Title	Disjunction of Metal/Glass Anodically-bonded Interface by Application of Reverse Voltage(Materials, Metallurgy & Weldability)
Author(s)	Takahashi, Makoto; Yasuda, Hiroki; Ikeuchi, Kenji
Citation	Transactions of JWRI. 2004, 33(1), p. 25-32
Version Type	VoR
URL	https://doi.org/10.18910/6796
rights	
Note	

Disjunction of Metal/Glass Anodically-bonded Interface by Application of Reverse Voltage[†]

Makoto TAKAHASHI*, Hiroki YASUDA, Kenji IKEUCHI*****

Abstract

A voltage in the opposite direction to that of anodic bonding was applied to anodically-bonded joints of Fe and Kovar alloy (Fe-Ni-Co alloy) to borosilicate glass at a temperature at which thermal diffusion of the alkali ions in the glass was activated. Disjunction of the bond interfaces occurred in the Kovar/glass joints. On the other hand, the Fe/glass joints retained cohesion of their bond interface after a long application of reverse voltage. At the bond interface in an as-bonded Kovar/glass joint, a reaction layer of crystalline Fe oxide formed by the reaction between Fe from the Kovar alloy and O from the glass. The content of Fe in the Kovar alloy adjacent to the bond interface decreased. In an Fe/glass joint a reaction layer of amorphous Fe-Si oxide formed. This layer was much thicker than the reaction layer in the Kovar/glass joint. After application of the reverse voltage, Fe in the amorphous oxide layer in the Fe/glass joint was replaced by alkali ions. It was suggested that this process mitigated concentration of alkali ions at the bond interface and the formation of a Na rich brittle phase. The Kovar alloy adjacent to the bond interface in the Kovar/glass joint was rich in Ni and Co contents. This result suggested that properties of the Kovar/glass bond interface were similar to those of Ni/glass or Co/glass bond interface to some extent. Effects of reverse voltage on anodically-bonded Ni/glass and Co/glass joints were examined, and disjunction occurred in both joints. From these results it was suggested that the disjunction in anodically-bonded Kovar/glass interface was caused by the alloying elements Ni and Co.

KEY WORDS: (anodic bonding), (disjunction of joints), (borosilicate glass), (iron), (nickel), (cobalt), (Kovar alloy), (ionic conduction), (alkali ion), (interfacial reaction)

1. Introduction

Anodic bonding is a method for bonding a metal or semiconductor to glass containing alkali ions by applying a D.C. voltage between them with the metal side being the anode. A glass sheet and the metal part to be joined are stacked on a conductor base plate. The materials are heated to a bonding temperature of 500-600 K. The metal to be bonded is connected to the positive terminal of a D.C. power source, and the base plate is connected to the negative terminal. A bonding voltage of 100-1000 V is applied to them. The alkali ions in the glass drift toward the cathode side, and an alkali ion depletion layer forms in the 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 ion. An electrostatic force acting between this charge and the charge appearing on the surface of the anode metal brings the glass and the metal in intimate contact, and a permanent bond is achieved by the chemical reaction at the interface [1)]. The bonding temperature for anodic bonding is relatively low and deformation of the glass does not occur in this temperature range [2)].

The application of voltage to an anodically-bonded joint in the opposite direction to that for bonding causes degradation of the joint: disjunction of the bond interface, cracks in the glass, discoloration of the bond interface, and so on [3,4,5,6)]. These phenomena have harmful effects on the reliability of anodically-bonded joints if the joints receive reverse voltages in the course of manufacturing or during use. The phenomena accompanying the application of reverse voltage change with the materials that are joined to the glass [5)]. It was found that the disjunction of anodically-bonded joints of a Kovar alloy to borosilicate glass was caused by the application of a reverse voltage [4)]. Kovar alloy is composed mainly of Fe, Ni, and Co, and the role of each component on the disjunction has not been clarified. In this study, a reverse voltage was applied to anodically-bonded joints of pure

---

† Received on July 8, 2004

* Assistant Professor
** Graduate Student (present affiliation: Fujitsu Co. Ltd.)
*** Professor

Transactions of JWRI is published by Joining and Welding Research Institute of Osaka University, Ibaraki, Osaka 567-0047, Japan

metals of Fe, Ni, and Co to borosilicate glass, and the effects were investigated macroscopically and microscopically.

