RADIOISOTOPE SPACE POWER GENERATOR ANNUAL REPORT

**FOR THE PERIOD JULY 1, 1975,
THROUGH SEPTEMBER 30, 1976**

by

**N. B. ELSNER, J. CHIN, H. G. STALEY,
E. J. STEEGER, and P. K. GANTZEL**

**Prepared under
Contract EY-76-C-03-0167
Project Agreement No. 60
for the San Francisco Operations Office
U.S. Energy Research and Development Administration**

SEPTEMBER 1977

GENERAL ATOMIC COMPANY

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ABSTRACT

TPM-217 P-type selenide usefulness in thermoelectric converters depends on its dimensional, electrical and thermal stability at high temperature and its compatibility with other converter component materials in a low pressure environment. Experimental efforts have been directed at determining: the vaporization behavior at 900°C, the partial pressures of vaporizing species versus temperature, vapor suppression coatings, thermal expansion, dimensional stability, and the high temperature compatibility of TPM-217 with proposed end cap materials.

Scanning electron examination shows as-cast TPM-217 P-type material has a lamellar structure with occasional layers of a ductile phase which is presumed to be copper.

TPM-217 when comminuted and vacuum hot pressed is dimensionally unstable in subsequent use. The material will grow in both length and diameter when subjected to several thermal cycles between room temperature and 500°C. Heat treatments during and after the vacuum hot pressing operation have made large gains in reducing this dimensional instability.

End cap bonding by the General Atomic mesh-in-cap techniques appears to have adequate joint strength for TPM-217 material but corrosive interaction occurs between the unprotected 316 stainless steel mesh and cap and the TPM-217 material at 600°C. Compatibility studies were conducted to determine if pyrocarbon, Mo, W, W-Re or Re were resistant to this corrosive interaction with TPM-217 P-type material. The application of these refractory metal coatings or carbon on 316 stainless steel will suppress the interaction and will also allow the high expansion stainless steels to be used with the very high expansion TPM-217 material ($\alpha = 24 \times 10^{-6}$ in/in/°C).

Rates of vaporization for unprotected TPM-217 P-type at 900°C in vacuum were measured at 1×10^{-4} gm/cm²-hr. Knudsen cell mass spectrometer examination of heated TPM-217 species show Se₂, Cu, Ag, and CuSe to be the major species. Se₂ comprises over 90% of the vapor species at 1100°C. One method of suppressing vaporization being evaluated is to coat the TPM-217 material with an insulating material which is molten at 900°C, yet is sufficiently viscous to relieve the thermal stresses caused by the high expansion of the TPM-217 material. Two glasses which show some promise contain B₂O₃ + graphite flakes and B₂O₃ + BN. TPM-217 material coated with these materials and aged for short periods at elevated temperatures (800° to 900°C) remained adherent to the TPM-217 and reduced the rate of vaporization by a factor of five. Other protective coating systems are being examined.

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1. INTRODUCTION

TPM-217 P-type selenide thermoelectric material is a promising high-temperature thermoelectric material from 3M that is being evaluated at General Atomic. Its usefulness in thermoelectric converters depends on its thermal stability at high temperature and its compatibility with other converter component materials in a low pressure environment. The first steps in the evaluation of this material were to examine its microstructure and dimensional stability at temperature and in a thermal gradient. The results of these tests were used as a guide in determining what coating and end cap joining techniques might be evaluated.

The expected useful life of any thermoelectric device operating in an elevated temperature, low pressure environment depends on its maintenance of its structural and chemical stability. The desired operating temperature of proposed thermoelectric generators using TPM-217 P-type material is 900°C. The vaporization behavior of this material at 900°C and the partial pressures of vaporizing species versus temperature were examined and reported last year in this program (Ref. 1). These tests were a further guide to possible vapor suppression coatings for these materials.

Details of FY 1976 experiments are described in the sections which follow. Experimental coatings for vapor suppression are also described as are joining and material compatibility problems associated with end cap bonding. For brevity, the designation TPM-217 P type material is sometimes designated TPM-217 or just TPM. No TPM-217 N material is included in work reported.

2. MICROSTRUCTURAL EXAMINATION

Two forms of TPM-217 P-type material are being evaluated. These are as-cast material prepared by the 3M Company and vacuum hot pressed material prepared at General Atomic. The vacuum hot pressed materials were prepared from ground as-cast material, sieved through a 270 mesh screen. The sieved powder was hot pressed in vacuo at 600°C and 10,000 psi. As-cast and vacuum hot pressed material were mounted and polished for metallurgical examination. Three phases observed in the metallographic examinations were: the matrix, a copper colored phase, and a white phase. Microprobe examinations showed the copper colored phase to be mainly copper. The white phase was 75-85% silver.

Scanning photomicrograph of fractured as-cast TPM-217 P-type material (Fig. 1) shows it to be composed to platelets. Fractures occur along platelet boundaries. Between these platelets, at irregular intervals, one can see columnar growth cones of a ductile phase (Fig. 2). This ductile phase is presumed to be copper or copper-silver. The morphology of these cones is similar to chemically vapor deposited metals from a low concentration reactant gas environment.

SEM photomicrographs of vacuum hot pressed TPM-217 P-type material are shown in Fig. 3. The destruction of the platelets are clearly seen in the photos. Seebeck measurements of as-cast and vacuum hot pressed TPM-217 were 184 and 185 $\mu\text{V}/^\circ\text{C}$ respectively. Thus the destruction of the gross platelet formations in the vacuum hot press process appears to have no apparent effect on the thermoelectric properties.

a

b

c

Fig. 2-1

SEM photomicrographs of a fractured surface of as-cast 3M, TPM-217 general views at (a) 100X, (b) 400X and (c) 1500X.

a

b

c

d

Fig. 2-2 SEM photomicrographs of a fractured surface of as-cast 3M, TPM-217 showing columnar second phase material planes of Cu_2Se at (a) 400X (b & c) 2000X and (d) 4000X

a

b

c

Fig. 2-3

SEM photos of fractured surface
of vacuum hot pressed TPM-217,
thermally cycled four times to
500°C

- (a) typical structure at 400X
- (b) coarse structure 1500X
- (c) fine grain structure 1500X

3. HOT PRESSING EVALUATION

An objective of the Isotec Materials fabrication study is to examine temperatures, pressures and other processing parameters used for vacuum hot pressing of TPM-217 P-type when fabricating mesh-in-cap bonded joints. The parameters for vacuum hot pressing of TPM-217 P-type material examined to date are summarized in Table 1. The results show the following:

1. Evacuating ground as-cast 3M, TPM-217 P-type material, then gradually increasing the pressure to 11,000 psi in steps yielded a good appearing hot pressed sample which was not (metallographically) different than 7,500 psi pressed samples without step increases in the pressure.
2. Boron nitride powder 95% plus Spraygraph 5% mold release gave the smoothest separation of the vacuum hot pressed samples from the hot pressing dies.
3. There was no visual advantage in using H_2 during the hot pressing process. Other properties must be evaluated before a complete assessment can be made. Conversely, no harm was found in using H_2 and from a quality control standpoint, it is probably wiser to use H_2 for possible reduction of surface oxides.
4. Post annealing to 800°C was necessary to insure cyclic thermal expansion behavior.

Room temperature, X-ray powder patterns of as-received 3M TPM-217 P-type material, and material after various fabrication steps were examined to determine microstructural stability. A Guinier camera was used for these measurements. A mixture equivalent to stoichiometric Cu_2Se was melted in vacuo in a sealed quartz vial. The resulting

TABLE 3-1

SUMMARY VACUUM HOT PRESSING PARAMETER STUDY

Sample No.	Powder Size (mesh)	Temp. (°C)	Pressure (psi)	Time at final Temp.	Gaseous Environment	Die Release	Results
6115-42	270	RT→450	1,000	0	H ₂	Spray-graph	Cu build up around the circumference of the sample; slight adhesion of sample to die.
		450→600	10,000	30 min	vac		
		600→RT	10,000		vac		
6115-44	270	RT→100	1,000	0	vac	Spray-graph + BN 50%	Better removal from die; copper still observed in cooler die areas.
		100→450	1,000	0	H ₂		
		450→600	10,000	30 min	vac		
		600→RT	0	--	vac		
6115-45-1	270	Die inverted to minimize free copper then processed the same as 6115-44.					Copper still collected on the cold sample side.
6115-45-2	270	Die pressing from 2 sides then processed the same as 6115-44					Copper uniformly coated the whole sample.

