Ceramic to metal seals metallized by sputtering

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Abstract A method for applying the metallizing layers to ceramics by a sputtering technique is described. The ceramic to metal seals produced using this method, which can be used on any grade or type of ceramic, are strong and vacuum tight.

1 Introduction

A ceramic to metal seal usually consists of a ceramic body with a sintered refractory metal coating, a secondary layer of nickel or copper to provide a wetting layer for the braze filler, and the metal member to which the metallized ceramic is brazed. This paper describes a method of applying the metal coatings to the ceramic (i.e. the use of sputtering).

In the conventional metallizing technique the metal, usually molybdenum, molybdenum–manganese, or molybdenum–manganese–titanium, is painted on to the ceramic surface as a suspension of fine particles in a binder. This is then bonded to the ceramic by furnacing, between 1300 and 1500°C depending on the paint mixture, in a controlled atmosphere. A second furnacing operation will be required if the wetting layer is applied in the form of an oxide or powder. The bond between the metal layer and the ceramic depends upon the formation of a glassy or melt phase in the ceramic which will wet the metal. When metallizing the higher grade aluminas (i.e. Coors AD 995) it is necessary to add a presintered glassy phase to the metallizing paint to obtain strong vacuum tight bonds. A full description of these techniques is given by Reed *et al.* (1965).

It has been found that the metallizing layer and the wetting layer can be applied to the ceramic by a sputtering technique to give a strong vacuum tight bond without sintering. Sputtering is essentially a low temperature process and hence there is no risk of the ceramic cracking or distorting during the metallizing. The use of a low temperature process is particularly useful in the case of beryllia because of its toxicity. The thickness of the sputter layers is approximately 1 μm instead of the 20 to 30 μm of the sintered layers, so the ceramic can be machined to close tolerances before metallizing. The same process can be used on any grade or type of ceramic, and can easily be operated by unskilled labour.

2 Sputtering

In the experiments, the sputtering was carried out in a conventional vacuum bell jar, pumped by an oil diffusion pump and rotary backing pump. The three electrode technique was used and figure 1 shows a schematic diagram of the apparatus.

A discharge was maintained between the anode and the cathode, a heated tungsten filament, in a pressure of a few millitorr of argon. A magnetic field of 5×10^{-3} tesla (50 G) confined the plasma to a column of approximately 8–10 cm diameter. The target, which was the material to be sputtered, and the substrate, the material to be coated, were placed about 6 cm apart so that both were immersed in the plasma beam. A negative potential was applied to the target and positive gas ions bombarded the target causing material to be removed or sputtered (Holland 1956). The substrate holder was kept at earth potential. Deposition rates varied from 10–1000 Å min^{-1} depending on the material and voltage used.

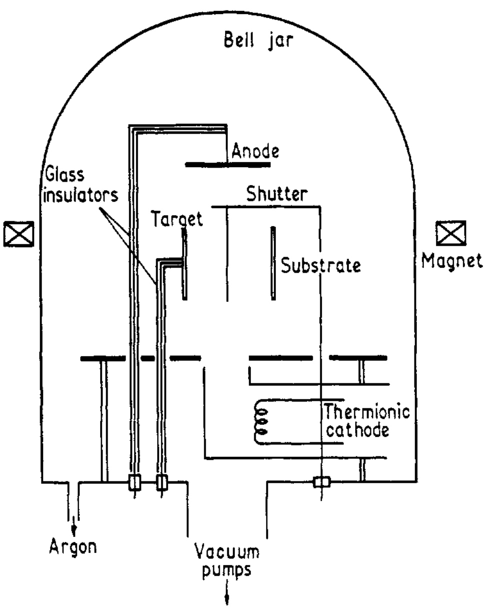

Figure 1 Schematic diagram of apparatus for three electrode sputtering process

3 Method

Ceramic test pieces to ASTM designation F19-61T/1961 (figure 2) made from Coors AD 94 and AD 995 alumina, Anderman and Ryder's Deranox 975 alumina, and Brush Thermalox 998 beryllium oxide were used in the experiments.

The ceramics were cleaned for 5 min in Genklene in an ultrasonic bath and then rinsed in acetone. The targets were made from sheet, 10 cm × 10 cm and 0·25–0·5 mm thick. A rotable holder was used so that two layers of different metals could be deposited without letting the system down to air.

Provision was made for a shutter to be placed between the target and substrate so that the surface layer of the target could be removed by sputtering, exposing clean metal for deposition on the substrate.

