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by

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CERAMIC MATERIALS FOR NUCLEAR THERMIONIC CONVERTERS

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The development of nuclear power has been accompanied by many different schemes of converting fission energy to electrical energy. Most of these involve the production of an expanding fluid such as steam which is converted to electricity through 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 prime 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 Figure 1. The emitter is made of a fissionable material and is heated by the energy released in controlled nuclear fission. The hot emitter ionizes cesium vapor which surrounds it forming a cesium plasma. A flow of electrons is established between the hot emitter through the cesium plasma to the cooler collector. An open circuit voltage of about three volts is established between the emitter and collector. A maximum current flow of 20 amperes per square centimeter of emitter area may 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 and a hermetic seal is required. The method of forming these seals is the subject of this paper. The operating conditions of this device are very unique and a brief description of them will illustrate the problems involved in developing materials for plasma thermocouple use. For maximum efficiency,

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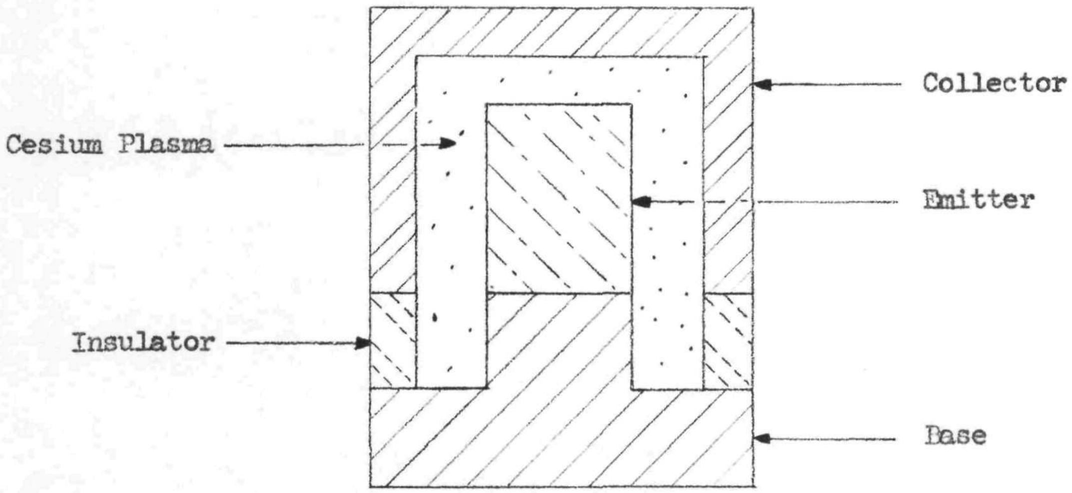
This work was performed under the auspices of the Atomic Energy Commission.

Figure 1

PLASMA THERMOCOUPLE CELL



this cell should operate at as high a temperature as possible. Through the proper choice of fissionable materials, the emitter may operate at 2000°C. The collector must operate at some lower temperature. This temperature must be high enough to allow for efficient cooling by radiation. A collector temperature of 1200°C is the maximum presently being considered. In some instances, lower collector temperatures may be used. 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 which will operate in the temperature range of 700° to 1200°C.

The choice of materials for the collector and insulator is based on several considerations. The collector must have a low electrical resistivity to minimize ohmic losses, have a low absorbtion cross-section for thermal neutrons, and have a thermal expansion which closely matches that of the insulator. The ceramic insulator must have a high electrical resistivity, and 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 the presence of cesium vapor. Cesium is an extremely corrosive material and 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 thermal expansion coefficients of these materials are similar which should lead to a minimum of thermal stresses. 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 may be made of nickel. To minimize thermal stresses, the ceramic may be made of magnesia which has a relatively high thermal expansion.

