Solid State Bonding of Ceramics with Platinum Foil

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The solid state reactions that take place between many ceramics and metals can be utilised to produce strong vacuum-tight joints that maintain their strength and durability even at elevated temperatures. In this context platinum can play an especially important role because of its high melting point and resistance to chemically aggressive environments. Some industrial applications of the solid state bonding process using platinum are described in this article, which also includes some data on the properties of joints made in this way.

Techniques for the bonding of ceramics to metals are continually being sought for applications as diverse as electronic circuitry, vacuum tube technology, nuclear engineering and high temperature sensing devices.

Many techniques involving welding or brazing are currently available for ceramic-metal bonding, but most are limited by their nature to specific pairs of materials, and to low temperature applications.

A process known as reaction bonding has been developed through a collaborative programme between the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and the School of Physical Sciences of Flinders University (1, 2, 3, 4). Patents for the process have been granted in several countries (5). In contrast to conventional brazing and metallising techniques, reaction bonding is a direct, solid state process, that is to say no intermediate materials are used and no melting of any component is involved.

Reaction bonding can be applied to a wide range of metals and ceramic oxides. For example, alumina, zirconia, beryllium oxide and alumina-silicate ceramics can be bonded to industrially important metals such as platinum, gold, nickel and copper.

With noble metals such as platinum and gold, the mechanism of the bonding process involves a chemical reaction taking place at the bond interface. Scanning electron microscopy and electron probe microanalysis have failed to detect any evidence of metal diffusion into the ceramic (3). A scanning electron micrograph of a sectioned alumina-platinum-zirconia bond is shown in Figure 1.

The technique of reaction bonding is relatively simple, with four main requirements:

(i) Bonding temperatures must be below the melting point of the lowest melting component of the system, usually about 90 per cent of the melting point of the metal.

(ii) Bonding time is usually 2 to 3 hours, but can be as low as a few minutes.

(iii) Clamping pressures of 0.5 to 1.5 MPa are required to ensure adequate physical contact at the interface during bonding.

(iv) For maximum bond strength, the surface of the ceramic to be bonded must be polished to near optical flatness.

Bonding is usually done in air or vacuum, but protective atmospheres of argon or nitrogen are sometimes used to prevent excessive oxidation of the metal during the process.

Bonds formed in these conditions are both strong and vacuum tight, and maintain their strength at temperatures approaching those at which they were formed.

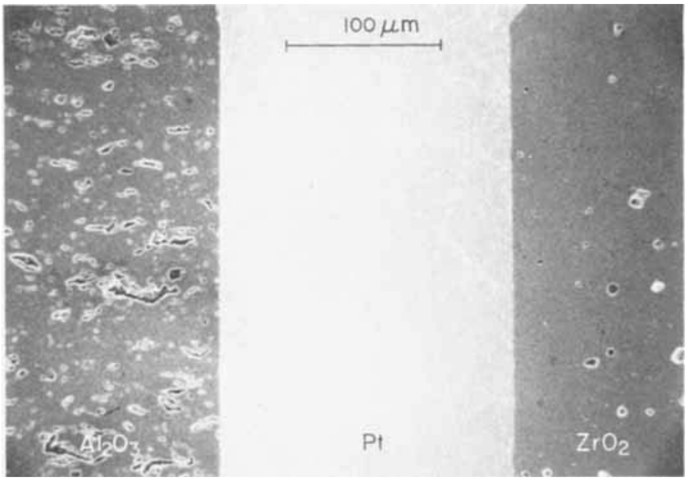

Fig. 1 A scanning electron photomicrograph of a sectioned alumina-platinum-zirconia reaction bond

In earlier papers (6, 7), factors that influence bond formation have been discussed with reference to alumina and gold. In the case of bonds involving platinum, optimum bonding conditions have been found to be 4 hours at 1450°C in air, with the ceramic and platinum foil held in contact by 1 MPa clamping pressure. Extensive mechanical strength testing in air at both room and elevated temperatures has been performed and some typical data are shown in Figure 2, demonstrating that the high bond strength is maintained at temperatures up to 1100°C. Specimen failure on testing in the moderate to high temperature range may occur in either the bond or the bulk of the alumina, as is clear from the closeness of curves A and B in Figure 2. Three pairs of alumina specimens bonded with platinum under identical conditions, and then tested to rupture are shown in Figure 3.

