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Effect of substituting cerium-rich mischmetal with lanthanum on high temperature properties of die-cast Mg–Zn–Al–Ca–RE alloys

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Abstract

Mg–Zn–Al–Ca–RE alloys have been found to be promising materials for substituting aluminum alloys used for automatic transmission case applications in the automobile industry. Particularly, Mg–0.5%Zn–6%Al–1%Ca–3%RE (ZAXE05613) alloy exhibits comparable creep resistance as ADC12 die-casting aluminum alloy that is currently used for automatic transmission case applications. Changing the rare earth (RE) content of the alloy from mischmetal to lanthanum gives a further improvement in the creep properties of the alloy. Lanthanum addition results in the crystallization of a large amount of acicular $Al_{11}RE_3$ ($Al_{11}La_3$) compound along the grain boundaries as well as across the grain boundaries and this effectively controls grain boundary sliding and dislocation motion in the vicinity of the grain boundaries. As a result, die-cast ZAXLa05613 alloy exhibits a higher creep resistance than that of ZAXE05613 alloy.

Keywords: Magnesium alloys; Die-casting; Grain boundary compounds; Heat resistance

1. Introduction

Light-weight magnesium alloys exhibit high specific strength and stiffness. Therefore, extensive application of magnesium alloys to various automobile parts is expected to enhance fuel efficiency through weight reduction. Although some magnesium alloys are already being applied to certain automobile parts, such as instrument panel, seat frame, valve cover, steering wheel and steering column parts, and others [1], more effective weight reductions could be achieved by applying magnesium alloys to powertrain parts. Powertrain components like automatic transmission cases operate at elevated temperatures and die-casting is usually the preferred method of production. However, current magnesium alloys exhibit either good die-casting characteristics with poor heat resistance (e.g. AZ91D) or good heat resistance with poor die-casting characteristics (e.g. AS21) [2].

Recently, Mg–Zn–Al–Ca–RE alloys in which RE is added in form of Ce-rich mischmetal (50%Ce–25%La–20%Nd–5%Pr) have been systematically developed to simultaneously satisfy the two requirements of high heat resistance and excellent die-casting properties [3–7]. Among the new Mg–Zn–Al–Ca–RE alloys, Mg–0.5%Zn–6%Al–1%Ca–3%RE (ZAXE05613) alloy combines excellent die-casting properties with satisfactory heat resistance that is close to that of ADC12 aluminum alloy currently used for transmission cases. The microstructure of the alloy shows that Al_2Ca compound crystallizes along the grain boundaries, and in addition, two types of Al–RE compounds, Al_2RE and $Al_{11}RE_3$ also crystallize in the alloy [7]. In this paper, a detailed analysis of the composition of the RE-containing compounds is carried out and the preliminary result is utilized to develop a new alloy with improved microstructure features that could offer higher resistance to creep deformation. Consequently, the rare earth content of ZAXE05613 alloy was changed from ordinary Ce-rich mischmetal to lanthanum and the microstructure, high temperature tensile properties and creep resistance of the resulting alloy, ZAXLa05613, were investigated.

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Table 1
Chemical composition of investigated alloys (mass percentage)

Alloy	Zn	Al	Ca	RE	Mn	Mg
ZAXE05613	0.53	5.97	0.99	2.94[a]	0.24	Balance
ZAXLa05613	0.47	5.44	0.89	2.96[b]	0.21	Balance

[a] Ce-rich mischmetal.
[b] Lanthanum.

2. Experimental procedure

Die-casting of the investigated alloys was carried out using an 850 t cold chamber die-casting machine. Rectangular die-cast samples of 190 mm length, 115 mm width and 5 mm thickness were obtained. Table 1 shows the chemical compositions of the investigated alloys. Hereafter, the marks given in Table 1, which indicate alloy compositions, are used as alloy names.

