Materials Today Sustainability 26 (2024) 100787

Contents lists available at ScienceDirect

Materials Today Sustainability

journal homepage: www.journals.elsevier.com/materials-today-sustainability

Valorization of wood ash for sustainable *in situ* reinforced Ti composites with tailorable mechanical behavior manufactured via powder metallurgy

L. Bolzoni *, F. Yang

School of engineering, The University of Waikato, Hamilton, 3240, New Zealand

ARTICLE INFO

Keywords:
Composites
Powder metallurgy
Wood ash
Mechanical properties

ABSTRACT

The aim of this work is to investigate the feasibility of revalorizing commonly disposed wood ash as source to produce more sustainable *in situ* reinforced Ti composites. We propose a manufacturing process based on the powder metallurgy green technology and further increase the energy efficiency of the process by analyzing reactive induction sintering as the primary consolidation method. The feasibility of the proposed approach is demonstrated through the characterization of the physical, microstructural, and mechanical performance. It is found that compressibility decreases and the amount of residual porosity increases (6.0–11.7% for pressureless sintering) with the amount of wood ash used (0–0.25 wt%). However, the effective *in situ* creation of the reinforcement is always guaranteed by the proposed approach. Furthermore, minor adjustments of the manufacturing route can be used to maximize the amount of ash to be added for higher sustainability. The *in situ* reinforced Ti composites are commonly characterized by both elastic and plastic deformation and fail non-catastrophically, where for vacuum sintering ductility decreases (13.7 → 8.7%) but strength (497 → 653 MPa) and hardness (47.8 → 55.0 HRA) increase with the amount of ash used. The *in situ* reinforced Ti composites produced from revalorized wood ash have overall comparable or better mechanical properties in comparison to other Ti-based composites bearing a higher amount of generally more expensive reinforcements.

1. Introduction

The current widely adopted linear economy entails mining of raw materials, transformation of these resources into useful products, use of the products by the consumers, and final disposal of the products that most of the time end up in landfills. Conversely, the evolving paradigm shift of circular economy pushes the more efficient utilization of the available resources through reducing, reusing, and recycling. The implementation of this new paradigm is supported by mandatory regulations aiming at reducing consumption (e.g. energy, virgin materials, etc.) for CO_2 emission's reduction gains. Revalorization of currently considered wastes is a key aspect to pursue the virtuous path of a circular economy. Although neither sustainable nor energy efficient, the reality is that wood burning to produce heat is still widely used, and this results in the generation of a significant amount of wood ashes [1].

Ti alloys are the ideal materials for a wide range of engineering applications due to the combination of properties they afford, which include the highest relative mechanical properties (i.e. in relation to the density of the alloy), outstanding corrosion resistance, and biocompatibility [2]. The wider adoption of Ti alloys would result in significant environmental and social benefits exemplified, amongst others, by the reduction of CO_2 pollution from the transportation sector and lower maintenance of infrastructure due to the avoidance of corrosion. However, there are two key problems, respectively, preventing and limiting the wider adoption of Ti alloys to harvest such benefits. Specifically, Ti alloys are more expensive than other structural metal counterparts [3] and they are characterized by relatively low wear resistance due to their low hardness. Solutions to these two problems can be sought via investigating alternative manufacturing processes (e.g. powder metallurgy) and creating composite materials, respectively [4,5].

Powder metallurgy is a recognized green technology as its methods are more energy efficient, produce less waste, and allow the flexibility of easily creating new high-performance materials. In particular, most powder metallurgy techniques rely on solid-state processing (i.e. low temperature) resulting in less energy demand due to the avoidance of the need to melt the materials for their shaping. Powder metallurgy techniques are net- or near-net-shape methods characterized by high

* Corresponding author.
E-mail address: bolzoni.leandro@gmail.com (L. Bolzoni).

https://doi.org/10.1016/j.mtsust.2024.100787
Received 31 January 2024; Received in revised form 26 March 2024; Accepted 25 April 2024
Available online 27 April 2024
2589-2347/

yields of material where the amount of waste (i.e. energy/metal) is limited as a consequence of the reduced number of steps needed and the reduced amount of machining required [6]. Finally, powder metallurgy is ideally suited to create metal-based composite materials with ceramic reinforcements.

Composites made out of a metallic matrix with ceramic reinforcements are commonly divided in continuously and discontinuously reinforced, and depending on whether the reinforcement is directly added (i.e. *ex situ*) or formed *in situ* through the addition of appropriate precursors. Regardless of these distinctions, it is accepted and established that metal matrix composites are characterized by higher service temperatures and better wear performance due to their higher hardness. When it comes to Ti matrix composites, a variety of *ex situ* and *in situ* ceramic reinforcements including carbon nanotubes [7], graphene [8], graphite [9], SiC [10], TiN [11], B_4C [12] and Ti_5Si_3 [13] as well as TiB whiskers [14] and TiC particles [15] are used. TiC is one of the best reinforcements as it exhibits both wear- and corrosion resistance and high stiffness [4]. Moreover, its density and coefficient of thermal expansion are similar to those of Ti, which leads to reduced interfacial residual stresses [5].

With reference to TiC reinforced Ti, casting [16] can be used as exemplified by the work of Lu et al. [9] who used the self-propagation high-temperature synthesis reaction between titanium and graphite during melting in a non-consumable vacuum arc remelting furnace to produce *in situ* reinforced Ti/TiC composites. However, powder metallurgy is preferred as it permits to avoid segregation of the reinforcement and a variety of techniques including pressureless sintering [17,18], vacuum hot-pressing [19], spark plasma sintering [8,20–22], hot isostatic pressing [23], powder extrusion [23], selective laser sintering [24], and electron beam melting [25] have been investigated.

For instance, Peillon et al. [17] and Zhang et al. [18], respectively, used uniaxial pressing and cold isostatic pressing followed by pressureless sintering in Ar or under vacuum. Sun et al. [19] produced TiC reinforced Ti composites by means of hot-pressing at 900 °C applying a uniaxial pressure of 30 MPa during 10 min. Vasanthakumar et al. [20] and Lee et al. [21] analyzed the effect of using different combinations of sintering parameters, respectively 800–1200 °C/50 MPa/5 min and 1170 °C/80 MPa/10 min, during spark plasma sintering. Fruhauf et al. [23] produced Ti reinforced with 15 vol% TiC particles by means of hot isostatic pressing of encapsulated powder blends consolidated at 920 °C for 2 h under a load of 100 MPa. Fruhauf et al. [23] also analyzed powder extrusion of the same composition using steel cans filled with powder, which were heated to 920 °C for 1 h before extrusion with an extrusion ratio of approximately 4. He et al. [24] used scan speed of 200 mm/s, laser power of 100 W, laser spot of 100 mm, powder layer thickness of 50 mm, and hatch spacing of 70 mm to manufacture a Ti-5wt.% TiC composite via selective laser sintering. Valkov et al. [25] used a two-step electron beam surface modification technique including injection of C powder within the Ti substrates and refinement and homogenization of the microstructure to form Ti/TiC composite layers.

Apart from the direct addition of micro/nano TiC particles [17,21, 23,24], a wide range of C sources to create the TiC reinforcing particles *in situ* can be used. This includes graphite [9], methane [18], *n*-hexane [26], B_4C [27], polycarbosilane [28], carbon powder [25], activated carbon powder [29], carbon black [30], continuous carbon fibers [31], plain weave carbon fabric [32], carbon nanotubes [19,20], graphene [8, 22], and diamond [33]. Additionally, coal fly ash has been evaluated to make metal matrix composites [34–36] using powder metallurgy.

Therefore, it is found that specialized and expensive high-temperature equipment as well as special conditions for handling the raw materials are generally needed and researching a suitable process with a simple sintering route will be beneficial [26] from a sustainable point of view. Moreover, the trend found in literature points towards the use of progressively more expensive C sources, namely nanotubes, graphene, and diamond, which are far less than sustainable. From that, the aim of this work is to investigate the possibility of revalorizing commonly disposed ashes derived from wood burning as source to produce more sustainable *in situ* reinforced Ti composites by quantifying their physical, microstructural, and mechanical behaviors. To further enhance sustainability, the present work also put particular emphasis on the consolidation of the composites by means of reactive induction sintering [37]. The latter is a far more energy efficient method with respect to other more conventional and well-established powder metallurgy techniques due to its characteristic much higher heat transfer mode [38,39].

