JOURNAL OF MATERIALS SCIENCE 18 (1983) 2835–2843

Solid state metal–ceramic bonding of platinum to alumina

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The formation and resulting mechanical strength of solid state metal–ceramic reaction bonds of alumina to platinum are investigated in terms of the effects of three main parameters – bonding temperature, time at temperature and contact pressure. Also the effect of the subsequent operating temperature on the bond strength is examined. An optimum bonding regime can be devised to create platinum–alumina bonds of optimum strength and durability, suitable for use in practical bonding applications.

1. Introduction

Reaction bonding is a solid state process for joining metals to ceramics, developed initially on the basis of observations of de Bruin and co-workers [1–3]. Patents for the process are held jointly by the CSIRO and Flinders University of South Australia [4]. A wide variety of metals and oxide ceramics can be bonded using this technique; both noble metals (e.g. platinum, palladium, gold, silver) and transition metals (e.g. iron, cobalt, nickel, copper) can be bonded to ceramics such as alumina, zirconia, magnesia, silica and beryllia.

In recent years, our research on metal–ceramic bonding has been directed mainly towards exploting the bonding technique as a practical solution to technological problems. Several commercial applications of reaction bonding have been developed, some of which have been discussed elsewhere [5]. In the development of these applications it has been important to determine appropriate bonding conditions to provide bonds of optimum strength and durability for the particular pair of materials used. Results of research on gold–alumina solid state reaction bonding have been published, where the effects of various parameters on the bond formation in this system were discussed [6, 7].

An important feature of reaction bonding, which distinguishes it from many alternative metal–ceramic bonding techniques is that the bonds so formed generally retain their strength at high temperatures, indeed even at temperatures approaching those at which they were formed. This means that the bonds can be used in applications at temperatures which would normally be above the limit for metal–ceramic joints formed by the commonly used metallizing or brazing techniques. In these high temperature applications platinum is a commonly used metal, due to its high metling point (1769° C) and chemical inertness in many hostile environments. Two of the more important commercial applications of reaction bonding, the fast response thermocouple sheath and oxygen probe [5], use platinum–ceramic bonds which are required to withstand in-service operating temperatures up to about 1200° C. The development of these applications has therefore necessitated a more complete study of the effects of the basic parameters of bonding in this system, so that appropriate bonding conditions can be established suitable for commercial production of reaction bonded devices.

The parameters shown to be important in determining bond strength in the alumina–gold system, i.e. temperature, time at temperature and contact pressure [6], have also been investigated in this study of the alumina–platinum bonding system. In addition this paper examines the effect of subsequent operating temperature on the mechanical strength of the bonds.

Finally, on the basis of the experimental results, an optimum bonding regime can be devised to form bonds of a certain minimum strength, which will retain their strength at high operating temperatures.

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2. Experimental details

2.1. Materials

The alumina ceramic selected as standard for the experimental work was Degussit A123 recrystallized alumina tubing, 10 mm OD (outer diameter) by 6 mm ID (inner diameter). This material was claimed by the manufacturer to be at least 99.5% Al_2O_3.

To make test pieces, the alumina tubing was sawn into 25 mm lengths, ground each end to form flat, parallel surfaces, then polished to optical flatness on one end only, using 2 to 6 μm diamond powder as the final abrasive.

Platinum was purchased as "pure", in the form of 0.18 mm thick sheet. This was rolled down to 0.08 mm, after which 10 mm diameter discs were pressed out of the sheet material using a press tool. The discs were then lightly pressed between optically flat steel platens to ensure flatness. A sample of the platinum used was assayed by atomic absorption analysis and found to be $>99.98\%$ Pt.

Prior to bonding, both the ceramics and platinum foils were cleaned identically using ultrasonic agitation, firstly in 60 to 80° C BP petroleum ether, then in 10% HNO_3 in ethanol. The specimens were then rinsed in water and allowed to air dry.

As a final pre-treatment both the ceramics and platinum foils were pre-baked to 1000° C for 3 h in air. It is considered that such a treatment would effectively clean the surfaces of any hydrocarbons remaining after the solvent cleaning procedure.

This type of pre-treatment of the materials before bonding, that is polishing, cleaning and pre-baking, was found to be beneficial for optimizing bond strength in the alumina–gold system [6] and was therefore adopted as a standard pre-treatment routine for the materials used in this study.

