

Parameters in solid-state bonding of metals to oxide materials and the adherence of bonds

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Temperature, pressure and time are parameters in the solid-state bonding of metals to oxide materials. The role of these parameters in the bonding of metals with low melting point to glass and ceramic and their interrelationship is experimentally investigated in relation to the adherence of the bonds. The influence of the surface structure and the unevenness of the bonding surfaces is also considered.

1. Introduction

During the past ten years many studies on solid-state interactions between metals and oxide materials (ceramics and glasses) have been published. Most of them were concerned with fibre-reinforced materials [1, 2], but a few of the papers were devoted to the bonding of structural parts which can satisfy high demands regarding tightness and mechanical loadability [3-5]. The bonding of metals with low melting points (Al, Pb and In) to ceramic material and glass has not received much attention until now. These metals can be bonded in the solid-state to oxide materials at relatively low temperatures [6, 7], which can be of interest in industrial applications. In any bonding process, the primary condition is that intimate contact between the materials is established, so that interaction can occur. In solid-state bonding, this is achieved, at least partly, by exerting pressure at the interface. To achieve a high rate of interaction, the temperature should be as high as possible in the most reactive state, so that bonding is completed in a reasonable time. This implies that, at the bonding temperature, the metal surface is free of oxide and the other surface is free of contaminants. However, metals with low melting-points form stable oxides which cannot be reduced in a gas atmosphere below the melting temperature of the metal in a reasonable time. The solubility of oxygen in these metals is too low to remove the oxide film by the dissolution of the oxygen in the bulk metal. The only way to present clean metal to the ceramic

or glass surface is to destroy the oxide film by plastic deformation of the metal during the bonding process. So the parameters in the bonding process are: pressure, temperature and time.

In this paper the parameters and their interrelationship in the solid-state bonding of aluminium, lead and indium to ceramic and glass are discussed in relation to the adherence of the bonds.

2. Parameters

2.1. Pressure

The function of pressure in the solid-state bonding of the oxygen-active metals to oxide materials is to create a highly active metal surface by the *in situ* destruction of the surface oxide layer. The flowing metal must also be expected to affect the contaminants on the surface of the oxide material. On bonding aluminium to semiconductors Krasulin [8] found that active centres form at the interface, and that plastic deformation of the softer material is the determining factor for this effect. The effect of plastic deformation of the metal in between two fused silica discs is shown in Fig. 1, which is a photograph taken through glass that is bonded to lead. The bright zones are the bonded areas and are almost free of lead oxide, while the centre zone and the edge zones are not bonded due to the presence of the lead oxide. This will be discussed in more detail. Analysis of the process of plastic deformation of a metal between hard, smooth surfaces in two dimensional plane strain is known

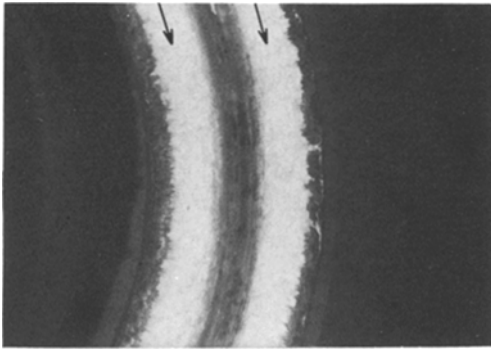


Figure 1 Fused silica-lead bond. Arrows indicate the adherence zones, (X 6).

from the literature [9]. This can be applied to explain the formation of the different zones in the contact area. The equilibrium of forces in the x -direction (see Fig. 2) gives

$$[(\sigma_x - d\sigma_x) - \sigma_x]h - 2\tau_{xy} dx = 0. \quad (1)$$

The shear stress (τ_{xy}) occurs by friction at the interface.

In order to get the metal to bond to the other surface, locally, the shear stress τ_{xy} in the metal should reach at least the value τ_{max} required for plastic flow.

