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Effect of ion beam irradiation surface treatment on solid-state bonding of Zr-based bulk metallic glass to pure copper

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The surface of Zr-based bulk metallic glass and pure copper was irradiated by 1 keV argon ion beam before solid-state bonding. In addition, the sound solid-state joints without macroscopic deformation were obtained at 440°C for 15 min. Argon ion beam irradiation has a positive effect on the removal of oxide film on the bulk metallic glass and pure copper. The maximum tensile strength of joints was 131.06 MPa, which is much higher than the joints without surface treatment. The bulk metallic glass after bonding retained the unique amorphous structure, indicating that thermal cycle, microscopic deformation and atomic diffusion caused no crystallization of bulk metallic glass. Argon ion beam surface treatment provides a feasible route for the sound solid-state bonding of bulk metallic glass.

Keywords: Bulk metallic glass, Solid-state bonding, Surface treatment, Copper

1 Introduction

The bulk metallic glasses (BMGs) have many potential applications due to their unique properties, such as superior strength and hardness, excellent corrosion resistance[1-3] and so on. However, the availability and weldability of BMG is limited by the poor plasticity at ambient temperature and the poor glass-forming ability[4]. In order to extend the application of BMG, the joining of BMG was tried by various welding technologies one after another[5-7]. In particular, the joining of BMG to crystalline alloys was developed with emphasis.

Based on the homogenous flow in supercooled liquid region[8], the shaping and welding of BMG has been studied widely. However, there is a lack of research on the solid-state bonding of BMG without macroscopic deformation. Two main barriers, the lower atomic diffusion coefficient and the stable oxide film, hindered the solid-state bonding[9] of BMG. Therefore, the surface treatment of specimens is a feasible way to overcome the barrier of oxide film during the solid-state bonding[10,11] of BMG. By surface treatment before solid-state bonding, the joints of Si/Si, SiO_2/SiO_2 and GaAs/Si were obtained at a low temperature[12-14].

Zr-based metallic glasses have the high glass formability and a wide supercooled region [15] and pure copper is one of materials widely used in the field of industry. Therefore, the solid-state bonded joints of Zr-based BMG to pure copper without macroscopic deformation are attractive not only in regard to fundamental research but also in practical applications. In the present paper, the surface of BMG and pure copper was etched by 1 keV argon ion beam. Subsequently, the specimens were bonded in vacuum furnace without exposing them to the atmosphere.

2 Materials and Methods

The $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG plates and pure copper plates (99.9 wt.%) have been used in the present study. The two kinds of plates were cut into blocks with the sizes of 4 mm × 4 mm × 5 mm (for microstructure observation) and 4 mm × 4 mm × 15 mm (for tensile tests) by electrical discharge machining. All specimens were polished by SiC papers up to grit 1000, and ultrasonically cleaned in acetone prior to solid-state bonding. The glass-transition temperature (T_g) and the crystallization onset temperature (T_x) of $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG are 410°C and 494°C, respectively. In order to determine the bonding parameters, the time-temperature-transformation curve was measured by differential scanning calorimetry (DSC, Netzsch-DSC 404) with a heating rate of 30°C/min.

Surface treatment process, as well as the solid-state bonding process, was carried out in the surface activation assisted vacuum solid-state bonding furnace. The schematic representation of the furnace is shown in Fig. 1. Firstly, the BMG and pure copper specimens were irradiated by 1 keV argon ion beam in surface treatment chamber for 0, 10 and 20 min, and then the treated surface was abutted by the fold of specimen holder. Subsequently, the specimens were sent into the solid-state bonding chamber ($<3\times10^{-5}$ Pa) and bonded at 440°C under the pressure of 80 MPa. The joints quality was assessed by scanning electron microscopy (SEM) and tensile test at a displacement speed of 0.5 mm/min at room temperature. The structure of the optical joints was investigated by micro-focused X-ray diffractometry (MF-XRD) with a beam size of about 50 μm and transmission electron microscopy selected area electron diffraction (TEM-SAED).

3 Results and Discussion

Figure 2 shows the time-temperature-transformation (T-T-T) curve of $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG and the thermal cycling process of solid-state bonding in our study. The onset times for isothermal crystallization are plotted as a function of temperature. It can be found that the crystallization time becomes shorter with the increase of temperature. In order to retain the amorphous structure of BMG specimens after solid-state bonding, the holding time should be less than the crystallization time in the corresponding temperature. According to the supercooled liquid region and the T-T-T curve, the feasible solid-state bonding temperature and holding time are 440°C and 15 min (less than 32.5 min).