TABLE 3-1 (continued)

Sample No.	Powder Size (mesh)	Temp. (°C)	Pressure (psi)	Time at Final Temp.	Gaseous Environment	Die Release	Results
6115-46-1	270	Die plungers at both ends					
		RT→100	3,250	0	vac	Spray-graph + BN 50%	No copper observed
		100→400	5,000	0	H ₂		
		400→500	7,500	0	vac		
		500→600	10,000	15 min	vac		
		600→RT	0	--	vac		
6115-46-2	270	Repeat of 6115-46-1				Spray-graph + BN 50%	Copper observed but no extrusion
6115-49-1	300	RT	0	16 hrs	vac	Spray-graph	Mesh in cap failed on removal from the die due to technique used; copper was not noticed on the TPM material, sample looked intact, no copper detected.
		RT→200	3,750	0	vac		
		200→400	6,250	0	H ₂		
		400→500	6,250	0	vac		
		500→600	7,500	0	vac		
		600	11,000	15 min	vac		
		600→RT	1,000	0	vac		

TABLE 3-1 (continued)

Sample No.	Powder Size (mesh)	Temp. (°C)	Pressure (psi)	Time at Final Temp.	Gaseous Environment	Die Release	Results
6115-49-2	Repeat of above, but part carefully removed from the die						
6115-61	270	RT→250	3,000	0	vac	Spray-graph	Slight copper tinted surfaces but no major problems otherwise; samples had no visible imperfections
		250→300	3,000	0	H ₂		
		300→350	3,750	0	H ₂		
		350→375	5,000	0	H ₂		
		375→400	6,250	0	H ₂		
		400→425	7,500	0	H ₂		
		425→450	8,750	0	H ₂		
		450→500	10,000	0	H ₂		
		500→600	11,000	0	vac		
		600	11,000	10 min	vac		
	600→RT	1,000	0	vac			
6115-62	Same parameters as 6115-61						Samples had no visible imperfections, dimensional changes occurred when thermal cycled

TABLE 3-1 (continued)

Sample No.	Powder Size (mesh)	Temp. (°C)	Pressure (psi)	Time at Final Temp.	Gaseous Environment	Die Release	Results
6115-65	Same parameters as 6115-61, plus a postanneal to 800°C for 1 hr at 2000 psi load after the 600°C heating.						Good appearance, good thermal cycle expansion behavior.
6115-88	270-400	RT→300	3,000	0	vac	Spray-graph	Samples had no visible imperfections
		300→450	7,500	0	H ₂		
		450→600	8,750	0	vac		
		600	11,000	10 min	vac		
		600→RT	11,000	0	vac		
6115-112	270-400	RT→300	2,000	0	vac		Sample had no visible imperfections, essentially the same as run 6115-65.
		300→400	4,500	0	vac		
		400→600	7,250	0	vac		
		600→800	2,000	0	vac		
		800	500-2,500 3 times	60 min	vac		
		800→RT	500	0	vac		

TABLE 3-1 (continued)

Sample No.	Powder Size (mesh)	Temp. (°C)	Pressure (psi)	Time at Final Temp.	Gaseous Environment	Die Release	Results
6115-121	270-400	RT→300	3,000	0	vac	Spray-graph	2 of 8 samples separated at cap joint
		300→450	7,500	0	vac		
		450→600	8,750	0	vac		
		600	11,000	10 min	vac		
		600→800	light	30 min	vac		
		800→RT	11,000-3,000	0	vac		
6115-123	270-400	Repeat of 6115-121				Spray-graph	All 8 samples were without visible imperfections
6115-125	270-400	RT→300			vac	Spray-graph	All 8 samples were without visible imperfections
		300→450			vac		
		450→600	6,500		vac		
		600→800	1,000	30 min	vac		
		800→RT	1,000		vac		

TABLE 3-1 (continued)

Sample No.	Powder Size (mesh)	Temp. (°C)	Pressure (psi)	Time at Final Temp.	Gaseous Environment	Die Release	Results
6115-134	270-400	RT→600	1,000	0	vac	BN 95% + Spray-graph	Good appearance; easy mold release
		600	6,700-7,000	15 min	vac		
		600→800	1,000	30 min	vac		
		800→RT	1,000	0	vac		
6115-137	-400	RT→600	1,000	0	vac	BN 95% + Spray-graph	Good appearance; no copper noted
		600	7,250	15 min	vac		
		600→800	0	30 min	vac		
		800→RT	0	0	vac		
6115-140	-400	Repeat of run 6115-137				BN 95% + Spray-graph	Good appearance; easy mold release; no copper noted

TABLE 3-2
TPM P-TYPE MATERIAL GUINIER CAMERA RESULTS

Material	Material Process Treatment	Orthorhombic α -Cu ₂ Se Patterns	Cubic Cu _{2-x} Se	AgCuSe
As Cast TPM P type #1	As received	Diffuse peaks	No	Yes
	Ground to powder	Diffuse peaks	No	
	Powder anneal 900°C 1 hr	Sharp--some position peaks	No	Unknown
	Reground 900°C annealed powder	Diffuse peaks	No	Yes
	Vacuum hot pressed	Diffuse peaks	No	Yes
As-cast TPM P type #2	As received	Diffuse peaks	Yes	Yes
As Cast TPM P type #3	Vacuum hot pressed	Diffuse peaks	No	Yes

sample was used as an α -Cu₂Se standard. The results of the examination are shown in Table 3-2. The samples generally showed the presence of α -Cu₂Se which is in agreement with phase diagrams described in Murray and Heydings (Ref. 2). The cubic phase in a second batch of TPM-217 P-type material follows the observations of Slevels and Jellinck (Ref. 3). A thorough examination of these microstructures require hot stage metallography and hot stage X-ray examinations.

Lines corresponding to AgCuSe were observed in all samples except one which had been annealed for 1 hr at 900°C.

The X-ray examinations show the processes used to prepare vacuum hot pressed TPM-217 P-type material do not observably change its crystal structure. Some variations in as-received material were noted but cannot be explained. Other variations can be attributed to thermal annealing. Microprobe examinations of as-received, and vacuum hot pressed TPM-217 P-type samples, had the same Cu/Se ratios within the error of the measurements. This again shows the vacuum hot pressing does not alter the material.

4. DIMENSIONAL STABILITY

Vacuum hot pressed TPM-217 material was found to undergo large dimensional changes after conventional hot pressing (600°C, 20 min). Fig. 4-1 is an example of the hysteresis one observes in the first three heatings to 500°C. To alleviate this expansion, an 800°C, 1 hour anneal was added to the vacuum hot pressing operation. The results obtained on a specimen pressed in this manner are given in Table 4-1. The previously observed expansion in non-annealed samples is no longer evident in the first thermal cycles. Also shown in Table 4-2 are the smaller dimensional changes noted with as-cast material.

Volume expansion and density changes in thermal cycled as-cast and vacuum hot pressed TPM-217 were also measured. The results, in Table 4-2, show that the density of both as-cast and vacuum hot pressed material approach a common value of about 6.64 gm/cm^3 . Continuous heating can cause a slight decrease in this value.

One peculiarity with TPM-217 which was observed in these experiments and also reported by 3M (Ref. 4) was extrusion of copper out of the cold side of this material. If the cold side has a mechanical barrier, copper will collect at the barrier.

Fig. 4-1 Example of hysteresis observed in first three heatings to 500°C for TPM-217 vacuum hot-pressed at 600°C for 20 min

TABLE 4-1
THERMAL EXPANSION COMPARISON OF
AS-CAST AND ANNEALED VACUUM HOT PRESSED TPM-217

The as-cast sample was sliced and diced from a 3M cast element. The VHP sample was hot-pressed in the normal way, but was subsequently reheated to 800°C and held for 1 hour.

