JOURNAL OF MATERIALS SCIENCE 13 (1978) 1045–1052

Gold-to-alumina solid state reaction bonding

F. P. BAILEY, K. J. T. BLACK
Division of Chemical Physics, CSIRO, Clayton, Victoria, Australia 3168

This paper describes methods by which strong vacuum-tight bonds between gold and alumina can be fabricated in an air atmosphere. Temperature was found to be a sensitive factor in bond formation; the higher the temperature, the stronger the bond, provided that the temperature remained below the melting point of gold. Intimate contact between the bonding gold and alumina surfaces during formation of the bond was also an important consideration. This was achieved by using an optically flat and polished ceramic surface and applying a low pressure of about 1 MPa to the bonding couple. Further enhancement of the contact can be achieved by depositing an additional thin layer of gold onto the ceramic surface by evaporation or by other means, and by thorough cleaning by high temperature heat treatment prior to bonding. Good bonding occurs in the range of 1 to 100 h. Bond strengths as high as 80 MPa were achieved.

1. Introduction

Strong bonds between gold and alumina have been sought by many workers in the field of solid state bonding technology. Potential uses of such bonds include their application in electronic circuit components and in high-temperature and/or corrosive environments. Observations by de Bruin, Moodie and Warble [1–4] have led to the development of a solid state process known as reaction bonding, which has been patented in several countries [5–9]. This process encompasses a wide variety of metal–ceramic bonds. This paper reports the results of a development programme to establish the basic bonding factors of the gold–alumina bond couple, thus extending the preliminary work on this process.

Bonds made by this process represent an improvement on other bonding processes in that they can be manufactured under conditions which need not be critically controlled: the fabrication process requires only low contact pressure, moderate temperature and an air atmosphere, and bonds of high strength can be made reliably and economically.

2. Experimental procedures

2.1. Material selection and specimen preparation

2.1.1. Ceramic preparation

Two commercially available and widely accepted polycrystalline alumina ceramics were used in this study: Coors AD99 in 9.5 mm solid rods and Degussa AL23 in 10 mm o.d. × 6 mm i.d. tubes. These were prepared for bonding by sawing into pieces approximately 15 mm long which were then ground to give flat, parallel ends. The ground specimens were then polished on one end by optical finishing techniques to a final polish with 2 to 4 μm diamond paste on a nylon lap. The polished surface of the rods was flat to within 250 nm. Additionally, single crystals of alumina (sapphire) obtained from Saphirwerk Switzerland were trepanned out of Verneuil boules and highly polished to a final finish with 1 μm diamond paste.

2.1.2. Metal preparation

Three batches of gold foil were used. The thicknesses of these samples are given in Table I. Using atomic absorption spectroscopy, foils were

TABLE I Gold samples used

Batch	Thickness of foil (mm)	Difference purity (%)	Impurities (p.p.m.)							
			Cu	Ag	Fe	Zn	Pd	Mg	Cd	Pb
A	0.065	99.88	696	315	97	5	93	0	0	<15
B	0.045	99.96	138	108	59	18	105	0	0	<15
C	0.060	99.85	550	790	67	55	-	-	-	-

