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Brazing of Cu with Pd-based metallic glass filler

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Abstract

Metallic glass has several unique properties, including high mechanical strength, small solidification shrinkage, small elastic modulus and supercooling state, all of which are well suited as a residual stress buffer for metal and ceramic joining. In the present preliminary study, we demonstrated brazing of Cu rods with $Pd_{40}Cu_{30}Ni_{10}P_{20}$ metallic glass filler. The brazing was carried out at 873 K for 1 min in a vacuum atmosphere (1×10^{-3} Pa), and then the specimens were quenched at the rate of 30 K/s by blowing He. The metallic glass brazing of Cu using $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler was successful, with the exception that several voids remained in the filler. According to micro-focused X-ray diffraction, no diffraction patterns were observed at both the center of the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler and the Cu/$Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface. The result showed that the Cu specimens were joined with $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler in the glassy state. The tensile fracture strength of the brazed specimens ranged from 20 to 250 MPa. The crack extension from the voids in the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler may have caused the results to be uneven and very low compared to the strength of Pd-based bulk metallic glass.

Keywords: Amorphous materials; Copper; Brazing; Glass transitions; Metastable phase; Pd-based metallic glass

1. Introduction

Metallic glasses have many unique properties, such as high mechanical strength, low elastic coefficient, small solidification shrinkage and high corrosion resistance. Because of these valuable properties, which cannot be found in crystalline metals, metallic glass has attracted many researchers and shows potential for use in various industrial applications. Bulk metallic glass is ordinarily fabricated from a molten base alloy by the melt spinning method or casting method. Some types of metallic glass, such as Mg- [1], Zr- [2,3], Fe- [4,5], Pd- [6] and Ni-based [7] alloys, have a low critical cooling rate, R_c. Especially, $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ has an R_c of 0.067 K/s [8]. Such high glass forming ability enables the production of bulk amorphous alloys that are several centimeters in thickness. Up to now, the joining of metallic glasses has been attempted by using electron beam welding [9], explosive welding [10], pulse current welding [11], friction welding [12] and laser welding [13,14]. These welding techniques are classified into two types according to welding temperature. For example, friction welding is performed around the glass transition temperature, at which metallic glass is in a supercooling liquid state. In this type of welding, the temperature and welding time needs to be precisely controlled so that the metallic glass does not cross the crystal-formation curve in the time-temperature transformation (TTT) diagram. Once on the other side of the curve, metallic glass immediately transforms into the crystal phases. In contrast, electron beam and laser welding are performed at a temperature higher than the melting temperature. This type of welding needs a rapid cooling rate that does not cross the crystal-formation curve in the continuous cooling transition (CCT) diagram. Small energy injection by a high-energy density source is preferable for this type of welding to suppress crystallization. In this work, we demonstrated the brazing of copper using $Pd_{40}Cu_{30}Ni_{10}P_{20}$ metallic glass filler.

2. Experimental

Two oxygen-free Cu rods (99.994%), Ø 6 mm in diameter, were brazed with $Pd_{40}Cu_{30}Ni_{10}P_{20}$ in an inductive heating

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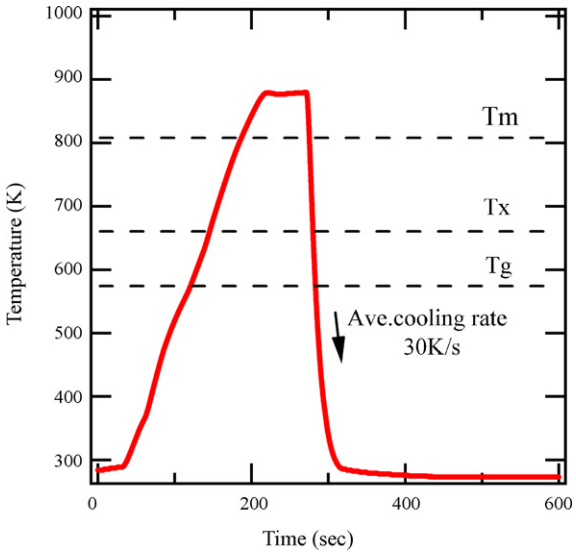

Fig. 1. Thermal cycle of metallic glass brazing.