Thermal Cycles to 500°C	As-Cast		Vacuum Hot Pressed	
	Widths	Length	Diameter	Length
Initially	0.096/ 0.090	0.2385	0.1275	0.2833
After first cycle	0.0910/ 0.0905	0.2392	0.1282	0.2848
After second cycle	0.0913/ 0.0902	0.2392	0.1282	0.2845
After third cycle	0.0912/ 0.0904	0.2392	0.1280	0.2845

TABLE 4-2

VOLUME EXPANSION AND DENSITY CHANGES IN 500°C THERMAL CYCLES

	As-Cast			Vacuum Hot Pressed and 1 hour 800°C Reheat		
	Volume (Cm ³)	Density (gm/cm ³)	Total Wt Loss (10 ⁻⁴ gms)	Volume (Cm ³)	Density (gm/cm ³)	Total Wt Loss (10 ⁻⁴ gms)
As prepared	0.0337	6.39	0	0.0593	6.75	0
500°C, 20 min (slow heat & cool)	0.0323	6.65	6	0.0602	6.64	0
500°C, 20 min (2nd heating)	0.0323	6.66	3	0.0602	6.63	7
500°C, 20 min (3rd heating)	0.0323	6.64	8	0.0600	6.65	13
500°C, 65 hours (4th heating)	0.0321	6.67	13	0.0603	6.59	15

5. VAPORIZATION

In the initial vaporization study utilizing the graphite Knudsen cell, a Cu colored deposit was observed outside the cell after the run. How this Cu colored deposit occurred is not known; but since Se readily wets graphite, it was postulated that a Cu_xSe_z compound migrated through the graphite cell. Based upon this anomalous behavior with the graphite cell, the analysis was repeated with a BN cell and reported last year (Ref. 1). For the above analyses, the Knudsen cells were temperature and pressure calibrated by observing the melting point signal of Ag in separate experiments. The melting point can be observed because there is a constant pressure period while the Ag goes from solid to liquid; thus the thermocouple being used for the Knudsen cell experiment is calibrated in the geometry and environment in which it is actually used.

Vaporization behavior of as-received TPM-217 P material was measured and reported last year (Ref. 1). This year one cast and one vacuum hot pressed specimen were held at 900°C for a total of 368 hours in vacuo. The samples were removed and placed in the BN Knudsen cell. The vapor pressures of the species of the cast TPM-217 after this test were measured from the BN Knudsen cell (Fig. 5-1). The cell had been out-gassed at 1125°C. At this temperature, a small steady B_2O_3 signal was observed. It was probably caused by hydrolysis of the BN while the cell was opened to air at room temperature. At no time during the run were any B_2O_3 /TPM-217 compounds observed in the spectrum. Heats of vaporization were:

$\Delta H \text{ Se}_2$	=	56.2 ± 0.7 kcal/mole
$\Delta H \text{ Cu}$	=	79.8 ± 1.1 kcal/mole
$\Delta H \text{ Ag}$	=	76.4 ± 2.7 kcal/mole
$\Delta H \text{ CuSe}$	=	89.7 ± 3.2 kcal/mole

Fig. 5-1 Vapor species above cast TPM-217 heated to 900°C for 368 hr at less than 10^{-8} torr

○ Se_2

□ Cu

△ Ag

◇ CuSe

The CuAg species was not observed. Se_2 , Cu and CuSe vapor pressures were approximately the same as those measured on unaged vacuum hot pressed TPM-217 P-type material from Knudsen cell. Ag was down by over two orders of magnitude. The final vapor pressure point for CuSe was inadvertently made above the melting point of the material. This data point was the final measurement of the series and seemed to have no affect on the CuSe vapor pressure curve.

The drop in Ag vapor pressure was as expected. Prior metallographic examination of the cast sample tested at 900°C in vacuum showed no Ag-rich second phase.

One of the best coating systems evaluated to date to suppress vaporization of TPM-217 at 900°C in vacuo has been B_2O_3 + graphite. The graphite was added to the B_2O_3 to increase the 900°C viscosity of the glass. The system is thought to work, because the viscous glass can follow the dimensional changes in the TPM material during thermal excursions. Two speculated shortcomings of this system were experimentally examined. These were: (1) the reactions between B_2O_3 and graphite or B_2O_3 + graphite and (2) water absorbed by the B_2O_3 .

5.1 RESULTS OF MASS SPECTROMETRIC AND THERMOGRAVIMETRIC ANALYSIS OF A B_2O_3 -C COATING ON TPM-217

The vapor pressures of the major vapor species over an uncoated and a B_2O_3 -12% graphite coated TPM-217 element were measured. The weight loss was measured and the vapor species identified as a function of temperature, for the coating alone. The vapor pressure of B_2O_3 was measured.

The BN Knudsen cell, and mass spectrometer used in previous TPM-217 vapor pressure studies, was used. Identical calibration procedures were followed. The results for the control uncoated TPM-217 element were very

similar to previous measurements. The vapor pressure results are shown in Fig. 5-2. The heats of vaporization measured for the major vaporizing species were:

$\Delta H \text{ Se}_2$	=	$59.5 \pm 1.2 \text{ kcal/mole}$
$\Delta H \text{ Cu}$	=	$72.8 \pm 1.4 \text{ kcal/mole}$
$\Delta H \text{ Ag}$	=	$64.9 \pm 1.1 \text{ kcal/mole}$

A TPM-217 element, which had been plasma sprayed with a B_2O_3 -12% graphite coating to suppress vaporization, was then run. A large amount of H_2O vaporized around 100°C . Se_2 was observed vaporizing at a factor of 30 times higher vapor pressure than from the uncoated element. The element was held at 880°C for approximately 20 hours. At this time the Se_2 pressure, which was still slowly decreasing, had gone down by a factor of 50. The data in Fig. 5-3 shows the vapor pressures of the major vapor species at this time along with the initial Se_2 pressure. Vapor pressure above the B_2O_3 used is plotted in Fig. 5-4 for comparison. The heats of vaporization measured for the major vaporizing species from the coated element were:

$\Delta H \text{ Se}_2$	=	$59.3 \pm 0.7 \text{ kcal/mole}$
$\Delta H \text{ Cu}$	=	$82.0 \pm 0.9 \text{ kcal/mole}$
$\Delta H \text{ Ag}$	=	$63.2 \pm 1.2 \text{ kcal/mole}$
$\Delta H \text{ B}_2\text{O}_3$	=	$100.5 \pm 2.1 \text{ kcal/mole}$

It should be noted that B_2O_3 has approximately the same vapor pressure as Cu.

Samples of the coating were obtained by plasma spraying B_2O_3 onto stainless steel and then scraping off small pieces. The coating was run on a thermogravimetric analysis apparatus which is connected to a quadruple

Fig. 5-2 Vapor pressure over uncoated TPM-217

Fig. 5-3 Vapor pressure over B_2O_3 -C coated TPM-417 after 220 hr at $\sim 880^\circ C$

Fig. 5-4 Vapor pressure over B_2O_3 powder

type spectrometer. This allowed weight losses and vaporizing products to be measured and identified.

H_2O and H_3BO_3 were seen vaporizing between 80° and $200^\circ C$. CO_2 , changing to CO was seen from 700° to $900^\circ C$. The sample lost 31% of its weight. The heating rate was $5^\circ/min$. The run is shown in Fig. 5-5.

The weight loss was almost all H_2O and H_3BO_3 . The CO_2 and CO seen at the higher temperature presumably is the onset of the $C-B_2O_3$ reaction.

Several attempts to dry the B_2O_3 in an oven showed that, unless the vapor products were removed from the area of the B_2O_3 , hydrates would form.

Thermo-analysis showed that these hydrates would not decompose until temperatures were reached which were above those of the oven. Melting and sintering were also encountered at the higher temperatures.

5.2 PLASMA SPRAYED ANHYDROUS B_2O_3

The excess water content of the B_2O_3 seen in the mass spectrometer and thermogravimetric analysis was obviously effecting the coating effectiveness in suppressing vaporization of TPM-217. Samples of B_2O_3 powder were dried for up to 48 hours at $205^\circ \pm 5^\circ C$. This material was mixed with BN to circumvent potential reactions between B_2O_3 and graphite. Coatings containing 15, 25, 40, and 75% BN, were plasma sprayed on 316 stainless steel pins and heated to $900^\circ C$ for 1 hour (Fig. 5-6). Coatings containing 25 and 40% BN looked excellent at the end of the test. This was a marked improvement over earlier tests with hydrated $B_2O_3 + BN$ coatings.

