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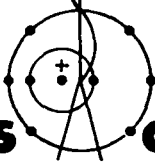
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by

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CERAMIC MATERIALS FOR NUCLEAR THERMIONIC CONVERTERS*

by

Robert E. Cowan and Stephen D. Stoddard

ABSTRACT

Ceramic-to-metal seals and pure oxide ceramics for use in the plasma thermocouple concept of nuclear thermionic power converters were developed to operate in a cesium-vapor environment at 1200°C. Hermetic seals of tungsten-metallized alumina brazed to niobium were developed that could be thermal cycled to above 1200°C. Magnesia-nickel ceramic-to-metal seals showed promise for use in thermal cycling to 700°C. An alumina-yttria body was used for metallizing with tungsten.

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The development of nuclear power has been accompanied by many different schemes for converting fission energy to electrical energy. Most plans involve the production of an expanding fluid such as steam that is converted to electricity by means of turbines and generators. It has long been realized that the direct conversion of fission energy to electrical energy would have many advantages. The elimination of heat exchangers, turbines, and generators would result in a greater electrical output per unit of weight and possibly realize a greater overall efficiency. This concept is particularly attractive for space vehicle applications where weight is of primary concern.

At the Los Alamos Scientific Laboratory, the nuclear thermionic converter is known as the plasma thermocouple.¹ A cross-sectional view of one design of this device is shown in Fig. 1. The emitter, a fissionable material, is heated by the energy released in controlled nuclear fission. The hot emitter ionizes cesium vapor surrounding it to form cesium plasma. A flow of electrons between the hot emitter through the cesium plasma to the cooler collector establishes

*Presented at 65th Annual Meeting of the American Ceramic Society, Pittsburgh, Pennsylvania, May 1, 1963.

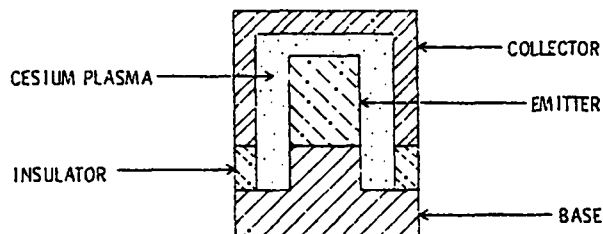


Fig. 1.
Plasma thermocouple cell.

an open-circuit voltage of ~ 3 V. A maximum current flow of 20 A per square centimeter of emitter area can be obtained. An insulator must be used to prevent the collector and emitter from forming a short circuit. The junctions between the insulator and collector and base must not allow air to penetrate: a hermetic seal is required. The method of forming such seals is the subject of this report.

The operating conditions of this device are unique, and a brief description of them will illustrate the problems involved in developing materials for plasma thermocouple use. For maximum efficiency,

this cell should operate at as high a temperature as possible. Through the proper choice of fissionable materials, the emitter can operate at 2000°C. The collector must operate at some lower temperature that is still high enough for efficient cooling by radiation. A collector temperature of 1200°C is the maximum presently being considered, and lower collector temperatures can be used in some instances. The insulator of course must operate at the same temperature as the collector. The objective of this development program has been to fabricate ceramic-to-metal seals that will operate in the 700 to 1200°C range.

The choice of materials for collector and insulator is based on several considerations. The collector must have a low electrical resistivity to minimize ohmic losses, a low absorption cross section for thermal neutrons, and a thermal expansion closely matching that of the insulator. The ceramic insulator must have a high electrical resistivity and must withstand the effects of high neutron fluxes. Its expansion must, of course, match that of the collector. In addition, the ceramic must not be affected by cesium vapor. Cesium is an extremely corrosive material that reacts extensively with some oxides, notably silica. These considerations have led to the development of two different ceramic-to-metal seal combinations. For use at 1200°C, a combination of a silica-free alumina ceramic and niobium appears to be the most promising. The similar thermal expansion coefficients of these materials should develop a minimum of thermal stress. Other oxides, such as beryllia or spinel, might also be used with niobium, but these have not been studied extensively. At 700°C, the collector can be made of nickel. To minimize thermal stresses, the ceramic can be made of magnesia, which has a relatively high thermal expansion.

