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Research Article

Surface Crystallization in Mg-Based Bulk Metallic Glass during Copper Mold Casting

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The localized crystallization of $Mg_{54}Cu_{28}Ag_7Y_{11}$ bulk metallic glass (BMG) in the injection casting process using a copper mold was investigated. It has been found that several crystalline phases were formed close to the as-cast surface but did not exist in the internal part of the BMG plate. It is abnormal that the as-cast surface is partially crystallized with higher cooling rate than that of inside. Overheating of the melt and nucleation induced by the surface of copper mold play key roles in the abnormal crystallization. It is suggested that the function of copper mold to trigger heterogeneous nucleation cannot be totally ignored, although it provides the high cooling rate for the glass formation during casting.

1. Introduction

Bulk metallic glass (BMG) has attracted much attention since the rapid cooling solidification technology was developed which mainly includes melt quenching, fluxing, and copper mold casting [1–4]. The unique structure of metallic glass (MG) formed by rapid cooling solidification endows this new comer of metal materials many special properties such as good compression ductility, high corrosion resistance, good wear resistance, and special functional properties [5–14]. In general, BMG is fabricated by quenching the melt without incurring crystallization. Therefore, the forming of MG is determined by the inherent glass forming ability (GFA) of the alloy itself and the preparation conditions. Meanwhile, the GFA of one alloy is the major factor to control the thermal stability of the glass forming liquid. The other factor, which is related to the preparation technologies, also plays an important role to obtain full amorphous structure frozen from the melt.

Mg-based BMG is one-kind lightweight amorphous alloy, few in amount, which possesses both good GFA and low density. Inoue et al. [15] firstly discovered the $Mg_{65}Cu_{25}Y_{10}$ BMG in 1991. Next, Park et al. [16] investigated the effect of Ag substitution for Cu and improved the critical diameter (D_c) for amorphous phase formation from 4 mm to 6 mm. Ma et al. [17, 18] optimized the composition of Mg-Cu-Y ternary alloy and Mg-Cu-Ag-Y quaternary alloy, improving the D_c values to 9 mm and 16 mm, respectively. Up to date, this class of BMG can be made into 27 mm [19] and can be significantly toughened by ex situ addition of some second phases [20, 21]. Therefore, Mg-based BMG and composites have been regarded as promising materials for engineering application. It is necessary to investigate the processing properties of this BMG alloy system.

In the present work, $Mg_{54}Cu_{28}Ag_7Y_{11}$ alloy [18] was selected as the experimental material to investigate the casting formability of typical Mg-based BMG. The crystallization related to the cast technology aspect will be discussed.

2. Experimental

The raw materials with purity better than 99.9% were used to fabricate the BMG alloy. An intermediate alloy with the nominal composition $Cu_{28}Ag_7Y_{11}$ was firstly prepared by arc melting method under a Ti-gettered argon atmosphere. This intermediate alloy was then melted with Mg pieces by induction melting under inert atmosphere to obtain a master alloy with the nominal composition $Mg_{54}Cu_{28}Ag_7Y_{11}$. Subsequently, the master alloy was then remelted in the quartz

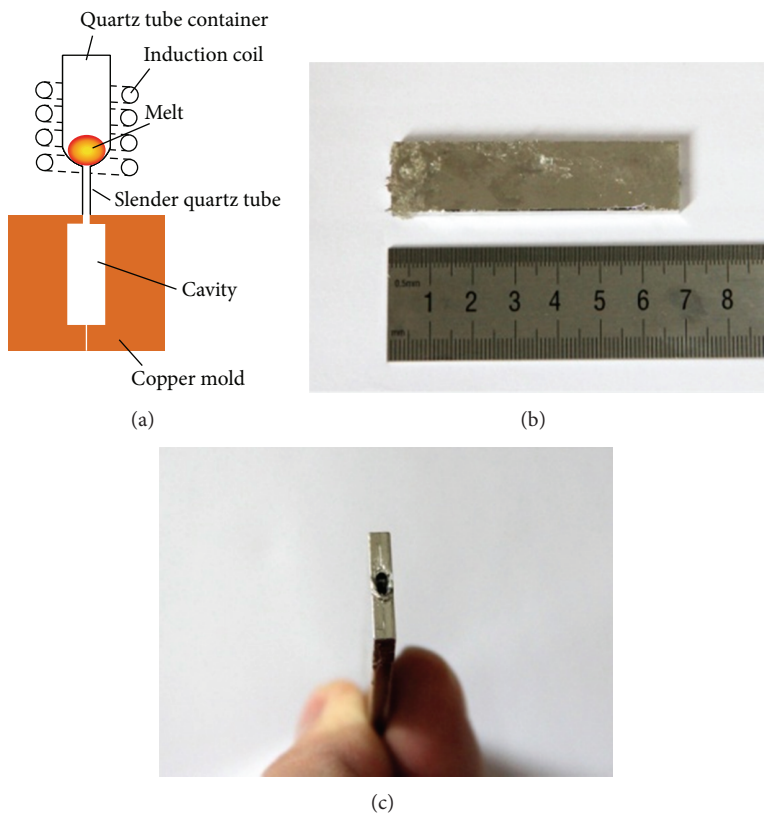

Figure 1: (a) Schematic diagram of the applied injection casting, (b) image of the BMG plate, and (c) top view of the plate.

