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MASTER

LARGE RADIOISOTOPE HEAT SOURCE
CAPSULE PROGRAM
TOPICAL REPORT NO. 11
MATERIALS COMPATIBILITY

AEC Research and Development Report

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BY JH Kahn/amb
DATE 7/25/70

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North American Rockwell

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CAPSULE PROGRAM
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BY
ROBERT G. BRENGLE

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ABSTRACT

Various interfaces of T-111 (Ta-8W -2Hf) Ta-10W, TZM (Mo -0.5 Ti-0.08Zr, 0.02C), Nb-1Zr, Mo-50Re, Pt-20Rh, AXF-5Q graphite, RPG graphite, alumina, platinized alumina and iron titanate were tested in combinations and at temperatures that would simulate a radioisotope heat source. Testing was conducted at 2000 °F, 2250 °F and 2500 °F for times between 10 and 1000 hours in a hard vacuum. Results showed that the refractory metals are compatible except for an apparent instability in the TZM. Hard phases were observed in the graphite to metal interfaces and in the interdiffusion areas of the refractory metals in contact with Pt-20Rh. A new emittance coating, platinized alumina, was tested and found to be compatible with T-111. Finally, a useful equation for predicting interdiffusion distances in T-111 vs. Pt-20Rh was derived.

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I. INTRODUCTION

Radioisotope heat source design requires many dissimilar materials including noble metals, refractory metals and various ceramics be placed in close proximity or in contact with one another. Two capsule designs, the LRHS and the Transit (Figures 1 and 2 respectively), illustrate the material compatibility problems that are associated with radioisotope heat source capsules that must operate, at or near 2000°F for five years. At these temperatures, rates of solid state and vapor diffusion become significant and must be evaluated in order to reliably predict the lifetime of a capsule. The LRHS compatibility task was initiated to fulfill this purpose and the results of the GFY 1970 program are the substance of this report.

The LRHS, Transit, and Pioneer capsules contain three basic subassemblies: a fuel container of Ta-10W, a structural member of T-111, and a platinum alloy oxidation barrier. An emittance coating is applied to the exterior of the Pt alloy oxidation barrier for heat transfer purposes.

LRHSC Topical Report No. 5, by E. Benn, investigated most of the interfaces critical in the Ta-10W, T-111, Pt-10Rh capsules. The report concluded that the only situation that must be avoided is that which places iron titanate, the LRHSC reference emittance coating, in contact with the tantalum alloys. This condition produces degradation of the T-111 or Ta-10W in times as short as 100 hours at 2000°F.

The GFY 1970 compatibility task investigated compatibility of materials in three areas:

- 1) Alternate structural and liner materials
- 2) Emittance coatings vs. structural materials
- 3) Reentry materials vs. structural materials and emittance coatings.

These materials were tested in combinations that would simulate capsules designed with the various alternate materials.

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Figure 1. Large Radioisotope Heat Source Capsule (LRHSC)

70-M13-026-2-1

Figure 2. Transit Capsule Design

		STRUCTURAL MATERIALS					
		T-111	Nb-1Zr	TZM	T-111 Al_2O_3	TZM Al_2O_3	Nb-1Zr Al_2O_3
LINER MATERIALS	Pt-20Rh (Also an oxidation barrier)						
	Ta-10W	X			X	X	X
	TZM			X	X	X	X
	Mo-50Re			X	X	X	X

Al_2O_3 is a coating applied to T-111, TZM, and Nb-1Zr as a diffusion barrier
 T-111 (Ta-8W - 2.0 Hf)
 TZM (Mo-0.5 Ti-0.08 Zr-0.02C)
 Other alloys are in weight percent of the respective elements

Figure 3. Structural Materials vs. Liner Materials

Figure 3 shows the interface combinations that were tested in the first area. T-111 was previously tested with Ta-10W and was not duplicated in GFY 1970. Nb-1Zr was not tested with Mo50Re for funding reasons. The liner materials were chosen from fuel compatibility data and the structural alternates are representative of three classes of refractory alloys, tantalum base, niobium (columbium) base, and molybdenum base.

