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Rate controlling processes in anodic bonding of boroslicate glass-to-Kovar alloy coated with Al film①

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[Abstract] The Kovar alloy disks coated with Al film were anode-bonded to the glass at temperatures of 513~ 713 K under the static voltage of 500 V. The kinetics of enlargement of intimate contact area between the Kovar alloy and the glass was examined, and the joint strength was determined by the shear tests. It is suggested that a critical temperature of about 663 K exists. The enlargement of intimate contact area is achieved mainly by elastic deformation of the glass at temperature lower than the critical temperature. The estimated activation energy is close to that of conductivity of the glass. Whereas, the enlargement of intimate contact area is achieved mainly by viscous flow of the glass, and the corresponding activation energy is higher than the former and is a combination of the activation energies of conductivity and viscous flow of the glass. Examination of joint strength reveals that the chemical bond or complete bonding is formed as soon as the surfaces are brought into intimate contact, and rate-controlling process in anodic bonding is considered to be the rate of enlargement of intimate contact area.

[Key words] anodic bonding; kinetics; elastic deformation; viscous flow; charge transfer; activation energy; joint strength

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1 INTRODUCTION

Extensive researches of anodic bonding suggest that oxidation of the anode metal into the glass is responsible for bond formation[1~ 4]. During bonding, an electric field-assisted movement of stronger bound atoms, such as nonbridging oxygen (NBO) ions in Na ions depletion layer becomes possible due to the high electric field in the depletion region. In particular, the drift of oxygen ions and subsequent anodic oxidation of anode materials are considered to be a reaction pathway that governs the formation of chemical bonds at the interface. Direct evidence, observed by TEM, for the anodic oxidation as the essential interface reaction in anodic glass-Kovar bonding was recently given by Ikeuchi et al[5].

In order to establish a chemical bond at the glass/metal interface, a primary requirement is to bring the glass and the metal parts into intimate contact. For blocking anode materials, that is, neglecting the migration of cations from the anode materials into the glass, the drift of alkali ions in glasses under the electric field applied during bonding results in a polarized depletion layer in the glass adjacent to the anode. The formation of such depletion layer can generate an electrostatic force to bring the surfaces into intimate contact over a large area through elastic deformation or viscous flow of the glass[6]. At bonding temperatures lower than 663 K, Morsy et al[7] found that the activation energy of enlargement of intimate contact area (ICA) was similar to that of the conduction of the glass. However, the kinetics of enlargement of ICA has not been clarified in detail. There are relatively little investigations on joint strength of Al-to-glass bond. In the previous paper, the authors examined the interfacial phenomena in anodic bonding of Kovar/Al-glass[8]. The purpose of present work is to examine the kinetics of the enlargement of ICA by considering the development of electric force and the deformation of the glass, as well as the establishment of interfacial strength of the joint. The rate controlling processes are also proposed.

2 EXPERIMENTAL

The borosilicate glass (d 25 mm × 1 mm, with chemical composition of 68.7% SiO_2, 3.60% Al_2O_3, 18.8% B_2O_3, 3.83% Na_2O and 4.06% K_2O) and Kovar alloy (Fe-Ni-Co alloy, d 20 mm × 5 mm) coated with Al film were used as pair for bonding. Since they provide much similar thermal expansion coefficient, the residual thermal stress was minimized. Diamond paste of 1 μm was used for final polishing of Kovar alloy. Al film with a thickness of about 0.1 μm was RF sputtered on the surface of Kovar alloy. The anodic bonding was conducted in a vacuum chamber of 10^{-3} Pa. A copper plate was employed as the cathode, on which the specimen couple was placed with

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the glass at the cathode side[8]. After bonding, the intimate contact area (defined as bonded area after cooling to room temperature) was computed by image processing. When intimate contact was achieved, the interface became a uniform dark color and Newton's rings were present at the edge of the contacted region. In order to determine the joint strength, shear tests were carried out and the fracture surfaces were also examined by SEM.

3 RESULTS

3.1 Enlargement of ICA

The ICA fraction (S/S_0, where S is contact area after bonding for t time and S_0 is nominal area) as a function of bonding time is shown in Fig. 1. It is clear that intimate contact area is enlarged, and the required time for obtaining ≈ 100% ICA fraction is decreased with increasing bonding temperature. The activation energy (Q) was calculated from the bonding time needed to form ≈ 100% ICA fraction. The corresponding Arrhenius plot is shown in Fig. 2. The activation energy from the slope of the linear fit is determined to be 67 kJ/mol when temperature below 663 K, which is within the range of that of sodium conduction in silica (65~ 145 kJ/mol). The activation energy for conduction within the particular glass examined is 65 kJ/mol. These results indicate that the enlargement of ICA is controlled by the drift of Na ions under this temperature ranges.

