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In-situ formation behaviors of Al_8Mn_5 particles in Mg-Al alloys

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Abstract

Al_8Mn_5 aluminide particles were in-situ formed in an Mg-Al alloy with Mn addition. The effects of Mn content and melting temperature on the in-situ formation behaviors of Al_8Mn_5 aluminide were investigated. It was found that increasing Mn content or melting temperature promoted the formation of Al_8Mn_5 , and also the segregation tendency of these in-situ formed aluminide particles.

Key words: Magnesium matrix composite, Manganese aluminide, In-situ formation, Casting

1. Introduction

Magnesium is attracting increased interest for applications in transportation industry due to its high specific strength, good damping capacity, excellent castability, and superior machinability. Currently, the most widely used commercial magnesium alloys, such as AM60B and AZ91, are based on Mg-Al system. These alloys can only be used at a temperature of up to 120°C because of a rapid decrease of mechanical properties with

increasing temperature, due mainly to the relatively low thermal stability of the $\text{Mg}_{17}\text{Al}_{12}$ [1], the main precipitates in the alloys. Reinforcing the magnesium alloys with a hard and thermally stable second phase has been widely explored to improve the mechanical properties of the materials at high temperatures. The reinforcements can be ceramic particles or fibers, or with elemental metal particles. Ceramics, such as SiC [2] and Al_2O_3 [3], provides high hardness, high strength and thermal stability, but they generally do not wet well with molten magnesium. Elemental metal powders, such as Ni [4] and Cu [5], on the other hand, generally have good wettability with molten magnesium, and can strengthen the magnesium alloys without sacrifice in ductility. However, the high density of the most elemental metals may not only compromise the lightweight of the final composites, but also make it difficult to uniformly distribute these reinforcing materials in the matrix.

In addition, the high manufacturing cost of composite materials hinders their industrial applications. In-situ fabrication is a promising approach to eliminating this prohibitive cost of composite materials. Thus, in-situ forming intermetallic particulate reinforcement, of high melting point, is considered a promising approach for fabricating lightweight magnesium matrix composites. The Al-Mn binary phase diagram [6] shows that a series of manganese aluminides can be formed between Al and Mn, and the aluminum-rich manganese aluminides Al_6Mn is stable at temperatures up to 658°C [6]. The Mg-Al-Mn ternary phase diagram [7] shows that solid Al_8Mn_5 aluminide phase coexists with Mg-Al-Mn melt in a wide temperature range. These phase diagrams indicate that manganese aluminides are promising candidates for reinforcement phases in the magnesium alloys,

and they can be potentially in-situ formed in these alloys. In this paper, the formation behavior of the manganese aluminide particles in a Mg-Al alloy was examined.

2. Experimental methods

2.1. Sample preparation

AM60B magnesium alloy was used as the matrix. The composition of the alloy is listed in Table 1. Al and Mn are two major alloying elements. In order to promote the formation of aluminide, the Al content was increased to 10wt.%. The Mn content was varied from 0.5wt.% to 2.5wt.% by adding Mn powders with an irregular shape and $<45\ \mu\text{m}$ in size. The melting was performed in a vacuum casting furnace using a plain carbon steel crucible, as schematically shown in Fig. 1. When the AM60B and Al blocks were melted, the plain carbon steel tubing for argon gas and a thermocouple was lowered into the melt, and argon gas of industrial purity was bubbled through the melt to promote metallurgical reactions and homogenization. The melt was homogenized at either 750 °C or 850 °C for 60 minutes before being poured into a steel receiving crucible which was kept at room temperature or preheated to 450 °C. The ingots were then subject to various characterizations.

2.2. Material characterization

Samples were sectioned from the cast ingots and analyzed by an Olympus PMG3 optical microscope, a Hitachi S-3500 scanning electron microscope (SEM), with an energy dispersive spectrometer (EDS) attachment, and a Philips Xpert XRD diffractometer using $\text{Cu-K}\alpha$ radiation. In addition, the precipitates in selected samples were extracted by

dissolving the samples in an ethanol solution containing 25vol.% acetic acid and then characterized for phase constitution and composition by X-ray diffraction and EDS analysis.

