

Full Length Article

# A novel approach to melt purification of magnesium alloys

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## Abstract

A novel low-cost method for melt purification of magnesium alloys, the melt self-purifying technology (MSPT), has been developed successfully based on a low temperature melt treatment (LTMT) without adding any fluxes. The iron solubility in the molten liquid of magnesium and its alloys, and the settlement velocity of iron particles were calculated. It is shown that the low temperature melt treatment is an effective method to decrease the impurity Fe content in magnesium and its alloys. Without any additions, the Fe content in the AZ31 alloy was reduced to 15 ppm from the initial 65 ppm, and the Fe content in the AZ61 melt was decreased to 20 ppm from the initial 150 ppm after the low temperature melt treatment. The results also showed that the Fe content in AM60 and AM50 dropped to 15 and 18 ppm, respectively, from the initial 150 ppm after the low temperature melt treatment. For ZK 60, the Fe content in the melt down to less than 5 ppm was achieved. After the low temperature melt treatment, the Si content in the above alloys was also decreased obviously.

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## 1. Introduction

The demand for applications of magnesium alloys in transport and structural fields is continuously increasing due to their low density and high strength-to-weight ratio [1–4]. However, their poor corrosion resistance and low plastic formability limit the viability of the increasing magnesium usage. The corrosion rate of commercial magnesium alloys is usually high in inorganic acidic and neutral solutions [5–10], which results from its high intrinsic dissolution tendency. It was reported that the presence of impurities (Fe, Si, Cu and Ni) with high standard electrode potential and second phases acting as local cathodes caused local galvanic acceleration of corrosion [5–7]. Among these impurities, Fe element, even with a small amount, can severely deteriorate the corrosion resistance of magnesium alloys [2].

Liu et al. [11,12], and Inoue et al. [13] reported that the corrosion rate of the alloy is substantially high due to its contamination with Fe, Ni, or Cu above the tolerance limit. Liu et al. [11,12] theoretically explained the corrosion tolerance limit for Fe through the Mg–Fe phase diagram. It is reported that the corrosion resistance of magnesium alloys is possibly not lower than that of aluminum alloys if the content of iron in magnesium alloys is less than 20 ppm [14]. Additionally, it has been reported that impurity Fe has a harmful effect on grain refinement, mechanical properties and rolling formability in AZ and ZK alloys [15–17]. Therefore, Fe content must be controlled to an extremely low level [2,18] in order to further improve the properties of magnesium alloys, especially corrosion resistance and formability.

At present, the purity of commercial primary magnesium used in industrial production of magnesium alloys is very high. The content of impurity iron in the primary magnesium is usually higher than 100 ppm, which is thought to be one of the main causes of poor corrosion resistance and low plasticity in commercial magnesium alloys. So far, several methods have been used to purify the magnesium alloy melt. The most conventional way of melt purification is adding fluxes to the melt during melting, which contains chloride salts [19,20] or fluoride salts [21]. It is true that some commercial fluxes can effectively

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remove nonmetallic inclusions from the melt of magnesium alloys, but the effects of these flux additions on decreasing the impurity elements of magnesium melt are not very satisfactory [22]. What is more, using fluxes may result in loss of alloying elements from the melt and secondary pollution through bringing in some nonmetallic impurity elements like F and Cl. For example. It is reported that  $\text{MgCl}_2$  in the flux may cause the loss of Gd and Y from the melt [19–21,23,24]. The Mn addition with reasonable ratio of Fe/Mn has been employed to remove Fe [22,25], but it is difficult to control the ratio of Fe/Mn [26–28], and the content of iron in the melt is still unsatisfactory by using normal melting and casting process. In addition, Haitani et al. and Tamura et al. found that manganese disturbed grain refinement of magnesium alloys [29,30]. Zr, Ti, B or their compounds have also been used to remove Fe, and Atrens's group [5,11,18] has done excellent work on purification of magnesium alloy with Zr addition in lab in the past five years. However, the content of iron in commercial magnesium alloys is usually still higher than 20 ppm after using these additions when traditional melting and casting process is conducted [18,25,27,31–40]. In fact, little work has been carried out about the effects of low temperature melt treatment on the efficacy of removing Fe from the melt.

In order to overcome the disadvantages of flux additions and to decrease the content of iron in the melt to a much lower level, a novel approach for melt purification without adding fluxes, i.e. the melt self-purifying technologies (MSPT), has been developed by using low temperature melt treatment (LTMT), which is obviously different from traditional high temperature treatment methods [26,27,34–39]. The effects of different melt treatment temperature and the combination with Mn/Zr additions on the Fe content in the melt of magnesium and its alloys were investigated in the present work, and the super high-purity alloys with less than 5 ppm Fe were prepared.

