Effects of Manganese and/or Carbon on the Grain Refinement of Mg-3Al Alloy

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The effects of manganese and/or carbon on the grain refinement of Mg-3Al alloy have been investigated in the present study. Significant grain refinement was obtained for the Mg-3Al alloy modified with either carbon or Al-Mn master alloy. There existed an optimal content of 0.1~0.2 mass%Mn to obtain refining grain size for the Mg-3Al alloy. The Al-Mn intermetallic particles with a molar ratio of 1:1 were considered as potent nuclei for Mg grains. The addition of Mn had no obvious effect on the grain size for the Mg-3Al alloy which was refined by 0.2 mass%C. The Al-C-O-Mn compounds were considered as the potent nuclei for Mg grains. A new hypothesis that the particles of Al-Mn compounds with Al2C3 coating film can act as potent nuclei for Mg grains was proposed.

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1. Introduction

Mg-Al alloys play a dominant role in magnesium alloys which are the lightest structural materials. Since the 1930s, the grain refinement of Mg-Al alloys has been extensively studied by many researchers. The grain refining method of the carbon inoculation has been emphasized due to its practical advantages in the low cost, the low operating temperature and the less fading. The hypothesis was widely accepted that Al4C3 particles act as the nuclei for Mg grains in the refining method of carbon inoculation.

Recently, Tamura et al. performed significant researches on the grain refinement of ultra-high purity Mg-Al alloys by carbon inoculation. The Al-C-O particles as the nuclei for Mg grains were found. Moreover, they concluded that Fe and/or Mn were the inhibiting elements for grain refinement by transforming Al-C-O into Al-C-O-Fe(Mn). However, the different conclusions have been made by Pan et al. and Pan et al. suggested that Fe played an important role in the formation of the nucleating particles rather than an inhibiting element for the commercial AZ63 alloy when it was refined by Al-1.5C master alloy. In these studies, the remarkable grain refining effects modified by carbon inoculation were obtained although the commercial magnesium alloy with high contents of Fe and Mn were used.

It is difficult to understand clearly why the inconsistent conclusions were made for the same phenomenon. In fact, Fe is an inevitable impurity element and Mn is an important alloyed element as Fe remover in the commercial Mg-Al alloys. In the present study, the following research works have been carried out to clarify: (1) whether Mn is an inhibiting element for grain refinement of Mg-Al alloys refined by carbon; (2) how grain size changes after addition of Mn in the Mg-Al alloys melt which have been modified with carbon or not. The ultimate purpose is to provide the important data to develop a suitable and reliable grain refiner to be applied for Mg-Al alloys.

2. Experimental Procedures

The raw materials used in the present study included relatively high purity magnesium (99.95 mass%Mg, 0.002 mass%Fe, 0.002 mass%Mn), high purity aluminum (99.99 mass%Al), carbon powder (45 μm in average diameter and purity of higher than 99 mass%), magnesium powder (200~400 μm in size and purity of higher than 99 mass%) and aluminum powder (70~150 μm in size and purity of higher than 99.5 mass%).

The pellets (about 3 mm in diameter and 5~10 mm in height) comprised of carbon powder, magnesium powder and aluminum powder at a mass ratio of 1:5:4 were prepared by using a cold isostatic press (CIP) under a pressure of 150MPa for 1 h. The Al-20 mass%Mn master alloy was prepared in advance as follows. The pure aluminium and electrolytic manganese were melted together at 950°C, and then the Al-Mn melt was poured into a copper mould at a high cooling rate.

The MgO crucible having high purity of more than 99.5 mass% was used in the present study. The pure Mg and Al as well as Al-20 mass%Mn master alloy were melted together in an electric resistance furnace at the temperature of 780°C. In the present study, the Al content in the prepared samples was controlled to be at constant 3 mass% and the Mn content was controlled to be at 0.05 mass%, 0.1 mass%, 0.2 mass%, 0.5 mass% in turn. After the pellets containing carbon were plunged into the melt, the melt was held for 10 min. Then it was manually stirred for 1 min with a magnesia rod, and continued to be held for 10 min at the temperature of 780°C. The addition amount of carbon is 0.2 mass% of the melt. The melt was poured into a truncated cone-shaped iron-mould with the size of $20 \times 25 \times 20$ mm³, which had been preheated at 600°C.