3. Experimental results and discussions

3.1. Effect of Mn content on Microstructures

For the melting at 750 °C for 60 minutes, the samples containing 0.5wt.% and 1.5wt.% of Mn were produced without difficulty by following the procedures described in Section 2. For the sample containing 2.5wt.% Mn, however, a portion of the melt solidified at the bottom of the melting crucible and could not be poured out. The sample solidified at the bottom of the melting crucible was cut out and analyzed along with the cast ingot samples.

The optical microstructures of the ingots with different amounts of Mn are shown in Fig. 2. All the samples showed in-situ formed particles with an irregular shape and up to 10 μm in size. Increasing Mn content led to higher density of the particles, but did not have apparent effect on the particles size. For the sample with 0.5wt.% Mn, the particles were uniformly distributed (Fig. 2a). When the Mn content was increased to 1.5wt.% and 2.5wt.%, increased local clustering of the particles could be observed, as shown in Fig. 2c and 2e.

Table 2 shows the results of EDS analysis for the samples containing different amounts of Mn. The composition of the matrix showed essentially no changes with the Mn content

varying in the range of 0.5wt.% and 2.5 wt.%, and was close to the nominal composition of AM60B. The particles were rich in Al, Mn and Mg, with a minor amount of Fe. Due to the facts that the particles size analyzed is relatively small, and the EDS signals normally comes from approximately an spherical volume of 2 μm in diameter, it is possible that the magnesium detected comes partially or totally from the matrix around the particles, depending on the particle size and shape. Given that the EDS results could not tell decisively whether and how much magnesium is contained in the particles, the Mn/Al ratio is calculated and compared to examine the effect of Mn content on the particle compositions. It could be seen observed that the Mn/Al ratio increased from 0.88 for the sample with 0.5wt.% Mn to 1.30 and 1.13 for the samples with 1.5wt.% and 2.5wt.% of Mn, respectively. From the EDS results, it can be inferred that the in-situ formed particles in the samples were intermetallic compounds containing manganese and aluminum, and possibly magnesium.

The microstructure of the sample containing 2.5wt.% Mn and solidified in the melting crucible is illustrated in Fig. 3. A high volume fraction of large particles with a size of 20 μm to 60 μm were embedded in the matrix. EDS analysis revealed that the large particles in the samples contained 94.2wt.%Mn-3.9wt.%Al-0.6wt.%Fe-0.1wt.%Mg-1.2wt.%O, indicating that these large particles were predominantly elemental Mn. Apparently, the Mn particles settled to the bottom of the melting crucible were the added particles that did not dissolve during melting. Such a high concentration of solid particles significantly increased the viscosity of the melt and prevented the surrounding melt from being poured

out. It was concluded that a melting temperature of 750°C was not sufficient for completely dissolving 2.5wt.%Mn in the Mg-Al melt.

3.2. Effect of melting temperature on microstructure

The effect of melting temperature on microstructures was investigated by melting the AM60B alloy with 10wt.%Al and 2.5wt.%Mn for 60min at 750°C, 800°C, and 850°C, respectively. After melting, the molten alloy was poured into a receiving crucible preheated to 450°C. It was observed that for all the three melting temperatures, a certain mass of the melt containing high concentration of Mn particles solidified at the bottom of the melting crucible and could not be pour out, indicating that 2.5wt.% of Mn could not be completely dissolved into the Mg-Al melt even at 850°C for 60 minutes. The volume of the solidified mass, however, decreased with increasing melting temperature, resulting from higher solubility of Mn in Mg-Al alloy and faster reaction kinetics at increased temperature. Microstructures observations also revealed that the top and central sections of the ingots melted at 800 °C and 850 °C had similar particle distribution to the ingot melted at 750 °C (shown in Figs. 2e and 2f), with a majority of the particles uniformly distributed in the ingot and a small degree of clustering. Figs. 4a and 4b show typical microstructures of the central and top sections of the ingots melted at 800 °C. A major difference in the microstructures of the ingots melted at 750 °C and at higher temperatures was that, a thick layer (approximately 10 mm in thickness) containing high concentration of coarse particles was observed at the bottom of the ingots cast at 800°C and 850°C, while such a layer is absent from the ingot melted at 750 °C. Figs. 4c and 4d show the high-concentration of particles found in the bottom layer of the ingot melted at 800°C. A

closed-up view of the particles showed that the particles in the bottom layer of the ingot were slightly larger than those found in the central and top sections. The relatively uniform thickness of the bottom layer indicates that it was formed by sedimentation of the particles in the receiving crucible before the melt solidified, due to the slow cooling of the ingot as a result of the high melting temperature and the preheating of the receiving crucible to 450°C.

