

Uptake of iron and its effect on grain refinement of pure magnesium by zirconium

P. Cao, Ma Qian, D. H. StJohn and M. T. Frost

The uptake of iron by molten magnesium from uncoated new mild steel crucibles at temperatures 680 °C, 730 °C, and 780 °C has been investigated. It was shown that the uptake of iron was sluggish at 680 °C and the use of 0.05% zirconium addition could effectively suppress the increase in iron content within the first 2 h of holding at temperature. Rapid and severe uptake of iron was observed at 780 °C. As a consequence, it was found that the grain refinement of pure magnesium achieved by 1% zirconium addition nearly vanished after 60 min hold at 780 °C due to the depletion of soluble zirconium. The uptake of iron at 730 °C was conspicuous but it was still controllable by use of 0.05% zirconium addition within the first 60 min of holding at temperature. The work conducted using an aluminium titanite crucible and a boron nitride coated mild steel crucible at 730 °C further confirmed the highly detrimental influence of the uptake of iron on the grain refinement of pure magnesium by zirconium. The characteristic zirconium rich coring structures developed from circular to rosette like when the melt was held at 730 °C in an uncoated mild steel crucible, while no such evolution was observed when held in an aluminium titanite crucible at the same temperature. Recommendations to minimise the consumption of zirconium by the uptake of iron were made based on the results obtained from this investigation. The mechanism of grain refinement of magnesium by a low concentration of zirconium is discussed.

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Keywords: Magnesium, Zirconium, Grain refinement, Iron

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Introduction

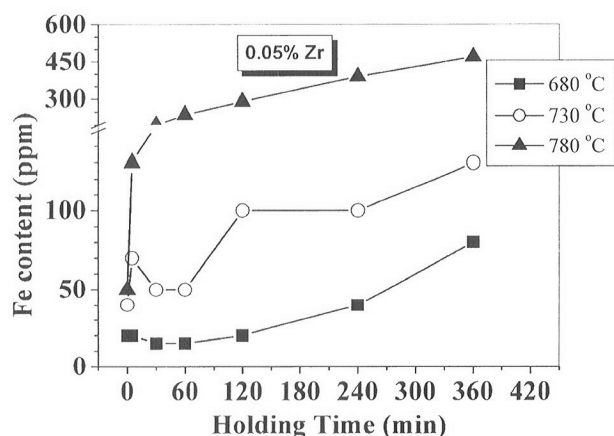
Zirconium is a potent grain refiner for magnesium alloys that do not contain aluminum such as Mg–Zn or Mg–RE–Zn alloys with or without calcium (zirconium forms stable intermetallic phases with aluminum).^{1–3} Zirconium is also a powerful iron removal agent. It reacts with any iron in molten magnesium (magnesium alloys containing zirconium normally contain less than 50 ppm of iron).⁴ Because of this, when introduced into a magnesium melt, zirconium will first remove iron from the melt. The resultant very low iron content will consequently provide an aggressive driving force for the uptake of iron by the melt from the alloying vessel, which is normally made of mild steel. This uptake of iron has two consequences. The first is the rapid consumption of zirconium in the melt and the second is the increased buildup of sludge at the bottom of the crucible due to the formation of iron–zirconium intermetallic compounds. As such, the uptake of iron has been one of the key issues affecting alloying zirconium to magnesium in the commercial production of magnesium alloys containing zirconium.

In order to offset the influence of the uptake of iron on the consumption of zirconium, an excess of zirconium is usually alloyed to the melt in practice. Although this remedy has technically worked, zirconium is a very expensive alloying material. Moreover, the use of excessive zirconium often produces a large amount of sludge, leading to increased operating cost and low yield of expensive magnesium alloys containing zirconium. Unfortunately, few economically viable alternative materials that are suitable for processing molten magnesium currently exist other than the use of mild steel crucibles. On the other hand, although the detrimental influence of the uptake of iron has long been recognised in the commercial production of magnesium alloys containing zirconium, little detailed information can be found in the literature about this important issue. This work has been

carried out to investigate the influence of the uptake of iron on the consumption of zirconium and the subsequent grain refinement of the final as cast alloy under various operating conditions. For comparison, iron free ceramic crucibles have also been used. Recommendations to minimise the consumption of zirconium by the uptake of iron are made based on the results obtained from this investigation.

Experimental procedure

Melting of magnesium was conducted in an electrical resistance furnace with temperature control in the range of ± 3 –5 K. The protective cover gas used was 1.0% SiF₆ in a mixture of 49% dry air and 50% CO₂. The uptake of iron was investigated at three different temperatures, 680 °C, 730 °C, and 780 °C. Three new mild steel crucibles (inner diameter 130 mm; depth 240 mm) were used in order to avoid the seasoning effect of zirconium that occurs from the repeated use of steel crucibles.⁴ Commercial purity magnesium ingots were used as the base material. The zirconium was introduced in the form of a Mg–30Zr master alloy, named AM-cast.⁵ Two tests were conducted at each temperature and each new crucible was thus used twice. In each test, the weight of magnesium charge was ~4 kg. The depth of melt in the crucible was ~190 mm. The specific contact surface, calculated as the ratio of the total melt/crucible contact surface to the volume of the melt, was ~0.36 cm^{–1}. In the first test conducted at each temperature, 0.05% zirconium was added while in the second test 0.25% zirconium was used. The melt was hand stirred using a boron nitride (BN) coated mild steel spoon for 5 min at ~100 strokes min^{–1} following addition of the AM-cast master alloy. After that, the melt was held at temperature for 6 h and small cone samples (diameter 20 mm × diameter 30 mm × height 25 mm) were taken from the top of the melt at different holding times using a BN coated cone ladle.