2. Experimental

The experimental materials were Kovar alloy and borosilicate glass "Matsunami #0700". The chemical compositions of both materials are shown in **Table 1**. The expansion coefficient of the glass was similar to that of Kovar alloy in a temperature range of room temperature to ~800 K. The glass was supplied as disks of 1 mm in thickness and 25 mm in diameter. The surfaces of the glass disk were polished. The Kovar alloy was cut into disks of 2 mm in thickness and 20 mm in diameter. One side of the disk was given a glossy finish by grinding with metallographic paper and buffing with 0.25 μm diamond paste. In order to produce an anodically-bonded interface of pure Fe, Ni, and Co to glass, the buffed surface of the Kovar disk was coated with a pure metal layer by RF sputtering in an Ar atmosphere of ~2 Pa at an RF power of 250 W for 4800 s, and this coated surface was bonded to the glass. The purity of the sputter targets was 99.9wt%. Deposited layers were ~1 μm thick. Some of the coated disks were annealed at 873 K for 3600 s in a vacuum of ~10^{-4} Pa in order to increase the size of crystal grains in the sputtered layers. The coated surface was buffed with diamond paste for a short time to remove contamination and roughness of the deposited layer just before the bonding. The atmosphere of the anodic bonding was a vacuum of ~10^{-4} Pa. The bonding temperature (T_b) was 613 K, the bonding voltage (V_b) was 500 V, and the bonding time (t_b) was 300 s. Joints of the Kovar alloy without pure metal coating to the glass were produced for comparison.

Table 1 Compositions of the Kovar alloy (a) and the borosilicate glass (b) (mass%).

	C	Co	Fe	Mn	Ni	Si
Composition	0.003	16.2	53.65	0.45	29.6	0.1

	SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	Li_2O	BaO	Fe_2O_3	Sb_2O_3
Composition	70.4	3.16	18.5	3.42	3.74	0.36	0.04	0.02	0.36

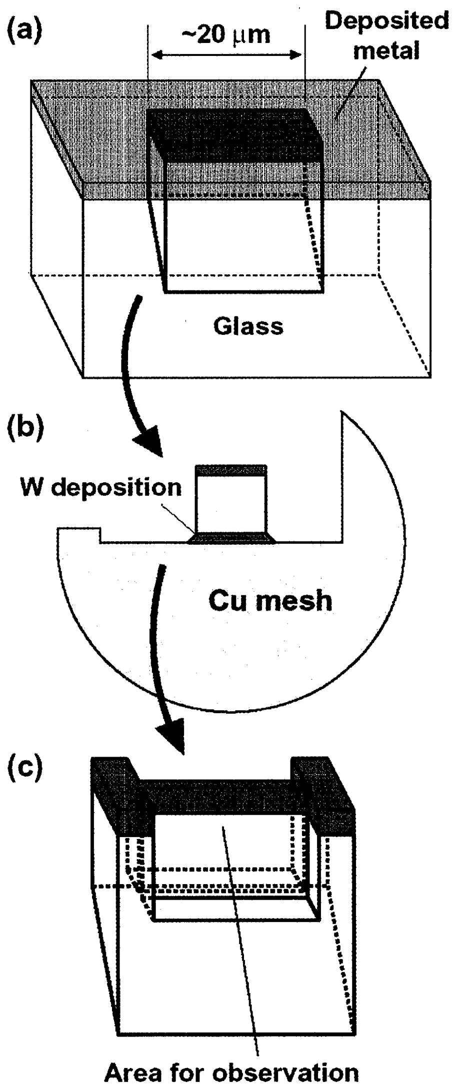


Fig. 1 Preparation of TEM specimen by m-sampling FIB. A small piece was cut out from the surface of the specimen (a), the piece was fixed on the Cu mesh (b), and the observation area of the piece was made into thin film (c).

A reverse voltage (V_r) of 500 V was applied to the joints at 613 K (T_r) in a vacuum of ~10^{-4} Pa. The application time of the voltage (t_r) was changed from 300 s to 2400 s. After that, visual examinations of the bond interfaces were carried out.

The as-bonded interfaces of the Fe/glass joint and the Kovar alloy/glass joint were observed by transmission electron microscopy (TEM). These joints were cut in a direction perpendicular to the bond interfaces, and the cross-sections were ground with metallographic paper and buffed. A thin foil for TEM was cut out from the bond interface region on the cross-section, with HITACHI FB-2000S focused ion beam (FIB) processing system, equipped with a micro-sampling system. With this system, the TEM specimens can be produced from the surface of bulk specimens in a perfectly dry process. It was difficult to prepare TEM specimens of the bond interface in the joints receiving reverse voltage using the same technique as for specimens of as-bonded joints, because of the high concentration of Na in the area around the interface. During mechanical polishing the specimen was exposed to water, and Na rich structures were washed away. For TEM observation of anodically-bonded Fe/glass interface, anodically-bonded joints of thin Fe film to glass were prepared. A layer of Fe ~1 μm thick was deposited on surface of the glass by RF sputtering, and a bonding voltage and reverse voltage were applied to this layer and the glass substrate. After that, a thin foil specimen for TEM was cut out from the area around the interface between the Fe layer and glass by a micro-sampling FIB processing. In **Fig. 1** is shown the procedure for the preparation of TEM specimens. In this way, TEM specimens of an anodically-bonded interface receiving reverse voltage were prepared without exposure of the interface to water.