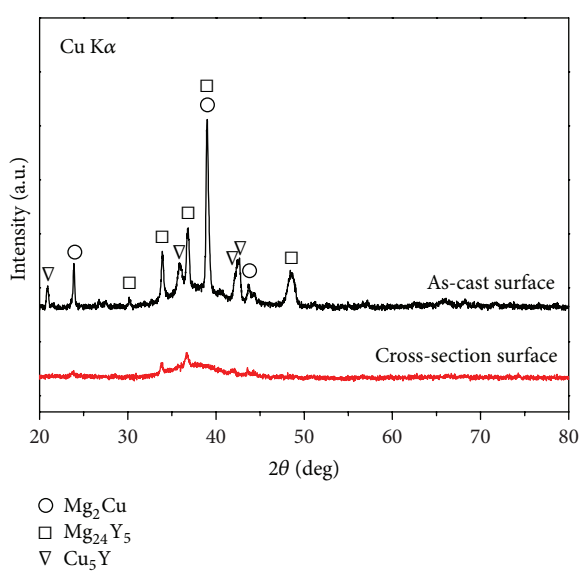

Figure 2: XRD spectra of the $Mg_{54}Cu_{28}Ag_7Y_{11}$ plate for different parts.

tubes using induction melting and injected into the copper mold which had an internal plate-shaped cavity of about 3 × 14 × 70 mm in size. The applied injection casting method was optimized by Xie et al. [22] as shown in Figure 1(a). A slender quartz tube was placed between the quartz tube (melt container) and the mold to keep gas impermeability for improving the mold-filling capacity.

The as-cast BMG sample was examined by X-ray diffraction (XRD) analysis using Rigaku D/max-RB XRD spectrometry with Cu Kα radiation. The thermal stability of the as-cast BMG sample was measured by differential scanning calorimeter (DSC, TA Instruments) at a constant heating rate of 20 K/min. The surface morphology was investigated by a LEO1530 scanning electron microscope (SEM) with a field emission gun. The composition of the BMG samples was examined by energy dispersive X-ray spectroscopy (EDS).

3. Results and Discussion

Figure 1 shows the pictures of one cast plate together with the schematic diagram of the applied injection casting. The as-cast plate has a perfect shape which completely matches the cavity size of the copper mold as shown in Figures 1(b) and 1(c). The good mold-filling capacity is attributed to the following two aspects: the good gas impermeability and a higher cast temperature of the melt. The good gas impermeability is favorable for improving the pressure of the melt during filling in the mold. Overheating is beneficial for improving the fluidity of the melt. These two aspects collaboratively work, resulting in significant improvement of mold-filling capacity.

Figure 2 shows the XRD spectra of the as-cast surface and the cross-section surface of the $Mg_{54}Cu_{28}Ag_7Y_{11}$ alloy plate.

It was found that the spectrum of the as-cast surface has many sharp peaks corresponding to the crystalline phases such as Mg_2Cu, $Mg_{24}Y_5$ and Cu_5Y. However, for the cross-section, the intensities of the crystalline phase peaks are much lower than that of the as-cast surface. It was demonstrated that the amount of crystalline phase in the cross-section surface is smaller than that of the as-cast surface. Moreover, one typical amorphous structure feature, the hump-like diffuse scattering peak, can be identified as existing on the spectrum of the cross-section surface. It is then suggested that the plate contains certain amount of amorphous phase. As we speculated, the crystalline phases might be precipitated in the as-cast surface in contact with the copper mold.

The as-cast sample, which has been examined by XRD in Figure 2, was grinded using sandpaper and hereafter reexamined to confirm whether the crystallization partially occurs on the surface. After wearing off ~0.1 mm and ~0.2 mm from the as-cast surface, the sample was rescanned by XRD, respectively. Figure 3 displays the XRD spectra of the sample with different wear depths. It shows that the intensities of the crystalline phase peaks are decreased with the increased wear depth. Moreover, the sample is found to be composed of full amorphous structure after wearing off ~0.2 mm. The inset of Figure 3 shows the DSC curve of the sample after wearing. It possesses a typical glass transition followed by an obvious crystallization process which is consistent with the result in the earlier work [18]. It is demonstrated again that the centre part of the as-cast plate possesses a full amorphous structure.