1 Uptake of iron by molten magnesium at 680 °C, 730 °C, and 780 °C with 0.05%Zr addition in each case

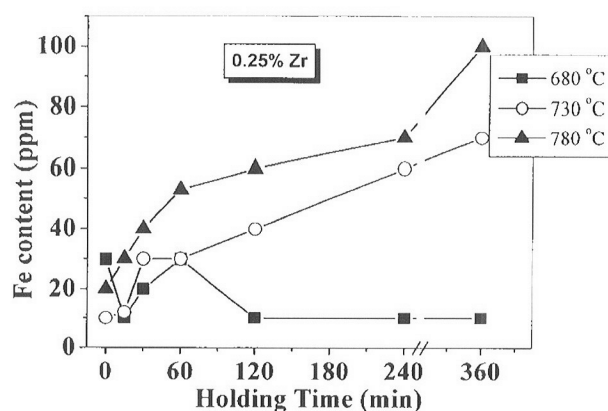
Grain refinement experiments were conducted at 680, 730, and 780 °C using three other new mild steel crucibles for comparison. The zirconium addition was fixed at 1% in these tests. Similar melting and sampling procedures were followed but the holding time was limited to 2 h in each test. To further clarify the influence of the uptake of iron on the grain refinement of pure magnesium by zirconium, similar grain refinement tests were conducted using aluminium titanite crucibles (nominal composition: AlTi_2O_5) with the dimensions diameter 80 mm \times depth 190 mm and a BN coated mild steel crucible.

Each cone sample was sectioned into halves along its axis. One half was ground and polished for metallographic analysis and the other half for wet chemical analysis. The etchant used contained 10 mL acetic acid, 4.2 g picric acid, 10 mL H_2O , and 70 mL ethanol. The grain size was measured from the central region of each sample in accordance with the intercept method described in the ASTM standard E112–96. The grain structures of each sample were analysed using a Philips XL–30 scanning electron microscope (SEM) in the backscattered electron (BSE) mode, assisted by an energy dispersive X-ray spectrometer (EDS). Quantitative analyses were performed using a JXA-8800L electron probe microanalyser (EPMA) with a beam voltage of 15 kV. The iron and zirconium contents were chemically determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) based on an approach previously developed for the determination of soluble zirconium in magnesium alloys.⁶

Results

UPTAKE OF IRON FROM MILD STEEL CRUCIBLES

Figure 1 shows the uptake of iron as a function of holding time at each of the three temperatures 680, 730, and 780 °C with 0.05% zirconium addition in each case. A gradual increase in the iron content was observed after 2 h at 680 °C but before that little increase was detected. The total increase in the iron content registered 60 ppm after 6 h at 680 °C. By contrast, a conspicuous increase in the iron content was observed after 2 h at 730 °C. The length of time registering little increase in the iron content was reduced from 2 h at 680 °C to 1 h at 730 °C. When alloyed and held at 780 °C, the melt demonstrated a rapid and significant increase in the iron content with increasing holding time. The iron content increased by 80 ppm within the first 5 min at 780 °C. In fact, the increase in the iron content started before the melt reached 780 °C, as can be inferred from the data corresponding to zero holding time shown in Fig. 1,



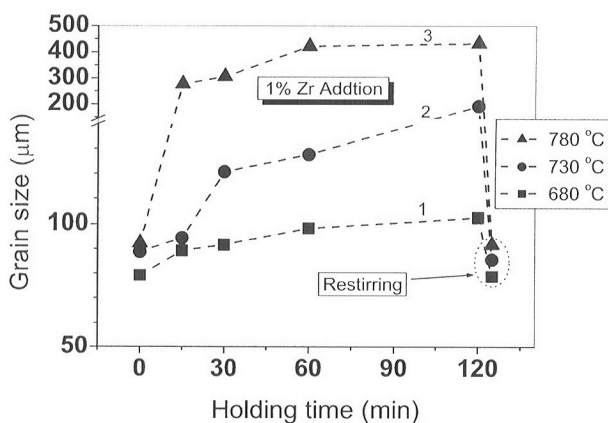
2 Uptake of iron by molten magnesium at 680 °C, 730 °C and 780 °C with 0.25% Zr addition in each case

suggesting that the 0.05% zirconium addition had been consumed before the melt reached 780 °C.

