

Anodic Bonding of Zirconium-based Metallic Glass[†]

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Abstract

Zirconium-based metallic glass was anodically-bonded to soda-lime glass as a trial. Faying surfaces of the joint pieces were finished by buffing and bonded in a pure argon atmosphere with a bonding voltage of 500 V. At a bonding temperature of 473 K intimate contact all over the joint interface was achieved with a bonding time of 7200 s. The bonding process was accelerated with increase of the bonding temperature. The obtained bond interfaces were strong, but cracks occurred in the soda-lime glass due to the residual stress caused by the difference in expansion coefficients of the metallic glass and the soda-lime glass. By transmission electron microscopy, it was found that the metallic glass kept its amorphous nature through the anodic bonding process. An oxidation layer ~100 nm thick was found at the bond interface. The oxidation layer was composed of a crystalline sublayer contacting to the metallic glass and an amorphous sublayer contacting to the soda-lime glass.

KEY WORDS: (Anodic bonding), (Metallic glass), (Silicate glass), (Joinability), (Microstructure)

1. Introduction

Anodic bonding is a method for bonding metals or semiconductors to silicate glass containing alkali ions by applying a D.C. voltage of 100-1000 V between them with the metal side anodic. The bonding temperature for anodic bonding is usually 500-700 K, and the adequate temperature is determined mainly by the type of the silicate glass. With heating to the bonding temperature, thermal diffusion of alkali ions in silicate glass is activated, and under the influence of the electric field induced by applied voltage, these ions drift toward the cathode side, and an alkali ion depletion layer forms in the silicate glass near the joint surface. This layer has a strong negative charge because of the presence of non-bridging oxygen (O) anions that lose their bonds with the alkali ions. A Coulomb force acting between this charge and the charge appearing on the surface of the anode conductor brings the silicate glass and the conductor into intimate contact, and a permanent bond is achieved by the oxidation of the surface of the conductor by oxygen derived from the alkali ion depletion layer in the silicate glass¹⁾. Anodic bonding achieves direct bonding of conductor to silicate glass without intermediates such as solder or adhesive, and it is workable at a temperature low enough not to cause deformation of the silicate glass²⁾. These features make anodic bonding a powerful method for precise bonding of conductors to silicate glass. Anodic bonding is commonly

used in sealing of silicon micro devices, for example, sensors for pressure or acceleration.

Bulk metallic glasses (BMG) have many attractive features, such as high strength, low Young's Modulus, or high corrosion resistance^{3, 4)}. And they have excellent compatibility with microfabrication by imprinting or beam processing because of their isotropic nature⁵⁾. Coupled with peculiar mechanical properties of BMGs, compatibility with microfabrication makes BMGs promising materials for microsensors or micromachines. As mentioned above, today most such devices are fabricated from silicon by applying microfabrication techniques developed for electronics, and the major application of anodic bonding is the sealing of silicon micro devices with silicate glass. Therefore, it is desirable to establish anodic bonding of metallic glass in order to realize micro devices made of metallic glass. There are some problems in anodic bonding of metallic glass, for example, applicability of anodic bonding to metallic glass, selection of adequate silicate glass, and influence of the process of anodic bonding on the amorphous nature of metallic glass. In this study, zirconium-based metallic glass was anodically-bonded to soda-lime glass in order to examine joinability of the metallic glass to silicate glass by anodic bonding. The microstructure of the obtained joint was investigated by transmission electron microscopy (TEM).

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2. Experimental

Experimental materials are zirconium-based metallic glass ($Zr_{55}Cu_{30}Al_{10}Ni_5$) and soda-lime glass Matsunami 0050. Typical soda-lime glass contains 71-73mass% SiO_2 , 9-10.5mass% CaO , 13-15mass% Na_2O , ~2mass% Al_2O_3 , and traces of Fe_2O_3 , MgO , and K_2O . Linear expansion coefficients of the metallic glass and soda-lime glass are $\sim 10 \times 10^{-6} / K$ ⁶⁾ and $8.7 \times 10^{-6} / K$ ⁷⁾, respectively. Crystallization temperature of the metallic glass is $\sim 750 K$ ⁸⁾. Metallic glass was provided as plates 2 mm thick and 25 mm square. One side of each plate was finished flat and glossy by mechanical grinding and buffing. After that these plates were cut into pieces 10 mm square. Buffed sides of these pieces were used as faying surfaces. The soda-lime glass was cut into pieces of 26 mm square, and faying surfaces of these pieces were finished by mechanical grinding and buffing.

