

Microstructure and Mechanical Properties of Heat-resistant Mg-Zn-Y Cast Alloys with Addition of Fourth Elements

Yuichi IENAGA* Kenshi INOUE* Mitsumoto KAWAI*

ABSTRACT

Extruded Mg-Zn-Y alloys with long-period stacking ordered (LPSO) structures are known to display increased strength at high temperatures, and are therefore useful in achieving weight savings in automotive components. Seeking to realize these attractive properties in cast components, the project discussed in this paper focused on controlling the microstructure of $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ (at.%) cast alloy by the addition of a fourth element. First, the effects of refining the crystal grains through the addition of zirconium and modification of the cooling rate on microstructure and mechanical properties were investigated. With the addition of Zr and the achievement of a high rate of cooling, the resulting $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ cast alloy displayed fine equiaxed grains (approx. 10 μm in diameter) and excellent tensile and fatigue properties, equivalent to or greater than those of commercial aluminum alloys at high temperatures above 200°C. At 250°C, this alloy exhibited a tensile strength of 223 MPa, approximately twice that of the A4032-T6 alloy used for automotive pistons. The project also focused on strengthening LPSO structures by means of stacking fault energy (SFE), and used a first principle calculation to select a further element for addition to the alloy. The addition of Ag increased yield strength by 60 percent.

1. Introduction

Magnesium alloys are the lightest of the metal materials in practical use, and are therefore expected to contribute to the resolution of environmental issues, for example by reducing automotive fuel consumption. Among these alloys, it is known that the strength characteristic of Mg-Zn-Y alloys, which possess long-period stacking ordered (LPSO) structures, can be increased even in high temperature ranges by extrusion processing and refinement of the microstructure^{(1),(2)}. Processing including forging and machining is necessary following extrusion in order to form parts; in the case of parts for automotive and other engines, it would be desirable to achieve increased strength in cast materials, helping to enable cost reductions through near-net shape formation. However, standard cast magnesium alloys are lower in strength than heat-resistant aluminum alloys. The project discussed here, therefore, set out to develop a cast heat-resistant magnesium alloy displaying a higher level of strength than heat-resistant aluminum alloys. The project sought to control the solidified microstructure

of the alloy, refining the microstructure through the addition of crystal grain refining elements and increasing the rate of cooling, in addition to increasing the strength of the LPSO strengthening phase through the addition of a fourth element. This paper will discuss the achieved structural morphology, mechanical properties, and physical properties of the alloy.

2. Method of Development of New Cast Alloy

A strength characteristic exceeding the strength characteristics of heat-resistant aluminum alloys can be achieved in Mg-Zn-Y magnesium alloys by subjecting them to extrusion and other plastic working processes⁽²⁾. In addition to compound dispersion strengthening during casting, this is due to strengthening due to work hardening during extrusion, texturing, and refinement of the crystal grains. However, casting in isolation coarsens the LPSO phase (the strengthening phase) and the other compound phases, and only a level of strength equivalent to that of conventional magnesium alloys can be obtained.

* Fundamental Technology Research Center

Experimentation therefore proceeded with a focus, from among the abovementioned factors producing increased strength, on refinement of the crystal grains and the compound phase morphology, which could be expected to result in increased strength even simply by casting. The effect of refining the crystal grains in increasing strength is much higher in the case of magnesium than in other metals such as iron and aluminum. The present project sought to refine the crystal grains through the addition of Zr, which has a high melting point and was expected to act as the point of origin of crystal nucleation. It was considered that by this means it would also be possible to refine the LPSO phase and other compound phases crystallizing at the grain boundary. It was also considered that the achievement of a higher rate of cooling would promote refinement of the crystal grains, and would also control the coarsening of the compound phases formed by diffusion of the constituent elements. These effects were demonstrated in the study.

Next, in order to achieve a further strength increase by increasing the strength of the LPSO phase, the main strengthening phase in the alloy, first principle calculations were employed in LPSO phase strength design. Stacking faults identified during localization of the structure of the LPSO phase were the focus in materials modeling. If the LPSO phase is considered as the strengthening phase, then increasing this stacking fault energy could be expected to increase the yield strength of the alloy. This consideration was based on the concept that because the LPSO phase is coherent with the α -Mg phase (the matrix), the difference in stacking fault energy with the matrix would represent a migration barrier to dislocation. The Vienna Ab-initio Simulation Package (VASP), a first principle calculation software package based on a density-functional calculation method, was used to determine the elements that would increase the stacking fault energy (strengthen the LPSO phase) by substitution for other elements in the materials model. Based on the results of these calculations, it was judged that Ag would be an effective candidate for addition, and tests were conducted with Ag as an additive element.

3. Test Method

Tests employed $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$, $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ and $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ alloys as test materials. The alloys were melted in a graphite crucible in an Ar gas environment using a high-frequency induction melting system, and the melted alloys were cast in copper ship-shaped molds with an average width of 18 mm, height of 25 mm, and length of 160 mm, and similar transverse cross-sections to those specified for casting molds by JIS H 5203. Table 1 shows the chemical composition of the alloys employed. In order to study the effect of the rate of cooling, the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy was cast in 50 mm-wide step-shaped molds of 2 mm, 4 mm, and 8 mm in thickness, as shown in Fig. 1. Following casting, the phases formed were identified using powder X-ray diffraction (XRD), and the microstructures

Table 1 Chemical composition of Mg alloys used in this study (at. %)

Alloy	Zn	Y	Zr	Ag	Mg
$\text{Mg}_{96}\text{Zn}_2\text{Y}_2$	2.11	2.06	–	–	Bal.
$\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$	1.86	1.81	0.21	–	Bal.
$\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$	2.31	2.02	–	2.96	Bal.

were examined by means of scanning electron microscopy (SEM). An analysis was also conducted using electron back-scatter diffraction (EBSD) to evaluate the diameter of the crystal grains.