2. Experimental procedure

The raw materials of the present study were a commercially available Ti powder and wood ash. The Ti powder was obtained by means of the comminution hydride-dehydride process and it is, therefore, characterized by an irregular powder morphology, particle size lower than 75 μm, and oxygen content of 0.27 wt%. The morphology and particle size make the powder ideal to be shape via the simple uniaxial pressing method and the oxygen content indicate that the material is equivalent to pure Ti grade 3 [40]. The desired proportions of raw materials were mixed by means of a V-shape blender operated at 45 rpm for 30 min. The overall study is divided into three parts, each one aiming at optimizing one aspect leveraging the findings of the previous sub-study, and the overall conditions are reported in Table 1. Part I analyzed the effect of the sintering method to prove the viability of using reactive induction sintering to manufacture Ti composites. For that, powder blends with 0–0.25 wt% wood ash were cold uniaxially pressed into 40 mm cylindrical samples and sintered at the same temperature (i.e. 1250 °C) either using vacuum or induction sintering. It is worth mentioning the 1250 °C was initially selected because it is one of the most common temperatures used to pressureless sinter Ti-based materials [14,18,41,42]. Vacuum sintering is the standard powder metallurgy route used to consolidate Ti alloys [43]. As the technique relies on conventional electrical-resistant heating elements, the maximum heating rate is approximately 10 °C/min and the overall sintering cycle time is around 12 h. During induction sintering the metallic samples are heated from the inside out thanks to the Eddy currents generated by the applied magnetic field, resulting in much faster heating rates. Ti samples with relative density of approx. 88% can be heated up to 1300 °C in less than 2 min with an effective heating rate of 15 °C/s (i.e. 900 °C/min) [38]. This allows to

Table 1
Details of the compositions and related processing conditions used in the study.

Project	Ash content	Shaping	Sintering	Forging
Part I	0 wt% 0.05 wt% 0.15 wt% 0.25 wt%	Cold uniaxial pressing: 600 MPa, 25 °C	Vacuum, 1250 °C, 2 h, 10 °C/min	–
	0 wt% 0.05 wt% 0.15 wt% 0.25 wt%	Cold uniaxial pressing: 600 MPa, 25 °C	Induction, 1250 °C, 2 min, Ar	–
Part II	0 wt% 0.1 wt% 0.3 wt% 0.6 wt%	Cold uniaxial pressing: 600 MPa, 25 °C	Induction, 1300 °C, 5 min, Ar	–
Part III	0.5 wt% 1 wt%	Warm uniaxial pressing: 600 MPa, 200 °C	Induction, 1300 °C, 5 min, Ar	–
	0.5 wt% 1 wt%		–	Induction, 1100 °C, 5 min, Ar

significantly shorten the overall sintering cycle from hours to min with the associated energy saving, increasing the overall sustainability of the manufacturing process.

Using exclusively reactive induction sintering, Part II investigated the effect of a wider range of wood ash additions, precisely 0–0.6 wt%. 40 mm cylindrical samples were shaped at room temperature and sintered at 1300 °C for 5 min. It is worth noting that, from the findings of Part I, the sintering temperature was raised aiming at enhancing the densification of the Ti composites as it was found that the addition of the wood ash decreases the density of the induction sintered samples. Finally, part III considered the effect of using warm pressing without and with forging to further enhance the densification of the Ti composites with 0.5–1.0 wt% of wood ash additions.

The density of the samples after shaping (i.e. green density) was calculated as mass/volume ratio. For that, the weight of the samples was obtained by means of a 4-digit analytical balance and the dimensions were measured using a 2-decimal digital caliper. The density of the sintered samples was quantified using water displacement measurements based on Archimedes' principle. Porosity is the difference between the relative and the theoretical density. Relative density values were calculated by dividing the measured density value by the theoretical density of the composite assuming, for the sake of simplicity, that all the wood ash transforms into stoichiometric TiC. The densification parameter was calculated as sintered minus green density divided by theoretical minus green density. Preparation of the samples for metallographic analysis followed the classical route, which includes grinding with Emery papers, polishing, and chemical etching (Kroll solution: 2 ml HF, 5 ml HNO_3, and distilled H_2O). Quantification of the mechanical behavior was done through both hardness (HRA) and tensile testing. For the latter, dogbone samples (2 × 2 mm^2) were tested using a strain rate of $5 \cdot 10^{-3}$ 1/s. The offset method was used to calculate the yield stress.

3. Results

3.1. Part I – Vacuum sintering vs. induction sintering

Fig. 1 shows the variation of the physical properties, namely density, porosity, and densification parameter, of the Ti composites as a function of the ash content. Although from Fig. 1a) it seems constant, in reality the theoretical density slightly increases as the density of TiC (i.e. 4.93 g/cm^3) is marginally higher than that of Ti (i.e. 4.51 g/cm^3). The green density continuously decreases with the progressive addition of a greater amount of wood ash. The values achieved in the sintered samples are dependent on the sintering technique used and remain almost constant for vacuum sintering whereas constantly decrease in the case of reactive induction sintering. This behavior is reflected on the porosity values (Fig. 1b). Consequently, the amount of porosity in the green samples linearly increases from 12.0% to 13.2% as the amount of ash increases from 0 wt% to 0.25 wt%. From the analysis of the vacuum sintered composites, there are minor local variations but the amount of porosity remains almost constant at 6.3 ± 0.2% regardless of the amount of ash. In the case of the induction sintered composites, the porosity increases from 9.6% to 11.7% as the ash content increases. The combination of decreasing green density and constant/decreasing sintered density, respectively, leads to a slight increase for vacuum sintering and a decrease for induction sintering in terms of the densification of the composite with the amount of ash added (Fig. 1c).

Representative micrographs of the composites manufactured by means of vacuum and induction sintering are shown in Fig. 2. Regardless of the actual composition, porosity is present in the microstructure in agreement with the data of Fig. 1. However, the features of the residual pores are different depending on the manufacturing process used. Specifically, the majority of the pores are spherical in shape, are isolated, and primarily found at the grain boundaries in the case of vacuum sintering. Conversely, more irregularly shaped, and more interconnected residual pores are found in the induction sintered composites.

In terms of phases, the microstructure of the Ti composites is

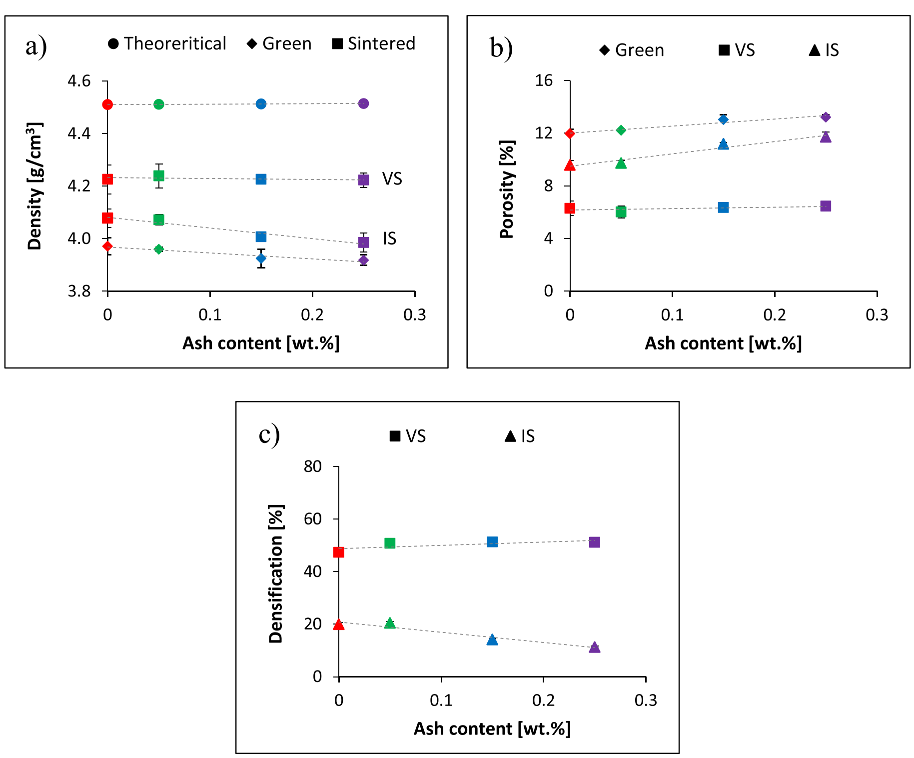

Fig. 1. Variation of the physical properties of the vacuum and induction sintered Ti composites as a function of the ash content: a) density, b) porosity, and c) densification parameter. Legend: VS – vacuum sintering, and IS – induction sintering.