The system was pumped down to better than 5 μtorr, the diffusion pump throttled and argon let into the system via a gas leak to a pressure of 1 to 3 mtorr. To obtain strong seals, it was necessary for the system to be leak tight and pure dry argon used. The argon was dried by passing it through coils immersed in freezing methyl alcohol. The tungsten cathode was heated and approximately 100 V applied to the anode. It was sometimes necessary to use a tesla coil to start the discharge. The anode volts dropped to 40–50 and the cathode temperature was adjusted to give 3·5–4 A anode current. The magnet coil, positioned level with the target and substrate but outside the vacuum system, was energized. The discharge was maintained for 15–20 min to clean the surface by plasma 'scrubbing' before 1000 V was applied to the selected target,

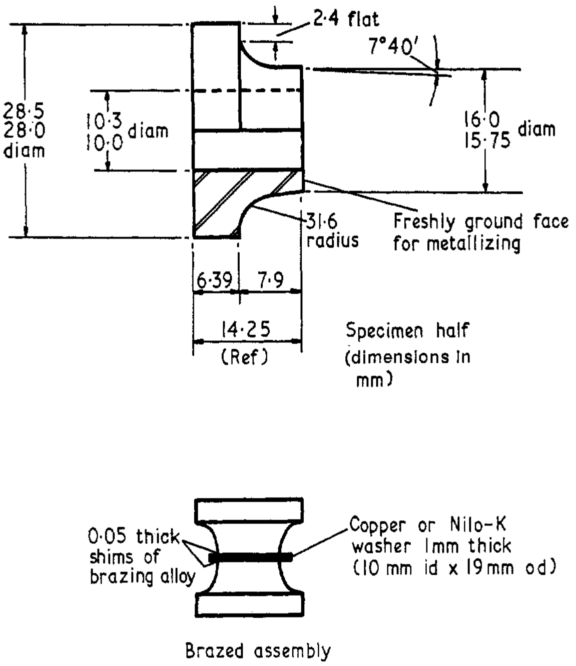

Figure 2 ASTM F19-61T/1961 test piece and brazed assembly. Area of metallized face, 1·17 cm^2; breaking load 1000 kg (0·98 ton), 850 kg cm^{-2} (12 000 lb in^{-2}); breaking load 820 kg (0·8 ton), 700 kg cm^{-2} (10 000 lb in^{-2})

which was presputtered for approximately 5 min with the shutter in position between the target and substrate. The shutter was removed and substrate sputtered to give the required thickness. The sputtering rates were determined in separate experiments by weighing the material deposited on glass sides. The same size target was used throughout the experiments; and with 1000 V applied a current of 100 mA was drawn. The deposition rate for a target-to-substrate spacing of 6 cm was approximately 100 Å min^{-1} for molybdenum, tungsten, tantalum, titanium and chromium; and approximately 300 Å min^{-1} for copper, gold and silver. When the required amount had been deposited the target voltage was switched off and the target holder rotated so that the second target faced the substrate. This was also presputtered before exposing to the substrate. The target, anode and cathode were switched off when both layers had been sputtered and the substrate allowed to cool. The substrate temperature rose to 150–200°C during the sputtering operation.

4 Brazing and testing

Two ASTM test pieces were joined together via a 1 mm copper, Nilo-K or molybdenum washer, using 0·05 mm shims of braze material.

The assembly was loaded in the brazing jig (figure 3), the centralizing pin being removed before closing the furnace. The weight of the top member ensured sufficient loading to maintain contact of the mating surface while the braze material was molten.

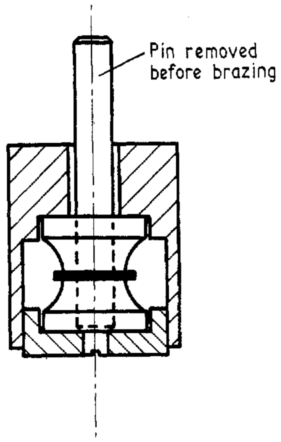

Figure 3 Brazing jig for tensile test specimen

The brazed seal was vacuum checked using a Beckman mass spectrometer leak-detector with helium as the probe gas. The seals were finally tensile tested with a Hounsfield tensometer using adaptors (figure 4) with PTFE washers to cushion the shoulders of the ceramics against the metal flanges. A successful ceramic to metal seal was taken as one which was vacuum tight and had a tensile strength in excess of 700 kg cm^{-2} (10 000 lb in^{-2}).

5 Results and discussion

Various combinations of metals were tried in these experiments. Primary layers of molybdenum, tantalum or tungsten followed by a secondary layer of copper, silver or gold have produced successful seals. All the seals produced with titanium as the primary layer, or with nickel as the secondary layer leaked. To obtain a good seal using chromium as the primary layer it is necessary to sputter a thick (>1 μm) layer of chromium. The braze temperature and the time the seal is at that temperature must be kept to a minimum to prevent diffusion of the secondary layer metal through the chromium to the ceramic.

The solubility of copper, silver or gold in molybdenum, tantalum or tunsgten is reported by Hansen (1958) as very small or 'vanishingly small'; their solubilities in chromium are small but sufficient to make the seals unreliable. The solubilities of these metals in titanium are of the order of a few per cent at the brazing temperature. Nickel alloys readily with all the metals used as primary layers.

The requirement for a vacuum tight seal then is for a primary layer of metal to be sputtered on to the ceramic, followed by a secondary layer of metal which is not soluble in the metal used for the primary layer but is readily wetted by the braze material.