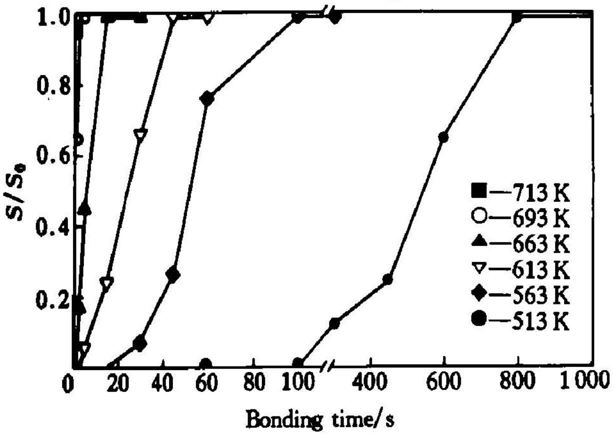

Fig. 1 Effect of bonding time on ICA fraction at various bonding temperatures

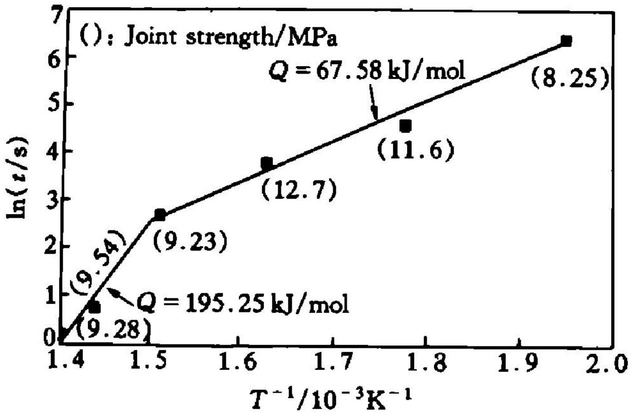

Fig. 2 Bonding time required to attain ≈ 100% ICA fraction as function of bonding temperature at applied voltage of 500 V

The bonding time at temperatures above 663 K, however, becomes shorter than that predicted from the linear fit with activation energy of 67 kJ/mol. This implies that another process, which is different from the former and corresponding to larger activation energy, controls the enlargement of ICA. This activation energy is estimated to be about 195 kJ/mol and is different from that obtained by Morsy[7].

3.2 Charge transfer during bonding

Amount of charge transfer at various temperatures is measured by integrating current with time, as shown in Fig. 3. The time interval for integration is from the initial application of the voltage to the time when the bonding of the surface is completed over. It is notable that the charge transfer is nearly constant ranging from 45 mC to 50 mC at temperatures lower than 663 K. While it is decreased to 15~ 17 mC at temperatures of 693~ 713 K. This result is contrary to the result in the previous papers[2,4].

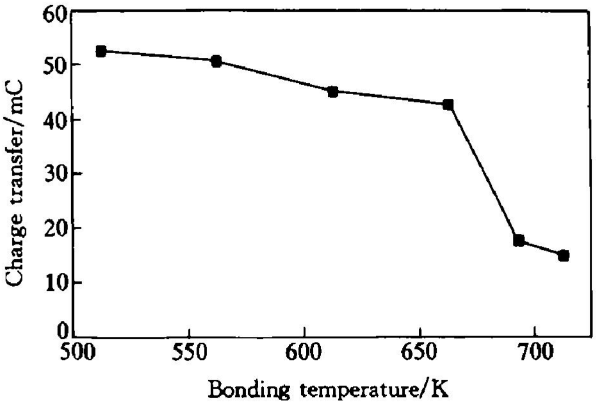

Fig. 3 Charge transfer required forming ≈ 100% ICA fraction at various temperatures

3.3 Joint strength

It is known that the metal and glass must be brought into intimate contact by the electrostatic force before they are bonded and the bonded area increases with increasing bonding time[2,7]. This is also clarified by present work. So the strength of these Kovar/ Al-glass joints bonded at different temperature, is first examined, as shown in Fig. 2. These joints have probably approximate strengths ranged from 8 MPa to 12 MPa, regardless of the bonding temperature and time. Fig. 4 shows the effect of bonding time on joint strength at temperature of 613 K. It is found that the bonding time has no significant effect on the joint strength as long as the whole surface is intimately contacted and bonded. Similar tendency can also be observed from the dependence of the joint strength on bonding temperature, as shown in Fig. 5. These results imply that stable strength has been reached immediately as the surfaces of parts are brought into intimate contact. Either prolonging bonding time or increasing bonding temperature can hardly change the joint strength. So in most cases fracture occurs within the Al film that is transformed into alumina after anodic bonding[8].

