The Effect of Cerium on Microstructures and Mechanical Properties of Mg-4Al-2Sn-1Ca Alloy

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The development of new creep resistant magnesium alloys has become a major research focus. This study examined the microstructure and creep properties of Mg-4.0 mass%Al-2.0 mass% Sn-1.0 mass%Ca alloys containing Ce. The results showed that Ce could improve dramatically the tensile strength and ductility of the alloy at room temperature and increase the creep resistance at elevated temperatures significantly. With a trace amount of Ce, the morphology changed from a coarse CaMgSn phase to a refined shape and the microstructure of the alloy was remarkably refined. [doi:10.2320/matertrans.M2010042]

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1. Introduction

As one of the lightest structural metal materials available, magnesium alloys are the most attractive candidates for automotive and aerospace applications.^{1,2)} However, these alloys need to meet certain mechanical criteria when used for structural applications. Mg-Al based alloys, such as AZ91D and AM60B, which exhibit superior die castability and a good balance of strength and ductility, have been used increasingly in automotive products. However, these alloys have poor creep resistance at temperatures above 125°C, making them unsuitable for major engine and power-train components.³⁻⁵⁾ Early developed creep-resistant Mg-Al based alloys were based on the Mg-Al-RE (AE series) and Mg-Al-Si (AS series) systems. The disadvantages of both alloy systems, such as the high cost or less than optimal properties, has prompted further research.⁶⁻⁸⁾ The addition of Sn and alkaline earth metals (Sr and Ca) is a potential way of producing heat-resistant Mg-Al alloys due to the formation of highly stable intermetallic compounds. Several studies⁹⁻¹¹⁾ reported that Mg-Sn-Ca and Mg-Al-Sn-Ca based alloys exhibit good creep resistance at low cost. However, there are only a few reports on the Mg-Al-Sn-Ca quaternary system. The results reported in previous work showed that the addition of Sn and Ca to the binary alloy, Mg-4Al, is quite effective in improving the creep resistance at temperatures > 150°C.^{12,13)} This paper reports the effects of the trace element Ce on the microstructure, tensile and creep properties of Mg-4Al-2Sn-1Ca alloys to provide a reference for the development of creep resistant magnesium alloys.

2. Experimental Procedures

Mg-4.0 mass%Al-2.0 mass% Sn-1.0 mass%Ca and 1.0 mass%Ce (simply noted as Mg-4Al-2Sn-1Ca and Mg-4Al-2Sn-1Ca-1Ce in this paper) containing alloys were prepared from high purity magnesium (99.9%), aluminum (99.99%), tin (99.9), and Mg-40 mass%Ca and Mg-40 mass%Ce master alloys. The alloys were melted at 750°C in a mild steel crucible under a CO₂+SF₆ atmosphere and then poured into preheated permanent mold at 200°C. The samples selected at

the corresponding position were homogenized at 420°C for 4 h in order to delineate the grains. Microstructural analysis was carried out using an optical microscope and a scanning electron microscope equipped with an energy dispersive X-ray spectrometer. The phases of the as-cast alloys were examined by X-ray diffraction (XRD) using monochromatic CuK α radiation. The tensile and creep test specimens were 3 mm $\times$ 6 mm $\times$ 30 mm in size. The tensile tests were performed at an initial engineering strain rate of $3.33 \times 10^{-2} \text{ s}^{-1}$ at room temperature. The tensile creep tests were conducted using a lever arm type creep tester in a box chamber (450 mm $\times$ 250 mm $\times$ 250 mm) for temperature control. The creep tests were carried out at constant temperatures between 150°C and 200°C and at constant applied stresses of 70 MPa. The tests were performed until the specimen broke or the minimum creep rate averaged over three tests had been reached.