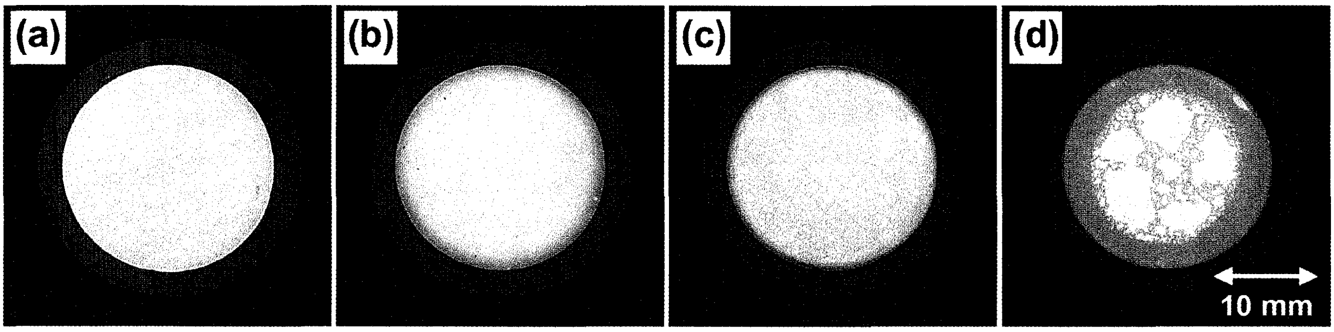


Fig. 2 Anodically-bonded Kovar alloy/borosilicate glass joints as-bonded (a), receiving the reverse voltage for 300 s (b), 420 s (c), and 600 s (d).

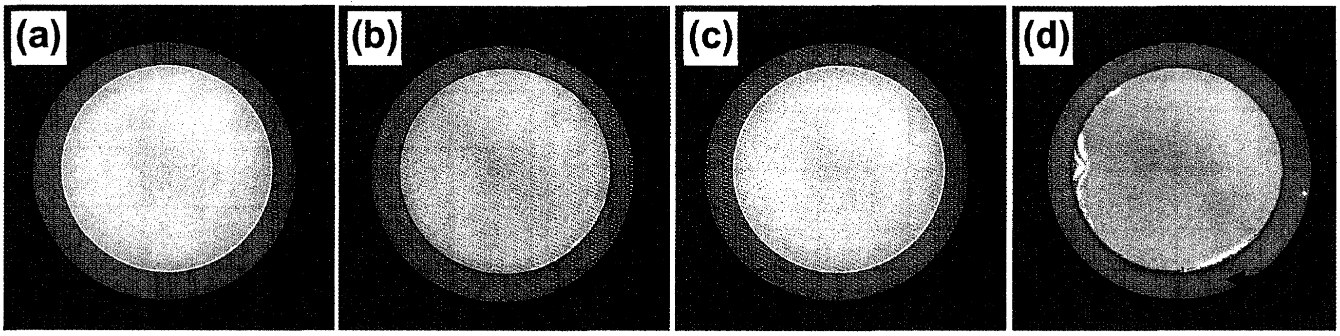


Fig. 3 Anodically-bonded Fe/borosilicate glass joints as-bonded (a), receiving the reverse voltage for 600 s (b), 1200 s (c), and 2400 s (d).

The TEM observations and EDS analyses were carried out with a JEOL JEM-2010 transmission electron microscope operating at 200 kV.

3. Results and Discussion

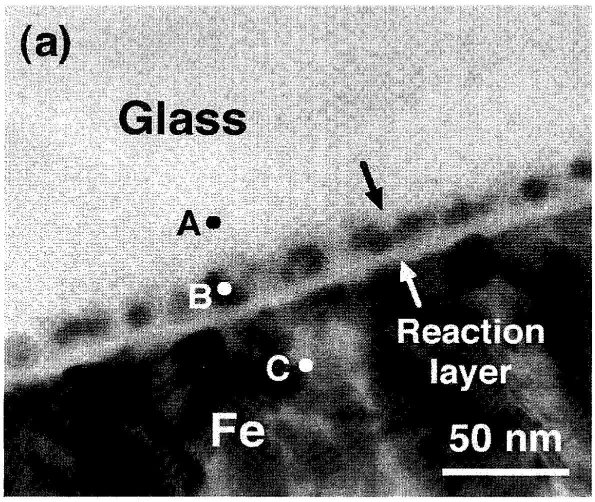
The macroscopic changes in bond interfaces of anodically-bonded Kovar alloy/glass joints with the application of the reverse voltage are shown in **Fig. 2**. In the as-bonded joint (Fig. 2(a)), intimate contact was achieved on the whole joint interface. In the joint receiving the reverse voltage for 300 s (Fig. 2(b)), obvious disjunction could not be detected by visual inspection. After application of the reverse voltage for 420 s (Fig. 2(c)), many small exfoliations appeared on the joint interface. In the joint receiving the reverse voltage for 600 s (Fig. 2(d)), the exfoliations aggregated and large disjunction areas were formed in the central part of the joint interface. Cracks in the glass (another typical defect found in anodically-bonded joints receiving reverse voltage [5, 6]) were not found in these joints.