The composition of the ceramic bodies used in these seals is determined by their ability to withstand attack by cesium vapor and their ability to be metallized. The problem of resistance to cesium vapor may be minimized by avoiding the intentional use of silica in the ceramic. The limits of silica concentration have not been established but at temperatures below 1000°C approximately one percent silica does not appear to be harmful. For the ultimate seal utilizing alumina and operating at 1200°C for 10,000 hours, it is probably wise to keep the silica content as low as possible. This limitation on the use of silica creates problems in the fabrication of the ceramic and in its metallizing. It is common practice to add silicate materials to alumina to promote sintering. In addition, the presence of a silicate glass appears to promote the adherence of a metallizing material. It has been found that yttria is both an effective flux for alumina and aids in the formation of a strong ceramic-metal bond. Yttria is also unaffected by cesium vapor. The addition of two weight percent yttria to alumina results in a body which can be fired to vitrification at approximately 1700°C. The sintering process is apparently enhanced by compound formation which results in a yttria-rich phase being formed at the grain boundaries of the alumina.

The magnesia body used for making seals to nickel contains 0.5 percent calcia and 0.3 percent silica as the major impurities. These contaminants have not proven to be 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 range of 1400°-1600°C. These temperature requirements precluded the use of active metal sealing techniques since it was feared that excessive diffusion of titanium or zirconium into the ceramic would destroy the bond. For this reason, the refractory metal techniques were used exclusively. Many of the refractory metal processes utilize a composition which contains materials which are unstable in contact with cesium. These include 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 material for 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. It has been found that an adherent coating of tungsten may be applied to a yttria-bearing alumina without the use of additional fluxes, such as might be found in conventional molybdenum-manganese processes.

The tungsten may 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 volume percent water and 34 volume percent tungsten oxide which has an average particle size of one micron. The addition of a small amount of methyl cellulose improves the strength of the dry, unfired coating. The use of tungsten oxide has been found to be somewhat unreliable since a volume decrease of 170 percent occurs during reduction in hydrogen. This frequently results in coatings which tend to crack and peel. This difficulty can be alleviated through the application of tungsten metal. A mixture of 83 volume percent water and 17 volume percent tungsten metal produces a suspension having satisfactory viscosity. Binders and deflocculants may also be added if necessary. The application of the tungsten to the alumina may be done by brushing with a red sable artist brush or by spraying with an air brush. An application of about 60 milligrams per square inch of surface yields a coating thickness of 0.0005 inch. This coating is fired at 1650°C with a 30-minute soak in hydrogen having a dew point of 25°C.

For metallizing magnesia which is to be used in the less severe service conditions, a conventional molybdenum-manganese process has been used. This composition is composed of approximately 75 weight percent molybdenum and 15 percent manganese. The remaining 10 percent 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 minutes in an atmosphere of hydrogen having a dew point of 25°C.

The joining of the metallized ceramic to the metal is done by conventional brazing techniques using filler metals which are chosen according to the final service conditions. For the alumina-niobium seal operating at 1200°C, a braze metal of palladium appears to be the most promising. 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 which may operate at somewhat lower temperatures may be 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 which contain gold is not possible since cesium attacks gold and its alloys very severely.

Brazing to magnesia which was metallized with molybdenum has been done most extensively with the common silver-copper eutectic alloy. It is necessary to first coat the molybdenum with a thin layer of nickel in order for it to be wet by the silver-copper alloy. This can be done by electroplating or by the reduction of nickel oxide at 1000°C in hydrogen.

