Novel hexagonal structure and ultrahigh strength of magnesium solid solution in the Mg–Zn–Y system

Akihisa Inoue[a)]
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Yoshihito Kawamura
Mechanical Engineering, Kumamoto University, Kumamoto 860-0862, Japan

Mitsuhide Matsushita
Inoue Superliquid Glass Project, Exploratory Research for Advanced Technology, Japan Science and Technology Corporation, Sendai 982-0807, Japan

Kentaro Hayashi
Graduate School, Tohoku University, Sendai, Japan

Junichi Koike
Materials Science and Engineering, Tohoku University, Sendai, Japan

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A magnesium (Mg) solid solution with a long periodic hexagonal structure was found in a $Mg_{97}Zn_1Y_2$ (at.%) alloy in a bulk form prepared by warm extrusion of atomized powders at 573 K. The novel structure has an ABACAB-type six layered packing with lattice parameters of a = 0.322 nm and c = 3 × 0.521 nm. The Mg solid solution has fine grain sizes of 100 to 150 nm and contains 0.78 at.% Zn and 1.82 at.% Y. In addition, cubic $Mg_{24}Y_5$ particles with a size of about 7 nm are dispersed at small volume fractions of less than 10% in the Mg matrix. The specific density (ρ) of the extruded bulk Mg–Zn–Y alloy was 1.84 Mg/m^3. The tensile yield strength (σ_y) and elongation (δ) are 610 MPa and 5%, respectively, at room temperature, and the specific yield strength defined by the ratio of σ_y to ρ is as high as 3.3×10^5 Nm/kg. High σ_y values exceeding 400 MPa are also maintained at temperatures up to 473 K. It is noticed that the σ_y levels are 2.5 to 5 times higher than those for conventional high-strength type Mg-based alloys. The Mg-based alloy also exhibits a high-strain-rate superplasticity with large δ of 700 to 800% at high strain rates of 0.1 to 0.2 s^{-1} and 623 K. The excellent mechanical properties are due to the combination of the fine grain size, new long periodic hexagonal solid solution containing Y and Zn, and dispersion of fine $Mg_{24}Y_5$ particles. The new Mg-based alloy is expected to be used in many fields.

I. INTRODUCTION

In recent years, there have been strong demands of energy saving and maintenance of a clean atmosphere on earth. One of the ways that satisfies these demands is to fabricate an ultrahigh-strength material with light specific weight by using raw materials which are abundant resources and have high recycling ratios. Among conventional metals, a Mg metal with a hexagonal closed-packed (hcp) structure has the lowest specific weight of 1.74 Mg/m^3 and is one of abundant metallic resources on earth.[1] It is well-known that a Mg-based alloy is an easy recycling material.[1] On the basis of the above-described social demands and advantage points, Mg-based alloys have been used in a number of fields such as case materials for televisions, cameras, portable telephones, and word processors and part materials in automobiles, bicycles, and robots.[1] However, the tensile yield strengths (σ_y) and elongations (δ) of conventional Mg-based alloys are 70 to 180 MPa and 2 to 10% for the casting type and 90 to 230 MPa and 4 to 13% for the heat treatment type.[1] Very recently, we have examined systematically the compositional dependence of ductility and strength of Mg-based solid solutions in the Mg–M_1–M_2 ternary system where the three elements have significant atomic size mismatches above 12% and negative heats of

[a)]Address all correspondence to this author.
e-mail: ainoue@imr.tohoku.ac.jp

mixing. The combination of such three elements is expected to cause an anomalous effect in the structure and properties of the multicomponent solid solution. This is evidenced from the results that such ternary alloys have anomalous effects such as stabilization of metallic supercooled liquid and high glass-forming ability which enable us to form bulk amorphous alloys.[2–4] In the systematic study on the development of a new Mg-based alloy by use of the novel concept, we have succeeded in fabricating a high-strength Mg-based $Mg_{97}Zn_1Y_2$ alloy with a new long periodic hexagonal structure by the warm extrusion process of atomized powders (RS/PM process). The new Mg-based alloy exhibited good mechanical properties, i.e., 425 to 610 MPa for tensile yield strength and 5 to 16% for elongation, depending on extrusion temperature from 573 to 723 K. This paper is intended to present the structure and mechanical properties of the new hexagonal RS/PM $Mg_{97}Zn_1Y_2$ alloy.