The appearances of the Fe/glass joints receiving the reverse voltage are shown in **Fig. 3**. The Kovar disks (and Fe layers on their surfaces) used in these joints were not annealed. Good bonding was achieved on the whole joint interface in the as-bonded joint (Fig. 3(a)). After application of reverse voltage, peripherally areas of the bond interfaces were colored brown slightly (Fig. 3 (b)-(d)), but even in the joint receiving the reverse voltage for 2400 s (Fig. 3(d)), no disjunction was detected. The joint faults that were found in the joints receiving the reverse voltage for 600 s and 2400 s (Figs. 3(b) and (d)) had already existed before the application of the reverse voltage.

In order to investigate the origin of the difference between Kovar/glass and Fe/glass joints to the application of the reverse voltage from the viewpoint of microstructure, the joint areas in as-bonded Fe/glass and Kovar/glass joints were observed by TEM.

The results from TEM observations of the microstructure around the bond interface in an Fe/glass joint and EDS point analyses are shown in **Fig. 4**. At the bond interface a reaction layer was found. This layer appeared as if the interface was lined with particles 20-30 nm in size. By EDS, it was found that this layer contained Fe and Si at high concentrations (point 'B' in Fig. 4(a)). This layer contained much O also (though in the tables in Fig. 4 and Fig. 5 the content of O is omitted because the precise quantification of light elements like O is difficult by EDS). In the selected area electron diffraction (SAD) pattern from the area around the interface, no reflection from the layer was found. These results showed that this layer consisted of an amorphous Fe-Si complex oxide. It was thought that the Fe atoms from the Fe layer penetrated into the glass, and reacted with excess O ions in the alkali depletion layer to form the complex oxide layer.

In **Fig. 5** is shown the microstructure around the bond interface in a Kovar/glass joint and the results from the EDS point analyses. At the bond interface, a reaction layer 5-10 nm thick was found. By EDS analysis, it was found that this layer contained Fe and O of high concentration (point 'B' in Fig. 5 (a)). In the SAD pattern

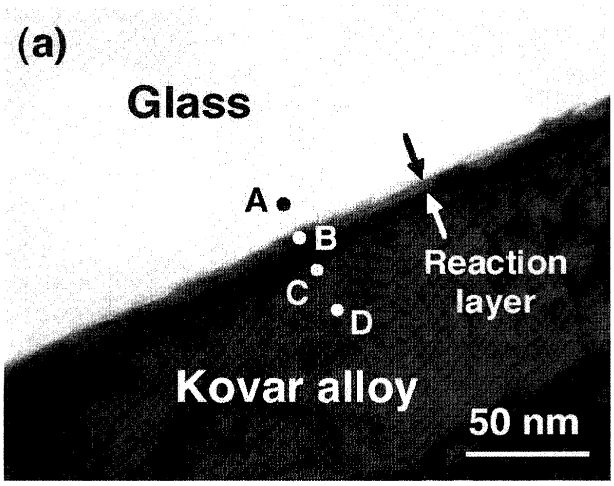


(b)

	Si	Fe	Al	K	Na
A	98.6	0.7	0.2	0.0	0.5
B	50.8	45.5	1.7	2.0	0.0
C	1.6	97.4	0.6	0.0	0.4

(unit: at%)

Fig. 4 Microstructure around the bond interface in an anodically-bonded Fe/borosilicate glass joint as bonded (a) and the chemical compositions derived by EDS at points indicated in **a** (b). From points 'A' and 'B,' strong characteristic X-rays of oxygen were detected by EDS in addition to the elements listed in **b**.



(b)

	Si	Fe	Ni	Co	Al
A	95.7	1.5	0.4	0.3	2.1
B	14.1	80.6	3.2	1.2	0.9
C	1.5	45.1	32.9	20.4	0.1
D	0.1	57.6	26.4	15.9	0.0

(unit: at%)

Fig. 5 Microstructure around the bond interface in an anodically-bonded Kovar alloy/borosilicate glass joint as bonded (a) and chemical compositions derived by EDS at points indicated in **a** (b). From points 'A' and 'B', strong characteristic X-rays of oxygen were detected by EDS in addition to the elements listed in **b**.

from the area around the interface, the reflections from the layer were found. These results showed that this layer consisted of a crystalline Fe oxide. Analyses of the Kovar alloy showed that, in the area in the Kovar alloy adjacent to the bond interface (point 'C' in Fig. 5(a)), the content of Fe was lower than that in the inside area (point 'D' in Fig. 5(a)). Composition of the Kovar alloy in the inside area is very similar to that of the as-received Kovar alloy (shown in Table 1). It was thought that Fe in the area near the interface was oxidized preferentially by excess O ions from the alkali depletion layer in the glass to form the Fe oxide layer. It can be thought that this Ni and Co rich layer acted as a barrier against further penetration of Fe into the glass and prevented growth of the reaction layer.

From the observations by TEM, two possible mechanisms can be thought to cause the difference between Kovar/glass joints and Fe/glass joints in behavior with application of reverse voltage. One possibility is as follows:

The cause of the disjunction of anodically-bonded Kovar alloy/glass joints is thought to be the degradation of glass near the bond interface with the accumulation of Na during the application of reverse voltage [5]. The concentration of Na in the glass causes the formation of a brittle Na-Si crystalline complex oxide phase, and rupture of joints occurs through this brittle phase. An anodically-bonded Fe/glass joint had a much thicker reaction layer at the bond interface than that in the Kovar alloy/glass joint. This thicker reaction layer blocked accumulation of Na at the bond interface and formation of the brittle Na-Si crystalline complex oxide.

