Effects of Carbon and/or Alkaline Earth Elements on Grain Refinement and Tensile Strength of AZ31 Alloy

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The effects of carbon and/or alkaline earth elements Ca and Sr on the grain refinement and tensile properties of the AZ31 alloy have been investigated in the present study. A significant grain refining efficiency could be obtained for the AZ31 alloy modified by carbon inoculation and the grain refining efficiency could be further improved by the combination of 0.2 mass%C and alkaline earth elements of 0.2 mass%Ca or 0.2 mass%Sr. Compared to the AZ31 alloy without any treatment, the tensile properties of the AZ31 alloy were remarkably improved after being modified by the combination of carbon and a little addition of alkaline earth elements. The ultimate tensile strength and elongation to failure were improved by about 20% and 40%, respectively. After being refined either by 0.2 mass%C or by the combination of 0.2 mass%C and a little addition of alkaline earth elements (0.2 mass%Ca or 0.2 mass%Sr), the main fracture mechanism was changed from cleavage mode with large cleavage planes for the unrefined AZ31 alloy to mixed mode of cleavage and quasi-cleavage fracture. The fracture surfaces were almost composed of small cleavage planes with thin rive patterns and quasi-cleavage planes with small dimples and severe plastic deformation.

Keywords: AZ31 magnesium alloy, grain refinement, alkaline earth elements, carbon, tensile properties

1. Introduction

Recently, the demand for magnesium alloys has been increased rapidly owing to applying more and more light materials in the automobile industry, in order to reduce fuel consumption and lower waste gas emission.1) Among the broad range of magnesium alloys, aluminum bearing magnesium alloys (Mg-Al alloys) take a dominating position of consumption. High pressure die casting is the dominant process for magnesium components to be applied in the automobile industry. Recently, increasing attentions have been paid to wrought magnesium alloys, i.e., extrusions and sheet products due to their better mechanical properties.2,3) Among the Mg-Al alloys, AZ31 alloy is the most widely used as commercial wrought magnesium alloy.3,4)

Compared to aluminium alloys, the ductility and formability of magnesium alloys are relatively poor at room temperature because magnesium has hexagonal close packed (HCP) crystal structure and highly anisotropic dislocation slip behaviour.5) It is well known that the grain refinement, often combined with finer and uniform distribution of intermetallic phases, can effectively improve the mechanical properties and formability of the cast metal products. Therefore, it is very important to investigate the grain refinement of magnesium alloys, especially for the Mg-Al alloys.

Many investigations have been performed on the grain refinement for the Mg-Al alloys since 1930s.6,7) The main grain refining methods for this group alloys are superheating8,9) FeCl3 inoculation,10) carbon inoculation11–19) and addition of solute elements.20–22) Among them, the carbon inoculation has the advantages in the low cost, the low operating temperature and the less fading. For the carbon inoculation, the most possible refining mechanism proposed by Emley in his book7) is that Al3C3 particles formed in the Mg-Al melt act as nuclei for the α-Mg grains during solidification. This hypothesis has been widely appreciated by other researchers.11–16)

As for the Mg-Al alloys, the addition of solute elements (e.g., Ca, Sr, RE) is another important grain refining method. For example, small amount of addition of alkaline earth elements Ca or Sr was found to be very effective in refining the microstructures of the Mg-Al alloys.20–22) The significant grain refinement potential of Ca or Sr is associated with higher constitutional undercooling at the advancing solid/liquid (S/L) interface during solidification due to the strong segregating power of Ca or Sr in the magnesium melt.20,21) This refining mechanism is completely different from that of the carbon inoculation.