II. EXPERIMENTAL PROCEDURE

Ternary alloy ingots in Mg–Zn–Y system were prepared by high-frequency induction heating in an argon atmosphere. Ribbon samples with a cross section of $0.02 \times 1.2\ \mathrm{mm}^2$ were produced by the melt-spinning technique. Bend ductility and hardness in as-spun and annealed states were measured by the simple bend test and Vickers hardness tester under a load of 25 g, respectively. Alloy powders were produced by helium gas atomization with an applied pressure of 9.8 MPa and then sieved in the particle size fraction below 32 μm. The sieved powder was precompacted into a copper can, followed by evacuating and then sealing. The sealed atomized powder was extruded at an extrusion ratio of 10 in the extrusion temperature range from 573 to 723 K. The extruded alloy has a rod shape with a diameter of 6 mm and a length of 800 mm. The structure was examined by x-ray diffraction and transmission electron microscopy (TEM). Atomic configuration was also examined by high-resolution TEM, and the atomic component was evaluated by EDX spectroscopy. Mechanical properties were measured with an Instron testing machine in the temperature range from room temperature to 673 K and in a wide initial strain rate range from 0.02 to 0.8 s^{-1}. The gauge dimensions of tensile test specimens are 2.5 mm in diameter and 16 mm in length for ordinary strength and elongation measurements at an initial strain rate of $5.0 \times 10^{-4}\ s^{-1}$ and 2 mm in diameter and 10 mm in length for superplasticity measurement at an initial strain rates of 0.02 to 0.8 s^{-1}. Deformation marking and fracture surface were examined by scanning electron microscopy (SEM).

III. RESULTS

We confirmed that the $Mg_{97}Zn_1Y_2$ alloy had the highest Vickers hardness in the maintenance of good bend ductility in the as-quenched state as well as in annealed states for 1.2 ks at 573 and 673 K. The "ductile" implies that the melt-spun ribbon sample can be bent through 180° without fracture. The annealing temperatures correspond to the extrusion temperatures. Consequently, the $Mg_{97}Zn_1Y_2$ alloy was chosen in the subsequent study.

Figure 1 shows the changes in the tensile yield strength (σ_y) and elongation (δ) with extrusion temperature (T_e) for the RS/PM Mg–Zn–Y alloy rods. The σ_y and δ are 610 MPa and 5%, respectively, at $T_e = 573$ K, and the increase in T_e causes a decrease in σ_y and an increase in δ, resulting in good combined values of $\sigma_y = 570$ MPa and $\delta = 7\%$ at $T_e = 623$ K, $\sigma_y = 490$ MPa and $\delta = 8\%$ at $T_e = 673$ K, and $\sigma_y = 420$ MPa and $\delta = 16\%$ at $T_e = 723$ K. Figure 2 shows the relation between tensile yield strength (σ_y) and plastic elongation (δ) for the new RS/PM Mg–Zn–Y alloy rods produced by extrusion at different temperatures, together with the data for conventional Mg-based alloys developed to date. It is noticed that the σ_y and δ of the RS/PM Mg–Zn–Y alloy rods are about 2–3 times higher than those for the

