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# Formation of reaction layers at anodically-bonded metallic glass/silicate glass interfaces<sup>†</sup>

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

## 1. Introduction

Anodic bonding is a method for bonding conductive materials to silicate glass containing alkali ions by applying a D.C. voltage of 100-1000 V between them with the conductive material side anodic. With adequate heating thermal diffusion of alkali ions in silicate glass is activated. Under the influence of the electric field induced by the 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 anions that lose their bonds with the alkali ions. A Coulomb force acting between this negative charge and the positive charge appearing at 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 glass<sup>1)</sup>. 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 softening of the silicate glass<sup>2)</sup>. 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, and high corrosion resistance<sup>3, 4)</sup>. And they have excellent compatibility with microfabrication because of their isotropic nature<sup>5)</sup>. These features make BMGs promising materials for microsensors or micromachines. It is desirable to establish anodic bonding of metallic glass in order to realize micro devices made of metallic glass. In this study, anodic bonding of zirconium-based metallic glass to two different kinds of silicate glass, soda-aluminosilicate glass Matsunami 801 and soda-potassia glass Matsunami 7622 was tried with various bonding temperatures and voltage application times. These silicate glass materials have thermal expansion coefficients near to that of the used metallic glass. Joint interfaces in the obtained joints were examined by appearance and the microstructure around the joint interface was observed by transmission electron

microscopy (TEM).

## 2. Experimental

Experimental materials are zirconium-based metallic glass ( $Zr_{55}Cu_{30}Al_{10}Ni_5$ ) and silicate glass, soda-aluminosilicate glass Matsunami 801 and soda-potassia glass Matsunami 7622. Linear expansion coefficients of the metallic glass, 801 glass, and 7622 glass are  $\sim 10 \times 10^{-6} / K$ <sup>6)</sup>,  $10.7 \times 10^{-6} / K$  and  $12 \times 10^{-6} / K$ <sup>7)</sup>, respectively. Crystallization temperature of the metallic glass is  $\sim 750 K$ <sup>8)</sup>. 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 silicate glass was provided as disks of 1 mm in thickness and 25 mm in diameter. Both sides of the disks were finished by mechanical grinding and polishing.

The procedure of anodic bonding was as follows.

The silicate glass piece was placed on the negative electrode plate. The surface of the silicate 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 silicate 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. Bonding temperatures adopted for 801 glass joints were 483 K, 523 K, and 563 K, and those for 7622 glass joints were 523 K, 564 K, and 603 K. After the temperature of specimens settled, a bonding voltage of 500 V was applied to the specimens for a predetermined bonding time ( $t_b$ ) with the metallic glass side anodic. The electric current that passed through the specimens ( $i_b$ ) was monitored during the application of the voltage. After the voltage application, specimens were cooled slowly in the bonding apparatus.

In order to evaluate the progress of bonding, the appearances of joint interfaces of the obtained joints were examined visually through the silicate glass. Microstructure around the joint interfaces was investigated closely by TEM. Thin foil specimens for TEM were cut from the

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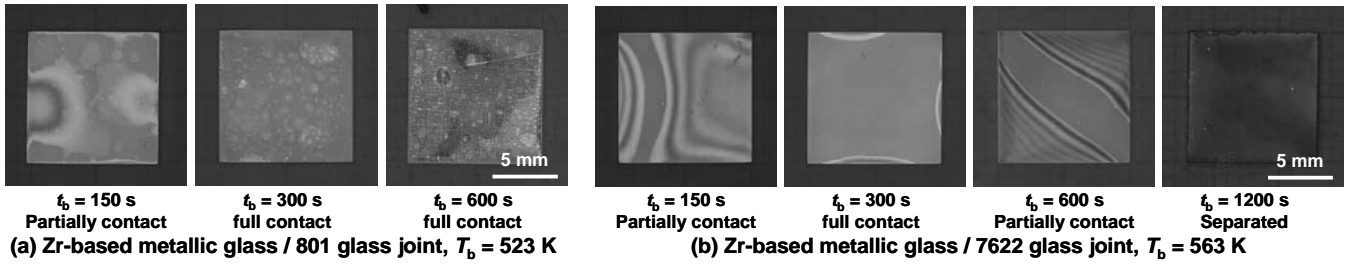


Fig. 1 Appearances of the metallic glass / silicate glass anodically-bonded interface.