According to the classical solidification theory, the grain size of a casting can be refined by increasing the number of potent nuclei in the melt and constitutional undercooling at the advancing solid/liquid interface during solidification.20) Recently, the authors reported that the higher grain refining efficiency could be obtained for the Mg-3Al alloy modified by the combination of carbon and alkaline earth elements Ca or Sr due to the synergistic action of more potent nuclei and higher constitutional undercooling.20,21)

In the present study, the AZ31 alloy was used and the following research works have been carried out to clarify: (1) whether the high grain refinement could also be obtained for the AZ31 alloy which was modified by the combination of carbon and alkaline earth elements Ca or Sr; (2) how mechanical properties change for the AZ31 alloy which was modified with only carbon and alkaline earth elements Ca or Sr, as well as the combination of carbon and alkaline earth

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elements. The ultimate purpose is that some important data were provided to develop a suitable and reliable grain refiner to be applied for the Mg-Al alloys.

2. Experimental Procedure

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), high purity zinc (99.99 mass%Zn), electrolytic manganese (99.9 mass%Mn), Al-15 mass%Ca and Al-15 mass%Sr master alloy, 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%).

To ensure the carbon powder can be dispersed into the melt slowly and uniformly, the cylindrical pellets containing carbon powder were prepared in advance, having about 3 mm in diameter and about 5 ~ 10 mm in height. The mixtures comprising carbon powder, magnesium powder and aluminum powder were blended at a mass ratio of 1 : 5 : 4 firstly, then the pellets were formed by using a cold isostatic press (CIP) under a pressure of 150 MPa for 1 h.

The AZ31 alloy was used in the present study. Its nominal compositions were 3 mass%Al, 1 mass%Zn, 0.15 mass%Mn, the rest Mg. The AZ31 melt was alloyed with Ca or Sr in the form of Al-15 mass%Ca or Al-15 mass%Sr master alloys, respectively. The addition of carbon is 0.2 mass% of the melt. To exactly control the Al content in the AZ31 melt, the contents of Al in the pellets and Al-15 mass%Ca or Al-15 mass%Sr master alloys were carefully taken into consideration.

The MgO crucible having high purity of more than 99.5 mass% was used. Pure Mg, Al, Zn, Mn and Al-15 mass%Ca or Al-15 mass%Sr master alloys were molten together with an electric resistance furnace at the temperature of 750°C. After that, the pellets were plunged into the melt. Then the melt was held for 10 min, was manually stirred for 1 min with a magnesia rod, and then was held for additional 10 min. Then the melt was poured into tabulate shaped copper mould with the size of 10 × 60 × 70 mm³, which was preheated at 600°C.

There were six kinds of samples were prepared in the present study. They were the AZ31 alloy which was modified without any treatment, with treatment by 0.2 mass%Ca or by the combination of 0.2 mass%Ca and 0.2 mass%Sr separately, with treatment by the combination of 0.2 mass%Ca and 0.2 mass%Sr and by the combination of 0.2 mass%Ca and 0.2 mass%Sr.

Metallographic samples were cut at the same position that was 20 mm from the bottom and 10 mm from one side of the tabulate ingots. To reveal grain boundaries, the samples were polished by nitride acid ethanol solution and then were etched by electric spark machine. Five specimens were prepared for every ingot. The tensile tests were performed on AG-2000 type material test machine in a crosshead speed of 1 mm/min at room temperature. The tensile fracture surfaces were observed by JEOL JSM 6606 scanning electron microscope (SEM).

3. Results and Discussion

3.1 Microstructures

3.1.1 Grain refining efficiency

Figure 1 shows the comparison of grain morphologies for the AZ31 alloy modified without any treatment, with treatment by 0.2 mass%Ca, 0.2 mass%Sr, and with treatment by 0.2 mass%Ca combined with 0.2 mass%Ca or 0.2 mass%Sr. For the sample without any treatment, the grain size was about 480 μm (Fig. 1(a)). The grain size was refined from about 480 to 180 μm after the sample was modified by 0.2 mass%Ca (Fig. 1(b)). For the samples modified by either 0.2 mass%Ca or 0.2 mass%Sr, the grain sizes were both about 220 μm (Figs. 1(c) and 1(d)). It is found from Figs. 1(e) and 1(f) that the grain sizes were further drastically refined after being modified by the combination of carbon and alkaline earth elements. The grain sizes were 130 μm and 140 μm for the samples modified by 0.2 mass%Ca combined with 0.2 mass%Ca and 0.2 mass%Sr, respectively.