## 2. Experimental procedures

### 2.1. Melt purification processes

The commercial purity magnesium, commercial purity AZ31, AZ61, AZ91, AM50, AM60 and ZK60 magnesium alloys were used in the present work. The used materials were melted in a stainless steel crucible in an electric-resistant furnace under an inert atmosphere with a  $\text{CO}_2$  and  $\text{SF}_6$  mixture. For commercial magnesium, when the temperature reached 730 °C, the magnesium melt was stirred for 5 min and subsequently held at 710 °C for 45 min, then cooled to different relative low temperatures of 650–690 °C for 30–90 min. For AZ31, AZ61, AZ91, AM50 and AM60 magnesium alloys, when the temperature reached 750 °C, the magnesium melt was stirred for 5 min and then cooled to different relative low temperatures of 610–670 °C for 30–90 min. For ZK60 alloy, when the temperature reached 760 °C, the magnesium melt was stirred for 5 min and subsequently held at 630–750 °C for 30–90 min. The samples for chemical composition analysis were taken from the upper melt in the crucible.

### 2.2. Melt purification with addition of Zr/Mn

The aim was to investigate the efficiency of Fe removal from magnesium melt using a fixed amount of Zr and Mn at different temperature for different holding time. The experimental procedure was similar to that of melt purification in commercial magnesium. Mg-30 wt.%Zr and Mg-4.27 wt.%Mn master alloys were added to the Mg melt at 740 °C. The melts were held at 730 °C for 45 min after being stirred for 5 min, then held at relatively low temperature for 30–120 min.

### 2.3. Analysis of chemical composition and second phases

The chemical composition of samples was analyzed using inductively coupled plasma-emission spectrometry (ICP, Optima 8300). Samples for scanning electron microscopy (SEM) were mechanically polished using 1  $\mu\text{m}$  diamond paste, and etched for the same period of 1 min in 4%  $\text{HNO}_3$  in  $\text{C}_2\text{H}_5\text{OH}$  dried in cool air stream. A TESCAN VEGA 3 LMH SEM, equipped with energy dispersive X-ray spectroscopy (EDX), was employed to characterize the microstructure and impurity particles containing iron in Mg alloys. X-ray diffraction analyses were carried out using Rigaku D/MAX-2500PC with Cu K radiation.

## 3. Results

### 3.1. Iron solubility, solid phases and their settlement velocity in the melts

The novel approach for purification is based on the solubility decrease of impurities in the magnesium melt by lowering the melt temperature, and iron particles or compounds containing iron are expected to form and settle out in magnesium melt. Early Mg–Fe and Mg–Fe–X phase diagrams show that Fe solubility in magnesium melt decreases with the lowering melt temperature [11,18]; however, there is the lack of detailed data in the very low iron content corner for most of commercial magnesium alloys. The change of iron solubility in the molten liquid of magnesium and its alloys has been calculated in the present work by using the Pandat Software Package (Database PanMg-2013), and the calculated results are shown in Fig. 1. It is shown from Fig. 1a that iron solubility in the magnesium melt is very high, and the calculated value is about 350 ppm at temperature of 710 °C. When the magnesium melt temperature drops to 650 °C, the iron solubility decreases to 180 ppm. From Fig. 1b, it can be seen that the additions of alloying elements can decrease obviously the iron solubility in the melt. With the decrease of the melt temperature, the iron solubility drops to less than 5 ppm for commercial magnesium alloys, AZ31, AZ91, AM60 and ZK60, which means that it is possible to prepare super-purity magnesium alloys by using suitable low temperature treatment as an additional step of melting and casting processes.

The experimental results by SEM and X-ray analysis showed that the remaining iron existed in the melt as single iron phase or compounds containing iron for commercial primary magnesium due to existence of other minor elements (Fig. 2a). For commercial magnesium alloys, no single iron phase is found and the remaining iron existed in the melt as compounds

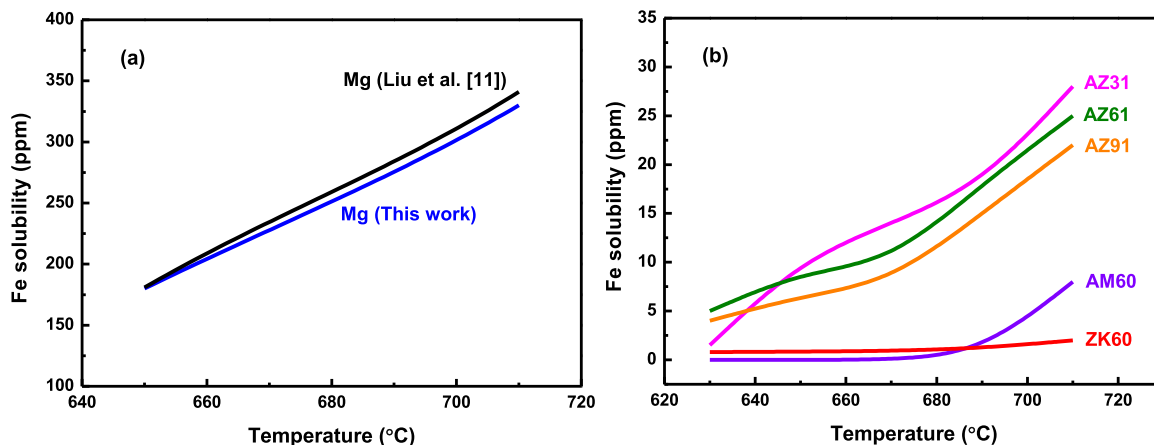


Fig. 1. Fe solubility in the melt of magnesium (a) and its alloys (b) at different temperatures.

containing iron (Fig. 2b). The size of iron particles or compounds containing iron was normally about 5 μm (Fig. 3), and some big particles with the size of bigger than 100 μm were also found in the melt, which is similar to that of Fe–Mn compound in Mg–(Mn,Zr)–Fe system found by Gandel et al. [41]. The detailed information for the compounds containing iron needs to be investigated.