Figure 4 shows the combinations of reentry materials, structural materials and emittance coatings that were tested.

The test conditions (Figure 5) were chosen to produce data that could be used to give both a temperature dependent and a time dependent relationship for the various reactions that would occur. The 2000 °F temperature is the reference LRHSC operating temperature and the higher temperatures are of interest to Pioneer and future capsules. All testing was carried out in vacuum of 10^{-7} Torr or better.

During GFY 1970, twelve (12) coupon stacks containing 168 interfaces were tested and evaluated.

The metallographic examination was thorough and complete; and a temperature and time dependence was derived for the T-111 vs. Pt-20Rh reaction.

		STRUCTURAL			EMITTANCE	
		T-111	TZM	Nb-1Zr	Plati- nized Alumina	Iron Titanate
REENTRY MATERIALS	RPG					
	AXF-5Q POCO GRAPH.					
STRUCTURAL AND CLAD	T-111					
	TZM					
	Nb-1Zr					
	Pt-20Rh					

Figure 4. Structural Materials and Emittance Coating vs. Reentry Materials; and Structural and Clad Materials vs. Emittance Coatings

Figure 5. Test Parameters

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II. COMPATIBILITY TESTING

A. TEST DESIGN

Compatibility test design was essentially the same as that used previously⁽¹⁾. Some changes were considered desirable noting the difficulties that were previously encountered in preparation of metallographic and electron beam microprobe samples. Figure 6 shows the coupon holder and coupon design that were used in this year's program. Sealing the stacks by electron beam welding was a cost savings over the old threaded design and the 1-inch OD of the coupon stack holder made preparation for the microprobe relatively easy. A simple clamping arrangement provided the initial pressure on the stacks during welding and test results showed that this method was entirely adequate. Tapers were included on the coupon edges to provide a gradual separation of the materials to give an indication of any vapor transport phenomena.

Since two basically different types of material were being tested, they were segregated into separate coupon stacks. The refractory and noble metal diffusion couples were placed in one stack and were labeled a dash one (-1) type. The second coupon stack for each test condition contained reentry materials, Pt-20Rh coated with either iron titanate or platinized alumina and refractory metals. This stack was labeled a dash two (-2) type. The method for identifying coupon stacks with test parameters is shown in Figure 7.

All metal coupons that were assembled into this year's coupon stacks were polished on both sides to a 600 grit finish (≈ 2 microinches). Since the number of coupons in a coupon stack is approximately fourteen (14), parallelism of the coupon faces becomes more important than surface finish in obtaining contact. Coupons ground as mentioned were generally within 0.0002-inches of parallel. The arrangement of coupons in the various coupon stacks is shown in Figure 8.

(1) LRHSC Topical Report No. 5, by E. Benn, page 11.

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-01 HOLDER

-02 CAP

DASH NO.	A DIM	MATERIAL
-03	.035	Ta-10W
-04	.040	T-111
-05	.040	ASTAR B11C
-06	.040	Ud-1Er
-07	.030	Pa-20Rh
-08	.030	Mo-50Re
-09	.040	TEM
-10	.050	REENTRY MATL.

-03 THRU -09
COUPON
&
-10 REENTRY MATL.

ASSEMBLY

1. COUPON & REENTRY MATL. ARRANGEMENT & QUANTITY TO BE DETERMINED BY DEPT. 737-76
 2. SERIAL NO. TO BE ASSIGNED BY DEPT. 737-76
 3. APPLY & MAINTAIN A LOAD OF 100 ± 10 PSI ON -02 CAP WHILE PINNING.
- NOTE: UNLESS OTHERWISE SPECIFIED