Fig. 5-5 TGA run on B_2O_3 -12% graphite

(a)

(b)

(c)

(d)

Fig. 5-6 Plasma sprayed coatings of B_2O_3 dried for 48 hr at $205^\circ \pm 5^\circ C$ plus (a) 15% BN, (b) 25% BN, (c) 40% BN, and (d) 75% BN, on 316 stainless steel pins after a 1 hr, $900^\circ C$ heating in vacuo

6. THERMAL CONDUCTANCE PENALTIES OF VAPOR SUPPRESSION COATINGS

Any coating creates a secondary heat leakage path which can result in efficiency losses in thermoelectric generators. The following paragraphs describe a conservative scheme for estimating the penalties in thermal conductivity and performance one might expect from thick coatings used for vapor suppression.

The thermal effect of coating the "P" element to suppress vaporization was investigated using a simple one-dimensional heat transfer model as shown in Fig. 6-1. The results of these calculations are conservative.

When an element is coated one half of its length, then heat is shorted through the coating and back into the element and the amount of heat shorted is a function of the thermal conductivity of the coating and the coating thickness. This heat path outside of the element changes the midpoint temperature and increases the apparent thermal k of the material. The effect of coating thickness and coating material on the element midpoint temperature for two sizes of elements is shown in Figs. 6-2 and 6-3. The increase in apparent thermal k for the same size elements is shown in Fig. 6-4.

Since the heat shorted through the coating does not produce power, the efficiency of the couple will be lowered. Fig. 6-5 shows the relation between couple efficiency and increase in apparent k for a couple operating with $T_H = 900^\circ\text{C}$ and $T_C = 200^\circ\text{C}$.

Simplified
One-dimensional
Model

Model Requiring
Computer Solution

Fig. 6-1 Heat paths in coated element

Fig. 642

Fig. 6-3

Fig. 6-4

TPM-217-P

PERCENT INCREASE IN APPARENT
INTERNAL CONDUCTIVITY
ELEMENT COATED 1/2 WAY

Fig. 6-5

EFFECT OF SHIELDING OF "P" ELEMENT
ON COUPLE PERFORMANCE

TPM-217

7. VAPOR SUPPRESSION

Three potential methods of suppressing the rate of evaporation of TPM-217 materials are:

1. Coating with a material which is chemically stable in contact with TPM-217 at 900°C, which acts as a mechanical barrier to vaporization.
2. Coating with a material which reacts with volatile materials coming from heated TPM-217 to form a self-healing barrier.
3. Coating with a material which reacts with TPM-217 to form a new stable layer between the TPM-217 and the coating which inhibits evaporation.

7.1 VAPOR SUPPRESSION - INERT COATINGS

The present experimental work has been concentrating on coating materials which are reasonably stable in contact with each other. The first material types being evaluated are glass based. The rationale for using glass based materials in the possible accommodation of the large thermal expansion of the TPM-217 material by a material such as glass which can be made slightly viscous at the operating temperature of the thermoelectric generator. Of the glasses tested to date, B_2O_3 based glasses showed the fewest cracks and the best wetting. A variety of additives to B_2O_3 were examined to see if some modification in its apparent 900°C viscosity and mud cracking on cooling could be realized. A summary of some trial melting experiments is given in Table 7-1. Trial coating results are shown in Table 7-2. The results show two

promising mixes, B_2O_3 + 5.26% graphite flakes and B_2O_3 + 10% BN. Finely divided graphite flakes were better than finely divided carbon in reducing cracking.

Weight loss rates for TPM-217 coating candidates were measured in the following test. Stainless steel 316 0.010 in. sheet stock was cut into 1.0 in. squares and dimpled with an 0.550 in. diameter die. Powder mixes of the coatings were put in each dimple and all samples were mounted in a 900°C vacuum furnace set at 900°C with a control stainless steel sheet with no coating mixture. The tests were run for 111 hours with samples removed 7 times for periodic observations and weight loss measurements. The results of the examinations are shown in Table 7-3. Since mixtures used in these experiments were powders, the weight lost rate differences for B_2O_3 , B_2O_3 + graphite, B_2O_3 + La_2O_3 , B_2O_3 + BN are not considered significant since surface areas are only approximate. An apparent reaction between B_2O_3 and Pr_2O_3 or $PrCl_3$ caused higher weight loss rates in these samples. Weight gains in the control sample probably mirror these reactions between B_2O_3 and the praseodymium compounds.

Brush coatings of the glass mixes from water-ethanol slurries were not satisfactory in terms of coating uniformity. An attempt was made to improve coating uniformity by rotating the specimen in a 900°C furnace in air while observing coating uniformity. Using this technique reasonably uniform coatings were applied to TPM-217 samples. The results of the slurry coatings can be summarized as follows:

1. B_2O_3 + graphite flake and B_2O_3 + BN are the most promising glassy coatings tried thus far. These coatings are prepared by mixing the dry powders with water or organic liquids or both brush coating the resulting slurry on the TPM material then firing the coated element at 900°C in vacuum. The rates of reaction between graphite or BN with B_2O_3 are not known and can be a limitation on their use at these temperatures. As

TABLE 7-1

B₂O₃ BASE GLASSES, MELTING EXPERIMENTS

Sample	Composition			Vehicle	After 900°C, 2-5 min. in Vacuum ^(a)	
	B ₂ O ₃ (Wt %)	Additive	Additive (Wt %)		Fluidity	Appearance
6115-81A	99.00	Al ₂ O ₃	1.00	H ₂ O	Viscous	Al ₂ O ₃ suspended, cracks
6115-81B	99.00	SiO ₃	1.00	H ₂ O	Runny	Clear, cracked
6115-81C	99.00	CeO ₂	1.00	H ₂ O	Runny	CeO ₂ suspended, cracked
6115-81D	99.00	Graphite Flakes	1.00	H ₂ O	Moderate-Viscous	Smooth, few cracks
6115-81E	95.20	GeO ₂	4.80	H ₂ O	Moderate	GeO ₂ suspended cracked
6115-82A	99.95	Graphite Flakes	0.05	H ₂ O	Runny	Edgecracks
6115-82B	99.75	Graphite Flakes	0.25	H ₂ O	Moderate-Runny	Few cracks
6115-82C	99.75	Spray Graphite	0.25	H ₂ O	Moderate	Poor wetting, few cracks
6115-82D	94.74	Graphite Flakes	5.26	H ₂ O	Viscous	One crack at edge
6115-82E	94.74	Carbon Black	5.26	H ₂ O	Viscous	Few cracks
6115-82F	90.00	BN	10.00	H ₂ O	Viscous	Few cracks

(a) Melted in a tantalum crucible

TABLE 7-2

B₂O₃ BASED GLASSES EVALUATION

Sample No.	Composition			Vehicle	Substrate	Firing Temp. °C (time)	As-coated Appearance	After Thermal Anneal
	B ₂ O ₃ (Wt %)	Additive	Additive (Wt %)					
6115-78	100	-	0	None	Graphite	850 (16 hr)	Clumps	-
6115-79A	100	-	0	None	TPM-217	900 (30 min)	Non-uniform	-
6115-79B	100	-	0	Amylacetate	TPM-217	900 (15 min)	Dark	Large corrosion pits(a)
6115-79C	100	-	0	Oronite Polybetene 32	TPM-217	900 (15 min)	Clear	-
6115-79D	31	Al ₂ O ₃	69	Amylacetate	TPM-217	900 (15 min)	Powdery	Massive cracks
6115-79E	31	Al ₂ O ₃	69	H ₂ O	TPM-217	900 (15 min)	Mudcracked	Cracking and pits(b)
6115-83A	90	BN	10	H ₂ O	TPM-217	900 (10 min)	Bubbles, pits	Extruded Cu No cracks(b)
6115-83B	95	Microfine Graphite	5	H ₂ O	TPM-217	900 (10 min)	Pits	No cracks hole with some loss TPM-217(b)
6115-83C	90	Dissolved	10	H ₂ O	TPM-217	900 (10 min)	Wrinkled thin	-
6115-84A	90	Nd ₂ O ₃	10	H ₂ O	TPM-217	900 (10 min)	Poor mix	-