Figure 4 shows a typical backscattered electron image of the sample after wearing off ~0.1 mm in depth. It is clearly observed that some phases, with simple geometric shapes such as triangle, quadrilateral, and hexagon, are existing on the worn surface which is near the as-cast surface. A further examination on these polygon phases by EDX proved that they are all Cu-rich and Y-rich. The ratio of Cu and Y in atom is less than 6 : 1. It is considered that, by combining this result with the XRD spectra shown in Figure 2, this phase may be Cu_5Y, a common compound in ternary Mg-Cu-Y alloys. The investigation result shown in Figure 4 agrees well with the discovery in a very recent work by Mezbahul-Islam and Medraj [23]. They reported on the phase formation in the ternary Mg-Cu-Y system, revealing that the metallographic shapes of the phases with Cu-rich and Y-rich have small plane features as well as simple geometric shapes.

For copper mold casting, it has been reported that the cooling rate is decreased with the increased diameter size. In other words, the center of a rod or plate should have relatively lower cooling rates which negatively affect the glass forming. Therefore, the crystallization is mostly identified in the center region [24, 25]. However, the crystallization in the present work is quite different: the major crystalline phases are all segregation on the as-cast surface where the cooling rate is relatively higher. It is thus suggested that the copper mold does not completely play a single role to supply the high cooling rate for glass formation.

The possible reason of the abnormal crystallization may be attributed to the two following aspects. The first one is that the GFA of the $Mg_{54}Cu_{28}Ag_7Y_{11}$ alloy is decreased by some preparation technologies such as the cast temperature

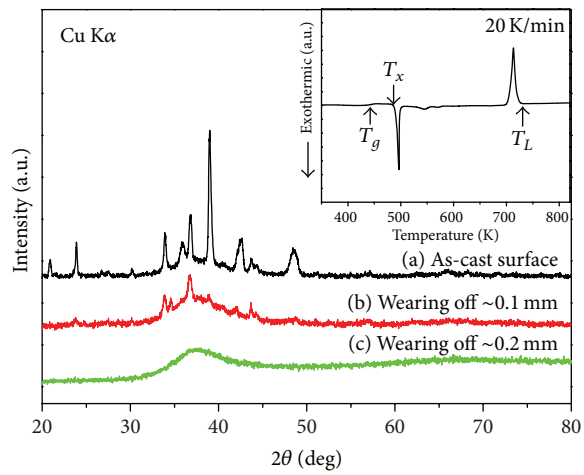

Figure 3: XRD spectra of the $Mg_{54}Cu_{28}Ag_7Y_{11}$ plate with different surface treatments. The inset is the DSC curve of the sample after wearing off the crystalline surface.

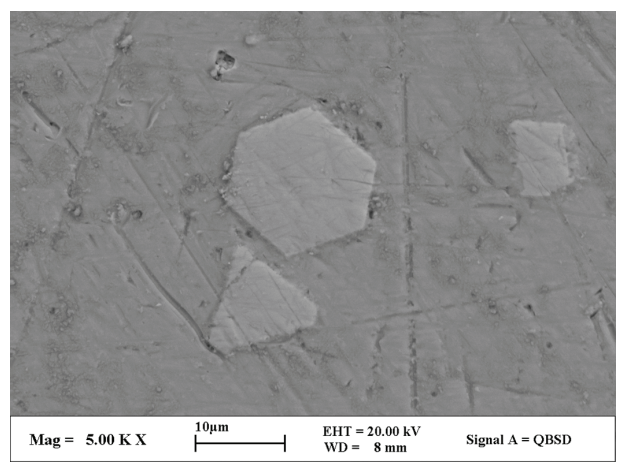

Figure 4: Typical BSE image of some crystalline phases near the as-cast surface.

and the use of quartz tube. It is known that overheating of the melt significantly affects the GFA of BMG [26]. In this work, a higher cast temperature together with a high Ar pressure of ~10^5 Pa was applied to improve the fluidity of the melt to fill the mold. Moreover, in the $Mg_{54}Cu_{28}Ag_7Y_{11}$ alloy, the melt point and boiling point of Mg are both low; thus the Mg atoms in the overheating melt are energetic and active. It is then become harder that the atoms should be frozen into an amorphous solid. Thus, the GFA of the $Mg_{54}Cu_{28}Ag_7Y_{11}$ alloy may be decreased by the high casting temperature. In addition, the quartz tube can react with Mg melt, resulting in the reduction of Mg content. Therefore, the actual composition of the BMG plate may be changed deviating from the nominal composition which has the best GFA in this quaternary alloy system. The second aspect is related to the copper mold. In our opinion, the copper mold not only provides the high cooling rate during casting, but

also supplies many favorable sites for heterogeneous nucleation. These both aspects mentioned above might jointly work during the injection casting process, resulting in the apparently abnormal surface crystallization.

4. Conclusions

In the present work, the $Mg_{54}Cu_{28}Ag_7Y_{11}$ bulk metallic glass plate was obtained by an injection casting method using copper mold. It has been found that several crystalline phases were formed close to the as-cast surface but did not exist in the internal part of the plate. The surface crystallization is attributed to the overheating of the melt and nucleation induced by the surface of copper mold. It is demonstrated that the function of copper mold to trigger heterogeneous nucleation cannot be totally ignored, although it provides the high cooling rate for glass formation during the casting.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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