Eutectic Phase Investigation in a Ca-added AM50 Magnesium Alloy Produced by Die Casting

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The eutectic phase in a 1.72 mass pct calcium added AM50 die-cast alloy homogenized at 673 K has been investigated by X-ray diffraction (XRD) and energy dispersive spectrometry (EDS). The XRD and EDS experiments indicate that the eutectic phase consists of a Al_2Ca phase with the C15 structure and contains 10.76 atomic pct magnesium in the equilibrium state. The solubility lobe of the Al_2Ca phase lies parallel to the equi-66.7 at%Al composition line in the Mg-Al-Ca ternary grid, indicating that magnesium preferentially substitutes the calcium site of the Al_2Ca phase.

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1. Introduction

Magnesium has the lowest density among the conventional engineering metals.¹⁾ The automotive use of magnesium alloys has been growing for the past decade to reduce weight and improve fuel economy;^{2,3)} however, the applications are currently limited to a few room-temperature components such as instrument panels, steering wheels, *etc.*^{4,5)} The additional substantial increase of magnesium alloys is achieved by utilizing the alloys for powertrain components, namely, transmission cases and engine blocks,^{6,7)} where the operating temperatures can be as high as around 450 K.⁸⁾ A major requirement for these applications is a good high-temperature performance of magnesium alloys.^{9–12)}

Calcium is a cost effective and lighter alternative to rare-earth elements to improve high-temperature mechanical properties of Mg-Al alloys.^{13–15)} A thousandfold increase in creep strength has been successfully achieved in the die-cast AM50 alloy by the addition of 1.72 mass pct calcium,^{16,17)} where AM50 offers good combination of die-castability, ductility and fracture toughness among the conventional commercial magnesium alloys.¹⁸⁾ The improvement in creep resistance of the AM50 alloy by the calcium addition is ascribed to the eutectic phase surrounding the α -Mg grains as shown in Fig. 1. The characteristic feature of the eutectic phase is expected to contribute to effective grain boundary strengthening or to resist the plastic flow of the α -Mg grains during the creep deformation.¹⁷⁾

The aim of the present study is to identify the eutectic phase formed in the 1.72 mass pct calcium added AM50 die-cast alloy through the combination of the X-ray diffraction (XRD) and energy dispersive spectrometry (EDS). Non-equilibrium phases may appear in the as die-cast state of Mg-Al-Ca alloys.^{19,20)} In this study, the isothermal homogenization treatment at 673 K is employed for the die-cast alloy to produce the equilibrium state of the alloy.

Fig. 1 FE-SEM micrograph of the eutectic phase formed in the AM50-1.72 mass%Ca die-cast alloy.

2. Experimental

The magnesium alloy of 1.72 mass pct calcium added AM50 (Mg-4.98Al-1.72Ca-0.29Mn in mass pct) was produced using a cold chamber die-casting machine at the casting and die temperatures of 993 and 473 K, respectively. The materials were obtained in the form of plates of 150 mm length, 70 mm width and thickness varying in steps from 1 to 3 mm. Specimens for the phase analysis were taken from the 3 mm thickness sections of the plates. The die-cast materials were homogenized at 673 K for 36 ks followed by water quenching.

The microstructure was observed by the field emission scanning electron microscopy (FE-SEM) operated at 5 kV. A metallographic sample was polished by the conventional mechanical polishing and etched in a solution of 2 ml HNO_3 and 98 ml ethyl-alcohol. The XRD experiments were carried out at room temperature using a diffractometer with a $\text{CuK}\alpha$ radiation operated at 40 kV and 30 mA. X-ray data was collected for the scanning angles of $20^\circ < 2\theta < 80^\circ$ using a 0.02° step scan. Compositional analysis was performed by the EDS attached to the transmission electron microscope

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Fig. 2 FE-SEM micrograph of the eutectic phase in the AM50-1.72 mass%Ca die-cast alloy homogenized at 673 K for 36 ks.

(TEM) operated at an accelerating voltage of 200 kV. Thin foils were prepared using twin-jet polishing with an electrolyte of 6 vol% perchloric acid and 94 vol% methanol at a temperature of 243 K.

3. Results and Discussion

The microstructure of the AM50-1.72 mass%Ca die-cast alloy homogenized at 673 K for 36 ks is presented in Fig. 2. The alloy consists of the eutectic phase on a grain boundary of the α magnesium solid solution. The eutectic phase changes into spherical in shape by the homogenization treatment, while the average grain diameter of the α grains is 5.3 μm almost identical with that of the as die-cast alloy shown in Fig. 1.

