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A REVIEW OF THE REACTION BONDING TECHNIQUE FOR JOINING CERAMICS TO METALS

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Résumé - Le scellement réactif est un procédé direct pour former à l'état solide des scellements solides et étanches au vide entre des céramiques et des métaux. Plusieurs domaines d'applications potentielles sont présentés; ils nécessitent de former des liaisons entre de très grands nombres de matériaux - les aciers, le cuivre, le titane, le platine et l'or pour les métaux - l'alumine, la PSZ et le nitrure de silicium pour les céramiques.

Abstract - Reaction Bonding is a direct solid-state process for forming strong, vacuum-tight seals between ceramics and metals. Several potential new application areas for the process are discussed, which involve bonds formed between a wide range of materials - metals such as steels, copper, titanium, platinum, and gold, and the ceramics Al_2O_3 , PSZ and silicon nitride.

I - INTRODUCTION

Solid-state bonding processes are coming increasingly under study, for the potential advantages they have to offer as a practical joining technique for advanced engineering materials.

The ability to form strong bonds between materials in the solid state is however not a new technology. Thousands of years ago, metals such as silver, gold and iron are known to have been joined by solid-state processes such as hammering or forging. Development has proceeded over the years, to the point where solid-phase welding now covers a range of related industrial processes - cold pressure welding, friction welding, explosive welding and diffusion bonding. All are solid state processes, the basic difference being in the interchange of the three elements of temperature, pressure and time /1,2/.

The joining of metals by these solid-state welding processes is widely used and becoming more relevant today, the particular advantage being the ease with which widely dissimilar metals can be joined.

The advent of new engineering materials has posed a challenge to the development of suitable joining techniques, so as to allow these materials to be used to their full potential. In the field of

ceramics this is especially true. Solid-state metal-ceramic bonding is a technique which follows the general principles of solid-phase metal-metal joining techniques, i.e. the application of temperature, pressure and time, in a new way, to form bonds between a wide range of metals and ceramics. These bonds have characteristics ideally suitable for use with these materials - high strength at high operating temperatures, the ability to join materials of differing thermal expansion, and if required, vacuum-tightness of the bonded seal.

II - REACTION BONDING

The process of solid-state bonding of metals to ceramics has been studied for some years at the CSIRO Division of Chemical Physics, based on original observations by De Bruin, Moodie and Warble /3/. This process has come to be known as reaction bonding. A large number of bond combinations have been examined, some of which have been developed commercially into practical applications, such as a ZrO_2 based oxygen sensor, and a fast response thermocouple sheath /4/.

The bonding of the noble metals Pt and Au, to Al_2O_3 /5,6/, and Pd to MgO have been studied in detail, the latter as a model system using high resolution electron microscopy /7/. In this work, the reaction between Pd and MgO has been observed directly in the microscope, and it has been established that the reaction proceeds by means of a liquid-like amorphous phase at a temperature lower than the melting point of either material. However micro-diffraction to within $10\text{\AA}$ of the metal/oxide interface has shown no evidence of any material other than pure Pd or pure MgO.

Solid-state bonding involving the non-noble metals would seem to take place via a different mechanism altogether, and is often referred to by other workers as diffusion bonding /8/, as it tends to involve diffusion of the metal into the ceramic, the formation of reaction zones, and in the cases of nickel and copper with Al_2O_3 , reactions to form spinel phases at the interface. This is analogous to the solid-phase diffusion bonding processes discussed above, involving metals only.

(i) Bonding using interlayers - With some metals it can be difficult to form reliably strong reaction bonds directly to a ceramic - the ferrous alloys are an important example. So far it has not been established which of the possible causes is responsible i.e. thermal expansion mis-match, chemical incompatibility, structural changes in the metal on heating to the bonding temperature, or problems with oxide formation at the bond interface.

