Effects of Eutectic Compounds Formed along Grain Boundaries in Thixomolded® Alloy Mg96Zn2Y2 on Creep Deformation

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During thixomolding® of Mg alloys, fine grains (size of ~10 μm) and continuous eutectic compounds are formed along grain boundaries. These compounds are partly responsible for the superior creep strength of Mg alloys. In this study, we investigate the effects of eutectic compounds formed along grain boundaries in thixomolded® Mg96Zn2Y2 on creep deformation at 573 K. By performing microstructure analyses, we find that two types of continuous eutectic compounds—Mg3Y2Zn6 and Mg12YZn—are formed in the alloy. The stress exponent n of Mg96Zn2Y2 is about two orders of magnitude lower than that of a heat-resistant alloy Mg93Al5Ca9 (Mg-6 mass%Al-3 mass%Ca) at 573 K. The stress exponent n at 573 K is approximately 7, and it is considered that creep deformation is controlled by dislocation motion. All scribe lines produced on a specimen of Mg96Zn2Y2 are curved. Furthermore, in the case of a specimen with a creep strain of 7%, no abrupt steps are observed at grain boundaries and interfaces between the α-Mg matrix and eutectic compounds. Our results indicate that eutectic compounds formed along grain boundaries are effective in suppressing grain boundary sliding. [doi:10.2320/matertrans.MBW200831]

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1. Introduction

Magnesium (Mg) alloys are the lightest structural materials. It is expected that they will be used in the manufacture of vehicles in order to improve their fuel efficiency. However, the high temperature strength of these alloys, especially their creep strength, is not sufficient to use them to manufacture engine parts. Therefore, their application temperature is limited to ambient temperature. In order to increase the applicability of Mg alloys, it is necessary to improve their creep strength.

Recently, a new rapidly solidified powder metallurgy alloy Mg97Zn2Y2 that has a high strength has been produced. It exhibits a tensile yield strength of more than 600 MPa and an elongation of 5% at room temperature.1,2) This alloy has excellent mechanical properties because it consists of fine grains (100~200 nm in diameter) and twinning deformation occurring in the α-Mg matrix is suppressed by secondary phases with a long period stacking ordered structure.3) In contrast, Yamaguchi et al.4,5) have produced such alloys with excellent creep strength by Thixomolding® process, which is a combination of casting and injection molding. A thixomolded® alloy Mg96Zn2Y2 has higher creep strength than a die-cast aluminum alloy ADC12 at 473, 498 and 523 K.

It is reported that eutectic compounds are formed along grain boundaries in some types of Mg alloys (e.g., Mg-Al,6,7) Mg-Al-Ca,6,7) Mg-Al-Sr6) and Mg-Al-Zn6,10) fabricated by Thixomolding® process. According to Huang et al., solidification of the alloy ZW66 (Mg-5.52 mass%Zn-6.48 mass%Y), whose chemical composition is similar to that of Mg96Zn2Y2 (Mg-5 mass%Zn-6.7 mass%Y), occurs in three stages: (1) first, the α-Mg matrix is formed, (2) then, Mg12YZn is formed by the pseudobinary eutectic reaction, and (3) finally, Mg3Y2Zn3 is formed by the same reaction.11) In the case of Mg alloys in which eutectic compounds are formed along grain boundaries, suppression of grain boundary sliding by these compounds is considered one of the important creep strengthening mechanisms7,12–14) It is expected that creep strengthening will also occur in the thixomolded® alloy Mg96Zn2Y2, because it consists of an α-Mg matrix and eutectic compounds formed along grain boundaries. However, the strengthening effects of the eutectic compounds in Mg96Zn2Y2 during high-temperature creep deformation have not been described in detail. Therefore, in this study, we investigate the effects of eutectic compounds formed along grain boundaries in Mg96Zn2Y2 on its creep strength by analysis of creep parameters and microstructure observations.

