Mechanism of Enlargement of Intimately Contacted Area in Anodic Bonding of Kovar Alloy to Borosilicate Glass

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The effects of the bonding temperature and voltage on the rate of the enlargement of intimately contacted area in the anodic bonding of the Kovar alloy to borosilicate glass have been studied systematically in order to obtain better understanding of the rate controlling factor of the process. It was suggested that the attainment of intimate contact was controlled by two factors having different activation energies depending on the bonding temperature. At bonding temperatures higher than 669–687 K (depending on the bonding voltage), the estimated activation energy was close to that of the viscous flow of the glass. At lower bonding temperatures, the estimated activation energy was close to that of the conductivity of the glass. A mechanism of the enlargement of intimately contacted area during the anodic bonding is proposed to explain these results.

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I. Introduction

Anodic bonding is a process by which certain metals or semiconductors can be bonded to glass at temperatures below the softening point of the glass under a high electrostatic field that is usually applied by connecting the glass and metal with cathode and anode, respectively⁽¹⁾. Application of the anodic bonding has also been extended to bonding of metal to ceramic, ex., β -alumina and zirconia⁽²⁾⁽³⁾. The low bonding temperature broadens the area of application to those devices whose characteristics are impaired by exposure to high temperatures, ex., electronic sensors and micromachining. Also the lower bonding temperature allows the bonding process to be applied to materials of low melting point, ex., aluminum. The process can also be applied to optics and electronic optics since no macroscopic distortion takes place.

According to Wallis and Pomerantz⁽¹⁾, the application of electric field to glass in a range of temperatures at which cations in glass, viz., Na^+ ions are mobile, moves them toward the cathode electrode from the anode, resulting in the formation of Na^+ -depleted layer adjacent to the glass/anode interface. In this Na^+ -depleted layer, negative charges will be accumulated unless the number of cations ejected into the glass from the anode is enough to compensate the charge accumulation due to the Na^+ depletion. The charge accumulation in the depletion layer exerts electrostatic force that attracts the anode metal surface to the glass surface to bring them into intimate contact.

Wallis⁽⁴⁾, DeNee⁽⁵⁾ and Borom⁽⁶⁾ suggested that the surface of the anode metal was oxidized by oxygen supplied from the glass and the formation of the oxide layer con-

tributed significantly to the bond strength.

On the other hand, Brownlow⁽⁷⁾ has suggested that the Joule heating of the glass layer adjacent to the anode metal was needed to increase its temperature so that it can deform and conform to the metal anode. However, Kanda *et al.*⁽⁸⁾ measured the temperature surge during the anodic bonding at glass-metal interfaces using emissivity calibrated temperature thermography. He suggested that the Joule heating at the interface was insignificant and the temperature of the glass was still below its annealing point. However, this does not mean that the contribution of the viscous flow to the anodic bonding is insignificant, since several authors have suggested that the glass can viscously flow even below its annealing point⁽⁹⁾⁻⁽¹¹⁾.

Polarization study by Albaugh⁽¹²⁾ indicated that current flow was controlled by the resistance of the bulk glass rather than by the rate of interfacial charge transfer. Albaugh⁽¹³⁾ showed that after the applied voltage was removed, no significant discharge current was detected, suggesting that the depletion layer was nearly charge neutral. This also suggested that the contribution of electrostatic force to bond strength is insignificant.

Arata *et al.*⁽¹⁴⁾ carried out anodic bonding of aluminum to glass under external pressure, and they found that applying pressure resulted in a lower temperature and voltage required for bonding. On the basis of the results of Arata *et al.*⁽¹⁴⁾, Albaugh⁽¹⁵⁾ pointed out that the anodic bonding was completed when the amount of charge transfer exceeded a certain value, and indicated that the charge transfer was related directly to the amount of anodic oxidation; i.e., the electrochemical reaction was the rate limiting factor. However, he also suggested that the anodic bonding process was controlled by the conductivity of glass.

According to observations reported by several authors⁽¹⁾⁽¹⁴⁾, the anodic bonding process proceeded through contact area enlargement. However, almost all previous papers of the anodic bonding discussed their results without taking into account the enlargement mechanism of intimately contacted area. In this paper, the effects of temperature and voltage on the rate of enlargement of intimately contacted area in anodic bonding of Kovar alloy to borosilicate glass have been studied systematically, and the rate controlling steps of the attainment of intimate contact have been proposed.