According to the size of solid phases, the settlement velocity of iron particles in the melt has been calculated by using different data for density, viscosity and surface tension at different temperatures, and the calculated results are in Fig. 4. It can be seen that the difference of settlement velocity between 650 °C and 750 °C is not so big, and the effective settlement of iron particles may be achieved if there is enough holding time at lower temperatures. Because the compounds containing iron present in the melt normally has lower density than iron particles, the settlement velocity of these phases will be lower than that of iron particles. Of course, the presence of other compounds in commercial magnesium alloys will also affect the

settlement of iron particles or compounds containing iron, and the detailed investigation for effect of other solid phases on the settlement of iron particles or compounds containing iron is being carried out.

### 3.2. Effects of melt holding temperature on melt purification of commercial magnesium

The results of the effect of melt temperature on the melt purification of commercial Mg, which shows that the Fe content can be decreased obviously by lowering melt treatment temperature, is shown in Fig. 5. The Fe content in the as-received commercial magnesium was about 100 ppm, and the treatment at 650 °C for 90 min resulted in the decrease of the Fe content down to 40 ppm in the melt. The addition of Mn and Zr was found to have an important effect on the purification of magnesium melt, and the results showed the combination of low temperature melt treatment and Zr/Mn addition was more effective in impurity reduction. It is found from Fig. 5 that the efficacy of Zr in removing Fe from the melt is obvious by using

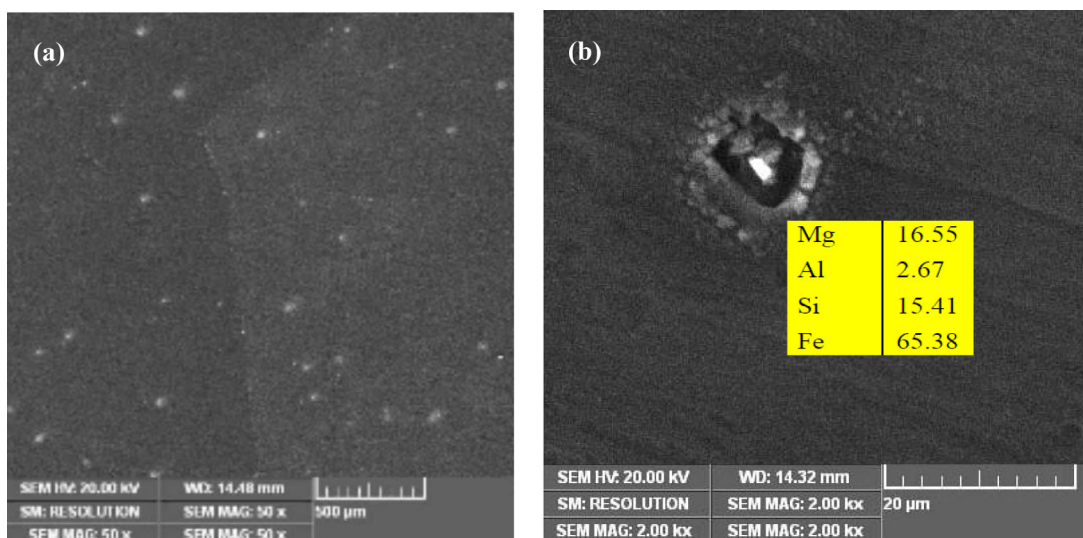


Fig. 2. SEM images of the particles in the melt. (a) Iron particle and compounds containing iron; (b) morphology and EDS analysis result (wt%) of the compound cluster containing iron.