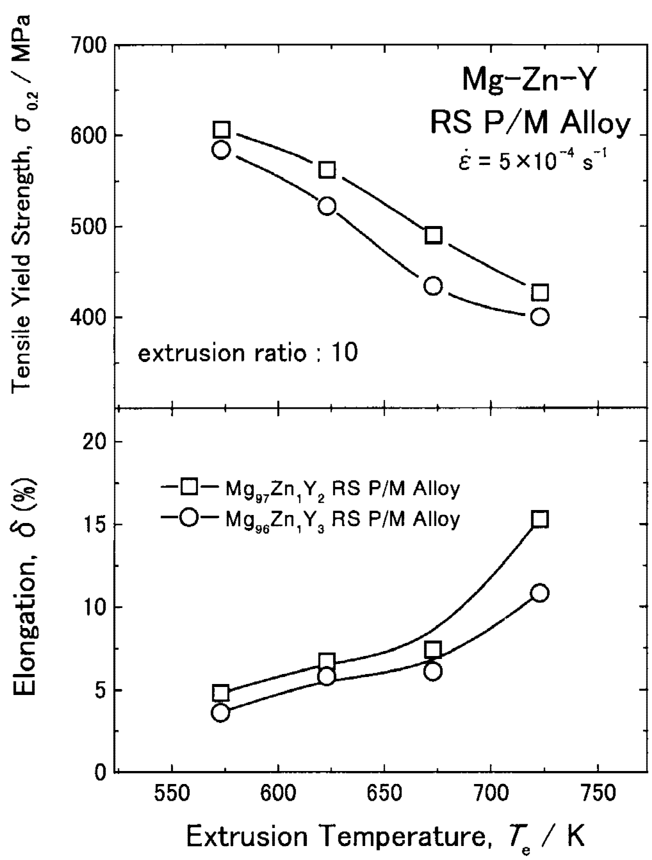

FIG. 1. Changes in the tensile yield strength and elongation at room temperature with extrusion temperature (T_e) for the RS/PM $Mg_{97}Zn_1Y_2$ alloy.

conventional Mg-based alloys marked with ingot metallurgy (IM) and heat treatment (aging). Furthermore, even in comparison with the conventional Mg-based alloys developed previously by the rapid solidification technique, the σ_y values of the present alloy rods are higher by about 1.5 times. Here, it is important to point out that the RS/PM Mg–Zn–Y alloy also exhibits high elevated temperature strength above 400 MPa in the temperature range up to 473 K and the further increase in testing temperature causes a rapid decrease in σ_y. Figure 3 summarizes the specific yield strength (σ_y/ρ) of the RS/PM $Mg_{97}Zn_1Y_2$ and $Mg_{96}Zn_1Y_3$ alloys, together with the data of other conventional alloys in Mg-, Al-, and Ti-based systems. The densities of the RS/PM $Mg_{97}Zn_1Y_2$ and $Mg_{96}Zn_1Y_3$ alloys produced by extrusion at 573 K were measured as 1.84 and 1.86 Mg/m^3, respectively. It is noticed that the $Mg_{97}Zn_1Y_2$ alloy has the highest specific yield strength and the increased ratio reaches four times as compared with conventional Mg-based alloys.

Figure 4 shows the temperature dependence of σ_y and δ for the RS/PM $Mg_{97}Zn_1Y_2$ alloy deformed at an initial strain rate of $5.0 \times 10^{-4}\ s^{-1}$. As the testing temperature increases, σ_y decreases gradually to 400 MPa in the temperature range up to 473 K and then rapidly in the higher temperature range. On the other hand, δ increases gradually to 25% at the temperatures up to 473 K, followed by

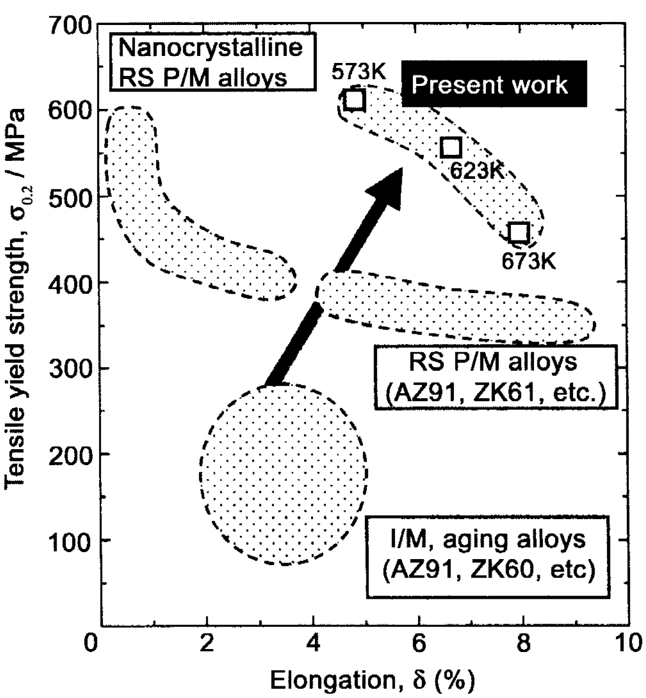

FIG. 2. Relation between tensile yield strength (σ_y) and plastic elongation (δ) for the RS/PM $Mg_{97}Zn_1Y_2$ alloy rods produced at various extrusion temperatures. The data of conventional Mg-based alloys produced by ingot metallurgy (IM) and heat treatment (aging) as well as previously developed RS/PM Mg-based alloys are also shown for comparison.