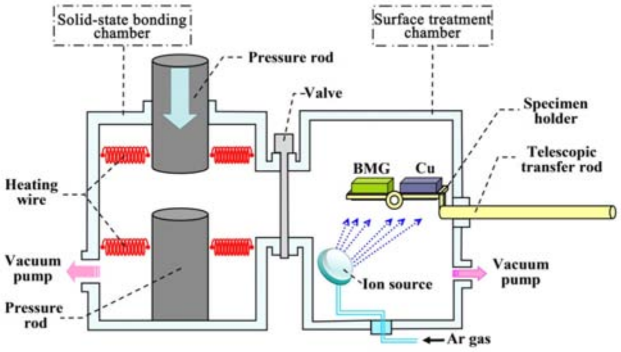

Fig. 1 — Schematic representation of the surface activation assisted vacuum solid-state bonding furnace

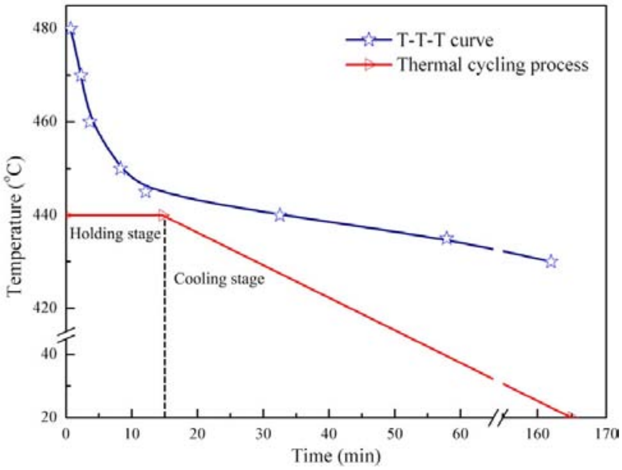

Fig. 2 — Time-temperature-transformation (T-T-T) curve of $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG and the thermal cycling process of solid-state bonding of BMG to pure copper

Figure 3 shows the scanning electron micrographs of the joints with and without surface treatment, respectively. The joint interface in Fig. 3(a) shows an incomplete weld between BMG and pure copper. In addition, there are some imperfections, such as cracks and voids at the interface. When the specimens were treated by argon ion beam for 10 min, there are no voids and only some tiny cracks were found at the interface of joints as shown in Fig. 3(b). The lack of some imperfection is attributed to the effect of surface treatment on the surface state, namely, argon ion beam removes the organic pollution and parts of oxide film on the surface of specimens. The irradiated surface provides the opportunity of close contact between atoms, and the contiguous atoms can form the reliable bonding. With the increase of surface treatment time, the organic pollution and residual oxide film are less and less. From Fig. 3(c), it can be seen that the joint interface was well bonded and devoid of imperfections such as cracks and voids. The micrographs of joint after surface treatment demonstrated the argon ion beam irradiation is beneficial to the solid-state and non-macroscopic deformation bonding of BMG to pure copper.

Figure 4 shows the micro-focused X-ray diffraction patterns of the cross-section around the interface of BMG/Cu joint with surface treatment for 20 min. The positions of diffraction spots with a beam spot diameter of 50 μm were at the interface line and 100 μm away from the interface, respectively as

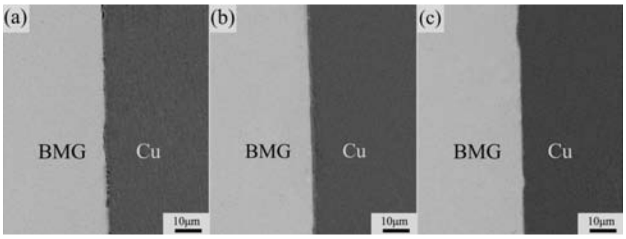

Fig. 3 — Backscattered electron images of the joints with ion irradiation for different time (a) 0 min (b) 10 min (c) 20 min