REVISIONS		DATE	APPROVED
SYN	DESCRIPTION		
A		10-18-67	

QTY REQD	PART OR IDENTIFYING NO	NOMENCLATURE OR DESCRIPTION	CODE IDENT	MATERIAL	DATA SPECIFICATIONS SIZES, NOTES, VENDORS	LINE NO.
3	-13	PIN		Ta-10W BAR	.062 DIA	014
	-12					013
	-11					012
AS REQD	-10	REENTRY MATL				011
	-09	COUPON		TEM		010
	-08			Mo-50Re		009
	-07			Pa-20Rh		008
	-06			Ud-1Er		007
	-05			ASTAR B11C		006
	-04			T-111		005
AS REQD	-03	COUPON		Ta-10W		004
2	-02	CAP		Ta-10W BAR	1.000 DIA	003
1	-01	HOLDER		Ta-10W TUBE	1.000 OD x .100 WALL	002
		ASSEMBLY				001

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES. TOLERANCES ON DECIMALS ANGLES FRACTIONS .001 = .001 .002 = .002 .003 = .003 200 = .010 .002 = .002 .003 = .003				LIST OF MATERIALS OR PARTS		ATOMIC INTERNATIONAL A Division of North American Aviation, Inc. CANOGA PARK, CALIFORNIA	
				DR BY CHK BY	V. Weillio 8/6/69
APPROVED BY				COUPON ASSEMBLY (69) LRHSC			
ITEM QTY MODEL PART NO. DRAWING				CODE IDENT NO. SIZE			
REQD PER END ITEM				09974 D SK-N 73419019			
APPLICATION (USAGE) DATA				SCALE 4:1 SHEET			

	10 Hr.	100 Hr.	1000 Hr.
2000 °F		CS-21-2	CS-22-1 Test Time 400 Hrs. CS-22-2
2250 °F	CS-23-1 CS-23-2	CS-24-1	CS-25-1 CS-25-2
2500 °F		CS-27-1 Test Time 75 Hrs. CS-27-2	

Key: CS-2X-Y

CS: Indicates "coupon stack"

CS-2X: The digit two indicates the second series of coupon stacks. The X digit will be from 1 to 8 and corresponds to the test parameters.

CS-2X-Y: The Y digit indicates the type of coupon stack. A-1 type contains only refractory metals, platinum alloys and alumina coating. The -2 type contains emittance coatings, reentry materials as well as refractory metals.

Figure 7. Method for Identifying Coupon Stacks with Test Parameters

<u>CS-21-1</u>	<u>CS-21-2</u>	<u>CS-22-1</u>	<u>CS-22-2</u>
T-111	RPG	TZM	RPG
Pt-20Rh	TZM	Cb-3015	TZM
TZM	AXf-5Q	T-111	AXf-5Q
Ta-10W	T-111	Pt-20Rh	T-111
Nb-1Zr	RPG	TZM	RPG
<u>Pt-20Rh</u>	Pt-(Al ₂ O ₃)	Ta-10W	Pt-(Al ₂ O ₃)
<u>T-111</u>	AXf-5Q	Nb-1Zr	AXf-5Q
<u>TZM</u>	Nb-1Zr	<u>Pt-20Rh</u>	Nb-1Zr
<u>Pt-20Rh</u>	Pt-(Al ₂ O ₃)	T-111	Pt-(Al ₂ O ₃)
Nb-1Zr	TZM	<u>TZM</u>	TZM
TZM	FeTiO ₅	<u>Pt-20Rh</u>	FeTiO ₅
Mo-50Re	AXf-5Q	TZM	AXf-5Q
T-111	Pt-(Al ₂ O ₃)	Mo-50Re	Pt-(Al ₂ O ₃)
	T-111	T-111	T-111
<u>CS-23-1</u>	<u>CS-23-2</u>	<u>CS-24-1</u>	<u>CS-25-1</u>
T-111	RPG	T-111	T-111
Pt-20Rh	TZM	Pt-20Rh	Pt-20Rh
TZM	AXf-5Q	TZM	TZM
Ta-10W	T-111	Ta-10W	Ta-10W
Nb-1Zr	RPG	Nb-1Zr	Nb-1Zr
<u>Pt-20Rh</u>	Pt (Al ₂ O ₃)	TZM	<u>Pt-20Rh</u>
<u>T-111</u>	AXf-5Q	T-111	T-111
<u>TZM</u>	Nb-1Zr	Mo-50Re	<u>TZM</u>
<u>Pt-20Rh</u>	Pt-(Al ₂ O ₃)	TZM	<u>Pt-20Rh</u>
Nb-1Zr	TZM	Pt-20Rh	Nb-1Zr
TZM	Fe-TiO ₅	Nb-1Zr	TZM
Mo-50Re	AXf-5Q	Al ₂ O ₃	Mo-50Re
T-111	Pt-(Al ₂ O ₃)		T-111
Cb-3015	T-111		Cb-3015
TZM			TZM