The results of EDS analysis for the sample melted at 800°C are given in Table 3. The compositions of the sample melted at 850°C were similar to the results shown in the table and were not included. From the table it could be observed that the compositions of the matrix were almost the same for the ingots melted at different temperatures, with the top and central sections of ingot melted at 800°C showing slight lower aluminum content. The particles from different ingots and locations were all rich in Al, Mn and Mg and containing a small amount of Fe. The concentrations of Al and Mn in the particles, however, were different from ingot to ingot and from location to location for the ingot melted at 800 °C. The Mn/Al weight ratio for the particles in the top and central sections of the ingot was 1.35, while the ratio for the particles in the bottom layer was 0.89.

3.3. Effect of receiving crucible temperature on microstructures

To avoid sedimentation of manganese aluminide particles to the bottom of the ingots, a sample was melted at 850 °C for 60 minutes and subsequently poured into a receiving crucible set at room temperature. Microstructure observation using an optical microscope confirmed that by lower the temperature of the receiving crucible from 450°C to room

temperature, macroscopic segregation of particles to the bottom of the ingot was eliminated. Typical microstructure of the ingot is shown in Figure 5. Small particles distributed uniformly across the whole ingot, with scattered clusters of large particles. The result confirmed that the macroscopic segregation was due to the sedimentation of the particles in the receiving crucible resulting from slow cooling of the melt.

The SEM image of the particles extracted from the sample melted at 850°C is shown in Fig. 6. EDS analysis revealed that the particles had an average composition of 53.8wt.%Al-43.8wt.%Mn-2.2wt.%Fe-0.2wt.%Mg. The X-ray diffraction pattern of the extracted particles, as shown in Figure 7, revealed that the particles in-situ formed in the AM60B with different Mn content were Al_8Mn_5 type manganese aluminide, as expected from the ternary Mg-Al-Mn phase diagram [7]. The sedimentation of the particles to the bottom of the receiving crucible when the cooling rate was slow indicates that the Al_8Mn_5 manganese aluminide was formed in molten Mg-Al during the melting process.

3.4. Effect of melting sequence on the formation of Al_8Mn_5

To investigate the effect of alloying sequence on the formation behavior of the Al_8Mn_5 type manganese aluminide, a different melting sequence was employed to form a magnesium alloy containing 10 wt.% of Al and 2.5 wt.% of Mn. In the first step, a Mg-2.5 wt.% Mn ingot was produced by melting pure Mg blocks and elemental Mn powder at 850 °C for 2 hours. Microstructure examination revealed that that Mn was completely dissolved into the Mg melt with the absence of Al. Optical micrographs of the resulting

Mg-Mn ingot showed that fine Mn particles were evenly distributed in the Mg matrix, as illustrated in Fig. 8. Such fine and homogeneously distributed Mn particles reportedly had minor reinforcing effect to the Mg matrix [8]. In the second step, the Mg-Mn ingot was melted with 10wt.% of Al at 650°C for 2 minutes and poured to a receiving crucible at room temperature. Again, a portion of the melt was observed to solidify at the bottom of the melting crucible and could not be poured out.

The microstructure of the solid piece solidified at the bottom of the melting crucible is shown in Fig. 9. Particles with a size of up to 10 μm and a high concentration were formed uniformly in the matrix. EDS and X-ray diffraction analysis of the extracted particles from the sample showed that the particles contained 40.2wt.%Al-49.6wt.%Mn-8.9wt.%Fe-1.3wt.%O. The corresponding Mn/Al weight ratio in the particles is 1.23, which is very close to the ratio of 1.27 for Al_8Mn_5 , indicating that the particles settled to the bottom of the melt during melting was Al_8Mn_5 . The XRD diffraction pattern for the particles shown in Figure 10 confirmed that the particles formed during the two-step melting process were indeed the Al_8Mn_5 type of manganese aluminide.