2. Experimental Procedure

2.1 Test specimen

The alloy used in this study was a thixomolded® alloy Mg96Zn2Y2. From the Mg-Zn-Y ternary phase diagram at 573 K,15) it was found that the alloy consisted of three phases—α-Mg, Mg12YZn, and Mg3Y2Zn3. Thixomolding® process is a combination of die casting and plastic injection molding.5,7) Its merits are described below:

1. It is an environmentally friendly and safe process, because it is carried out without using the inert gas SF6, a greenhouse effects gas. Moreover, it is a closed-loop system.
2. It can be used for near-net-shape forming by injecting metallic slurry that is in the semi-solid or molten state into a die cavity.
3. Some Mg alloys produced by this process have better mechanical properties and corrosion resistance than alloys produced by die casting.

In this study, injection molding was carried out under the following conditions: cylinder temperature of 903 K (molten state), injection speed of 2 m/s, and die temperature of 433 K.
2.2 Creep tests

Compressive creep tests were performed on thixomolded\textsuperscript{\textregistered} specimens at 523\textdegree{}C\textdegree{} to 573\textdegree{}C in air under constant stresses of 50\textdegree{} to 130 MPa. The variations in temperature and stress were within \pm{} 1 K and \pm{} 0.5\%, respectively. Creep specimens were produced in the form of rectangular solids with dimensions of 2 \times{} 2 \times{} 3 mm by mechanical polishing with water-proof emery papers. No abnormal changes in the surfaces of the specimens were observed during preliminary examination. Therefore, inert gases were not used in the creep tests.

2.3 Microstructure observation and analyses

The microstructures of Mg\textsubscript{96}Zn\textsubscript{2}Y\textsubscript{2} were observed by field emission scanning electron microscopy (FE-SEM). The chemical compositions and crystal structures of eutectic compounds were analyzed by SEM equipped with energy-dispersive X-ray spectrometry (SEM-EDX) and X-ray diffraction (XRD) with Cu-K\alpha radiation (40 kV, 100 mA).

Distortion of scribe lines on the surface of a specimen during creep deformation was observed by FE-SEM, and the possibility of grain boundary sliding during the deformation was examined. The scribe lines were produced by focused-ion-beam scanning electron microscopy (FIB-SEM); they had a length of 50 \mu{}m, width of 1 \mu{}m, and depth of 1 \mu{}m. The ion beam source was gallium (Ga), and the acceleration voltage was 30 kV. Creep deformation occurred at 573 K under a stress of less than 70 MPa, and the interrupted strain was 7\%. Before SEM observation, the crept specimen was polished to remove contamination from its surface.

3. Results and Discussion

3.1 Microstructure of Mg\textsubscript{96}Zn\textsubscript{2}Y\textsubscript{2}

A typical microstructure of Mg\textsubscript{96}Zn\textsubscript{2}Y\textsubscript{2} is shown in Fig. 1. Fine \alpha{}-Mg matrix grains (about 10 \mu{}m in size) and two types of eutectic compounds—white (indicated by “a” in Fig. 1) and gray eutectic compounds (indicated by “b”)—were formed along the grain boundaries. The grain boundary coverage was 0.8; it is defined as the ratio of the grain boundary length by the eutectic compounds to the total grain boundary length. The area fraction of the eutectic compounds was 0.24. The XRD profile of Mg\textsubscript{96}Zn\textsubscript{2}Y\textsubscript{2} is shown in Fig. 2. Peaks corresponding to the \alpha{}-Mg matrix, Mg\textsubscript{12}YZn (hexagonal structure: \(a = 0.3224 \text{ nm}, c = 4.6985 \text{ nm}\))\textsuperscript{16} and Mg\textsubscript{3}Y\textsubscript{2}Zn\textsubscript{3} (AlMnCu\textsubscript{2}-type structure: \(a = 0.69116 \text{ nm}\))\textsuperscript{17} are observed in the profile. Results of SEM-EDX elemental mapping and point analyses of Mg, Zn, and Y are shown in Fig. 3 and Table 1, respectively. In Fig. 3 and Table 1, white eutectic compound is indicated by “A” and gray eutectic compound is also indicated by “B” and “C”. These results

