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THERMIONIC TECHNOLOGY PROGRAM

Fiscal Year 1986 - Final Technical Report

By
Velma P. Cone and John B. Dunlay

December 1987

Work Performed Under Contract No. DE-AC03-86SF15955

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San Francisco Operations Office
Department of Energy

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TABLE OF CONTENTS

<u>Chapter</u>		<u>Page</u>
1	INTRODUCTION AND SUMMARY	1
2	CERMET TRILAYER DEVELOPMENT	3
	2.1 THE SPHERE-COATING PROCESS	3
	2.1.1 Powder Spheroidizing	3
	2.1.2 Ceramic Powder Coating	5
	2.2 SLURRY CERMET FORMING TECHNIQUES	8
	2.2.1 Spraying and Tape Casting	8
	2.2.2 Slip Casting	9
	2.2.3 Filter Pressing	10
	2.3 ELECTRICAL CONSIDERATIONS	10
	2.4 STRENGTH TESTS	12
	2.5 YAG CERMETS	18
	2.6 COMPOSITE AND OXYNITRIDE TRILAYERS	22
	2.7 UCA-1 SAMPLE FABRICATION	26
	2.8 SHEATH INSULATOR STRESS ANALYSIS	32
	2.8.1 Design Considerations	32
	2.8.2 ANSYS Finite Element Code	33
	2.8.3 Discussion of Stress Analysis	34
3	ADDITIVE EFFECTS WITH SUBLIMED MOLYBDENUM COLLECTORS	51
	3.1 REVIEW OF PRIOR WORK	51
	3.2 THE ADDITIVE PROCESS	54
	3.3 ADDITIVE THERMIONIC PERFORMANCE	57
	3.4 DIODE FABRICATION	65

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LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
2.1	Layered Cermet Cross Section	13
2.2	Tensile Test Configuration.....	14
2.3	Cermet Tensile Strength.....	16
2.4	Test Specimen Fracture Surfaces	17
2.5	Linear Thermal Expansion	20
2.6	Thermal Expansion Coefficient	21
2.7	ESCA - Coating on YAG/Nb Cermet.....	23
2.8	SEM - Coating on YAG/Nb Cermet	24
2.9	Reaction Bond Interface	27
2.10	Electrical Resistivity of Ceramic Matrix Composite (Si ₃ N ₄ Whiskers/Al ₂ O ₃ Matrix) Trilayer.....	28
2.11	UCA-1 Al ₂ O ₃ Sheath Insulator Configuration	29
2.12	UCA-1 YAG Sheath Insulator Configuration	31
2.13	Trilayer Dimensions	35
2.14	Enclosed Ceramic (Far From End).....	36
2.15	Enclosed Ceramic (End of Metal).....	37
2.16	Enclosed Ceramic (Interface - Metal Side).....	38
2.17	Enclosed Ceramic (Interface - Ceramic Side)	39
2.18	Enclosed Ceramic	41
2.19	Outer Nb Slotted	42
2.20	Outer Nb Removed (0.1 inch)	43
2.21	Flat End	44
2.22	Recessed Ceramic (0.01 inch).....	45
2.23	Inner Nb Removed (0.1 inch).....	46
2.24	Inner Nb Removed (0.07 inch).....	47
2.25	Stress Relieved End Configurations	49

LIST OF ILLUSTRATIONS (Continued)

<u>Figure</u>		<u>Page</u>
3.1	Typical Nonadditive Thermionic Performance	58
3.2	Typical Additive Thermionic Performance.....	60
3.3	Output Power Density Comparison	63
3.4	Conversion Efficiency Comparison.....	64
3.5	PD-1 Performance Curves.....	69
3.6	PD-2 Performance Curves.....	70
3.7	PD-3 Performance Curves.....	71
3.8	PD-4 Performance Curves.....	73
3.9	PD-4 Collector Temperature Dependence	74
3.10	Pressure Bonded Emitter Design	75
3.11	PD-5 Performance Curves.....	76
3.12	PD-6 Performance Curves.....	79
3.13	PD-7 Performance Curves.....	80
3.14	PD-8 Performance Curves.....	81
3.15	CD-1 Performance Curves	83
3.16	CD-2 Performance Curves	84

LIST OF TABLES

<u>Table</u>		<u>Page</u>
2.1	Composition at YAG/Nb Interface	25
3.1	Nonadditive Performance Calculations	61
3.2	Additive Performance Calculations.....	62
3.3	Diode Test Conditions	66
3.4	Diode Electrode Materials	67

1. INTRODUCTION AND SUMMARY

During FY 1986, the Thermionic Technology Program at Thermo Electron Corporation concentrated on advancing the development of cermet sheath insulators and additive converters. Both development efforts were based on the thermionic technology established by thermionic reactor programs during the 1960's and early 1970's. Improved sheath insulators and additive converters were fabricated during FY 1986 and delivered to Rasor Associates Incorporated, for extensive testing and evaluation.

The most promising cermet fabrication process changed from dry ceramic powder coating of niobium spherical particles to the use of water-based slurries of ceramic powder and fine, irregularly shaped, niobium powder. Slurry processing is much more controlled and reproducible.

The fabrication of crack-free, fully dense yttria alumina garnet (YAG) sheath insulator trilayers remains to be accomplished. Measurements of the thermal expansion of YAG indicate that the expansion mismatch with niobium (particularly from 1300 to 1500 C) may cause cracking. Limited evidence also suggests that high-temperature (1500 C and higher) reactions between YAG and niobium may also contribute to cracking. Alternative fabrication schedules need to be explored to minimize these adverse high-temperature effects. Preliminary tests indicate that alternative ceramics, such as oxide composites and aluminum oxynitride (ALON), show promise as improved sheath insulators.

Finite element analysis was used to investigate mechanical stresses in sheath insulators resulting from radiation-induced swelling. Stress relieved end configurations were established and were included in the UCA-1 sample designs. Three $\text{Al}_2\text{O}_3/\text{Nb}$ and three YAG/Nb cermet trilayer samples were fabricated for fast reactor testing in the UCA-1 capsules.

The use of sublimed molybdenum collector coatings continues to be the most promising approach for achieving additive thermionic performance. Four fixed spacing planar diodes were fabricated and tested to investigate the effect of selected fabrication conditions on additive operation. These tests, in addition to x-ray diffraction analysis and metallurgical examination, confirmed that the MoO_3 formed during the sublimation process is rapidly converted to MoO_2 in the molybdenum coating, and is not subject to evaporation losses during subsequent diode fabrication steps or operation. Eight variable spacing planar diodes and two cylindrical diodes were fabricated and sent to Rasor Associates, Incorporated. During performance checkout of these diodes, some abnormal operating characteristics were observed. These results demonstrate the need for a better understanding of the fabrication processes, including the importance of individual steps to the overall additive effect. Most of the experimental results are compared using the oxygen content of the sublimed coatings as a basis. These oxygen values, however, are highly suspect and should not be considered reliable. Improved measurement techniques or alternative bases of comparison are required. Finally, additives offer improved thermionic performance (higher power densities and high conversion efficiencies) only at high current densities. Accordingly, to be meaningful, performance comparisons with nonadditive diodes should include data at high current densities.

2. CERMET TRILAYER DEVELOPMENT

In a series-connected, multicell, thermionic fuel element (TFE), sheath insulators are required to electrically insulate the thermionic collectors from the outer metallic sheath tube. The sheath insulator is a trilayer consisting of an insulator bonded between two concentric niobium tubes. Rejected heat from the collector flows radially outward through the trilayer to the surrounding coolant. Both the thermal and electrical performance of the trilayer must remain stable over the design lifetime of the thermionic reactor (currently about 7 years).

Based on work performed in the early 1970's, a cermet was selected for the insulator. The cermet consisted of a dispersion of niobium metal particles or spheres in a ceramic matrix. The niobium metal was added to strengthen the ceramic layer and increase the bond strength at the niobium-ceramic interface. Strengthening the ceramic matrix and the metal-to-ceramic bond is important if the insulator is to withstand the stresses induced by swelling of the materials because of nuclear radiation.

2.1 THE SPHERE-COATING PROCESS

In the early 1970's, Thermo Electron developed a method for forming electrically insulating cermet trilayers containing 30 volume percent niobium metal. In this process, niobium spheres 30 to 50 microns in diameter were tumbled in a wax-coated jar. The wax-coated spheres were then placed in a second jar containing alumina powder. The jar was agitated, and the powder formed coatings around the spheres. The coated spheres were formed into a tube by hydrostatic pressing. The tube was fired, machined and then pressure bonded to niobium cylinders. This simple process was very difficult to duplicate in the 1980's.