The relation between the normal stress (σ_y) and the longitudinal stress (σ_x) is given by the deformation energy criterion for this stress condition

$$\sigma_x - \sigma_y = \frac{2}{\sqrt{3}} \sigma_0 = \sigma_x + p \quad (2)$$

in which σ_0 is the flow stress under uniaxial load. The stress distribution for the various zones can be calculated using Equations 1 and 2 from which the following expressions are obtained [9]

Zone I (Coulomb friction zone)

$$\sigma_{yI} = \frac{2}{\sqrt{3}} \sigma_0 \exp \frac{2\mu(b/2) - x}{h} \quad (3)$$

$$\tau_{xy} = \mu\sigma_y \quad (4)$$

(μ is the coefficient of friction)

Zone II (adherence zone)

$$\sigma_{yII} = \frac{\sigma_0}{\mu\sqrt{3}} \left[1 + \frac{2\mu(x_b - x)}{h} \right] \quad (5)$$

$$\tau_{xy} = \tau_{max} = \frac{\sigma_0}{\sqrt{3}} \quad (6)$$

Zone III (hydrostatic pressure zone)

$$\sigma_{yIII} = \sigma_{yII} + \frac{\sigma_0}{h\sqrt{3}} \left(\frac{x_c^2 - x^2}{x_c} \right) \quad (7)$$

$$\tau_{xy} = \tau_{max} \frac{x}{x_c} \quad (8)$$

The specific pressure (P) to be applied is obtained by integrating Equations 3, 5 and 7 over $x = b/2$

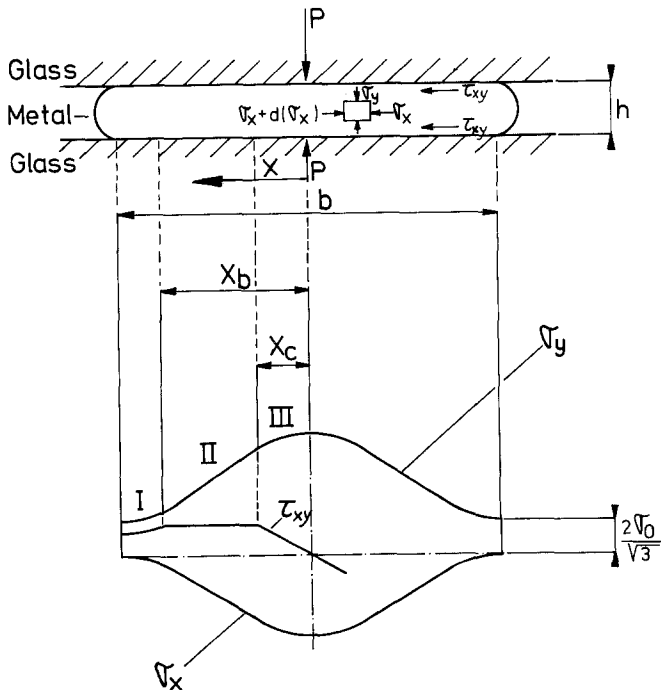


Figure 2 Contact stress distribution for plane compression of a metal between flat glass surfaces. σ_y = normal stress, τ_{xy} = shear stress, σ_x = longitudinal compression stress. $2\sigma_0/\sqrt{3}$ = stress required for flow.

and $-b/2$ which gives the following

$$P = \frac{4h\sigma_0}{\mu b\sqrt{3}} \left[\frac{1}{2\mu} + \frac{2\mu}{3} + \phi(1 + \mu\phi + 2\mu) \right] \quad (9)$$

in which

$$\phi = \left(\frac{b}{2h} - \frac{\ln 2\mu}{2\mu} - 1 \right)$$

Using Equation 9 to calculate the pressure for given $b/2h$ ratios, a nearly linear relationship between these variables is found if μ exceeds the value of 0.25, see Fig. 3. The slope of the curves is 0.25.