Differential scanning calorimetry (DSC) was used to evaluate the solidification characteristics of the alloys and their microstructures were observed using an optical microscope after polishing and etching in 0.5% HF solution. The microstructures of the alloys were also observed using a transmission electron microscope (TEM) and a scanning electron microscope (SEM) equipped with a wavelength dispersive X-ray (WDX) spectrometer for electron probe micro-analysis (EPMA). X-ray diffraction patterns of the alloys were obtained and analyzed using an X-ray diffractometer operating at 40 kV and 30 mA. Furthermore, area fraction of eutectic compounds was evaluated using an image analyzer attached to a personal computer that has Image-Pro Plus software. Tensile creep test was carried out at 175–200 °C with a small fluctuation of ±2 °C under an applied stress of 50 MPa from 100 to 1200 h. Flat specimens having reduced cross-sectional dimension of 10 mm × 5 mm were used. High temperature tensile test of the die-cast samples was carried out from room temperature to 250 °C using specimens having a reduced cross-sectional dimension of 10 mm × 5 mm and a gauge length of 30 mm.

3. Results

3.1. Analysis of microstructures

Fig. 1 shows the microstructures of die-cast specimens of ZAXE05613 alloy that contains Ce-rich mischmetal. As shown in Fig. 1(a), eutectic compounds finely crystallize both inside the grains and along the grain boundaries. SEM images, Fig. 1(b) and (c), show that acicular compounds crystallize both along and across the grain boundaries, while fine particle-like compounds crystallize both within the grains and at the grain boundaries. Subsequently, proper identification of the compounds was done by carrying out EPMA using DSC specimens. The EPMA result is shown in Fig. 2. As shown in the figure, in addition to Al_2Ca, two types of Al–RE compounds, acicular $Al_{11}RE_3$ and particle-like Al_2RE compounds crystallize in the alloy [7]. Further investigation of the RE content of the Al–RE compounds shows that Al_2RE has higher content of cerium than other constituents of the Ce-rich mischmetal, while $Al_{11}RE_3$ has higher content of lanthanum than the others. As shown in Fig. 1, the acicular $Al_{11}RE_3$ compound occupies a large grain boundary area and this is considered

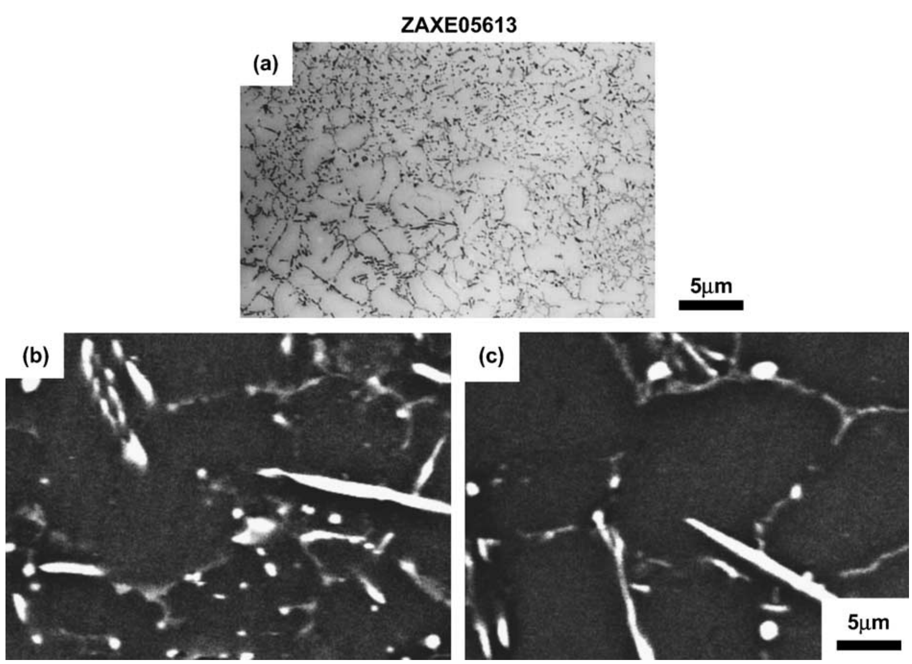

Fig. 1. Optical micrograph (a) and SEM images (b) and (c) of die-cast specimens of ZAXE05613 alloy.