The other possibility is as follows:

By EDS analysis of the Kovar/glass joint it was shown that, in the area adjacent to the bond interface the Fe content of the Kovar alloy had decreased from that of the as-received Kovar alloy, and consequently Ni and Co contents had increased. Therefore, these alloying elements should have strong influences on the properties of anodically-bonded Kovar/glass interfaces. If anodically-bonded Ni/glass or Co/glass joints are easily unjointed by application of reverse voltage, this property may be reflected in the behaviors of Kovar/glass joints.

Reaction of the Fe-Si complex oxide layer at the bond interface in an Fe/glass joint with Na accumulating at the interface with application of reverse voltage was observed by TEM in order to confirm the capability of the layer to avoid build-up of Na. The microstructure around the bond interface in an anodically-bonded joint

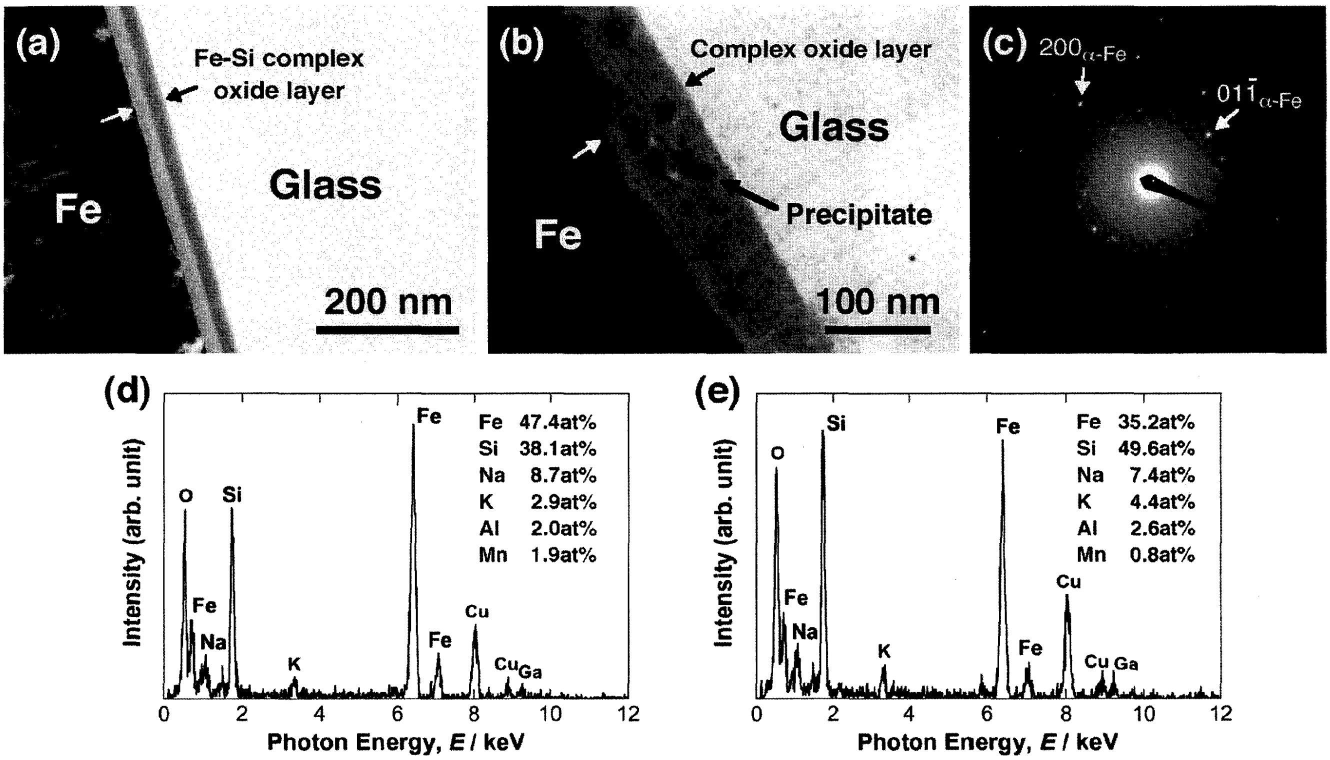


Fig. 6. The changes in microstructure around the bond interface in an anodically-bonded Fe/borosilicate glass joint with the application of reverse voltage: TEM micrographs of bond interfaces as-bonded (a) and receiving the reverse voltage (b), SAD pattern from the complex oxide layer in **b** (c), EDS spectra from the precipitate indicated in b (d) and a position in the complex oxide layer in **b** other than the precipitates (e). (Signals for Cu and Ga in the EDS spectra were from the Cu mesh sheet for TEM and contamination from the Ga FIB process. The specimen materials contained none of these elements.)

of the Fe layer deposited on the glass with the glass substrate and its change with the application of reverse voltage are shown in **Fig. 6**. The TEM micrograph of the interfacial area in an as-bonded joint (T_b = 613 K, the V_b = 500 V, and t_b = 300 s) is shown in Fig. 6(a). A reaction layer ~40 nm thick was found between the Fe layer and the glass. By EDS, Fe, Si, and O of high concentration were detected in this layer, and the SAD pattern taken from this layer was a halo pattern. This layer consisted of an amorphous Fe-Si complex oxide. The difference in morphology between this layer and the layer shown in Fig. 4 might reflect the difference in the closeness of Fe to the glass before the bonding process.

