Microalloying Effects of Ca and Ni on High-Temperature Creep Behavior in Mg-Y-Zn Alloys

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High temperature creep strength at 650 K and microstructures of Mg-Y-Zn-based alloys with four elements (nickel and calcium) have been investigated. The microalloying of 0.5 mass% calcium markedly increases the stacking fault density in the Mg-3 mass% Y-0.5 mass% Zn alloy. Furthermore, the addition of calcium can decrease the size of stacking faults. On the other hand, in the nickel-added alloy, many precipitates were formed and the estimated stacking faults density decreased significantly. The creep strength of the Mg-Y-Zn-Ca alloy is higher than that of the base alloy (Mg-3 mass% Y-0.5 mass% Zn, WZ305). Transmission electron microscopic (TEM) observations revealed that many a-dislocations on the basal planes in the magnesium matrix are extended during creep deformation in Mg-Y-Zn-based alloys. There was significant consumption of solute atoms in the matrix and deterioration of creep strength in the Mg-Y-Zn-Ni alloy, because the formation of a large number of precipitates began before creep. On the other hand, both the low mobile dislocation density and the large separation width of extended a-dislocations were observed in the Mg-Y-Zn-Ca alloy, which exhibits excellent creep strength at 650 K under 20 MPa.

Keywords: magnesium-yttrium-zinc-based alloys, deformation substructures, high temperature creep, extended dislocations, stacking faults

1. Introduction

Recently, environmental issues have been getting greater international attention. Magnesium-based alloys have been investigated as a possible lightweight structural material because of their many advantages, such as high specific strength, low density, good damping capability, and high recyclability. Magnesium-based alloys have potential uses in aerospace and automobile parts to increase the fuel efficiency and speed of the transportation vehicles. However, the low mechanical properties of magnesium-based alloys, especially poor high temperature creep strength, hinder their widespread application. The addition of a rare earth (RE) element is a known method of improving the strength of magnesium.1–5) At the beginning of this decade, Kawamura et al. developed a new Mg72Y2Zn1 alloy (in mol%) alloy produced by the rapidly solidified powder metallurgy (RS P/M) processing method5) which exhibited a high yield stress of 610 MPa at room temperature. The details of the microstructures of this alloy have been reported by Abe et al.7) According to them, a long period stacking ordered (LPSO) structure including periodic aligned stacking faults is formed in this alloy, and zinc and yttrium atoms are segregated in two layers on each stacking fault. This LPSO structure has been reported as a stable phase in Mg-Y-Zn-Zr alloy by Luo et al.,9) and in several kinds of Mg-Zn-RE systems.9) More recently, several transition metals (TM) have been shown to have an effect similar to zinc in Mg-TM-RE ternary systems.10,11) However, from an engineering viewpoint, the dilute addition of an RE element is must be kept as small as possible to minimize the cost of the magnesium-based alloys. Suzuki et al. reported that the creep strength of an Mg-1 mol%Y (3 mass%Y) alloy is significantly improved by the microalloying of zinc for 0.04 mol% (0.1 mass%).12,13) They also reported that the stacking fault energy decreases in these alloys so that many stacking faults, which do not form the LPSO structure, are extended significantly during creep deformation, and these extended dislocations are considered to reduce their mobility under high temperature creep conditions.14) The formation of stacking faults is thought to be due to a decrease in the stacking fault energy by the segregation of RE and TM elements. Therefore, it should be possible to control this segregation behavior by varying the alloying elements. In this paper, creep strength and deformation microstructures of Mg-Y-Zn-based alloys containing additional microalloying elements of MX (nickel and calcium, respectively) are reported. The formability of the stacking faults and their strengthening effects are also discussed based on microstructure observations.

2. Experimental Procedures

Three kinds of Mg-3 mass%Y-0.5 mass%Zn-based alloys with and without a fourth MX element were used in this investigation, and their target compositions are listed in Table 1. The concentrations of yttrium and zinc were nearly the same among these three alloys from the results of the area quantitative analyses by scanning electron microscopy with energy dispersive X-ray spectrometer (SEM-EDS) after the heat treatment described below.

