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Influence of structural relaxation on wetting behavior of molten In–Sn alloy on $Cu_{40}Zr_{44}Al_8Ag_8$ bulk metallic glass

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ABSTRACT

Influence of structural relaxation on wetting behavior of molten In–Sn alloy on $Cu_{40}Zr_{44}Al_8Ag_8$ bulk metallic glass (BMG) was studied using the sessile-drop method at isothermal condition in high vacuum. It was found that the equilibrium contact angle increased with the increase of the pre-annealing temperature of $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate. Moreover, the high-temperature structural relaxation greatly affected wetting behavior of molten In–Sn alloy on $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate. By analyses of interfacial microstructure, the interface between In–Sn alloy and pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG was continuous, while no interfacial reaction layer formed in the temperature range studied.

1. Introduction

Bulk metallic glasses (BMGs) have emerged over the past 50 years as materials with unique and attractive properties, such as excellent corrosion resistance, high formability and low damping [1]. However, BMGs are thermodynamically metastable and can transform into stable crystalline phases in heating process. Prior to crystallization, a process for atoms gradually to approach their equilibrium sites in the amorphous phase is called "structural relaxation" [2]. Until recently, many models have been developed to describe and explain the structural relaxation of BMGs. The free volume model is one of the most commonly used models [3]. Furthermore, generation, annihilation and redistribution of the free volume play an important role in the properties of the metallic glass [4,5].

The wetting behavior of liquid metals on solids is of fundamental and scientific interest in understanding the development of liquid metal-solid bonding during brazing, soldering and composites [6–8]. Recently a few studies had been carried out on the wetting behavior of liquid alloy on BMGs substrate. For example, Inoue et al. [9] demonstrated wetting behavior of Sn–Ag–Cu solder on Pd-based bulk metallic glass. Similarly, Zhang group [10] reported contact angle and interfacial characteristics between molten In–Sn alloy and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG. However, none of these studies focused on the relationship between the structural relaxation and wetting behavior of molten alloy on BMGs substrate.

The present work is dedicated to investigate the effect of structural relaxation on wetting behavior of molten In–Sn alloy on $Cu_{40}Zr_{44}Al_8Ag_8$ BMG at isothermal condition. The free volume model is employed to describe relationship between the structural relaxation and wetting behavior of molten In–Sn alloy on $Cu_{40}Zr_{44}Al_8Ag_8$ BMG.

2. Experimental procedure

The eutectic alloy composition (49.1Sn–50.9In wt%) was prepared by induction melting in high purity argon atmosphere (99.99%). $Cu_{40}Zr_{44}Al_8Ag_8$ alloy was produced by arc melting under a Ti-gettered Ar atmosphere. $Cu_{40}Zr_{44}Al_8Ag_8$ alloys were remelted in a quartz tube by induction melting, followed by casting into copper moulds with plate cavity of 2 mm in thickness. $Cu_{40}Zr_{44}Al_8Ag_8$ BMG plates were cut into small substrates of 20 mm × 20 mm and were annealed for 20 min at different temperature under vacuum furnace. A differential scanning calorimetry (DSC) was used to investigate $Cu_{40}Zr_{44}Al_8Ag_8$ BMG plates at different annealing temperature.

Wetting experiments were performed by the sessile drop method in a high vacuum furnace described in detail elsewhere [11]. After the desired experimental temperature was achieved, wetting angles were recorded photographically using back lighting at various times until an equilibrium angle could be recorded. After completion of the sessile drop experiments, the solidified samples were sectioned to examine the interface. Cross sections were polished to examine the possible interfacial reactions using scanning electron microscopy (SEM).

