Microstructural development at weld interface between Zr-based glassy alloy and stainless steel by resistance microwelding

S Fukumoto¹, M Minami¹, A Soeda¹, M Matsushima¹, M Takahashi², Y Yokoyama³ and K Fujimoto¹

¹Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.
²Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka, Japan
³Institute for Materials Research, Tohoku University, Sendai, Miyagi, Japan

E-mail: fukumoto@mapse.eng.osaka-u.ac.jp

Abstract. Zr-based bulk metallic glasses are expected to be welded to conventional structural alloys. Dissimilar welding of metallic glasses to stainless steel was carried out by resistance microwelding. The metallurgical analysis of the weld interface revealed the welding mechanism. A thin reaction layer was formed between the two liquid materials. The melting of stainless steel should be limited to obtain sound joints.

1. Introduction
Zr-based bulk metallic glasses (BMGs), which are kinds of amorphous alloys, not only have superior mechanical properties such as high strength and high elastic limit but also a low Young's modulus. It is expected that high-performance devices could be developed using BMGs for energy saving. On the other hand, it is well known that BMGs are often crystallized due to heat hysteresis during welding processes, which causes embrittlement in a weld and a heat affected zone (HAZ). A fast heating and cooling rate are necessary to avoid crystallization in the fusion welding of BMGs. It has been reported that electron beam welding[1-2] and laser welding [3-5] are appropriate fusion processes to weld BMGs successfully. The authors have reported that resistance micro-spot welding is also a suitable fusion welding process to weld BMG without crystallization even in an air atmosphere.[6-7] Recently, BMGs are also expected to be welded to conventional structural alloys such as stainless steels to produce functional small devices such as pressure sensors. However, as is well known, it would be unfavorable to form brittle intermetallic compounds (IMCs) in a weld in the case of dissimilar welding. The reaction between dissimilar metals must be limited to avoid brittleness in the weld.

In the present study, the microstructural development of a weld interface between Zr-based BMG and austenitic stainless steel formed by resistance microwelding was investigated to clarify the welding process. The relation between interfacial strength and the microstructure was also investigated.

2. Experimental procedures
The materials used are Zr₅₀Cu₃₀Ni₁₀Al₁₀ bulk metallic glass and type 304 austenitic stainless steel (SS) sheets of 0.2 mm in thickness. The geometry of the sheet was 20×6 mm. The faying surfaces of the
BMG sheet were polished by #2000 emery paper and cleaned with acetone. The physical properties are shown in Table 1. The BMG was welded to the stainless steel by resistance micro-spot and micro-seam welding. The experimental setups are shown in Figure 1. The welding current was varied from 300 to 700 A, and the weld time and the electrode force were 9 ms and 49 N, respectively, in the case of resistance micro-spot welding, and Cu-Cr electrodes with an R-type tip-face were used. The welding current, impulse time including on-time and off-time, welding speed, and electrode force are the parameters in resistance micro-seam welding. In the present study, only the welding current was varied from 600 to 950 A, and the other parameters, that is to say, impulse time of 30 ms, welding speed of 10 mm/s, and electrode force of 49 N, were kept constant. On-time is 33% of impulse time, while off-time is 66% of impulse time. The basic welding mechanism of both processes are similar.[8] Resistance seam welding is like resistance “multi-spot” welding. Therefore, in the present work, both processes are treated as the same process to explain microstructural development.

Cross sections were observed by optical microscopy and scanning electron microscopy (SEM). The fracture surfaces were also observed by SEM and energy dispersive X-ray analysis (EDX). The weld interface was observed by transmission electron microscopy (TEM) (JFM-2100). The TEM sample was prepared by the focused ion beam system. The joint strengths of the seam-welded joints were evaluated by a tensile shear test with a crosshead speed of 0.017 mm/s. The fracture surfaces of the spot-welded joints were obtained by the peel test. The experimental setups of the mechanical tests are shown in Figure 2.

### Table 1. Physical properties of materials.

| Material | Zr50Cu30Ni10Al10 | SUS304 |
|----------|------------------|--------|
| Electrical resistivity ($10^{-8}$ Ωm) | 205 | 72 |
| Thermal conductivity (W/m·K) | ~10 | 16.7 |
| Melting point (K) | 1133 | 1673–1723 |
| Glass transition temperature (K) | 706* | - |

* The values depend on the cooling rate.