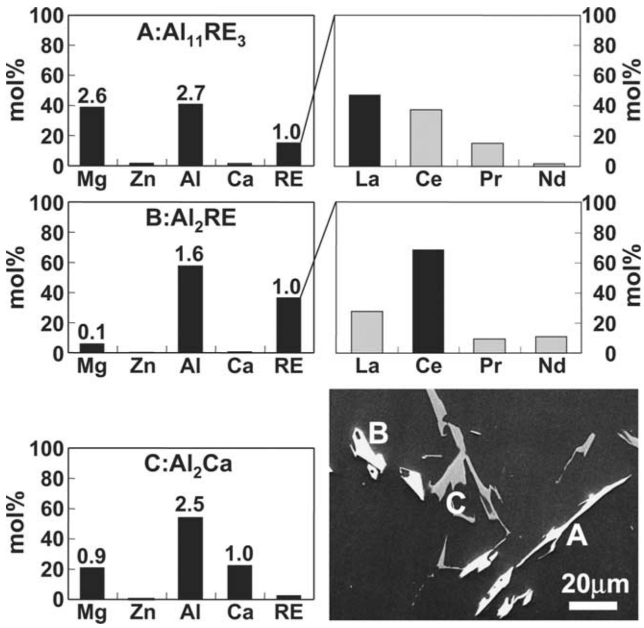

Fig. 2. EPMA result obtained for ZAXE05613 alloy using DSC specimen of the die-cast sample.

to be an effective obstacle to grain boundary sliding and dislocation motion in the vicinity of the grain boundaries during high temperature creep. Since grain boundary sliding has been shown to play a significant role in the creep deformation of die-cast magnesium alloys [8], compounds that could effectively strengthen the grain boundaries are needed to improve the creep resistance of die-cast magnesium alloys [9]. Consequently, an alloy based on the same composition as ZAXE05613 alloy but whose Al–RE compound would be mostly $Al_{11}RE_3$ compound was desired and the Ce-rich mischmetal was substituted with lanthanum in order to improve the creep properties of the alloy.

Fig. 3 shows the microstructure of die-cast specimen of the new alloy that contains lanthanum instead of cerium-rich mischmetal. The microstructure of the alloy, Mg–0.5%Zn–6%Al–1%Ca–3%La (ZAXLa05613) is similar to that of ZAXE05613 shown in Fig. 1(a), but the grain size of ZAXLa05613 alloy is finer than that of ZAXE05613 alloy. Furthermore, the area fraction of Al–RE compounds

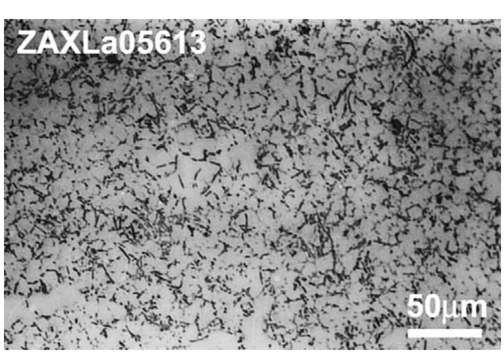

Fig. 3. Microstructure of die-cast specimen of ZAXLa05613 alloy.

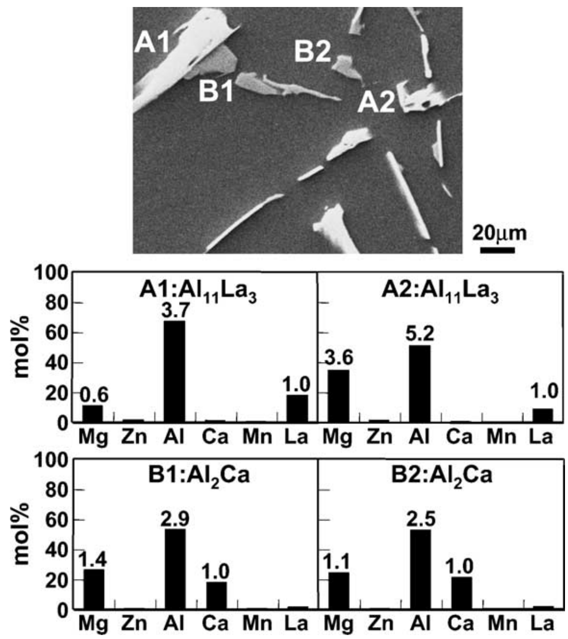

Fig. 4. EPMA result obtained for ZAXLa05613 alloy using DSC specimen of the die-cast sample.