The primary layer can be quite thin (500 Å), but the secondary layer needs to be thick enough (10 000 Å) to allow for diffusion of the braze material. The braze materials used in these tests were copper–silver eutectic, silver, 9 carat copper–gold, and various copper–silver palladium alloys,

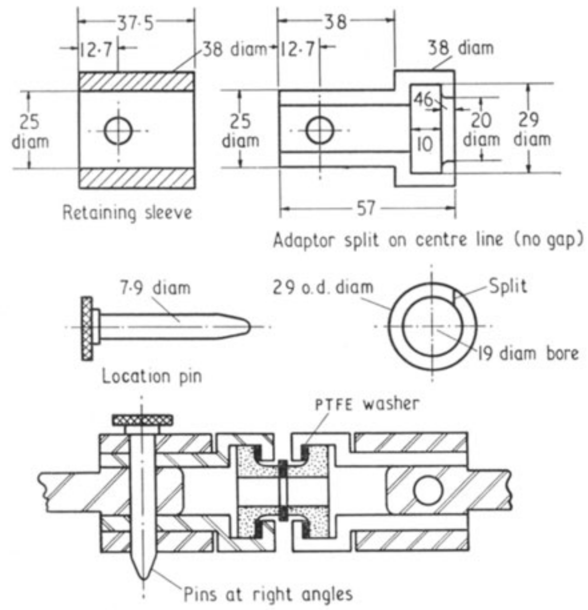

Figure 4 Adaptor for tensile test specimens on Hounsfield tensometer. All dimensions in millimetres

melting between 800 and 1000°C. Brazing was carried out in either a dry hydrogen atmosphere or in a vacuum furnace.

The fracture in a good joint will occur completely in the ceramic, leaving a layer of ceramic still adhering to the metal member (figure 5). The strength of the joint depends on the quality of the ceramic as no glass phase or weak intermediate layer is produced. Joint strengths of 1750 kg cm^{-2} (25 000 lb in^{-2}) have been recorded for the alumina ceramic to metal seals; and 850 kg cm^{-2} (12 000 lb in^{-2}) for the beryllia ceramic to metal seals. However, different batches of AD 94 and AD 995 alumina test pieces fractured at values as low as 700 kg cm^{-2} (10 000 lb in^{-2}).

The sputtered layers adhere well to the ceramic and do not require a sintering or diffusion treatment to bond them to the ceramic. To prove this, sputtered test pieces have been joined together using an impact adhesive (Eastman Kodak 910) and require a pull of 1000 to 1150 kg cm^{-2} (14 000 to 16 000 lb in^{-2}) to separate them. There was no sign of the sputtered layers pulling off. Metal test pieces joined in the same way gave similar tensile figures.

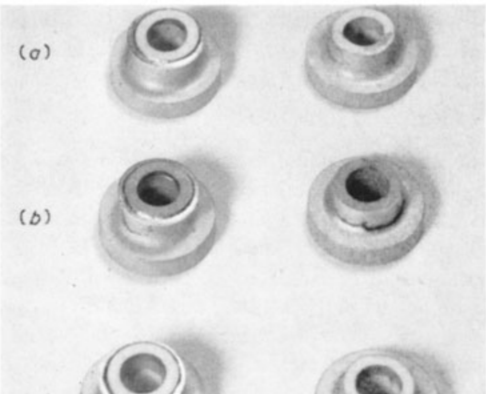

Figure 5 Fractured test pieces. (*a*) 99·8% beryllium oxide; (*b*) 99·5% aluminium oxide; (*c*) 94% aluminium oxide

Brazed test pieces have been temperature cycled to see if the seal will withstand refurnacing as might be expected if the ceramic part were used in a valve. A ceramic copper joint fails (i.e. becomes no longer vacuum tight) if reheated above 500°C. However, it will withstand heating to 400°C for several hours and still remain vacuum tight although its tensile strength is reduced to half the expected value. Joints of ceramic to metals with a closer thermal expansion match will withstand repeated temperature cycling to within a few degrees of the braze melting temperature. Test pieces joined by Nilo-K (nickel–cobalt–iron alloy) or molybdenum washers and alumina to alumina joints have been successfully cycled five times and were still vacuum tight. The tensile strength of these joints was only slightly reduced.

Heil and Morozovsky (1966) obtained tensile strengths up to 850 kg cm^{-2} (12 000 lb in^{-2}) for ceramic to metal seals using a particle bombardment method, a combination of rf sputtering and vaporization of the metal layers. Mattox (1965) and Culbertson and Mattox (1966) report strengths of 560 kg cm^{-2} (8000 lb in^{-2}) by evaporating the metal layers on to the ceramic in a gas discharge, a technique known as ion plating. Buck and White (1966) used a diode sputtering technique to apply metal layers to ferrimagnetic materials and obtained good adhesion.

6 Conclusion

Sputtering is a clean and simple technique for metallizing ceramics, which can be operated by unskilled labour. The same process can be used for any grade of ceramic, and it is particularly useful for beryllia. It is essentially a 'cold' process so there is no risk of distortion or cracking of the ceramics during metallizing. The metal layers are thin ($\simeq 1\ \mu m$) and hence the ceramics can be machined to close tolerances before metallizing.

Acknowledgments

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