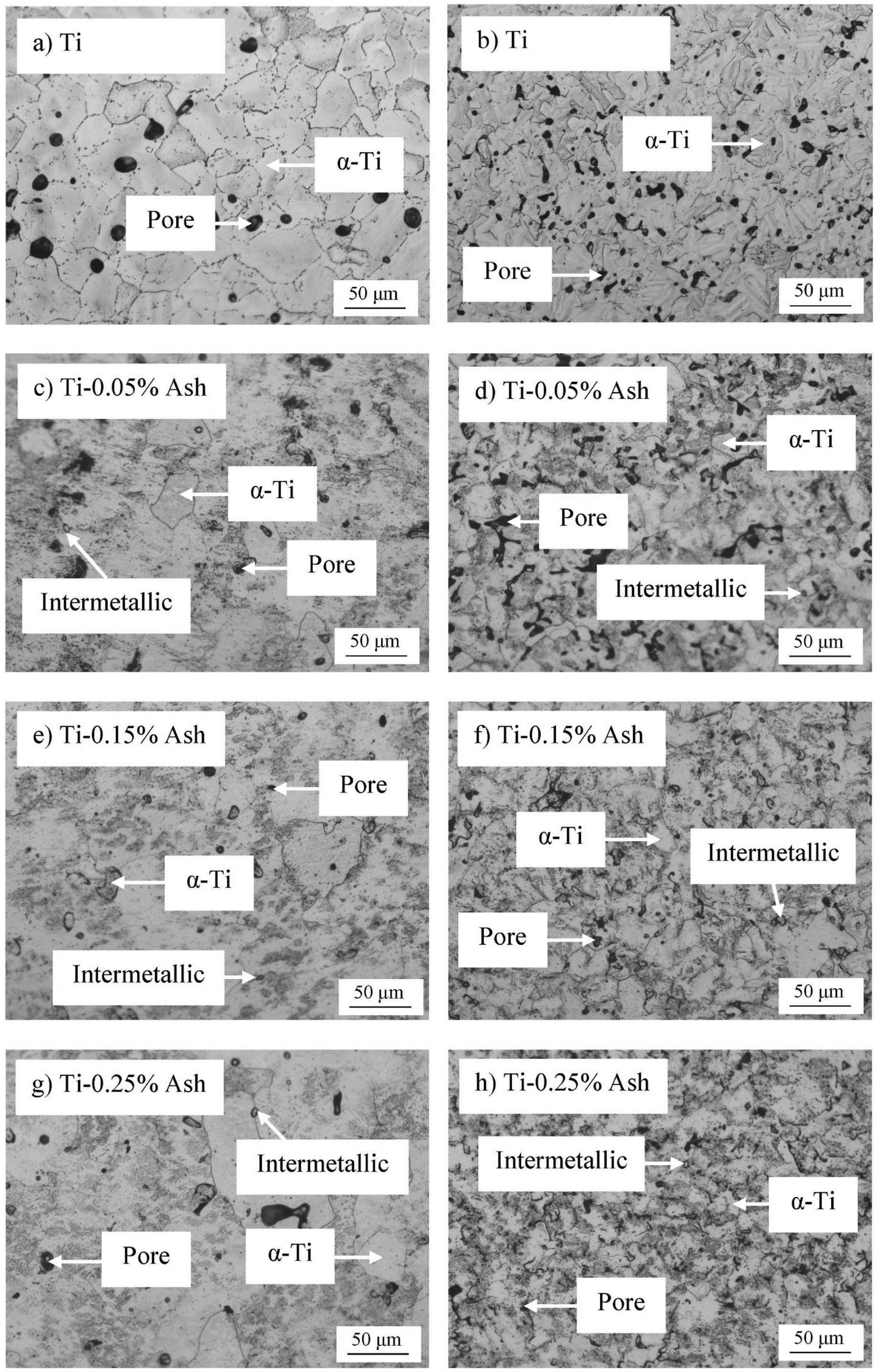

Fig. 2. Representative micrographs of the Ti composites, respectively, vacuum and induction sintered: a-b) Ti, c-d) Ti-0.05% Ash, e-f) Ti-0.15% Ash, and g-h) Ti-0.25% Ash.

composed of grains of the equilibrium α-Ti phase; however, their morphology is different. In particular, equiaxed or coarse acicular grains are, respectively, found in the vacuum or induction sintered composites. This is due to the intrinsically different cooling rate, which is much faster in the case of induction sintering leading to the formation of a martensitic-like acicular structure rather than an equiaxed one. This is coherent with the physical metallurgy of Ti where massive martensite can be obtained [40]. Both type of grains form upon cooling from sintering in the β field, above the allotropic β transus temperature of Ti (i.e. approximately 920 °C for Ti grade 3 [40]). The equiaxed β-Ti phase grains, thus, transform into equiaxed or acicular α-Ti phase grains as the degree of cooling increases. The addition of the wood ash leads to the precipitation of equiaxed intermetallic particles (representative average EDS analysis in at.%: 55.49%Ti-43.03%C-1.48%Si) with particle size in the 5–10 μm range at the grain boundary of the α-Ti phase regardless of the amount of ash used.

Fig. 3 shows representative tensile stress-strain curves of the vacuum and induction sintered composites as well as their average mechanical properties. It can be seen that, regardless of the composition or the manufacturing process, the sintered composites are characterized by

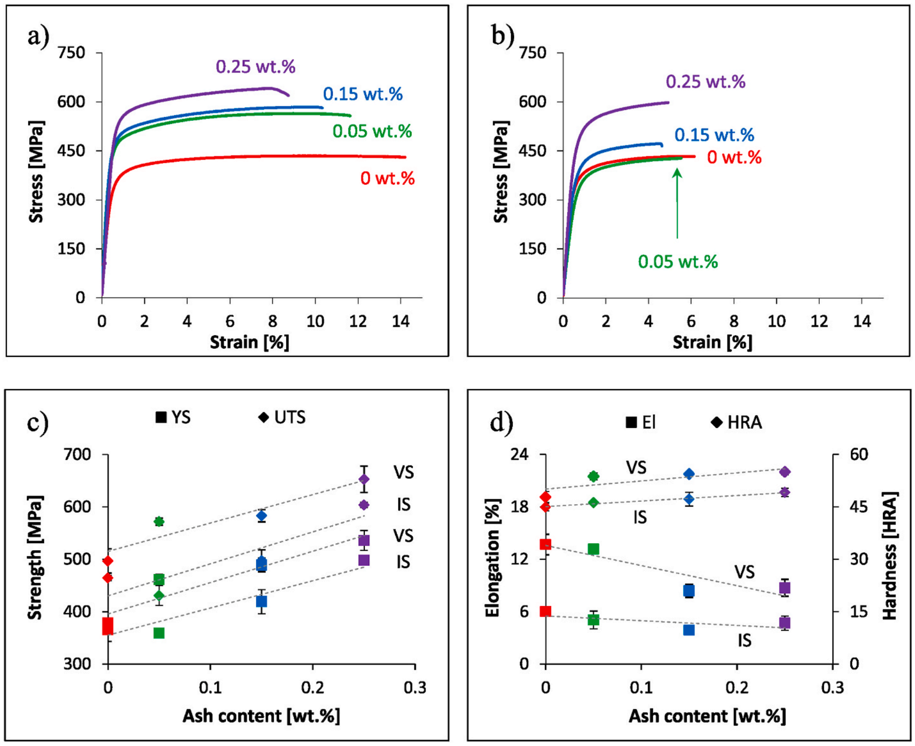

Fig. 3. Variation of the mechanical properties of the Ti composites: a) representative stress-strain curves of the vacuum sintered samples, b) representative stress-strain curves of the induction sintered samples, c) strength vs. ash content, and d) elongation and hardness vs. ash content. Legend: VS – vacuum sintering, and IS – induction sintering.

both elastic and plastic deformation before non-catastrophic failure. The different composites have comparable elastic modulus as their curves overlap in the elastic region. Generally the composites get stronger and more brittle as the amount of ash added increases; however, there is also a clear influence from the manufacturing method employed.

More in detail, both the yield stress and ultimate tensile strength of the Ti composites linearly increase with the amount of ash added (Fig. 3c). However, the initial addition of 0.05 wt% of ash has a much greater effect on the vacuum sintered (i.e. 85 MPa increase on average) rather than on the induction sintered samples. For the latter, the initial addition actually slightly decreases (i.e. 26 MPa on average) the strength and the highest increment is obtained when increasing the ash content from 0.15 wt% to 0.25 wt% (i.e. 93 MPa on average). It can also be noticed that, generally, the average strength of the induction sintered samples is lower (i.e. 63 MPa on average) than that of the vacuum sintered one. This is due to the lower amount of porosity of the latter (Fig. 1b) as a consequence of the higher densification experienced. As it could have been expected, similar trends are found for the hardness of the Ti composites. Therefore, the hardness continuously increases with the amount of ash and higher values (i.e. 5.9 HRA on average) are obtained in the vacuum sintered specimens. In terms of elongation to fracture, the ability to withstand plastic deformation before failure linearly decreases for both types of Ti composites. Nevertheless, in this case the trend is reversed and a smaller loss of ductility is found in the induction sintered samples (Fig. 3d).

From this initial part of the study it is found that the manufacturing of Ti composites by means of induction sintering generally leads to lower performance. However, especially for the case of the Ti composites with 0.25 wt% of ash addition, the difference in strength and elongation is not as pronounced. Considering that induction sintering is a more sustainable and much less energy demanding process, this was selected as the manufacturing method moving forward to analyze the effect of higher ash additions. Taking into account that the compressibility and the densification decrease and the amount of porosity increases with the amount ash (Fig. 1), both the sintering temperature and time were slightly increased, respectively, to 1300 °C and 5 min for Part II of the study.

3.2. Part II – Effect of higher wood ash additions

The variation of the physical properties of the Ti composites induction sintered at 1300 °C for 5 min with ash contents up to 0.6 wt% are shown in Fig. 4. Not surprisingly, both the green and sintered density values decrease with the amount of ash added and the theoretical density slightly increases linearly. Consequently, the amount of residual porosity present in the green and sintered samples continuously increases whereas the densification parameter monotonically decreases as a greater amount of ash is added into the composition of the Ti composites (Fig. 4b). The trends found are consistent with the results shown in Fig. 1. However, a lower amount of porosity (i.e. 1.3% on average) and a higher degree of densification (i.e. 13.6% on average) is achieved as a consequence of the slightly higher temperature and longer time used during the reactive induction sintering process.

