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**Study on the Formation Mechanisms of Core–Shell Structures and
Their Influence on the Properties of Ni-Co-Al-Ti-Based
High-Entropy Intermetallic**

A thesis

submitted in fulfilment

of the requirements for the degree

of

Doctor of Philosophy in Materials Manufacturing Engineering

at

The University of Waikato

by

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THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

Year of submission

2026

Abstract

The advancement of aerospace technology imposes increasingly stringent requirements on the mechanical properties of structural materials at both room and elevated temperatures. Intermetallic compounds have attracted considerable attention due to their excellent specific strength and high-temperature performance. However, their engineering applications are persistently constrained by issues such as room-temperature brittleness or insufficient high-temperature strength. Inspired by the concept of high-entropy design, this study employs a sublattice high-entropy alloying strategy to improve the mechanical properties of conventional intermetallic compounds, developing Ni-Co-Al-Ti-based high-entropy intermetallics with a core-shell structure that exhibit favorable room-temperature ductility. Through further compositional tuning, the core-shell structure evolves toward multi-scale characteristics, achieving synergistic enhancement of strength and ductility. This work reveals the formation mechanism of the multi-scale core-shell structure and its influence on room-temperature mechanical properties, while also elucidating the strengthening-ductilization mechanism of the multi-scale core-shell structured high-entropy intermetallics. In addition, the mechanical properties over a wide temperature range are investigated, revealing the embrittlement at intermediate temperature and an anomalous yield effect, along with the corresponding microscopic mechanisms.

First, through thermodynamic and solidification analyses, the effect of Co addition on the $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ series alloys is studied. The results show that Co addition favors the stable formation of an $\text{L1}_2/\text{FCC}$ dual-phase structure. Further microstructural characterization reveals that, at a Co content of 25 at.%, a dual-phase core-shell structure consisting of ordered L1_2 cores and disordered FCC shells forms within the grains. Based on these observations, the mechanism by which Co addition promotes the formation of the core-shell structure is analyzed. On the one hand, Co addition induces the formation of the FCC phase and promotes the precipitation of the L1_2 phase, providing the phase-structural basis for the core-shell structure. On the other hand, it maintains a low $\text{L1}_2/\text{FCC}$ interfacial energy, supplying an stable interfacial condition for core-shell formation. Mechanical testing indicates that the formation of this structure effectively improves the room-temperature ductility of the alloy. The $\text{Ni}_{25}\text{Co}_{25}\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy exhibits a yield

strength of approximately 450 MPa, an ultimate tensile strength of about 650 MPa, and a plastic elongation of roughly 10%.

Building upon the alloy in which the core-shell structure has already been established, compositional adjustments are performed to promote the development of the core-shell structure toward multi-scale features. The addition of Ta induces the formation of a dual-scale core-shell structure with micron- and submicron-scale in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy, effectively enhancing the room-temperature strength. This alloy shows a yield strength of about 800 MPa, an ultimate tensile strength of approximately 1000 MPa, and a plastic strain of about 8%. Further increasing the Al/Ti ratio promotes the formation of a multi-scale core-shell structure comprising micron-scale, submicron-scale, and nanoscale in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys, achieving a synergistic improvement in room-temperature strength and ductility. Among them, the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy exhibits a yield strength of approximately 1000 MPa, an ultimate tensile strength of about 1250 MPa, and a plastic strain of roughly 12.5%. The formation mechanism of the multi-scale core-shell structure can be summarized as follows: Ta addition exacerbates compositional segregation at grain boundaries, inducing the formation of micron-scale core-shell structure. Meanwhile, an increased Al/Ti ratio enhances the sluggish diffusion effect, promoting the precipitation of submicron-scale and nanoscale core-shell structures.

Furthermore, $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy with multi-scale core-shell structure is selected as the research object. The evolution of dislocation substructures during room-temperature deformation was systematically characterized, revealing that the room-temperature deformation mechanism of this alloy is synergistically governed by superlattice intrinsic/extrinsic stacking faults, stacking faults, Lomer-Cottrell locks, dislocation forests, and dislocation walls.. On this basis, combined with theoretical calculations, the strengthening-ductilization mechanism is thoroughly elucidated. The results indicate that the high strength of the alloy mainly originates from precipitation strengthening arising from the high-volume-fraction ordered L1_2 cores and hetero-deformation-induced strengthening caused by the multi-scale core-shell structure, while the favorable ductility is attributed to continuous ($\text{FCC}+\text{nanoscale } \text{L1}_2$) dislocation motion channels and hetero-deformation-induced strain hardening. In addition, the highly coherent core-shell interfaces and serrated

grain boundaries jointly promote cooperative deformation, enabling the material to achieve an excellent combination of strength and ductility at room temperature.

Subsequently, the microstructural stability and mechanical properties of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy at 800 °C are investigated, revealing a good thermal stability and relatively high yield strength, but with almost zero plastic elongation. Vacuum comparative tensile tests indicate that this intermediate-temperature embrittlement originates from grain-boundary weakening caused by oxygen penetration and stress concentration induced by grain-boundary sliding. By increasing the Cr content to 20 at.%, discontinuous α -Cr phases and small-scale core-shell structures are induced to form at grain boundaries, which effectively hinder oxygen diffusion and restore the 800 °C plastic elongation to about 5%, thereby mitigating the embrittlement issue at intermediate temperature. In addition, the mechanical properties of the high-Cr alloy over a wide temperature range from 25 to 1000 °C are evaluated. The results show that the yield strength first increases and then decreases with rising temperature, reaching a peak value of about 920 MPa at 800 °C, exhibiting a clear anomalous yield effect. TEM characterization reveals that this effect is attributable to the transition of the deformation mechanism to anti-phase boundary shearing at elevated temperatures, as well as the formation of Kear-Wilsdorf locks and Lomer-Cottrell locks.

Keywords: High-entropy intermetallic; Core-shell structure; Deformation mechanism; Strengthening-ductilization mechanism; Intermediate-temperature embrittlement; Anomalous yield effect

List of Publications

I: Publications in international journals

Publications related to this thesis

- [1] **Junqi Liu**, Xiaopeng Wang, Xiao Zong, Xianfei Ding, Hui Xu, Fei Yang, Fantao Kong. Superior strength-ductility synergy in novel as-cast L1₂-type HEI Ni₅₀Co₂₅Cr_{9.5}Al₉Ti₅Ta_{1.5} with hierarchical core-shell structure[J]. *Acta Materialia*, 2025, 288, 120811. **Corresponding to the contents in Chapter 4 and 5.**
- [2] **Junqi Liu**, Xiaopeng Wang, Xiao Zong, Xianfei Ding, Hui Xu, Fei Yang, Fantao Kong. The evolution of dual-phase core-shell structure and mechanical properties induced by Co addition in as-cast high-entropy intermetallic[J]. *Materials & Design*, 2023, 232, 112120. **Corresponding to the contents in Chapter 3.**
- [3] **Junqi Liu**, Xiaopeng Wang, Ajit Pal Singh, Hui Xu, Fantao Kong, Fei Yang. The evolution of intermetallic compounds in high-entropy alloys: from the secondary phase to the main phase[J]. *Metals*, 2021, 11, 2054. **Corresponding to the contents in Chapter 1.**

II: Applied & granted patents

- [1] Fantao Kong, **Junqi Liu**, Xiaopeng Wang, A high-temperature resistant multi-principal-element intermetallic and its preparation method. **Application No.: CN115976391A, 2023.**

Acknowledgements

I would like to express my sincere gratitude to my PhD supervisor Professor Fei Yang for his guidance and kind support throughout the fulfillment of my PhD degree.

I would like to express my sincere gratitude to my co supervisors Professor Fantao Kong and Associate Professor Leandro Bolzoni for providing a firm support throughout the pursuit of my PhD degree.

I would like to acknowledge the supports and beneficial discussions from my coworkers Rui Zhang, Jingnan Ma, Yaqi Chang, Qinghe Zheng, Ziyao Fan, Pan Gao and Yutao Zhai.

I would like to thank everyone who directly or indirectly contributed to the preparation of this thesis.

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List of abbreviations

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HEAs: High-entropy alloys

HEIs: High-entropy intermetallics

FCC: Faced-centered cubic

SFE: Stacking fault energy

TWIP: Twinning-induced plasticity

TRIP: Transformation-induced plasticity

VEC: Valence electron concentration

BCC: Body-centered cubic

APB: Anti-phase boundary

HDI: Hetero-deformation induced

GNDs: Geometrically necessary dislocations

XRD: X-ray diffraction

SEM: Scanning electron microscope

EDS: Energy dispersive spectroscopy

EBSD: Electron backscatter diffraction

IPF: Inverse pole figures

KAM: Kernel average misorientation

TEM: Transmission electron microscope

BF: Bright field

HAADF-STEM: High-angle annular dark-field scanning transmission electron microscopy

SAED: Selected area electron diffraction

HRTEM: High-resolution transmission electron microscopy

LUR: Loading–unloading–reloading

CALPHAD: Calculation of phase diagrams

FFT: Fast fourier transform

IFFT: Inverse fast fourier transform

SFs: Stacking faults

SISF: Superlattice intrinsic stacking fault

SESF: Superlattice extrinsic stacking fault

L-C locks: Lomer-Cottrell locks

K-W locks: Kear-Wilsdorf locks

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Chapter 1 Introduction

With the advancement of new-generation aerospace and astronautics vehicle technologies, the performance requirements for high-temperature structural materials in terms of lightweight characteristics, high-temperature strength, creep resistance, and oxidation resistance have been increasingly elevated. Intermetallic compounds exhibit strong atomic bonding, low density, high specific strength, and excellent elevated-temperature resistance, making them important candidates to replace superalloys as structural materials in aerospace, astronautics, transportation, and other industries [1-3]. However, most high-temperature intermetallic structural materials, such as the widely studied Ni-Al, Ti-Al, and Fe-Al systems, generally suffer from pronounced room-temperature brittleness or insufficient high-temperature strength, severely restricting their engineering applications [4].

To overcome the performance bottlenecks of conventional structural materials, Yeh and Cantor et al. proposed the concept of high-entropy alloys (HEAs) in 2014 based on the equiatomic multi-principal-element design strategy [5]. This class of materials, leveraging the unique high-entropy effect, sluggish diffusion effect, lattice distortion effect, and “cocktail” effect, exhibits outstanding mechanical properties and holds significant promise for structural material applications [6,7]. Building on this foundation, the University of North Carolina proposed the concept of high-entropy oxide ceramics in 2015, pointing a new direction toward solving the difficulty of simultaneously enhancing hardness and toughness in traditional ceramic materials [8]. Inspired by the design rationale of HEAs and high-entropy ceramics, and to address the persistent challenges of pronounced room-temperature brittleness and insufficient high-temperature strength in conventional intermetallics, Harbin Institute of Technology proposed the concept of sublattice high-entropy alloying for ordered crystal structures in 2017, leading to a novel multi-principal-element intermetallics, namely high-entropy intermetallics (HEIs) [9-11].

From a thermodynamic perspective, the formation enthalpy of intermetallic compounds is generally negative, and sublattice high-entropy alloying substantially increases the configurational entropy. The combined effect renders the Gibbs free energy of high-entropy intermetallics significantly lower than that of HEAs, thereby

endowing them with greater structural stability. Furthermore, owing to their ordered superlattice structure and strong atomic bonding characteristics, HEIs effectively impede dislocation slip and maintain high strength at elevated temperatures. This circumvents the limitation of traditional Ni-based or Co-based superalloys, which rely heavily on high-density refractory alloying elements, enabling simultaneous lightweight characteristics and excellent high-temperature mechanical properties [12]. Moreover, sublattice high-entropy alloying can reduce the intrinsic brittleness of ordered structures by modulating the electronic structure and bonding character, resulting in superior ductility of HEIs compared to conventional intermetallics. Consequently, HEIs are expected to achieve a favorable balance of strength and ductility at both room and elevated temperatures [13].

In recent years, research on high-entropy intermetallics has attracted widespread attention. However, existing studies have predominantly focused on room-temperature mechanical properties, while investigations of high-temperature performance remain relatively scarce. Meanwhile, the room-temperature mechanical properties of as-cast high-entropy intermetallics still exhibit considerable room for improvement, and the underlying strengthening–plasticizing mechanism and room-temperature deformation mechanism warrant in-depth exploration. Therefore, it is imperative to optimize the microstructure and room-temperature properties of as-cast alloys through compositional regulation, and to systematically evaluate their high-temperature mechanical performance. Against this backdrop, this dissertation takes as-cast Ni-Co-Al-Ti-based high-entropy intermetallics as the research object and conducts a systematic investigation of their solidification microstructure and room-/high-temperature mechanical properties. The objective is to elucidate the influence of compositional regulation on microstructural evolution and mechanical properties, clarify the room-temperature strengthening–plasticizing mechanism and deformation mechanism, and explore the characteristics of high-temperature mechanical properties, thereby providing a theoretical and technical foundation for the research and fabrication of high-performance high-entropy intermetallics.

Chapter 2 Literature review

2.1 Research progress on advanced structural materials

2.1.1 Research progress on intermetallic compounds

Intermetallic compounds are a class of materials formed by metallic and/or metalloid elements combined in near-stoichiometric ratios, characterized by superlattice structural features [14]. These materials simultaneously possess long-range ordered crystal structures, strong atomic bonding, and close-packed atomic arrangements, thereby exhibiting high strength, high melting points, and outstanding corrosion and oxidation resistance [15]. Among them, certain intermetallic compounds can retain a stable long-range ordered structure at temperatures approaching their melting points, demonstrating favorable microstructural stability [16]. Concurrently, the strong atomic bonding imparts low atomic mobility and sluggish lattice diffusion kinetics to these materials, endowing them with excellent creep resistance [17]. Owing to these performance advantages, intermetallic compounds exhibit significant application potential as structural materials in critical fields such as aerospace, nuclear energy, and chemical engineering.

However, conventional intermetallic structural materials typically exhibit inadequate ductility and a propensity for brittle fracture at room temperature, severely constraining their engineering application. This embrittlement behavior primarily arises from two factors. On the one hand, the limited number of independently activated slip systems leads to intrinsic brittleness. On the other hand, the relatively low grain-boundary cohesion in certain material systems readily induces intergranular fracture [18]. To address these critical issues, researchers have conducted systematic investigations on the microstructure and mechanical properties of ordered intermetallics, with a particular focus on cubic ordered systems [19]. Through the development of multi-scale alloying strategies, including macro-alloying and micro-alloying, the intrinsic plastic deformation capacity of these materials has been enhanced to a certain extent [20]. For instance, in the $\text{Ni}_3\text{V-Co}_3\text{V-Fe}_3\text{V}$ alloy system, the design of ductile ordered intermetallics can be realized by tailoring the valence electron concentration (e/a ratio). Studies have shown that

when Fe addition lowers the valence electron concentration to below approximately 7.85, the originally brittle $(\text{Ni,Co})_3\text{V}$ alloy exhibits significantly improved ductility [21]. Additionally, in the Co_3Ti and Ni_3Al alloy systems, moderate deviation from the ideal stoichiometric ratio can regulate the long-range order parameter, thereby relaxing the constraints of the L1_2 ordered structure on dislocation slip, promoting dislocation motion and enhancing alloy ductility [22,23]. Moreover, the minor addition of elements such as B, Zr, and Hf to polycrystalline Ni_3Al alloys can suppress rapid crack propagation along grain boundaries through grain-boundary segregation, effectively improving ductility [24].

Although previous research results indicate that alloying-based compositional design can, to some degree, improve the room-temperature ductility of intermetallic structural materials, their overall mechanical properties still fall short of the requirements for practical application. From the perspective of alloy composition, current alloying studies have primarily focused on relatively simple compositional systems, wherein only one or two alloying elements are added to improve properties. In such alloy systems containing only a limited number of element species, the available compositional design space is relatively restricted, making it difficult to achieve substantial breakthroughs in mechanical properties. Consequently, there is an urgent need to develop new compositional design concepts to transcend the performance limitations of conventional alloy systems.

2.1.2 Research progress on high-entropy alloys

In contrast to intermetallic compounds with long-range ordered crystal structures, solid-solution alloys are primarily characterized by solute atoms randomly occupying lattice sites, resulting in a disordered atomic arrangement. Conventional solid-solution alloys typically employ one or two elements as the base matrix, achieving property regulation through the addition of minor alloying elements. However, as application environments increasingly extend toward extreme conditions, the limitations of property regulation in traditional single-principal-element solid-solution alloys have become progressively more pronounced [25]. Against this backdrop, the multi-principal-element alloy design strategy has transcended conventional paradigm and propelled the development of high-entropy alloy systems [26]. HEAs adopt an equiatomic or near-equiatomic multi-principal-

element design, substantially expanding the alloy composition space and enabling diverse property profiles, as illustrated in Fig. 2.1 [27]. Among them, face-centered cubic (FCC) structured HEAs demonstrate broader application prospects owing to their higher crystal symmetry. In light of this, the following sections provide a classified review of the mechanical property characteristics of different types of FCC-structured HEA systems.

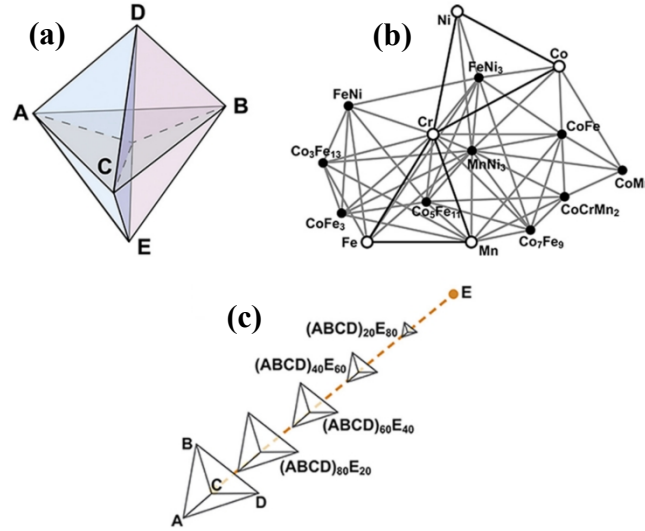


Fig. 2.1 Schematic diagram of expanded composition space for multi-principal-element alloys [27]-454

(a) high-dimensional composition space; (b) potential phase combinations in multi-component systems; (c) compositional evolution pathway from single-principal-element to multi-principal-element alloys

(1) Equiatomic single-phase FCC high-entropy alloys

In the early developmental stage of HEAs, single-phase FCC solid-solution HEAs garnered extensive attention due to their excellent plastic deformation capacity, with the most representative system being the equiatomic CrMnFeCoNi (Cantor) alloy [28]. Studies have shown that such single-phase FCC HEAs generally exhibit a highly homogeneous solid-solution structure, and their strengthening mechanisms are primarily derived from the multi-principal-element solid-solution strengthening effect and the pronounced lattice distortion effect [29]. During room-temperature deformation, this class of alloys primarily achieves plastic deformation through the planar slip of $\{111\}\langle 110 \rangle$ dislocations. The large dissociation width of Shockley partial dislocations and the restricted cross-slip behavior jointly promote dislocation pile-up, thereby sustaining a high strain-hardening capacity [30]. As plastic deformation proceeds, multiple slip systems are progressively activated, forming

complex dislocation interaction structures that further enhance the strain-hardening capability. Under high-temperature conditions, the strength of single-phase FCC HEAs is relatively insensitive to temperature variations, enabling stable mechanical property retention over a wide temperature range [31]. However, owing to the absence of stable second-phase strengthening structures, the strength enhancement potential of this class of alloys is limited, making it difficult to meet the stringent requirements of demanding engineering applications, as shown in Fig. 2.2 [32].

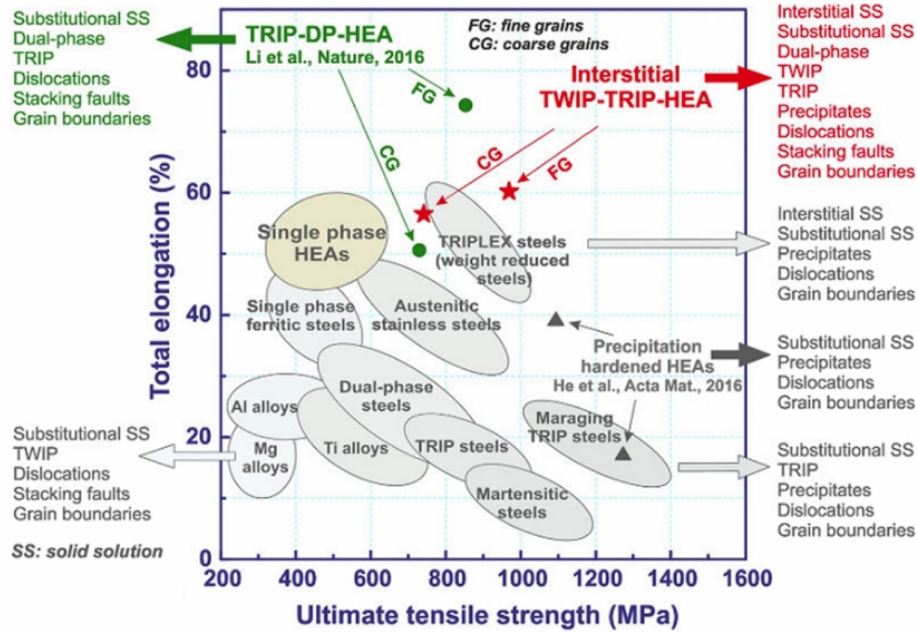


Fig. 2.2 Strength–ductility property distribution of different types of metallic materials [32]–45

(2) Non-equiatomic multi-phase FCC high-entropy alloys

Building upon single-phase FCC HEAs, non-equiatomic compositional design and multi-phase microstructural tailoring can further enhance their strength–ductility synergy. Research has demonstrated that deviation from the equiatomic ratio can effectively regulate the stacking fault energy (SFE), thereby altering the dislocation slip mode and improving the mechanical properties. For example, the CrCoNi medium-entropy alloy can achieve a more favorable strength–ductility balance by lowering the SFE to promote twin-assisted plastic deformation [33]. Further investigations have revealed that various deformation mechanisms—including dislocation slip, twinning-induced plasticity (TWIP), and transformation-induced plasticity (TRIP)—can be controllably switched in non-equiatomic FCC HEAs

through continuous compositional tuning [34]. For instance, in the $\text{Fe}_{(80-x)}\text{Mn}_x\text{Co}_{10}\text{Cr}_{10}$ alloy, as the Mn content decreases, the deformation mechanism can sequentially transition from dislocation slip to TWIP, TRIP, and even synergistic deformation involving both FCC and hexagonal close-packed (HCP) phases, as illustrated in Fig. 2.3 [35]. However, existing research results indicate that relying solely on solid-solution strengthening or conventional dual-phase structural strengthening is insufficient to sustain adequate dislocation impedance under high-temperature conditions.

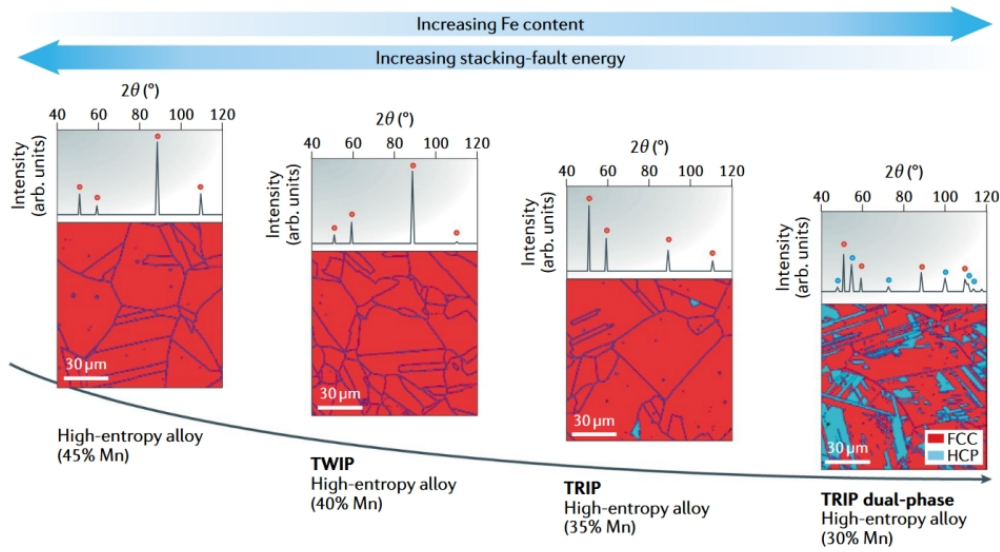


Fig. 2.3 Regulation of stacking fault energy and phase constitution in non-equiatomc derivative systems of the Cantor alloy [35]-524

(3) L_{12} nanoparticle precipitation-strengthened FCC high-entropy alloys

To overcome the limitations of single-phase and conventional multiphase FCC-type high-entropy alloys in terms of strength and high-temperature performance, precipitation-strengthened HEAs have been developed in recent years, among which the L_{12} nanoparticle precipitation-strengthened FCC-type HEAs are the most representative. Studies have shown that introducing a high density of coherent L_{12} nanoprecipitates into the FCC-type HEA matrix can effectively impede dislocation motion, thereby achieving a synergistic optimization of strength and ductility. For instance, in the $(\text{FeCoCrNi})_{96}\text{Ti}_2\text{Al}_4$ alloy, the introduction of L_{12} nanoprecipitates enables a yield strength of approximately 1.2 GPa at room temperature while maintaining a tensile ductility of about 17% [36]. Furthermore, by tailoring the precipitation behavior to achieve the simultaneous occurrence of continuous and

discontinuous precipitation, different morphology of L_{12} nanoprecipitates were introduced into the CoCrNi medium-entropy alloy, attaining a tensile strength of ~ 1.3 GPa with a ductility of $\sim 45\%$ [37]. On this basis, a design concept of “dual high-entropy synergy” was further proposed, which leverages the synergistic interplay between the multi-principal-element matrix and multi-principal-element intermetallic nanoprecipitates to improve the strength–ductility trade-off, as schematically illustrated in Fig. 2.4 [38]. This work was published in 《Science》 in 2018. It was revealed that, owing to the presence of $(\text{Ni,Co,Fe})_3(\text{Ti,Al,Fe})$ multi-principal-element intermetallic precipitates, this FCC-type HEA achieves both an ultrahigh strength of ~ 1.5 GPa and an excellent ductility of $\sim 50\%$ at room temperature.

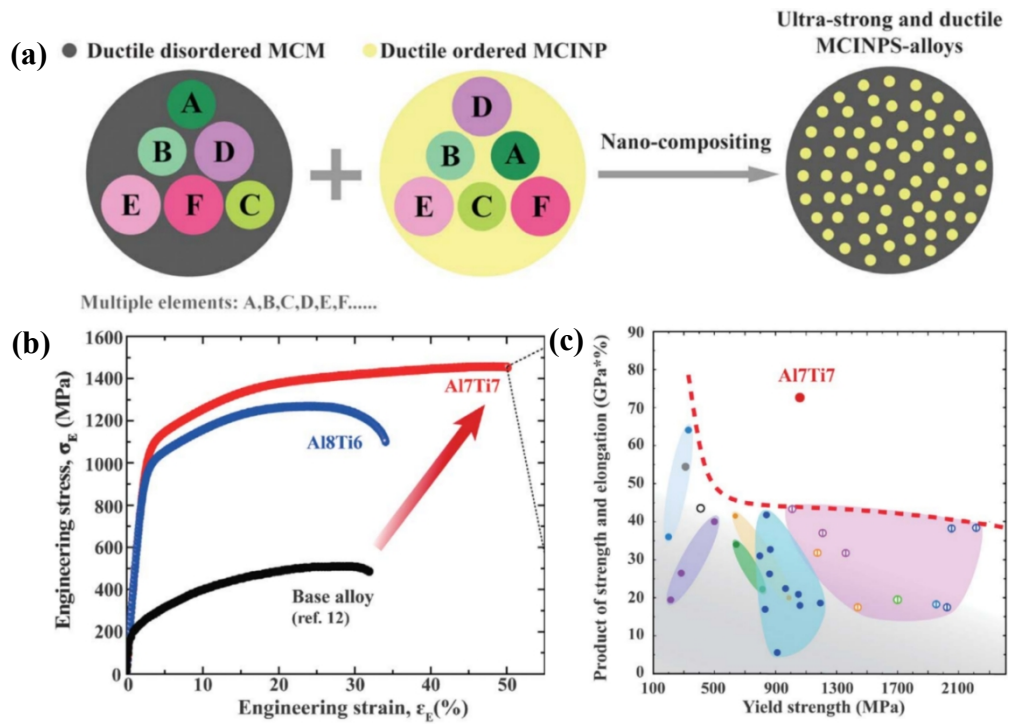


Fig. 2.4 Schematic microstructures of high-entropy alloys strengthened by multi-component nanoparticles and their excellent room-temperature mechanical properties [38]–1,3
(a) microstructure schematic; (b) tensile engineering stress–strain curves; (c) performance comparison

More importantly, the multi-principal-element L_{12} strengthening phase generally exhibits favorable thermal stability, enabling these alloys to maintain relatively high mechanical performance at elevated temperatures. For example, Zhao et al. [39] found that the coarsening kinetics of the L_{12} strengthening phase in the $(\text{NiCoCrFe})_{94}\text{Al}_4\text{Ti}_2$ alloy are substantially slower than those in conventional

nickel-based superalloys, and similar results were also confirmed in the $(\text{NiCoCr})_{94}\text{Al}_3\text{Ti}_3$ alloy [40]. In addition, the $\text{Ni}_{39.9}\text{Co}_{20}\text{Fe}_{10}\text{Cr}_{20}\text{Al}_6\text{Ti}_4\text{B}_{0.1}$ alloy achieves a yield strength of ~ 900 MPa and a tensile ductility of $\sim 25\%$ at 600°C , facilitated by stacking-fault-related deformation mechanisms [41]. However, it should be noted that L1_2 -precipitation-strengthened FCC-type HEAs often suffer from severe embrittlement in the intermediate-temperature regime. For instance, the Ni-Co-Cr-Al-based L1_2 -precipitation-strengthened HEA exhibits a yield strength of ~ 1000 MPa and a tensile ductility of $\sim 23\%$ at room temperature. However, the tensile ductility drops sharply to $\sim 3\%$ when the temperature is elevated to 750°C , although the yield strength remains at ~ 800 MPa [42]. These characteristics indicate that L1_2 -nanoprecipitate strengthening can effectively enhance both the strength and high-temperature mechanical properties of FCC-type HEAs, endowing them with promising potential for applications across a wide temperature range. Nevertheless, the pronounced ductility degradation in the intermediate-temperature regime imposes certain constraints on their overall wide-temperature-range performance.

In summary, the strengthening strategies for FCC-type HEAs have progressively evolved from early solid-solution strengthening to multiphase strengthening and precipitation strengthening, resulting in sustained improvements in both room-temperature and high-temperature mechanical properties. However, even in L1_2 -nanoprecipitate-strengthened FCC-type HEAs, there remains considerable room for further enhancement of mechanical performance across a broad temperature range. Against this background, alloy systems that rely solely on a single strengthening mechanism are no longer sufficient to meet the ever-increasing demands for performance breakthroughs. There is an urgent need to develop novel high-performance structural materials that integrate multiple strengthening mechanisms and multi-principal-element chemical complexity, thereby offering new pathways for the optimization of comprehensive performance over a wide temperature range.

2.2 Research progress on high-entropy intermetallics

Research progress on high-entropy alloys demonstrates that the synergistic high-entropy effect between the solid-solution matrix and intermetallic precipitates contributes to further enhancement of the overall mechanical properties of

precipitation-strengthened high-entropy alloys. Meanwhile, studies have shown that multi-principal-element L1₂-type intermetallics themselves possess favorable mechanical properties [38]-4. Inspired by this, Harbin Institute of Technology introduced the multi-principal-element alloying design concept into conventional intermetallics and proposed high-entropy intermetallics as a novel material system, with the aim of improving the mechanical properties of conventional intermetallics [10]-13. Based on the structural characteristics of this material, this section focuses on summarizing the thermodynamic phase stability and the characteristics of sublattice high-entropy alloying, providing theoretical support for subsequent investigations into microstructure and properties.

2.2.1 Structural characteristics of high-entropy intermetallics

In the early stages of research on multi-principal-element alloys, the focus was primarily directed toward disordered solid-solution structures. This was largely attributed to the early understanding of entropy stabilization theory, which holds that mixing multiple principal elements in equiatomic ratios markedly increases the configurational entropy, thereby lowering the Gibbs free energy and stabilizing single-phase solid-solution structures [43]. However, as research has progressed, it has gradually been recognized that stable ordered structures can also form in multi-principal-element alloy systems. For instance, Tong et al. [44], in their study of Al_xCoCrCuFeNi high-entropy alloys, discovered that a single B2 ordered structure can form when the Al content exceeds 2.8 at.%. Subsequently, Li et al. [45] further demonstrated that AlCrCoNiFe can also crystallize into a B2-type ordered structure. These findings indicate that multi-principal-element alloy systems are capable of stabilizing not only disordered solid-solution structures but also stable ordered intermetallic phases.

Concurrently, Harbin Institute of Technology, through analysis of the atomic arrangements in typical structural materials, identified a distinctive mode of atomic arrangement lying between the ordered arrangement of intermetallics and the disordered arrangement of high-entropy alloys. Taking the (100) plane of the face-centered cubic structure illustrated in Fig. 2.5 as an example, the atom sizes in the figure are used to differentiate the sublattice types, while the atom colors are used to distinguish the elemental species within the same sublattice. As can be seen from

Fig. 2.5 (c) and (d), while preserving the long-range ordered structure characteristic of intermetallics, introducing multi-principal-element atoms into at least one sublattice to achieve sublattice high-entropy alloying can yield a novel alloy system. This alloy simultaneously possesses the ordered crystal structure of intermetallics and the multi-principal-element compositional characteristics of high-entropy alloys, and is therefore designated as a high-entropy intermetallic [9-11]-1,13.

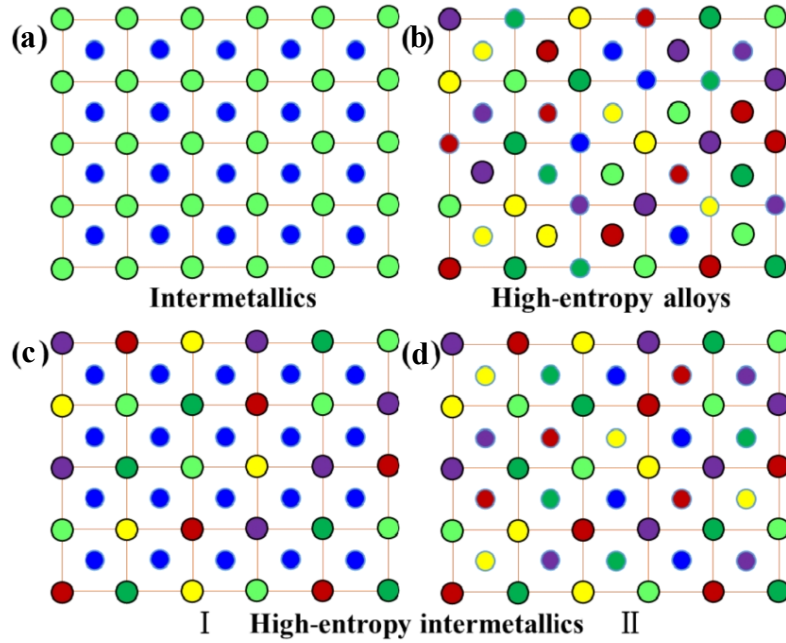


Fig. 2.5 Atomic arrangement on the (100) plane of the face-centered cubic structure [9]-21

(a) binary intermetallic; (b) high-entropy alloy; (c) type I high-entropy intermetallic; (d) type II high-entropy intermetallic

High-entropy intermetallics are essentially ordered intermetallic compounds that possess multi-principal-element characteristics. However, such compositional complexity is restricted to particular sublattice sites, whereas the overall ratio of principal elements occupying distinct sublattices remains in rigorous compliance with the stoichiometric constraints of the intermetallic compound. Consequently, their formation process is termed sublattice high-entropy alloying, which is distinctly different from the overall high-entropy alloying that arises from the random occupation of all principal elements across lattice sites in high-entropy alloys [10]-13. In addition, similar to the case in conventional alloys or high-entropy alloys, where the solid solution serves as the primary phase with a small amount of ordered secondary phase permitted, high-entropy intermetallics may also contain a limited amount of disordered solid-solution phase. In this thesis, it is held

that as long as the multi-principal-element intermetallic phase constitutes the dominant phase, the material can be designated as a high-entropy intermetallic.

Since its introduction, high-entropy intermetallics have rapidly emerged as a research hotspot in the field of metallic materials, with extensive research efforts systematically devoted to composition design, phase structure evolution, and property optimization [46-48]. To date, high-entropy intermetallics with various crystal structure types have been successively reported, encompassing ordered structures such as $L1_2$, B2, and $L2_1$. These materials have demonstrated outstanding overall performance in fields including high-temperature structural materials, catalytic electrodes, magnetic functional devices, and energy storage and conversion. In 2023, researchers systematically reviewed and categorized over 60 high-entropy intermetallics and their related compositional systems reported at the time, and published the findings in the form of a review in an academic journal [43]-7,11. This review classifies high-entropy intermetallics according to their crystal structure type, among which $L1_2$ - and B2-structured ones have been widely employed in structural materials due to their excellent high-temperature strength, favorable thermal stability, and relatively prominent strength–ductility synergy. The relevant compositional information, melting methods, and phase constitutions are listed in Table 2.1. It is thus evident that high-entropy intermetallics have progressively evolved into an important bridge connecting conventional ordered intermetallics and disordered high-entropy alloys.

Table 2.1 Reported $L1_2$ and B2 structured high-entropy intermetallics [43]-7,11

Chemical formula	Melting method	Phase constitution
FeCoNiV	Induction melting	$L1_2$
$Al_{0.25}FeCoNiV$	Arc melting	$L1_2 + B2$
$Ni_{43.9}Co_{22.4}Fe_{8.8}Al_{10.7}Ti_{11.7}B_{2.5}$	Arc melting	$L1_2 + FCC$
Co-30Ni-11Al-5.5 W-4Ti-2.5Ta-0.10B	Arc melting	$L1_2$
(FeCoNi)(AlTi)	Chemical dealloying	$L1_2$
$Co_{0.31}Fe_{0.27}Ni_{0.19}Cu_{0.09}Pd_{0.14}$	Annealing superstructures in NH_3 atmosphere	$L1_2$
$Al_xCoCrCuFeNi$ ($x \geq 2.8$)	Arc-melting	B2
$AlCoCr_xFeMo_{0.5}Ni$ ($x=0-2.0$)	Arc-melting	$B2+\sigma$
AlCoFeMnNi	Arc-melting	B2
AlTiVCr	Arc melting	B2
AlCoCrFeNi	Arc-melting	B2
ZrTiHfCuNiFe	Arc-melting	B2

2.2.2 Thermodynamic phase stability of high-entropy intermetallics

From a thermodynamic perspective, the phase stability of an alloy is fundamentally governed by the change in Gibbs free energy, expressed as [49]:

$$\Delta G = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (2-1)$$

where ΔG — Gibbs free energy ($\text{J}\cdot\text{mol}^{-1}$);

ΔH_{mix} — enthalpy of mixing ($\text{J}\cdot\text{mol}^{-1}$);

ΔS_{mix} — entropy of mixing ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$);

T — absolute temperature (K).

For an N-component system, the entropy of mixing can be expressed as [50]:

$$\Delta S = -R \sum_{i=1}^N x_i \ln x_i \quad (2-2)$$

where x_i — atomic fraction of the i-th element;

R — gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

Theoretically, the entropy of mixing of a system increases markedly with the number of principal elements. When the contribution of the entropy of mixing is sufficiently large, it can effectively lower the Gibbs free energy, thereby enhancing phase stability—this serves as the fundamental thermodynamic rationale for designing solid-solution high-entropy alloys [51]. For high-entropy intermetallics, the long-range ordered crystal structure generally results in a low, or even negative, enthalpy of mixing (or formation enthalpy), while the high-entropy effect within the sublattice markedly increases the overall entropy of mixing of the alloy. According to the Gibbs free energy equation, the combined action of a higher entropy of mixing and a lower enthalpy of mixing/formation enthalpy inevitably leads to a decrease in the free energy, thereby favoring the formation of high-entropy intermetallics and the stabilization of their phase structure. Preliminary research in this project calculated the free energies of 15 L1₂-structured high-entropy intermetallics and compared them with over 40 L1₂-structured intermetallics and FCC-type high-entropy alloys, the results are presented in Fig. 2.6. As can be seen, high-entropy intermetallics exhibit a distinctly lower Gibbs free energy, thereby validating their thermodynamic phase stability. Nevertheless, the final phase constitution of the alloy depends not only on the mixing entropy across sublattices and the effect of enthalpy–entropy competition from ordered structures

on phase stability, but also on achieving a coordinated balance between the local chemical environment and the crystal structure. Consequently, extensive research efforts have been devoted to establishing suitable phase formation criteria for high-entropy intermetallics.

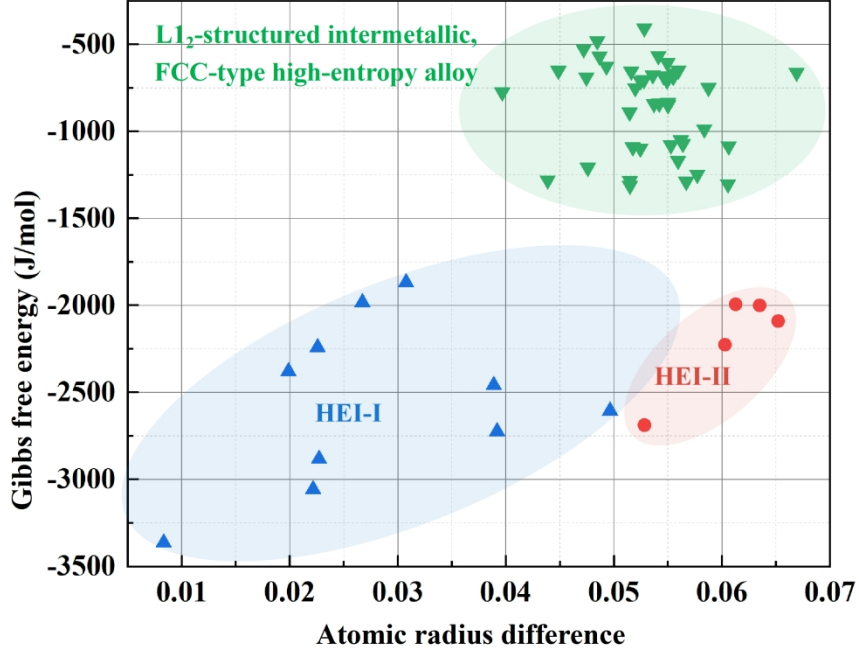


Fig. 2.6 Comparison of Gibbs free energy between HEIs and HEAs [11]-47

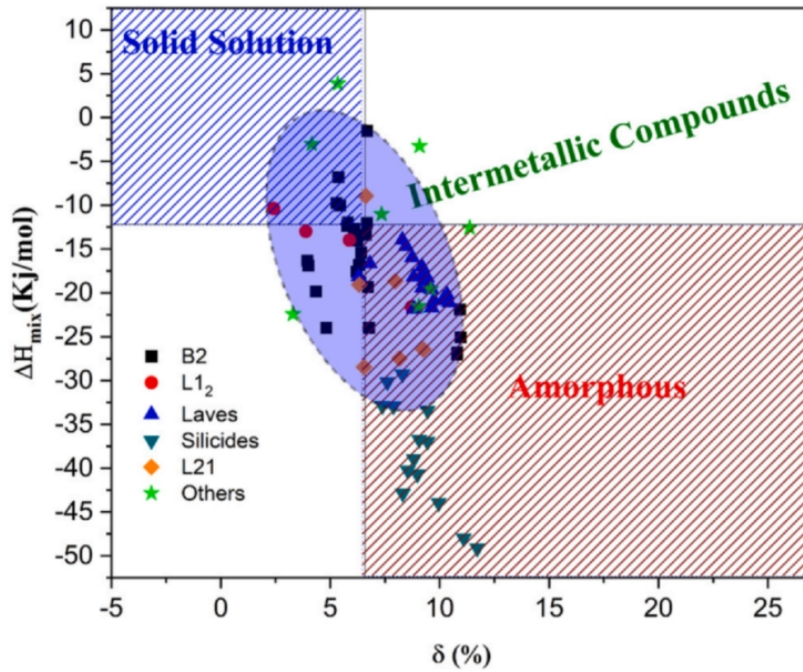


Fig. 2.7 δ - ΔH_{mix} relationship diagram for delineating different phase formation regions [43]-15

Existing studies have shown that, in multi-principal-element alloy systems, factors such as chemical bonding characteristics, atomic size matching relationships, and geometric compatibility of crystal structures exert significant influence on phase stability. On this basis, several phase formation prediction approaches have been established using thermodynamic and structural parameters. Among these, the δ - ΔH_{mix} criterion proposed by Zhang et al. [52] and Guo et al. [53] has been widely employed to distinguish the formation regions of solid solutions, amorphous phases, and intermetallics. As shown in Fig. 2.7, when ΔH_{mix} is between -11.6 kJ/mol and 5 kJ/mol and $\delta \leq 6.6\%$, the system tends to form a solid-solution structure. In addition, the valence electron concentration (VEC) is also commonly used to predict crystal structure type. A VEC below 6.87 favors the formation of body-centered cubic (BCC) structures, whereas a VEC greater than 8 favors the formation of FCC structures [54].

Electronegativity difference is likewise regarded as an important factor influencing phase stability. Phase stability criteria constructed by Pauling and Allen based on electronegativity have been widely applied in multi-principal-element systems [55]. For example, Yurchenko et al. [56] proposed that, when $\delta \geq 5\%$ and $\Delta x_{\text{Allen}} \geq 7\%$, the system exhibits a stronger tendency to form a Laves phase structure. Further, Yao et al. [57] proposed an overall electronegativity difference criterion, achieving effective delineation of the formation regions of solid solutions, intermetallics, and amorphous phases. Subsequent studies have revealed that, in multi-principal-element ordered intermetallic systems, the lattice site occupancy environment within the sublattice and the local chemical bonding characteristics exert a significant influence on phase stability. Accordingly, a sublattice electronegativity difference criterion was proposed to characterize the effect of local chemical environment differences among elements at different lattice sites within the same sublattice on structural stability [58]. The results demonstrate that the majority of reported single-phase high-entropy intermetallics are distributed within a specific stable region ($\Delta x_{\text{A}_i\text{-B}_i} \geq 5$, and $1.2 \leq \delta^* \leq 3.3$), as illustrated in Fig. 2.8 [59]. Overall, both existing theoretical and experimental studies confirm that high-entropy intermetallics possess a well-defined thermodynamic foundation for phase stability and constitute a class of ordered multi-principal-element structural materials capable of stable existence.

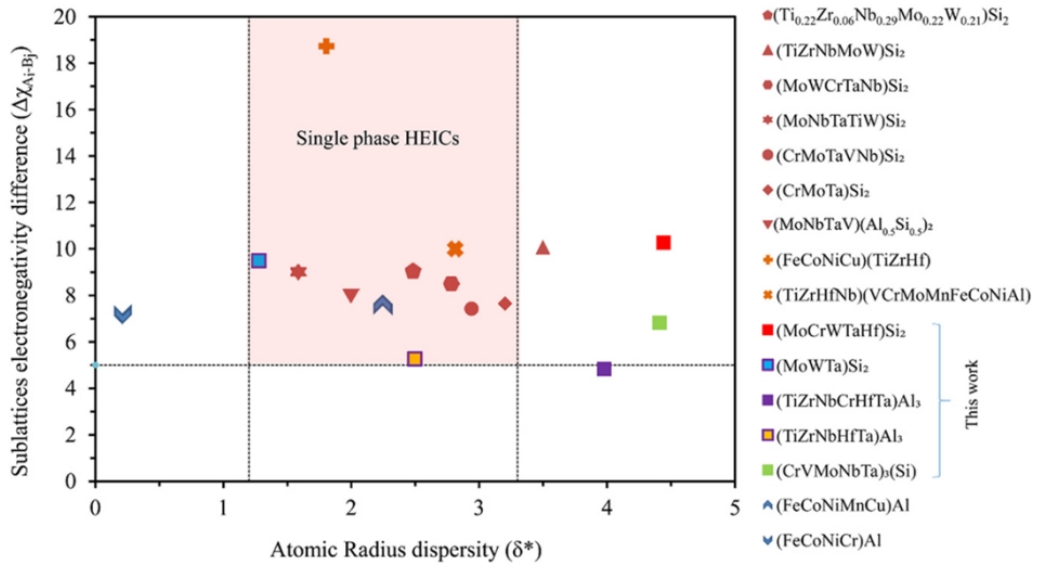


Fig. 2.8 $\Delta\chi_{A_i-B_j}$ - δ^* relationship diagram for delineating the single-phase formation region [59]-6

2.2.3 Sublattice high-entropy alloying of high-entropy intermetallics

Distinguished from conventional intermetallics, high-entropy intermetallics offer a vast compositional design space for alloy development owing to their unique sublattice high-entropy alloying characteristics [9]-22. Unlike disordered solid solutions, ordered intermetallics possess well-defined sublattice site occupancy rules, with each element typically preferentially occupying specific lattice sites. Taking the L1₂ (A₃B) ordered structure as an example, A corresponds to the face-centered sites and B to the corner sites. By integrating the physicochemical properties of the elements with existing experimental results, the multi-principal elements can be classified into two categories: one tending to occupy the A sublattice and the other tending to occupy the B sublattice. During composition design, provided that the total atomic amounts of the A-type and B-type elements satisfy the 3:1 stoichiometric ratio, the compositional proportions of the two categories of elements can be freely combined. This process not only increases the configurational entropy of each sublattice but also modifies the local coordination environment and electronic structure within the sublattice, thereby influencing the atomic bonding strength, interfacial defect energy, and dislocation motion characteristics, as shown in Fig. 2.9 [60].

The essence of sublattice high-entropy alloying lies in the enhancement of the

mixing entropy of a specific sublattice through multi-principal-element occupancy, and this multi-principal-element alloying process itself is conducive to improving the mechanical properties of the material. For instance, Niu et al. [61] found that, through sublattice multi-principal-element alloying, the anti-phase boundary energy (APB energy) of the B2 precipitate phase was reduced to half that of the conventional binary intermetallic NiAl in their investigation of Al-Co-Cr-Fe-Ni high-entropy alloys. This enabled the B2 phase to exhibit pronounced dislocation activity during tensile deformation, thereby improving the ductility of the alloy and enhancing its strain hardening capacity. Similarly, Chiba et al. [62] found that multi-principal-element alloying of the A sublattice enables phase structure transformation and improved room-temperature ductility in A_3B -type intermetallics. For example, in the case of $(Co,Ni,Fe)_3V$, the addition of Ni and Fe converts Co_3V from a hexagonal ordered structure to a cubic $L1_2$ structure, resulting in a room-temperature tensile ductility of approximately 40% [63]. Hence, further realizing sublattice high-entropy alloying on the basis of sublattice multi-principal-element alloying holds promise for simultaneously ensuring phase stability and further optimizing the mechanical properties of the alloy, thereby providing new degrees of freedom for the property control of high-entropy intermetallics.

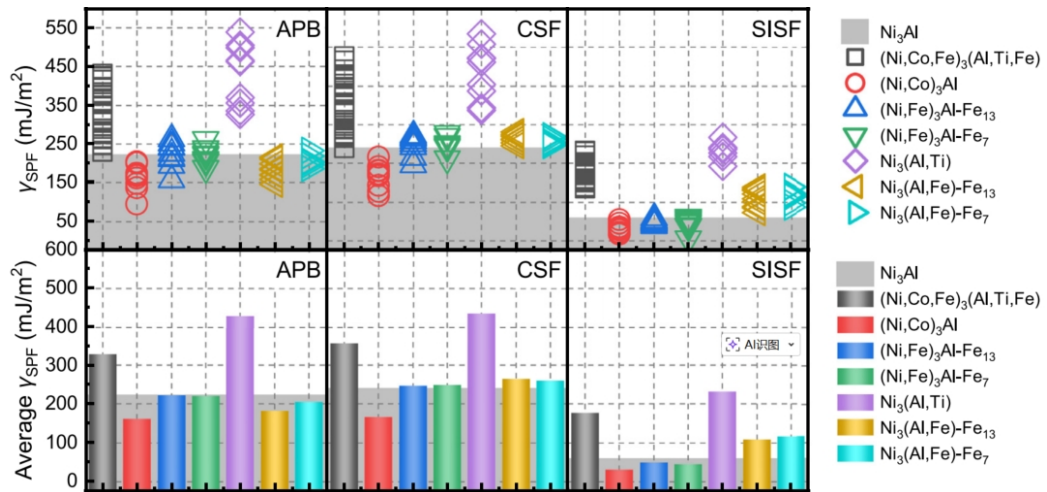


Fig. 2.9 Defect energy distribution in Ni_3Al and multicomponent intermetallic [60]-6

Although sublattice high-entropy alloying is an effective approach for tailoring the mechanical properties of intermetallics, the site occupancy behavior of multi-principal elements exhibits a pronounced dependence on the alloy composition. For example, Cr atoms preferentially occupy the B sites in binary Ni_3Al [64], but tend to substitute for the A sites in multi-component $L1_2$ systems [65]. This composition-

dependent site occupancy behavior not only modifies the local chemical environment within the sublattice, but also affects the degree of sublattice high-entropy alloying and consequently influences the material properties. Therefore, the strategy of tailoring the mechanical properties of high-entropy intermetallics based on sublattice high-entropy alloying still warrants further in-depth investigation.

2.3 Performance characteristics of $L1_2$ -type high-entropy intermetallics

High-entropy intermetallics combine long-range ordered crystallographic structures with multi-principal-element chemical compositions. They can maintain high strength and high-temperature stability while improving ductility through sublattice high-entropy alloying, thereby offering a promising solution to the long-standing strength–ductility trade-off in conventional intermetallics [66]. Kolli et al. [67] surveyed over 4000 binary intermetallic compounds and found that ordered structures derived from BCC and FCC parent phases are the most abundant, with B2 and $L1_2$ types being the most prevalent, respectively, as shown in Fig. 2.10. Among them, the $L1_2$ structure, as the ordered counterpart of the FCC solid solution, possesses cubic high symmetry and provides an adequate number of slip systems, which is favorable for achieving coordinated plastic deformation [68]. Accordingly, this section focuses on the mechanical properties of $L1_2$ -type high-entropy intermetallics, including the strength–ductility relationship at room temperature and the microstructural stability at elevated temperatures.

2.3.1 Synergistic improvement of room-temperature strength and ductility

Although conventional ordered intermetallics exhibit high strength, their increasing of order degree impedes dislocation glide, rendering them susceptible to brittle fracture during deformation [69]. In contrast, sublattice high-entropy alloying provides a new strategy for overcoming the room-temperature strength–ductility limitation. For example, the $L1_2$ -type alloy $\text{Ni}_{43.9}\text{Co}_{22.4}\text{Fe}_{8.8}\text{Al}_{10.7}\text{Ti}_{11.7}\text{B}_{2.5}$ achieves a yield strength exceeding 1 GPa, approximately 2.6 times that of Ni_3Al , as shown in Fig. 2.11. This remarkable strengthening effect originates primarily from the enhancement of anti-phase boundary energy induced by sublattice multi-principal-

element alloying. In the Ni_3Al -type ordered structure, Ti atoms preferentially occupy the Al sublattice sites, thereby significantly increasing the APB energy. The elevated APB energy increases the energy barrier for anti-phase boundary formation when dislocations shear through the ordered lattice. This implies that leading dislocations must overcome greater resistance to bow out and propagate, thereby increasing the macroscopic flow stress of the material [70]. Experimental results indicate that the APB energy of this alloy system is approximately 296 mJ/m^2 , in contrast to only about 110 mJ/m^2 for binary Ni_3Al [71]. The resulting additional interfacial energy substantially raises the critical stress required for dislocation nucleation and motion, endowing the $(\text{Ni},\text{Co},\text{Fe})_3(\text{Al},\text{Ti},\text{Fe})$ alloy with an exceptionally high strength level during tensile deformation.

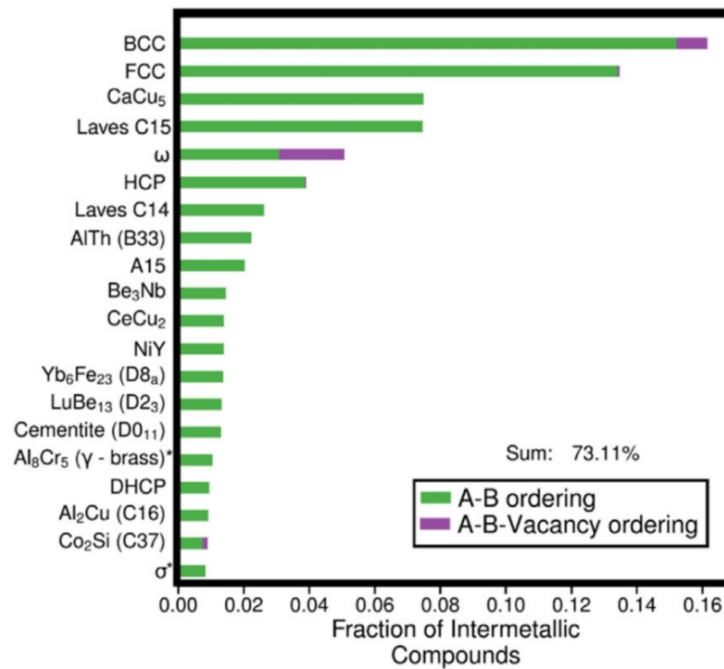


Fig. 2.10 Distribution of intermetallic compounds corresponding to the 20 most common parent crystal structures in binary metal alloys [67]-4

Meanwhile, the grain-boundary structural regulation effect brought about by sublattice high-entropy alloying can further enhance the room-temperature ductility. Studies have shown that multi-principal-element co-segregation can induce the formation of a nanoscale disordered layer near grain boundaries, which effectively suppresses intergranular fracture. As shown in Fig. 2.12, Fe, Co, and B exhibit pronounced segregation near grain boundaries. This compositional segregation reduces the stability of the L1_2 ordered structure, inducing the formation of an FCC-type solid solution at the grain boundaries. The formation of the FCC phase

effectively promotes dislocation glide and coordinated deformation, alleviates local stress concentration caused by dislocation pile-up, and ultimately prevents premature intergranular fracture [72]. Furthermore, constructing a dual-phase microstructure through compositional design can also facilitate the synergistic improvement of room-temperature strength and ductility in $L1_2$ -type high-entropy intermetallics. For instance, $Al_{0.25}FeCoNiV$ achieves a tensile strength of approximately 1530 MPa and a ductility of about 20% through the formation of a fine-grained $L1_2/B2$ dual-phase microstructure [73].

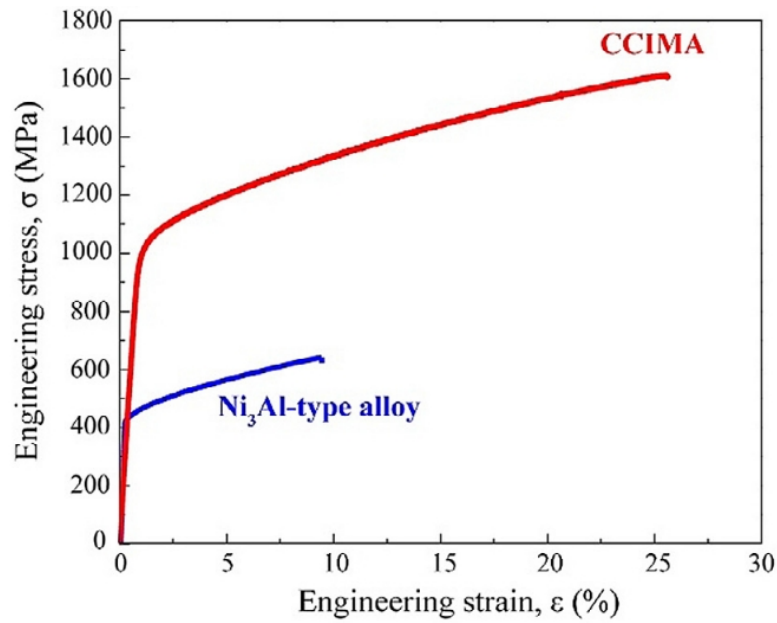


Fig. 2.11 Room-temperature tensile properties of the $L1_2$ -type high-entropy intermetallic $Ni_{43.9}Co_{22.4}Fe_{8.8}Al_{10.7}Ti_{11.7}B_{2.5}$ with a disordered grain-boundary nanolayer [13]-169

2.3.2 High-temperature microstructural and performance stability

Conventional $L1_2$ -type Ni_3Al has been widely employed in high-temperature structural material research owing to its low atomic diffusivity and excellent high-temperature strength [74]. However, certain $L1_2$ systems are metastable and tend to decompose during prolonged high-temperature service, leading to microstructural coarsening and degradation of mechanical properties [75]. In contrast, $L1_2$ -type high-entropy intermetallics effectively enhance the thermal stability of the microstructure through sublattice high-entropy alloying, which is beneficial for advancing their applications at elevated temperature. For example, a recently developed $(Co,Ni)_3(Al,W,Ti,Ta)$ -type high-entropy intermetallic, with a specific

composition of $\text{Co}_{46.9}\text{Ni}_{30}\text{Al}_{11}\text{W}_{5.5}\text{Ti}_4\text{Ta}_{2.5}\text{B}_{0.1}$ [76], exhibits excellent high-temperature phase stability with a solvus temperature as high as 1296 °C. In addition, this material displays a pronounced anomalous yield effect. When the deformation temperature is raised from 250 °C to 800 °C, its yield strength increases continuously, reaching a peak of approximately 700 MPa in the high-temperature regime. Moreover, the steady-state creep rate of this alloy is more than one order of magnitude lower than that of conventional Ni_3Al -based intermetallics, indicating superior creep resistance at elevated temperatures.

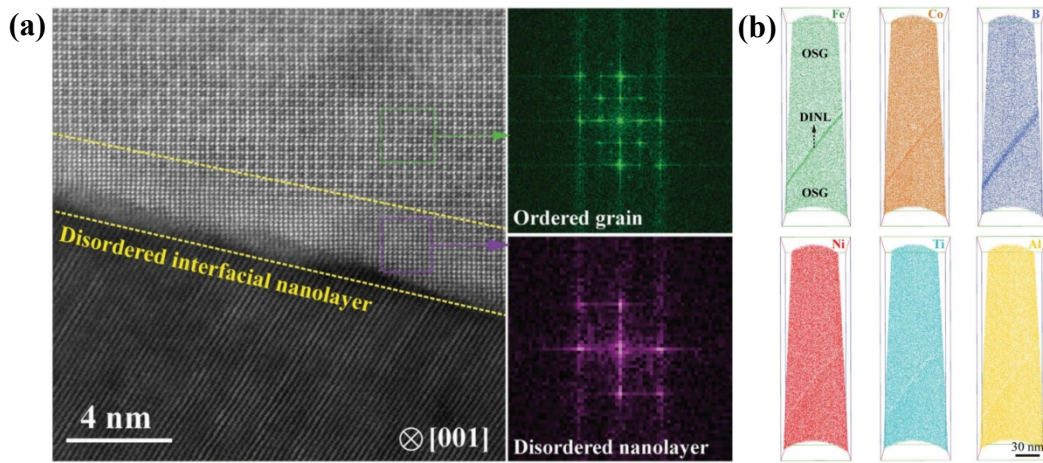


Fig. 2.12 Nanoscale disordering and multi-element synergistic segregation near grain boundaries in the $\text{Ni}_{43.9}\text{Co}_{22.4}\text{Fe}_{8.8}\text{Al}_{10.7}\text{Ti}_{11.7}\text{B}_{2.5}$ superlattice alloy [13]-167
(a) high-resolution image and the corresponding fast Fourier transform pattern showing the presence of a nanoscale-thick ultra-thin disordered layer at the grain boundary; (b) atom distribution map reconstructed from three-dimensional atom probe tomography, indicating the enrichment of multiple elements at the disordered interfacial nanolayer

Under high-temperature conditions, rapid grain coarsening constitutes one of the critical issues limiting the engineering application of polycrystalline materials. Studies have demonstrated that the L_{12} -type $\text{Ni}_{43.9}\text{Co}_{22.4}\text{Fe}_{8.8}\text{Al}_{10.7}\text{Ti}_{11.7}\text{B}_{2.5}$ alloy with a nanoscale disordered interface exhibits excellent resistance to grain coarsening at elevated temperatures, with virtually no significant grain growth observed after annealing at 1050 °C for 120 h, as shown in Fig. 2.13. The high-temperature stability originates primarily from the synergistic effects of multiple elements in the grain-boundary region, which increases the configurational entropy of the grain boundary and reduces the Gibbs free energy, thereby diminishing the driving force for grain coarsening [13]-170. Concurrently, the solubility difference between the grain boundary and the grain interior can retard solute diffusion and

suppress grain-boundary migration, while the local enrichment of elements at grain boundaries can further stabilize grain kinetics through the solute drag effect [77]. Furthermore, this alloy demonstrates excellent high-temperature softening resistance, with the microhardness at 800 °C decreasing only marginally from 417 ± 8 HV at room temperature to 392 ± 3 HV [43]-17.