We have found that successful bonds can be achieved with the use of a suitable metal interlayer between the ceramic and metal to be joined, all bonds still being solid-state however. This effectively combines the old metal-metal solid-phase diffusion bonding with the newer metal-ceramic solid-state bonding. Suitable interlayer materials have so far been found to be the noble metals Pt and Au, in the form of thin foils, and also ductile metals like copper. Copper as an interlayer has been found to be particularly useful in facilitating the bonding of stainless steels to ceramics such as Al_2O_3 and partially stabilized ZrO_2 (PSZ). The ductility of copper aids the bonding process in that the interlayer material can be deformed sufficiently under moderate pressure (3MPa at $\sim 950^\circ\text{C}$ bonding temperature) to provide a good contact between itself and ceramic on one side and the steel on the other, without the fine surface finishing of the materials normally required prior to direct reaction bonding of ceramic to metal/5,6/.

Aluminium has been used by others /9/ as an interlayer material between

Al_2O_3 and stainless steel. This has the advantage of low bonding temperatures ($\sim 600^\circ\text{C}$), however the application temperatures are similarly limited. The contact pressures required to bond using aluminium are exceedingly high (50MPa), it has been necessary to deform the metal extensively to break open the oxide layer which is preventing reaction occurring, to expose clean Al to the ceramic. Aluminium also suffers the disadvantage of forming intermetallic layers with stainless steel, which tend to grow in thickness and degrade in strength with time at temperature /9/.

III-APPLICATIONS

Reaction bonding, in combination with solid-phase metal bonding via the use of metal interlayers, has been studied in relation to a number of application areas. These have included the electrical/electronic area, a traditional user of ceramics, and the newer structural applications, where the relatively new engineering ceramics, like PSZ, Syalon and silicon nitrides are coming into prominence. Also of interest is the bio-medical area, where the reaction bonding technique has special benefits to offer.

(i) Electrical/Electronic Applications - Ceramic-metal bonds are required in a wide range of electrical/electronic components. These include insulators, capacitors, discharge housings, X-ray tubes, heat sinks, feed-throughs and surge suppressors amongst many others. Almost all of these components require the sealing of copper to an electrically insulating ceramic, usually Al_2O_3 .

Reaction bonding of copper to these ceramics is readily achieved, the average bond strength being 124MPa for Al_2O_3 -Cu- Al_2O_3 sandwich type specimens (1) bonded at 1040°C .

The bonding of copper to alumina has been found to be sensitive to impurity levels in the copper, specifically oxygen, and correspondingly sensitive to the bonding atmosphere, in relation to oxygen content. The strength figure quoted above, 124MPa, is achieved for standard electrolytic grade copper sheet, which contains $\sim 0.04\%$ oxygen as an impurity, and bonds well in an inert atmosphere (pure argon). High conductivity oxygen free copper however, with an oxygen content of 0.0002%, tends to bond weakly in argon atmosphere ($< 20\text{MPa}$), however the addition of some oxygen into the atmosphere during the bonding process can improve this strength considerably. For one type of copper foil tested, bond strength was increased from about 10MPa (2 hours at 1040°C , 2MPa contact pressure) to 223MPa by flushing a mixture of 0.1% oxygen in nitrogen through the furnace during the bonding process.

These results support the mechanism of Cu- Al_2O_3 adherence in the solid state, as proposed by others /10/, i.e. the formation of a copper aluminate spinel CuAl_2O_3 , arising from reaction between CuO and Al_2O_3 . This is reported to result in a gradual change of structure at the bond interface, rather than a well-defined boundary.

Another technique for bonding copper to alumina, known as eutectic bonding, proceeds via a completely different mechanism. This involves the formation of a eutectic phase of Cu-Cu₂O at the interface, which wets the ceramic, forming a strong bond. This process requires a minimum bonding temperature of 1065°C , and very closely controlled atmosphere conditions /11/.

(1) Specimens formed from 99% Al_2O_3 tubing 8mm O.D. by 5mm I.D., copper discs 0.5mm thick. Bonding conditions: 2MPa clamping pressure, argon atmosphere.