The composition of the ceramic bodies used in seals is governed by their ability to withstand attack by cesium vapor and by their ability to be metallized. Cesium corrosion can be minimized by avoiding silica in the ceramic. The limits of silica concentration have not been established, but ~1% silica does not appear to be harmful at temperatures below 1000°C. The alumina seal operating at 1200°C for 10 000 h will require a silica content as low as possible. This silica constraint creates problems in ceramic fabrication and metallizing. Adding silicate materials to alumina promotes both sintering and

the adherence of a metallizing material. But it has been found that yttria, which is unaffected by cesium vapor, is an effective flux for alumina and aids in the formation of a strong ceramic-metal bond. The addition of 2 wt% yttria to alumina results in a body that can be fired to vitrification at ~1700°C. The sintering process is apparently enhanced by compound formation that develops a yttria-rich phase at the alumina grain boundaries.

The magnesia body used for making seals to nickel contains 0.5 wt% calcia and 0.3 wt% silica as the major impurities. These contaminants have not proved harmful from the standpoint of resistance to attack by cesium vapor.

The metallizing technique used for the alumina ceramic was determined by the service conditions of the seal. An operating temperature of 1200°C required that the braze be made in the 1400 to 1600°C range. These temperature requirements precluded the use of active metal sealing techniques because excessive titanium or zirconium diffusion into the ceramic could destroy the bond. For this reason, refractory metal techniques were used exclusively. Many of the refractory metal processes use a composition containing oxides that are unstable in contact with cesium, among them silica, titania, manganous oxide, and manganic oxide. These oxides are frequently added to refractory metals to promote ceramic-metal adherence. Although their use could be tolerated for the low-temperature magnesia seals, they could not be used for the more severe service conditions of the alumina seals. Tungsten was chosen as the metallizing layer primarily because it has a higher recrystallization temperature than does molybdenum. For high-temperature brazing, less grain growth might be expected from tungsten than from molybdenum. An adherent coating of tungsten can be applied to a yttria-bearing alumina without adding the fluxes used in conventional molybdenum-manganese processes.

The tungsten can be applied in powder form either as the oxide (WO_3) or as the metal. The oxide has a lower density and is much softer than the metal, which simplifies the preparation of finely divided stable suspensions for brushing or spraying. A satisfactory suspension can be made from 66 vol% water and 34 vol% tungsten oxide that has an average particle size of 1 μ m. Adding a small amount of methyl cellulose improves the strength of

the dry, unfired coating. Tungsten oxide is somewhat unreliable because a volume decrease of 170% occurs during reduction in hydrogen, causing the coatings to crack and peel. Application of tungsten metal solves the problem. A mixture of 83 vol% water and 17 vol% tungsten metal produces a suspension having satisfactory viscosity. Binders and deflocculants can also be added. The tungsten can be applied to the alumina by brushing with a red sable artist brush or by spraying with an air brush. An application of about 9.3 mg per square centimeter of surface yields a coating thickness of 0.0013 cm. This coating is fired at 1650°C with a 30-min soak in wet hydrogen.*

For metallizing magnesia for use in less severe service conditions, a conventional molybdenum-manganese process has been used. This composition is composed of ~75 wt% molybdenum and 15 wt% manganese. The remaining 10% consists of iron, titanium hydride, alumina, and silica.² An organic vehicle is used to form a suspension for spraying or brushing. Firing is carried out at 1650°C for 30 min in a wet hydrogen soak.

The metallized ceramic is joined to the metal by conventional brazing techniques using filler metals chosen according to the final service conditions. For the alumina-niobium seal operating at 1200°C, palladium appears to be the most promising braze metal. Palladium melts at 1554°C, has a fairly low vapor pressure, and wets both tungsten and niobium. A brazing temperature of 1600°C in vacuum has been used to form hermetic seals with palladium.³ Seals that can operate at lower temperatures are made using an alloy of palladium and cobalt.** This alloy has a liquidus temperature of 1235°C and wets tungsten and niobium. A brazing temperature of 1250°C is used with this alloy. The use of brazing filler metals that contain gold is not possible because cesium attacks gold and its alloys very severely.