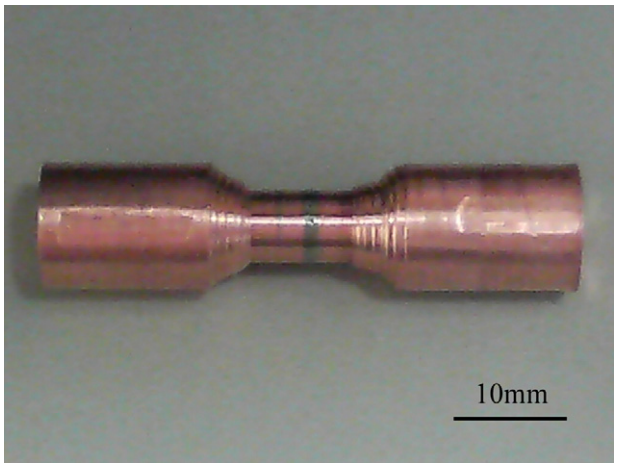

Fig. 2. Photograph of the brazed specimen.

furnace. $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler was prepared by arc-melting a mixture of pre-alloyed PdP, Cu, Ni and Pd together with B_2O_3 flux under an Ar atmosphere. Flux treatment was repeated five times to remove impurities of the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy. The resulting alloy buttons were cast to form a metallic glass plate. The plate was cut into a disk shape Ø 5 mm in diameter and 1.5 mm in thickness. The glass transition temperature, crystallization temperature and melting temperature of the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ were 574, 660 and 808 K, respectively. A shallow hole, which was Ø 5 mm in diameter and 0.5 mm in depth, was machined at the center of the Cu surface. $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler was set in this hole and joined to the other Cu rod with a flat surface. The brazing was carried out at 873 K for 1 min in a vacuum atmosphere (1×10^{-3} Pa), and then the joint sample was quenched at the rate of 30 K/s by blowing He. The thermal cycle of the brazing is shown in Fig. 1. Tensile testing was carried out at a strain rate of 1×10^{-4}/s. Micro-focused X-ray diffraction (XRD) using Cu Kα radiation ($\lambda = 0.1790$ nm) with spot size of Ø 50 μm in diameter was used to identify the crystallinity of the metallic glass filler. A cross section of the joint was polished and etched with 50% HNO_3 aq. at room temperature. The microstructure was analyzed by an optical microscope and energy dispersive X-ray (EDX) spectroscopy.

3. Results and discussion

The Cu specimens were successfully brazed with the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler of 0.5 mm in thickness. Pressure was not applied to the metallic glass filler during brazing, and so several voids remained in the filler. The appearance of the brazed specimen is shown in Fig. 2. Fig. 3 shows the micro-focused XRD patterns taken from the cross section of the Cu, $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler and Cu/$Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface. A broad peak around $2\theta = 42°$, which is characteristic of the amorphous state, was observed in the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler. Sharp peaks at $2\theta = 44°$ and 51°, characteristic of Cu (1 1 1) and (2 0 0), respectively, were observed in Cu. Cu peaks and a broad peak were observed in the Cu/$Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface, at which an X-ray beam was irradiated to both Cu and $Pd_{40}Cu_{30}Ni_{10}P_{20}$, but no detectable diffraction pattern of the reaction layer was observed. The smallest six compounds such as the monoclinic structure, tetragonal Cu_3Pd-like structure, rhombohedral $Pd_{15}P_2$-like structure, Ni_2Pd_2P intermetallic compound, fcc-(Ni, Pd) solid solution and bct-Ni_3P-like structure, are known as crystal phases of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ [15,16]. These intermetallic compounds are brittle, so the mechanical strength of crystallized $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy is less than that of the amorphous state. But, the results showed $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler could be joined to Cu in the amorphous state, since the metallic glass filler was quenched at the rate of 30 K/s, which is faster than the critical cooling rate of the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler ($R_c = 0.1$ K/s). Fig. 4 shows an optical micrograph of the cross section of the Cu/$Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface. Although the XRD data did