that crystallize in ZAXLa05613 alloy is 8.1% and it is higher than that of ZAXE05613 alloy, which is 6.8%. This is because most or all of the lanthanum atoms are utilized in the formation of acicular $A1_{11}La_3$ compound. On the other hand, when mischmetal is added, a significant amount of the rare earth atoms are utilized in the formation of particle-like Al_2RE compound as well as acicular $A1_{11}RE_3$ compound. EPMA was carried out in order to characterize the compounds that crystallize in the ZAXLa05613 alloy and the result is shown in Fig. 4. As expected, apart from Al_2Ca, $Al_{11}La_3$ compound seems to have been the only Al–RE compound that crystallizes in the alloy. X-ray diffraction patterns obtained for the alloy confirms that Al_2Ca and $Al_{11}La_3$ are the main compounds that crystallize in the ZAXLa05613 alloy as shown in Fig. 5. However, it should be noted that Al_2La compound may also have crystallized in the alloy but the amount is too small to be detected by X-ray diffraction.

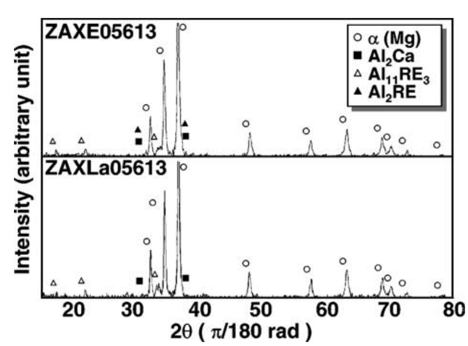

Fig. 5. X-ray diffraction patterns of die-cast specimens of ZAXE05613 and ZAXLa05613 alloys.

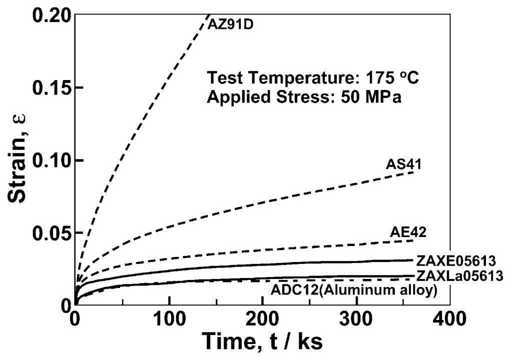

Fig. 6. Creep curves of die-cast specimens of investigated alloys tested at 175 °C under an applied stress of 50 MPa.

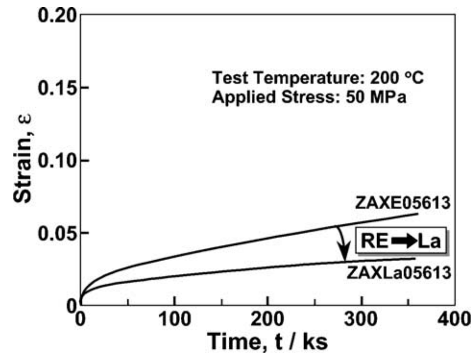

Fig. 8. Effect of lanthanum substitution on the creep resistance of die-cast specimens of Mg–Zn–Al–Ca–RE alloys tested at 200 °C under an applied stress of 50 MPa.

3.2. Evaluation of heat resistance

Fig. 6 shows the tensile creep curve of die-cast specimen of the new ZAXLa05613 alloy compared to those of other magnesium die-casting alloys and ADC12 aluminum alloy that is currently used for automatic transmission case application. The creep test was carried out at 175 °C under a load of 50 MPa. As shown in the figure, there is a significant improvement in the creep resistance of the new ZAXLa05613 alloy over that of the mischmetal-containing ZAXE05613 alloy. Furthermore, the new ZAXLa05613 alloy exhibits a similar creep behavior as the aluminum alloy, ADC12. This indicates that ZAXLa05613 alloy can be applied to automatic transmission cases. However, the compressive creep and bolt-load-retention properties of the alloy have to be evaluated before practical application can be realized.

The high temperature tensile properties of die-cast specimens of the alloys are shown in Fig. 7. Those of AZ91D alloy are also shown for comparison. The difference between the tensile properties of AZ91D alloy and those of the Mg–Zn–Al–Ca–RE alloys has been discussed elsewhere [7]. However, ZAXE05613 and ZAXLa05613 alloys exhibit comparable tensile properties although, the elongation of ZAXE05613 alloy is slightly higher than that of ZAXLa05613 alloy at all test temperatures.