2.2. Bonding arrangement

All bonds were of a "sandwich" type, that is alumina–Pt–alumina, and were formed either singly or in groups of three, using a bonding arrangement similar to that used for gold–alumina bonding [6]. Contact pressures between 0.13 and 3 MPa were applied using this arrangement, a gravity loading technique, where the materials to be bonded are assembled and held between a ceramic pedestal on the bottom and a ceramic push-rod on the top, by which a load is applied via a lever arm and ball-joint system. Contact pressures above 3 MPa were applied by an air piston system driven by a pressurized gas cylinder, as shown in Fig. 1. Contact pressures up to 10 MPa were successfully achieved using this technique, however, higher pressures could not be attained due to softening and subsequent distortion of the alumina push-rod at the bond temperatures used (1450° C), resulting in collapse of the rig after 1 to 2 h at temperature.

A Pt–20% Rh wound resistance tube furnace was used for bonding at temperatures up to 1450° C. For bonding at temperatures between 1450 and 1650° C, a molybdenum wound furnace was used. An r.f. induction type furnace was used to attain temperatures above the melting point of platinum (1769° C). A limited number of bonds were attempted under these conditions, as a comparison with the standard solid-state reaction bond, which is generally considered to achieve maximum strength at a temperature of about 90% of the melting point of the metal in degrees absolute [5]. All bonds were formed in an air atmosphere.

The rate of heating of the furnace to the bond temperature was fairly slow, generally 10° C min^{-1} on average. Bonds to be formed were held at the selected bonding temperature for times varying between 12 min and 10 h. After the allotted time at temperature, the bonds were allowed to cool slowly at the natural rate of the furnace. The load creating the contact pressure was removed shortly after cooling commenced.

A set of operating conditions was selected as standard for all the experimental work involved in this study and these conditions were only altered in respect of the parameters being investigated, that is bonding temperature, time or contact pressure. These standard operating conditions were:

(a) bonding temperature, 1450° C,

(b) bonding time (at temperature), 4 h,

(c) contact pressure, 0.8 MPa.

Although 1450° C is less than 90% of the melting point of platinum (1769° C), which is generally considered the optimum bonding temperature, 1450° C was the maximum temperature which could be simply and routinely obtained using our apparatus, for the numerous and repetitive bonding experiments required for this study, and was therefore selected as standard.

2.3. Bond evaluation

The strength of the bonds formed was evaluated in

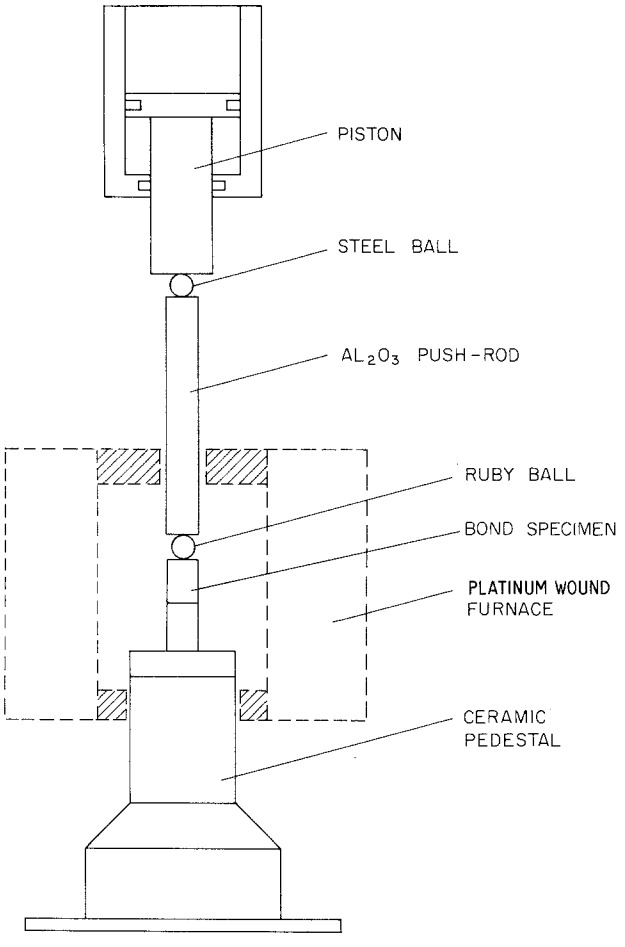

Figure 1 Schematic diagram of the furnace and bonding assembly.

terms of modulus of rupture, using a standard 4-point bend test. The configuration of the test is shown in Fig. 2.