Testing of the alumina-niobium seal brazed with palladium has been carried out as high as 1450°C without loss of integrity. One seal was cycled in vacuum from room temperature to various temperatures between 1200° and 1450°C with a one-hour soak at temperature for 100 cycles without the hermetic seal being destroyed. Magnesia-

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

nickel seals which were 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.** The alumina plus two percent yttria composition was metallized with tungsten and fired at 1600°, 1650°, and 1700°C in hydrogen having a dew point of 25°C. The samples were brazed with a nickel-gold alloy and tested at a strain rate of 0.010 inch per minute. The results indicated that the seal strength increased as the firing temperature was increased. Strengths of 7690 psi at 1600°C, 8130 psi at 1650°C, and 9040 psi at 1700°C were obtained. These data are probably not representative of the true strength of the seal since some of the specimens fractured in the shoulder rather than at the joint. Further measurements are planned which 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 two weight percent yttria is shown in Figure 2. The tungsten layer is approximately 0.0005 inch 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 an electron beam measuring one micron in diameter. The X-rays emitted from the various elements in the interface were recorded allowing an analysis of the positions of the constituents to be made. In addition, the intensity of the back-reflected electrons was recorded. Since the heavy elements scatter electrons more effectively than the light elements, a qualitative cross-sectional view of the interface was obtained. A photograph of the back-reflected electron distribution is shown in Figure 3. 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 plus

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** ASTM Test F19-61T.