3. Results and Discussion

3.1 Microstructure

Figure 1 shows the XRD patterns of the as-cast Mg-4Al-2Sn-1Ca alloys. The XRD results showed that the Mg-4Al-2Sn-1Ca alloy was composed mainly of α -Mg (hexagonal, P6₃/mmc), Mg₁₇Al₁₂ (Cubic, I $\bar{4}$ 3m), Mg₂Sn (Cubic, Fm3m) and CaMgSn (Orthorhombic, Pnma) phase. With the addition of Ce, peaks for an Al₁₁Ce₃ phase appeared. Figure 2 shows the microstructures of the as-cast and homogenized Mg-4Al-2Sn-1Ca and the Mg-4Al-2Sn-1Ca-1Ce alloys. The CaMgSn phase was distributed in the grain interior of the Mg-4Al-2Sn-1Ca alloy, and the Mg₁₇Al₁₂ and Mg₂Sn phase formed at the grain boundaries (Fig. 2(a)). With the addition of 1.0 mass% Ce, the microstructure of the as-cast Mg-4Al-2Sn-1Ca alloy was remarkably refined and the morphology changed from a coarse CaMgSn phase to a refined shape (Fig. 2(b)). The distribution coefficient of the solute Ce was found to be <1 according to the fundamentals of solidification and the binary phase diagram of the Mg-Ce system. Therefore, solute Ce atoms are enriched in the liquid ahead of the solid-liquid interface during the solidification process.¹⁴⁾ This might result in constitutional undercooling and a

Fig. 1 XRD patterns of as-cast alloys: (a) Mg-4Al-2Sn-1Ca, (b) Mg-4Al-2Sn-1Ca-1Ce.

decrease in rate of Sn and Ca diffusion, which would increase the number of nuclei and restrict the growth of the CaMgSn phase. However, the reason for the morphology change in the CaMgSn phase in the Ce-containing Mg-4Al-2Sn-1Ca alloy is unclear and further study will be needed. Figure 2(c)–(d) shows the microstructures of the homogenized alloys. With the addition of 1.0 mass% Ce, the mean grain sizes of the Mg-4Al-2Sn-1Ca alloy decreased from 105 to 63 μm . The reduced grain size by Ce addition might be due to the enrichment of solute atoms leading to the formation of $\text{Al}_{11}\text{Ce}_3$ phase, which are distributed mainly in the grain boundary areas, further restricting grain growth.¹²⁾

3.2 Tensile properties

Figure 3 shows the stress-strain curves and fractography of the alloys tested at room temperature. As shown in Fig. 3(a), the ultimate tensile strength and elongation of the as-cast Mg-4Al-2Sn-1Ca alloy were 150 MPa and 5.5% respectively, while the ultimate tensile strength and elongation of the Mg-4Al-2Sn-1Ca-1Ce alloy were 194 MPa and 11.4% respectively. The addition of 1 mass% Ce to the alloy had an effect on the mechanical properties of the Mg-4Al-2Sn-1Ca alloy. Both the fracture strength and ductility increased. This situation was possibly related to the refinement of the CaMgSn phase in the Mg-4Al-2Sn-1Ca-1Ce alloy. It is well known that the initiation of microcracks can be greatly influenced by the presence and nature of the second phase.⁷⁾ A common situation is for the particle to be cracked during deformation. Resistance to cracking is improved if the particle is well bonded to the matrix. Small and spherical particles are more resistant to cracking. However, the bigger the particle size is, the more easily the particle can be fractured. Addition of 1 mass% Ce content resulted in the morphological change from coarse CaMgSn to a refined shape. In addition, grain size was decreased from 105 to 63 μm . Therefore, the tensile strength of as-cast Mg-4Al-2Sn-1Ca-1Ce alloy was enhanced by second phase strengthening and fine grain strengthening.