The mechanical properties of the alloys were evaluated in tensile tests, tension-compression fatigue tests, creep tests, Rockwell hardness tests, and Charpy impact tests. For the tensile tests, the ship-shaped castings were formed into ASTM E8 standard test piece forms, with a diameter of 6.35 mm in the parallel portions and a gauge length of 25.4 mm, and the step-shaped castings were formed into mini test pieces with a thickness of 2 mm, a width of 4 mm, in the parallel portions, and a gauge length of 4 mm. The tests were conducted using a strain rate of 5×10^{-4} /s, at temperatures ranging from 25 to 300°C. The fatigue tests were conducted on the mini test pieces described above, using a stress ratio of $R = -1$, sine wave frequencies of 20–40 Hz, a maximum number of repetitions of 10^7 times, and a temperature of 200°C. The creep tests were conducted at 200°C $\times$ 90 MPa, and the hardness tests, based on JIS Z 2245, used the Rockwell B scale and a total test force of 980 N. The Charpy impact tests were based on JIS Z 2242, and used V-notch test pieces at room temperature. Thermal conductivity was measured using the laser flash method specified in JIS R 1611, coefficient of thermal expansion was measured using the thermo-mechanical analysis method specified in JIS R 1618, Young's modulus was measured using ultrasonic method, as specified in JIS Z 2280, and density was measured using the Archimedes method, as specified in JIS Z 8807. Results were compared with results for existing materials.

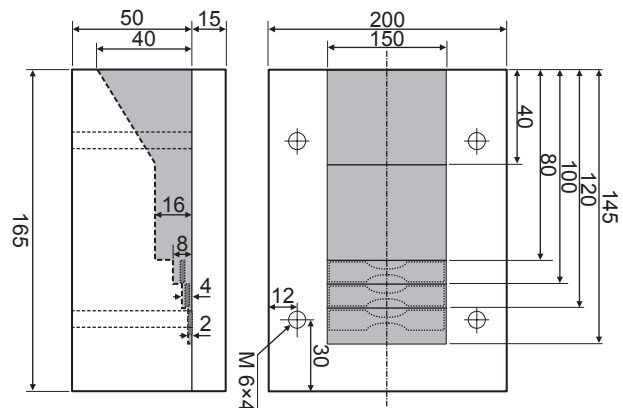


Fig. 1 Step-shaped copper mold and sampling points

4. Test Results and Discussions

4.1. Strength Increase due to Refinement of Crystal Grains

4.1.1. Effect of addition of Zr on microstructure

The refining effect of the addition of Zr on the microstructures of Mg-Zn-RE (rare earth) alloys is well known⁽³⁾. $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ and $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloys were cast in ship-shaped molds in order to study the effect of the addition of Zr in refining the microstructure of $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ alloy. Figure 2 shows XRD patterns for both the alloys. The addition of Zr produces no change in the structural phases, with both alloys being made up of α -Mg, Mg_{12}ZnY (LPSO), and $\text{Mg}_3\text{Zn}_3\text{Y}_2$ phases. Figure 3 shows back-scattered

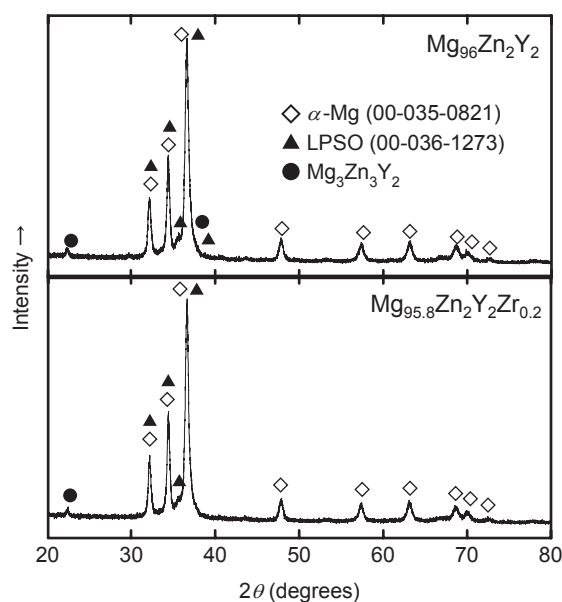


Fig. 2 XRD patterns of $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ and $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloys

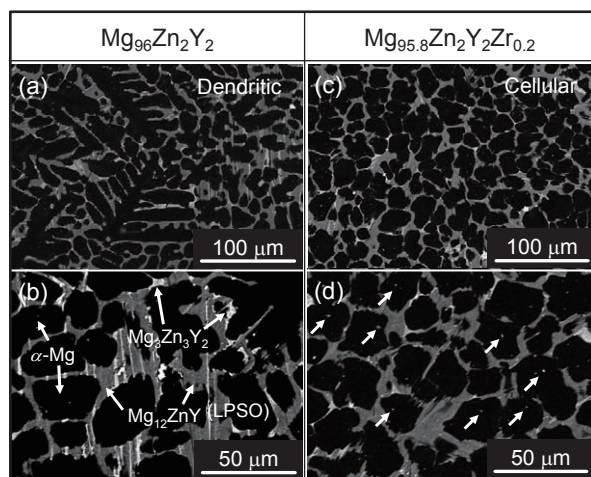


Fig. 3 BSE (Back scattered electron)-SEM images of $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ and $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloys

electron (BSE) SEM images for the alloys. Based on the results of energy-dispersive X-ray spectrometry (EDS) and previously published reports⁽⁴⁾, the black areas can be assumed to represent the α -Mg phase, and the gray and white areas the LPSO and $\text{Mg}_3\text{Zn}_3\text{Y}_2$ phases, respectively. As Fig. 3(a) shows, the α -Mg phase in the $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ alloy frequently forms dendritic structures. Figure 3(b) shows that the $\text{Mg}_3\text{Zn}_3\text{Y}_2$ phase displays a coarse morphology that disrupts the LPSO phase that crystallizes in a network around the α -Mg phase. By contrast, in the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy, the α -Mg phase forms cell shapes, as shown in Fig. 3(c), and the $\text{Mg}_3\text{Zn}_3\text{Y}_2$ phase is refined, as indicated in Fig. 3(d). Because, however, no significant difference in the diameter of the α -Mg grains was observed with the addition of the Zr, EBSD analysis was used to study the crystal grains. The results are shown in Fig. 4. The figure shows that the grain diameters of the $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ and the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloys are approximately 200 μm and 20 μm , respectively, indicating a significant refining effect with the addition of the Zr. In addition, as indicated by the arrow in Fig. 3(d), large numbers of fine particles can be observed among the α -Mg grains. Figures 5(a) and 5(b) respectively show a transmission electron microscope (TEM) image and the results of EDS analysis of these fine particles. The results show that the fine particles are angular, block-shaped, Zr-rich particles of approximately 0.5 μm . It is

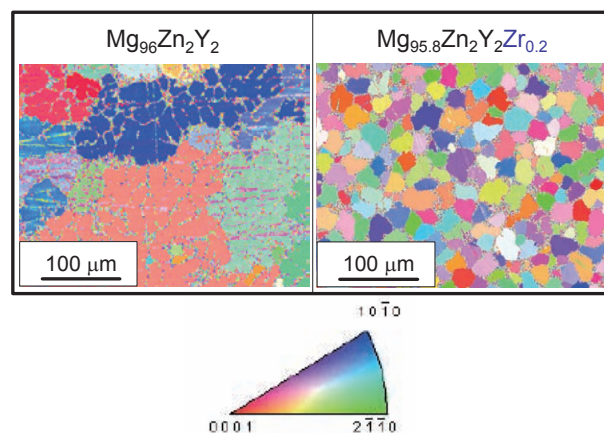


Fig. 4 Crystal orientation imaging maps of $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ and $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloys

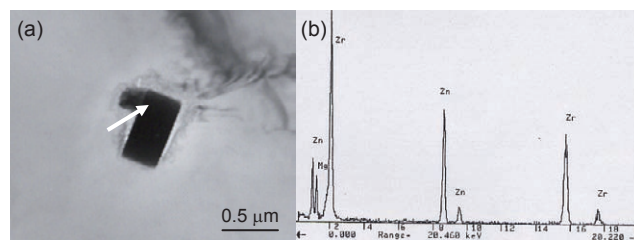


Fig. 5 (a) TEM image of Mg grains in $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy (b) TEM-EDS analysis obtained from particle indicated by white arrow in Fig. 5 (a)

thought that because the solid solubility limit of Zr in Mg (0.12 at.%(⁵)) is lower than the additive amount of Zr (0.2 at.%), Zr that is not in solid solution exists in the alloy, and this forms the point of origin for nucleation of the α -Mg phase, resulting in the refinement of the microstructure of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy.

4.1.2. Effect of cooling rate on microstructure

In order to study the effect of the cooling rate on the microstructure of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy, $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy castings of 2 mm, 4 mm, and 8 mm in thickness were produced using step-shaped molds. XRD results showed that differences in the cooling rate did not produce any changes in the structural phases, with the thick areas of each casting being composed of α -Mg, LPSO, and $\text{Mg}_3\text{Zn}_3\text{Y}_2$ phases. Figure 6 shows BSE-SEM images, and Fig. 7 shows EBSD crystal orientation maps for the 2 mm-, 4 mm-, and 8 mm-thick $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy castings. Figure 6 indicates that the microstructure tends to become more refined as the cooling rate increases. Figure 7 shows that the average crystal grain diameters for the three thicknesses of casting are 8 μm , 11 μm , and

16 μm . By contrast, the crystal grains were coarse (50-100 μm) in the 2 mm-thick casting using the alloy to which Zr was not added. Therefore, in the range of thicknesses from 2-20 mm, the addition of Zr, which reduced the crystal grain diameter from 200 μm to 20 μm , can be considered to have a greater effect than the cooling rate. Refinement of the alloy microstructure through the addition of Zr can therefore be indicated as being more effective in the case of engine parts, the majority of which are no greater than 20 mm in thickness.