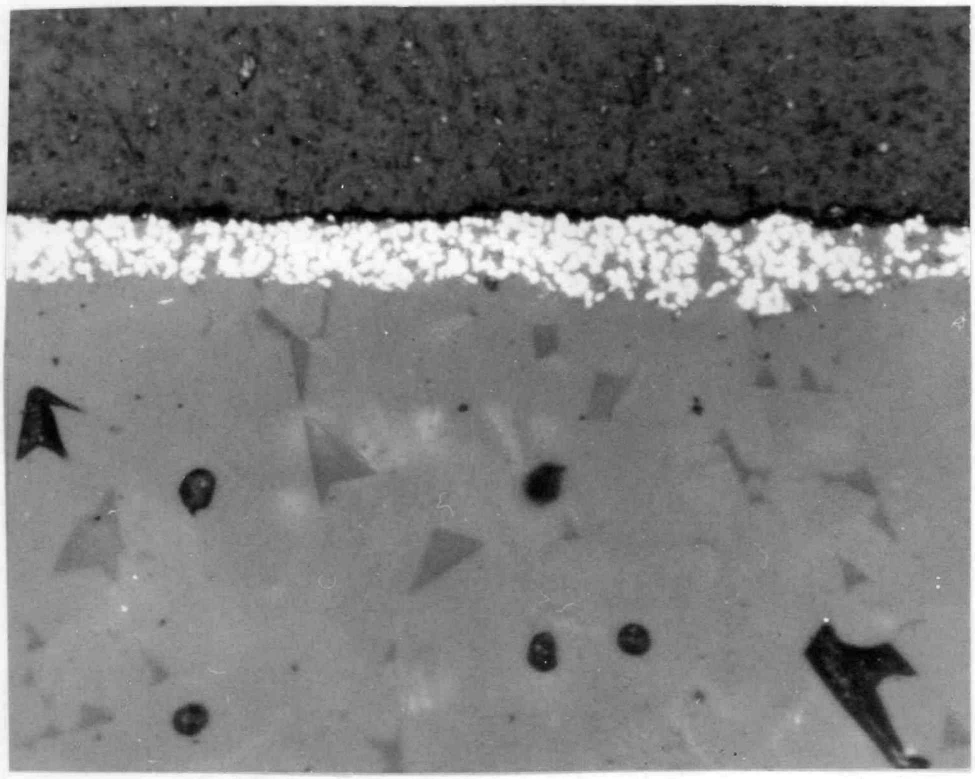

Figure 2
Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
800X

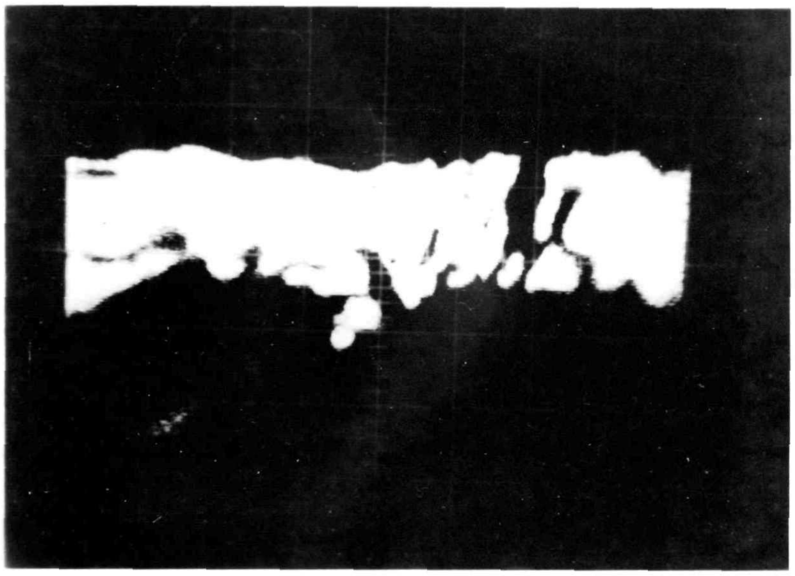

Figure 3

Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten

Electron Back Scatter

two percent yttria ceramic. The spacing between the grid lines is 5.6 microns and the overall magnification if 1600 diameters. The interface is very rough and several areas are present where the tungsten "undercuts" the alumina. This should provide an excellent mechanical bond between the two. The area at the right side of the photograph shows a gap in the tungsten coating. Reference will be made to this area in subsequent figures. The light area at the lower left side of the view was caused by the reflection of electrons from yttria present as an inclusion between alumina grains. Figure 4 is a photograph of 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 that was shown in the previous figure does not appear in this case, indicating that the inclusion was not tungsten. The dark areas correspond to the gaps in the coating which were noted in the previous figure. The distribution of aluminum $K\alpha$ lines is shown in Figure 5. 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 side of the photograph. This corresponds to the yttria inclusion which was mentioned earlier. Figure 6 is a view of the yttrium $K\alpha$ lines from the sample. The inclusion here shows up plainly and is positively identified as yttrium. Two interesting features are revealed by this figure. First, note that the area corresponding to a gap in the tungsten contains no yttrium. The yttrium is found to be associated with the tungsten in the metallic coating. The yttrium appears to be concentrated in an area near the alumina-tungsten interface. Figure 7 shows the preceding four photographs together. Their individual detail was reduced in order to place all the photographs on one slide. The relative positions of the various constituents are more easily observed in this arrangement.

A different area of this sample was also examined and other interesting details were revealed. Figure 8 shows the electron back scatter from the heavy elements. Several isolated tungsten grains are at the right side and an yttria inclusion appears at the bottom. The distribution of the tungsten $L\alpha_1$ line is shown in Figure 9 and conforms to the general outline of the electron back scatter photograph. The aluminum $K\alpha$ lines are shown in Figure 10. A dark line near the center of the alumina indicates the absence of alumina. This is a grain boundary. A dark area near the bottom of the field corresponds to the yttria inclusion which was observed in an earlier figure. The yttrium $K\alpha$ lines are shown in Figure 11. The yttria was present in the grain boundary, in the inclusion, and also in the tungsten layer. In addition to these