Metallographic samples were cut in the horizontal direction at the position of 10 mm from the bottom of the ingots. To reveal grain boundaries, the samples were held at 420°C.
for 6 h, and then were air-cooled. The samples for grain morphology observation were prepared using a standard procedure with a final polishing with 0.05 μm colloidal alumina suspension. After that, the samples were chemically polished by nitride acid, and then were etched with acetic-picric acid to reveal the grain morphology. The grain microstructures were observed by use of the Olympus BX50 type optical microscope. The average grain size of each truncated cone sample was measured from the central of a longitudinal section of the truncated cone. Linear intercept method described in ASTM standard E112-88 was used to evaluate the grain size. As cast samples etched with 2 vol% nitride acid ethanol solution were further studied by scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDX) spectrometer.

3. Results

3.1 Grain refining efficiency

Figure 1 shows the typical grain morphologies of Mg-3Al alloy with the grain size of about 300 μm for the sample without any treatment, and about 140 μm for the samples treated by either 0.2 mass% C or the combination of 0.2 mass% C and 0.2 mass% Mn. Figure 2 illustrates the effect of Mn content on the grain size of the Mg-3Al alloy with and without being treated by 0.2 mass% C. Under the condition without 0.2 mass% C treatment, the grain size decreased steeply with increasing the Mn content when it was lower than 0.1 mass%. No obvious change in the grain size of Mg-3Al alloy was observed when the Mn content increased from 0.1 mass% to 0.2 mass%. The further increase in the Mn addition to 0.5 mass% led to a re-increase in the grain size. However, it was found that the addition of Mn had no obvious effect on the grain size for Mg-3Al alloy which was refined by 0.2 mass% C.
3.2 SEM observations

By SEM observation, many Al-Mn-rich intermetallic particles were found in the samples of Mg-3Al alloy modified by Mn. Judged by SEM observations, the higher was the content of Mn, the larger was the number of the Al-Mn-rich particles. Figure 3(a) shows the morphologies of the Al-Mn-rich particles in the sample of the Mg-3Al alloy modified by 0.2 mass%Mn. On the basis of the EDS analyses for about 30 particles, it was found that there existed two types of Al-Mn-rich intermetallic compounds with the average molar ratio between Al and Mn of about 1:1 and 3:2 in the samples modified by Mn. The result indicates that the Al-Mn intermetallic compounds were AlMn and Al$_3$Mn$_2$ phases under the present experimental conditions. The EDS analyses represented that the particles denoted by A and B in Fig. 3(a) were the AlMn phase particles and particle C was Al$_3$Mn$_2$ phase particle. The typical spectra of AlMn and Al$_3$Mn$_2$ phase are shown in Figs. 3(b) and (c), which were measured from the particles A and C in Fig. 3(a), respectively. The AlMn phase was the main Al-Mn-rich intermetallic compounds in the samples of Mg-3Al alloy modified by Al-20 mass%Mn because it was found that the number of AlMn particles was much more than that of Al$_3$Mn$_2$ particle.

Under the condition of Mg-3Al alloy modified by the combination of C and Mn, the Al-C-O-Mn-rich particles were easily captured in the samples. The types of intermetallic particles comprised both of only Al, C and O and of the Al-Mn-rich particles not containing C could hardly be found in the samples modified by the combination of C and Mn. By EDS analyses, the particles denoted by A, B and C in Fig. 4(a) are all Al-C-O-Mn-rich intermetallic particles. Figure 4(b) shows the typical EDS spectrum of Al-C-O-Mn-rich particle measured from the particle B.