![Fig. 1 SEM micrograph of the thixomolded\textsuperscript{\textregistered} alloy Mg\textsubscript{96}Zn\textsubscript{2}Y\textsubscript{2}. Two types of eutectic compounds (indicated by “a” and “b”) are formed along grain boundaries.](image1)

![Fig. 2 XRD profile of Mg\textsubscript{96}Zn\textsubscript{2}Y\textsubscript{2}.](image2)
show that the concentrations of Zn and Y are higher in the white eutectic compound than in the gray eutectic compound. In addition, the ratios of the concentrations of Zn and Y in the white and gray eutectic compounds are 3:2 and 1:1, respectively. These ratios are similar to those of Mg$_3$Y$_2$Zn$_3$ and Mg$_{12}$YZn, respectively. Point analyses also show high concentrations of Mg in Mg$_3$Y$_2$Zn$_3$ and Mg$_{12}$YZn. It is suggested that these results include Mg matrix effects because the acceleration voltage and spot size used in the quantitative analyses were large. Thus, it can be concluded that the white and gray eutectic compounds are Mg$_3$Y$_2$Zn$_3$ and Mg$_{12}$YZn, respectively.

### 3.2 Creep curve

A typical creep curve of Mg$_{96}$Zn$_2$Y$_2$ obtained at 573 K under a stress of 90 MPa is shown in Fig. 4. The creep curve of a thixomolded alloy Mg$_{93}$Al$_5$Ca$_2$ (Mg-6 mass%Al-3 mass%Ca), whose microstructure is similar to that of Mg$_{96}$Zn$_2$Y$_2$, obtained under the same conditions is also shown in this figure. In the case of Mg$_{93}$Al$_5$Ca$_2$, the average grain size is 8.7 µm, grain boundary coverage is 0.76, and area fraction of eutectic compounds is 0.18. The creep curves of both the alloys are normal, and the strain rate of Mg$_{96}$Zn$_2$Y$_2$ is about two orders of magnitude lower than that of Mg$_{93}$Al$_5$Ca$_2$. The effects of the alloying elements on the stacking fault energy are considered responsible for the large difference in strain rates as described in section 3.6.

### 3.3 Stress exponent

The minimum strain rate is plotted as a function of the applied stress, as shown in Fig. 5. Creep behavior at high temperature is generally described by the following power-law equation:

$$\dot{\epsilon} = A\sigma^n \exp(-Q_C/RT)$$

(1)

where $A$ is a material-related constant, $\sigma$ is the applied stress, $n$ is the stress exponent, $Q_C$ is the creep activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. The $n$ value of Mg$_{96}$Zn$_2$Y$_2$, i.e., the slope of the line in Fig. 5, is approximately 7, which is higher than the $n$ values of other Mg alloys that have similar grain sizes. Several studies have determined the dominant creep mechanisms of these alloys. Mabuchi et al. have reported that extruded AZ91 (Mg-9

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Table 1 Chemical compositions of eutectic compounds in the thixomolded alloy Mg$_{96}$Zn$_2$Y$_2$. These compounds were analyzed by SEM-EDX.

<table>
<thead>
<tr>
<th>Analysis Point</th>
<th>Y (at%)</th>
<th>Zn (at%)</th>
<th>Mg (at%)</th>
<th>Y : Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.36</td>
<td>7.01</td>
<td>87.62</td>
<td>2 : 3</td>
</tr>
<tr>
<td>B</td>
<td>3.32</td>
<td>3.98</td>
<td>92.70</td>
<td>1 : 1</td>
</tr>
<tr>
<td>C</td>
<td>3.75</td>
<td>4.65</td>
<td>91.60</td>
<td>1 : 1</td>
</tr>
</tbody>
</table>

