Precipitation of bcc nanocrystals in bulk Mg–Cu–Y amorphous alloys

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Coexistent amorphous and nanoscale bcc-Mg₇Li₃ phases were found in slowly quenched alloys of the Mg_{65-x}Li_xCu₂₅Y₁₀ system containing 3 to 15 at. % Li. The crystallization behavior of these alloys has been studied. The grain size of the nanocrystalline bcc phase which is formed ranges from 2 to 20 nm. The volume fraction of nanocrystalline phases as well as the grain size of the nanocrystals increase as the Li composition increases. Transmission electron microscopy studies suggest that the alloy exhibits phase separation in the undercooled liquid state and that the nucleation and growth of the bcc-nanocrystals is related to the phase separation. Some characteristic thermal properties of the glassy phase are presented, and the composition dependence of T_g and T_x is discussed. It is concluded that the addition of a small amount of Li is essential for the production of a bcc nanocrystalline phase in the Mg–Li–Cu–Y system.

I. INTRODUCTION

In the past few years, both nanocrystalline and amorphous metallic materials have attracted increasing interest because they exhibit different physical properties than conventional crystalline materials. Several systems have been reported that exhibit coexistent nanocrystalline and amorphous phases, such as fcc-Ni in Ni–Si–B,¹ fcc-Al in Al–Ni–Ce,² hcp-Mg in Mg–Zn–La,³ and hcp-Co in Co–Zr–B,⁴ and have been observed to form using rapid cooling techniques like splat-quenching or melt-spinning. The thickness of these samples is below 50 μm , and the estimated cooling rate is about 10^6 K/s. Such nanoscale amorphous structures have not been generally found when lower cooling rates are used. Recently, a new family of bulk metallic glasses in the Mg–Cu–Y system having a wide supercooled liquid region were found.^{5,6} Fully glassy rods with a diameter of 7 mm were obtained by high-pressure die-casting. We have observed that a nanocrystalline bcc intermetallic phase forms in an amorphous matrix at relatively low cooling rates when a few percent of Li is added to the Mg–Cu–Y system. Here we define a bulk metallic glass as having a minimum dimension of 1 mm which is equivalent to a critical cooling rate of about 10^3 to 10^4 K/s.

II. EXPERIMENTAL PROCEDURE

Mg–Li–Cu–Y ingots were alloyed by induction melting a mixture of the elements of purity ranging from 99.9% to 99.999% on a water-cooled silver boat under a Ti-gettered argon atmosphere. The ingots were repeatedly turned over and remelted to ensure homo-

geneity. Then they were further processed by casting into copper molds under inert gas atmosphere to form strip samples with 1 mm thickness. The structure of the strips was examined by x-ray diffraction with an Inel position sensitive detector using Co $K\alpha$ radiation ($\lambda = 1.790$ Å). Thermal properties, including the glass transition, crystallization, and melting behavior, were measured by using a Perkin-Elmer differential scanning calorimeter (DSC-4) interfaced to a personal computer for data processing and analysis. The samples were contained in molybdenum pans and scanned in a flowing argon atmosphere to reduce oxidation. Microstructural characterization was performed by a Philips TEM430 operating at 300 kV.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of the surfaces of as-cast Mg₆₅Cu₂₅Y₁₀ and Mg_{65-x}Li_xCu₂₅Y₁₀ ($x = 3, 6, 8, 10$, and 15 at. %) strip samples with a fixed thickness of 1 mm. It is clear that the alloys with Li content higher than 6% are partially amorphous and partially crystalline. The Mg₅₀Li₁₅Cu₂₅Y₁₀ sample has a complex structure containing several crystalline phases while Mg₅₇Li₈Cu₂₅Y₁₀ and Mg₅₅Li₁₀Cu₂₅Y₁₀ contain only one simple crystal phase identified as bcc-Mg₇Li₃ with lattice constant $a = 3.52$ Å. The grain size of the bcc phase is about 10 to 20 nm as estimated by full-width at half maximum of diffraction peaks. The x-ray patterns taken from interior cross-sectioned surfaces of the samples are the same as those taken from exterior surfaces. This implies that the bcc nanocrystalline phase is nucleated not only on external surfaces but also throughout the bulk samples (i.e., it is nucleated

FIG. 1. X-ray diffraction patterns of as-cast strips of 1 mm thickness for $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ and $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$ ($x = 3, 6, 8, 10$, and 15).