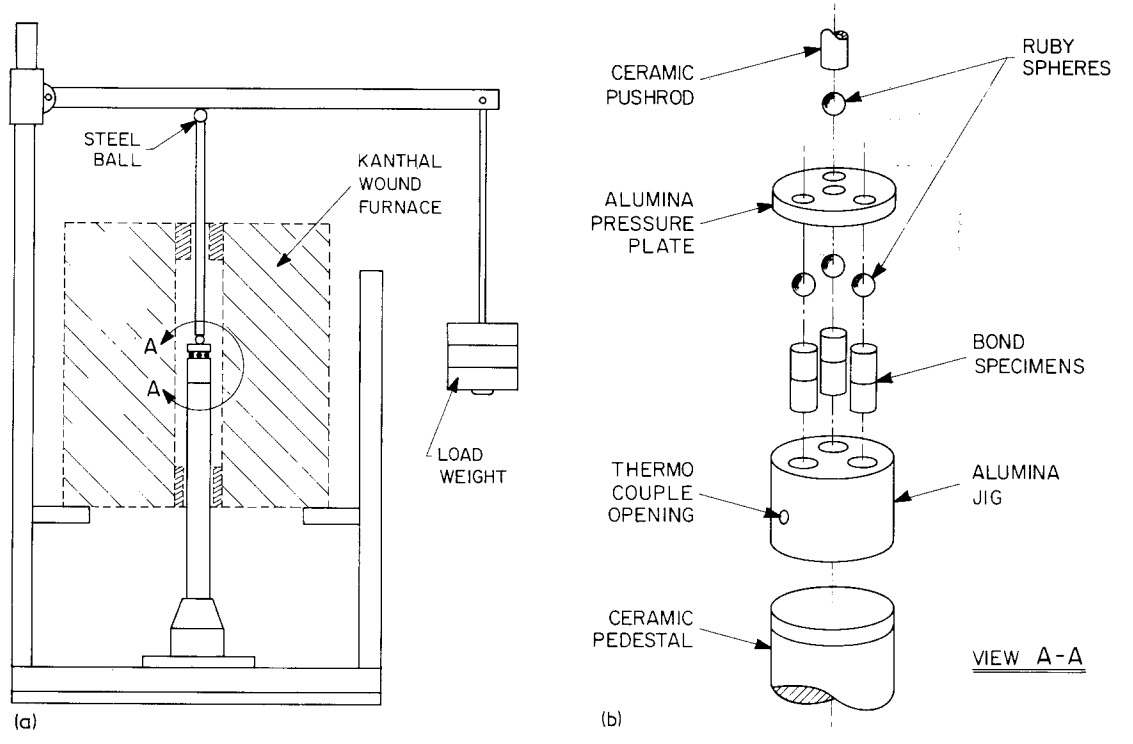

Figure 1 Schematic diagram of the furnace and bonding assembly (a) with a more detailed view of the apparatus along A–A (b).

analysed in this laboratory for those impurities commonly found in gold; the difference purities (obtained by subtracting the amounts of these impurities from 100%) are also given in Table I. Disks of 10 mm diameter were pressed out from the foil, carefully deburred, and planished between optically-flat steel platens to ensure flatness.

2.1.3. Cleaning procedures and other pre-treatments

Immediately prior to use, ceramics and metal foils were cleaned successively in (1) 60 to 80° C b.p. petroleum ether, (2) 10% HNO_3 in ethanol and (3) hot water. Steps (1) and (2) were accompanied by ultrasonic agitation. The pieces were then air-dried or wiped with a clean lint-free tissue.

In specific cases the ceramic and/or metal pieces were given one or more additional pre-treatments: (1) heat treatment at 1030° C for 3 h in air; (2) boiling in HCl (conc.) for 10 min followed by several boiling water baths and subsequent heat treatment as in (1); (3) evaporation of 300 nm of gold onto the ceramic bond surfaces. Both the evaporated gold and the disk used in (3) were gold batch B.

2.2. Formation of the bond

The specimens were placed in a ceramic jig to hold them in alignment during the furnace loading procedure. "Sandwich" bonds of alumina/gold/alumina were formed singly or in groups of three. All bonds were formed in an air atmosphere*. A Kanthal-wound resistance tube furnace with a

*Bonding in other atmospheres will be dealt with in a subsequent paper.

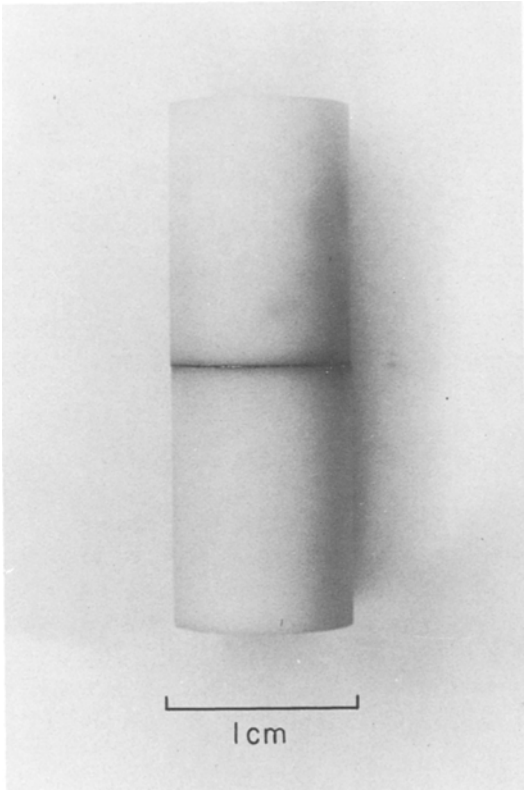

Figure 2 A bonded, unbroken specimen.