Applications of Reaction Bonding with Platinum

As discussed above, a wide range of metals can be reaction-bonded to ceramics. However, the process lends itself mainly to high temperature applications which are best served by noble metals such as gold and platinum. Platinum in particular, with its high melting point (1769°C) and chemical inertness in many hostile environments, is the preferred metal for many bonding applications. Two of these are considered below.

Fast Response Thermocouple Sheath

Thermocouple elements are traditionally sheathed in closed end ceramic tubes, in order

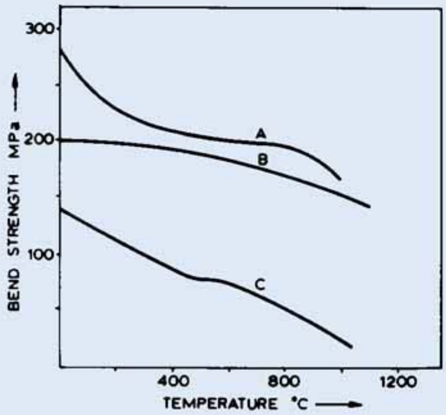

Fig. 2 Typical mechanical bend strength data for alumina-platinum-alumina bonds over a range of temperatures. Comparable data for commercial alumina, and tensile strength data for platinum are also given.
A: commercial alumina, 99 per cent dense. (Data – Coors Porcelain Co.)
B: alumina-platinum-alumina bond.
C: platinum, tensile strength, (Data – International Nickel Ltd.)

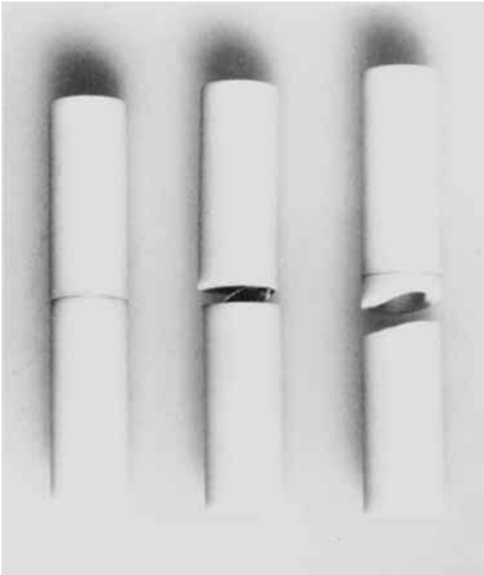

Fig. 3 Hot modulus-of-rupture test specimens of alumina-platinum-alumina bonds formed in identical conditions. Left: unbroken specimen, middle: specimen fractured through the bond, right: specimen fractured through the alumina

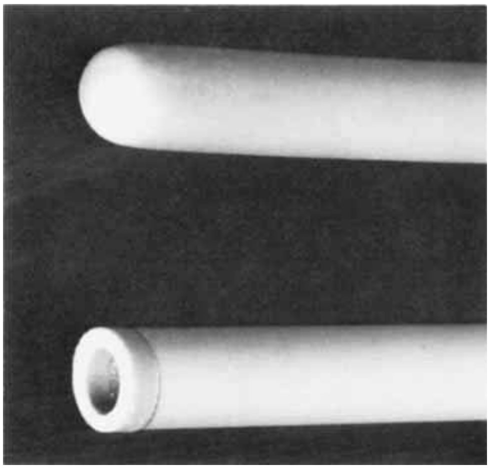

Fig. 4 Compared with a conventional domed end ceramic sheath (top), the sheath with a platinum foil window (bottom) permits a more rapid response to temperature change

to protect them from chemical attack or physical damage which can occur in many industrial and laboratory applications. The response to temperature changes of thermocouples within these sheaths is slow, and rapid temperature fluctuations will thus remain undetected. Reaction bonding has been used to overcome this problem; a new type of sheath known as a "fast response thermocouple sheath" has been designed. As shown in Figure 4, it consists of an open ended ceramic tube across the end of which platinum foil has been reaction-bonded, so as to form a thermal partition or window. The platinum foil window replaces the conventional domed end of a closed end ceramic sheath. In Figure 4 a thin ceramic ring bonded across the platinum window can be seen; this has no effect on the function of the sheath and protects the foil under rough service conditions and manufacture.