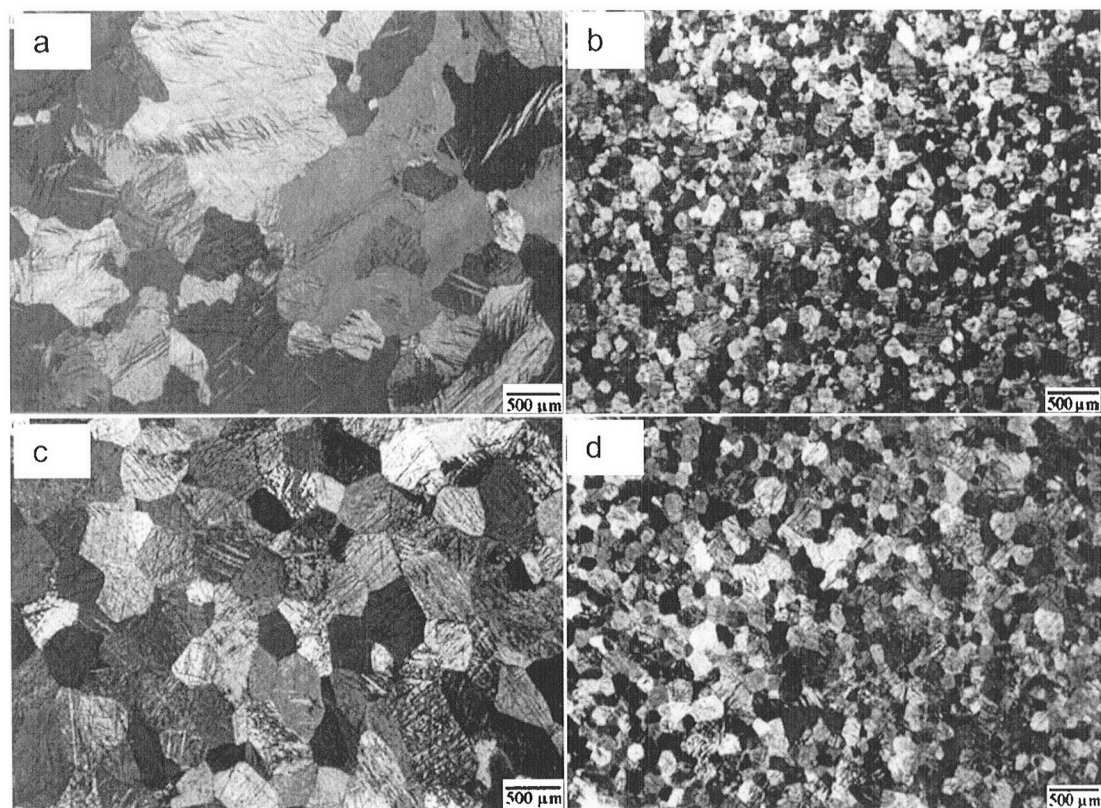
The increase in the iron content with 0.25% zirconium addition was much slower at each temperature, as shown in Fig. 2. Little increase in the iron content was observed throughout 6 h of holding at 680 °C, while at 730 °C the increase in Fe content was limited to 60 ppm after 6 h at temperature. The use of 0.25% zirconium also significantly suppressed the increase in the iron content at 780 °C. For example, the Fe content increased mildly from 20 to 100 ppm after 6 h at 780 °C compared to a dramatic increase from 50 to 470 ppm in the case of 0.05% zirconium addition.

GRAIN REFINEMENT OF PURE MAGNESIUM BY ZIRCONIUM WHEN ALLOYED IN UNCOATED MILD STEEL CRUCIBLES

Figure 3 shows the average grain size measured on samples taken from the grain refinement tests conducted at 680, 730, and 780 °C. In each test, the first sample was taken immediately after 5 min manual stirring. Similar to the observations made from the use of boron nitride coated mild steel crucibles,³ the average grain size was found to increase with increasing holding time at each temperature. However, the growth rate was obviously different at each temperature. As shown in Fig. 3, the average grain size increased from 79.2 to 102.7 μm after the melt was held for 2 h at 680 °C (curve 1) while an increase from 89 to 190 μm was observed after the same holding time at 730 °C (curve 2). On the other hand, the 2 h of holding at 780 °C led to a dramatic increase



3 Average grain size as a function of holding time at 680 °C, 730 °C, and 780 °C when uncoated mild steel crucibles were employed



4 Typical views of the grain structures of samples taken at 780°C a before adding zirconium, average grain size (AGS) 860 μm; b after 5 min stirring following addition of zirconium, AGS=92.3 μm; c after 2 h of holding, AGS=433 μm; d after restirring the melt for 2 min, AGS=91.7 μm. An uncoated mild steel crucible was used in this test

in the average grain size from 92 to 433 μm (curve 3). Table 1 shows the chemical analytical results of both soluble and total zirconium contents of samples taken before settling and after 2 h of settling. There was a significant decrease in the soluble zirconium content after 2 h of settling at 780°C (down from 0.36% to 0.19%), while the decrease in the soluble zirconium content at 680°C was negligible. At 730°C, the soluble zirconium content registered a limited decrease from 0.42% to 0.37%. This is a tolerable loss, suggesting that if a magnesium melt is alloyed and held at 730°C in an uncoated mild steel crucible for no more than 2 h, then the consumption of zirconium by the uptake of iron will not be a major concern. The total zirconium content dropped conspicuously at each temperature due to the settling of undissolved zirconium particles.^{3,6–9}

Figure 4a–d show typical views of the grain structures of samples taken before adding zirconium, after 5 min of stirring following addition, after 2 h of settling at 780°C, and after restirring the melt. It has been shown that restirring the melt can bring the average grain size back to the level obtained before settling when alloyed in boron nitride coated crucibles or magnesia crucibles due to the positive role of undissolved zirconium particles.^{6–9} As shown in Fig. 3, restirring the melt also worked to restore the average grain size of the final alloy at each temperature in this investigation. The soluble and total zirconium contents of

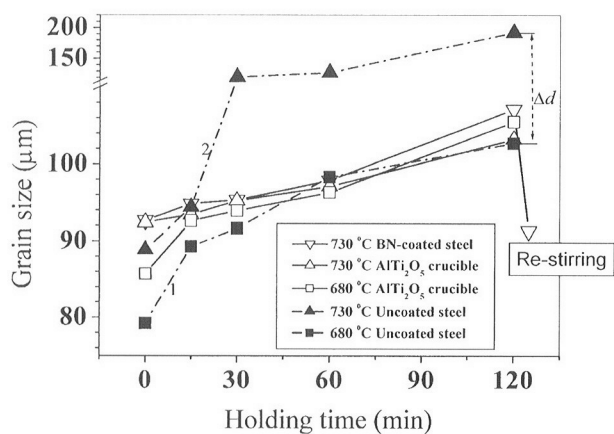
the samples taken after restirring the melt have also been listed in Table 1. As can be seen, the reason why restirring the melt worked at 680°C and 730°C was due primarily to the increased total zirconium content, while at 780°C it was because of the obvious increase in both the soluble zirconium content and the total zirconium content, of which the former played a more profound role.^{6–9}

