Microstructure of Bonding Interface for Resistance Welding of Zr-Based Metallic Glass Sheets

Toshio Kuroda¹, Kenji Ikeuchi¹, Masahiro Shimada¹, Akira Kobayashi¹, Hisamichi Kimura² and Akihisa Inoue²

¹Joining and Welding Research Institute, Osaka University, Ibaraki 567-0047, Japan
²Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Resistance welding of Zr₅₅Cu₃₀Al₁₀Ni₅ metallic glass sheets was investigated at 723 K in a supercooled liquid region. The welding time was changed from 5 s to 20 s at 723 K. The joint interface of the metallic glass was no defect and no crack. X-ray diffraction technique of the bonding interface of specimens was performed. The specimens showed halo patterns showing existence of only glassy phase, when the welding time was 5 s and 10 s. X-ray diffraction patterns of specimen bonded for 20 s showed crystalline peaks with halo patterns for the welding for 20 s. The crystalline phase at the bonding interface was small. Transmission electron micrograph at the bonding interface showed nanostructures of NiZr₂ and Al₅Ni₃Zr₂.

Keywords: zirconium-based metallic glass, resistance welding, transmission electron microscopy, X-ray diffraction analysis, nanostructure

1. Introduction

Metallic glasses have been studied for their mechanical,¹ corrosion resistance,² and magnetic³ properties. However, when subjected to heating to exceed the crystallization temperature, followed by slow cooling, metallic glasses crystallize and their advantageous properties disappear. Thus, the welding of metallic glasses has generally been limited to the electron,⁴ laser,⁵ and friction welding.⁶ There are only a few reports on other welding methods.⁷ There is a demand for a method for welding metallic glasses. Resistance welding was carried out at 723 K, which lies in the supercooled liquid region. The main aim of the present study was to examine the bonding interface microstructure of resistance welding using optical, scanning and transmission electron microscopies.

2. Experimental

A Zr₅₅Cu₃₀Ni₅Al₁₀ metallic glass with a thickness of 50 μm was used in the present study. The glass transition temperature (Tₐ) and the crystallization temperature (Tₓ) were 683 K and 769 K, respectively.⁹

Figure 1 schematically illustrates resistance welding using the Gleeble thermomechanical simulator. Four overlapped metallic glass sheets were placed between the electrodes, and resistance welding was carried out under a pressure of 20 MPa in a He atmosphere. The welding temperature was controlled by a thermocouple located 1 mm from the bonding interface. The thermocouple was set at 723 K, i.e., at a temperature between the Tₐ and Tₓ. The welding time at 723 K was varied from 5 s to 20 s. The welded specimens were examined in cross-sections by optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). Thinning treatment of the specimens at the bonding interface was achieved by the focused ion beam (FIB) technique. The glassy structure was examined by X-ray diffraction using Cu-Kα irradiation.

3. Results and Discussion

Figure 2 shows the temperature-time curve during resistance welding at 723 K for 20 s. During the heating process, the temperature-time curves for the different conditions showed non-linear rises, although rise and drop phenomena¹⁰ were also shown in Fig. 2. As the contact surfaces were irregular, localized heating occurred, which resulted in short-circuiting of the electric current and halting of the resistance heating. This stop-start pattern of resistance heating gener-
ated the rise and drop phenomena. At around 700 K, the metallic glass began to deform and to fill the gaps between the sheets, such that the contact surfaces were extended, which resulted in a small change in the temperature. The same phenomenon was observed for the welding times of 5 s and 10 s.

Figure 3 presents the cross-sectional microstructures at the bonding interface for resistance welding at 723 K for 20 s, both before etching (a) and after etching (b). Etching was carried out in a solution of 10% hydrofluoric acid and 90% distilled water. As shown in Fig. 3(a), there was no evidence of a defect or pore at the interface, and welding was completed around the center of the specimen. With increased welding time, the efficiency of joining increased. The joining efficiency of the four welded sheets was 80% for a welding time of 20 s. The total thickness of the four sheets of metallic glass before welding was 200 μm, and the thickness after welding was 150 μm. The joining of the four sheets of metallic glass was performed in the supercooled liquid temperature region between the \( T_g \) and \( T_x \).11) In the present study, the thickness of the metallic glass was not changed sufficiently. Superplastic deformations of the metallic glasses generally occur at high strain rates. However, in the present study, the metallic glass was placed under a pressure of 20 MPa from the beginning of the experiment, and the load was maintained at a constant level until the end of experiment. Therefore, the strain rate was considered to be slow at the welding temperature. As a consequence, superplastic deformation at the bonding interface was negligible.

As shown in Fig. 3(b), etched black lines were observed near the bonding interface. Zirconium has a high chemical affinity for O\(_2\), and reacts readily with O\(_2\) to form ZrO\(_2\). A reduction in the Zr concentration in the matrix would disrupt the equilibrium of the amorphous composition, so that the structure would be crystallized below the crystallization temperature. Therefore, we hypothesized that the metallic glass would be crystallized at the zones of etching. In the case of resistance welding, the heat for welding is generated by the resistance to the flow electric current at the bonding interface.12) Therefore, the temperature of the bonding interface may be higher than 723 K. Since the thermocouple was positioned 1 mm from the interface, the temperature of the interface was considered to exceed the \( T_x \).

