Thermal Stability and Mechanical Properties of Mg–Y–Cu–M (M = Ag, Pd) Bulk Amorphous Alloys

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Magnesium-based bulk amorphous alloys with a diameter of 7 mm for Mg₆₅Y₁₀Cu₁₅Ag₅Pd₅ were produced by a metallic mold casting method. The glass transition temperature (T_g), crystallization temperature (T_x), the temperature interval of the supercooled liquid region ($\Delta T_x = T_x - T_g$) and the melting temperature (T_m) are measured to be 437, 472, 35 and 707 K, respectively, for the Mg₆₅Y₁₀Cu₁₅Ag₅Pd₅ alloy. The simultaneous addition of Ag and Pd to Mg–Y–Cu system causes a steep decrease in T_m and an increase in the reduced glass transition temperature (T_g/T_m), leading to an increase in the glass-forming ability. The Mg–Y–Cu–(Ag, Pd) bulk amorphous alloys have a high compressive fracture strength of 770 MPa. The simultaneous addition of Ag and Pd is useful for the improvements of glass-forming ability and fracture strength.

(Received May 22, 2000; Accepted August 29, 2000)

Keywords: bulk amorphous alloy, magnesium base alloy, supercooled liquid region, reduced glass transition temperature, high glass-forming ability

1. Introduction

For energy saving and reduction of carbon dioxide gas, it is important to develop a new alloy with high strength, light weight and good corrosion resistance. It is known that amorphous alloys have much higher mechanical strength as compared with those for the corresponding crystalline alloys.¹⁾ Furthermore, when the specific weight of metallic alloys is taken into consideration, Mg-based alloys are attractive materials among a number of metallic alloys. Consequently, great efforts have been devoted to the development of Mg-based amorphous alloys with high specific strength in a bulk-form with a thickness of over several millimeters because the bulk form is essential for application as structural materials. Inoue *et al.* have found that amorphous alloys in Mg–Ln–(Ni, Cu) (Ln = lanthanide metal) systems have a large supercooled liquid region before crystallization^{2,3)} and the high stability of the supercooled liquid against crystallization has enabled us to produce bulk amorphous alloys with diameters up to about 4 mm.^{3,4)} Furthermore, the Mg-based bulk amorphous alloys exhibit high tensile fracture strength reaching 850 MPa and fracture along the maximum shear plane which is declined by about 45 degrees to the direction of tensile load.⁵⁾ Subsequently, similar data on the formation of bulk amorphous Mg-based alloys have also been presented by the other groups.⁶⁾ It is noted that the tensile strength is about twice as high as the highest strength for conventional Mg-based crystalline alloys. However, the Mg-based amorphous alloys with the highest glass-forming ability have a great disadvantage leading to embrittlement upon elevated temperature aging. The improvement against the aging-induced embrittlement in the maintenance of high strength level has strongly been desired for practical use of Mg-based bulk amorphous alloys. Very recently, the simultaneous addition of Ag and Pd to Mg–Cu–Y system is expected to causes the formation of a bulk amorphous alloy with high glass-forming ability, high tensile frac-

ture strength and high resistance against the aging-induced embrittlement. This paper is intended to present the composition range in which amorphous Mg–Cu–Y–(Ag, Pd) alloys are formed in a bulk form with diameters above 5 mm by copper mold casting, and thermal stability and mechanical properties of the bulk amorphous alloys and to discuss the reason for the effectiveness of the simultaneous addition of Ag and Pd elements.

2. Experimental Procedure

Multicomponent alloys with compositions of Mg₆₅Y₁₀Cu_{25–x–y}Ag_xPd_y were examined because the Mg₆₅Y₁₀Cu₂₅ amorphous alloy had the largest supercooled liquid region before crystallization and the highest glass-forming ability in the Mg–Ln–Cu (Ln = lanthanide metal) ternary systems. Alloy ingots were prepared by induction melting the mixtures of pure Mg, Cu, Ag and Pd metals in an argon atmosphere. The alloy compositions represent nominal atomic percentages of the mixtures because the weight loss after melting was less than 0.2%. Bulk amorphous alloys in a cylindrical form with a constant length of 60 mm and different diameters of 3 to 7 mm were produced by a copper mold casting method. Amorphous alloy ribbons with a cross section of 0.02 × 1.2 mm² were also produced by melt spinning. The amorphous structure was examined by X-ray diffraction and optical microscopy. Thermal stability associated with glass transition, supercooled liquid region and crystallization was evaluated by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Mechanical properties were measured with an Instron testing machine at room temperature. Fracture surface was examined by scanning electron microscopy.

3. Results and Discussion

Figure 1 shows the outer surface appearance of the as-

Fig. 1 Outer shape and surface morphology of a cast $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ alloy rod with a diameter of 7 mm and a length of 60 mm.

Fig. 2 X-ray diffraction patterns of cast $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ alloy rods with different diameters of 5 to 7 mm.

cast $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ rod with a diameter of 7 mm and a length of 60 mm prepared by the copper mold. Neither holes nor cavities are seen on the outer surface of the as-cast samples and their surface has a good luster. Considering that the shape and dimension of the as-cast sample are just the same as the inner shape of the copper mold, the metallic mold pressure casting method seems to be useful of the production of the bulk samples with various shapes and dimensions.