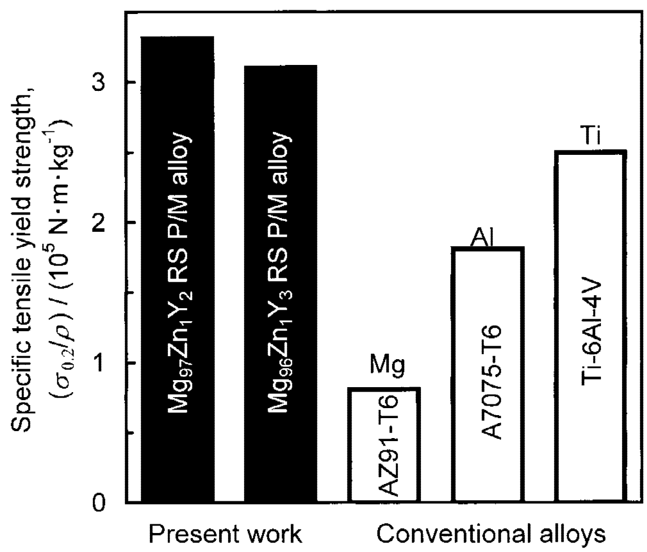

FIG. 3. Tensile specific yield strength defined by the ratio of σ_y to specific density (ρ) for the RS/PM $Mg_{97}Zn_1Y_2$ and $Mg_{96}Zn_1Y_3$ alloy rods produced at $T_e = 573$ K in comparison with those for other conventional metallic alloys.

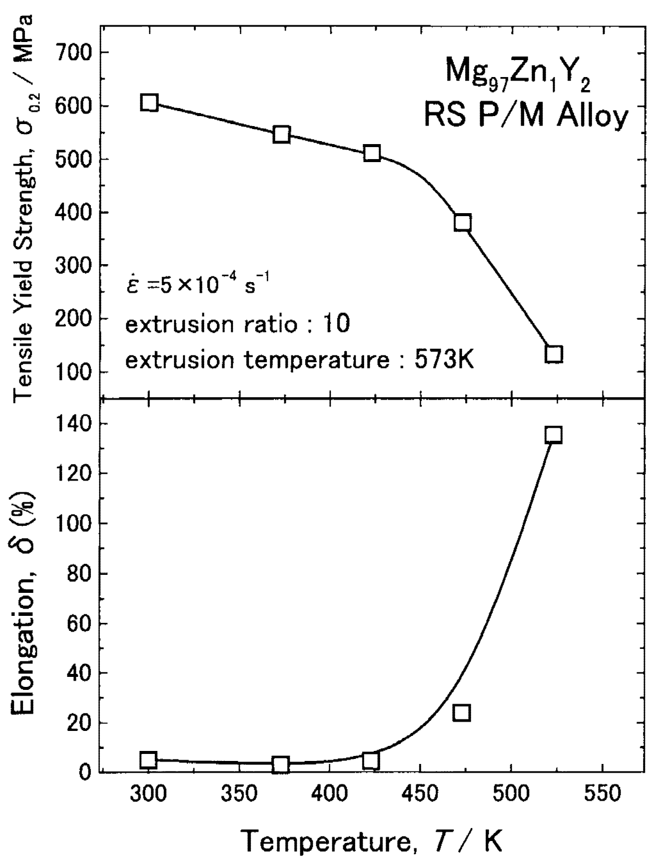

FIG. 4. Changes in the tensile yield strength and elongation with testing temperature for the RS/PM $Mg_{97}Zn_1Y_2$ alloy produced at $T_e = 573$ K.

a rapid increase to 135% at 523 K. It is noticed that the Mg-based alloy keeps an extremely high elevated temperature strength of 400 MPa at 473 K. Figure 5 shows the relation between δ and strain rate ($\dot{\epsilon}$) for the $Mg_{97}Zn_1Y_2$ alloy subjected to tensile deformation at elevated temperatures, in comparison with that for other Mg- and Al-based alloys. The Mg–Zn–Y alloy exhibits large elongations of 700 to 800% at the high initial strain rates of 0.1 to 0.2 s^{-1}, indicating the achievement of much better high-strain-rate superplasticity which cannot be obtained for any other Mg- and Al-based alloys. Figure 6 shows the change in the sample shape of the RS/PM $Mg_{97}Zn_1Y_2$ alloy before and after the deformation tests at 623 K under different strain rates from 0.02 to 0.8 s^{-1}. It can be clearly confirmed that the alloy exhibits maximum elongations of 700 to 800% at high strain rates of 0.1 and 0.2 s^{-1}. In addition, no distinct change in the color on the surface of the deformed specimens is seen, indicating that the Mg-based alloy also has rather high resistance against oxidation in the temperature range up to 623 K.