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Fig. 3 Results of SEM-EDX elemental mapping of Mg$_{96}$Zn$_2$Y$_2$. (a) SEM image, (b) Mg, (c) Zn, and (d) Y. A, B, and C in (a) represent the points at which SEM-EDX point analyses were performed.
mass%Al-1 mass%Zn) alloys varying grain size from 7.6 to 15.4 \( \mu \)m have strain rate sensitivity of \( \frac{m}{n} = 0.5 \) (\( m \) is defined as \( 1/n \), where \( n = 2 \)) at 573 K. \[1\] From this high value of \( m \), grain boundary sliding is the deformation mechanism in this alloys. Similar results have been obtained in the case of extruded AZ61 (Mg-6 mass%Al-1 mass%Zn) alloys that contain fine grains with a size of 6~17 \( \mu \)m. \[22, 23\] Further, Valle et al. have reported that grain boundary sliding (\( n = 2 \)) occurs in fine-grained AM60 (Mg-6 mass%Al) alloys (grain size of \(<28.1 \mu \)m) during high-temperature creep deformation. \[24\] Therefore, grain boundary sliding in fine-grained Mg alloys significantly affects their creep strength. However, the \( n \) value of Mg\(_{90}\)Zn\(_2\)Y\(_2\) is higher than that of Mg alloys (\( n = 2, m = 0.45 \sim 0.5 \)) in which grain boundary sliding is dominant deformation mechanism. This result suggests that grain boundary sliding in Mg\(_{90}\)Zn\(_2\)Y\(_2\) is suppressed, and a different rate-controlling mechanism is dominant. Climb-controlled dislocation creep is reported to be the dominant deformation mechanism of \( n = 7 \) in Mg-Al-Zn alloys. \[25\] This mechanism is considered to be controlled by pipe diffusion or lattice diffusion. \[26\] On the other hand, reaching a \( n \) value \( \sim 8 \) with increasing temperature for non-basal cross slip was reported in Mg. \[27, 28\]

### 3.4 Activation energy

The temperature dependence of the minimum strain rate of Mg\(_{90}\)Zn\(_2\)Y\(_2\) is shown in Fig. 6. The apparent activation energy for creep (\( Q_C \)) is 205 kJ/mol, which can be calculated from the slope of the line shown in this figure. It has been reported that the activation energy for lattice diffusion (\( Q_L \)) and that for pipe diffusion (\( Q_P \)) are 135 kJ/mol and 92 kJ/mol, respectively. \[29\] The activation energy for creep, controlled by the dislocation climb, should be equal to \( Q_C \) or \( Q_P \). According to Vagarali et al., when the rate-controlling mechanism of Mg is non-basal cross slip, \( Q_C \sim 220 \) kJ/mol. \[30\] The activation energy for creep in Mg\(_{90}\)Zn\(_2\)Y\(_2\) is significantly higher than both \( Q_C \) and \( Q_P \), but close to the non-basal cross slip in Mg. Therefore, it is considered that cross slip is the rate-controlling mechanism of Mg\(_{90}\)Zn\(_2\)Y\(_2\) under the present experimental conditions.