4.1.3. Mechanical properties

Figure 8 shows the test-temperature dependence of the tensile strength of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy castings (2 mm, 4 mm, and 8 mm in thickness). Results for the tensile strength of A4032-T6 aluminum alloy are shown for

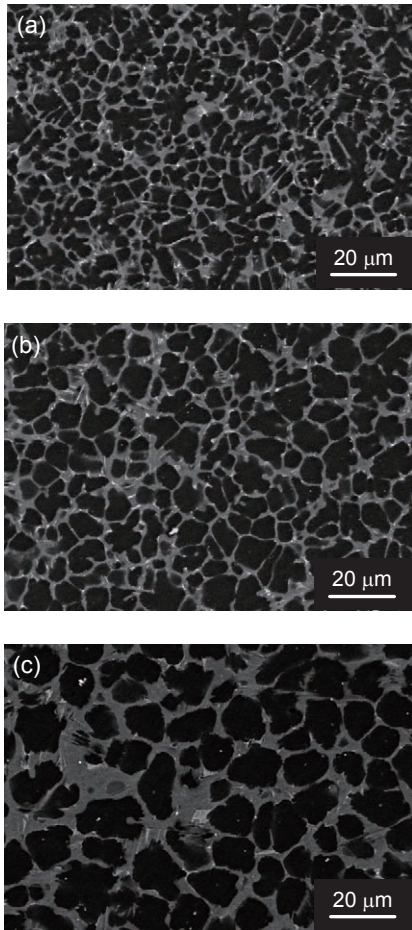


Fig. 6 BSE-SEM images of $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy in thickness of (a) $t = 2$ mm, (b) $t = 4$ mm and (c) $t = 8$ mm

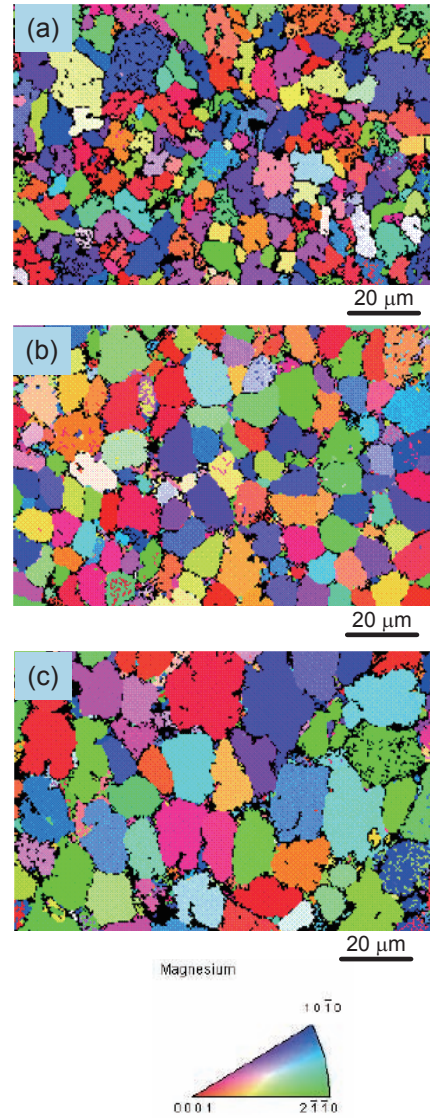


Fig. 7 Crystal orientation imaging maps of $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy with (a) $t = 2$ mm, (b) $t = 4$ mm and (c) $t = 8$ mm

comparison. By contrast with A4032-T6, which displays a decline in strength at 200°C and above, no rapid decline in strength is observed in the case of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy. In addition, the strength of the alloy increases with greater refinement of the crystal grains, and it is particularly noteworthy that the alloy displaying a fine microstructure with a crystal grain diameter of 10 μm or below achieves a high-temperature strength exceeding that of the A4032-T6 alloy, displaying a tensile strength (223 MPa) approximately twice that of the latter at 250°C, and close to three times in magnitude at 300°C. Even at a thickness of 8 mm, the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displays approximately 1.5-times greater tensile strength than the A4032-T6 alloy.

Figure 9 shows the relationship between the crystal grain diameter and yield strength at room temperature, plotted to help enable study of the relationship between

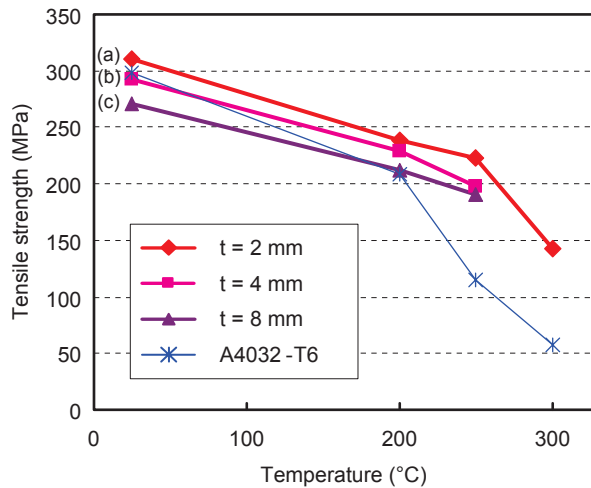


Fig. 8 Tensile properties of $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy with (a) $t = 2$ mm (b) $t = 4$ mm and (c) $t = 8$ mm at 25 °C, 200 °C, 250 °C and 300 °C