The width of Zone I can be derived from Equation 3 since if $\tau = \mu$, σ_y reaches the value $\tau_{\max} = \sigma_0/\sqrt{3}$ and sliding friction no longer occurs. Then

$$\frac{-\ln 2\mu}{2\mu} = \frac{(b/2) - x}{h} \quad (10)$$

with $x = x_b$ and for given values of μ , the relative width of Zone I is obtained. For the deformation process considered here, using Prandtl's solution [9], the width of Zone III is found to be $1.29h$. Data for σ_0 and μ , for a given material combination, are scarcely available. We have therefore experimentally determined the values of σ_0 and μ .

Experiments have been carried out from which

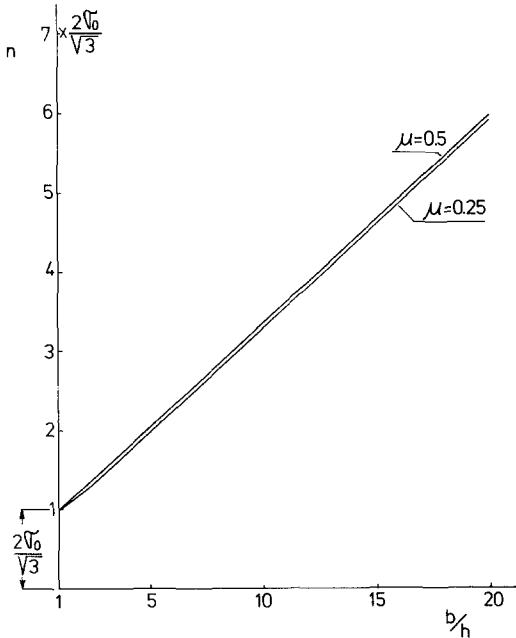


Figure 3 Theoretical relationship between the pressure and the ratio b/h for $0.25 < \mu < 0.5$.

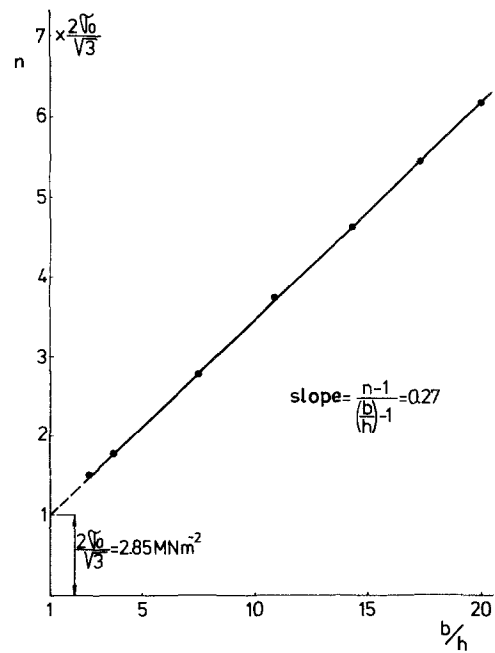


Figure 4 Experimental relationship between the pressure and the ratio b/h . Aluminium-fused silica bonded at 630°C . Deformation rate 2 to 8 sec^{-1} .

the relations between the applied pressure (P) and the relative widths b/h , $(x_b - x_c)/h$ and x_c/h have been determined. For this, two fused silica discs, 5 mm thick, were bounded by deforming two $0.8 \times 0.8 \times 18 \text{ mm}^3$ aluminium bars between the discs at 630°C in H_2/N_2 gas, the pressure being maintained for 60 sec.

The result of the measurements, as shown in Fig. 4, indicates that there is a linear relationship between P and b/h . The slope of the curve is 0.27, which is in good agreement with the theory. The width of Zone I ($(b/2h - x_b)/h$) was found to be $0.65h$. By substitution of this value in Equation 10 the value of $\mu = 0.31$ is obtained for this zone.