Reaction bonding between Cu and ceramics is not critical with temperature in this way. Solid-state bonds with copper can be formed down to $\sim 800^{\circ}\text{C}$, however the strengths of reaction bonds do decrease as the bonding temperature is lowered /5/.

For the electrical/electronic applications mentioned above, metallizing

Fig.1. Electrically isolated Pt pads bonded to an Al_2O_3 substrate, to form part of a multi-contact electrical device. The Pt is bonded as a ring (figure 1a), which is later machined to leave the high-profile, hermetically-sealed Pt pads, as shown in figure 1b.

and brazing techniques are widely used at present to form the required metal-ceramic seals. These techniques have the advantage over solid-state processes like reaction bonding, in that they are readily adaptable to mass-production techniques. Their disadvantage however, is that metallized layers have poor electrical and thermal conductivity. With the current demand for higher density and speed of integrated circuit elements, there is a need for improved heat dissipation, and the thermal properties of the metal-ceramic seals are now of great importance. Direct bonding processes like reaction bonding or the eutectic bonding process described above must lead to improvement in thermal properties. For the eutectic bonding process for example, an estimate has been made of $0.02^{\circ}\text{C}\text{W}^{-1}\text{cm}^{-2}$ as the contribution of the Cu-ceramic interface to the total thermal impedance of a $\text{Cu}/0.63\text{mm Al}_2\text{O}_3/\text{Cu}$ sandwich measured at $0.36^{\circ}\text{C}\text{W}^{-1}\text{cm}^{-2}$ /11/.

Apart from improved heat dissipation across a direct-bonded interface, an advantage of reaction bonding is that the bonds are suitable for applications at high temperatures, above the maximum limits of $\sim 500^{\circ}\text{C}$ for metallized layers. Other metals may need to replace copper in these applications. Platinum-alumina reaction bonds have been tested up to 1100°C , where vacuum-tightness and strength of 150MPa (by 4-point bend test) is retained.

Figure 1 shows part of an electrical device where a ring of platinum has been reaction-bonded to an Al_2O_3 substrate, the ring later having been cut through at intervals so as to form tiny Pt pads arranged in a circular pattern. Variations of this technique could be used to form almost any required pattern of metal on a substrate, the reaction bond being sufficiently strong to withstand the cutting operation.

(ii) Bio-medical applications - Several million artificial or prosthetic parts are implanted into individuals each year. Of these many involve ceramics, particularly alumina, with PSZ presently under investigation for its bio-compatibility. Metals used include stainless steels, Ti and Ti alloys and often noble metals, particularly Pt or Ir /12/.

Vacuum-tight seals can often be required between these materials,

particularly in cases where electrical feed-through connections are required into circuitry and components to be implanted. In such cases of course, the ceramic-metal joining process must be just as bio-compatible as the materials themselves. The direct nature of reaction bonding, with its lack of any intermediary substances between metal and ceramic, gives it a special advantage in this area. The inert noble metals are especially suitable for many bio-medical applications, used

Fig.2. Materials to be used in bio-medical devices, such as titanium and PSZ, may need to be joined via noble metal interlayers. Here a PSZ insulator is joined to a titanium alloy case on one side, and a screw terminal on the other, via gold foil interlayers.

either on their own as connectors or lead-through wires, or as we have found, as interlayer metals to facilitate bonding of non-noble metals like titanium.

Figure 2 shows a test piece of a PSZ insulator bonded between a titanium alloy case on one side, and a screw terminal on the other, both bonds being made via a thin foil of noble metal, in this case gold. This bond combination has a bend strength of 102MPa, (formed under conditions of 1 hour at 890°C, contact pressure 7MPa). Similar bonds can be formed using platinum if required.

(iii) Structural Applications - Ceramics are increasingly being considered for use in structural applications, where the properties required are toughness, resistance to wear, corrosion and erosion, and ability to tolerate high temperature operation.