Figure 2 shows the X-ray diffraction patterns of the as-cast $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ rods with different diameters of 5 to 7 mm. These rods have a broad diffraction peak around $K_p = 25.4 \text{ nm}^{-1}$ and no diffraction peak corresponding to a crystalline phase is seen in all the samples, indicating that a mostly single amorphous phase is formed by the casting method. No appreciable difference in the K_p value is observed among the three samples. The good agreement in the K_p value is confirmed between the rods and the corresponding melt-spun ribbon. The agreement indicates that there is no significant change in the amorphicity of the Mg–Y–Cu–(Ag, Pd) samples prepared by casting and melt spinning, in spite of the large difference in cooling rate of the melt. In ad-

Fig. 3 DSC curves of the amorphous $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ alloy rods with different diameters of 5 to 7 mm.

dition, it is noted that the $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ alloy has the very large glass-forming ability enough to produce an amorphous single phase even in the 7 mm rod sample.

The DSC curves of the amorphous $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ rods with different diameters are shown in Fig. 3, along with that of the melt-spun amorphous ribbon. The T_g and T_x of the bulk samples are 437 and 471 K, respectively, independent of the diameter of the rods. Furthermore, there is no appreciable difference in the T_g and T_x values between the cast and melt-spun samples. The heats of crystallization (ΔH_x) for the first and second exothermic peaks were measured to be 2.3 to 2.4 kJ/mol for the rods with diameters of 5 to 7 mm and 2.3 kJ/mol for the ribbon, being nearly the same among the four samples. It is thus concluded that the sequent transition behavior of glass transition, supercooled liquid and crystallization is independent of the preparation conditions. However, there is an appreciable difference in the DSC curves at the temperatures below T_g between the cast and melt-spun samples as shown in Fig. 3. That is the heat of irreversible structural relaxation has a significant difference in both states because of a significant difference in cooling rate. Figure 3 also shows the melting point of the Mg–Y–Cu–(Ag, Pd) alloy. The onset temperature (T_m) is 707 K and hence the T_g/T_m is as high as 0.62 which exceeds 0.59 for the Mg–Y–Cu alloy. The higher T_g/T_m value is thought to be the origin for the larger glass-forming ability for the Mg–Y–Cu–Ag–Pd alloy than for the Mg–Y–Cu alloy.

Figure 4 shows the nominal compressive stress-strain curves of the $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ amorphous rod with a diameter of 5 mm. The Young's modulus, compressive fracture strength (σ_f) and fracture elongation are 59 GPa, 770 MPa and 1.3% respectively. The σ_f value of the $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ rod is higher by 90 MPa than that of the $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{25}$ amorphous rod with a diameter of 2 mm. It is noted that the new alloy has the higher strength even in the bulk sample with

Fig. 4 Compressive stress-strain curves of the amorphous $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ alloy rod with a diameter of 5 mm.

Fig. 5 Fracture surface appearance of the amorphous $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ alloy rod with a diameter of 5 mm.

larger diameter. Figure 5 shows the compressive fracture surface appearance of the $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ amorphous rod. The rod is fractured along the maximum shear plane which is declined by about 45 degrees to the direction of compressive load and the fracture surface consists of smooth and vein regions. The features of the fracture behavior and fracture surface appearance are just the same as those for other bulk amorphous alloys with good ductility.

It has been reported⁷⁻¹⁰⁾ that a bulk amorphous alloy is formed in the alloy system which satisfies the following conditions, i.e., (1) multicomponent alloy systems consisting of more than three elements, (2) significantly difference in atomic size ratios above about 12%, and (3) negative heats of mixing. Although the three conditions are satisfied for the Mg–Y–Cu system, the simultaneous addition of Ag and Pd causes more systematic changes in the atomic sizes and the negative heats of mixing, which seem to be more favorable for the formation of a stabilized supercooled liquid with a higher degree of dense random packed structure and more homogeneously mixed atomic configurations.

4. Summary

It was found that bulk amorphous alloys in a rod form in the Mg–Y–Cu–(Ag, Pd) system were produced in a wide diameter range up to 7 mm by copper mold casting. The bulk alloys have a good luster on the outer surface and neither holes nor cavities are seen on the outer surface. The T_g , T_x and ΔH_x values of the $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{15}\text{Ag}_5\text{Pd}_5$ bulk amorphous rods are

independent of sample diameter and are nearly the same as those for the corresponding melt-spun ribbon with a thickness of about 0.02 mm. The compressive fracture strength of the bulk amorphous Mg–Y–Cu–(Ag, Pd) alloy rod with a diameter of 5 mm is 770 MPa which is higher by 90 MPa than that of the bulk amorphous $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{25}$ rod with a diameter of 2 mm. The simultaneous addition of Ag and Pd elements are very effective for the improvements of glass-forming ability and mechanical strength.

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