To clarify the reason for the excellent mechanical properties, we examined the microstructure of the RS/PM $Mg_{97}Zn_1Y_2$ rod obtained at the extrusion temperature of 573 K. Figure 7 shows its bright-field TEM image. The grain size of the Mg matrix phase is as small as 100 to 150 nm even in the extruded bulk Mg alloy with the low solute concentration. In addition, one can see a high density of plane faults and fine precipitates with a rectangular shape in almost all the matrix grains. However, no appreciable precipitates are observed on the grain boundary. Figure 8 shows a high-resolution TEM image and a selected-area electron diffraction pattern of the Mg matrix phase including a high density of plane faults. In the diffraction pattern revealing the hexagonal structure, one can see extra reflection spots at the positions of 1/3(0001) and 2/3(0001) and strong streaks along the [0001] direction. This reveals clearly the existence of a high density of plane faults along the (0001) plane. The diffraction pattern also indicates the formation of a new hexagonal structure with lattice parameters of a = 0.322 nm and c = 3 × 0.521 nm. The c value is three times larger than that of the ordinary hexagonal closed packed (hcp) Mg phase. Besides, the EDX spectrum taken from the long periodic hexagonal grain shown in Fig. 8 demonstrated that the new hexagonal Mg phase is a solid solution containing 0.78 at.% Zn and 1.82 at.% Y. Figure 9 shows the high-resolution TEM image of the plane faults in the long periodic hexagonal grain. As identified in the figure, the long periodic hexagonal phase has a six layered atomic packing of ABACAB type

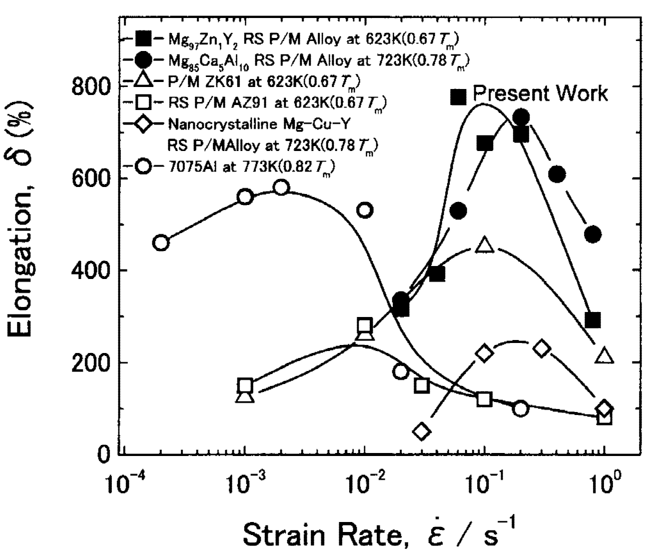

FIG. 5. Relation between δ and strain rate for the RS/PM $Mg_{97}Zn_1Y_2$ alloy produced at T_e = 573 K. The data of other conventional metallic alloys are also shown for comparison.

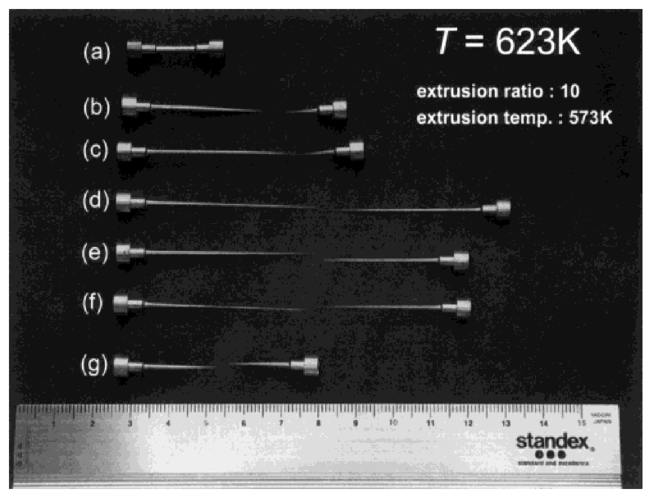

FIG. 6. Outer shape of the RS/PM $Mg_{97}Zn_1Y_2$ alloy produced at T_e = 573 K before and after the tensile deformation tests at 623 K under different strain rates of (a) before deformation, (b) 0.02 s^{-1}, (c) 0.04 s^{-1}, (d) 0.06 s^{-1}, (e) 0.1 s^{-1}, (f) 0.2 s^{-1}, and (g) 0.8 s^{-1}.