3.1.2 SEM observation of Al-C-O particles

In the authors’ previous studies, the Al-C-O particles were observed in the samples of the Mg-3Al alloy modified either by 0.2 mass%Ca or by the combination of 0.2 mass%Ca and alkaline earth elements. In the Al-C-O particles, the alkaline earth elements were hardly detected by EDS when the addition contents of Ca or Sr were less than 0.2 mass%. In the present studies, the Al-C-O particles were also found in the samples of the AZ31 alloy modified either by 0.2 mass%Ca or by the combination of 0.2 mass%Ca and alkaline earth elements. Under the present conditions, not only the elements Ca or Sr but also Zn were not detected in the Al-C-O particles, even if high content Zn was added in the AZ31 alloy. The typical features of these Al-C-O particles are shown in Fig. 2, which was observed from the sample of the AZ31 alloy modified by the combination of 0.2 mass%Ca and 0.2 mass%Ca. Figure 2(a) shows the distribution of the Al-C-O particles which were denoted by A, B and C. The highly magnified features of these particles with size about 2 μm are shown in Fig. 2(b), corresponding to the particles denoted by A, B and C in Fig. 2(a). The typical EDS spectrum of the Al-C-O particle is shown in Fig. 2(c), which was measured for particle C.

The significant refining efficiency was obtained for the AZ31 alloy modified by 0.2 mass%Ca in the present study, as shown in Fig. 1. For the grain refinement of Mg-Al alloys by carbon, the hypothesis that the Al₄C₃ particles should play an
important role in grain refinement has been widely accepted by many researchers,11–19 although Al-C-O particles were usually found in Mg-Al alloys modified by carbon.11,12,16 From the viewpoint of lattice disregistry, both Al$_4$C$_3$ and Al$_2$CO are suitable for acting as nucleating particles for the magnesium phase with the planar disregistry of only 4% and 0.9%, respectively. Their crystal structures and lattice parameters are listed in Table 1.13 Recently, the theoretical results calculated by Zhang et al.30 showed that the Al-C-O particles with the form of Al$_2$CO are effective nucleating particles for α-Mg grains. However, the grain refinement of Mg-Al alloys resulting from carbon inoculation was attributed to Al$_4$C$_3$ particles could not be accepted because the formation of Al$_4$C$_3$ phase in magnesium melt is impossible in the molten Mg-Al alloys from the viewpoint of thermodynamic consideration.31 It is therefore deduced that Al$_4$C$_3$ particles should act as nuclei for α-Mg grains in the AZ31 alloy, while O in nucleating particles comes from contamination during the process of sample preparation because Al$_4$C$_3$ is extremely reactive to water.16

Figures 1(c) and 1(d) show that a small amount (0.2 mass%) of addition of Ca or Sr can effectively refine the grain size of the AZ31 alloy. For magnesium alloys, Ca and Sr have been usually regarded as the very effective elements for inhibiting grain growth due to their high segregating power in the magnesium melt.2,20 The segregating power of a solute can be evaluated by $GRF = mC_0(k - 1)$, where $GRF$ is the growth restriction factor which reflects the segregating power of the solute, $m$ is the slope of the liquidus line, $k$ is the equilibrium distribution coefficient and $C_0$ is the initial concentration of the solute.2 The effect of $GRF$ resulting from Ca or Sr in the Mg-Al melt
on the grain refinement has been discussed in detail in the authors’ previous studies.\textsuperscript{26,27}) Judged by Fig. 1, much higher refining efficiency could be obtained for the samples of the AZ31 alloy modified by 0.2 mass% C combined with either 0.2 mass% Ca or 0.2 mass% Sr, compared to the other samples of the AZ31 alloy modified separately by 0.2 mass% C, 0.2 mass% Ca and 0.2 mass% Sr. A conclusion could be drawn in the present study that alkaline earth elements Ca or Sr are effective elements to improve the grain refining efficiency for the AZ31 alloy modified by carbon inoculation.