Nickel and calcium were chosen as the fourth alloying MX element. Nickel has small solubility for magnesium15) and a low impurity diffusion coefficient in magnesium.16) On the
other hand, nickel has recently been reported as a new TM element to form LPSO structures by simultaneous addition with several kinds of RE elements to magnesium.\textsuperscript{10,11)\textsuperscript{12}} The solubility of calcium in magnesium (1.3 mass% at 516.5°C)\textsuperscript{15)\textsuperscript{16}} is as small as nickel, however, a first-principles calculation revealed that the stacking fault energy of magnesium is decreased by the addition of calcium.\textsuperscript{17)

All the alloys were arc-melted and cast into water cooled copper cylindrical molds (30 mm in diameter and 8 mm in height) in argon atmosphere. These alloy ingots were hot-rolled at 673 K by 40\% reduction to a plate shape of 5 mm in thickness. All the alloys were solution-treated in an argon atmosphere at 770 K for 2 h and then water quenched. These heat-treated alloys were machined to a rectangular solid (2 mm × 2 mm × 3 mm) for compressive creep specimens. The average grain diameters of these alloys ranged from 110 to 200 μm.

Compression creep tests were carried out under a constant stress of 20 MPa at 650 K in air. The stress axis was parallel to the rolling direction and the specimens were held at the test temperature for about 14.4 ks (4 h) before creep tests to maintain the temperature stability of the testing system. The crept specimens were water-quenched under a load for microstructural observations.

Microstructures before and after creep tests were investigated by a scanning electron microscopy (SEM) and also with a transmission electron microscope (TEM) at an acceleration voltage of 200 kV. The chemical composition of second phases in specimens was analyzed by SEM-EDS.

3. Results and Discussion

3.1 Initial microstructures of Mg-Y-Zn-MX alloys

TEM microstructures of Mg-Y-Zn-MX alloys after solution treatment and heat treatment at 650 K for 4 h are shown in Fig. 1. This heat treatment is the same as the thermal history before creep tests in this investigation. The incident beam directions in Fig. 1 are parallel to [2110] for WZNi30505 and [0110] for other alloys. Many stacking faults (SF) are known to form parallel to the trace of the basal planes in the magnesium matrix as straight-line contrasts. The morphology of these stacking faults is typical of those found in dilute Mg-Y-Zn-based alloys,\textsuperscript{13)\textsuperscript{14}} thus the displacement vector of these stacking faults is the same as other dilute Mg-Y-Zn-based alloys and is considered to be 1/3(1100) (intrinsic type II) or 1/6(2203) (intrinsic type I). On the other hand, the size and density of stacking faults depend on the alloy composition. Among the alloys in this investigation, the highest stacking fault density was seen in the WZX30505 alloy. The estimated value of the average spacing between stacking faults in the c-direction of the magnesium matrix is about 40 nm in the WZX30505 alloy.\textsuperscript{18)\textsuperscript{19}} This value is significantly smaller than that of the WZ305 alloy (about 130 nm).\textsuperscript{18)\textsuperscript{20}} It was noted that the average size of stacking faults on the matrix basal planes in the WZX30505 alloy is significantly smaller compared with that in the WZ305 alloy. Although the average stacking fault size in the WZNi30505 alloy is similar to the WZX305 alloy, the values of the stacking fault density in these alloys are lower than that of the WZ305 alloy.

SEM back-scattered electron (SEM-BSE) images of some Mg-Y-Zn-MX alloys heat treated at 650 K for 4 h are shown in Fig. 2. The typical point analysis results by energy dispersive X-ray spectrometer (EDS) in these alloys are also shown in this figure. There are many white contrasts along grain boundaries of the magnesium matrix in all Mg-Y-Zn-MX alloys. These contrasts are considered to be precipitates which nucleate and grow during heat treatment because
no such contrasts were observed by SEM-BSE in either the cast or the hot-rolled specimens. In the WZ305 alloy, coarse second phases are observed within grains, but they are small in number. The SEM-EDS analysis revealed that the coarse second phase mainly consists of yttrium and magnesium, and it is considered to be an Mg-Y-based intermetallic compound of Mg\(_{24+x}\)Y\(_5\). The high zinc concentration is measured from fine precipitates on grain boundaries in the WZ305 alloy, and these precipitates are considered to be Y-Zn-based compounds. Similar grain boundary precipitates were observed in the WZX30505 alloy. In addition, there are other precipitates of the Mg\(_2\)Ca intermetallic compounds which have a morphology different from the above one in the WZX30505 alloy.