An Instron universal testing machine of type 1115, with a crosshead speed of 0.05 mm min^{-1}, was used for the general test work.

Bond specimens used to evaluate the effect of operating temperature on strength were tested in a hot bend test furnace constructed in these laboratories, using an alumina bend rig of the same dimensions as the steel rig used in the Instron test machine.

The modulus of rupture was calculated as though the entire area of the alumina ceramic had fully bonded, that is over the full cross-sectional area of the specimen.

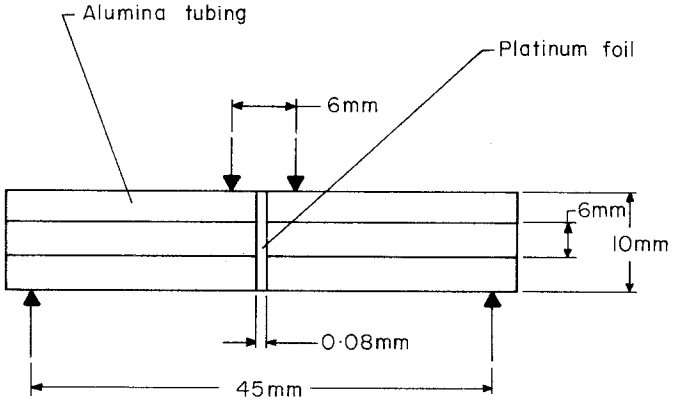

Figure 2 Schematic diagram showing the configuration of the 4-point bend test used for bond evaluation.

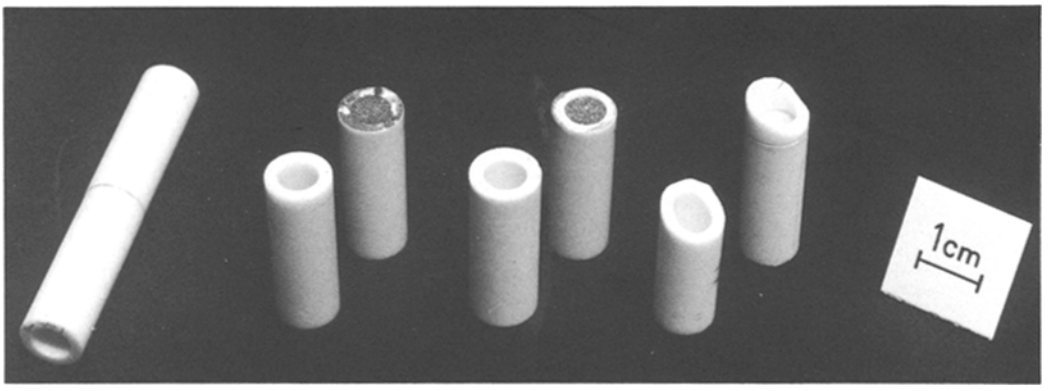

Figure 3 Four typical bond sepcimens. One as formed, unbroken, and three showing the different modes of failure on bend testing. Failure can occur at the alumina–Pt interface, or partially at the interface and partially within the ceramic, or completely within the ceramic.

For most bonds failure occurred at one or the other alumina–Pt interface. However some bonds failed partially at the interface and partially within the ceramic, while others failed completely within the ceramic, at some distance away from the bond interface (see Fig. 3).

3. Results and discussion

3.1. Bonding temperature

To study the effect of bonding temperature on strength, a series of bonds was formed at various temperatures in the range 1100 to 1800° C, with all other parameters standard, as described above.

The bonds formed at temperatures up to 1450° C were made in groups of three in one firing; those formed at higher temperatures were made singly.

Fig. 4 shows the results of modulus of rupture tests on the bonds formed.