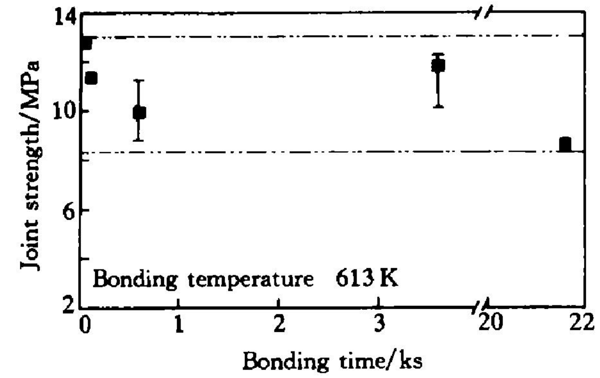

Fig. 4 Effect of bonding time on joint strength at bonding temperature of 613 K

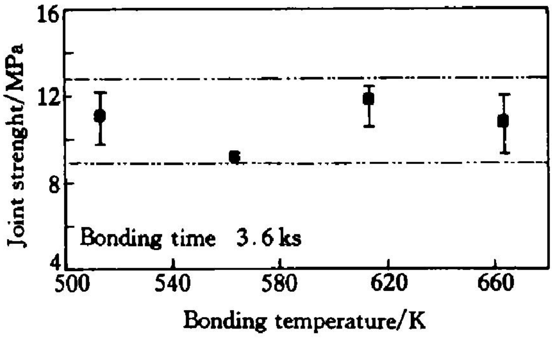

Fig. 5 Dependence of joint strength on bonding temperature at bonding time of 3.6 ks

4 DISCUSSION

4.1 Establishment of interfacial chemical bond

It is suggested that the time required to achieve complete bonding can be considered to be kinetics data available for bonding, where the complete bonding is either the achievement of maximum strength in the case of the bonds that are weaker than surrounding materials or the achievement of bonds that are stronger than the weaker of the surrounding materials[2]. From Fig. 2 and Fig. 4, it can be seen that: 1) fracture strength of the joints that are just brought into ≈100% ICA fraction is about the same; 2) bonding time has no visible effect on joint strength. Moreover, fracture occurs within the Al film. These indicates that complete bonding has been achieved immediately as the parts are brought into intimate contact.

Enlargement of intimate contact area between the metal and the glass results from the polarization of the glass[1,2,6]. Therefore, abundant negative charge such as NBO should be present in the depletion layer (polarized region) before intimate contact is achieved. The migration of NBO toward the anode surface of the glass is likely under high electric field. Immediately as the surfaces are brought into intimate contact, anodic oxidation at the anode takes place to form chemical bond at the interface. Also, the depletion layer is known to be radically different from the bulk glass. The polarization process depletes a substantial volume of the materials from the depletion layer, resulting in a very open structure near the metal anode. Abundant vacancy should be present there which is easily occupied by metal ions from anode resulted from the large local electric fields across the thin depletion layer, leading to fast reactions and solutions. Stable chemical thermodynamic equilibrium at the interface that is required for strong sealing[9] is established immediately as the metal and the glass is brought into intimate contact. On the other hand, the growth of the interfacial oxide is relatively slow[10], since the local electrostatic field decreases with the bonding time due to the growth of the polarization layer.

4.2 Rate controlling processes

Albaugh[2] suggested that the kinetic data is consistent with an electrochemical oxidation model, that is the rate of bonding is limited by the rate of establishment of the depletion layer. He also proposed that the anodic oxidation is rate-controlling process so that a fixed amount of charge transfer (representing a fixed amount of oxide growth) is required for bonding. The establishment of the depletion layer or the charge transfer, however, is required for both the contact of the surfaces and the oxidation of the anode metal, since intimate contact precedes bond formation. As soon as the surfaces are brought into intimate contact, saturation of the interface with the oxide formed by anodic oxidation and subsequent formation of oxides even if a molecular oxide results in equilibrium and chemical bonding at the interface[9]. It seems to be that fixed amount of oxide growth is not necessary for such equilibrium and chemical bonding at the interface. Therefore, a fixed amount of charge transfer required for bonding should be corresponding to that for intimate contact. As a result, rate-controlling processes during anodic bonding are considered to be the attainment of intimate contact.