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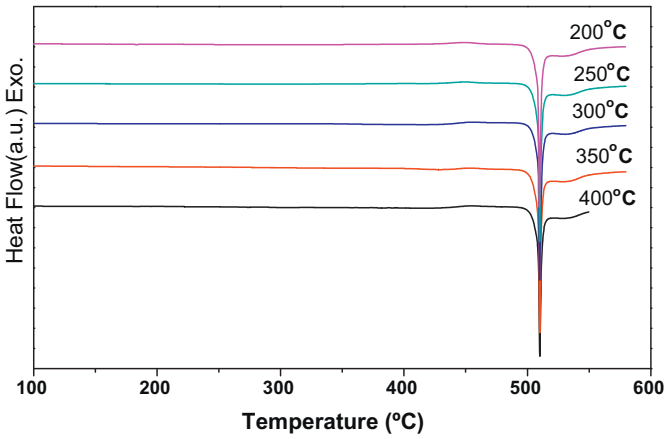

Fig. 1. DSC curves for $Cu_{40}Zr_{44}Al_8Ag_8$ BMG after pre-annealed treatment for 20 min.

3. Results and discussions

3.1. Structural relaxation

Fig. 1 shows the DSC curves of $Cu_{40}Zr_{44}Al_8Ag_8$ BMG plates of different pre-annealing temperature. From these curves, it can be seen that all pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG are fully amorphous, and the glass transition temperature T_g is observed at about 430 °C.

Generally, the free volume model of the structural relaxation described well the results of DSC experiments of metallic glasses, especially the glass transition phenomenon [12,13]. Van den Beukel [12] assumed that the change of enthalpy ΔH due to change in free volume is

$$(\Delta H)_{fv} = \beta.\Delta v_f \quad (1)$$

where β is constant and Δv_f is the change of the free volume per atomic volume. By the experiment, Eckert [14] proved that there was a linear dependence between enthalpy change ΔH and free volume change Δv_f over a wide temperature. Thus, relative value of relaxation enthalpy between as-cast sample and the annealed sample of BMGs could be used to describe quantificationally variation trend of the free volume.

According to Eq. (1), quantification of the enthalpy change between as-cast $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates and pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates was achieved. Based on repetitious experiments, the average and standard deviation of enthalpy change were shown in Fig. 2. It is seen that average value of the enthalpy change increases with the increase of pre-annealing temperature of $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates, and achieves nearly a stable level by end of 350 °C.

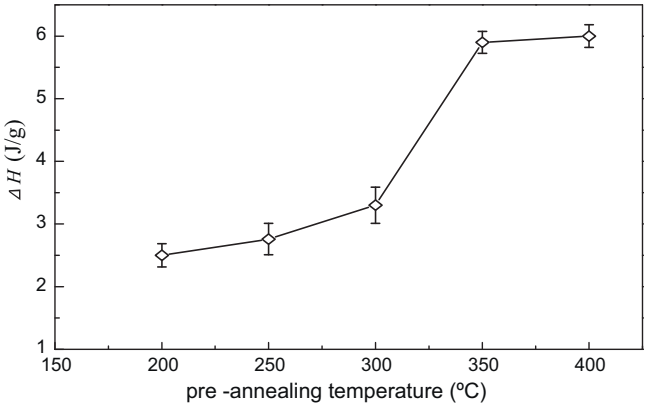

Fig. 2. Quantification of the enthalpy change of $Cu_{40}Zr_{44}Al_8Ag_8$ BMG at different pre-annealing temperature.

The structural relaxation can be divided into two stages corresponding to two different temperature regions for $Cu_{40}Zr_{44}Al_8Ag_8$ BMG. In the pre-annealing temperature range from 200 °C to 300 °C, the low-temperature structural relaxation occurs. Moreover, in the pre-annealing temperature range from 300 °C to T_g, the high-temperature structural relaxation occurs. According to the free volume model of the structural relaxation [12], there are large numbers of superfluous free volume in the as-cast BMGs. The low-temperature relaxation is thought to lead to local atomic structural rearrangement and the free volume do not considerably annihilate out. However, in high temperature region, all of the atoms in BMG shift to the stable sites by co-operative mode instead of the independent or local mode, and the free volume can rapidly move and annihilate out. Thus, with the increase of annealing temperature, the amount of free volume reduces gradually and achieves a stable level in the end, as shown in Fig. 2.

3.2. Wetting behavior

Scanning electron microscopic (SEM) micrographs for the cross section of molten In–Sn on $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates at 150 °C for 20 min are presented in Fig. 3. It is found that the interface is continuous, while no interfacial reaction layer formed at the interface of In–Sn alloy on pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates.