The response time of a thermocouple within the reaction-bonded sheath has been shown to be up to five times faster than for a thermocouple in a conventional closed end sheath. Such a rapid response ensures accurate temperature control, resulting in fuel savings by preventing overshoot and leading in many cases to improved quality control. The sheath has potential for use in many industrial applications, for example glass re-melt furnaces, where

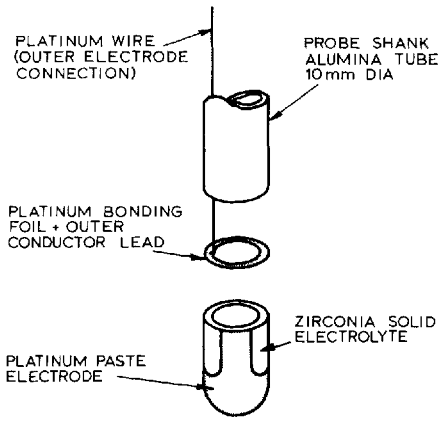

Fig. 5 Here reaction bonding is used to join an alumina tube of appropriate length to a zirconia cup. This is platinised on both the inner and outer surfaces to form the electrodes of an oxygen sensor. The outer electrode is connected by the platinum foil bond to a platinum wire and hence to the terminal head

Fig. 6 The bare oxygen sensor (top) is normally used mounted in a probe assembly complete with protective metal sheath and terminal head (bottom)

the rapid response of a bare thermocouple is required, while at the same time it must be protected against a corrosive environment.

Oxygen Analysing Sensor

An oxygen sensor using reaction bonding has been developed by CSIRO. The sensor is capable of in situ monitoring of oxygen concentrations in hot gaseous environments (600 to 1400°C). Oxygen sensors of this type are increasingly used in controlling fuel combustion in power generation and metallurgical processes where control of gas atmosphere and efficient energy usage are important.

The oxygen sensor is of the zirconia solid electrolyte type which relies for its operation on the high mobility of oxygen ions within the zirconia electrolyte. If differing concentrations of oxygen are present on either side of a zirconia barrier, an e.m.f. will be generated across that barrier depending on the magnitude of the difference in oxygen concentrations (8, 9). The reaction-bonded oxygen sensor is constructed by using a zirconia (calcia or yttria stabilised) cup, reaction-bonded with platinum to an alumina tube of a length to suit the installation, see Figure 5.

A thermocouple element (not shown in Figure 5) is fitted within the body of the sensor, so as to contact the inner platinised surface of the zirconia; the negative lead of the thermocouple also acts as the inner electrode wire.

Air is pumped to the inside of the sensor to provide a reference oxygen concentration, while the outside of the zirconia is exposed to the atmosphere to be analysed. The sensor is normally mounted in a protective metal sheath with terminal head, as shown in Figure 6.

For direct in situ operation of the sensor, the temperature of the process to be monitored must lie within the ionic conducting temperature range for zirconia, that is, between 600 and 1400°C. In cooler situations, a heater element can be fitted to the sensor to raise the temperature of the zirconia above 600°C. The reaction-bonded oxygen sensor has been licensed through CSIRO for manufacture in Australia.

Conclusions

Although only a few examples of reaction bonding have been discussed, it is believed that the technique has a scope for a wide range of applications. Although it appears to have most potential in the high temperature field, the simplicity of the technique lends itself to many ambient temperature applications where it could effectively replace many of the more complicated techniques used at present.

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