Joining of Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ Bulk Metallic Glasses by a Friction Welding Method*1

Takuo Shoji*2, Yoshihito Kawamura and Yasuhide Ohno

1Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan  
2Department of Materials Science, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

In order to establish metallurgical bonding technology of bulk metallic glasses, friction welding of Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ bulk metallic glass with a wide supercooled liquid region and high glass forming ability has been tried. The Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ bulk metallic glass has successfully welded to the same bulk metallic glass together. Moreover, the effects of friction-welding conditions such as friction time, rotational speed and upsetting pressure have been investigated under a wide range of conditions, no crystallization and no defects were observed in the interface.

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1. Introduction

Amorphous alloys suffered from three major issues, i.e., a limitation of product size and lacks of workability and weldability. Recently, amorphous alloys having a high glass-forming ability and a wide supercooled liquid region have been attracted increasing attention because of the high interests on basic science and engineering applications. The new amorphous alloys are called bulk metallic glasses (BMGs). They have superior mechanical properties such as high strength at ambient temperature and high-strain-rate superplasticity above the glass transition temperature. Large BMGs can be fabricated by casting of the melt and by consolidation of the glass powders. These results demonstrate that the BMGs have solved two major subjects of a limitation of product size and a lack of workability. However, the problem of welding has been left unsolved. In 2001, it has been reported that Pd$_{40}$Ni$_{40}$P$_{20}$ BMGs were successfully welded together having amorphous structure and full strength by a friction welding. Zr-based BMGs, which are commercially used as a face material of golf club heads, are typical BMGs as well as the Pd$_{40}$Ni$_{40}$P$_{20}$ BMG. In this paper, we will report the friction welding of Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ BMGs, and the effects of friction-welding conditions such as friction time, rotational speed and upsetting pressure on weldability.

2. Experimental Procedure

Figure 1(a) shows a schematic illustration of the friction-welding apparatus. The joining was performed using a conventional friction-welding machine in the air. The dimensions of workpieces and the welding conditions are shown in Figs. 1(b) and (c), respectively. One specimen of a pair to be welded was rotated at a rate of 6000 min$^{-1}$. The pressures of the friction and upsetting were 100 and 150 MPa, respectively. The times of the friction and upsetting were 0.2 and 3.0 s, respectively. These conditions are the same as the

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*2Graduate Student, Kumamoto University.

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Fig. 1 Schematic illustrations of (a) an employed friction joining method, (b) dimension of work pieces to be welded and (c) changes in the applied pressure ($P$) and rotational speed ($N$) during the friction welding.
friction welding of the PdNiP BMGs which has been reported previously.\textsuperscript{5)} ZrBeTiCuNi BMG samples to be welded were prepared by machining the cast BMG rods. The ZrBeTiCuNi BMGs, of which glass transition, crystallization and melting temperature were 639, 748 and 1030 K, respectively, using differential scanning calorimetry (DSC) apparatus at a heating rate of 0.67 K/s. The thermal properties of the ZrBeTiCuNi BMG used in this study are given in Table 1. The effects of friction-welding conditions on weldability were investigated, where the friction time, rotational speed and upsetting pressure were in the range of 0.05 to 0.4 s, 1500 to 6000 min\(^{-1}\) and 50 to 150 MPa, respectively, as shown in Table 2. The welded specimens were investigated by optical microscopy, scanning electron microscopy (SEM) of their polished cross-section. The glassy structure was examined by micro-focused X-ray diffractometry using CuK\(\alpha\) radiation. The diameter of the X-ray beam was 100\(\mu\)m. The joining strength of the welded BMGs was estimated by tensile tests. Tensile test specimens with a gauge length of 3.0 mm and a diameter of 2.1 mm were prepared by machining the welded BMGs. The tensile tests were carried out using an Instron tensile test machine at a strain rate of 5\(\times\)10\(^{-4}\) s\(^{-1}\). The fracture surface was observed using SEM.

3. Results

3.1 Friction welding of ZrBeTiCuNi BMGs

Figure 2 shows the outer appearance of the ZrBeTiCuNi BMGs friction-welded under a rotational speed of 6000 min\(^{-1}\), a friction time of 0.2 s, a friction pressure of 100 MPa, an upsetting time of 3 s and an upsetting pressure of 150 MPa. The ZrBeTiCuNi BMGs were successfully welded together as well as the PdNiP BMGs.\textsuperscript{5)}

Table 2 Welding conditions of same ZrBeTiCuNi bulk metallic glasses together.

