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Characterization of Mg-rich clusters in the C36 phase of the Mg–5Al–3Ca–0.7Sr–0.2Mn alloy

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ABSTRACT

In this paper, characterization of clusters embedded in the C36 eutectic phase using TEM, STEM and XRD methods is presented. Disk-shaped Mg-rich clusters with sizes less than 150 nm were observed in the sand-cast Mg–5Al–3Ca–0.7Sr–0.2Mn alloy. The composition of the C36 eutectic phase was 24.1Mg–47.2Al–27.8Ca–0.9Sr and that of the Mg-rich clusters was 53.1Mg–33Al–13.1Ca–0.8Sr in at.%. The lattice parameters of the C36 phase were determined to be a_0 = 5.827 Å and c_0 = 18.834 Å, whereas for the clusters they were determined to be a_0 = 5.586 Å and c_0 = 18.834 Å. The chemical compositions of the eutectic phase and clusters, and the decrease of the lattice parameters with increasing magnesium content in the C36 phases suggest that Mg atoms occupy both Al and Ca sites in the C36 phase.

1. Introduction

In the last decade, Ca-containing magnesium alloys have been the subject of numerous studies because calcium addition has proven to be beneficial for the mechanical properties of alloys at elevated temperature and also because Ca is a cheap and light alloying element [1,2]. Mg–Al–Ca–Sr alloys are mainly used in the automotive industry for components with complex shape, and the alloys can be used at temperatures up to 200 °C [3]. The most commonly used method for the fabrication of these alloys is high-pressure die casting [1,4]. Die cast Mg–Al–Ca–Sr alloys can achieve a tensile strength of around 250 MPa. However, the mechanical properties greatly depend on the gas porosity, which is due to gas entrapment during the high-speed injection in the die casting process [2,4,5]. Good mechanical properties of die cast Mg–Al–Ca–Sr alloy are dependent on a high cooling rate during the die cast. The use of casting methods, which are characterized by low solidification rates, promotes castings with a coarse-grained microstructure and low mechanical properties [6,7]. However, after gravity casting the mechanical properties of these alloys are comparable to those of expensive Mg–RE–Zn–Zr (ZRE1) alloys (tensile strength about 140 MPa and yield strength about 90 MPa) [8]. Thus, these alloys are a cheaper alternative to more expensive magnesium alloys containing zinc and rare earth metals.

The good creep resistance of Mg–Al–Ca–Sr alloys up to 200 °C can be attributed to the formation of high melting temperature compounds located in both the interdendritic regions and within the grains [1,9]. Depending on the chemical composition of the Mg–Al–Ca–Sr alloys, a few eutectic compounds in the interdendritic areas can be observed: (1) $(Mg,Al)_2Ca$ Laves phase with a C36 hexagonal structure, (2) Mg_2Ca Laves phase with a C14 hexagonal structure, (3) Al_4Sr phase with a tetragonal crystal structure, (4) $(Mg,Al)_{17}Sr_2$ with a hexagonal crystal structure, and (5) $Mg_{17}Al_{12}$ phase with an A12 crystal structure [4,9–15]. The first four phases have a favorable effect on the creep properties, whereas the low-melting point $Mg_{17}Al_{12}$ phase favors low creep resistance of magnesium alloys. Moreover, precipitates of the Al_2Ca Laves phase (C15, cubic crystal structure) were found within the α-Mg grains in the permanent-mold-cast Mg–5Al–3Ca–0.15Sr alloy. Finely distributed Al_2Ca precipitates can also be formed in die-cast Mg–5Al–3Ca–0.15Sr alloy as a result of aging in the temperature range from 175 °C to 350 °C, because precipitation is suppressed by the faster cooling rate of the die-casting process compared with the slower cooling rate of the permanent mold-casting process [13].