II. Experimental

Borosilicate glass of #0700 produced by Matsunami glass Co. Ltd. and a Kovar alloy were used as bonding specimens. The glass has a thermal expansion coefficient close to that of the Kovar alloy. The chemical compositions of the alloy and the glass are shown in Tables 1 and 2, respectively. The Kovar alloy specimen was a disk of 20 mm diameter and 5 mm thickness, and the glass specimen was also a disk of 25 mm diameter and 1 mm thickness. The surfaces of the glass and Kovar alloy specimens were optically finished by mechanical polishing. The bonding experiment was conducted in a vacuum chamber of $\sim 10^{-3}$ Pa. The schematic diagram of the apparatus for anodic bonding is shown in Fig. 1(a). In this apparatus, a copper plate was employed as the cathode electrode on which bonding specimens and a Dummy specimen were placed closely. The bonding temperature was monitored using a chromel-alumel thermocouple percussion-welded in the vicinity of the bond interface of the Dummy specimen. After the specimens were heated to a desired temperature, a DC voltage was applied for a required time as shown in Fig. 1(b). A 500 Ω resistance was connected in series with the specimen for recording the current-time curve. After the bonding operation, the specimens were cooled to a temperature below 423 K at a rate of $4.6 \text{ K} \cdot \text{s}^{-1}$. The charge transfer during the bonding was estimated from the integration of the current density over the time interval for which the voltage was applied. The tensile test of the joint was carried out by sticking steel rods to both sides of the joint using an adhesive (see Fig. 2). An additional device was used in order to conduct the test without machining of the bonded specimen.

Table 1 Chemical composition of the Kovar alloy specimen (mass%).

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

Table 2 Chemical composition of borosilicate glass specimen (mass%).

SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	K ₂ O	Li ₂ O	CaO	BaO
≤ 70	4	9	2-4	2-4	2-4	2-4	2-4

Fig. 1 (a) Schematic diagram of the assembly of anodic bonding apparatus. (b) The temperature and voltage profiles during the anodic bonding process.

The complex impedance method was employed to estimate the conductivity of the glass specimen. The conductivity measurement was carried out at frequencies ranging from 10 Hz to 100 kHz using a frequency response analyzer with swept frequency signal.

III. Results

1. Effects of Cu coating of cathode-side surface of glass on anodic bonding phenomena

In this investigation, we coated the cathode-side surface of the glass specimen with an evaporated film of copper in order to obtain homogeneous distribution of the electrical potential over the whole cathode area. The effects of Cu coating on the current density flowing through the specimen and the intimately contacted area[†] at the glass/anode metal interface are shown in Figs. 3(a) and (b), respectively. The application of the Cu-coating film to the cathode side surface of the glass specimen increased significantly both the current density and the intimately contacted area.

Increasing the bonding temperature resulted in a significant increase in current density and intimately contacted area as shown in Figs. 4(a) and (b), respectively. The current-time curves showed a typical profile when the cathode side surface of the glass specimen was coated with Cu; i.e., the current increased rapidly to a peak

[†] We could recognize the intimately contacted area by the appearance of Newton's rings around its edge.

Fig. 2 Schematic diagram of the assembly for bond strength measurement.

Fig. 3 (a) Effect of Cu coating of the cathode-side surface of the glass specimen on the current-time curve during the anodic bonding process (V_b , T_b , and t_b are bonding voltage, temperature and time, respectively). (b) Comparison of intimately contacted areas between Cu-coated and uncoated glass specimens.

value, and then decreased gradually to an almost steady-state value passing through a transition region. In addition, the reproducibility of the bonding phenomena was much improved by the application of the Cu-coating film to the cathode side surface of the glass specimen. For these reasons, we employed the glass specimen whose cathode side surface was coated with a Cu film.

Fig. 4 (a) Effect of Cu coating of the cathode-side surface of the glass specimen on the current-time curve during the anodic bonding process (V_b , T_b , and t_b are bonding voltage, temperature and time, respectively). (b) Comparison of intimately contacted areas between Cu-coated and uncoated glass specimens.