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<th>Friction pressure (P_1) (MPa)</th>
<th>Friction time (t_1) (s)</th>
<th>Rotational speed (N) (min(^{-1}))</th>
<th>Upsetting pressure (P_2) (MPa)</th>
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Figure 3 shows the optical micrograph of the polished cross section of the interface in the friction-welded Zr\textsubscript{41}Be\textsubscript{23}Ti\textsubscript{14}Cu\textsubscript{12}Ni\textsubscript{10} BMGs. No defects were observed, showing the achievement of metallurgical bonding. A large thin protrusion with a thickness of about 400\textmu m was observed on the outside of the interface, as shown in Fig. 4. It should be noticed that neither deformation nor swelling was observed beside the thin protrusion. Figure 5 shows the micro-focused X-ray diffraction patterns of the cross-section around the interface of the friction-welded Zr\textsubscript{41}Be\textsubscript{23}Ti\textsubscript{14}Cu\textsubscript{12}Ni\textsubscript{10} BMGs. Each diffraction pattern consisted of a halo pattern, showing the existence of only glassy phase. No detectable diffraction of any crystalline phases were observed. These results demonstrated that the interface maintained the amorphous structure and no devitrification was occurred. The tensile strength of the friction-welded Zr\textsubscript{41}Be\textsubscript{23}Ti\textsubscript{14}Cu\textsubscript{12}Ni\textsubscript{10} BMGs was 1870 MPa, that was almost the same as that of the original BMG. The fracture took place along the maximum shear plane that was inclined by about 55 degrees to the direction of tensile load, as shown in Fig. 6(a). Vein patterns, which are typical for amorphous alloys with good bending ductility, were observed over the whole fracture surface, as shown in the magnified SEM micrograph of Fig. 6(b). This confirmed that the Zr\textsubscript{41}Be\textsubscript{23}Ti\textsubscript{14}Cu\textsubscript{12}Ni\textsubscript{10} BMGs were successfully welded with maintaining amorphous structure and full strength in spite of the welding processing in the air.

### 3.2 Effects of friction-welding conditions on weldability

The effects of friction-welding conditions such as friction time, rotational speed and upsetting pressure on weldability were investigated for Zr\textsubscript{41}Be\textsubscript{23}Ti\textsubscript{14}Cu\textsubscript{12}Ni\textsubscript{10} BMGs. Figures 7 to 9 show optical micrographs of the Zr\textsubscript{41}Be\textsubscript{23}Ti\textsubscript{14}Cu\textsubscript{12}Ni\textsubscript{10} BMGs welded under different conditions. In all conditions, no defects were observed, showing the achievement of metallurgical bonding, it was confirmed by micro-focused X-ray diffractometry that the interface of these friction-welded BMGs kept the amorphous state. As shown in Fig. 7, although the volume of protrusion increased with increasing the friction time, its thickness was identical to about 400\textmu m. Both the volume and thickness of the protrusion were
increased with increasing the rotational speed, as shown in Fig. 8. Joining part was not reached outside under a condition of 1500 min\(^{-1}\). As shown in Fig. 9, both the volume and thickness of protrusion were independent of the upsetting pressure. Therefore, it was found that the BMGs could be friction-welded keeping amorphous structure and full strength under a wide range of conditions. It should be noticed that the Zr\(_{41}\)Be\(_{23}\)Ti\(_{14}\)Cu\(_{12}\)Ni\(_{10}\) BMGs were successfully welded even at a short friction time of 0.05 s or a low rotational speed of 1500 min\(^{-1}\).

4. Discussion

4.1 Friction welding of Zr\(_{41}\)Be\(_{23}\)Ti\(_{14}\)Cu\(_{12}\)Ni\(_{10}\) BMGs

The glass transition temperature \(T_g\) of the Zr\(_{41}\)Be\(_{23}\)Ti\(_{14}\)Cu\(_{12}\)Ni\(_{10}\) BMG was 639 K, that was higher by 50 K than that of the Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) BMG. Although Zr-based BMGs are very easy to be oxidized by heating above 600 K in the air, as compared with the Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) BMG. The Zr\(_{41}\)Be\(_{23}\)Ti\(_{14}\)Cu\(_{12}\)Ni\(_{10}\) BMGs were, however, friction-welded successfully in the air without defects and with amorphous structure and original strength.