As shown in Fig. 3(b)–(c), the fracture surface of the Mg-4Al-2Sn-1Ca alloy exhibited large cleavage-type facets (arrow 'A' in Fig. 3(b)). Apparently, the coarse CaMgSn phase in the Mg-4Al-2Sn-1Ca alloy would have a detrimental effect on the room temperature mechanical properties because the cracks could easily nucleate along the interface

Fig. 2 Optical micrographs of as-cast (a) Mg-4Al-2Sn-1Ca and (b) Mg-4Al-2Sn-1Ca-1Ce alloys and homogenized (c) Mg-4Al-2Sn-1Ca and (d) Mg-4Al-2Sn-1Ca-1Ce alloys.

Fig. 3 Stress-strain curves (a) and fractography of the as-cast alloys (b) Mg-4Al-2Sn-1Ca and (c) Mg-4Al-2Sn-1Ca-1Ce at room temperature.

Fig. 4 Creep curves at (a) 150°C, 70 MPa and (b) 200°C, 70 MPa and SEM micrographs of transverse section of the (c) etched Mg-4Al-2Sn and (d) Mg-4Al-2Sn-1Ca alloy and (e) non-etched and (f) etched Mg-4Al-2Sn-1Ca-1Ce alloy after creep at 200°C, 70 MPa.

between the CaMgSn phase and α -Mg matrix. Figure 3(a) highlights the difference in the tensile properties of the as-cast alloys. On the other hand, the fracture surfaces of the Mg-4Al-2Sn-1Ca-1Ce alloy showed only small cleavage-

type facets (arrow 'B' in Fig. 3(c)). This might be one reason for the difference in the tensile properties, particularly the elongation of the Mg-4Al-2Sn-1Ca alloys with and without Ce addition.

3.3 Creep behavior

Figure 4 shows the creep curves of the as-cast alloys obtained at 150°C, 200°C and 70 MPa and SEM micrographs of transverse section of the Mg-4Al-2Sn alloys after creep. The as-cast Mg-4Al-2Sn-1Ca and Mg-4Al-2Sn-1Ca-1Ce alloys exhibited higher creep-resistance than the Mg-4Al-2Sn alloy. The high creep-resistant properties of Mg-4Al-2Sn-1Ca and Mg-4Al-2Sn-1Ca-1Ce alloys were attributed mainly to the CaMgSn and Al₁₁Ce₃ phase in the alloys.

In general, the increase in the volume fraction of the thermally stable phases for magnesium alloys commonly results in an increase in creep-resistance.¹³⁾ Therefore, the minimum creep rate of the Mg-4Al-2Sn alloys at 150°C and 70 MPa changes from 1.01×10^{-7} to $9.15 \times 10^{-9} \text{ s}^{-1}$, indicating that the presence of Ce in the Mg-4Al-2Sn-1Ca-1Ce alloy improves the creep-resistance. Figure 4(c)–(f) shows SEM images of Mg-4Al-2Sn alloys obtained after creep rupture at 200°C and 70 MPa. Voids were initiated mainly at the Mg₁₇Al₁₂ phase and cracks propagated along the grain boundaries, suggesting that deformation by boundary sliding played an important role during the creep of these alloys. However, the propagation of cracks normally stopped in front of the CaMgSn or Al₁₁Ce₃ phase, indicating that the existence of these two phases inhibits sliding of the grain boundaries.

4. Conclusions

With the addition of 1.0 mass% Ce, the average grain size of primary α -Mg phase in the as-cast Mg-4Al-2Sn-1Ca alloy decreased from 105 to 63 μm and the refined CaMgSn phase was distributed uniformly within the grains of the as-cast Mg-4Al-2Sn-1Ca alloys. The ultimate tensile strength and elongation of the as-cast Mg-4Al-2Sn-1Ca-1Ce alloy were 194 MPa and 11.4%, respectively. The creep resistance was increased significantly by the addition of Ce due to the formation of thermally stable Al₁₁Ce₃ phase in the grain boundaries. The addition of Ce in the Mg-4Al-2Sn-1Ca alloy

led to the formation of a fine CaMgSn phase and a thermally stable second phase in the as-cast alloy, which accounted for the improvement in the tensile and creep properties in the Mg-4Al-2Sn-1Ca alloy.

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