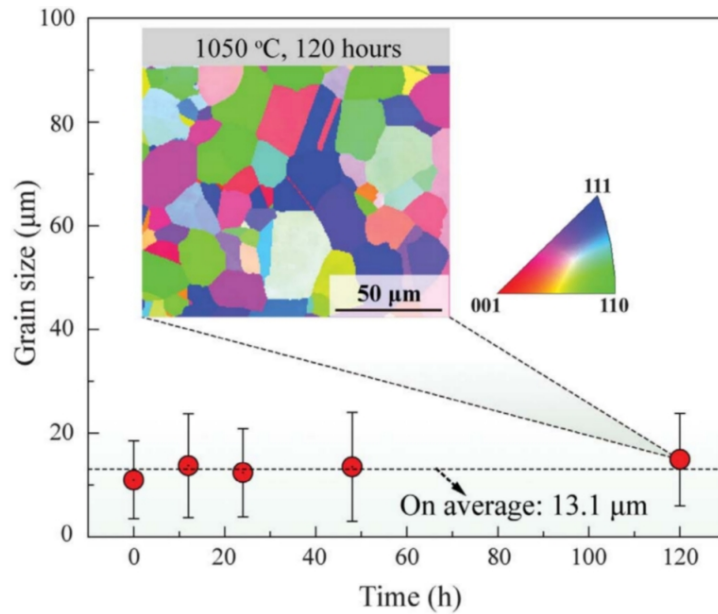


Fig. 2.13 Evolution of grain size during high-temperature treatment at 1050 °C with different holding times [78]

In summary, L1₂-type high-entropy intermetallics exhibit significant advantages in both room-temperature and high-temperature mechanical properties. Compared with disordered high-entropy alloys, they achieve higher strength owing to the ordered superlattice strengthening effect and elevated APB energy. Compared with conventional intermetallics, sublattice high-entropy alloying helps alleviate dislocation glide constraints, thereby enhancing ductility. Meanwhile, these materials also surpass conventional nickel-based superalloys in terms of high-temperature softening resistance and microstructural stability, maintaining a high strength level over a broad temperature range. Nevertheless, the room-temperature comprehensive mechanical properties of these alloys still offer further room for optimization, and the corresponding deformation mechanisms and strengthening–plasticizing mechanisms require in-depth elucidation. Moreover, research on their high-temperature mechanical properties remains relatively scarce, and systematic investigations combining fracture behavior with deformation mechanisms are needed.

2.4 Current status of heterostructured materials research

Microstructure is the core factor governing the mechanical properties of metallic materials. Conventional material design typically aims to obtain a homogeneous microstructure so as to ensure stable and reliable performance. However, continued exploration of deformation mechanisms has revealed that heterostructured systems built upon the synergistic deformation of soft and hard structural units can enhance the strength of materials while maintaining or even improving ductility, as illustrated in Fig. 2.14. Based on this, the present section first introduces the characteristics of heterostructured materials, then reviews the research progress of representative heterostructured material systems, and analyzes their microstructural features and property enhancement mechanisms, thereby providing a theoretical basis for the microstructural design and property optimization of high-entropy intermetallics.

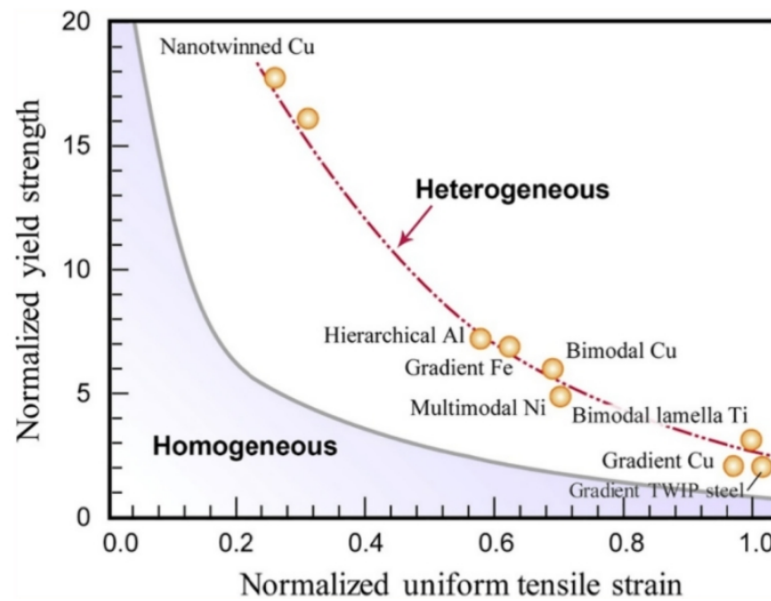


Fig. 2.14 Relationship between normalized yield strength and normalized uniform tensile strain of homogeneous materials and heterostructured materials [79]

2.4.1 Classification of heterostructured materials

Heterostructured materials represent a new class of material systems comprising regions with distinct mechanical or physical properties [80]. Heterostructures are widely prevalent in nature. For instance, biological materials such as bamboo, seashells, and bones are all composed of different structural units with significantly varying properties, as illustrated in Fig. 2.15. Through the synergistic interaction

between different structural regions, these natural materials achieve a concurrent optimization of high strength and high toughness while maintaining lightweight characteristics, demonstrating exceptional overall performance. Inspired by these structural design principles in nature, the concept of heterostructure design has been progressively introduced into the field of engineering metallic materials.

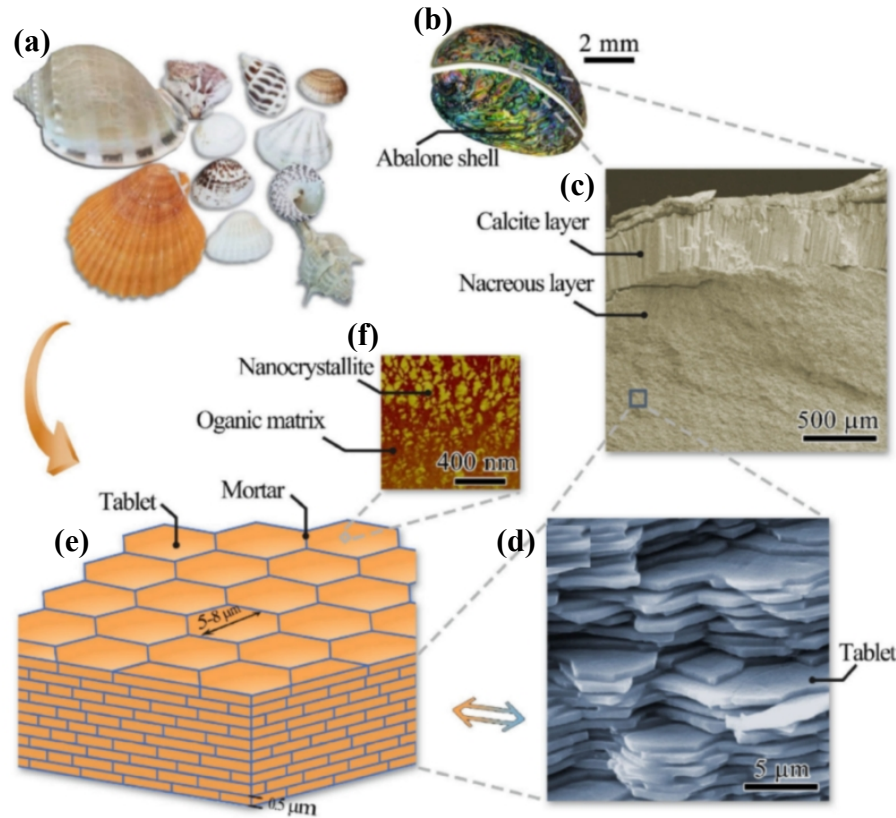


Fig. 2.15 Heterostructure of mollusk shells [80]-3

(a) mollusk shell; (b) abalone shell; (c) cross-section of the abalone shell, showing the outer hard calcite layer and the inner nacreous layer; (d) fracture surface of abalone nacre; (e) schematic illustration of the “brick-and-mortar” structure of the nacreous layer; (f) platelet structure of aragonite nanocrystals embedded in the organic matrix

It is generally accepted that materials can be defined as heterostructured when they contain heterogeneous regions with pronounced differences in mechanical or physical properties [80]-4. The coupling effect between different regions gives rise to a synergistic strengthening effect, enabling the overall performance of the material to surpass the predictions of the conventional rule of mixtures. In a broad sense, materials with non-uniform microstructures can all be regarded as heterostructured materials [81]. However, in the field of structural materials, research has primarily focused on material systems capable of generating a hetero-deformation induced (HDI) strengthening effect during deformation. From a

mechanical perspective, the essence of heterostructured materials lies in the existence of significant differences in flow stress among different structural regions. Under external loading, the soft zones preferentially undergo plastic deformation and accumulate geometrically necessary dislocations (GNDs) near the interfaces, giving rise to a back stress in the soft zones and a forward stress in the hard zones. The combined action of these stresses produces both HDI strengthening and HDI strain hardening effects, as schematically shown in Fig. 2.16. Among these, HDI strengthening contributes to enhancing the yield strength, while HDI strain hardening helps to maintain ductility, thereby enabling an excellent combination of mechanical properties [82].

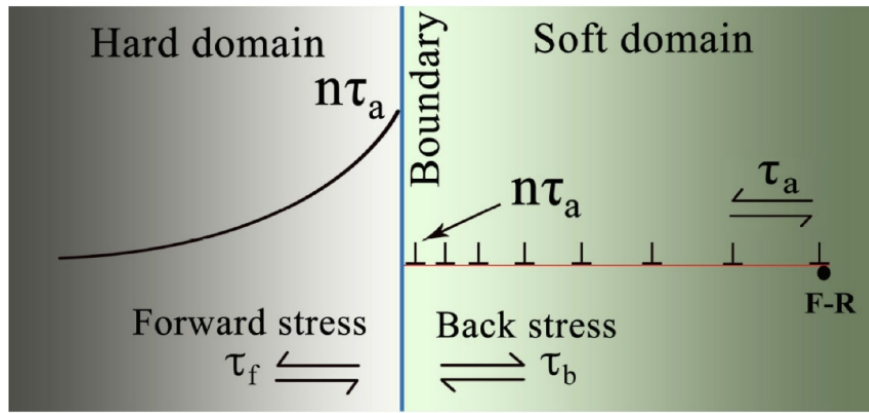


Fig. 2.16 Schematic diagram of geometrically necessary dislocation pile-up [83]

Based on the above definition, heterostructured materials can exhibit a wide range of microstructural morphologies, including heterogeneous laminated structure, bimodal grain structure, gradient structure, dual-phase structure, harmonic structure (core-shell structure), metal matrix composite, and multi-scale hierarchical structure [80]-5. Although these structures differ in morphology, their performance advantages fundamentally originate from the flow stress differences between structural regions and the resulting HDI effects. Among them, dual-phase core-shell structure materials constructed through the spatial combination of soft and hard phases are particularly outstanding in enhancing comprehensive mechanical properties and have become an important research direction for advanced structural materials in recent years. Accordingly, the following section will focus on the microstructural characteristics and mechanical property regulation mechanisms of dual-phase core-shell structure materials.

2.4.2 Effect of core–shell structure on mechanical properties

Core–shell structured materials belong to the harmonic structure class and represent a typical category of heterostructured systems. Their fundamental characteristic lies in the spatial combination of two types of structural units with significantly different mechanical properties—namely, soft and hard regions [84]. These materials typically exhibit a spatial encapsulation structure featuring a high-strength core region surrounded by a high-plasticity shell region. Alternatively, an inverse configuration in which the hard phase encloses the soft phase can also be realized, as schematically shown in Fig. 2.17. Owing to the pronounced differences in flow stress between different structural regions, heterogeneous deformation behavior is readily induced under external loading, thereby triggering the HDI effect. This enables a substantial enhancement in strength while maintaining good plastic deformability [85].

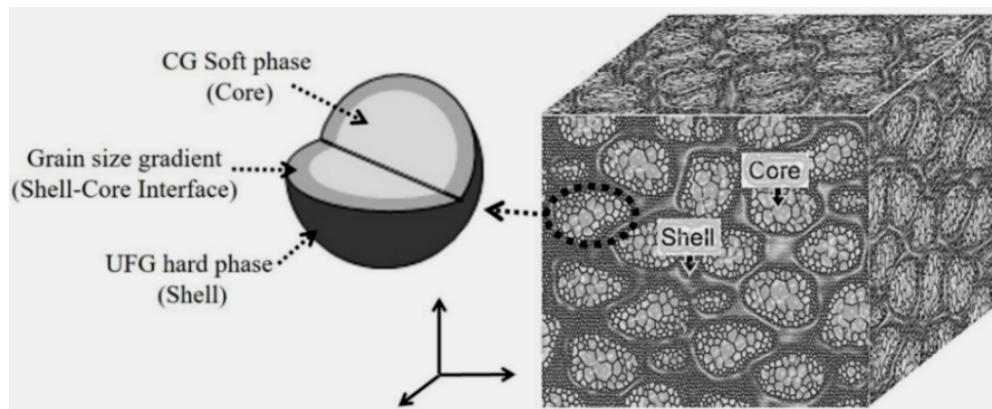


Fig. 2.17 Schematic diagram of the harmonic structure design concept [84]-4

In recent years, the core–shell structural design concept has been validated across a variety of metallic material systems. For instance, Xue et al. [86] investigated the formation mechanism and strengthening behavior of multilayer core–shell nanoprecipitates in Al–Li alloys and found that these alloys develop a core–shell architecture comprising Zr–Ti-enriched cores and Li-enriched shells.. First-principles calculations further indicated that this structure exhibits a lower nucleation energy barrier and higher thermal stability, enabling the as-cast Al–Li alloy to achieve a strength approaching 500 MPa. The core–shell structure also demonstrates promising application potential in high-specific-strength structural material systems. Wang et al. [87] successfully fabricated a nanocrystalline α -Ti core/Ti₂Cu+ β dual-phase shell structure through element alloying, quenching, and

thermomechanical processing. This dual-phase shell simultaneously enhances the thermodynamic stability of low-energy interfaces and introduces a kinetic dislocation-pinning effect, thereby achieving an excellent combination of room-temperature strength and ductility, along with significantly improved microstructural stability at elevated temperatures, as illustrated in Fig. 2.18.

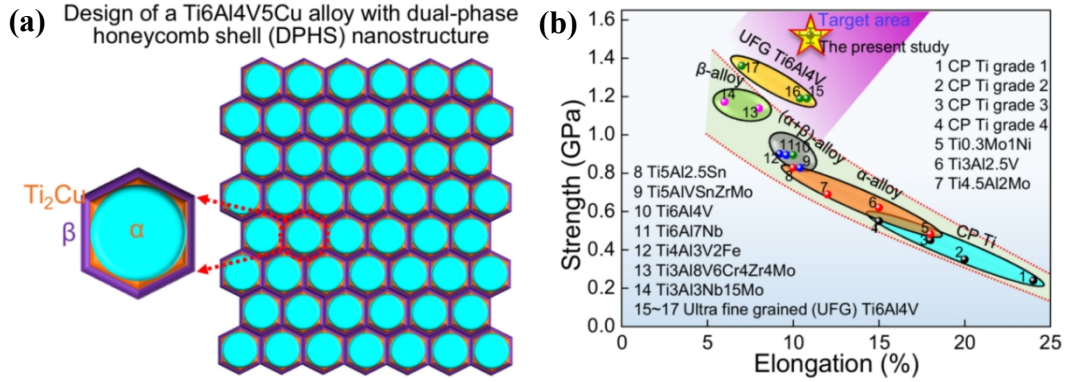


Fig. 2.18 Microstructure and mechanical properties of nanocrystalline Ti6Al4V5Cu alloy [87]-3

(a) schematic diagram of the dual-phase cellular shell nanostructure; (b) tensile strength versus elongation diagram

In high-temperature intermetallic systems, the core-shell structure exhibits excellent capabilities for microstructural and property regulation. For example, Yu et al. [88] obtained a core-shell microstructure with $(\alpha_2+\gamma)$ lamellar colonies as the core and α_2 matrix as the shell by controlling the lamellar decomposition behavior of β -solidified TiAl alloys. Hot compression test results demonstrated that this structure can reduce the anisotropy of the lamellar microstructure and optimize strain partitioning behavior, thereby significantly improving the hot workability and plastic deformation capability of the TiAl alloy. In the Ni-Co-Fe-Al-Ti-B multi-principal-element alloy system, Yang et al. [89] exhibited superior comprehensive mechanical properties through the introduction of a nanocrystalline core-shell structure. This alloy achieves a strength exceeding 2 GPa at room temperature while maintaining a plastic deformation capacity above 15%, and demonstrates microstructural stability up to approximately $0.78 T_m$ under elevated-temperature conditions, exhibiting remarkable strength-ductility synergy and thermal stability advantages. Further analysis revealed that these outstanding properties originate from ordering strengthening, Hall-Petch strengthening, and the dislocation storage and work hardening capacity induced by the core-shell interface, indicating that the core-shell structure retains excellent comprehensive property regulation capability

in multi-principal-element systems.

In summary, although the formation mechanisms and structural scales of core–shell structures vary across different material systems, the underlying origin of their performance enhancement fundamentally lies in the deformation coordination and load transfer effects dominated by the core–shell interfaces. By tailoring the property mismatch between the core and the shell, as well as the interfacial structural characteristics, synergistic optimization of strength enhancement, strain hardening capability, and ductility stability can be achieved.

2.5 Research gap

Based on the comprehensive review presented above, the following research gaps have been identified:

(1) Although L1₂-type high-entropy intermetallics have demonstrated promising potential for both room-temperature and high-temperature applications by combining ordered lattice strengthening with sublattice high-entropy alloying design, their room-temperature mechanical properties still require further improvement. The underlying mechanisms of room-temperature strengthening and ductilization remain incompletely understood, and the microstructural stability as well as mechanical performance at elevated temperatures have yet to be systematically investigated.

(2) Core–shell structured materials, as a typical category of heterostructured systems, have been extensively studied in various metallic material systems and have proven effective in achieving synergistic enhancement of strength and ductility at room temperature, as well as improved microstructural stability and mechanical properties at high temperatures. However, to date, no studies have reported the formation or utilization of core–shell structures in high-entropy intermetallic compounds.

(3) The integration of core–shell structural design with L1₂-type high-entropy intermetallics has not been explored. Given that core–shell structures offer a viable pathway for enhancing mechanical performance across a wide temperature range,

their introduction into L1₂-type HEIs may provide a new strategy to overcome the longstanding trade-off between strength and ductility in ordered intermetallic compounds. Nevertheless, experimental investigations concerning the mechanical properties of core-shell structured high-entropy intermetallics are completely lacking, making the actual effectiveness of this strategy uncertain.

2.6 Hypothesis, research objectives, and structure of thesis

Hypothesis:

In the present research, we propose the following hypotheses:

- (1) Compositional regulation, particularly through Co addition, can promote the formation of L1₂-FCC dual-phase core-shell structures in Ni-Co-Al-Ti-based L1₂-type high-entropy intermetallics, driven by solute partitioning behavior and phase stability modulation during solidification.
- (2) Further compositional optimization, such as Ta addition and adjustment of the Al/Ti ratio, can facilitate the development of multi-scale core-shell structures, thereby enabling hierarchical microstructural design.
- (3) The presence of multi-scale core-shell structures can simultaneously enhance room-temperature strength and ductility through heterogeneous deformation-induced strengthening and strain hardening, while also improving high-temperature microstructural stability and mechanical performance

Research objectives

This study takes Ni-Co-Al-Ti-based L1₂-type high-entropy intermetallics as the research subject, aiming to systematically investigate the influence of compositional regulation on the microstructure and mechanical properties. The major objectives are as follows:

- (1) To investigate the formation of core-shell structures and their effects on room-temperature mechanical properties. Using Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloys, thermodynamic and solidification calculations will be employed to study the effects

of Co addition on phase stability, solute partitioning at the solid–liquid interface, and interfacial stability. Combined with microstructural characterization, the formation of core–shell structures will be analyzed, and the underlying mechanism by which Co addition promotes the formation of L1₂–FCC dual-phase core–shell structures will be elucidated. Subsequently, room-temperature mechanical testing and deformation substructure analysis will be conducted to clarify the influence of core–shell structure formation on room-temperature mechanical properties.

(2) To promote the formation of multi-scale core–shell structures through compositional regulation. Based on alloys in which core–shell structures have already been formed, further compositional adjustments will be made to facilitate the development of multi-scale characteristics. Thermodynamic calculations and microstructural characterization will be systematically employed to analyze the effects of Ta addition and Al/Ti ratio increase on microstructural evolution, thereby clarifying the role of compositional variation in the formation of multi-scale core–shell structures. Additionally, differential thermal analysis and solidification path analysis will be conducted to investigate the nucleation and growth processes of L1₂ ordered cores at different scales, thus revealing the formation and transformation mechanisms of multi-scale core–shell structures.

(3) To investigate the room-temperature mechanical properties of multi-scale core–shell structured HEIs. Alloy samples with multi-scale core–shell structures obtained through compositional regulation will be selected for room-temperature mechanical testing to systematically examine the influence of multi-scale structural transformation on mechanical properties. Subsequently, TEM characterization will be employed to clarify the evolution of dislocation substructures during room-temperature tensile deformation, revealing the room-temperature deformation mechanisms of multi-scale core–shell structured HEIs. Combined with quantitative calculations, the room-temperature strengthening and ductilization mechanisms will be elucidated, and the fundamental origin of the excellent room-temperature mechanical properties will be analyzed from a microscopic perspective.

(4) To investigate the high-temperature mechanical properties of multi-scale core–shell structured HEIs. Alloy samples with multi-scale core–shell structures will be subjected to long-term isothermal aging at 800 °C to observe their microstructural

thermal stability. On this basis, tensile properties at 800 °C will be evaluated, with particular attention to intermediate-temperature embrittlement and their underlying mechanisms. By increasing the Cr content, the effects of compositional variation on microstructural evolution and the improvement of intermediate-temperature embrittlement will be investigated. Furthermore, wide-temperature-range tensile testing and dislocation substructure analysis will be performed on high-Cr-content alloys to reveal the temperature-dependent evolution of deformation mechanisms and the microscopic mechanism underlying the anomalous yield effect

The structure of thesis

This thesis is organized as follows:

Chapter 1 introduces the research background, reviews the development of high-entropy intermetallics, identifies the research gaps, and presents the research objectives and plan of this thesis.

Chapter 2 provides a comprehensive literature review on advanced structural materials, including ordered intermetallics, high-entropy alloys, L1₂-type high-entropy intermetallics, heterostructured materials, and core-shell structured materials, establishing the research background and significance.

Chapter 3 presents the experimental procedures, including material preparation, compositional design, characterization techniques, and mechanical testing methods employed throughout this study.

Chapter 4 investigates the formation of core-shell structures and their influence on room-temperature mechanical properties, focusing on the role of Co addition.

Chapter 5 addresses the promotion of multi-scale core-shell structures through further compositional regulation, emphasizing the effects of Ta addition and Al/Ti ratio adjustment.

Chapter 6 examines the room-temperature deformation mechanisms and strengthening-ductilization mechanisms of multi-scale core-shell structured HEIs.

Chapter 7 investigates the high-temperature microstructural stability and mechanical properties, with emphasis on intermediate-temperature embrittlement and the anomalous yield effect.

Chapter 8 summarizes the major conclusions of this study and provides perspectives for future work.

Chapter 3 Methodology and experimental materials

3.1 Experimental materials and sample preparation

(1) Selection of alloy composition system

This study focuses on the Ni-Co-Al-Ti-based L1₂-type high-entropy intermetallics, with Ta and Cr selected as sublattice high-entropy alloying elements. The microstructure and mechanical properties of the alloys are optimized through composition regulation. The composition system of this study starts from the single-phase L1₂-type high-entropy intermetallic Ni₇₅Al_{8.33}Si_{8.33}Ti_{8.34}. This alloy is based on the typical L1₂-type intermetallic Ni₃Al, and high-entropy is achieved by introducing equiatomic Si and Ti into the Al sublattice while strictly maintaining a stoichiometric ratio of 3:1 between the total atomic content of the Ni sublattice and the Al sublattice, thereby ensuring the formation of a single-phase L1₂ structure.

To improve the ductility of the alloy, Co is added to the Ni₅₀Co₂₅Al_{8.33}Si_{8.33}Ti_{8.34} alloy. Previous studies have shown that Co can stabilize the FCC phase in multi-principal-element alloys and tends to occupy the Ni sublattice [90]. The softer FCC disordered phase can form a highly coherent phase interface with the L1₂ ordered phase to stabilize the microstructure, which is beneficial for enhancing the room-temperature ductility of the material. To this end, sublattice high-entropy alloying with Co is performed on the alloy while maintaining the 3:1 stoichiometric ratio, and the microstructural evolution and property variations of the Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} ($x=0, 5, 25, 37.5$) series alloys are investigated. The results show that the Ni₅₀Co₂₅Al_{8.33}Si_{8.33}Ti_{8.34} alloy exhibits the optimal room-temperature ductility.

To further enhance the strength of the alloy, a small amount of the refractory element Ta is added on the basis of Ni₅₀Co₂₅Al_{8.33}Si_{8.33}Ti_{8.34}. Thermodynamic calculations indicate that the Ta addition should be controlled within 1.5 at.% to avoid the precipitation of detrimental brittle intermetallic phases. Meanwhile, microstructural analysis reveals that Si promotes the formation of Si- and Ti-rich intergranular secondary phases. Therefore, the addition of Si is eliminated. Under the constraints of maintaining the 3:1 stoichiometric ratio and an equiatomic Al/Ti

ratio, the optimized alloy composition is determined as $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$. Mechanical property tests demonstrate that this alloy achieves a significant enhancement in room-temperature strength with only a slight decrease in ductility.

To promote synergistic enhancement of strength and ductility, the Al/Ti ratio, which has a significant influence on room-temperature mechanical properties, is further regulated. While keeping the total content of Al and Ti constant, the critical addition amounts that avoid introducing secondary phases are determined through thermodynamic calculations, thereby establishing three alloy compositions with Al/Ti ratios of 8/6, 9/5, and 10/4, i.e., $\text{Ni}_{50}\text{Co}_{25}\text{Al}_8\text{Ti}_6\text{Ta}_{1.5}\text{Cr}_{9.5}$, $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$, and $\text{Ni}_{50}\text{Co}_{25}\text{Al}_{10}\text{Ti}_4\text{Ta}_{1.5}\text{Cr}_{9.5}$. Systematic microstructural characterization and mechanical property testing of the three alloys reveal that the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy possesses the most outstanding strength–ductility combination. Consequently, this alloy is selected for further analysis of its room-temperature deformation mechanisms and strengthening–plasticizing mechanisms.

To further enhance the high-temperature mechanical properties of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy, its Cr content is increased to 20 at.%, yielding an optimized alloy composition of $\text{Ni}_{43}\text{Co}_{21.5}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{20}$. Systematic microstructural characterization and wide-temperature-range tensile testing are conducted on this alloy to elucidate the improvement mechanism of intermediate-temperature embrittlement. A comparative analysis of the differences in mechanical properties and deformation mechanisms between room temperature and elevated temperatures is performed to reveal the operative mechanism of the anomalous yield effect. The alloy composition system selected for this study is illustrated in Fig. 3.1.

(2) Preparation and of raw materials

The elemental metallic raw materials used in the experiments include Ni, Co, Cr, Al, Ti, and Ta, all with a purity of no less than 99.99 wt.%. Among them, Ni, Co, and Cr are primarily in granular form, Al and Ti are in wire or small-block form, and Ta is in powder form. To prevent the introduction of oxygen impurities during melting from the oxide layers on the raw material surfaces, mechanical grinding of the surfaces of each metallic element is performed using a grinding wheel and

abrasive paper before weighing to remove surface oxide scales and contamination layers. Subsequently, the raw materials are weighed according to the designed nominal alloy compositions using a precision electronic balance, with the weighing error controlled within ± 0.005 g. After weighing, each element is stored in clean sealed bags to prevent environmental contamination and oxidation.

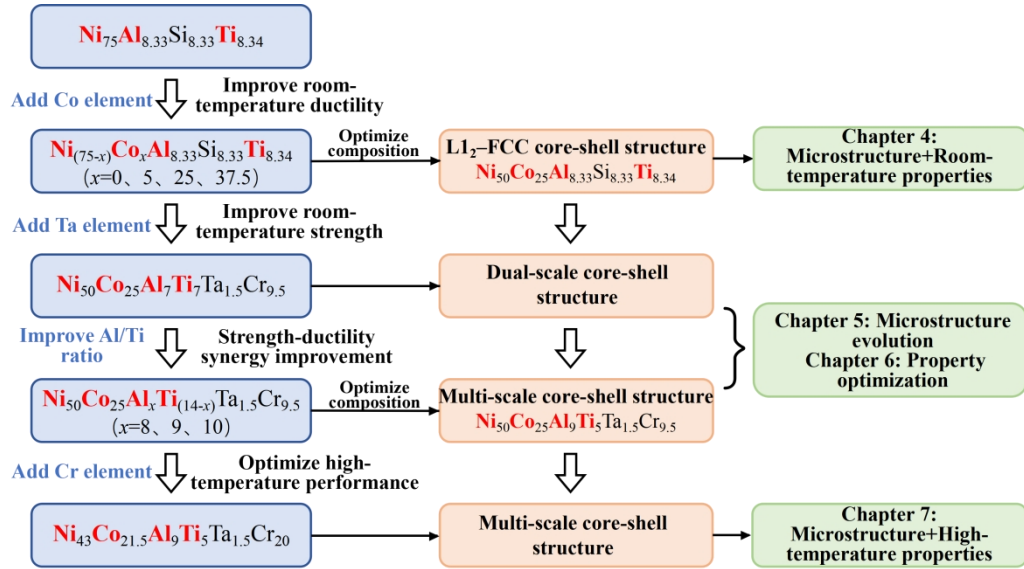


Fig. 3.1 Schematic diagram of the alloy composition system

(3) Vacuum Arc Melting

All alloy ingots used in the experiments were prepared by high-vacuum non-consumable arc melting furnace. According to the nominal composition, the raw materials were weighed and placed in the water-cooled copper crucible, with low-melting-point elements positioned at the bottom and high-melting-point elements at the top, so as to minimize volatilization loss of low-melting-point elements and improve the uniformity of overall melting during the melting process.

Prior to melting, the furnace chamber was pre-evacuated by a mechanical pump. After the vacuum level reached below 10 Pa, the pumping system was switched to a molecular pump to continue evacuation until a vacuum level higher than 5×10^{-3} Pa was achieved. Subsequently, high-purity argon gas (purity $\geq 99.999\%$) was backfilled into the chamber to a pressure of approximately 0.04–0.05 MPa. To minimize the residual oxygen content in the chamber, the above evacuation and argon backfilling cycle was repeated 2–3 times. After the gas purging procedure,

melting was initiated with an arc ignition current of 60–80 A. A pure titanium ingot placed in the crucible was pre-melted for about 1–2 minutes to absorb residual oxygen and improve the purity of the furnace atmosphere. The melting current was then increased to 200–300 A to melt the alloy raw materials. To ensure compositional homogeneity, each ingot was flipped over using a manipulator after each melting cycle, and the melting process was repeated 5–6 times. Finally, as-cast high-entropy intermetallic button ingots were obtained, with a weight of approximately 350 g per ingot. All specimens used for subsequent microstructural observation and mechanical property testing were taken from the central region of the arc-melted button ingots.

3.2 Microstructural characterization

(1) X-ray diffraction (XRD)

To analyze the phase constitution and crystal structure characteristics of L1₂-type high-entropy intermetallic samples, an X-ray diffractometer was employed for phase characterization and structural refinement analysis.

XRD specimens were prepared from the as-cast alloy ingot by wire electrical discharge machining, with dimensions of approximately 10 mm×10 mm×2 mm. The specimen surfaces were sequentially ground using SiC abrasive papers with grit sizes of 400#, 800#, 1500#, and 2000# to remove the surface oxide layer and the deformation layer introduced during machining. After grinding, the specimens were ultrasonically cleaned in anhydrous ethanol for approximately 10 min, dried, and then used for testing. XRD measurements were performed using Cu K α radiation ($\lambda=1.5406$ Å). The operating voltage was 20–40 kV, the operating current was 20–40 mA, the scanning range was $2\theta=20$ – 100° , the scanning step size was 0.02° , and the scanning rate was 0.5 – $10^\circ/\text{min}$.

The acquired data were subjected to phase identification using Jade software in conjunction with PDF standard reference cards. Subsequently, Rietveld refinement analysis was performed using MAUD software to obtain the lattice constant, order parameter, and related crystal structure parameters. Finally, Origin software was employed for pattern plotting and data processing.

(2) Scanning electron microscope (SEM)

Scanning electron microscopy was employed to observe the microstructural morphology and tensile fracture characteristics of the alloys, combined with energy dispersive spectroscopy (EDS) for analyzing elemental distribution features.

SEM specimens were prepared from the as-cast alloy ingot by wire electrical discharge machining, with dimensions of approximately 10 mm×10 mm×6 mm. The specimen surfaces were sequentially ground using SiC abrasive papers with grit sizes of 240#, 600#, 1200#, 2000#, and 3000#, with the grinding direction at each step oriented perpendicular to the previous one to effectively eliminate scratches. Subsequently, mechanical polishing was performed using diamond suspensions with particle sizes of 3 μm and 1 μm to achieve a mirror-like surface finish. To remove the surface strain layer introduced by mechanical preparation and to enhance microstructural contrast, the polished specimens were subjected to electrolytic polishing followed by electrolytic etching. The electrolytic polishing solution was prepared by mixing C₂H₅OH and HClO₄ at a volume ratio of approximately 90% to 10%, and polishing was conducted at 30 V for approximately 20 s to eliminate fine scratches on the specimen surface. Subsequently, the specimens were electrolytically etched in a mixed solution of 170 mL H₃PO₄+10 mL H₂SO₄+15 g CrO₃ at 5 V for approximately 5 s to remove the FCC phase and expose the L1₂ phase. After etching, the specimens were thoroughly rinsed with deionized water, ultrasonically cleaned in anhydrous ethanol for approximately 10 min, dried, and then sputter-coated with a conductive gold layer.

(3) Electron backscatter diffraction (EBSD)

Electron backscatter diffraction was employed to characterize and analyze the crystallographic orientation distribution, grain boundary structure characteristics, and local plastic deformation information of the specimens, with the aim of revealing the coordinated deformation mechanism and load transfer mechanism in heterogeneous structures.

EBSD test specimens were prepared from the as-cast alloy ingot by wire electrical discharge machining, with dimensions of approximately 10 mm×10 mm×6 mm.

After sequential mechanical grinding and fine polishing, the specimens were further subjected to electrolytic polishing to remove the surface strain layer introduced during preparation, thereby enabling high-quality diffraction patterns. After polishing, the specimens were ultrasonically cleaned in anhydrous ethanol and dried for subsequent use. EBSD measurements were performed using an Oxford EBSD detector system mounted on a field-emission scanning electron microscope platform. The accelerating voltage was 20 kV, and the scanning step size was selected as 0.2–0.5 μm depending on the microstructural scale.

The acquired data were post-processed using AZtecCrystal software. Based on the EBSD results, inverse pole figures (IPF) were obtained to characterize the grain orientation distribution; the kernel average misorientation (KAM) was calculated to reflect the local orientation gradient within individual grains; the grain boundary misorientation angle distribution was statistically analyzed to determine the proportions of high-angle and low-angle grain boundaries; and the Schmid factor distribution was calculated under a prescribed loading direction to evaluate the magnitude of resolved shear stress on specific slip systems and their potential for activation.

(4) Transmission electron microscope (TEM)

Transmission electron microscopy was employed to analyze nanoscale microstructural features and dislocation substructures.

TEM test specimens were prepared from the as-cast alloy ingot by wire electrical discharge machining, with dimensions of approximately 10 mm×10 mm×1 mm. The specimens were mechanically thinned to a thickness of approximately 40 μm by sequential grinding. Disc specimens with a diameter of approximately 3 mm were then punched out and further thinned by ion milling to obtain electron-transparent thin foil specimens. Ion milling was performed in a Gatan ion milling system to produce electron-transparent regions. After ion milling, the specimens were cleaned in anhydrous ethanol and dried for subsequent use.

TEM observations were mainly conducted using bright field (BF), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM),

selected area electron diffraction (SAED), and high-resolution transmission electron microscopy (HRTEM) modes for microstructural observation and dislocation structure analysis.

3.3 Mechanical property testing

(1) Tensile testing at room and elevated temperatures

Tensile tests were conducted to evaluate the room-temperature and high-temperature mechanical properties of the alloys.

Tensile specimens were prepared from the as-cast alloys by wire electrical discharge machining with a standard flat-sheet geometry, having a gauge length of approximately 15 mm, a width of approximately 2 mm, and a thickness of approximately 2 mm. To minimize the influence of machining-induced stresses and surface defects, the specimen surfaces were progressively ground with SiC abrasive papers until no visible scratches remained, after which the tests were performed.

The strain rate for both room-temperature and high-temperature tensile tests was set to $1 \times 10^{-3} \text{ s}^{-1}$. During testing, an extensometer was employed to measure the specimen deformation in real time, thereby improving the accuracy of strain measurement. At least three specimens were tested for each alloy to ensure the reliability of the results, and the yield strength was determined by the 0.2% offset method. The high-temperature tensile test temperature was set according to the research requirements, and the specimens were held at the target temperature for 5 min prior to tensile loading to ensure a stable temperature field.

(2) Compression testing at room and elevated temperatures

An electronic universal testing machine, Instron-5569, was used to conduct room-temperature compression performance tests on the alloy. The compression specimens were prepared from the as-cast alloy by wire cutting, in the shape of cylinders with dimensions of $\Phi 4 \text{ mm} \times 6 \text{ mm}$ (diameter $\times$ height). Both end faces were ground and polished to ensure parallelism and flatness, thereby reducing the influence of end friction on the test results. The strain rate for the room-temperature compression experiments was set at $1 \times 10^{-3} \text{ s}^{-1}$. To ensure the accuracy and

repeatability of the data, at least three specimens were tested for each alloy. The yield strength was determined by the 0.2% offset method, and the compressive strength and compressive plasticity were recorded and calculated from the stress–strain curves.

(3) Loading–unloading–reloading (LUR) tests

To quantitatively analyze the back stress evolution behavior and the heterogeneous deformation accommodation capability of the material during plastic deformation, LUR tensile tests were carried out.

The strain rate for LUR tests was set to $1 \times 10^{-3} \text{ s}^{-1}$. During the test, the specimen was first loaded to a true strain of approximately 0.5%, then unloaded to approximately 20 N under load control mode at an unloading rate of approximately $2000 \text{ N} \cdot \text{min}^{-1}$. Subsequently, the specimen was reloaded at the same strain rate to the next preset strain point, with the unloading–reloading cycle interval set to approximately 0.5% strain. Throughout the entire test, an extensometer was used to measure the specimen deformation in real time to ensure the accuracy of strain measurement during the unloading springback stage.

After the test, the stress–strain response curve of the material during the unloading–reloading process was obtained. Based on the unloading springback behavior and the variation in reloading yield stress, the back stress and effective stress of the material during plastic deformation were separated and analyzed. On this basis, the back stress evolution behavior at different strain stages was quantitatively characterized.

(4) Nanoindentation testing

Nanoindentation was employed to measure the local mechanical properties of different microstructural regions, in order to analyze the contribution of micro-scale structural units to the overall mechanical properties of the alloy.

Nanoindentation specimens were prepared from the as-cast alloys by wire electrical discharge machining, with dimensions of approximately $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$. To

ensure that the indentation positions within the microstructure could be accurately located under SEM after nanoindentation testing, thereby enabling a correlative analysis between local mechanical properties and microstructural features, the preparation procedure for nanoindentation specimens was kept consistent with that for SEM specimens. Nanoindentation testing was performed using a standard Berkovich triangular pyramid indenter with a tip radius of approximately 20 nm. Prior to testing, the instrument was calibrated using a fused silica standard specimen. During testing, the maximum indentation depth for each indent was controlled at approximately 500 nm, and the loading strain rate was approximately $5 \times 10^{-2} \text{ s}^{-1}$. At least six repeated indentations were performed in each test region, and the average value was taken as the final result.

After testing, the nanoindentation load–displacement (P-h) curve was obtained. The relevant data were processed using the instrument's built-in analysis software based on the Oliver-Pharr method to determine the nanohardness and elastic modulus of the material.

3.4 Thermodynamics and solidification analysis calculations

To provide theoretical support for the analysis of alloy composition regulation and core–shell structure formation mechanisms, JMatPro software (Sente Software Ltd.) was employed to perform thermodynamic phase diagram calculations and Scheil-Gulliver solidification calculations for Ni-Co-Al-Ti-based high-entropy intermetallics. The calculations were based on the built-in nickel-based superalloy thermodynamic database of the JMatPro software. By selecting the corresponding alloy system and calculation module in the software interface, inputting the nominal alloy composition, and setting the temperature range and solidification model, the software outputs information such as thermodynamic phase diagrams and the evolution of solute concentration in the liquid phase during solidification. Combining the calculation results with experimental microstructural characterization results enables thermodynamic phase stability analysis and solidification path analysis.

(1) Thermodynamic phase diagram calculations

Thermodynamic phase diagram calculations aim to elucidate the influence of alloy composition on phase constitution and stability, providing a theoretical basis for the analysis of the formation mechanism of multi-scale core-shell structures. These calculations are based on the CALPHAD (CALculation of PHase Diagrams) method, which uses the minimization of the total Gibbs free energy of the system as the criterion and solves the thermodynamic equilibrium equations of multi-component, multi-phase systems to obtain the phase constitution, phase fractions, and thermodynamic properties of each phase under different temperature and composition conditions.

Through thermodynamic phase diagram calculations, the stable temperature ranges of each phase in the alloy system at a given composition, the variation curves of the phase fractions of the L1₂ and FCC phases with temperature and their dissolution temperatures, as well as the formation temperature ranges and volume fraction variation trends of competing phases can be obtained. The relevant calculation results can be used to evaluate the thermodynamic stability of different phase structures, providing a thermodynamic basis for composition optimization design. Furthermore, the thermodynamic calculation results can be compared and validated with experimental characterization results from XRD, SEM, and TEM, thereby offering reliable theoretical support for elucidating the formation mechanism and transformation behavior of core-shell structures.

(2) Scheil-Gulliver solidification calculations

Solidification calculations aim to reveal the phase precipitation behavior and solute redistribution during the solidification process of the alloy, providing support for the analysis of the formation process of multi-scale core-shell structures from the perspective of the solidification path. The ingots used in this study were all prepared by arc melting. This process features a relatively high cooling rate, and the diffusion time of solute atoms within the solid phase during solidification is extremely short. Therefore, it can be approximately assumed that there is no solute diffusion in the solid phase. Based on this, the Scheil-Gulliver solidification model was selected for the calculations. This model assumes no solute diffusion in the solid phase and complete mixing of solute in the liquid phase, which is highly consistent with the actual solidification conditions of arc melting and can adequately describe the

solute redistribution behavior and the degree of microsegregation under these conditions.

Through Scheil-Gulliver solidification calculations, the precipitation sequence and phase transformation temperatures of the $L1_2$ and FCC phases during solidification, as well as the evolution trend of solute element concentrations in the liquid phase with solidification progress, can be obtained. The relevant calculation results can be used to analyze the microsegregation behavior of alloying elements, assess the formation tendency of each phase under solidification conditions, and reveal the formation and transformation behavior of the core-shell structure during solidification. Combining the calculation results with microstructural characterization results can provide theoretical guidance for the microstructural control of core-shell structure.

Chapter 4 Formation of core-shell structure and the effect on room-temperature mechanical property

4.1 Introduction

In the field of materials science, simultaneously achieving high strength and good ductility is one of the long-standing challenges in the development of structural materials [91]. Traditional strengthening mechanisms, including solid solution strengthening, precipitation strengthening, and grain refinement strengthening, generally increase the resistance to dislocation motion to enhance material strength, which inevitably leads to a decline in plastic deformation capacity [92-94]. In contrast, $L1_2$ -type high-entropy intermetallics possess relatively strong directional covalent/metallic bonds and inherit the high-strength characteristics of conventional intermetallics. Meanwhile, sublattice high-entropy alloying can modify the bonding type and reduce periodic voids at grain boundaries, thereby alleviating room-temperature brittleness to a certain extent [10]-13. Nevertheless, the room-temperature mechanical properties of this alloy system still fall short of meeting practical engineering requirements.

The design of high-entropy intermetallics typically takes an ordered crystal structure as the foundation and introduces multiple alloying elements to achieve high-entropy effect of specific sublattice. Taking the typical $L1_2$ -type intermetallic Ni_3Al as an example, applying sublattice high-entropy alloying to the corner site using Si and Ti yields a high-entropy intermetallic with a nominal composition of $Ni_{75}Al_{8.33}Si_{8.33}Ti_{8.34}$. In this alloy, the atomic contents of the face-centered sublattice and the corner sublattice satisfy the stoichiometric ratio of 3:1, thus favoring the formation of a stable $L1_2$ single-phase structure. Extensive studies have shown that alloys exhibiting a favorable strength-ductility synergy are generally not single-phase. In contrast, they consist of a combination of hard and soft phases, wherein the primary phase is typically separated or enveloped by the secondary phase [95]. Therefore, the FCC-phase-forming element Co, which has an atomic size similar to that of Ni and favorable crystallographic compatibility, was selected to induce sublattice high-entropy alloying on the face-centered lattice of the $Ni_{75}Al_{8.33}Si_{8.33}Ti_{8.34}$ alloy, with the aim of improving the room-temperature

plasticity of the L1₂-type high-entropy intermetallics [96].

This chapter takes the series of alloys Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} ($x = 0, 5, 25, 37.5$, hereinafter referred to as Co0, Co5, Co25, and Co37.5 alloys) as the research object and systematically analyzes the effect of composition regulation on microstructure and mechanical properties. First, the influence of Co addition on the phase stability and solidification behavior was examined through combined thermodynamic and solidification analyses. On this basis, a series of alloy ingots are prepared and subjected to microstructural characterization to clarify the evolution of the actual microstructure with Co content, with particular emphasis on the formation of the core-shell structure. Subsequently, the formation mechanism of the core-shell structure was elucidated through experimental compositional analysis. Finally, the effects of microstructural evolution and core-shell structure formation on the mechanical properties were elucidated through room-temperature mechanical testing and deformation microstructure characterization. The findings of this chapter can provide experimental basis and theoretical guidance for subsequent microstructural regulation and mechanical property optimization.

4.2 Effect of Co addition on Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloys

As an FCC-phase-forming element, Co can theoretically induce the formation of an FCC phase in multi-principal-element alloy systems. In addition, compositional regulation also affects the solidification behavior of the alloy, which in turn influences the subsequent microstructure and properties. Therefore, this section combines thermodynamic and solidification analyses to systematically examine the effect of Co addition on the Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloy system from three perspectives: phase constitution, solute partitioning behavior during solidification, and phase interface stability.

4.2.1 Co-addition-induced FCC phase formation

First, the effect of Co addition on the phase structure was analyzed from a thermodynamic perspective, based on the equilibrium phase fraction-temperature relationship of the Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloys. Figure 4.1 illustrates the evolution of phase fractions with temperature for this series of alloys under equilibrium conditions.

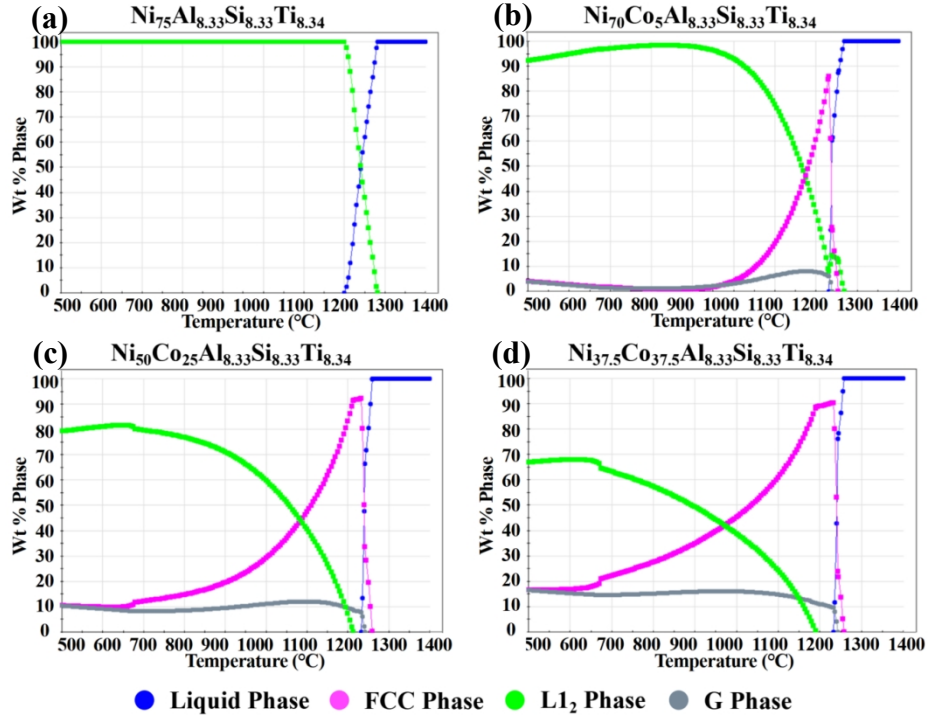


Fig. 4.1 Temperature dependence of equilibrium phase fraction in $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy
 (a) Co0 alloy; (b) Co5 alloy; (c) Co25 alloy; (d) Co37.5 alloy

For the Co0 alloy, the equilibrium phases are completely dominated by L_{12} , indicating that the alloy forms a single-phase L_{12} -type high-entropy intermetallic without Co addition. At a Co content of 5 at.%, the FCC phase emerges above the solidus temperature and remains stable within the solid-phase region, albeit with a relatively low fraction of approximately 5%. Meanwhile, a brittle intermetallic G-phase begins to appear. When the Co content is increased to 25 at.%, only the FCC phase exists above the solidus temperature. As the temperature decreases, the FCC phase continues to increase. As the temperature falls below the solidus, the L_{12} phase forms while the FCC phase is progressively consumed with increasing L_{12} content. Under this composition condition, the fractions of both the FCC and G phases are approximately 10%, while the L_{12} phase accounts for about 80%. When the Co content reaches 37.5 at.%, the formation temperature of the L_{12} phase further decreases, and the fractions of the FCC and G phases increase to approximately 15%, while the L_{12} phase fraction decreases to 70%. These results indicate that Co addition can introduce an FCC phase into this alloy system, and the FCC phase fraction increases with increasing Co content.

To investigate the underlying cause of Co addition promoting the formation of the

FCC phase, the Gibbs free energies of the L1₂ and FCC phases in the Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloys were further calculated. Figure 4.2 presents the temperature-dependent curves of the Gibbs free energy, where the relative positions and variation trends of the two phase curves directly reflect the differences in their thermodynamic stability. The results indicate that for the Co-free alloy, only the L1₂ free energy curve appears, suggesting that the FCC phase lacks the thermodynamic stability to exist independently, and the alloy remains in the single-phase L1₂ region. When the Co content increases to 5 at.%, both the L1₂ and FCC phase curves emerge simultaneously. However, the L1₂ phase consistently exhibits a lower free energy throughout the entire temperature range, indicating that despite the stable existence of the FCC phase, the microstructure remains dominated by the L1₂ phase. As the Co content is further increased to 25 at.%, the free-energy curves of the two phases tend to converge at elevated temperatures, with only the FCC curve persisting near the solidus temperature, demonstrating that the FCC phase obtains an independent thermodynamic stability window in the high-temperature region. When the Co content is increased to 37.5 at.%, the independent stability window of the FCC phase expands further, and its thermodynamic stability in the high-temperature region is continuously enhanced, which is consistent with the thermodynamic phase diagram calculation results.

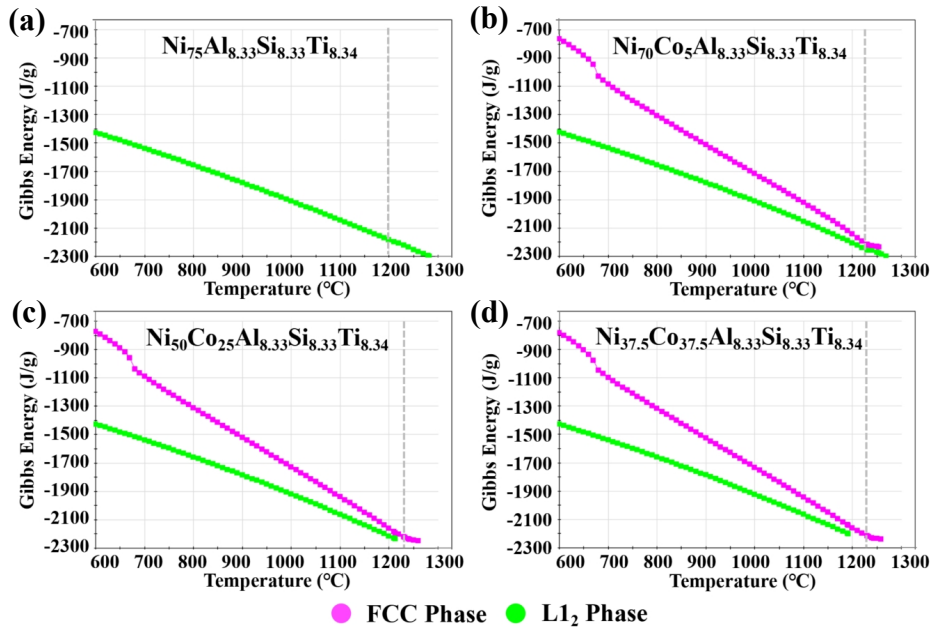


Fig. 4.2 Temperature dependence of the Gibbs free energy of the L1₂ and FCC phases in Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloy
 (a) Co0 alloy; (b) Co5 alloy; (c) Co25 alloy; (d) Co37.5 alloy

From the thermodynamic calculation results, it can be seen that Co addition enhances the thermodynamic stability of the FCC phase by modulating the competition between the Gibbs free energies of the L1₂ and FCC phases in the Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloy system. With increasing Co content, the alloy system gradually transforms from a single-phase L1₂-type high-entropy intermetallic into an L1₂/FCC dual-phase coexisting system.

4.2.2 Co-addition-promoted L1₂ phase precipitation

Considering that compositional regulation may affect the solidification behavior of the alloys, the solidification behavior of the Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloys was analyzed in this section using the Scheil-Gulliver solidification model. First, the influence of Co addition on the solidification path and primary phase formation was examined through the variation of solid fraction with temperature, with the results presented in Figure 4.3.

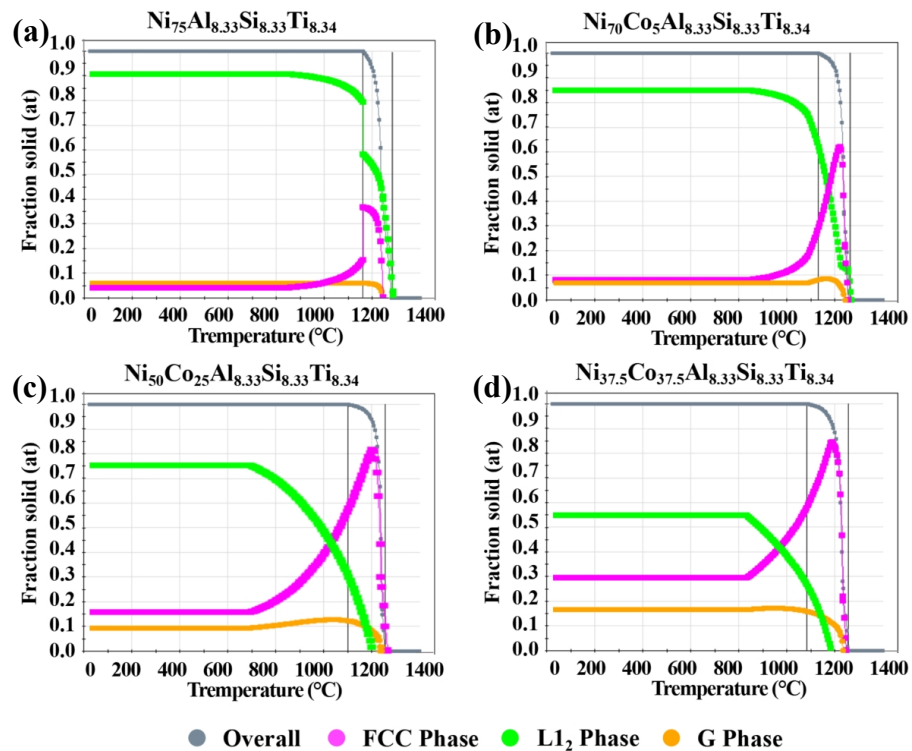


Fig. 4.3 Temperature dependence of solidification phase fraction in Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloy
(a) Co0 alloy; (b) Co5 alloy; (c) Co25 alloy; (d) Co37.5 alloy

In the Co-free alloy, the L1₂ phase precipitates from the onset of solidification and remains dominant, whereas the FCC phase emerges only transiently during the late

stage and then rapidly disappears, indicating that the solidification path involves direct formation of the $L1_2$ phase from the liquid. With the addition of 5 at.% Co, the FCC and $L1_2$ phases precipitate simultaneously from the onset of solidification, as evidenced by a rapid rise of the FCC fraction to a peak followed by a subsequent decline, accompanied by a corresponding increase in the $L1_2$ fraction. This change indicates the emergence of a solidification path in which the FCC phase forms directly from the liquid, while the origin of the $L1_2$ phase shifts from complete liquid solidification to partial precipitation in the solid state. When the Co content increases to 25 at.%, the FCC phase forms prior to the $L1_2$ phase and reaches a peak, and the solidification path completely transforms into one in which the FCC phase forms directly from the liquid, with the $L1_2$ phase forming entirely through solid-state precipitation. When the Co content is further increased to 37.5 at.%, the dominance of the FCC phase is further strengthened, while the $L1_2$ phase emerges only near the final stage of solidification, a trend that is consistent with the thermodynamic calculations. In summary, Co addition causes a transition in the solidification path of the alloy from $L1_2$ -dominant to FCC-dominant, altering the formation mechanism of the $L1_2$ phase.

On the basis of clarifying the solidification paths of the alloys with different Co contents, the effect of Co addition on the solidification microstructure was further analyzed from the perspective of liquid composition evolution. Figure 4.4 presents the concentration variations of each element in the liquid phase as a function of solid fraction during solidification. For the Co0 alloy, the Ni content remains almost constant throughout the solidification process, indicating a uniform distribution of Ni within the dendrites. The contents of Al and Ti in the liquid phase decrease continuously, suggesting that the formation of the primary phase involves the consumption of Al and Ti. In contrast, the Si content in the liquid phase increases continuously and becomes significantly enriched toward the end of solidification. This solidification mode, characterized by the continuous uptake of Al and Ti into the solid phase, is consistent with the compositional evolution associated with the direct formation of the $L1_2$ phase from the liquid. The solute partitioning behavior of the Co5 alloy during solidification is similar to that of the Co0 alloy. However, the partitioning curves of individual elements become more moderate, exhibiting reduced chemical gradients at the solid–liquid interface and a more homogeneous

chemical environment ahead of the solidification front. Nevertheless, the Co addition reduces the Ti content in the liquid phase, implying a higher Ti supersaturation in the primary phase and consequently enhancing the driving force for subsequent solid-state precipitation. In addition, Co exhibits a distribution pattern similar to that of Ni throughout the solidification process, with a smooth and stable profile, suggesting that Co is uniformly distributed within the dendrites.

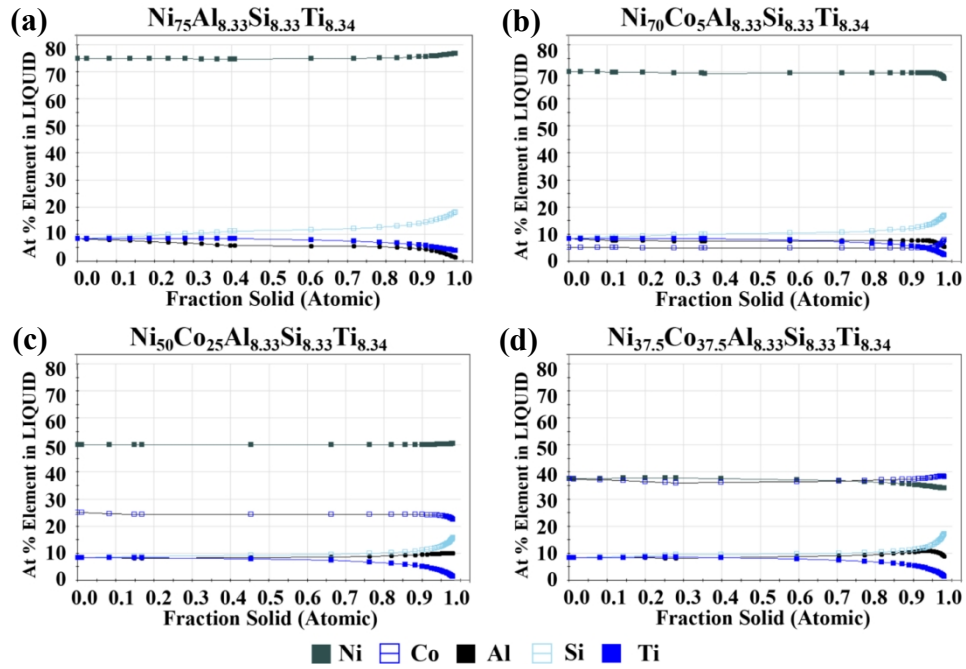


Fig. 4.4 Variation of solute concentration in the liquid phase as a function of solid fraction during solidification of $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy
(a) Co0 alloy; (b) Co5 alloy; (c) Co25 alloy; (d) Co37.5 alloy

When the Co content is increased to 25 at.%, the solute partitioning behavior undergoes a distinct change. The Ni and Co contents remain stable, while the Si content increases more gradually, further enhancing the chemical stability of the solidification front. Al no longer continuously enters the solid phase but tends toward a stable distribution, indicating that the primary phase structure transitions from L1_2 -dominant to FCC-dominant. Ti continuously partitions into the solid phase, exhibiting a more gradual decline yet a greater degree of depletion at the end, thereby providing a stronger driving force for the subsequent solid-state precipitation of the L1_2 phase. The solute partitioning behavior of the Co37.5 alloy is largely consistent with that of the Co25 alloy, except that a reverse fluctuation in Ni and Al contents occurs near the end of solidification. This phenomenon is related to the enhanced thermodynamic stability of the G-phase at high Co contents. Si is

significantly enriched at the end of solidification, promoting G-phase formation and consuming some Ni and Co, and together with the extreme depletion of Ti, jointly disrupts the chemical field at the end of solidification. Thus, appropriate Co addition can regulate the solute partitioning behavior, providing a compositional driving force for the subsequent solid-state precipitation of the L1₂ phase.

The temperature dependence of the solute partition coefficient k further reveals the nature of elemental partitioning behavior during solidification, with the results shown in Figure 4.5. For the Co0 alloy, the k values of all elements increase significantly near the liquidus temperature, where the differences among the elements are most pronounced. Among them, Al exhibits the fastest increase rate, followed by Ni and Ti, whereas Si shows the slowest increase, displaying a typical “strong partitioning” characteristic that is consistent with the significant solute redistribution observed in the liquid composition during the early stage of solidification..

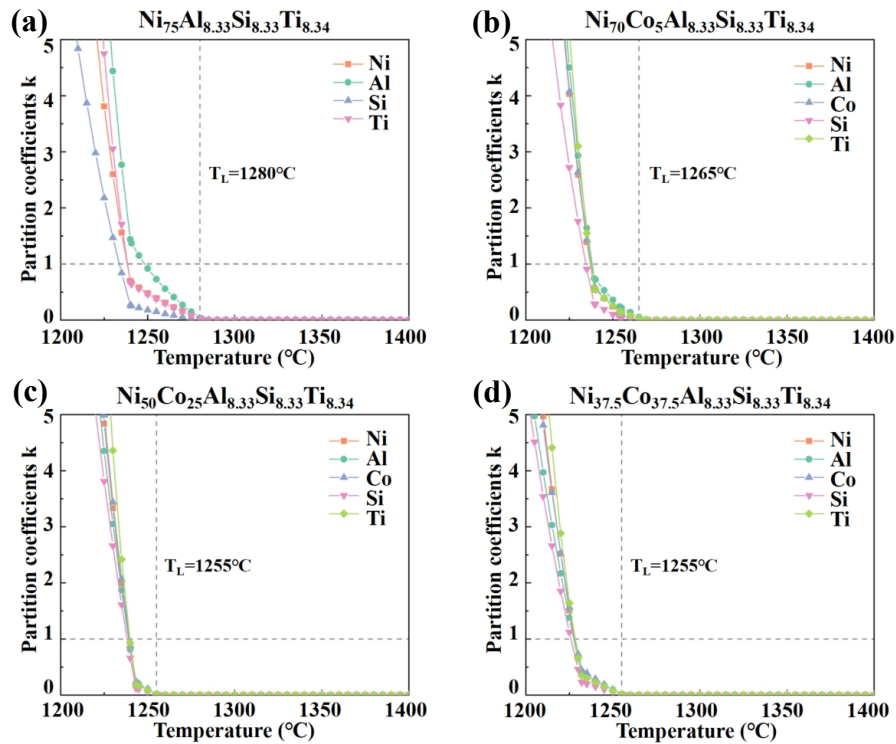


Fig. 4.5 Temperature dependence of solute partition coefficient k during solidification of $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy
(a) Co0 alloy; (b) Co5 alloy; (c) Co25 alloy; (d) Co37.5 alloy

When the Co content increases to 5 at.%, the k curves of all elements converge toward 1 as a whole, with a gentler increasing trend and reduced differences among

elements. This indicates that the driving force for solute partitioning is significantly weakened and the chemical gradient at the solidification front is effectively suppressed. However, the increase rate of Si still falls behind that of the other elements, corresponding to the Si enrichment observed at the late stage of solidification in the liquid phase. When the Co content is increased to 25 at.%, the k curves of all elements nearly overlap, indicating that solute partitioning is at its weakest, which is consistent with the gentle fluctuations observed in the liquid-phase composition evolution. When the Co content is further increased to 37.5 at.%, the overall k distribution is comparable to that of the Co25 alloy, except for a slight deviation near the end of solidification, which is consistent with the enhanced fluctuations in the liquid-phase composition at the end. Collectively, these results reveal that compositional homogenization and the tuning of precipitation driving force during solidification originate from the altered solute partition coefficients resulting from sublattice multi-principal-element alloying with Co.