2.1.1 Powder Spheroidizing

Niobium spheres are produced by passing powder through a plasma torch and into a chamber filled with inert gas. The powder melts in

the torch and collapses into spheres. The niobium solidifies as it travels through the chamber before falling onto the walls of the vessel. While this process is conceptually simple, there are several practical difficulties in making spheres. The diameter of the sphere desired for use in the cermet is 25 microns or less. Particles in this small size range are very difficult to handle. They are so fine that it is impossible to pass them through sieves. However, close control of particle size is necessary to minimize the formation of pyrophoric dust during plasma spraying. Since niobium powder contains a wide distribution of particle sizes, a fluid bed classifier had to be constructed to remove particles less than 2 to 5 microns from the feed powder.

Another difficulty is the sensitivity of the torch to the alignment of the electrodes. Any misalignment will cause incomplete melting of the powders. The velocity of the gas flowing through the torch and powder feeder is also critical to the formation of spheres. The manufacturer of the torch recommends that gas flows be set so that the powder flows in the plane of the arc. However, the best spheres were made when the powder flowed through the arc and out the opposite side at about a 25 degree angle. The yield of spherical particles increased from about 80 to over 95 percent when the powder was forced to overshoot the arc in this way.

The size of the particle and the location where the powder flows through the arc determine how much energy is transferred to the spheres. Overheated powder is a problem because niobium vapors condense in the chamber as an extremely fine pyrophoric dust. This dust is difficult to remove from the niobium spheres. The only practical method of separating the dust from the spheres is rinsing in soap and water. Even after repeated rinsing in water and agitation in ultrasonic cleaners, there was still some niobium dust adhering to the surface of the spheres. Some of this dust was found in the cermets fabricated

for electrical testing. Because this powder was concentrated in the grain boundaries, it probably had adverse effects on the long-term electrical properties of the cermets.

A mechanical vibrator was constructed to separate unmelted powder from the spheres. This separator was made from a finely polished metal sheet and a small vibrating feeder. The powder-sphere mixture was fed onto the table and forced to roll up an incline. The incline was such that the irregular-shaped unmelted powder was driven up the polished sheet while the spheres rolled downward. The table works well for powders that are greater than 25 microns in diameter. It is difficult to separate smaller particles using this method. Any flaws in the surface, such as a scratch or fingerprint, will obstruct the flow of the powders. Static charging and high humidity also influence the separation process. It was found that coating the metal sheet with an antistatic agent helped prevent sticking.

2.1.2 Ceramic Powder Coating

An experimental approach was used to select a combination of wax and ceramic that would form coatings on the spheres. Many powders would not form coatings on the spheres. Powders that did coat the spheres left a large fraction of the powder as agglomerates that were indistinguishable from the coated spheres. Many different waxes of various hardness and tack were used in combination with approximately 15 different grades of alumina and yttria. One grade of alumina was significantly better than all of the others. This was Alcoa Al6 Super-ground (Al6) alumina. Al6 alumina is essentially the same material that was used with success in the early 1970's. The coated spheres do not appear to be different from the as-received Al6 alumina, which is highly agglomerated. This is because of the very small particle size (about 0.5 micron). Particles of this size are strongly affected by interatomic and electrostatic forces that cause particles to be

attracted to one another. This agglomeration phenomenon was expected to be the key to the success of the sphere-coating process.

At first, static charging was thought to be the driving force behind the sphere-coating process. This was because the spheres were coated with wax, a good insulator, and then agitated in a ceramic material. This process could be expected to form static charges similar to the static charge found on clothing in a dryer. In an effort to quantify this effect, an electrometer and a Faraday cup were used to measure static charges placed on the ceramic and metal powders. Charges of different polarity were placed on the powders by rolling them in containers of different electrostatic potential, i.e., glass, plastic, and metal. The charging capacity was increased by coating the spheres with camphor, stearic acid and carnauba wax. Although it was possible to establish a charge on the powder or the spheres, the powder would not form coatings on the spheres.

Agglomeration of particulate materials can result from electrostatic forces, Van der Waals forces, liquid bridges and solid bridges. (These forces are listed in order of increasing strength.) Van der Waals forces are interatomic forces that result from dipole effects. If a particle is small (<10 microns), these attractive forces are many times greater than that of gravity. The individual crystallites of Al₆ alumina, and most commercial grades of alumina, are held together very strongly by Van der Waals attractions. As these materials are exposed to moisture in the air, the alumina or other ceramic reacts with the water in the air to form hydrates. These hydrates form a chemical bridge between the particles that is very difficult to break down. It is thought that the ceramic used in the previous work had a particle size and degree of hydration that allowed weak agglomerates to break up and re-form around the spheres.

Alumina ceramic manufacturers usually grind alumina with dispersants, lubricants and binders to break up agglomerates. This produces a more manageable raw material and a uniform finished part. Organic binders such as polyvinyl alcohol (PVA) have been added to alumina to make extrudable clays, castable slurries and free-flowing powders. The organic binder gives strength to unfired shapes. It also acts as a lubricant that improves the formability of the powders. Many manufacturers spray dry slurries of ceramic and binders so that the ceramic can be easily handled and processed into shapes.

Spray drying was investigated at Thermo Electron using milled alumina in a water slurry containing PVA as a binder. This material was atomized in a hot environment so that small, soft spheres of alumina were formed. The binder was then fired away in an air furnace. It was hoped that the binder would separate the individual crystallites and leave behind an agglomerate that was much weaker than those in the as-received powder. Unfortunately, the resulting agglomerates were even harder to break up than the originals.

Mechanical stresses imposed by cold forming also help to disperse the agglomerates. If Al6 or A39 superground aluminas are pressed in the hydrostatic press, thin layers of alumina can be scraped off with an alumina doctor blade. If the layers are extremely fine, the powder forms good coatings on niobium spheres coated with a hard paraffin. Another technique is to mix two grades of alumina with different particle sizes and agglomeration characteristics. One that worked reasonably well was two parts Al6 alumina to one part by volume Union Carbide 0.3 micron micropolish milled in methanol.

The sphere-coating characteristics of yttria powder were found to be improved by grinding in an attrition mill to reduce the particle size. However, the powder was never improved to the point where coatings could be made that completely obscured the surface of the spheres.

In general, the powder coating process was found to be very difficult to control. Coating reproducibility relied heavily on the availability of very small particle size raw materials as well as the skill of the technician. Because of these difficulties, slurry processing was developed to achieve improved niobium dispersions in ceramic.

2.2 SLURRY CERMET FORMING TECHNIQUES

2.2.1 Spraying and Tape Casting

One promising process was the spraying of alternating layers of a slurry of ceramic and a slurry of ceramic plus niobium on a niobium mandrel. After multiple layers were deposited, the layers were compressed in the hydrostatic press. One of these cermets containing about 25 volume percent niobium was pressure bonded inside of a niobium tube. Unfortunately, the ceramic cracked during the pressure bonding. The cermet was electrically insulating and would probably have good resistance to an electrical potential because of the layered microstructure. If the cracks could be eliminated, this would be an attractive method for forming cermet insulators.

A second promising method is that of tape casting. In this process, a ceramic slurry is made with organic solvents and an acrylic binder. The slurry can then be cast in a thin, flexible film referred to as a tape. Ceramic or metal particle tapes can be wound around a mandrel in alternating layers. After the tapes are secured inside of niobium tubes, the binder can be removed and the cermet processed in the normal way. The limitation to this process is in the removal of the binder; the binder burns off at temperatures above the oxidizing temperature of niobium. Acrylic binders are claimed to decompose without the presence of oxygen and also leave no carbon residue. However, some small amount (0.1 to 1 percent) of the binder remained in the powder even after carefully controlled burnout experiments. The amount of carbon that remained in the cermet would be small (approximately 0.01 percent).

2.2.2 Slip Casting

Slip casting is a traditional ceramic processing technique used to produce items such as dinnerware and decorative ceramics. In this process, a highly dispersed, fluid slurry of ceramic is poured into a porous mold. As the mold absorbs liquid from the slurry, the ceramic is drawn against the sides of the mold forming a soft shell on the surface of the mold. Excess slurry (usually called a slip) is drained out and the shell of ceramic is allowed to dry. As the casting dries, the ceramic shrinks away from the sides of the mold so that it is easily removed.