profile giving a 75 mm uniform hot zone was used. Temperature measurements were made using a Pt/Pt 13% Rh thermocouple placed within 5 mm of the gold foil. Temperatures were selected from the range 880° C to 1080° C (m.p. of gold, 1063° C). A gravity-loaded ceramic push-rod system applied the requisite contact pressure to the top of the bond specimens via ruby spheres and an alumina pressure plate. Pressures were selected from the range 5×10^{-4} to 1.8×10^{1} MPa. Fig. 1 depicts the furnace assembly.

The heating rate of the furnace averaged 15° C min^{-1} and the specimens were held at the required temperature for times ranging between 0.5 and 100 h. The furnace was turned off and allowed to cool after removing the loading. Fig. 2 shows a bonded specimen.

2.3. Evaluation of bonds

The bonds were tested for strength by direct shear. Early results showed that the areas of maximum bonding were occasionally "rings" within the total circular disk (see Fig. 3). Therefore shear tests most accurately represent the average strength over the full bond area,

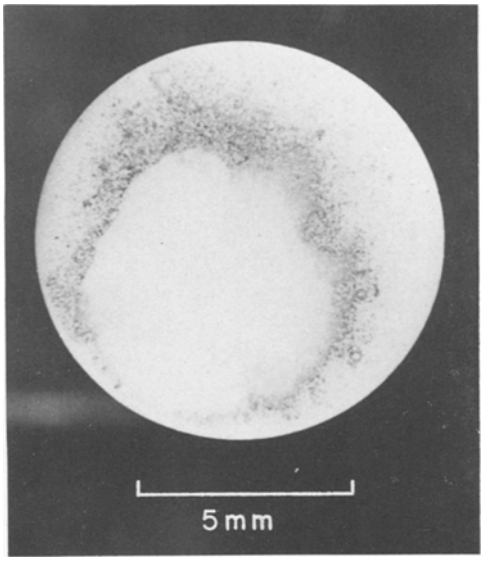

Figure 3 Optical micrograph showing "ring" effect in some bonds.

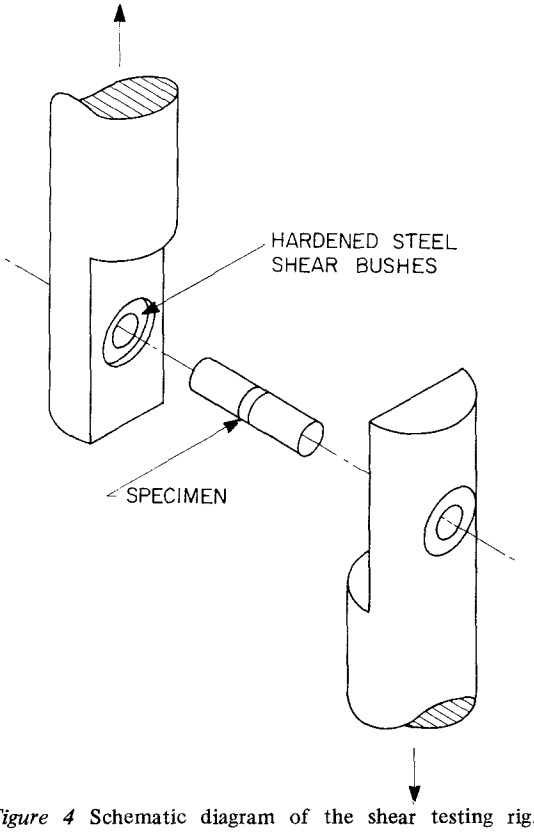

Figure 4 Schematic diagram of the shear testing rig. Retaining sleeve is not shown. Shear bushes are recessed giving minimal clearance over gold foil.

whereas bend testing is unduly sensitive to the position of the rings with respect to the extreme fibre. The geometry of the specimens makes tensile testing very difficult to perform.