GRAIN REFINEMENT OF PURE MAGNESIUM BY ZIRCONIUM WHEN ALLOYED IN IRON FREE CERAMIC CRUCIBLES AND COATED MILD STEEL CRUCIBLES

In order to further clarify the influence of the uptake of iron, similar tests were carried out using iron free aluminum titanite crucibles at 680°C and 730°C and a boron nitride coated mild steel crucible at 730°C. The results obtained from these tests are shown in Fig. 5. For easy comparison, the data shown in Fig. 3 for curves 1 and 2 are replotted in Fig. 5. As expected, not much difference was observed at 680°C because of the less severe uptake of iron at this temperature. However, the difference was conspicuous at 730°C. The use of an aluminum titanite crucible and a boron nitride coated mild steel crucible led to a much slower increase in the average grain size than did the use of an uncoated mild steel crucible. The limited increase in the

Table 1 Soluble and total zirconium contents of samples taken from grain refinement tests conducted at different temperatures using uncoated mild steel crucibles and aluminium titanite crucible. Analytical method: ICP-AES

Crucible	Temperature	Before settling		2 h of settling		Restirring	
		Soluble Zr, %	Total Zr, %	Soluble Zr, %	Total Zr, %	Soluble Zr, %	Total Zr, %
Uncoated mild steel	680 °C	0.43	0.62	0.41	0.43	0.37	0.58
	730 °C	0.42	0.65	0.37	0.41	0.37	0.57
	780 °C	0.36	0.62	0.19	0.30	0.34	0.46
Aluminium titanite	730 °C	0.45	0.62	0.45	0.48	0.48	0.60



5 Average grain size as a function of holding time at 680°C and 730°C when aluminium titanite crucible and boron nitride coated steel crucible used. 1%Zr was alloyed to the melt in each test. Curves 1 and 2 reproduced from Fig. 3 for comparison

average grain size observed from the use of both an aluminum titanite crucible and a BN coated crucible is mainly attributed to the settling of undissolved zirconium particles in the melt.⁷⁻⁹ By contrast, the difference in grain size Δd arising from the use of an uncoated mild steel crucible and an aluminum titanite crucible at 730°C, as shown in Fig. 5, is due primarily to the uptake of iron by molten magnesium from the uncoated mild steel crucible at 730°C. Figure 6a–c show typical views of the grain structures of respective samples taken from the test conducted at 730°C in an aluminum titanite crucible.