The TEM micrograph shown in Fig. 6(b) shows the changes in microstructure around the bond interface with the application of the reverse voltage of 500 V at 613 K for 1200 s. The thickness of the reaction layer increased to ~80 nm, and particles of 10~30 nm in size were precipitated in the layer. A SAD pattern from the central area in Fig. 6(b) is shown in Fig. 6(c). The spots indicated by white arrows were from the precipitate indicated by a black arrow in Fig. 6(b). These spots constituted a 011 pole figure of an α-Fe crystal. The EDS spectrum from the position of the same precipitate is shown in Fig. 6(d). An EDS spectrum from a position other than the precipitates is shown in Fig. 6(e). The content of Fe at the position of the precipitate was higher than that at the other position. (Strong characteristic X-rays of Si and O were observed in the EDS spectrum in Fig. 6(d) because the precipitate was buried in the reaction layer. The composition observed by EDS did not reflect only the composition of the precipitate). These results show that the precipitates consisted of metallic Fe. A high concentration of Na and K in the layer was found from the EDS results. It was believed that, Fe atoms in the Fe-Si complex oxide were substituted by alkali ions that migrated toward the bond interface with application of the reverse voltage. Then the Fe precipitated as metal Fe in the reaction layer. The Na ions substituting for Fe ions in the reaction layer were dispersed in the layer instead of concentrating at the interface.

Effect of reverse voltage on anodically-bonded Ni/glass and Co/glass interfaces was investigated. Pure Ni and Co layers on Kovar disks were anodically-bonded to glass. Crystal grains in as-deposited metal layers had very fine columnar structures (Fig. 4). The thickness of a column was ~50 nm. This extremely fine structure could have some effect on susceptibility of anodically-bonded interfaces to application of reverse voltage, for example, through enhancement of grain boundary diffusion. In order to increase the crystal grain size in deposited metal layers, Kovar plates coated with Ni and Co were annealed at 873 K for 3600 s. With this heat treatment, the crystal grain size in the layers increased to several micrometers.

In **Fig. 7** are shown the changes in anodically-bonded Ni/glass interfaces with application of

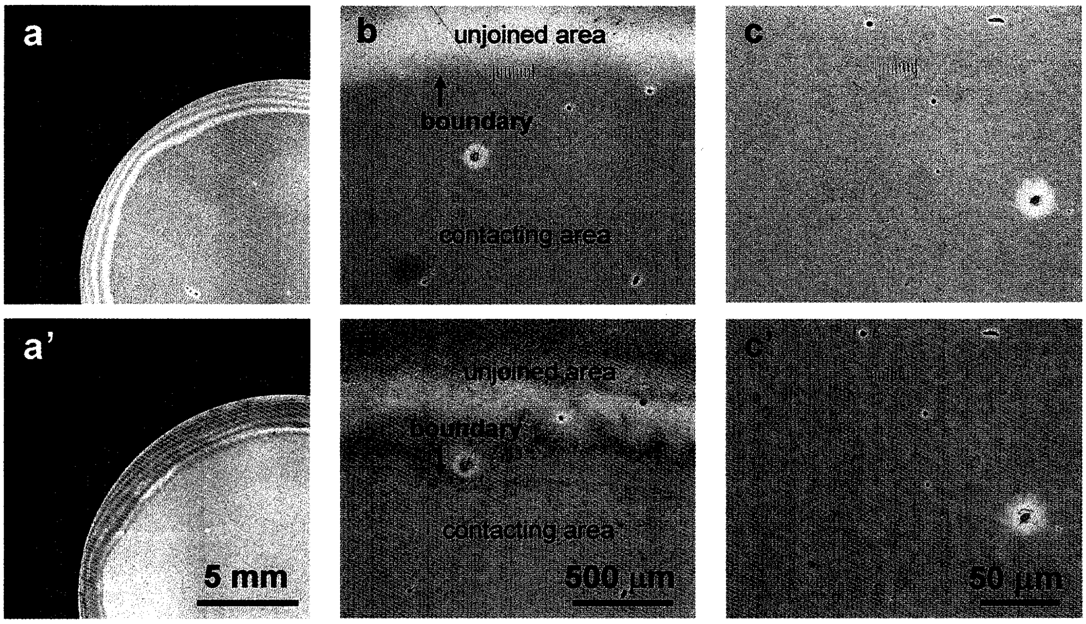


Fig. 7 Changes in an anodically-bonded Ni (annealed at 873 K)/glass interface by application of reverse voltage. The as-bonded state (a, b, and c) and the state after the application of reverse voltage. Macroscopic photographs (a, a'), and optical micrographs of the periphery (b, b') and the central part (c, c').