### 3.5 Microstructures of crept specimen with scribe lines

The scribe lines produced on the surface of a specimen by FIB-SEM are shown in Fig. 7. As mentioned earlier, these scribe lines have a length of about 50 \( \mu \)m, and width and depth of about 1 \( \mu \)m. The white contrast around them is attributed to the presence of Ga atoms and/or the edge effect. The contrast decreased after the creep test because the crept specimen was polished again to remove contamination from...
its surface. The morphology of a curved scribe line after the creep test (7% creep) of Mg\(_{96}\)Zn\(_2\)Y\(_2\) and a schematic illustration are shown in Fig. 8(a) and 8(b), respectively. In Fig. 8(b), grain boundaries and a scribe line are shown by solid lines and broken line, respectively. Any crack was not formed at the grain boundaries and interfaces between the \(\alpha\)-Mg matrix and eutectic compounds. Koike et al. have reported that when grain boundary sliding occurs in the tensile-tested alloy AZ31-O (Mg-3 mass\%Al-1 mass\%Zn-0.3 mass\%Mn), some abrupt steps were formed at the grain boundaries observed even at room temperature.\(^{31}\) In this study, however, the scribe lines on the crept specimen were curved, and no abrupt step was formed at the grain boundaries between the matrix and eutectic phases (indicated by arrows in Fig. 8). The curvature of the scribe lines can be attributed to dislocation pile-up at the grain boundaries. We conclude that grain boundary sliding in Mg\(_{96}\)Zn\(_2\)Y\(_2\) is suppressed by the eutectic compounds, and dislocation motion is its main deformation mechanism, although it consists of fine grains with a size of 10\(\mu\)m. Our findings about scribe line morphology of the crept specimen are consistent with the creep strengthening mechanism based on the creep parameters \(n\) and \(Q_C\).

### 3.6 Creep deformation mechanism of Mg\(_{96}\)Zn\(_2\)Y\(_2\)

As mentioned in section 3.3, two rate-controlling mechanisms—dislocation climb and non-basal cross slip—are the possible creep deformation mechanisms of Mg\(_{96}\)Zn\(_2\)Y\(_2\) with \(n = 7\). Due to the activation energy \(Q_C = 205\) kJ/mol, non-basal cross slip is considered as the rate-controlling mechanism under the present experimental conditions. On the other hand, dislocation climb is reported as an important rate-controlling mechanism on high temperature creep in many metallic materials. Therefore, the suppression mechanism of dislocation climb should be considered in this alloy. As the mechanism for suppression of dislocation climb, decreasing...
of stacking fault energy occurred by Y solved into α-Mg matrix is suggested. Uesugi et al. have determined the relationship between the concentration of solute elements and the stacking fault energy of Mg by first principle calculations.\(^{32}\) Their results indicate that the effect of Y on the decrease in the stacking fault energy is more than the effects of Zn, Al, and Ca. In h.c.p. lattice, a-dislocations on basal planes can extend according to the stacking fault energy.\(^{33}\) During dislocation climb, the most part of edge dislocations are extended on basal plane except of jogs. For climbing of extended edge dislocation, constriction of partial dislocations pair is required.\(^{34}\) The separation width of extended dislocations increases with decreasing stacking fault energy.\(^{35}\) Segregation of solute atoms at stacking fault (Suzuki effect) on extended dislocations is also expected in the present alloy, increasing the separation of extended dislocations.\(^{30}\) On the other hand, the dislocation expansion and Suzuki effect can affect the suppression of dislocation cross-slip.\(^{33}\) However, separation width of a screw dislocation is smaller than that of an edge dislocation with same stacking fault energy.\(^{33}\) Due to difference of separation width, extended screw dislocation could be constricted easier than edge dislocation. Additionally, the dislocation locking force by Suzuki effect can be negligible on a segment of a-dislocations cross slipping on non-basal plane, because it does not extend until it start moving on another basal plane after double cross-slip. These dislocation climb and cross slip are independent deformation mechanisms.\(^{30}\) By comparison of dislocation climb and cross slip, dislocation climb is more significantly suppressed by decreased stacking fault energy and Suzuki effect than cross slip. As a result, it is considered that the dislocation cross-slip occurs predominantly as the rate-controlling mechanism on creep deformation in Mg\(_{96}\)Zn\(_2\)Y\(_2\). Other solution hardening effects (e.g. Cottrell atmosphere for dislocation climb and dislocation slip) could affect the selection of rate-controlling process.\(^{33}\) However, their effects have not been cleared in this investigation, and further researches are required. It have been reported that polycrystalline magnesium has two temperature regions with different activation energies.\(^{30}\) At the low temperature region (\(T < 600 \sim 750\)K), the activation energy is fairly constant at \(135\) kJ/mol. On the other hand, at the high temperature region (\(T > 600 \sim 750\)K), the activation energy increases to \(220\) kJ/mol. In this study, it is suggested that the transition temperature between two regions with different activation energies decreases with the decreasing of the stacking fault energy. Therefore, creep deformation is controlled by non-basal cross slip. Hence, the apparent activation energy (\(Q_a\)) is considered to be equal to the activation energy for non-basal cross slip.