The slip casting technique was adapted to the fabrication of cermets by developing a slurry containing both metal and ceramic powder. The powder was fluid enough to be poured into the molds, but viscous enough to keep niobium particles in suspension. The casting slip was, by necessity, a compromise between uniformity of the metal dispersion and suitability for producing flaw-free castings. A more viscous slip prevented the niobium from settling, but slips that are too thick usually crack in the mold. High solid content slips can be made with the addition of organic deflocculents which put a charge on individual particles in the slip. This charge essentially lubricates the particles because Coulomb repulsion prevents particle contact. Without mechanical contact, there is no friction or interlocking as the particles move in the suspension. These suspensions are much more uniform, and can have higher solids contents so that there is less segregation of the niobium. The amount of organic deflocculent that can be added is limited because of problems with contamination. However, cermets have been made with about 0.2 percent Darvan* C without negative consequence in electrical performance.

*Darvan is a trademark of L.T. Vanderbilt Company.

One interesting discovery was that yttria is a very effective deflocculent of alumina slurries. This is no doubt a complicated effect arising from the change in zeta potential of the alumina particles by the adsorption of dissolved yttrium. While no effort was made to understand this phenomenon for the UCA-1 experiments, the effect was used to decrease the viscosity of a slip that produced alumina cermets with 2 volume percent yttria.

2.2.3 Filter Pressing

Slip casting was not found to be a suitable method for making YAG cermets since commercially available yttria powders were too large to form a suspension with the low viscosity needed for slip casting. However, a similar technique called filter pressing was successful. In this process, a viscous slurry was made from ceramic, a liquid medium, the niobium powder and a dispersant. Water was removed from the slurry by pressing the slurry in a cylindrical die. The die was equipped with hollow plungers that were fitted with filters where the water was allowed to flow out, but the ceramic was forced to stay behind. The resulting briquettes were dried, fired and then machined to the dimensions required for pressure bonding. Outgassing of the slurries before pressing was found to be very important. Adsorbed air bubbles that were not visible in the starting mixture formed voids which would not close up even after sintering at high temperature and pressure.

2.3 ELECTRICAL CONSIDERATIONS

Six slip cast alumina cermets were delivered to Rasor Associates Inc., for measurements of resistivity versus temperature and life testing. The finished cermets contained 25 volume percent niobium spheres approximately 25 microns in diameter. These cermets were produced by milling a 40-volume-percent slurry of Al₆ alumina with an addition of 2 percent yttria for 12 hours in a ball mill. The slurries were

evacuated with a rough pump to remove air bubbles and then cast into a cylindrical mold. This mold was a block of U.S. Gypsum's Pottery Grade No. 1 plaster with a 0.9-inch-diameter hole in the center. The castings were dried and then presintered at 1400 C. This high pre-sintering temperature was necessary to densify the ceramics so that they could be easily machined, but hard enough so that spheres were not pulled from the surface but were sliced by the tool.

The cermets shorted electrically after several days at 1250 K and 30 volts. With one exception, all of the cermets shorted across the ends. The shorting paths are believed to result from contamination of the cermet by pyrophoric niobium dust, the products of a reaction between niobium and YAG formed by the addition of 2 percent yttria or contamination by diffusion pump oil.

High metal contents increase the strength and toughness of the cermets, but also increase the possibility of creating metal chains which may lead to electrical shorts. Depending upon the mathematical construction used, the theoretical limit of the amount of a conductive material that can be randomly dispersed in an insulating matrix before a conductive path is formed is between 14 and 25 volume percent. This limit is called the percolation threshold. The actual limit to the volume of niobium that can be added to the alumina or other ceramic is dependent upon gravitational effects, the chemical and electrostatic interaction of the niobium with the ceramic powders, and the nature of the suspending medium. Surface charges on particles in suspension and surface tension of the medium can completely dominate many forces, such as the Van der Waals and gravity. These charges are often opposite for different materials in a suspension, tending to cause agglomeration of unlike species. The complexity of a mixed suspension of powders makes it difficult to characterize the dispersion of niobium. Since cermets can be fabricated with 25 volume percent niobium on a routine basis, it appears that the niobium particles may be somewhat insulated

from one another. Physical evidence of this has been seen by observing the interface between a niobium sheath and a layered cermet (Figure 2.1). This niobium sheath did not form a good bond to the spheres because the spheres are almost completely surrounded by alumina. Ceramic still surrounds the niobium particles deformed in the pressure bonding cycle.

2.4 STRENGTH TESTS

The niobium metal content of a cermet trilayer insulator generally increases the bond strength at the sheath tube interface. The niobium also increases the toughness of the insulator by increasing the amount of energy required to propagate a crack through the ceramic.

Mechanical tensile tests were performed to investigate the increase in strength of the trilayer as the metal content is increased. Three to five samples of each of ten cermet compositions were tested. The samples were: pure alumina; alumina with 10, 20, and 30 percent niobium spheres; alumina with 10, 20, and 30 percent niobium powder; and several layered samples. The design of the tensile test configuration is shown in Figure 2.2. The test bars were made by pressure bonding partially sintered disks of the cermet materials at 10,000 psi and 1550 C. The cermets were produced by filter pressing the slurries and presintering to 1250 C. The 50-percent niobium-layered samples were made by applying a slurry to the insulator disks with a doctor blade. The water was drawn out of the slurry by the porous cermet much the same way as in slip casting. The layer of ceramic adhered well to the disks and the test pieces remained intact even after a second sintering to 1200 C. Another set of layered cermets was made using a dilute slurry of aluminum nitride. The nitride slurry was brushed directly on the inside surface of the niobium capsule. Disks of alumina were then sealed in the nitride-coated niobium capsules and pressure bonded.

57-188

Figure 2.1 Layered Cermet Cross Section

Figure 2.2 Tensile Test Configuration

The results of the tensile tests are shown in Figure 2.3. The error bars represent the standard deviation of the measurements. All of the pure ceramics failed at the interface indicating that this was the weakest link in the trilayer. All of the other samples had a mixture of failure modes through the ceramic and at the interface. Representative samples are shown in cross section in Figure 2.4.

The strength of the bond formed between the niobium and pure alumina is about 7000 psi. The bond is probably a combination of a very limited chemical interaction, as well as the adhesion from charge transfer that all materials show when brought in very close contact. M. Rühle has reported a slight solubility of alumina in niobium when they are bonded at temperatures above 1700 C.¹ Cermets bonded at 1550 C probably have a similar, but smaller, interaction with niobium. Visual evidence of this interaction is seen in the alumina as a color change from white to blue-gray. This color change has been associated with the formation of oxygen defects and is to be expected with the low oxygen potential induced by the niobium.

The tensile strength of the trilayer doubled with only 10 volume percent niobium sphere addition. The test results indicated a diminishing increase of strength with increasing metal content in the 20- to 30-volume-percent range. The cermets failed primarily through the bulk of the insulator rather than at the interface. This shows that a small metal addition significantly increases the strength of the interface.

A consistent finding in all of the test samples was an increase in strength from the addition of fine (10-micron), rough, niobium powder as opposed to niobium spheres. This is a logical result since

1. Rühle, M., Burger, K. and Mader, W., "Structure and Chemistry of Grain Boundaries in Ceramics and Metal/Ceramic Interfaces," J. Microsc. Spectrosc. Electron., Vol. 11, pp. 163-177, 1986.

Figure 2.3 Cermet Tensile Strength

Ten v/o Nb Spheres

Ten v/o Nb Powder

20 v/o Nb Spheres

Fracture Surface, Layered Cermet

Figure 2.4 Test Specimen Fracture Surfaces (x165)

the energy required for a crack to propagate around an irregular particle is greater than the energy of a sphere, and the greater number of particles resulting from the fine powder are more likely to interact with a propagating crack. A similar increase in strength in ceramics with high surface area inclusions, as opposed to spherical powder, has been observed at Sandia Laboratories during a study of glass-to-metal seals.²

None of the layered samples showed any real improvement in strength over the 10-volume-percent cermets. This is probably an artifact of the fabrication technique. The niobium in the slurries tends to be covered with alumina. This phenomenon may be electrostatic or just a function of surface tension. Since this layer was not machined to expose the niobium spheres, the bond between the surfaces was not increased.

The coating layer of aluminum nitride appears to provide additional strength to the interface equivalent to the strength obtained with the 10-volume-percent cermets. This method of bonding may be of some help in the fabrication of yttria trilayers. Because of the extremely high free energy of formation of yttria, the interface between niobium and yttria should be more inert than that between niobium and alumina, and the interface bond strength of yttria trilayers would be expected to be low. The bond should be strengthened by using a thin layer of aluminum nitride as an aid to reaction bonding.

2.5 YAG CERMETS

YAG has reported values of thermal expansion similar to those of niobium, excellent radiation resistance and good electrical resistivity.

2. Kunz, S.C. and Moore, R.H., "Kovar Particle Toughened Scaling Glass," Ceramic Proceedings, 10th Annual Conference on Composites and Advanced Materials, American Ceramic Society, 1986.