The X-ray diffraction spectrum of the homogenized alloy is shown in Fig. 3. The XRD spectra of the phases expected to appear in the alloy are also included in the figure along with their crystal structures.^{14,21)} The scattering angle and intensity for each phase were derived from the JCPDS card data. The identification of the crystal structure was attempted by fitting the XRD result to the spectra in Fig. 3. It was confirmed that the spectrum of the alloy consists of two phases, α -Mg phase with the A3 structure and Al_2Ca phase with the C15 structure. Then, the eutectic phase in the AM50-1.72 mass%Ca die-cast alloy is deduced to be the Al_2Ca phase in the equilibrium state.

The TEM/EDS results of the two phases in the homogenized alloy are summarized in Table 1, together with the results of the eutectic phase observed in the as die-cast alloy. It is found that the α -Mg phase contains 3.55 atomic pct aluminum and 0.18 atomic pct calcium in equilibrium of the alloy. The eutectic phase of the as die-cast alloy contains 17.47 atomic pct magnesium, while the concentration decreases to 10.76 atomic pct in the Al_2Ca phase of the homogenized alloy. The calcium concentration of the eutectic phase remains unchanged during the homogenization treatment.

The compositions of the eutectic phase presented in Table 1 are plotted in the Mg-Al-Ca ternary grid (Fig. 4). The Al_2Ca is known to be a Daltonide compound according to the recent binary phase diagram of the Al-Ca system,^{22–24)}

Fig. 3 X-ray diffraction spectra for four kinds of phases expected to appear in the AM50-1.72 mass%Ca die-cast alloy homogenized at 673 K for 36 ks ((a)–(d)). The scattering angle and intensity for each phase are derived from the JCPDS card data. The experimentally obtained XRD spectrum for the homogenized alloy is shown in (e).

Table 1 Phase compositions of the AM50-1.72 mass%Ca die-cast alloy homogenized at 673 K for 36 ks (in atomic pct), together with the data of the as die-cast alloy.

Sample	Phase	Mg	Al	Ca
Homogenized	α -Mg	96.03	3.55	0.18
	Al_2Ca	10.76	66.66	22.35
As die-cast	eutectic compound	17.47	59.80	22.87

however the Al-rich corner of the Mg-Al-Ca ternary phase diagram is not well established yet.^{25,26)} It is found in Fig. 4 that the composition of the eutectic phase shifts along the equi-Ca composition line through the homogenization treatment and the composition is placed on the equi-66.7 at%Al composition line in the equilibrium state.

It is well accepted that the site preference of the third element in a binary intermetallic compound is deduced from the direction of the solubility lobe in the corresponding ternary phase diagram.^{27,28)} The directions of the solubility lobe of the γ' - Ni_3Al phase with the L_{12} structure at 1273 K obtained by Ochiai *et al.* are reproduced in Fig. 5 for 21 kinds of the third elements as typical examples.²⁹⁾ Ochiai *et al.* suggested that if the γ' solubility lobe of the Ni_3Al -X extends to the direction from Ni_3Al to X_3Al in the Ni-Al-X ternary phase diagram, the third element X will preferentially occupy

Fig. 4 Composition of the Al_2Ca phase appeared in the AM50-1.72 mass%Ca die-cast alloy homogenized at 673 K for 36 ks (solid symbol), together with that of the eutectic phase in the as die-cast alloy (open symbol).

Fig. 5 Direction of solubility lobes of the ternary Ni_3Al phase at 1273 K reported by Ochiai *et al.*²⁹⁾

the nickel site. On the other hand, if the lobe direction is from Ni_3Al to Ni_3X , the third element X will preferentially occupy the aluminum site. Finally, for the γ' solubility lobe bisecting both directions, the third element will substitute both the nickel and aluminum sites. Then, Fig. 5 indicates that Co, Pt and Cu substitute preferentially for nickel, while Ti, Hf, V, Nb, Ta, Mo, W, *etc.* substitute for aluminum and Cr, Mn and Fe occupy both nickel and aluminum sites.

One certainly finds from Fig. 4 that the solubility lobe of Al_2Ca phase directs parallel to the equi-66.7 at%Al composition line in the Mg-Al-Ca ternary grid. Hence, it is claimed in the AM50-1.72 mass%Ca die-cast alloy homogenized at 423 K that magnesium of the order of 10.76 atomic pct substitutes preferentially the calcium site of Al_2Ca in the equilibrium state. The solubility limit of magnesium into the Al_2Ca phase has not been clarified yet and will be reported elsewhere.

4. Conclusions

The eutectic phase of a 1.72 mass pct Ca added AM50 die-

cast alloy homogenized at 673 K for 36 ks was identified by the combination of the XRD and TEM/EDS. The XRD and TEM/EDS experiments indicate that the eutectic phase is a Al_2Ca phase with the C15 structure and contains 10.76 atomic pct magnesium in the equilibrium state. The solubility lobe of the Al_2Ca phase directs parallel to the equi-66.7 at%Al composition line in the Mg-Al-Ca ternary grid, indicating that magnesium preferentially substitutes the calcium site of the Al_2Ca phase.

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