From the above solidification calculation results, it is evident that Co addition significantly alters the solidification path of the alloy, transforming the primary solid phase from $L1_2$ to FCC. Meanwhile, Co addition regulates the solute partitioning behavior at the solid–liquid interface and increases the compositional supersaturation of the primary solid phase upon completion of solidification, thereby establishing favorable conditions for the subsequent solid-state precipitation of the $L1_2$ phase.

4.2.3 Co addition maintains $L1_2$ /FCC interface stability

In a dual-phase alloy system, the stability of the phase interface directly affects the microstructural stability and mechanical properties of the alloy. Therefore, it is necessary to examine the effect of Co addition on the structural stability of the $L1_2$ /FCC interface. The lattice misfit and interfacial energy are two core parameters that govern interface stability, which together determine whether two phases can be stably combined in a coherent or nearly coherent manner. Fig. 4.6 shows the temperature dependence of the lattice misfit between the $L1_2$ and FCC phases.

The calculation results show that the lattice misfit of all three Co-containing alloys at room temperature is maintained within the range of 0.5–1.0% (Table 4.1).

Previous studies have demonstrated that when the misfit is below 1%, the L1₂/FCC system typically forms a coherent or nearly coherent interface, which is favorable for promoting L1₂ phase nucleation and significantly suppressing precipitate growth and coarsening [97]. In this alloy system, although the misfit increases slightly with Co content, its absolute value remains extremely low, thereby providing the necessary interfacial conditions for coherent precipitation of the L1₂ phase within the FCC matrix and ensuring its long-term stability.

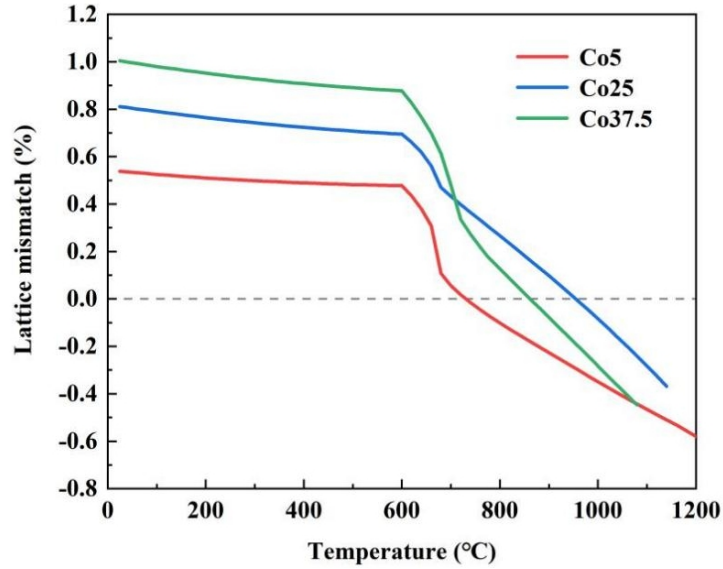


Fig. 4.6 Temperature dependence of the lattice misfit between the L1₂ and FCC phases in Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloys

Table 4.1 Interface stability parameters of Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloy at room temperature

	Shear modulus G (GPa)	Misfit δ (%)	Elastic interfacial energy γ_{elastic} (mJ·m ⁻²)
Co0	74.3	—	—
Co5	74.6	0.5	1.87
Co25	75.6	0.8	4.84
Co37.5	74.6	1	7.46

The interfacial energy further determines whether the L1₂ and FCC phases can coexist stably with a coherent interface. This interfacial energy arises primarily from the elastic strain energy induced by lattice misfit, which is concentrated in the interface region and constitutes the elastic interfacial energy. Therefore, it can be quantitatively characterized using the elastic interfacial energy, expressed as follows [98]:

$$\gamma_{\text{elastic}} = E_{\text{strain}} h \quad (4-1)$$

where γ_{elastic} — elastic interfacial energy ($\text{J}\cdot\text{m}^{-2}$);
 E_{strain} — elastic strain energy density ($\text{J}\cdot\text{m}^{-3}$);
 h — thickness of the misfit-strain-affected layer (m, typically taken as 2 nm).

Further, the approximate expression of the elastic strain energy density is [99]:

$$E_{\text{strain}} = \frac{1}{2} G \delta^2 \quad (4-2)$$

where G — shear modulus (Pa);
 δ — $\text{L1}_2/\text{FCC}$ two-phase misfit.

Combined with the temperature dependence curve of the shear modulus shown in Fig. 4.7, the elastic interfacial energies of the three Co-containing alloys at room temperature are obtained to be approximately $1.9\text{--}7.5 \text{ mJ}\cdot\text{m}^{-2}$ (Table 4.1). These values are significantly lower than the γ/γ' interfacial energy in Ni-based superalloys ($6\text{--}15 \text{ mJ}\cdot\text{m}^{-2}$) and far below the $10\text{--}50 \text{ mJ}\cdot\text{m}^{-2}$ level reported for most intermetallics [100,101]. The above comparison indicates that the $\text{L1}_2/\text{FCC}$ interface in this alloy system is in an extremely low-energy stable state, possessing the interfacial thermodynamic advantage for forming a stable dual-phase structure. Notably, although Co addition leads to a certain increase in elastic interfacial energy, its absolute value consistently remains within the low-energy range required for a stable coherent interface, indicating that Co addition does not compromise the microstructural stability of the dual-phase structure..

In summary, the effect of Co addition on the $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy is manifested in promoting the stable formation of the $\text{L1}_2/\text{FCC}$ dual-phase structure. First, Co enhances the thermodynamic stability of the FCC phase by modulating the competitive relationship between the Gibbs free energies of the L1_2 and FCC phases, thereby gradually transforming the alloy system from an L1_2 single-phase into $\text{L1}_2/\text{FCC}$ dual-phase coexistence. Second, Co addition alters the solidification path by switching the primary solid phase from L1_2 to FCC, while simultaneously enhancing the compositional supersaturation of the primary solid phase upon solidification completion through regulation of solute partitioning at the solid–

liquid interface, thereby providing a compositional driving force for the subsequent solid-state precipitation of the $L1_2$ phase. Furthermore, Co addition maintains a low lattice misfit and elastic interfacial energy between the $L1_2$ and FCC phases, offering favorable interfacial thermodynamic conditions for the stable coexistence of the dual-phase structure. Nevertheless, the above calculation results still require experimental verification in subsequent studies.

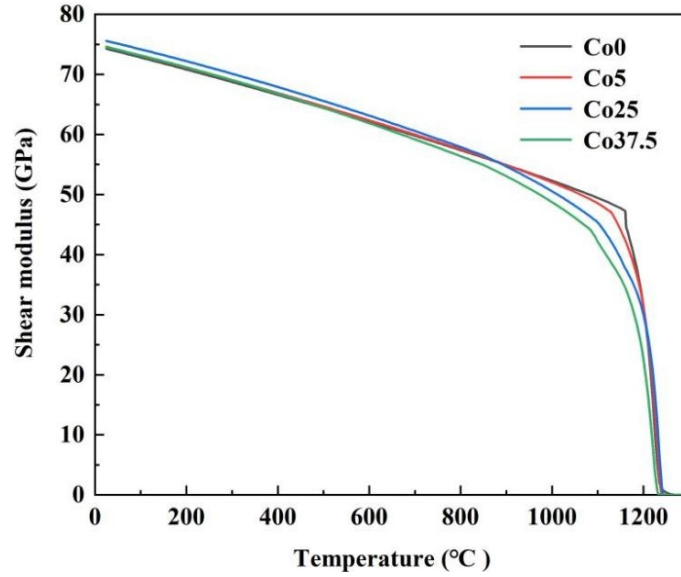


Fig. 4.7 Temperature dependence of shear modulus for $Ni_{(75-x)}Co_xAl_{8.33}Si_{8.33}Ti_{8.34}$ alloy

4.3 Characterization and formation mechanism analysis of the core-shell structure

The calculations in the previous section indicate that Co addition facilitates the stable formation of an $L1_2$ /FCC dual-phase structure in the $Ni_{(75-x)}Co_xAl_{8.33}Si_{8.33}Ti_{8.34}$ alloy. To verify this theoretical analysis, the microstructure of this series of alloys is investigated in this section. Given that the calculated equilibrium fraction of the $L1_2$ phase in the Co37.5 alloy at room temperature is less than 75%, three as-cast alloys with compositions of Co0, Co5, and Co25 are selected as the subjects of this investigation.

4.3.1 Microstructure of the $Ni_{(75-x)}Co_xAl_{8.33}Si_{8.33}Ti_{8.34}$ alloy

To investigate the influence of Co content variation on the phase constitution of the $Ni_{(75-x)}Co_xAl_{8.33}Si_{8.33}Ti_{8.34}$ alloy, X-ray diffraction analysis was first performed on the three as-cast alloy compositions, and the results are shown in Fig. 4.8. For the

Co0 alloy, only diffraction peaks corresponding to the $L1_2/FCC$ structure were detected. With the addition of Co, new diffraction peaks appeared in the patterns of the Co5 and Co25 alloys, corresponding to an unknown phase with an FCC crystal structure, whose PDF card number is 5-0628. Notably, distinct $(100)_{FCC}/(110)_{FCC}$ superlattice diffraction peaks were detected in the diffraction patterns of all alloys, indicating the presence of an ordered $L1_2$ phase in all three alloys.

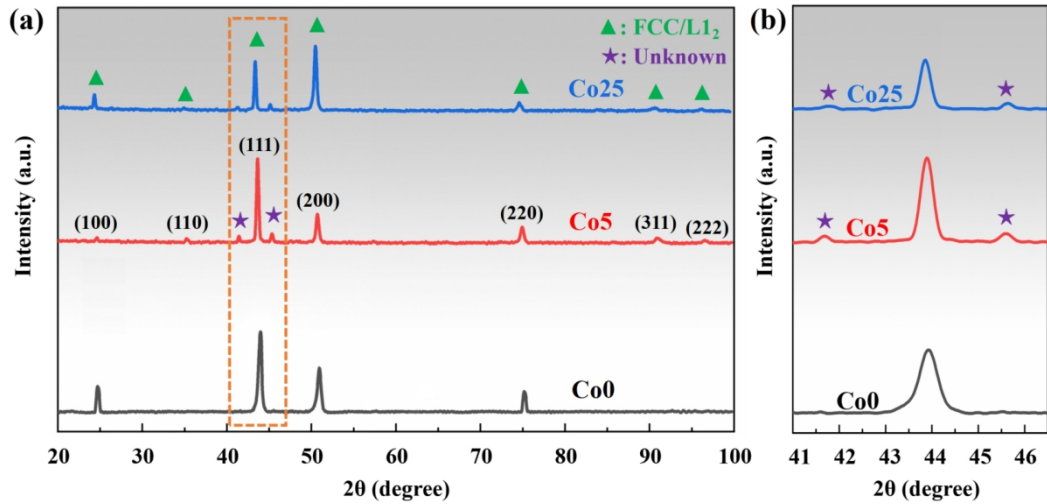


Fig. 4.8 XRD patterns of the three as-cast alloys
(a) full XRD spectra and phase identification; (b) fine-scan patterns of the (111)
crystal plane diffraction peak of the FCC phase

The fine XRD analysis of the (111) crystal plane diffraction peak of the FCC phase for the three as-cast alloys is shown in Fig. 4.8 (b). It can be seen that no diffraction peaks of the unknown phase exist in the Co0 alloy, further confirming that this alloy consists solely of the $L1_2/FCC$ dual phase. Meanwhile, a slight shift in the $(111)_{FCC}$ diffraction peak position with increasing Co content is observed, which is related to the lattice distortion effect induced by Co addition. The atomic radius of Co (0.126 nm) is slightly larger than that of Ni (0.124 nm). Therefore, as the Co content increases, the lattice constant of the FCC phase gradually increases, causing the $(111)_{FCC}$ diffraction peak to shift toward smaller 2θ angles. This conclusion is further corroborated by the XRD fitting results. Based on the $(111)_{FCC}$ diffraction peak analysis, the lattice constants of the FCC phase in the Co0, Co5, and Co25 alloys are 0.3598, 0.3602, and 0.3606 nm, respectively. In addition, according to the XRD fitting results of the 45° diffraction peak, the lattice constants of the unknown phase in the Co5 and Co25 alloys are determined to be 0.5342 and 0.5340 nm, respectively. The XRD analysis reveals that Co addition does not induce

significant changes in the crystal structure of the alloy system, and the alloy consistently retains the ordered crystal structure characteristics dominated by the $L1_2$ -type high-entropy intermetallic.

To reveal the microstructural evolution associated with increasing Co content, backscattered electron microscopy characterization was performed on the three alloys, and the results are shown in Fig. 4.9. As can be seen from Fig. 4.9 (a), the Co0 alloy exhibits a uniform solidification microstructure with relatively large grains of approximately 200 μm . Meanwhile, grain boundaries are clearly visible, and no secondary phase precipitation is observed within the grains. EDS analysis of the grain interior (results listed in Table 4.2) shows that its composition is consistent with the nominal composition. The magnified image of the grain interior further confirms that the grain consists of a single $L1_2$ phase. Combined with the XRD results, it can be confirmed that this alloy is a single-phase $L1_2$ -type high-entropy intermetallic $\text{Ni}_3(\text{Al},\text{Si},\text{Ti})$. As shown in Fig. 4.9 (b), the solidification microstructure of the Co5 alloy consists of grains with light gray contrast and irregular grain-boundary precipitates with dark gray contrast. The grain size is approximately 150 μm , and the volume fraction of grain-boundary precipitates is approximately 12%. From the magnified intragranular image in the upper right corner, it can be seen that no distinct secondary phase is present within the grains. The SEM-EDS analysis reveals that the grain interior composition is essentially consistent with the nominal composition. In contrast, the grain-boundary precipitates show significant enrichment in Si and Ti, along with a lower Al content and Ni and Co levels close to their nominal values. Combined with the XRD analysis, it can be inferred that the intragranular phase of the Co5 alloy has an $L1_2$ structure, while the grain-boundary phase is an unknown Si,Ti-rich phase.

The solidification microstructure of the Co25 alloy is similar to that of the Co5 alloy, as shown in Fig. 4.9 (c). Its average grain size is approximately 180 μm , and the volume fraction of grain-boundary precipitates is approximately 8%. The chemical composition of the grain interior remains close to the nominal composition, and the grain-boundary precipitates similarly exhibit Si and Ti enrichment and Al depletion, while Ni and Co are close to their nominal values. Notably, under high-magnification observation, a secondary phase with white contrast appears within

the grain interior, as shown in Fig. 4. 9 (d) and (e). This white secondary phase is extremely thin and separates the gray grains into numerous nearly spherical isolated domains, each composed of a gray grain core enveloped by the white secondary phase, exhibiting a core–shell structure morphology, as illustrated in Fig. 4.9 (f). Therefore, the grains of the Co25 alloy are actually composed of a large number of core–shell structural units, in which the average diameter of the gray cores is approximately 200 nm and the volume fraction is approximately 85%. Based on the XRD results, it is inferred that the white-contrast secondary phase should be a disordered FCC structure, and its precise structure requires confirmation by higher-resolution characterization.

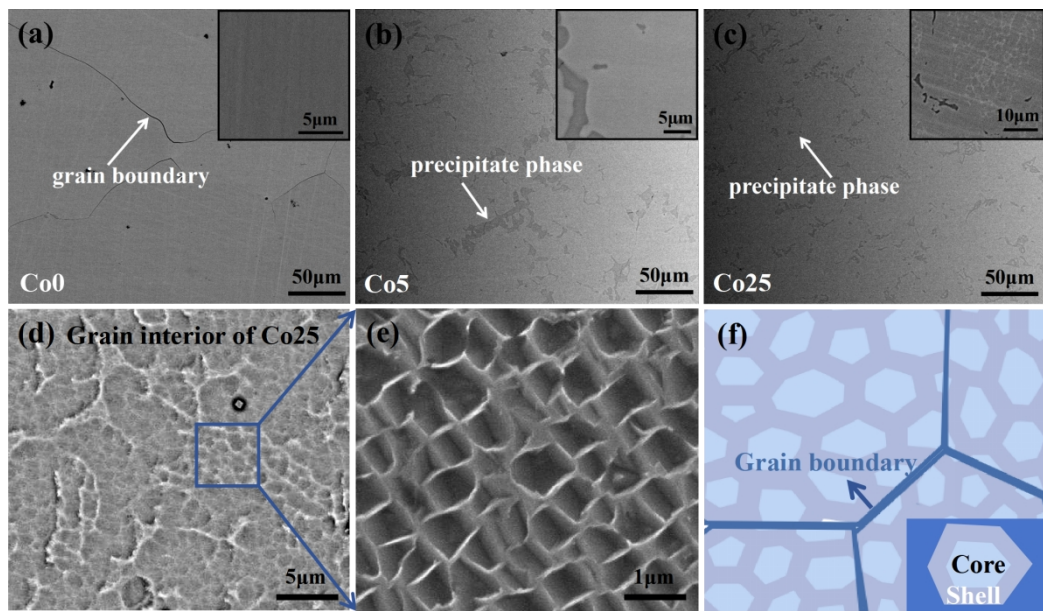


Fig. 4.9 Microstructure of the three as-cast alloys
(a) Co0 alloy; (b) Co5 alloy; (c) Co25 alloy; (d) high-magnification image of the grain interior of the Co25 alloy; (e) microstructural features of the core–shell structure within the grain interior; (f) schematic illustration of the core–shell structure

To further investigate the white-contrast secondary phase within the grain interior of the Co25 alloy and the resulting core–shell structure, TEM analysis was performed, and the results are presented in Fig. 4.10 (a). From the HAADF-STEM image, it can be observed that the white-contrast secondary phase is uniformly distributed at the nanoscale within the grain interior, interconnecting to form a network-like structure that isolates the other phase into independent nearly spherical domains, thus forming a dual-phase core–shell structure. The corresponding SAED analysis further clarifies the crystal structures of the two

phases. When the electron beam is incident along the $[\bar{1}\bar{1}0]$ zone axis, the white secondary phase exhibits a diffraction pattern characteristic of an FCC disordered solid solution, as shown in Fig. 4.10 (b). When the electron beam is incident along the $[101]$ zone axis, the other phase within the grain displays a diffraction pattern with superlattice spots characteristic of an $L1_2$ ordered structure, as shown in Fig. 4.10 (c). It can thus be concluded that, in the Co25 alloy, the nearly spherical $L1_2$ ordered phase is enveloped by a thin FCC disordered layer of only tens of nanometers in thickness, thereby forming a dual-phase core-shell structure characterized by an “ $L1_2$ ordered core-FCC disordered shell”. After this structure was proposed, similar “ordered-disordered” core-shell structures were observed in other material systems. For example, a study published in 《Nature Communications》 revealed that in nanocrystalline high-entropy alloys, FCC disordered shells were found at grain boundaries, enveloping $L1_2$ ordered nanograins and rendering each nanograin an independent “ordered-disordered” core-shell structural unit [89]-2. However, the disordered shells in that high-entropy alloy were mainly distributed at grain boundary positions, which is significantly different from the case in the present study, where FCC disordered shells form within the grain interior of the Co25 alloy.

Table 4.2 Chemical compositions of different microstructural constituents in the three as-cast alloys determined by SEM-EDS analysis

Alloy	Microstructural constituent	Ni	Co	Al	Si	Ti	Volume fraction
Co0	Nominal composition	75.00	—	8.33	8.33	8.34	—
	Grain	72.75	—	9.23	9.32	8.70	100%
Co5	Nominal composition	70.00	5.00	8.33	8.33	8.34	—
	Grain	70.54	4.54	9.52	8.66	6.74	88%
	Grain-boundary precipitate	41.32	22.35	1.96	17.42	16.95	12%
Co25	Nominal composition	50.00	25.00	8.33	8.33	8.34	—
	Grain	50.98	24.54	9.58	8.13	6.77	92%
	Grain-boundary precipitate	41.41	23.21	1.75	18.37	15.26	8%

The TEM-EDS elemental mapping results (Fig. 4.10 (d)) show that the white-contrast secondary phase is significantly enriched in Co, whereas Ni, Al, and Ti are mainly distributed in the nearly spherical other phase. Further HRTEM characterization reveals the thickness of the secondary phase and its interfacial structure with the other phase. From Fig. 4.11 (a), it can be observed that the average thickness of the FCC secondary phase is approximately 10 nm, and it maintains a good coherent relationship with the $L1_2$ phase, similar to the interfacial matching characteristics of the γ/γ' phase in nickel-based superalloys. In addition, Fast Fourier Transform (FFT) and Inverse Fast Fourier Transform (IFFT) were performed on both sides of the interface, and the results further verify the crystal structures of the two phases, as shown in Fig. 4.11 (b)–(e).

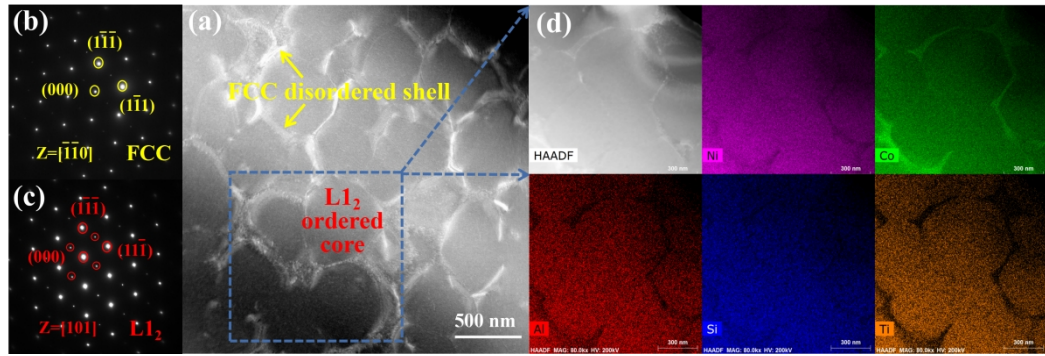


Fig. 4.10 TEM characterization of the intragranular structure in the Co25 alloy (a) high-angle annular dark-field image of the intragranular region; (b) selected-area electron diffraction pattern corresponding to the shell structure; (c) SAED pattern corresponding to the core structure; (d) elemental mapping showing the compositional distribution within the grain

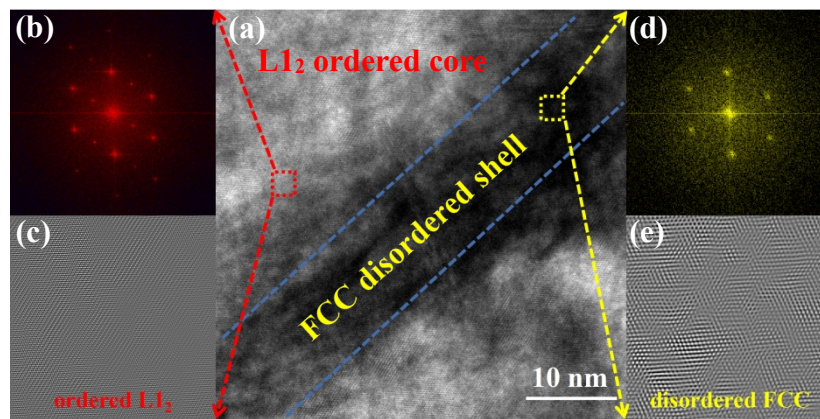


Fig. 4.11 TEM characterization of the interface between $L1_2$ core and FCC shell in the Co25 alloy (a) high-resolution image of the interface; (b) fast Fourier transform pattern of the $L1_2$ core; (c) inverse fast Fourier transform pattern of the $L1_2$ core; (d) fast Fourier transform pattern of the FCC shell; (e) inverse fast Fourier transform pattern of the FCC shell

Furthermore, the crystal structure of the grain boundary precipitates was further confirmed by TEM characterization. Fig. 4.12 presents the morphology of the precipitates, together with the corresponding SAED pattern and TEM-EDS elemental mapping results. As shown in Fig. 4.12 (b), when the incident electron beam was parallel to the [001] zone axis, the phase exhibited typical diffraction spots characteristic of an FCC crystal structure, consistent with the diffraction features of the “unknown phase” detected in the XRD analysis. Compositional analysis further revealed that the precipitate was significantly enriched in Si and Ti, while Al was markedly depleted, with Ni and Co contents close to the nominal composition, as illustrated in Fig. 4.12 (c). Combined with the SEM-EDS results, it can be confirmed that this precipitate corresponds to the FCC-type phase formed at grain boundaries. Based on the chemical composition and crystal structure characteristics of this grain boundary precipitate, it can be inferred to be the G phase reported in the literature (with a structural formula of $(\text{Ni,Co})_{16}\text{Ti}_6\text{Si}_7$) [102]. The G phase belongs to a typical class of Si-rich intermetallic compounds that commonly appear in high-Si alloy systems [103]. The fundamental reason for its formation lies in the strongly negative mixing enthalpy between Si and Ni, Co, and Ti, which drives these elements to segregate toward grain boundaries during solidification and subsequently combine with Si to form a stable intermetallic compound.

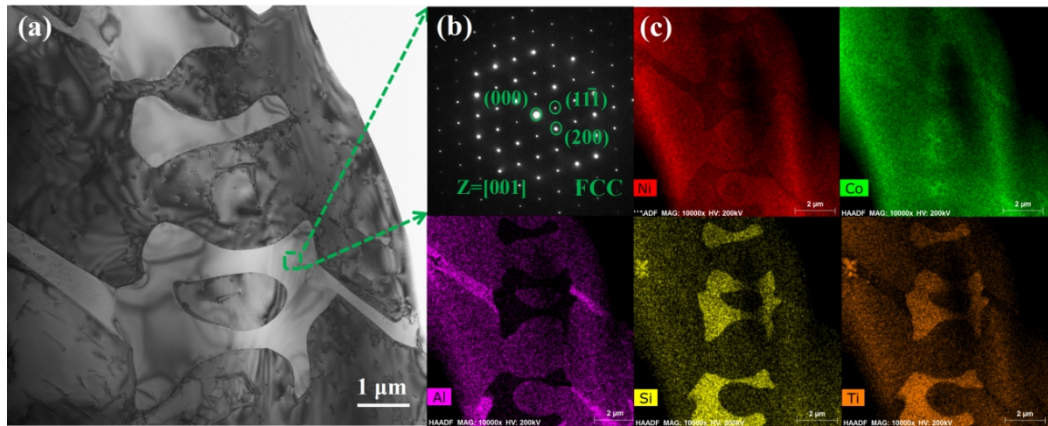


Fig. 4.12 TEM characterization of grain boundary precipitates in the Co25 alloy
(a) High-angle annular dark-field image of the precipitate; (b) selected-area electron diffraction pattern of the precipitate; (c) elemental mapping of the precipitate

The above microstructural analysis shows that the solidification microstructure evolves from a single $L1_2$ phase to an $L1_2$ /FCC dual-phase structure with increasing Co content. When the Co content reaches 25 at.%, a dual-phase core-shell structure characterized by an “ $L1_2$ ordered core–FCC disordered shell” is further developed.

These results not only confirm the reliability of the preceding computational analysis and clarify the effect of Co addition on solidification microstructure evolution and core-shell formation, but also establish a reasonable Co content window for achieving the L1₂-FCC dual-phase core-shell structure.

4.3.2 Mechanism of Co addition in promoting core-shell structure formation

To elucidate the mechanism by which Co addition promotes the formation of the L1₂-FCC dual-phase core-shell structure, the solidification microstructure evolution pathways of the Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloy under different Co content conditions were first analyzed by integrating thermodynamic calculations, microstructural characterization, and alloy compositional characteristics.

For the Co0 alloy, both thermodynamic calculations and microstructural characterization results confirmed it to be a single-phase L1₂ ordered structure, indicating that its solidification process follows the solidification pathway of a single-phase L1₂-type high-entropy intermetallic. Since both Si and Ti exhibit a strong tendency to preferentially occupy the Al sublattice, the intragranular region satisfies the stoichiometric relationship of Ni:(Al+Si+Ti)=3:1 under the nominal composition, thereby directly forming a single L1₂ ordered phase. For the Co5 alloy, theoretical calculations indicated that a small amount of FCC phase might form under equilibrium conditions. However, the actual microstructure revealed that the introduction of a small amount of Co was insufficient to drive FCC phase nucleation within the grains and maintain its stability. Therefore, the solidification process still tended to directly form the L1₂ ordered phase according to the nominal composition. From a compositional perspective, the partial substitution of Ni by Co resulted in an intragranular Ni:(Al+Si+Ti) ratio slightly below 3:1. According to the mixing enthalpy rule, the binding energies of Si and Ti with Ni are lower than those with Co. Consequently, Si and Ti preferentially combine with Ni to form the L1₂ phase during solidification. This elemental bonding preference caused small amounts of Si/Ti to be expelled to grain boundaries at the terminal stage of solidification, where they co-precipitated with a minor amount of Co to form Si- and Ti-rich grain boundary precipitates, i.e., the G phase. Ultimately, the actual microstructure of the Co5 alloy exhibited the coexistence of an intragranular L1₂ primary phase and grain

boundary G phase.

For the Co25 alloy, theoretical calculations indicated that the stability landscape of the L1₂/FCC two-phase system had changed, and the solidification process tended to preferentially form the FCC phase according to the nominal composition. Owing to the substantial substitution of Ni by Co, the composition of the primary FCC matrix exhibited a marked Ni:(Al+Si+Ti)<3:1 ratio. As the temperature decreased, L1₂ began to precipitate from the FCC phase. Similarly, according to the mixing enthalpy rule, Si and Ti preferentially combine with Ni, resulting in more Si and Ti being rejected to grain boundaries during solidification, where they form the G phase in conjunction with Co. However, the precipitation of the G phase was insufficient to fully consume the added Co. Therefore, a portion of Co was forced to remain within the grains, shifting the intragranular chemical composition to (Ni+Co):(Al+Si+Ti)>3:1. Under this condition, part of the Co atoms within the grains combined with Ni at the stoichiometric ratio of (Ni+Co):(Al+Si+Ti)=3:1 to form the L1₂ ordered core, while the remaining Co atoms, along with other principal elements, maintained the stability of the FCC disordered shell. Consequently, an L1₂–FCC dual-phase core–shell structure was formed in the actual microstructure of the Co25 alloy. Based on the thermodynamic calculation results, microstructural characterization, and alloy compositional characteristics, the influence of Co content on the solidification microstructure evolution pathway of the Ni_(75-x)Co_xAl_{8.33}Si_{8.33}Ti_{8.34} alloy is summarized in Fig. 4.13.

It can be reasonably inferred that a further increase in Co content would further enhance the thermodynamic stability of the FCC phase, and the solidification process would persistently tend to preferentially form the FCC matrix according to the nominal composition. However, owing to the extensive substitution of Ni atoms by Co, the intragranular (Ni+Co):(Al+Si+Ti) ratio during solidification would become significantly higher than 3:1. To approach the stoichiometric window required for L1₂ precipitation, more Co atoms would be retained in the matrix, forming the disordered FCC shell. In this case, the precipitation amount of the ordered L1₂ core is significantly restricted, as evidenced by the equilibrium phase diagram calculation of the Co37.5 alloy, which shows that the L1₂ phase content is below 70%.. Therefore, theoretically, when the Co addition exceeds 25 at.%, the

alloy would still exhibit an $L1_2$ –FCC dual-phase core–shell structure. Nevertheless, the resulting phase constitution would not satisfy the ordered phase content requirement for high-entropy intermetallics, owing to the low volume fraction of the $L1_2$ phase.

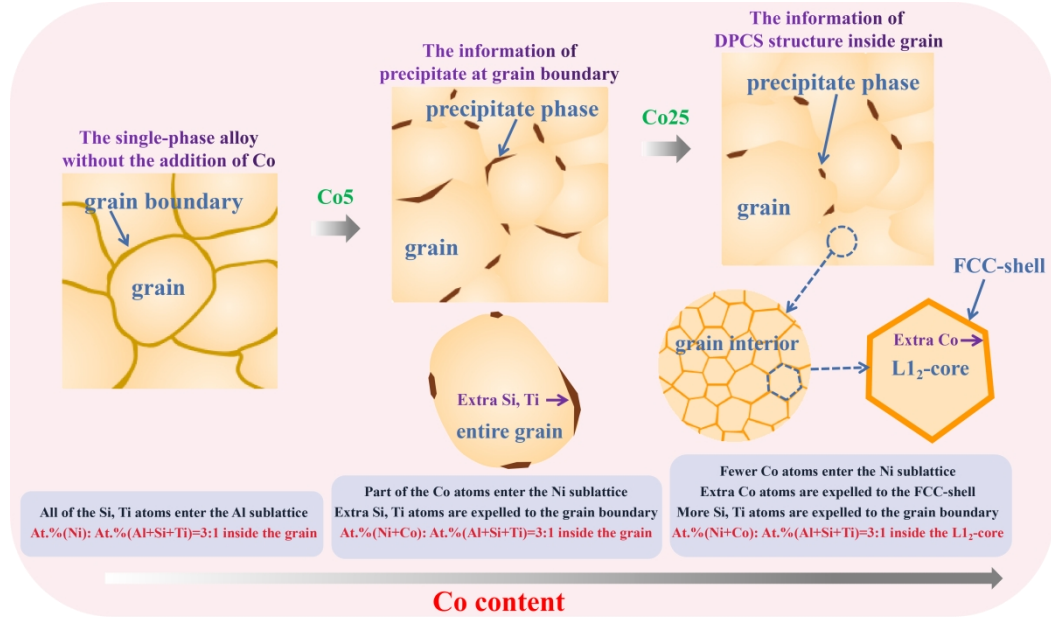


Fig. 4.13 Schematic illustration of the solidification microstructure evolution in $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy as a function of increasing Co content

In summary, the mechanism by which Co addition promotes the formation of the $L1_2$ –FCC dual-phase core–shell structure can be attributed to the combined effects of four factors: phase stability, solidification chemical field, interfacial stability, and elemental physicochemical characteristics. First, Co addition provides the phase-structural foundation for the $L1_2$ –FCC dual-phase core–shell structure by enhancing the thermodynamic stability of the FCC phase. In the Co-free alloy, the solid-phase region is entirely dominated by the $L1_2$ phase, and the FCC phase lacks independent stability. Consequently, the solidification process can only proceed along the pathway of directly forming a single-phase $L1_2$ intermetallic from the liquid. As the Co content increases, the stability temperature range of the FCC phase expands toward the lower-temperature side, and the alloy system gradually transitions from $L1_2$ single-phase dominance to $L1_2$ /FCC dual-phase coexistence. Thus, Co addition establishes the phase-structural foundation for the formation of the $L1_2$ –FCC dual-phase core–shell structure by modulating the free-energy competition between the $L1_2$ and FCC phases.

Second, Co addition establishes the compositional foundation for the subsequent solid-state precipitation process by regulating the solute partitioning behavior at the solid–liquid interface front during solidification. The introduction of Co shifts the solidification pathway from direct $L1_2$ formation in the liquid to primary FCC solidification, followed by $L1_2$ precipitation from the FCC phase. Concurrently, Co addition intensifies the depletion of Ti in the liquid phase at the end stage of solidification, imparting a stronger supersaturation driving force to the FCC primary solid phase and thereby promoting the subsequent solid-state precipitation of the $L1_2$ phase. It is thus evident that Co addition creates favorable solidification conditions for the formation of the $L1_2$ –FCC dual-phase core–shell structure by regulating the solidification pathway and solute partitioning behavior.

Finally, Co addition enables the stable existence of the core–shell structure by maintaining a low-energy state of the $L1_2$ /FCC interface. Co addition keeps the lattice misfit and interfacial elastic energy between the $L1_2$ /FCC two phases in this alloy system at a low level, thereby promoting the formation of a stable coherent interface between the two phases. From an interface science perspective, low misfit and low interfacial energy provide favorable conditions for the stable existence of $L1_2$ precipitates within the FCC matrix. On the one hand, the coherent interface can significantly reduce the nucleation energy barrier, promoting the precipitation of the $L1_2$ phase at fine scales. On the other hand, the low interfacial energy can suppress the coarsening behavior of the precipitates, maintaining the morphological stability of the core–shell structure. It can thus be concluded that Co addition provides stable interfacial conditions for the formation of the $L1_2$ –FCC dual-phase core–shell structure by maintaining a low interfacial energy.

Furthermore, the physicochemical characteristics of the Co element also constitute an important factor in promoting the formation of the $L1_2$ –FCC dual-phase core–shell structure. Co possesses an atomic radius close to that of Ni and a similar crystal structure, enabling it to achieve favorable solid solution behavior in the FCC lattice, thereby avoiding the introduction of additional lattice distortion or interfacial stress and facilitating the structural stability of the FCC matrix. Meanwhile, Co exhibits high compatibility with the $L1_2$ structure, as it can participate in the ordered site occupancy of the Ni sublattice without disrupting the long-range order

characteristics of the $L1_2$ phase. More importantly, Co plays the dual role of stabilizing the FCC phase and regulating $L1_2$ phase precipitation, preserving the precipitation potential of the $L1_2$ phase while promoting the formation of the FCC primary phase. This makes Co a key sublattice high-entropization alloying element that promotes the formation of the $L1_2$ –FCC dual-phase core–shell structure.

4.4 Effect of core–shell structure on room-temperature mechanical property

The experimental results in the preceding section demonstrated that, the microstructure of the $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy undergoes a systematic transformation with increasing Co content. When the Co addition reached 25 at.%, an $L1_2$ –FCC dual-phase core–shell structure was formed in the microstructure. To investigate the effect of this structure on the room-temperature mechanical properties of the alloy, this section employs systematic mechanical property testing to analyze the property characteristics corresponding to different microstructures, while also revealing the room-temperature deformation mechanism of the Co25 alloy possessing the core–shell structure, thereby providing reliable experimental evidence for optimizing the microstructure and properties of $L1_2$ -type high-entropy intermetallics.

4.4.1 Room-temperature mechanical property of the

$\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy

As an important indicator reflecting local deformation resistance, microhardness can reveal the strength differences corresponding to different phase structures at the microscopic scale. Therefore, this section first compares the microhardness of three $L1_2$ -type high-entropy intermetallics, with the results presented in Table 4.3 and the typical indentation morphologies shown in Fig. 4.14.

For the single-phase Co0 alloy, the indentations fell entirely within the grain interior, yielding a grain hardness of approximately 450 ± 10 HV. With the introduction of Co, the grain hardness of the Co5 alloy decreased slightly to 445 ± 12 HV. Hardness measurements performed on the Si- and Ti-rich precipitates formed at its grain boundaries gave a value of approximately 530 ± 10 HV, noticeably higher than that

of the grain interior. When the Co content was further increased to 25 at.%, the intragranular hardness of the Co25 alloy decreased significantly to 306 ± 15 HV. Based on the microstructural analysis, this change can be attributed to the $L1_2$ –FCC dual-phase core–shell structure formed within the grains. Since the intrinsic hardness of the continuously distributed FCC disordered phase is markedly lower than that of the $L1_2$ ordered phase, the solid-solution strengthening effect is insufficient to compensate for the low hardness characteristic of the disordered solid solution, resulting in a substantial decrease in intragranular hardness. Meanwhile, the grain boundary precipitates maintained a relatively high hardness level of approximately 518 ± 12 HV, and their hardness did not change appreciably with increasing Co content. It is thus evident that the microstructural transformation induced by Co addition exerts a significant influence on material hardness, wherein the intragranular hardness gradually decreases with the formation of the FCC shell layer, while the hardness of grain boundary precipitates remains essentially unaffected by changes in Co content.

Table 4.3 Microhardness of the three as-cast alloys

Alloys	Grain hardness (HV)	Grain boundary precipitate hardness (HV)
Co0	450 ± 10	—
Co5	445 ± 12	534 ± 10
Co25	306 ± 15	518 ± 12

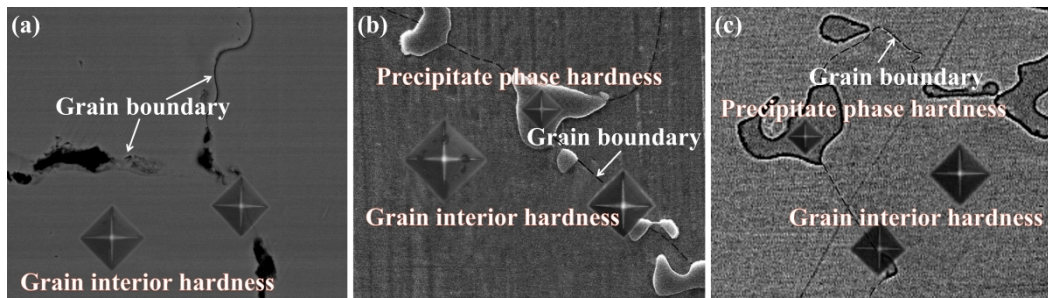


Fig. 4.14 SEM images of indentation regions at different locations in the three as-cast alloys

(a) Co0 alloy; (b) Co5 alloy; (c) Co25 alloy

Building upon the microhardness analysis, the effect of increasing Co content on the macroscopic mechanical properties of the alloys was further investigated. The room-temperature compressive engineering stress–strain curves of the three as-cast alloys are presented in Fig. 4.15, and the corresponding mechanical property

parameters are listed in Table 4.4. The results indicate that Co content exerts a significant influence on the mechanical properties of the alloys. Specifically, the single-phase $L1_2$ structured Co0 alloy exhibited a yield strength of approximately 757 MPa and a compressive strength of about 1048 MPa, yet its fracture strain is relatively low, exhibiting the typical high-strength and low-ductility characteristics of intermetallic compounds. With the addition of a small amount of Co, the yield strength of the Co5 alloy increased slightly to approximately 786 MPa, while the fracture strain was substantially elevated to approximately 37.5%. The trend of property changes in the Co5 alloy corresponded to the microstructural evolution. On the one hand, the high-hardness grain boundary precipitates enhanced the load-bearing capacity of the alloy, substantially increasing the fracture strain by extending the loading stroke. On the other hand, since the intragranular $L1_2$ phase still remained predominant, the intrinsic yield strength of the alloy did not undergo a significant change.

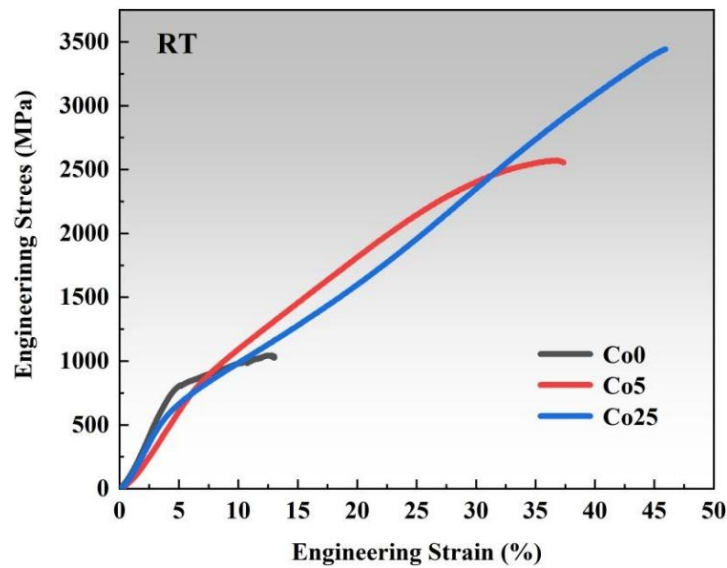


Fig. 4.15 Room-temperature compressive engineering stress–strain curves of three as-cast alloy

When the Co content was further increased to 25 at.%, the yield strength of the Co25 alloy decreased to approximately 510 MPa. However, the fracture strain was remarkably elevated to approximately 46%, representing a nearly threefold increase compared with the Co0 alloy. Based on the microstructural analysis, the improvement in room-temperature ductility is closely associated with the formation of the $L1_2$ –FCC dual-phase core–shell structure. The softer FCC disordered shell layer enhances the ductility of the material while leading to a reduction in yield

strength, whereas the harder ordered $L1_2$ core continues to exert the strengthening effect with increasing loading stroke, resulting in a further increase in compressive strength. This “soft shell–hard core” synergistic deformation mechanism enables the Co25 alloy to achieve a substantial improvement in room-temperature ductility under the premise of a modest reduction in yield strength.

Table 4.4 Room-temperature compressive mechanical properties of the three as-cast alloys

Alloys	Yield strength	Compressive strength	Fracture strain
	σ_y (MPa)	$\sigma_{\max}$ (MPa)	ε (%)
Co0	757±20	1048±30	13.0±1.3
Co5	786±20	2569±50	37.5±1.3
Co25	510±18	3441±50	46.0±1.5

To further analyze the influence of the $L1_2$ –FCC dual-phase core–shell structure on the room-temperature mechanical properties of the alloy, room-temperature tensile tests were conducted on the Co25 alloy, and the results are presented in Fig. 4.16. As shown in the figure, the alloy exhibits a room-temperature yield strength of approximately 450 MPa, an ultimate tensile strength of approximately 650 MPa, and a plastic strain of approximately 10%, which is markedly different from the low-ductility characteristics typically exhibited by conventional as-cast intermetallics at room temperature. From the fracture morphology shown in Fig. 4.16 (b), the Co25 alloy does not display cleavage steps or intergranular brittle fracture features commonly observed in intermetallics during tensile fracture. Conversely, a small number of uniformly distributed fine dimples appear in localized regions, indicating a certain degree of microscopic plastic deformation capability. Meanwhile, the strain hardening rate curve shown in Fig. 4.16 (c) demonstrates that the alloy maintains a stable strain hardening capacity throughout the entire deformation process, implying the existence of a sustainable plastic deformation mechanism that can delay necking and sustain a larger plastic strain. Overall, the formation of the $L1_2$ –FCC dual-phase core–shell structure in the Co25 alloy effectively alleviates the room-temperature brittleness problem of conventional intermetallics, enabling the material to exhibit appreciable plastic deformation capacity under tensile loading.

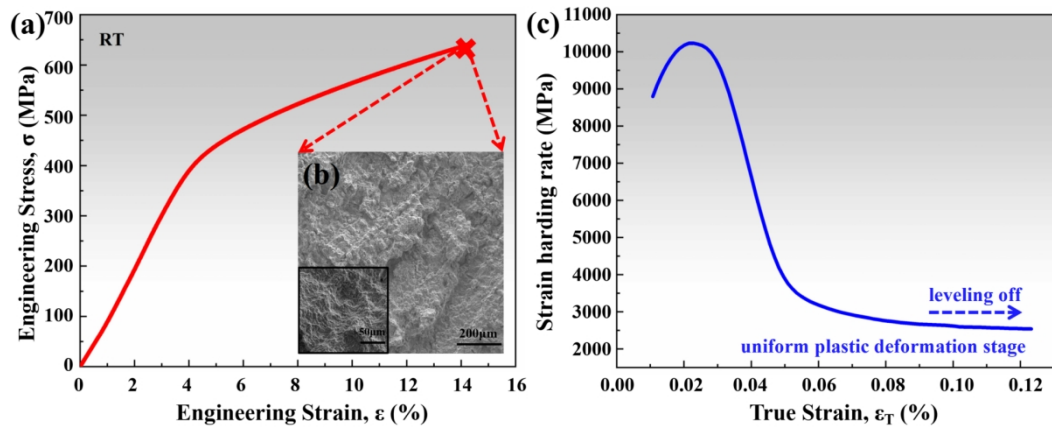


Fig. 4.16 Room-temperature tensile mechanical properties of the Co25 alloy
(a) Engineering stress–strain curve; (b) fracture morphology; (c) strain hardening rate–true strain curve

In summary, the addition of Co significantly influences the room-temperature mechanical properties of the three as-cast alloys by modulating the microstructural evolution within the grains. Among them, the $L1_2$ –FCC dual-phase core–shell structure formed in the Co25 alloy leads to a certain reduction in yield strength, but significantly enhances the compressive strength and compressive plasticity, while also effectively suppressing brittle fracture behavior under room-temperature tensile conditions.. The above results indicate that the formation of the dual-phase core–shell structure is conducive to mitigating the room-temperature brittleness problem of the material, thereby achieving comprehensive optimization of mechanical properties.

4.4.2 Room-temperature deformation mechanism of the $Ni_{50}Co_{25}Al_{8.33}Si_{8.33}Ti_{8.34}$ alloy

Through a systematic investigation of the room-temperature mechanical properties of $Ni_{(75-x)}Co_xAl_{8.33}Si_{8.33}Ti_{8.34}$ alloys, it was found that the formation of the $L1_2$ –FCC dual-phase core–shell structure significantly enhances the room-temperature ductility of the Co25 alloy, with an increase of nearly three times relative to the Co0 alloy in which this structure is absent. To elucidate the underlying mechanism responsible for the favorable room-temperature ductility of this alloy, it is necessary to conduct an in-depth analysis of its room-temperature deformation mechanism, thereby clarifying the critical role played by the core–shell structure in performance optimization.

To reveal the deformation mechanism of the Co25 alloy at room temperature, TEM was employed to systematically characterize its dislocation substructure. Fig. 4.17 presents TEM images of the microscopic dislocation substructure of the Co25 alloy at different deformation levels. In the mild plastic deformation stage, as shown in Figure 4.17 (a), only a small number of dislocations are observed within the FCC shell, indicating that the softer disordered FCC shell undergoes preferential plastic deformation during tensile loading. Owing to the relatively small overall deformation, the dislocation density remains low, and dislocations move relatively freely in the FCC channels primarily through slip, without significant tangling or pile-ups, nor any appreciable interaction with the phase interfaces. Therefore, the plastic deformation at this stage is predominantly accommodated by the FCC shell, while the $L1_2$ ordered core essentially maintains an elastic response.

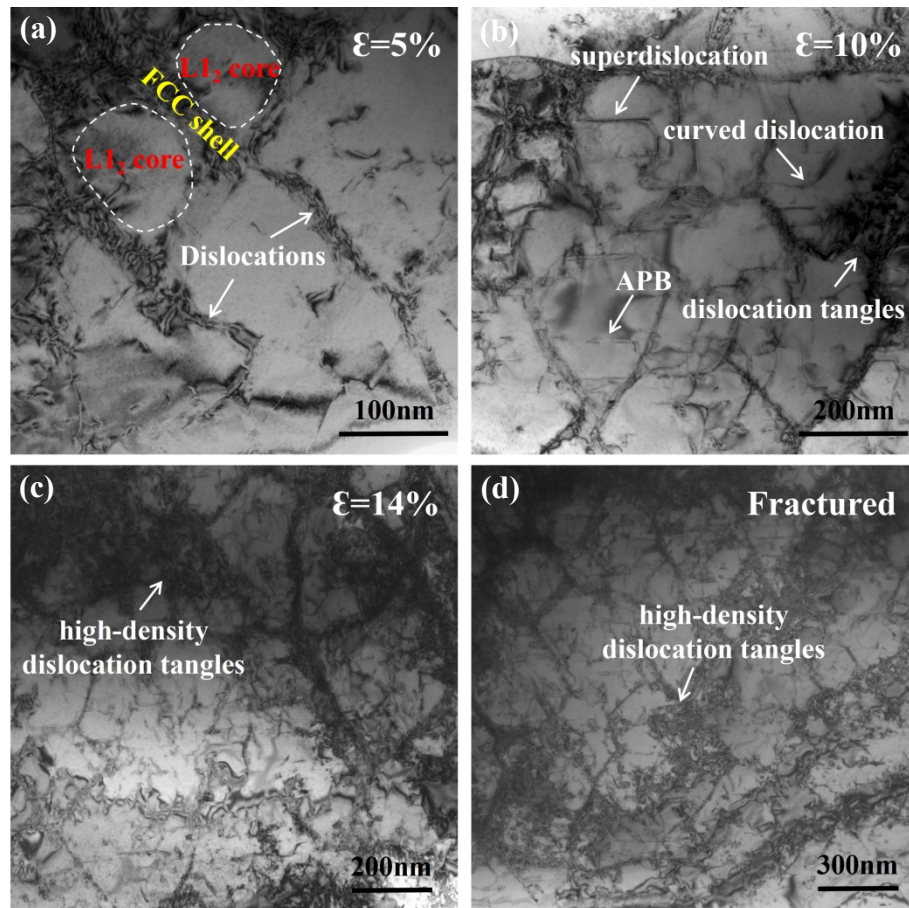


Fig. 4.17 Evolution of the dislocation substructure in the Co25 alloy with increasing strain during tensile deformation
(a) tensile strain of 5%; (b) tensile strain of 10%; (c) tensile strain of 14%; (d) fractured specimen

When the deformation level increases to 10%, as shown in Fig. 4.17 (b), the

dislocation density within the FCC shell rises significantly, and pronounced dislocation entanglement appears. Concurrently, the increased deformation causes some dislocations to pile up at the FCC/L1₂ phase interface, indicating that the interface acts as a barrier to dislocation motion. Driven by the continuously applied stress, a fraction of dislocations can penetrate the interface via a shearing mechanism and enter the interior of the L1₂ ordered phase. Generally, dislocations in the FCC matrix can overcome L1₂ precipitates through two typical mechanisms: directly shearing the precipitates or bypassing them via the Orowan mechanism [104]. At room temperature, the occurrence of the Orowan bypass mechanism typically implies that the precipitates are non-deformable. However, in the Co25 alloy, the L1₂ ordered phase exhibits not only pronounced superdislocations and anti-phase boundaries but also curved dislocations induced by the stress field associated with APBs.

The above analysis indicates that the L1₂ ordered core provides a considerable barrier to dislocation motion and serves as an important source of strength enhancement for the material. At the same time, owing to the highly coherent nature of the L1₂/FCC interface, dislocations can be transmitted from the FCC shell into the L1₂ core, thereby effectively relieving stress concentration at the core-shell interface and reducing the risk of interfacial instability and premature fracture. Furthermore, the coexistence of curved dislocations and APBs within the L1₂ ordered phase indicates that dislocations shear the ordered phase in the form of superdislocations or paired dislocations. Therefore, the L1₂ phase is capable of contributing to plastic deformation via dislocation transfer and shear mechanisms without sacrificing its strengthening capacity, which fundamentally constitutes the critical microscopic mechanism responsible for the substantial ductility enhancement achieved by the L1₂-FCC core-shell structure, while maintaining the yield strength at a reasonable level.

As the deformation proceeds further toward the fracture stage, as presented in Figure 4.17 (c), a notable increase in dislocation density is observed in both the FCC shell and the L1₂ ordered core, accompanied by continuously enhanced dislocation interactions, which are evidenced by more pronounced dislocation entanglement and pile-up configurations at the phase boundaries. With the

progressive accumulation of plastic deformation, the dislocation activity gradually transitions from homogeneous to highly localized, leading to a marked increase in the degree of local stress concentration. When the stress concentration caused by heavily piled-up dislocations in local regions exceeds the load-bearing capacity of relatively weak sites within the material, microcracks initiate and propagate rapidly, ultimately resulting in fracture failure of the material, as shown in Fig. 4.17 (d).

In addition, further characterization of the FCC shell in the fractured sample reveals the presence of a small number of parallel stacking faults (SFs) in localized regions, as shown in Fig. 4.18. As a common deformation substructure in FCC alloys, the formation of SFs can effectively impede dislocation slip, increase the resistance to dislocation motion, thereby enhancing the strain hardening capacity of the material and contributing to the maintenance of plastic deformation capability. The appearance of SFs in the Co25 alloy can be attributed primarily to the following two aspects. First, the addition of Co reduces the stacking fault energy of the FCC disordered phase, thereby lowering the energy barrier required for SFs formation. Studies have demonstrated that Co has a pronounced SFE-lowering effect in various FCC alloy systems [105]. Second, the Co25 alloy possesses a certain degree of plastic deformability, which enables it to sustain a relatively high flow stress during deformation. When the applied stress exceeds the critical stress required for SFs formation, SFs begin to appear in localized regions. It should be noted that the overall number of SFs in this alloy remains relatively small. Therefore, the primary deformation mechanism of the material is still dominated by dislocation slip and the formation of APBs within the $L1_2$ ordered phase.

It can be concluded that the formation of the $L1_2$ -FCC dual-phase core-shell structure is beneficial to the enhancement of the room-temperature mechanical properties of the Co25 alloy. In this structure, the continuously distributed FCC shell in the intragranular region, characterized by a lower yield resistance, is preferentially deformed during the initial stage of loading, which supplies efficient strain accommodation pathways and serves as a stress relaxation medium, thus notably enhancing the overall plastic deformability of the alloy. Meanwhile, the $L1_2$ ordered core, encased by the FCC shell, continuously exerts a strengthening effect during the middle and later stages of deformation, enabling the alloy to maintain

relatively high strength while retaining high ductility. This “soft shell–hard core” synergistic deformation mechanism effectively avoids the premature brittle instability commonly observed in conventional single-phase $L1_2$ alloys, enabling the Co25 alloy to achieve favorable room-temperature ductility.

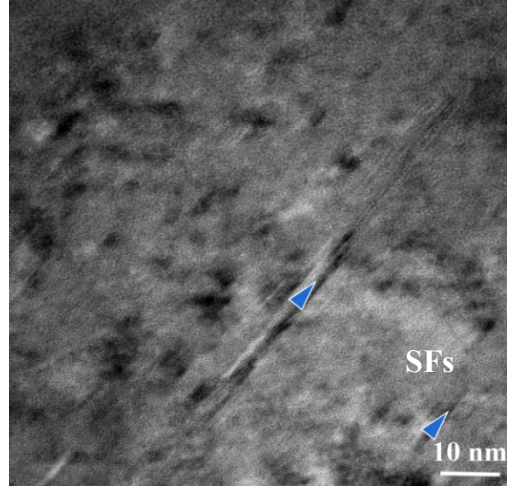


Fig. 4.18 A small number of SFs within the FCC shell of the fractured Co25 alloy sample

In addition, the deformation mechanism of the disordered FCC shell in the Co25 alloy is analogous to that of the FCC-type disordered nanolayers observed at grain boundaries in the $\text{Ni}_{43.9}\text{Co}_{22.4}\text{Fe}_{8.8}\text{Al}_{10.7}\text{Ti}_{11.7}\text{B}_{2.5}$ alloy. In both cases, the disordered nanolayers are embedded in multi-principal-element intermetallic and serve to improve plastic deformability by promoting dislocation glide. Tensile tests at ambient temperature reveal that the $\text{Ni}_{43.9}\text{Co}_{22.4}\text{Fe}_{8.8}\text{Al}_{10.7}\text{Ti}_{11.7}\text{B}_{2.5}$ alloy exhibits a yield strength of ~ 1040 MPa and a plastic strain of $\sim 25\%$, substantially outperforming the Co25 alloy [78]-3. It should be noted that this alloy was processed via a combination of arc melting and deformation-recrystallization, and the complex thermomechanical treatment resulted in significant grain refinement. Concurrently, the co-segregation of multiple solutes at grain boundaries induced pronounced high-entropy and sluggish diffusion effects, which effectively restrained grain coarsening during recrystallization, ultimately yielding an average grain diameter of merely ~ 11 μm . Given the well-established principle that grain refinement concurrently enhances both strength and ductility, the superior room-temperature performance of this alloy is intimately associated with the grain-refinement strengthening mechanism.

In contrast, the Co25 alloy was tested in the as-cast condition following arc melting, with the solidification microstructure characterized by coarse dendrites and an average grain size of $\sim 180\ \mu\text{m}$. At this length scale, the contribution of grain-refinement strengthening is marginal. Consequently, the property enhancement observed in the Co25 alloy can be ascribed almost exclusively to the formation of the disordered FCC shell. To quantitatively assess the role of the FCC shell in modifying the room-temperature mechanical response, Figure 4.19 compiles the yield strength and tensile ductility of Ni_3Al alloys over a range of grain sizes. As depicted in the figure, both yield strength and tensile elongation degrade with increasing grain size. For the Ni_3Al alloy with a grain size comparable to that of the Co25 alloy ($\sim 180\ \mu\text{m}$), the yield strength falls below 300 MPa and the tensile elongation approaches zero, that are considerably inferior to those of the Co25 alloy ($\sim 450\ \text{MPa}$ and $\sim 10\%$, respectively). These results clearly demonstrate that the introduction of Co, which gives rise to the disordered FCC shell, effectively mitigates the room-temperature brittleness of intermetallic compounds even in the coarse-grained solidification microstructure. This finding implies that, for coarse-grained intermetallics, the intrinsic brittleness can be circumvented by sublattice high-entropy alloying that promotes core-shell structure formation, avoiding the need for deformation-induced grain refinement or thermomechanical processing.

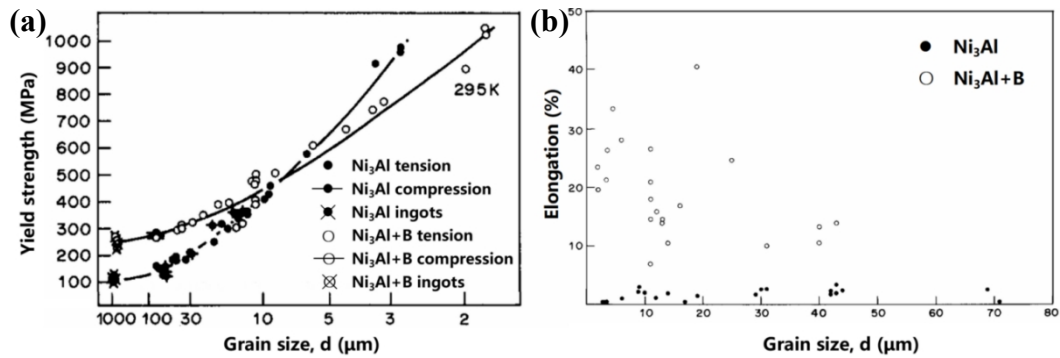


Fig. 4.19 Room-temperature yield strength and elongation of Ni_3Al alloy as a function of grain size [106]
(a) yield strength–grain size; (b) elongation–grain size

In summary, the formation of the L_{12} –FCC dual-phase core-shell structure in the Co25 alloy effectively overcomes the inherent room-temperature brittleness characteristic of conventional single-phase L_{12} -type intermetallics. Within this structure, the disordered FCC shell undergoes preferential deformation to accommodate dislocation activity, while the ordered L_{12} core sustains its

strengthening function throughout the deformation process. The synergistic interplay between the two constituents enables a substantial enhancement in room-temperature ductility while preserving a moderate level of yield strength. Distinct from conventional strategies that rely on severe plastic deformation and grain-refinement strengthening, the sublattice high-entropy alloying approach achieves desirable mechanical performance in the as-cast coarse-grained microstructure without requiring complex deformation or heat-treatment processes. This observation offers a new paradigm for attaining an optimal balance of strength and ductility in coarse-grained intermetallic compounds.

4.5 Chapter summary

In this chapter, the $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ series alloys were taken as the research object, and the effect of increasing Co content on the microstructure of the alloys was systematically investigated through both theoretical and experimental approaches, elucidating the formation mechanism of the L1_2 –FCC dual-phase core–shell structure induced by Co addition. Meanwhile, combined with mechanical property testing and TEM characterization, the influence of microstructural evolution on room-temperature mechanical properties was revealed, and the room-temperature deformation mechanism of the Co25 alloy featuring the L1_2 –FCC dual-phase core–shell structure was clarified. The main conclusions are as follows:

(1) Co addition promotes the formation of the dual-phase core–shell structure. In the absence of Co, the Co0 alloy exhibits a single-phase L1_2 structure. When the Co content reaches 25 at.%, a dual-phase core–shell structure characterized by an “ L1_2 ordered core–FCC disordered shell” is formed within the grains of the Co25 alloy. The average diameter of the cores is approximately 200 nm, with a volume fraction of about 85%, and the shell thickness is around 10 nm. The interface between the shell and the core is coherent.

(2) The dual-phase core–shell structure effectively improves the room-temperature plasticity of the material. The Co25 alloy, which possesses the L1_2 –FCC dual-phase core–shell structure, exhibits a maximum compressive strength of approximately 3441 MPa and a fracture strain of about 46%, representing an approximately threefold increase in fracture strain compared with the single-phase Co0 alloy

without this structure.

(3) The mechanism by which Co addition promotes the formation of the $L1_2$ –FCC dual-phase core–shell structure is revealed. Co induces the formation of the FCC phase by enhancing its thermodynamic stability, and promotes the solid-state precipitation of the $L1_2$ phase by regulating the solid–liquid partitioning behavior, thereby providing the phase-structure basis for the formation of the core–shell structure. In addition, Co maintains a low $L1_2$ /FCC interfacial energy, which ensures the stability of the $L1_2$ /FCC interface and provides favorable interfacial conditions for the formation of the core–shell structure.