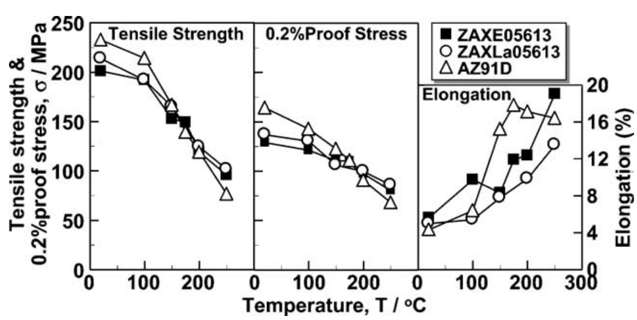

Fig. 7. Tensile properties of investigated alloys as function of temperature.

4. Discussion

The present investigation shows that substituting Ce-rich mischmetal with lanthanum in Mg–Zn–Al–Ca–RE alloys results in a significant alteration of their microstructures and this leads to an increase in the creep resistance of the alloys at 175 °C. A more substantial improvement in creep resistance is obtained even at a higher temperature of 200 °C, as shown in Fig. 8. This implies that lanthanum addition is more effective for strengthening the alloys against creep deformation than cerium-rich mischmetal. Since Al_2Ca compound crystallize in both alloys, the only major difference between their microstructures is the crystallization of a large amount of $Al_{11}La_3$ as the main Al–RE compound in ZAXLa05613, while ZAXE05613 alloy contains a mixture of Al_2RE and $Al_{11}RE_3$ compounds. Although both rare earth-containing compounds could be effective for improving the creep resistance of magnesium alloys [9,10], the nature of the crystallization of $Al_{11}RE_3$ compound (e.g. $Al_{11}La_3$ in ZAXLa05613) appears to be responsible for its higher creep resistance performance as discussed below. Fig. 9 shows SEM images of die-cast specimens of ZAXLa05613 alloy before and after creep test. The microstructures of the die-cast specimens of the alloy in which $Al_{11}La_3$ compound appears to be the main RE-containing compound show that the acicular $Al_{11}La_3$ compound crystallizes both across the grain boundaries (Fig. 9(a)) and along the grain boundaries (Fig. 9(b)). Some fine particles that could be Al_2La compound are also observed within the grain interiors. However, EPMA and X-ray diffraction analysis could not detect the presence of Al_2La compound as shown in Figs. 4 and 5, respectively. Fig. 9(c) and (d) show the microstructures of the alloy observed after creep test at 175 °C under an applied stress of 50 MPa for 1200 h. As shown in the figure, the micrographs are similar to those observed before creep test (Fig. 9(a) and (b)), indicating that the microstructure of the new alloy remains stable after the creep test. Although it has been reported that $Al_{11}RE_3$ compound decomposes during creep of AE42 alloy and leads to the formation of Al_2RE and $Mg_{17}Al_{12}$ compounds