The results of the microstructural characterization performed on the Ti composites induction sintered at 1300 °C for 5 min are displayed in Fig. 5. The microstructure is still characterized by the presence of residual pores, coarse acicular α-Ti phase grains, and the precipitation of intermetallic particles primarily found at the α-Ti grain boundaries. However, the total amount of porosity is obviously lower and their morphology tends to be more equiaxed as a result of the higher densification experienced during sintering. Moreover, the size of the acicular α-Ti phase grains is slightly bigger as a consequence of the longer time spent at the higher sintering temperature above the allotropic β transus temperature. No remarkable differences were found in terms of size and distribution of the intermetallic particles.

From the representative stress vs. strain curves of the Ti composites induction sintered at 1300 °C for 5 min plotted in Fig. 6, it can be seen that they are still characterized by an elasto-plastic behavior in response

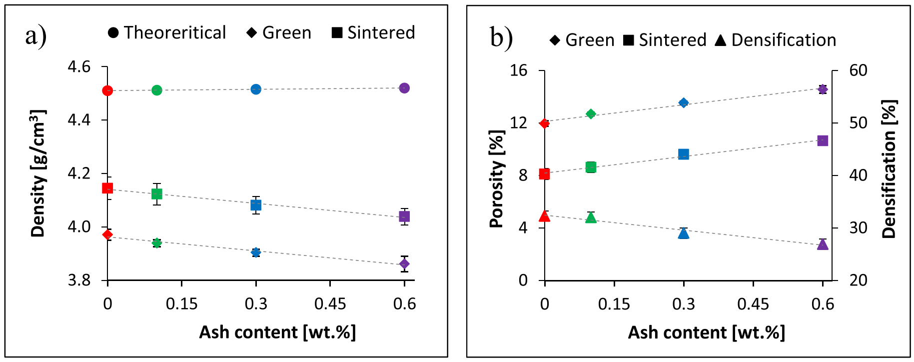

Fig. 4. Variation of the physical properties of the Ti composites induction sintered at 1300 °C for 5 min as a function of the ash content: a) density, and b) porosity/densification parameter.

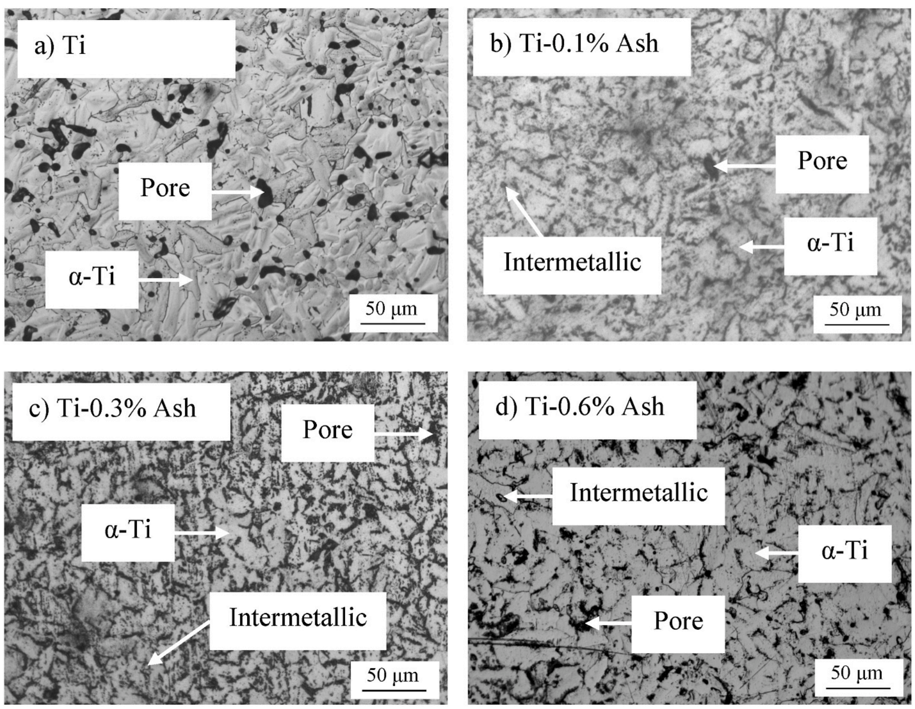

Fig. 5. Representative micrographs of the Ti composites induction sintered at 1300 °C for 5 min: a) Ti, b) Ti-0.1% Ash, c) Ti-0.3% Ash, and d) Ti-0.6% Ash.

to the applied uniaxial tensile load. As the amount of ash added increases, the resistance to plastic deformation increases and the ductility decreases, but the elastic modulus remains fairly constant. On average, the progressive addition of a greater amount of ash leads to a more significant increment of the yield strength (i.e. 30 MPa) compared to the ultimate tensile strength (i.e. 15 MPa) resulting in an increasingly lower gap between the two of them as seen in Fig. 6b). Associated to that, there is a monotonic increase of the hardness (i.e. 3.0 HRA) and an almost linear decrease of the elongation to fracture (i.e. 0.4%) for higher additions of ash (Fig. 6c). The described mechanical behavior is the compromise between different counteracting aspects induced by the higher amount of ash added and the increase of the temperature, which can reduce the mechanical strength. Specifically, the addition of a progressively higher amount of ash induces both greater solid solution/precipitation strengthening effects and the formation of a higher amount of residual pores. Furthermore, the longer sintering at higher temperature leads to coarsening of the microstructural features. Strengthening increases strength but reduces ductility, porosity reduces both strength and ductility, although theoretically linearly and parabolically respectively [42], whereas microstructure coarsening favors ductility (decreasing strength) due to the resulting lower amount of grain boundaries.

From this part of the study it is concluded that Ti composites with higher amount of ash additions can successfully be manufactured using reactive induction sintering still maintaining a ductile behavior. Nevertheless, from the characterization of the mechanical behavior it is found that the Ti-0.6% ash composites have almost a brittle behavior due to their limited ductility (i.e. 1.0 ± 0.4%). If the aim is to use a greater amount of ash in the Ti composites to make them more sustainable, the amount of porosity needs to be reduced. This is generally associated with the need to enhance the densification of the material. Significantly increasing the sintering temperature or using much longer sintering times would be the obvious option; however, this would increase the energy demand, making the process less sustainable. Alternatively, reduction of porosity can be achieved by either increasing the green density, which is expected to result in higher sintered density values, or by subjecting the Ti composites to a thermomechanical deformation process. The advantage of induction sintering is that sintering is directly used as preheating step for the subsequent thermomechanical deformation process [37]. This avoids the need for reheating

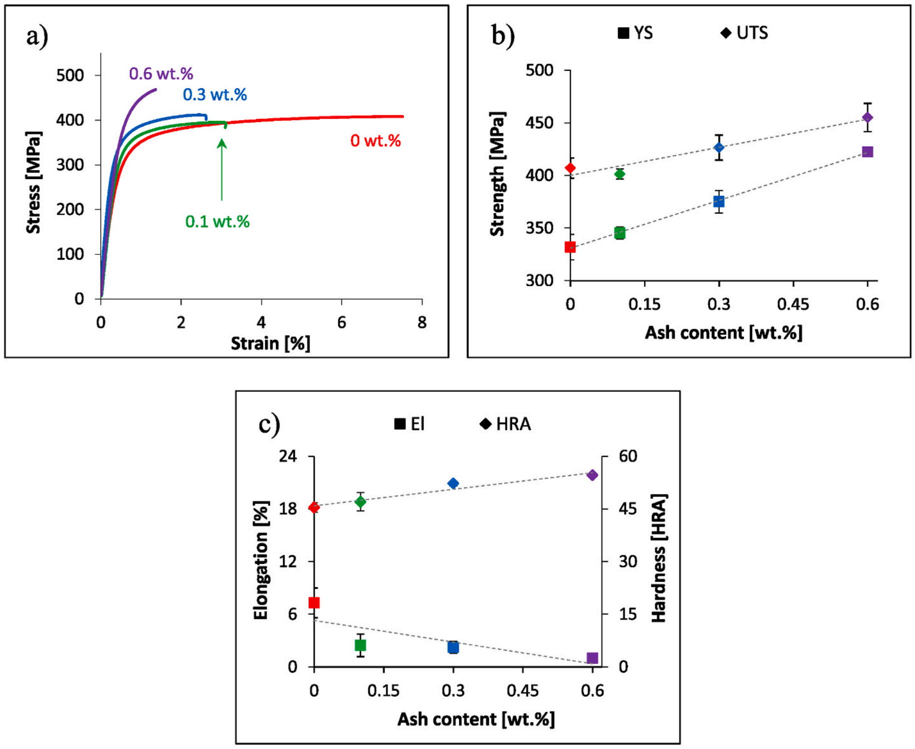

Fig. 6. Variation of the mechanical properties of the Ti composites induction sintered at 1300 °C for 5 min: a) representative stress-strain curves, b) strength vs. ash content, and c) elongation and hardness vs. ash content.

the Ti composites, if they were vacuum sintered for instance, resulting in a more energy efficient process. With that in mind, the concurrent effects of a higher green density and thermomechanical deformation via hot forging was analyzed in part III of this study.