(a) 900°C, 65 hour anneal 10⁻⁶ ton(b) 800°C, 67 hour anneal 10⁻¹ ton

TABLE 7-3
WEIGHT LOSS RATES FOR B_2O_3 WITH ADDITIVES ON 316 STAINLESS STEEL

Sample No.	Coating Mixture			Average ^(a) Wt Loss Rate (gm/cm ² -hr)
	B ₂ O ₃ (Wt %)	Additive		
		Powder	Wt %	
6115-132-6	100	--	--	1.2 x 10 ⁻⁵
6115-130-1	85	Graphite	15	1.5 x 10 ⁻⁵
6115-131-5	60	BN	40	2.6 x 10 ⁻⁵
6115-130-3	75	La ₂ O ₃	25	2.2 x 10 ⁻⁵
6115-130-2	75	Pr ₂ O ₃	25	6.5 x 10 ⁻⁵
6115-131-4	75	PrCl ₃	25	6.5 x 10 ⁻⁵
6115-132-7	Control, no mixture			2.0 x 10 ^{-6(b)}

(a) Average of 6 measurements in 111 hour tests

(b) An average weight gain

B_2O_3 melts it is adsorbed on the graphite or BN. This inhibits the free movement of the molten B_2O_3 and thus raises its viscosity. Therefore by experimental iteration one should find the optimum concentration of inert additive to B_2O_3 which will minimize creep but accommodate the high thermal expansion of the TPM-217 material at normal service temperatures.

2. Porosity and spalling of the coatings due to trapped water or organic liquids was difficult to avoid in these slurry coatings.
3. Some creep does occur in aged coatings. As previously mentioned this can be minimized through the optimum addition of graphite flakes, BN powder, or some other addition. Creep in the final thermoelectric converter is less critical in operation since the generator will be operating in a near zero gravity environment.

The GA DC plasma spray system was activated to attempt to overcome some of the problems noted in the brush-coated glass coatings. The plasma spray system, built by Plasmadyne, has a 40 kW power supply. The plasma spray gun is designed to operate with argon or argon helium gas mixtures. Adjusting the gas mixtures, gas flows, gun to substrate distance, power input to the gun, the powder size and the powder feed rate, controls the quality of the coating. The advantages in using the plasma spray over brush coating are:

1. Volatile vehicles do not have to be removed after the coating is applied.
2. Materials with a higher melting temperature than the substrate, can be applied to the substrate.
3. Mixtures with widely differing melting points can be made molten at the same time.

The first coatings plasma sprayed were those which were most promising from earlier brush coating experiments. Table 7-4 summarizes the experimental conditions for the coating application and the preliminary observations of the resulting coatings. Table 7-5 summarizes the coating work with the second group of plasma sprayed coatings. Most of these coatings contained rare-earth oxide additions.

As noted in the tables, B_2O_3 + graphite flakes and B_2O_3 + BN continue to have the best post coating macro appearance. Scanning electron photomicrographs of these coatings (Figs. 7-1 through 7-3) show that it is possible to apply smooth appearing, reasonably pore free coatings of these mixtures on 316 stainless steel. Coatings on TPM-217 were rougher and more porous than those on stainless steel. One possible explanation is that the TPM-217 material outgasses as the coating is applied, resulting in surface cooling.

Coating experiments were followed by thermal annealing tests of coated TPM-217 samples.

Weight loss rate tests were made of plasma sprayed and solution applied glassy coating on TPM-217 bonded to niobium caps. Samples were removed, weighed and observed four times. Weight loss rate measurements on these samples are shown in Fig. 7-4. The B_2O_3 -BN samples were removed from the test after 101 and 150 test hours when spalling and degradation of these coatings were observed. A third sample was removed after the first 16 hours due to specimen adhesion to the specimen holder. The results of a similar test repeated with B_2O_3 + graphite and B_2O_3 carbon are shown in Fig. 7-5.

Weight loss rates for B_2O_3 + graphite coated TPM-217 P-type material determined from intermediate sample weights are 1/5 those of uncoated samples previously tested. The most promising coating continues to be 90% B_2O_3 + 10% graphite. The coating was free of apparent microcracks

TABLE 7-4

PLASMA SPRAYED GLASSY COATINGS THAT WERE INITIALLY APPLIED BY SLURRY TECHNIQUES

Sample No.	Spray Powder Mix Weight %							Coating Appearance After Brief 800°-900°C Thermal Treatment
	Substance	B ₂ O ₃	BN	Graphite	Al ₂ O ₃	Corning 1990	Ferro 2255	
6115-86A	316SS	50.6	--	--	49.4	--	--	(b) rough at 1X
6115-86B	316SS	2.2	--	--	--	95.6	2.2	(b) fell apart
6115-86C	316SS	97.6	2.4	--	--	--	--	(b) smooth <180X
6115-86D	316SS	96.7	--	3.3	--	--	--	(b) smooth <180X
6115-87A	316SS	90.0	10	--	--	--	--	(c) smooth <20X
6115-87B	316SS	90.4	--	9.6	--	--	--	(c) smooth <20X
6115-89A	TPM-217	90.4	--	9.6	--	--	--	(c) rough, porous at 1X
6115-89B	TPM-217	90.0	10	--	--	--	--	(c) rough, porous at 1X
6115-89C	TPM-217	90.0	10	--	--	--	--	(c) rough, porous at 1X
6115-91A ^(a)	TPM-217	90.0	10	--	--	--	--	(c) rough, porous at 1X

(a) All samples sprayed from a gas mixture of 50 CFM Ar, 20 CFM He, 50 CFM powder feed gas with power settings of 50 volts, 400 amps 60% on the powder feeder, 4-5 inches between the Plasmadyne SGIB gun and the substrate except sample 6115-91A. This sample was sprayed with all the same conditions except the gun to substrate distance which was 3-4 inches.

(b) Thermal treatment 65 hours at 800°C

(c) Thermal treatment 16 hours at 900°C

TABLE 7-5
SECOND GROUP OF PLASMA SPRAYED COATINGS

Sample No.	Substrate	Spray Powder Mix			Coating Appearance After Brief 900°C Thermal Treatment
		B ₂ O ₃ (wt. %)	Second Material	Wt. %	
6115-94A	316SS	10	CeO ₂	90	Powdery, spalled, cracked
6115-94B	316SS	10	Y ₂ O ₃	90	Powdery, spalled, cracked
6115-94C	316SS	10	La ₂ O ₃	90	Slightly, rough, adherent
6115-94D	316SS	85	Carbon Black	15	Powdery, adherent
6115-95A	316SS	23	Pr ₂ O ₃	77	Cracked, poorly adherent
6115-95B	316SS	75	Nd ₂ O ₃	25	Full of pin holes
6115-95C	316SS	50	Y ₂ O ₃	50	Rough, adherent
6115-96	TPM-217	85	Y ₂ O ₃	15	Microcracked, rough
6115-97A	TPM-217	85	Y ₂ O ₃	15	Rough, adherent
6115-97B	TPM-217	50	Nd ₂ O ₃	50	Rough coating, adherent
6115-97C	TPM-217	75	CeO ₂	25	Rough coating, adherent
6115-97D	TPM-217	75	Pn ₂ O ₃	75	Rough coating, adherent
6115-98A	TPM-217	88	Carbon Black	12	Adherent, copper extruded through
6115-98B	TPM-217	90	Graphite Flake	10	Adherent, copper extruded through
6115-98C	TPM-217	50	Graphite	50	Adherent, good

and was significantly smoother than the as-applied coating. Smoothing was less prominent in the 50/50 carbon-graphite coating. Weight loss rates at 900°C for these carbon or graphite-containing glasses are 10-20% of the controls. This is equivalent to operating uncoated TPM-217 in a temperature range of 810-865°C.

Besides estimating performance penalties, effectiveness of unyielding shells to suppress vaporization was experimentally examined. Several sleeved samples have been run in thermal stability tests. Figs. 7-6 and 7-7 show TPM-217 with BN sleeves after 7 and 327 hours at 900°C in vacuo. Glassy B_2O_3 was used to fillet the edge where BN and TPM contact ended. This is the only place where damage was visible in the fully sleeved sample after the test. Corrosion of unprotected half of TPM-217 in a half sleeved sample was greater than that noticed on a totally unprotected sample.