![Figure 1](image1.png)

**Figure 1.** Experimental setups of resistance micro-spot, (a); and micro-seam, (b), welding.

![Figure 2](image2.png)

**Figure 2.** Schematic illustration of (a) tensile shear and (b) peel tests. (unit: mm)
3. Results

3.1. Cross sections

Figure 3 shows cross sections of resistance micro-spot welded dissimilar joints for various welding currents. At a welding current of 300 A, no fusion nuggets were observed. As the welding current increased, the stainless steel started to melt and penetrate into the BMG sheet. At a welding current of 700 A, an oval fusion nugget was formed and many cracks were introduced due to the formation of brittle IMCs.

The fusion of both alloy sheets is obvious when the welding current is higher than 500 A as shown in Figure 3b. On the other hand, a weld nugget was not observed in a weld made at 300 A. It has been reported that a weld nugget is invisible as long as the BMG maintains an amorphous structure, even if there is a fusion zone.[7] The electric resistivity of Zr-based BMG is three times larger than that of stainless steel, and the thermal conductivity of BMG is less than that of stainless steels (Table 1). Moreover, the melting point of BMG is less than that of stainless steel. Therefore, even at a small welding current, the BMG could have melted, even though a fusion zone was not observed. In this study, the BMG was squeezed out in a liquid state or a supercooled liquid state at the edges of the weld interface to form an expulsion. Once the stainless steel melts, both the liquid phases mix together, resulting in the formation of a brittle IMC nugget. Therefore, the amount of the liquid phase of stainless steel should be limited at the weld interface as shown in Figure 3a.

Figure 4 shows a detailed weld interface, in which only limited fusion occurs in the stainless steel sheet. At the outmost region, squeezed out BMG is observed. There are principally three kinds of interfaces. The contact between sheets was insufficient and there are some small gaps, hereafter called interface-A. At the center is the weld interface, where fusion of the stainless steel occurred and where it mixed with the liquid BMG in a limited area, which is called interface-C. Between interface-A and interface-C lies interface-B, where both materials show good contact without fusion of the stainless steel.

![Figure 3. Cross sections of resistance micro-spot welds at various welding currents. (a) 300 A, (b) 500 A, (c) 700 A.](image)

![Figure 4. Three kinds of weld interface between BMG and stainless steel. Images (b) and (c) correspond to the highlighted areas in (a).](image)

3.2. Fracture surfaces

Figure 5 shows fracture surfaces on a BMG sheet with a micro-spot weld with a welding current of 300 A, before the formation of an IMC nugget. Squeezed out BMG, like an expulsion, was observed. Three kinds of regions—in addition to the squeezed out BMG—were observed on the fracture surface.
At the center, there is the brightest region, which contains not only Zr, Al, Cu and Ni but also Fe and Cr, and where no flat-surface morphology was observed (Figure 5b). It is believed that the region corresponds to interface-C, where a limited reaction occurred between the liquid BMG and stainless steel. A small IMC reaction layer formed at this region. Next to this region, there is another region where the surface morphology was relatively flat, while small amounts of elements of stainless steel were detected (Figure 5c). The region most likely corresponds to interface-B. At the outmost region, there are many straight lines in one direction (Figure 5d). These line patterns were transferred from the surface of the stainless steel, and no Cr or Fe was detected there. It is believed that the stainless steel in a solid state did not react but contacted with the BMG in a liquid or supercooled liquid state at this region. Therefore, this region probably corresponds to interface-A.

As described above, the welding mechanism of resistance seam welding is basically similar to that of resistance spot welding. Figure 6 shows the fracture surface of a micro-seam weld. A brittle fracture surface morphology, including elements of stainless steel, was observed at the center area of the weld bead and there was also dimple morphology in places. The transfer printing of the surface of the stainless steel sheet were also observed at the outmost region. Between those two regions, a slightly bright region was observed in comparison with the BMG base alloy, which means the area includes a small amount of elements of stainless steel. The regions are almost similar to those observed on the fracture surfaces of the resistance micro-spot welds. Each region increased with an increase in the welding current.

3.3. Interfacial strength

It is difficult to estimate the interfacial strength of resistance micro-spot welds accurately since the area is relatively small. Therefore, the joint strength of resistance micro-seam welds was evaluated since the weld area is larger than that of micro-spot welding. Figure 7 shows the shear breaking force of the seam welds and the shear stress against each region for various welding currents. Each region was measured on the fractured surfaces of BMGs. Most of the joints were fractured at the weld interface. When the welding current was 950 A, a fracture occurred in the BMG base alloy.