These results show that Al_8Mn_5 is a stable phase in the Mg-Al-Mn system, and sedimentation to the bottom of the melt indicated that the Al_8Mn_5 are formed in the liquid phase during melting. Unlike many compounds formed in liquid phase, the Al_8Mn_5 particles seem to resist coarsening in the melt at high temperature even at a very high concentration. For melting at temperatures up to 850°C for 60 minutes, a majority of the

Al_8Mn_5 particles remained smaller than 10 μm . This attribute makes Al_8Mn_5 a very desirable reinforcement phase in the Mg alloys. Al_8Mn_5 tends to settle to the bottom of the melt in both the melting crucible and the receiving crucible, due to the density difference between Al_8Mn_5 and the magnesium melt. The segregation can be potentially avoided by strong agitation and control the solidification rate of the melt.

4. Summary

The in-situ forming behaviors of Al_8Mn_5 aluminide particles in Mg-Al-Mn melt were examined for magnesium matrix composite applications. It has been found that Al_8Mn_5 is a stable phase in the Mg-Al-Mn system, and is formed in the liquid phase during melting. Unlike many compounds formed in liquid phase, the Al_8Mn_5 particles seem to resist coarsening in the melt at high temperature even at a very high concentration, which makes it desirable as reinforcements in magnesium alloys. Increase in Mn content and/or melting temperature promoted the in-situ formation of Al_8Mn_5 particles. However, segregation of the Al_8Mn_5 particles through gravitational sedimentation needs to be carefully controlled.

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Table 1. The composition of AM60B alloy.

Elements	Al	Mn	Zn	Si	Cu	Fe	Ni	Mg
Content (wt.%)	5.6-6.4	0.26-0.5	<0.2	<0.05	<0.008	<0.004	<0.001	Bal.

Table 2. The matrix and particles compositions (wt.%) of the samples with different Mn content

Samples		Al	Mn	Fe	Mg	Mn/Al
0.5Mn ingot	Matrix	5.3	Undetected	Undetected	94.7	-
	Particle	30.4	26.7	2.2	40.7	0.88
1.5Mn ingot	Matrix	5.3	Undetected	Undetected	94.7	
	Particle	35.7	46.6	2.8	14.9	1.30
2.5Mn ingot	Matrix	5.2	Undetected	Undetected	94.8	
	Particle	27.9	31.7	1.2	39.3	1.14

Table 3. EDS analysis results for the ingot cast at 750°C and 800°C.

Sampling locations		Al	Mn	Fe	Mg	Mn/Al
Top and central sections of ingot melted at 800°C	Matrix	4.1	Undetected	Undetected	95.9	-
	Particle	32.9	44.3	2.7	20.1	1.35
Bottom layer of ingot melted at 800°C	Matrix	5.0	Undetected	Undetected	95.0	-
	Particle	37.3	33.3	4.8	24.6	0.89
Ingot melted at 750°C	Matrix	5.2	Undetected	Undetected	94.8	
	Particle	27.9	31.7	1.2	39.3	1.14

Fig. 1. Schematic illustration of the melting setup.

Fig. 2. The optical microstructures of ingots with different amounts of Mn, (a)/(b). 0.5wt.%Mn; (c)/(d). 1.5wt.%Mn; (e)/(f). 2.5wt.%Mn.

Fig. 3. Optical microstructure of the sample containing 2.5wt.% Mn and solidified in the melting crucible.

(a)

(b)

(c)

(d)

Fig. 4. Optical micrographs of the ingot cast at 800°C: (a)&(b) central and top areas; (c)&(d) bottom layer with high concentration of particles.

Fig. 5. Optical micrographs of the ingot cast at 850°C into a receiving crucible at room temperature.

Fig. 6. SEM image of the particles extracted from the ingot cast at 850°C into a receiving crucible at room temperature.

Fig. 7. (Cu-K_α) XRD pattern for the particles extracted from ingot cast in room-temperature receiving crucible.

Fig. 8. The optical microstructure of Mg-2.5wt.%Mn ingot.

Fig. 9. Optical micrographs of Mg-10wt.%Al-2.5wt.%Mn ingot remaining in the melting crucible.

Fig. 10. (Cu-K α) XRD pattern for the particles formed in the two-step melting.

Table and figure caption

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