It is supposed that two major reasons result in no interfacial reaction layer. Usually, the structural relaxation induces the decrease of free volume or of the number of defects existing in the BMG alloy. This reduction limits the atomic diffusion and increases the activation energy of diffusion evidently [15]. And the thermodynamic data suggest that Zr–Cu bonds are much stronger than other atom bonds (Cu–In and Zr–In). The structural relaxation, especially the high-temperature relaxation, makes Zr and Cu form various chemical short range orders easily. Therefore, the high atomic bonding energy of Zr–Cu can restrain active Zr and Cu atoms diffusing in molten In–Sn alloy. The liquid–solid interfacial reaction can be greatly impeded by the decrease of atomic diffusion. Secondly, the Gibbs free-energy change ΔG_r is not only affected by the activity of the atoms, but also is affected by experimental temperature. In this study, the wettability of pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates by molten In–Sn alloy was preformed at lower temperature (150 °C). Hence, the intermetallic compound does not form at the interface between pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG and molten In–Sn alloy.

Fig. 4 shows the pattern for the contact angles of pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates by molten In–Sn alloy at 150 °C as a function of pre-annealing temperature. These curves describe a similar behavior and exhibit three characteristic regions of the contact angle with respect to time: the first stage is characterized by a slope where the contact angle decreased at a specific rate, the second stage presents a slighter slope and the third stage demonstrates that the value of θ is nearly constant. It is also found that the equilibrium contact angle increases monotonically with the increase of pre-annealing temperature: the mean equilibrium contact angle is 33.2°, 37.8°, 39°, and 58.1° and, 62.5°, respectively. And variation trend of equilibrium contact angle for pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates is in good agreement with variation trend of the free volume.

The equilibrium contact angle (θ_{eq}) is defined by Yong's equation for nonreactive wetting:

$$\cos\theta_{eq} = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} \quad (2)$$

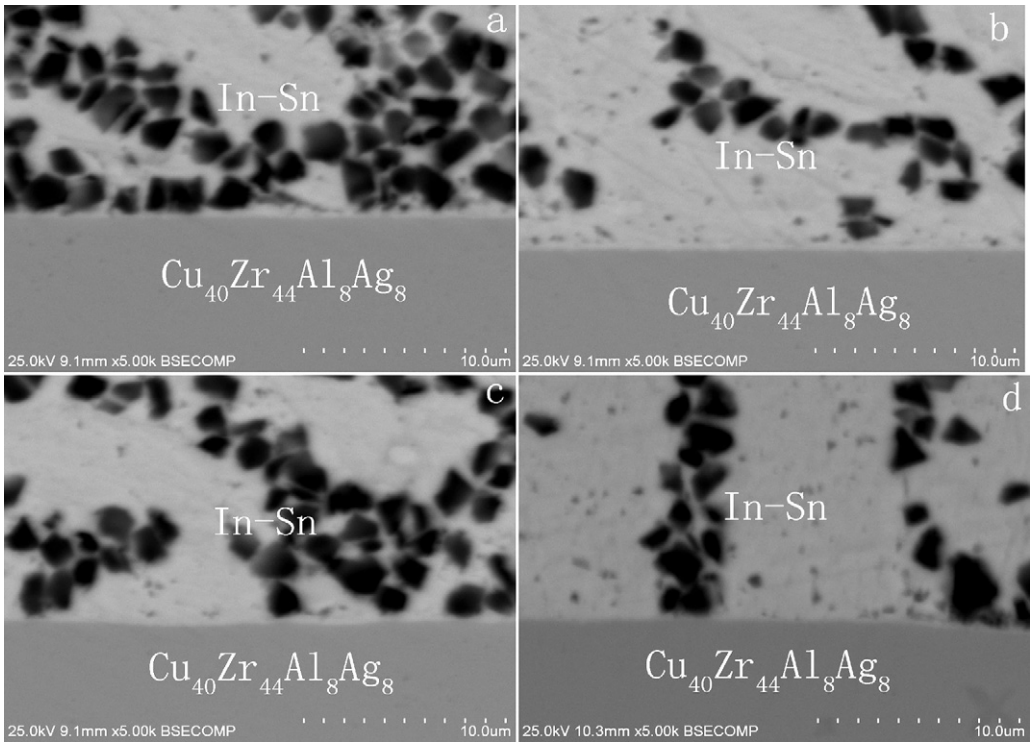

Fig. 3. SEM micrographs for the interfaces between molten In–Sn and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate (pre-annealed at various temperature: a, 250 °C; b, 300 °C; c, 350 °C; d, 400 °C) after spreading at 150 °C for 20 min.