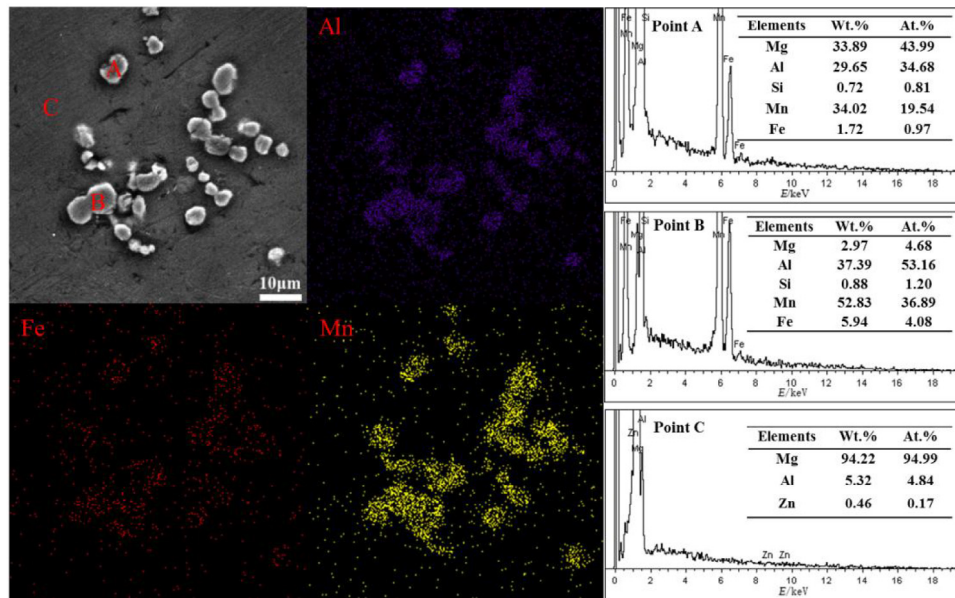


Fig. 3. SEM image and EDS analysis results of the particles containing Fe in AZ61 alloy.

normal melting temperature, which is similar to the experimental and calculated results by Prasad et al. [18], but the content of iron in the melt is still higher than 30 ppm. When the melt holding temperature decreased to 650 °C, the content of iron in the melt dropped to 5 ppm after 90 min. The effect of Mn addition was found to be more apparent, and the iron content down to 2 ppm in the melt was achieved when the melt was held at 650 °C for 90 min. At the same time, the silicon content in the melt with additions of Zr and Mn was also decreased remarkably from 170 ppm to 10 ppm after the low temperature treatment. By conducting suitable production process, the melt with Mn or Zr addition after the low temperature treatment may be used to prepare super high-purity Mg–Mn–X or Mg–Zr–X alloys.

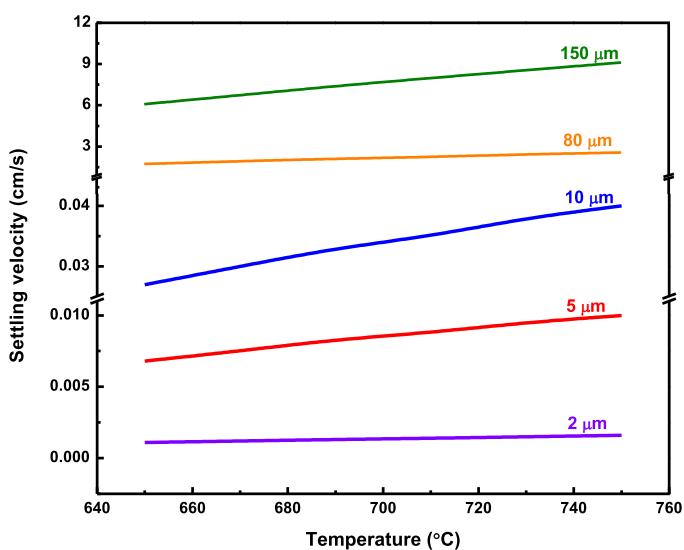


Fig. 4. The settlement velocity of iron particles in the melt at different temperature.

### 3.3. Effects of melt holding temperature on melt purification of AZ alloys

Fig. 6 shows the effects of melt treatment temperature on Fe removal in AZ31, AZ61 and AZ91 alloys. With the decrease of melt temperature, the Fe content in the melt is obviously below the starting Fe concentration for these alloys. The Fe content was reduced to 15 ppm from the initial 65 ppm when the AZ31 melt was treated at 620 °C for 90 min. There are similar changes in the Fe content in the melt of AZ61 and AZ91 alloys. The experimental results showed that the Fe content in the AZ61 melt was decreased from 150 ppm to 20 ppm, and that in the AZ91 melt was decreased from 140 ppm to 37 ppm after holding at 630 °C. These results indicate that the low temperature melt treatment is very effective in further decreasing the impurity Fe content in the AZ series magnesium alloys. The results in Fig. 6 also show that the impurity Si content in the AZ61 alloy can be decreased from 210 ppm to 110 ppm. It is evident that the efficacy of Fe removal is better for the AZ series alloys as compared to pure magnesium by conducting the low temperature melt purification process. Moreover, Al and Zn concentrations in the melt were found to have no obvious changes after the low temperature melt purification process (as shown in Table 1), which is different from what happened in magnesium alloys subjected to flux purification treatment [19–21].

### 3.4. Effects of melt holding temperature on melt purification of AM and ZK alloys

In Fig. 7 are the results about the effect of melt holding temperature on the melt purification of AM60, AM50 and ZK60 alloys. The initial Fe concentration of both AM60 and AM50 is about 150 ppm. The low temperature treatment leads to a decrease of Fe content in all the samples, and the lowest Fe content is 15 and 18 ppm for AM60 and AM50, respectively. It