uniformly throughout the sample). It is also observed that the relative intensity of the diffraction peaks corresponding to bcc nanocrystalline Mg_7Li_3 phase increases as the Li content increases. This indicates that the amount of bcc- Mg_7Li_3 phase increases with increasing Li content. The fact that the bcc- Mg_7Li_3 phase is still found in $\text{Mg}_{50}\text{Li}_{15}\text{Cu}_{25}\text{Y}_{10}$ means this phase is relatively stable. This can also be seen in the x-ray diffraction patterns of $\text{Mg}_{59}\text{Li}_6\text{Cu}_{25}\text{Y}_{10}$ samples which were heated to 170 °C or 230 °C in the DSC at a heating rate of 20 K/min and then subsequently cooled to ambient temperature as shown in Fig. 2. While the alloys with 3 or 6% Li look fully amorphous by x-ray diffraction, from the selected area diffraction patterns and dark-field TEM images of these alloys shown in Fig. 3, one can see that there are

FIG. 2. X-ray diffraction patterns of $\text{Mg}_{59}\text{Li}_6\text{Cu}_{25}\text{Y}_{10}$ in the as-cast state and in samples heated to 170 °C and 230 °C, respectively, in a DSC at a heating rate of 20 K/min and then subsequently cooled to ambient temperature.

ultrafine nanocrystals distributed uniformly throughout the amorphous matrix. The crystallite sizes range from 2 to 6 nm.

DSC traces at various compositions for $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$ ($x = 3, 6, 8, 10$, and 15) taken using a heating rate of 10 K/min are shown in Fig. 4. Two exothermic peaks are observed in the scan of $\text{Mg}_{59}\text{Li}_6\text{Cu}_{25}\text{Y}_{10}$ beginning at 141 °C and 208 °C, respectively. It was confirmed from the x-ray diffraction patterns for annealed samples shown in Fig. 2 that the first peak was due to precipitation and grain growth of the nanoscale bcc- Mg_7Li_3 while the second peak was due to the transformation of the remaining amorphous matrix to the intermetallic phase Mg_2Cu . The glass transition endotherm and crystallization exotherm to bcc- Mg_7Li_3 are overlapping in other scans. One also notes that the total heat release for crystallization of bcc- Mg_7Li_3 phase is relatively small, estimated to be about 90 cal/mol. This means the free energy difference between the purely amorphous phase and the partially crystallized nanocrystalline phase is small, suggesting that the driving force for nanoscale precipitation of the bcc- Mg_7Li_3 phase is small.

Figure 5 shows a comparison of DSC scans for $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$ ($x = 6, 8$, and 10) in the as-cast state (solid line) to the state previously annealed at 170 °C to crystallize Mg_7Li_3 (dash line). In the scans for

FIG. 3. Selected area diffraction patterns and dark-field TEM images of as-cast (a) $\text{Mg}_{62}\text{Li}_3\text{Cu}_{25}\text{Y}_{10}$ and (b) $\text{Mg}_{59}\text{Li}_6\text{Cu}_{25}\text{Y}_{10}$. The dark-field images were taken from the ring indicated by the arrow.

the annealed Mg–Li–Cu–Y, the T_g of the amorphous matrix increases with both annealing and increasing Li content. It is known⁷ that T_g tends to increase with an increase of magnitude and number of the attractive bonds among the constituent atoms. As the volume fraction of the bcc Mg_7Li_3 phase increases, one expects the Y and Cu contents of the remaining amorphous matrix to increase. In the amorphous Mg–Cu–Y system, both increasing Cu and Y content will result in an increase of T_g . Also, after annealing, the crystallization temperature, T_x , for Mg_2Cu decreases since the remaining amorphous matrix has been enriched in copper due to the precipitation of Mg_7Li_3 .