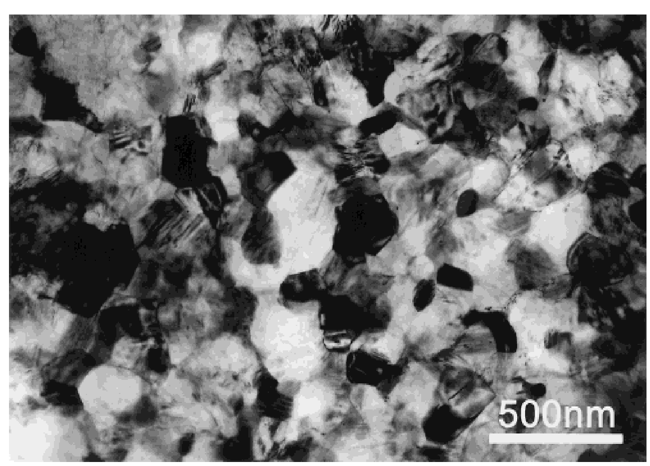

FIG. 7. Bright-field TEM image of the RS/PM $Mg_{97}Zn_1Y_2$ alloy produced at T_e = 573 K.

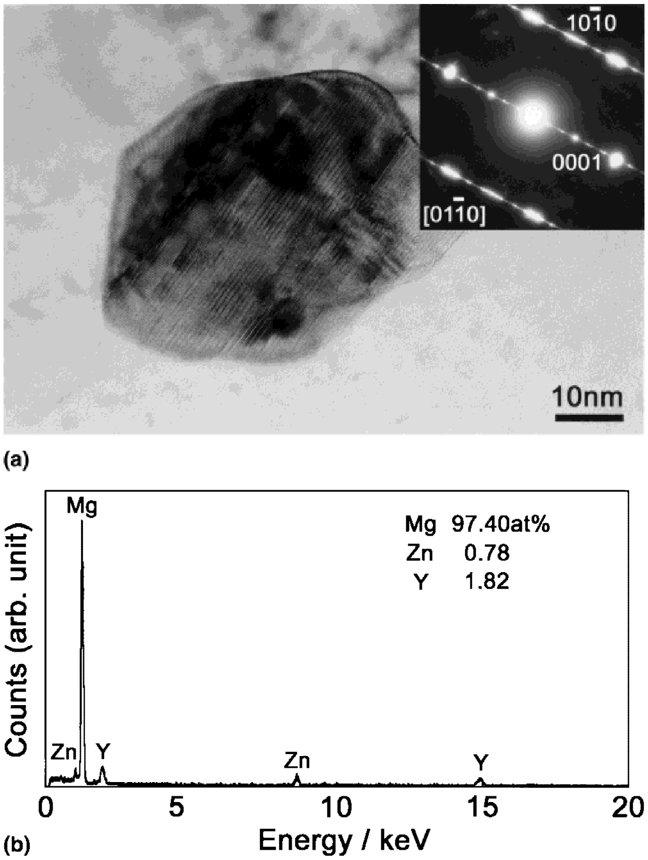

FIG. 8. High-resolution TEM image and selected-area electron diffraction pattern of the RS/PM $Mg_{97}Zn_1Y_2$ alloy produced at T_e = 573 K. The diffraction pattern and EDX spectrum were taken from one grain in the high-resolution TEM image.

which is three times longer than the ordinary AB-type two layered atomic configuration. The change from the AB-type hexagonal packing to the ABACAB-type long periodic hexagonal packing is presumed to result from significant strains generated by the reinforced solution of Y with a larger atomic size of 0.180 nm and Zn with a smaller size of 0.131 nm into hcp Mg phase.[5] This is believed to be the first evidence for the formation of the new long periodic hexagonal structure for the Mg-rich alloy containing only 3% solute elements. In addition, Fig. 10 shows a high-resolution TEM image and a nanobeam electron diffraction pattern of the fine precipitate with a rectangular shape, together with the nanobeam EDX spectrum. The nanobeam diffraction pattern and EDX spectrum reveal that the rectangular precipitate with an edge size of about 7 nm is a cubic $Mg_{24}Y_5$ phase with a lattice parameter of 1.1 nm. However, one can notice that the composition in the $Mg_{24}Y_5$ compound obtained from the EDX spectrum is slightly higher than the stoichiometric Y content (17.2 at.%). The deviation seems to reflect the result that the data by the EDX spectroscopy include those from the two phases of $Mg_{24}Y_5$ compound and Mg-based solid solution.