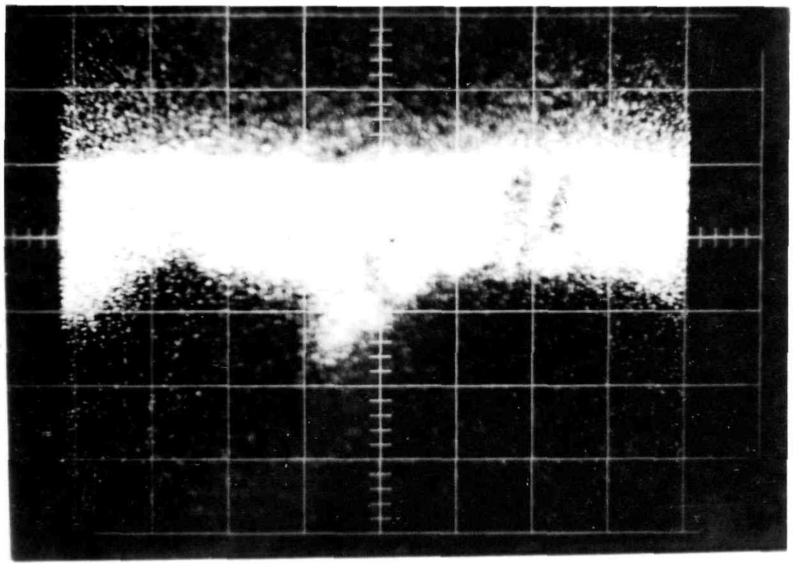

Figure 4
Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
Tungsten $L\alpha_1$ X-ray Distribution

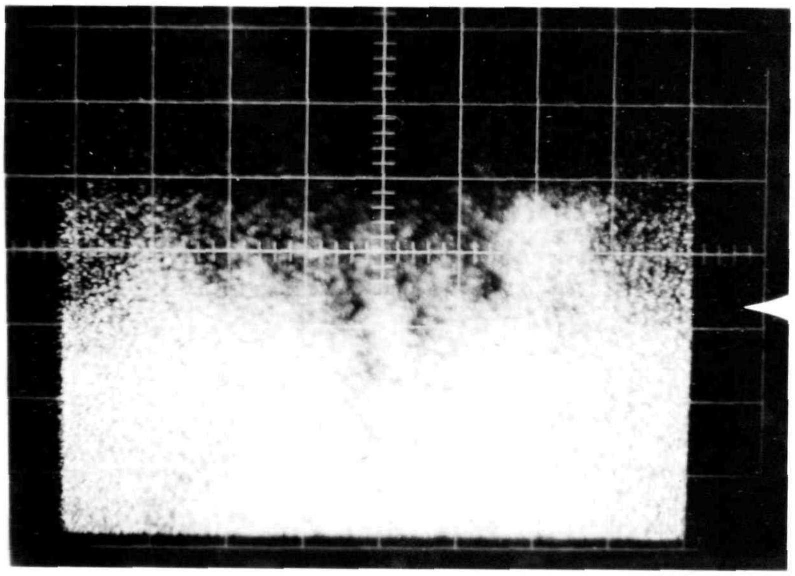

Figure 5
Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
Aluminum Kα X-ray Distribution