(4) The room-temperature deformation mechanism of the Co25 alloy is clarified. During tensile deformation, the FCC shell deforms preferentially to accommodate dislocations, after which dislocations shear into the $L1_2$ core, forming superdislocations and APBs. This “soft shell–hard core” cooperative deformation mechanism alleviates interfacial stress concentration while ensuring strain hardening, enabling the Co25 alloy to achieve a significant improvement in room-temperature ductility while maintaining a moderate level of yield strength.

(5) The critical role of the $L1_2$ –FCC dual-phase core–shell structure in optimizing mechanical performance is elucidated. Without relying on grain-refinement strengthening, the Co25 alloy achieves excellent room-temperature mechanical properties through sublattice high-entropy alloying that promotes the formation of the $L1_2$ –FCC core–shell structure. It exhibits a yield strength of approximately 450 MPa, an ultimate tensile strength of about 650 MPa, and a plastic strain of roughly 10%, which are significantly superior to those of the Ni_3Al alloy with a comparable grain size.

Chapter 5 Composition regulation promotes the formation of multi-scale core-shell structure

5.1 Introduction

Traditional material design philosophy generally holds that microstructural homogeneity is fundamental for ensuring stable and reliable mechanical properties of materials [107]. A homogeneous microstructure helps suppress localized stress concentration and mitigate property fluctuations, thereby imparting better controllability and predictability to materials during deformation and failure. However, recent studies have increasingly demonstrated that the rational introduction of heterogeneous microstructures into alloy systems may instead overcome the conventional strength–ductility trade-off, enabling superior comprehensive mechanical properties [108].

Heterogeneous microstructures refer to the simultaneous presence of spatially distinct structural units with different mechanical response characteristics within a material. Specific forms include heterogeneity arising from grain size differences (e.g., coexistence of coarse and fine grains), heterogeneity arising from phase structure differences (e.g., coexistence of soft and hard phases), and heterogeneity induced by variations in the size, morphology, and distribution of secondary phases [109]. Among these, heterogeneous microstructures constructed from precipitates of different scales have been demonstrated to offer significant advantages in various alloy systems, such as dual-scale γ' precipitates in Ni-based superalloys and multi-scale precipitate particles in advanced high-entropy alloys [110]. Such structures are capable of maintaining high strength while effectively delaying the onset of localized instability and premature fracture.

Inspired by the above research progress, this chapter builds upon the Co25 alloy, in which an $L1_2$ –FCC dual-phase core-shell structure has already been established, and combines thermodynamic and solidification analysis calculations to further optimize the alloy composition and tailor the microstructure, so as to promote the evolution of the core-shell structure toward multi-scale characteristics. Through systematic microstructural characterization, the transformation behavior of the

microstructure under different compositional conditions is clarified, while thermal analysis experiments are employed to reveal the underlying mechanisms of microstructural transformation. This chapter aims to introduce heterogeneous microstructures through composition regulation, thereby providing microstructural design principles and experimental foundations for optimizing the mechanical properties of core-shell structured Ni-Co-Al-Ti-based high-entropy intermetallics.

5.2 Ta addition promoting the formation of dual-scale core-shell structure

Research in the preceding chapter has shown that in the $\text{Ni}_{(75-x)}\text{Co}_x\text{Al}_{8.33}\text{Si}_{8.33}\text{Ti}_{8.34}$ alloy, a stable L_{12} -FCC dual-phase core-shell structure can be formed when the Co content is 25 at.%. On this basis, the present section employs thermodynamic calculations to perform composition regulation on the Co25 alloy, with the aim of promoting the formation of heterogeneous microstructures. Furthermore, systematic microstructural characterization is conducted to elucidate the influence of compositional variations on the microstructure.

5.2.1 Composition regulation based on thermodynamic calculation

According to the findings of the preceding chapter, to ensure the formation of the L_{12} -FCC dual-phase core-shell structure, the contents of Ni and Co are maintained at 50 at.% and 25 at.%, respectively. In addition, Si not only induces the undesired brittle intermetallic G phase but also suppresses the precipitation of the L_{12} phase; therefore, Si is no longer considered in the composition regulation of this section. The analysis results of the preceding chapter also indicate that the appearance of the intragranular FCC disordered shell leads to a decrease in the yield strength of the material. For this reason, while retaining the existing Al and Ti contents, it is necessary to introduce additional L_{12} -forming elements to promote the formation of L_{12} ordered cores, thereby further enhancing material strength. Moreover, to obtain heterogeneous microstructures, the newly added L_{12} -forming elements should also facilitate the formation of multi-scale L_{12} ordered cores. Among numerous candidate alloying elements, Ta can simultaneously satisfy both of the above requirements. Existing studies have noted that in Ni-based superalloys and related multi-principal-element alloy systems, Ta not only promotes the

precipitation of the $L1_2$ ordered phase but also significantly modifies its size distribution characteristics, inducing the formation of dual-scale or even multi-scale precipitates [111–113]. Based on this, the present section first considers the addition of Ta to achieve microstructural regulation of the alloy.

As a typical $L1_2$ -stabilizing element, Ta can not only promote sufficient precipitation of the $L1_2$ phase by increasing its nucleation driving force but also achieve a relatively high degree of solid solution within the $L1_2$ phase, thereby enhancing material strength in multiple respects. However, excessive addition of Ta promotes the formation of Ta-rich brittle phases. Similarly, excessive addition of Al and Ti can also induce the formation of brittle phases such as BCC, σ , and η . Therefore, it is necessary to rationally regulate the contents of the $L1_2$ -forming elements Al, Ti, and Ta, ensuring that the ordered phase fraction is no less than 75% while avoiding the precipitation of detrimental phases. To achieve this objective, JMatPro is first employed to perform room-temperature phase equilibrium calculations for the new alloy system in order to determine the addition level of Ta. In principle, the Ta content should be set as the independent variable, while the content of another alloying element should be taken as the dependent variable. Through the synergistic variation of these two variables, the room-temperature equilibrium phase constitution should be observed to screen for elemental ratios that meet the requirements. However, in this alloy system, the contents of Al, Ti, and Ta are all undetermined, making it impossible to directly identify the dependent variable element. Consequently, an approximation treatment based on the characteristics of the alloying elements is required. The TEM-EDS results of the preceding chapter indicate that both Al and Ti tend to partition into the $L1_2$ ordered core, and extensive studies have confirmed that both elements predominantly occupy the corner sublattice sites of the $L1_2$ ordered crystal structure. Furthermore, compared with the mixing enthalpy of 1 kJ/mol between Ti and Ta, the mixing enthalpy between Al and Ta is more negative, at -19 kJ/mol [114]. This implies that Al and Ta are more prone to combine and form secondary phases. Based on the above analysis, Al and Ti are uniformly treated as the Al element, serving as the dependent variable in the room-temperature phase equilibrium calculation, thereby determining the critical addition level of Ta at which detrimental phases are not introduced.

Based on the above discussion, room-temperature equilibrium phase fraction calculations were performed for the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_{(25-x)}\text{Ta}_x$ alloy, and the results are shown in Fig. 5.1. It can be seen from the calculated phase diagram that when the Ta content is below 1.5 at.%, only the L1₂ and FCC phases exist in the alloy system, and the L1₂ ordered phase fraction is maintained at approximately 80%, satisfying the requirements of L1₂-type high-entropy intermetallics for phase constitution and phase fraction. When the Ta content exceeds 1.5 at.%, detrimental phases such as η appear in the alloy system, and their proportion gradually increases with increasing Ta content. Therefore, the Ta addition level is determined to be 1.5 at.%, so as to fully exploit its strengthening effect while avoiding the formation of detrimental phases.

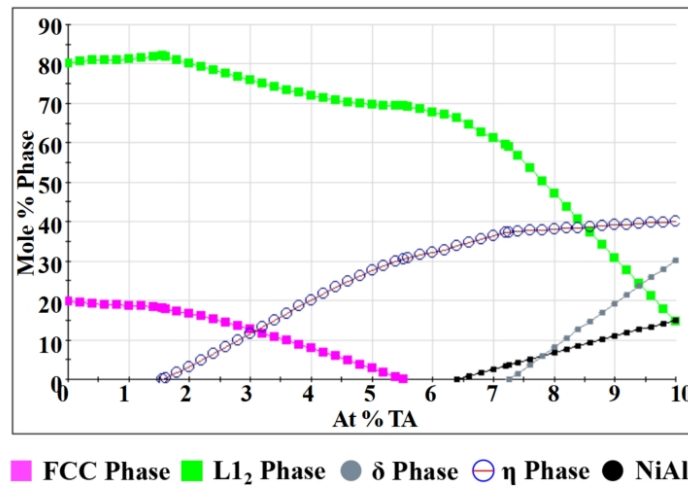


Fig. 5.1 Room-temperature equilibrium phase fractions of $\text{Ni}_{50}\text{Co}_{25}\text{Al}_{(25-x)}\text{Ta}_x$ alloy

After determining the Ta addition level, in order to enable the L1₂-type high-entropy intermetallic to meet both room-temperature and high-temperature application requirements, an appropriate amount of Cr is further introduced into the new alloy system, laying the foundation for subsequent optimization of high-temperature performance. Cr is an effective high-temperature oxidation-resistant element, which has a relatively minor effect on alloy properties at room temperature, mainly dissolving in the FCC matrix to provide solid-solution strengthening. Therefore, the principle for Cr addition is to regulate its content without introducing other detrimental phases. Considering that the mixing enthalpy between Al and Cr is -10 kJ/mol, which is more negative than the mixing enthalpy of -7 kJ/mol between Ti and Cr, indicating that Al and Cr are more likely to combine and form secondary phases [114]-2819. For this reason, Al and Ti are uniformly treated as the Al

element, and room-temperature equilibrium phase fraction calculations are performed for the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_{(23.5-x)}\text{Ta}_{1.5}\text{Cr}_x$ alloy system to determine the Cr addition level. The calculated phase diagram shown in Fig. 5.2 indicates that when the Cr content is below 9.5 at.%, the room-temperature phase constitution of the alloy system is not affected. However, when the Cr content exceeds 9.5 at.%, the BCC phase begins to appear in the alloy. Therefore, the Cr addition level in the new alloy system is determined to be 9.5 at.%.

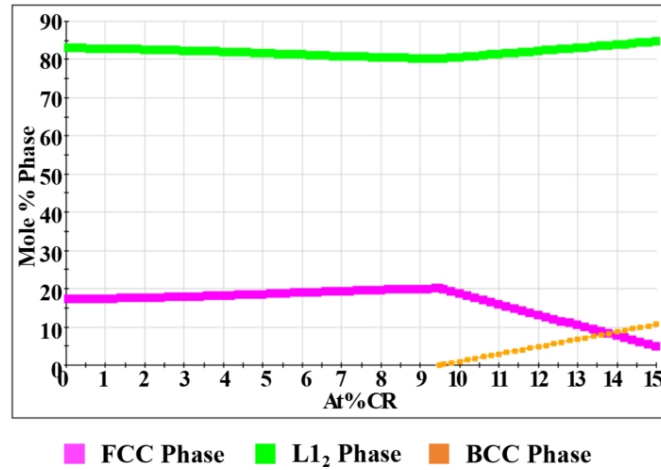


Fig. 5.2 Room-temperature equilibrium phase fractions of $\text{Ni}_{50}\text{Co}_{25}\text{Al}_{(23.5-x)}\text{Ta}_{1.5}\text{Cr}_x$ alloy

Based on the above analysis, 1.5 at.% Ta and 9.5 at.% Cr were added to the new alloy system. This composition ensures the desired L1₂ ordered phase fraction while avoiding other detrimental phases. Additionally, the formation of multi-scale core-shell structures and their application in high-temperature environments are also taken into account. Concurrently, according to the composition of the Co25 alloy with an L1₂–FCC dual-phase core-shell structure, the ratio of Al to Ti was set at 1:1. Thus, a model alloy with the nominal composition of $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ was obtained. Equilibrium phase diagram calculations were performed for this alloy, and the results are shown in Fig. 5.3. The phase diagram results indicate that the primary phase of this alloy is the FCC disordered phase. As the temperature decreases, the L1₂ phase and the η phase gradually form. It is noteworthy that when the temperature drops to the solidus, the fractions of both the FCC phase and the η phase reach their maximum values. During the subsequent solid-state phase transformation, the η phase fraction gradually decreases until it completely disappears at approximately 900 °C. In contrast, upon the onset of the solid-state

transformation of the FCC phase, its fraction declines sharply, accompanied by a continuous increase in the L1₂ phase fraction. This trend is presumably attributable largely to the precipitation of the L1₂ phase from the FCC matrix. Ultimately, the room-temperature equilibrium solidification microstructure contains only 80% L1₂ phase and 20% FCC phase. According to the equilibrium phase diagram, this model alloy possesses the thermodynamic conditions required for the formation of an L1₂–FCC dual-phase core–shell structure. Therefore, an alloy ingot of this composition was further prepared to observe the formation of the core–shell structure in its microstructure.

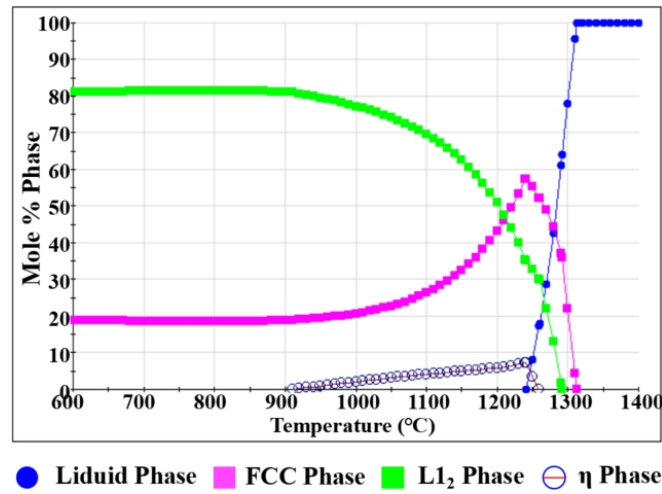


Fig. 5.3 Temperature dependence of equilibrium phase fractions in Ni₅₀Co₂₅Al₇Ti₇Ta_{1.5}Cr_{9.5} alloy

5.2.2 Microstructure of the Ni₅₀Co₂₅Al₇Ti₇Ta_{1.5}Cr_{9.5} alloy

Based on the calculation result in the preceding section, the Ni₅₀Co₂₅Al₇Ti₇Ta_{1.5}Cr_{9.5} alloy is thermodynamically an L1₂/FCC two-phase coexistence system. However, these calculation results only reflect the phase stability under equilibrium condition, and the actual formation and morphological characteristics of the core–shell structure in the as-cast alloy still require further verification through microstructural characterization. To clarify the actual phase constitution of the alloy, XRD testing was first performed on the as-cast specimen, and the results are shown in Fig. 5.4. As can be seen from the figure, the alloy overall exhibits typical FCC/L1₂ dual-phase characteristics, with the main diffraction peaks corresponding to the (111), (200), (220), and (311) crystal planes of the FCC/L1₂ phases.

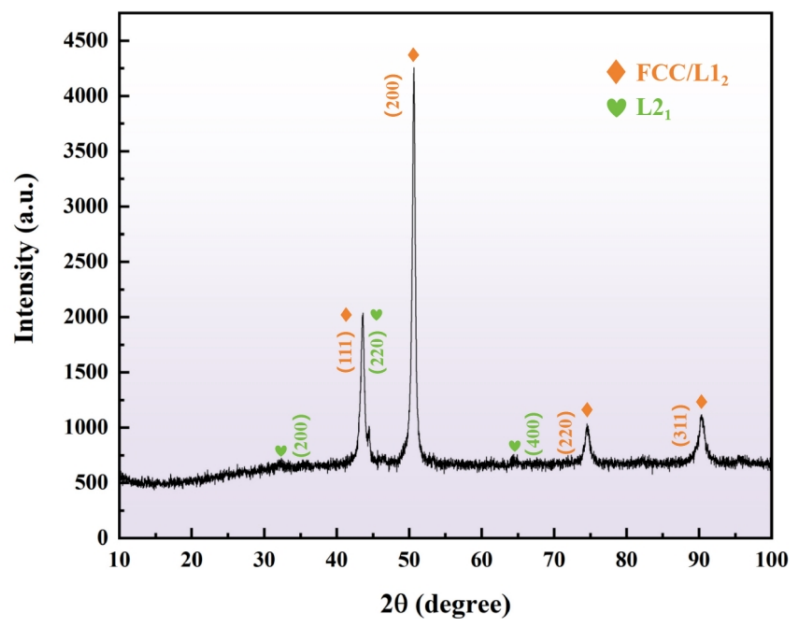


Fig. 5.4 XRD pattern of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

It is noteworthy that no distinct L_{12} superlattice diffraction peaks were detected under the present testing conditions, which may be attributable to the weak superlattice reflection structure factor. Theoretically, the intensity of the superlattice diffraction peaks of the L_{12} phase depends on the difference in the mean scattering factors of atoms on the two types of sublattices. When the scattering contrast between the two sublattices is insufficient, or when significant antisite occupancy and cross-sublattice mixing occupancy exist, the intensity of superlattice peaks is substantially weakened and may even approach the background level. In the present alloy, a certain degree of cross-sublattice mixing occupancy may exist between Ni/Co/Cr and Al/Ti/Ta, while the high-entropy effect of the sublattice simultaneously reduces the order parameter. The combined effect of these two factors significantly decreases the superlattice reflection intensity of the L_{12} phase, making it difficult to resolve clear superlattice diffraction peaks under conventional XRD conditions. In addition, a set of weak diffraction peaks not belonging to the FCC/ L_{12} system also appeared in the pattern. By comparison with PDF standard cards, this set of diffraction peaks corresponds to the L_{21} crystal structure, belonging to the $\text{Fm-3m}(225)$ space group, with a lattice constant of approximately 0.585 nm. Overall, the XRD results are largely consistent with the thermodynamic calculation results, indicating that the alloy is predominantly composed of the FCC/ L_{12} dual phases, accompanied by a small amount of secondary phase.

To further reveal the microstructural characteristics of the alloy and the formation of the core-shell structure, SEM characterization was performed on the as-cast specimen, with the results shown in Fig. 5.5. As can be seen from Fig. 5.5 (a), the alloy exhibits a typical dendritic solidification microstructure in the as-cast condition. Further magnified observation reveals that two regions with distinctly different contrast spontaneously form within each dendrite, namely a light-contrast region located at the dendrite boundary and the dark-contrast region within the dendrite core enveloped by the former, as shown in Fig. 5.5 (b). Statistical analysis of multiple dendrites indicates that the average dendrite size is approximately 150 μm , with the thickness of the light-contrast region at the dendrite boundary being approximately 20 μm . From Fig. 5.5 (c), it can be observed that a small number of blocky precipitates exist in the interdendritic region, with an average size of approximately 5 μm and an irregular morphology, exhibiting typical intergranular precipitation characteristics. High-magnification observation at the interface between regions of different contrast within the dendrite clearly reveals the core-shell structural features, as shown in Fig. 5.5 (d). Specifically, the dark-contrast region within the dendrite core is composed of core-shell structures that are small in size and approximately spherical in morphology. Statistical calculations show that the diameter of the nearly spherical cores is approximately 150 nm, belonging to the submicron scale. In contrast, the light-contrast region at the dendrite boundary is composed of core-shell structures that are larger in size and approximately cellular in morphology. Size statistics of the cellular cores indicate an average length of approximately 3 μm and an average width of approximately 2 μm , belonging to the micrometer scale. The above results demonstrate that this alloy undergoes microstructural partitioning during the as-cast solidification process, and core-shell structures with distinct morphologies and scales further develop within different regions, thereby exhibiting a microstructure characterized by dual-scale core-shell structural features.

To further analyze the compositional differences between the two scales of core-shell structures within the dendrite interior, two typical regions, as marked in Fig. 5.6 (a), were selected for EDS analysis. Region A corresponds to the dendrite center composed of submicron-scale core-shell structures, while Region B corresponds to the dendrite boundary region consisting of micron-scale core-shell structures. The

corresponding SEM-EDS analysis results are listed in Table 5.1. As shown in the table, the Co and Cr contents in the submicron-scale core–shell structure region at the dendrite center (Region A) are markedly higher than those in the micron-scale core–shell structure region at the dendrite boundary (Region B). Conversely, the Ti and Ta contents in Region B are significantly higher than those in Region A. In contrast, the differences in Ni and Al contents between the two scales of core–shell structure regions are relatively small, remaining at similar levels overall. These results indicate that, during the as-cast solidification process, the formation of core–shell structures with different morphologies and scales is accompanied by pronounced elemental segregation behavior. A schematic illustration of the specific dual-scale core–shell structure is presented in Fig. 5.6 (b).

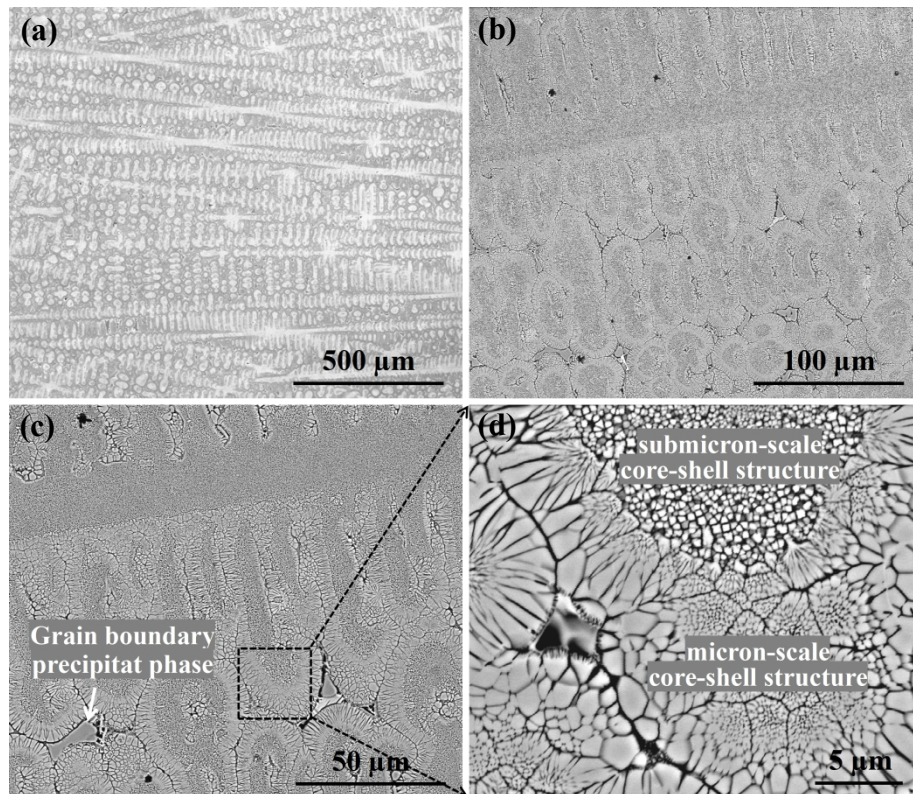


Fig. 5.5 Microstructures of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy
(a) as-cast dendritic morphology; (b) higher-magnification dendritic image; (c)
morphology of precipitates in the interdendritic region; (d) core–shell structure
microstructure at the dendrite interior and dendrite boundary

Based on the microstructural observations, the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy indeed forms two types of core–shell structures with significantly different morphologies and scales. To further identify the phase structure types of the core and shell, TEM characterization was performed on the as-cast alloy specimen, with the results

shown in Fig. 5.7. First, a typical field of view containing both scales of core–shell structures was selected under the HAADF-STEM mode, with its morphology presented in Fig. 5.7 (a). Subsequently, TEM-EDS elemental mapping was conducted over this region, and the results are shown in Fig. 5.8. The elemental mapping results reveal that the two scales of core–shell structures exhibit highly consistent elemental partitioning characteristics: the shell layers are both enriched in Co and Cr, whereas the cores are enriched in Ni, Al, Ti, and Ta. This finding suggests that, despite the difference in scale, the compositional preferences of the core–shell structures follow the same partitioning pattern, implying that they may possess the same phase structure type.

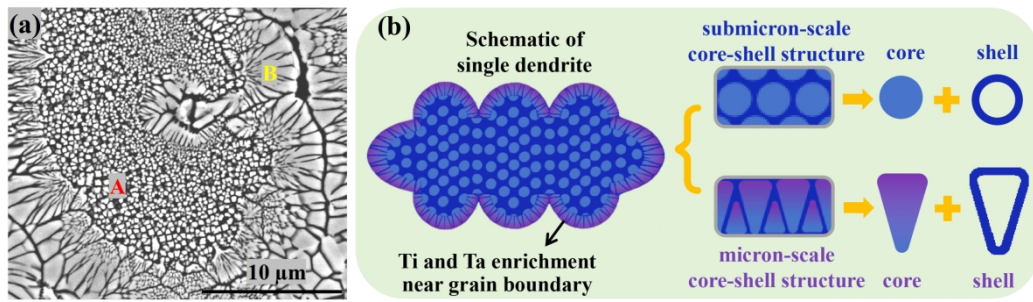


Fig. 5.6 Characterization of the dual-scale core–shell structure in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

(a) microstructure of the dual-scale core–shell structure; (b) schematic illustration of the dual-scale core–shell structure

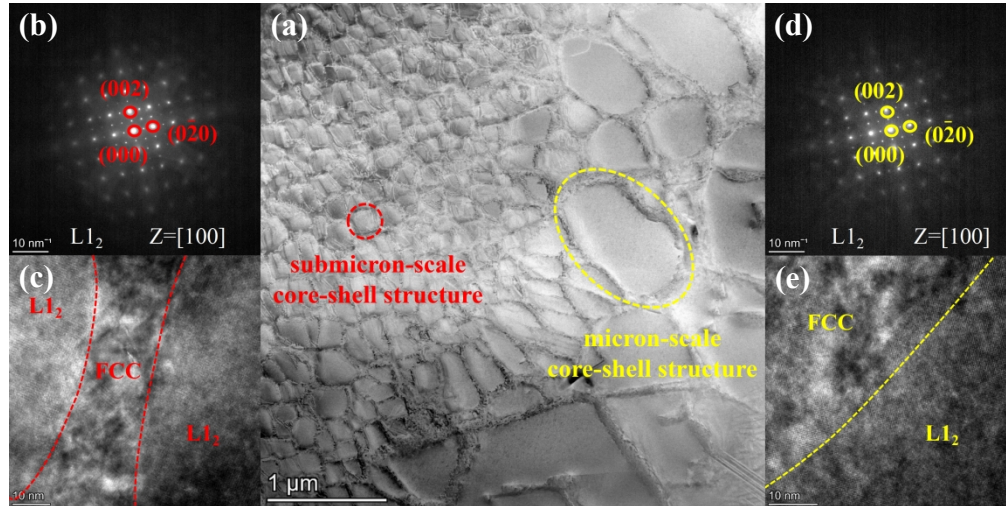


Fig. 5.7 TEM characterization of dendrite interior in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

(a) HAADF-STEM image of the dual-scale core–shell structures; (b) SAED pattern corresponding to the submicron-scale core–shell structure; (c) high-resolution image of the interface within the submicron-scale core–shell structure; (d) SAED pattern corresponding to the micron-scale core–shell structure; (e) high-resolution image of the interface within the micron-scale core–shell structure

Table 5.1 SEM-EDS compositional analysis of the regions corresponding to the two scales of core–shell structures

Regions	Ni	Co	Al	Ti	Ta	Cr
A	50.60	24.78	6.09	7.10	1.88	9.55
B	49.68	22.60	7.92	10.25	2.98	6.57

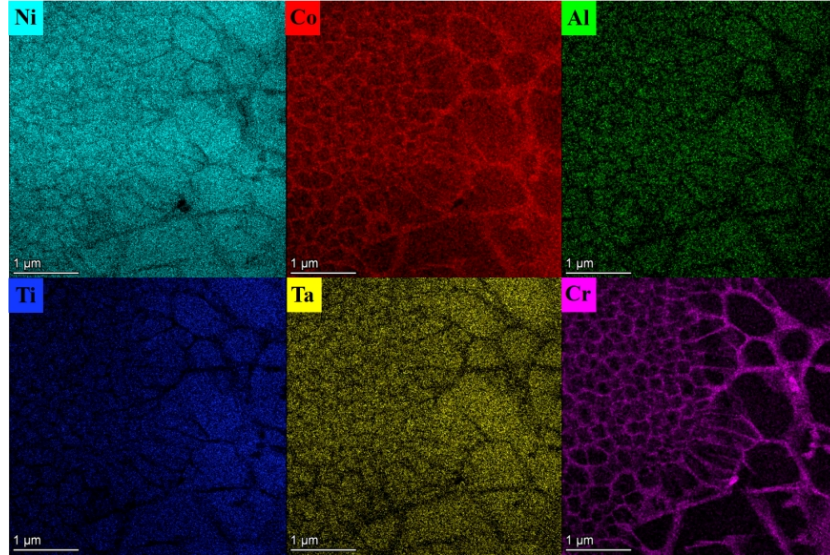


Fig. 5.8 Elemental mapping of the composition distribution within the dendrite interior of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

To further identify the submicron-scale core–shell structures of smaller dimensions, selected area electron diffraction analysis was performed, with the results shown in Fig. 5.7 (b). When the electron beam was incident along the $[100]$ zone axis direction, this region exhibited typical FCC crystal structure diffraction characteristics accompanied by clear superlattice diffraction spots, indicating that the region contains both ordered and disordered structures. Subsequently, high-resolution characterization was conducted on this region under the scanning transmission electron microscopy mode, with the results shown in Fig. 5.7 (c). The high-resolution image reveals that the outer FCC disordered shell has a thickness of approximately 15 nm and maintains a well-defined coherent interface with the inner L1_2 ordered core. Accordingly, it can be confirmed that this submicron-scale core–shell structure is an L1_2 –FCC dual-phase core–shell structure.

Following the same characterization approach, the micron-scale core–shell structures were analyzed, and the results are shown in Fig. 5.7 (d) and (e). The characterization results reveal that the micron-scale core–shell structures are similar

to their submicron-scale counterparts, consisting of an $L1_2$ -ordered core and an FCC-disordered shell, and thus essentially remain a dual-phase $L1_2$ -FCC core-shell structure. The above TEM results further indicate that the core-shell structures at different scales are consistent in phase constitution, with their differences mainly lying in geometric size and morphology. To further clarify the crystal structure of the interdendritic precipitates, TEM characterization was performed, and the results are presented in Fig. 5.9.

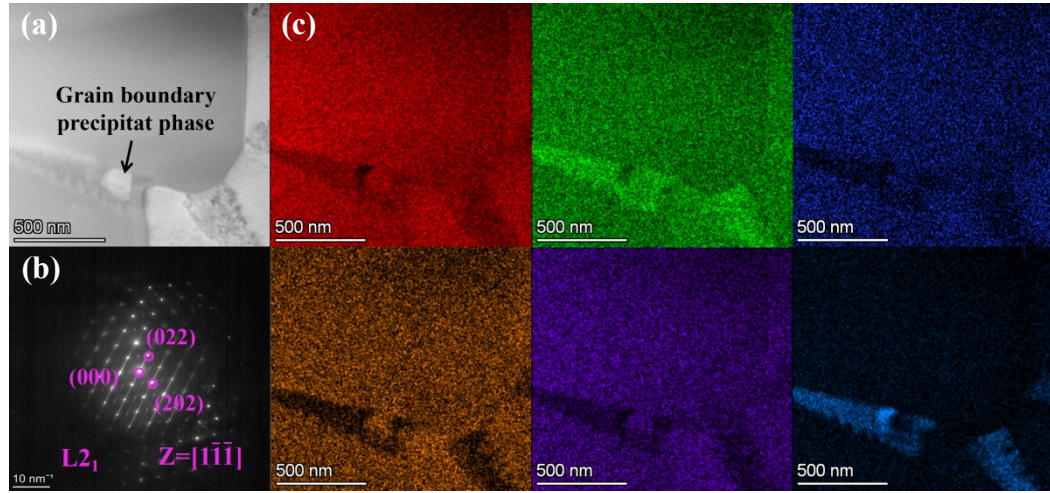


Fig. 5.9 TEM characterization of interdendritic precipitates in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy
(a) HAADF-STEM image of interdendritic precipitates; (b) SAED pattern corresponding to the interdendritic precipitates; (c) elemental mapping of the composition distribution in the interdendritic region

The presence of interdendritic precipitates can be clearly observed in the HAADF-STEM image, as shown in Fig. 5.9 (a). SAED analysis was performed on this region, with the results presented in Fig. 5.9 (b). When the electron beam was incident along the $[1\bar{1}\bar{1}]$ zone axis direction, this precipitate exhibited $L2_1$ crystal structure diffraction characteristics, consistent with the second-phase diffraction results detected in the XRD pattern. Subsequently, TEM-EDS elemental mapping was conducted, and the results show that this precipitate is significantly enriched in Ni, Al, Ti, and Ta, as illustrated in Fig. 5.9 (c). Based on its crystal structure characteristics, elemental composition, and the additional diffraction peaks observed in the XRD pattern, it is inferred that the small amount of interdendritic precipitates present in this alloy is a Heusler phase with the chemical formula Ni_2AlTi . The Heusler phase is a class of ternary intermetallic compounds with a stoichiometric ratio of XYZ, possessing an $L2_1$ ordered structure, and is commonly

found in nickel-based/cobalt-based superalloys and high-entropy alloys, where it contributes to precipitation strengthening. In summary, through comprehensive validation by multi-scale characterization techniques including XRD, SEM, and TEM-EDS, the microstructure of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy primarily consists of L_{12} –FCC dual-phase core–shell structures at two scales, accompanied by a small amount of Heusler phase precipitation in the interdendritic regions.

5.3 Increasing Al/Ti ratio promoting the formation of multi-scale core–shell structure

The preceding section demonstrated that the addition of Ta to the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy successfully introduced a dual-scale core–shell structure. However, the microstructural characterization results revealed the presence of a small amount of secondary phase in the interdendritic regions. Moreover, the relative contents of Al and Ti in this alloy composition have not yet been finely tuned; only the total amount of the two elements was determined via thermodynamic calculations. These findings indicate that there remains room for further optimization of the alloy composition and microstructure. Therefore, in this section, based on the $\text{Ni}_{50}\text{Co}_{25}(\text{Al}+\text{Ti})_{14}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy composition, the Al/Ti ratio is adjusted to suppress the precipitation of the secondary phase in the interdendritic regions, while further optimizing the microstructural characteristics of the multi-scale core–shell structure, thereby laying a microstructural foundation for the subsequent synergistic enhancement of strength and ductility.

5.3.1 Composition regulation based on thermodynamic calculation

The Al/Ti ratio is a key factor influencing the microstructure and properties of L_{12} -type high-entropy intermetallics. On one hand, the Al content directly affects the crystal structure of multi-principal-element alloy systems: excessive Al promotes the transformation from an FCC structure to a BCC structure, whereas insufficient Al addition tends to induce the formation of detrimental phases. On the other hand, Ti is an important element that promotes the precipitation of the L_{12} phase, but its excessive addition intensifies elemental segregation in the interdendritic regions and alters the structure and morphology of the precipitates near the dendrite boundaries. Therefore, reasonably tuning the Al/Ti ratio not only facilitates the

optimization of the distribution characteristics of the L1₂–FCC core–shell structure, but also effectively suppresses the precipitation of detrimental interdendritic phases, thereby enhancing the overall mechanical properties of the material.

To determine the appropriate Al/Ti ratio, room-temperature equilibrium phase fraction calculations were performed on the Ni₅₀Co₂₅(Al+Ti)₁₄Ta_{1.5}Cr_{9.5} alloy system, with the results shown in Fig. 5.10. Figure 5.10 (a) presents the room-temperature equilibrium phase fraction diagram of the Ni₅₀Co₂₅Al_xTi_(14-x)Ta_{1.5}Cr_{9.5} alloy. As can be seen from the diagram, when the Al content is below 8 at.%, the alloy system begins to favor the formation of the brittle η phase. Therefore, the Al content in the new alloy composition must exceed 8 at.%. Furthermore, Fig. 5.10 (b) shows the room-temperature equilibrium phase fraction diagram of the Ni₅₀Co₂₅Al_(14-x)Ti_xTa_{1.5}Cr_{9.5} alloy. The results indicate that when the Ti content exceeds 6 at.%, the alloy system likewise begins to favor the formation of the brittle η phase. Consequently, the Ti content in the new alloy composition must be below 6 at.% to avoid the formation of detrimental phases.

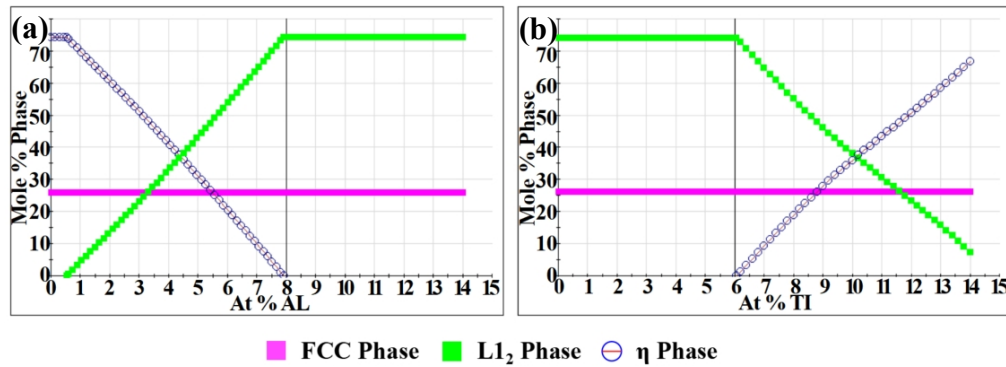


Fig. 5.10 Room-temperature equilibrium phase fractions of the Ni₅₀Co₂₅(Al+Ti)₁₄Ta_{1.5}Cr_{9.5} alloys
(a) Ni₅₀Co₂₅Al_xTi_(14-x)Ta_{1.5}Cr_{9.5}; (b) Ni₅₀Co₂₅Al_(14-x)Ti_xTa_{1.5}Cr_{9.5}

Based on the above thermodynamic calculation results, three alloy compositions with Al/Ti ratios of 8/6, 9/5, and 10/4 were selected in this section, namely Ni₅₀Co₂₅Al₈Ti₆Ta_{1.5}Cr_{9.5}, Ni₅₀Co₂₅Al₉Ti₅Ta_{1.5}Cr_{9.5}, and Ni₅₀Co₂₅Al₁₀Ti₄Ta_{1.5}Cr_{9.5} (hereinafter abbreviated as Al8, Al9, and Al10 alloys, respectively), to systematically investigate the effect of increasing the Al/Ti ratio on the alloy microstructure. Figure 5.11 presents the equilibrium phase diagrams of the three alloy compositions. It can be seen that all three alloys form a stable L1₂/FCC dual-phase structure at room temperature with comparable volume fractions of the two

phases. The primary difference among the three alloys lies in the thermodynamic stability range of the L_{12} phase. Specifically, with increasing Al content, the high-temperature stability range of the L_{12} phase above the solidus gradually diminishes, implying that the amount of L_{12} phase formed directly from the liquid during solidification decreases. It can thus be inferred that increasing the Al/Ti ratio can alter the formation pathway of the L_{12} phase, thereby further optimizing the microstructural characteristics of the multi-scale core-shell structure.

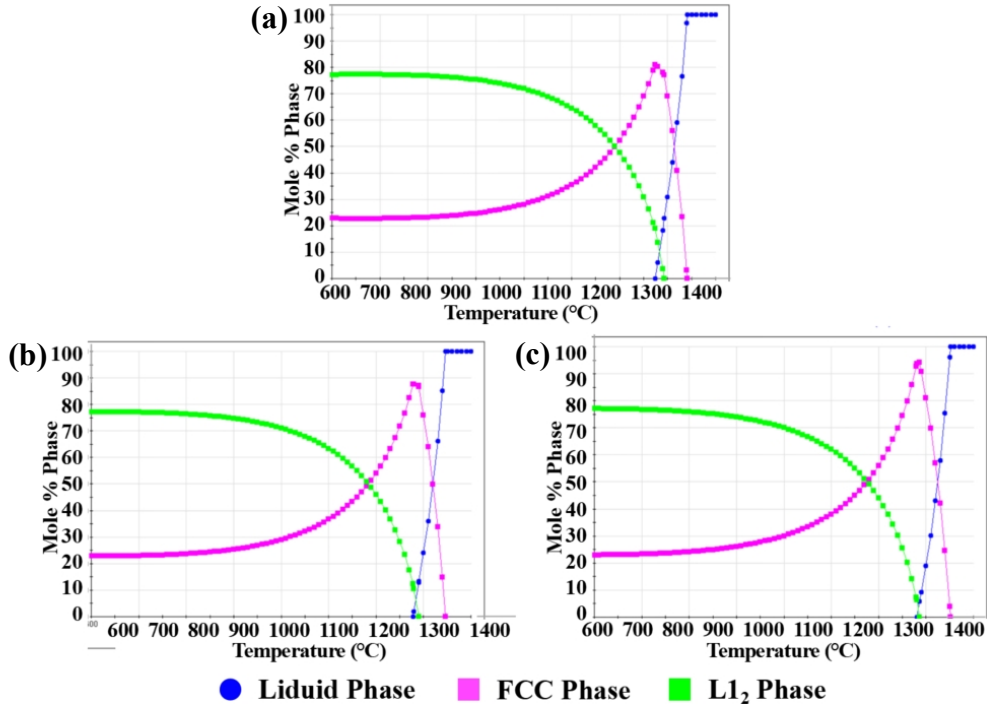


Fig. 5.11 Temperature dependence of equilibrium phase fractions in $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents
(a) Al8 alloy; (b) Al9 alloy; (c) Al10 alloy

5.3.2 Microstructure of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

From the thermodynamic calculation results in the previous section, the Al8, Al9, and Al10 alloys all fall within the L_{12} /FCC two-phase coexistence regime thermodynamically. To further analyze the actual phase constitution of the alloys, XRD measurements were performed on the as-cast specimens, and the results are shown in Fig. 5.12. As can be seen, all three alloys exhibit typical L_{12} /FCC dual-phase diffraction characteristics, with the main diffraction peaks corresponding to the (111), (200), and (220) planes of the FCC/ L_{12} phases. Notably, all three as-cast alloys display a superlattice diffraction peak corresponding to the (100) plane of the L_{12} phase near $2\theta=25^\circ$, which unequivocally confirms the presence of the L_{12}

ordered phase in the alloy system. In addition, no characteristic peaks of other secondary phases were detected in the patterns, indicating that the as-cast alloys largely maintain an L1₂/FCC dual-phase structure.

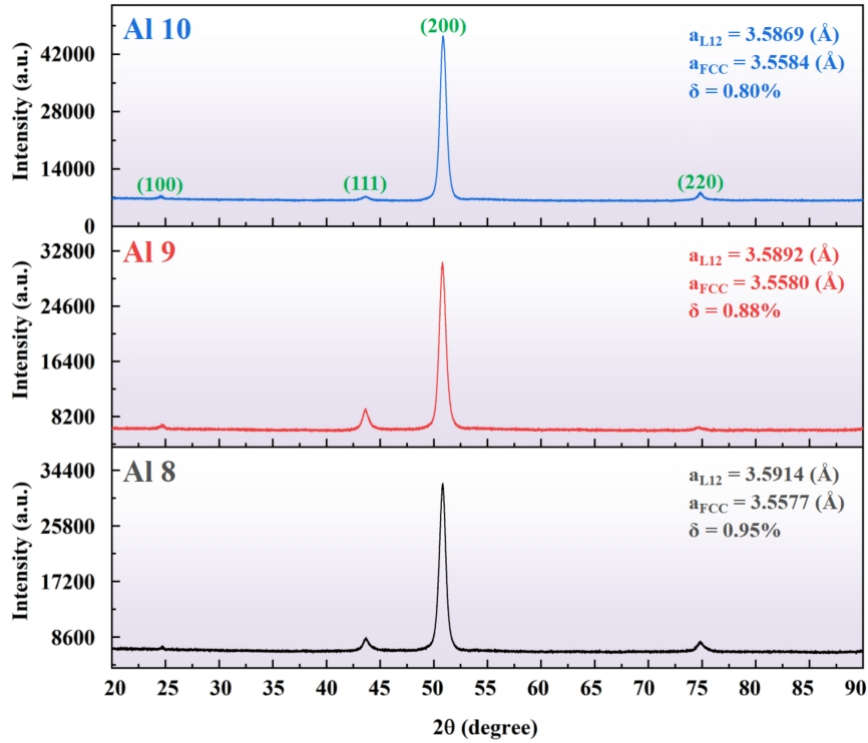


Fig. 5.12 XRD patterns of the Ni₅₀Co₂₅Al_xTi_(14-x)Ta_{1.5}Cr_{9.5} alloys with varying Al contents

To quantitatively characterize the lattice misfit relationship between the FCC and L1₂ phases in the three alloys and to provide a reliable basis for subsequent microstructural evolution and interfacial feature analysis, deconvolution peak fitting was performed on the (200)_{FCC/L1₂} diffraction peaks of the three alloys. Based on the fitting results, the lattice constants of the FCC and L1₂ phases in each alloy were calculated, and the corresponding lattice misfit was further determined; the relevant values are summarized in Table 5.2. The results show that with a gradual increase in the Al/Ti ratio, the lattice misfit between the FCC and L1₂ phases in the alloys exhibits a continuously decreasing trend, indicating that compositional regulation can effectively tune the degree of coherency between the two phases.

To further reveal the microstructural characteristics and the formation of the multi-scale core-shell structure in the Ni₅₀Co₂₅Al_xTi_(14-x)Ta_{1.5}Cr_{9.5} alloys, SEM characterization was carried out on the as-cast specimens of the three compositions,

with the results presented in Fig. 5.13. From Fig. 5.13 (a)–(c), it can be seen that all three alloys developed typical as-cast dendritic solidification microstructures, and, similar to the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy, there is a pronounced contrast difference between the dendrite interior and the grain boundary vicinity. Further observation reveals that with increasing Al/Ti ratio, the volume fraction of the light-contrast microstructure near the grain boundaries gradually decreases. This change is manifested not only in the reduction of the thickness of this region but also in the significant weakening of its continuity. Ultimately, the light-contrast microstructure exhibits a discontinuous distribution along the grain boundaries in the Al10 alloy.

Table 5.2 FCC and L1₂ lattice constants and the corresponding lattice misfit between the two phases in $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents as determined by XRD analysis

Alloys	FCC phase lattice constant (Å)	L1 ₂ phase lattice constant (Å)	FCC/L1 ₂ lattice misfit (%)
Al8	3.5577	3.5914	0.95
Al9	3.5580	3.5892	0.88
Al10	3.5584	3.5869	0.80

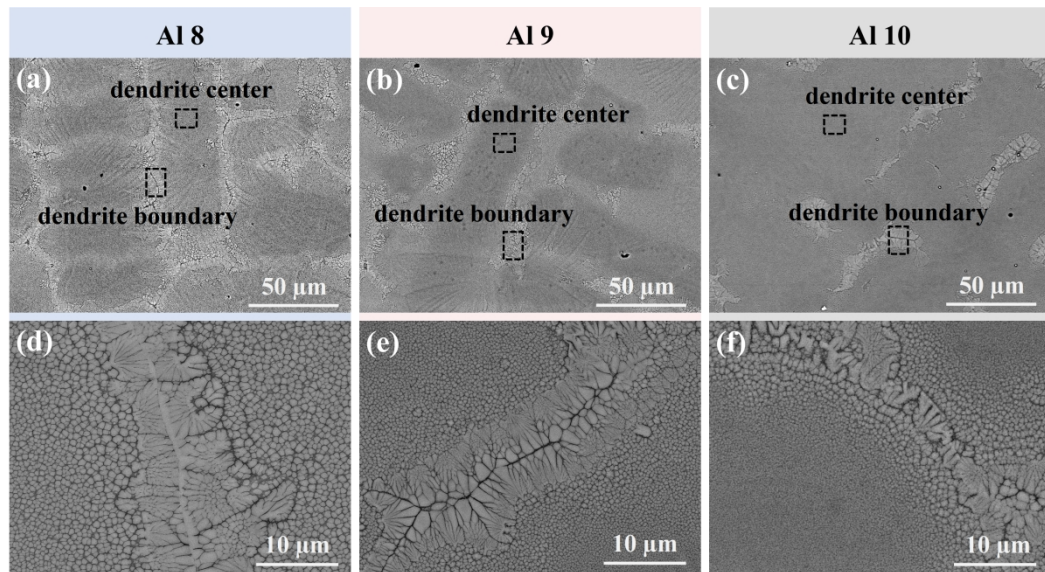


Fig. 5.13 Microstructure of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

(a) Al8 alloy overview; (b) Al9 alloy overview; (c) Al10 alloy overview; (d) Al8 alloy grain boundary; (e) Al9 alloy grain boundary; (f) Al10 alloy grain boundary

Subsequently, high-magnification characterization was performed on the light-contrast regions near the grain boundaries of the three alloys, with the results shown in Fig. 4.13 (d)–(f). As can be seen from the images, these regions are still composed

of micron-scale cellular core–shell structures whose morphological characteristics are consistent with the microstructure observed in the same region of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy. Furthermore, statistical measurements were carried out on the thickness of the region containing the micron-scale core–shell structures in the three alloys. The results indicate that with increasing Al/Ti ratio, the average thickness of this region progressively decreases from approximately 18 μm in the Al8 alloy to approximately 15 μm in the Al9 alloy, and further to approximately 10 μm in the Al10 alloy. Meanwhile, the characteristic size of individual micron-scale cellular L_{12} ordered cores also exhibits a decreasing trend. The above results demonstrate that raising the Al/Ti ratio can reduce the size and volume fraction of the micron-scale core–shell structures and weaken the continuity of the region in which they reside.

Meanwhile, characterization of the microstructure within the dendrite interior of the three alloys revealed that this region still exhibits fine core–shell structural features. However, unlike the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy, the size of the core–shell structures within the dendrite interior in this series of alloys is not uniform but instead displays a gradient size distribution that gradually decreases from the vicinity of the dendrite boundary toward the dendrite center, as shown in Fig. 5.14.

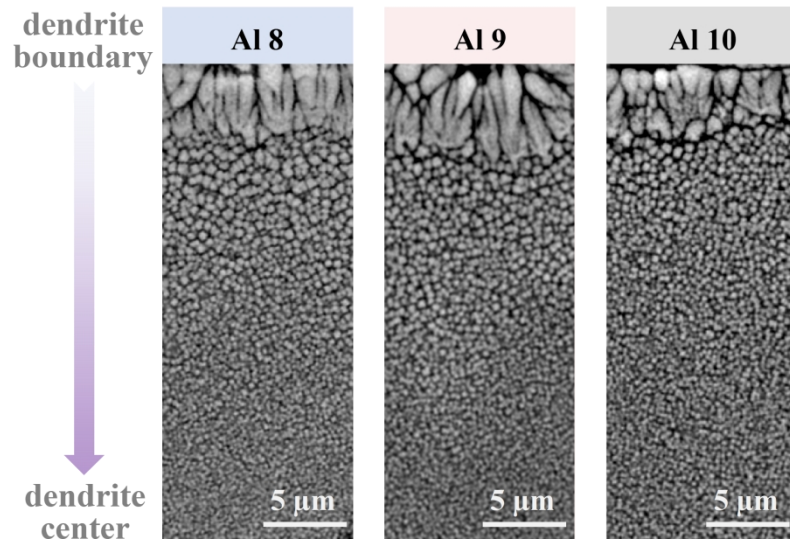


Fig. 5.14 Microstructure within dendrite interior of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

Based on the above observations, further characterization was conducted on the microstructure within the dendrite interior of this series of alloys, and the results

are presented in Fig. 5.15. As shown in Fig. 5.15 (a), the dendrite boundary region of the Al8 alloy consists of micron-scale cellular core-shell structures, which exhibit progressively larger volumes and higher aspect ratios as the dendrite boundary is approached. With increasing distance from the dendrite boundary, the aspect ratio of the cellular cores gradually decreases and their morphology progressively transforms into a cuboidal shape. In the region adjacent to the micron-scale cellular core-shell structures, submicron-scale cuboidal core-shell structures are formed, as shown in Fig. 5.15 (b). With further distance from the grain boundary, the size of these submicron-scale cuboidal core-shell structures gradually decreases, while their morphology undergoes no significant change. At the dendrite center region, the size of the submicron-scale cuboidal core-shell structures reaches its minimum, as shown in Fig. 5.15 (c). Statistical analysis of the cuboidal core size within the dendrite interior of the Al8 alloy indicates an average diameter of approximately 127.38 nm, as shown in Fig. 5.15 (d).

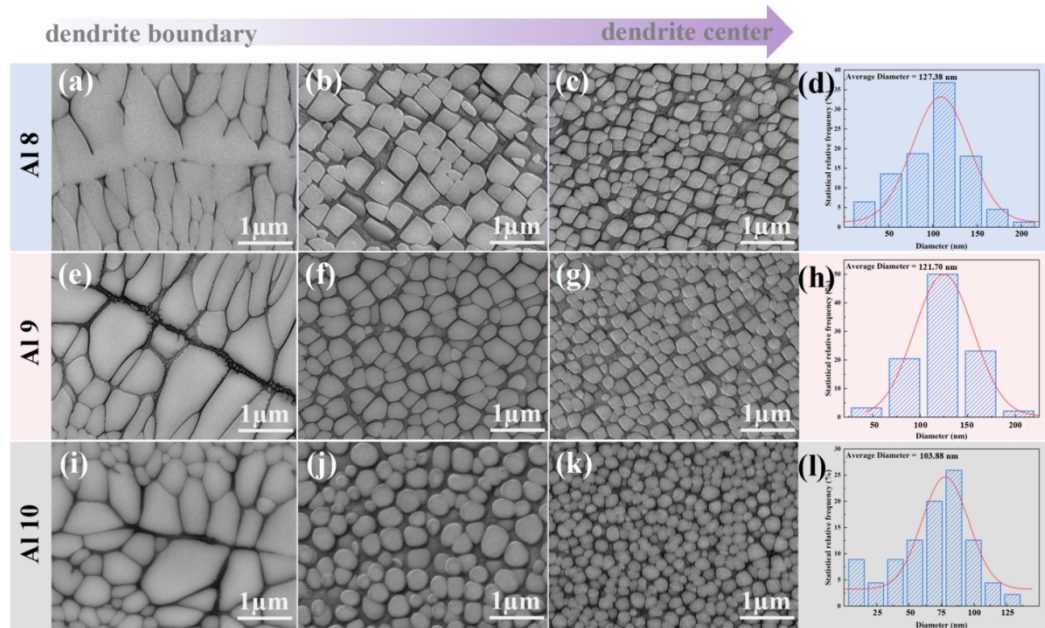


Fig. 5.15 Microstructural characterization of different regions in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

(a) dendrite boundary region of the Al8 alloy; (b) region adjacent to the dendrite boundary of the Al8 alloy; (c) dendrite center region of the Al8 alloy; (d) frequency distribution histogram of core diameters in the dendrite center region of the Al8 alloy; (e) dendrite boundary region of the Al9 alloy; (f) region adjacent to the dendrite boundary of the Al9 alloy; (g) dendrite center region of the Al9 alloy; (h) frequency distribution histogram of core diameters in the dendrite center region of the Al9 alloy; (i) dendrite boundary region of the Al10 alloy; (j) region adjacent to the dendrite boundary of the Al10 alloy; (k) dendrite center region of the Al10 alloy; (l) frequency distribution histogram of core diameters in the dendrite center region of the Al10 alloy

The microstructural characteristics of the Al9 alloy are essentially consistent with those of the Al8 alloy, as shown in Fig. 5.15 (e)–(g). The main difference between the two lies in that the submicron-scale core–shell structures in the Al9 alloy exhibit a morphology that tends more toward a near-spherical cuboidal shape, and their average core diameter decreases to 121.70 nm, as shown in Fig. 5.15 (h). For the Al10 alloy, the dendrite interior still retains a pronounced structural gradient, as shown in Fig. 5.15 (i)–(k). Unlike the former two alloys, the morphology of the submicron-scale core–shell structures in the Al10 alloy has completely transformed into a spherical shape, while the average core diameter further decreases to 103.88 nm, as shown in Fig. 5.15 (l). Thus, it can be seen that with increasing Al/Ti ratio, the size of the submicron-scale core–shell structures exhibits a continuous gradient distribution, while the core size decreases and the morphology gradually transforms from cuboidal to spherical.

At present, dual-scale core–shell structures exhibiting a structural gradient have been observed in all three alloys. To further clarify their crystal structure, TEM characterization was performed on the core–shell structures at different scales in the three alloys, and the results are shown in Fig. 5.16 and 5.17. Fig. 5.16 (a)–(c) presents the high-angle annular dark-field images of the micron-scale core–shell structures in the three alloys, from which the morphological features of both the core and the shell can be clearly distinguished. Further selected area electron diffraction analysis of the core regions reveals distinct superlattice diffraction spots in the insets, indicating that the micron-scale cores in all three alloys possess an $L1_2$ ordered structure.

Subsequently, high-resolution scanning transmission electron microscopy characterization was performed on the micron-scale core–shell interface regions of the three alloys, and the results are shown in Fig. 5.16 (d)–(f). The high-resolution images reveal that a well-maintained coherent interface exists between the core and the shell. Further FFT analysis was conducted on the regions on both sides of the interface. The results show that the core region exhibits only superlattice diffraction spots corresponding to the $L1_2$ ordered structure, confirming it to be an $L1_2$ ordered phase. In contrast, in the shell region, in addition to distinct diffraction spots of the disordered FCC structure, faint ordered superlattice reflections are also observed. It

can thus be inferred that the micron-scale core–shell structure as a whole belongs to an $L1_2$ –FCC dual-phase core–shell structure, but $L1_2$ ordered phases may exist within the FCC shell. Furthermore, the TEM results also indicate that the shell thickness in this region does not change significantly with increasing Al/Ti ratio, with the average shell thickness in all three alloys remaining consistently at approximately 10 nm.

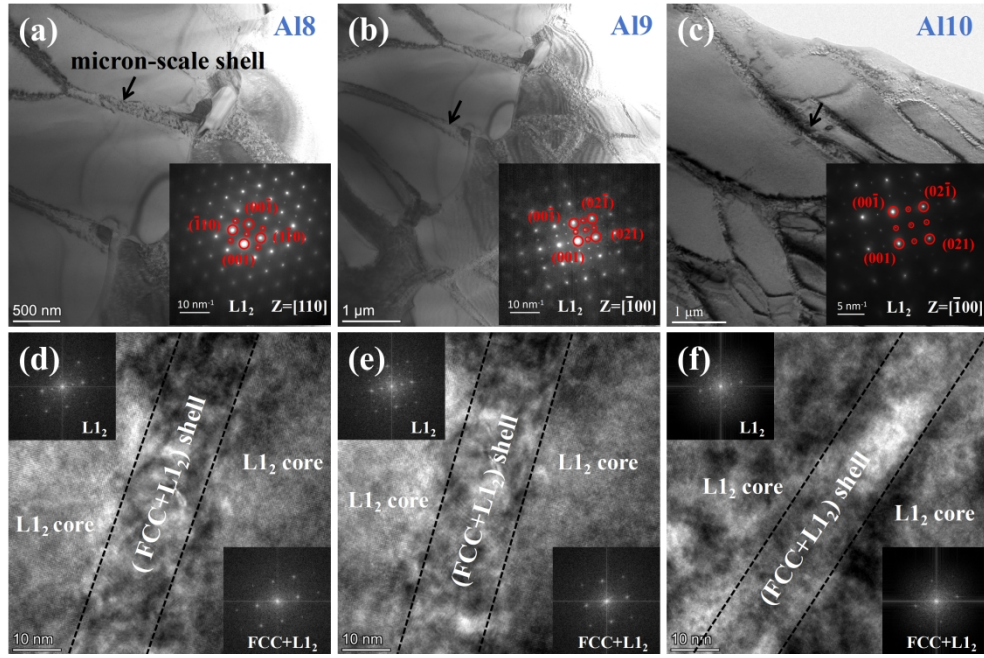


Fig. 5.16 TEM characterization of the micron-scale core–shell structure in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

(a) HAADF-STEM image and corresponding SAED pattern of the core in the Al8 alloy; (b) HAADF-STEM image and corresponding SAED pattern of the core in the Al9 alloy; (c) HAADF-STEM image and corresponding SAED pattern of the core in the Al10 alloy; (d) HR-STEM image and FFT analysis of the core–shell interface in the Al8 alloy; (e) HR-STEM image and FFT analysis of the core–shell interface in the Al9 alloy; (f) HR-STEM image and FFT analysis of the core–shell interface in the Al10 alloy

Fig. 5.17 (a)–(c) shows the HAADF-STEM images of the submicron-scale core–shell structures in the three alloys, from which the densely distributed cores and their surrounding shells can be clearly observed. Selected-area electron diffraction analysis of the core regions reveals distinct superlattice diffraction spots in the insets, indicating that the submicron-scale cores in all three alloys adopt the $L1_2$ ordered structure. Fig. 5.17 (d)–(f) presents the high-resolution scanning transmission electron microscopy images of the submicron-scale core–shell interface regions in the three alloys.

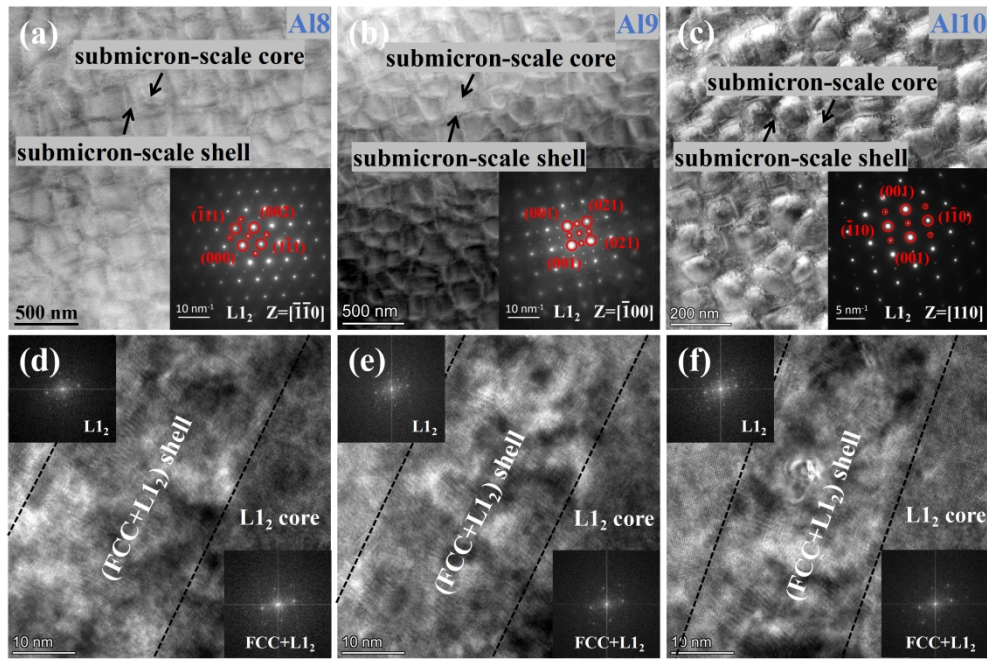


Fig. 5.17 TEM characterization of the submicron-scale core-shell structure in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

(a) HAADF-STEM image and corresponding SAED pattern of the core in the Al8 alloy; (b) HAADF-STEM image and corresponding SAED pattern of the core in the Al9 alloy; (c) HAADF-STEM image and corresponding SAED pattern of the core in the Al10 alloy; (d) HR-STEM image and FFT analysis of the core-shell interface in the Al8 alloy; (e) HR-STEM image and FFT analysis of the core-shell interface in the Al9 alloy; (f) HR-STEM image and FFT analysis of the core-shell interface in the Al10 alloy

It can be seen from the figure that the core and the shell likewise maintain a good coherent interface relationship, and the shell thickness in this region is significantly greater than that in the micron-scale core-shell structure. The FFT analysis results on both sides of the interface, as shown in the insets, further indicate that the core region corresponds to the ordered L_{12} crystal structure, while the shell region simultaneously exhibits the FCC crystal structure and weak ordered superlattice reflections. Unlike the micron-scale core-shell structure, the variation in the Al/Ti ratio exerts a pronounced effect on the shell thickness of the submicron-scale core-shell structure. As the Al/Ti ratio increases, the shell thickness decreases markedly. Specifically, the shell thickness is ~ 25 nm in the Al8 alloy, decreases to ~ 20 nm in the Al9 alloy, and further reduces to ~ 15 nm in the Al10 alloy.

The above TEM analysis results demonstrate that core-shell structures at two distinct length scales exist in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys. Among them, the submicron-scale core-shell structures exhibit a continuous gradient size distribution within the dendrite interiors. Further analysis reveals that the cores at

both scales are the $L1_2$ ordered phase, whereas the shell regions at both scales display a two-phase structure consisting of coexisting FCC and $L1_2$ phases. Notably, the diffraction spots of the $L1_2$ phase in the shell are extremely weak, which is presumably attributable to their small size. To further clarify the microstructural characteristics of the shell regions in this series of alloys, high-magnification SEM analysis was performed on the dendrite interiors of the three alloys. For each alloy composition, three typical locations were selected for characterization: the micron-scale core-shell structure region, the submicron-scale core-shell structure region, and the transitional region between the two, with the results presented in Fig. 5.18. It can be observed from the figure that nanoscale tiny particles are visible in the shell regions of core-shell structures at all scales, and these are speculated to be the cause of the weak $L1_2$ diffraction spots observed in the shell regions in the aforementioned TEM analysis.