It is well known that the properties of materials strongly depend on the microstructure, and especially on the phase composition. In sand-cast Mg–5Al–3Ca–0.7Sr–0.2Mn and Mg–7Al–3Ca–0.7Sr–0.3Mn alloys the Mg-rich clusters within the C36 phase are observed. These clusters can play important role in the structural stability of C36 phase at elevated temperature. Our investigations (details results will be published in future) shows that these

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clusters transforms to needle-shaped precipitates within the C36 eutectic compound at 400 °C (these alloys cannot operate above 200 °C, however, short-term overheating above 200 °C can occur during exploitation) and contribute to the formation of cracks inside the C36 phase. Formation of these cracks causes significant deterioration of mechanical properties. Despite numerous studies of Mg alloys with Al and Ca [1–33], characterization of the clusters embedded in the eutectic compound in the Mg–Al–Ca–Sr alloys has not been performed. Thus, the objective of the present work is to characterize these clusters using transmission electron microscopy (TEM) and X-ray diffraction (XRD).

2. Experimental procedures

The Mg–5Al–3Ca–0.7Sr–0.2Mn magnesium alloy containing Al, Ca, Sr and Mn was prepared, and its composition was analyzed by X-ray fluorescence spectroscopy and determined to be Mg–5.1Al–2.96Ca–0.69Sr–0.15Mn in wt.%. Commercially pure Mg (99,8%), Al (99,8%), and Mn (99,7%) were used, and Sr and Ca were added in the form of Al–10 wt.% Sr and Al–85 wt.% Ca master alloys, respectively. Melting of the alloys was performed by induction melting in an alumina crucible under the protection of an argon atmosphere. The melt was maintained at 730 °C for 3 min then poured into sand moulds.

The microstructure of the Mg–5Al–3Ca–0.7Sr–0.2Mn alloy was analyzed by scanning electron microscopy (SEM) using a FE SEM Hitachi S-3400 N scanning electron microscope. Microstructure observations were preformed on the unetched samples. To reveal the precipitates located within the α-Mg grains, samples were etched in reagent containing 3 mL HNO_3 and 97 mL C_2H_5OH.

A Hitachi HD-2300A scanning transmission electron microscope (STEM) equipped with an energy dispersive X-ray (EDX) detector was used to identify the phase appearing in the Mg–5Al–3Ca–0.7Sr alloy, and for chemical microanalysis of the phases. To identify the phases, especially to characterize the clusters, a nanodiffraction technique was used. This technique enables acquisition of diffraction patterns from a small area (2 mrad). However, STEM possesses have limited ability to rotate the sample during analysis, thus the possibility of choosing a specific zone axis is hindered. Therefore, the FEI Titan 83/300 transmission electron microscope (TEM) was also used to analyze the phase composition and chemical composition of the intermetallic phases. Thin foils were prepared by electrolytic polishing. The electrolyte composition was 5.3 g lithium chloride, 11.16 g magnesium perchlorate, 500 mL methanol, and 100 mL 2-butoxyethanol. Polishing was performed at −45 °C and 20 V.

XRD patterns were obtained with a JEOL JDX-7S diffractometer with a copper anode. Registration was performed by 0.02° stepwise regression for 2θ ranging from 10° to 140°. Phase identification was performed using the ICDD PDF-4+database. The Rietveld method was used to determine the lattice parameters of the C36 phase. The structure models for the α-Mg, $Mg_{17}Sr_2$, Al_2Ca, Mg_2Ca, and $Al_{1.34}CaMg_{0.66}$ phases were taken from the ICDD PDF-4+database.

3. Results

The microstructure of the Mg–5Al–3Ca–0.7Sr alloy is composed of primary α-Mg solid solution grains and intermetallic compounds located in the interdendritic regions (Fig. 1). The intermetallic compounds that form eutectics with the α-Mg phase can be classified into three types: (1) lamellar eutectic consisting of Al- and Ca-rich phase (A type), (2) fine lamellar eutectic with Mg-, Al-, Ca-rich compound (B type), and (3) eutectic containing bulky Sr-rich phase (C type). Moreover, observations of the etched samples in light and scanning electron microscopes revealed the presence of needle-shaped precipitates (D type) in the α-Mg eutectic cells. Because the Mg–5Al–3Ca–0.7Sr alloy has a multi-phase structure and the volume fraction of the intermetallic phases is low, XRD analysis is hindered. An additional complication is the similarity of the crystal structures of the C36 and C14 phases, resulting in the peaks belonging to these Laves compounds overlapping in the XRD pattern. Therefore, to identify the crystalline structure of these intermetallic compounds, TEM observations were performed.