4. Discussion

Mn is a very important alloying element and exists in virtually all kinds of commercial Mg-Al alloys as Fe remover due to the formation of Al-Fe-Mn-rich compounds. A few detailed studies to reveal the effect of Mn on the microstructures of Mg-Al alloys have been done so far. In the present study, one conclusion can be drawn from Figs. 1 and 2 that there existed the optimal content of 0.1~0.2 mass%Mn
to obtain the refining grain size of the Mg-3Al alloy. The result is almost consistent with that obtained recently by Cao et al.\textsuperscript{15)\textsuperscript{2}}

In Cao’s study, the refining mechanism of $\varepsilon$-AlMn particles existing in Al-60 mass$\%$Mn master alloy splatter as nuclei for Mg grains was proposed.\textsuperscript{15)\textsuperscript{3}} Nevertheless, some doubts about whether grain refinement is really attributed to the $\varepsilon$-AlMn phase or not were pointed out recently by Qiu et al.\textsuperscript{16)\textsuperscript{4}} The theoretically calculated results based on the edge-on-edge matching model show that the meta-stable $\tau$-AlMn phase possesses a significant heterogeneous nucleating potency whereas $\varepsilon$-AlMn phase has not nucleating potency for Mg grains.\textsuperscript{16)\textsuperscript{5}} The meta-stable $\tau$-AlMn phase is only generated from the high temperature $\varepsilon$-AlMn phase through mass transformation. In the present study, it is believed that the $\varepsilon$-AlMn phase exists in the Al-20 mass$\%$Mn master alloy due to the rapid cooling rate and the high heating temperature of 950°C, which is higher than the temperature of 870°C for obtaining the stable $\varepsilon$-AlMn phase,\textsuperscript{17)\textsuperscript{6}} and the temperature of 780°C that is the transition temperature of AlMn phase from the $\varepsilon$ phase to the $\tau$ phase.\textsuperscript{17)\textsuperscript{7}}

For ordinary metal alloys, the number of potent nuclei in the melt and the constitutional undercooling at the advancing solid/liquid (S/L) interface are the very important factors to determine the final grain size of casting.\textsuperscript{18)\textsuperscript{8}} The constitutional undercooling is controlled by the segregation of solutes in the melt. The segregating power of a solute can be evaluated by the value of $m(k - 1)$, where $m$ is the slope of the liquidus line, $k$ is the equilibrium distribution coefficient.\textsuperscript{19)\textsuperscript{9}} For Mg alloys, the effect of constitutional undercooling resulting from Mn on grain size is negligible because Mn has a very low value $m(k - 1)$ of 0.15 in the Mg-Mn binary alloy system.\textsuperscript{20)\textsuperscript{10}} So it is believed that the grain refinement of Mg-3Al alloy resulting from Mn is attributed to the increase in the number of potent nuclei. Based on the viewpoints supported by Cao et al.\textsuperscript{15)\textsuperscript{11}} and Qiu et al.\textsuperscript{16)\textsuperscript{12}} and the experimental results in the present study, it can be rather deduced that the AlMn phase particles play an important role in the grain refinement, acting as nuclei for Mg grains during solidification for the Mg-3Al alloy.

When an excess amount of Mn is added, the Al content in the melt gradually decreases due to the formation of Al-Mn compounds, which will result in the decrease in the constitutional undercooling. The low constitutional undercooling can not effectively limit the growth of grains. In addition, further nucleation can not occur effectively in front of the S/L interface because the constitutional undercooling is the major driving force for nucleation.\textsuperscript{31)\textsuperscript{13}} So the grain size obviously increases after further increase in the Mn content to 0.5 mass$\%$ although more AlMn particles are formed.