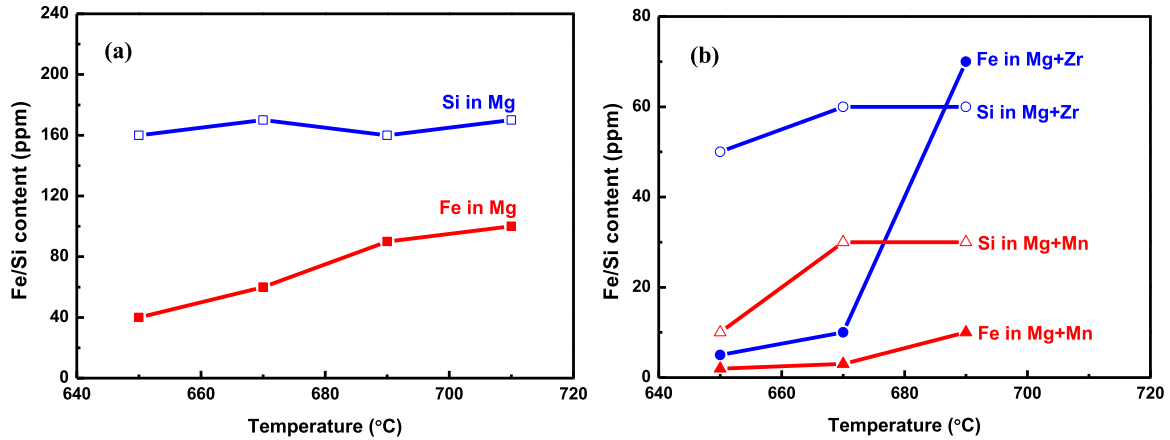


Fig. 5. Variations of Fe and Si contents in the magnesium melt after the melt treatment. (a) Commercial Mg; (b) commercial Mg with additions of Zr and Mn. The content of Fe and Si in the as-received Mg is about 100 ppm and 170 ppm, respectively.

can be found that the purification efficacy of the AM alloys is thus similar to that of the AZ alloys when the low temperature melt treatment is applied. For ZK60 alloy, the experimental results show that melt holding even at high temperature also apparently reduces the initial Fe content. The lower the melt temperature is, the more effective the Fe removal is. The low temperature treatment was found to result in a more dramatic decrease of the Fe content from 80 ppm to 5 ppm in the melt.

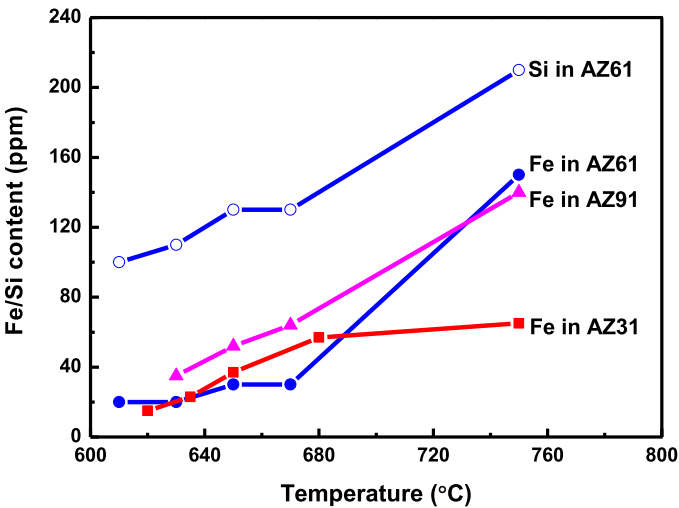


Fig. 6. Variations of Fe and Si contents in the melt after the melt treatment for AZ alloys.

Table 1  
Effects of melt holding temperature on the content of main elements in the melt of the AZ31 and AZ61 alloys.

Material	Sample	Temperature/°C	Time/min	Al /wt.%	Zn/wt.%
AZ31	As-received	–	–	3.15	0.82
AZ31	1	650	90	3.15	0.86
AZ31	2	620	90	3.15	0.83
AZ61	As-received	–	–	7.44	0.71
AZ61	1	670	60	7.45	0.65
AZ61	2	650	60	7.52	0.70

Furthermore, the impurity Si was also decreased to a relatively low level in this process, which was less than 20 ppm. The purified ZK60 melt had been used to prepare successfully the magnesium alloy with the Fe content of about 5 ppm at normal casting temperature by using the low-cost special technique to avoid the re-dissolving of solid phases containing iron at higher temperatures.

#### 4. Discussion

The low temperature melt treatment (LTMT) developed in the present work is a melt self-purifying technology (MSPT) without any melt pollution. The decrease of impurity iron in the melt depends on not only the solubility of iron in the molten liquid but also the settlement velocity of iron particles or compounds containing iron. If the solid phases with remaining iron do not settle out, the effective decrease of iron content in the melt is impossible. The experimental results indicate that the low temperature melt treatment is able to remove impurity Fe effectively, which indicates that the effective settlement of the