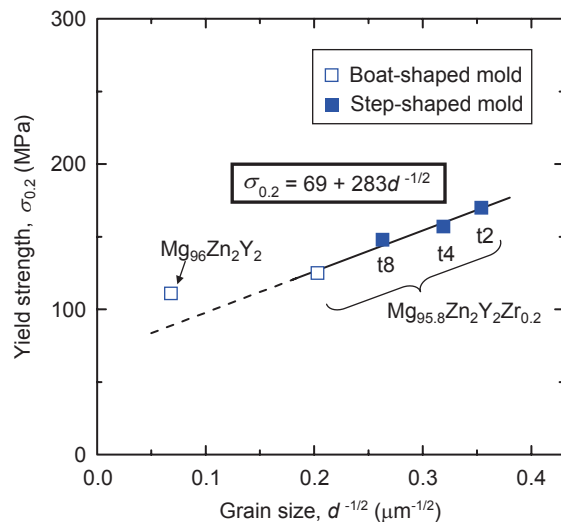


Fig. 9 Relationship between yield strength and grain size for Mg-Zn-Y alloys

crystal grain diameter and yield strength. The 0.2% proof strength was employed as yield strength. The $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ alloy with no added Zr displays a dendritic microstructure, and because it is thought that this contributes to strength at the dendritic interface in addition to the grain boundary, calculations were performed for four points in the case of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy. The results derived from a least squares analysis can be arrayed along the straight line obtained using Hall-Petch equation in the figure, indicating that strength increases with the greater refinement of the grains, in accordance with the aim of the project. Figure 10 compares the fatigue strength characteristics (S-N curves) of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy and A4032-T6 aluminum alloy at 200°C. The arrows show test pieces that have not yet failed. Despite having been cast, the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displays almost identical fatigue strength (10^7 cycle) to the A4032-T6 alloy at 200°C. In addition, while the strength of the aluminum alloy continues to decline as the number of repetitions increases, it can be conjectured that the fatigue strength of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy will remain stably higher than that of the A4032-T6 alloy at 10^7 cycles and above, making the material preferable from the perspective of design. It is reported that the LPSO phase increases fatigue strength in Mg-Zn-Y alloys⁽⁶⁾, and the existence of the LPSO phase can similarly be considered to increase fatigue strength in the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy. Figure 11 shows alloy creep properties at 200°C and 90 MPa. The $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displays greater creep properties than the heat-resistant ACM522⁽⁷⁾ magnesium alloy employed in hybrid vehicle oil pans, and an identical level of creep strain to the ADC12 aluminum alloy used in transmission cases, for which a higher level of heat resistance is demanded. In addition, the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displays a failure life approximately twice that of ADC12 under high stress (110 MPa), and approximately four times greater at the higher temperature of 300°C at 50 MPa. It is reported that control of grain boundary sliding by the compound phases that

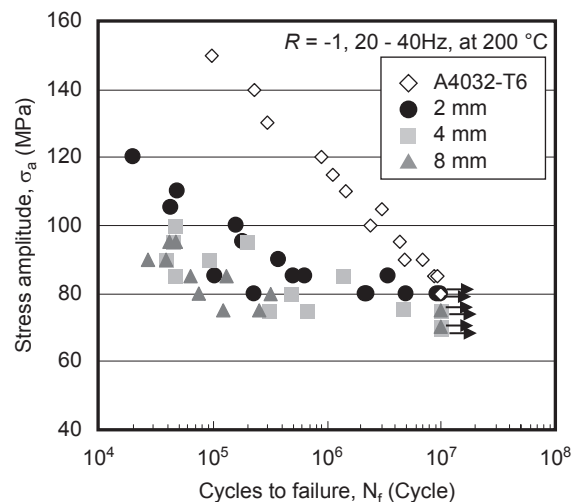


Fig. 10 S-N curves of $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ and A4032-T6 alloys

crystallize at the grain boundary and strengthening of the matrix by stacking faults enhances creep properties at high temperatures⁽⁸⁾. As indicated above, the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy demonstrated strength characteristics equivalent to or greater than those of high heat-resistance aluminum alloys in the high-temperature range of 200°C and above.

Next, the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy was subjected to a high-temperature dimensional stability test (at 230°C) and a softening test (at 250°C), in order to study factors producing the alloy's superior high-temperature strength. The change in dimension of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy following 100 h of the high-temperature dimensional stability test, at $4 \times 10^{-3}\%$, was lower than that of the A4032-T6 alloy at $33 \times 10^{-3}\%$. Figure 12 shows changes in the hardness of the alloys when soaked for 100 h at 250°C.

In the time range of 100 h, while the A4032-T6 alloy undergoes a rapid decline in hardness (from HRB60 to

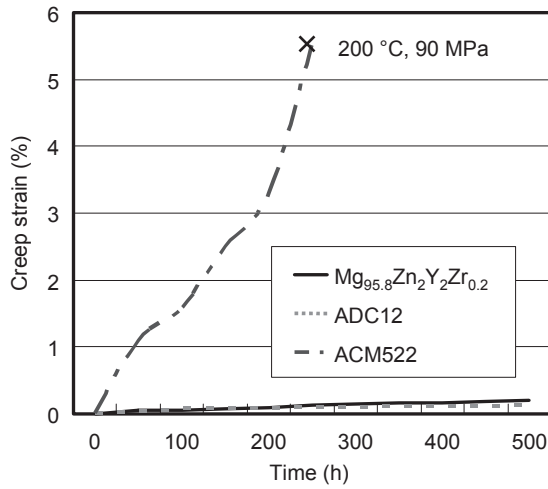


Fig. 11 Creep properties of $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ ($t = 8$ mm), ADC12 and ACM522 alloys