3.3. *Part III – Effect of reduced porosity striving for higher ash contents*

Fig. 7 shows the variation of the physical properties including density, porosity, and densification parameter, of the induction sintered and

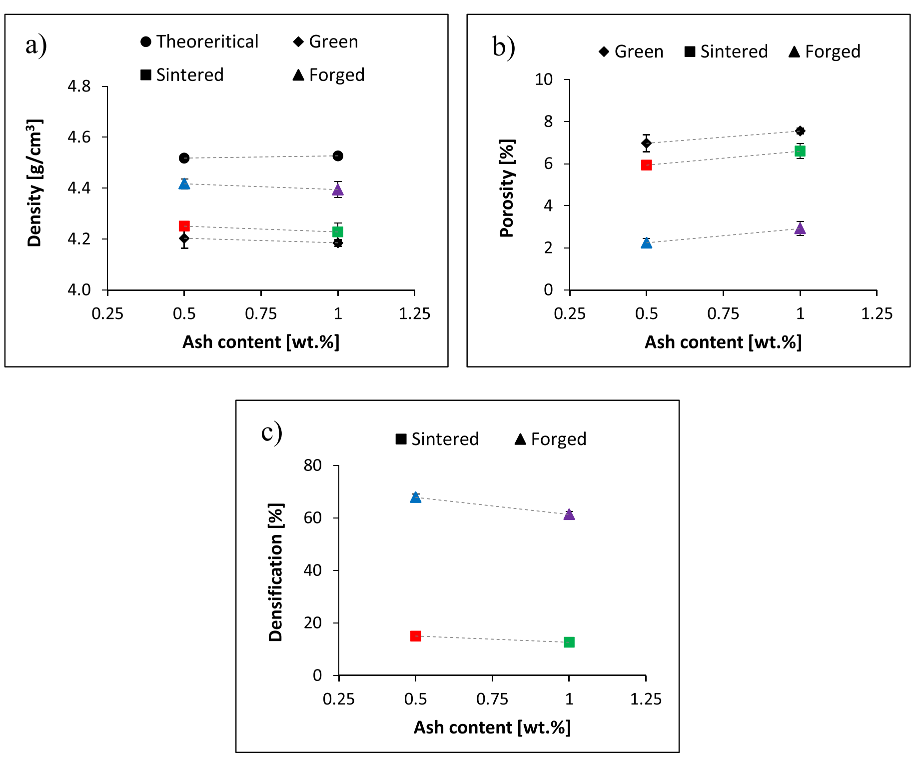

Fig. 7. Variation of the physical properties of the induction sintered and forged Ti composites as a function of the ash content: a) density, b) porosity, and c) densification parameter.

forged Ti composites with ash content of 0.5–1.0 wt%. As for the other Ti composites, the theoretical density slightly increases and the green density as well as the density after consolidation (i.e. sintering or forging) marginally decreases. Consequently, the amount of residual porosity increases (i.e. 0.7% on average) and the values of the densification parameter decrease (i.e. 4.4% on average) with the amount of ash added. However, it is found that the total amount of porosity is significantly lower in the forged samples as a consequence of the plastic deformation experienced during the thermomechanical processing. This, concurrently, translates into much higher densification parameter values (Fig. 7c). Moreover, it can be noticed that the amount of porosity present in the induction sintered samples is lower (i.e. 3.0% on average) with respect to the those analyzed in part II (Fig. 4b), although of the higher amount of ash added. That is the outcome of using warm pressing (Table 1) to achieve higher density values in the green samples. However, it can also be noticed that the values of the densification parameter (Fig. 7c) are also lower (i.e. 16.2% on average) compared to Fig. 4b), even though they were sintered under the same conditions (i.e. 1300 °C for 5 min). This is the consequence of the combined effects of bearing a higher amount of ash and starting from a higher green density.

Fig. 8 shows representative optical micrographs of the induction sintered and forged Ti composites. No remarkable differences can be highlighted for the induction sintered samples in comparison to those characterized in part II (Fig. 5). Furthermore, regardless of the manufacturing process used, the Ti composites are still characterized by the same phases entailing α-Ti phase grains and intermetallic particles formed at the grain boundaries. The most noticeable difference is the features of the microstructure of the forged Ti composites (Fig. 8c–d). Even though still composed of acicular α-Ti phase grains, the size of these grains is significantly smaller compared to those of the sintered samples. Moreover, there is a clear distinguishable texture with the acicular grain elongated in the perpendicular direction to the applied load during forging. This is evidently the combined effect of the applied load and the faster cooling experienced by the Ti composites upon forging in air. It can also be noticed that the volumetric amount of porosity is lower but the residual pores are characterized by a lenticular shape rather than an almost spherical morphology, which could be detrimental for the mechanical behavior. This is once again due to the plastic deformation experienced during their processing via thermomechanical deformation.

The representative stress-strain curves of the induction sintered and forged Ti composites (Fig. 9a) shows that, independently of the manufacturing process used, the Ti-1.0% ash composites display purely elastic behavior whilst the Ti-0.5% ash composites undergo both elastic and plastic deformation, although quite limited. Conversely to previous results (i.e. Figs. 3 and 6), the strength of the Ti composites decreases with the amount of ash added due to the embrittlement of the material, up to the point that it was not possible to determine the yield stress of the Ti-1.0% ash composites due to their brittle nature. Therefore, the elongation to fracture also decreases as the amount of ash increases whereas the hardness of the Ti composites is the only property that constantly increases. Analysis of the mechanical properties also denotes that the forged Ti composites are always characterized by better mechanical behavior with respect to their induction sintered counterparts with an average increase of 64 MPa in strength and 4.1 HRA in hardness but a slight decrease of 0.3% in terms of elongation to fracture. This behavior is the consequence of the differences highlighted in terms of microstructural features, precisely finer acicular α-Ti phase grains and elongated residual pores.

4. Discussion

The circular economy paradigm aims at recovering materials at their highest utility reducing or avoiding waste. Other key aspects are minimization/elimination of raw materials from fossil sources and reduction of greenhouse gas emissions [44]. Local circular economy can surge considering regional available wastes and the revalorization of waste products in the composites industry is being investigated. However, it is clear that research on more sustainable polymer-based composites is well ahead and its metal-based counterparts. Therefore, this study analyzed the feasibility of revalorizing commonly disposed wood ash for manufacturing more sustainable *in situ* reinforced Ti composites. To maximize sustainability, this research proposes and primarily investigated reactive induction sintering for manufacturing the Ti composites.

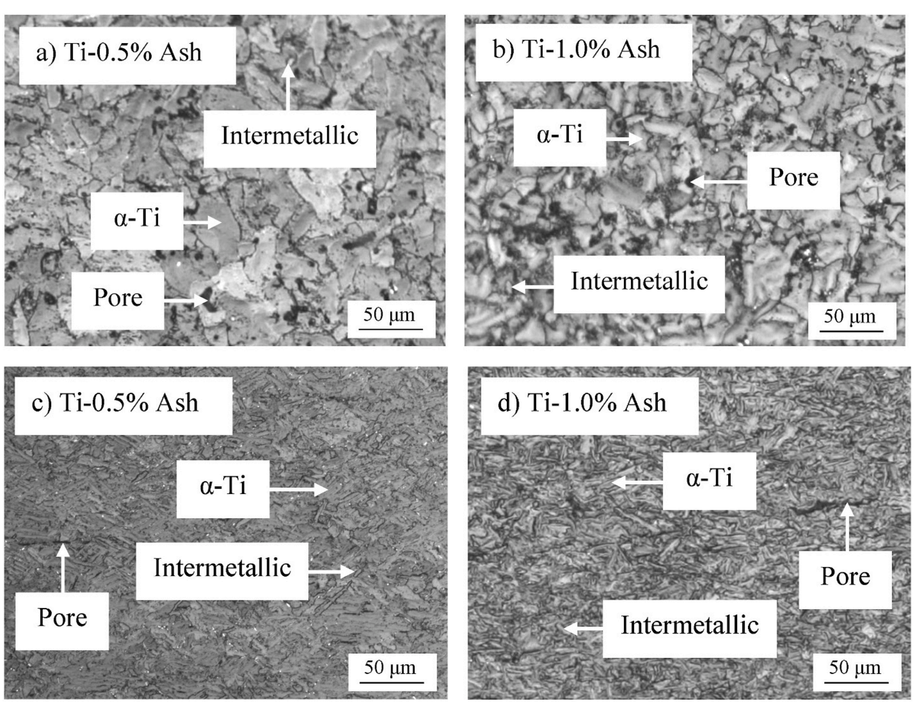

Fig. 8. Representative micrographs of the induction sintered and forged Ti composites: a) sintered Ti-0.5% Ash, b) sintered Ti-1.0% Ash, c) forged Ti-0.5% Ash, and d) forged Ti-1.0% Ash.