To further identify the crystal structure of the nanoscale tiny particles, detailed TEM characterization was carried out. Since the shell of the submicron-scale core-shell structure region in the Al8 alloy is thicker, which is more conducive to observing the presence of tiny particles, the Al8 alloy was selected as the object of study, and the results are shown in Fig. 5.19. First, a field of view encompassing the submicron-scale core-shell structure region was selected in HAADF-STEM mode, as shown in Fig. 5.19 (a). Owing to the extremely small size of the nanoparticles, it is difficult to directly resolve their distinct morphology in this imaging mode. Therefore, the shell region marked by the pink dashed rectangle in Fig. 5.19 (a) was examined by high-resolution scanning transmission electron microscopy, with the result shown in Fig. 5.19 (b). In the high-resolution image, a small number of ordered atomic clusters exhibiting regular periodicity can be observed (as indicated by the white dashed circles in the figure), suggesting the presence of locally ordered structures within this region. An area with a relatively high concentration of ordered atomic clusters in Fig. 5.19 (b) (marked by the blue dashed rectangle) was further selected for FFT analysis, and the result is presented in Fig. 5.19 (c). It can be seen that, in addition to the diffraction spots corresponding to the FCC structure, a series of periodic superlattice diffraction spots located at positions such as $[0\bar{1}\bar{1}]$ also appear (as indicated by the yellow arrows in the figure). The above superlattice reflections are typical reciprocal-space characteristics of the $L1_2$ ordered structure,

indicating the presence of a phase with long-range ordered arrangement within this region.

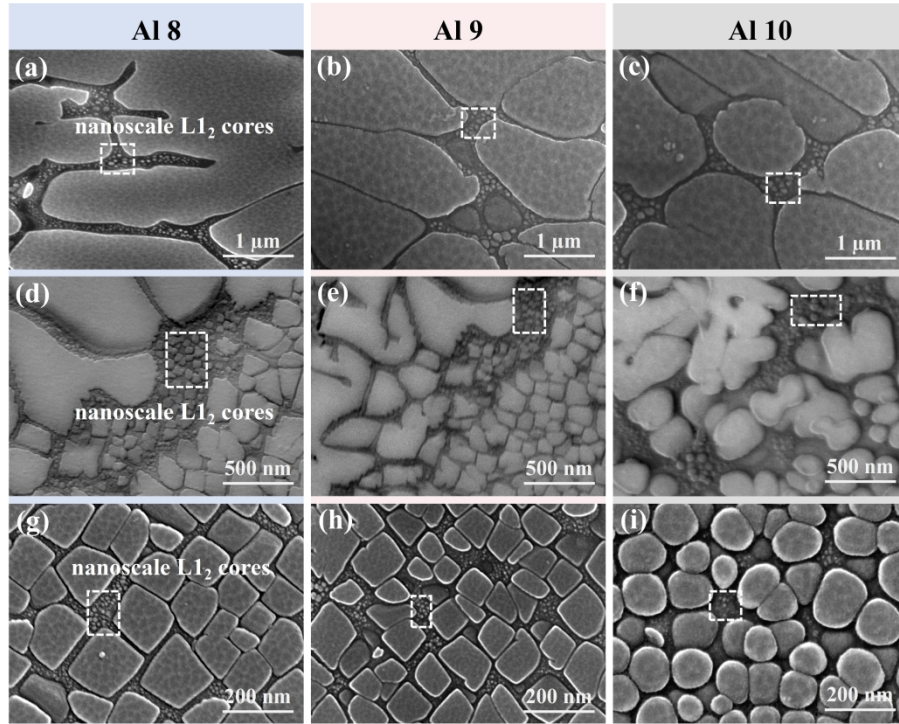


Fig. 5.18 Microstructural characterization of nanoscale particles within the different shell regions of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents (a) micron-scale core-shell structure region in the Al8 alloy; (b) micron-scale core-shell structure region in the Al9 alloy; (c) micron-scale core-shell structure region in the Al10 alloy; (d) transitional region between the micron- and submicron-scale core-shell structures in the Al8 alloy; (e) transitional region between the micron- and submicron-scale core-shell structures in the Al9 alloy; (f) transitional region between the micron- and submicron-scale core-shell structures in the Al10 alloy; (g) submicron-scale core-shell structure region in the Al8 alloy; (h) submicron-scale core-shell structure region in the Al9 alloy; (i) submicron-scale core-shell structure region in the Al10 alloy

To further intuitively reveal the distribution characteristics of these ordered structures in real space, a spot-masking treatment was applied to the superlattice diffraction spots in Fig. 5.19 (c), followed by inverse fast Fourier transform analysis, with the result shown in Fig. 5.19 (d). It can be seen from the figure that, after the spot-masked IFFT reconstruction, several periodically arranged ordered atomic regions exhibiting bright contrast are clearly revealed within the shell region. These bright regions correspond to the real-space ordered structures reconstructed from the superlattice frequency components, essentially reflecting regions where the local atomic arrangement undergoes a transition from disorder to order. Further observation reveals that these ordered atomic regions maintain a good coherent

relationship with the surrounding FCC shell in terms of crystallographic orientation, consistent with the structural characteristic of the $L1_2$ ordered phase precipitating coherently from the FCC matrix. Magnification of the ordered region marked by the white dashed rectangle in Fig. 5.19 (d) yields the result shown in Fig. 5.19 (e). It can be observed that the average diameter of such ordered atomic clusters is ~ 5 nm. The measured (111) interplanar spacing of ~ 0.213 nm is in excellent agreement with the characteristic spacing of the $L1_2$ crystal structure, further confirming the $L1_2$ ordered structure at the atomic scale.

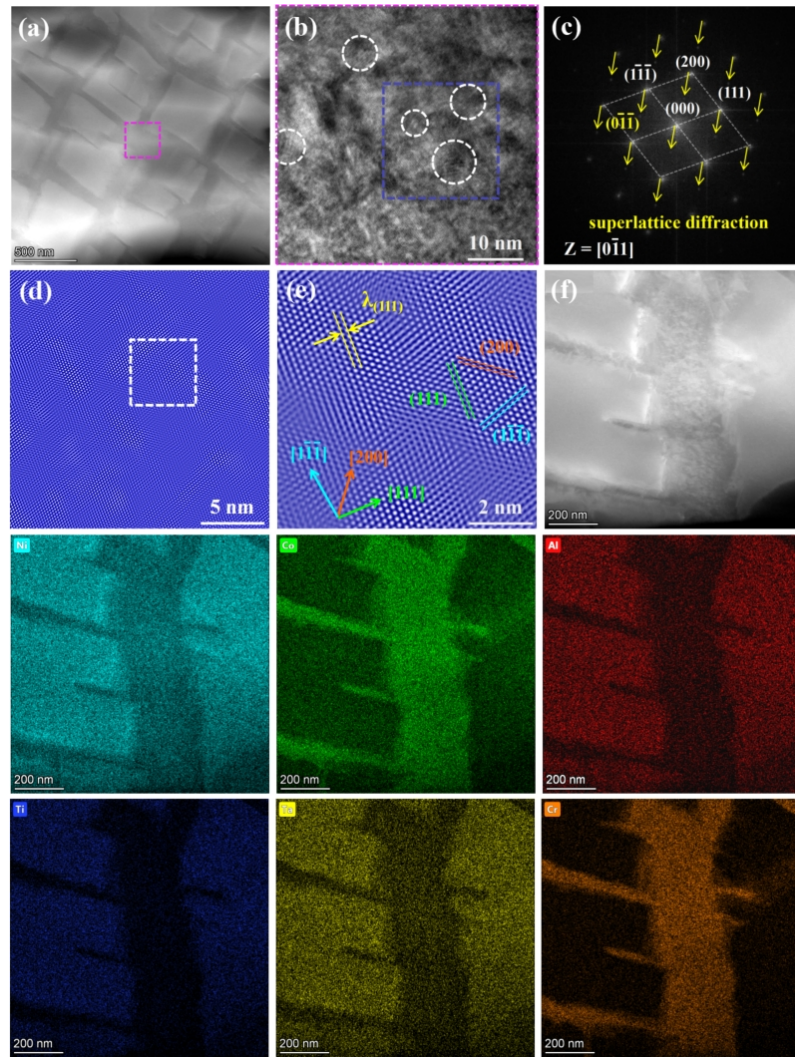


Fig. 5.19 TEM characterization of nanoscale particles in the Al8 alloy
(a) HAADF-STEM image of the submicron-scale core-shell structure region; (b)
high-resolution image of the area marked by the pink dashed rectangle in (a); (c)
FFT analysis of the area marked by the blue dashed rectangle in (b); (d) IFFT
analysis after spot-masking treatment of (c); (e) magnified image of the area marked
by the white dashed rectangle in (d); (f) elemental mapping of the submicron-scale
core-shell structure

In addition, TEM-EDS elemental mapping analysis was performed on the shell region, with the result shown in Fig. 5.19 (f). It can be seen that all major alloying elements are uniformly distributed within this region, without any obvious elemental enrichment or compositional segregation. This indicates that the ordered atomic clusters observed in the high-resolution images are not artifacts arising from local compositional fluctuations or imaging artifacts, but represent genuine physical structural features resulting from crystalline ordering. Combining the superlattice reflections and periodic atomic arrangement characteristics revealed by the aforementioned FFT/IFFT analyses, it can be further confirmed that the nanoscale clusters formed in the shell region are essentially nanophases possessing the $L1_2$ ordered structure. It can thus be confirmed that, within the shell region of the Al8 alloy, a nanoscale $L1_2$ -FCC core-shell structure is further developed.

Summarizing the above TEM characterization results, by increasing the Al/Ti ratio, multi-scale core-shell structures spanning the micron, submicron, and nanometer scales are formed in the microstructure of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys. Among them, the submicron-scale core-shell structures exhibit a gradient size distribution that changes continuously from the boundary toward the center within the dendrite interiors. Furthermore, the effect of increasing the Al/Ti ratio differs significantly among core-shell structures at different scales. For the micron-scale core-shell structure, increasing the Al/Ti ratio reduces the core size and simultaneously decreases the volume fraction and continuity of the region where this structure resides. For the submicron-scale core-shell structure, increasing the Al/Ti ratio likewise reduces the core size and causes the morphology to transform from cuboidal to nearly spherical. At the same time, increasing the Al/Ti ratio also reduces the shell thickness of the submicron-scale core-shell structure, but has no significant effect on the shell thickness of the micron-scale core-shell structure.

5.4 Analysis of the formation mechanism and morphology transition mechanism of the multi-scale core-shell structure

The experimental results presented in the preceding two sections demonstrate that composition regulation can drive the core-shell structure to undergo a transition toward a multi-scale configuration, in which the morphology of the submicron-scale core-shell structure transforms as the Al/Ti ratio increases. However, the

formation mechanism and transition mechanism of these microstructural features remain unclear at present. To this end, this section takes the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys, which exhibit multi-scale core-shell structure characteristics, as the model system, and combines thermodynamic calculations with thermal analysis experiments to elucidate the formation mechanism of the multi-scale core-shell structure and the morphology transition mechanism of the submicron-scale core-shell structure.

5.4.1 Formation mechanism of multi-scale core-shell structure

As previously noted in the compositional regulation of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy, the key to the formation of multi-scale core-shell structures lies in the generation of multi-scale L1_2 ordered phases. Therefore, investigating the formation mechanism of multi-scale core-shell structures essentially amounts to a deeper understanding of the formation process of multi-scale L1_2 ordered phases. Considering that the L1_2 phase may form either directly during solidification or through solid-state precipitation in the subsequent cooling stage, this section first systematically analyzes the formation of the L1_2 phase during the solidification stage by examining the variation of the solid fraction with temperature during alloy solidification. The solidification phase fraction as a function of temperature for the three alloys is presented in Fig. 5.20.

As can be seen from the figure, the three alloys exhibit highly similar solidification pathways. As the temperature decreases, an FCC phase first forms from the liquid, and its volume fraction increases rapidly. In the middle-to-late stages of solidification, a small amount of the L1_2 phase begins to appear in all three alloys and gradually increases with further decreasing temperature. Concurrently, the growth rate of the FCC phase slows down markedly, and after reaching its maximum, it starts to decline. When the temperature drops below the solidus, the L1_2 phase continues to increase while the FCC phase continues to decrease. As the temperature further decreases to approximately 800 °C the solid fractions of the three alloys tend to stabilize. Ultimately, at room temperature, the phase constitutions of the three alloys are essentially identical, in good agreement with the equilibrium phase diagram calculations.

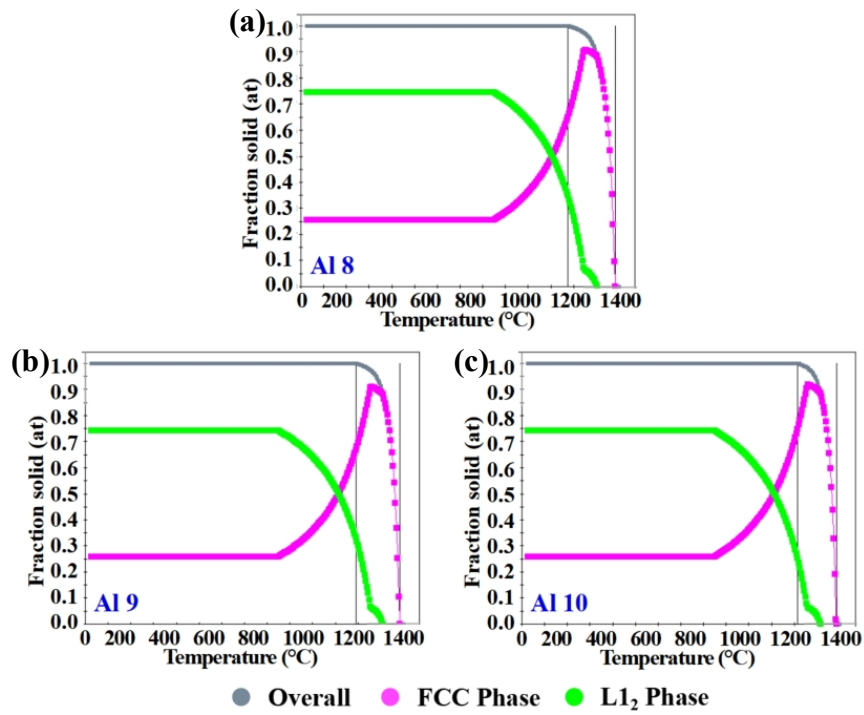


Fig. 5.20 Temperature dependence of solidification phase fractions in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents
(a) Al8 alloy; (b) Al9 alloy; (c) Al10 alloy

The primary difference among the three alloys lies in the solidification interval above the solidus temperature. As can be seen from the figure, with an increasing Al/Ti ratio, the solidus temperature of the alloys rises slightly, and the solidification interval is correspondingly shortened. Under the premise that the temperature at which the L_{12} phase first begins to form does not change significantly, the formation window of the L_{12} phase during the solidification stage is thereby narrowed, leading to a decrease in the amount of L_{12} phase formed during solidification. In conjunction with the actual microstructural observations of the three alloys, it can be found that with an increasing Al/Ti ratio, the micron-scale core-shell structures at grain boundaries are significantly reduced. It can thus be inferred that the micron-scale L_{12} ordered cores primarily form during the solidification process. To further verify this inference, differential scanning calorimetry (DSC) measurements were performed to investigate the thermal behavior of the three alloys during cooling, and the results are presented in Fig. 5.21.

As can be seen from the figure, the three alloys exhibit similar exothermic behavior during cooling, with three distinct exothermic peaks appearing in all the curves. With decreasing temperature, all three alloys first exhibit a sharp main exothermic

peak at approximately 1330 °C, corresponding to the latent heat released during the solidification of the primary FCC phase. In the late stage of FCC solidification, a smaller but equally sharp exothermic peak appears in all three alloys. In general, such a small exothermic peak accompanying the main peak before the completion of solidification usually corresponds to a eutectic reaction at the late stage of solidification. This reaction involves the direct transformation of the liquid into two solid phases and is a first-order phase transformation. Accordingly, its exothermic peak exhibits a relatively sharp profile. In the present alloy system, this reaction occurs at the late stage of solidification within a narrow reaction window, with a limited amount of liquid phase participating in the reaction. Consequently, the heat released is relatively small, manifesting as a low-height small exothermic peak. In combination with the calculated results of the solid phase formation sequence during solidification, it can be inferred that this eutectic reaction corresponds to the formation of the $L1_2$ phase in the solidification stage. The variations in the relative position and peak height of this eutectic reaction exothermic peak with the Al/Ti ratio in the DSC curves of the three alloys provide supporting evidence for this inference. Specifically, as the Al/Ti ratio increases, both the peak height and the corresponding characteristic temperature gradually decrease. This trend is consistent with two observations: the marked reduction in the number of micron-scale core-shell structures in the actual microstructure, and the calculated result showing that the appearance window of the $L1_2$ phase within the solidification interval is relatively delayed.

Studies have shown that the solid phases formed by eutectic reactions near grain boundaries at the late stage of solidification generally follow a discontinuous precipitation mechanism [115]. In this mechanism, the grain boundary serves as the nucleation and growth front, accompanied by interface migration and compositional redistribution, which enables the new phase to grow rapidly along the grain boundary direction, thereby resulting in solid phases on the micron scale. Their morphology often appears as elongated cellular features, being broader and thicker on the side adjacent to the grain boundary. The morphological characteristics of solid phases formed by this discontinuous precipitation mechanism are highly consistent with the micron-scale $L1_2$ ordered cores observed near the dendrite boundaries in the present alloy system. Therefore, by integrating

the solidification pathway calculations, microstructural characterization, and DSC results, it can be concluded that the micron-scale $L1_2$ ordered cores near the dendrite boundaries are primarily formed through a eutectic reaction at the late stage of solidification, and this formation process belongs to the discontinuous precipitation mechanism.

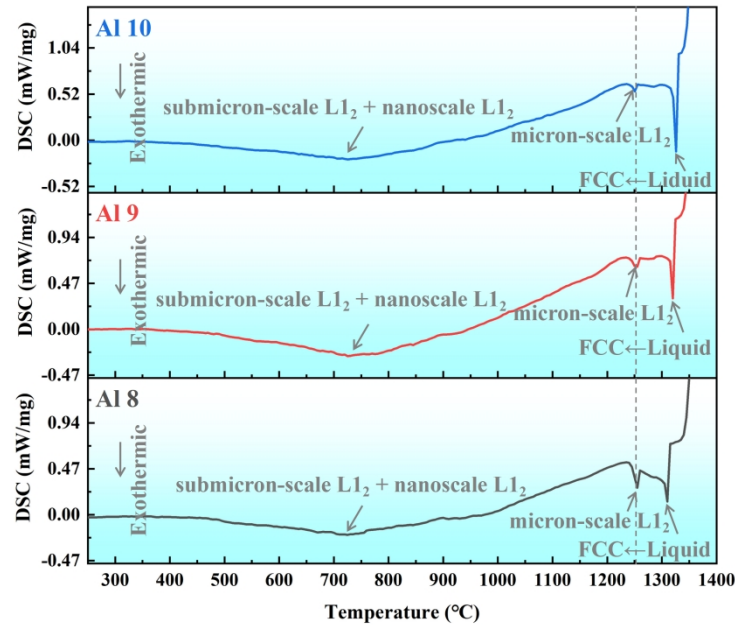


Fig. 5.21 DSC curves of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

After the appearance of the sharp small exothermic peak, as the temperature decreases further, all three alloys exhibit a broad and gentle exothermic peak in their DSC curves. This exothermic process becomes evident immediately upon the completion of solidification, persists up to approximately 500 °C, with its peak located at around 800 °C. Such a broad exothermic peak typically corresponds to the precipitation of solid phases within the matrix. This is because the formation of this type of phase is primarily diffusion-controlled and belongs to a continuous solid-state phase transformation. In essence, it involves neither abrupt interface migration nor a concentrated release of latent heat by phase transformation, and therefore does not manifest as a sharp exothermic peak.

In combination with the microstructural characteristics of the three alloys, it can be inferred that this broad exothermic peak corresponds to the solid-state precipitation process of submicron-scale and nano-scale $L1_2$ ordered cores. Generally, such broad exothermic peaks are commonly observed in alloys exhibiting precipitation

behavior and typically correspond to the exothermic process caused by precipitates of a single scale, such as the γ' phase precipitation in precipitation-strengthened Ni-based superalloys. However, in the present alloy system, the multi-principal-element compositional characteristics introduce a pronounced sluggish diffusion effect, so that the initially formed $L1_2$ ordered cores cannot rapidly deplete the alloying elements participating in the $L1_2$ phase formation in the surrounding FCC matrix. As the temperature further decreases, the FCC matrix once again reaches a supersaturated state, thereby triggering secondary nucleation of the $L1_2$ ordered phase at a lower temperature range. Since the initially formed $L1_2$ ordered cores nucleate immediately upon the completion of solidification, they experience a higher nucleation temperature, a broader growth temperature window, and a longer growth duration. As a result, they can grow to the submicron scale. In contrast, the subsequently formed $L1_2$ ordered cores nucleate at a lower temperature and have limited growth time. Furthermore, the atomic diffusion capability is significantly restricted at low temperatures, so they can only develop to the nano-scale. In addition, the low-temperature nucleation process of the nano-scale $L1_2$ ordered cores overlaps extensively in temperature range with the continued growth of the submicron-scale $L1_2$ ordered cores, making the two processes difficult to distinguish thermally. Therefore, the heat released by both processes is collectively incorporated into the broad and gentle exothermic peak corresponding to the solid-state precipitation of the $L1_2$ ordered phase.

In addition, the submicron-scale $L1_2$ ordered cores in all three alloys exhibit a distinctive gradient size distribution. From the thermodynamic calculation analysis in Section 4.2.2, it is known that the precipitation of the $L1_2$ phase is related to the supersaturation driving force of the primary solid phase. Therefore, the variation of the solute concentration in the liquid phase as a function of the solid fraction during solidification is first analyzed for the three alloys, so as to reveal the formation mechanism of the gradient microstructural characteristics. Fig. 5.22 shows the real-time evolution of elemental concentrations in the liquid phase as the solid fraction increases during the solidification of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys. As can be seen, the three alloys exhibit highly similar solute partitioning characteristics. With increasing solid fraction, the concentrations of Ni and Al in the liquid phase remain essentially constant, indicating that these two elements are distributed

relatively uniformly within the dendrite interior. In contrast, the concentrations of Co and Cr in the liquid phase decrease significantly, with a more pronounced decreasing trend for Co, suggesting that Co and Cr tend to be enriched in the central region of the early-formed dendrites. Meanwhile, the concentrations of Ti and Ta in the liquid phase continue to increase after the onset of solidification, indicating that the growing primary FCC solid phase continuously rejects these strong L1₂-forming elements into the remaining liquid. Consequently, at the late stage of solidification, a pronounced enrichment of Ti and Ta gradually develops in the interdendritic regions. When the solute concentration of the residual interdendritic liquid enters the eutectic reaction regime, the eutectic reaction that directly produces FCC and L1₂ phases from the liquid is initiated, corresponding to the first appearance of the L1₂ phase in the solidification phase diagram. Thereafter, elements such as Ni, Al, and Ti in the liquid are rapidly consumed, generating the FCC phase and micron-scale L1₂ ordered cores until the completion of solidification. It can thus be seen that the driving force for the formation of micron-scale L1₂ ordered cores essentially originates from the compositional segregation induced by solute redistribution at the late stage of solidification. Ta, as a strong L1₂-forming element, further intensifies the segregation behavior in the liquid, thereby promoting the formation of micron-scale core-shell structures at the dendrite boundaries.

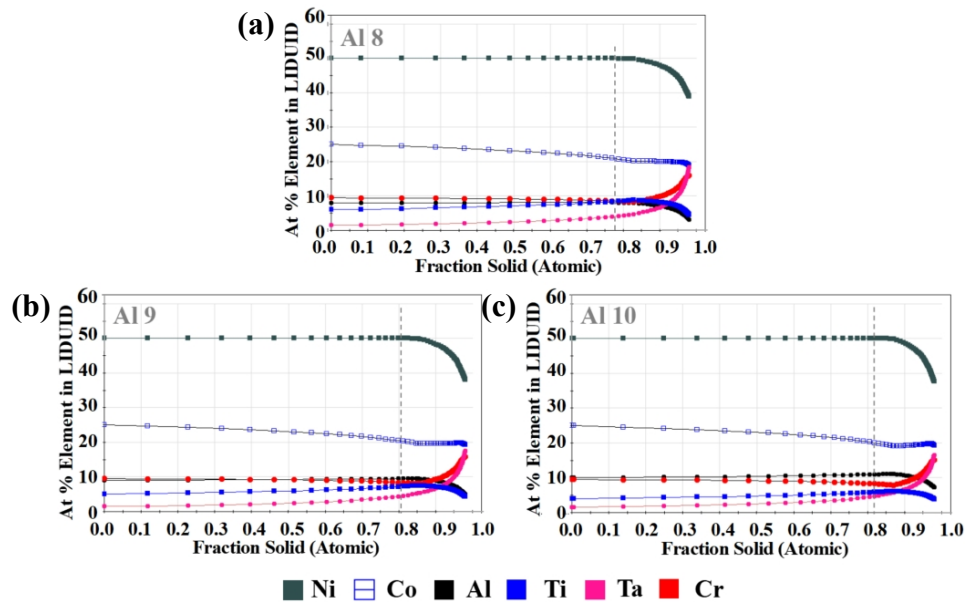


Fig. 5.22 Variation of solute concentration in the liquid phase as a function of solid fraction during solidification of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

(a) Al8 alloy; (b) Al9 alloy; (c) Al10 alloy

It is noteworthy that with an increasing Al/Ti ratio, the turning points at which the elemental concentrations begin to exhibit significant fluctuations during the late stage of solidification are shifted to later stages overall. This changing trend is consistent with the delayed appearance of the L1₂ phase in the solidification pathway calculations and the decrease in the characteristic temperature of the eutectic reaction exothermic peak in the DSC measurements. Meanwhile, the increase in the Al/Ti ratio also reduces the amplitude of elemental fluctuations at the late stage of solidification, indicating that the extent of the eutectic reaction gradually weakens. This characteristic directly corresponds to the progressive decrease in the volume fraction of micron-scale core–shell structures observed in the microstructures of the three alloys. Furthermore, compared with the Co25 alloy, the elemental concentration variations during solidification are more pronounced in the Ni₅₀Co₂₅Al_xTi_(14-x)Ta_{1.5}Cr_{9.5} alloys, as manifested by an overall increase in the absolute values of the curve slopes. This implies that the primary FCC solid phase develops a stronger compositional gradient from the dendrite center to the boundary, thereby establishing a significant chemical field gradient upon the completion of solidification, which lays the foundation for the gradient-type continuous size distribution of the submicron-scale L1₂ ordered cores during the subsequent cooling process.

Furthermore, SEM-EDS line-scan compositional analysis was conducted across the dendrite boundary regions of the Ni₅₀Co₂₅Al_xTi_(14-x)Ta_{1.5}Cr_{9.5} alloys, and the results are shown in Fig. 5.23. As can be seen from the figure, the contents of Ti and Ta exhibit a continuously decreasing distribution from the dendrite boundary toward the dendrite center, whereas Co and Cr show a continuously increasing trend, and the contents of Ni and Al remain essentially constant. This indicates that the addition of Ta significantly slows down the diffusion kinetics in the multi-principal-element alloy system at the late stage of solidification, enabling the compositional gradient established during solidification to be effectively preserved in the solid state. Within such a chemical field characterized by a spatial gradient, the FCC matrix in the region adjacent to the dendrite boundary is the first to reach a supersaturated state and thus preferentially nucleates the L1₂ ordered phase. As the nucleation site advances toward the dendrite center, the local chemical driving force gradually weakens, and the nucleation of the L1₂ phase is correspondingly delayed.

Consequently, the $L1_2$ ordered cores precipitated near the dendrite boundary, owing to their higher nucleation temperature and longer effective growth time, attain a final size that is markedly larger than that of the $L1_2$ ordered cores formed in the central region of the dendrite. Nevertheless, the $L1_2$ ordered cores formed at this stage all originate from solid-state precipitation, and their scale remains confined to the submicron range, thereby producing submicron-scale core–shell structures with a gradient size distribution characteristic within the dendrite interior.

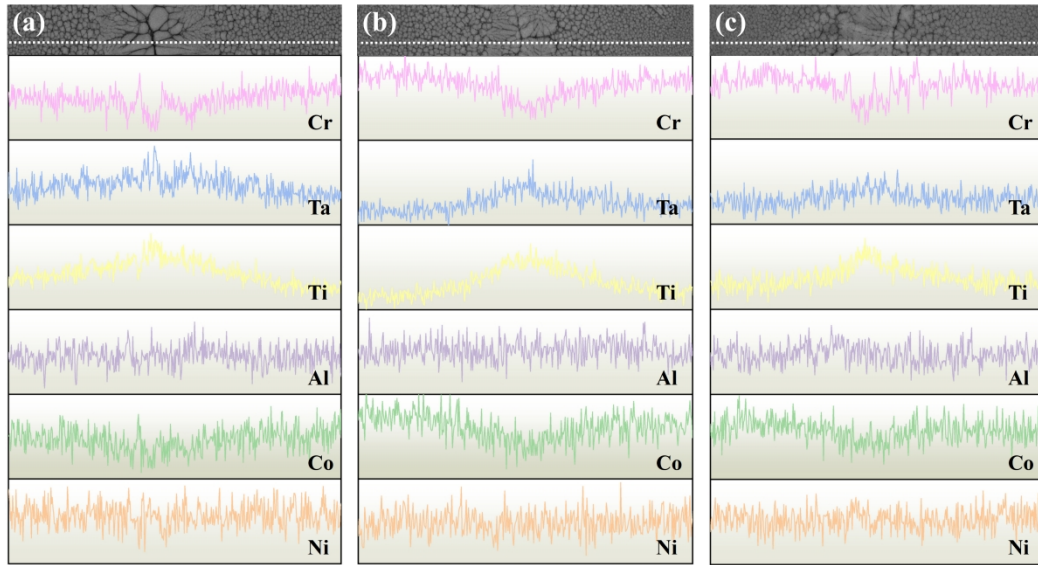


Fig. 5.23 SEM-EDS line-scan compositional analysis across the dendrite boundary regions of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents (a) Al8 alloy; (b) Al9 alloy; (c) Al10 alloy

In summary, the formation mechanisms of multi-scale core–shell structures in this alloy system can be classified into two categories: first, micron-scale $L1_2$ ordered cores formed directly through a eutectic reaction at the late stage of solidification; second, submicron-scale and nano-scale $L1_2$ ordered cores formed through solid-state precipitation below the solidus. The formation of submicron-scale $L1_2$ ordered cores is primarily dominated by composition-driven supersaturation, while the formation of the structural gradient within the dendrite interior originates from the difference in $L1_2$ nucleation onset time caused by the compositional gradient. Moreover, the sluggish diffusion effect inherent to the multi-principal-element alloy system not only helps preserve the compositional gradient established during solidification but also suppresses the continued growth of submicron-scale $L1_2$ ordered cores, making it difficult for them to fully deplete the solute elements participating in $L1_2$ formation within the surrounding FCC shell. Consequently, as

the temperature further decreases, the submicron-scale FCC disordered shell can once again reach a supersaturated state, thereby triggering the formation of nano-scale $L1_2$ ordered cores. Studies have shown that in FCC-type multi-principal-element alloy systems, the diffusion rate of Al atoms is the slowest and is significantly lower than that of Ti atoms [116]. Compared with the $Ni_{50}Co_{25}Al_7Ti_7Ta_{1.5}Cr_{9.5}$ alloy, the higher proportion of Al in the $Ni_{50}Co_{25}Al_xTi_{(14-x)}Ta_{1.5}Cr_{9.5}$ series alloys renders the sluggish diffusion effect of the alloy system more pronounced, which in turn reduces the long-range diffusion capability of atoms and provides a compositional window for the formation of nano-scale $L1_2$ ordered cores.

5.4.2 Morphology transition mechanism of submicron-scale core-shell structure

Microstructural characterization reveals that the morphology of submicron-scale $L1_2$ ordered cores in the $Ni_{50}Co_{25}Al_xTi_{(14-x)}Ta_{1.5}Cr_{9.5}$ alloys gradually transitions from cuboidal to near-spherical with the increase of Al/Ti ratio. Studies have demonstrated that the morphology of solid-state precipitates is primarily governed by the competition between interfacial energy and elastic strain energy during nucleation and growth. On this basis, the interfacial energy and elastic strain energy of submicron-scale $L1_2$ ordered cores in the three alloys are quantitatively calculated in this section, aiming to elucidate the morphological transition mechanism from an energetic perspective.

Overall, the total energy change ΔE_{el} induced by precipitate formation consists of two components: interfacial energy ΔE_{tot} and elastic strain energy ΔE_{surf} . For precipitates of the same volume, the spherical morphology is thermodynamically more favorable when its corresponding total energy change $\Delta E_{tot}^{(s)}$ is lower than that of the cuboidal morphology $\Delta E_{tot}^{(c)}$. Conversely, the cuboidal morphology becomes more stable under the opposite condition. Therefore, the total energy change of equal-volume precipitates in the two morphologies can serve as a criterion for morphological stability. When the two energy values are equal, the two morphologies are energetically equivalent, representing the critical condition for the morphological transition from one state to the other. The characteristic size

corresponding to this critical condition can be defined as the critical diameter for morphological transition.

First, assuming that the submicron-scale L1₂ ordered core precipitates as a sphere with radius r , its surface area A is:

$$A = 4\pi r^2 \quad (5-1)$$

The corresponding interfacial energy increment $E_{\text{surf}}^{(s)}$ is:

$$E_{\text{surf}}^{(s)} = 4\pi r^2 \gamma_{\text{int}} \quad (5-2)$$

where γ_{int} — interfacial energy per unit area ($\text{J}\cdot\text{m}^{-2}$).

Furthermore, the interfacial energy per unit area between the core and the shell can be expressed as [117]:

$$\gamma_{\text{int}} = \left(\frac{3\Delta G^* (\Delta G_v)^2}{16\pi} \right)^{1/3} \quad (5-3)$$

where ΔG_v — nucleation driving force ($\text{J}\cdot\text{m}^{-3}$);

ΔG^* — critical nucleation energy barrier of the precipitate (J).

The ΔG_v is calculated by the JMatPro software, corresponding to the Gibbs free energy change when the system transforms from the FCC single phase to the L1₂/FCC dual phase; ΔG^* can be further expressed as [118]:

$$\Delta G^* = kT_{\text{max}} \ln\left(\frac{I_0}{I_{\text{max}}}\right) \quad (5-4)$$

where k — Boltzmann constant ($1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$);

T_{max} — maximum nucleation rate temperature (K);

I_0 — nucleation pre-exponential factor ($\text{m}^{-3}\text{s}^{-1}$, typically taken as $10^{39-43} \text{ m}^{-3}\text{s}^{-1}$ for the L1₂ phase);

I_{max} — maximum nucleation rate ($\text{m}^{-3}\text{s}^{-1}$).

The T_{max} was determined by the isothermal transformation curves obtained from JMatPro calculations, as shown in Figure 5.24. I_{max} is the reciprocal of the minimum incubation time for nucleation, which was determined by the nose time of the isothermal transformation curves.

Combining the above equations, the interfacial energy change caused by the precipitation of a spherical L1₂ ordered core is:

$$E_{\text{surf}}^{(s)} = 4\pi r^2 \left(\frac{3kT_{\text{max}} (\Delta G_v)^2 \ln(I_0 t_{\text{min}})}{16\pi} \right)^{1/3} \quad (5-5)$$

For a spherical L1₂ ordered core with radius r , its volume is:

$$V = \frac{4}{3}\pi r^3 \quad (5-6)$$

The corresponding elastic strain energy increment resulting from the precipitation of a spherical L1₂ ordered core is [119]:

$$E_{\text{el}}^{(s)} = \Phi_s G \delta^2 V \quad (5-7)$$

where Φ_s — elastic shape factor;

δ — lattice misfit at the temperature corresponding to the minimum incubation time (obtained by JMatPro calculation).

Combining the above equations, the elastic strain energy change caused by the precipitation of a spherical L1₂ ordered core is obtained as:

$$E_{\text{el}}^{(s)} = \Phi_s G \delta^2 \frac{4}{3}\pi r^3 \quad (5-8)$$

Adding the equation (5-5) and (5-8), the total energy change caused by the precipitation of submicron-scale L1₂ ordered cores with a spherical morphology $\Delta E_{\text{tot}}^{(s)}$ can be further determined as:

$$\Delta E_{\text{tot}}^{(s)} = 4\pi r^2 \left(\frac{3kT_{\text{max}} (\Delta G_v)^2 \ln(I_0 t_{\text{min}})}{16\pi} \right)^{1/3} + \Phi_s G \delta^2 \frac{4}{3}\pi r^3 \quad (5-9)$$

In contrast, for a submicron-scale L1₂ ordered core with the same volume but precipitating in a cuboidal morphology, the corresponding side length is $1.61r$. From this, the expressions for the interfacial energy and elastic strain energy changes when the L1₂ ordered core precipitates with a cuboidal morphology can be derived as:

$$E_{\text{surf}}^{(c)} = 6 \cdot (1.61r)^2 \left(\frac{3kT_{\text{max}} (\Delta G_v)^2 \ln(I_0 t_{\text{min}})}{16\pi} \right)^{1/3} \quad (5-10)$$

$$E_{\text{el}}^{(c)} = \Phi_c G \delta^2 (1.61r)^3 \quad (5-11)$$

Combining the equation (5-10) and (5-11), the total energy change caused by the precipitation of submicron-scale L1₂ ordered cores with a cuboidal morphology $\Delta E_{\text{tot}}^{(c)}$ can be calculated as:

$$\Delta E_{\text{tot}}^{(c)} = 6 \cdot (1.61r)^2 \left(\frac{3kT_{\text{max}} (\Delta G_v)^2 \ln(I_0 t_{\text{min}})}{16\pi} \right)^{1/3} + \Phi_c G \delta^2 (1.61r)^3 \quad (5-12)$$

Setting the energy changes in the two morphological states to be equal, i.e., the equation (5-9) and (5-12), the critical diameter d_c for morphological transition can be derived as:

$$d_c = \frac{3}{2G\delta^2(\Phi_s - \Phi_c)} \cdot \left(\frac{3kT_{\text{max}} (\Delta G_v)^2 \ln(I_0 t_{\text{min}})}{16\pi} \right)^{1/3} \quad (5-13)$$

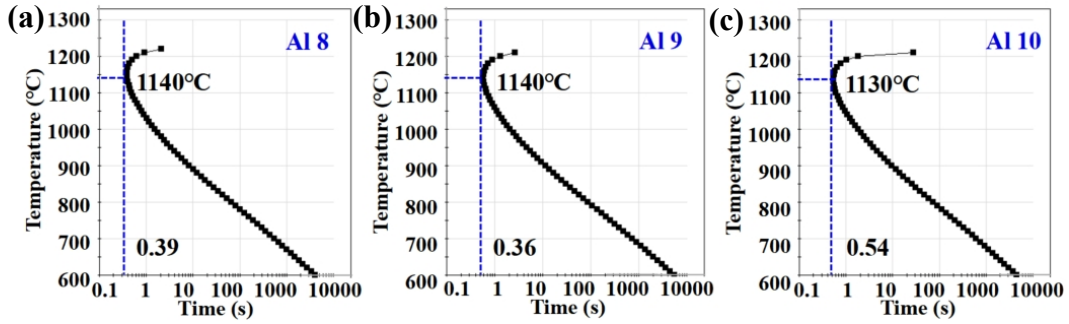


Fig. 5.24 Isothermal transformation curves of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents calculated by JMatPro
(a) Al8 alloy; (b) Al9 alloy; (c) Al10 alloy

The relevant parameters involved in the above calculations are summarized in Table 5.3. It should be emphasized that the final morphology of the precipitate is largely determined during the early growth stage following nucleation. Therefore, in the calculation of isothermal transformation curves, the volume fraction of the L1₂ precipitate was set to an extremely small value of 0.5%, and the minimum incubation time obtained under this condition was taken as the shortest incubation time of the submicron-scale L1₂ ordered cores. This assumption is reasonable, as in the present alloy system, the precipitation of submicron-scale L1₂ ordered cores precedes that of nanoscale L1₂ ordered cores. Under this assumption, the temperature corresponding to the minimum incubation time can be regarded as the characteristic temperature at which the submicron-scale L1₂ ordered cores reach their maximum nucleation rate and enter the early growth stage. Accordingly, all temperature-dependent parameters calculated by JMatPro in this study are uniformly evaluated at this characteristic temperature, ensuring physical consistency and self-consistency in the subsequent analysis.

Table 5.3 Calculation parameters for the morphological transition of submicron-scale ordered core in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

Parameters	Al8		Al9		Al10	
	Spherical	Cuboidal	Spherical	Cuboidal	Spherical	Cuboidal
Temperature of maximum nucleation rate ($^{\circ}\text{C}$)	1140		1140		1130	
Minimum incubation time (s)	0.39		0.46		0.54	
Nucleation driving force (J/mol)	36.33		36.46		47.72	
Shear modulus (GPa)	44.76		44.04		45.88	
$\text{L1}_2/\text{FCC}$ lattice misfit	0.029%		0.005%		0.008%	
Elastic shape factor	2.56	2.39	2.56	2.39	2.56	2.39

Substituting the various parameters into the above model, the critical diameters for morphological transition of the submicron-scale L1_2 ordered cores in the three alloys are calculated to be 107 nm, 130 nm, and 160 nm, respectively. According to the microstructural statistical results, the actual average diameters of the submicron-scale L1_2 ordered cores in the three alloys are approximately 127 nm, 122 nm, and 104 nm, respectively. For the Al8 alloy, the actual size of the majority of submicron-scale L1_2 ordered cores exceeds their critical diameter for morphological transition. Therefore, the L1_2 ordered cores in this alloy predominantly exhibit a cuboidal morphology. For the Al10 alloy, the size of nearly all submicron-scale L1_2 ordered cores is smaller than the critical diameter, causing them to adopt a lower-energy spherical configuration during growth and ultimately exhibit a spherical morphology. The Al9 alloy represents an intermediate state between the two, with its submicron-scale L1_2 ordered cores exhibiting the coexistence of cuboidal and spherical morphologies.

The above analysis indicates that the increase in Al/Ti ratio significantly enlarges the critical diameter for morphological transition, thereby broadening the size range favorable for spherical precipitates. Meanwhile, it also substantially reduces the actual size of the submicron-scale L1_2 ordered cores. When the actual size becomes smaller than the corresponding critical diameter, the precipitates tend to adopt the lower-energy spherical configuration during the early growth stage and eventually

stabilize in this morphology. It can thus be concluded that the Al/Ti ratio governs the cuboidal-to-spherical morphological transition of the submicron-scale $L1_2$ ordered cores through a dual mechanism: On one hand, it modifies the critical condition for transition by regulating the competition between interfacial energy and elastic strain energy; On the other hand, it directly reduces the actual size of the precipitates. The synergistic effect of these two aspects ultimately dictates the morphological evolution in this alloy system.

5.5 Chapter summary

In this chapter, the microstructure of the Ni-Co-Al-Ti-based high-entropy intermetallic was further optimized through compositional regulation. A multi-scale core-shell structure was successfully introduced, and microstructural features with a structural gradient were formed within the dendrites. By combining thermodynamic calculations with multi-scale microstructural characterization, the influence of compositional variations on the formation of the multi-scale core-shell structure was clarified. On this basis, the formation mechanism of the multi-scale core-shell structure was systematically revealed, and the morphological transition mechanism of the submicron-scale core-shell structure was further elucidated. The main conclusions are as follows:

(1) Through the addition of Ta, a dual-scale core-shell structure was formed in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy. The micron-scale core-shell structures are distributed in the dendrite boundary region, with the cores exhibiting a cellular morphology, an average length of approximately 3 μm , and an average width of approximately 2 μm . The submicron-scale core-shell structures are distributed within the dendrite interior, with the cores exhibiting a near-spherical morphology and an average diameter of approximately 150 nm.

(2) By further increasing the Al/Ti ratio, a multi-scale core-shell structure spanning the micron ($\sim 2 \mu\text{m}$), submicron ($\sim 120 \text{ nm}$), and nano ($\sim 5 \text{ nm}$) scales was formed in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys. With increasing Al/Ti ratio, the core size of the micron-scale core-shell structure decreased, and the morphology of the submicron-scale core-shell structure transformed from cuboidal to spherical.

(3) The formation mechanism of the multi-scale core–shell structure was elucidated. The addition of Ta intensified compositional segregation at the interdendritic boundaries during the late stage of solidification, thereby promoting the formation of micron-scale $L1_2$ ordered cores in these regions through a eutectic reaction. Simultaneously, the increase in Al/Ti ratio enhanced the sluggish diffusion effect of the alloy and increased the supersaturation driving force of the primary solid phase, thereby promoting the formation of submicron- and nanoscale $L1_2$ ordered cores through solid-state precipitation.

(4) The formation mechanism of the structurally gradient microstructure was revealed. During solidification, solute redistribution caused the contents of the $L1_2$ -forming elements Ti and Ta to exhibit a continuously decreasing distribution from the interdendritic boundaries toward the dendrite centers. The sluggish diffusion effect of the multi-principal-element alloy enabled this compositional gradient to be preserved during the solid-state stage, thereby inducing the sequential nucleation of submicron-scale $L1_2$ ordered cores from the interdendritic boundaries toward the centers, resulting in structurally gradient microstructural features.

(5) The morphological transition mechanism of the submicron-scale core–shell structure was elucidated. Based on the competitive relationship between interfacial energy and elastic strain energy, the critical diameters for morphological transition of the three alloys were calculated to be 107 nm, 130 nm, and 160 nm, respectively, while the actual average diameters of the three alloys were 127 nm, 122 nm, and 104 nm, respectively. In the Al10 alloy, the actual size is smaller than the critical diameter, making the spherical configuration thermodynamically more favorable.

Chapter 6 Room-temperature mechanical property and strengthening–plasticizing mechanism of multi-scale core–shell structured high-entropy intermetallic

6.1 Introduction

In the preceding two chapters, the microstructure of Ni-Co-Al-Ti-based high-entropy intermetallics was systematically optimized through compositional tailoring. The phase constitution progressively evolved from an initial $L1_2$ single-phase structure to an $L1_2$ /FCC dual-phase coexistence system. Accompanying this transition, an $L1_2$ –FCC dual-phase core–shell structure emerged in the alloys and further developed toward multi-scale microstructural features. Previous studies have demonstrated that the $L1_2$ –FCC dual-phase core–shell structure contributes to improving the room-temperature ductility of Ni-Co-Al-Ti-based high-entropy intermetallics. However, systematic investigations into the influence of the multi-scale core–shell structure on the room-temperature mechanical properties of this class of materials remain lacking, and the corresponding deformation and fracture mechanisms warrant in-depth elucidation.

On this basis, the present chapter conducts systematic mechanical property tests on Ni-Co-Al-Ti-based high-entropy intermetallics featuring a multi-scale core–shell structure, with the aim of clarifying the influence of the multi-scale core–shell structure on the room-temperature mechanical properties of $L1_2$ -type high-entropy intermetallics. Furthermore, by means of characterization techniques including SEM, TEM, and EBSD, the room-temperature deformation and fracture mechanisms of multi-scale core–shell structured high-entropy intermetallics are revealed. Building on this, the strengthening and plasticizing mechanisms of multi-scale core–shell structured high-entropy intermetallics are explored in depth by focusing on the microscopic substructures formed during plastic deformation. Through the above investigations, the intrinsic correlation between the multi-scale core–shell structure and room-temperature mechanical properties is established, and the synergistic contribution of core–shell structures at different scales to the mechanical properties is elucidated, thereby providing a transferable design

rationale for subsequent structural regulation and property optimization of high-performance high-entropy intermetallics.

6.2 Influence of the dual-scale core–shell structure on the room-temperature mechanical property of high-entropy intermetallic

The research presented in the previous chapter demonstrated that adding Ta to the base composition of the Co25 alloy promotes the formation of a dual-scale core–shell structure in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy. Although systematic thermodynamic calculations and microstructural characterization have clarified the formation mechanism of the dual-scale core–shell structure, the room-temperature mechanical properties of this alloy remain to be investigated. Therefore, this section conducts systematic room-temperature mechanical property tests on the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy, complemented by SEM characterization to analyze its fracture mechanism, with the aim of further elucidating the influence of the dual-scale core–shell structure on the room-temperature mechanical properties of L1₂-type high-entropy intermetallics.

6.2.1 Room-temperature mechanical property of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

Room-temperature compression and tensile tests were first performed on the as-cast $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy specimens; the results are presented in Fig. 6.1. As shown in Fig. 6.1 (a), this alloy exhibits a compressive yield strength exceeding 800 MPa, which is significantly higher than the room-temperature compressive yield strength of 510 MPa for the Co25 alloy, which possesses a single-scale core–shell structure. While attaining high yield strength, the alloy still retains a fracture strain of approximately 35% and displays pronounced strain hardening behavior during deformation, resulting in an ultimate compressive strength exceeding 1400 MPa. Fig. 6.1 (b) displays the tensile engineering stress–strain curve of the alloy. As can be seen from the figure, its tensile yield strength approaches 800 MPa, considerably higher than the 450 MPa of the Co25 alloy. It is noteworthy that the tensile and compressive yield strengths of this alloy are comparable, with no pronounced tension–compression asymmetry, as expected for the typical plastic material. Meanwhile, the alloy exhibits a room-temperature tensile plastic

elongation of approximately 8%. Although slightly lower than the 10% of the Co25 alloy, this value already meets the level required for engineering applications. Moreover, the alloy also exhibits sustained strain hardening behavior during tensile plastic deformation, yielding an ultimate tensile strength approaching 1000 MPa, which is markedly superior to the 650 MPa of the Co25 alloy. The above results indicate that the introduction of the micron-scale core-shell structure can significantly enhance the room-temperature strength of the material, while incurring only a modest decrease in ductility.

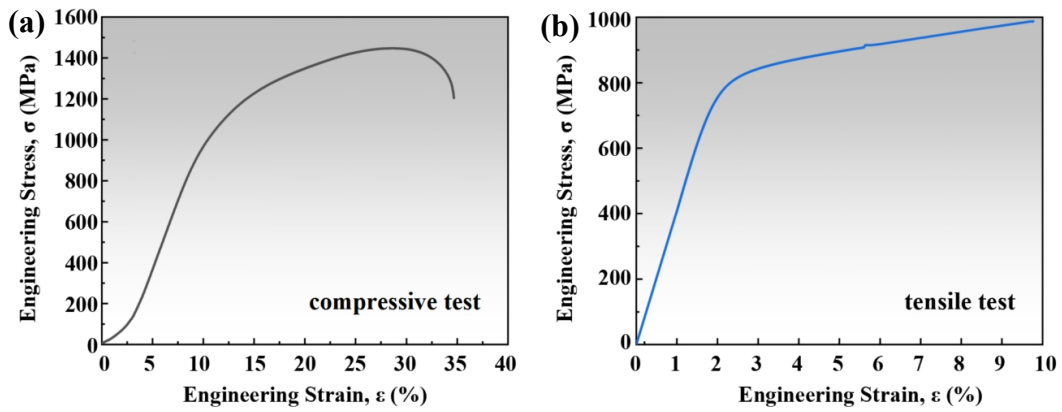


Fig. 6.1 Room-temperature mechanical properties of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy
(a) room-temperature compressive engineering stress-strain curve; (b) room-temperature tensile engineering stress-strain curve

To further analyze the influence of the micron-scale core-shell structure on the mechanical properties of the material, site-specific in-situ nanoindentation tests were performed on the alloy specimen to characterize the differences in mechanical response between the micron-scale and submicron-scale core-shell structures, and the results are shown in Fig. 6.2. Multiple sets of indentation tests were conducted in the respective regions containing the two scales of core-shell structures, and only those indentations that fell entirely within the corresponding regions were selected as valid data. The representative indentation morphologies are presented in Fig. 6.2 (a) and (b). As can be observed from the figures, the indentation profiles formed in both regions are clear and complete, without significant boundary crossing or distortion, indicating that the collected data possess good validity and comparability. In addition, the indentations in both regions exhibit typical triangular pyramidal residual impressions, and no brittle damage features such as radial cracks or spallation are observed around the indentations. Meanwhile, localized areas

adjacent to the indentation edges are accompanied by slight material pile-down behavior, suggesting that the material accommodates local deformation primarily through plastic flow under high strain gradients, thereby exhibiting favorable plastic deformation capability at room temperature. It is noteworthy that, under comparable indentation depth conditions, the projected area of the indentations in the submicron-scale core-shell structure region is noticeably larger than that in the micron-scale core-shell structure region, suggesting lower resistance to deformation and thus a lower average microhardness.

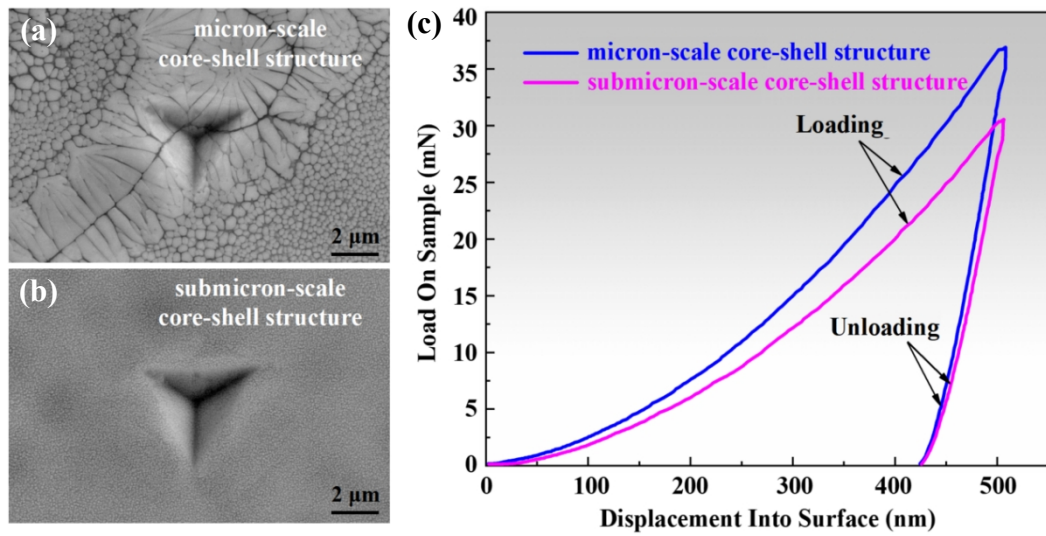


Fig. 6.2 In-situ nanoindentation test results of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy
(a) indentation morphology in the micron-scale core-shell structure region; (b)
indentation morphology in the submicron-scale core-shell structure region; (c) load-
displacement curves

Furthermore, the representative load-displacement curves for the two regions are presented in Figure 6.2 (c). It can be observed that distinct hysteresis loops are formed between the loading and unloading curves, indicating that a significant residual indentation depth remains after unloading, which is characteristic of typical irreversible plastic deformation. Meanwhile, the loading-stage curves are smooth and continuous throughout, without any pop-in or sudden fluctuations, suggesting that the deformation process is predominantly governed by the gradual activation and propagation of dislocations rather than by brittle damage. These features further demonstrate that both the submicron-scale and micron-scale core-shell structure regions are essentially plastic in nature. However, at a given indentation displacement during loading, the micron-scale core-shell structure region consistently requires a higher applied load, directly reflecting its higher average

microhardness. It can thus be inferred that the micron-scale core–shell structure region exhibits stronger resistance to deformation, enabling more effective obstruction of dislocation motion and suppression of localized plastic flow, thereby significantly enhancing the overall room-temperature strength of the material.

6.2.2 Room-temperature fracture mechanism of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

To elucidate the fracture mode of this alloy under room-temperature tensile conditions and its intrinsic correlation with the mechanical properties, SEM characterization was performed on the tensile fracture surfaces of the alloy specimens; the results are presented in Fig. 6.3. As can be seen from Fig. 6.3 (a), the overall tensile fracture surface displays pronounced ductile features, characterized by tear ridges and river patterns across the entire surface, along with extensive undulating traces of plastic flow, indicating substantial plastic deformation prior to failure. Localized tear sources are observed in the central region of the fracture surface, from which cracks radiate in multiple directions and eventually coalesce, reflecting the multi-path crack propagation in a complex stress field. Enlarged observations of local regions clearly reveal a large number of dimples, with the dimple edges displaying conspicuous plastic flow traces, as shown in Fig. 6.3 (b). This dimple-dominated fracture characteristic is consistent with the appreciable fracture elongation and pronounced strain hardening behavior observed in the aforementioned mechanical properties, demonstrating that the alloy possesses favorable plastic deformation capability at room temperature.

Further observations were conducted on the side-surface microstructure adjacent to the tensile fracture; the results are shown in Fig. 6.4. It can be seen that various forms of microscopic damage have developed within the material prior to macroscopic fracture. As evident from Fig. 6.4 (a), dispersed microcracks are present in the region near the fracture surface, indicating that localized stress concentration has occurred and damage has gradually accumulated in certain areas during tensile loading. Furthermore, as shown in Fig. 6.4 (b), the cracks preferentially propagate along interdendritic regions, forming a characteristic interdendritic cracking pattern, suggesting that interdendritic regions are more susceptible to becoming favorable paths for crack propagation during deformation.

Concurrently, both Fig. 6.4 (c) and (d) clearly reveal that the interdendritic secondary phase induces crack initiation and subsequent propagation into the surrounding regions. This indicates that, under external loading, the interdendritic secondary phase acts as a site of local stress concentration and serves as a preferential nucleation site for microcracks. As deformation continues to increase, these microcracks initiated from the interdendritic secondary phase progressively propagate and interconnect, ultimately coalescing with the main crack and causing macroscopic fracture of the material. Notably, based on the arrested positions of crack tips emanating from the secondary phase, the micron-scale core-shell structure adjacent to the dendrite boundaries exerts a buffering effect on crack propagation, effectively suppressing crack growth and coalescence and thus delaying premature material failure.

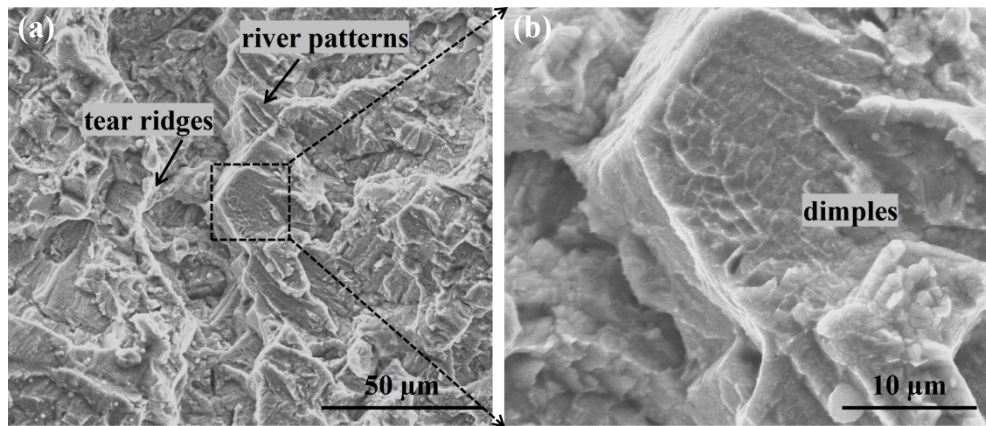


Fig. 6.3 Room-temperature tensile fracture surfaces of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy
(a) overall fracture surface morphology; (b) enlarged view of the dimple region

In combination with the aforementioned fracture surface morphological features, it can be concluded that the room-temperature fracture mechanism of this alloy belongs to a mixed fracture mode. Specifically, owing to the presence of the dual-scale core-shell structure within the dendrites, the intradendritic regions undergo sufficient plastic deformation during deformation, thereby producing a large number of dimples on the fracture surface and reflecting the favorable ductility of the core-shell structure. In contrast, the interdendritic secondary phase becomes a preferential site for crack initiation and a favorable path for crack propagation, accelerating microcrack coalescence and the occurrence of intergranular brittle fracture. Consequently, the fracture of this alloy is characterized by dominant plastic fracture within the dendrites, accompanied by localized brittle secondary-

phase-induced crack initiation in the interdendritic regions. This mixed fracture mechanism is precisely responsible for the favorable trade-off between high strength and ~8% plastic elongation at room temperature.

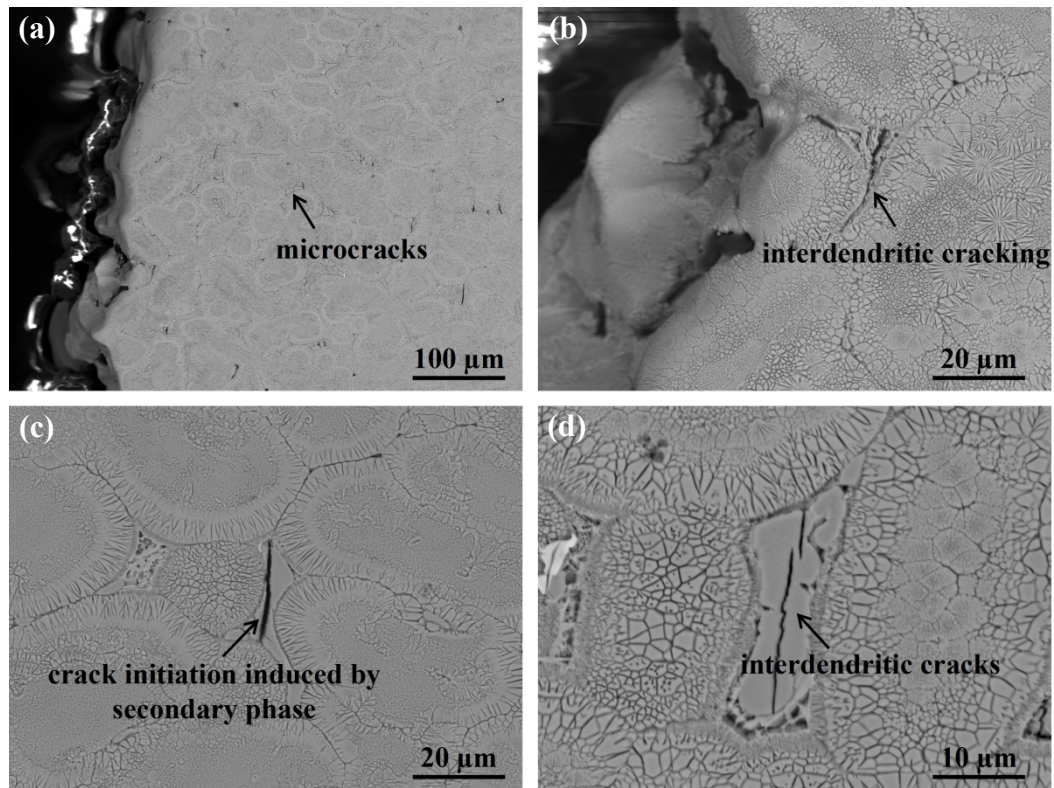


Fig. 6.4 Side-surface microstructures adjacent to the fracture in the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_7\text{Ti}_7\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

(a) overall morphology of the side-surface microstructure; (b) local magnified view of the side-surface microstructure; (c) interdendritic region near the fracture; (d) high-magnification image of the interdendritic region near the fracture

By integrating the macroscopic room-temperature mechanical property test results with the microscopic fracture behavior characteristics, it can be concluded that the dual-scale core-shell structure does not induce brittle failure while providing high strength. On the contrary, the micron-scale core-shell structure can effectively retard rapid crack propagation, enabling the material to maintain a high strength level while remaining dominated by ductile fracture. However, it should be noted that intergranular precipitates tend to act as crack initiation sites, while interdendritic regions provide preferential paths for crack propagation. The synergy between these two effects readily promotes premature cracking, thereby degrading the overall mechanical properties. Therefore, subsequent property optimization should aim to suppress intergranular precipitate formation and reduce both the volume fraction and connectivity of interdendritic regions. This would minimize

crack initiation sites and disrupt rapid propagation pathways, thereby further enhancing the mechanical properties.

6.3 Influence of the multi-scale core–shell structure on the room-temperature mechanical property of high-entropy intermetallic

The analysis in the preceding section demonstrates that the introduction of the micron-scale core–shell structure can significantly enhance the room-temperature strength of L1₂-type high-entropy intermetallics while maintaining high ductility. On this basis, this section further investigates the room-temperature mechanical properties of the Ni₅₀Co₂₅Al_xTi_(14-x)Ta_{1.5}Cr_{9.5} alloys possessing a multi-scale core–shell structure, and systematically elucidates the influence of this structure on their mechanical properties in conjunction with fracture mechanism analysis.

6.3.1 Room-temperature mechanical property of the

Ni₅₀Co₂₅Al_xTi_(14-x)Ta_{1.5}Cr_{9.5} alloys

Room-temperature tensile tests were conducted on the three as-cast alloys with varying Al/Ti ratios. The resulting engineering stress–strain curves are presented in Fig. 6.5 (a), and the corresponding mechanical properties are summarized in Table 6.1. As shown in the figure, the Al₈ alloy achieves the highest yield strength among the three alloys, at approximately 1100 MPa, yet its plastic elongation is merely ~6.5%. With increasing Al/Ti ratio, the yield strength of the Al₉ alloy decreases slightly to approximately 1000 MPa, whereas its plastic elongation increases markedly to approximately 12.5%, achieving a synergistic enhancement of strength and ductility. When the Al/Ti ratio is further increased, the Al₁₀ alloy shows a further decrease in yield strength to approximately 800 MPa, while its plastic elongation significantly increases to approximately 23.5%. This trend indicates that increasing the Al/Ti ratio can effectively improve the ductility of the alloys, albeit at the cost of a certain reduction in strength. Notably, the mechanical property data of these three alloys are superior to those of the previously studied dual-scale core–shell structured alloy, demonstrating that the multi-scale core–shell structure plays a critical role in optimizing the room-temperature comprehensive mechanical properties of high-entropy intermetallics.