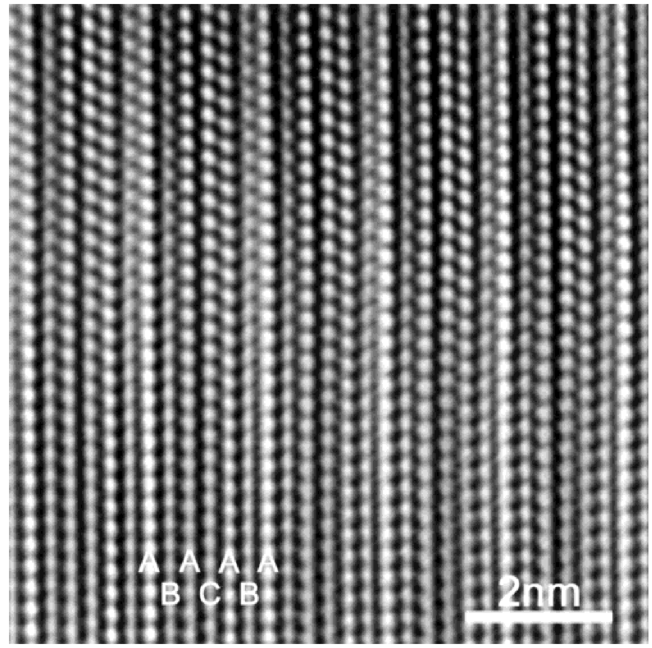

FIG. 9. High-resolution TEM image of the RS/PM $Mg_{97}Zn_1Y_2$ alloy produced at T_e = 573 K.

IV. DISCUSSION

It is thus characterized that the RS/PM $Mg_{97}Zn_1Y_2$ alloy has the following structural features: (i) fine grain sizes of 100 to 150 nm; (ii) formation of a new long periodic hexagonal structure of ABACAB type packing with lattice parameters of a = 0.322 nm and c = 3 × 0.521 nm which is different from the ordinary hcp Mg structure of the AB type packing with the lattice parameters of a = 0.321 nm and c = 0.521 nm; (iii) dissolution of 0.78 at.% Zn and 1.82 at.% Y in the long periodic hexagonal Mg phase; (iv) homogeneous dispersion of cubic $Mg_{24}Y_5$ precipitates with a rectangular shape of about 7 nm in the Mg phase. The maximum solid solubility of each solute element into the hcp Mg phase is 0.07 at.%[6] for Zn and nearly zero[7] for Y at room temperature, and no appreciable solid solubility of Zn + Y elements is also recognized in the Mg–Zn–Y ternary system.[8] Consequently, the long periodic hexagonal phase is concluded to be a solid solution saturated with Zn and Y. On the basis of the structural features of the RS/PM Mg–Zn–Y alloy, it may be concluded that the high strength is due to the combination of (i) strengthening by the grain size refinement, (ii) solid solution strengthening, (iii) introduction of a high density of plane faults caused by the formation of the long periodic hexagonal Mg phase, and (iv) dispersion strengthening by fine $Mg_{24}Y_5$ compound particles. In addition, the good elongation may be attributed to the fine grain structure without any precipitates on the grain boundary as well as the homogeneous dispersion and small volume fraction of the fine $Mg_{24}Y_5$ compound particles. In addition, the