It has been reported that the BMGs exhibit high-strain-rate superplasticity in the supercooled liquid state.\(^2\) The interface corresponding the thickness of protrusion seems to be heated above the glass transition temperature, the projection seems to be formed by superplastic deformation of the interface, because the thin protrusion was rapidly formed within 0.2 to 0.3 s. The friction welding is generally classified into a solid phase welding process. However, it can be said that the friction welding of BMGs is a supercooled liquid phase welding process. In the friction welding, the relative motion of the two interfaces causes the heating of the interface above \(T_g\). The BMG in the interface seems to be discharged as a protrusion with oxide films on the original interface, resulting in metallurgical bonding through the freshened surfaces.

The calorific value in the interface during friction welding is shown approximately by a summation of friction work consumed at the section of its phase. The rate of heat generation \(q\) is expressed by the equation.

\[
q = \alpha \cdot N \cdot T,
\]

where \(\alpha\) is constant, \(N\) is the rotational speed and \(T\) is the torque.\(^9\)

The interface with the same thickness as the protrusion may become supercooled liquid, because friction-welded
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Fig. 8 Optical micrographs of the polished cross section of the interface in the Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ BMGs welded under the conditions of rotation speeds ($N$) of (a) 1500 min$^{-1}$, (b) 3000 min$^{-1}$, (c) 6000 min$^{-1}$, and $t_1 = 0.2$ s, and $P_2 = 150$ MPa.

Fig. 9 Optical micrographs of the polished cross section of the interface in the Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ BMGs welded under conditions of upsetting pressures ($P_2$) of (a) 50 MPa, (b) 150 MPa, (c) 200 MPa, and $t_1 = 0.2$ s, and $N = 6000$ min$^{-1}$. 
BMGs were not deformed except the part of protrusion. This phenomenon may be regarded as relative rotation of the two solid BMGs sandwiching a supercooled liquid with a thickness of $\tau$ and a viscosity $\eta$, as shown in Fig. 10. This phenomenon in friction welding of BMGs can be expressed by a rotational parallel plate rheometer (RPPR) model which is one of methods for measuring of viscosity. In this RPPR model, the relationship between the viscosity $\eta$ of the supercooled liquid and friction torque $T$ of liquids can be expressed by

$$\eta = \frac{30\tau T}{\pi^3 r^4 N^1}.$$  \hspace{1cm} (2)

where $\tau$ is the thickness of supercooled liquid in interface which corresponds to the thickness of the protrusion, $r$ is the radius of sample and $N$ is the rotational speed. The following equation can be obtained by substituting the eqs. (2) to (1).

$$q = \frac{\alpha}{30\tau} \frac{\pi^3 r^4 \eta N^2}{\pi^3 r^4 N^1}.$$  \hspace{1cm} (3)

This equation means that the heat generation rate $q$ is proportional to the viscosity $\eta$ and square of rotational speed.

Figure 11 shows the temperature dependence of the viscosity of the $\text{Zr}_{41}\text{Be}_{23}\text{Ti}_{14}\text{Cu}_{12}\text{Ni}_{10}$ BMG which has been already reported. \(^7\) The viscosity of supercooled liquid above $T_g$ depends significantly on the temperature. Temperature increment of 15 K results in a decrease in viscosity by one order of magnitude. Therefore, it is expected from eq. (3) and Fig. 11 that the temperature of the interface can be self-controlled so as not to over-heat. The time-temperature-transition ($TTT$) diagram of the crystallization for the heating of the amorphous solid is different from one for the cooling of the melt. The nose time of the $TTT$ diagram of the $\text{Zr}_{41}\text{Be}_{23}\text{Ti}_{14}\text{Cu}_{12}\text{Ni}_{10}$ BMG is 70 s for the melt cooling and 5 s for the solid heating. \(^7\) The friction time of 0.2 s is much short than the nose time of two crystallization $TTT$ diagrams.

As above mentioned, it can be considered that the crystallization during the friction welding was avoided due to the short friction time and the self-control of the temperature of two interface.