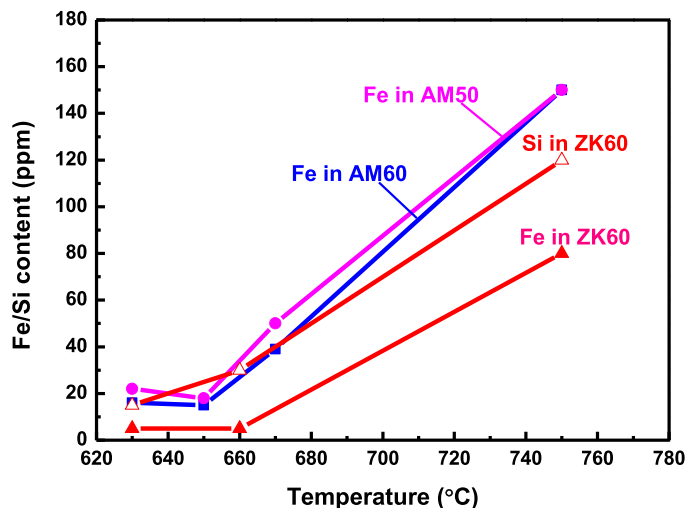


Fig. 7. Variations of Fe and Si contents in the melt after the melt treatment for AM50, AM60 and ZK60 alloys.

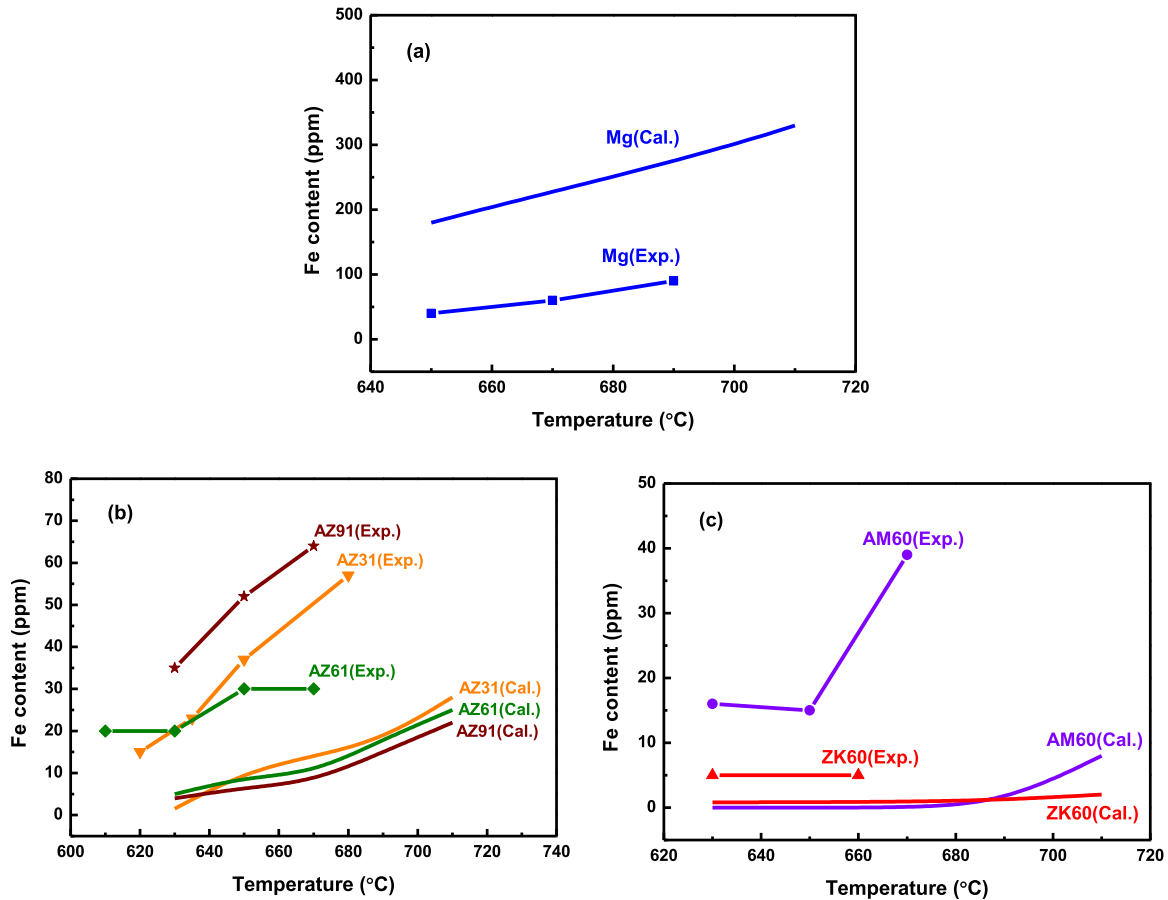


Fig. 8. The comparison between the measured Fe content after LTMT and calculated Fe solubility in magnesium and its alloys at different temperatures. (a) Commercial magnesium, (b) AZ alloys, and (c) AM60 and ZK60 alloys.

iron particles or compounds containing iron in used commercial magnesium and its alloys has been achieved, and high purity melt or super high-purity melt can be prepared by this method. However, the Fe content in the alloy melt after low temperature melt treatment is still higher than the Fe solubility in the melt (see Fig. 8b and c), which means that there are some remaining iron as solid phases in the alloy melt that does not settle out from the melt. The difference between the measured Fe content after LTMT and calculated Fe solubility is 5–30 ppm. This may be ascribed to two factors: one is that the degree of accuracy for calculation of Fe solubility needs to be improved, and the other is that longer holding time at lower temperature has to be used or other ways, such as ultrasonic technique, can be used to accelerate the settlement of iron particles or compounds containing iron. The high temperature melt treatment has been proved to be helpful to the settlement of iron particles or compounds containing iron [22,27,34–39], but it is difficult to prepare super-high purity magnesium alloys because part of iron particles or compounds containing iron will re-dissolve in the molten liquid at a higher temperature. Filtering technology has been successfully used to decrease the amount of inclusions in the melt [42], which should be helpful to decreasing the amount of iron particles or compounds containing iron. However, the iron's re-entering to the molten

liquid also has to be overcome because the filtering process is normally carried out in higher temperature similarly due to requirement of high melt fluidity.