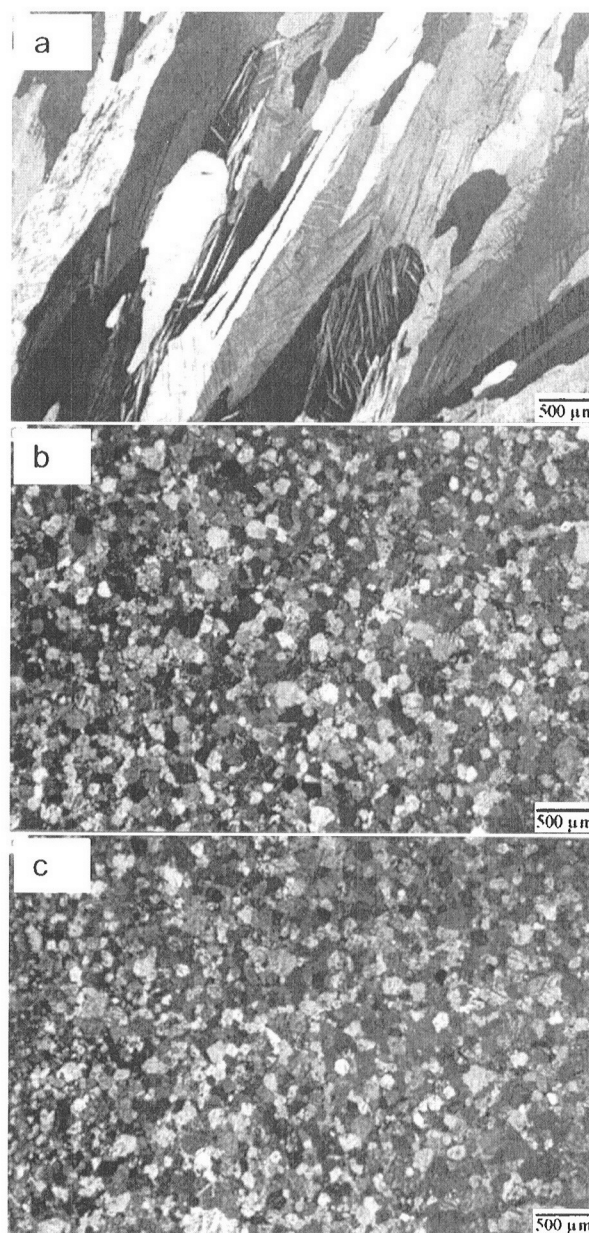
TYPICAL GRAIN STRUCTURES

The characteristic zirconium rich coring structures of a magnesium alloy containing zirconium are readily visible when observed under an SEM in the BSE mode.¹⁰ Figures 7a–d show typical views of the zirconium rich coring structures observed in samples taken from the grain refinement test conducted at 730°C using an uncoated mild steel crucible. The zirconium rich cores were generally elliptical or circular after 5 min stirring following the addition of 1% zirconium (Fig. 7a). Little change was observed in their morphologies after 30 min of holding at 730°C except for a decrease in the number density (Fig. 7b). However, most of the elliptical or circular cores developed into rosette like structures after a further 30 min of holding at temperature (Fig. 7c). Similar observations were made from samples taken from the grain refinement test conducted at 780°C using an uncoated mild steel crucible except that the rosette like cores were observed after only 15 min hold at 780°C. By contrast, no such morphological changes were observed from samples taken from similar grain refinement tests conducted using an iron free aluminum titanite crucible, as shown in Fig. 8a and b. Quantitative compositional analyses by EPMA showed that about 0.6–1.5% zirconium was detected in the central regions of some of the circular cores observed in the sample shown in Fig. 7b, whereas 0.37–0.5%Zr was observed in the central regions of some of the rosette like cores in the sample shown in Fig. 7c.

Discussion

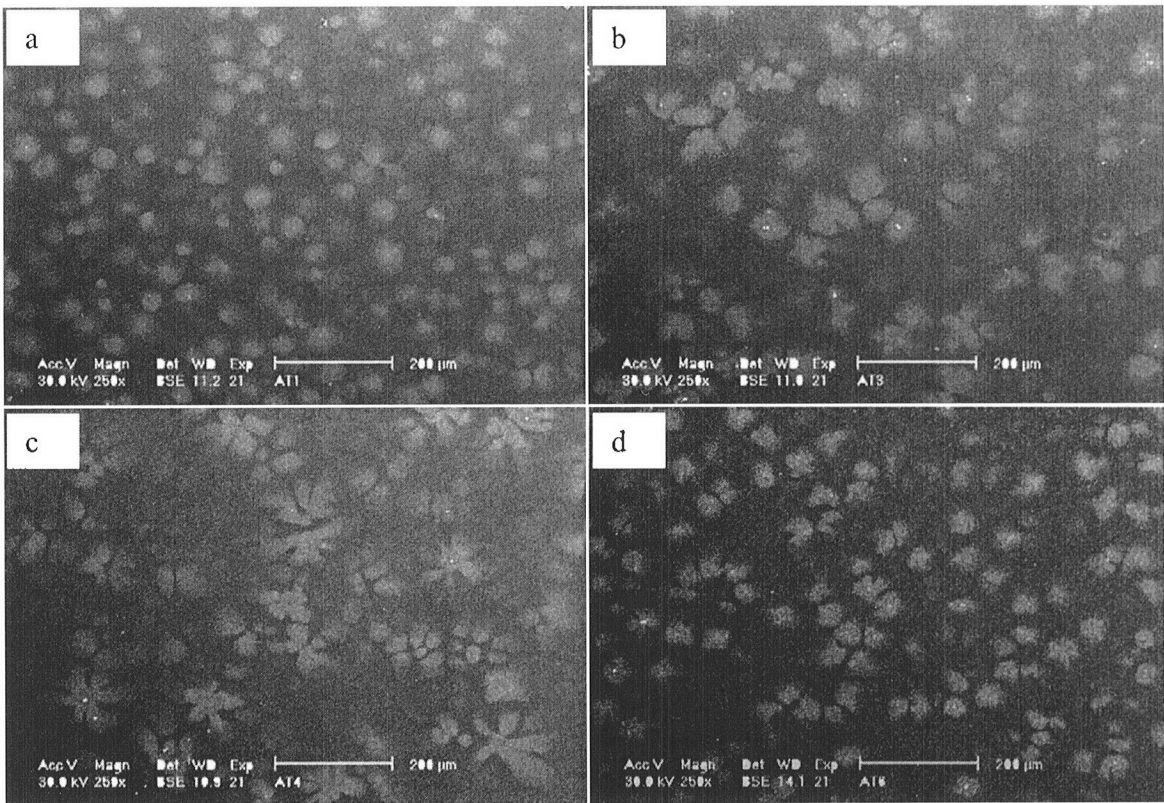
CONSUMPTION OF SOLUBLE ZIRCONIUM BY THE UPTAKE OF IRON

It is known within the magnesium industry that zirconium removes iron from molten magnesium by forming Fe–Zr



6 Typical views of grain structure of samples taken from grain refinement test conducted at 730°C using aluminium titanite crucible: a before adding zirconium, AGS=1090 μm; b after 2 h settling at 730°C, AGS=103 μm; c after restirring melt for 2 min, AGS=91 μm

intermetallics and these intermetallic particles settle out very fast in molten magnesium due to their high densities. To confirm this understanding, two separate experiments were conducted at the 30 kg scale of magnesium melt using an uncoated mild steel crucible (diameter 250 mm; depth 500 mm). In each test, 30 kg of pure magnesium ingots containing 160–180 ppm of iron was melted at 730°C. Then 1%Zr was added to the melt in the form of a Mg–33.3Zr master alloy, followed by 10 min stirring at 250 rev min⁻¹ to assist the dissolution of zirconium. The melt was allowed to settle for 15 min before two plate samples (160 × 140 × 30 mm) were sand cast. A sludge sample was taken from the bottom of the crucible after casting. The iron and zirconium contents in both the plate sample and the sludge sample were analysed using a chemical approach developed previously.⁶ Table 2 shows the analytical results obtained from these samples. In both cases, a substantial difference was observed between the total iron content in the plate sample and the total iron content in the sludge



7 Morphological evolution of zirconium rich coring structures observed from samples taken from the grain refinement test conducted at 730 °C using uncoated mild steel crucible: *a* after 5 min stirring following addition of zirconium; *b* after 30 min of holding at temperature; *c* after 60 min of holding at temperature; *d* after restirring melt for 2 min

sample, where the total iron content refers to the sum of the iron in solution (i.e. the soluble iron) and the iron in various iron containing intermetallics (i.e. the insoluble iron). On the other hand, little difference was observed between the soluble iron content and the total iron content in each plate sample. These observations support the understanding that zirconium removes iron from molten magnesium by forming Fe–Zr intermetallics, which then quickly settle out in molten magnesium. The settling time is typically around 30 min after alloying a magnesium melt with zirconium in the commercial production of magnesium alloys containing zirconium in order to eliminate the undesirable Fe–Zr intermetallic particles and undissolved large zirconium particles. The exceedingly high zirconium contents detected in the sludge samples were due to settled undissolved zirconium particles.