However, a dense, crack-free YAG trilayer has not been fabricated. Additional differential expansion measurements were made to better define the thermal expansion characteristics of YAG, especially at temperatures close to 1500 C, the trilayer pressure bonding temperature.

A thermal expansion test bar was fabricated by pressure bonding a mixture of yttria and alumina inside of a niobium tube. After bonding, the niobium was removed by acid etching. Analysis by x-ray diffractometer showed only a YAG x-ray pattern and no other oxides. No appreciable shifting of the peaks from their normal values was seen. This diffraction pattern indicated that the transformation from the reactant materials was essentially complete and there were few impurities. The test bar was shipped to Theta-J Corporation* for measurement of thermal expansion. A graph of the measured thermal expansion of YAG, together with literature values for the expansion of polycrystalline alumina, yttria, and niobium, is shown in Figure 2.5.^{3,4} YAG expansion is the highest of the three ceramics and the most positive relative to niobium. The expansion coefficients for these materials are shown in Figure 2.6 and exhibit similar relative values. These thermal expansion data suggest that yttria should be the easiest to bond to niobium without cracking, followed by alumina, and then by YAG as the most prone to cracking. Experiments support this ranking. In addition, there is some evidence of an adverse reaction between YAG and niobium.

Coatings form on the surface of YAG cermets when sintered prior to the machining operation. These coatings are dark gray and become more pronounced the higher the firing temperature. Cermets fired at 1700 C were coated with a thick, electrically conductive film. This surface film was analyzed by microprobe and Auger spectroscopy.

*Theta Industries, Port Washington, N.Y.

3. Thermophysical Properties Research Center (TPRC), Purdue University, West Lafayette, Indiana.
4. CONF-8308130, "Refractory Alloy Technology for Space Nuclear Power Applications," Proceedings of a Symposium held at Oak Ridge, Tennessee, August 1983.

Figure 2.5 Linear Thermal Expansion

Figure 2.6 Thermal Expansion Coefficient

The results of some of these studies are shown in Figures 2.7 and 2.8. The analysis shows that the films contained niobium metal and yttria but no alumina. These films formed when stoichiometric YAG was used, as well as when mixed oxides were fired in contact with niobium. To study this phenomenon more closely, niobium capsules were made with YAG cylindrical rods that were pressure bonded inside. These YAG samples were not cracked. The cracking appears to occur only when there is niobium on the inside of the ceramic and the ceramic fails in tension.

The interface between the ceramic and the niobium was examined with an electron microprobe for evidence of reactions (Table 2.1). Within the limit of the detectability of this instrument (about 0.1 percent) no reactions were found. An unexpected result was the detection of the migration of SiO_2 impurities to the outside of the capsule. This may indicate that the solubility of silica in YAG is extremely small. Segregation of impurities to grain boundaries can significantly weaken a ceramic. However, the high purity of the materials used (>99.9 percent) makes impurities seem an unlikely cause of the cracking phenomenon.

The cracking appears to be due either to an interaction of YAG with niobium or with the thermal expansion mismatch between YAG and niobium. The pressure bonding procedure produces a great deal of stress on any ceramic as the temperature or the pressure is reduced. A weakened material, or one that is highly stressed by thermal expansion differences, may be unable to survive the procedure. However, there may be some alternative materials to YAG.

2.6 COMPOSITE AND OXYNITRIDE TRILAYERS

Composites of ceramic materials may have the high strength and low swelling characteristics required to survive in a radiation environment. A second phase, like Sialon or boron nitride dispersed in alumina, can increase the strength almost as much as a metal dispersion

12-Aug-1986 10:52:42

YAG CERMET AREA 1

Vert= 1000 counts Disp= 1

Preset=

100 secs

Elapsed=

50 secs

Figure 2.8 SEM - Coating on YAG/Nb Cermet

TABLE 2.1
COMPOSITION AT YAG/Nb INTERFACE

Sample Area	Elements - Weight Percent			
	Al	Y	Nb	Si
Area Scan on Interface	20.4	32.4	47.3	-
YAG (10 μ from Interface)	36.0	64.1	-	-
YAG (5 μ from Interface)	35.1	64.9	-	-
Interface	0.8	-	95.0	4.2
Nb (5 μ from Interface)	0.1	-	99.9	-
Nb (10 μ from Interface)	-	-	100.0	-

without greatly reducing the electrical properties. The Sialons and boron nitride have low swelling which will also help to minimize stresses. A preliminary attempt was made to fabricate an all-ceramic composite. The ceramic was a mixture of aluminum oxide powder and silicon nitride fibers. The nitride and the alumina reacted to form a Sialon phase and the excess remained as free alumina. The interesting feature of this trilayer is that a good metallurgical bond was formed between the nitride and the niobium. This bond is shown in cross section in Figure 2.9. The trilayer was placed on test and found to have an electrical resistivity over 10^9 ohm-cm at 1250 K. A graph of resistance versus time for this ceramic is shown in Figure 2.10. The sample was taken off test after three weeks at 1250 K and 15 to 100 volts. These conditions exceed the requirements of accelerated life testing established for the Thermionic Fuel Element (TFE) Verification Program. The ceramic and the bond looked unchanged.

Another promising material is aluminum oxynitride (ALON). This material is comparable to alumina in strength and electrical resistivity, but it has a spinel structure. Preliminary results by R. Clinard⁵ suggest that ALON is more radiation resistant than even magnesia alumina spinel. ALON has been pressure bonded to niobium and shows the same type of reaction bond seen in the composite trilayers. If this material can be fabricated as a trilayer, it would, in all likelihood, be an ideal insulator.

2.7 UCA-1 SAMPLE FABRICATION

Three $\text{Al}_2\text{O}_3/\text{Nb}$ and three YAG/Nb cermet trilayer samples were fabricated for fast reactor testing in the UCA-1 capsules. The design and as-built dimensions of the $\text{Al}_2\text{O}_3/\text{Nb}$ samples are shown in Figure 2.11.

5. Clinard, R. and Maguire, E., "Effect of Gamma Radiation on the Color Transmittance of Aluminum Oxynitride," Intersociety of Optical Engineering, SPIE, Vol. 683, p. 49, 1986.

Figure 2.9 Reaction Bond Interface

Figure 2.10 Electrical Resistivity of Ceramic Matrix Composite (Si_3N_4 Whiskers/ Al_2O_3 Matrix) Trilayer

Figure 2.11 UCA-1 Al_2O_3 Sheath Insulator Configuration

The $\text{Al}_2\text{O}_3/\text{Nb}$ samples have stress relieved end configurations (outer layer metal removal on one end and inner layer metal removal on the other end). Fabrication data for the samples are as follows:

- Sample Numbers
 - TE-A-1
 - TE-A-2
 - TE-A-3
- Cermet
 - 25 volume percent niobium spheres
 - Alcoa Al6 alumina with 2 weight percent Atomergic Chemicals yttria
 - Slip cast
- Sphere Diameter
 - 20 micron average
- Pressure Bonded
 - 1550 C
 - 10,000 psi

The design and as-built dimensions of the YAG/Nb samples are shown in Figure 2.12. Because YAG swelling due to radiation is relatively small, the samples were machined with flat ends (no stress relieving). Fabrication data for the samples are as follows:

- Sample Numbers
 - TE-YAG-1
 - TE-YAG-2
 - YAG formed by reacting Alcoa Al6 alumina and Atomergic Chemicals yttria
 - TE-YAG-4
 - Cerac YAG

ACTUAL DIMENSIONS						
I.D. NO.	A	B	C	D	E	F
TE-YAG-1	.6890 .6888	.6195	.5803	.520	.0196	.7491 .7489
TE-YAG-2	.6897 .6898	.6202	.5809	.5199 .5200	.0195	.7475 .7472
TE-YAG-4	.6900	.6465	.5793	.5201 .5200	.0335	.7485 .7486

Figure 2.12 UCA-1 YAG Sheath Insulator Configuration

- Cermet
 - 25-volume-percent niobium spheres
 - Filter press
- Sphere Diameter
 - 20 micron average
- Pressure Bonded
 - 1600 C
 - 1000 psi

The UCA-1 irradiation tests started in October 1986 with a scheduled completion date of October 1987.

2.8 SHEATH INSULATOR STRESS ANALYSIS

2.8.1 Design Considerations

The sheath insulator trilayer assembly is exposed to high neutron fluxes in a thermionic reactor. Over the operating life of the reactor, the neutron fluence (integrated flux) is sufficiently high to cause radiative induced swelling in the materials. Depending on the ceramics used, the swelling in the sheath insulator is generally different than the surrounding niobium. The volume changes cause mechanical stresses in the ceramic which can result in brittle fracture of the sheath insulator or separation at the metal-to-ceramic interfaces.