2. Effects of temperature and voltage on rate of enlargement of intimately contacted area

The changes in intimately contacted area and current density with time at bonding temperatures from 563 to 683 K are shown in Figs. 5(a) and (b), respectively. At a bonding temperature of 563 K, an incubation period was observed in the relation between intimately contacted area and time. As the bonding temperature was increased, this incubation period became unobservable, and the rate of enlargement of intimately contacted area increased. From the corresponding current-time curves (Fig. 5(b)), it can be seen that current density was increased rapidly to a peak value and then decreased gradually to an almost steady state value passing through a transition region. Increasing temperature increased both the peak value and the steady state value of the current. The changes in intimately contacted area and current density with time at different voltages are shown in Figs. 6(a) and (b), respectively. The rate of enlargement of intimately contacted area was accelerated with increasing voltage (Fig. 6(a)). Increasing voltage increased the peak and steady state current density. The arrows in Figs. 5(b) and 6(b) indicate the bonding times required to obtain intimately contacted area of 80%. Increasing the bonding temperature and voltage shifted this time from the steady state region to the transition region.

Fig. 5 Change in intimately contacted area (a) and current density (b) with bonding time at bonding temperatures of 563, 613 and 683 K and at a bonding voltage of 500 V. The arrows in (b) indicate the bonding times required for attainment of intimately contacted area of 80%.

Results from the tensile test of bonded specimens are listed in Table 3. The strength level was scattered widely, which is probably due to the residual stress generated during the cooling process after the bonding operation by the difference in the thermal expansion coefficients between the glass and Kovar alloy. Fracture modes of the joint in the tensile test are shown schematically in Fig. 7. Almost all the specimens having an intimately contacted area of more than 80% were fractured at the glass (mode C) except for those bonded under the conditions of short bonding time, high bonding temperature, and low bonding voltage.

In order to estimate the activation energy, $\ln t$ (t : bonding time corresponding to 80% intimately contacted area) was plotted against $1/T$ (T : bonding temperature) as shown in Fig. 8. The results suggest that two different processes with different activation energies controlled the enlargement rate of intimately contacted area. A critical temperature at which the change from one activation energy process to the other occurred ranged from 669 to 687 K, and decreased with increasing the bonding voltage. At temperatures lower than the critical temperatures, the activation energy was 65 ± 5 kJ/mol, and at higher temperatures, the activation energy was 460 ± 50 kJ/mol.

As there were reports⁽¹⁴⁾⁽¹⁵⁾ suggesting that the amount

Fig. 6 Change in intimately contacted area (a) and current density (b) with bonding time at a bonding temperature of 613 K and at bonding voltages of 400, 500 and 600 V. The arrows in (b) indicate the bonding times required for attainment of intimately contacted area of 80%.

of charge transfer could be taken as a measure of the progress of the anodic bonding process, we estimated the charge transfer required to obtain joints presenting fracture mode C at various temperatures and voltages. As shown in Fig. 9, the charge transfer necessary for the fracture mode C decreased with increasing the bonding temperature and voltage. This results is contrary to the suggestion reported in the previous papers⁽¹⁴⁾⁽¹⁵⁾.

IV. Discussion

Although the glass and metal surfaces were optically polished, the intimate contact between the glass and metal surfaces started at one spot owing to the inflatness of the surfaces, and expanded gradually over the whole interface with the bonding time. Therefore, the intimately contacted part and the uncontacted part coexisted at the bond interface in the early stage of the process. When a voltage is applied to an intimately contacted part, the current flows which is carried by mobile cations migrating from the glass surface contacted to the anode metal towards the cathode. This results in the formation of cation depleted layer where a negative charge will be accumulated. When a voltage is applied to an uncontacted part, a negative charge will also be accumulated which is approximated by the following equation⁽⁹⁾:

Table 3 Results of tensile tests.

Voltage (V)	Temperature (K)	Time (s)	Bond strength (MPa)	Intimate contact area (%)	Fracture mode*
200	613	600	2.3	31	A
300	613	600	3.2	43	B (26% at glass and 74% at glass/metal interface)
400	703	7	4.2	83	B (33% at glass and 67% at glass/metal interface)
400	683	90	1.6	81	C
500	753	600	2.8	93	C
500	703	1.3	4	90	A
500	703	3	9.4	93	C
500	703	10	3.9	91	C
500	683	10	1.9	85	C
500	663	600	5.1	93	C
500	613	600	7.8	81	C
500	563	480	8.1	81	C
600	663	30	2.3	84	C
600	613	60	1.6	84	C
600	563	300	5.1	81	C

* Fracture modes A, B, and C are shown in Fig. 7.