According to the binary Fe–Zr phase diagram,¹¹ zirconium can form four different types of Fe–Zr intermetallic phases, namely, FeZr₃, FeZr₂, Fe₂Zr, and Fe₂₃Zr₆. However, it is not clear exactly what type of Fe–Zr intermetallic forms in molten magnesium. Early work by Schneider and Stendel⁴ shows that there is a mutual solubility relationship existing between zirconium and iron in molten pure magnesium. Figure 9 shows the mutual solubility relationships between zirconium and iron in the molten magnesium

at 700, 750, and 800 °C.⁴ Assuming the formation of a Fe–Zr intermetallic phase in molten magnesium is described by the following reaction



then the solubility product constant, *K*_{sp}, can be written as

$$K_{sp} = [\text{Fe}]^m [\text{Zr}]^n \quad \dots \quad (2)$$

where [Fe] and [Zr] are the concentrations of Fe and Zr in the melt. Using equation (2), the logarithms of the concentrations of Fe and Zr can be expressed linearly by

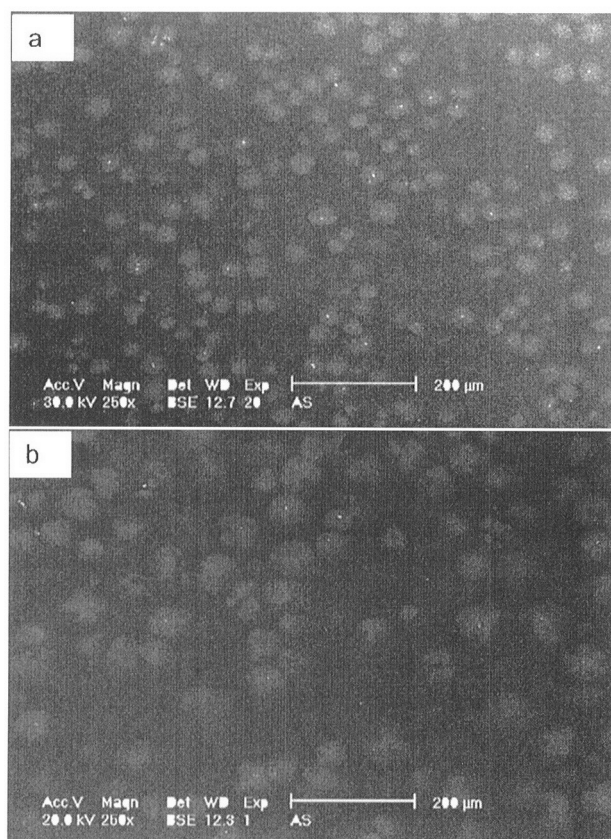
$$\log [\text{Zr}] = -\frac{m}{n} \log [\text{Fe}] + \frac{1}{n} \log K_{sp} \quad \dots \quad (3)$$

All of the mutual solubility relationships shown in Fig. 9 obviously obey the linear relationship predicted by equation (3). Moreover, the slope of each of the three lines shown in Fig. 9 was found to be just equal to –2, suggesting that Fe₂Zr is formed in molten magnesium in the temperature range between 700 and 800 °C rather than FeZr₃, FeZr₂ and Fe₂₃Zr₆. In this work, the consumption of soluble zirconium in the magnesium melt is regarded as a consequence of the formation of Fe–Zr intermetallic, probably Fe₂Zr. Transmission electron microscopy may be needed to clarify the nature of the intermetallic particles formed in the melt.

Table 2 Settling of Fe_mZr_n intermetallic particles in molten magnesium*

Trials	Sample	Soluble Fe, %	Total Fe, %	Soluble Zr, %	Total Zr, %
1	Plate sample†	<0.005	<0.005	0.43	0.52
	Sludge sample		0.56		18.2
2	Plate sample†	<0.005	<0.005	0.53	0.66
	Sludge sample		0.23		4.35

*In these two trials, 30 kg of magnesium ingot was melted at 730 °C using an uncoated mild steel crucible (diameter 250 mm, height 500 mm). 1%Zr was added to the melt followed by 120 rev min^{–1}. Plate samples were sand cast after the melt settled for 15 min.
†Dimensions of sand cast plate samples: 160 × 140 × 30 mm.