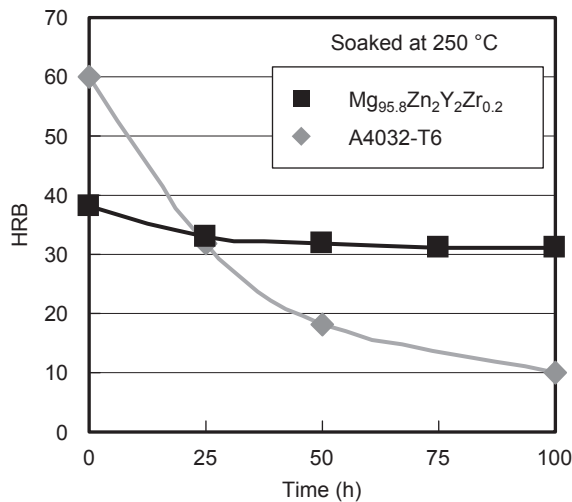


Fig. 12 Relationship between hardness and soak time for $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ ($t = 8$ mm) and A4032-T6 alloys

Table 2 Mechanical properties of $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ and $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloys

Alloy	Tensile strength (MPa)	Yield strength (MPa)	Elongation (%)
$\text{Mg}_{96}\text{Zn}_2\text{Y}_2$	216	116	4.3
$\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$	249	125	10.5

HRB10), the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displays almost no decline in hardness. It was conjectured that the rapid decline in hardness in the A4032-T6 alloy was due to the coarsening of the compound phases. Figure 13 shows the microstructures of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ and A4032-T6 alloys before and after the test. The microstructure of the A4032-T6 alloy has actually coarsened, but no change can be observed in the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy microstructure. It can therefore be considered that the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displays better high-temperature characteristics than age-hardening aluminum alloys such as A4032-T6 due to the greater stability of its microstructure at high temperatures.

Despite being cast, the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displayed better characteristics than the forged A4032-T6 alloy in the Charpy impact test, with a result of 3.6×10^4 J/m² against the latter's 2.0×10^4 J/m². These results were for V-notch shapes, and the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displayed similarly superior characteristics when tested as plane-type specimens. Next, to study ductility, the $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ and $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloys were cast in ship-shaped molds, in order to help ensure a sufficient gauge length. Table 2 shows the tensile properties of the alloys at room temperatures. In addition to increasing the strength of the alloy, the refinement of the material's microstructure through the addition of Zr also increased its elongation. The elongation of age-hardened heat-resistant magnesium alloys to which Zr has been added in order to

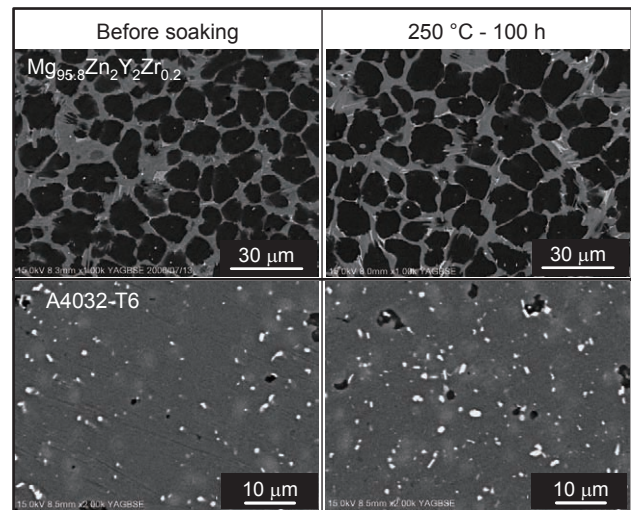


Fig. 13 BSE-SEM images of $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ and A4032-T6 alloys before and after soaking

Table 3 Characteristics of $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy compared to commercial aluminum and magnesium alloys

Alloy	Thermal conductivity (W/m·°C) at 200 °C (25 °C)	Thermal expansion coefficient (1/°C) at 25 - 300 °C	Young's modulus (GPa)	Density (kg/m ³)
$\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$	102 (92.5)	26.6×10^{-6}	45.8	1890
A4032-T6	141	21.5×10^{-6}	73	2690
AC8A-T6	128	21.4×10^{-6}	78	2720
AZ91D-T6	(51)	27.2×10^{-6}	45	1830
WE54-T6	(52)	24.6×10^{-6}	44	1850

refine the microstructure (EZ33A, QE22A, EQ21A, ZE41A, WE54A, and others) is generally around 4%, despite of their refined microstructures⁽⁹⁾. By contrast, the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displays superior elongation, recording a figure of more than 10%. While the test conditions do not necessarily match exactly, for reference Fig. 14 shows the relationship between tensile strength at 250°C and elongation at room temperature for $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ and a variety of light alloys. The $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy not only displays good high-temperature strength, but also exhibits a high ductility at room temperatures, and can therefore be indicated as possessing a good strength-ductility balance.

4.1.4. Physical properties

Table 3 shows various properties of the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy. Results for commercial aluminum alloys (A4032, AC8A) and commercial magnesium alloys (AZ91, WE54) are also shown for comparison. Thermal conductivity represents an issue from the perspective of cooling performance when a material is considered for use in an automotive part that will experience high temperatures (for example, pistons). The $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ displays superior results in terms of this property, with a level of thermal

conductivity higher than that of the commercial magnesium alloys, and close to that of the commercial aluminum alloys.

The $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displays a similar thermal expansion coefficient and Young's modulus to the commercial magnesium alloys, with figures lower than those for the commercial aluminum alloys in both cases. However, the material displays a low density like the commercial magnesium alloys, recording a figure of around 70% of the figures for the commercial aluminum alloys, and can therefore be expected to be effective in reducing the weight of engine parts in automotive and other applications.