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

In Fig. 1 are shown the appearances of the metallic glass silicate glass anodically-bonded interfaces. The 801 joints shown in Fig. 1 were bonded at 563 K, and the 7622 joints were bonded at 563 K. In the joint interfaces, the areas in which intimate contact of the metallic glass to the silicate glass showed a little dark tone, and the areas in which metallic glass was separated from the silicate glass showed bright tone with Newton fringes. (In the 7622 glass joint of  $t_b = 1200$  s all the joint interface was separated. The appearance was observed without 7622 silicate glass.) As is shown in Fig. 1(a), in 801 glass joints the ratio of the intimate contacting area increased with the voltage application time, and progress of the bonding became faster at higher bonding temperatures. This is a usual tendency in

anodic bonding. At a higher temperature drift of alkali ions in silicate glass with voltage application is enhanced more strongly, and buildup of the alkali ion depletion layer and consequently the bonding process become quicker. On the other hand, anodic bonding of metallic glass to 7622 glass showed a peculiar progress (Fig. 1(b)). At  $T_b = 563$  K, the 7622 glass joints once achieved intimate contact of almost all the joint interface with the voltage application for 300 s. But the joint interfaces were separated again with longer voltage application. At a higher  $T_b$  of 603 K, all the metallic glass / 7622 glass joint interfaces remained separated with the voltage application from 75 s to 300 s.

Microstructures around the joint interfaces in a 801 glass joint anodically-bonded at 563 K with voltage application for 300 s and a 7622 joint bonded at 523 K with voltage application for 4800 s were observed by TEM. In Fig. 2 is shown the microstructure of the joint interface in the 801 joint. Reaction products formed two layers at the joint interface. One is a crystalline layer  $\sim 70$  nm thick contacting the metallic glass, and another is an amorphous layer  $\sim 20$  nm thick contacting the silicate glass. Chemical analysis by energy dispersion X-ray Spectroscopy (EDS) showed existence of high-concentrations of oxygen in these layers. Therefore, these reaction layers were thought to be of oxide formed by reaction of elements from the metallic glass with oxygen from the silicate glass in anodic bonding. And Cu concentration in the amorphous oxide layer was very low. The microstructure around the joint interface in the 7622 joint is shown in Fig. 3. Reaction products were found at the joint interface also. But the reaction layer in the 7622 joint formed a single layer  $\sim 40$  nm thick. This layer contained some crystals, but mainly formed of amorphous. EDS analysis showed high oxygen concentration and low Cu concentration in the reaction layer.

Results from TEM observation suggest that the peculiar progress of metallic glass / 7622 glass is concerned with the formation of Cu-poor amorphous oxide layer at the joint interface.

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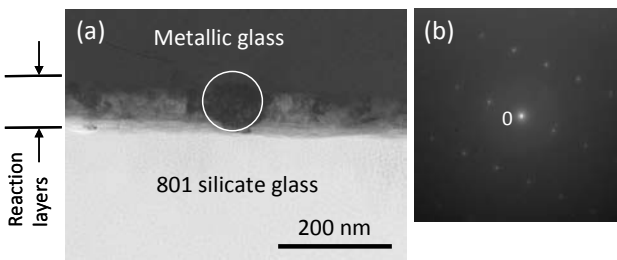


Fig. 2 Microstructure around the metallic glass / 801 silicate glass anodically-bonded joint interface. Bright-field image (a), and SAD pattern taken from the area indicated by the circle in the image a (b).

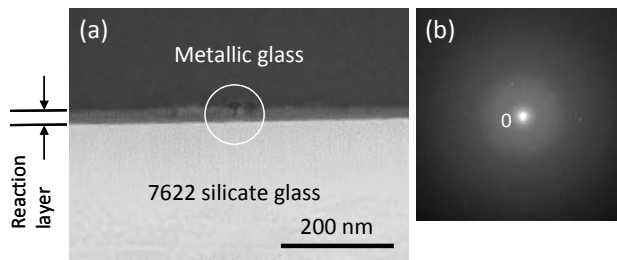


Fig. 3 Microstructure around the metallic glass / 7622 silicate glass anodically-bonded joint interface. Bright-field image (a), and SAD pattern taken from the area indicated by the circle in the image a (b).

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