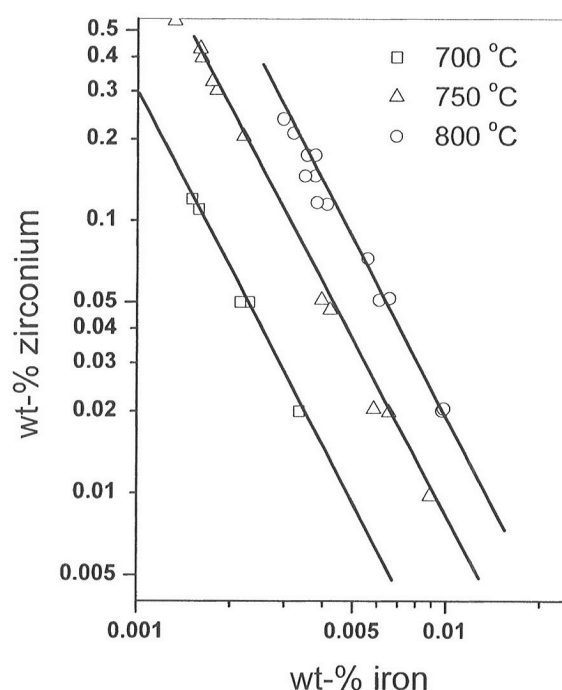


8 Typical views of zirconium rich coring structures observed from samples taken from grain refinement test conducted at 730 °C using aluminium titanite crucible: a after 5 min stirring following addition of zirconium; b after 2 h settling at 730 °C; 1%Zr was added to the melt in this test; zirconium rich cores remained circular or elliptical after 2 h settling at 730 °C

EFFECT OF UPTAKE OF IRON ON GRAIN REFINEMENT

It has been clarified that grain refinement of magnesium by zirconium is mainly attributable to the soluble zirconium content in the melt before casting, although insoluble zirconium as suitably sized undissolved zirconium particles also plays a positive role.^{2,6,8,9} As evident from comparing Figs. 1 and 3, there is good agreement between the trend in uptake of iron and the trend in increase in the average grain size at each temperature. Since the uptake of iron by a low iron magnesium melt from a mild steel crucible is unavoidable at high temperature (≥ 730 °C), the procedures used to alloy zirconium to magnesium should be designed to ensure a minimal consumption of zirconium based on the dissolution kinetics of zirconium in molten magnesium and the kinetics of the uptake of iron. For example, it has been found that stirring or puddling plays a key role in assisting the dissolution of zirconium into molten magnesium when introduced in the form of a Mg–Zr master alloy, and without proper stirring or puddling little dissolution occurs.^{9,12} In addition, it has been found that melt temperature has little influence on the dissolution of a Mg–Zr master alloy in molten magnesium in the range 680–780 °C.⁹ Therefore, in order to reduce the consumption of zirconium, the master alloy should be introduced into the melt immediately before casting at the lowest melt temperature that is suitable for casting, for example, 730 °C, if practical. Also, stirring or puddling should be applied about 30 min before casting.

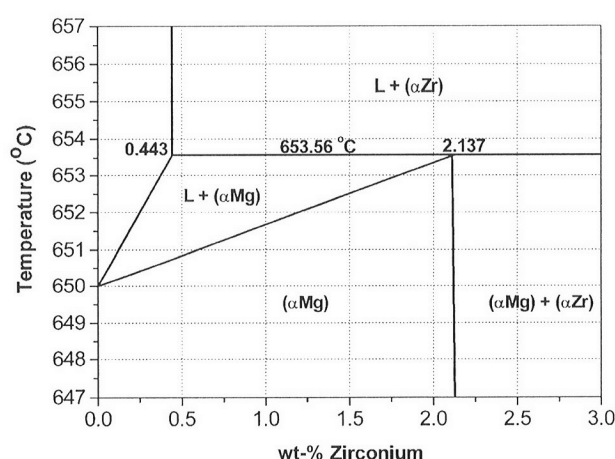
The gradual increase in the average grain size shown in Fig. 5 for the two tests conducted using an aluminium



9 Mutual solubility relationship between Zr and Fe in molten magnesium at different temperatures (replotted from Ref. 4)

titanite crucible and the test conducted using a BN coated mild steel crucible is mainly due to the settling of undissolved zirconium particles with increasing holding time in the crucible,^{6–9} as can be judged from the soluble and total zirconium results shown in Table 1. This is similar to the gradual increase in the average grain size observed at 680 °C when a mild steel crucible was used (Fig. 3). It can also be seen from Fig. 5 that the growth rate of grain size over the holding time was nearly the same in all cases studied at both 680 °C and 730 °C. This coincides with the theoretical predictions that melt temperature has a negligible effect on the settling behaviour of undissolved zirconium particles in molten magnesium.⁷

Restirring the melt can bring settled undissolved zirconium particles from the bottom into the melt, therefore providing more nucleants for magnesium grains during the solidification of the final alloy. This is the mechanism by which restirring works when a ceramic crucible or a well coated mild steel crucible is used. However, the mechanism differs when an uncoated mild steel crucible is employed, particularly when there is severe uptake of iron. This has been the case for the test conducted at 780 °C, where the soluble zirconium content decreased from 0.36% to 0.19% after 2 h holding at temperature and increased to 0.34% after restirring the melt (Table 1). In these cases, restirring has played a role in both reactivating the dissolution of zirconium into the melt and bringing the particles from the bottom back to the body of the melt. It should be noted that apart from bringing settled undissolved zirconium particles from the bottom into the melt, restirring also simultaneously brings settled Fe–Zr intermetallic particles back to the melt. The possibility that these Fe–Zr intermetallic particles may be returned to the melt, either partially or completely, by vigorous restirring cannot be excluded. This will be governed by the mutual solubility relationship existing between Fe and Zr in the melt, as shown in Fig. 9. Considering that the iron level in a magnesium alloy containing zirconium is typically less than 50 ppm, fine experimental work is needed to clarify this point.