An attempt was made to form two bonds at temperatures above the melting point of platinum, using r.f. induction heating. One of these was attempted under the usual standard conditions with 0.8 MPa contact pressure, but after about 10 min at the bond temperature 1800° C, the height of the ceramic push-rod fell slightly, indicating some disturbance and possible imminent collapse of the bond materials. The bond was then

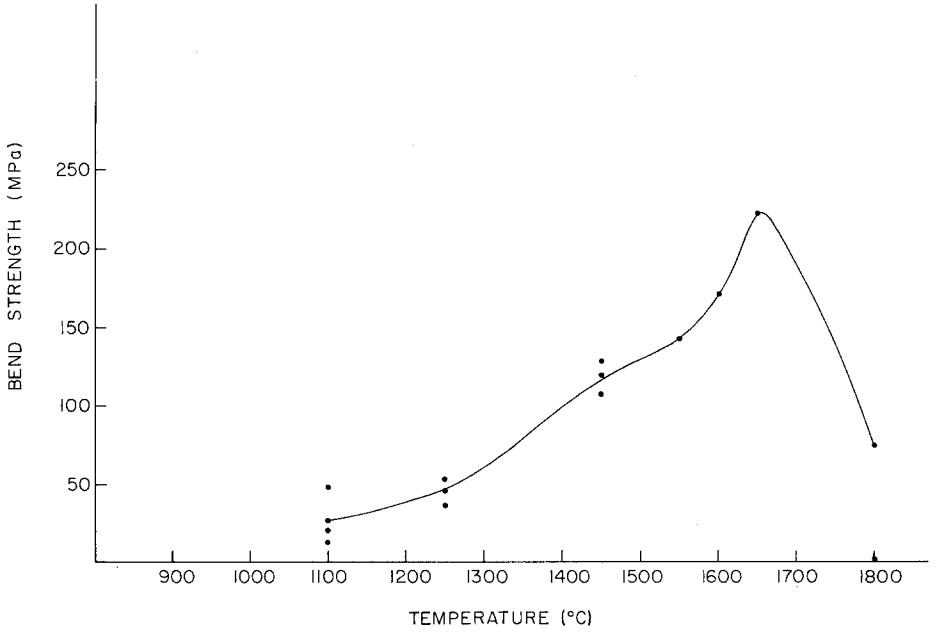

Figure 4 The relationship between bond strength and bonding temperature.

allowed to cool slowly (to ambient temperature in 60 min). Later examination showed that the ceramics had softened and distorted badly and that the molten platinum seemed to have been completely squeezed out of the bond area, so that the bond formed was in fact directly between the two alumina pieces. When tested for strength by the standard bend test, failure occurred by a jagged break roughly through the centre of the test piece, the line of failure not following the previous position of the platinum foil in any way. The strength measured was 76 MPa, considerably lower than that achieved for bonds formed below the melting point of platinum, generally greater than 200 MPa.

For the second bond attempted above the melting point of platinum, no load was applied to the specimen while bonding, i.e. the contact pressure was almost zero (the weight of the upper alumina tube would contribute only 1×10^{-3} MPa contact pressure), so that the platinum, once melted, might be retained in the bond area. This specimen was held at temperature (1800° C) about 30 min. Later examination showed no obvious distortion of the ceramic, however, again the platinum appeared to have melted and run out from the bond area, depositing on the support pedestal underneath the bond. The bond later failed at virtually zero applied stress, while loading into the bend test rig. The exposed ceramic bond faces showed no signs of any remaining platinum.

For the bonds formed at temperatures below the melting point of platinum, however, the strength was found to steadily increase as the bonding temperature was increased, as shown in Fig. 4. The optimum temperature for bonding, to produce bonds of maximum strength, would appear to be just below the melting point of platinum; however under the standard contact pressure of 0.8 MPa, the alumina ceramic can soften and bend slightly at such a high temperature, causing distortion in the shape of the bonded specimen. No such distortion was observed in specimens bonded below about 1500° C; therefore this temperature would probably be the optimum for bonding in practical terms.

These results are in accord with those obtained for the alumina–gold bonding system, where it was similarly shown that the optimum point for the formation of the reaction bond occurs just below the melting point of the metal and that the bond formed above the melting point, if any, is of an entirely different nature to the true solid-state reaction bond. If any of the metal can be retained in contact with the ceramic above the melting point, the bond formed would be via a sessile drop contact, which though strong at the area of contact, would result in a weak bond when considered over the entire area of the ceramic.

3.2. Bonding time

A series of bonds was formed under the usual standard conditions, varying only the time held at temperature to form the bond, from 12 min to 10 h. Fig. 5 shows the effect on the bond strength (modulus of rupture) of this variation in the bonding time. It can be seen from Fig. 5 that considerable strength (70 MPa) was attained even after the minimum period of 12 min, however the strength of the bonds was still increasing with time after 10 h at temperature.