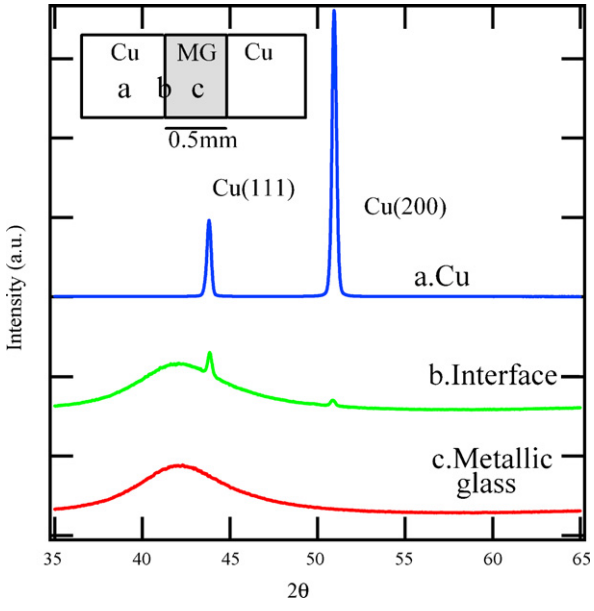

Fig. 3. Micro-focused X-ray diffraction patterns of the cross section of (a) the base material, (b) Cu/$Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface and (c) center of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler.

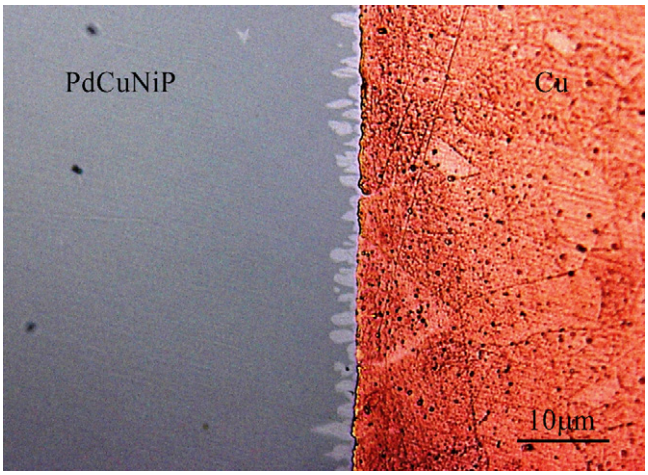

Fig. 4. Microstructure of the $Cu/Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface.

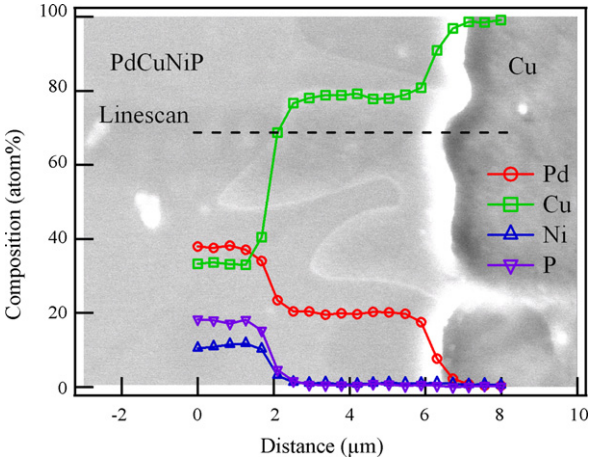

Fig. 5. Elemental analysis of the $Cu/Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface.

not show diffraction patterns, dendrites approximately 4 μm in length and 3 μm in width were observed. Elemental analysis of the $Cu/Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface is shown in Fig. 5. The elemental composition of the filler was almost the same as that before brazing, but the Cu content was about 80% in the dendrites due to elution during brazing. When Cu exceeds more than 80% in the Pd–Cu–Ni–P alloy, the glass forming ability is greatly decreased compared to that of $Pd_{40}Cu_{30}Ni_{10}P_{20}$. Therefore, dendrites seemed to grow at the $Cu/Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface during quenching. Fig. 6 shows the tensile fracture strength of the brazed specimens. The tensile test was repeated four times at the same conditions. The true fracture strength ranged from 20 to 250 MPa and most of the specimens fractured in the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler. The strength decreased with the increase of the void area ratio, which is defined as the ratio of the cross-sectional area of the void to the cross-sectional area of the joint. The fracture surface that fractured at 250 MPa and showed a partial vein pattern, which is unique to metallic glass, but the fracture surface that fractured at less than 100 MPa showed a river pattern, which is characteristic of brittle material.