TABLE II Pre-treatments (Standard bond conditions: 1050° C for 4 h with 0.5 MPa contact pressure.)

Treatment	Bond shear strength (MPa)	Number of bonds	Standard deviation
Nil	22	14	8.5
Evaporation of gold	39	6	3.4
Gold heated	40	6	4.8
Alumina heated	41	3	4.1
Gold heated and acid treated	43	2	1.4
Gold and alumina both heat-treated	51	12	5.8
Gold heated, alumina acid-treated then heated	53	9	9.1

Fig. 4 shows a diagram of the shear rig, which was mounted in an Instron universal testing machine, type 1082. A slow cross-head speed of 5 mm min^{-1} was used. The reported strengths were calculated with respect to the full cross-sectional area of the specimen, corrected for any obvious lateral misalignment of the two ceramic rods, but not corrected for any apparently non-bonding areas across the fractured interface.

3. Observations and results

3.1. Optimum bond preparation

3.1.1. Surface finish

3.1.1.1. Gold. Gold A had a smooth, highly reflective surface which was seen to be nearly scratch-free under the optical microscope at 90 x magnification. On the other hand, gold B had a matte surface which was roughly textured in a rumpled pattern. Both gold samples, however, showed the phenomenon of perfectly matching the ceramic surface structure after bonding. Burnishing gold B to a comparable finish to gold A did not influence the strength of bonds made with it.

3.1.1.2. Ceramics. The bonds made in the initial stages of this work showed that the contact area of the bond would be critically dependent on the flatness of the ceramic surface at the low pressures commonly used. The procedure used to achieve a high degree of flatness also produced a highly polished surface free of loosened grains. The importance of the surface condition to the strength of similarly produced bonds has been well covered by Schmidt-Brüchen and Schlapp [10], whose polarized light procedure was used to confirm the optimum quality of our final surfaces.

3.1.2. Pre-treatments of bond components

3.1.2.1. Heat treatments. In all cases, heat treatment increased bond strength considerably. For example, gold B which had been bonded to Coors alumina at 1050° C for 4 h gave an average bond strength of 22 MPa (14 bonds in sample) when neither the metal nor the ceramic components had been heat-treated prior to bonding. When all components were heated, however, the average bond strength increased to 51 MPa (12 bonds). In addition, if only the gold was heated, and not the ceramic, the strength increased to a lesser extent, to 40 MPa (6 bonds). Similar results were obtained when only the ceramic and not the metal was heated: 41 MPa average (3 bonds).

3.1.2.2. Acid and heat treatments. For bonds where the ceramic only was boiled in acid and then both metal and ceramic were heated, bond strengths averaged 53 MPa (9 bonds). When only the gold was heated and then given the acid-treatment described, and the alumina was not treated, bond strengths averaged 43 MPa (2 bonds).

3.1.2.3. Gold evaporation. The bonds with evaporated gold averaged 39 MPa (6 bonds). These bonds had no other pre-treatment, and are therefore to be compared with the bonds averaging 22 MPa. Results of all the pre-treatments are summarized in Table II.

3.2. Optimum bonding temperature

The main criterion for the reaction-bonding process is that the temperature shall not exceed the melting point of any of the bond materials. Maximum bond strength was found to develop at