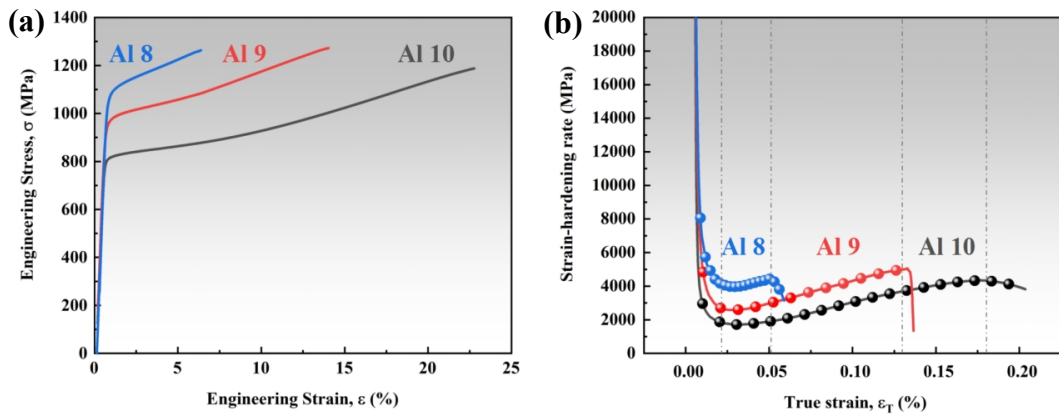


Fig. 6.5 Room-temperature mechanical properties of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents
(a) room-temperature tensile engineering stress–strain curves; (b) strain hardening rate–true strain curves

Table 6.1 Room-temperature tensile properties of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents

Alloys	Yield strength	Ultimate tensile	Elongation
	σ_y (MPa)	strength σ_{UTS} (MPa)	e (%)
A18	1100±20	1250±50	6.5±1.3
A19	1000±20	1250±30	12.5±1.3
A110	800 ± 18	1180±50	23.5±1.5

Further analysis of the tensile curve characteristics reveals that all three alloys exhibit pronounced strain hardening behavior during tensile deformation. Taking the Al8 alloy as an example, its flow stress increases continuously and steadily after yielding until fracture, which is consistent with the strain hardening behavior characteristics of the single-scale and dual-scale core–shell structured alloys. With increasing Al/Ti ratio, this series of alloys displays a distinct two-stage strain hardening characteristic during the plastic deformation stage. This suggests that, additional deformation mechanisms are progressively activated with ongoing deformation, endowing the alloys with enhanced load-bearing capacity beyond that of initial strengthening and thereby revealing potential for further performance optimization. Notably, this multi-staged strain hardening behavior is particularly prominent in the Al10 alloy. Although its yield strength is approximately 200 MPa lower than that of the Al9 alloy, its elongation increases approximately twofold, resulting in an ultimate tensile strength of approximately 1180 MPa.

To further elucidate the relationship between strain hardening behavior and the

mechanical properties of the alloys, the strain hardening rate curves were calculated and plotted based on the true stress–true strain curves of the three alloys, as shown in Fig. 6.5 (b). It can be seen that the three alloys exhibit distinctly different strain hardening behavior characteristics. The deformation behavior of the Al8 alloy is similar to that of conventional as-cast intermetallics, and its strain hardening process can be divided into three stages. In the elastic deformation stage (Stage I), the strain hardening rate decreases rapidly. Upon entering the plastic deformation stage (Stage II), the strain hardening rate increases continuously. When deformation enters Stage III, the strain hardening rate decays rapidly, and the material undergoes unstable deformation and fractures. This variation trend is consistent with its mechanical property characteristics. On the one hand, the continuously enhancing strain hardening capacity in Stage II endows the Al8 alloy with a high ultimate tensile strength. On the other hand, the material undergoes unstable fracture at a relatively low strain level, thereby resulting in a low elongation.

With increasing Al/Ti ratio, the Al9 alloy, upon entering Stage III, shows no decrease in strain hardening rate. Instead, the rate rises further with a steeper slope, and unstable fracture does not occur until Stage IV, accompanied by a sharp drop in the hardening rate. This behavioral characteristic indicates that the Al9 alloy can sustain stable plastic deformation over a relatively wide strain range. Furthermore, this alloy is highly likely to activate new deformation mechanisms in the later stage of deformation, thereby effectively delaying unstable fracture and simultaneously enhancing both strength and ductility. With further increase in the Al/Ti ratio, the Al10 alloy exhibits more complex multi-stage plastic deformation behavior during room-temperature tensile testing. Its strain hardening rate increases continuously with different slopes over the Stage II to Stage IV interval, constituting a distinctive three-stage strain hardening process. This sustained and progressively intensifying strain hardening capacity substantially prolongs the stable plastic deformation stage, providing the basis for the high room-temperature elongation of the Al10 alloy. In summary, the introduction of the nanoscale core–shell structure can further enhance the strength of the material, but inevitably results in a decrease in elongation. However, increasing the Al/Ti ratio facilitates the activation of multi-stage strain hardening behavior in the material, thereby significantly improving ductility while maintaining a high strength level and achieving superior strength–ductility synergy.

Concurrently, the introduction of the nanoscale core–shell structure promotes the synergistic deformation capability of the alloy.

Comprehensively, the Al8 alloy exhibits a relatively low plastic elongation, while the Al10 alloy shows a relatively poor yield strength. In contrast, the Al9 alloy achieves a more favorable balance between room-temperature strength and ductility, with its yield strength and tensile strength reaching approximately 1000 MPa and 1250 MPa, respectively, while still maintaining a plastic elongation of about 12%. Notably, without undergoing any complex thermomechanical processing, the room-temperature mechanical properties of this as-cast alloy are already comparable to those of L_{12} nanoprecipitate-strengthened FCC-structured high-entropy alloys prepared by intricate processing routes, such as the $\text{CoCrFeNi}(\text{Ni}_3\text{Al})_{0.75}$ alloy, with a yield strength of 910 MPa, a tensile strength of 1200 MPa, and an elongation of 14% [120]. To objectively assess the overall room-temperature mechanical property of the Al9 alloy, its tensile properties are compared with those of other as-cast structural materials rich in $\text{Ni}_3\text{Al}/L_{12}$ ordered phases, with the results presented in Fig. 6.6. The comparison demonstrates that the strength–ductility synergy of the Al9 alloy significantly surpasses that of representative material systems, including typical Ni-based superalloys, ductilized Ni_3Al alloys, and L_{12} nanoprecipitate-strengthened FCC-structured high-entropy alloys.

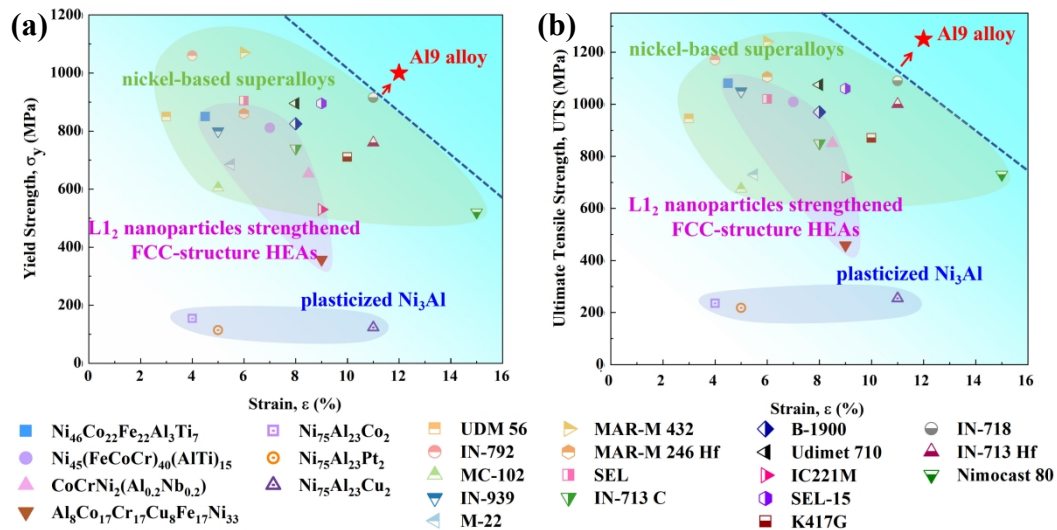


Fig. 6.6 Comparison of room-temperature mechanical properties between the Al9 alloy and other representative material systems containing $\text{Ni}_3\text{Al}/L_{12}$ ordered phase [121-126]

(a) yield strength–tensile strain; (b) ultimate tensile strength–tensile strain

6.3.2 Room-temperature fracture mechanism of the

$\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys

To further understand the influence of the increasing Al/Ti ratio on the mechanical properties of the multi-scale core-shell structured high-entropy intermetallics, SEM characterization was performed on the tensile fracture morphologies of the three alloys, with the results shown in Fig. 6.7. From Fig. 6.7 (a)–(c), it can be observed that the room-temperature tensile fracture surfaces of all three alloys exhibit typical mixed fracture characteristics. Specifically, tear ridges and river patterns resulting from brittle fracture can be observed on the fracture surfaces, along with dimples formed by ductile fracture. However, the proportions of ductile and brittle fracture features differ markedly among the alloys. With increasing Al/Ti ratio, the dimple regions indicated in red on the fracture surfaces increase significantly, while the tear ridge and river pattern regions indicated in green decrease markedly. This indicates that increasing the Al/Ti ratio can suppress brittle fracture of the material, thereby substantially increasing the elongation of the alloys.

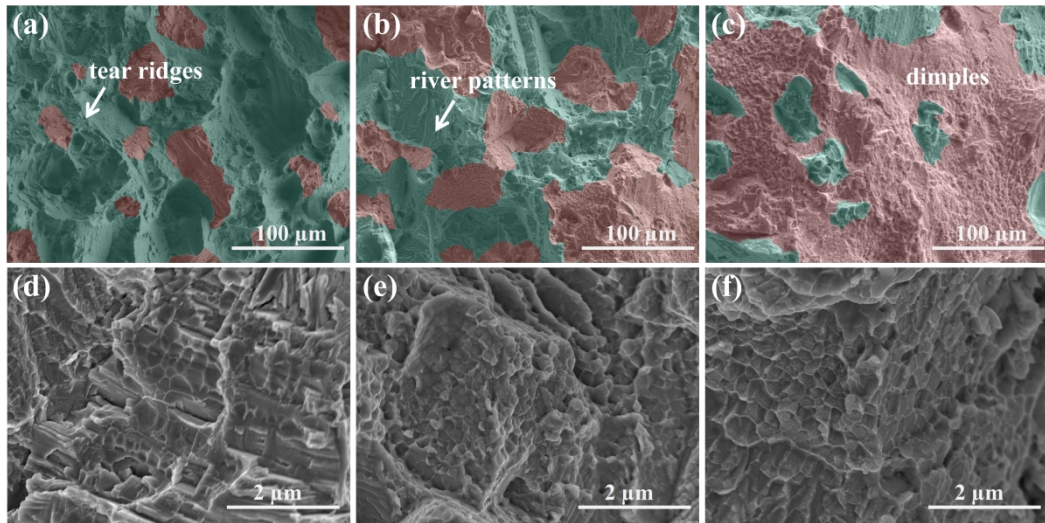


Fig. 6.7 Room-temperature tensile fracture surfaces of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys with varying Al contents
(a) overall morphology of the Al8 alloy; (b) overall morphology of the Al9 alloy; (c) overall morphology of the Al10 alloy; (d) local dimples in the Al8 alloy; (e) local dimples in the Al9 alloy; (f) local dimples in the Al10 alloy

Further magnified observations of the dimple regions in the three alloys were conducted, with the results shown in Fig. 6.7 (d)–(f). It can be found that the morphology and size of the dimples are highly consistent with the submicron-scale L_{12} ordered cores in the alloys. In view of the microstructural characteristics of this

series of alloys, nanoscale $L1_2$ cores exist within the shell of the submicron-scale core-shell structure. These ordered cores can enhance the strength of the shell, thereby narrowing the strength disparity between the core and the shell in the submicron-scale core-shell structure. In this case, the synergistic deformation between the core and the shell is enhanced, effectively delaying unstable fracture caused by property mismatch and allowing more extensive plastic deformation during tensile testing. However, the nanoscale $L1_2$ ordered cores are too small to adequately strengthen the shell, preventing the shell strength from reaching that of cores. Consequently, uneven stress partitioning still exists between the submicron-scale core and shell during deformation. When localized stress concentration cannot be effectively relieved through synergistic deformation, cracks initiate and propagate at the core-shell interface, ultimately forming dimple morphologies on the fracture surface that correspond to the size of the submicron-scale $L1_2$ ordered cores. Therefore, the introduction of the nanoscale core-shell structure enhances the synergistic deformation capability of the submicron-scale core-shell structure, promoting sufficient plastic deformation in this region, which ultimately leaves behind a large number of dimples in the form of ductile fracture.

To analyze the room-temperature fracture mechanisms of the multi-scale core-shell structured high-entropy intermetallics, the representative Al9 alloy was selected, and the side-surface microstructures adjacent to its tensile fracture were observed, with the results presented in Fig. 6.8. From Fig. 6.8 (a), it can be clearly seen that numerous micro-damage features exist in the region near the fracture, with the damage density increasing progressively toward the fracture surface. This indicates that fracture of this alloy is not an instantaneous event but a progressive damage process involving the gradual accumulation of microscopic defects. Further high-magnification observations of the microstructures near the fracture were conducted, with the results shown in Fig. 6.8 (b₁) and (b₂). From these two images, microstructural features corresponding to two fracture modes can be clearly observed: one is transgranular fracture where the fracture edge directly cuts through the interior of the dendrite, and the other is intergranular fracture where the fracture edge propagates along the dendrite boundary. Further magnified observations of the micro-defects appearing in the region adjacent to the fracture edge were performed, with the results presented in Fig. 6.8 (c₁) and (c₂). From these images, it can be seen

that two types of micro-defects appear on the side surface of the fractured specimen of this alloy. One type is microvoids located at the interface between the micron-scale and submicron-scale core-shell structures, and the other is microcracks present in the interdendritic region.

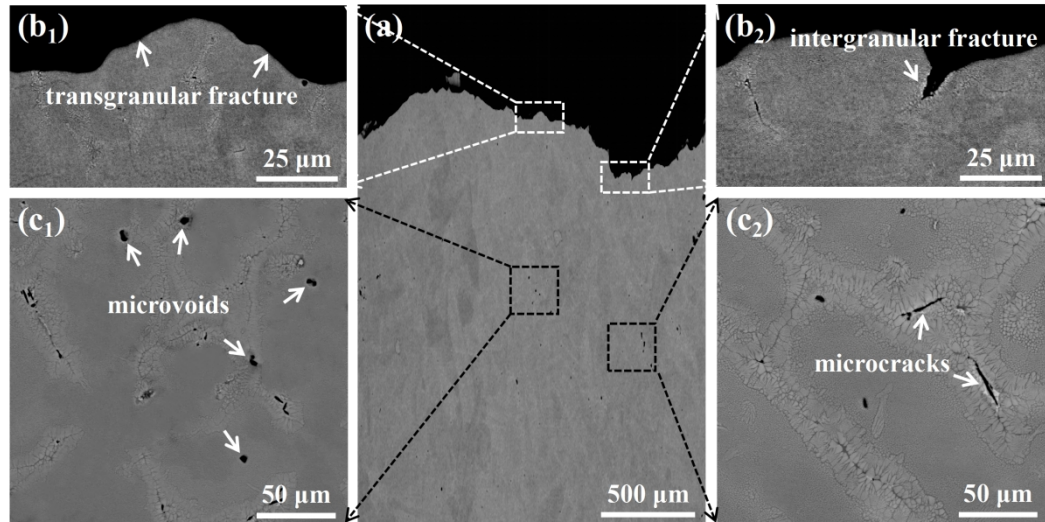


Fig. 6.8 Side-surface microstructures adjacent to the fracture in the Al9 alloy
(a) overall morphology of the side-surface microstructure; (b₁) local magnified
image of the transgranular fracture region; (b₂) local magnified image of the
intergranular fracture region; (c₁) high-magnification image of the microvoid; (c₂)
high-magnification image of the microcrack

The nucleation of microvoids originates from the accumulation of local strain and stress concentration. Nanoindentation test results indicate that there is a significant difference in microhardness between the micron-scale and submicron-scale core-shell structure regions. During the tensile process, the two regions differ in deformation capability, leading to incompatible deformation in adjacent regions and thus generating stress concentration at the interfaces. When the local stress cannot be relieved through coordinated deformation of the surrounding microstructure, microvoids preferentially form at these locations. As deformation continues, some voids grow and coalesce under the applied stress, eventually developing into cracks that penetrate through the grains and leading to transgranular fracture. The formation of microcracks is generally associated with factors such as dislocation pile-up, slip band evolution, and grain boundary sliding [127]. In as-cast dendritic materials, the interdendritic region is a microstructurally weak location with relatively low interfacial bonding strength. Moreover, this region is subject to complex geometric and mechanical constraints, which promote slip discontinuity

and impede dislocation motion during deformation, making it a preferential site for dislocation pile-up. When the applied stress continues to increase and the local stress concentration induced by dislocation pile-up exceeds the interfacial bonding strength of the interdendritic region, microcracks preferentially nucleate in this region. As analyzed in Section 6.2.2, the micron-scale core-shell structure exerts a pronounced impeding effect on crack propagation, such that only a limited number of microcracks can propagate continuously and induce intergranular fracture. In most structural materials, the formation and propagation of intergranular microcracks are often critical to final failure. However, microcracks nucleated in the interdendritic region are difficult to propagate over long distances in the present alloy, thereby effectively suppressing catastrophic failure and enabling the material to maintain good room-temperature ductility.

In summary, the introduction of the nanoscale core-shell structure effectively enhances the coordinated deformation capability of the material, such that the fracture mechanism of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_x\text{Ti}_{(14-x)}\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloys is jointly governed by brittle fracture and ductile fracture. With increasing Al/Ti ratio, the material progressively transitions toward ductile fracture, and the elongation increases correspondingly. The Al9 alloy, which achieves the best strength-ductility synergy, exhibits a coexistence of transgranular and intergranular fracture during room-temperature tensile testing. Transgranular fracture is primarily attributed to microvoid nucleation and coalescence driven by deformation mismatch between the micron-scale and submicron-scale core-shell structures, whereas intergranular fracture stems from microcrack nucleation and propagation caused by dislocation pile-up at the interdendritic regions.

6.4 Analysis of the strengthening and plasticizing mechanisms of multi-scale core-shell structured high-entropy intermetallic

From the room-temperature mechanical property test results presented in Section 6.3.1, it can be seen that the multi-scale core-shell structure high-entropy intermetallic exhibits multi-stage strain hardening behavior during room-temperature plastic deformation, thereby effectively enhancing its overall mechanical properties. Considering that the strain hardening behavior is closely related to the evolution of dislocation substructures during deformation, this section

first employs TEM characterization to systematically analyze the evolution of dislocation substructures in the representative Al9 alloy during tensile deformation, thereby revealing its room-temperature deformation mechanism. On this basis, combined with theoretical calculations and experimental results, the strengthening and plasticizing mechanisms of this alloy are further explored, providing a theoretical foundation for the microstructural design and property optimization of multi-scale core-shell structure high-entropy intermetallics.

6.4.1 Room-temperature deformation mechanisms of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

Since the submicron-scale core-shell structure constitutes a large proportion of the microstructure in the Al9 alloy, the evolution of dislocation substructures in this region during tensile deformation is first examined, and the results are shown in Fig. 6.9. TEM observation was performed on the tensile specimen of this alloy interrupted near the yield point, and the obtained bright-field image is shown in Fig. 6.9 (a). The micron-scale L1_2 ordered cores and the surrounding shells can be clearly observed in the image. However, since the material is at the critical elastic-to-plastic transition stage at this point, no significant dislocations have yet appeared within the material. When the tensile strain increases to 5%, the bright-field TEM image of the interrupted specimen is shown in Fig. 6.9 (b). As can be seen from the image, a large number of dense dislocation structures have appeared in the shell, whereas only very few dislocations have entered the core interior. This pronounced difference indicates that the core and the shell play distinct roles during plastic deformation. Specifically, the shell, based on a disordered FCC matrix, is relatively soft and therefore preferentially undergoes plastic deformation and accommodates most of the dislocation activity. In contrast, the core consists of the L1_2 ordered structure, which possesses higher shear resistance and thus effectively impedes dislocation motion. As the deformation increases further, some dislocations piled up at the interface can overcome the interfacial energy barrier and enter the L1_2 ordered core. From Fig. 6.9 (c) and (d), it can be seen that under the 5% strain condition, dislocations enter the L1_2 ordered core primarily through two mechanisms. First, they enter in the form of superdislocations, introducing anti-phase boundaries into the ordered phase. Second, they enter as partial dislocations,

forming superlattice intrinsic/extrinsic stacking faults (SISF/SESF) within the $L1_2$ ordered core. The formation of both types of dislocation substructures can introduce stable defect configurations within the core, thereby significantly increasing the critical stress required for dislocation transmission and continued slip, enabling the material to exhibit pronounced strain hardening capacity during plastic deformation.

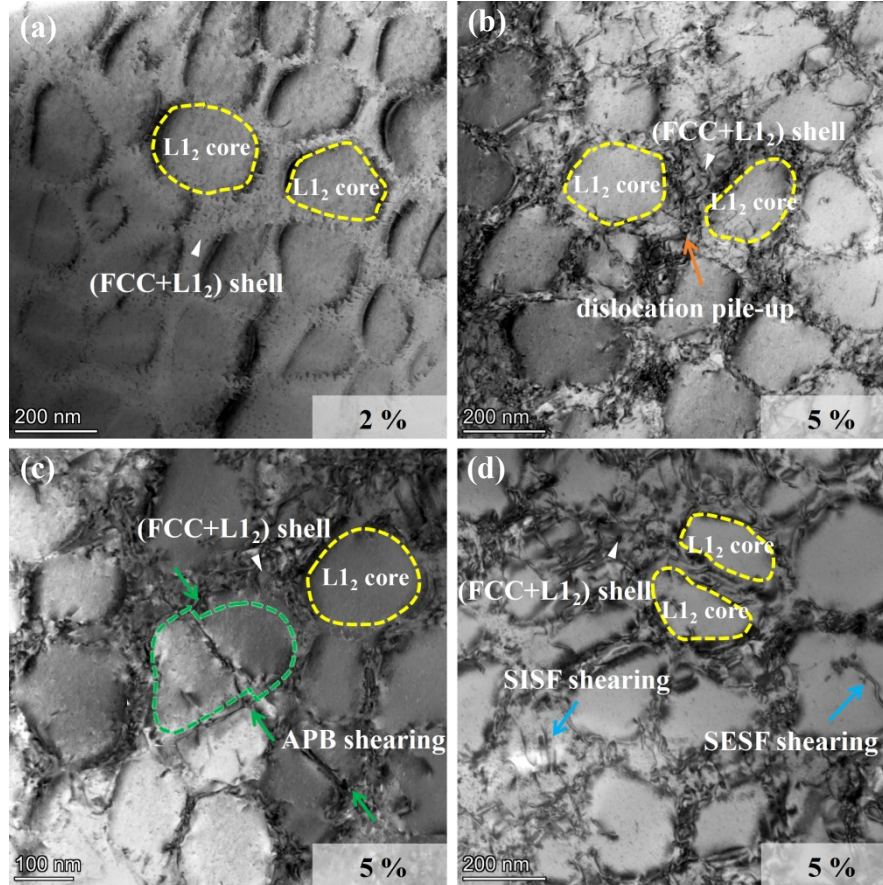


Fig. 6.9 Evolution of dislocation substructures with increasing strain in the submicron-scale core-shell structure region of the Al9 alloy during low-strain tensile deformation

(a) tensile strain of 2%; (b) tensile strain of 5%; (c) magnified view of the APB region; (d) magnified view of the SISF/SESF region

It should be noted that under low-strain conditions, dislocations more preferentially enter the $L1_2$ phase in the form of superdislocations and leave behind APBs, as demonstrated by the deformation mechanism of the Co25 alloy in Section 4.4.2. Meanwhile, this is also the typical deformation mode of conventional Ni_3Al alloys and other alloys containing the $L1_2$ ordered phase. However, the Al9 alloy already exhibits the phenomenon of $L1_2$ phase shearing by partial dislocations under the low-strain condition of 5%, and it is therefore necessary to systematically investigate this behavior. In practical materials, the choice between superdislocation

and partial-dislocation shearing of the $L1_2$ ordered phase is governed largely by the energetic competition among the various defects within the ordered phase, specifically the relative values of the anti-phase boundary energy γ_{APB} and the superlattice stacking fault energy λ_{SFE} . To this end, the average composition of the submicron-scale $L1_2$ ordered core was first obtained by TEM characterization, and the results are shown in Table 6.2. Based on this composition, the stacking fault energy of the $L1_2$ ordered core at room temperature was calculated using JMatPro software to be approximately 20.8 mJ/m². Although this value is typically slightly smaller than λ_{SFE} , it is significantly lower than the γ_{APB} values reported for other FCC-structured high-entropy alloys, thereby providing an energetic basis for the partial-dislocation shearing of the $L1_2$ ordered phase and the formation of SISF/SESF under low-strain conditions [128].

Table 6.2 Chemical compositions of the submicron-scale core-shell structure regions in the Al9 alloy determined by TEM-EDS

Regions		Elements (at. %)					
		Ni	Co	Al	Ti	Ta	Cr
Submicron-scale core-shell structure	Core	54.9±0.4	21.4±0.3	8.7±0.2	4.7±0.2	0.8±0.1	9.5±0.2
	Shell	41.3±0.5	31.6±0.3	7.7±0.3	2.7±0.1	0.6±0.1	16.1±0.4

Furthermore, the size of the $L1_2$ ordered phase is also an important factor influencing the dislocation shearing mode. As the size of the $L1_2$ ordered phase decreases, the activity of perfect dislocations is gradually suppressed, whereas the activity of partial dislocations becomes relatively more favorable. Therefore, dislocations tend to shear through partial dislocations and form SISF/SESF when the $L1_2$ ordered core size is sufficiently small. The critical $L1_2$ phase size for the activation of perfect dislocation versus partial dislocation shearing modes can be obtained based on the Orowan-type size criterion. This criterion, rooted in the universal size effect where the critical shear stress decreases with increasing obstacle size, provides a comparative framework for assessing the relative favorability of perfect versus partial dislocations across different length scales. First, the critical shear stresses required for the activation of the two types of dislocations are expressed as [129]:

$$\tau_F(d) = \tau_0 + \frac{2\alpha\mu b}{d} \quad (6-1)$$

$$\tau_P(d) = \frac{\lambda_{\text{SFE}}}{b_P} + \frac{2\alpha\mu b_P}{d} \quad (6-2)$$

By combining the two equations, the expression for the critical $L1_2$ ordered core diameter at which the dominant mechanism transitions from perfect dislocations to more readily activated partial dislocations can be obtained:

$$d_c = \frac{2\alpha\mu(b - b_P)}{\lambda_{\text{SFE}}/b_P - \tau_0} \quad (6-3)$$

where τ_0 — lattice friction shear stress (Pa);

μ — shear modulus (Pa);

α — dislocation type related geometric constant (approximately 1 for mixed dislocations);

b — Burgers vector of the perfect dislocation (m);

b_P — Burgers vector of the partial dislocation (m).

Among these parameters, τ_0 is approximately 65 MPa, borrowed from an FCC-type high-entropy alloy system of the same composition system [130]; μ is calculated by JMatPro to be 84.25 GPa; γ_{SFE} is replaced by 20.8 mJ/m² to calculate the maximum critical radius; b and b_P are calculated from the lattice constant obtained by XRD refinement to be 0.2532 nm and 0.1462 nm, respectively. Substituting the above parameters into the formula yields a critical diameter of $d_c = 250$ nm.

According to the microstructural statistics of the Al9 alloy presented in section 5.3.2, the average diameter of the submicron-scale $L1_2$ ordered phase is approximately 121 nm, which is significantly smaller than the aforementioned critical diameter. Therefore, in the submicron-scale core-shell structure region, tensile-induced localized plasticity is preferentially accommodated by Shockley partial dislocation glide, resulting in SISF/SESF formation within the $L1_2$ ordered phase under low-strain conditions. It can thus be concluded that the relatively small submicron-scale $L1_2$ ordered cores in the alloy provide a structural basis for the shearing of the $L1_2$ ordered phase by partial dislocations and the formation of SISF/SESF under low-strain conditions. It should be noted that the λ_{SFE} used in the above calculation is the stacking fault energy rather than the superlattice stacking fault energy. In general,

the stacking fault energy is smaller than the superlattice stacking fault energy, and therefore the calculated critical radius is overestimated. In addition, the submicron-scale $L1_2$ ordered cores exhibit a gradient size distribution, with the maximum diameter approaching 200 nm. This implies that the diameters of some ordered cores may exceed the critical diameter, so that a small fraction of dislocations still tend to shear the $L1_2$ ordered cores in the form of perfect dislocations and form APBs.

As the strain level further increases to 8%, the stress level gradually rises. From Fig. 6.10 (a), it can be seen that the dislocation density within the material further increases at this stage, and the dislocation motion mode gradually transforms from dislocation pile-up within a single slip system to dislocation entanglement involving multiple slip systems. From the magnified image at this strain condition, it can be observed that the deformation of the material is almost entirely dominated by SISF/SESF at this stage, as shown in Fig. 6.10 (b). Combined with the analysis of the strain hardening rate curve, the high density of dislocation entanglements and the strong pinning effect of SISF/SESF enable the strain hardening rate of the material to continuously increase under the 8% strain condition. When the strain level is further increased to 10%, numerous dislocations from different slip systems become spatially cross-distributed, mutually hindering one another and gradually evolving into a dislocation forest, as shown in Fig. 6.10 (c). The dislocation forest exhibits a disordered internal orientation, and the dislocations provide forest hardening through mutual blocking, intersection, and entanglement. As the strain level continues to increase, dislocations begin to undergo spatial rearrangement and self-organization, progressively transforming from a disordered state into an ordered state. Driven by the stress field and energy minimization, dislocations undergo directional clustering, promoting the further development of the dislocation forest into a substructural aggregate composed of dense dislocations, i.e., deformation microbands. Under local strain, some deformation microbands can further evolve into interfaces with high energy density, i.e., dislocation walls, as shown in Fig. 6.10 (d).

To reveal the origin of the partial dislocations required for shearing the $L1_2$ ordered phase, the shell of the submicron-scale core-shell structure in the undeformed

tensile specimen was further examined, and the results are shown in Fig. 6.11. As can be seen from the figure, even in the absence of any plastic deformation, a large number of stacking faults already exist in the shell, which is closely related to the low stacking fault energy of this region. Based on the compositions listed in Table 6.2, the stacking fault energy of the shell at room temperature was calculated using JMatPro to be 8.3 mJ/m². It is worth noting that this value is far lower than that of previously reported FCC-structured high-entropy alloys with low stacking fault energy [131]. This is primarily attributed to the addition of elements such as Co, Cr, Al, Ti, and Ta, all of which can effectively reduce the stacking fault energy of the alloy system. Under such an extremely low stacking fault energy, the perfect dislocations within the shell tend to spontaneously dissociate to form SFs, thereby supplying the partial dislocations required for shearing the L1₂ ordered core.

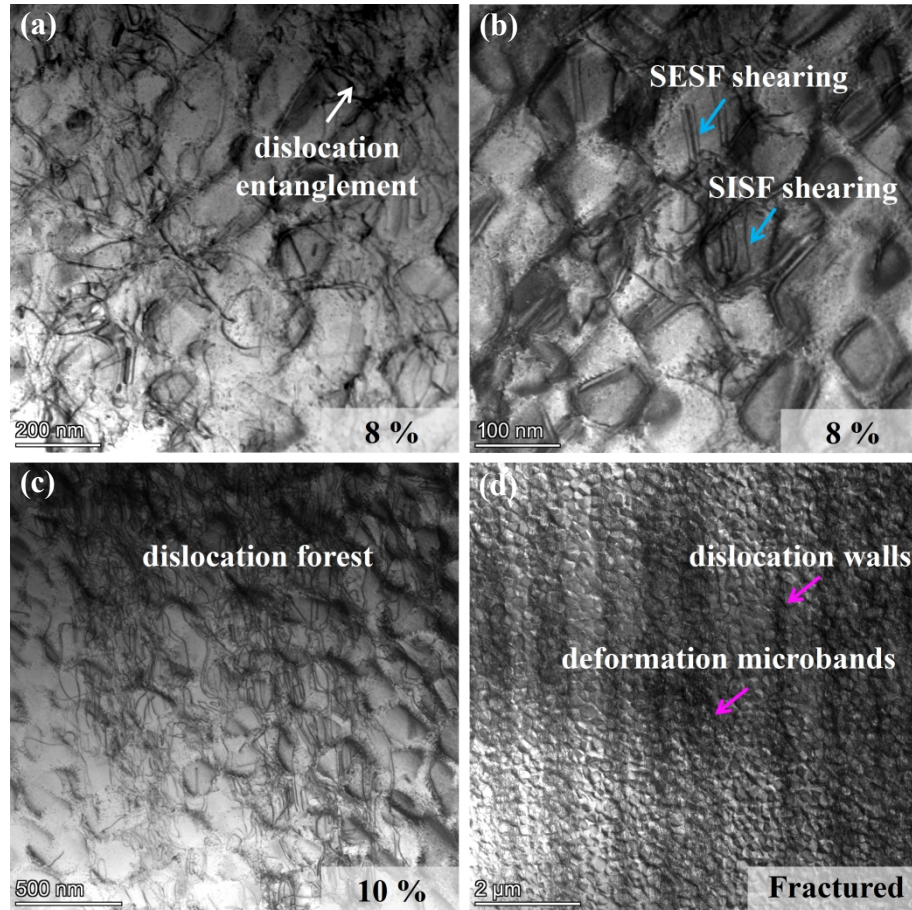


Fig. 6.10 Evolution of dislocation substructures with increasing strain in the submicron-scale core-shell structure region of the Al9 alloy during high-strain tensile deformation

(a) dislocation entanglement; (b) SISF/SESF; (c) dislocation forest; (d) dislocation walls and microbands

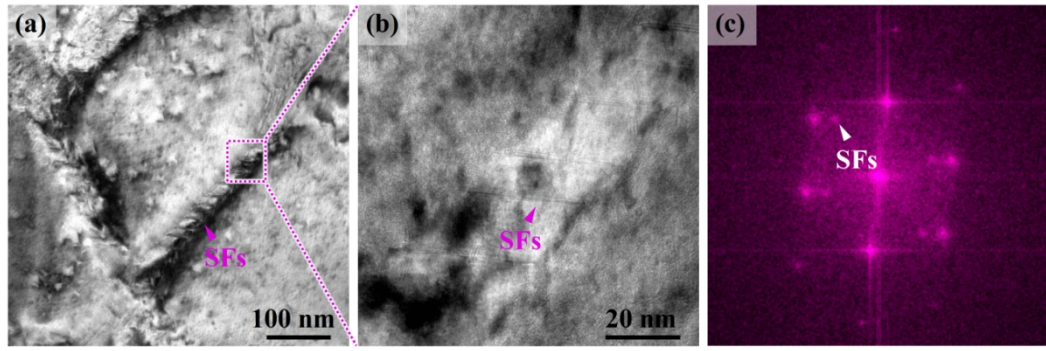


Fig. 6.11 Dislocation substructures in the shell of the submicron-scale core-shell structure region of the undeformed Al9 alloy
(a) shell morphology; (b) magnified view of SFs; (c) diffraction pattern of SFs

Furthermore, the SFs in the shell undergo multiplication and interact with one another as deformation increases. To this end, the shell region was further characterized, and the obtained high-resolution images are shown in Fig. 6.12. As can be seen from the figure, at approximately 4% strain, only SFs with a single slip direction exist in the shell, corresponding to the dislocation pile-up caused by a single slip system under the same strain condition in the bright-field image. When the strain increases to approximately 8%, the density of SFs increases, and SFs with another slip direction appear, corresponding to the dislocation entanglement caused by the activation of multiple slip systems in the bright-field image. When the tensile strain further increases to approximately 10%, special Lomer-Cottrell locks (L-C locks) appear in the shell. This structure is a dislocation locking substructure formed by the interaction between SFs of different slip directions, which can significantly hinder dislocation glide and enhance the dislocation accumulation capacity, thereby continuously providing an additional strain hardening contribution at high strain levels. The formation of L-C locks accounts for the further rise of the strain hardening curve at medium-to-high strains and manifests in the bright-field image as a dislocation forest arising from intensified entanglement. This indicates that dislocation motion is more severely confined spatially and that substantial dislocation accumulation has taken place.

Thus, the deformation mechanism in the submicron-scale core-shell structure region begins with the dissociation of perfect dislocations into partial dislocations and the formation of SFs in the shell, followed by the progressive formation of L-C locks through the synergistic action of multiple slip systems. Concurrently, the partial dislocations shear the ordered $L1_2$ core, thereby forming SISF/SESF within

it. With increasing strain, hierarchical dislocation substructures including dislocation forests, deformation microbands, and dislocation walls are successively generated in the material. On the one hand, these dislocation substructures strongly hinder dislocation motion through enhanced dislocation interactions and pinning effects, thereby imparting high strength to the material. On the other hand, they continuously enhance the dislocation storage capacity and retard the dynamic recovery of dislocations, enabling the material to sustain a relatively high level of strain hardening capacity over a large strain range.

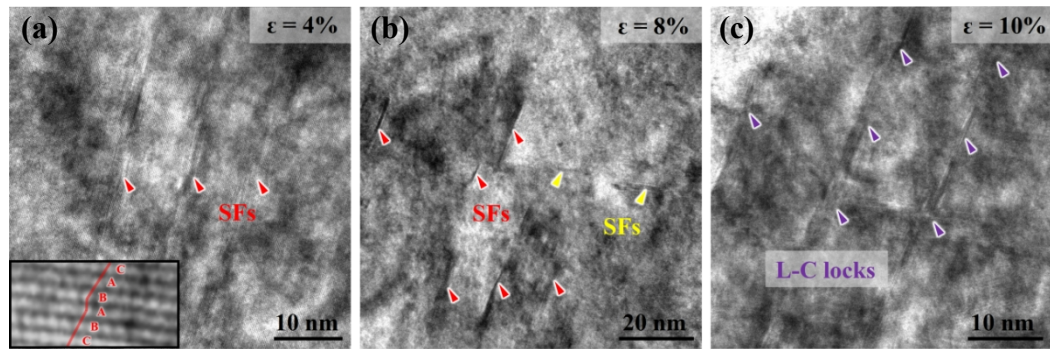


Fig. 6.12 Evolution of dislocation substructures with increasing strain in the shell of the submicron-scale core-shell structure region of the Al₉ alloy
(a) tensile strain of 4%; (b) tensile strain of 8%; (c) tensile strain of 10%

Similarly, TEM was employed to characterize the dislocation substructures in the micron-scale core-shell structure of the fractured tensile specimen, in order to reveal the room-temperature deformation mechanism of this region. The resulting bright-field images are presented in Fig. 6.13. Unlike in the submicron-scale core-shell structure, no apparent dislocation shearing of the L₁₂ ordered cores is observed in this region, suggesting that dislocations do not interact with the ordered phase predominantly via a shearing mechanism. However, pronounced dislocation pile-up can be observed in the vicinity of the larger ordered phases. Meanwhile, clear dislocation bowing and individual dislocation lines bypassing the phases are observed around the relatively smaller ordered phases. Such dislocation configurations suggest that, in the micron-scale L₁₂ ordered cores with elongated cellular morphology, gliding dislocations are largely prevented from direct shearing and instead preferentially accumulate at the core-shell interface. As plastic deformation proceeds, when the local stress reaches a critical level, some dislocations bypass the L₁₂ ordered cores via the Orowan mechanism, thereby contributing to the strengthening of the material. In addition, TEM characterization

was performed on the shell of the micron-scale core–shell structure region in the undeformed specimen, and the results are shown in Fig. 6.14. It was observed that a high density of SFs is also present within the shell of this region. These SFs can multiply and interact with one another during subsequent plastic deformation, progressively evolving into higher-density dislocation substructures and further enhancing the mechanical properties of the material.

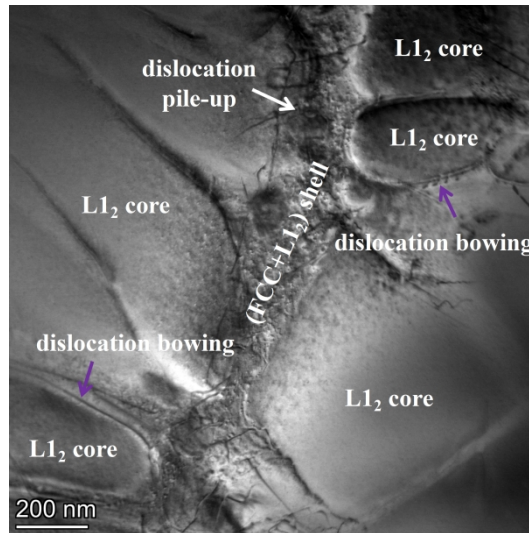


Fig. 6.13 Dislocation substructures in the micron-scale core–shell structure region of the fractured Al9 alloy tensile specimen

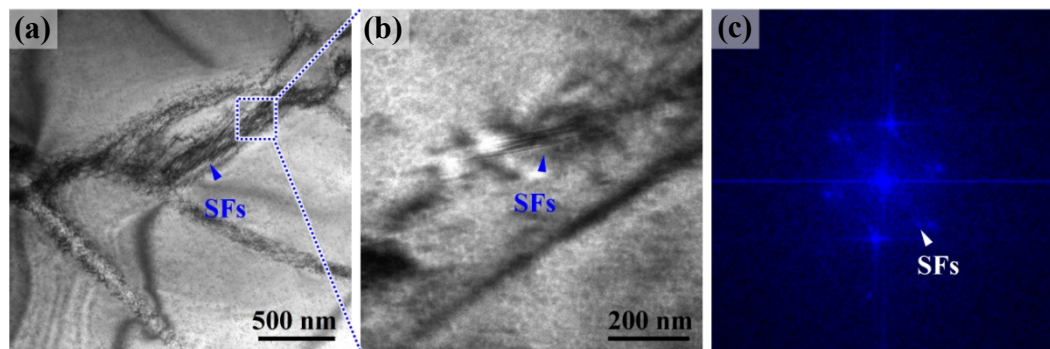


Fig. 6.14 Dislocation substructures in the shell of the micron-scale core–shell structure region of the undeformed Al9 alloy
(a) shell morphology; (b) magnified image of SFs; (c) diffraction pattern of SFs

In summary, the room-temperature deformation mechanism of this alloy is jointly governed by a variety of microscopic dislocation substructures, including dislocation glide, SFs, L-C locks, SISF/SESF, as well as dislocation forests, deformation microbands, and dislocation walls. Overall, the deformation process can be divided into two stages. Before a tensile strain of approximately 8%, the deformation of the ordered cores in the submicron-scale core–shell structure is

primarily controlled by SISF/SESF, while the deformation of the shell is dominated by SFs. In contrast, the ordered phases in the micron-scale core-shell structure essentially undergo no appreciable plastic deformation, and their outer shells accommodate the deformation mainly through dislocation glide, with significant dislocation pile-up occurring at the core-shell interfaces. When the tensile strain exceeds approximately 8%, the deformation of the ordered cores in the submicron-scale core-shell structure gradually transitions to being dominated by complex dislocation substructures such as dislocation forests, deformation microbands, and dislocation walls, while the deformation of the shell is synergistically controlled by SFs and L-C lock configurations. Concurrently, in the micron-scale core-shell structure, the ordered phases still undergo no appreciable deformation, and the deformation of the surrounding shells is mainly governed by SFs, with the partial dislocations interacting with the ordered phases through a bypass mechanism. Collectively, the progressive activation of multiple dislocation substructures endows the material with a continuously enhanced multi-stage strain hardening behavior during deformation, thereby conferring its excellent room-temperature tensile properties.

6.4.2 Room-temperature strengthening mechanisms of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

The Al9 alloy exhibits an outstanding level of strength at room temperature. According to classical strengthening theory and the microstructural characterization results described above, the high strength of this alloy does not originate from a single factor but rather from the synergistic action of multiple strengthening mechanisms, primarily including lattice friction stress (σ_0), grain boundary strengthening (σ_G), solid solution strengthening (σ_s), dislocation strengthening (σ_D), and precipitation strengthening (σ_p). On this basis, the present section first quantitatively evaluates the contribution of each strengthening mechanism through systematic calculation and performs a comparative analysis, thereby elucidating the room-temperature strengthening mechanisms of the Al9 alloy.

First, the contributions of lattice friction stress and solid solution strengthening are calculated. Classical solid solution strengthening theory considers that the size and

modulus mismatch between solute and solvent atoms constitutes the fundamental origin of the strengthening contribution. However, in high-entropy intermetallics, sublattice high-entropy alloying makes it difficult to distinguish between solute and solvent. Therefore, approximate evaluation is carried out with the aid of material systems of similar composition. With reference to the $(\text{FeCoNi})_{78.5}\text{Cr}_{10.5}\text{Al}_5\text{Ti}_5\text{Ta}_1$ alloy, whose composition is close to that of the Al9 alloy, the solid solution strengthening contribution is estimated to be approximately 86.5 MPa [132]. Furthermore, the L1_2 -type high-entropy intermetallic can be regarded as the product of sublattice high-entropy alloying of Ni_3Al . Consequently, the lattice friction stress is approximately taken as 180 MPa, based on the value for Ni_3Al [133].

After that, the grain boundary strengthening contribution is calculated. In general, a reduction in grain size leads to a significant increase in grain boundary density, thereby enhancing the impeding effect of grain boundaries on dislocation motion and improving the strength of the material. The quantitative relationship between grain size and yield strength can be described by the Hall-Petch equation, as expressed in equation (6-4) [134]:

$$\sigma_y = \sigma_0 + kd^{-1/2} \quad (6-4)$$

where σ_y — yield strength (Pa);

σ_0 — lattice friction stress (Pa);

k — strengthening coefficient ($\text{Pa} \cdot \text{m}^{1/2}$);

d — average grain diameter (m).

In the present alloy, σ_0 is taken as 180 MPa; k is taken from the experimental data of the L1_2 -strengthened high-entropy alloy $(\text{FeCoNi})_{78.5}\text{Cr}_{10.5}\text{Al}_5\text{Ti}_5\text{Ta}_1$, i.e., $276 \text{ MPa} \cdot \mu\text{m}^{1/2}$; d was obtained through statistical analysis using Image Pro software, yielding an average dendrite diameter of approximately $118.5 \mu\text{m}$ for the Al9 alloy. On this basis, the grain boundary strengthening contribution can be expressed as equation (6-5) [135]:

$$\sigma_G = k(d^{-1/2} - d_0^{-1/2}) \quad (6-5)$$

where d_0 — initial coarse grain size (nm).

For this as-cast alloy, d_0 can be approximately regarded as infinite. It can thus be calculated that the contribution of grain boundary strengthening to the enhancement of material strength is approximately 25.4 MPa.

Subsequently, the dislocation strengthening contribution is calculated. As the primary carrier of plastic deformation, dislocations are continuously generated and accumulated during cold deformation. The interactions among pre-existing dislocations significantly impede their mutual motion, thereby producing a considerable dislocation strengthening effect. The contribution of dislocation strengthening to the enhancement of material strength can be described by the Bailey-Hirsch equation, as given in equation (6-6) [136]:

$$\sigma_D = M\alpha Gb\rho^{-1/2} \quad (6-6)$$

where M —Taylor factor;

α —dislocation strengthening coefficient;

G —shear modulus (Pa);

b —Burgers vector (m);

ρ —dislocation density (m⁻²).

Since the present alloy specimen was prepared by a direct casting process and did not experience any plastic deformation procedure, its dislocation density ρ can be approximately regarded as zero. Although a small number of dislocations may be induced by internal stresses during rapid cooling, their contribution to the strength is exceedingly limited compared with other strengthening mechanisms and can be reasonably neglected. Hence, in this alloy, the dislocation strengthening contribution is approximately taken as 0.

Finally, the precipitation strengthening contribution is calculated. In classical precipitation strengthening theory, the high-strength phase is generally regarded as the precipitate phase, while the continuously distributed phase is treated as the matrix phase. Therefore, in order to quantitatively evaluate the precipitation strengthening contribution, the high-strength L1₂ cores are regarded as the precipitate phase and the surrounding shells are treated as the matrix phase in the calculations, and a reasonable quantitative evaluation is performed on this basis.

According to the deformation mechanism analysis presented in Section 6.4.1, dislocations primarily bypass the micron-scale $L1_2$ ordered cores through the Orowan bypass mechanism in the dendrite boundary region. In contrast, dislocations tend to penetrate the ordered phase through a shearing mechanism in the dendrite interior region. Hence, the total strength increment induced by precipitation strengthening in this alloy is calculated using the rule of mixtures [137], which can be expressed as equation. (6-7):

$$\Delta\sigma_p = C_s \cdot \Delta\sigma_{p-s} + C_c \cdot \Delta\sigma_{p-c} \quad (6-7)$$

where C_s — volume fraction of the submicron-scale core-shell structure region;

C_c — volume fraction of the micron-scale core-shell structure region;

$\Delta\sigma_{p-s}$ — precipitation strengthening increment induced by the submicron-scale $L1_2$ ordered cores (Pa);

$\Delta\sigma_{p-c}$ — precipitation strengthening increment induced by the micron-scale $L1_2$ ordered cores (Pa).

Based on SEM images and statistical analysis using Image Pro software, the volume fractions C_s and C_c were determined to be approximately 85% and 15%, respectively. $\Delta\sigma_{p-s}$ is primarily generated by the dislocation shearing mechanism, and its strengthening contribution comprises coherency strengthening ($\Delta\sigma_{cs}$), elastic modulus mismatch strengthening ($\Delta\sigma_{ms}$), and order strengthening ($\Delta\sigma_{os}$). The calculation formulae for the aforementioned strengthening contributions can be expressed as [138]:

$$\Delta\sigma_{cs} = M \cdot \alpha_\epsilon (G \cdot \epsilon)^{3/2} \left(\frac{rf}{0.5Gb} \right)^{1/2} \quad (6-8)$$

$$\Delta\sigma_{ms} = M \cdot 0.0055 (\Delta G)^{3/2} \left(\frac{2f}{G} \right)^{1/2} \left(\frac{r}{b} \right)^{(3m/2)-1} \quad (6-9)$$

$$\Delta\sigma_{os} = \frac{\gamma_{SFE}}{2b} \left[(3\pi^2 \gamma_{SFE} \cdot \frac{rf}{32T})^{1/2} - f \right] \quad (6-10)$$

where α_ϵ — empirical constant for FCC-type alloys;

ϵ — misfit strain;

r — precipitate radius (m);

f ——precipitate volume fraction;
 m ——precipitate volume fraction;
 T ——dislocation line tension ($\text{J}\cdot\text{m}^{-1}$).

In these expressions, the room-temperature shear modulus G was calculated by JMatPro software to be 81.5 GPa; M for an FCC polycrystalline matrix is taken as 3.06 [139]; the Burgers vector b of the matrix phase can be obtained from $b = (\sqrt{2}/2) \cdot a_{\text{matrix}}$, where the lattice constant a was calculated from XRD diffraction results to be 0.3558 nm, corresponding to $b=0.2516$ nm; the lattice misfit between the shell and the core can be obtained from $\varepsilon=(2/3) \cdot (\Delta a/a)$, and based on the XRD results, ε was calculated to be 0.585%; the stacking fault energy γ_{SFE} of the L1_2 ordered core is 20.8 mJ/m²; α_ε and m are taken as 2.6 and 0.85, respectively [140]; T can be calculated from $T=G \cdot b^2/2$. In addition, the volume fraction f and the average radius r of the precipitate phase were determined through statistical analysis using Image Pro software to be 75% and 60.5 nm, respectively. Based on the above parameters and calculation formulae, the contributions of coherency strengthening, elastic modulus mismatch strengthening, and order strengthening are obtained as 164 MPa, 78.2 MPa, and 282.7 MPa, respectively. Hence, the precipitation strengthening contribution induced by the submicron-scale L1_2 ordered cores is 524.9 MPa.

$\Delta\sigma_{\text{P-C}}$ is primarily generated through the Orowan-type dislocation bypass mechanism, and its expression can be expressed as equation. (6-11) [141]:

$$\Delta\sigma_{\text{P-C}} = 0.4MGb \frac{1}{\pi\sqrt{1-\nu}} \frac{\ln(\frac{2\bar{r}}{b})}{\lambda_p} \quad (6-11)$$

where $\bar{r}$ ——mean radius of precipitates on the slip plane (m);

λ_p ——equivalent inter-precipitate spacing (m);

ν ——Poisson's ratio (taken as 0.25).

In these expressions, $\bar{r}$ can be obtained from $\bar{r} = \sqrt{2/3} \cdot r$, where r is the average radius of the micron-scale L1_2 ordered cores, determined through statistical analysis

using Image Pro software to be approximately 400 nm; λ_p can be calculated from $\lambda_p = d \cdot (1 - f) \cdot \sqrt{2/3f}$ [142], where d is the average equivalent diameter of the micron-scale L1₂ ordered cores, approximately 800 nm, and the precipitate volume fraction f is approximately 90%. Substituting the above parameters into the formula, the precipitation strengthening contribution of the micron-scale L1₂ ordered cores is calculated to be 524.9 MPa. Comprehensively considering the volume fractions of the submicron-scale and micron-scale core-shell structure regions, the total precipitation strengthening contribution of the Al9 alloy is calculated to be 616.9 MPa.

Based on the above calculation results, the theoretical yield strength of the Al9 alloy is about 908.8 MPa. Among these contributions, precipitation strengthening accounts for approximately 68%, occupying a dominant position among all strengthening mechanisms. It is therefore necessary to further analyze the origin of the outstanding room-temperature yield strength with a focus on the precipitation strengthening mechanism. According to the precipitation strengthening formulae, an increase in the volume fraction of the L1₂ ordered phase, regardless of whether dislocations shear or bypass, leads to greater resistance to dislocation motion and thus a significantly enhanced precipitation strengthening contribution to the yield strength. Both thermodynamic calculations and microstructural statistical analyses demonstrate that the L1₂ ordered phase content approaches 80% in the Al9 alloy. By comparison, in conventional L1₂-particle-strengthened FCC-type high-entropy alloys and precipitation-strengthened nickel-based superalloys, the volume fraction of the L1₂ ordered phase is generally below 60%. It can thus be concluded that the outstanding room-temperature yield strength of the Al9 alloy primarily originates from the precipitation strengthening mechanism dominated by the high volume fraction of L1₂ ordered cores.

Building upon the high yield strength, the excellent ultimate tensile strength of the Al9 alloy primarily originates from the pronounced strain hardening behavior during plastic deformation. The strain hardening capability of a material is conventionally characterized by the strain hardening exponent n , which can be

calculated using the logarithmic form of the Hollomon equation, expressed as equation. (6-12) [143]:

$$\ln(\sigma) = \ln(K) + n\ln(\varepsilon) \quad (6-12)$$

where σ —true stress in the uniform plastic deformation stage (Pa);

ε —true strain in the uniform plastic deformation stage;

K —strength coefficient (Pa);

n —strain hardening exponent.

Therefore, the slope of the $\ln(\sigma)$ – $\ln(\varepsilon)$ curve represents the n value of the material. Based on the true stress–true strain data of the Al9 alloy, this curve is plotted, as shown by the black curve in Fig. 6.15 (a). It is evident that the curve rises slowly in the early stage of deformation and increases rapidly near fracture. Further fitting of the first-order derivative of this curve yields the variation of the n value with true strain, as shown by the blue curve in Fig. 6.15 (a). As can be seen from the figure, the n value of the Al9 alloy can reach 0.4 in the later stage of deformation, which is significantly superior to that of most conventional structural materials, as shown in Fig. 6.15 (b) [144–147]. The above results indicate that the Al9 alloy possesses excellent strain hardening capability.

This pronounced strain hardening capability originates from the synergistic strengthening effect of the multi-scale $L1_2$ ordered cores. In the early deformation stage, the softer shell accommodates plasticity preferentially, while the dispersed nano-scale ordered cores within it impede the motion of partial dislocations and stacking faults. Although the ordered phase at this scale is relatively small in size and has a limited capacity to impede individual dislocations, its high-density distribution characteristic significantly shortens the mean free path of dislocations, thereby enabling the material to exhibit a high strain hardening even at the early stage of plastic deformation. As strain increases, the submicron-scale ordered cores progressively dominate the deformation. Dislocations shear through them, forming complex substructures within the cores, including SISFs/SESFs, forests, and walls. This significantly enhances dislocation storage and suppresses dynamic recovery, enabling the material to sustain high strain hardening at intermediate strains. Entering the late deformation stage, the micron-scale ordered cores persistently

impede dislocation motion through the Orowan bypass mechanism, providing long-term stable obstacles for dislocations and thereby maintaining a high strain hardening level at the high strain stage. In summary, the multi-scale $L1_2$ ordered cores sequentially exert strengthening effects at different stages of deformation, achieving a continuous increase in the strain hardening rate and consequently significantly enhancing the ultimate tensile strength of the material. In contrast, the strengthening effect of single-scale precipitates is typically concentrated in a specific deformation stage. As deformation proceeds, the strain hardening rate decreases rapidly once dislocations gradually adapt to a single type of obstacle and undergo dynamic recovery or rearrangement, thus limiting further improvement of the ultimate tensile strength.

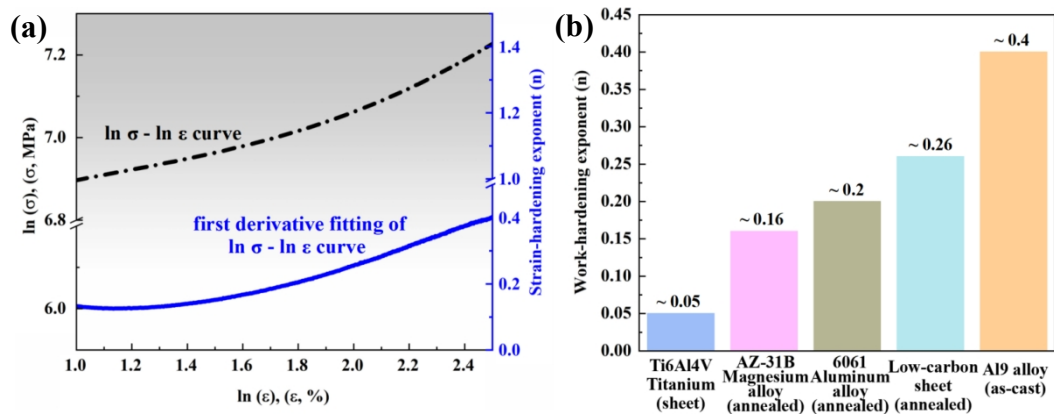


Fig. 6.15 Analysis of the strain hardening capability of the A19 alloy
(a) $\ln(\sigma)$ – $\ln(\epsilon)$ curve and variation of the n value with true strain; (b) comparison of n values for different structural materials

Furthermore, the coexistence of multi-scale core-shell structures imparts heterogeneous structural characteristics to the microstructure of the A19 alloy, thereby further enhancing its strength. According to the strengthening contribution calculations, a discrepancy of approximately 100 MPa exists between the theoretical and experimental yield strengths, as shown in Fig. 6.16. In addition to the strengthening contribution from nano-scale $L1_2$ ordered phases that was not included in the calculation, there may also be other strengthening mechanisms that jointly contribute to the excellent room-temperature yield strength of the A19 alloy. It is well known that the flow stress consists of two components: the effective stress and the HDI stress [148]. The effective stress is a short-range local stress, which includes the lattice friction stress and the interaction between moving dislocations, corresponding to the five conventional strengthening mechanisms described above.

The HDI stress, on the other hand, is a long-range internal stress arising from the property differences between heterogeneous structures within the material. In the Al9 alloy, HDI stress exists at both macroscopic and microscopic levels. At the macroscopic level, a pronounced property difference exists between the relatively soft submicron-scale core–shell region within the dendrite interior and the harder micron-scale core–shell region at the dendrite boundary. During plastic deformation, back stress develops within the dendrite interior, exerting a strengthening effect on this region. Simultaneously, forward stress develops at the dendrite boundary to balance the stress concentration induced by the strength difference. At the microscopic level, within the micron-, submicron-, and nano-scale core–shell structures, back stress and forward stress are similarly generated within the respective shells and cores due to the strength differences between them. However, they cannot completely counteract each other, since back stress decays more slowly than forward stress, thereby generating a net strengthening effect, i.e., the HDI stress. It can thus be inferred that the pronounced heterogeneous microstructural characteristics of the Al9 alloy jointly activate the HDI strengthening effect at both macroscopic and microscopic levels, thereby further enhancing the yield strength of the material.

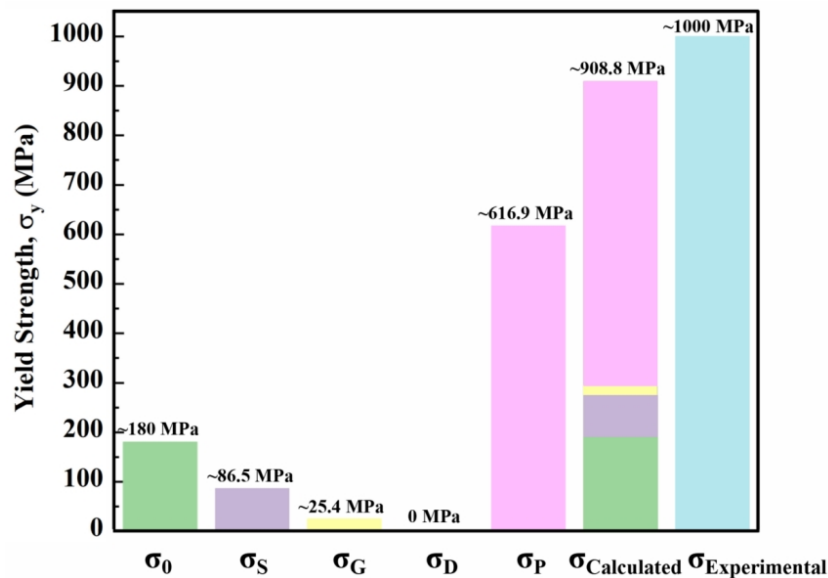


Fig. 6.16 Comparison between the theoretically calculated and experimentally measured yield strengths of the Al9 alloy

Notably, while the strengthening effect arising from microscopic HDI stress has been extensively validated, macroscopic HDI strengthening has received far less

resulting engineering stress–strain curves are shown in Fig. 6.17 (f). The results indicate that the room-temperature yield strength of the heat-treated alloy decreased to approximately 825 MPa. Further calculation of the strength contributions yielded the friction stress, grain boundary strengthening, solid-solution strengthening, dislocation strengthening, and precipitation strengthening of the heat-treated alloy as 180 MPa, 86.5 MPa, 17.5 MPa, 0 MPa, and 504.2 MPa, respectively. Based on these values, the theoretical yield strength was calculated to be approximately 788.2 MPa, which deviates from the experimental value by about 37 MPa. Assuming the strengthening contribution of the nanoscale $L1_2$ ordered phases is neglected and the discrepancy between the experimental and theoretical yield strengths is ascribed exclusively to the HDI strengthening effect, the HDI strengthening in the heat-treated Al9 alloy is still substantially lower than that in the as-cast alloy. Considering that the submicron- and nano-scale core–shell structures remained essentially unchanged, the reduction in HDI strengthening in the heat-treated Al9 alloy is primarily attributed to the absence of macroscopic-level HDI strengthening caused by the disappearance of the micron-scale core–shell structures at the grain boundary. This demonstrates that macroscopic-level HDI strengthening plays a critical role in enabling the Al9 alloy to achieve excellent room-temperature yield strength.

In summary, the excellent room-temperature strength of the Al9 alloy primarily originates from the synergistic strengthening effect of the multi-scale core–shell structures. From a structural perspective, the high volume fraction of $L1_2$ ordered cores provides a substantial precipitation strengthening contribution, laying a solid foundation for the achievement of high yield strength. Building upon this, the heterogeneous microstructure formed by the multi-scale core–shell structures further induces the HDI strengthening effect, additionally elevating the yield strength level of the material. Simultaneously, the $L1_2$ ordered cores at different scales exhibit distinct strengthening characteristics at progressive deformation stages, wherein dislocations are continuously impeded by multi-scale obstacles throughout the entire process. Such sustained dislocation–obstacle interactions preserve a high strain hardening rate, ultimately endowing the alloy with excellent room-temperature ultimate tensile strength.

6.4.3 Room-temperature plasticizing mechanisms of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

Based on the analysis of room-temperature deformation mechanisms, the shell within each scale of the core–shell structures serves as the preferential deformation region and exerts a significant influence on dislocation motion and material plasticity. Therefore, this section systematically analyzes the room-temperature plasticizing mechanism of the Al9 alloy, starting from the shell of the core–shell structure, to further elucidate the microscopic origin of its excellent tensile ductility.