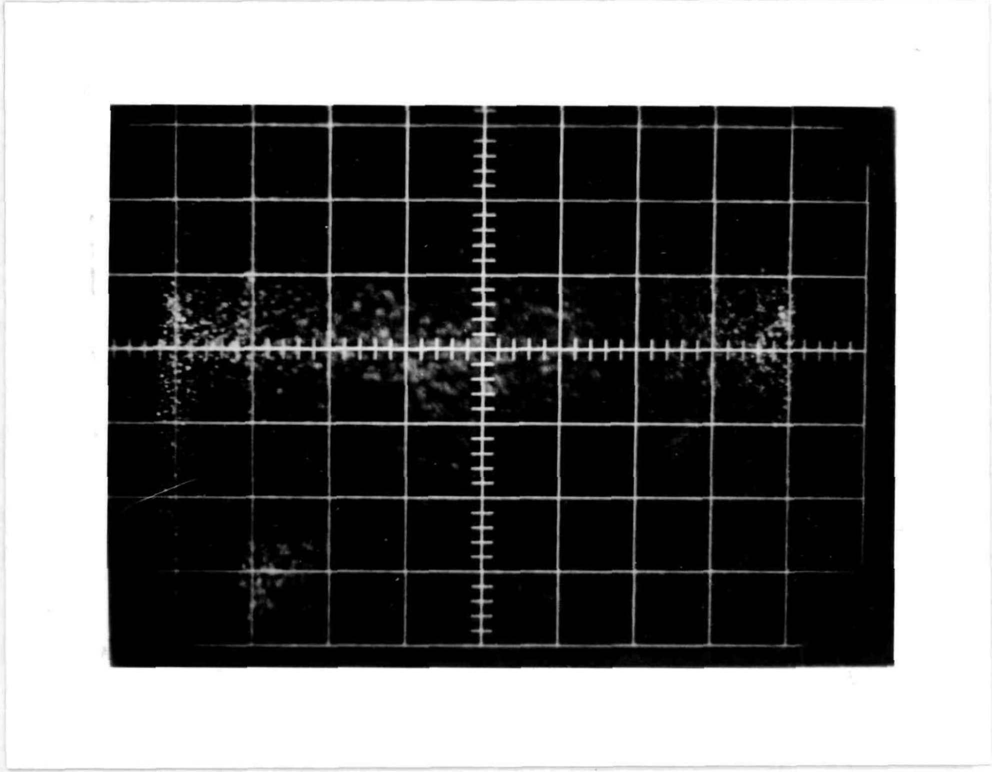

Figure 6

Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
Yttrium Kα X-ray Distribution

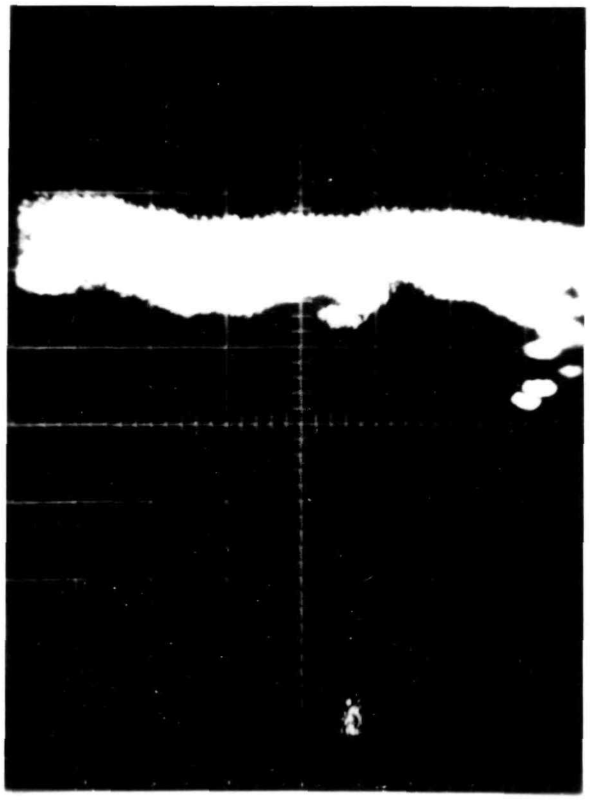

Figure 8
Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
Electron Back Scatter

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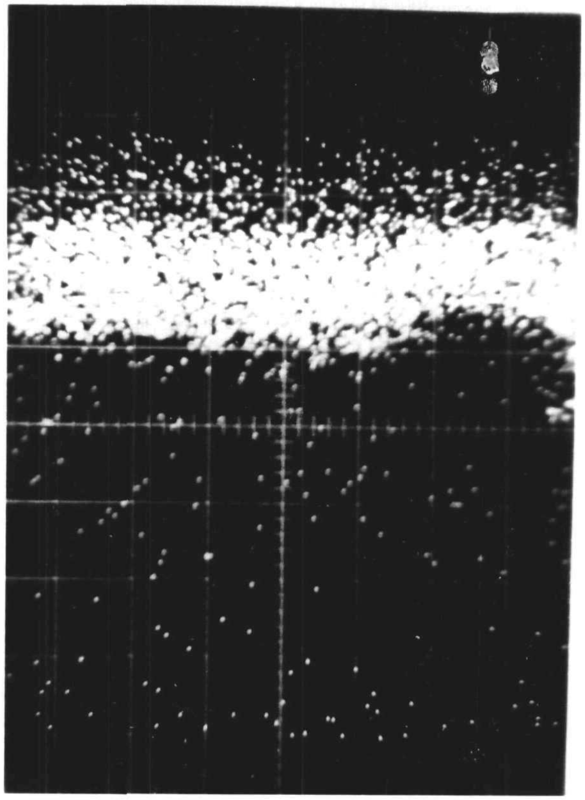