The ceramics of interest here are PSZ, silicon nitrides, silicon carbide and alumina. The structural applications include extrusion dies, spray nozzles, wear pads, pump parts, bearings and components for gas turbine and diesel engines. In all these areas, a means of attachment of ceramic to metal is nearly always required. For many applications however, the traditional techniques of shrink-fitting, mechanical fastening, or low temperature adhesives or cements are inadequate, and new joining processes must be developed which can satisfy the demands of the new application areas.

Our investigations have been orientated towards studying the reaction bonding behaviour of the materials likely to be involved in these structural applications. As ceramics, PSZ and alumina bond readily to a large range of metals, although as described above, an interlayer of a ductile metal such as copper is generally necessary to obtain a strong bond with ferrous metals. Alumina will generally form the strongest bonds of this type, up to 167MPa for the combination stainless steel-Cu-Al₂O₃, for example, (formed at 1040°C for 4 hours at 4MPa contact pressure, tested by 4 point bend). PSZ also bonds well, but bond

strengths are limited by the restrictions on bonding temperature for PSZ, i.e. for maximum long-term stability, this material is not recommended to be heated for long periods above $\sim 800^{\circ}\text{C}$ /13/. At this bonding temperature the strength of bonds formed between PSZ (2) and

Fig.3. Copper is a useful interlayer material, facilitating bonding between a wide range of materials:

- (a) Aluminium joined to PSZ via copper
- (b) A steel alloy engine valve, bonded at the tip to PSZ via a copper interlayer.

copper is around 70MPa (3).

Bonds between the silicon nitride materials and copper have also been attempted, although this work is at an early stage. These materials are also restricted in bonding temperature, due to the presence of glassy phases within the ceramic which limit their maximum operating temperature to $\sim 800^{\circ}\text{C}$. Maximum bond strength obtained so far for SYALON-copper is 90MPa, bonded under conditions of 870°C , for 1 hour at 5MPa contact pressure (4).

Much has been claimed about the prospects for ceramics in internal combustion engines, with the emphasis being on the superior physical and mechanical properties offered by these materials in replacing metal components. One important factor however, which may impede acceptance of ceramics for engine components, is their substantially higher cost, the fabrication of complex shapes in ceramic being inherently more costly than for metals. A large part of this extra cost is incurred in the necessary machining of ceramic components to the required tolerance which by its nature is more expensive for ceramics than for metals. There is therefore a need to restrict the use of ceramics to those areas where their superior properties are required, i.e. areas of high wear and thermal stress. If metal and ceramic are to be used in combination, then inevitably a demand is created for suitable metal-ceramic joining techniques. The engine application is most severe, in that the joints in most cases must perform reliably under considerable applied stress.

Possible areas where reaction bonding could be applicable to engine components are piston caps and valve stem tips. The purpose of a ceramic cap on either an aluminium or cast iron piston is to act as a load-bearing heat shield, while a valve tip is an area suffering high wear.

(2) PSZ here refers to MgO partially stab. ZrO_2 , as supplied by Nilcra Ceramics Pty Ltd (Australia).

(3) Sandwich type bonds formed from PSZ rod 13mm dia., and Cu discs 0.5mm thick, tested by 4 point bend.

(4) SYALON supplied by Lucas Cookson (U.K.)

In these applications, a 2-stage process may be required, for example, a direct reaction bond formed between the ceramic and a copper layer (such as foil), followed by some form of metal-metal joining process between the copper and the piston or valve metal, e.g. brazing or even solid-phase bonding. Figure 3a shows an aluminium alloy-copper-PSZ bond, made in this way. The Cu-Al joint is solid-state, heated at 500°C for 2 hours at 2MPa contact pressure.

A one-stage process may be possible in certain cases. Figure 3b shows a steel valve stem, which has been bonded in one heating cycle to a PSZ tip via a copper foil interlayer.

Conclusion

Being a direct, solid-state process, reaction bonding can be used to join a wide variety of ceramics to metals. Interlayers of suitable metals can be used to facilitate bonding in those cases where strong, reliable bonds cannot readily be formed directly. The versatility of the process, in both range of materials which can be joined and flexibility of bonding conditions, lends it to application areas as diverse as electronics, bio-medicine and engine components.

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