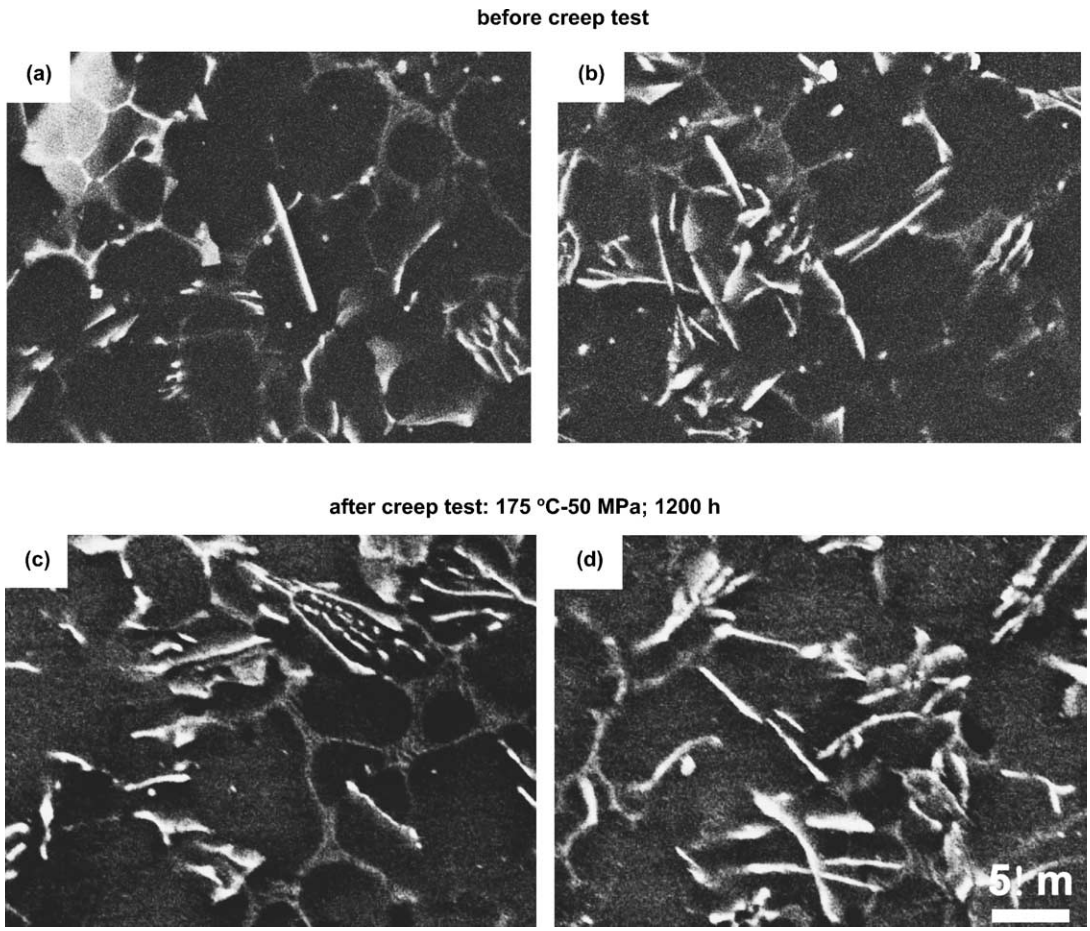

Fig. 9. SEM images of die-cast specimens of ZAXLa05613 alloy before and after creep test.

[10], no such microstructural changes relating to the decomposition of $Al_{11}La_3$ compound have been observed in ZAXLa05613 alloy as shown in Fig. 9. $Al_{11}La_3$ compound is apparently more thermally stable than $Al_{11}RE_3$ compound, which contains different rare earth atoms like cerium and neodymium that may readily form Al_2RE compound under severe creep conditions. Furthermore, the presence of calcium in ZAXLa05613 alloy, which forms stable Al_2Ca compound, helps to stabilize the microstructure of the alloy. Fig. 10 shows a transmission electron micrograph of ZAXLa05613 alloy after creep test at 175 °C under an applied stress of 50 MPa for 1200 h. Numerous dislocations are observed around the acicular $Al_{11}La_3$ compound and there are no indications of its decomposition even after prolonged (1200 h) creep test under sever creep conditions of 175 °C and stress of 50 MPa.

A model of the microstructure of ZAXLa05613 alloy is shown in Fig. 11. From the model, four major reasons are considered to be responsible for the higher creep resistance performance of $Al_{11}La_3$ compound, which makes ZAXLa05613 alloy to be more creep resistant than ZAXE05613 alloy. (1) The $Al_{11}La_3$ compound that crystallizes across the grain boundaries, such as A_1 in Fig. 11, provides a bridging effect between two adjacent grains. Consequently, while blocking the sliding of the grain boundary between the two grains, it also impedes dislocation motion in the vicinity of the grain boundary as shown in the TEM image of Fig. 10. That is, as shown in Fig. 11, A_1 simultane-

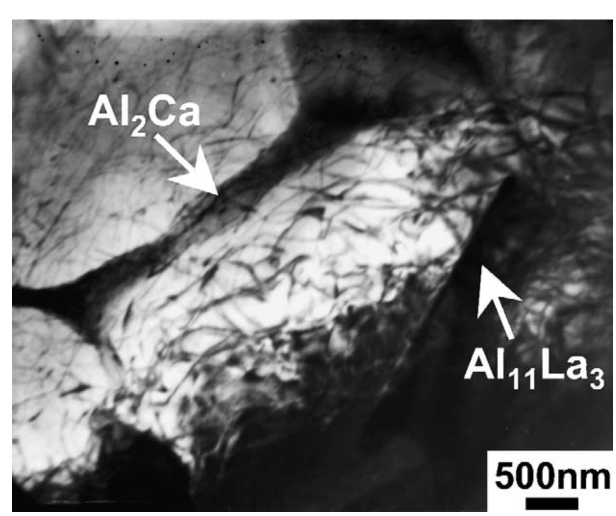

Fig. 10. Transmission electron micrograph of ZAXLa05613 alloy after creep test at 175 °C under applied stress of 50 MPa for 1200 h.