3.3. Bonding pressure

To investigate the effect of contact pressure on bond strength, bonds were formed at various contact pressures, in the range 0.13 to 10 MPa, with all other parameters held constant at the standard conditions. From the results presented in Fig. 6, the bond strength appears to increase with increasing applied contact pressure, up to about 2 MPa, above which little further increase in strength is attained.

Figs. 7 to 10 are photographs of the exposed platinum interfaces of four bonds formed at 0.13, 0.8, 2 and 6.7 MPa, respectively, which have been bend tested to failure. The central areas of each specimen have not been in contact with alumina (the alumina used being tubing), therefore only the outer annular areas of each specimen are the areas which show the effect of having been reaction bonded. The heavy rumples and distortions which can be seen in the platinum foils are brought about by the failure of the bond during bend testing and should be disregarded when examining the surfaces for variations due to the contact pressure. The four photographs clearly show the effect of contact pressure in that there is a distinct variation in the extent of the matt bonded surface, particularly evident between the specimens bonded at 0.13 and 0.8 MPa (Figs. 7 and 8). The matt appearance has been brought about by the imprint of the alumina ceramic, which has been intimately pressed against the platinum during bonding; the higher the pressure,

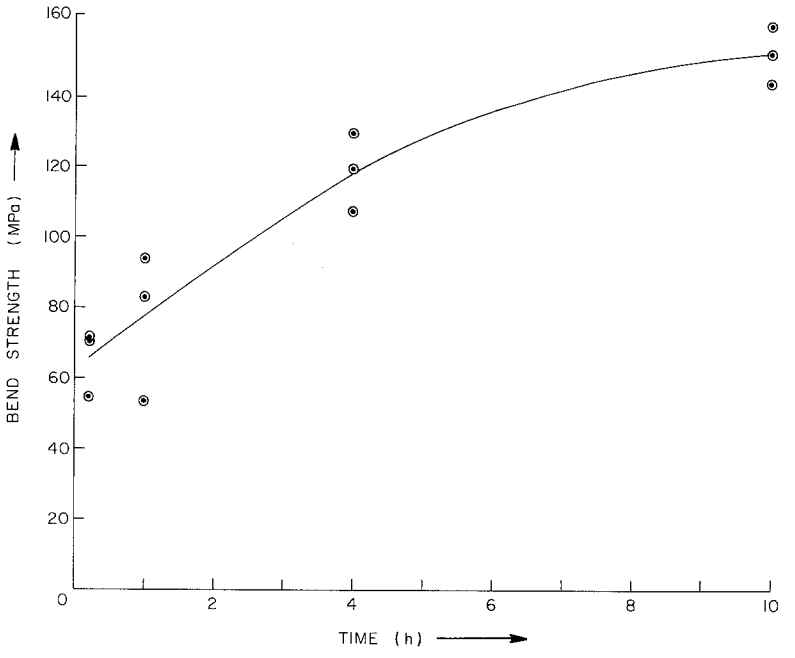

Figure 5 The relationship between bond strength and bonding time.

the better the contact between metal and ceramic and the more extensive this matt surface would be expected to be.

The specimen bonded at 0.13 MPa shows only patchy areas of the matt surface, which is in accord with the correspondingly low strength of this specimen (55 MPa). In Fig. 8, it can be seen that having used 0.8 MPa pressure for bonding has markedly improved the quality of the bond in that the matt surface now appears fairly evenly over the whole annular bond area of the specimen and the strength figure is correspondingly higher (120 MPa). For the specimen bonded at 2 MPa, Fig. 9 shows that the matt appearance is very even over the whole bond surface and seems slightly more "dense" than in Fig. 8. The strength of specimens bonded at this pressure, as shown in Fig. 6, is higher than that achieved for the lower bond pressures. Fig. 10, of the specimen bonded at 6.7 MPa, shows little variation from Fig. 9 in the appearance of the matt surface, which supports the strength data in that little increase in strength is attained by