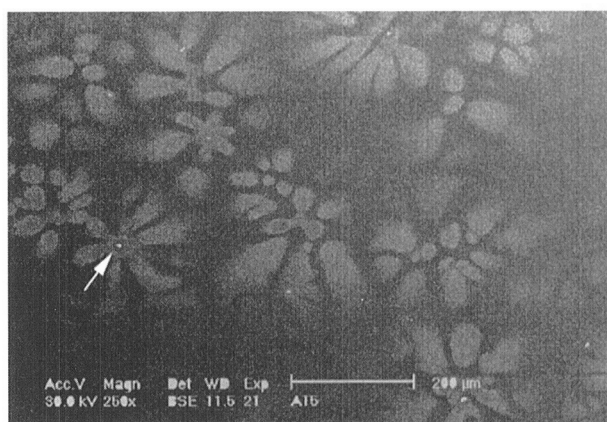


10 Portion of Mg rich region of the Mg-Zr phase diagram (after Refs. 14,15)

MECHANISM OF GRAIN REFINEMENT OF MAGNESIUM BY LOW CONCENTRATION OF ZIRCONIUM

It is generally agreed that the grain refinement of magnesium by zirconium occurs via a peritectic reaction.^{2,10,13} According to the Mg-Zr phase diagram,^{14,15} in order for the peritectic reaction to occur, the melt needs to contain ~0.45% zirconium in solution when cooled in an equilibrium state (Fig. 10). However, obvious grain refinement is observed with a low concentration of zirconium in the liquid. Figure 11 shows a typical view of the microstructure of a sample taken from the grain refinement test conducted at 780°C using an uncoated mild steel crucible. The melt was held for 2 h at 780°C before the sample was taken. As a result, the sample contains only 0.19% zirconium in solution due to the uptake of iron (Table I). The total zirconium content is 0.30%, which is also well below 0.45%. As shown in Fig. 11, characteristic zirconium rich structures still form in this alloy. Quantitative microprobe analyses showed that almost all of the soluble zirconium contained in the alloy is concentrated in these structures and other areas basically contain no zirconium. This is similar to the observations made previously for the case of a high zirconium content alloy.¹⁰ In addition, fine zirconium particles can also be found at the centres of the rosette like zirconium rich structures shown in Fig. 11. For example, a well developed rosette like structure, which contains a tiny zirconium particle at the centre, a circular core surrounding the particle, and a number of dendrite branches surrounding the core, has been captured in Fig. 11 (the arrowed structure). The rosette like zirconium rich structures shown in Fig. 11 should be similar in nature although most of them do not show a particle at the centre in this particular field of view. This is because only those particles that happen to have been sectioned through are visible in the subsequently polished microstructure. The major difference between the zirconium rich structures shown in Fig. 11 and those shown in Fig. 7a are therefore the morphologies of the zirconium rich structures due probably to the different zirconium and iron contents in the melt before casting.

The presence of zirconium particles and a low zirconium matrix indicates that zirconium has not dissolved sufficiently to bring the liquid to the equilibrium content of 0.45%Zr (Fig. 10). Therefore, a melt that contains much less than 0.45%Zr, say 0.2%, is stable to a temperature below the α -Mg liquidus at approximately 652°C, α -Mg begins to solidify according to the Mg-Zr phase diagram (Fig. 10). Since the zirconium particles are excellent nucleants for α -Mg, the α -Mg grains will nucleate on zirconium



11 Rosette like zirconium rich structures observed in sample containing only 0.19% soluble zirconium. Note that the structure arrowed in this micrograph contains a tiny zirconium particle at the centre, a circular core surrounding the particle, and developed dendrite branches surrounding the core

particles in the melt. A peritectic reaction is not necessary and plays no part in this process. In fact, even if the liquid composition reached equilibrium during solidification, a peritectic reaction is probably not likely to occur as observed in other peritectic systems such as Al-Ti alloys.¹⁶ The solidification process of a low zirconium content magnesium alloy is therefore simply the crystallisation of α -Mg grains onto the zirconium particles, which are excellent nucleants for α -Mg. It is proposed that the rosette morphology of the zirconium rich α -Mg is related to the soluble zirconium and iron contents in the melt before casting (Fig. 11). Further work is required to fully understand the formation of rosette like zirconium rich structures in low zirconium content magnesium alloys.

Summary

1. The uptake of iron by molten magnesium from uncoated mild steel crucibles was sluggish at 680°C. The use of 0.05%Zr addition could effectively suppress the increase in the iron content within the first 2 h of hold at 680°C. Little increase in the iron content was observed throughout the 6 h of holding at 680°C when 0.25%Zr was alloyed to the melt.

2. Rapid and severe uptake of iron was observed at 780°C. The uptake of iron at 730°C was conspicuous but was still controllable by use of 0.05%Zr within the first hour of holding at 730°C. The use of 0.25%Zr could significantly suppress the increase in the iron content at both temperatures.

3. The uptake of iron demonstrated a significant influence on the grain refinement of pure magnesium by zirconium at both 730°C and 780°C. It was found that the grain refinement of pure magnesium achieved by 1%Zr addition nearly vanished after 1 h of holding at 780°C due to the uptake of iron. The work conducted using an aluminium titanite crucible and a boron nitride coated mild steel crucible at 730°C further confirmed the highly detrimental influence of the uptake of iron. In these experiments, the soluble zirconium remained constant and excellent grain refinement was readily restored by stirring and bringing the zirconium particles back to the melt.

4. The zirconium rich coring structures were observed to develop from circular to rosette like when the melt was held in an uncoated steel crucible at 730°C and 780°C due to the consumption of soluble zirconium and the uptake of

iron. No such morphological evolution was observed when aluminium titanite crucibles were used. It is proposed that the rosette morphology of zirconium rich α -Mg is related to the soluble zirconium and iron contents in the melt before casting.

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