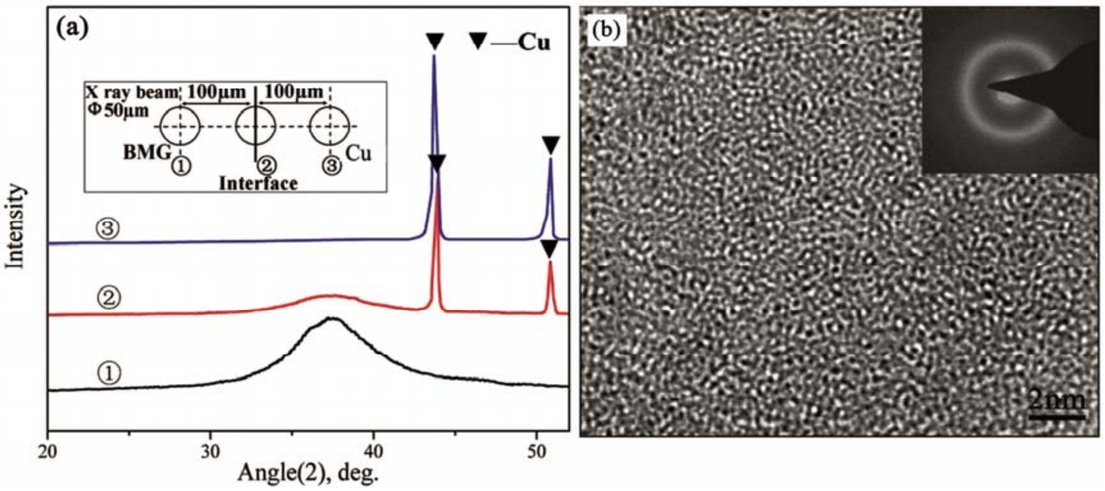

Fig. 4 — (a) Micro-focused X-ray diffraction patterns of the cross-section around the interface of BMG/Cu joint as marked in Fig. 3(c), (b) TEM bright field images of specimens taken from the BMG near the interface and its corresponding SAED pattern

shown in the inset of Fig. 4(a). Diffraction pattern of the BMG side in Fig. 4(a) shows the same diffuse peak showing the existence of only amorphous phase. The diffraction pattern at the joint interface exhibits a diffuse peak with the diffraction peaks of copper, demonstrating that the diffusion of copper atoms and micro-area deformation do not cause crystallization and the BMG at the interface still retains amorphous structure. TEM bright field image of specimen taken from the BMG near the interface and its corresponding SAED pattern in Fig. 4(b) also shows clearly that only diffuse halo rings are observed. The results of MF-XRD and TEM demonstrate that thermal cycle, micro-area deformation and interface atomic diffusion cause no crystallization of BMG.

The tensile strength is used to assess the quality of joints. The results of all tensile tests are summarized in Table 1. From Table 1, it can be found that the tensile strength of the joints without surface treatment is only 12.70 ± 6.11 MPa, which is about 4.98% of pure copper substrate. While the specimens were irradiated by argon ion beam for 10 min, the tensile strength of joint has a drastic improvement and reaches up to 37.44% of pure copper substrate. When the surface treatment time increased to 20 min, the tensile strength of joints increases to 131.06 ± 14.29 MPa, which is about 51.40% of pure copper substrate. The improvement of bonding quality is attributed to the argon ion beam irradiation mechanism, which removes the organic pollution and oxide film on the surface of specimens. The mechanism of surface activation assisted solid-state bonding is as follows: When the organic pollution and oxide film on the surface of pure copper and BMG are removed, asperities on the two surfaces contact at the microscopic level and plastically deform. As these asperities deform, they interlink forming interfaces between the two surfaces. Elevated temperature and pressure cause larger deformation in pure copper and BMG, which reduces gaps between the two surfaces to isolated voids. Superplastic deformation of BMG and creep of pure copper play a main role in the above process. In addition, atomic diffusion resulting from surface source mechanism and interface source mechanism causes the voids at the interface becomes tiny and small. For the specimens without surface treatment, it is difficult to achieve the close contact of specimens. Therefore, argon ion beam irradiation plays an important role in creating the cleaned surface.

Table 1 — Tensile strength of joints bonded with different parameters

Surface treatment time	Tensile strength (MPa)	σ_j/σ_b (%)
0 min	12.70 ± 6.11	4.98
10 min	95.48 ± 19.06	37.44
20 min	131.06 ± 14.29	51.40

Generally, it is difficult to obtain a solid-state and non-macroscopic deformation joint of BMG at a low temperature for a short time. However, the sound bonding of BMG to pure copper is realized by surface activation assisted solid-state bonding in our study. At present, the major barrier for low-temperature solid-state bonding of BMG is attributed to oxide film and low atomic diffusion coefficient. According to surface activation assisted solid-state bonding, ion irradiation eliminates the barrier of oxide film and provides a favourable condition for solid-state bonding of BMG to pure copper. Therefore, it looked forward in providing a new way to the precise solid-state bonding of BMG to pure copper, as well as other materials with oxide film.

4 Conclusions

The surface activation assisted solid-state bonding of $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG to pure copper was carried out and the effect of argon ion beam irradiation surface treatment has been investigated in the present paper. The ion beam irradiation process improved the bonding quality of BMG to pure copper drastically. No observable crystallization was detected by MF-XRD and TEM after bonding. The results indicated the precise solid-state bonding of BMG to crystalline materials, are feasible. The ion beam irradiation surface treatment provides a route to the high-quality solid-state bonding.

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