It is known that intimate contact is accomplished in anodic bonding by the electrostatic field in the gap between the glass and the metal, which in turn generates an electrostatic force that pulls the parts together. The electrostatic force can be expressed as follows for conductible glass[6]:

$$p = \frac{\sigma_s^2}{2\varepsilon_0} \tag{1}$$

where σ_s is surface charge density on metal anode.

At the onset of anodic bonding, the situation is that much of the applied voltage drop is across the bulk glass rather than across the gap between the parts, since the capacitance of the gap is much larger than that of the glass. The positive ions contained in the glass, therefore, move toward the cathode resulting in a depleted layer of positive ions and thus produce a space charge of negative ions near the anode. As well known, the electric current in the glass is carried mainly by Na ions. Because of the low electric field intensity across the bulk glass, the drift rate of Na ions is

$$v = \frac{\nu_0 e\delta^2}{\gamma kT}\exp\left(-\frac{Q_c}{kT}\right)E \qquad (2)$$

where ν_0 is vibrational frequency of the ion, δ the average jump distance of mobile ion, Q_c the activation energy required for a jump, k Boltzman's constant, γ the number of possible jump directions and E the average electric field across the glass which will decreases with the growth of depletion layer.

The average width of depletion layer X_p at bonding time is

$$X_p = vt = \frac{\nu_0 e\delta^2}{\gamma kT}\exp\left(-\frac{Q_c}{kT}\right)Et \qquad (3)$$

As shown in Eqn. (3), several studies[11, 12] have found that the width of depletion layer approximately increases linearly with time in the initial stage of the bonding.

The surface charge density on the metal side is equal to the total charge density in the depletion layer (polarized zone), thus:

$$\sigma_s = \rho X_p \qquad (4)$$

The electrostatic pressure is found by substituting Eqn. (4) into Eqn. (1):

$$p = \frac{(\rho X_p)^2}{2\varepsilon_0} \qquad (5)$$

Since the charge density ρ is not strongly time-dependent before intimate contact, the electrostatic pressure will increase with the growth of depletion layer.

During anodic bonding as the average separation distance, H, between the surface decreases, the area of contact of the surfaces increases proportionately. In the simplest case, the intimate contact area, S, increases with decreasing surface separation, thus

$$\frac{S}{S_0} = \frac{H_0 - H}{H_0} \qquad (6)$$

where H_0 is the initial average separation distance between the surfaces at the start of anodic bonding.

The intimate contact required for anodic bonding can be achieved under the electrostatic pressure by elastic deformation or viscous flow of the glass[6]. The strain associated with elastic deformation is:

$$\varepsilon_E = \frac{\sigma}{K} \qquad (7)$$

where σ is the stress on the un-contact area ($S_0 - S$), K is the elastic modulus. Since σ is time dependent, the strain rate of elastic deformation can be found by substituting Eqns. (3) and (5) into Eqn. (7),

$$\frac{d\varepsilon_E}{dt} = -\frac{dH}{H\,dt} = -\frac{d\ln H}{dt} = \frac{m}{2\varepsilon_0 K(S_0 - S)}\left[\exp\left(-\frac{Q_c}{kT}\right)\right]^2 2t, \qquad (8)$$

$$m = \left[\frac{\nu_0 e\rho\delta^2 E}{\gamma kT}\right]^2 \qquad (9)$$

The strain rate associated with the Newtonian vicious flow of the glass is

$$\frac{d\varepsilon_V}{dt} = \frac{d\ln H}{dt} = \frac{\sigma}{3\eta} \qquad (10)$$

where η is the viscosity of the glass which can be expressed as

$$\eta = \eta_0\exp\left(\frac{Q_\eta}{kT}\right) \qquad (11)$$

The elastic modulus K or the viscosity of the glass can be considered to be resistance force for deformation. If ε_E and ε_V are set equal to each other and substituting Eqns. (7) and (10) into the equation of $\varepsilon_E = \varepsilon_V$, a critical condition can be found as follows and illustrated in the form of Arrhenius plot in Fig. 6.