![Figure 5. Fracture surface of BMG sheet of resistance micro-spot welding at a current of 300 A. (a) Macroscopic view. Images (b) to (d) correspond to the higher magnifications of each region indicated in (a).](image-url)
The interfacial shear breaking force of interfacial fractured joints increases as the welding current increases because the weld area increases. The weld area includes three kinds of regions as described in Section 3.2. The shear stress against the area including all kinds of interfaces, that is to say interfaces-A, -B and -C, increased with an increase in the welding current (Figure 7b). The shear stress against the area including interfaces-B and -C also increased with an increase in welding current. On the other hand, the shear stress of the joint against interface-C, which is indicated as solid circles in Figure 7b, shows almost a constant value of approximately 220 MPa regardless of the welding current. It is believed that interface-C, where a limited fusion of stainless steel occurs, is most likely dominant in terms of joint strength.

4. Discussion
A weld interface has three kinds of interfaces as shown in Figure 4. Among them, interface-C is dominant for joint strength. Detailed microstructures of interfaces-B and -C are shown in Figure 8. A reaction layer and a plane interface were observed at the weld interface. They correspond to interface-C and interface-B, respectively. An amorphous structure was maintained in the BMG sheet except for

Figure 6. Typical fracture surface of BMG sheet of resistance micro-seam welding. Each kind of white dotted line corresponds to that shown in Figure 5a.

Figure 7. Joint shear breaking force of resistance micro-seam welds, (a); and interfacial shear stress for various weld interfaces, (b).
the area close to interface-B. A reaction layer was formed at weld interface-C. A eutectic structure was observed in the reaction layer, and the selected area diffraction pattern reveals that one of the phases was Fe23Zr6 (Figures 9a and 9b). Therefore, it is believed that interface-C was produced by a reaction between molten stainless steel and molten BMGs.

A crystalline phase of the stainless steel was observed in the amorphous phase close to both interface-B and the reaction layer, that is interface-C. The area is shown by white dotted lines in Figure 8a, and there is not only a crystalline phase but also an amorphous phase (Figures 9c and 9d). It is believed that the molten stainless steel flows into the liquid phase of BMG from the reaction layer to form such an area. Since the stainless steel was melted at interface-C, the temperature at interface-C must be higher than 1673 K. As shown in Table 1, the melting point of BMG is much lower than that of stainless steel. Hence, the BMG would be the liquid phase near interface-B. On the other hand, interface-B was a plane, which suggests the stainless steel was in a solid state at interface-B during the welding. Figure 10 shows the distribution of Zr in the stainless steel near interface-B. Zr was detected in the range of 100 to 150 nm from interface-B, and the concentration decreases with an increase in the distance. Although the weld time was just 9 ms, the diffusion should not be ignored near the weld interface. The welding mechanism at the weld interface-B is based on the interdiffusion between solid stainless steel and liquid BMG. So interface-B contributes to the joint strength to some degree, although it is probably smaller than that of interface-C. Further study is necessary to clarify the relation between interfacial strength and the microstructure.

5. Conclusions

Zr-based BMG was welded to stainless steel by resistance microwelding. The weld interface consisted of three kinds of interfaces. There was a reaction layer composed of a eutectic structure at the center of the weld interface. Next to the reaction layer, there was an interface formed by the liquid/solid interdiffusion between BMG and stainless steel. There are some gaps in the outermost region where interfacial strength cannot be expected. An interface with a limited reaction layer might be dominant for the joint strength.
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Figure 9. Detailed microstructures of highlighted areas shown in Figure 8a. (a)-(b) Microstructure of reaction layer and selected area diffraction patterns. (c)-(d) Microstructure of BMG sheet near interface-B and selected area diffraction patterns.

Figure 10. Distribution of Zr in stainless steel near weld interface-B, which is the highlighted area in Figure 9c. (a) Bright-field image, (b) Concentration of Zr near weld interface. Crosses indicate analysis points. The diameter of electron beam is 1 nm.
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References
[1] Yokoyama Y et al 2002 Mater. Trans. JIM 43 2509
[2] Kawamura Y and Ohno Y 2001 Mater. Trans. JIM 42 2476
[3] Li B et al 2006 J. Alloy and Compound 1-2 118
[4] Kim J H et al 2007 Mater. Sci. Eng. A 449-451 872
[5] Tsumura T and K Nakata 2011 Weld. Inter. 27 491
[6] Fukumoto S et al 2007 Mater. Sci. Forum 562-565 1307
[7] Fujiwara K, Fukumoto S et al 2008 Mater. Sci. Eng. A 498 302
[8] Karagoulis M J 2000 Resisatace seam welding ASM Handbook Vol.6 Welding, Brazing, and Soldering ed Olson D L et al (Materials Park, OH) pp238-246