From Fig. 8a, it can be seen that the Fe content in the commercial magnesium melt after LTMT is much lower than the calculated Fe solubility. This is because most of minor elements may decrease the Fe solubility in the Mg melt, and there are other minor impurity elements in the commercial magnesium used in the present work. The experimental work has showed that there are still some phases containing iron present in the Mg melt after LTMT. Because the purity of magnesium alloys depends mainly on the purity of primary magnesium, the development of new ways to accelerate the settlement of iron particles or compounds containing iron or the additions of minor elements to decrease the Fe solubility in primary magnesium is much more important in order to produce high quality magnesium alloys. In fact, It has been reported that the addition of 50 ppm Mn could result in a dramatic decrease of the Fe solubility in the magnesium melt down to less than 20 ppm [43].

Because the high purity melt is the base of the industrial production of high purity magnesium alloys, how to avoid iron's re-entering to the melt from melting and casting tools is a challenge due to rise of the Fe solubility in the melt with the

increase of melt temperature. In the National Engineering research Center for Magnesium Alloys at Chongqing University (CCMg), the special low-cost techniques for solving this problem have been developed, and the detailed investigation will be reported in another paper.

## 5. Conclusions

- (1) A new method for melt purification of magnesium alloys, the melt self-purifying technology (MSPT), has been developed successfully based on the low temperature melt treatment (LTMT) without adding any fluxes. After the low temperature met treatment, the alloy melt with the iron content of less than 5 ppm can be achieved.
- (2) Without any additions, the impurity Fe content in the commercial magnesium was decreased from 100 ppm to 40 ppm after the low temperature met treatment at 650 °C. The remaining iron existed in the melt as single iron phase or compounds containing iron due to existence of other minor elements. The Fe content as low as 2 ppm can be achieved by appropriate melt treatment plus adding Mn for commercial magnesium.
- (3) Without any additions, the Fe content in the AZ31 alloy was reduced to 15 ppm from the initial 65 ppm when the melt was treated at 620 °C. The Fe content in the AZ61 melt was decreased from 150 ppm to 20 ppm after holding at 630 °C.
- (4) Without any additions, the Fe content in AM60 and AM50 dropped to 15 and 18 ppm from the initial 150 ppm after the low temperature melt treatment, respectively. For ZK60, the low temperature melt treatment resulted in the dramatic decrease of the Fe content in the alloy from 80 ppm to less than 5 ppm.
- (5) After the low temperature melt treatment, the Si content in the AZ alloys, AM alloys and ZK alloy used in the present work was also decreased obviously.