Brazing to magnesia metallized with molybdenum has been done most extensively with the common silver-copper eutectic alloy. To promote wetting by the silver-copper alloy, the molybdenum is first coated with a thin layer of nickel by electroplating or by reducing nickel oxide at 1000°C in hydrogen.

*All hydrogen soaks in this study have a dew point of 25°C.

**This alloy, sold under the trade name "Palco," is a product of Western Gold and Platinum Co., Belmont, California.

The alumina-niobium seal brazed with palladium has been tested as high as 1450°C without loss of integrity. One seal was cycled in vacuum from room temperature to various temperatures between 1200°C and 1450°C with a 1-h soak at temperature for 100 cycles without destruction of the hermetic seal. Magnesia-nickel seals made using the copper-silver brazing alloy were tested in air at 700°C. The seals were intact after 25 cycles of heating from room temperature to 700°C.

Some investigations have been made into the strength and nature of the bond between tungsten and the alumina-yttria ceramic. A series of tensile strength measurements were made using the ASTM method (ASTM Test F19-61T). The alumina plus 2 wt% yttria was metallized with tungsten and fired at 1600°C, 1650°C, and 1700°C in wet hydrogen. The samples were brazed with a nickel-gold alloy and tested at a strain rate of 0.015 m/s (0.010 in./min). The results indicated that the seal strength increased as the firing temperature increased. Strengths of 53 MPa (7690 psi) at 1600°C, 56 MPa (8130 psi) at 1650°C, and 62 MPa (9040 psi) at 1700°C were obtained. These data are probably not representative of the true strength of the seal because some of the specimens fractured in the shoulder rather than at the joint. Further measurements are planned that will use the modified ASTM sample configuration.

An examination of the bond between the tungsten and the alumina-yttria ceramic was made by metallography. A polished section of an alumina ceramic containing 2 wt% yttria is shown in Fig. 2. The tungsten layer is approximately 0.0013 cm thick. It is apparent that the metal is very well bonded to the ceramic even though no glassy phase is present. The alumina appears to have migrated into the area between the tungsten grains, firmly bonding the metal and ceramic together. Although the tungsten grains appear isolated from each other, the coating exhibited a low electrical resistivity, indicating that the metal surface was continuous.

The ceramic-metal interface was also examined by the electron microprobe technique. The area under study was traversed by a 1- μ m-diam electron beam. The x rays emitted from the various elements in the interface were recorded, allowing analysis of the positions of the constituents. The intensity of