The width of Zone III was found to be $1.3h$, which is nearly equal to the theoretical value. The stress at which the deformation of the aluminium starts to occur is found by extrapolation (see Fig. 4) to be 2.85 MNm^{-2} . From this it follows that the flow stress (σ_0) of aluminium ($(2.85 \times \sqrt{3})/2 = 2.47 \text{ MNm}^{-2}$).

The relative width of the adherence zone $(x_b - x_c)/h$, which determines the bonding process, is related to b/h as in Fig. 5. This shows that, for adhesion to occur, the metal has to be deformed to a ratio of at least $b/h = 4$. Identical relationships were found when lead and indium wires 1 mm thick were bonded to fused silica at 290 and

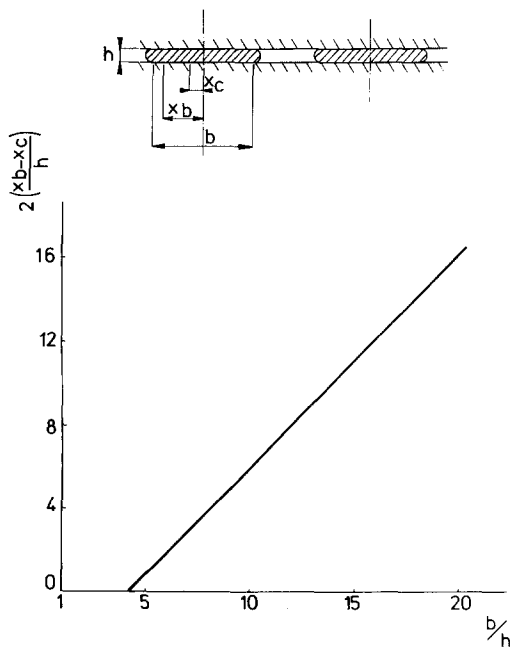


Figure 5 Width of the adherence zone in relation to the ratio b/h in the aluminium-fused silica bond.

130°C respectively and the pressure maintained for 60 sec. The flow stresses were found to be 0.85 MNm^{-2} for lead and about 0.15 MNm^{-2} for indium. The coefficient of friction was found to be 0.45 for both metals.

It should be mentioned that the flow stress of a metal increases with increasing deformation rate. To indicate the effect of the deformation rate on the strength of a metal, the ultimate change in the strength of aluminium with the deformation rate is given in Fig. 6. In our experimental work the deformation rate was 2 to 8 sec^{-1} .

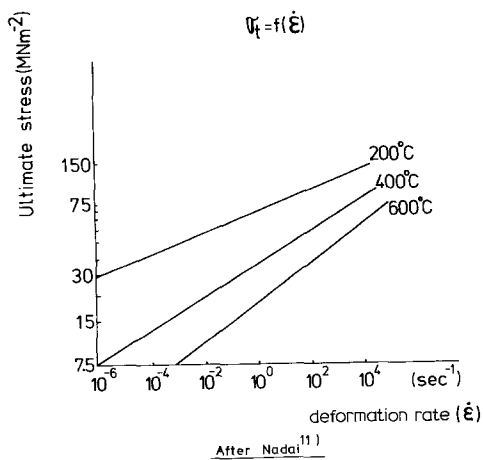


Figure 6 Tensile strength versus the deformation rate of aluminium, Nadai [11].

2.2. Temperature

The function of the temperature is to activate the interaction by increasing the mobility of the atomic species and also the mobility of the dislocations in the metal. The latter is found with a decrease of the flow stress of a metal and with an increase of the creep rate with increasing temperature. From this it will be obvious that the pressure to be applied for a given b/h ratio decreases with increasing temperature.

The bonding of aluminium to fused silica is accompanied by chemical reaction at the interface [10]. It is to be expected that this can also occur at the interface of aluminium with a debased alumina containing silicon.