Figure 9
Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
Tungsten $L\alpha_1$ X-ray Distribution

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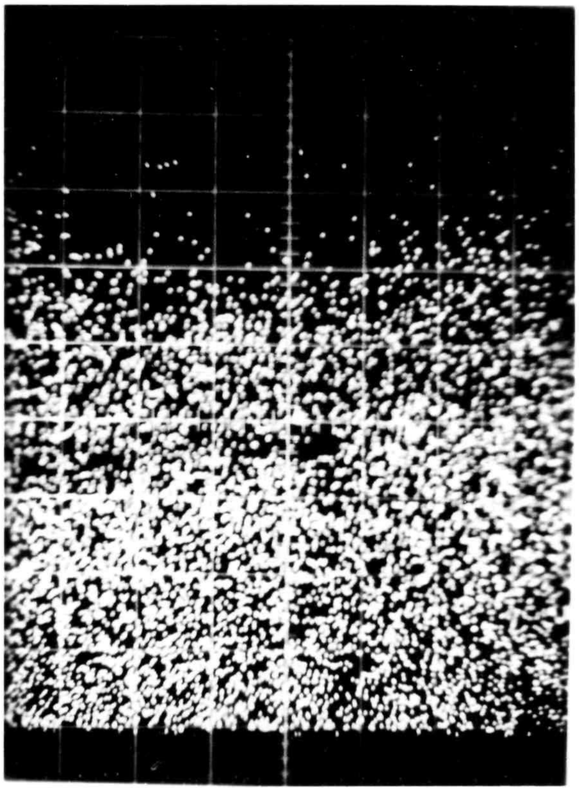

Figure 10
Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
Aluminum Kα X-ray Distribution