Fig. 7 Fracture modes of tensile tested specimens.

Fig. 8 Time required for attainment of intimately contacted area of 80% as a function of reciprocal temperature at voltages of 400, 500 and 600 V.

$$\sigma = \epsilon_0 \frac{V}{d}, \quad (1)$$

where σ is the charge density, ϵ_0 is the permittivity of free

Fig. 9 Charge transfer required to obtain joints presenting fracture mode C at various temperatures and voltages.

space, d is the gap width and V is the voltage applied. According to eq. (1), although it is based on the parallel condenser approximation, the charge distribution in the surface layer of the anode metal side glass can be illustrated in Fig. 10. The charge accumulated at the uncontacted spot decreased, as the distance from the edge of the intimately contacted part is increased, namely as the gap width is increased. Electrostatic force P between the negatively charged glass surface and the positively charged metal surface is approximately given by⁽⁹⁾:

$$P = \frac{\sigma^2}{2\epsilon_0} \quad (2)$$

According to eqs. (1) and (2), the electrostatic attractive force decreases gradually with the increase in the distance from the contacted part because of the increase in gap width d . Increasing bonding time increases the charge density and the electrostatic attraction, resulting in closing the gap between glass and metal from the periphery of the intimately contacted part through the deformation of glass. Thus the intimate contact proceeds

Fig. 10 Charge distribution at the glass surface contacted to the anode metal and the periphery of the contact.

through the area enlargement rather than the increase in the number of contacted spots. As described in Section I, several authors^{(4)–(6)} have proposed that the anodic oxidation is necessary for the completion of the anodic bonding. Owing to the high electric field in the depletion layer, the metal surface is oxidized anodically in the intimate contacted part, and a thin oxide film is formed. By this way, the intimately contacted area spreads outward until the whole area is contacted, and the anodic bonding is completed after the whole area is anodically oxidized.

1. Effect of Cu coating of cathode-side surface of glass on enlargement of intimately contacted area

As described in Section III.1, the Cu coating of the cathode-side surface of the glass specimen increased the current density, and accelerated the rate of enlargement of intimately contacted area. In this investigation, we employed a Cu plate as a cathode electrode, and because of the roughness and the infatness of its surface, the contact between the Cu-plate cathode and glass occurs only in a limited area (Fig. 11(b)). Therefore, if the Cu coating is not applied, the flow of cations in the glass near the cathode-side surface will be restricted mostly within the cathode-side contacted spots as shown in Fig. 11(b). When the Cu coating is applied to the cathode-side surface of the glass specimen, the distribution of the electrical potential on the cathode-side surface becomes rather uniform. For this, cations can flow into the Cu-coated surface, as if the intimate contact was achieved over the whole cathode area, since the conductivity of copper is much higher than that of the glass. By this way, the charge density accumulated on anode-side surface of the glass and the electrostatic force are increased as suggested from eq. (2). Probably from this reason, the enlargement rate of intimately contacted area was accelerated by the Cu coating of the cathode-side surface of the glass specimen.

Fig. 11 Flow lines of cations towards the cathode: (a) Cu-coated glass and (b) Uncoated glass.

2. Kinetics of attainment of intimate contact in anodic bonding

As mentioned in Section I, it has been suggested that the attainment of intimate contact and the subsequent anodic oxidation are necessary for anodic bonding process⁽¹⁵⁾. From our experimental results, however, almost all the joint with intimately contacted area more than 80% are fractured at glass (mode C) except joints bonded under the conditions of very high temperature, low voltage, and very short time. This suggests that the anodic oxidation, if it is required for the establishment of strong bond across the glass/metal interface, is completed in a very short time after the attainment of intimate contact. For this, in the present investigation, the discussion will be focused on the enlargement of intimately contacted area.