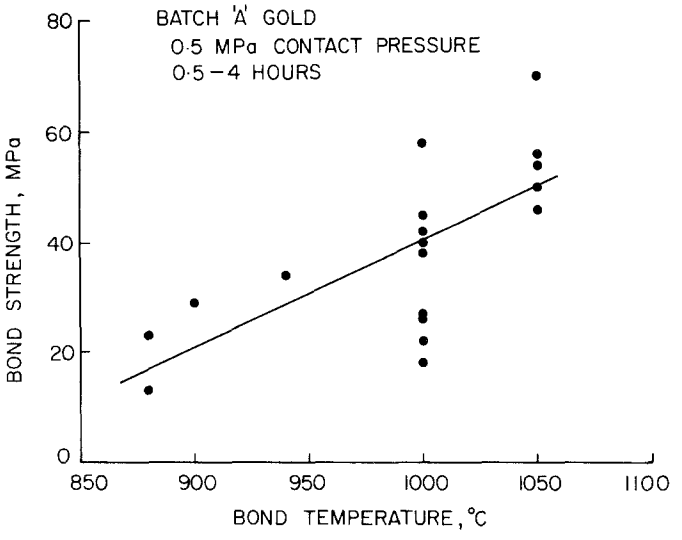

Figure 5 The relationship between bond strength and bonding temperature.

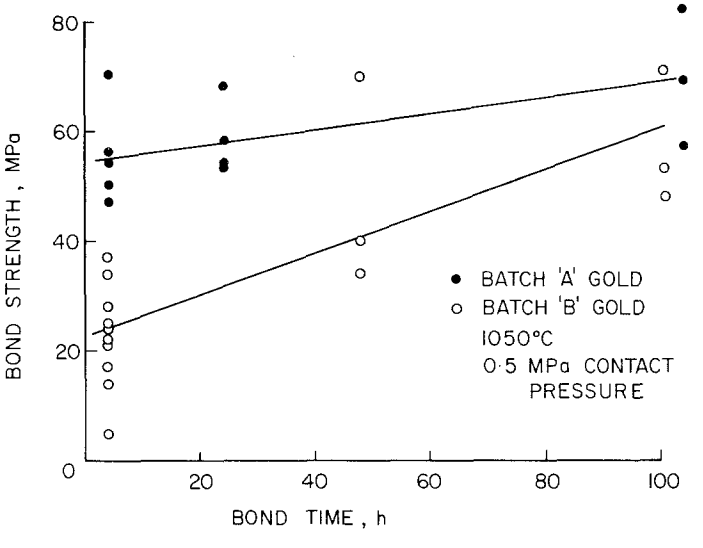

Figure 6 The relationship between bond strength and bonding time.

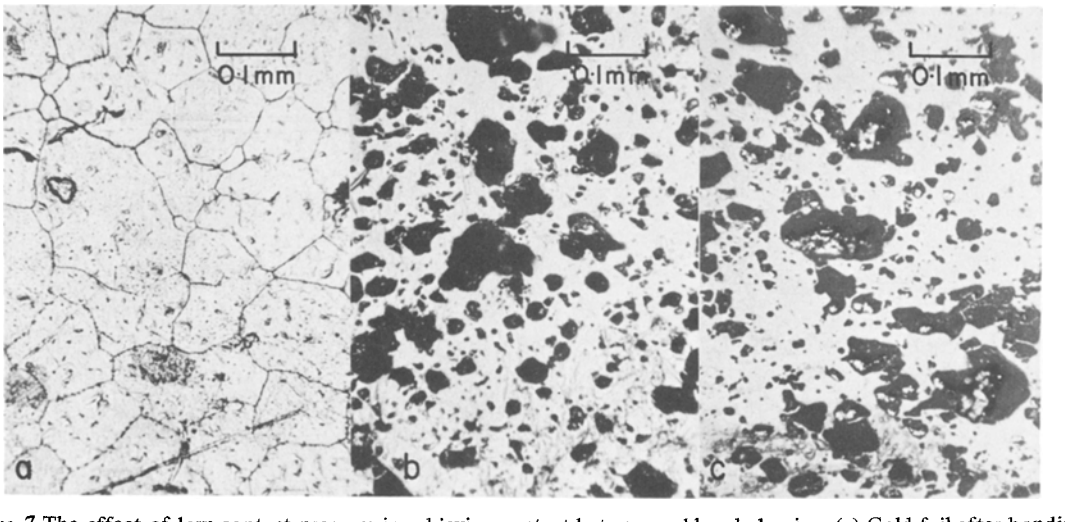

Figure 7 The effect of low contact pressure in achieving contact between gold and alumina. (a) Gold foil after bonding under no pressure. (b) Gold foil after bonding with 5×10^{-1} MPa pressure. (c) Alumina interface after bonding with 5×10^{-1} MPa pressure.

temperatures close to the melting point of gold, strength decreasing as the temperature was lowered. Fig. 5 illustrates this relationship. However, if the gold is allowed to melt, the bond is very weak when considered on an overall area basis, but is quite strong in the areas of contact. In this case, the gold does not wet the ceramic, but forms into sessile balls, which are strongly adherent to the ceramic – many cannot be prized off the surface even with the laboratory pliers.

