RAPID PUBLICATION

Increase of Mechanical Strength of a Mg85Zn12Ce3
Amorphous Alloy by Dispersion of
Ultrafine hcp-Mg Particles

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A Mg85Zn12Ce3 amorphous alloy containing finely dispersed hcp-Mg particles was found to form either by melt spinning or by heat treatment of the melt-spun ribbon. The particle size and interparticle distance of the hcp-Mg phase can be controlled in the range of 3 to 20 nm and 5 to 10 nm, respectively. The mixed phase alloy prepared thus has a good bending ductility and exhibits a high ultimate tensile strength (σu) ranging from 655 to 935 MPa and a fracture elongation including elastic elongation (εf) of 2.9 to 7.0%. The highest specific strength (σu/density=σu) reached 3.6×10^5 N·m/kg. It should be noted that the highest values of σu, σf, and εf are considerably higher than those (690 MPa, 2.5×10^2 N·m/kg and 2.5%) for amorphous Mg-Zn-Ce alloys. The increase of the mechanical strengths by the formation of the mixed phase structure is presumably due to a dispersion hardening of the hcp supersaturated solution which has the hardness higher than that of the amorphous phase with the same composition.

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I. Introduction

A Mg element is the lightest in metals which have been used as a major component in construction materials and hence an amorphization of Mg-base alloys is expected to bring about a high specific strength material. Recently, Inoue et al. have reported that an amorphous phase with high strength and good bending ductility is formed in rapidly solidified Mg–Ln–TM (Ln=lanthanide metal, TM=transition metal) alloys. However, the Mg content in their amorphous alloys is usually less than 83 at% and the formation of a further Mg-rich amorphous phase has strongly been desired because of an expectation of the development of Mg-based alloys with a higher specific strength.

More recently, it has been found that the Al-rich alloys with Al compositions (85 to 90 at%Al) higher than the glass-formation range in the Al–Ln–TM ternary system have a rapidly solidified structure consisting of fcc Al particles embedded in an amorphous matrix. Furthermore, the mixed phase alloys have been found to exhibit excellent mechanical strengths which are about two times as high as those of amorphous single phase alloys with the same alloy compositions. It is expected that a similar mixed structure is formed at Mg-rich compositions in Mg–Ln–TM alloys and high mechanical strengths exceeding those of an amorphous single phase are obtained in the mixed phase alloys. In the systematic research on the formation and mechanical strengths of Mg-rich alloys consisting of amorphous and hcp Mg phases, the present authors have found that the mixed phase exhibiting high mechanical strength and good bending ductility is formed in the Mg–Zn–Ln ternary alloys. This paper is intended to clarify the microstructure and mechanical strengths of a rapidly solidified Mg85Zn12Ce3 alloy consisting of amorphous and hcp Mg phases.

II. Experimental Procedure

A Mg85Zn12Ce3 ingot was prepared by induction melting a mixture of pure Mg (99.99 mass%) metal and Zn–Ce alloy in a purified argon atmosphere. The composition is chemically expressed in atomic per cent. From the master alloy ingot, a rapidly solidified ribbon with a cross-section of 1.5×0.02 mm² was produced by a single roller melt-spinning technique and the precipitation amount of a hcp-Mg phase was controlled either by changing the rotation speed of roller or by subsequent heating for 20 s in the temperature range of 363 to 423 K. Rapidly solidified structure was examined by X-ray diffraction and transmission electron microscopy (TEM) techniques. The TEM sample was prepared by thinning electrolytically the melt-spun ribbon in a solution of 20% nitric acid and 80% methanol at 273 K. Crystallization temperature (Tc) and heat of crystallization (∆Hf) were measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Hard-
ness and tensile strengths were examined by a Vickers microhardness tester with 0.49 N (50 gf) load and an Instron-type tensile testing machine at a strain rate of $8.3 \times 10^{-4} \text{s}^{-1}$, respectively.

III. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of as-quenched and annealed (383 K-20 s) phases of a melt-spun Mg$_{85}$Zn$_{15}$Ce$_{5}$ alloy. Sharp diffraction peaks due to the precipitation of a crystalline phase are seen, in addition to a broad diffraction peak revealing the formation of an amorphous phase. All the crystalline peaks are identified to be a hcp Mg phase and hence the as-quenched and annealed phases are concluded to consist of amorphous and hcp Mg phases. In addition, it is seen that the precipitation amount of the hcp Mg phase increases significantly by annealing. The lattice parameter of the hcp Mg phase was measured to be $c_0=0.5163$ nm in the as-quenched state and $a_0=0.3236$ nm and $c_0=0.5168$ nm in the annealed state, though the $a_0$ value of the Mg phase in the as-quenched alloy remains unidentified because of the absence of the diffraction peaks corresponding to the $a_0$ axis. There is a tendency for the $c_0$ value to increase upon annealing. When these lattice parameters are compared with that ($a_0=0.3209$ nm, $c_0=0.5211$ nm)$^{(5)}$ of pure Mg metal, one can notice that the $a_0$ value is larger and the $c_0$ value is smaller. The atomic size of the three constituent elements is the largest for Ce, followed by Mg and then Zn. The data$^{(5)}$ on the lattice parameters of the equilibrium hcp solid solution in Mg–Zn binary system indicate that the $a_0$ and $c_0$ values decrease linearly with increasing Zn content and are 0.3195 and 0.5186 nm, respectively, at 2.85%Zn. If it is assumed that the linearity is valid up to 12 at%Zn, the $a_0$ and $c_0$ values of the hcp Mg–Zn supersaturated solution containing 12 at%Zn are extrapolated to be 0.3150 and 0.5106 nm, respectively. In comparison of the extrapolated values with the actually measured values of the hcp solution in Mg$_{85}$Zn$_{15}$Ce$_{5}$, the hcp Mg–Zn–Ce phase has the $a_0$ and $c_0$ values much larger than those of the hypothetical Mg–Zn supersaturated solution. The significant difference is reasonably interpreted to result from the quenching induced dissolution of the Ce atom with the largest atomic size into the hcp phase. It is therefore concluded that the hcp particle embedded in the amorphous phase is a supersaturated solution containing Zn and Ce contents above their equilibrium solubility limits.

In order to clarify the dispersed state of the as-quenched structure consisting of amorphous and hcp Mg phases, the TEM observation was carried out for the Mg$_{85}$Zn$_{15}$Ce$_{5}$ alloy. As shown in Fig. 2, the as-quenched alloy consists of a crystalline phase with a particle size of about 3 nm homogeneously dispersed in an amorphous matrix. It is seen from the electron diffraction pattern that the crystalline phase has a hcp structure with a lattice parameter of $a_0=0.324$ nm and $c_0=0.517$ nm and hence can be identified to be a Mg-based solid solution. It has furthermore been observed that the volume fraction of the Mg particles increases significantly by annealing for 20 s at 383 K, accompanied by an increase of the average particle size from 3 to 20 nm and a decrease of the interparticle distance from 10 to 5 nm.

Figure 3 shows the DSC curves of the as-quenched and annealed Mg$_{85}$Zn$_{15}$Ce$_{5}$ ribbons having the mixed struc-

![Fig. 1 X-ray diffraction patterns of a melt-spun Mg$_{85}$Zn$_{15}$Ce$_{5}$ alloy. (a) as-quenched, (b) annealed for 20 s at 383 K.](image1)