4.2. Increasing Strength by Increasing LPSO Phase Strength

The tests conducted to this point had indicated that the $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy displayed good high-temperature characteristics, but the result for yield strength at room temperatures, as shown in Fig. 9, could not necessarily be considered a high figure. Further strengthening of the material was therefore attempted through the addition of Ag, which had been selected based on calculation results. Figure 15 shows XRD patterns for $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ and $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ alloys. The results show that in addition to the three phases that form in the $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ alloy, it was possible that the $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ alloy had formed the new

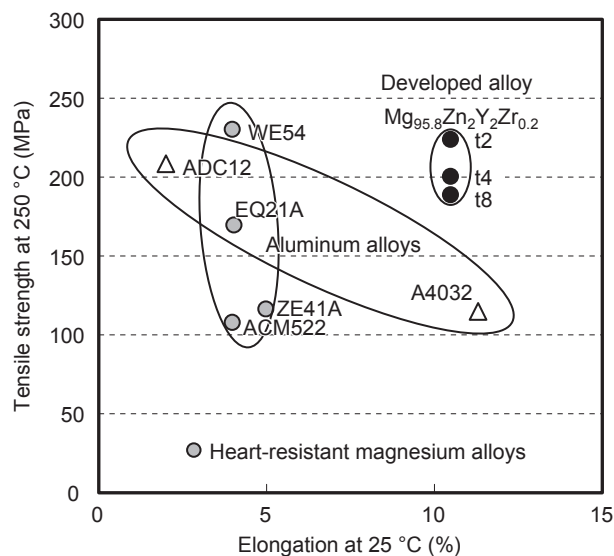


Fig. 14 Relationship between tensile strength at 250 °C and elongation at 25 °C

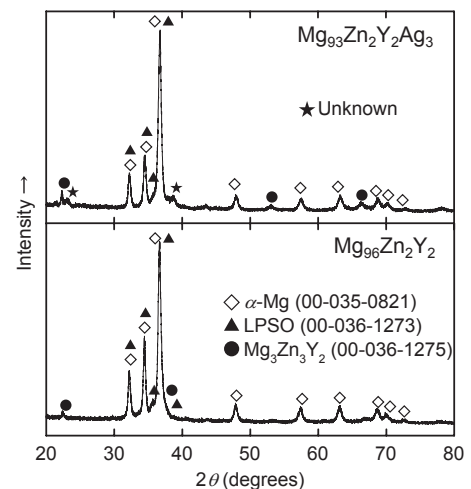


Fig. 15 XRD patterns of $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ and $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ alloys

phase marked in the figure by the star. Figure 16 shows a BSE-SEM image of the $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ alloy and the results of an EDS analysis of the phases making it up. As in the XRD results, the $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ alloy is made up of four phases, the α -Mg matrix, an LPSO phase, an $\text{Mg}_3\text{Zn}_3\text{Y}_2$ phase, and an unknown X' phase. The results of EDS analysis indicated that Ag was present in the matrix in solid solution, and was present in the X' phase in a quantity that exceeded the solid solubility limit of Mg (approximately 4 at.%). This indicated that it was possible that the Ag did not simply exist in solid solution, but had formed a new phase. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was applied to this phase. Figure 17 compares HAADF-STEM images of the LPSO and X' phases. In HAADF-STEM images, contrasts are produced by differences in atomic number; the higher the atomic number, the whiter the appearance in the image. The base LPSO phase displays a cyclic alternation of 2 monolayers (ML) which appear white, indicating a high concentration of Zn or Y, which have higher atomic numbers than Mg⁽¹⁰⁾. The alloy with added Ag displays further white areas in addition to the concentrated 2 ML, and with consideration of the results of the EDS analysis,

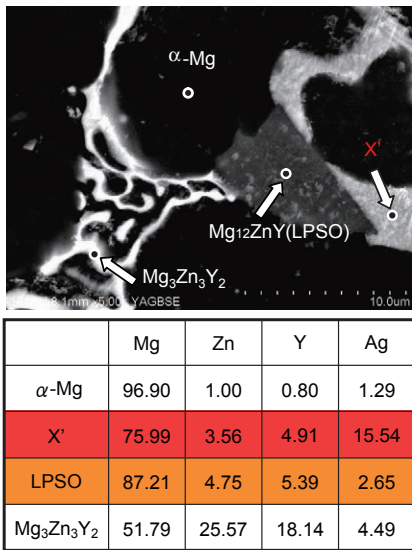


Fig. 16 BSE-SEM image and point EDS analysis of $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ alloy (at. %)

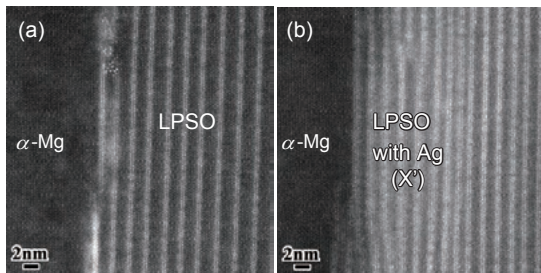


Fig. 17 HAADF-STEM images of (a) $\text{Mg}_{95.8}\text{Zn}_2\text{Y}_2\text{Zr}_{0.2}$ alloy and (b) $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ alloy

it can be conjectured that Ag has been substituted for Mg here. It can therefore be considered that an LPSO phase in which Ag has been substituted has been formed in accordance with the desired atomic model.