3.3. Optimum bonding time

Bonding time was taken to be the length of time the furnace was held at the maximum temperature. In general, the longer the bonding time, the stronger the bond, in the range of 0.5 to 100 h. Fig. 6 illustrates this relationship.

3.4. Optimum bonding pressure

Optical microscope examination of the sheared bond faces has shown that a typical pressure of 0.5 to 0.6 MPa gives very intimate contact between the metal and ceramic. This can be seen from the gold surface after bonding, which usually shows a perfect imprint of the alumina structure (see Fig. 7). On the other hand, very low pressures (5×10^{-4} MPa) give bonds with no strength at all, nor does the gold foil show any imprint of the alumina structure. The rise in strength with increasing pressure is rapid up to the point where intimate contact is seen to be achieved. Further increasing the pressure to 18 MPa apparently does not increase the bond strength. Fig. 8 illustrates these relationships.

Very high pressure (e.g. 18 MPa) does increase the mechanical keying of the gold in the alumina pores; however, our work shows that this contribution to bond strength is small compared to that of the chemical bond. Several bonds were made in the hydrogen atmosphere, the effect of which was to reduce the chemical bonding to near zero. Bonds to highly polished sapphire single crystals averaged 2 MPa, whereas bonds to a porous Degussa alumina averaged 19 MPa under identical conditions*. Thus it is estimated that mechanical keying contributes, at most, about 15 MPa to a bond. This is to be contrasted to air bonds with sapphire which are greater than 90 MPa in strength, yet have no mechanical keying.

A final confirmation that low pressures are adequate for bond formation is given by the results of vacuum tests on several of the bonds. Bonds made with 5×10^{-1} MPa contact pressure proved to be completely leak-free when helium-leak tested.

4. Conclusions

4.1. Pre-treatments

The marked increase in strength observed after heat treatment could be due to several factors. The first considered was the annealing of the ceramic surfaces; however, the low temperature of the heating and similar results with only the gold being heated would make this an unlikely explanation. The second was the possibility that the heating procedure brought about a diffusion of active impurities of the metal to the surface†. It would be expected that these impurities would be removed by treatment with acid. However, bonds

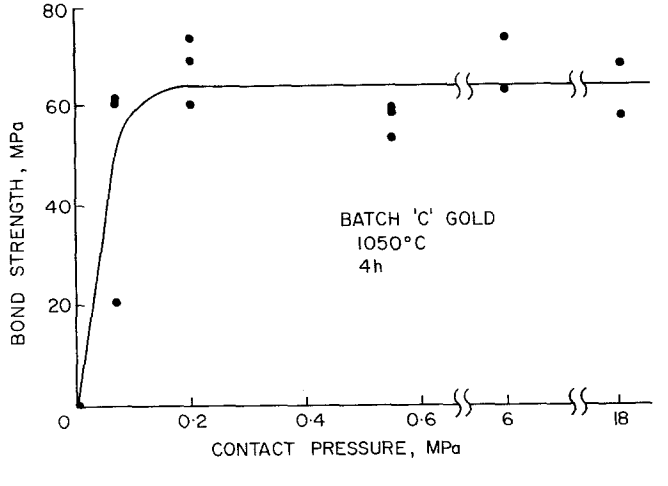

Figure 8 The relationship between bond strength and bonding contact pressure.

*930° C, 0.5 h, 15 MPa contact pressure, Gold B, hydrogen at 1 atm.

† The effect of impurities on bonding will be dealt with in a subsequent paper.

made in this way had strengths which were similar to those of bonds made from components which had received only the heat treatment. The third and final possibility considered was the simple one that the heat treatment is a very effective cleaning procedure, and that the thin film of hydrocarbons left after the standard solvent cleaning is enough to inhibit bonding. Indeed, Holloway [11] has shown that a carbon residue as little as 1 nm thick is sufficient to degrade gold thermocompression bonds. This explanation is consistent with the absence of any effect on acid-treatment of the components, and also with the fact that heat-treating either the gold or the alumina gave a bond-strength lower than that obtained by heat-treating both components (Table II).