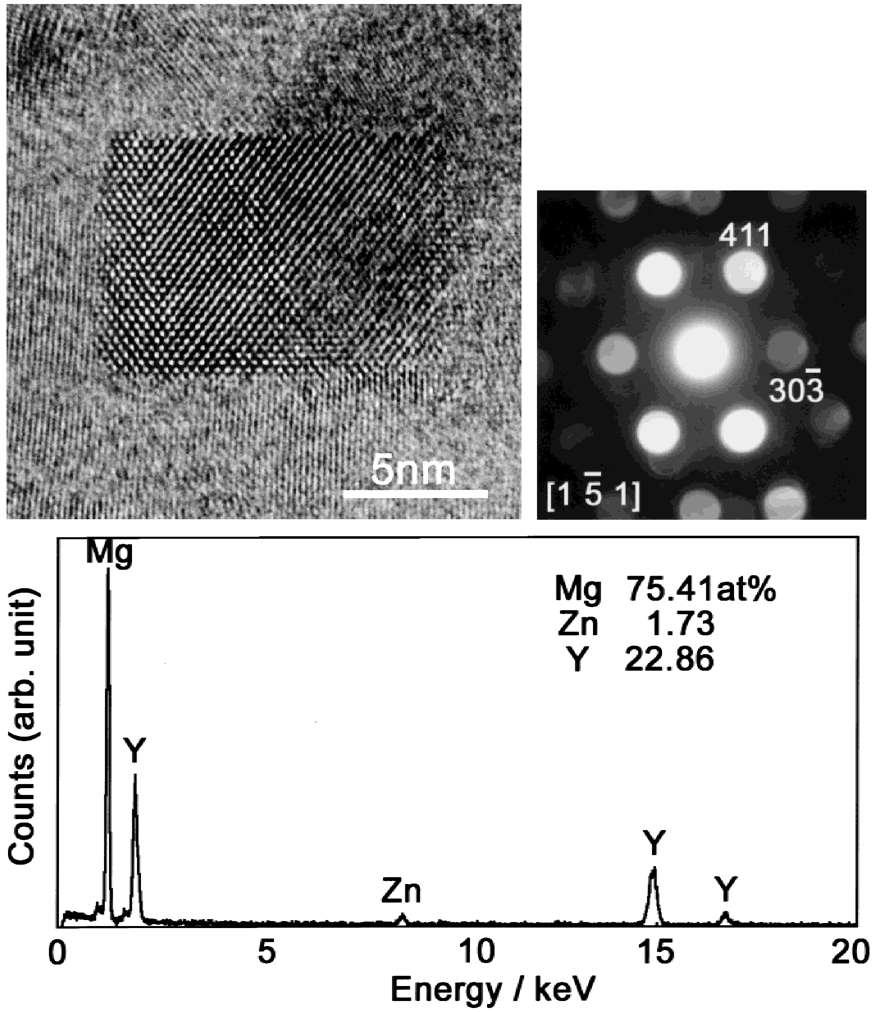

FIG. 10. High-resolution TEM image, nanobeam electron diffraction pattern and EDX spectrum of the RS/PM $Mg_{97}Zn_1Y_2$ alloy produced at $T_e = 573$ K. The diffraction pattern and EDX spectrum were taken from the second phase with rectangular shape.

excellent high-strain-rate superplasticity with large elongation of 700 to 800% at high strain rates of 0.1 to 0.2 s^{-1} results from the fine grain structure without second phase on the grain boundary. The maintenance of the fine grain structure during deformation which is an essential factor for the achievement of the high-strain-rate superplasticity is presumably due to the homogeneous dispersion of the fine $Mg_{24}Y_5$ compound particles and the formation of the new long periodic hexagonal atomic configurations leading to the difficulty of atomic movement.

V. SUMMARY

A novel Mg-based solid solution with a long periodic ABACAB type layered packing was found to be formed in the $Mg_{97}Zn_1Y_2$ alloy produced by extrusion of atomized powders at 573 K. The hexagonal phase contains 0.78 at.% Zn and 1.82 at.% Y and has fine grain sizes of 100 to 150 nm containing fine $Mg_{24}Y_5$ compound particles with a size of about 10 nm. The RS/PM alloy exhibits good mechanical properties, i.e., high tensile yield strength and large elongation of 610 MPa and 5% at the extrusion temperature (T_e) of 573 K and 570 MPa and 7% at $T_e = 623$ K. The RS/PM alloy produced at $T_e = 573$ K has a small density of 1.84 Mg/m^3 and high specific yield strength of 3.3×10^5 Nm/kg. The high tensile yield strength exceeding 400 MPa is also maintained in the temperature range up to 473 K. The further increase in testing temperature to 623 K caused the high-strain-rate superplasticity of 700 to 800% in elongation at high strain rates of 0.1 to 0.2 s^{-1}. The combination of high strength, large elongation, light weight, high elevated temperature strength, and high-strain-rate superplasticity is encouraging for future uses as various kinds of structural materials.

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