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## References

- [1] T. Morishige, K. Ueno, M. Okano, T. Goto, E. Nakamura, T. Takenaka, *Mater. Trans.* 55 (2014) 1506–1509.
- [2] L. Yang, X. Zhou, S.M. Liang, R. Schmid-Fetzer, Z. Fan, G. Scamans, et al., *J. Alloys Compd.* 619 (2015) 396–400.
- [3] H. Matsubara, Y. Ichige, K. Fujita, H. Nishiyama, K. Hodouchi, *Corros. Sci.* 66 (2013) 203–210.
- [4] A.A. Luo, *J. Magnes. Alloys* 1 (2013) 2–22.
- [5] A. Atrens, G.-L. Song, M. Liu, Z. Shi, F. Cao, M.S. Dargusch, *Adv. Eng. Mater.* 17 (2015) 400–453.
- [6] B.G. Song, *Adv. Eng. Mater.* 7 (2005) 563–586.
- [7] G.L. Makar, J. Kruger, *Int. Mater. Rev.* 38 (1993) 138–153.
- [8] A. Atrens, G.L. Song, F. Cao, Z. Shi, P.K. Bowen, *J. Magnes. Alloys* 1 (2013) 177–200.
- [9] G. Song, D. StJohn, *Corros. Sci.* 46 (2004) 1381–1399.
- [10] Y. Zhang, C. Yan, F. Wang, W. Li, Y. Zhang, C. Yan, et al., *Corros. Sci.* 47 (2005) 2816–2831.
- [11] M. Liu, P.J. Uggowitzer, A.V. Nagasekhar, P. Schmutz, M. Easton, G.L. Song, et al., *Corros. Sci.* 51 (2009) 602–619.
- [12] M. Liu, P.J. Uggowitzer, P. Schmutz, A. Atrens, *JOM* 60 (2008) 39–44.
- [13] M. Inoue, M. Iwai, K. Matuzawa, S. Kamado, Y. Kojima, *Light Met.* 48 (1998) 257–262.
- [14] Y.Z. Wang, *Foundry* 50 (2001) 61–66 (in Chinese).
- [15] X.H. Chen, F.S. Pan, J.J. Mao, J.S. Huang, *J. Mater. Sci.* 47 (2012) 514–520.
- [16] X.H. Chen, F.S. Pan, J.J. Mao, Z.S. Zhang, *J. Wuhan Univ. Technol. (Mater. Sci. Ed.)* 28 (2013) 1207–1211.
- [17] F.S. Pan, J.J. Mao, X.H. Chen, J. Peng, J.F. Wang, *Trans. Nonferrous Met. Soc. China* 20 (2010) 1299–1304.
- [18] A. Prasad, P.J. Uggowitzer, Z. Shi, A. Atrens, *Adv. Engin. Mater.* 14 (2012) 477–490.
- [19] W. Wang, G.H. Wu, Q.D. Wang, Y.G. Huang, M. Sun, W.J. Ding, *Trans. Nonferrous Met. Soc. China* 18 (S1) (2008) s292–s298.
- [20] G.H. Wu, W. Wang, M. Sun, Q.D. Wang, W.J. Ding, *Trans. Nonferrous Met. Soc. China* 20 (2010) 1177–1183.
- [21] W. Jie, J.X. Zhou, W.H. Tong, Y.S. Yang, *Trans. Nonferrous Met. Soc. China* 20 (2010) 1235–1239.
- [22] O. Lunder, T.K. Aune, K. Nisancioglu, *Corros. Sci.* 43 (1987) 291–295.
- [23] W. Wang, Y. Huang, G. Wu, Q. Wang, M. Sun, W. Ding, *J. Alloys Compd.* 480 (2009) 386–391.
- [24] W. Wang, G. Wu, Q. Wang, Y. Huang, W. Ding, *Mater. Sci. Eng. A* 507 (2009) 207–214.
- [25] E. Emley, *Principles of Magnesium Technology*, Pergamon Press, London, 1966.
- [26] H. Gao, G. Wu, W. Ding, L. Liu, X. Zeng, Y. Zhu, *Mater. Sci. Eng. A* 368 (2004) 311–317.
- [27] G. Wu, H. Gao, W. Ding, Y. Zhu, *J. Mater. Sci.* 368 (2005) 6175–6180.
- [28] Y.J. Li, T.J. Luo, Y.S. Yang, *Trans. Nonferrous Met. Soc. China* 20 (2010) s407–s410.
- [29] T. Haitani, Y. Tamura, E. Yano, T. Motegi, N. Kono, E. Sato, *J. Jpn. Inst. Light Met.* 51 (2001) 403–408.
- [30] Y. Tamura, T. Motegi, N. Kono, E. Sato, *Mater. Sci. Forum Trans Tech Publ* (2000) 199–204.
- [31] C.S. Roberts, *Magnesium and Its Alloys*, Wiley, 1960.
- [32] D.H. StJohn, M. Qian, M.A. Easton, P. Cao, Z. Hildebrand, *Metall. Mater. Trans. A* 36 (2005) 1669–1679.
- [33] D.H. StJohn, P. Cao, M. Qian, M.A. Easton, *Adv. Eng. Mater.* 9 (2007) 739–746.
- [34] H. Gao, *Flux purification behavior and theory for magnesium alloy*. Ph. D thesis, Shanghai Jiao Tong University, 2006. (in Chinese).
- [35] H. Gao, G. Wu, W. Ding, Y. Zhu, *Trans. Nonferrous Met. Soc. China* 14 (2004) 530–536.
- [36] H. Gao, G. Wu, W. Ding, Y. Zhu, *J. Mater. Sci.* 39 (2005) 6449–6456.
- [37] H. Gao, G. Wu, Y. Fan, W. Ding, *Mater. Sci. Forum* 488–489 (2005) 25–30.
- [38] G. Wu, H. Zou, C. Zhai, K. Zeng, W. Ding, *Foundry* 52 (2003) 167–170 (in Chinese).
- [39] G. Wu, C. Lu, C. Zhai, X. Zeng, W. Ding, Y. Zhu, *Foundry* 52 (2003) 1166–1169 (in Chinese).
- [40] P. Wan, X. Fan, S. Hu, H. Wen, *Res. Stud. Foundry Equip.* 1 (2008) 11–14 (in Chinese).
- [41] D.S. Gandel, M.A. Easton, M.A. Gibson, N. Birbilis, *Mater. Chem. Phys.* 143 (2014) 1082–1091.
- [42] G. Wu, M. Sun, W. Wang, W. Ding, *Chin. J. Nonferr. Met.* 20 (2010) 1021–1031 (in Chinese).
- [43] P.S. Wang, *Investigation on phase diagrams and thermodynamics of Mg-Mn-Fe-Ni, Mg-Mn-Ca-Zr, Mg-Mn-Al-Li systems*. Ph. D thesis, Central South University, 2012. (in Chinese).