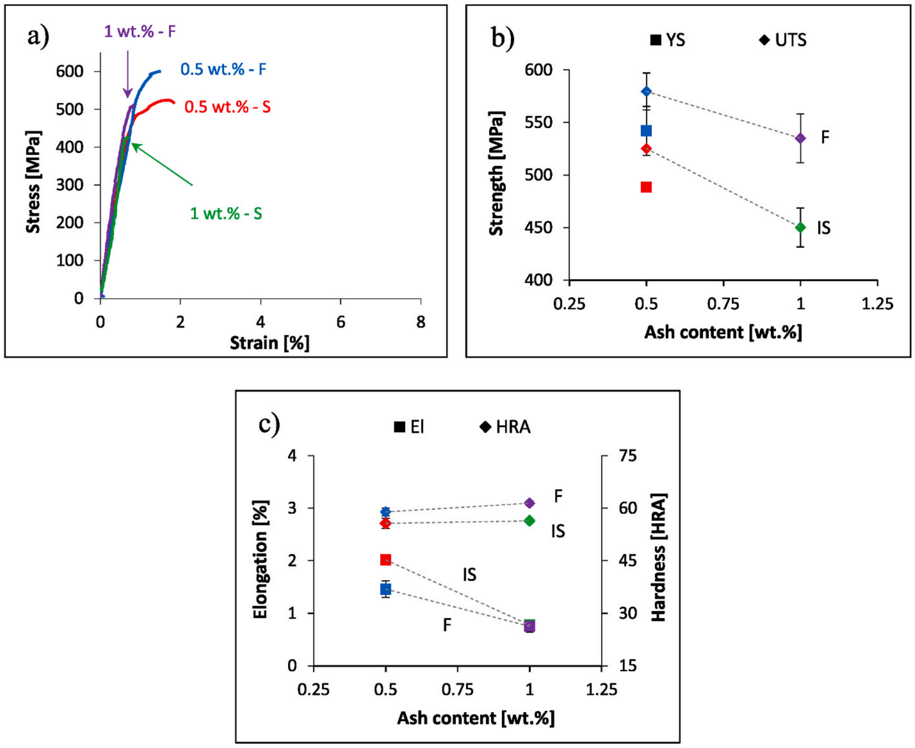

Fig. 9. Variation of the mechanical properties of the induction sintered and forged Ti composites: a) representative stress-strain curves, b) strength vs. ash content, and c) elongation and hardness vs. ash content. Legend: IS – induction sintering, and F – forged.

This approach simultaneously harvests all the intrinsic advantages of the green powder metallurgy technology including high materials' yield and reduced energy demand combined with the exploitation of the much more energy efficient induction heating method. Specifically, for a single component, this cuts the consolidation processing time from tenths of hours to few min resulting in significant energy saving, reduced emission, and enhanced overall sustainability. Therefore, both materials and manufacturing advantages characterize the proposed approach.

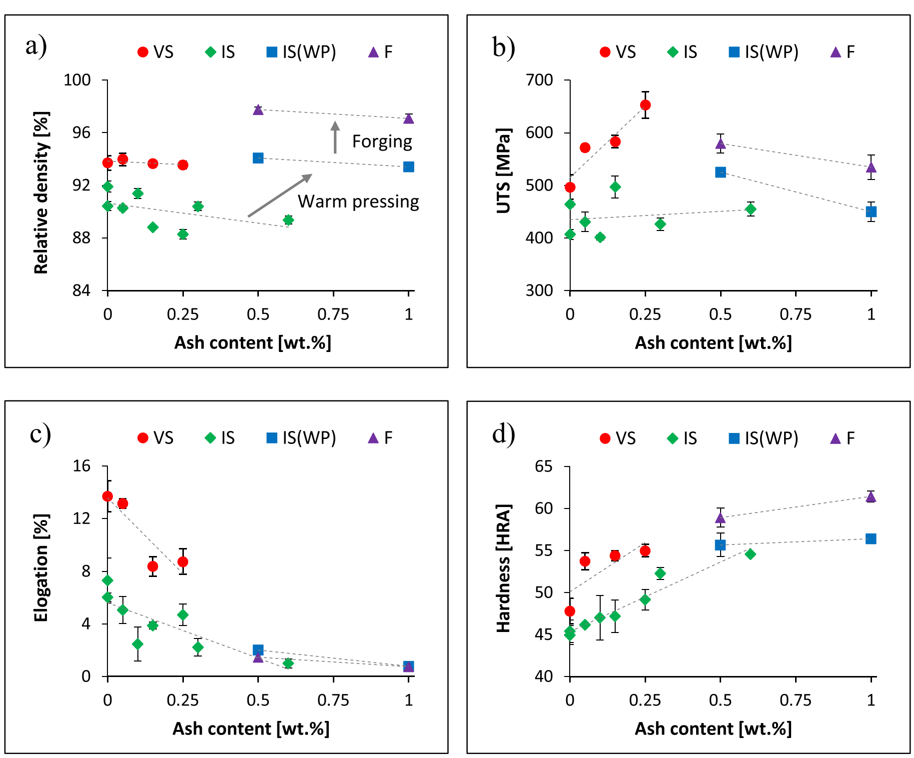

Fig. 10. Variation of the performance of the *in situ* reinforced Ti composites manufactured via induction sintering as a function of the ash content: a) relative density, b) UTS, c) elongation, and d) hardness. Legend: VS - vacuum sintering, IS - induction sintering, IS(WP) - induction sintering of warm pressed samples, and F - forged.

Form a materials point of view, advantages are the use of a cheap readily available reinforcement source as compared to more extensive reinforcements (e.g. nanotubes), and the valorization of a byproduct which is otherwise a waste material. From a manufacturing point of view, advantages include the ability to produce near-net-shape components, reduced energy consumption and environmental impact, and ability to tailor the mechanical response by easily changing the amount of ash added.

Part I of this study comparatively and systematically analyzed the physical, microstructural, and mechanical performance of *in situ* reinforced Ti composites manufactured via the conventional vacuum sintering and the induction sintering methods. The main conclusion drawn from the analysis of the Ti composites with up to 0.25 wt% of ash addition is that reactive induction sintering is a viable method to manufacture these materials. The properties are generally slightly lower compared to those of vacuum sintered samples, but the gap closes, especially in terms of mechanical behavior, with the amount of added ash. In terms of properties, it is found that, regardless of the manufacturing route used, the theoretical density slightly increases and the compressibility decreases (i.e. lower green density values). Considering relative density, porosity and densification, vacuum sintering leads to a fairly constant behavior independently of the amount of ash (Fig. 1). Conversely, porosity increases and densification decreases with the ash content in the induction sintered samples and, consequently, the relative density values decrease as shown in Fig. 10a). As for the vacuum sintered samples, induction sintering leads to the formation of a microstructure composed of α-Ti phase grains and equiaxed intermetallic particles, and porosity is present. However, the morphology of the α-Ti phase grains is acicular and the residual pores are more irregular and interconnected (Fig. 2). Despite these differences, the resistance to plastic deformation (i.e. strength and hardness) increases and, consequently, the ability to withstand the applied load in a ductile manner decreases with the amount of ash used (Fig. 3). However, ductility, which is much more critical than strength to prevent catastrophic failure, decreases at a much faster pace in the vacuum sintered composites in comparison to the induction sintered ones (Fig. 10c).

Once established that reaction induction sintering is a competitive process to manufacture *in situ* reinforced Ti composites, part II investigated the possibility to increase the amount of revalorized wood ash added into the Ti composites. To compensate for the forecast loss of compressibility and densification, the sintering temperature and time were slightly increased to, respectively, 1300 °C and 5 min for manufacturing Ti composites with ash contents up to 0.6 wt%. Such increments do not significantly impact the sustainability of the process, which remains still much more energy efficient and environmentally friendly compared to vacuum sintering. It is found that Ti composites with ash contents up to 0.6 wt% can successfully be manufactured and are characterized by higher relative density values (Fig. 10a, diamonds above the trendline) due to the higher degree of densification (Fig. 4). The microstructure is still composed of acicular α-Ti phase grains and intermetallic particles precipitated at the grain boundaries, but the α-Ti phase grains are coarser and the residual pores more spherical and less interconnected (Fig. 5). The Ti composites still undergo both elastic and plastic behavior upon uniaxial loading (Fig. 6) and their trend in terms of ultimate tensile strength (Fig. 10b), elongation (Fig. 10c), and hardness (Fig. 10d) aligns with that of the Ti composites bearing a lower amount of wood ash.

With the aim of increasing even further the amount of ash bore by the Ti composites, and considering that the Ti-0.6% ash composite has almost a brittle behavior, part III analyzed a slight modification of the manufacturing process. On the one side, cold pressing was replaced by warm pressing. This entails quickly preheating the Ti composites powder blends to 200 °C through induction heating but permits to achieve high relative sintered density values in the Ti composites with ash contents up to 1.0 wt% (Fig. 10a). In the other side, thermomechanical plastic deformation by means of hot forging was considered taking advantage of the fact that the induction heating cycle used to sinter the samples can directly be employed as preheating step for forging. This avoids the need of a secondary reheating stage, which is typical of thermomechanical deformation processes carried out on wrought/already sintered materials [45]. Forging further increases the relative density values of the Ti composites (Fig. 10a) due to the applied load, but the amount of residual porosity still increases with the amount of ash added (Fig. 7). Warm pressing does not change the resulting microstructure of the Ti composites but forging does, resulting in significantly smaller textured acicular α-Ti phase grains and lenticularly shaped residual pores (Fig. 8). The enhanced relative density and the microstructural changes associated with forging, generally, lead to better mechanical performance with respect to the other Ti composites analyzed in previous parts of the study (Fig. 10). However, in terms of tensile behavior, it is also found that the Ti-1.0% ash composites are brittle in nature (Fig. 9) regardless of the manufacturing process used. This results in the strength decreasing with the content of wood ash added and indicates that 1.0 wt% of ash is the maximum amount useable. Nevertheless, it is worth mentioning that this is only true for the manufacturing processes studied and when and if ductility is a requirement of a specific application. The hardness of the Ti composites is the only properties that is always higher for higher amounts of wood ash added and for higher relative density values, which is expected to result in enhanced wear resistance. Moreover, composites are highly used in engineering applications where compression is the main loading mode. In such instances, the amount of revalorized wood ash added to manufacture *in situ* reinforced Ti composites could potentially be further increased.