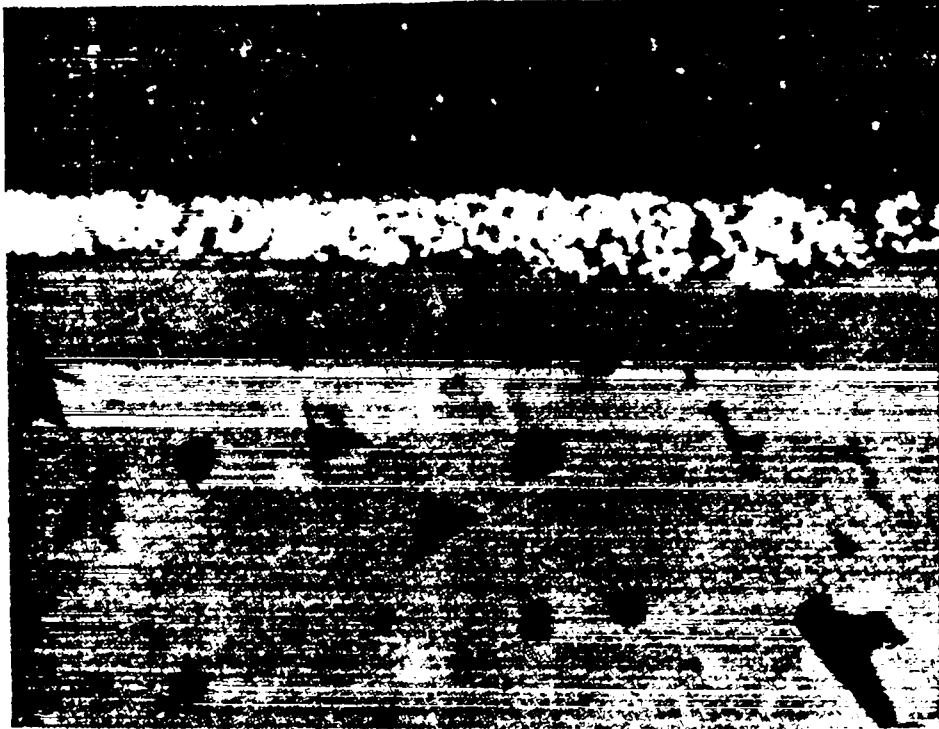
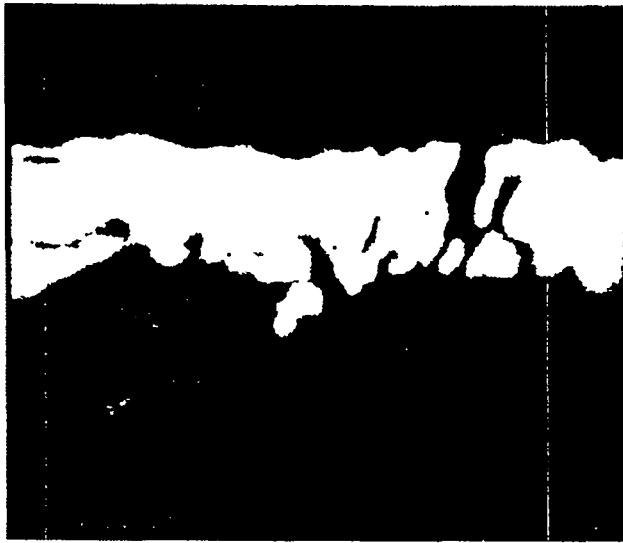


Fig. 2.
 $Al_2O_3 + 2\% Y_2O_3$ metallized with tungsten. 800X.

the back-reflected electrons was also recorded. Because the heavy elements scatter electrons more effectively than the light elements, a qualitative cross-sectional view of the interface was obtained. Figure 3 shows four electron microprobe photographs of the alumina-yttria interface. A photograph of the back-reflected electron distribution is shown in Fig. 3a. The dark area at the top of the field is the plastic mount, the light zone in the center is the tungsten coating, and the dark area at the bottom is the alumina-yttria ceramic. The interface is very rough, and in several areas the tungsten "undercuts" the alumina, providing an excellent mechanical bond between the two. The area at the right shows a gap in the tungsten coating. The light area at the lower left was caused by the reflection of electrons from yttria present as an inclusion between alumina grains. Fig. 3b shows the distribution of tungsten $L_{\alpha 1}$ x-ray lines from the sample. The x rays are more easily scattered and their distribution appears more diffuse. This photograph merely confirms that the material at the surface is tungsten. The inclusion shown in Fig. 3a does not

appear here, indicating that the inclusion was not tungsten. The dark areas correspond to the gap noted in Fig. 3a. The distribution of aluminum K_{α} lines is shown in Fig. 3c. It is evident that alumina is present in the gaps in the tungsten coating. Note also the absence of alumina in an area at the lower left corresponding to the yttria inclusion shown in Fig. 3a. Figure 3d is a view of the yttrium K_{α} lines from the sample. The inclusion here shows up plainly and is positively identified as yttrium. This photograph shows two interesting features. First, the area corresponding to a gap in the tungsten contains no yttrium. The yttrium is associated with the tungsten in the metallic coating. Second, the yttrium appears to be concentrated in an area near the alumina-tungsten interface.