The procedure of anodic bonding was as follows.

The soda-lime glass piece was placed on the negative electrode plate with the polished surface up. The surface of the soda-lime glass piece contacting the electrode plate was painted with a carbon conductive coating (Aquadag: colloidal graphite) in order to obtain a uniform electric potential at the surface. The metallic glass piece was placed on the soda-lime glass piece with the faying surface down, and connected with the positive electrode. These specimens were heated to a predetermined bonding temperature (T_b) by surrounding graphite heaters in a pure argon atmosphere of 0.12 MPa. Four different bonding temperatures, T_b , 473 K, 523 K, 573 K, and 623 K were adopted. After the temperature of specimens stabilized, a bonding voltage of 500 V was applied to the specimens for a predetermined bonding time (t_b) with the metallic glass side anodic. During the voltage application, the electric current that passed through the specimens was recorded digitally. The major carriers of the current in silicate glass are mobile cations, and the current represents the drift of the cations. After the voltage application, specimens were cooled slowly in the bonding apparatus.

In order to evaluate progress of bonding, the appearance of joint interfaces of the obtained joints was examined visually through the soda-lime glass. Microstructure around the joint interfaces was

investigated closely by TEM. Thin foil specimens for TEM were cut from the anodically-bonded joint across the bond interface with the focused ion-beam (FIB) system. The FIB system used was Hitachi FB-2000A, and TEM observation was performed by JEOL JEM-2010 operating at an accelerating voltage of 200 kV.

3. Results and Discussions

Appearances of the joint interfaces of the metallic glass anodically-bonded to the soda-lime glass at various bonding temperatures from 473 K to 623 K are shown in **Fig. 1**. At all T_b , intimate contact of the joint interfaces was achieved. The color of the joint interfaces was changed with bonding, and a higher T_b caused a darker joint interface. The bonding process progressed faster at a higher bonding temperature. In **Fig. 1** is shown the t_b of each joint. The t_b of the joint bonded at 473 K was 7200 s, and that of the joint bonded at 623 K was much shorter 60 s. The acceleration of the bonding process is caused by increase of mobility of alkali ions in soda-lime glass with rising temperature. The T_b of 473 K is rather low as the bonding temperature for anodic bonding. Anodic bonding of silicon to heat resistant borosilicate glass, the most typical combination of materials in practical anodic bonding, is usually done at a bonding temperature of $\sim 600 K$ ⁸⁾. The composition of Na in soda-lime glass (13-15mass% as Na_2O) is much higher than that in heat resistant borosilicate glass (~ 2 mass% as Na_2O). Sodium acts as a mobile cation in anodic bonding. Joinability at a low bonding temperature of soda-lime glass with anodic bonding is thought to result from the high Na content.

The current that passes through the joints during the voltage application and the charge that was transferred by the current are shown in **Fig. 2** as functions of the voltage application time for various T_b . At 473 K, an initial current of $\sim 1.5 A/m^2$ flowed at the beginning of the voltage application. The initial current increased with T_b to $\sim 300 A/m^2$ at 623 K. The bonding current decreases with the voltage application time. The decrease of the current like this occurs generally in anodic bonding. The cation depletion layer grows with the drift of cations in silicate glass induced by the voltage application in anodic bonding. Cations are the major carrier of the electric current in silicate glass, and the electric conductivity of