The thermal behavior of $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$ alloys near the melting temperature is shown in Fig. 6. $\text{Mg}_{62}\text{Li}_3\text{Cu}_{25}\text{Y}_{10}$ shows a relatively sharp melting endotherm while $\text{Mg}_{50}\text{Li}_{15}\text{Cu}_{25}\text{Y}_{10}$ has a more complicated melting structure exhibiting a series of exotherms. The latter alloy starts to melt at a solidus temperature

FIG. 4. DSC scans for as-cast $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$ ($x = 3, 6, 8, 10$, and 15) at a heating rate of 10 K/min .

of 433°C followed by complete melting at liquidus temperature 495°C . Table I summarizes the thermal parameters including the glass transition temperature, T_g , the crystallization temperature, T_x , for Mg_2Cu , the total heat of crystallization, ΔH_x , the melting temperature, T_m , and the latent heat, L_m , where T_g , T_x , and T_m are defined as the onset points of corresponding events. In the case of melting, the solidus and liquidus temperatures are given.

Figure 7 shows the high resolution electron micrograph for $\text{Mg}_{62}\text{Li}_3\text{Cu}_{25}\text{Y}_{10}$. There is an obvious contrast in the TEM image which suggests two apparently different amorphous regions in the image. These amorphous domains are separated by a relatively sharp boundary. Based on these images, we suggest that the amorphous alloy has undergone phase separation during solidification. The domains that exhibit lighter contrast appear to be fully amorphous. On the other hand, one observes well-developed groups of crystalline lattice fringes within the darker domains. These fringes can be identified with the bcc nanocrystalline phase. The overall domain sizes are about 10 nm while the grain size of the nanocrystalline phase is even smaller. Since

FIG. 5. DSC scans for $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$ ($x = 6, 8$, and 10) in the as-cast state (solid-line) and previously heated up to 170°C to crystallize Mg_7Li_3 (dashed line).

the nanocrystalline phase is bcc- Mg_7Li_3 , this suggests that the darker regions are Mg–Li rich, while the lighter regions are Mg–Li poor. It appears that phase separation occurs in the liquid state prior to crystallization of the nanophase during cooling from the melt. Nucleation of the bcc nanophase then occurs preferentially in the

FIG. 6. DSC scans for as-cast $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$ ($x = 3, 6, 8, 10$, and 15) near melting point.

Mg–Li-rich amorphous phase. The subsequent growth of these Mg–Li-rich nanocrystals would then be restricted by the size of the phase-separated domains in which they nucleated. Thus, the phase separation acts both to trigger the nucleation and to limit the growth of the Mg_7Li_3 crystals.

IV. SUMMARY

It is found that a nanoscale intermetallic phase bcc- Mg_7Li_3 with a grain size of 2 to 20 nm is formed by nucleation in the bulk amorphous $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$

TABLE I. Thermal parameters for $\text{Mg}_{65-x}\text{Li}_x\text{Cu}_{25}\text{Y}_{10}$ ($x = 3, 6, 8, 10$, and 15) alloys. T_g is the glass transition temperature of amorphous matrix. T_x is the crystallization temperature of Mg_2Cu . ΔH_x is the heat of crystallization. T_m^{sol} is the solidus temperature, T_m^{liq} is the liquidus temperature, and L_m is latent heat.

Li (at.)	T_g ($^\circ\text{C}$)	T_x ($^\circ\text{C}$)	ΔH_x (cal/mol)	T_m^{sol} ($^\circ\text{C}$)	T_m^{liq} ($^\circ\text{C}$)	L_m (cal/mol)
3	141	214	708	454	472	2051
6	150	208	385	433	460	1961
8	154	205	336	433	464	1768
10	155	204	288	434	476	1777
15	...	210	361	433	495	1537

FIG. 7. The high resolution electron micrograph for as-cast $\text{Mg}_{62}\text{Li}_3\text{Cu}_{25}\text{Y}_{10}$.

system. The nanocrystalline particles are homogeneously distributed throughout the bulk sample. The ratio of nanocrystal to amorphous phase and the grain size of the nanocrystalline both increase as Li content increases.

Adding Li changes the structure of Mg–Li–Cu–Y alloys from bulk amorphous to amorphous plus nanocrystalline, then finally to a mixture of several intermetallic phases. From TEM, we suggest that $\text{Mg}_{62}\text{Li}_3\text{Cu}_{25}\text{Y}_{10}$ undergoes phase separation during cooling in the liquid state and forms two phases that are, respectively, Mg–Li rich and Mg–Li poor with a length scale of about 10 nm. The primary crystallization occurs in the Mg–Li-rich regions, and the crystallines are restricted to nanometer size because the boundaries of these two regions constrain the growth of the crystals. It has been found that the presence of Li plays an important role in the formation of nanoscale bcc structure.

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