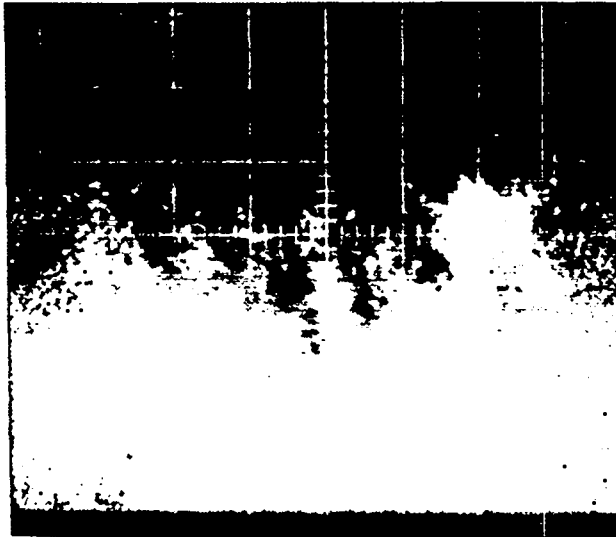
Figure 4 shows five electron-microprobe photographs of a different area of this sample. Figure 4a shows the electron backscatter from the heavy elements. Several isolated tungsten grains are at the right, and an yttria inclusion appears at the bottom. The distribution of the tungsten $L_{\alpha 1}$ line shown in Fig. 4b conforms to the general outline of



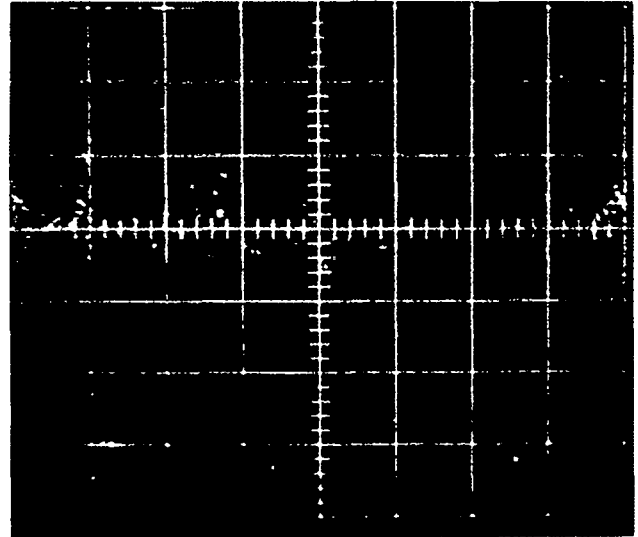
(a) *Electron backscatter*



(b) *Tungsten $L_{\alpha 1}$ x-ray distribution*



(c) *Aluminum K_{α} x-ray distribution*



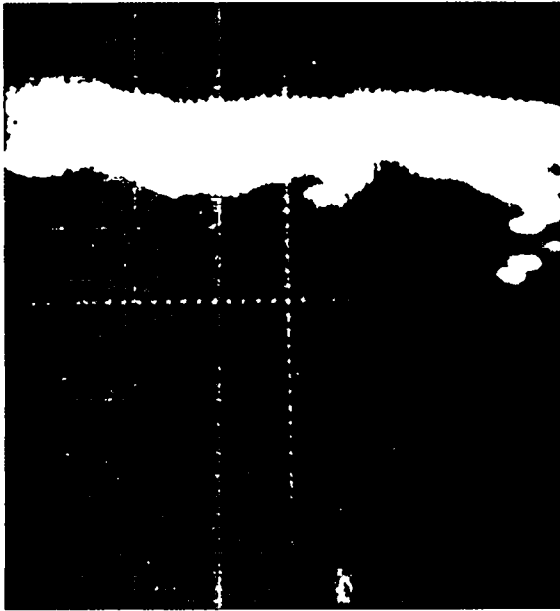
(d) *Yttrium K_{α} x-ray distribution*

Fig. 3.