The significant increase in bond strength observed in the specimens with additional evaporated gold is attributed to the improvement in contact area that such a treatment promotes. This effectively puts a layer of ductile metal into exceptionally intimate contact with the ceramic, bridging the subsequent contact to the bulk metal disc. The evaporated layer was, significantly, approximately equal in thickness to the extent of deviation from flatness of the ceramic surface, and it might be expected that a flatter ceramic surface would not show so great an enhancement of strength. Practical considerations determine the choice between the additional enhancement of the surface finish and the addition of an extra layer of gold. Apart from methods involving evaporation, additional gold layers can be deposited by several well-known methods, which would no doubt give similarly effective results.

4.2. Temperature

It is clear that bond strength increases with increasing temperature up to the melting point of gold, decreasing rapidly upon melting. In spite of this, there is still great strength in the small contact area of dewetted specimens. Here it is felt that the gold bonds to the alumina on passing just below its melting point during the cooling cycle; therefore, the bond developed is exceptionally strong. For practical bonding of components, of course, this is not a controllable method of creating seals, and a temperature which is as close to the melting point as the control equipment permits is the most satisfactory.

4.3. Time

A bonding time of 100 h may increase the bond strength by two- to three-fold, but as this increase may also be achieved by optimizing other parameters, a time of 1 to 4 h was deemed to be the most practical. The greater the strength that can be achieved at short times, the less is the effect of increased bonding time on the bond strength.

4.4. Pressure

Contrary to the reports of many recently developed solid-state bonding techniques, it was found that large contact pressures are not necessary to produce leak-tight, strong bonds. Only that pressure necessary to ensure intimate contact between the ceramic and metal is required. This optimum pressure will vary with the degree of flatness of the ceramic and the bonding temperature, as surface flatness and the ductility of gold near its melting point in themselves promote good contact and therefore make high pressures unnecessary. In other words, increased pressure can compensate, to some degree, for the departure of other factors from the optimum.

5. Summary

The investigation has shown that temperature is a sensitive bonding factor, as is also the degree of contact between the metal and the ceramic.

The strongest bond which could be achieved would be formed from alumina gently polished to the best flatness that optical finishing techniques permit. The gold batch would be carefully selected, and all components, after cleaning in solvents, would be heat treated at high temperature. Next a thin layer of gold would be deposited on the alumina. The bond would be made under about 1 MPa contact pressure just below the melting point for 100 h in air.

As has been discussed, strong bonding occurs over a wide range of conditions, and benefits gained diminish on approaching extreme values of temperature, pressure and time.

Acknowledgements

We acknowledge the assistance of Mr P. L. Larkins of the Spectroscopy Section of this laboratory for assistance with the atomic absorption analyses of gold samples.

References

1. A. F. MOODIE and C. E. WARBLE, paper presented at XXII International Congress of Pure and Applied Chemistry, Sydney, Australia, August (1969).
2. *Idem, Phil. Mag.* **35** (1977) 201.
3. H. J. DE BRUIN, A. F. MOODIE and C. E. WARBLE, *J. Mater. Sci.* **7** (1972) 909.
4. *Idem, Gold Bull.* **5** (1972 62.
5. C.S.I.R.O. and the Flinders University, South Australia, "Chemical Bonding of Metals to Ceramic Materials", Australian Patent No. 452651.
6. *Idem, ibid,* Italian Patent No. 920003.
7. *Idem, ibid,* British Patent No. 1352775.
8. *Idem, ibid,* United States Patent 4050956.
9. *Idem, ibid,* Japanese Patent Application No. 7473/71.
10. H. SCHMIDT-BRÜCHEN and W. SCHLAPP, *Keram. Z.* **24** (1972) 427.
11. P. H. HOLLOWAY, Sandia Laboratory, Albuquerque, New Mexico, Report SLA-73-1099 (1974).

Received 27 May and accepted 2 August 1977.