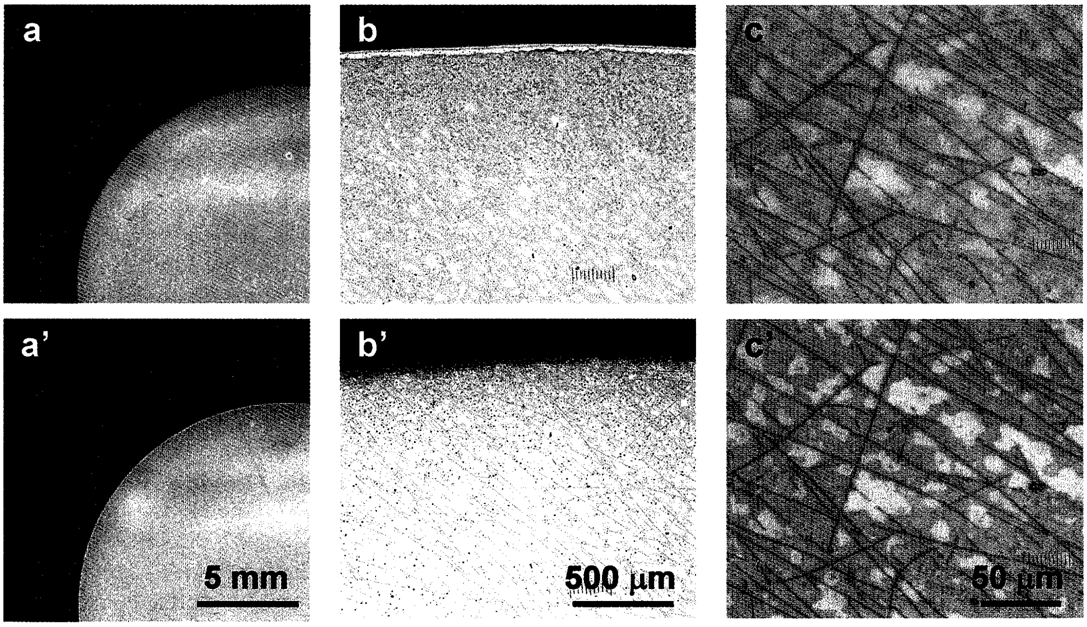


Fig. 8 Changes in an anodically-bonded Co (annealed at 873 K)/glass interface by application of reverse voltage. The as-bonded state (a, b, and c) and the state after the application of reverse voltage. Macroscopic photographs (a, a'), and optical micrographs of the periphery (b, b') and the central part (c, c').

a reverse voltage of 500 V for 600 s. Bonding parameters of the joints were as listed in the experimental section. With these parameters, intimate contact of the whole joint interface was not achieved, and unjoined areas remained in the periphery (Fig. 7(a)). Bondability of Ni to glass by anodic bonding is lower than for Fe and Kovar alloy. After the application of reverse voltage, the unjoined area broadened a little (Fig. 7(a')). This disjunction could be observed clearly by optical microscopy (Fig. 7(b) and (b')). After application of reverse voltage, the boundary between unjoined area and joined area continued inside the joint interface. In the central part of the joint interface, the change was not obvious with the application of reverse voltage.

As is shown in **Fig. 8**, anodically-bonded Co/glass interfaces were also unjointed by application of reverse voltage. In the as-bonded state, intimate contact was achieved all over the joint interface (Fig. 8(a)).