Table 1 summarizes the chemical compositions of the phases determined on the thin foils. The fine lamellar compound (B type) was identified as the C14 Laves phase with a hexagonal crystal structure (a_0 = 6.076 Å, c_0 = 9.771 Å) (Fig. 2). As shown in Table 1,

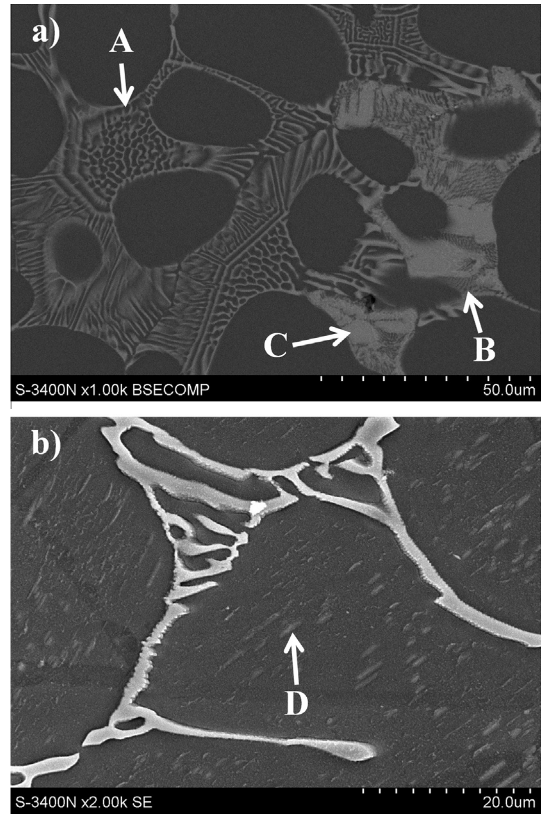

Fig. 1. SEM micrographs of the as-cast Mg–5Al–3Ca–0.7Sr alloy (a) BSE image, unetched sample, and (b) needle-shaped precipitates inside the α-Mg grains, SE image, etched in 3% HNO_3.

the Mg_2Ca Laves phase dissolved a large amount of aluminum. The bulky phase (C type) was identified as the $Mg_{17}Sr_2$ phase with hexagonal crystal structure (a_0 = 10.533 Å, c_0 = 10.342 Å) (Fig. 2). The EDX results indicate the solubilities of Al and Ca in the binary $Mg_{17}Sr_2$ phase. In view of the fact that the atomic sizes of Ca and Sr are similar, these elements could replace each other in the $Mg_{17}Sr_2$ phase. In the case of Mg and Al atoms, a similar rule can be applied and the formula can be written as (Mg, Al)$_{17}$(Sr, Ca)$_2$.

Inside the α-Mg grains, needle-shaped precipitates of the Al_2Ca phase with the C15 structure (D type) are visible (Fig. 3). The ratio of Al/Ca was close to 2, suggesting an Al_2Ca phase without Mg atoms. The high Mg content in the results of the EDX analysis is caused by the small size of the precipitates and the interaction between the electron beam and the Mg matrix.

Fig. 4 shows a TEM image taken of the lamellar phase (A type), and this region was used to identify the crystal structure of this phase by selected area diffraction (SAED). Several zone axes were imaged, and one of these is shown in Fig. 4. The [2 −1 −1 0] zone axis diffraction pattern from the lamellar eutectic compound confirms that it has the C36 crystal structure, because additional reflections along the 000l systematic set of reflections are visible. All of the obtained SAED patterns indicate that the dihexagonal C36 structure is present, with the lattice parameter in the a axis close to 5.9 Å and that in the c axis close to 20 Å.

Detailed observations of the C36 phase reveal the existence of fine rectangular and round clusters within the eutectic compound (Fig. 5). However, we also found regions of the C36 phase in which these clusters (islands) are not visible. The area fraction of clusters within the C36 phase, determined by quantitative metallography, is 9.7 ± 2.1%. The area fraction of C36 phase in the Mg–5Al–3Ca–0.7Sr–0.2Mn alloy is 6.6 ± 3.1%, thus the area fraction in alloy is about 0.65%. The maximum length of the rectangular-shaped