For the Mg-Al alloys modified by carbon, the Al-C-O particles were also found in Mg-3Al alloy modified by 0.2 mass$\%$C in the present study. This fact may suggest that Al$_4$C$_3$ particles act as nucleants in Mg-Al alloys while O in nucleating particles comes from contamination during sample preparation because Al$_4$C$_3$ is extremely reactive to water.\textsuperscript{19)\textsuperscript{14}} After addition of Mn, the Al-C-O nucleating particles were completely transformed into Al-C-O-Mn intermetallic compounds, as shown in Fig. 4. Moreover, it was found that Mn had no obvious effect on the grain refining efficiency for the Mg-3Al alloy modified by carbon in the present study. The results are inconsistent with the results obtained by Tamura and Ma et al.\textsuperscript{5–10)\textsuperscript{15}} who stated that Mn is an inhibiting element which poisons the nucleating potency of Al-C-O particles by transforming them to Al-C-O-Mn intermetallic particles. However, the present results are consistent with the results obtained by Pan and Ma et al.\textsuperscript{11,13)\textsuperscript{16}} In their studies, the remarkable refining effects were obtained for the commercial Mg-Al alloys modified by carbon containing agents although the Al-C-O-Mn(Fe)-rich heterogeneous nucleating particles were also found.

In the Tamura’s researches, the Al$_4$C$_3$ particles existed in the ultra-high-purity Mg-Al alloys in advance although the Mg melt was not modified by carbon containing agents.\textsuperscript{5)\textsuperscript{17}} These particles were termed as the native nucleating particles by Ma et al.\textsuperscript{9)\textsuperscript{18}} After addition of Mn or Fe, the grain size of ultra-high-purity Mg-9Al alloys increased and Al-C-O-Mn(Fe) particles were found.\textsuperscript{7)\textsuperscript{19}} In the latest research, a new hypothesis was proposed by Cao et al.\textsuperscript{10)\textsuperscript{20}} who attributed the poisoning effect to the formation of a coating film containing Fe and/or Mn on the Al$_4$C$_3$ nucleant particles. This hypothesis was differentiated from traditional viewpoint of the Al-C-O-Mn compounds and was used rationally to explain the refining mechanism for the Mg-Al alloys treated by superheating. Nevertheless, in the research results conducted by Pan et al.\textsuperscript{11)\textsuperscript{21}} and present study, the Al-Mn intermetallic compounds existed in the melt in advance and then the melt was modified by carbon. The Al-C-O-Mn compounds are probably formed by two ways. One is that the Al-C compounds are formed by a reaction between Al and C firstly, then the Al-C compounds are adsorbed on the surface of Al-Mn compounds. The other is the Al-C-O-Mn compounds are directly formed by a reaction between C and Al-Mn compounds on the surface. Anyway, it is possible that Al$_4$C$_3$ coating film can be formed on the surface of Al-Mn compounds. Figure 5 schematically shows the possible evolution of the Al$_4$C$_3$ coating film formed on the Al-Mn intermetallic compounds. The Al$_4$C$_3$ coating film is formed on the surface of Al-Mn compounds and then grows gradually. As a result, the particles of the Al-Mn compounds with Al$_4$C$_3$ coating film act as nuclei for Mg grains. So the same refining efficiency can be expected for the Mg-Al alloys modified only by carbon, although Mn has been added in the Mg-Al melt. Further indepth microscopic work should be needed to support the new concept and to find detailed description of the coating behavior of Al$_4$C$_3$ on the Al-Mn-rich intermetallic compounds.

5. Summary

(1) There existed the optimal content of 0.1–0.2 mass$\%$Mn to obtain refining grain size for the Mg-3Al alloy. The
particles of Al-Mn compound with the molar ratio of 1 : 1 were considered as the potent nuclei for Mg grains.

2) Significant grain refinement was obtained for the Mg-3%Al alloy modified with carbon. The addition of Mn had no obvious effect on the grain size of Mg-3Al alloy which was refined by 0.2 mass%C and the grain size was kept constant with increase in the Mn content.

3) The Al-C-O-Mn compounds were considered as the potent nuclei for Mg grains. A new hypothesis that the particles of Al-Mn compounds with Al\(_4\)C\(_3\) coating film can act as potent nuclei for Mg grains was proposed.

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REFERENCES