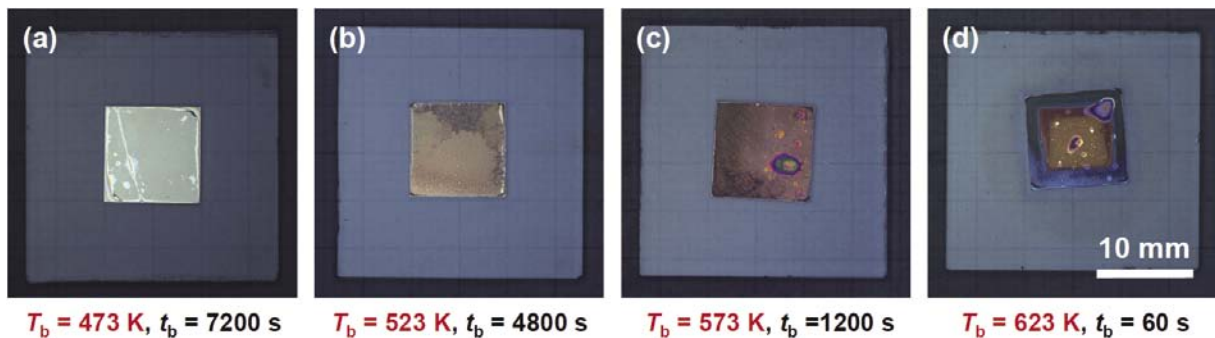


Fig. 1 Appearance of anodically-bonded joints of zirconium-based metallic glass to soda-lime glass. Bonding voltage was 500 V, and bonding temperature (T_b) and bonding time (t_b) of each joint are shown in the figure.

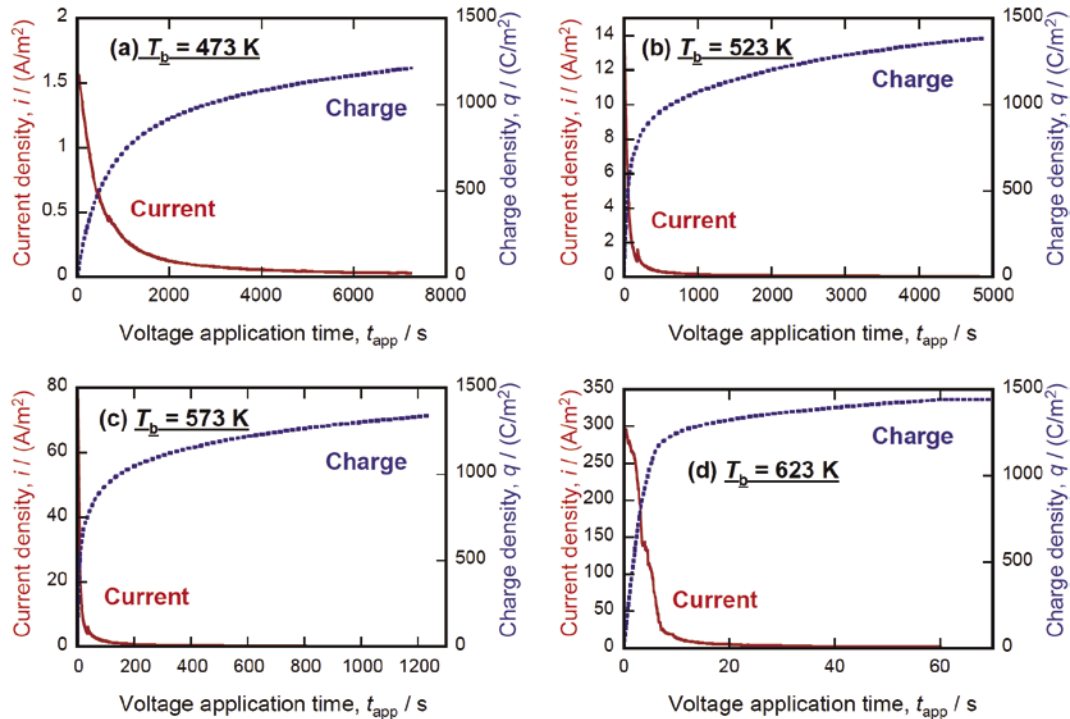


Fig. 2 Current passing through the joints and charge transferred by the current during anodic bonding of zirconium-based metallic glass to soda-lime glass. Bonding temperature (T_b) is shown in the figure.

the cation depletion layer is much lower than that of the original silicate glass¹⁰⁾. At higher T_b the current dropped more quickly because of the faster growth of the cation depletion layer. At all T_b , the charge transferred by the current reached 1200-1500 C/m² at late stages of the voltage application. The transferred charge represents the amount of cations that drifted in the soda-lime glass during the voltage application.