$$9\eta = Kt \qquad (12)$$

$$\ln t = \ln\frac{9\eta_0}{K} + \frac{Q_\eta}{kT} \qquad (13)$$

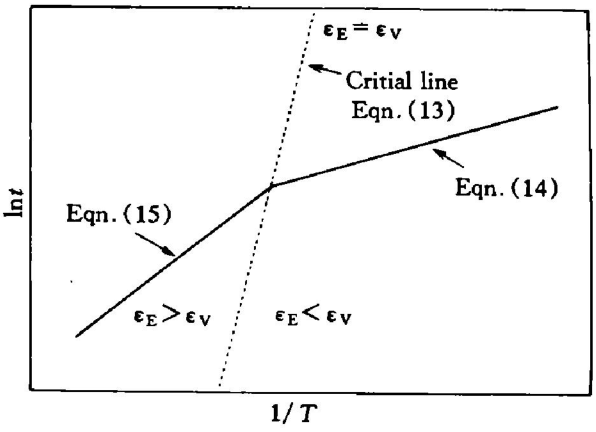

Fig. 6 Schematic illustration of critical condition of Eqn. (13), Eqn. (14) and Eqn. (15)

The slope of the critical line is equal to the activation energy Q_η of Newtonian viscous flow. Eqn. (13) implies that at low temperatures, i. e. on the right of this line, the strain produced through elastic deformation is larger than that through viscous flow, indicating the contact can be achieved through elastic deformation. Whereas, the viscous flow becomes the main contribution to intimate contact at high temperatures. Therefore, the contact process through either elastic deformation or viscous flow should depend on the bonding temperature and time.

In the case of contact achieved through elastic deformation, the time required to obtain 100% ICA fraction can be found by integrating Eqn. (8) with respect to time and an Arrhenius form in Fig. 6.

$$\ln t = \frac{1}{2}\ln S_0 - \frac{1}{2}\ln\frac{m}{2\varepsilon_0 K} + \frac{Q_c}{kT} \qquad (14)$$

Eqn. (14) indicates the activation energy of enlargement of ICA is equal to that of ion conductivity. This is consistent with the result in Fig. 2 at low temperature range.

On the other hand, if the contact process is achieved through viscous flow, the time required can be found from Eqns. (11) and (12) and an Arrhenius form also shown in Fig. 6.

$$\ln t = \frac{1}{3}\ln S_0 - \frac{1}{3}\ln\frac{m}{18\varepsilon_0 \eta_0} + \frac{Q_\eta + 2Q_C}{3kT} \qquad (15)$$

In this case, the activation energy of enlargement of ICA is a combination form of activation energies of both the conductivity and the viscosity of the glass. The activation energy of viscosity of the glass examined is determined to be 430 kJ/mol using the beam bending viscosity test. Therefore, the activation energy of enlargement of ICA is estimated to be 185 kJ/mol. The activation energy of 195.25 kJ/mol at high temperatures shown in Fig. 2 is similar to this value. The critical temperature of about 663 K at which the activation energy changes from 67 kJ/mol to 195 kJ/mol can be considered to be the critical condition as shown in Eqn. (13) and in Fig. 6. Since the elastic modulus K is not strongly temperature dependent, the electrostatic force required to bring whole area into intimate contact should be constant in spite of bonding temperatures if the contact is achieved through elastic deformation of the glass. This is confirmed by the constant amount of charge transfer shown in Fig. 3, since the electrostatic force is proportional to the charge transfer. At high temperatures, however, the amount of charge transfer required is quite smaller than that at low temperature. This implies that vicious flow of the glass occurs at high temperatures under the electrostatic force smaller than that required for elastic deformation at low temperatures.

5 CONCLUSIONS

1) The intimately contacted area is increased with increasing bonding time. The rate of enlargement of ICA is accelerated with increasing bonding temperature.

2) The activation energy is obtained from Arrhenius plot of time ($\ln t$) vs. bonding temperature ($1/T$) for attainment of 100% ICA fraction. At temperature range lower than 663 K, the activation energy is 67 kJ/mol which is close to that of the conductivity of the glass. At temperatures higher than 663 K, whereas, it is estimated to be 195 kJ/mol.

3) With increasing temperature, the amount of charge transfer required for complete contact between the surfaces is also changed from about 45~ 50 mC to 15~ 17 mC at this critical temperature.

4) Joint strength determined by shear tests is 8 ~ 12 MPa as long as the joint is brought into ≈100% ICA fraction, regardless the bonding temperature and time.

5) Rate controlling processes in anodic bonding are considered to be the rate of the enlargement of ICA. A mechanism of the enlargement of ICA is proposed.

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