First, the continuously distributed (FCC+L1₂) shell provides the foundation for dislocation motion. In the early stage of plastic deformation, dislocations are preferentially initiated and glide within the relatively soft shell. This is because the dislocation glide process induces local disordering of the slip plane, causing dislocations to preferentially move along paths with lower ordering energy. Consequently, the shell with a disordered FCC matrix provides favorable space for dislocation motion and multiplication, serving as an important foundation for the stable progression of plastic deformation. From a compositional perspective, the alloy incorporates FCC-phase-forming elements Co and Cr at a total content of 34.5 at.%, which generates abundant FCC-type slip paths in the microstructure, providing sufficient channels for the continuous motion of dislocations. Simultaneously, the addition of these FCC-phase-forming elements also reduces the ordering energy of the shell, further facilitating dislocation glide within it. From a structural perspective, the shells of the core–shell structures at each scale are continuously distributed, forming an uninterrupted slip channel network at the microscopic level. This structural feature significantly reduces the likelihood of dislocation pile-up within the shell, thereby ensuring the stable progression of the plastic deformation process. Thus, owing to the high content of FCC-forming elements, the continuous (FCC+L1₂) shell enables dislocations to move under a low energy barrier and effectively suppresses local pile-up, thereby laying the foundation for the alloy to achieve good ductility.

Second, the excellent strain hardening capability promotes a synergistic enhancement of strength and ductility in the material. It is well known that alloys with excellent strain hardening capability can effectively suppress microcrack

propagation and necking, thereby achieving uniform plastic deformation and further promoting the synergistic enhancement of strength and ductility [149]. Deformation mechanism analysis reveals that the excellent strain hardening capability of the Al9 alloy originates from two main sources: the stage-specific interaction between $L1_2$ ordered cores of different scales and dislocation substructures, and the additional hardening contribution from the interaction between HDI stress and mobile dislocations [150]. The strain hardening induced by HDI stress can be quantitatively characterized by the rate of change of HDI stress with increasing strain, a parameter obtainable through LUR experiments. To analyze the microscopic-level HDI strain hardening, LUR tests were conducted on the heat-treated alloy, the results of which are shown in Fig. 6.18 (a) and (b). The distinct hysteresis loops observed in the LUR curves of the heat-treated alloy indicate the presence of microscopic-level HDI stress induced by the submicron- and nano-scale core-shell structures. This stress can be determined according to equation (6-13) [151]:

$$\sigma_{\text{HDI}} = \frac{1}{2}(\sigma_u + \sigma_r) \quad (6-13)$$

where σ_u — unloading yield stress (Pa);

σ_r — reloading yield stress (Pa).

Here, σ_u and σ_r were determined according to the calculation method provided in Ref. [152]. Furthermore, the effective stress generated by the submicron- and nano-scale core-shell structures can be calculated using equation (6-14):

$$\sigma_{\text{flow}} = \sigma_{\text{effective}} + \sigma_{\text{HDI}} \quad (6-14)$$

where σ_{flow} — flow stress (Pa);

$\sigma_{\text{effective}}$ — effective stress (Pa).

The calculated results are plotted in Fig. 6.18 (c), with the error bars representing the standard deviation of multiple repeated measurements at each data point. As can be seen from the figure, the HDI stress curve of the heat-treated alloy exhibits a continuously increasing trend with increasing strain, confirming the existence of microscopic-level HDI strain hardening. LUR tests were also conducted on the as-cast alloy sample using the same measurement parameters, and the resulting LUR

curves are shown in Fig. 6.18 (a) and (b). The larger hysteresis loops observed in Fig. 6.18 (b) indicate that the introduction of micron-scale core-shell structures activated a more pronounced HDI stress. The HDI stress and effective stress of the as-cast alloy were similarly calculated according to the above formulas, and the results are plotted in Fig. 6.18 (d). As can be seen from the figure, the growth trend of the HDI stress in the as-cast alloy is steeper than that in the heat-treated alloy. It can thus be inferred that the introduction of micron-scale core-shell structures simultaneously activates HDI strain hardening at both microscopic and macroscopic levels, providing the plastic deformation of the Al9 alloy with additional dislocation accumulation capacity. Consequently, the multi-scale core-shell structures are capable of providing an additional HDI strain hardening effect, enabling the alloy to maintain a high level of strain hardening capability throughout the deformation process, thereby effectively delaying the onset of local plastic instability and further enhancing the plastic performance of the material.

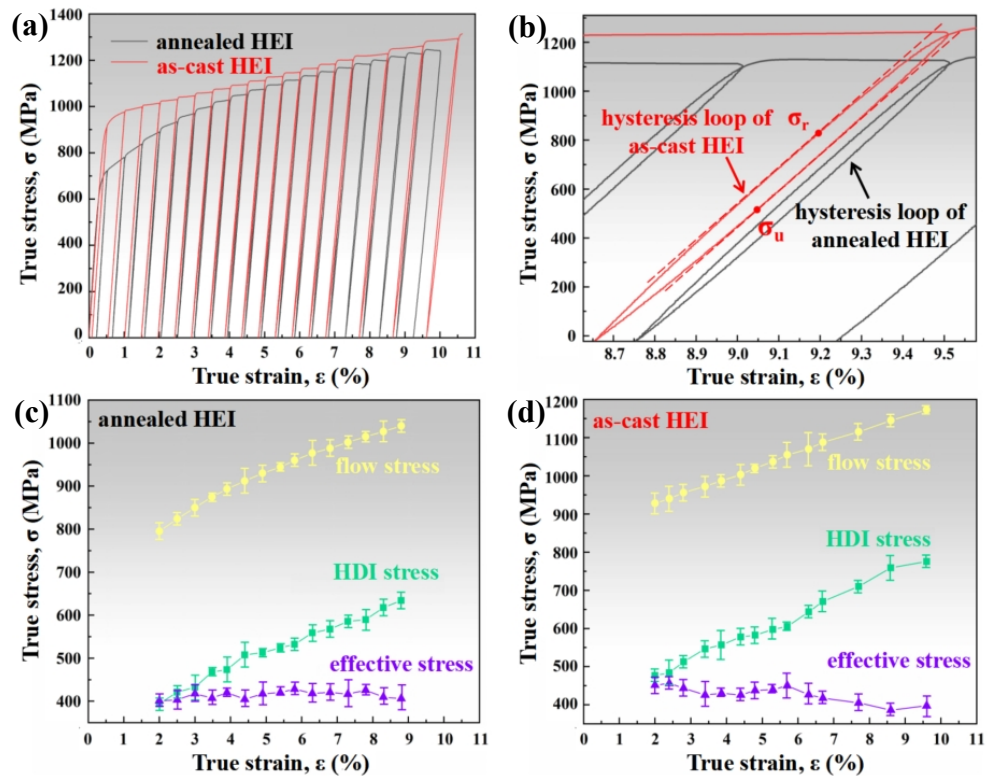


Fig. 6.18 HDI strain hardening capability of the as-cast and heat-treated Al9 alloy
 (a) LUR curves; (b) magnified view of the LUR curves; (c) variation of HDI stress with true strain for the heat-treated alloy; (d) variation of HDI stress with true strain for the as-cast alloy

Furthermore, the unique gradient microstructure extends the stable plastic deformation stage of the alloy. Combined with the analysis in Section 6.3.1, it is

evident that the Al9 alloy exhibits a continuously rising strain hardening rate over a broad strain range. This indicates that dislocations can undergo sustained multiplication and storage during deformation, thereby enabling the material to maintain stable plastic flow over a wide strain interval. Such persistently stable and continuously intensifying strain hardening behavior is closely associated with the continuous gradient size distribution formed within the dendrite interior by the submicron-scale core-shell structure. According to equation (6-2), the critical stress required to promote partial dislocation shearing exhibits an inverse relationship with the size of the L_{12} ordered phase. Consequently, in the low-strain stage, the larger submicron-scale L_{12} ordered cores near the dendrite boundary are preferentially sheared by partial dislocations. As the strain further increases, the partial dislocation shearing behavior gradually extends from the larger cores in the dendrite boundary region to the smaller cores in the dendrite center region. During this process, SISFs/SESFs progressively form and continuously accumulate within the L_{12} ordered cores, thereby producing sustained interactions over a wide strain range, which drives the strain hardening rate to maintain an ascending trend across a broad strain interval. Hence, the gradient microstructure can promote the progressive activation of strain hardening capacity, thereby significantly broadening the stable plastic deformation range of the material and ultimately achieving excellent room-temperature ductility.

Thus, the outstanding room-temperature ductility of the Al9 alloy originates from the synergistic effects of the multi-scale core-shell structure. On the one hand, the continuously distributed network of low-energy dislocation channels provides the structural foundation for steady plastic deformation. On the other hand, the activation of multi-scale HDI strain hardening effects enables the alloy to maintain a high level of strain hardening capacity throughout the entire deformation stage, thereby sustaining stable plastic deformation while ensuring high strength. In addition, the gradient microstructure promotes the progressive activation of strain hardening, enabling the strengthening effect to persist continuously over an extended strain range, thereby substantially broadening the stable plastic deformation interval.

It is noteworthy that the deformation of the multi-scale core-shell structured high-

entropy intermetallic involves interactions among multiple structural units with distinct mechanical properties, and the coordinated deformation capability among these units directly determines the overall mechanical performance of the material. Therefore, it is necessary to further analyze the coordinated deformation mechanism of the Al9 alloy to elucidate the microstructural origin of its excellent room-temperature comprehensive properties. The first aspect is the coordinated deformation between the core and the shell within each scale of the core-shell structure. TEM high-resolution characterization in Section 5.3.2 shows that both the micron-scale and submicron-scale core-shell structures in the Al9 alloy exhibit highly coherent interfacial characteristics. The XRD fitting results indicate that the average lattice misfit between the core and shell phases is only 0.88%. Consequently, the elastic strain energy at the core-shell interface is low, which is favorable for dislocation transmission across the interface. According to the room-temperature deformation mechanism, dislocations can traverse the core-shell interface through either shearing or bypassing to participate in plastic deformation, demonstrating good coordinated deformation capability between the two phases. This compatibility can reduce stress concentration at the interface, suppress microvoid initiation and coalescence, and prevent premature failure of the material due to microvoid aggregation. Thus, the highly coherent core-shell interface can both provide strengthening by impeding dislocation motion and promote dislocation transmission to sustain ductility by reducing the lattice misfit, thereby laying the microstructural foundation for the Al9 alloy to achieve an excellent strength-ductility synergy.

Meanwhile, the micron-scale and submicron-scale core-shell structure regions also exhibit good coordinated deformation capability. Nanoindentation results reveal a pronounced strength difference between the two regions. Typically, such a strength disparity can easily induce deformation incompatibility at the inter-regional interface, which in turn triggers local stress concentration and may even lead to premature cracking. However, fracture mechanism analysis of the Al9 alloy reveals that, despite the presence of a small number of microvoids at the interface between the two scale-level core-shell structural regions, neither crack initiation nor propagation occurs at these sites, indicating the existence of an effective coordinated deformation mode between the two regions. Theoretically, coordinated

deformation between regions of different strengths relies on the accumulation of GNDs. In the Al9 alloy, the submicron-scale core-shell structure region within the dendrite interior has a lower strength and undergoes preferential deformation during the early stage of plastic deformation. In contrast, the micron-scale core-shell structure region at the dendrite boundary possesses a higher deformation resistance and thus deforms with a relative delay. To accommodate the deformation mismatch between the two regions, a large number of GNDs must be generated at the inter-regional interface to accommodate the local strain gradient and achieve continuous load transfer. To further verify the actual activation of this coordinated deformation mechanism in the Al9 alloy, TEM characterization was performed at the interface between the two scale-level core-shell structure regions, and the bright-field image is presented in Fig. 6.19. It can be clearly observed from the image that a high-density GNDs accumulation zone exists near the interface. Thus, the Al9 alloy effectively regulates the coordinated deformation capability between the micron-scale and submicron-scale core-shell structure regions through the formation of high-density GNDs, enabling the interfacial region to provide strengthening while avoiding ductility loss due to local deformation incompatibility, thereby achieving a synergistic enhancement of strength and ductility.

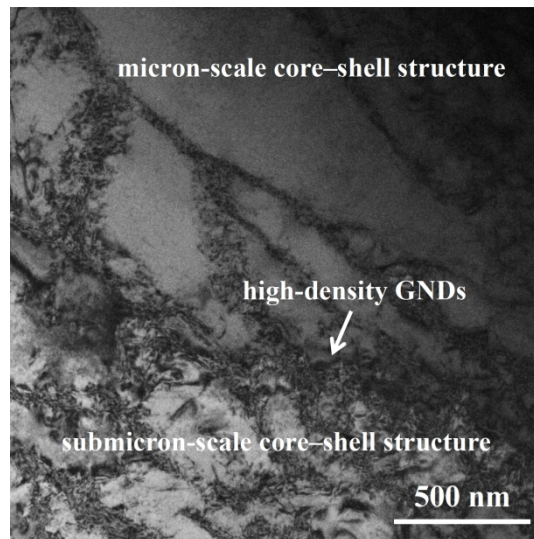


Fig. 6.19 GNDs at the interface between micron-scale and submicron-scale core-shell structure region in the Al9 alloy

In addition, the different grains in the Al9 alloy also exhibit excellent coordinated deformation capability. Generally, grain boundaries in polycrystalline alloys tend to become sites of dislocation pile-up and stress concentration, owing to their

disordered atomic arrangement and low bonding strength, thereby inducing microcrack initiation and leading to intergranular fracture. Based on the fracture mode analysis, the Al9 alloy exhibits a mixed fracture mode with coexisting intergranular and transgranular fracture, and the intergranular fracture accounts for a relatively small proportion alongside transgranular fracture. This indicates that the grain boundary regions of the alloy possess good coordinated deformation capability, enabling effective alleviation of local stress concentration during plastic deformation and preventing intergranular fracture of the material. To validate this conclusion, TEM characterization was performed on the region near the grain boundary, and the bright-field image is shown in Fig. 6.20. It can be clearly observed from the image that the grain boundary exhibits a serrated morphology, with a high-density dislocation accumulation zone in the adjacent region. This suggests that the grain boundary can actively participate in the plastic deformation process, contributing to local strain accommodation and load transfer, rather than merely serving as a dislocation termination site.

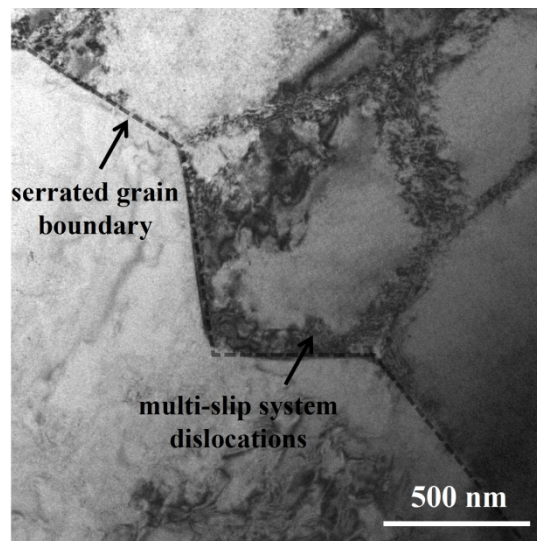


Fig. 6.20 Serrated grain boundary and surrounding dislocation structures in the Al9 alloy

Previous studies have indicated that serrated grain boundaries are conducive to promoting coordinated deformation among grains. On the one hand, the serrated morphology introduces local orientation gradients, which facilitate the activation of multiple slip systems, thereby promoting continuous load transfer. On the other hand, the serrated structure can disperse local stress concentration, reducing the stress level on individual grain boundary segments and consequently delaying crack

initiation. Serrated grain boundaries typically originate from instabilities in the interface migration rate during solidification or phase transformation, as well as morphological perturbations during the cooperative growth of multi-phase interfaces. For the Al9 alloy, both sides of the grain boundary consist of micron-scale core-shell structures formed through the eutectic reaction. During eutectic growth, differences in diffusion kinetics, interfacial energy characteristics, and growth kinetics at the solidification front between the $L1_2$ and FCC phases give rise to inconsistent growth rates, which in turn induce periodic perturbations in the interface morphology and ultimately result in the formation of serrated grain boundaries.

To further investigate the influence of serrated grain boundaries on coordinated deformation, EBSD characterization was carried out on the region adjacent to the grain boundary, and the results are presented in Fig. 6.21. First, the grain boundary morphology can be clearly identified in the band contrast mode, and distinct micron-scale core-shell structures are observed on both sides of the grain boundary, as shown in Fig. 6.21 (a). On this basis, a statistical analysis of the misorientation angle distribution was performed on the grain boundary neighborhood, yielding the misorientation angle distribution map, as shown in Fig. 6.21 (b). The results show that the correlated orientation pairs have a significant statistical weight in the low-angle region, while the medium-to-high-angle region exhibits a multi-peak distribution, indicating the presence of segmented orientation variation characteristics along the grain boundary. Simultaneously, the correlated pair distribution clearly deviates from the random distribution, indicating that the grain boundary structure possesses high stability and continuity, which statistically confirms the existence of serrated grain boundaries. Further statistical analysis of the grain boundary angles in this alloy reveals that high-angle grain boundaries ($>15^\circ$) account for approximately 75%, while low-angle grain boundaries ($2-15^\circ$) account for approximately 25%. This implies that, during the formation of serrated grain boundaries, local regions of the grain boundary can develop graded-orientation interfaces and exhibit the structural characteristics of low-angle grain boundaries. Low-angle grain boundaries are typically composed of dislocation arrays, which can provide effective pathways for dislocation transmission across grain boundaries, thereby facilitating the enhancement of coordinated deformation

capability among grains. Meanwhile, high-angle grain boundaries still maintain a strong dislocation-blocking capacity. The synergistic coexistence of both types enables the grain boundary to improve strength while simultaneously possessing good deformation compatibility.

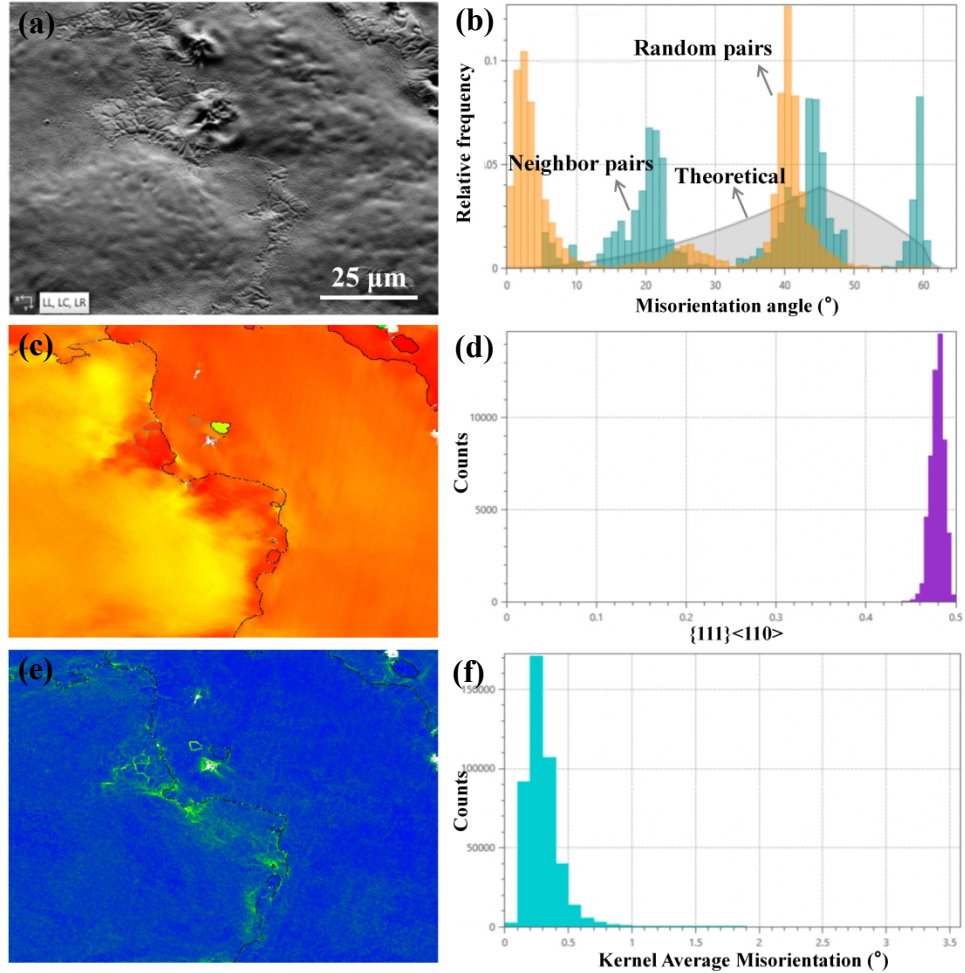


Fig. 6.21 EBSD characterization of serrated grain boundaries and nearby areas in the Al9 alloy

(a) serrated grain boundary morphology; (b) grain boundary misorientation angle distribution map; (c) spatial distribution map of Schmid factor in the grain boundary region; (d) statistical frequency distribution histogram of Schmid factor for the {111}<110> slip system; (e) KAM spatial distribution map in the grain boundary region; (f) KAM statistical frequency distribution histogram

To intuitively demonstrate the effect of serrated grain boundaries on coordinated deformation, Schmid factor calculations were performed on the grain boundary region, and the spatial distribution map is shown in Fig. 6.21 (c). The results reveal that the Schmid factor at the grain boundary is significantly higher than that within the grain interior, indicating that the serrated grain boundary alters the local slip geometry conditions, thereby promoting the synergistic activation of multiple slip

systems. Further statistical analysis was conducted on a region approximately 2 μm wide adjacent to the grain boundary, yielding the frequency distribution map shown in Fig. 6.21 (d). The statistical results indicate that the average Schmid factor in this region is approximately 0.5. Such a high Schmid factor level suggests that this region readily participates in load transfer through slip, which is beneficial for grain boundary coordinated deformation. Meanwhile, KAM analysis was performed on the same region to evaluate local stress concentration, yielding the KAM spatial distribution map shown in Fig. 6.21 (e). It can be seen that the KAM distribution is generally uniform both within the grain interior and at the grain boundary, with only slight strain concentration observed at localized grain boundary segments, indicating that the serrated grain boundary can effectively regulate the strain distribution. A KAM statistical analysis was further performed on a region approximately 2 μm wide adjacent to the grain boundary, yielding the KAM frequency distribution histogram shown in Fig. 6.21 (f). The figure shows that the KAM values are primarily concentrated in the range of 0–0.5°, with an average value of approximately 0.3°. The relatively low KAM value at the grain boundary further demonstrates that the serrated grain boundary can effectively promote coordinated deformation, resulting in a more uniform strain distribution, thereby avoiding premature brittle fracture caused by local stress concentration. Thus, the serrated grain boundary not only promotes the evolution of certain boundary segments into low-angle grain boundaries, providing channels for dislocation transmission, but also facilitates the synergistic activation of multiple slip systems and enhances load transfer capability. The synergistic effect of these two aspects leads to a more uniform strain distribution in the grain boundary neighborhood and effective alleviation of local stress concentration.

In summary, the Al9 alloy exhibits good coordinated deformation capability at multiple structural levels, including the core–shell interface, grain boundaries, and between different scale-level core–shell structures. This multi-level coordinated deformation mechanism can effectively alleviate the local stress concentration generated during the tensile process, suppress premature instability and cracking behavior, thereby enabling the alloy to simultaneously possess excellent strength and good ductility at room temperature.

6.5 Chapter summary

This chapter systematically investigated the room-temperature mechanical properties of high-entropy intermetallics with a multi-scale core-shell structure. Through the integrated application of multi-scale characterization techniques including SEM, TEM, and EBSD, together with mechanical testing methods such as room-temperature tensile testing, nanoindentation, and LUR experiments, an in-depth analysis of the room-temperature fracture mechanism of this class of alloys was conducted, and the influence of the multi-scale core-shell structure on room-temperature mechanical properties was elucidated. On this basis, the Al9 alloy, which exhibits the best overall properties, was selected as the representative material for systematic analysis of its room-temperature deformation mechanism and further elucidation of its strengthening and toughening mechanisms. The main conclusions are as follows:

(1) The multi-scale core-shell structure can significantly enhance the room-temperature comprehensive mechanical properties of high-entropy intermetallics. The dual-scale core-shell structure can improve strength, and the multi-scale core-shell structure can promote synergistic enhancement of strength and ductility through the activation of multi-stage strain hardening. Among them, the Al9 alloy exhibits the best comprehensive performance, with a yield strength of approximately 1000 MPa, an ultimate tensile strength of approximately 1250 MPa, and a plastic elongation of approximately 12.5%.

(2) The room-temperature deformation mechanism of the multi-scale core-shell structured high-entropy intermetallic was elucidated. In the submicron-scale core-shell structure of the Al9 alloy, partial dislocations interact with the $L1_2$ ordered core by shearing, and the deformation mechanism is governed by SISFs/SESFs, dislocation forests, deformation microbands, dislocation walls, and L-C locks. In the micron-scale core-shell structure, partial dislocations interact with the $L1_2$ ordered core through bypassing, and the shell deformation is dominated by SFs.

(3) The room-temperature strengthening mechanism of the multi-scale core-shell structured high-entropy intermetallic was revealed. The $L1_2$ ordered cores, with a volume fraction approaching 80% in the Al9 alloy, provide a significant

precipitation strengthening contribution, promoting an increase in yield strength. In addition, the multi-stage strain hardening behavior effectively enhances the ultimate tensile strength. Meanwhile, the multi-scale core–shell structure activates the HDI strengthening effect, enhancing the overall strength of the alloy.

(4) The room-temperature plasticizing mechanism of the multi-scale core–shell structured high-entropy intermetallic was revealed. The continuously distributed (FCC+L1₂) shell in the Al9 alloy effectively accommodates dislocation motion and multiplication, providing the structural foundation for plastic deformation. Meanwhile, the multi-scale core–shell structure activates the HDI strain hardening effect, enabling the alloy to maintain a high level of strain hardening and stable plastic deformation capacity throughout the entire deformation stage.

(5) The coordinated deformation mechanism of the multi-scale core–shell structured high-entropy intermetallic was systematically investigated. In the Al9 alloy, deformation coordination is achieved across multiple scales: at the microscale, dislocation transmission enables coordination between the L1₂ core and the surrounding shell; at the macroscale, high-density GNDs facilitate coordination between the micron-scale and submicron-scale core–shell regions; and at the grain scale, serrated grain boundaries promote intergranular coordination by inducing low-angle grain boundary transformation and activating multiple slip systems.

Chapter 7 Intermediate-temperature embrittlement characteristic and abnormal yield effect of multi-scale core-shell structured high-entropy intermetallic

7.1 Introduction

As a class of intermetallic compounds, multi-scale core-shell structured high-entropy intermetallics hold substantial promise for achieving superior mechanical performance at elevated temperatures. This potential is twofold. On one hand, they inherit a long-range ordered superlattice structure, which is conducive to high-temperature strength and exceptional property stability. On the other hand, the sluggish diffusion effect, arising from the high-entropy alloying of sublattices, effectively retards diffusion-driven microstructural evolution at high temperatures, thereby enhancing both the microstructural and structural integrity of the material. Consequently, these materials exhibit significant development potential for demanding high-temperature applications, such as those encountered in the aerospace industry.

Common high-temperature structural materials, including Ni-based superalloys, Co-based superalloys, and Ni₃Al-type intermetallics, are highly susceptible to abnormal microstructural coarsening and intermediate-temperature embrittlement within the range of approximately 600–900 °C. This embrittlement leads to a marked reduction in ductility and fracture resistance [153], which compromises material reliability and damage tolerance and consequently restricts its practical applicability. Previous studies have linked this phenomenon to grain boundary weakening, environmentally sensitive effects, and the competitive interplay between dislocation slip and diffusion mechanisms [154]. However, systematic observation and analysis of this intermediate-temperature embrittlement in multi-scale core-shell structured high-entropy intermetallics remain absent to date.

Furthermore, L1₂-ordered materials frequently exhibit an anomalous yield effect over a specific temperature range, where the yield strength initially increases with rising temperature before subsequently decreasing. This results in intermediate-to-high-temperature yield strengths exceeding the room-temperature value. This

behavior, regarded as a hallmark of ordered intermetallics that distinguishes them from disordered solid-solution alloys, is critically important for enhancing load-bearing capacity at elevated temperatures. Although extensive studies have been conducted on this phenomenon in conventional $L1_2$ -type intermetallics, it has yet to be thoroughly explored in high-entropy intermetallic systems that concurrently exhibit sublattice high-entropy alloying and a multi-scale core-shell structure.

To address these gaps, this chapter systematically investigates the mechanical properties of the Al9 alloy, a representative multi-scale core-shell structured material, over a broad temperature range. First, the microstructural characteristics and tensile properties at 800 °C are evaluated, with a focus on microstructural stability and intermediate-temperature embrittlement. Subsequently, composition optimization is employed to mitigate this embrittlement, and the resulting microstructural and mechanical changes are analyzed to elucidate the underlying improvement mechanisms. Finally, tensile properties are characterized over a wide temperature range. Combined with microstructural observations and deformation mechanism analyses, the anomalous yield effect is revealed, thereby providing a foundation for designing structural materials for wide-temperature-range applications.

7.2 Intermediate-temperature microstructure and property analysis of multi-scale core-shell structured high-entropy intermetallic

For high-temperature structural materials, microstructural stability and mechanical properties in the intermediate-temperature regime are key indicators of application potential. The temperature of 800 °C falls within the typical service range of $L1_2$ -type intermetallics, a regime characterized by accelerated diffusion, more apparent microstructural instability, and relatively high susceptibility to intermediate-temperature embrittlement [155]. Accordingly, this section focuses on the Al9 alloy, with a systematic analysis of its microstructural stability, tensile properties, and embrittlement characteristics at 800 °C, aiming to establish a foundation for subsequent composition optimization and property enhancement.

7.2.1 Microstructural stability of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy at 800 °C

A stable microstructure is essential for achieving excellent high-temperature mechanical properties. In multi-scale core-shell structured high-entropy intermetallics, the thermal stability of the L_{12} ordered core critically influences high-temperature performance, as its morphology and distribution directly determine the characteristics of the core-shell structure and significantly affect the heterogeneous microstructure. To systematically assess this thermal stability, the Al9 alloy was aged isothermally at 800 °C for extended periods, with the microstructural evolution, especially of the L_{12} -ordered core, tracked over time.

Fig. 7.1 presents multi-scale microstructural characterization of the Al9 alloy after isothermal aging at 800 °C for 10 h, 20 h, and 30 h. Overall, extended aging did not cause significant microstructural changes. At the macroscopic scale, a dendritic morphology persisted, with clear color contrast between interdendritic boundaries and dendrite interiors (Fig. 7.1 (a₁)–(a₃)). Statistical analysis of dendrite arm width showed a slight increase with aging time. At higher magnification, micron-scale core-shell structures remained evident at interdendritic boundaries, although their area fraction decreased slightly with time (Fig. 7.1 (b₁)–(b₃)). Within the dendrite interiors, submicron-scale core-shell structure exhibited a gradient size distribution, decreasing from boundary toward center. Characterization of these submicron-scale structures (Fig. 7.1 (c₁)–(c₃)) revealed no pronounced morphological changes, but their average diameter increased with aging time, from 127 nm at 10 h to 135 nm at 20 h, and finally to 142 nm at 30 h.

To further verify the stability of the nanoscale features, higher-magnification observations of the submicron-scale core-shell regions were performed (Fig. 7.1 (d₁)–(d₃)). Nanoscale L_{12} ordered cores were still present within the shell (indicated by white arrows). These results demonstrate that, even after prolonged aging at 800 °C, the multi-scale core-shell microstructure remained essentially intact, with only a slight coarsening of the submicron-scale L_{12} cores as the notable change. This confirms the excellent intermediate-temperature microstructural stability of the Al9 alloy.

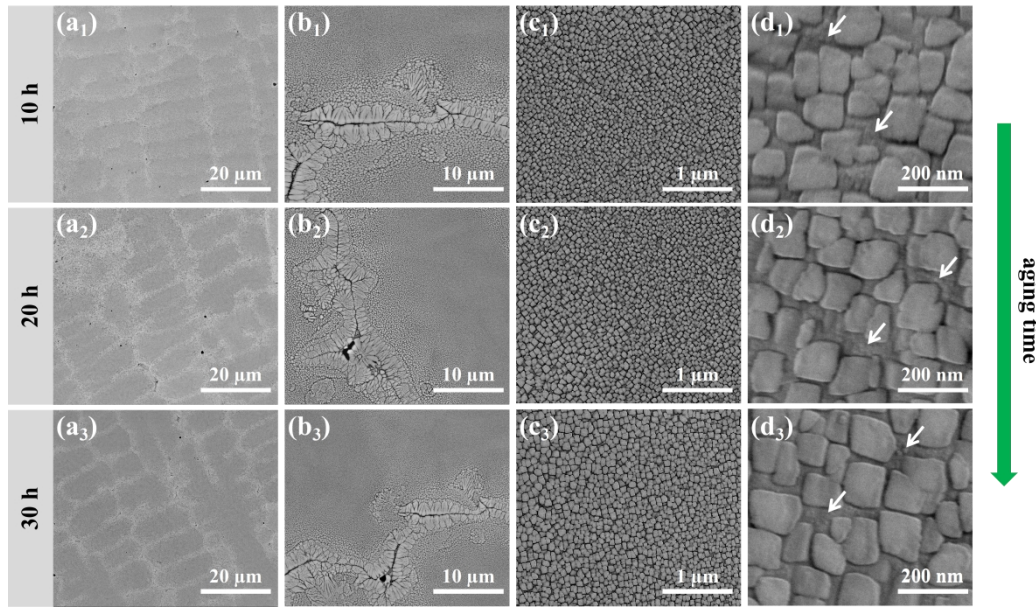


Fig. 7.1 Microstructural evolution of the Al9 alloy as a function of aging time during isothermal aging at 800 °C

(a₁) 10 h/macro-scale; (a₂) 20 h/macro-scale; (a₃) 30 h/macro-scale; (b₁) 10 h/submicron-scale; (b₂) 20 h/submicron-scale; (b₃) 30 h/submicron-scale; (c₁) 10 h/micrometer-scale; (c₂) 20 h/micrometer-scale; (c₃) 30 h/micrometer-scale; (d₁) 10 h/nanoscale; (d₂) 20 h/nanoscale; (d₃) 30 h/nanoscale

To elucidate the origin of this remarkable stability, the coarsening kinetics of the submicron-scale L1₂ ordered cores were quantitatively characterized. These cores form through precipitation from the supersaturated FCC phase during cooling, analogous to γ' precipitation in Ni-based superalloys. In such systems, coarsening is primarily controlled by solute diffusion in the matrix and is described by the classical Lifshitz-Slyozov-Wagner (LSW) theory [156]. This time-dependent process follows a power-law relationship:

$$r^3(t) - r^3(t_0) = k(t - t_0) \quad (7-1)$$

where $r(t)$ —average precipitate radius at aging time t (m);

k —coarsening rate constant ($\text{m}^3 \cdot \text{s}^{-1}$).

To determine k for the Al9 alloy, additional aging treatments at 800 °C for 15 h and 25 h were conducted, yielding average L1₂ core diameters of 130 nm and 138 nm, respectively. Combined with the 10 h, 20 h, and 30 h data, the variation of r^3 with t is plotted in Fig. 7.2, showing an excellent fit to the LSW model. The slope of the linear fit gives $k = 9.90 \times 10^{-28} \cdot \text{m}^3/\text{s}$ ($R^2 = 0.981$). This value is notably lower than those reported for many Ni- and Co-based superalloys, even those containing high

fractions of slow-diffusing elements like W, Mo, or Re [157].

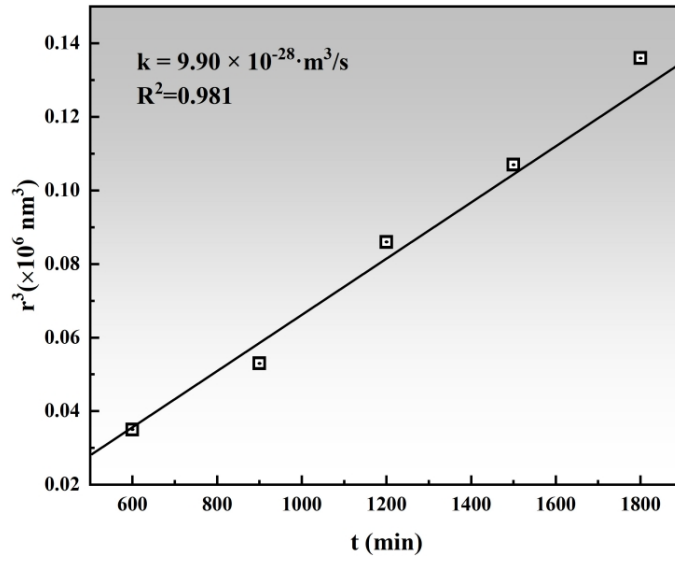


Fig. 7.2 Linear fitting relationship between the cube of the submicron-scale L1₂ ordered core radius (r^3) and the aging time (t) for the Al9 alloy under isothermal aging at 800 °C

Recently, Philippe and Voorhees extended LSW theory to multi-principal-element systems [158]. In such complex alloys, the coarsening kinetics are typically governed by the slowest-diffusing principal element [159], and the rate constant can be expressed as:

$$k \approx \frac{8V_m \sigma D c_i^M}{9RT(c_i^P - c_i^M)^2} \quad (7-2)$$

where V_m —molar volume of the precipitate (m^3);

σ —interfacial energy ($\text{J} \cdot \text{m}^{-2}$)

c_i^M —equilibrium molar concentration of i in matrix ($\text{mol} \cdot \text{m}^{-3}$);

c_i^P —equilibrium molar concentration of i in precipitate ($\text{mol} \cdot \text{m}^{-3}$);

D —diffusion coefficient of the slow-diffusing element ($\text{m}^2 \cdot \text{s}^{-1}$).

The temperature dependence of D follows the Arrhenius relation:

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (7-3)$$

where D_0 —pre-exponential factor ($\text{m}^2 \cdot \text{s}^{-1}$);

Q —activation energy for diffusion ($\text{J} \cdot \text{mol}^{-1}$).

To further investigate the origin of the low coarsening rate, the coarsening rate constants at 700 °C, 750 °C, 850 °C, and 900 °C were similarly calculated, yielding values of $1.94 \times 10^{-29} \cdot \text{m}^3/\text{s}$ ($R^2=0.987$), $1.42 \times 10^{-28} \cdot \text{m}^3/\text{s}$ ($R^2=0.973$), $5.68 \times 10^{-27} \cdot \text{m}^3/\text{s}$ ($R^2=0.982$) and $2.57 \times 10^{-26} \cdot \text{m}^3/\text{s}$ ($R^2=0.992$), respectively. Assuming weak temperature dependence of V_m , c_i^M and c_i^P , equation (7-3) was fitted (Fig. 7.3). The derived diffusion activation energy is $Q=350 \text{ kJ/mol}$, which is substantially higher than the typical range of 257–274 kJ/mol for most Ni- and Co-based superalloys (Table 7.1).

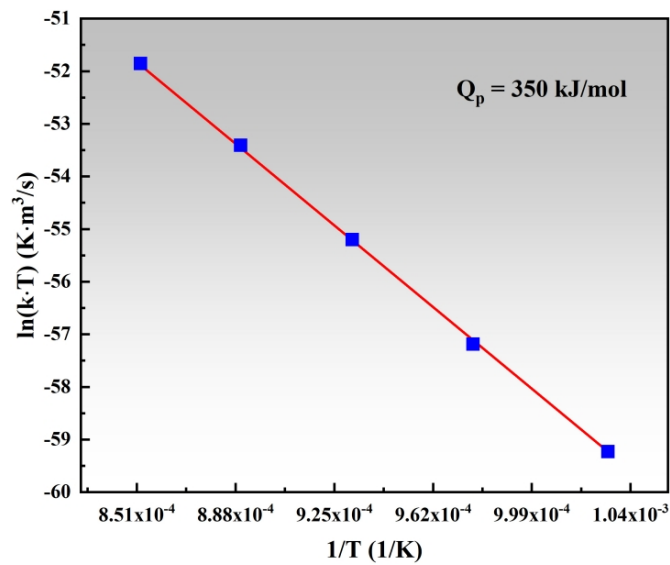


Fig. 7.3 Arrhenius plot of the coarsening rate constant $\ln(k \cdot T)$ as a function of the reciprocal of aging temperature ($1/T$) of the Al9 alloy

Table 7.1 Diffusion activation energies of common Ni-based and Co-based superalloys obtained by precipitation coarsening calculation methods [39]-190

Alloys	Activation energy for diffusion
	Q (kJ/mol)
Inconel 738	269
Inconel 939	266
CMSX-2	260
CMSX-4	272
Udimet 700	270
Nimonic 80A	274
Nimonic 90	257
Nimonic 105	264

In general, a higher diffusion activation energy implies a greater energy barrier for vacancy formation and solute migration, consistent with the “sluggish diffusion”

characteristic of multi-principal-element alloys [160]. From a kinetic perspective, this high activation energy suppresses precipitate coarsening, thus the excellent coarsening resistance of the Al9 alloy is primarily attributed to its high elemental diffusion activation energy.

7.2.2 800 °C tensile property of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

Microstructural characterization after prolonged isothermal aging at 800 °C confirmed that the Al9 alloy exhibits good thermal stability at this temperature. To evaluate its application potential at elevated temperatures, tensile tests were conducted at 800 °C, and the resulting engineering stress–strain curves are presented in Fig. 7.4. It can be seen that the Al9 alloy exhibits an excellent yield strength of approximately 925 MPa at 800 °C, slightly lower than its room-temperature value of about 1000 MPa. However, in contrast to its outstanding room-temperature tensile ductility, the alloy failed immediately upon yielding during tensile deformation at 800 °C, displaying typical brittle fracture characteristic.

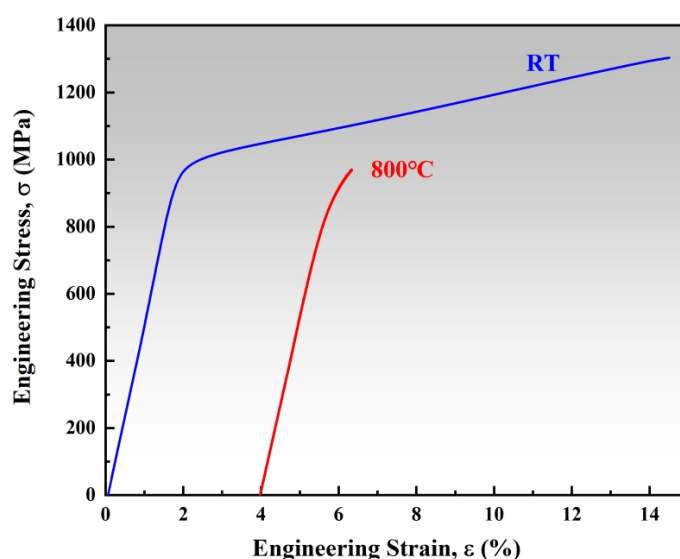


Fig. 7.4 Tensile engineering stress–strain curves of the Al9 alloy at room temperature and 800 °C

Furthermore, the fracture behavior at 800 °C is entirely different from that at room temperature. Fracture surface morphology analysis (Fig. 7.5) reveals an overall dendritic pattern (Fig. 7.5 (a)), indicating a close correspondence between crack path and dendritic structure. Higher magnification (Fig. 7.5 (b)) shows pronounced intergranular fracture features, with extensive intergranular cracking in interdendritic regions. Local fracture morphology (Fig. 7.5 (c) and (d)) reveals

numerous tear ridges indicative of brittle fracture and a limited number of fine dimples from ductile fracture. Notably, intergranular cracks remain evident in the vicinity of these tear ridges and dimples, implying that even in regions where localized plasticity takes place, grain boundary cracking can readily interconnect, ultimately constraining the overall ductility. These observations confirm that the Al9 alloy fails predominantly by intergranular brittle fracture at 800 °C, and its rapid failure is closely associated with premature cracking in interdendritic regions.

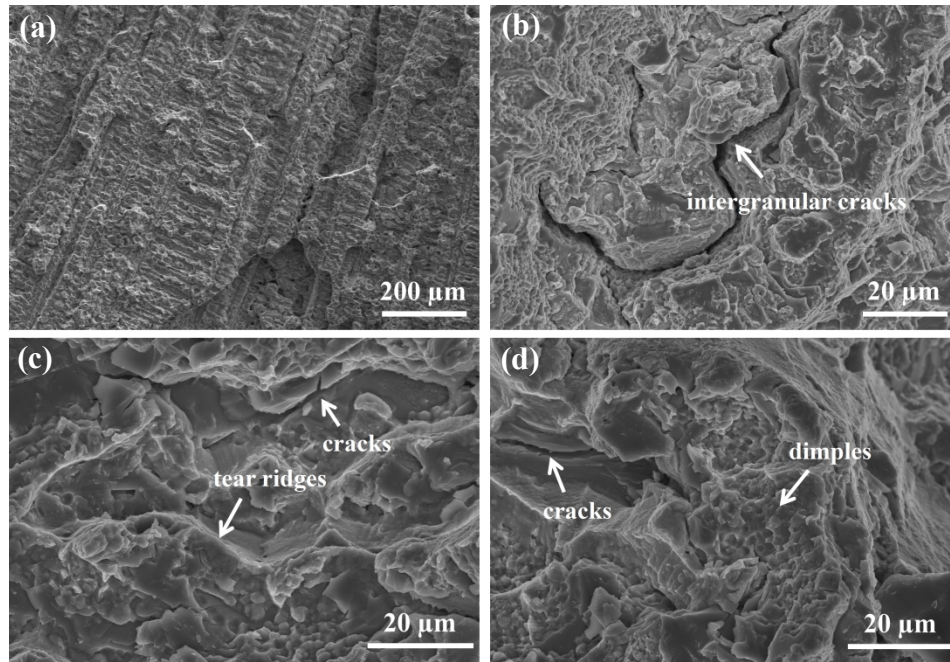


Fig. 7.5 Fracture morphology characteristics of the Al9 alloy after tensile fracture at 800 °C

(a) overall morphology; (b) intergranular cracks; (c) brittle fracture features; (d) ductile fracture features

To further identify crack initiation sites and propagation paths, the side-surface microstructure adjacent to fracture was analyzed (Fig. 7.6). Cracks predominantly originate in interdendritic regions and propagate preferentially along dendritic boundaries (Fig. 7.6 (a)), confirming the intergranular fracture mode. No significant plastic deformation traces are observed near the crack paths, indicating rapid crack linkage once initiated. At locations slightly farther from the fracture surface (Fig. 7.6 (b)), interdendritic cracks are still evident, suggesting that intergranular cracking initiates well before final fracture and gradually propagates during tensile loading. Notably, all interdendritic cracks are oriented approximately perpendicular to the tensile direction, indicating their formation is driven by the principal tensile

stress. High-magnification observations (Fig. 7.6 (c) and (d)) further confirm that crack initiation and propagation in interdendritic regions dominate failure, while the intra-dendrite multi-scale core–shell structure remains largely stable, indicating that crack propagation is primarily controlled by the weaker interdendritic regions.

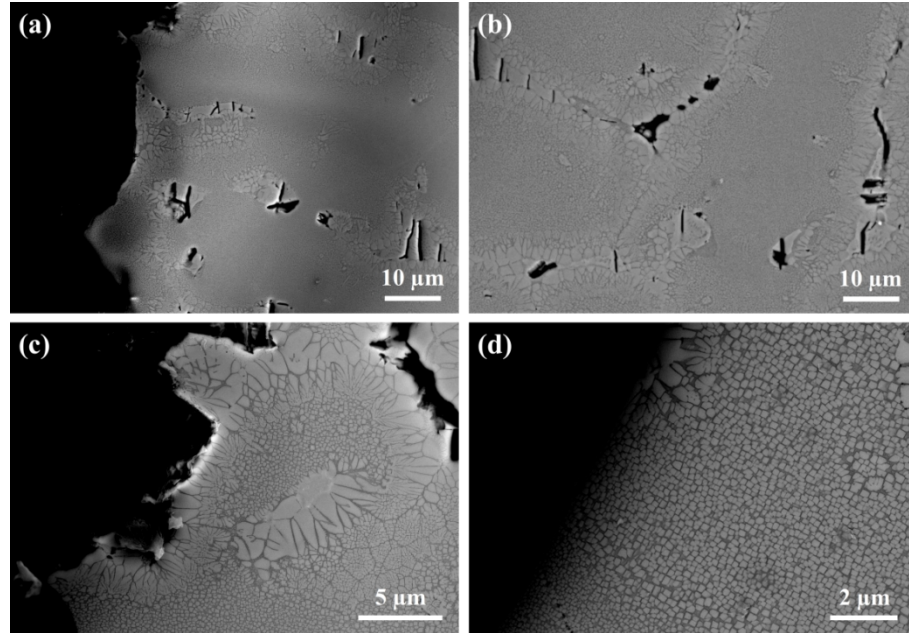


Fig. 7.6 Side-surface microstructures adjacent to the fracture region of the Al9 alloy after tensile testing at 800 °C

(a) microstructure near the fracture surface; (b) microstructure away from the fracture surface; (c) interdendritic region near the fracture; (d) intragranular region near the fracture

In summary, while the Al9 alloy retains high yield strength and excellent microstructural stability at 800 °C, its plastic deformation capacity is severely constrained, leading to rapid failure via intergranular cracking at the onset of yielding. Both fracture surface and side-surface analyses indicate that cracks preferentially initiate and propagate along interdendritic grain boundaries, with no significant damage within the dendrite interiors. These results demonstrate that the Al9 alloy exhibits typical intermediate-temperature embrittlement at 800 °C, with failure dominated by crack initiation and propagation in interdendritic regions.

7.2.3 Intermediate-temperature embrittlement initiation mechanism of the $\text{Ni}_{50}\text{Co}_{25}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{9.5}$ alloy

Extensive studies have shown that this type of intergranular brittle fracture is closely associated with stress-assisted oxygen penetration along grain boundaries,

which leads to decohesion [161]. To elucidate the cause of embrittlement in the Al9 alloy, tensile tests were conducted at 800 °C in a vacuum environment (Fig. 7.7). Compared to the air-tested sample, the vacuum environment enabled a recovery of tensile ductility, with plastic elongation increasing from nearly 0 to ~4%.

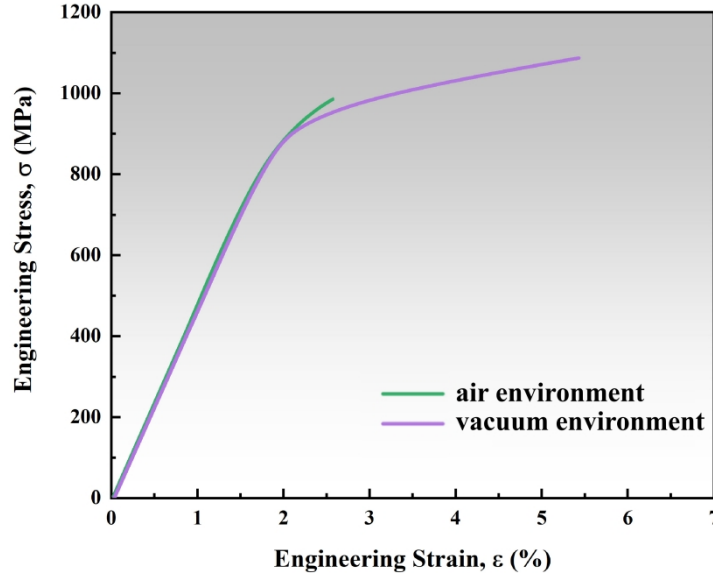


Fig. 7.7 Engineering stress–strain curves of the Al9 alloy under air and vacuum environments during tensile testing at 800 °C

Microstructural characterization of the vacuum-tested sample (Fig. 7.8) shows a fracture surface dominated by dimples, along with some tear ridges and intergranular cracks (Fig. 7.8 (a)), indicating a transition from brittle to a mixed-mode fracture. Side-surface observations (Fig. 7.8 (b)) reveal a significant reduction in both the number and propagation length of intergranular cracks, indicating substantially less grain boundary damage. This confirms that oxygen in the air plays a critical role in inducing intergranular brittle fracture, while a vacuum environment effectively isolates oxygen, protecting the specimen from intergranular oxygen penetration and significantly restoring ductility.

Regarding the influence of environmental oxygen on embrittlement in multi-principal-element alloys, previous studies on a Ni-Co-Fe-Cr-Al-Ti system have analyzed elemental distributions near fracture surfaces [41]-9. An oxide layer (~250 nm thick) consisting of an outer CoO sublayer and an inner NiO sublayer formed on the specimen surface. While NiO is thermodynamically favored to form beneath the reaction interface, its relatively loose and non-protective structure fails to provide an effective diffusion barrier [162]. No continuous Al₂O₃ layer was

observed, likely due to the low Al content (~9 at.%), which hinders the formation of a protective film. Moreover, the sluggish nucleation and growth kinetics of Al_2O_3 at intermediate temperatures further suppress its formation [163]. Given the compositional similarity, a comparable CoO/NiO double-layer oxide structure is inferred for the Al9 alloy during 800 °C tensile testing in air. Consequently, oxygen can readily penetrate along grain boundaries through the loose oxide scale, inducing grain boundary weakening and decohesion, leading to intergranular brittle fracture at the onset of yielding, a hallmark of intermediate-temperature embrittlement.

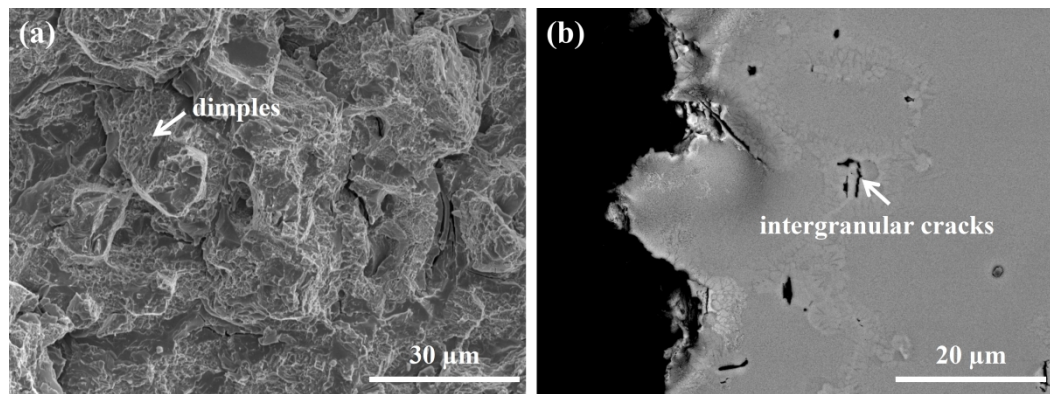


Fig. 7.8 Fracture morphology and the adjacent side-surface microstructure of the Al9 alloy after tensile deformation at 800 °C in a vacuum environment
(a) fracture morphology; (b) side-surface microstructure

Additionally, KAM analysis using EBSD was performed on the side-surface region adjacent to the fracture of the air-tested sample to characterize intergranular stress distribution (Fig. 7.9). Significant stress concentration is evident near the fracture, correlating with the change in grain boundary deformation mechanisms at elevated temperatures. As temperature increases, grain boundary sliding and diffusion-assisted deformation become active [61]-15. While activated grain boundary sliding provides an additional deformation mode, it also promotes dislocation migration and pile-up near grain boundaries and interdendritic regions, resulting in increased dislocation density and pronounced stress concentration [164]. Extensive studies indicate that high grain boundary stress enhances the adsorption and diffusion of oxygen atoms, promoting oxygen enrichment and the formation of brittle oxidation products at grain boundaries [165]. Therefore, the mutual reinforcement between grain boundary stress concentration and intergranular oxygen penetration significantly exacerbates crack propagation, intensifying intermediate-temperature embrittlement.

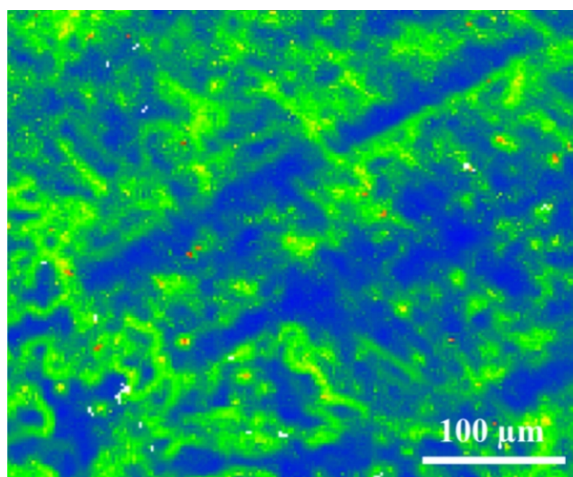


Fig. 7.9 KAM spatial distribution map of the side-surface region adjacent to the fracture of the Al9 alloy after tensile testing in air environment at 800 °C

These observations suggest that controlling the enrichment and diffusion of oxygen along grain boundaries is an effective strategy for mitigating intermediate-temperature embrittlement. Given that oxygen diffusion is a time-dependent process, shortening the diffusion time is expected to alleviate the performance degradation caused by this embrittlement. Following this rationale, tensile tests were conducted on the Al9 alloy at 800 °C under different strain rates, and the results are presented in Fig. 7.10. The engineering stress–strain curves indicate that increasing the strain rate, and thereby shortening the deformation time, can partially suppress the onset of intermediate-temperature embrittlement. A similar phenomenon has also been reported in the Inconel 718Plus nickel-based superalloy [166].

In summary, the intermediate-temperature embrittlement of the Al9 alloy in air at 800 °C arises from the combined effects of oxygen penetration along grain boundaries and stress concentration induced by grain boundary sliding. As temperature rises, the grain boundary diffusion coefficient increases exponentially, allowing oxygen atoms to rapidly enrich and form detrimental oxides along grain boundaries, weakening their cohesive strength [167]. Concurrently, grain boundary sliding is significantly activated at 800 °C, elevating dislocation density near interfaces and causing stress concentration. With the intrinsic grain boundary strength already compromised, such localized stress concentration readily induces decohesion and crack initiation, promoting rapid intergranular crack propagation and ultimately leading to brittle fracture. Conversely, the significant ductility

recovery under vacuum confirms that isolating oxygen effectively mitigates this environmentally-assisted embrittlement. Similarly, increasing the strain rate shortens the time window for oxygen diffusion, providing another means to alleviate embrittlement.

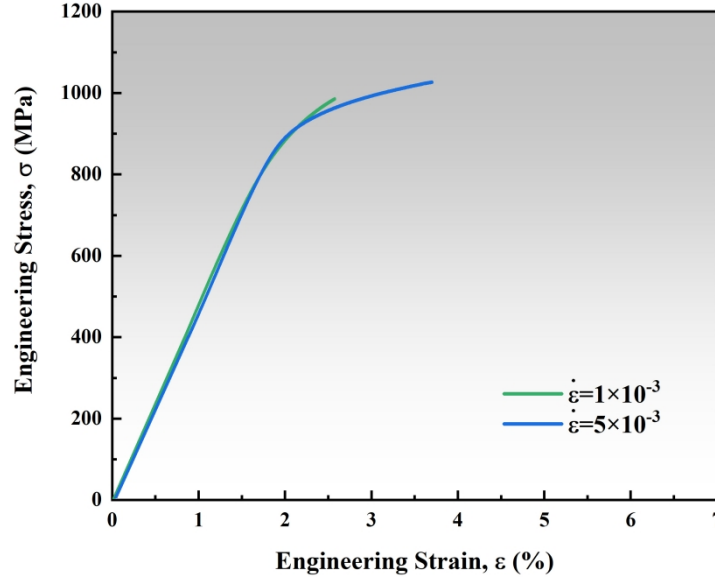


Fig. 7.10 Engineering stress–strain curves of the Al9 alloy at 800 °C under different strain rates

7.3 Improvement of intermediate-temperature embrittlement in multi-scale core–shell structured high-entropy intermetallic through Cr addition

The preceding section elucidated the mechanism of intermediate-temperature embrittlement driven by stress-assisted oxygen diffusion and proposed mitigation strategies based on testing environment and loading conditions. However, precise control over environmental atmosphere and loading parameters is often challenging in practical applications, and external adjustments alone are insufficient. Therefore, intrinsic material modifications via composition and microstructural regulation are necessary. In this section, the multi-scale core–shell microstructure is optimized through composition control, the influence of microstructural evolution on embrittlement behavior is systematically analyzed, and new design strategies for improving intermediate-temperature embrittlement are provided.

7.3.1 Microstructure of the $\text{Ni}_{43}\text{Co}_{21.5}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{20}$ alloy

Elements such as Al, Si, Nb, and Cr are widely used to enhance the oxidation

resistance and high-temperature stability of structural materials [168]. Among these, Cr significantly suppresses oxygen diffusion into the matrix by promoting the formation of a dense Cr_2O_3 protective film, thereby mitigating embrittlement. Although the Al9 alloy already contains a moderate amount of Cr, it still exhibits pronounced embrittlement at 800 °C. Therefore, the Cr content was increased to 20 at.% to improve performance. Simultaneously, the total (Ni+Co) content was reduced while maintaining the Ni:Co atomic ratio at 2:1, with other elements unchanged to preserve the core-shell structure. The resulting composition, $\text{Ni}_{43}\text{Co}_{21.5}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{20}$, is hereafter designated as the Cr20 alloy.

To analyze the influence of microstructural evolution on embrittlement behavior, the as-cast Cr20 alloy was characterized. XRD analysis (Fig. 7.11) confirms the coexistence of FCC and L_{12} phases, evidenced by the (100) superlattice peak. Additionally, a new set of peaks corresponding to a BCC crystal structure (lattice parameter ~ 0.288 nm) appears.

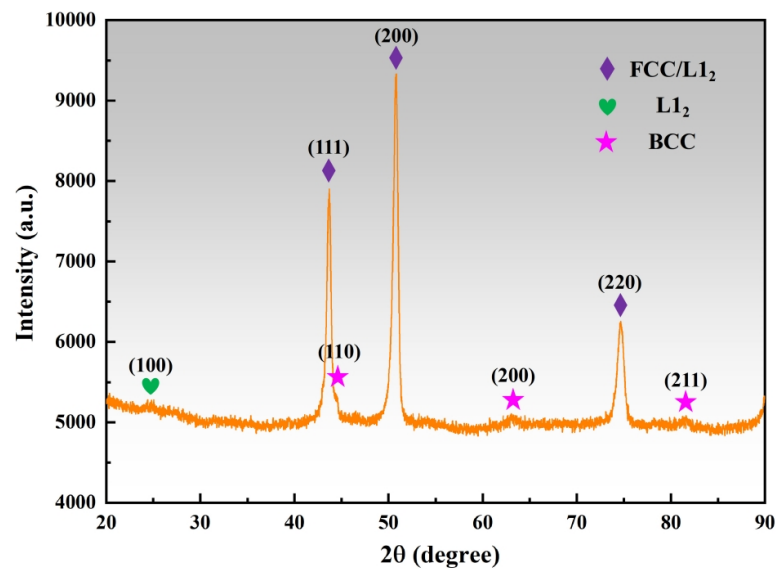


Fig. 7.11 XRD pattern of the Cr20 alloy

Further microstructural characterization (Fig. 7.12) shows that the as-cast Cr20 alloy retains an overall dendritic morphology (Fig. 7.12 (a)). However, a significant number of dark-contrast precipitates appear at dendrite boundaries (Fig. 7.12 (b)). Higher magnification (Fig. 7.12 (c)) reveals that these precipitates typically form as strip-like features attached to the surfaces of light-contrast regions, while granular precipitates form inside the light-contrast regions. Notably, the strip-like

precipitates and adjacent light-contrast regions are primarily distributed along grain boundaries, disrupting the continuity of the micron-scale core-shell structures in these areas. Within the grain interior (Fig. 7.12 (d)), a gradient-type microstructure persists, characterized by continuously varying submicron-scale core-shell diameters. The increased Cr content transforms the morphology of the submicron-scale L_{12} ordered cores from cuboidal to spherical, with an average diameter of ~ 110 nm (Fig. 7.12 (e)). High-magnification observation (Fig. 7.12 (f)) shows that nano-scale fine particles still exist within the submicron-scale shell (indicated by white circles). In summary, the as-cast alloy retains the multi-scale core-shell microstructure. The increase in Cr primarily promotes the formation of strip-like precipitates and small particulate regions at grain boundaries while altering the morphology of the submicron-scale cores within the grains.