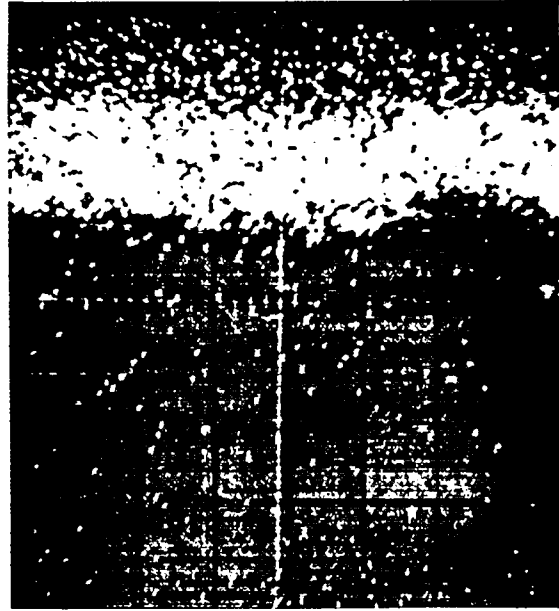
$Al_2O_3 + 2\% Y_2O_3$ metallized with tungsten. Grid spacing = $5.6 \mu m$. 1600X.

the electron backscatter photograph. The aluminum K_{α} lines are shown in Fig. 4c. A dark line near the center of the alumina, indicating the absence of alumina, is a grain boundary. A dark area near the bottom of the field corresponds to the yttria inclusion observed in Fig. 4a. The yttrium K_{α} lines are shown in Fig. 4d. The yttria was present in the grain boundary, in the inclusion, and also in the tungsten

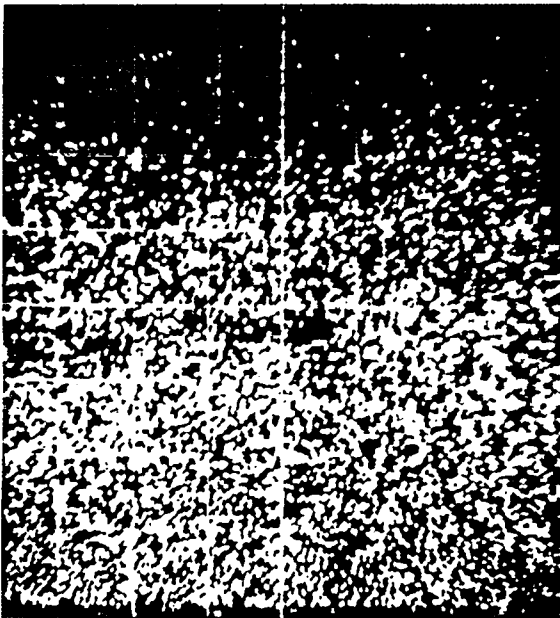
layer. Silicon was also present. The silicon K_{α} lines are shown in Fig. 4e. Silicon was observed at the grain boundary and in the inclusion, indicating that silica and yttria occurred together here. Silicon was also present in the tungsten layer: it appears that the silicon extended farther into the tungsten than did the yttrium.