Polycrystalline Al_2O_3 is a possible ceramic material for the sheath insulator. When exposed to high neutron fluences, Al_2O_3 swells more than niobium. The Al_2O_3 sheath insulator pushes outward on the exterior sheath tube and pulls outward on the interior collector. Stress patterns in the niobium sheath tube and the niobium collector are characteristic of pressure vessels with internal pressure. Both the axial and tangential stresses are tensile and relatively large. In the sheath tube, the radial stress is compressive due to pressure from the sheath insulator and is relatively small. In the collector, the radial

stress is tensile due to the pull of the sheath insulator and again relatively small in magnitude. The axial and tangential stresses in the sheath insulator are compressive and large. The radial stress in the insulator is tensile on the inside toward the collector (to match the collector radial stress), and changes to compressive on the outside toward the sheath tube (to match the sheath tube radial stress).

This swelling induced pattern of stress is relatively uniform throughout the trilayer. Rapidly changing stresses are not evident except at material interfaces and at the ends of the trilayer. End effects can introduce large radial tensile stresses in the sheath insulator. These effects are very localized. Under typical conditions, the end effected region may be only 0.01-inch thick. Fractures in this localized region may propagate, however, leading to more extensive damage. Study of these end stresses is greatly aided by the use of computer programs such as the finite element code discussed in the following section.

2.8.2 ANSYS Finite Element Code

The ANSYS finite element computer program was used to analyze the trilayer end stresses. The program, available from Swanson Analysis System, Inc., is capable of both static and dynamic analyses. The static analysis is used to solve for the displacements, stresses, strains, and forces in structures under the action of applied loads. Capabilities include elastic, plastic, creep, swelling, large deflections, stress stiffening, and geometrically nonlinear elements. Dynamic analysis is an extension of the static analysis and solves for the dynamic response of a structure under the action of applied time-dependent loads.

Static elastic calculations were performed to establish stress pattern trends while minimizing computer time. This type of calculation is linear and requires only a single solution. Introducing plastic or creep

properties makes the solution nonlinear and requires multiple iterations. Two-dimensional modeling of the trilayer was used. The geometry was axisymmetric with the trilayer structure defined in the radial and axial directions.

Swelling in the sheath insulator was simulated by thermal expansion. The product of the expansion coefficient times the change in temperature ($\alpha\Delta T$) was adjusted to yield an insulator linear increase of 0.005 relative to the surrounding niobium. This linear increase corresponds to a volume increase of 1.5 percent. Actual volume increases in Al_2O_3 may be greater than 3 percent at end-of-life conditions.

The trilayer dimensional array used in the calculations is illustrated in Figure 2.13. The trilayer cross section is shown with the cylindrical axis on the left. The inside niobium layer extends from a radius of 0.260 to 0.290 inch, the sheath insulator from 0.290 to 0.305 inch, and the outside niobium layer from 0.305 inch to an outer radius of 0.341 inch. In the axial direction, the end of the sheath insulator is 0.70 inch from the midpoint of the trilayer length. The inner and outer niobium layers are shown connected by a niobium cap around the end of the insulator. The following section describes the stresses that result when niobium is removed at various locations in the end region to allow the inner and outer niobium layers to be electrically insulated from each other.

2.8.3 Discussion of Stress Analysis

Stresses as a function of radius through the trilayer are shown at different positions in the enclosed ceramic configuration in Figures 2.14 through 2.17. Figure 2.14 shows the stress patterns far removed from the end effects. Radial stresses in the ceramic are very small. Axial and tangential stresses are large but compressive (negative).

Figure 2.15 illustrates the stresses in the all-metal cap at the end of the trilayer. The radial and tangential stresses are tensile;

Figure 2.13 Trilayer Dimensions

Figure 2.14 Enclosed Ceramic (Far From End)

Figure 2.15 Enclosed Ceramic (End of Metal)

Figure 2.16 Enclosed Ceramic (Interface - Metal Side)

Figure 2.17 Enclosed Ceramic (Interface - Ceramic Side)

the inner and outer niobium walls are essentially joined together by the metal cap across the end. A similar (but larger) pattern of stresses exists on the metal side of the ceramic-metal interface, as shown in Figure 2.16. On the ceramic side of this interface, the stresses in the ceramic are compressive and relatively large, as shown in Figure 2.17. The stress patterns as a function of axial position are shown in Figure 2.18. These patterns suggest that differential ceramic expansion in an enclosed end trilayer does not introduce, anywhere in the ceramic, large tensile stresses that would lead to failure by cracking.

The requirement for cutting the end cap to provide electrical insulation between the inner and outer niobium layers changes the stress patterns. Figure 2.19 illustrates the effects of slotting the outer niobium layer. The end section is displaced radially outward less than the bulk of the trilayer. The end section lags behind and localized tensile stresses develop in the ceramic. A similar displacement occurs when the slot is widened to include 0.1 inch outer metal removal at the end. The stress patterns are smoothed toward the end of the ceramic layer (as shown in Figure 2.20), but the maximum tensile stresses are about the same.

Removing the metal cap and forming a flat-ended configuration result in large localized, tensile radial stresses, as illustrated in Figure 2.21. Recessing the ceramic, as shown in Figure 2.22, does not significantly reduce these radial stresses, but merely shifts the stresses toward the new ceramic surface.

Removing metal from the inner layer of the trilayer results in the end section displacing radially outward faster than the bulk, as illustrated in Figure 2.23, and localized tensile stresses form in the ceramic. These stresses tend to become larger and more localized if the length of the removed inner layer is shortened, as shown in Figure 2.24.

AXIS

Figure 2.18 Enclosed Ceramic

Figure 2.19 Outer Nb Slotted

Figure 2.20 Outer Nb Removed (0.1 inch)

Figure 2.21 Flat End

Figure 2.22 Recessed Ceramic (0.01 inch)

Figure 2.23 Inner Nb Removed (0.1 inch)

Figure 2.24 Inner Nb Removed (0.07 inch)

Figure 2.25 summarizes the maximum tensile stresses calculated for each of the end configurations. The flat end results in the highest stresses. Recessing the ceramic does not reduce the stresses. Removing metal from either the outer or inner layers significantly reduces the stress levels, with removal of the inner layer achieving the lowest stresses.

σ_r = RADIAL
 σ_z = AXIAL
 σ_θ = TANGENTIAL

MAXIMUM TENSILE STRESS (psi)

Figure 2.25 Stress Relieved End Configurations

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3. ADDITIVE EFFECTS WITH SUBLIMED MOLYBDENUM COLLECTORS

3.1 REVIEW OF PRIOR WORK

The use of collector coatings formed by the sublimation of molybdenum onto niobium substrates originated during the 1960's. Niobium was, and still is, the standard collector substrate material primarily because of the close thermal expansion match with Al_2O_3 (the collector and sheath insulator can be bonded together to achieve good heat transfer across the interface). However, collector surfaces of niobium did not consistently yield the highest thermionic converter performance. With molybdenum surfaces, for example, significantly higher thermionic output was occasionally observed. Such converters were called "Super Diodes," and the performance was characterized by reduced optimum cesium reservoir temperatures and very steep I-V curves. Eventually, the term super diode shifted to oxygen additive diode when the effect of oxygen on converter performance was realized. Oxygen lowers the emitter cesiated work function, allows converter operation at reduced cesium pressures with less electron scattering, and results in improved high-current capacity (steep I-V curves). If the system design can be adjusted to accept high current density operation, significant increases in converter performance can be achieved.

Evaporation (sublimation) was selected as a relatively simple fabrication technique to form a thin coating of molybdenum on a niobium substrate. Initially, the sublimation process was performed in a diffusion-pumped vacuum system at pressures in the 10^{-5} torr range. Later, coatings were produced with oxygen introduced into the vacuum system. When properly made, the coatings consistently resulted in the expected oxygen additive effect. These "vintage" coatings contained 5,000 to 10,000 ppm of oxygen. Since the solubility limit of oxygen in molybdenum is about 40 ppm, the oxygen content was almost totally

in the oxide form. The sublimation conditions were adjusted to maximize the MoO_3 content in the belief that the trioxide was the additive source or precursor.

The longest life test of an oxygen additive diode was the electrically heated "G" series converter fabricated in 1971. The "G" series converter used a sublimed molybdenum collector coating with an oxygen content of approximately 6000 ppm. The design operating conditions were:

Emitter Temperature	1800°K
Current Density	6 A/cm ²
Output Voltage	0.77 V
Output Power Density	4.6 W/cm ²
Collector Temperature	870°K
Cesium Reservoir Temperature	560°K
Electrode Area	35 cm ²

The life test of the converter extended to June 1973 with completely unattended testing during the last six months. The converter accumulated a total of approximately 14,000 hours of operation, and was fully operational when the test was shut down.