Fig. 11 shows the comparison of the tensile performance of the *in situ* reinforced Ti composites with other Ti-based composites bearing similar, but more costly, reinforcements found in literature [14,15,46,47]. From the analysis of the variation of the yield stress versus the amount of reinforcement it is, not surprisingly, found that it increases as more reinforcement is added. Nonetheless, it can be seen that, in general, the *in situ* reinforced Ti composites of this study have comparable yield stress to that of other Ti-based composites bearing a significantly higher amount of reinforcement (Fig. 11a). Specifically, the yield stress achievable using revalorized wood ash as reinforcement is better than that of cast Ti-1.5%B and similar to that of laser deposited Ti with 10 vol% and 20 vol% of TiC reinforcing particles and hot pressed Ti+1.5 vol% of TiB. Only the cast and forged Ti-2.0%B composite has slightly higher yield stress.

With respect to UTS-elongation pairs (Fig. 11b), it can be seen that the *in situ* reinforced Ti composites have comparable values to those of laser deposited Ti+10–20 vol% of TiC and cast Ti-1.5%B composites whereas the cast and forged Ti-2.0%B composite has higher strength. Moreover, similar elongation values are achieved via revalorized wood ash additions with respect to hot pressed Ti+1.5 vol% TiB and sintered Ti+3–5 vol% TiB composites, although the corresponding ultimate tensile strength is lower. However, it is worth mentioning that the best UTS-elongation pairs amongst all the materials analyzed in Fig. 11b) can be achieved in the wood ash *in situ* reinforced Ti composites if the slightly less energy efficient vacuum sintering technique is used to manufacture them. This analysis indicates that, from a mechanical point of view, the recycling of wood ash leads to the production of cheaper composites with comparable properties to those of others obtained using more expensive reinforcement sources.

5. Conclusions

This work aimed at investigating the possibility of revalorizing commonly disposed ash derived from wood burning as source to produce more sustainable *in situ* reinforced Ti composites. To maximize the sustainability from a manufacturing point of view, the composites were produced by means of the powder metallurgy green technology. Furthermore, reactive induction sintering, which has different

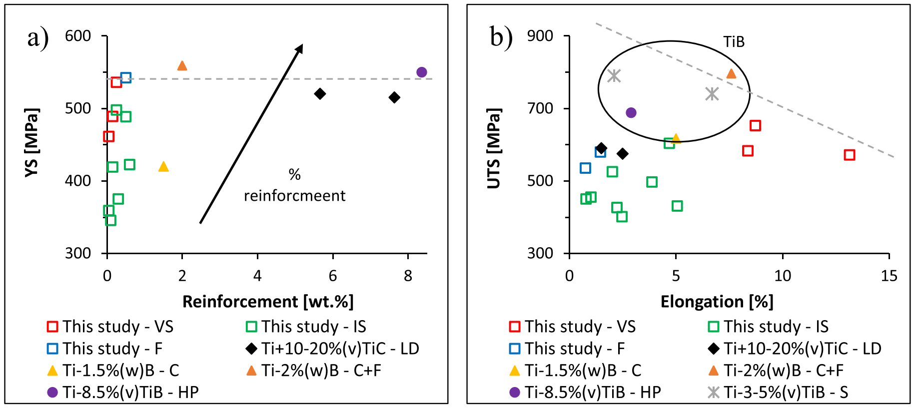

Fig. 11. Comparison of the tensile performance of the *in situ* reinforced Ti composites with other Ti-based composites [14,15,46,47]: a) YS vs. wt.% of reinforcement, and b) UTS vs. elongation. Legend: VS - vacuum sintered, IS - induction sintered, F - forged, LD - laser deposited, C - cast, HP - hot pressed, S - sintered, and (w) and (v) are weight and volume, respectively.

advantages including much higher energy efficiency, was proposed as the main consolidation method. Therefore, form this study the following conclusions can be drawn:

- The characterization of the physical, microstructural, and mechanical performance of the *in situ* reinforced Ti composites proves the feasibility of the proposed approach.
- The addition of wood ash generally decreases the compressibility of the composites' powder blend resulting in the progressive increase of the amount of residual porosity with the amount of ash added. However, slight increments of the sintering parameters (i.e. temperature and time) or minor modifications of the manufacturing route (i.e. warm pressing and forging) are effective in allowing to include a greater amount of wood ash. This is beneficial to maximize the reduction of the cost of the composites without sacrificing the sustainability of the manufacturing process.
- Regardless of the actual wood ash content and the manufacturing route used, the microstructure of the *in situ* reinforced Ti composites is composed of α-Ti phase grains, porosity, and intermetallic particles. Minor differences in the morphology of the grains and of the residual pores are found, but the proposed approach always leads to the effective creation of the reinforcement *in situ.*
- The *in situ* reinforced Ti composites are commonly characterized by both elastic and plastic deformation and fail non-catastrophically where the ductility decreases but the strength and hardness increase with the amount of ash used. The *in situ* reinforced Ti composites produced from revalorized wood ash have overall comparable or better mechanical properties, especially tensile performance, in comparison to other Ti-based composites bearing a significantly higher amount of generally more expensive reinforcements.

CRediT authorship contribution statement

L. Bolzoni: Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **F. Yang:** Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

[1] R. Siddique, Wood ash, in: R. Siddique (Ed.), Waste Materials and By-Products in Concrete, Springer Berlin Heidelberg, Berlin, Heidelberg, 2008, pp. 303–321.
[2] L. Bolzoni, M. Alqattan, L. Peters, Y. Alshammari, F. Yang, Ternary Ti alloys functionalised with antibacterial activity, Sci. Rep. 10 (1) (2020) 22201.
[3] L. Bolzoni, M. Xia, N. Hari Babu, Formation of equiaxed crystal structures in directionally solidified Al-Si alloys using Nb-based heterogeneous nuclei, Sci. Rep. 6 (1) (2016) 39554.
[4] X. Wang, S. Li, Y. Han, G. Huang, J. Mao, W. Lu, Visual assessment of special rod-like α-Ti Precipitates within the in situ TiC crystals and the mechanical responses of titanium matrix composites, Compos. B Eng. 230 (2022) 109511.
[5] Y. Jiao, L. Huang, L. Geng, Progress on discontinuously reinforced titanium matrix composites, J. Alloys Compd. 767 (2018) 1196–1215.
[6] L. Bolzoni, E.M. Ruiz-Navas, E. Gordo, Influence of vacuum hot-pressing temperature on the microstructure and mechanical properties of Ti-3Al-2.5V alloy obtained by blended elemental and master alloy addition powders, Mater. Chem. Phys. 137 (2012) 608–616.
[7] F.-C. Wang, Z.-H. Zhang, Y.-J. Sun, Y. Liu, Z.-Y. Hu, H. Wang, A.V. Korznikov, E. Korznikova, Z.-F. Liu, S. Osamu, Rapid and low temperature spark plasma sintering synthesis of novel carbon nanotube reinforced titanium matrix composites, Carbon 95 (2015) 396–407.
[8] X.N. Mu, H.M. Zhang, H.N. Cai, Q.B. Fan, Z.H. Zhang, Y. Wu, Z.J. Fu, D.H. Yu, Microstructure evolution and superior tensile properties of low content graphene nanoplatelets reinforced pure Ti matrix composites, Mater. Sci. Eng., A 687 (2017) 164–174.
[9] W. Lu, D. Zhang, X. Zhang, R. Wu, T. Sakata, H. Mori, Microstructural characterization of TiC in in situ synthesized titanium matrix composites prepared by common casting technique, J. Alloys Compd. 327 (1) (2001) 248–252.
[10] C. Poletti, M. Balog, T. Schubert, V. Liedtke, C. Edtmaier, Production of titanium matrix composites reinforced with SiC particles, Compos. Sci. Technol. 68 (9) (2008) 2171–2177.
[11] J. Umeda, H. Ishizaka, S. Li, A. Alhazaa, K. Kondoh, Comparison study on mechanical properties of powder metallurgy titanium materials with nitrogen solutes and TiN dispersoids, J. Alloys Compd. 846 (2020) 156455.
[12] F. Toptan, A. Rego, A.C. Alves, A. Guedes, Corrosion and tribocorrosion behavior of Ti-B4C composite intended for orthopaedic implants, J. Mech. Behav. Biomed. Mater. 61 (2016) 152–163.
[13] Z. Liu, B. Gao, Y. Liu, S. Ji, Q. Ao, Research on preparation and characterization of Ti-Ti5Si3 gradient composite porous material via in-situ reactive process, J. Alloys Compd. 899 (2022) 163405.
[14] C. Yang, J.C. Wang, L.M. Kang, T. Chen, W.W. Zhang, L.H. Liu, Y.Y. Li, Improvement in tensile plasticity of pressureless-sintered TiBw/Ti composites by evading Kirkendall's pore, Powder Technol. 396 (2022) 444–448.
[15] Y. Zhang, Z. Wei, L. Shi, M. Xi, Characterization of laser powder deposited Ti-TiC composites and functional gradient materials, J. Mater. Process. Technol. 206 (1) (2008) 438–444.