For ordinary metal alloys, the number of potent nuclei in the melt and constitutional undercooling at the advancing solid/liquid interface are very important factors to determine the final grain size of a cast. For the sample modified by the combination of carbon and alkaline earth elements, a large amount of Al\textsubscript{4}C\textsubscript{3} particles could be formed in the melt, which should act as potent nuclei for the α-Mg grains during solidification. On the other hand, the addition of alkaline earth elements can effectively restrict grain growth since the diffusion of the solute occurs slowly. In addition, further nucleation occurs in front of the diffusion layer because nucleants in the melt are more likely to survive and be activated in the constitutionally undercooled zone since constitutional undercooling is a major driving force for nucleation.\textsuperscript{2,20}) Therefore, further refining efficiency could be obtained for the Mg-Al alloy modified by the combination of carbon and alkaline earth elements.

### 3.2 Tensile properties

Figure 3 shows the typical curves of tensile strength vs tensile strain for the samples of the AZ31 alloy modified by the different routes. The tensile tests were performed five times for every sample prepared in the present study. And then the experimental results of ultimate tensile strength and elongation to failure were averaged. The average results and error bars are shown in Fig. 4. For the sample of the AZ31 alloy without any treatment, the ultimate tensile strength and elongation to failure were 168 MPa and 9.6%, respectively. For the three kinds of samples of the AZ31 alloy treated separately by 0.2 mass% C, 0.2 mass% Ca and 0.2 mass% Sr, the ultimate tensile strengths were all about 185 MPa and
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Fig. 3 Typical curves of tensile strength vs tensile strain for the samples of the AZ31 alloy modified by different routes.

Fig. 4 Mechanical properties of the samples of AZ31 alloy modified by different routes (1: without any treatment, 2: with treatment by 0.2 mass% C, 3: with treatment by 0.2 mass% Ca, 4: with treatment by 0.2 mass% Sr, 5: with treatment by 0.2 mass% C and 0.2 mass% Ca, 6: with treatment by 0.2 mass% C and 0.2 mass% Sr).

elongations to failure were in the range of 12–13%. For the other two samples of the AZ31 alloy which was modified by 0.2 mass% C combined with 0.2 mass% Ca or 0.2 mass% Sr, the ultimate tensile strengths were both about 200 MPa and elongations to failure were in the range of 14–15%. The results show that mechanical properties of the AZ31 alloy were remarkably improved after being modified by the combination of carbon and a little addition of alkaline earth elements. The ultimate tensile strength and elongation to failure were improved by about 20 and 40%, respectively.

Improvements of tensile strength and elongation are closely associated with the change of fracture mechanisms. For magnesium alloys, their fractures at room temperature are usually brittle in a cleavage or quasi-cleavage mode due to their HCP structure.5,32) Figure 5 shows the SEM images (shown in Fig. 5(a)) is mainly composed of smooth cleavage planes without river patterns (denoted by A) and rough cleavage planes with coarse river patterns (denoted by B). These features indicate the main fracture mechanism is cleavage mode for the AZ31 alloy having large grain size. The river pattern represents steps between local cleavage facets of the same general cleavage plane. The smooth cleavage planes (A in Fig. 5(a)) without river pattern observed indicate that the grain may have been orientated at a right angle to the main tensile axis, causing the fracture to propagate very easily on a single plane.