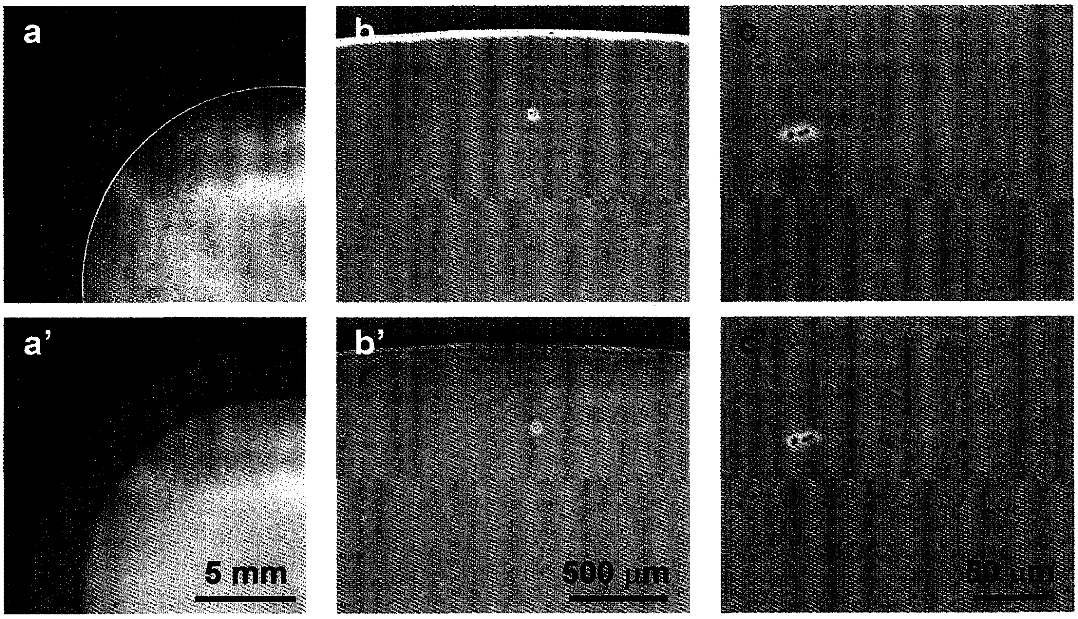


Fig. 9 Changes in an anodically-bonded Fe (annealed at 873 K)/glass interface by application of reverse voltage. The as-bonded state (a, b, and c) and the state after the application of reverse voltage. Macroscopic photographs (a, a'), and optical micrographs of the periphery (b, b') and the central part (c, c').

Bondability of Co to glass by anodic bonding was good. After the application of reverse voltage, obvious change was not detected in appearance of the joint interface (Fig. 8(a')), but by optical microscopy, formation of many exfoliations was found (Fig. 8(b')). These exfoliations were not observed before the application of reverse voltage (Fig. 8(a)). Formation of exfoliations was observed in the central part of the joint interface also (Fig. 8(c) and (c')).

In the experiment for which results are shown in Fig. 3 (effect of application of reverse voltage to anodically-bonded Fe/glass interfaces) as-deposited Fe layers were used. To ensure consistency with the experiments of Ni/glass joints and Co/glass joints, effect of reverse voltage on the anodically-bonded joint of an Fe deposited layer annealed at 873 K for 3600 s to borosilicate glass was investigated. The results were shown in **Fig. 9**. On the macroscopic scale (Fig. 9(a) and (a')) and also the microscopic scale (Fig. 9(b), (b'), (c), and (c')), no disjunction and other joint faults were induced by application of reverse voltage.

The thick reaction layer in the Fe/glass joint prevented concentration of Na at the bond interface through the substitution of Na for Fe in the layer. Growth of the reaction layer in the Kovar/glass joint was prevented by a Ni and Co rich layer forming in the area adjacent to the bond interface in the Kovar alloy. Anodically-bonded Ni/glass and Co/glass interfaces were unjointed by the application of reverse voltage. In particular, the mode of disjunction of the Co/glass interface (formation of small exfoliations) was similar to that of the Kovar/glass interface.

From these results, it was concluded that the disjunction of anodically-bonded Kovar/glass interfaces was the effect of the alloying elements Ni and Co.

4. Conclusions

Effects of the application of reverse voltage on anodically-bonded joints Fe, Ni, Co, and an alloy of these elements, Kovar alloy to borosilicate glass were examined macroscopically and microscopically. Summary of the results are listed below:

(1) Application of reverse voltage induced disjunction of anodically-bonded joints of Kovar alloy to glass, but no disjunction occurred in joints of Fe to glass by the same process.

(2) A reaction layer of crystalline Fe oxide 5-10 nm thick was found at the bond interface of the as-bonded Kovar/glass joint. The reaction layer in the Fe/glass joint was 20-30 nm thick and consisted of amorphous Fe-Si complex oxide. In the area adjacent to the joint interface, the Fe content of the Kovar alloy lowered by preferential oxidation of Fe.

(3) In the reaction layer at the bond interface in the Fe/glass joint receiving the reverse voltage, metal Fe particles were precipitated. This occurred as the result of the substitution for Fe in the reaction layer of the Fe-Si complex oxide by alkali ions accumulating at the bond interface, with the application of the reverse voltage.

(4) Anodically-bonded joints of Ni and Co were unjointed by application of reverse voltage. It was suggested that the disjunction of Kovar/glass joint by application of reverse voltage was due to the effect of Ni and Co that were concentrated at the Kovar/glass bond interface during anodic bonding.

REFERENCES

1) G. Wallis, D. I. Pomerantz, J. Appl. Phys., 40 (1969) 3976.
2) K. Hiller, R. Hahn, C. Kaufmann, S. Kurth, K. Kehr, T. Gessner, Proc. SPIE Int. Soc. for Optical Engineering, 3878 (1999) 58.
3) K. B. Albaugh, Materials Letters, 4 (1986) 465.
4) M. A. Morsy, K. Ikeuchi, M. Ushio, H. Abe, Mat. Trans. JIM, 37 (1996) 1511.
5) M. Takahashi, S. Nishikawa, K. Ikeuchi, Proc. the 7th Int. Symp. JWS, (2001) 851.
6) M. M. Visser, J. A. Plaza, D. T. Wang, A. B. Hanneborg, J. Micromechanics and Microengineering, 11 (2001) N1.