The possibility of improving thermionic performance is generally divided into two approaches: reducing the voltage drop occurring in the interelectrode space and reducing the collector work function. The sum of the interelectrode voltage drop plus the collector work function is called the barrier index. A low barrier index implies a high performance diode.

The pre-1973 work concentrated on reducing the interelectrode voltage drop. Electrons produced at the emitter by thermionic emission experienced numerous collisions while moving across the interelectrode space to the collector. The voltage or energy drop resulting from these collisions was dependent on the product of the cesium pressure in the space times the width of the space ($p \cdot d$). A minimum value in voltage drop of approximately 0.5 volt occurred at a $p \cdot d$

product of about 20 mil-torr. This value represented the energy required to ionize cesium atoms to form the plasma in the ignited mode of diode operation. The voltage drop increases for $p \cdot d$ values less than 20 mil-torr because of insufficient ionization and for $p \cdot d$ values greater than 20 mil-torr because of excess collisions.

The $p \cdot d$ product suggests that either the cesium pressure or the interelectrode spacing may be adjusted to minimize the voltage drop. The required cesium pressure is primarily controlled by the thermionic emission conditions at the emitter. Lower bare work function emitters (poor emitters) require higher cesium pressures. In general, a poor emitter can be compensated for by using a small spacing. Typical poor emitters with bare work functions of 4.5 to 4.6 volts require an optimum spacing of less than 1 mil. Such a small spacing becomes exceedingly difficult to physically maintain, especially in a nuclear reactor application where fueled emitter deformations occur.

The work function of crystalline materials depends on the orientation of the crystal relative to the surface. The overall average work function of a randomly oriented polycrystalline emitter can be increased by orienting the crystals during fabrication to preferentially expose high bare work surfaces. The $\langle 110 \rangle$ preferred orientation obtained with the chloride tungsten CVD process was developed specifically for reactor applications to permit wider spacings.

Further reductions in optimum cesium pressure are obtained as a result of the presence of a partial monolayer of oxygen on the emitter surface. The adsorbed oxygen significantly increases the effective work function of the emitter material. The increase in work function and the resultant decrease in cesium pressure depends on the surface coverage of oxygen. Thus, the technique used to supply oxygen is critically important in achieving the benefits of oxygen additives.

In the period from 1973 to 1984, research concentrated on the second means of improving performance: reducing the collector work function. Sublimed molybdenum collector coatings were reinvestigated toward the end of this time period for applications with reduced emitter and collector temperatures and at low power levels. Coating sublimation conditions were adjusted to optimize the barrier index at low current levels. Tests at various oxygen contents in the coatings suggested that the sensitivity of diode performance to collector temperature (back emission from the collector) could be reduced at low oxygen levels.

In 1985, two planar diodes were fabricated with collector coatings containing reduced oxygen contents to further investigate this collector temperature dependency. Short-term tests of these diodes revealed performance characteristics that were free of oxygen. The saturated emitter current densities did not depend on collector temperature (a standard test for detecting the presence of additives on the collector), the optimum cesium reservoir temperatures were high, and the I-V curves were not steep. The lack of additive performance demonstrated the need for further investigation and readjustment of the sublimation conditions for higher temperature and power conditions.

3.2 THE ADDITIVE PROCESS

The steps leading to and resulting in additive performance are believed to be the following:

- During Sublimation of the Molybdenum Coating
 - Oxygen in the vacuum chamber preferentially reacts with the molybdenum evaporator to form oxides.
 - Metal and oxides evaporate from the molybdenum evaporator.
 - The evaporated material is mostly metal with a small amount of oxide.
 - The molybdenum oxides formed at the evaporator preferentially evaporate as a trioxide.

- The sublimed coating forms as mostly metal with a small amount of dispersed (maybe at the grain boundaries) trioxide.
- A low substrate temperature (probably below 700 C) is necessary to prevent a rapid reaction from occurring between the trioxide and metal to form dioxide.
- The sublimed coating forms as columnar grains growing from the substrate surface.
- During Converter Outgassing
 - The dispersed trioxide in the coating reacts with metal to form molybdenum dioxide.
 - The trioxide-to-dioxide reaction results in a 16-percent-volume reduction.
 - The volume reduction forms connected pores (probably along grain boundaries).
- During Converter Operation
 - The connected pores provide limited access of cesium to the dispersed molybdenum dioxide.
 - Cesium reacts with molybdenum dioxide to form cesium oxides.
 - Cesium oxide evaporates from the pores and surface of the collector coating and diffuses to the emitter surface.
 - Cesium oxide is decomposed yielding oxygen to the emitter surface and cesium to the interelectrode space.
 - Tungsten oxides formed at the emitter evaporate and diffuse to the collector.
 - Cesium reacts with tungsten oxide on the collector and forms cesium oxide and tungsten.
 - Oxygen is continuously cycled between the collector and emitter.

- The oxygen reservoir is the dispersed molybdenum dioxide in the collector coating.
- The oxygen reservoir provides startup oxygen and makeup oxygen for any losses in the system.

X-ray diffraction analyses of mixtures of molybdenum and molybdenum oxide powders have provided better understanding of the sublimed molybdenum fabrication procedures. Tests with known concentrations of MoO_3 (and separate tests with known concentrations of MoO_2) establish the lower detectable limit (equivalent oxygen content) at about 10,000 ppm O_2 . Many of the earlier sublimation samples contained only several thousand ppm O_2 (determined by chemical analysis), and x-ray diffraction could not detect the presence of oxides.

Reactions between Mo metal and MoO_3 were studied as a function of temperature. Test samples were prepared by mixing metal and MoO_3 powders, cold pressing, and heating in vacuum. The presence and/or absence of MoO_3 and MoO_2 after heating provides insight for the following reaction:

Samples held at 500 C for five hours did not show any reaction between Mo and MoO_3 . Some reaction was observed in samples held at 600 C for one hour. The MoO_3 was completely converted to MoO_2 in samples held at 600 C for five hours.

These results show that MoO_3 can be retained in the sublimed coatings only at low temperatures. Operation at 600 C or higher will rapidly convert the trioxide to dioxide. Four fixed-spacing converters (using the planar variable-spacing design without the bellows) were fabricated and tested to study the effects of depositing and outgassing sublimed molybdenum coatings at different temperatures. Processing temperatures may effect diode performance because of the reaction between Mo and MoO_3 .

The four converters contained collector coatings prepared as follows:

Converter No.	Sublimation Temperature (°C)	Outgassing Temperature (°C)
1	600	500
2	500	500
3	500	750
4	750	750

All of the converters exhibited additive thermionic performances. The performances of Converters 1, 2 and 3 were the same. Converter 4 showed a slight loss in voltage. The results indicate that low sublimation temperatures are desirable (forming the coatings with MoO_3 appears to be beneficial). Subsequent outgassing to temperatures sufficiently high to convert the MoO_3 to MoO_2 does not cause a penalty.

The collector coatings were sublimed in a vac-ion chamber. The first hour of a run was made under vacuum conditions (mid- 10^{-7} -torr range). Oxygen was added during the remaining four hours to obtain a chamber pressure of 8×10^{-6} torr. The substrate temperature was approximately 900 C during the first hour and was lowered to the indicated sublimation temperature for the remaining four hours. The pressure levels and substrate temperatures were selected to obtain an initial high-purity molybdenum layer next to the substrate, followed by a MoO_3 -bearing layer with columnar grain structure. Cross sections of sample deposits distinctly showed this type of deposit formation.

3.3 ADDITIVE THERMIONIC PERFORMANCE

Additive effects resulting from the use of sublimed molybdenum collectors were evident during testing by a reduction in optimum cesium reservoir temperature and by steeper I-V curves. These changes become clear when a set of nonadditive performance curves shown in Figure 3.1 is compared to a set of additive performance curves shown

Figure 3.1 Typical Nonadditive Thermionic Performance

in Figure 3.2. The differences between these two sets of data are caused primarily by a reduction of the voltage drop in the interelectrode space. The voltage drop is reduced because the oxygen additive reduces the cesium pressure required to achieve adequate emission (emitter work function).

Further comparison of the data shows that the low current performance of additive and nonadditive diodes are very similar. This result is consistent with the primary difference being a reduction in cesium pressure. Excessive electron scattering from cesium atoms represents an internal electrical resistance in the diode. The effect of such a resistance is small for small currents, but becomes progressively more important as the current increases.