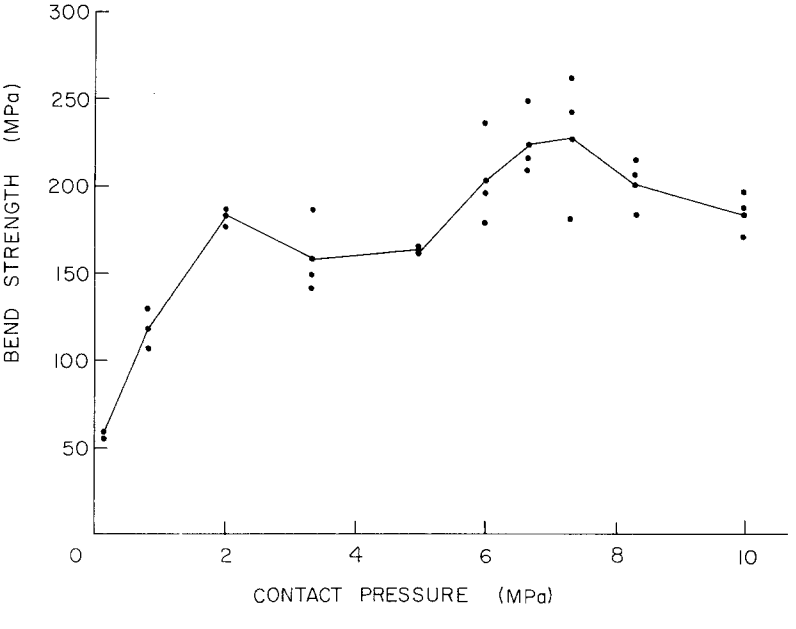

Figure 6 The relationship between bond strength and bonding contact pressure.

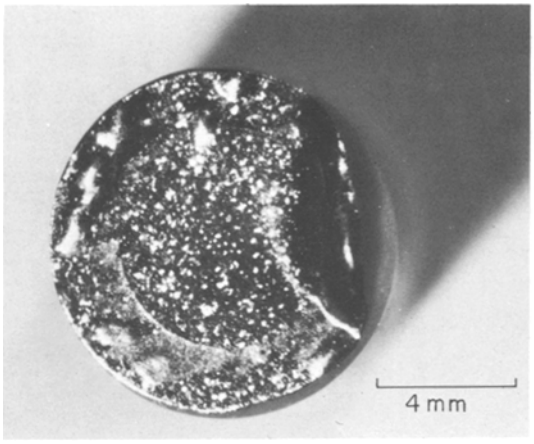

Figure 7 Exposed platinum interface of bond formed at 0.13 MPa contact pressure.

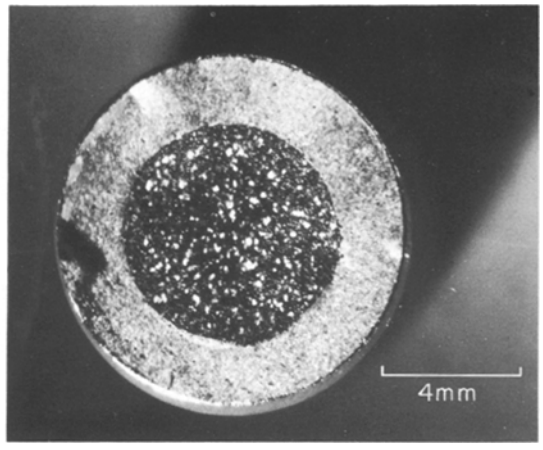

Figure 9 Exposed platinum interface of bond formed at 2 MPa contact pressure.

bonding at 6.7 MPa compared to 2 MPa. That is, optimum contact between metal and ceramic is achieved at 2 MPa bonding pressure. Any further increases in pressure would probably only increase the likelihood of mechanical interlocking of the platinum into the pores of the alumina.

The possibility of mechanical keying of the metal to the ceramic, brought about by high contact pressures, was discussed with reference to gold–alumina bonding [6]. The same considerations would apply for platinum–alumina and, for the same reasons, mechanical keying can be discounted as making any significant contribution to bond strength, when compared to the contribution made by the chemical bond between the two materials. Our results show that optimum bond strength is achieved at a relatively low contact pressure (2 MPa). If mechanical keying was a significant factor in bond formation, it would be expected that the bond strength would continue to increase with increasing pressure. This is not the case.

The effect of variation in contact pressure is also shown in Figs. 11 and 12, which are photomicrographs of two of the same specimens discussed above, bonded at 0.13 and 2 MPa, at a higher magnification than in Figs. 7 and 9. The left side of each photomicrograph is of the previously bonded platinum foil; the right side is the platinum which has not been in contact with alumina, that is the centre, non-bonded region of the platinum disc. At 2 MPa, the alumina ceramic has been evenly and completely impressed upon the platinum surface, while the contact between metal and ceramic has been very patchy over the specimen bonded at 0.13 MPa.