Appearances of the joint interfaces bonded for various t_b are shown in **Fig. 3** and **Fig. 4** for T_b of 523 K and 573 K, respectively. In these photographs areas with Newton fringes and without fringes are observed in the

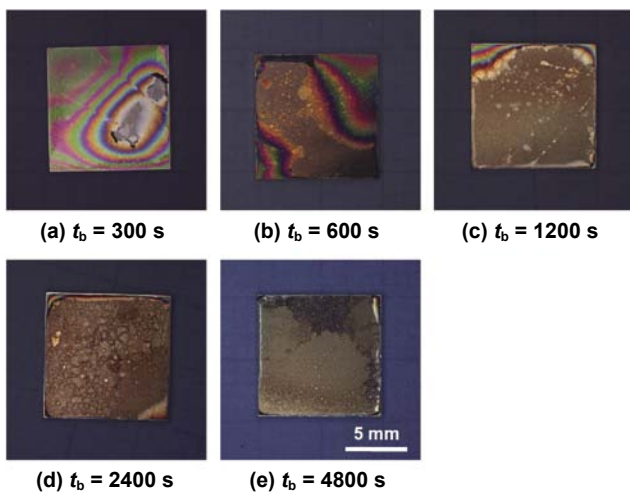


Fig. 3 Appearance of joint interfaces in anodically-bonded joints of zirconium-based metallic glass to soda-lime glass. Bonding temperature was 523 K, and bonding time (t_b) of each joint are shown in the figure.

joint interfaces. The Newton fringes reveal the existence of a gap between the surfaces of the metallic glass and the soda-lime glass, therefore the joint interfaces contacted intimately in the area without the fringes. In both T_b intimate contact areas expanded with t_b , and intimate contact all over the joint interface was achieved with t_b of 4800 s at T_b of 523 K, and with t_b of 1200 s at T_b of 573 K. As seen in Fig. 2, the electric current dropped in early stage of the voltage application, but expansion of the intimate contact areas continued till a later stage at both T_b .

In all obtained joints cracks in the soda-lime glass occurred. In **Fig. 5**, is shown a crack that was found in a joint bonded at T_b of 573 K for t_b of 1200 s for example. The crack started at the edge of the corner of the joint interface, and ran inside of the soda-lime glass. The expansion coefficient of the metallic glass is a little larger than that of the soda-lime glass. In the cooling path after bonding, the contraction of the metallic glass was larger than that of the soda-lime glass. This caused a tensile

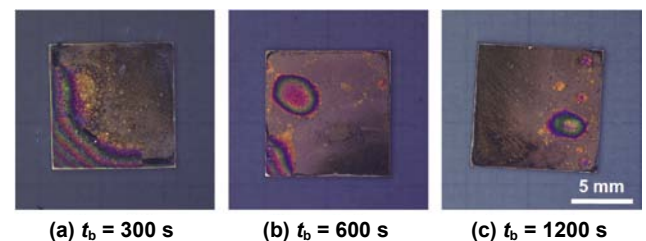


Fig. 4 Appearance of joint interfaces in anodically-bonded joints of zirconium-based metallic glass to soda-lime glass. Bonding temperature was 573 K, and bonding time (t_b) of each joint are shown in the figure.