TPM-217 coatings containing $B_2O_3 + 30\% SiO_2$ (Fig. 7-8) were visibly as poor as unprotected TPM-217 (Fig. 7-9). An examination of Figs. 7-10 and 7-11 show $B_2O_3 + BN$ coatings are effective in inhibiting vaporization of TPM-217 if porosity is not major in the as-prepared sample.

These coating and vaporization studies show:

1. B_2O_3 based glass coatings on TPM-217 survive thermal cycle tests from ambient to 900°C without spalling or cracking.
2. Viscosity control in the boron based glasses can be obtained with additives.
3. The most promising additive is BN. It is stable in the presence of B_2O_3 at 900°C and shows no adverse reaction with TPM-217 material. Originally carbon additives appeared promising but the carbon was shown to react with B_2O_3 to form CO. No adverse reactions have been noted with BN.

(a)

Fig. 7-1

(b) Scanning electron photo-
micrographs at (a) 22X,
(b) 180X and (c) 1400X of
plasma sprayed B_2O_3 +
2.4% BN (Sample 6115-86C)
on 316 stainless steel
after a 65 hr, 800°C
thermal aging

(c)

(a)

(b)

(c)

Fig. 7-2

Scanning electron photomicrographs at (a) 22X, (b) 180X and (c) 1800X of plasma sprayed $B_2O_3 + 3.3\%$ graphite flakes (sample 6115-86D) on 316 stainless steel after a 65 hr, $800^\circ C$ thermal aging

(a)

(b)

Fig. 7-3 Scanning electron photomicrographs at (a) 22X and (b) 180X of plasma sprayed B_2O_3 + 9.6% graphite flakes (sample 6115-87B) on 316 stainless steel after 16 hr at 900°C

Fig. 7-4

Weight Loss Rates for B_2O_3 -graphite and B_2O_3 -BN
Coatings on TPM-217 P-Type Material

Fig. 7-5 Weight loss rates for B_2O_3 -graphite, B_2O_3 -carbon coated
TPM-217 P-type material at 900°C in vacuo

Weight Loss Rate (Grams/cm²-hr)

348-712 KEUFFEL & ESSER CO.
Semi-Logarithmic, 3 Cycles X 10 to the 10th
5th lines omitted.
MADE IN U.S.A.

Time in Hours

- 90% B_2O_3 10% graphite 6115-98B
- 50% B_2O_3 50% graphite 6115-98C
- ⊕ 88% B_2O_3 12% carbon 6115-98A

CONTROL

a

b

Fig. 7-6 TPM-217 fitted with a full length BN sleeve containing B_2O_3 between the TPM and BN interfaces and over the end of the TPM-217 element after (a) 7 hr and (b) 327 hr at $900^\circ C$ in vacuo

a

b

c

Fig. 7-7 TPM-217 with a half BN sleeve with B_2O_3 at the BN-TPM interface
(a) as prepared, (b) after 7 hr and (c) after 327 hr at $900^\circ C$ in vacuo

a

b

Fig. 7-8 TPM-217 coated with $B_2O_3 + 30\% SiO_2$ after (a) 7 hr and (b) 327 hr at $900^\circ C$ in vacuo

a

b

Fig. 7-9 Sample of uncoated TPM-217 after (a) 7 hr and (b) 327 hr at 900°C in vacuo

a

b

Fig. 7-10 TPM-217 plasma spray coated with $B_2O_3 + 35\% BN$ after (a) 7 hr and (b) 327 hr at $900^\circ C$ in vacuo showing exaggerated failure due to initial porosity in the coating

a

b

Fig. 7-11 TPM-217 coated without major porosity with $B_2O_3 + 30\% BN$ after (a) 7 hr and (b) 327 hr at $900^\circ C$ in vacuo

4. Vaporization rates of B_2O_3 based glass coated TPM-217 samples at $900^\circ C$ were equivalent to vaporization rates of uncoated TPM-217 material operating between 810° and $865^\circ C$.
5. Up to 40% H_2O is commonly associated with B_2O_3 at room temperature as supplied by the vendor. Removing water from B_2O_3 by a thermal treatment is difficult because of a clumping tendency and a reactivity or adhesion of B_2O_3 at elevated temperatures with most crucible materials.

7.1.1 Removal of Water from B_2O_3 Used to Coat TPM-217

Experimental efforts were directed toward preparing dehydrated B_2O_3 plasma sprayed coatings on TPM-217 to compare the ability of these coatings to suppress the vaporization of TPM-217 at $900^\circ C$ operating temperatures. Fig. 7-12 shows results of thermal gravimetric examinations of B_2O_3 , as received, and after 110° , 180° and $200^\circ C$ 16 hour outgassings to remove moisture. Fig. 7-13 shows water pick up by B_2O_3 powder as a function of time, which was exposed to the ambient environment of the laboratory. Fig. 7-14 shows moisture in as-received anhydrous B_2O_3 after ball milling and as plasma sprayed.

These experiments showed water was very difficult to remove from B_2O_3 which had not been purposely prepared as anhydrous B_2O_3 . Commercially available anhydrous B_2O_3 was the best material for minimum water content to be used for TPM-217 coatings. Ball milling and plasma spraying did not significantly increase the water content of the B_2O_3 (commercial anhydrous material).

Allowed to sit open in the laboratory, powdered B_2O_3 picked up 6% moisture in the first eight hours. Its rate of moisture increase was slow after eight hours presumably due to the formation of a hydrated B_2O_3 diffusion barrier on the outside of the B_2O_3 powder particles.

TGA EXAMINATION RESULTS OF B_2O_3 OUTGASSING EXPERIMENTS

Fig. 7-12

Fig. 7-13

TGA EXAMINATIONS WEIGHT LOSS IN ANHYDROUS B_2O_3

Fig. 7-14

7.1.2 Glass Coatings Other than B_2O_3 Based for TPM-217

To avoid overlooking glasses, other than B_2O_3 based, which may be effective as inert coatings for TPM-217, several types of glasses were plasma sprayed on TPM-217. Glass coated samples were then thermal cycled to 900°C and examined. Some of the glasses applied had previously been tried in slurry applications to 316 SS steel and reported in earlier monthly progress reports.

The glasses sprayed were Corning 1990, 7052, 9010, Ferro Corporation 2255 and mixtures of Corning 9010 and 7052 with and without B_2O_3 . Coated samples were fired to 600°C in a gas mixture of 86% He and 14% CO_2 . After cooling to ambient temperature, all of these glasses popped off the TPM-217.

Attempts were made to stress relieve the coating by firing the samples at 850°C for 1 hour in the He- CO_2 gas mixture then stress relieving the samples with a static gas overnight heating at 600°C. Glass coatings still popped off of the TPM-217 samples when cooled to room temperature. Addition of large percentages of B_2O_3 to the coating finally prevented the instability of the coating but metallographic examination showed the TPM-217 to be badly attacked by these glasses. No further examination of these types of glass coatings are contemplated at this time. It is suspected the SiO_2 in the molten B_2O_3 based glasses is causing the aggressive reaction with the TPM-217.

7.2 VAPOR SUPPRESSION, REACTIVE COATINGS

Except for viscous coatings of the B_2O_3 + graphite type or vapor deposited pyrocarbon, inert coatings do not appear to offer a solution to the problem of vapor suppression in TPM material. An alternative approach is to apply coatings or treat the surface of the TPM material with a chemical compound which will react to form barriers to vaporization. Two approaches to this reactive coating are being examined. First, rare

earth halides mixed with rare earth or boron oxides are being applied to the TPM surface. The reaction of selenium with the rare earths are expected to generate rare earth selenides which have elevated temperature stability. Fig. 7-15 shows weight loss rates for B_2O_3 + rare earth oxide coatings on TPM-217. These results were comparable to B_2O_3 + graphite or BN additive coatings. The second approach is to coat the TPM material with a vapor deposited rare earth metal, which again reacts with selenium to form a high temperature stable selenide. Both of these approaches were tried. Weight loss rates for TPM-217 coated with 90% B_2O_3 + 10% $NdCl_3$ coated TPM-217 can be seen in Fig. 7-16. Coating appearances were not the best, but these approaches were very promising. Mud cracking was prominent, but a glassy material was seen in all cracks of the B_2O_3 + $NdCl_3$ samples. This glassy material has not been identified, but weight loss rates for these samples were lower than similar appearing rare earth oxide-boron oxide coatings.