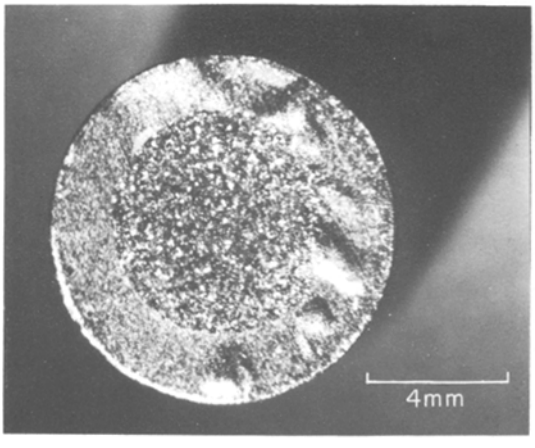

Figure 8 Exposed platinum interface of bond formed at 0.8 MPa contact pressure.

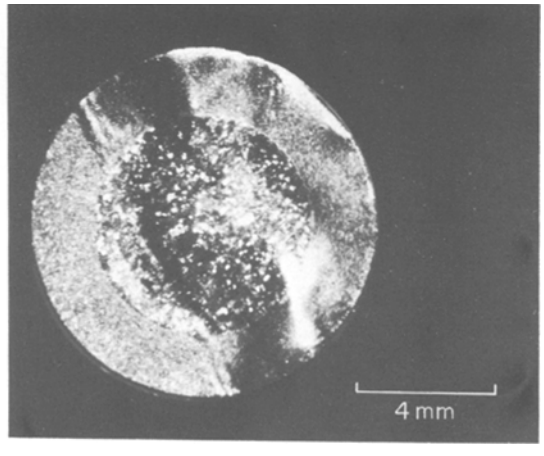

Figure 10 Exposed platinum interface of bond formed at 6.7 MPa contact pressure.

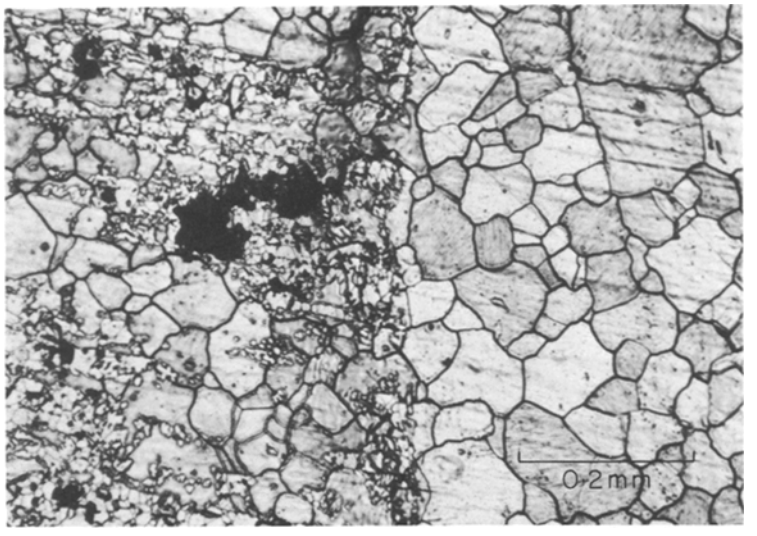

Figure 11 Photomicrograph of exposed platinum bond interface, showing previously bonded region (left) and non-bonded region (right). The imprint of the alumina is very patchy on the bond area, resulting from the low contact pressure (0.13 MPa).

3.4. Effect on bond strength of high temperature operation

A series of bonds was formed under the usual standard conditions of temperature, pressure and time, cooled to ambient temperature, then later tested to failure in a hot bend rig at temperatures between ambient and 1100° C, which is the maximum temperature attainable using our hot bend-test apparatus. The results are plotted in Fig. 13, against similar data obtained for commercial alumina (from the manufacturer's data sheet). It can be seen from Fig. 13 that the strength of the bonds does decrease slightly at elevated temperatures, however the decrease is no more than that observed for alumina alone, without any bond.

These results illustrate the excellent suitability of platinum–alumina reaction bonds for use in high temperature applications.

4. Conclusion

The parameters of bonding temperature, time and pressure have all been shown to markedly effect the mechanical strength of platinum–alumina reaction bonds.