where σ is the interfacial tension and the subscripts L, V, and S indicate the liquid metal, gas, and substrate, respectively. The liquid–gas surface energy σ_{LV} is determined by property of molten alloy, so σ_{LV} may be regarded as constant. The solid–gas surface energy σ_{SV} is determined by structure of material. The BMGs are thermodynamically metastable and atoms of the amorphous alloys are highly active, so the surface energy of the amorphous alloys is higher than that of crystals.

According to the free volume model, it is concluded that in the process of the structural relaxation, the activity of the atoms reduces and atoms gradually approach their equilibrium sites in the amorphous phase. Hence, with the increase of pre-annealing temperature of $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates, the surface energy σ_{SV} of the BMG decreases. And since the activity of the atoms reduces, the solid–liquid energy σ_{SL} which prevents molten alloy from spreading on solid surface increases. According to Eq. (2), the equilibrium contact angle increases with increasing the pre-annealing temperature. And similar reason result in the increase of the equilibrium contact angle with pre-annealing time of $Cu_{40}Zr_{44}Al_8Ag_8$ substrates.

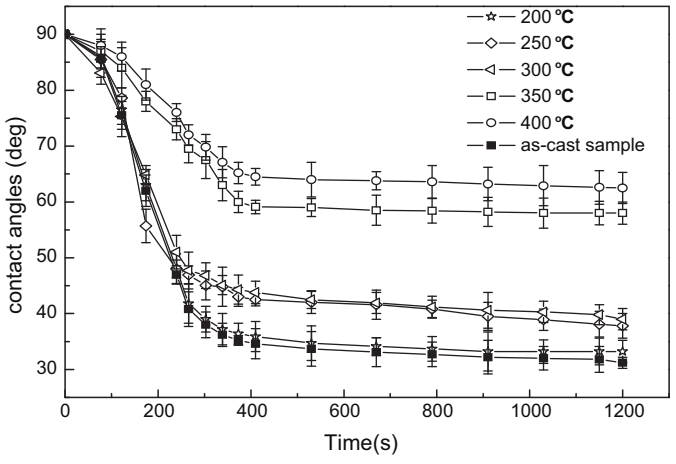

Fig. 4. Time dependence of contact angles of molten In–Sn and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate (pre-annealed at various temperature and as-cast sample) at 150 °C.

For the low-temperature structural relaxation, the structure change induced by local or short-range rearrangement and the free volume do not considerably annihilate out. In contrast to the contact angles of as-cast $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate by molten In–Sn alloy at 150 °C, the contact angles of $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates by molten In–Sn alloy only shows a slight change with the increase of the annealing temperature, as shown in Fig. 4. However, in the high-temperature structural relaxation region, the intermediate-range and long-range atomic diffusion can take place and the free volume in the bulk metallic glass can largely annihilate through sample surface. This causes a considerable increase in the contact angles of $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrates by molten In–Sn alloy with the annealing temperature, which can directly compared with the contact angles of as-cast $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate by molten In–Sn alloy at 150 °C. Hence, the high-temperature relaxation greatly affects wetting behavior of molten In–Sn alloy on $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate.

4. Conclusion

In this study, the free volume model was employed to investigate the effect of structural relaxation on wetting behavior of molten In–Sn alloy on $Cu_{40}Zr_{44}Al_8Ag_8$ BMG at isothermal condition. The equilibrium contact angle for pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate increases monotonically with the increase of pre-annealing temperature. No interfacial reaction layer formed at the interface between pre-annealed $Cu_{40}Zr_{44}Al_8Ag_8$ BMG and molten In–Sn alloy. The high-temperature relaxation greatly affected wetting behavior of molten In–Sn alloy on $Cu_{40}Zr_{44}Al_8Ag_8$ BMG substrate.

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