It now appears that the ideal coating is some combination of inert and reactive materials. The inert coating will provide gross protection to suppress vaporization. Rare earth and similar materials are expected to react with selenium to form a solid compound. This solid will hopefully act to plug holes formed in the glassy coatings.

Fig. 7-15 Weight loss rates for B_2O_3 + rare earth type oxides plasma spray coated TPM-217 P-type material at 900°C in vacuo

Fig. 7-16 Weight loss rates for $B_2O_3 + NdCl_3$ plasma spray coated TPM-217 P-type material at $900^\circ C$ in vacuo

8. MATERIAL COMPATIBILITY

Mesh-in-cap bonding and vaporization suppression both depend on having compatible material combinations. Experiments to determine the compatibility of proposed mesh-in-cap or vapor suppression materials with TPM-217 material at temperature are now in progress. Three types of tests prepared were:

1. Slab Tests

Slabs of TPM-217 material placed in mechanical contact with pyrocarbon, plasma sprayed vapor suppression coatings and rhenium. Samples will be held under a slight positive pressure in the vacuum hot press at 900°C.

2. Wire Mesh Tests

Mesh-in-cap type bonds prepared with vacuum hot pressed TPM-217. Wires used in these tests include W and W-Re. Material compatibility will be determined in 900°C, isothermal, high vacuum thermal aging tests.

3. Powder Tests

Beside BN and microfine graphite, other potential additives to B_2O_3 are Al_2O_3 , Y_2O_3 and rare earth. Powders of these oxides were mixed with TPM-217 and hot pressed. The hot pressed samples were heated for 174 hours at 900°C in vacuo. Metallographic cross sections of these samples (Fig. 8-1) showed neither the Al_2O_3 or Y_2O_3 were taken into solution. Whether reactions between these materials and TPM-217 occurred was not determined.

(a)

(b)

Fig. 8-1 Metallographic cross section at 400X of (a) Al_2O_3 and (b) Y_2O_3 particles hot pressed into TPM-217 and heated for 174 hours at 900°C in vacuo. The results show these materials were not taken into solution by the TPM-217 material

8.1 RARE EARTH OXIDES

Rare earth oxides have been considered for use in vapor suppression coatings to tie up volatile selenium. However, little information is known of their compatibility. Rare earth oxides of La_2O_3 , CeO_2 and Pr_2O_3 were mixed as powders with TPM-217 material, vacuum hot pressed, and heated for 900°C in vacuo for 174 hours. Metallographic cross sections of these samples (Fig. 8-2) show porosity associated with the powders and some indication of second phase formation. In addition, compatibility tests of these oxides with plasma sprayed on 316 stainless steel and in mechanical contact with TPM-217 material at 900°C in vacuo were made. After 88 hours at temperature, the samples were removed from the test. A second phase occurred in a reaction of La_2O_3 with TPM-217 (Fig. 8-3), but the 316 stainless steel beyond the La_2O_3 was undamaged. Where La_2O_3 protection ended, vapor phase transport of Se attacked the 316 stainless steel.

Plasma sprayed CeO_2 (Fig. 8-4) seems to catalyze the reaction between TPM-217 and 316 stainless steel. Pr_2O_3 (Fig. 8-5) showed little obvious reactivity with TPM-217 and offered excellent protection for the 316 stainless steel. Pr_2O_3 powder in TPM-217 inhibited the attack of TPM-217 in intimate contact with unprotected 316 stainless steel, but not 316 stainless steel exposed to Se-rich vapor.

8.2 RHENIUM, PYROCARBON VS. TPM

No reaction was observed between rhenium (Fig. 8-6) or pyrocarbon and TPM-217 in 88-hour mechanical contact tests.

8.3 MOLYBDENUM PLASMA SPRAYED MESH-IN-CAP PROTECTION

A niobium cap with a molybdenum mesh was plasma sprayed with molybdenum and bonded to TPM-217 in a vacuum hot pressing process. The

(a)

(b)

(c)

Fig. 8-2 Metallographic cross sections (a) La_2O_3 at 200X, (b) CeO_2 at 400X, and (c) Pr_2O_3 at 200X particles hot-pressed into TPM-217 and heated for 174 hours at 900°C in vacuo. Particles were not taken into solution, but reaction with the TPM is suggested by the porosity noted within the particles

Fig. 8-3

Metallographic cross sections at 200X of:

- (a) 316 stainless steel protected from TPM-217 by a plasma sprayed coating of La_2O_3 . A reaction zone presumed to be $\text{La}(\text{O},\text{Se})$ can be seen after 88 hrs at 900°C in vacuo.
- (b) 316 stainless steel in a TPM-217 - La_2O_3 environment removed from La_2O_3 . After 88 hrs at 900°C in vacuo, grain boundary loosening can be observed in the stainless steel.
- (c) 316 stainless steel cap in contact with TPM-217 into which 5% La_2O_3 powder had been hot pressed after 174 hrs at 900°C in vacuo.

Fig. 8-3

Fig. 8-4

Metallographic cross sections at 200X of:

- (a) 316 stainless steel protected from TPM-217 by a plasma sprayed coating of CeO_2 . The results show the CeO_2 reacted with the TPM-217 within 88 hrs at 900°C in vacuo and was not effective in preventing attack on the 316 stainless steel.
- (b) 316 stainless steel in a TPM-217 - CeO_2 environment removed from CeO_2 after 88 hrs at 900°C in vacuo.
- (c) 316 stainless steel wire taken into solution in a system of TPM-217 containing 5% CeO_2 powder, after 174 hrs at 900°C in vacuo.

Fig. 8-4
8-8

Fig. 8-5

Metallographic cross sections at 200X of:

- (a) 316 stainless steel protected from TPM-217 by a plasma sprayed coating of Pr_2O_3 . No reaction with 316 stainless steel occurred through the coating after 88 hrs at 900°C in vacuo.
- (b) 316 stainless steel in a TPM-217 - Pr_2O_3 slab test removed from the Pr_2O_3 after 88 hrs at 900°C in vacuo.
- (c) 316 stainless steel wire in contact with TPM-217 into which 5% Pr_2O_3 powder had been hot pressed after 174 hrs at 900°C in vacuo.

(a)

(b)

(c)

Fig. 8-5

Fig. 8-6 Metallographic cross sections at 200X of Re in contact with TPM-217 showing no observable reaction

sample was heated for 40 hours at 900°C in vacuo and the joint examined. Photomicrographs of cross sections of this sample (Fig. 8-7) show no reaction between the Mo and TPM-217, and no corrosion of the Nb even though the plasma sprayed molybdenum is porous.

(a)

(b)

(c)

Fig. 8-7 Metallographic cross sections at 200X of the (a) plasma sprayed Mo-TPM-217, (b) Nb cap - plasma sprayed Mo, and (c) Mo-plasma sprayed Mo interfaces after 40 hrs at 900°C in vacuo

9. JOINING

If the TPM-217 materials can be fabricated by powder metallurgy techniques presumably mesh-in-cap type bonds can be utilized (Fig. 9-1). The mesh-in-cap type bond, however, also requires that the mesh and end cap material be non-reactive with the thermoelectric material and possess a coefficient of thermal expansion that is not too different from the thermoelectric material being utilized. While the initial studies with TPM-217 have shown it is definitely amenable to fabrication by powder metallurgy techniques, the qualification of a compatible end cap material is not expected to be an easily accomplishable task. The end cap and mesh materials should be non-reactive and immiscible with TPM-217 and should also have matched thermal expansions. The materials which have shown the best compatibility with TPM-217 (Ref. 5) are W, W-25Re and Mo. Unfortunately, each of these materials has a very low thermal expansion that is approximately 1/3 that of TPM-217.

Metals which have thermal expansions closest to TPM-217 are the stainless steels and the nickel base superalloys. The Fe base ferritic alloys are ~60% lower in thermal expansion than TPM-217.