Creep deformation controlled by non-basal cross slip is expected to occur when some elements that can significantly decrease the stacking fault energy are alloyed. In the case of Mg-Y, Mg-Gd-Y-Zr, and Mg-Y-Nd-Zr alloys, the activation energies for creep are higher than those for lattice diffusion and pipe diffusion, and non-basal cross slip occurring in them is ascribe to their high activation energies for creep.\(^{37-39}\) It has also been reported that Al can decrease the stacking fault energy.\(^{32}\) However, the amount of decreased stacking fault energy from pure Mg (40.4 mJ/m\(^2\)) by Al addition is about 20 mJ/m\(^2\), which is smaller than that by Y addition (37.3 mJ/m\(^2\)). These values have been calculated by first principle theory assuming that 25% of the nearest positions of stacking fault on basal plane are substituted by solute atoms. It is suggested that transition temperature of activation energy is little decreased by Al addition, and dislocation climb is rate-controlling mechanism at 523 \(\sim\) 573 K. In fact, in some Mg-Al alloys, their creep deformation mechanism is reported dislocation climb which is controlled by lattice diffusion and/or pipe diffusion at 523 \(\sim\) 573 K.\(^{22,26,30}\) Therefore, the selection of rate-controlling mechanism is affected not only by eutectic compounds along grain boundaries as described in section 3.5, but also by the stacking fault energy.

The difference between the minimum strain rates of Mg\(_{96}\)Zn\(_2\)Y\(_2\) and Mg\(_{93}\)Al\(_7\)Ca\(_2\) could also explained by the effects of solute elements on the stacking fault energy. These alloys consist of fine grains and have a similar microstructure. Their grain boundary coverages are also high. However, the effects of solute elements on the stacking fault energy in these alloys are different. The decreasing effect of Y in the stacking fault energy is higher than these of Al and Ca. Therefore, the minimum strain rate of Mg\(_{96}\)Zn\(_2\)Y\(_2\) is lower than that of Mg\(_{93}\)Al\(_7\)Ca\(_2\). Moreover, the mechanical properties of the eutectic compounds could affect the creep strength. However, these properties have not been described in detail and should be examined quantitatively.

4. Conclusion

In this study, effects of eutectic compounds formed along grain boundaries on creep behavior at 573 K were investigated. The main results are summarized below:

1. The thixomolded\(^{\circ}\) alloy Mg\(_{96}\)Zn\(_2\)Y\(_2\) consists of a fine-grained matrix (\(< 10\) μm) and two types of eutectic compounds—Mg\(_{92}\)YZn and Mg\(_{92}\)Y\(_2\)Zn\(_3\)—formed along grain boundaries.
2. The scribe lines are curved, and no abrupt step is formed along them in the specimen with a creep strain 7%.
3. The stress exponent (\(n\)) and activation energy for creep (\(Q_C\)) in Mg\(_{96}\)Zn\(_2\)Y\(_2\) are obtained from creep tests as 7 and 205 kJ/mol, respectively. This stress exponent is higher than that for grain boundary sliding (\(n = 2\)), but close to that for dislocation creep (\(n = 7\)). The activation energy for creep in Mg\(_{96}\)Zn\(_2\)Y\(_2\) is higher than that for lattice diffusion (\(Q_l = 135\) kJ/mol) and pipe diffusion (\(Q_p = 92\) kJ/mol) in Mg, but close to that for creep in Mg (\(Q_C = \sim 220\) kJ/mol), which is controlled by non-basal cross slip.

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