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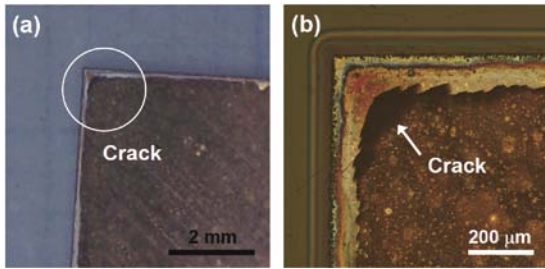


Fig. 5 Crack found in soda-lime glass anodically-bonded to zirconium-based metallic glass at 573 K for 1200 s. Low magnification (a) and enlargement of the area where the crack exists (b).

stress in the soda-lime glass at the edge of the joint interface and cracks in the pattern described above. The thermal stress caused cracks in the soda-lime glass, not separation in the joint interface. This result shows the bond strength of the anodically-bonded joint of zirconium-based metallic glass to silicate glass is rather high. Matching of expansion coefficients of the metallic glass and the soda-lime glass used in this study was not sufficient, but adoption of silicate glass whose expansion coefficient is closer to that of the zirconium-based metallic glass can achieve sound anodically-bonded joints on zirconium-based metallic glass.

In order to take advantage of various features of metallic glass in its joints, it is important to avoid crystallization of the metallic glass in the joining process. Crystallographic characteristics of the anodically-bonded joint of metallic glass to soda-lime glass were investigated by TEM at the nanoscale. A bright-field (BF) image around the anodically-bonded interface of the metallic glass to the soda-lime glass and selected area electron diffraction (SAD) patterns taken from areas shown in the BF image are shown in **Fig. 6**. In the BF

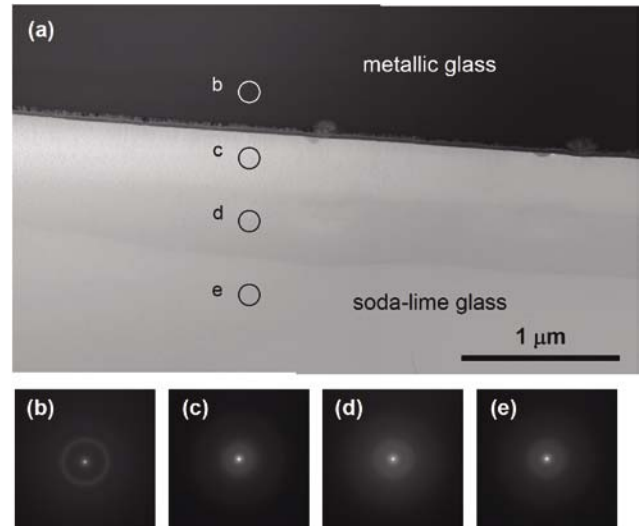


Fig. 6 Microstructure around a joint interface of zirconium-based metallic glass to soda-lime glass anodically-bonded at 573 K for 1200 s. Bright-field image by TEM (a) and SAD patterns taken from areas indicated by corresponding letters in the bright-field image (b)-(e).

image, the metallic glass shows a dark monotonic contrast. In the soda-lime glass two layers of some hundreds nm thick were observed along the bond interface. During anodic bonding some mobile cations drift and concentration distributions of those elements form in the silicate glass adjacent to the bond interface. The layers observed in the soda-lime glass are thought to reflect such concentration distributions. The SAD patterns taken from the metallic glass (Fig. 6(b)), layers in the soda-lime glass (Fig. 6(c) and (d)), and soda-lime glass out of the layers (Fig. 6(e)) all show non-spotty halo rings. These SAD patterns indicate the metallic glass and