Next, ship-shaped specimens were processed and subjected to tensile tests in order to study the increase in the yield strength of the $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ alloy. Figure 18 shows the relationship between grain size and yield strength at room temperature, compared with data obtained up to this point. The results show a clear increase in strength against the strength increase expressed by the Hall-Petch equation, which was achieved by refining the crystal grains through the addition of Zr and the modification of the cooling rate. An increase of approximately 60% in strength has been achieved when converted for the same grain size. This can be considered to be a strength increase brought about by the LPSO phase that contains Ag. The $\text{Mg}_{93}\text{Zn}_2\text{Y}_2\text{Ag}_3$ alloy fulfilled the design aims established for it by forming an LPSO phase containing Ag, and this contributed to an increase in yield strength.

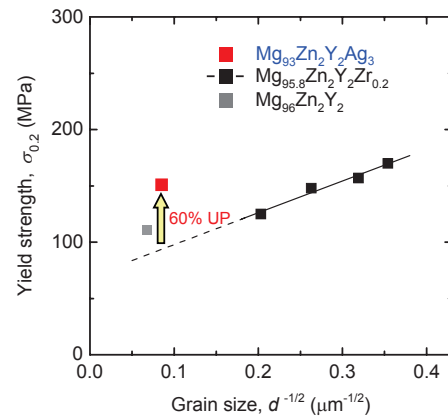


Fig. 18 Relationship between yield strength and grain size of Mg-Zn-Y-X alloys

5. Conclusions

The microstructure and various properties of Mg-Zn-Y alloys in which the solidified microstructure had been controlled were studied in an attempt to achieve weight savings in structural and other parts through the application of a high-strength, cast, heat-resistant magnesium alloy. The following results were obtained:

- (1) The addition of Zr to an $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ alloy transformed the α -Mg phase from dendritic to cell-shaped structures, and refined the microstructure of the cast alloy. In addition, increasing the rate of cooling when the alloy was cast tended to further refine the microstructure.
- (2) The alloy displayed high heat stability at high temperatures of 200°C and above, exhibiting a tensile strength (223 MPa) approximately twice that of A4032-T6 at 250°C, and close to three times its strength at 300°C. The alloy displayed equivalent or

better tensile, fatigue, and creep characteristics to heat-resistant aluminum alloys when cast, with no further treatment. In terms of physical properties, the material is low-density, with a density approximately 70% that of an aluminum alloy. In addition, its thermal conductivity, an issue when a material is used in parts, was higher than that of commercial magnesium alloys, and close to that of commercial aluminum alloys.

- (3) The addition of Ag, as selected based on the results of a first principle calculation, in order to produce a microstructure with a stronger LPSO phase, resulted in a 60% increase in yield strength at room temperatures.

As these results indicate, the new alloy can be considered as an effective cast alloy when seeking to achieve weight savings in heat-resistant components.

The first half of this paper is modified from the earlier paper published in the Journal of Japan Institute of Light Metals, Vol. 60, No. 6 (2010).

References

- (1) Yoshimoto, S., Yamasaki, M., Kawamura, Y.: Microstructure and Mechanical Properties of Extruded Mg-Zn-Y Alloys with 14H Long Period Ordered Structure, Mater. Trans., Vol.47, p.959-965 (2006)
- (2) Ienaga, Y., Inoue, K., Kawamura, Y.: Mechanical properties of large-scale extruded Mg-Zn-Y alloys, Proceedings of the 110th Conference of Japan Institute of Light Metals, p. 145-146 (2006)
- (3) Emley, E. F.: Principles of magnesium technology, Oxford, Pergamon press, p.126-156 (1966)
- (4) Yamaguchi, T., Saito, K., Kawamura, Y.: Mechanical properties of continuously consolidated $Mg_{96}Zn_2Y_2$ magnesium alloy chips, JILM, Vol. 57, No. 7, p. 286-292 (2007)
- (5) Okamoto, H.: Phase diagrams of dilute binary alloys, ASM International, p. 170 (2002)
- (6) Ando, S., Toda, K., Tsushida, M., Kitahara, H., Tonda, H., Kawamura, Y.: Fatigue Properties of Mg-Zn-Y Alloys with Long Period Ordered Structure, J. Japan Inst. Metals, Vol. 71, No. 9, p. 699-703 (2007)
- (7) Koike, S., Washizu, K., Tanaka, T., Baba, T., Kikawa, K.: Development of Lightweight Oil Pans Made of a Heat-Resistant Magnesium Alloy, HONDA R&D Technical Review, Vol. 12, No. 1, p. 167-174
- (8) Shibata, A., Suzuki, M., Maruyama, K.: Effects of Eutectic Compounds Formed along Grain Boundaries in Thixomolded Alloy $Mg_{96}Zn_2Y_2$ on Creep Deformation, Mater. Trans., Vol.50, p.1426-1432 (2009)
- (9) Busk, R. S.: Magnesium Products Design translated by the association of light metals, The association of light metals, p. 146 (1988)
- (10) Abe, E.: Jisedaino koukyoudo/koutainetsusei magunesiumugoukinno tokusyubisaikouzou-HAADF niyorukaiseiki, Proceedings of the 10th Conference of the Association of Magnesium Alloy Development and Processing, p. 61-62 (2006) (in Japanese)

■ Author ■



Yuichi IENAGA



Kenshi INOUE



Mitsumoto KAWAI