![Fig. 2 Bright- and dark-field images ((a) and (b)) and electron diffraction pattern (c) showing the as-quenched structure of a melt-spun Mg$_{85}$Zn$_{15}$Ce$_{5}$ alloy.](image2)
ture. Three exothermic peaks are seen in each temperature range of 371 to 415, 484 to 509 and 529 to 574 K. It was confirmed from the X-ray diffraction analyses and TEM observation that the three exothermic peaks are due to the precipitation of hcp-Mg phase from the amorphous matrix, the transformation of the remaining amorphous phase to compound phases and the recrystallization of crystallization-induced Mg and compound phases, respectively. The magnitude of the first exothermic peak due to the precipitation of Mg phase decreases significantly by heating for 20 s at 383 K because of the precipitation of Mg phase during heating, though there is no appreciable change in the magnitude of the second and third peaks upon heating. It is thus said that the precipitation amount of Mg phase can be controlled by subsequent heat treatment and the thermal stability of the remaining amorphous phase increases significantly after the precipitation of Mg phase. Here, it is important to point out that the mixed phase ribbons in as-quenched and annealed states exhibit a good bending ductility and can be bent through 180 degrees without fracture. Tensile strengths and fracture behavior were examined for these mixed phase ribbons with good bending ductility.

Figure 4 shows the nominal stress-strain curves of the Mg$_{80}$Zn$_{12}$Ce$_{8}$ ribbons in as quenched state and annealed for 20 s at 383 K. The proof stress at 0.2% elongation ($\sigma_{0.2}$), ultimate tensile strength ($\sigma_b$) and fracture elongation including elastic elongation ($\epsilon^e$) are 543 MPa, 655 MPa and 7.0%, respectively, for the as-quenched ribbon. The annealing treatment causes an increase of $\sigma_{0.2}$ and $\sigma_b$ to 735 MPa and 936 MPa and a decrease of $\epsilon^e$ to 2.9%. Thus, the $\sigma_{0.2}$ and $\sigma_b$ increase significantly by the increase in the precipitation amount of hcp Mg phase during heating. It is noticed that the $\sigma_b$ value for the annealed sample is about 3.2 times as high as the highest $\sigma_b$ value$^{(6)}$ for the conventional Mg-based crystalline alloys. Furthermore, the appearance of the significant plastic elongation is quite different from the previous result$^{(7)}$ that the amorphous ribbon with highly ductile nature fractures through an inhomogeneous shear sliding without distinct plastic elongation. The large plastic elongation indicates that the homogeneous dispersion of ultrafine hcp Mg particles embedded in the amorphous matrix suppresses the generation of local shear deformation and assists the homogeneous plastic deformation.

A typical example revealing a tensile fracture surface appearance for the as-quenched Mg$_{80}$Zn$_{12}$Ce$_{8}$ sample is shown in Fig. 5. The fracture surface consists of smooth and vein pattern regions. Although the feature is similar to that for an amorphous single phase with good bending ductility, one can notice a significant difference in which the smooth region occupies about 65% fraction in fracture surface area and distinctly developed ledges exist on the fracture surface of the mixed phase alloy. This
difference suggests that the fine hcp particles act as a resistance to local shear deformation and enhance the degree of local adiabatic heating in the final fracture stage, leading to a more significant viscous flow of the amorphous matrix. It is of great importance that the mixed phase alloy consisting of ultrafine hcp Mg particles embedded in an amorphous matrix exhibits the $\sigma_b$ and $\varepsilon_f$ values much higher than the highest values ($\sigma_b = 650$ MPa and $\varepsilon_f = 2.5\%$) for the amorphous single phase alloys in the Mg-Zn-Ce system.

In conclusion, it was found that a Mg$_{65}$Zn$_{35}$Ce$_{5}$ amorphous alloy containing finely dispersed hcp-Mg particles is formed either by melt spinning or heat treatment after melt spinning and exhibit high $\sigma_b$ values above 650 MPa and good ductility over a wide range of the precipitation amount of the hcp-Mg phase. The mixed alloys are highly attractive as a new type of high-strength materials with light weight because of an additional advantage that the optimum mixed structure is obtained by subsequent heat treatment of an amorphous phase. With the aim of enhancing the tensile fracture strength and elongation and clarifying the mechanism for the achievement of the high tensile strengths and good ductility, a subsequent investigation is in progress for Mg-Zn-Ln (Ln=lanthanide metal) amorphous alloys containing dispersed hcp-Mg particles.

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REFERENCES