Performance improvements from additive diodes, therefore, can be realized only at high current densities. Output power densities and electrical power conversion efficiencies are calculated for the illustrated additive and nonadditive performance data and are listed in Tables 3.1 and 3.2. The plot of power density as a function of voltage in Figure 3.3 shows a relatively flat characteristic for nonadditive diodes. The voltage rapidly falls off as the current increases with the product of voltage times current remaining approximately constant. A maximum does occur at 0.4 volt. The power density plot for additive diodes is quite different. The high current capability of additive diodes results in a rapid increase in power density as the voltage is reduced. For these data, the power output increases by a factor of almost 3, and the maximum is beyond the range of data at higher currents and lower voltages.

Conversion efficiency for both additive and nonadditive diodes increases with voltage. Considering only the energy removed from the emitter by electrons, the fraction converted to output power increases almost linearly with voltage, as illustrated in Figure 3.4. Both types of diodes exhibit "electron" conversion efficiencies up to

Figure 3.2 Typical Additive Thermionic Performance

TABLE 3.1
NONADDITIVE PERFORMANCE CALCULATIONS

V (volts)	J (A)	Power (W)	ϕ_E (V)	$Q_E (J\phi_E)$ (W)	Q_{cond} (W)	Q_{rad} (W)	$Q_E + Q_{\text{cond}} + Q_{\text{rad}}$	1.1 Q	$\eta (\%)$ $\left(\frac{\text{Power}}{1.1 Q}\right)$
0.15	20.4	3.06	2.60	53.0	1.9	11.3	66.2	72.8	4.20
0.2	18.2	3.64	2.62	47.7	1.9	11.3	60.9	67.0	5.43
0.25	16.3	4.07	2.64	42.8	1.9	11.3	56.0	61.6	6.61
0.3	14.6	4.38	2.66	38.8	1.9	11.3	52.0	57.2	7.66
0.35	13.3	4.65	2.67	35.5	1.9	11.3	48.7	53.6	8.68
0.4	12	4.8	2.68	32.2	1.9	11.3	45.4	49.9	9.61
0.45	10.6	4.77	2.70	28.6	1.9	11.3	41.8	46.0	10.4
0.5	9.3	4.65	2.72	25.3	1.9	11.3	38.5	42.3	11.0
0.55	8.3	4.56	2.74	22.7	1.9	11.3	35.9	39.5	11.5
0.6	7.2	4.32	2.76	19.9	1.9	11.3	33.1	36.4	11.9
0.65	~6	3.9	2.79	16.7	1.9	11.3	29.9	32.9	11.8

TABLE 3.2
ADDITIVE PERFORMANCE CALCULATIONS

V (volts)	J (A)	Power (W)	ϕ_E (V)	$Q_E (J\phi_E)$ (W)	Q_{cond} (W)	Q_{rad} (W)	Q ($Q_E + Q_{cond} + Q_{rad}$)	1.1 Q	η (%) $\left(\frac{Power}{1.1 Q}\right)$
0.4	28	11.2	2.55	71.4	1.4	11.3	84.1	92.5	12.1
0.45	22.3	10.0	2.59	57.7	1.4	11.3	70.4	77.4	12.9
0.5	17.2	8.6	2.63	45.2	1.4	11.3	57.9	63.7	13.5
0.55	12.4	6.8	2.68	33.2	1.4	11.3	45.9	50.5	13.5
0.6	9.0	5.4	2.73	24.6	1.4	11.3	37.3	41.0	13.2
0.65	~6.8	4.4	2.78	18.9	1.4	11.3	31.6	34.8	12.7

Figure 3.3 Output Power Density Comparison

Figure 3.4 Conversion Efficiency Comparison

about 24 percent. When radiation and other extraneous heat losses are included, the overall power conversion efficiency passes through a maximum in the 0.5- to 0.6-volt range, and these maxima are substantially reduced from the electron conversion values. The additive diode achieves a power conversion efficiency approximately 1.5 percentage points higher than the nonadditive diode because the extraneous losses are a smaller fraction of the electron cooling energy (The additive diode operates at higher currents.)

3.4 DIODE FABRICATION

Eight variable spacing planar and two fixed spacing cylindrical diodes were fabricated for testing at Rasor Associates to further evaluate the performance of additive diodes based on the use of sublimed molybdenum collector coatings. Table 3.3 lists the electrode surface conditions tested in each diode. The electrode combinations were chosen to: determine if the sensitivity of additive diode operation to collector temperature could be reduced by reducing the oxygen content of the coatings; determine if a high bare work function emitter improved additive performance over that obtained with a low work function surface; compare additive versus nonadditive diode performances; and compare planar versus cylindrical performance.

The electrode materials used in each diode are listed in Table 3.4. Planar diodes Nos. PD-1 and PD-2 used electroetched fluoride CVD tungsten emitters. The electroetched surface was used as a means of obtaining a relatively high work function surface early in the program while development continued on a chloride CVD tungsten process. The electroetching process preferentially attacks the low work function surfaces and exposes high work function surfaces. The actual increase in work function achieved on the emitters for PD-1 and PD-2 is uncertain because of the lack of test facilities for direct measurements.

TABLE 3.3
DIODE TEST CONDITIONS

<u>Diode No.</u>	
PD-1	High ϕ Emitter - Low O ₂ Additive
PD-2	High ϕ Emitter - No Additive
PD-3	Low ϕ Emitter - High O ₂ Additive
PD-4	Low ϕ Emitter - Medium O ₂ Additive
PD-5	Low ϕ Emitter - Low O ₂ Additive
PD-6	High ϕ Emitter - No Additive
PD-7	High ϕ Emitter - High O ₂ Additive
PD-8	High ϕ Emitter - Medium O ₂ Additive
CD-1	Low ϕ Emitter - High O ₂ Additive
CD-2	High ϕ Emitter - No Additive

Notes: PD = Planar Diode
 CD = Cylindrical Diode
 ϕ = Work Function

TABLE 3.4
DIODE ELECTRODE MATERIALS

<u>Diode No.</u>	<u>Emitter</u>	<u>Collector</u>
PD-1	EE W (F)	Sub Mo (3700 O ₂)
PD-2	EE W (F)	Mach. Nb
PD-3	EP W (F)	Sub Mo (15,000 O ₂)
PD-4	EP W (F)	Sub Mo (1/2 PD-3)
PD-5	EP W (F)	Sub Mo (1/4 PD-3)
PD-6	EP W (Duplex)	Mach. Nb
PD-7	EP W (Duplex)	Sub Mo (PD-3)
PD-8	EP W (Duplex)	Sub Mo (1/2 PD-3)
CD-1	EP W (F)	Sub Mo (PD-3)
CD-2	EP W (Duplex)	Mach. Nb

Notes: EE = Electroetched
 EP = Electropolished
 Duplex = CVD Cl/F W
 O₂ = Oxygen Content
 (Parts per million)

I-V curves obtained during performance checks of PD-1 and PD-2 are shown in Figures 3.5 and 3.6. Both diodes exhibited similar performance, performance characteristic of nonadditive diode operation. Nonadditive performance was expected from PD-2 which contained a machined niobium collector surface. PD-1, however, had a sublimed molybdenum collector coating with approximately 3700 ppm oxygen and should have exhibited additive performance. This coating was sublimed in a diffusion-pumped vacuum system that had been used for previous additive studies. While the system contained a liquid nitrogen cold trap to minimize pump oil contamination, analysis revealed the presence of silica and carbon in similar coatings. Since decomposition of pump oil was the most probable source of these contaminants, and these contaminants were probably the reason that PD-1 did not exhibit additive performance, the decision was made to sublime coatings only in a vac-ion pumped system for all future diodes.

PD-3 was fabricated with an electropolished fluoride CVD tungsten emitter and a sublimed molybdenum collector coating containing about 15,000 ppm O_2 . Figure 3.7 shows I-V curves obtained during performance checkout. The data are characteristic of additive performance (low cesium reservoir temperatures and steep I-V curves). PD-3 was the first variable spacing planar diode with a collector coating sublimed in a vac-ion pumped vacuum system. (The four fixed spacing planar diodes had used coatings formed in the vac-ion system to check out sublimation conditions.) The performance of PD-3 was considered to be excellent and the overall process appeared to be under reasonable control.