From Fig. 8, it is suggested that there were two processes controlling the attainment of intimate contact depending on the bonding temperature. In the higher temperature range (higher than 669–687 K depending on the bonding voltage), the activation energy was close to the reported values of the viscous flow of glass⁽¹¹⁾. The activation energy of the viscosity of the glass studied was also estimated from the strain point ($\log \eta = 14.5$, η : viscosity (poise)) and annealing point ($\log \eta = 13.0$). These points were determined using the beam bending viscosity test. The estimated value of the activation energy was 430 kJ/mol. This activation energy is also within the range of the activation energy of the intimate contact at higher temperatures. In the lower temperature range, the activation energy was nearly equal to that of the conductivity of the glass (65 kJ/mol). The Arrhenius plot of conductivity of the glass from which the activation energy was estimated is shown in Fig. 12. Albaugh⁽¹⁵⁾ has also suggested that the activation energy of the anodic bonding process is similar to that of the conduction of the glass, although his suggestion was based on the experimental results from the anodic bonding of aluminium to commercial soda-lime glass at bonding temperatures below 623 K.

These results suggest that the rate controlling factors are the viscous flow of the glass in the higher temperature

Fig. 12 The Arrhenius plot of the conductivity σ of the glass studied (at temperatures from 563 to 663 K).

range and the conductivity of the glass in the lower temperature range. Because of the roughness and the flatness of the surfaces, the specimens to be bonded have to undergo deformation to be contacted intimately during the anodic bonding. In the present investigation, we think that the glass specimen is deformed since its thickness, Young's modulus, and flow strength are smaller than those of the Kovar alloy specimen. As described in Section I, it has been accepted that the force for bringing the surfaces into intimate contact is due to the charge accumulated in the cations depleted layer of the glass surface. In the higher temperature range, since the mobility of Na^+ ions is high and the viscosity of the glass is low, the electric charges for generating the attractive force between the surfaces will be accumulated very quickly to the amount sufficient to expand the intimate contact area, so that the charge accumulation will not become a rate controlling factor for the enlargement of intimate contact. Therefore, we think that the viscous flow of the glass controlled the rate of the enlargement of intimately contacted area in the higher temperature range. In contrast to this, the charge accumulation sufficient to expand the intimately contacted area will take longer times in the lower temperature range, because of the lower mobility of Na^+ ions and the higher stress required to deform the glass. It can be considered that the conductivity of the glass controlled the enlargement of intimately contacted area in the lower temperature range, since the charge accumulation occurred through the migration of Na^+ ions (As well known, the electric current in the glass is carried mainly by Na^+ ions).

As shown in Fig. 8, increasing the applied voltage lowered the critical temperature at which the rate controlling factor changed from the conductivity to the viscous flow. This may be due to the acceleration of the Na^+ ion migration by the increase in the applied voltage, since the voltage is the driving force for the migration of Na^+ ions from the anode side to the cathode.

V. Conclusions

A parametric investigation has been made of the en-

largement of intimately contacted area in the anodic bonding process of the Kovar alloy to borosilicate glass. Bonding temperatures employed ranged from 563 to 703 K, bonding voltages from 200 to 600 V, and bonding times from 1 to 600 s. Factors controlling the enlargement of intimately contacted area have been discussed. From the results obtained we conclude the following:

(1) Coating the cathode-side surface of the glass specimen with an evaporated Cu film enhanced the enlargement of intimately contacted area and increased current density. The reproducibility of bonding phenomena was also much improved by the Cu coating.

(2) At bonding temperatures of 563 K or less, an incubation period was observed in the enlargement of intimately contacted area. This incubation period became unobservable with increasing temperature. Increasing the bonding temperature and voltage accelerated the rate of enlargement of intimately contacted area, and increased the current density.

(3) Plots of $\ln t$ against $1/T$ suggested that the enlargement of intimately contacted area in anodic bonding is controlled by two different factors depending on the bonding temperature. The activation energies obtained were close to that of the viscous flow of glass in the temperature range higher than 669–687 K (depending on the bonding voltage) and to that of the conductivity of the glass in the temperature range lower than 669–687 K. A mechanism of the enlargement of the intimately contacted area has been proposed which can explain these results.

(4) The charge transfer for the attainment of intimate contact in anodic bonding decreased with increasing bonding temperature and voltage.

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