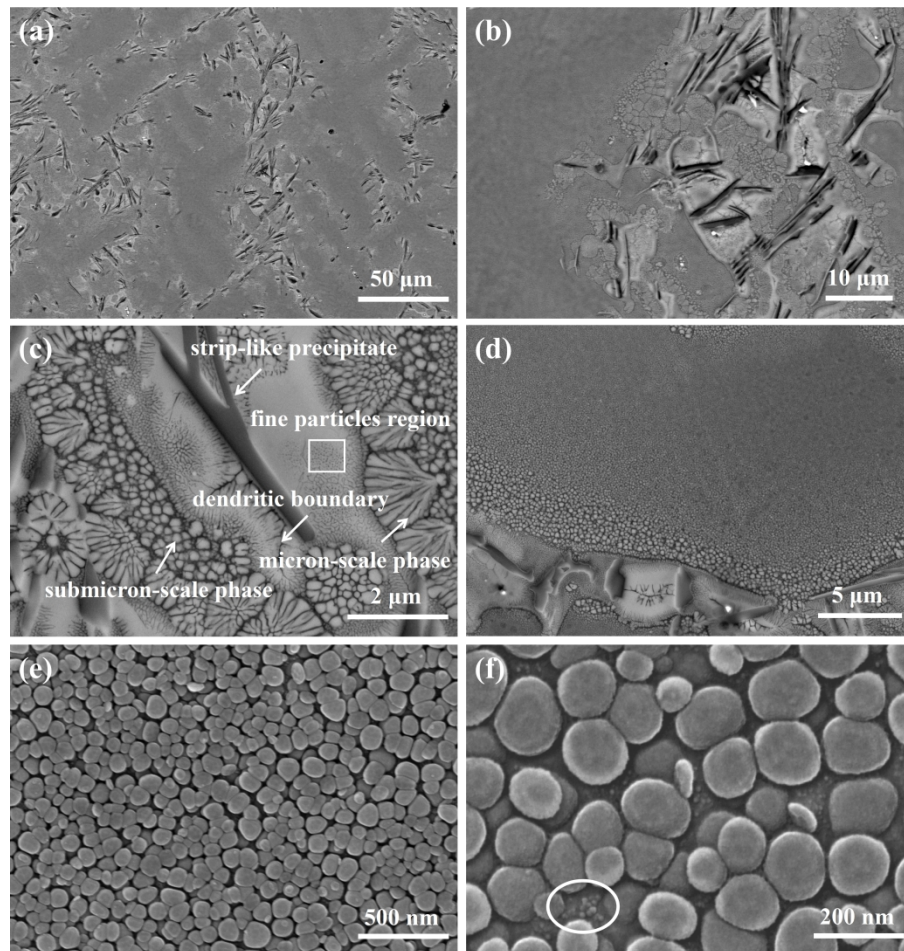


Fig. 7.12 Microstructural characterization of the Cr20 alloy
(a) overall microstructure; (b) dendrite boundary microstructure; (c)
microstructure in the vicinity of grain boundaries; (d) grain interior microstructure;
(e) core-shell structure at the grain center; (f) magnified image of the core-shell
structure at the grain center

To clarify the phase structure and composition of these new features, TEM-EDS analysis was conducted on the dendrite boundary region (Fig. 7.13). Elemental mapping reveals that the strip-like precipitates are significantly enriched in Cr, while other elements are depleted. In contrast, the surrounding small particulate regions show a lower Cr content, with other elements uniformly distributed. Quantitative EDS results (Table 7.2) show the strip-like precipitates contain ~90 at.% Cr, while the small particulate regions have a composition similar to the Al9 alloy but with only ~3.5 at.% Cr.

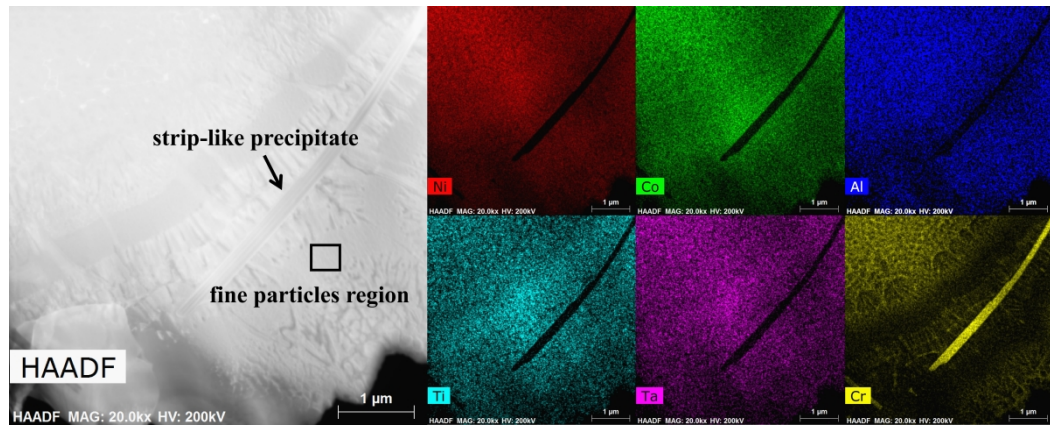


Fig. 7.13 Elemental mapping analysis of the dendrite boundary region in the Cr20 alloy

Table 7.2 Chemical composition of the dendrite boundary region in the Cr20 alloy determined by TEM-EDS

Regions	Elements (at. %)					
	Ni	Co	Al	Ti	Ta	Cr
Strip-like precipitate	2.4±0.2	6.8±0.2	0.3±0.1	0.6±0.2	0.6±0.2	89.3±0.4
Small particulate region	55.9±0.4	25.4±0.2	8.2±0.3	5.2±0.3	1.8±0.1	3.5±0.2

Further TEM analysis (Fig. 7.14) was performed to determine the phase structures. Bright-field imaging (Fig. 7.14 (a)) shows a high density of dark striations within the strip-like precipitates. SAED along the $[100]$ zone axis (Fig. 7.14 (b)) reveals a BCC pattern, consistent with XRD results, along with extra spots corresponding to the $L1_2$ structure from the surrounding regions. High-resolution TEM (Fig. 7.14 (c)) confirms a high density of SFs within the precipitates. SAED at the edge of a precipitate (Fig. 7.14 (d)) shows $L1_2$ diffraction features. SAED of a small particulate region (Fig. 7.14 (e) and (f)) along the $[\bar{1}10]$ zone axis shows an FCC structure with superlattice spots, confirming the $L1_2$ ordered phase.

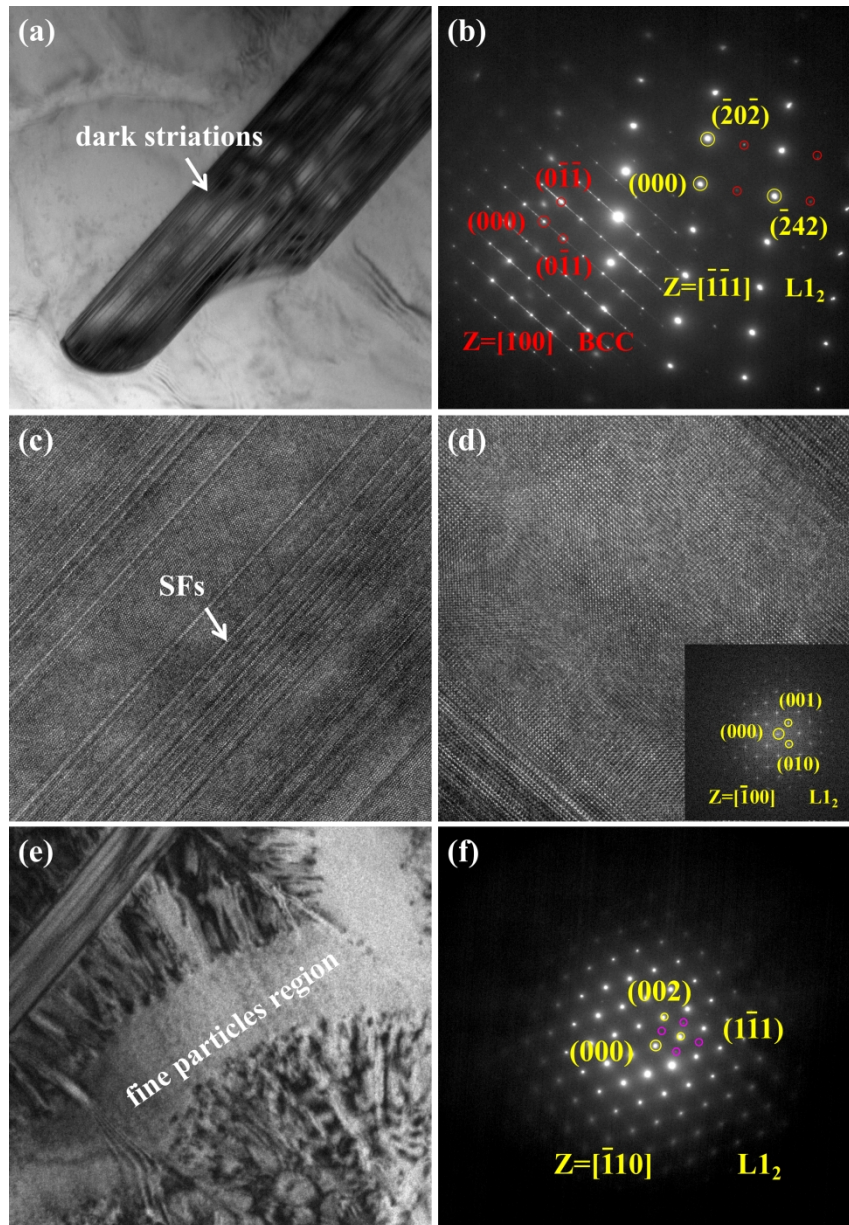


Fig. 7.14 TEM analysis of the dendrite boundary region in the Cr20 alloy
(a) bright-field image of the strip-like precipitates; (b) SAED pattern of the precipitates; (c) high-resolution image of the precipitates; (d) high-resolution image of the precipitate edge; (e) bright-field image of the small particulate region; (f) SAED pattern of the small particulate region

These results indicate that the strip-like precipitates are the α -Cr phase (a BCC Cr-rich solid solution), while the surrounding small particulate regions are finer $L1_2$ -FCC core-shell structures. Given the presence of $L1_2$ /FCC structures at the edges and surroundings, the α -Cr phase is inferred to have transformed from the FCC phase. Previous studies have shown that localized stress can induce FCC-to-BCC transformation [169]. The high Cr content in the precipitates creates significant lattice misfit, inducing stress concentration. When local stress reaches a critical

level, it drives the surrounding FCC to transform to BCC. Moreover, the local stress generates a high density of SFs within the FCC phase, providing preferential sites for BCC nucleation, consistent with the SFs observed within the α -Cr phase.

In summary, increasing Cr to 20 at.% does not destroy the multi-scale core-shell structure but significantly alters the dendrite boundary characteristics, forming discontinuous strip-like α -Cr phases and small-scale $L1_2$ -FCC core-shell regions. To analyze the transformation mechanism, thermodynamic and solidification calculations were performed. Equilibrium phase fraction calculations (Fig. 7.15) show that above the solidus temperature, liquid, $L1_2$, and FCC phases coexist. As the liquid fraction decreases, both $L1_2$ and FCC fractions increase, indicating direct $L1_2$ formation from the liquid. Below the solidus temperature, the FCC fraction decreases while $L1_2$ increases, suggesting $L1_2$ precipitation from FCC. These two formation modes correspond to the formation of core-shell structures at different scales. Upon further cooling to ~ 1100 °C, a BCC phase begins to precipitate while the FCC fraction fluctuates, indicating BCC formation via solid-state precipitation from FCC. The BCC phase remains stable down to near 400 °C, with a phase fraction of $\sim 10\%$, while FCC and $L1_2$ account for $\sim 10\%$ and $\sim 80\%$, respectively. These results confirm that Cr addition promotes BCC phase formation through solid-state transformation, and this phase is thermodynamically stable down to near room temperature.

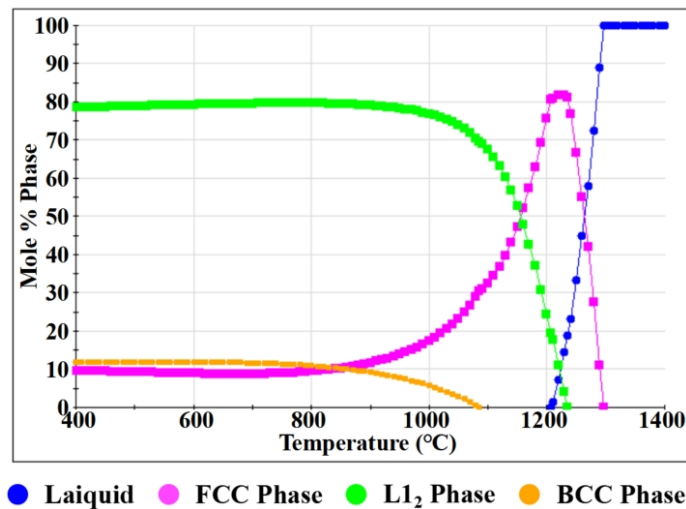


Fig. 7.15 Temperature dependence of equilibrium phase fractions in Cr20 alloy

Next, the formation mechanism of the phase structure in the dendrite boundary

region is further elucidated by analyzing the evolution of solute concentration in the liquid phase as a function of solid fraction during solidification of the Cr20 alloy. Fig. 7.16 presents the real-time evolution of elemental concentrations in the liquid phase of the Cr20 alloy with increasing solid fraction. As shown, the variation in solute content in the liquid phase is consistent with that of the Al9 alloy during the initial stage of solidification. Specifically, the FCC-forming elements Co and Cr preferentially partition into the solid grain interior, whereas the L1₂-forming elements Al, Ti, and Ta tend to enrich in the liquid phase. This elemental partitioning behavior promotes the formation of an FCC-type supersaturated solid solution, which provides a compositional basis for the subsequent precipitation of submicron-scale L1₂-ordered phases during cooling. Notably, the Cr20 alloy exhibits a unique two-stage feature in elemental concentration evolution during the later stage of solidification. In these two stages, the Ni and Cr contents in the liquid phase show opposite trends, suggesting that the two stages correspond to distinct reaction pathways. It is thus evident that the increase in Cr content alters the solidification path during the later stage, leading to significant microstructural changes in the vicinity of dendrite boundaries. In particular, the formation of the α -Cr phase is likely associated with the rapid consumption of Cr during the second stage of the later solidification.

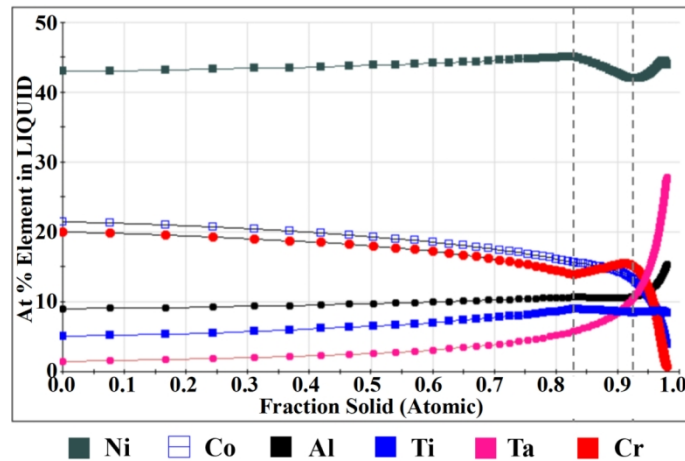
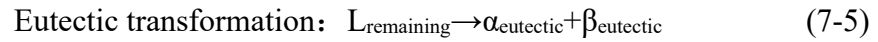
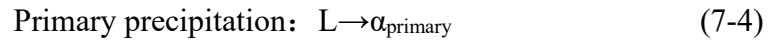


Fig. 7.16 Variation of solute concentration in the liquid phase as a function of solid fraction during solidification of Cr20 alloy

Based on these results, the phase transformation mechanism near dendrite boundaries is further analyzed. The boundary region is primarily composed of two phase structures: a relatively large proportion of small-scale L1₂-FCC core-shell regions, with submicron-scale L1₂ particles distributed around them, and strip-like

α -Cr phases formed on their surfaces. A small fraction of grain boundaries still exhibit cellular micron-scale core-shell structures similar to those in the Al9 alloy. These features are consistent with a divorced eutectic formation mechanism. Divorced eutectic does not refer to a specific reaction process, but rather a special solidification microstructure morphology, in which the two phases of the eutectic reaction products no longer maintain the typical alternating distribution of the symbiotic morphology, but instead undergo separated growth. Its formation process can generally be divided into two stages: primary phase precipitation and eutectic transformation of the remaining liquid, as shown in equations (7-4) and (7-5). During this process, primary α and eutectic α coalesce and grow, while eutectic β precipitates in isolation, resulting in divorced separation.



In the Cr20 alloy, the substantial increase in Cr causes the liquid composition in the late solidification stage to deviate significantly from the eutectic point, promoting a divorced eutectic reaction. As the solid fraction reaches ~ 0.82 , the FCC-forming elements Ni and Co are rapidly consumed, corresponding to the first-stage reaction, i.e., the precipitation of primary FCC. However, solute redistribution during solidification induces microsegregation, resulting in an uneven distribution of elemental concentrations ahead of the solid-liquid interface. This allows the composition in certain grain boundary regions to reach the eutectic point, directly triggering the eutectic reaction and forming cellular micron-scale core-shell structures. It should be noted that the eutectic reaction tends to reject Cr, while primary FCC precipitation consumes Cr. When the amount of Cr rejected by the eutectic reaction exceeds that consumed during primary FCC precipitation, the overall Cr content in the liquid phase increases accordingly, which is consistent with the slight rise in Cr content observed during the first-stage reaction. When the solid fraction reaches ~ 0.92 , the second-stage reaction occurs, where the remaining liquid undergoes a eutectic transformation to simultaneously generate a Cr-rich FCC eutectic phase and granular L1₂ eutectic phase. Owing to their identical lattice structure, the Cr-rich FCC eutectic phase tends to grow epitaxially on the surface of the primary FCC. Upon further cooling, solid-state transformations occur. The

supersaturated primary FCC precipitates $L1_2$ -ordered phases, corresponding to the small-scale $L1_2$ -FCC core-shell structured regions in the final microstructure. When the temperature decreases to approximately 1100 °C, the Cr-rich FCC eutectic transforms into the BCC phase under local stress, corresponding to the formation of strip-like α -Cr phase.

In summary, the microstructural transformation in the dendrite boundary region of the Cr20 alloy originates from a divorced eutectic reaction induced by the increased Cr content. This reaction occurs at the end of solidification and proceeds through two stages: FCC primary phase precipitation and a Cr-rich eutectic transformation. During subsequent cooling, the FCC primary phase precipitates the $L1_2$ ordered phase, while the strip-like Cr-rich eutectic transforms to the BCC α -Cr phase. In a small fraction of grain boundary regions where the local composition meets the eutectic point, cellular core-shell structures are still generated via the conventional eutectic pathway. The transformation mechanism is illustrated in Fig. 7.17.

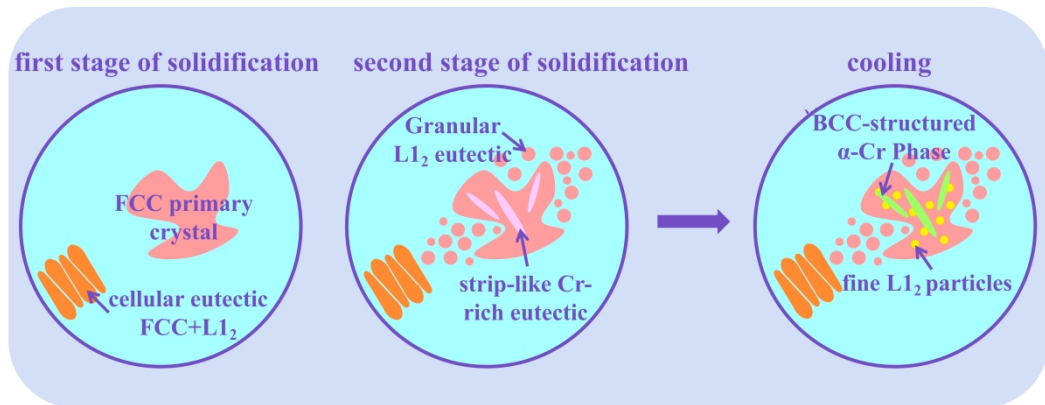


Fig. 7.17 Schematic diagram illustrating the evolution mechanism of the microstructure in the dendrite boundary region of the Cr20 alloy

7.3.2 Intermediate-temperature embrittlement characteristic of the $Ni_{43}Co_{21.5}Al_9Ti_5Ta_{1.5}Cr_{20}$ alloy

According to the analysis in Section 7.2.3, the development of intermediate-temperature embrittlement is closely related to the microstructure in grain boundary regions. Given the significant microstructural changes near the dendrite boundaries of the Cr20 alloy, this section systematically investigates its intermediate-temperature embrittlement characteristics through tensile property testing,

combined with fracture surface characterization to elucidate the influence of microstructural transformation on embrittlement behavior. Fig. 7.18 presents the engineering stress–strain curves of the Cr20 and Al9 alloys at 800 °C. Compared with the Al9 alloy, the Cr20 alloy exhibits a slightly improved yield strength of approximately 980 MPa, along with a plastic elongation of about 5%, which is markedly better than that of the Al9 alloy. These results indicate that the increased Cr content effectively mitigates the intermediate-temperature embrittlement issue in the multi-scale core–shell structured high-entropy intermetallic compound.

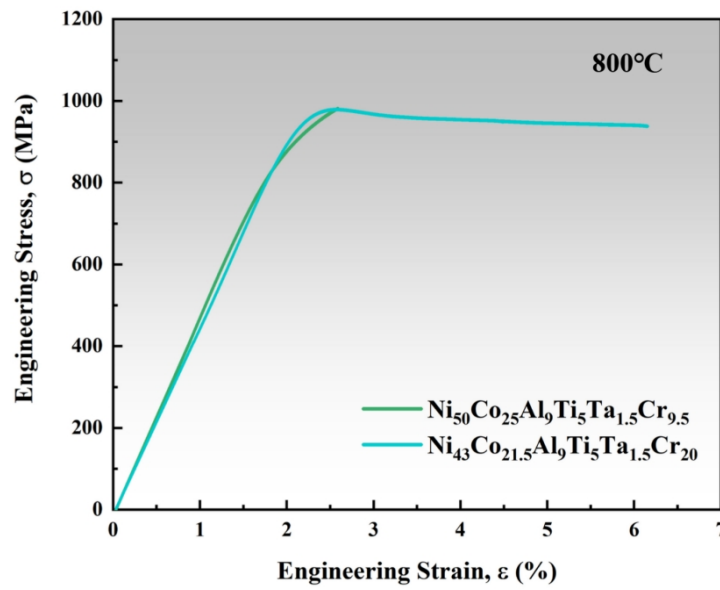


Fig. 7.18 Engineering stress-strain curves of Cr20 and Al9 alloys under tensile testing at 800 °C

To reveal the mechanism by which Cr addition enhances the intermediate-temperature ductility of the material, the fracture mechanism of the Cr20 alloy is further analyzed. Fracture surface morphologies were first examined, and the results are presented in Fig. 7.19. As can be seen from Fig. 7.19 (a), the overall fracture surface of the Cr20 alloy at 800 °C exhibits a mixed fracture feature characterized by the coexistence of tear ridges and dimples. In addition, a small number of microcracks are observed, among which those with longer propagation distances display a zigzag morphology. Further magnification of the microcrack formation regions (Fig. 7.19 (b)) reveals that microcracks predominantly initiate at the α -Cr phase adjacent to grain boundaries. This is attributed to the high strength but poor ductility of the BCC-structured α -Cr phase, which cannot readily accommodate deformation during straining, leading to stress concentration at phase

interfaces and consequently inducing microcrack initiation. Fig. 7.19 (c) shows the morphology of tear ridges, where a small number of dimples are observed in their vicinity, effectively suppressing propagation at the crack tips. Fig. 7.19 (d) displays a substantial number of dimples, indicating that the material underwent sufficient plastic deformation prior to fracture.

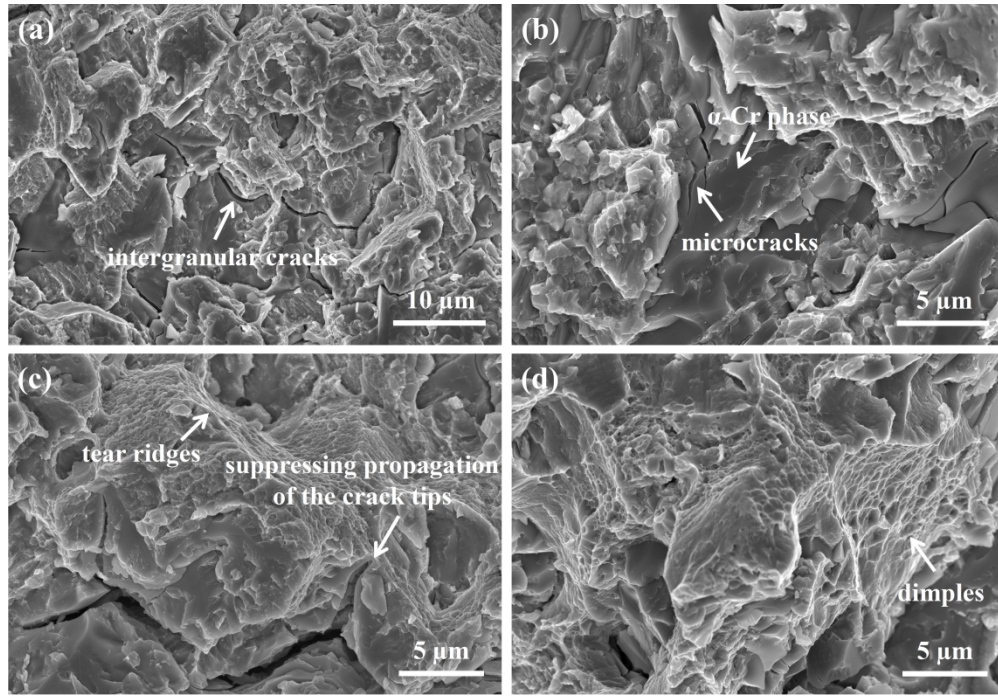


Fig. 7.19 Fracture morphology characteristics of Cr20 alloy after tensile fracture at 800 °C
(a) overall morphology; (b) microcracks; (c) tear ridges; (d) dimples

The lateral microstructure near the fracture surface of the Cr20 alloy tested at 800 °C was further characterized, and the results are presented in Fig. 7.20. As shown in Fig. 7.20 (a), the alloy exhibits pronounced transgranular fracture characteristics at 800 °C, which are distinctly different from the intergranular fracture features observed in the Al9 alloy under the same tensile conditions. In addition, relatively long propagating cracks are observed near the fracture surface. Magnified observation of the microstructure slightly away from the fracture surface (Fig. 7.20 (b)) reveals that numerous microcracks initiate and propagate within the strip-like α -Cr phase, consistent with the fracture surface morphology. Combining the tensile properties and fracture mechanism analysis of the Cr20 alloy at 800 °C, it is evident that the increased Cr content induces a transition in the intermediate-temperature fracture mechanism, from intergranular brittle fracture to a mixed fracture mode dominated by transgranular fracture, thereby effectively alleviating

the intermediate-temperature embrittlement of the alloy.

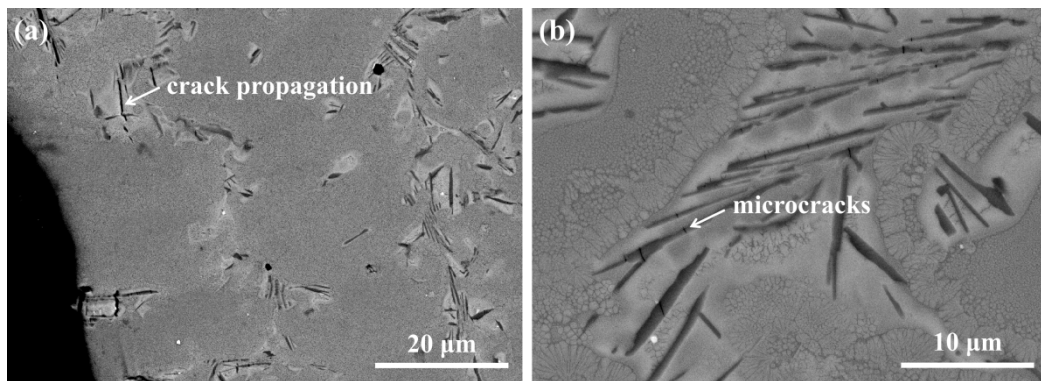


Fig. 7.20 Microstructure of the side surface near the tensile fracture region of Cr20 alloy at 800 °C
(a)overall microstructural morphology; (b) Microcracks in the local region.

Combined with the grain boundary microstructure of the Cr20 alloy, the underlying reasons for the improvement in intermediate-temperature embrittlement are elucidated. As analyzed in Section 7.2.3, intermediate-temperature embrittlement primarily originates from the synergistic effect of oxygen penetration and stress concentration, manifesting as brittle intergranular fracture with cracks preferentially propagating along grain boundaries. However, strip-like α -Cr phase and small-scale $L1_2$ -FCC core-shell structures form in the grain boundary regions of the Cr20 alloy. These phase structures disrupt the continuity of grain boundaries, effectively impeding oxygen penetration and crack propagation, and making it difficult for microcracks initiated at grain boundaries to coalesce. Furthermore, the less deformable strip-like α -Cr phase preferentially induces microcrack formation within itself, thereby relieving stress concentration at grain boundaries and preventing crack initiation there. Thus, by inducing the formation of discretely distributed strip-like α -Cr and small-scale $L1_2$ -FCC core-shell structures at grain boundaries, the increased Cr content simultaneously inhibits grain boundary crack initiation and impedes microcrack propagation and coalescence along grain boundaries, thereby avoiding intergranular fracture and mitigating intermediate-temperature embrittlement.

Additionally, the morphological change of the submicron-scale core-shell structure within the grain interior contributes to the improvement. Previous studies have shown that a significant strength difference between grain interiors and boundaries promotes stress concentration and embrittlement [167]-9. Therefore, increasing

grain boundary strength while moderately reducing grain interior strength helps mitigate this stress concentration. In the Cr20 alloy, the formation of the α -Cr phase enhances grain boundary strength to some degree. Meanwhile, the morphological transition of the core-shell structure reduces intragranular strengthening. Specifically, as an FCC-forming element, Cr enriches in the shell layer and affects the FCC lattice constant. Since Cr has a larger atomic radius than Ni and Co, increasing Cr content (while decreasing (Ni+Co)) raises the FCC lattice constant, thereby reducing the lattice misfit between the $L1_2$ and FCC phases. This promotes the morphological transition from cuboidal to spherical configurations with lower interfacial energy. The reduced lattice misfit also lowers the strain energy at the $L1_2$ /FCC interface, weakening coherency strengthening and HDI strengthening. As a result, the strength mismatch between the grain interior and boundary is reduced, alleviating stress concentration and suppressing crack initiation and propagation, thereby mitigating intermediate-temperature embrittlement.

In summary, the improved intermediate-temperature embrittlement resistance of the Cr20 alloy can be attributed to two synergistic effects. First, the formation of strip-like α -Cr and fine-scale $L1_2$ -FCC core-shell structures at grain boundaries serves to obstruct oxygen diffusion along grain boundaries. Second, the morphological evolution of the intragranular core-shell structures contributes to the relief of stress concentration at grain boundaries. The combined action of these mechanisms effectively inhibits intergranular crack initiation and propagation, leading to a substantial enhancement in the alloy's resistance to intermediate-temperature embrittlement.

7.4 Wide-temperature-range mechanical property analysis of the multi-scale core-shell structured high-entropy intermetallic

The previous section demonstrated that the Cr20 alloy possesses a degree of plastic deformation capability at 800 °C, effectively alleviating the embrittlement issue. To further determine whether this alloy suffers from severe brittle fracture at other temperatures, wide-temperature-range mechanical property testing was conducted. Particular attention was paid to the anomalous yield effect, and the variation of yield strength with temperature was revealed. Through characterization of dislocation substructures at different deformation temperatures, the evolution of deformation

mechanisms with temperature was elucidated. Based on these results, the intrinsic origin of the anomalous yield effect during wide-temperature-range tensile deformation is further analyzed, providing theoretical support for high-temperature applications.

7.4.1 Wide-temperature-range tensile property of the $\text{Ni}_{43}\text{Co}_{21.5}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{20}$ alloy

Tensile tests were conducted on the Cr20 alloy over the temperature range of 25–1000 °C, and the resulting engineering stress–strain curves are presented in Fig. 7.21. As shown, the alloy achieves a favorable combination of strength and ductility across a wide temperature range. At 25 °C, the alloy exhibits a yield strength of approximately 880 MPa, an ultimate tensile strength of about 1050 MPa, and a plastic elongation of roughly 18%. As the temperature rises, the yield strength does not decrease, but increases from approximately 890 MPa at 400 °C to about 920 MPa at 800 °C, exhibiting an anomalous yield behavior. However, concomitant with this increase in yield strength, the plastic elongation decreases markedly, from approximately 15% at 400 °C to about 5% at 800 °C. It is noteworthy that most conventional Ni-based and Co-based superalloys are susceptible to premature brittle fracture, i.e., intermediate-temperature embrittlement, in the temperature range of 600–800 °C [170]. In the present alloy, although the elevated temperature causes a pronounced reduction in ductility, an appreciable plastic deformability is retained up to 800 °C, indicating excellent potential for high-temperature applications. When the deformation temperature is further raised above 900 °C, the ductility of the alloy recovers to some extent, but the yield strength decreases notably. In particular, at 1000 °C, the yield strength drops to approximately 450 MPa, and the flow stress decreases with increasing strain after yielding, suggesting the onset of material softening.

Subsequently, the fracture surface morphologies of the Cr20 alloy after tensile testing over a wide temperature range were systematically characterized, and the results are presented in Fig. 7.22. As shown, the alloy exhibits typical ductile fracture characteristics at room temperature, 900 °C, and 1000 °C. The presence of extensive dimples indicates that the material underwent sufficient plastic deformation during tensile testing, which is consistent with the relatively high

plastic strains observed in the engineering stress–strain curves. In the temperature range of 400–800 °C, the fracture surfaces display a mixed fracture mode. Although dimples still dominate the fracture surface, a limited number of tear ridges and river-like patterns are also observed, corresponding to the relatively lower plastic deformability in this temperature regime. It is noteworthy that most alloys strengthened by the $L1_2$ phase typically exhibit severe brittle intergranular fracture in this temperature range, with the fracture surface morphology dominated entirely by brittle fracture features.

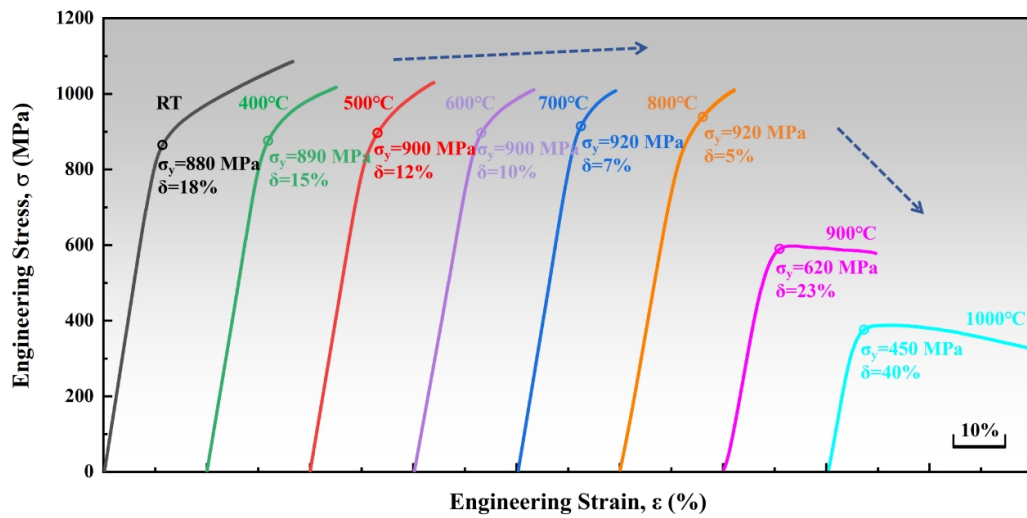


Fig. 7.21 Engineering stress–strain curves of the Cr20 alloy under tensile testing over a wide temperature range

To further clarify the high-temperature application potential of the Cr20 alloy, its yield strength over a wide temperature range is compared with that of other advanced alloys with promising high-temperature prospects, including FCC-structured high-entropy alloys and Ni-based superalloys, with the results shown in Fig. 7.23. As can be seen, the Cr20 alloy exhibits pronounced anomalous yield behavior over the entire tested temperature range, but its manifestation differs fundamentally from that of conventional alloys. In conventional alloys, the yield strength typically first decreases and then increases with rising temperature, reaching a peak at an intermediate temperature. In contrast, the yield strength of the Cr20 alloy increases continuously with temperature from room temperature upward. This unique characteristic not only endows the alloy with high-temperature yield strengths exceeding its room-temperature value but also renders its yield strength markedly superior to that of the other comparative alloys over a broader temperature range.

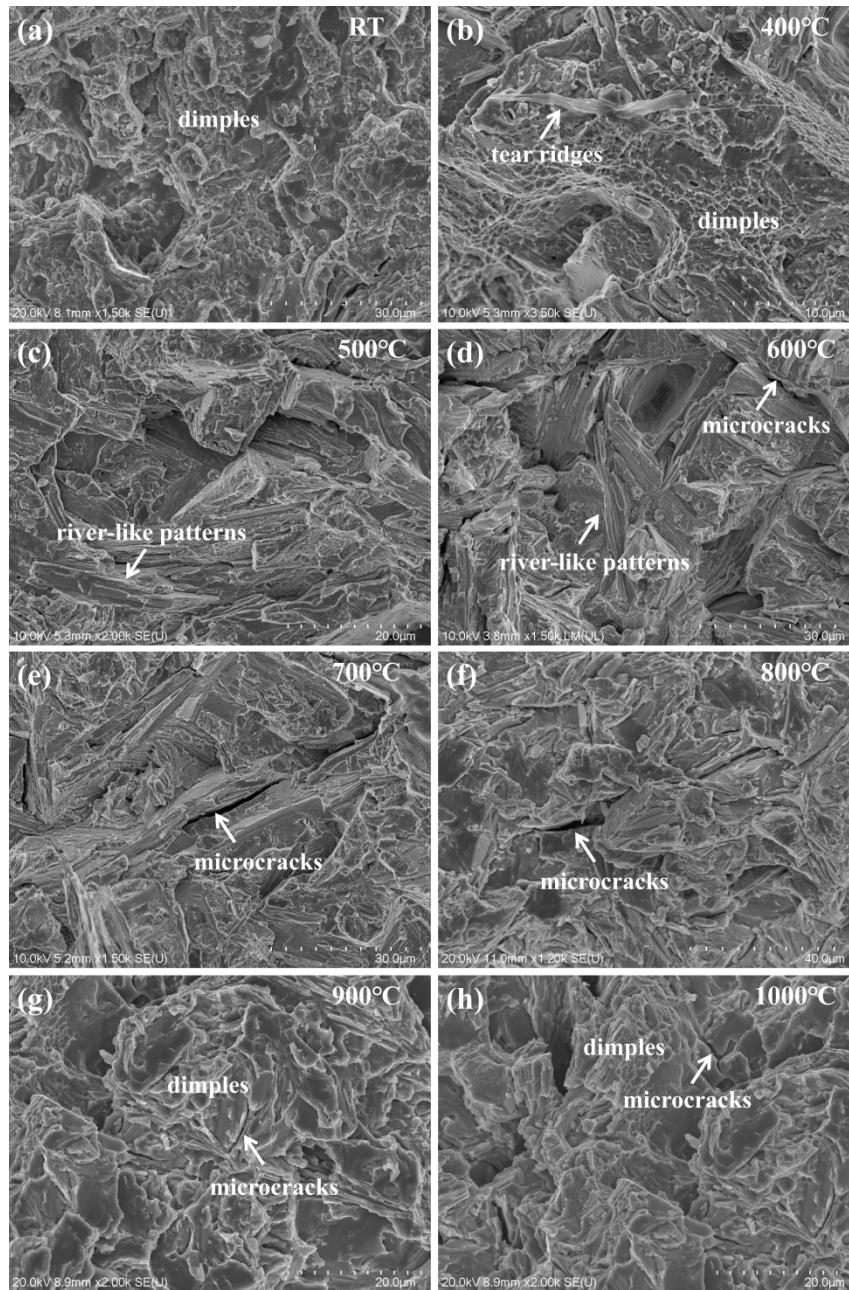


Fig. 7.22 Tensile fracture morphology characteristics of Cr20 alloy at different temperatures

(a) RT; (b) 400 °C; (c) 500 °C; (d) 600 °C; (e) 700 °C; (f) 800 °C; (g) 900 °C; (h) 1000 °C

In summary, the Cr20 alloy exhibits an excellent strength–ductility combination over the wide temperature range of 25–1000 °C. Its yield strength increases continuously with rising temperature, displaying a distinctive anomalous yield effect, while effectively overcoming the embrittlement issues commonly encountered in conventional superalloys at intermediate temperatures. Compared with FCC-structured high-entropy alloys and Ni-based superalloys, the Cr20 alloy offers higher yield strength and more stable mechanical properties over a broader

temperature range, demonstrating considerable promise for high-temperature applications.

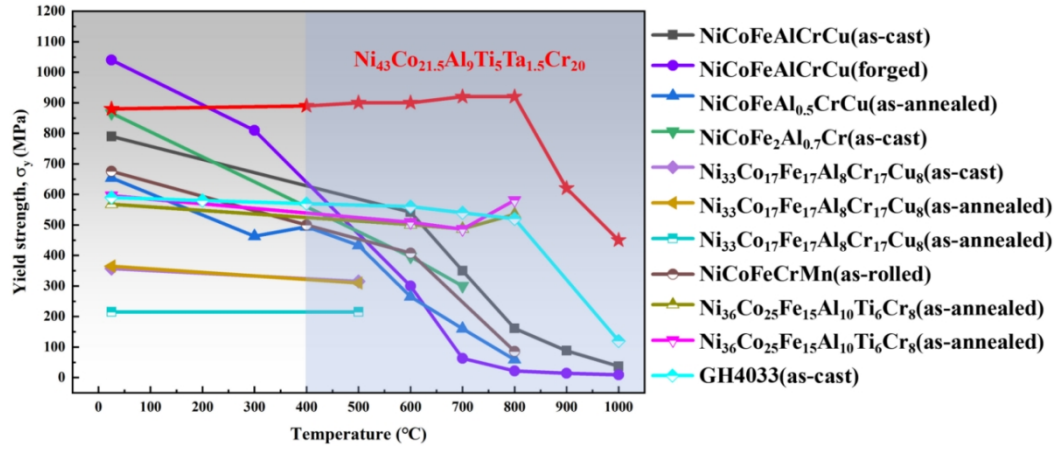


Fig. 7.23 Comparison of yield strength between the Cr20 alloy and FCC-structured high-entropy alloys as well as nickel-based superalloys over a wide temperature range [171-176]

7.4.2 Anomalous yield effect of the $\text{Ni}_{43}\text{Co}_{21.5}\text{Al}_9\text{Ti}_5\text{Ta}_{1.5}\text{Cr}_{20}$ alloy

Tensile test results indicate that the mechanical properties of the Cr20 alloy vary with temperature, which is closely associated with the deformation substructures activated at different temperature ranges. To elucidate the microscopic mechanisms underlying this temperature-dependent mechanical behavior and to further analyze the origin of the anomalous yield effect, the dislocation substructures of tensile-deformed specimens at various temperatures were systematically characterized by TEM. Fig. 7.24 presents the TEM results of dislocation substructures in Cr20 alloy specimens interrupted after 5% tensile strain at room temperature, 700 °C, 800 °C, and 900 °C.

As shown in Fig. 7.24 (a), the alloy primarily deforms through SISFs at room temperature. According to the discussion in Section 6.4.1 regarding the room-temperature deformation mechanism of the Al9 alloy, extended dislocations in the shell layer can shear the L_{12} -ordered phase by forming either APBs or SISFs during plastic deformation. The dominant mechanism in practice is governed by the superlattice stacking fault energy and the characteristic size of the L_{12} cores. When the L_{12} -ordered cores exhibit a low superlattice stacking fault energy and a small diameter, deformation tends to proceed through SISF formation. To verify this mechanism, the stacking fault energy of the Cr20 alloy was calculated using

JMatPro software, with the results shown in Fig. 7.25. As can be seen, the alloy exhibits a stacking fault energy of approximately 12.7 mJ/m² at room temperature, which is considerably lower than the 20.8 mJ/m² of the Al9 alloy. Moreover, the average diameter of the submicron-scale L1₂-ordered cores in the Cr20 alloy is approximately 110 nm, comparable to that of the Al9 alloy. Therefore, the Cr20 alloy tends to accommodate plastic deformation through SISF formation under room-temperature conditions. Notably, the density of SISFs in this alloy is significantly higher than that in the Al9 alloy at equivalent strain levels, which is likely attributable to the lower stacking fault energy of the Cr20 alloy.

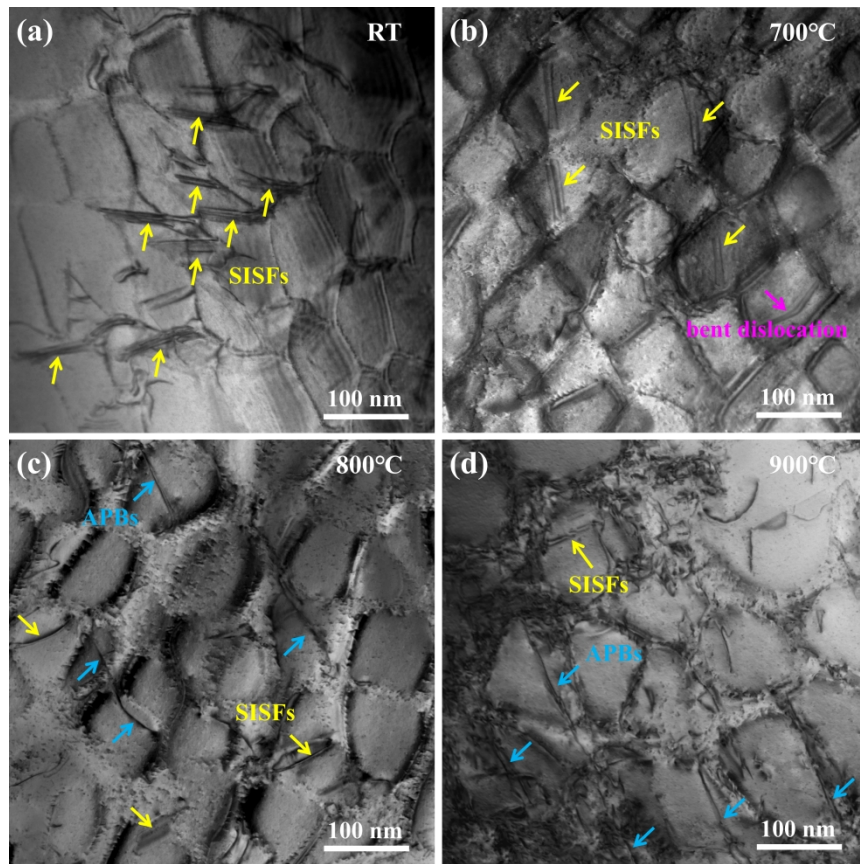


Fig. 7.24 Dislocation substructures of the Cr20 alloy interrupted at 5% tensile strain under different temperatures
(a) RT; (b) 700 °C; (c) 800 °C; (d) 900 °C

When the temperature is raised to 700 °C, the Cr20 alloy still accommodates plastic deformation primarily through SISF formation, as shown in Fig. 7.24 (b). Notably, the density of SISFs decreases significantly at this temperature, which is attributed to the inherent temperature dependence of stacking fault energy, as it generally increases with rising temperature [177]. As shown in Fig. 7.25, the SFE of the Cr20 alloy rises to approximately 75 mJ/m² at 700 °C. Under this condition, SISFs can

theoretically form only in smaller L_{12} -ordered cores. However, the critical stress required for extended dislocations to shear the L_{12} -ordered cores decreases with increasing temperature, which prompts extended dislocations to sustain plastic deformation through SISF formation [178]. On the other hand, the higher SFE increases the energy required for individual SISF formation, resulting in a reduced SISF density. In addition, pronouncedly bowed extended dislocations are observed at this temperature, which may be associated with dislocation cross-slip, indicating the onset of new dislocation motion modes under thermally activated conditions.

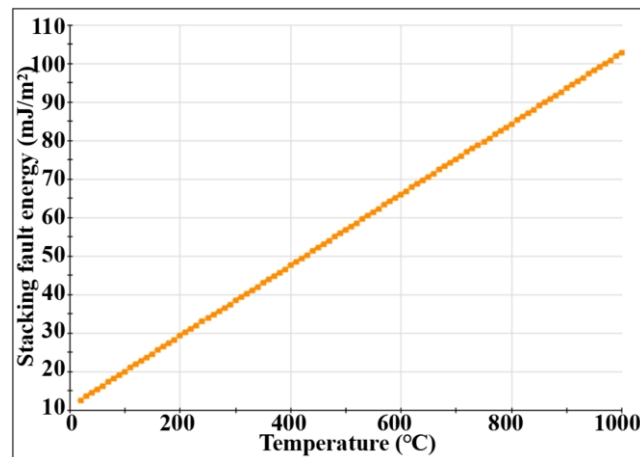


Fig. 7.25 Temperature dependence of stacking fault energy in the Cr20 alloy calculated by JMatPro software

When the temperature is further increased to 800 °C, APBs begin to appear in the L_{12} -ordered cores, while the density of SISFs decreases further, as shown in Fig. 7.24 (c). The formation of APBs is closely related to the anti-phase boundary energy; a lower anti-phase boundary energy is more favorable for the nucleation and propagation of APBs during tensile deformation. Notably, in contrast to the increasing trend of SFE with temperature, the anti-phase boundary energy tends to decrease with rising temperature [179]. Therefore, the lower anti-phase boundary energy significantly reduces the energy barrier for APB nucleation and propagation at 800 °C, while the higher SFE suppresses SISF formation. Consequently, the number of APBs increases markedly, and they jointly govern the plastic deformation of the material together with the remaining SISFs. When the temperature is further raised to 900 °C, under the combined effect of a continuously decreasing anti-phase boundary energy and an increasing SFE, plastic deformation is predominantly controlled by APBs, with SISFs rarely observed, as shown in Fig. 7.24 (d).

From this perspective, the wide-temperature-range deformation mechanism of the Cr20 alloy corresponds to its mechanical properties and exhibits a significant temperature-dependent characteristic. Before the peak yield strength is reached, i.e., from room temperature to 800 °C, the plastic deformation is dominated by SISFs, which impede dislocation motion and thereby sustain the strength. Although the density of SISFs gradually decreases with increasing temperature, APBs are generated and increase accordingly, so that the yield strength within this temperature range does not decline but instead increases slightly. When the temperature exceeds that corresponding to the peak yield strength, the deformation process is mainly dominated by APBs. On the one hand, the ability of APBs to hinder subsequent dislocation motion is generally weaker than that of SISFs. On the other hand, the critical stress required for forming APBs decreases with the reduction in antiphase boundary energy. These two factors together make it difficult for the APB-dominated deformation mechanism to maintain a strengthening effect equivalent to that of SISFs, leading to a decrease in the yield strength.

It is worth noting that this alloy already exhibits kinked dislocations caused by dislocation cross-slip at 700 °C. As a thermally activated process, the activity of cross-slip intensifies with increasing temperature. Meanwhile, a large number of studies on the anomalous yield effect of L1₂-structured alloys indicate that this phenomenon is closely related to dislocation cross-slip [180]. On this basis, further TEM analysis of the dislocation substructure under the deformation condition at 800 °C, corresponding to the peak yield strength, was conducted to reveal the microscopic reasons for the anomalous yield effect in the Cr20 alloy. As can be seen from Fig. 7.26 (a), the Cr20 alloy also exhibits obvious dislocation kinking at 800 °C. Further observation of Fig. 7.26 (b) reveals the formation of a large number of APBs and clear cross-slip traces. Previous studies have confirmed, via both density functional theory calculations and TEM characterization, that the (111) and (110) planes in L1₂-structured alloys possess distinct antiphase boundary energies, with that of the (111) plane being significantly higher than that of the (110) plane [181]. This anisotropy of antiphase boundary energy between the two crystal planes provides the driving force for APB-coupled dislocation pairs to undergo cross-slip. Specifically, APB-coupled dislocation pairs initially move on the (111) slip plane, which has lower energy. When they slip to the intersection of the (111) and (110)

planes, since the antiphase boundary energy of the (111) plane is significantly higher than that of the (110) plane, the system drives the dislocation pairs to cross-slip from the original (111) plane to the (110) plane, thereby reducing the energy of the system. After cross-slip, the two super-dislocation segments on the (111) and (110) planes are no longer coplanar and mutually constrain each other spatially, thereby forming a typical Kear-Wilsdorf (K-W) locks.

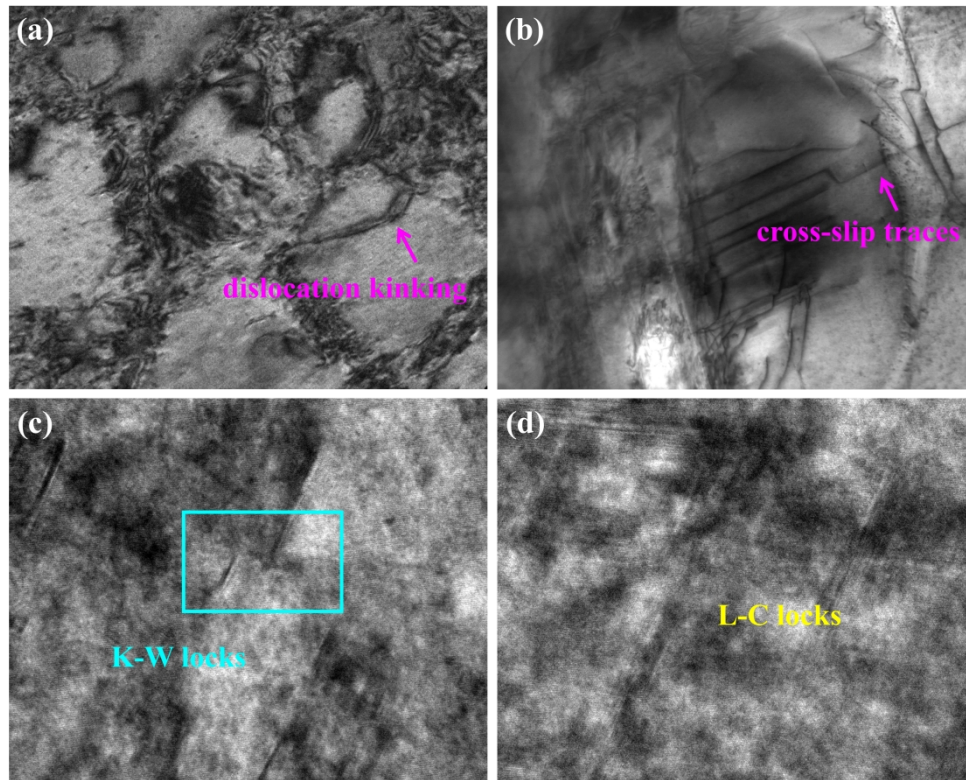


Fig. 7.26 Dislocation substructures of the Cr20 alloy interrupted after 5% tensile strain at 800 °C
(a) bright-field image of dislocation kinks; (b) bright-field image of dislocation slip;
(c) K-W locks; (d) L-C locks

As can be seen from Fig. 7.26 (c), a typical K-W lock structure appears in the Cr20 alloy after tensile fracture at 800 °C, and this dislocation configuration is the key factor responsible for the anomalous yield effect in the material [182]. Within a certain temperature range, an increase in temperature promotes the occurrence of cross-slip, thereby enhancing the pinning effect of K-W locks on dislocations and increasing the yield strength. When the temperature rises above a critical value, the dislocation pairs on the (110) plane gain sufficient thermal activation energy to move, thereby eliminating the pinning effect of the K-W locks and leading to a corresponding decrease in yield strength [183]. In addition, L-C locks formed by the interaction of SISFs are also observed at this temperature, as shown in Fig. 7.26

(d). The high density of L-C locks further impedes dislocation motion and, together with K-W locks, contributes to a higher peak yield strength [184].

In summary, the anomalous yield effect of the Cr20 alloy originates from the specific locked dislocation configurations formed by dislocation cross-slip. At 700 °C, dislocation kinks induced by cross-slip have already appeared in the alloy, indicating that thermally activated processes begin to participate in the deformation behavior. As the temperature rises to 800 °C, corresponding to the peak yield strength, the antiphase boundary energy anisotropy between the (111) and (110) planes drives APB-coupled dislocation pairs to cross-slip from the low-energy (111) plane onto the (110) plane, thereby forming spatially constrained K-W locks. From the perspective of alloy composition, the addition of Ta further enlarges the difference in antiphase boundary energy between the two slip planes, enhances the driving force for cross-slip, and thus promotes the formation of K-W locks [185]. This dislocation locking structure effectively pins dislocation motion and accounts for the anomalous increase in yield strength. When the temperature further exceeds the critical value, the dislocation pairs become unlocked due to sufficient thermal activation energy and resume motion, resulting in a decrease in yield strength. In addition, L-C locks formed by the interaction of SISFs play a supplementary strengthening role during deformation, enabling the alloy to exhibit a significant yield strength peak over a wide temperature range. Therefore, the anomalous yield effect of the Cr20 alloy is jointly governed by K-W locks and L-C locks, with the addition of Ta playing a crucial promoting role.

7.5 Chapter summary

In this chapter, the Al9 alloy was first taken as the research object to systematically evaluate its microstructural stability and tensile properties at intermediate temperatures, revealing the origin of intermediate-temperature brittleness in the multi-scale core-shell structured high-entropy intermetallic. On this basis, the Cr20 alloy was designed and fabricated by increasing the Cr content to alleviate the intermediate-temperature brittleness. The effects of Cr addition on the microstructure and mechanical properties were investigated, and the mechanism underlying the improvement in intermediate-temperature brittleness was elucidated. Furthermore, the tensile properties of the Cr20 alloy were tested over a wide

temperature range, the deformation mechanisms at different temperatures were identified, and the operative mechanism of the anomalous yield effect was revealed. The main conclusions are as follows:

(1) The Al9 alloy exhibits excellent microstructural stability at intermediate temperatures. After prolonged isothermal aging at 800 °C, the Al9 alloy retains the multi-scale core–shell structure, with only a slight increase in the diameter of the submicron-scale $L1_2$ -ordered cores. Calculation results indicate that the coarsening rate constant is $9.90 \times 10^{-28} \cdot \text{m}^3/\text{s}$, with a corresponding diffusion activation energy as high as 350 kJ/mol.

(2) The Al9 alloy exhibits intermediate-temperature brittleness. When tensile-tested at 800 °C in air, the Al9 alloy displays a high yield strength of approximately 925 MPa but with nearly zero plastic elongation, accompanied by typical intergranular brittle fracture characteristics. The intermediate-temperature brittleness originates from grain-boundary weakening caused by oxygen penetration along grain boundaries, as well as dislocation pile-ups and localized stress concentrations induced by high-temperature grain-boundary sliding.

(3) Increasing the Cr content to 20 at.% improves the intermediate-temperature brittleness of the alloy. The Cr20 alloy exhibits an increased yield strength of approximately 980 MPa at 800 °C, along with an improved plastic elongation of about 5%. The increase in Cr content transforms the fracture mechanism at 800 °C from intergranular brittle fracture to a mixed fracture mode dominated by transgranular fracture, thereby significantly alleviating the intermediate-temperature brittleness.

(4) The microscopic mechanism underlying the improvement in intermediate-temperature brittleness of the Cr20 alloy is revealed. The α -Cr phase formed at grain boundaries and the fine-scale $L1_2$ –FCC core–shell structures within the Cr20 alloy hinder oxygen diffusion along grain boundaries, while the morphological evolution of the intra-granular core–shell structures helps relieve stress concentrations at grain boundaries. The synergistic effect of these two factors effectively suppresses the initiation and propagation of intergranular cracks, thus improving the intermediate-temperature brittleness of the material.

(5) The anomalous yield effect of the Cr20 alloy and its operative mechanism are elucidated. In the temperature range of 25–1000 °C, the yield strength of the alloy first increases and then decreases, reaching a peak value of approximately 920 MPa at 800 °C. This effect originates from the temperature-induced transition to APB-dominated deformation, along with the pinning of dislocation motion by K-W locks formed through cross-slip of APB-coupled dislocation pairs. Meanwhile, L-C locks formed by the interaction of SISFs further enhance the yield strength of the material over a wide temperature range.

Chapter 8 Conclusions and perspectives

This paper focuses on Ni-Co-Al-Ti-based high-entropy intermetallics, and systematically conducts compositional design, microstructural characterization, and mechanical property testing with an emphasis on the formation and evolution of the multi-scale core-shell structure. Through thermodynamic and solidification analyses, the effects of Co and Ta additions as well as the increase in Al/Ti ratio on the microstructure were revealed, and the formation mechanism of the multi-scale core-shell structure was thereby elucidated. Combined with mechanical property testing, the influence of this structure on room-temperature mechanical properties was clarified. On this basis, the room-temperature deformation mechanism and the strengthening and ductilization mechanisms of the multi-scale core-shell structured HEIs were revealed. Meanwhile, based on wide-temperature-range mechanical property testing, the intermediate-temperature brittleness characteristics and the anomalous yield effect of this class of materials were investigated. The above studies have effectively enhanced the room-temperature ductility and significantly improved the high-temperature strength of conventional intermetallic compounds. The main conclusions are as follows:

(1) Co addition promotes the formation of the $L1_2$ -FCC dual-phase core-shell structure. By inducing the formation of the FCC phase, promoting the precipitation of the $L1_2$ phase, and stabilizing the $L1_2$ /FCC phase interface, the Co element enables the Co₂₅ alloy to develop a dual-phase core-shell structure with the $L1_2$ ordered phase as the core and the FCC disordered phase as the shell. The average core diameter is approximately 200 nm, the average shell thickness is about 10 nm, and the average grain size is roughly 180 μm . This dual-phase core-shell structure contributes to improved room-temperature ductility, enabling the Co₂₅ alloy to achieve a yield strength of 450 MPa, an ultimate tensile strength of 650 MPa, and a plastic elongation of 10%.

(2) The formation mechanism of the multi-scale core-shell structure is elucidated. Ta addition aggravates compositional segregation at dendrite boundaries, which promotes the formation of micron-scale $L1_2$ -ordered cores via eutectic reactions. On this basis, further increasing the Al/Ti ratio enhances the sluggish diffusion

effect, promoting the precipitation of submicron- and nanoscale $L1_2$ -ordered cores via solid-state precipitation and ultimately yielding a multi-scale core-shell structure with micron-, submicron-, and nanoscale features coexisting within the grains. This structure facilitates the synergistic improvement of room-temperature strength and ductility, enabling the Al9 alloy to achieve a yield strength of approximately 1000 MPa, an ultimate tensile strength of about 1250 MPa, and a plastic elongation of roughly 12.5%.

(3) The room-temperature deformation mechanism of the multi-scale core-shell structured HEI is revealed. The deformation of the Al9 alloy is dominated by multi-scale dislocation substructures. In the submicron-scale core-shell regions, owing to the low stacking fault energy and the average diameter of the $L1_2$ cores being smaller than the critical shear diameter of 250 nm, partial dislocations shear the $L1_2$ cores by forming SISFs/SESFs. With increasing strain, the dislocation substructures successively evolve into dislocation forests, deformation microbands, and dislocation walls, while L-C locks are formed in the shell layers. In the micron-scale core-shell regions, the $L1_2$ cores exhibit negligible plastic deformation, and dislocations interact with them primarily via the Orowan bypass mechanism.

(4) The room-temperature strengthening and ductilization mechanisms of the multi-scale core-shell structured HEI are elucidated. The high strength of the Al9 alloy mainly originates from the precipitation strengthening effect provided by the $L1_2$ -ordered cores, which account for nearly 80% by volume, as well as the HDI strengthening effect induced by the multi-scale core-shell structure. The good ductility benefits from the continuously distributed (FCC+ $L1_2$) shells, which provide effective channels for dislocation motion and multiplication, and from the significant HDI strain-hardening effect that promotes the synergistic enhancement of strength and ductility. In addition, the highly coherent $L1_2$ /FCC interfaces and serrated grain boundaries facilitate coordinated deformation, enabling the alloy to achieve both excellent strength and good ductility at room temperature.

(5) The intermediate-temperature brittleness characteristics and the improvement mechanism of the multi-scale core-shell structured HEI are revealed. The Al9 alloy exhibits a yield strength of approximately 925 MPa at 800 °C, but with a plastic elongation of nearly zero. This intermediate-temperature brittleness originates from

grain-boundary weakening caused by oxygen penetration and stress concentration induced by grain-boundary sliding. After increasing the Cr content to 20 at.%, the α -Cr phase formed at grain boundaries and the fine-scale core-shell structures effectively hinder oxygen diffusion along grain boundaries, while the morphological evolution of the intra-granular core-shell structures helps relieve stress concentrations at grain boundaries. The synergistic effect of these two factors restores the plastic elongation of the Cr20 alloy to approximately 5% at 800 °C, effectively alleviating the intermediate-temperature brittleness.

(6) The anomalous yield effect of the multi-scale core-shell structured HEI is elucidated. Over a wide temperature range of 25–1000 °C, the yield strength of the Cr20 alloy first increases and then decreases with rising temperature, reaching a peak value of approximately 920 MPa at 800 °C, which is higher than the room-temperature yield strength of about 880 MPa. This effect is attributed to the temperature-induced transition of the deformation mechanism to APB-dominated behavior, as well as the formation of K-W locks and L-C locks. Specifically, K-W locks are formed by cross-slip of APBs driven by the anisotropy of antiphase boundary energy, while L-C locks are generated by the interaction of SISFs. The synergistic pinning of dislocations by these two types of locks leads to an increase rather than a decrease in yield strength. When the temperature exceeds a critical value, the dislocations become thermally activated and unlock, resulting in a subsequent decrease in yield strength.

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