The effect of temperature on the bond strength and on the hermeticity of the bond was investigated on alumina-aluminium bonds, lead-fused silica and indium-fused silica bonds. The alumina contained 5% calcium silicate and the surface was in the as-sintered condition. For this purpose, the metals were used in the shape of an open ring of 1 mm-wire with an outside diameter of 18 mm. The end faces of the ring touched each other. The strength of alumina-aluminium bonds as a function of the b/h ratio at different bonding temperatures is given in Fig. 7. It is also indicated whether the bond is hermetic or not. The strength of alumina-aluminium bonds, fused silica-lead bonds and fused silica-indium bonds at a constant temperature as a function of the b/h ratio is given in Fig. 8. From the results it can be seen that the strength of alumina-aluminium bonds increases with increasing bonding temperature and with increasing b/h ratio. Chemical reactions

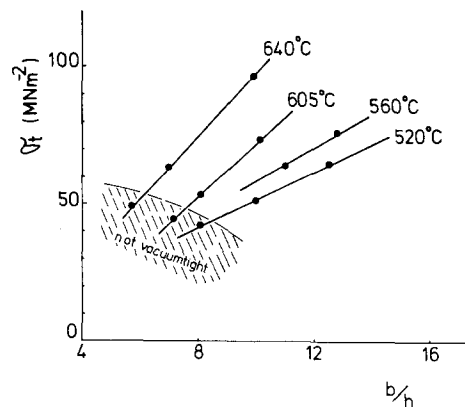


Figure 7 Tensile strength of aluminium-alumina (95%) bonds versus the ratio b/h with temperature as the parameter. Deformation rate 2 to 8 sec^{-1} .

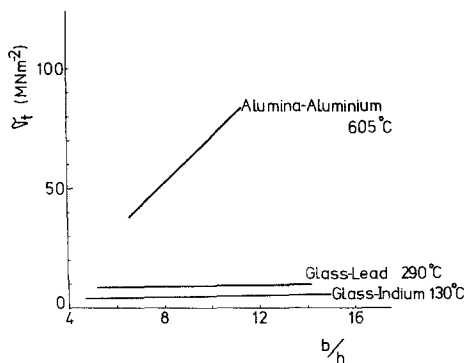


Figure 8 Tensile strength of different types of bonds made at constant temperature with varying b/h ratio. Deformation rate 2 to 8 sec^{-1} .

at the ceramic-metal interface may be responsible for this phenomenon [10]. The fused silica-lead bond strength did not change either with the bonding temperature or with the b/h ratio, see Fig. 8. The same is found in the fused silica-indium bonds.

The hermeticity of the bonds is reproducible if the b/h ratio is above a certain limit which is understandable from the fact that the adherence zone starts to occur if the b/h ratio is greater than or equal to 4.

A phenomenon observed in the seals, is the occurrence of a third adherence zone (Fig. 9) in the centre of Zone III. This is due to the curvature of the metal wire, because the original line of contact of the wire with the ceramic or glass surface moves outwards during the deformation process. The metal flowing inwards is under a combined compression stress while the outward-flowing metal is under combined tensile stress. Here the two-dimensional plane strain condition (see Section 2.1.) is not fulfilled.

2.3. Time

The bonding time, i.e. the time the pressure is maintained, will have a great effect if a chemical reaction occurs between the materials. If such reactions do not occur, the time required to deform the metal is the determining parameter, and so the deformation rate should be as high as possible to prevent oxygen penetration at the interface during the bonding process.

Seals between fused silica and lead and indium respectively have been made with a bonding time of between 0.1 and 1 sec ($\dot{\epsilon}$ between 8 and 0.8 sec^{-1} respectively) without differences in bond strength

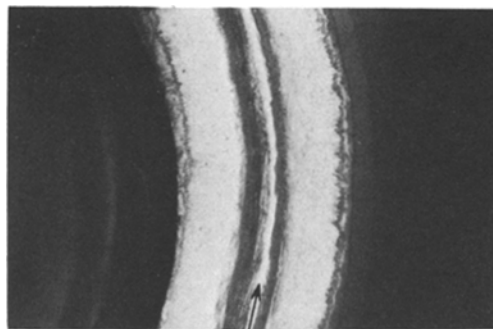


Figure 9 Occurrence of a third adherence zone, arrowed, in right shaped fused silica-lead bond, ($\times 6$).

occurring. However, with a deformation rate of $3 \times 10^{-2} \text{ sec}^{-1}$, the adherence zone was about 40% smaller than that obtained with a deformation rate of 8 sec^{-1} . This is probably due to the penetration of oxygen along the outer zone during the slowly proceeding deformation.