Figure 4 shows X-ray diffraction patterns of the as-received material and the Zr-based metallic glass welded at 723 K for 20 s. The surface of the welded metallic glass was analyzed. The diffraction patterns for welding times of 5 s and 10 s showed halo patterns and the existence of only glassy phase as well as as-received material. Crystallization peaks for NiZr\(_2\) and Al\(_5\)Ni\(_3\)Zr\(_2\) were observed with halo patterns for the welding time of 20 s. The NiZr\(_2\) phase is the first crystallite phase to be formed during the crystallization of a Zr-based metallic glass.13) As the temperature of the metallic glass rises above the \( T_g \), the time to crystallization is shortened.14) As the welding time is increased, the rate of crystallization increases. The crystallized metallic glass was harder than the non-crystallized metallic glass.15) However, the Vickers hardness of the specimen generated in a welding time of 20 s was almost identical to that of the original material.16) The crystalline phase at the bonding interface was small.

Figure 5 shows an SEM image of a cross-section of the bonding interface of the welded Zr-based metallic glass after welding at 723 K for 20 s. To compare the chemical compositions, marker B at the bonding interface and markers A and C in the matrix area were measured in the
EDX analysis. Markers A and C were located distal from the bonding area, while marker B was located at the bonding interface. Table 1 shows the EDX analysis results of the three markers shown in Fig. 5. 6 samples were measured. When Point B was measured, because the diameter of EDX was under 1 μm, the result was the value of Point B and its surrounding area. Therefore the difference of the value among Points A, C, and Point B was small and the standard deviation (SD) of the Points A, B, and C were in the range between 0.48 to 1.18.

The copper and nickel contents were higher at the bonding interface than in the matrix, and the Zr level was lower at the bonding interface than in the matrix. This suggests that ZrO₂ was formed. In the present study, resistance welding was performed initially in a vacuum, which was then filled with He gas. It is possible that residual O₂ was present during welding, with the consequence that the metallic glass surface was moderately oxidized during welding. It has been reported that when a metallic glass is heated at 723 K in air, the substrate became amorphous, it was crystallized in the oxide scale, and copper tended to segregate to the outer layer. 17,18 Oxide layers, consisting of ZrO₂ (tetragonal), CuO, NiZr₂, and Al₅Ni₃Zr₂ (Fig. 4), have been demonstrated at the surfaces of oxidized and crystallized metallic glasses. Similar layers are present at the bonding interface. As described previously, four chemical compounds are found at the bonding interface, with the levels of Cu and Ni being higher at the etched line.

Figure 6 shows a TEM bright field-image of a cross-section of the bonding interface of a Zr-based metallic glass that was subjected to resistance welding at 723 K for 20 s. The nanostructure phases are evident at the bonding interface. The thickness of the nanostructure was about 0.2 μm, which is similar to that seen in Fig. 5. Figure 7 shows the selected area diffraction patterns for area A and area B in Fig. 6.

In the present study, the oxide films was thin. It is considered that the X-ray diffraction method cannot confirm oxides, but the TEM observation will be possible to confirm oxides. “d” spacing by the relation of \( \lambda L = nd \) was calculated, where \( r \) is the distance from the central spot, \( \lambda \) is the electron wavelength, \( L \) is the distance of the specimen from the screen or plate and \( \lambda L \) is the diffraction constant of the microscope. The calculated “d” was compared with “d” of JCPDS cards within the range of 1.4% in the error margin. The selected area electron diffraction pattern for area A (in Fig. 6) shows a nanocrystal of NiZr₂ and Al₅Ni₃Zr₂ and fine granular oxides of ZrO₂ (tetragonal) and CuO. The oxide film of Zr-based metallic glass, ZrO₂ (tetragonal), is different from that of ZrO₂ (monoclinic) seen in Zr metals. ZrO₂ (tetragonal) was not in a passive state, and its thickness was substantial. The surface of the metallic glass was moderately oxidized and was readily crystallized. Therefore, two crystallized compounds of NiZr₂, Al₅Ni₃Zr₂, ZrO₂, and CuO were formed. Figure 7(b) shows the halo pattern that provides evidence of only a glassy phase for area B (in Fig. 6). Al₂O₃ was

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<th>Zr</th>
<th>Cu</th>
<th>Ni</th>
<th>Al</th>
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<tr>
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<td>50.36</td>
<td>30.72</td>
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<tr>
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Fig. 6 TEM bright-field image of the cross section at the bonding interface of the Zr-based metallic glass for the resistance welding at 723 K for 20 s.
excluded as a candidate, since the crystal structure of Al$_2$O$_3$ below 773 K had an amorphous structure.\textsuperscript{19)}

4. Conclusions

The joining of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ metallic glass sheets was achieved by resistance welding at 723 K, which lies in the supercooled liquid region. Welding at 723 K was conducted for time periods of 5 s to 20 s. The results are listed below.

(1) Welding of the metallic glass was performed for 5 s. As the welding time was increased, the joining efficiency increased up to 80\%, and the welding was progressive.

(2) X-ray diffraction analysis was carried out for the resistance-welded specimens. The diffraction patterns of the specimens welded for 5 s and 10 s showed halo patterns, as well as the as-received material. However, a crystallized diffraction pattern was observed together with the halo pattern for the specimens welded for 20 s. The crystallite phase was small.

(3) Transmission electron micrograph at the bonding interface of the resistance welding showed nanostructures of NiZr$_2$ and Al$_3$Ni$_3$Zr$_2$.

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REFERENCES