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TUNGSTEN METALLIZING ALUMINA-YTTRIA CERAMICS*

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Robert E. Cowan and Stephen D. Stoddard

ABSTRACT

The ease with which high-alumina bodies may be metallized with tungsten is improved by additions of yttria to the alumina. Mechanisms of this bonding process were studied by use of optical and electron microscopy, electron microprobe, and tensile tests. Variables studied included yttria content of the body and the firing temperature during metallizing. The study showed that a reaction between the tungsten and the yttrium grain boundary phase markedly improved adherence.

Recent developments in energy conversion techniques have resulted in the need for ceramic-to-metal seals that will operate under very severe environmental conditions. The principal problems, corrosion by alkali metal vapors and high service temperatures, have led to the development of highly specialized metallizing and brazing techniques.

The nuclear thermionic converter uses cesium vapor as the electrical conducting material in the diode. Cesium is incompatible with many oxides commonly used as fluxes and sintering aids in both body preparation and metallizing mixes.¹ This incompatibility precludes the use of SiO_2 , TiO_2 , MnO_2 , or MnO in any proposed metallized ceramic. Furthermore, the operating temperature of the seals for converter use is in the 1200 to 1500°C range in a nonoxidizing atmosphere. If the seals are to be assembled by conventional brazing techniques, the metallized ceramic must withstand brazing temperatures in the 1500 to 1900°C range. This requirement rules out the use of ceramics that contain a silicate glassy phase: these second phases migrate

through a metallizing layer at temperatures above 1500°C, producing an oxide film on the metallizing layer that cannot be wet by the brazing alloy.

The basic system chosen for this application was alumina metallized with tungsten. Fabrication technology is well established for alumina, and it has a thermal expansion coefficient closely matching that of niobium, which constitutes the remainder of the brazed assembly. The use of tungsten as a metallizing material was justified on the basis of its high recrystallization temperature. However, tungsten does not adhere directly to pure alumina. Adherence-promoting agents must be added either to the body or to the metallizing layer to produce a satisfactory bond.

Studies have shown that yttria additions to alumina are effective in lowering the firing temperature. These yttria-bearing bodies also may be readily metallized. The fluxing effect of yttria on alumina is shown in Fig. 1. These data show that increasing amounts of yttria lower the temperature at which maximum density is attained, an effect attributable to the formation of the compound $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ (yttrium aluminate) at the grain boundaries. X-ray diffraction analysis has confirmed the

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Fig. 1.

Effect of yttria content and firing temperature on alumina density.

presence of this phase. Figure 2, an electron micrograph of a body containing 2 wt% yttria, clearly shows the grain boundary phase.

The metallizing behavior of four yttria-bearing bodies was studied to determine the minimum amount of yttria needed to form a strong bond and

Fig. 2.

Ceramic metallized with tungsten.

to determine some of the basic mechanisms involved in the process. The raw materials were chosen to avoid the introduction of impurities that would deteriorate in contact with cesium. Spectrographic analyses of starting materials, mill batches, and fired bodies are shown in Table I.

Body preparation was done by ball milling the materials for 30-50 h. The shapes were fabricated by slip casting or cold pressing. Firing was carried out according to the schedule shown in Table I. The metallizing mixes were prepared by ball milling the tungsten powder for 4 h to break up agglomerates. The mill batch contained 100 g of tungsten powder, 22 ml of water, 0.6 ml of glycerine, and 0.3 ml of a commercial electrolyte (Darvan No. 7). The glycerine retards the drying rate of the slurry and allows a uniform coating to be applied by brushing.