LB

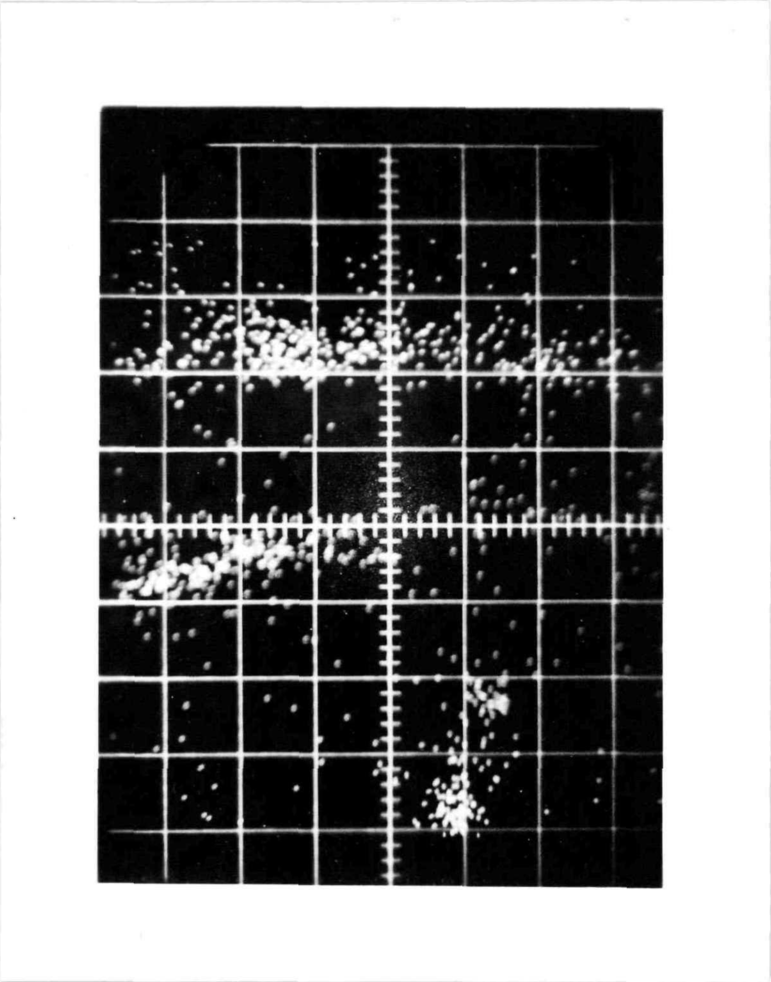

Figure 11
Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
Yttrium Kα X-ray Distribution

elements, the presence of silicon was also revealed. The silicon K lines are shown in Figure 12. Silicon is observed at the grain boundary and in the inclusion indicating that silica and yttria occur together. In addition, it is observed that silicon is present in the tungsten layer. It appears that the silicon extends further into the tungsten than does the yttrium. A compilation of the preceding five figures is shown in Figure 13.

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 of different yttria additions to the ceramic on the quality of the ceramic-metal bond. Alumina bodies containing as low as 0.05 percent 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 that alumina which contains no major impurities cannot be metallized with tungsten. The metallic layer may be easily removed following the firing operation.

Studies of the effect of various impurities on the adherence of tungsten to alumina are in progress. The experience to date indicates that the ceramic should contain a material which can react with the tungsten in order for good adherence to result. 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. In this situation, 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 which show promise for specialized applications. For operation in an oxidizing atmosphere at temperatures in the vicinity of 700°C, magnesia and nickel appear to be a good combination. Seals which are to operate at temperatures in the vicinity of 1200°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.

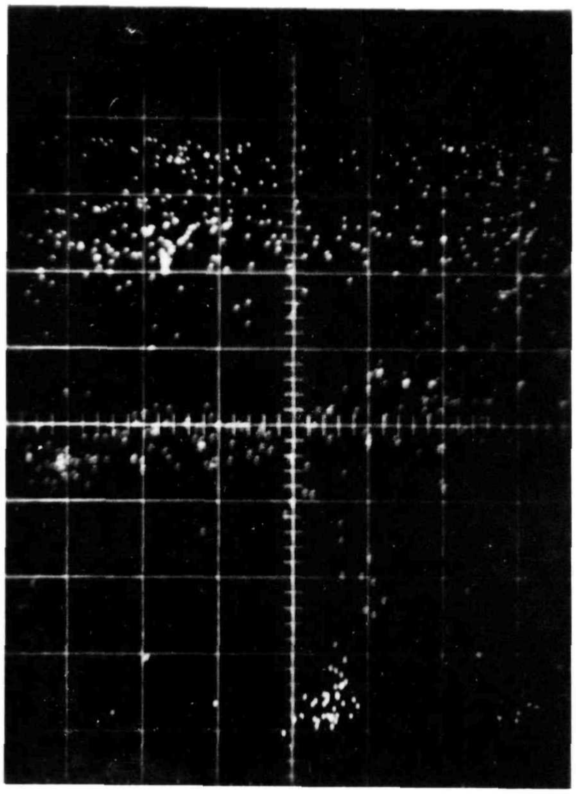

Figure 12
Al_2O_3 + 2% Y_2O_3 Metallized with Tungsten
Silicon Kα X-ray Distribution

The tungsten metallizing of alumina which contains yttria is a process which appears to have considerable merit. A reaction between the tungsten and yttria is thought to result in an improved ceramic-metal bond.

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Acknowledgements

Several members of this laboratory contributed to various phases of this investigation and the authors 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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