3. The effect of surface roughness

If the glass or ceramic surfaces are rough, the deformation process of the metal differs greatly from that of smooth surfaces and the description given in Section 2 no longer applies. The asperities prevent changes in the contact area from occurring during the deformation process, because the metal is anchored between the asperities. So there is no possibility of the metal extending the oxide-free contact area. Although there is adhesion of the metal, hermeticity is not reproducible. Joints of aluminium bonded to silica ground with abrasive having grains of the order of $36 \mu\text{m}$ appeared to be as strong as bonds with smooth fused silica, but the joints were not hermetic.

If the ground surfaces of glasses were etched or flame polished, thus removing the asperities and surface cracks, the strength and the hermeticity of bonds with aluminium, lead and indium were found to be equal to those on smooth surfaces. This was also found on surfaces obtained in common high-temperature glass treatments.

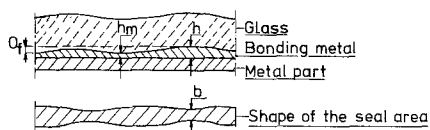


Figure 10 Permitted unevenness (O_f) for hermetic bonding of uneven rigid parts $O_f \leq b/4 - h_m$.

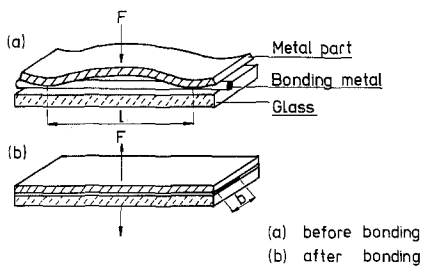


Figure 11 Bonding of uneven flexible parts (a) before bonding, (b) after bonding. The flattening force F should not exceed the loadability of the bond $F < \sigma_s \times l \times b$, σ_s = bond strength.

Alumina surfaces in the as-sintered condition are irregular due to the presence of grooves at the grain boundaries. The metal flowing during the bonding process cannot fill the pores completely and this affects the hermeticity of the joint. It appeared that such surfaces can be bonded so as to be hermetic if the seal width is about 30 times the grain size of the ceramic [10].

4. The effect of unevenness of the parts to be bonded

The tolerances for the unevenness of the surfaces to be bonded depend on the stiffness of the parts. If rigid parts have to be bonded, the degree of unevenness that can be tolerated is given by the minimum b/h ratio that is required to obtain a hermetic bond. This ratio was found (see Section 2) to be $b/h \geq 4$. On the other hand the maximum b/h ratio determines the pressure to be applied and this should not damage the parts (see Fig. 10).

From Fig. 10 the relation between the unevenness O_f and minimum b/h ratio is $O_f \leq b/4 - h_m$. For flexible parts, the permitted unevenness is given by well-known mechanical relations between the flattening force to be applied and the strength of the bonds.

In Fig. 11 a simplified model of such a combination is shown. From this it follows that

bond rupture occurs if the flattening force $F \geq \sigma_s \times l \times b$ (σ_s = seal strength, $l \times b$ = surface area).

5. Conclusion

It is shown that the parameters of the solid-state bonding process i.e. temperature, pressure and time are closely interrelated.

The lower limits of the bonding temperatures for hermetic sealing are: 80°C for indium, 260°C for lead and 500°C for aluminium. The adherence of the aluminium–alumina bonds increases with increasing bonding temperature, whereas the adherence of lead and indium bonds does not change with increasing bonding temperature.

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