[16] L. Bolzoni, N. Hari Babu, Engineering the Heterogeneous Nuclei in Al-Si alloys for Solidification control, Appl. Mater. Today 5 (2016) 255–259.

[17] N. Peillon, J.B. Fruhauf, S. Gourdet, J. Feraille, S. Saunier, C. Desrayaud, Effect of TiH2 in the preparation of MMC Ti based with TiC reinforcement, J. Alloys Compd. 619 (2015) 157–164.

[18] C. Zhang, Z. Guo, F. Yang, H. Wang, Y. Shao, B. Lu, In situ formation of low interstitials Ti-TiC composites by gas-solid reaction, J. Alloys Compd. 769 (2018) 37–44.

[19] X. Sun, Y. Han, S. Cao, P. Qiu, W. Lu, Rapid in-situ reaction synthesis of novel TiC and carbon nanotubes reinforced titanium matrix composites, J. Mater. Sci. Technol. 33 (10) (2017) 1165–1171.

[20] K. Vasanthakumar, N.S. Karthiselva, N.M. Chawake, S.R. Bakshi, Formation of TiCx during reactive spark plasma sintering of mechanically Milled Ti/carbon nanotube mixtures, J. Alloys Compd. 709 (2017) 829–841.

[21] W.H. Lee, J.G. Seong, Y.H. Yoon, C.H. Jeong, C.J. Van Tyne, H.G. Lee, S.Y. Chang, Synthesis of TiC reinforced Ti matrix composites by spark plasma sintering and electric discharge sintering: a comparative assessment of microstructural and mechanical properties, Ceram. Int. 45 (7) (2019) 8108–8114. Part A.

[22] J. Liu, M. Wu, Y. Yang, G. Yang, H. Yan, K. Jiang, Preparation and mechanical performance of graphene platelet reinforced titanium nanocomposites for high temperature applications, J. Alloys Compd. 765 (2018) 1111–1118.

[23] J.B. Fruhauf, J. Roger, O. Dezellus, S. Gourdet, N. Karnatak, N. Peillon, S. Saunier, F. Montheillet, C. Desrayaud, Microstructural and mechanical comparison of Ti+ 15%TiCp composites prepared by free sintering, HIP and extrusion, Mater. Sci. Eng., A 554 (2012) 22–32.

[24] B. He, K. Chang, W. Wu, C. Zhang, The Formation mechanism of TiC reinforcement and improved tensile strength in additive manufactured Ti matrix nanocomposite, Vacuum 143 (2017) 23–27.

[25] S. Valkov, D. Nedeva, V. Dunchev, F. Padikova, M. Ormanova, B. Stoyanov, N. Nedyalkov, Fabrication and characterization of Ti/TiC composite layers by an electron-beam surface modification, Coatings 13 (5) (2023) 951.

[26] A.H. Restrepo Carvajal, A.A. Zuleta Gil, J.G. Castaño G, J.M. Ríos Arbeláez, E. C. Bedoya, F.J. Bolívar Osorio, F.E. Echeverría, Influence of the milling conditions on the compressive strength of Ti/TiC composite materials sintered at atmospheric pressure, Ceram. Int. 49 (11) (2023) 17405–17414. Part A.

[27] K.D. Traxel, A. Bandyopadhyay, Influence of in situ ceramic reinforcement towards tailoring titanium matrix composites using laser-based additive manufacturing, Addit. Manuf. 31 (2020) 101004.

[28] X. Lu, Y. Pan, W. Li, M.D. Hayat, F. Yang, H. Singh, W. Song, X. Qu, Y. Xu, P. Cao, High-performance Ti composites reinforced with in-situ TiC derived from pyrolysis of polycarbosilane, Mater. Sci. Eng., A 795 (2020) 139924.

[29] B.H. Lohse, A. Calka, D. Wexler, Synthesis of TiC by controlled ball milling of titanium and carbon, J. Mater. Sci. 42 (2) (2007) 669–675.

[30] T. Threrujirapapong, K. Kondoh, H. Imai, J. Umeda, B. Fugetsu, Mechanical properties of a titanium matrix composite reinforced with low cost carbon black via powder metallurgy processing, Mater. Trans. 50 (12) (2009) 2757–2762.

[31] C. Even, C. Arvieu, J.M. Quenisset, Powder route processing of carbon fibres reinforced titanium matrix composites, Compos. Sci. Technol. 68 (6) (2008) 1273–1281.

[32] E. Ghasali, M.S. Ali Nezhad, S. Ghazvinian, Preparation of Ti-based laminated composites through spark plasma sintering with different carbon sources as the bonding layer, Ceram. Int. 45 (11) (2019) 14045–14057.

[33] F. Sun, L. Huang, R. Zhang, S. Wang, S. Jiang, Y. Sun, Q. An, Y. Jiao, L. Geng, In-situ synthesis and superhigh modulus of network structured TiC/Ti composites based on diamond-Ti system, J. Alloys Compd. 834 (2020) 155248.

[34] A. Singh, H.S. Dhami, M.K. Sinha, R. Kumar, Evaluation and comparison of mineralogical, micromeritics and rheological properties of waste machining chips, coal fly ash particulates with metal and ceramic powders, Powder Technol. 408 (2022) 117696.

[35] A. Singh, J. Singh, H.S. Dhami, M.K. Sinha, K. Viswanathan, R. Kumar, Quantifying the influences of coal fly ash on rheological and compaction behaviour of iron powder and mild steel machining chips, Adv. Powder Technol. 33 (11) (2022) 103819.

[36] A. Singh, M.K. Sinha, V. Jagota, R. Kumar, Production, characterisation and utilisation of grinding swarf/feedstock for synthesis of metal matrix composite through powder metallurgy process: a short communication, Sādhanā 47 (3) (2022) 160.

[37] M.T. Jia, B. Gabbitas, L. Bolzoni, Evaluation of reactive induction sintering as a manufacturing route for blended elemental Ti-5Al-2.5Fe alloy, J. Mater. Process. Technol. 255 (2018) 611–620.

[38] S. Raynova, Y. Collas, F. Yang, L. Bolzoni, Advancement in the pressureless sintering of CP titanium using high-frequency induction heating, Metall. Mater. Trans. 50 (10) (2019) 4732–4742.

[39] H.-C. Kim, D.-K. Kim, K.-D. Woo, I.-Y. Ko, I.-J. Shon, Consolidation of binderless WC-TiC by high frequency induction heating sintering, Int. J. Refract. Metals Hard Mater. 26 (1) (2008) 48–54.

[40] R. Boyer, G. Welsch, E.W. Collings, in: A. International (Ed.), Materials Properties Handbook: Titanium Alloys, Ohio, USA, 1998.

[41] S. Raynova, F. Yang, L. Bolzoni, Mechanical behaviour of induction sintered blended elemental powder metallurgy Ti alloys, Mater. Sci. Eng., A 799 (2021) 140157.

[42] H. Wang, Z.Z. Fang, P. Sun, A critical review of mechanical properties of powder metallurgy titanium, Int. J. Powder Metall. 46 (5) (2010) 45–57.

[43] L. Bolzoni, M. Paul, F. Yang, Effect of combined lean additions of isomorphous and Eutectoid Beta stabilisers on the properties of titanium, J. Mater. Res. Technol. 21 (2022) 3828–3843.

[44] M.V. Barros, R. Salvador, A.C. de Francisco, C.M. Piekarski, Mapping of research lines on circular economy practices in Agriculture: from waste to energy, Renew. Sustain. Energy Rev. 131 (2020) 109958.

[45] Y. Alshammari, M. Jia, F. Yang, L. Bolzoni, The effect of $\alpha+\beta$ forging on the mechanical properties and microstructure of Binary titanium alloys produced via a cost-effective powder metallurgy route, Mater. Sci. Eng., A 769 (2020) 138496.

[46] V. Imayev, R. Gaisin, E. Gaisina, R. Imayev, H.J. Fecht, F. Pyczak, Effect of hot forging on microstructure and tensile properties of Ti-TiB based composites produced by casting, Mater. Sci. Eng., A 609 (2014) 34–41.

[47] L.J. Huang, S. Wang, Y.S. Dong, Y.Z. Zhang, F. Pan, L. Geng, H.X. Peng, Tailoring a novel network reinforcement architecture exploiting superior tensile properties of in situ TiBw/Ti composites, Mater. Sci. Eng., A 545 (2012) 187–193.