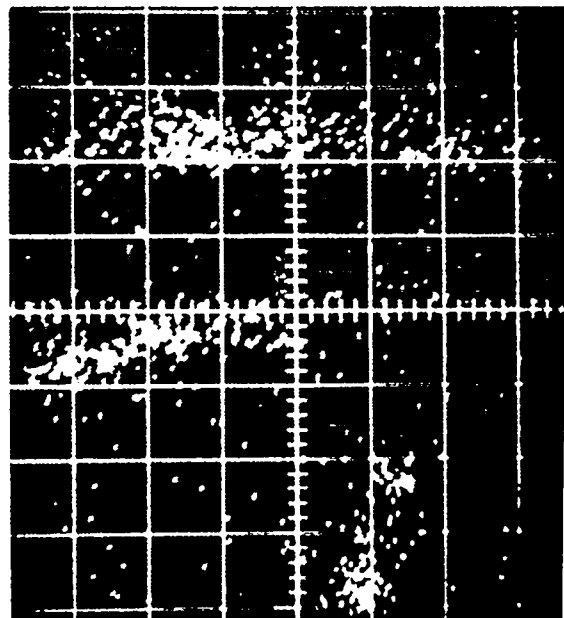
(a) *Electron backscatter*



(b) *Tungsten $L_{\alpha 1}$ x-ray distribution*



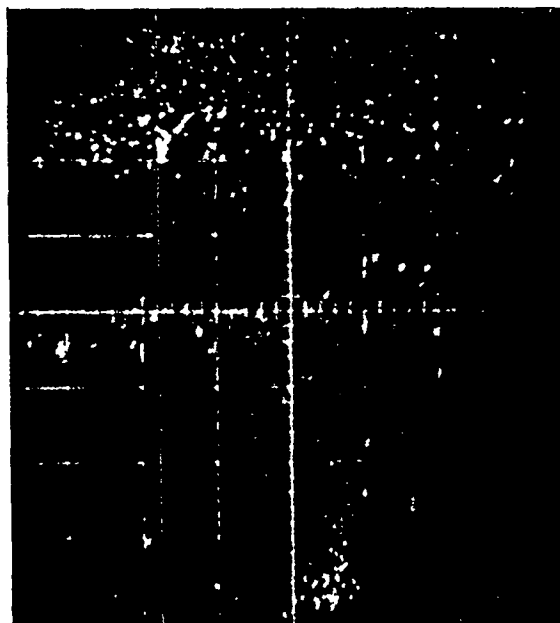
(c) *Aluminum K_{α} x-ray distribution*



(d) *Yttrium K_{α} x-ray distribution*

Fig. 4.

$Al_2O_3 + 2\% Y_2O_3$ metallized with tungsten. Grid spacing = $5.6 \mu m$. 1600X.



(e) Silicon K_{α} x-ray distribution

Fig. 4. (cont)

These analyses indicate that several chemical reactions can occur during this metallizing process. The grain boundary phase, which contains both yttria and silica, enters into a reaction with tungsten. If reduction to the respective metals occurred, diffusion of silicon and yttrium into the tungsten could be expected. These reactions would undoubtedly aid in the formation of a good ceramic-to-metal bond.

A limited amount of work has been done on the effect that adding different amounts of yttria to the ceramic has on the quality of the ceramic-metal bond. Alumina bodies containing as low as 0.05 wt% yttria have been metallized with tungsten and examined metallographically. Less reaction between ceramic and metal was observed with the lower yttria contents. No quantitative data have been obtained with these different compositions. It has been determined, however, that alumina containing no major impurities cannot be metallized with tungsten. The metallic layer can be easily removed following the firing operation.

Studies of the effects of various impurities on tungsten-alumina adherence are in progress. Experience to date indicates that the ceramic should contain a material that can react with the tungsten to give good adherence. Silica and yttria apparently fulfill this requirement, and other oxides, such as

manganese oxide and titanium oxide, might be expected to do likewise. This requirement may not be valid in cases where the alumina contains an appreciable amount of glassy phase: the glass may migrate to the surface and attach itself to the metal in accordance with the glass migration theory of ceramic-metal adherence.⁴

To summarize, two ceramic-to-metal seal combinations have been developed that show promise for specialized applications. For operation in an oxidizing atmosphere at $\sim 700^{\circ}\text{C}$, magnesia and nickel appear to be a good combination. Seals designed to operate at $\sim 1200^{\circ}\text{C}$ require a careful choice of materials. If an oxidizing atmosphere is not present, niobium and alumina can be used, with palladium serving as the brazing filler metal. For an oxidizing atmosphere, the tungsten metallizing of alumina that contains yttria appears to have considerable merit. A reaction between the tungsten and yttria results in an improved ceramic-metal bond.

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wish to acknowledge their kind assistance. Development of the metallizing techniques and sample preparation was done by J. E. Maestas. The preparation of the ceramic bodies was done by C. L. Martin. E. A. Hakkila provided the electron microprobe studies. The brazing development is the work of E. L. Brundige. The metallographic specimens were prepared by C. A. Javorsky, and the physical measurements were made by T. I. Jones.

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