The design objective of PD-4 was to obtain a collector coating with about one-half the oxygen content of that in PD-3. The oxygen content of sublimed coatings was varied by adjusting the partial pressure of oxygen in the bell jar during sublimation. For PD-3, the O_2 partial pressure (as indicated by a standard ionization gauge) had

Figure 3.5 PD-1 Performance Curves

Figure 3.6 PD-2 Performance Curves

Figure 3.7 PD-3 Performance Curves

been approximately 6.6×10^{-6} torr. The coating for PD-4 was therefore formed with the oxygen pressure reduced to 3.3×10^{-6} torr. Chemical analysis indicated the resultant coating contained about 3200 ppm O_2 . Performance data for PD-4 are shown in Figure 3.8. The data are only partially characteristic of additive performance. The cesium reservoir temperatures are low but the I-V curves are not steep. Significant back emission from the collector is also evident. This is the first time that large back emission effects had been observed at low collector temperatures. Figure 3.9 shows that the optimum collector temperature is less than 500 C. The slope of the I-V curves indicates some sort of internal resistance. The low cesium temperature, however, rules out excessive scattering by cesium vapor. A possible explanation is that the coating is poorly adhered to the niobium substrate. Such a condition could result in a high electrical resistance across the interface and a low thermal conductance. The coating would run at a substantially higher temperature than the measured substrate temperature and the observed back emission effects would result.

Approximately one-half of the oxygen content used in PD-4 was desired for the collector coating of PD-5. Sublimation was carried out in an oxygen partial pressure of 1.6×10^{-6} torr with a resultant oxygen content in the coating of about 1800 ppm. PD-5 also used a "first of its kind" emitter structure. All available full-diameter fluoride CVD tungsten emitter disks had been consumed in earlier diodes. The time required to fabricate additional full-size disks was excessive. Accordingly, a small-diameter fluoride CVD tungsten disk, available from the original deposition, was pressure bonded into a full-diameter powder metallurgy tungsten cup, as illustrated in Figure 3.10. Heating tests after machining indicated that the emitter disk was in good thermal contact with the substrate cup. I-V curves obtained for PD-5 (Figure 3.11) show characteristics similar to those observed from PD-4.

Figure 3.8 PD-4 Performance Curves

Figure 3.9 PD-4 Collector Temperature Dependence

Figure 3.10 Pressure Bonded Emitter Design

Figure 3.11 PD-5 Performance Curves

The cesium reservoir temperatures are characteristic of additive performance, but an internal resistance is evident and excessive back emission occurs. These abnormal effects are more pronounced in PD-5 than in PD-4.

The purpose of the next three planar diodes was to investigate the performance of duplex emitters (emitter structures simulating those planned for TFE applications). TFE emitter designs used a thick substrate of fluoride CVD tungsten covered with a thin coating of chloride CVD tungsten. The fluoride CVD tungsten (with a fluoride content of 5 to 15 ppm) exhibited a stable grain structure with good creep strength and is used to provide mechanical strength. The fluoride CVD tungsten, however, had poor thermionic emission properties (the grains were oriented to expose $\langle 100 \rangle$ crystal faces normal to the emitter surface). The chloride CVD tungsten layer was added to provide good thermionic performance. Chloride CVD tungsten can be deposited under controlled conditions with a $\langle 110 \rangle$ preferred orientation which results in a high bare work function with improved emission characteristics. The $\langle 110 \rangle$ chloride tungsten had a creep strength much lower than that of the fluoride CVD tungsten, and did not contribute significantly to the strength of the emitter body. Hence, only a thin layer (approximately 0.010 inch) of chloride tungsten is used.

Numerous trial depositions were performed to investigate the CVD conditions which led to the formation of $\langle 110 \rangle$ oriented tungsten. Favorable deposition parameters included a chamber pressure of 4 torr, a substrate mandrel temperature of 1100 C, and a Cl_2/H_2 ratio in the range of 1/2 to 1. Tests with both fluoride CVD tungsten and powder metallurgy tungsten mandrels indicated that the coating orientation was relatively independent of the substrate material. The coating orientation was determined using x-ray diffraction techniques. X-ray diffraction yields a qualitative indication of the preferred orientation but does not establish quantitative data. Cylindrical geometry coatings are particularly

difficult to analyze. Precision test equipment directly measuring thermionic emission (work function) is required to fully evaluate these coatings and to allow performance comparisons to be made among diodes containing these emitters.

Diode No. PD-6 contained a duplex emitter of chloride CVD tungsten on a substrate of fluoride CVD tungsten and a collector of machined niobium. I-V curves are shown in Figure 3.12. The performance of PD-6 is quite good and characteristic of a high bare work function emitter. There is no evidence of oxygen (the collector surface is niobium and an oxygen additive effect should not be expected). On a performance comparative basis, PD-6 is better than PD-2 (containing an electroetched emitter), but not as good as the reference duplex emitter diode tested in 1970. These results indicate that the emitter in PD-6 exhibits a higher bare work function than PD-2 but lower than the work function of the reference emitter. In nonadditive diodes, the thermionic performance is sensitive to the emitter bare work function with the performance increasing as the work function increases.

PD-7 used a duplex emitter of chloride CVD tungsten on a substrate of powder metallurgy tungsten. The collector was a sublimed molybdenum coating with an oxygen content of about 12,000 ppm. I-V curves obtained during the performance checkout are shown in Figure 3.13. The abnormal characteristics observed first in PD-4 and then seen as more pronounced in PD-5 are evident again.

PD-8 and PD-7 were fabricated at approximately the same time. PD-8 contained a duplex tungsten emitter with a fluoride CVD tungsten substrate and a sublimed molybdenum collector coating with an oxygen content of about 1000 ppm. Figure 3.14 shows that this diode exhibited typical additive performance and did not show the previously observed abnormal behavior. The cause of the abnormal I-V curves is unknown.

Figure 3.12 PD-6 Performance Curves

Figure 3.13 PD-7 Performance Curves

Figure 3.14 PD-8 Performance Curves

At first, the internal resistance effects appeared to be associated with low oxygen content collector coatings. The results from PD-7 and PD-8, however, do not agree with this association. The abnormal performance effects should not be directly related to the indicated oxygen measurements. Experience over the past two years suggests that the use of chemical analysis for determining oxygen content in this application is very marginal and probably very misleading. The significance of the stated values is questionable. Efforts to find a more accurate analysis method have been fruitless.

The first cylindrical diode (CD-1) used an electropolished fluoride CVD tungsten emitter and a sublimed molybdenum collector coating with an oxygen content of about 3000 ppm. The diode was operated in a slip-fit heat exchanger. The heat exchanger consisted of two concentric cylinders separated by a narrow gas gap. The diode was positioned in the central hole of the inner cylinder and water coolant flowed through the outer cylinder. The operating temperature of the collector was controlled by the thermal conductance (helium gas pressure) of the gap. The performance of CD-1 was that of an oxygen additive diode with characteristic low cesium reservoir temperatures. I-V curves obtained during performance checkout are shown in Figure 3.15. The indicated emitter temperature of 1800 K was observed by pyrometer at the center of the emitter. The center location operates at the highest temperature and an axial temperature difference of about 100 K exists along the emitter. The output voltage is measured electrode voltage.

Cylindrical diode No. CD-2 contained a duplex emitter with a chloride CVD tungsten layer on a fluoride CVD tungsten substrate. The collector was niobium. I-V curves are shown in Figure 3.16. The performance is characteristic of oxygen-free diode operation.

Figure 3.15 CD-1 Performance Curves

Figure 3.16 CD-2 Performance Curves

Diode performance curves necessarily represent an average of a range of emitter temperatures and a range of electrode voltages. Temperature gradients and voltage gradients exist in electrodes. These gradients tend to be greater in large cylindrical diodes and lesser in small planar diodes. The single most important factor influencing emitter temperature variations or gradients is electron beam heating, the usual means of electrically heating a diode. Bombardment power supplies control values of total voltage and total current. The distribution of this total current over the total emitting area of the bombardment filament depends on the localized filament temperature. If part of the filament tends to operate hotter than the rest of the filament, increased bombardment current will flow from the hotter section. The result is a localized increase in emitter temperature. This temperature perturbation is increased by thermal feedback from the emitter to the filament. The localized hot spot is self-generating and unstable. Bombardment heating is workable in practice because heat transfer (radiation and conduction) tends to smooth out temperature gradients formed as a result of localized heating.

Thermal feedback effects and the resultant nonuniform heating tend to be exaggerated in a large cylindrical diode configuration with the bombardment filament positioned in a deep well along the axis of the emitter. The end of the filament located at the bottom of the well is thermally coupled, more strongly to the local emitter temperature than the section of the filament at the open end of the well. The overall result is that the bottom part of the emitter inevitably operates at an elevated temperature. The emitter temperature gradient can be adjusted by positioning and shaping the filament to provide more uniform heat input to the emitter. Performance data obtained from cylindrical diodes can be altered significantly by these filament adjustment techniques.