A series of tensile tests was made in order to determine the effect of the yttria content of the body on the metallizing bond strength. Yttria contents of 0.05, 0.10, 0.50, and 2.0 wt% were used. The tensile specimens were modified slightly from the ASTM design in accordance with studies made by Sperry Gyroscope Company.³ The metallized coatings were fired at temperatures between 1400 and 1800°C with a 30-min soak at peak temperature. A hydrogen atmosphere having a dew point of 25°C was used for all firings. The specimens were brazed together using a nickel-gold eutectic brazing alloy. Testing was done on an Instron Testing Machine at a crosshead speed of 0.015 m/s (0.010 in./min). The tensile test results are shown in Fig. 3. These data show that the body containing 0.05% yttria produces significantly lower tensile strengths than do the bodies containing 0.1, 0.5, and 2.0% yttria. Firing temperature has a strong influence on the strength obtained with the 0.05% yttria body, whereas the other three bodies show much less dependence upon firing temperature. Mechanically strong (though not necessarily hermetic) joints can be made at temperatures as low as 1400°C with the three bodies of higher yttria content.

These data suggest that the presence of yttria in the form of yttrigarnet is responsible for the adherence obtained in this system. Some investigations have been made regarding the bonding mechanism. In some respects, this combination of materials is convenient to study, because the composition of the grain boundary phase is known, and it can be fabricated and examined separately. This

TABLE I
IMPURITY LEVEL OF MATERIALS USED IN METALLIZING DEVELOPMENT
(Units are in ppm)

	Tungsten As Received	Ball Milled	Yttria As Received	Alumina As Received	Body $Al_2O_3 + 0.5\% Y_2O_3$	
					Ball Milled (40 h)	Fired 1750 (2 h) H_2
Na	5	100	<20	40	400	<10
K	50	50	<100	<30	<30	<30
Mg	<1	50	<10	20	400	200
Ca	10	30	20	100	100	100
Si	20	300	100	100	2000	400
Al	<3	300	20	---	---	---
Fe	3	3	<30	400	400	100

Fig. 3.
Effect of yttria content and metallizing temperature on alumina-tungsten bond strength.

fabrication is more difficult to accomplish in conventional alumina bodies that contain a siliceous glassy phase.

An analysis of a tungsten-yttrigarnet interface was made by the electron microprobe technique. Tungsten coatings were applied to polycrystalline yttrigarnet and fired in wet hydrogen at 1500, 1600, and 1700°C. The samples were then polished ceramographically before the electron microprobe study. There appeared to be little difference among

the three firing temperatures; the results of the 1500°C firing are shown in Fig. 4. The electron backscatter photograph clearly shows the contour of the tungsten coating. The interface is very rough, and an excellent mechanical bond is to be expected. The x-ray distribution of the tungsten $L_{\alpha 1}$ lines shows little, if any, penetration of tungsten into the ceramic. The distribution of yttrium K_{α} x-rays is shown, and superimposed on it is the tungsten outline from the electron backscatter photograph. This photograph shows that the yttrium is present in the tungsten layer as well as the ceramic. A gradient of yttrium concentration across the tungsten suggests that a diffusion process has occurred. The distribution of aluminum K_{α} x-rays shows that the alumina is in contact with the tungsten at the interface. No diffusion of the aluminum has occurred. However, the voids in the tungsten layer contain alumina. These data indicate that the yttrigarnet has broken down into alumina and yttria, and that the alumina has remained between the tungsten particles while the yttria has diffused into the tungsten. This observation has also been made on a tungsten-coated body of alumina plus 2 wt% yttria and on pure yttria metallized with tungsten. Spectrographic analysis of the original tungsten powder used for metallizing showed that it contained less than 100 ppm yttrium. It is very unlikely that the electron

Fig. 4.

Electron microprobe examination of tungsten metallized yttrogarnet. Grid spacing = 5.6 μ m. 1600X.

microprobe technique could detect quantities of this magnitude.

Further studies of bonding in this system were made by electron microscopy. The sample preparation technique involved the preparation of 3.2-mm-thick ceramic discs lapped to a smooth finish. A tungsten slurry was applied to one surface of two discs and the pieces were then placed in contact, with the tungsten between them. The samples were

fired in wet hydrogen to bond the two coated pieces together. The piece was then sectioned and polished with silicon carbide and diamond abrasives. Structural details were developed either by polishing on a vibratory polisher or by thermal etching at 1500-1600°C for 5 min in wet hydrogen. For the electron micrographs, we prepared a negative parlodion replica and shadowed with carbon and chromium.