For the sample of the AZ31 alloy with treatment by 0.2 mass% C, the cleavage planes without river pattern are hardly observed in the fracture surface. Instead, the fracture surface is almost composed of small cleavage planes with thin river patterns and quasi-cleavage planes (denoted by C) with small dimples and severe plastic deformation spread in some regions. The dimples and plastic deformation zones with tear ridges can be clearly observed in the high magnification SEM image of the fracture surface, as shown in Fig. 6(a). These features indicate the fracture of the refined AZ31 alloy by carbon inoculation is mixed mode of quasi-cleavage and cleavage fracture. The plastic deformation zones with tear ridges indicate the improvement of ductility for the AZ31 alloy when it was refined by carbon inoculation. While comparing the fracture surface of the AZ31 alloy refined by carbon inoculation, quasi-cleavage planes with plastic deformation zones are relatively less in the fracture surfaces of the AZ31 alloy refined by 0.2 mass% Ca or 0.2 mass% Sr. Their fracture surfaces are almost composed of small cleavage planes with thin river patterns. The deformation zone is confined in the calcium and strontium added AZ31 alloy, which is possibly attributed to small amount of brittle metallurgical phases containing Ca or Sr formed in the AZ31 alloy.22–25)

For the samples with treatment by 0.2 mass% C combined with 0.2 mass% Ca or 0.2 mass% Sr, the characteristics of fracture surfaces are like that of the sample with treatment by 0.2 mass% C. Their fracture surfaces are also mainly composed of river patterns (denoted by B) and quasi-cleavage planes (denoted by C) with small dimples and severe plastic deformation in some regions. The small dimples can be clearly observed in the high magnification SEM image of the fracture surface, as shown in Fig. 6(b). Compared to the fracture surface of the AZ31 alloy refined by only 0.2 mass% C, the cleavage planes with thin river patterns are relatively small, otherwise the regions of quasi-cleavage planes with small dimples and severe plastic deformation increase. Small cleavage planes with thin river patterns and many quasi-cleavage planes connected by tear ridges and dimples ensure the high ductility and strength in these refined alloy, as shown in Figs. 3 and 4.

4. Conclusions

(1) A significant grain refining efficiency could be obtained for the AZ31 alloy modified by 0.2 mass% C and the grain refining efficiency could be further improved by the addition of 0.2 mass% C combined with alkaline earth elements of 0.2 mass% Ca or 0.2 mass% Sr.
Compared to the AZ31 alloy without any treatment, the tensile properties were slightly improved after being modified separately by 0.2 mass%C, 0.2 mass%Ca and 0.2 mass%Sr. The tensile properties of the AZ31 alloy were remarkably improved after being modified by the combination of carbon and a little addition of alkaline.

Fig. 5 SEM images of the tensile fracture surfaces for the samples of the AZ31 alloy without any treatment (a), with treatment by 0.2 mass%C (b), with treatment by 0.2 mass%Ca (c), with treatment by 0.2 mass%Sr (d), with treatment by the combination of 0.2 mass%C and 0.2 mass%Ca (e) and with treatment by the combination of 0.2 mass%C and 0.2 mass%Sr. (A) smooth cleavage plane, (B) cleavage plane with river pattern, (C) quasi-cleavage plane.

Fig. 6 High magnification SEM images of the tensile fracture surfaces for the samples of the AZ31 alloy with treatment by 0.2 mass%C (a) and with treatment by the combination of 0.2 mass%C and 0.2 mass%Ca (b).
earth elements. The ultimate tensile strength and elongation to failure were improved by about 20 and 40%, respectively.

(3) The main fracture mechanism is cleavage mode with large cleavage planes for the unrefined AZ31 alloy having large grain size. After being refined either by 0.2 mass% C or by the combination of 0.2 mass% C and a little addition of alkaline earth elements (0.2 mass% Ca or 0.2 mass% Sr), the main fracture mechanism was changed to the mixed mode of cleavage and quasi-cleavage fracture. The fracture surfaces were almost composed of small cleavage planes having thin river patterns and quasi-cleavage planes with small dimples and severe plastic deformation.

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