The precipitation contrasts and morphology in the WZNi30505 alloy are different from other alloys. The SEM-EDS analysis demonstrated that all alloying elements (nickel, yttrium and zinc) were present in high concentrations in these precipitates. Most of the precipitates in Mg-Y-Zn-MX alloys were not identified in this investigation; therefore, further microstructural investigation is needed. It should be noted that there are no such precipitates in the Mg-3 mass\%Y-0.1 mass\%Zn alloy, which has lower zinc concentration than the WZ305 alloy. The average spacing between stacking faults in the c-direction of magnesium has been reported to be about 200 nm in the Mg-3 mass\%Y-0.1 mass\%Zn alloy.\(^{13}\) This value is higher than that of the WZNi0505 alloy (290 nm) and lower than that of the WZ305 alloy.\(^{18}\)

Although evidence for the formation of the LPSO phase in Mg-Y-Ni ternary alloys has been reported,\(^{10,11}\) an estimate of the low stacking fault density in the WZNi30505 alloy was used in this investigation. The low stacking fault density observed in the WZNi30505 alloy is considered to be due to the low solubility of nickel in magnesium. The formation of the LPSO phase has been reported in Mg-Ni-Y alloys manufactured by rapid solidification processing. On the other hand, the present WZNi30505 alloys were manufactured by a standard arc melting technique, having a lower cooling rate than that of typical rapid solidification techniques, whereby nickel atoms were difficult to dissolve in matrix and formed a lot of precipitates. Moreover, the precipitates in the WZNi30505 include high yttrium and zinc contents (Fig. 2(c)). These two alloy elements are important for the formation and stabilization of stacking faults in magnesium. Consequently, the stacking fault density is sensitive to the concentration of solute atoms (yttrium and zinc) in magnesium matrix. The SEM-EDS analysis indicates that the matrix concentrations of yttrium and zinc are significantly low in the WZNi30505 alloy (Fig. 2(c)). Similar trends were seen to varying degrees to other alloys. The stacking fault density decreases with increasing of the solute atom (yttrium and zinc) consumption caused by the formation of precipitates in WZ305-based alloys except the WZX30505 alloy.

On the other hand, the measured stacking fault density was higher in the WZX30505 alloy as compared with the base alloy of WZ305. This can be explained by the effect of adding calcium. As mentioned in the experimental procedures, a first-principle calculation by Uesugi et al. has been reported whereby the alloying of the calcium decreases the stacking fault energy of magnesium.\(^{17}\) Their calculation
result suggests that adding calcium to magnesium increases the stacking fault density. Furthermore, the volume fraction of second phases in WZX30505 is smaller than those of WZ305 and WZNi30505. Therefore, the high stacking fault density in the WZX30505 alloy is ascribed to both the relative low consumption of yttrium atoms by the precipitation and the decreased stacking fault energy secondary to the microalloying of calcium.

### 3.2 Creep strength of Mg-Y-Zn-MX alloys

Creep curves of WZ305, WZNi30505, and WZX30505 alloys are shown in Fig. 3. The creep condition of these curves is 650 K and 20 MPa. The result of the Mg-3 mass%Y-0.1 mass%Zn alloy under the same creep condition is also shown in this figure as a thin dashed line. Except for the WZX30505 alloy, the shapes of the creep curves are similar: a long steady state is observed after a short primary stage, and then the creep rate increases slightly. On the other hand, the creep rate of the WZX30505 alloy increases from the beginning of creep and no steady state is observed.

The creep curves of the WZ305 alloy have a similar profile to that of Mg-3 mass%Y-0.1 mass%Zn alloy though their zinc contents are different. The creep strength of the WZX30505 alloy is higher than that of the WZ305 alloy, but the strengthening effect is only twofold at 10% creep strain. On the other hand, significant deterioration in creep properties was detected in the WZNi30505 alloy. The steady state condition was observed in WZX30505 (Fig. 3), so the creep rate increases slightly. One the other hand, the creep rate of the WZX30505 alloy increases from the beginning of creep and no steady state is observed.

As mentioned above, several kinds of precipitates are formed in the WZ305 alloy before creep (Fig. 2). However, the intragranular precipitates are coarse and the grain size of the WZ305 is about 130 μm. In addition, such precipitates are not formed in the Mg-3 mass%-0.1 mass%Zn alloy, therefore these precipitates cannot increase creep strength. On the other hand, the matrix contents of Y and Zn are decreased by the formation of precipitates. Therefore, the negligible strengthening of the WZ305 alloy from the Mg-3 mass%-0.1 mass%Zn alloy is considered to be due to decreased Y and Zn contents in matrix of this alloy.

The same argument is applies to the low creep strength of the WZNi30505 alloy, as it has a low stacking fault density. The SEM-EDS results of this alloy show that the concentration of yttrium in the matrix is significantly low. The yttrium concentration in matrix affects the creep strength of magnesium significantly compared with other typical alloy elements. Therefore, the low creep strength in the WZNi30505 alloy is very likely due to a decrease in the yttrium concentration in the magnesium matrix secondary to precipitation.