An electron micrograph of a ceramic (alumina plus 2 wt% yttria) metallized with tungsten is shown in Fig. 5. This sample was prepared by vibratory polishing, which distinguishes the metal and ceramic phases but fails to reveal a grain structure. The tungsten layer appears to be very dense, and isolated grains of the ceramic are present within the metal. A similar area is shown in Fig. 6. Here the tungsten and ceramic form a very rough interface, with the two materials penetrating each other to a great extent. Presumably, the electron microprobe would show that the material extending into the tungsten is alumina, with yttrium present in the tungsten.

A thermal etch at 1500°C on the same sample shows a somewhat different structure (Fig. 7). The two-phase structure of the ceramic is shown quite clearly. The grain structure of the tungsten is also revealed. The tungsten grains are $\sim 1 \mu\text{m}$ in diameter and are of fairly uniform size. Similar electron micrographs are shown in Figs. 8 and 9. Thermal etching at 1600°C tends to obliterate the microstructure (Fig. 10).

Fig. 5.
Ceramic metallized with tungsten. Sample 5538-2.

Fig. 6.
Ceramic metallized with tungsten. Sample 5538-1.

Electron microscopy has also been carried out on samples of pure grain boundary phase, yttrigarnet, using techniques similar to those just described. Figure 11 is an electron micrograph of tungsten-metallized yttrigarnet. Exaggerated grain growth had occurred in a portion of the ceramic. Again, the ceramic-tungsten bond is very intimate. It appears that the yttrigarnet has migrated into the tungsten for a few micrometers, and it is difficult to identify a true tungsten-yttrigarnet boundary in some areas.

A cermet composed of equal volumes of yttrigarnet and tungsten was also prepared for study. This mixture was cold pressed and sintered at 1700°C for 15 h in wet hydrogen. An electron micrograph of its microstructure is shown in Fig. 12. The yttrigarnet can be distinguished by its lack of detail on the surface of the grains. This sample contains virtually no porosity, and the bonding between the two dissimilar phases is excellent. There appear to be no reaction zones between the two phases. A microhardness measurement on the tungsten phase produced a Diamond Pyramid Hardness value of

Fig. 7.
Ceramic metallized with tungsten. Sample
5538-1.

Fig. 8.
Ceramic-tungsten interface. Sample 36.

445 using a 100-g load. This value is within the range expected for annealed tungsten.

These measurements have examined the improved bond obtained when yttria is added to the body. The possible beneficial effect of adding yttria to the metallizing mix has also been examined briefly. Two metallizing mixes, containing 2 wt% of yttria and yttrogarnet, respectively, have been studied. The coatings were applied to a body containing 0.05% yttria. Firing was done at 1700 and 1800°C for 30 min in wet hydrogen. The yttria addition fired at 1700°C produced a tensile strength of 51 MPa (7320 psi), whereas a firing temperature of 1800°C gave a value of 45 MPa (6550 psi). The strength produced by the yttrogarnet addition was 48 MPa (6900 psi) at 1700°C and 26 MPa (3790 psi) at 1800°C. These data indicate that adding yttria or yttrogarnet to the tungsten can produce strong joints, but that such additions to the body are more effective.

The data described here show that yttria has a strong influence on bond strength when added to either the body or tungsten. The mechanism for this behavior is apparently associated with a reaction between the yttrogarnet and the tungsten. The only direct evidence for such a reaction is given by the electron microprobe studies. A diffusion or migration of the yttrium into the tungsten occurs as a result of this reaction. The analytical techniques used here have not identified the chemical species of yttrium in the tungsten.

The metallizing technique using yttria as a bond-promoting agent has proved useful for seals operating at elevated temperatures. This combination of materials is stable in contact with cesium vapor and is a primary choice for seals to be used in nuclear thermionic converters.

Fig. 9.
Ceramic-tungsten interface. Sample 36.

Fig. 10.
Ceramic-tungsten interface. Sample 34.

Fig. 11.
Ceramic-tungsten interface. Sample 31A.

Fig. 12.
Typical cermet structure. Sample 37.

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