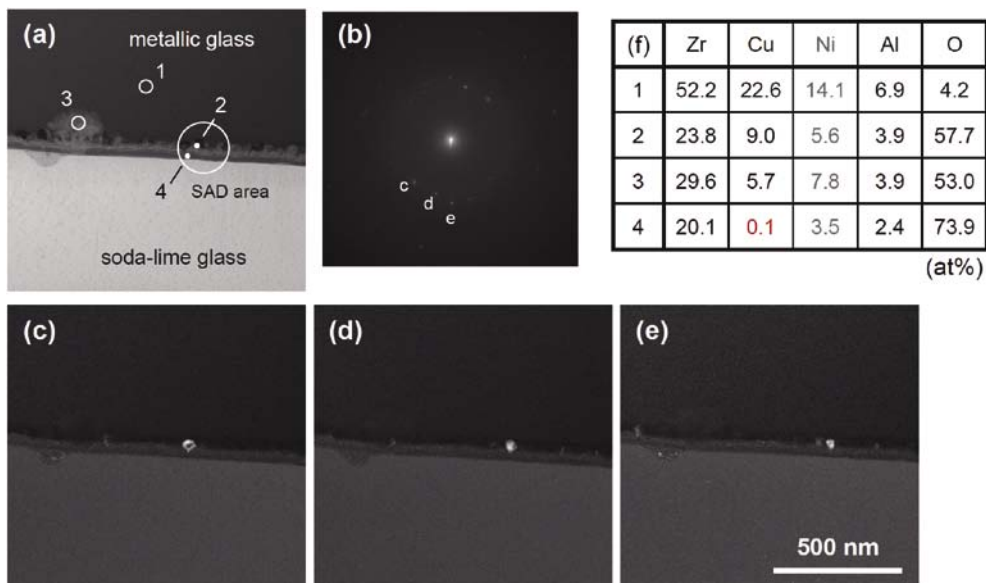


Fig. 7 Oxidation layer at the joint interface of zirconium-based metallic glass to soda-lime glass anodically-bonded at 573 K for 1200 s. Bright-field image (a), SAD pattern taken from the area indicated in the bright-field image (b), and dark-field images taken by reflections indicated by corresponding letters in the SAD pattern (c)-(e). Chemical compositions at points indicated by numbers in the bright-field image is shown in the inset table (f).

the soda-lime glass kept their amorphous states through the bonding process. No crystallization occurred because the bonding temperature of anodic bonding was rather lower than the crystallization temperatures of the metallic glass and soda-lime glass. In the BF image there was observed a layer of different contrast ~100 nm thick at the bond interface. This layer was observed more closely, and results are shown in Fig. 7. In the BF image (Fig. 7(a)), it can be seen the layer was composed of two sublayers. One was a rugged layer with nonuniform contrast contacting with the metallic glass, and the other is a smooth layer with nearly uniform contrast contacting with the soda-lime glass. In the SAD pattern taken from the area around the layer (Fig. 7(e)) some spotty crystalline reflections appeared. In the dark-field (DF) images taken by those reflections (Fig. 7(b)-(d)) particles in the layer contacting the metallic glass appeared bright. These observations revealed the layer contacting the metallic glass was crystalline and that contacting the soda-lime glass was amorphous. Results from energy dispersion X-ray spectroscopy (EDS) spot analysis at the metallic glass and the interfacial layers are shown in the inset table (Fig. 7(f)). High concentration of oxygen in the interfacial layers showed that these layers were of oxides that formed during anodic bonding by the reaction between the metallic glass and oxygen supplied from the soda-lime glass¹¹⁾. A depletion of Cu was observed in the amorphous layer. Ions of Cu have high mobility in the silicate glass, and it was suggested that Cu in the layer migrated to the soda-lime glass side. The change in concentration of Cu may affect the crystallinity of the layer.

It is thought that the formation of the oxidation layers caused the change in color of the joint interfaces that was observed in the appearance inspection.

4. Conclusions

Results from this study are summarized as follows.

- (1) Zr-based metallic glass can be anodically-bonded to soda-lime glass.
- (2) The bonding temperature can be as low as 473 K. Increase of the bonding temperature accelerated the bonding process through the increase of mobility of cations in the soda-lime glass.
- (3) Cracks in soda-lime glass occurred in anodically-bonded metallic glass joint to soda-lime glass. These cracks were thought to result from residual thermal stress. The thermal stress broke the soda-lime glass, but did not cause separation of the joint interfaces. It suggests that the anodically-bonded interface of metallic glass to soda-lime glass is rather strong.
- (4) No crystallization of the metallic glass or the soda-lime glass occurred through the anodic bonding process. At the bond interface, an oxidation layer ~100 nm thick formed. This layer was composed of a crystalline oxide layer contacting to the metallic glass and an amorphous layer with Cu depletion.

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