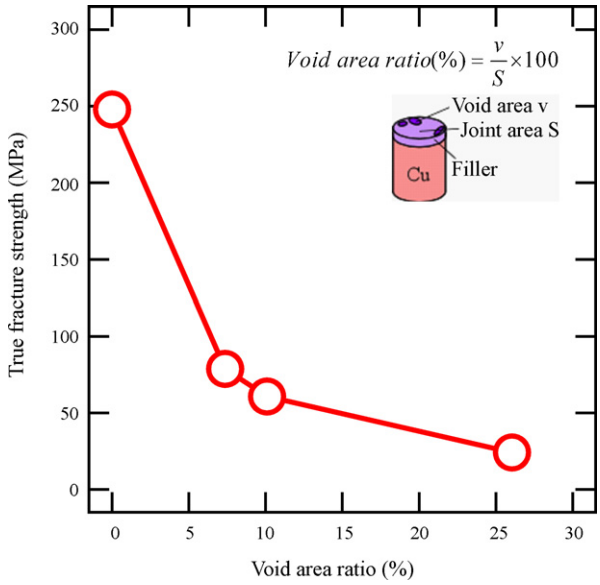

Fig. 6. True tensile fracture strength as a function of the void ratio.

It is known that the typical fracture surface of metallic glass shows a vein pattern because metallic glass fractures by transforming strain energy to heat energy and simultaneously forming

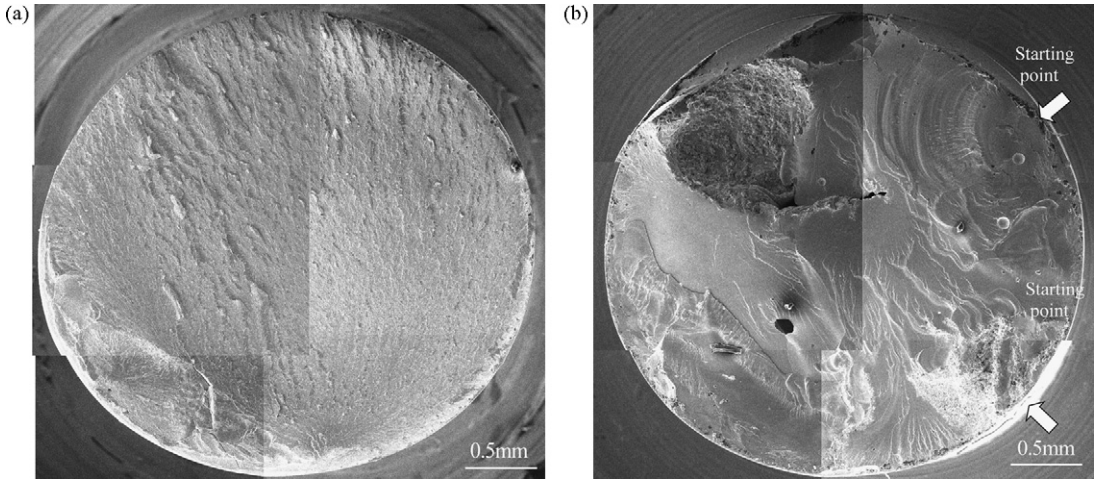

Fig. 7. Fracture surfaces of the brazed specimens. Void area ratios of (a) and (b) are 0 and 10%, respectively.

a pseudo-molten state. When the void content was more than 5%, the vein pattern was not observed in the fracture surface. In other words, the strain energy accumulated in the filler was not enough to form the pseudo-molten state. Moreover, the strength of these specimens was even less than 100 MPa although the fracture strength of Pd-based bulk metallic glass is 1.4 GPa [17]. The reason that the fracture strength was so low seemed to be the crack extension in the filler. Fig. 7 shows the fracture surfaces when the void content was 0% (fracture strength: 250 MPa) or 10% (52 MPa). For the 10% void content, the river patterns broadened radially from a void on the fracture surface. This means that voids played a role in the starting point of the crack extension. Consequently, the amount of the void affects the fracture strength and fracture types of the metallic glass filler.

4. Conclusion

Metallic glass brazing of Cu using $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler was successful, with the exception that several voids remained in the filler. From the results of micro-focused XRD, $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler was joined to Cu in the glassy state. Dendrites were observed along the Cu/$Pd_{40}Cu_{30}Ni_{10}P_{20}$ interface. The tensile fracture strength ranged from 20 to 250 MPa, and all specimens fractured in the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler. The fracture surface that fractured at 250 MPa showed a partial vein pattern, but the fracture surfaces that fractured at less than 100 MPa showed the river pattern that is characteristic of brittle material. Voids in the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ filler seemed to be a major factor for the low joint strength compared to the strength of the Pd-based bulk metallic glass.

Acknowledgements

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