Three methods are being considered for coating mesh-in-cap composites: (1) plasma spray, (2) CVD, and (3) ion plated. The purpose of this coating is to suppress any adverse reaction between the end cap materials and the TPM-217. The wire mesh is first tack welded to the caps and the coatings are then applied to the composite. A comparison of the physical appearance of these three coating techniques can be seen in Fig. 9-2.

Ion plating of these mesh-in-cap composites with carbon has shown good coverage. Coating the high expansion materials (stainless steels and nickel base alloys) with W or W-25Re by ion plating will occur in FY 77.

Fig. 9-1 TPM-217 P-type mesh-in-cap fabrication sequence

The adherence of the molybdenum plasma sprayed sample was good even though clogging of the wire mesh was observed. Electron microprobe examinations were made of wire caps where Mo and Nb came in contact with TPM material at 900°C. A coating-like layer developed on both materials. The composition of this layer on the molybdenum was found to be copper selenide with small concentrations of molybdenum. The layer on the niobium was thicker than that of molybdenum. It was predominantly copper selenide with a variable concentration of niobium from high on the niobium metal side to low on the TPM-217 side. It is not clear whether a reaction between the Mo and TPM-217 occurred.

Studies are in progress now to determine if these layers continue to grow. Initial experiments indicate carbon coatings on mesh-in-caps will reduce corrosive interactions between the TPM and mesh or cap material. First ion plated coatings were prepared in equipment now unavailable to this program and were too thin for a quantitative evaluation of these coatings.

Attempts were made to CVD coat pyrocarbon on molybdenum and iron wires rather than wait for a new ion plater. Only sooty coatings were applied to the iron wire because of the low temperature limits of the iron and the apparent catalytic effect of iron on the pyrolysis of propylene. Good appearing coatings were deposited on molybdenum but were poorly adherent. Further coating of the wire mesh by vapor deposition will be delayed until the more adherent ion plater carbon coatings can be applied to the mesh-in-cap system.

Visual examinations of joints in TPM end cap bonding studies are summarized in Table 9-1.

The results of the end cap bond studies show:

1. Iron in hot cap materials will be taken into solution by TPM-217 P-type material and cause joint failure.

Fig. 9-2 Molybdenum wire tack welded to 316 stainless steel cap with (a) no coating, (b) plasma sprayed molybdenum coating, (c) CVD-pyrocarbon coating, and (d) ion plated pyrocarbon coating.

TABLE 9-1

RESULTS OF VISUAL OBSERVATIONS OF JOINTS IN TPM-END CAP BONDING STUDIES

Sample No.	Cap	Mesh	Coatings Over Mesh and Cap	No. of Samples	% Failed	Time First Failure (hr)	Sample Test Time (hr)
6115-105-1 thru 6115-105-8	316 SS	316 SS	Carbon ion plate (very thin coating)	8	25.0	104	174
6115-89C	Nb	Mo	Carbon ion plate	1	0	--	101
6115-89A/ 6115-89B	Nb	Mo	None	2	0	--	101
6115-115-1/ 6115-115-2/ 6115-115-5	Fe	Mo	Mo plasma sprayed	5	40.0	254	326
6115-121-1 thru 6115-121-3	316 SS	316 SS	Mo plasma sprayed	3	0	--	327
6115-123-1 thru 6115-123-3	316 SS	W-Re	W plasma sprayed	3	33.3	7	327
6115-124-4/ 6115-124-5	316 SS	W-Re	W plasma sprayed	2	0	--	327
6115-125-1 thru 6115-125-3	Fe	W-Re	Mo plasma sprayed	3	100	7	327

2. Plasma sprayed Mo or W is porous and thus not an adequate barrier against Fe/TPM-217/P reactions even though no reaction between Mo, W and TPM-217/P could be observed.
3. Very thin ion plated carbon coatings did not adequately protect 316 stainless steel against corrosive interaction with TPM-217 material.

10. THERMAL GRADIENT TESTING

Construction of a two element thermal gradient test fixture was completed. The system is shown in Fig. 10-1. Heat is supplied by two molybdenum canned resistance heaters. Power required for each heater is approximately 100 watts. Thermocouple wires are embedded in the hot cap and the cold end of the TPM-217 P-type sample. A molybdenum sample holder acts as a thermal resistor between the water cooled base plate and the cold end of the test element. The hot side of the element is radiantly coupled and thus does not touch the heater. The system is vac-ion pumped and ion gauge monitored.

Two elements can be tested at a time. The first samples now being tested are vacuum hot pressed 3M/TPM-217 P-type material, bonded to iron caps with W-Re wire mesh which were plasma sprayed with molybdenum. A post anneal of 800°C for 30 minutes was used to stress relieve the elements.

One test was removed from test after 137 hours. This test sample was an as-cast, 3M/TPM-217 P-type element which was crushed and vacuum hot pressed bonded to an iron cap through a tungsten-rhenium wire mesh. The element and cap were annealed at 800°C for 30 minutes to stress relieve the sample. A plasma spray coating consisting of 70% B_2O_3 and 30% BN was put on the sample and baked for 10 minutes at 900°C. to homogenize the coating. Pock marks were seen in the elements before the homogenized disappeared after the homogenization.

The test began with the hot cap temperature measured at 900°C and the element cold side at 135°C. Within the first hour of testing a thermocouple failed and the test sample was removed from the system.

Fig. 10-1 Thermal gradient apparatus showing electrical heater leads to two molybdenum wound heaters, a TPM-217 P-type test element in place with thermocouple wires attached, and the water cooled plate for thermal gradient maintenance

The thermocouple was repaired and the sample was reinstalled. The hot cap temperature then averaged 870°C for the 137-hour test. The cold side thermocouple averaged 490°C for the test duration. Sample growth from thermal expansion during the test caused the sample to contact the molybdenum heated and bond to it. This joint was stronger than that mesh-in-cap bond. Copper movement down the thermal gradient and out the sides of the element can be seen in Fig. 10-3.

The second test sample was fabricated the same way as the first sample but tested in a different thermal gradient. The hot cap temperature is being held between 755° to 775°C; the element cold side is 28° to 33°C. The test has now exceeded 300 hours with no evidence of coating failure. What appeared to be a slight extrusion of copper at the base of the sample is gradually receding as the test continues. No new extrusions are visible.

Fig. 10-2 Samples of TPM-217 P-type material plasma spray coated with a 70% B_2O_3 -30% BN mixture before thermal gradient testing

Fig. 10-3

TPM-217 P-type material, coated with B_2O_3 + 30% BN, (a) before thermal gradient testing and (b,c,d) after 137 hr in a thermal gradient which averaged $870^\circ C$ on the hot cap and $490^\circ C$ on the cold end of the test element.

a

b

c

d

Fig. 10-3
10-6

11. SUMMARY

The cast material is composed of a coarse platelet structure with Ag and Cu dispersed in the matrix as second phases.

The TPM-217 material (270 mesh) when vacuum hot pressed at 600°C exhibited large dimensional changes in initial thermal cycling. This growth phenomena was greatly reduced by pressing at much higher temperatures. The cast material in comparison undergoes relatively minor dimensional changes. Copper within the hot pressed material was very mobile, migrating to cooler sides or partitions of the TPM material, similar to the as-cast material.

Vaporization behavior and heats of vaporization measurements of cast and vacuum hot pressed materials were similar. Dominant vapor species were Se_2 , Cu, and CuSe. Weight loss rates at 900°C in vacuum were found to be $2\text{--}2.5 \times 10^{-4} \text{ gm/cm}^2\text{-hour}$. This vaporization could be suppressed by applying glassy B_2O_3 + graphite or B_2O_3 + BN coatings to the TPM-217 material. Weight loss rates of $2\text{--}6 \times 10^{-5} \text{ gm/cm}^2\text{-hour}$ for 900°C vacuo tests of B_2O_3 + graphite coated TPM-217 samples were measured. This is equivalent to operating uncoated TPM-217 in a temperature range of 810° to 865°C.

Mesh-in-cap bonding of the hot junction of the TPM-217 P-type element was found to be a feasible modification of the vacuum hot pressing process. Refractory metal materials such as W, Mo and W-Re were found to be relatively inert in contact with TPM-217 material.

Mesh-in-cap bonded joints survived nine thermal cycles between ambient and 900°C over a 300-hour test without failure.

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