For maximum bond strength, the appropriate conditions would be:

(a) temperature, approximately 1700° C (or just below the melting point of platinum, 1769° C)

(b) time at temperature, 10 h or longer

(c) contact pressure, 2 MPa.

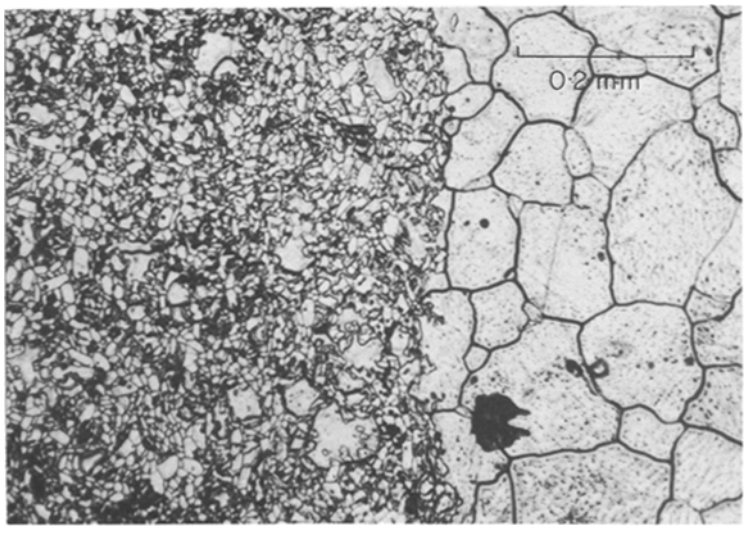

Figure 12 Photomicrograph of exposed platinum bond interface, showing previously bonded region (left) and non-bonded region (right). At the contact pressure of 2 MPa the alumina has been evenly and completely impressed upon the platinum bond area.

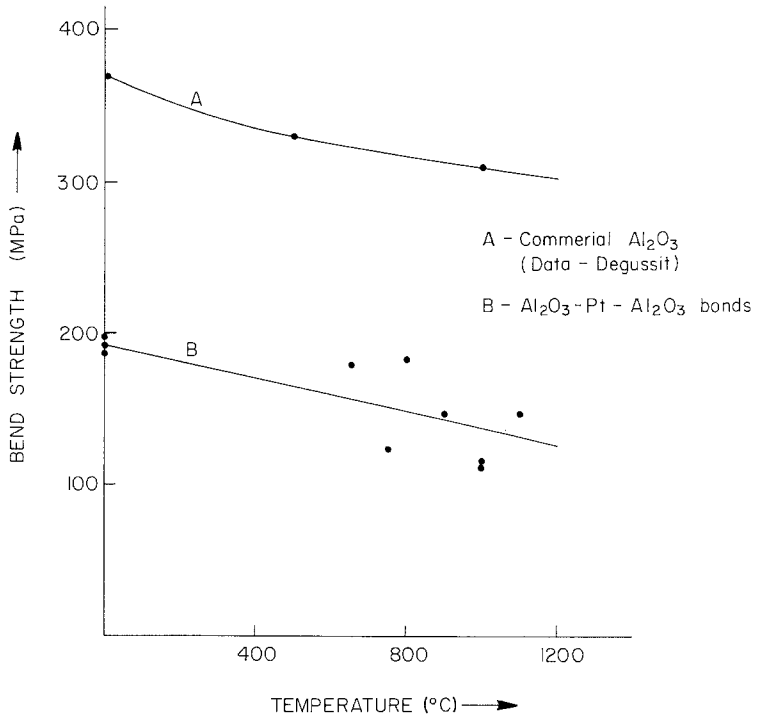

Figure 13 Relationship between bond strength and subsequent operating temperature.

However, very strong bonds can still be achieved at less rigorous conditions than these; for example, 4 h at 1450° C, and 2 MPa would produce bonds of more than adequate strength for most applications. The effects of the three bond parameters could be expected to be interrelated, for example, a shorter bonding time at a higher temperature may result in a bond of equal or even higher strength than could be achieved under the otherwise standard conditions.

The strength of the bonds at high operating temperatures was shown to be excellent, with the loss in strength at 1100° C being only about 25% of that at ambient temperature. This retention of strength at such high operating temperatures is a feature of solid-state reaction bonding which distinguishes it from other metal–ceramic bonding techniques.

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Received 22 November 1982
and accepted 18 February 1983