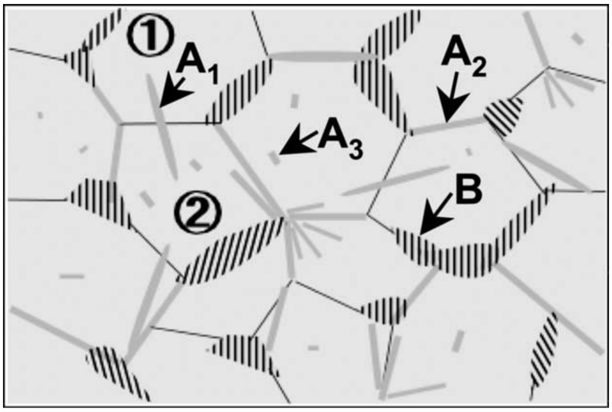

Fig. 11. A model of the microstructure of ZAXLa05613 alloy: A1 represents $Al_{11}La_3$ compound that crystallizes across the grain boundaries; A2 represents $Al_{11}La_3$ compound that crystallizes along the grain boundaries; and A3 represents $Al_{11}La_3$ compound that crystallizes inside the grains and B represents Al_2Ca compound.

ously impedes dislocation motion in the regions of grains ① and ② that are adjacent to the grain boundary between the two grains in addition to controlling the sliding of the grain boundary. (2) The length of the $Al_{11}La_3$ compound that crystallizes along the grain boundaries, such as A_2 in Fig. 11, ensures that a large portion of the grain boundary area is covered by second phase particles and this greatly complements the role of Al_2Ca compound (B in Fig. 11) in minimizing grain boundary sliding. (3) The $Al_{11}La_3$ compound that crystallizes in the grain interiors, such as A_3 in Fig. 11, helps to control dislocation motion within the grains. (4) The crystallization of $Al_{11}RE_3$ compound requires more aluminum atoms per RE atom than Al_2RE compound and this is expected to reduce the amount of aluminum atoms in solid solution. It has been observed that addition of RE to Mg–Al-based alloys restricts the crystallization of $Mg_{17}Al_{12}$ phase due to the preferential utilization of aluminum atoms to form Al–RE compounds [11]. Therefore, the chances of creep-induced precipitation of $Mg_{17}Al_{12}$ compound that deteriorates creep resistance of Mg–Al-based alloys is greatly reduced [8,9,12]. Furthermore, the diffusion of solute atoms of aluminum at elevated temperatures could be minimized if the amount of aluminum in solid solution is reduced.

The above four factors combine to yield an alloy having a stable matrix with well-fortified grain boundaries. This implies that microstructural instability in the near-grain boundary regions that is thought to significantly influence creep behavior in fine-grain magnesium die-castings [10,13], can be controlled. Consequently, a higher creep resistance is obtained in ZAXLa05613 alloy than in ZAXE05613 alloy. It should also be noted that the relatively more stable microstructure of ZAXLa05613 alloy is responsible for the lower elongation of the alloy since it is expected to provide a higher resistance to plastic deformation.

5. Conclusions

The effect of substituting cerium-rich mischmetal with lanthanum in Mg–Zn–Al–Ca–RE alloys has been studied. The results are summarized below.

(1) Lanthanum addition leads to the crystallization of a large amount of $Al_{11}RE_3$ ($Al_{11}La_3$) compound both across and along the grain boundaries and also within the grains.
(2) The particles of $Al_{11}La_3$ compound that crystallize across the grain boundaries provide a bridging effect between two adjacent grains and this simultaneously controls the sliding of the grain boundary between the two grains in addition to impeding dislocation motion in the vicinity of the grain boundary.
(3) The changes in microstructure that accompany lanthanum addition result in an alloy having a stable matrix with well-fortified grain boundaries. This is responsible for the higher creep resistance of ZAXLa05613 alloy in comparison with ZAXE05613 alloy.

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