### 4.2 Effects of friction-welding conditions for weldability

Figure 12 shows the changes in the volume of the protrusion as a function of friction time, rotational speed and upsetting pressure. The volume of protrusion is proportional to the friction time and rotational speed, but inde-
pendent of the upsetting pressure. The protrusion of about 10 mm$^3$ was formed even at zero friction time. This means that it took about $7.7 \times 10^{-2}$ s from the start of breaking to the stop of the rotation. The formation rate of the protrusion was estimated to be about $7.6 \times 10^{-3}$ mm$^3$ per one rotation and 137 mm$^3$ per one. The relationship between the strain rate $\dot{\varepsilon}$ and flow stress $\sigma$ can be expressed by

$$\dot{\varepsilon} = \frac{\pi^2 r^4 \sigma N}{90\tau T},$$

(4)

where $\eta$ is the viscosity. By substituting eqs. (2) to (4), the equation for the relationship between the formation rate of protrusion $\dot{\varepsilon}$ and flow stress $\sigma$ are obtained

$$\dot{\varepsilon} \propto \beta \frac{\pi^2 r^4 N}{\tau},$$

(6)

where $\beta$ is constant. In this eq. (6), the formation rate of protrusion is independent of time, showing that the volume of protrusion is proportional to the friction time. Moreover, the eq. (6) shows that the volume of protrusion is proportional to the rotational speed and independent of the friction pressure and upsetting pressure. These results are in good agreement with the experimental results shown in Fig. 12.

As described above, the volume of protrusion is proportional to the friction time and it takes a limited time with the rotation stops by breaking, as shown in Fig. 12(a).

The time required to stop the rotation may be proportional to the rotational speed. The time can be estimated to be $1.9 \times 10^{-2}$, $3.8 \times 10^{-2}$ and $7.6 \times 10^{-2}$ s for 1500, 3000 and 6000 min$^{-1}$, respectively. Therefore, the friction time dependence of the protrusion volume can be shown by Fig. 13(a) for each rotational speed, which is obtained Figs. 12(a) and (b). In this study, the minimum protrusion volume required in order to join through whole interface of the sample is about 10.5 mm$^3$. Figure 13(b) shows the rotational speed dependence of minimum friction time needed to join through whole interface. It is found that the minimum friction time increases exponentially with decreasing the rotational speed. At the rotational speed of 1500 min$^{-1}$ where joining was not obtained at a standard friction time of 0.2 s, whole joining can be achieved at a friction time of 0.75 s.

Figure 14 shows the changes in the thickness with friction time, rotational speed and upsetting pressure. The thickness of
the protrusion is independent of the friction time and upsetting pressure, but dependent on the rotational speed. Although the volume of the protrusion is proportional to the friction time as shown in Fig. 12(a), the thickness of protrusion is independent on that. This means that the protrusion with a constant thickness was formed continuously during the friction welding. It can be understood from the eq. (3) that the heated interface becomes thicker with increasing the rotational speed, because the heat generation is proportional to the rotational speed squared. As described above, the phenomenon during the friction welding of BMGs can be well expressed using the RPPR model shown in Fig. 10.

Conclusions

We have tried the friction welding of Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ BMG under different conditions. The results obtained are summarized as follows:

1) We successfully welded Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ BMG, which is oxidized easier than Pd$_{40}$Ni$_{40}$P$_{20}$ BMG by the friction welding in the air. The welded BMGs had amorphous structure and full strength.

2) Zr$_{41}$Be$_{23}$Ti$_{14}$Cu$_{12}$Ni$_{10}$ BMG was successfully welded under a wide range of conditions in which the friction time, the rotational speed and the upsetting pressure were 0.05 to 0.4 s, 1500 to 6000 min$^{-1}$ and 50 to 200 MPa, respectively.

3) The volume of the protrusion formed outside of the interface during the friction welding was proportional to the friction time and rotational speed, but was independent of the upsetting pressure. On the other hand, the thickness of the protrusion was proportional the rotational speed, but was independent of the friction time and upsetting pressure.

4) In the friction welding of BMGs, the temperature of the interface can be self-controlled in the range of the glass transition temperature to crystallization temperature due to the strong temperature sensitivity of the viscosity of the supercooled liquid.

5) The joining phenomenon during the friction welding of BMGs can be well expressed using a rotated parallel plate rheometer model.

REFERENCES