### 3.3 Deformation microstructures of Mg-Y-Zn-MX alloys

TEM deformation substructures in Mg-Y-Zn-MX alloys, which creep up to 4% of creep strain under 20 MPa at 650 K, are shown in Fig. 4. This creep strain is almost a steady-state condition for WZ305 and WZNi30505 alloys. No steady-state condition was observed in WZX30505 (Fig. 3), so the same strain value of the WZ305 and WZNi30505 alloys is used for its microstructural observation. The incident beams in these micrographs are parallel to the [2110] direction in the magnesium matrix and the g vector used was 011. There are many stacking faults as fringe contrasts in these photographs. The differences between Figs. 1 and 4 are due to the different diffraction conditions, namely, the use of different g-vectors. The stacking fault densities in the interior of the grains are similar to those seen in the heat-treated grains in each alloy.

In addition, the dislocation distribution in Mg-Y-Zn-MX alloys is similar to that of the Mg-Y-Zn ternary alloys. Most of the dislocations are parallel to the trace of the basal planes and they are not visible under g = 0002 condition, as shown in Fig. 4(d). From the g·b criteria, it is concluded that most of the dislocations have a 1/3(2110) type of Burgers vector and are activated on the magnesium basal planes. This dislocation morphology is generally observed in the deformation microstructure of magnesium-based alloys because the basal slip (1/3(2110)<0001>) is the primary slip system in magnesium. The dislocation density is different with each alloy. While dense dislocations are observed in WZ305 and WZNi30505 alloys, the number of dislocations in the WZX30505 alloy is small.

TEM micrographs of WZNi30505 and WZX30505 alloys are shown in Fig. 5. The creep condition is the same as in Fig. 4, and the incident beams are parallel to [2113] for the WZNi30505 alloy and to [001] for the WZX30505 alloy. There are many fringe contrasts within grains in both alloys. In the WZNi30505 alloy, the widths of these fringes are roughly estimated to range from less than 50 nm to 300 nm.
This value is lower than that of the stacking faults, which formed before creep (Fig. 1). Therefore, these contrasts represent the partial dislocation pairs having the $\frac{1}{3}\{1\overline{1}00\}$ type intrinsic stacking faults (intrinsic type II), as does the Mg-3 mass% Y-0.1 mass% Zn alloy. The average separation width of the Mg-3 mass% Y-0.1 mass% Zn alloy is about 260 nm, which is larger than that of the WZNi30505 alloy. In addition, there are many perfect dislocations in the WZNi30505 alloy. The existence of these "unextended" perfect dislocations can be explained by the argument above concerning the low solute concentrations in the WZNi30505 alloy. The dislocation dissociation is important in Mg-Y-Zn-based alloys because a chemical interaction is expected on the $1/3\{1\overline{1}00\}$ type (intrinsic type II) stacking fault between partial dislocations, which is stabilized by the segregation of solute atoms. This chemical interaction is not yet understood quantitatively, but the force of this chemical interaction is expected to decrease the dislocation mobility in a magnesium matrix. In the WZX30505 alloy, there are also many fringe contrasts within grains. It is difficult to distinguish between the stacking faults preformed before creep and the extended dislocations, because a large proportion of stacking faults are less than 1 μm (Figs. 1 and 4). However, the number of perfect dislocations in the WZX30505 alloy is obviously lower than that of the WZNi30505 alloy. From this result, it is indicated that the majority of dislocations are dissociated in the WZX30505 alloy. Both the dislocation mobility and the dislocation density are important to
determine creep strength. The high creep strength of the WZX30505 alloy is believed to be due to the low dislocation density (Fig. 4) and the large separation width between partial dislocations (Fig. 5).

4. Summary

Creep strength and microstructures of Mg-Y-Zn-based alloys with microalloying elements (nickel and calcium) have been investigated. The fine and dense stacking faults are formed in calcium-added alloy (WZX30505) after heat treatment at 650 K for 4 h. On the other hand, the addition of nickel inhibits the formation of dense stacking faults. Many precipitates were introduced in the WZNi30505 alloy due to the low solubility of nickel in magnesium. Additionally, the high yttrium and zinc contents were measured in these precipitates. The decrease in the matrix concentrations of alloy elements caused by the precipitation deteriorates the creep strength of the WZNi30505 alloy. On the other hand, the creep strength under 20 MPa of calcium-microalloyed alloy (WZX30505) is higher than the others. Both the low mobile dislocation density and the large separation width of extended $a$-dislocations on the basal planes are effective to improve creep strength of the WZX30505 alloy.

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REFERENCES