Pt-Al₂O₃ = A Pt-20Rh coupon plasma sprayed on both sides with platinized alumina.

Fe-TiO₅ = A Pt-20Rh coupon plasma sprayed on both sides with iron titanate.

_____ = Heavy line indicate alumina plasma sprayed on the refractory metal.

Figure 8. Arrangement of Interfaces in the Coupon Stacks

<u>CS-25-2</u>	<u>CS-27-1</u>	<u>CS-27-2</u>
RPG	T-111	RPG
TZM	Pt-20Rh	TZM
AXf-5Q	TZM	AXf-5Q
T-111	Ta-10W	T-111
RPG	Nb-1Zr	RPG
Pt-(Al ₂ O ₃)	<u>Pt-20Rh</u>	Pt-(Al ₂ O ₃)
AXf-5Q	T-111	AXf-5Q
Nb-1Zr	<u>TZM</u>	Nb-1Zr
Pt-(Al ₂ O ₃)	<u>Pt-20Rh</u>	Pt-(Al ₂ O ₃)
TZM	Nb-1Zr	TZM
Fe-TiO ₅	TZM	Fe-TiO ₅
AXf-5Q	Mo-50Re	AXf-5Q
Pt-(Al ₂ O ₃)	T-111	Pt-(Al ₂ O ₃)
T-111		T-111

Pt-Al₂O₃ = A Pt-20Rh coupon plasma sprayed on both sides with platinized alumina.

Fe-TiO₅ = A Pt-20Rh coupon plasma sprayed on both sides with iron titanate.

———— = Heavy line indicate alumina plasma sprayed on the refractory metal.

Figure 8. Arrangement of Interfaces in the Coupon Stacks (cont.)

Figure 9. Coupon Test Assembly in the Heater

7734-1815

B. TEST EQUIPMENT

The sealed coupon stacks were tested in ion pumped vacuum systems which could achieve pressures of 10^{-8} torr. The heaters were resistance type with coiled tantalum wire supported by high purity alumina insulators. Around the basic heating elements were several thicknesses of tantalum foil shielding (Figure 9). The testing unit ready for the vacuum chamber to be sealed is shown in Figure 10.

Temperature instrumentation was by Pt to Pt-10Rh thermocouples placed in various parts of the test rig. Temperatures were controlled within 1% of the absolute test temperature by using a central stack control thermocouple and manual variable resistors connected to a silicon rectifier controller.

C. TEST OPERATION

The vacuum system was pumped by mechanical and diffusion pumps to the 10^{-7} torr range, and then brought slowly to temperature maintaining a vacuum in the 10^{-6} torr range. After several hours at temperature the 10^{-7} torr to 10^{-8} torr range was achieved.

Figure 10. Compatibility Test Facility

III. TEST DATA EVALUATION

The methods for evaluating LRHSC coupon stacks are intended to reveal both gross reaction and areas of solid state and vapor diffusion. The test design limits the results to predicting mechanical properties rather than testing them. Various metallographic and etching techniques, microhardness and electron beam microprobe are utilized in the evaluation. The microstructures that are shown in this section may not be entirely representative of a single piece of a given material. This is understandable when one realizes that six (6) different materials in approximately fourteen (14) interfaces are being prepared in a single one inch metallographic mount. The areas that are not representative will be mentioned in the text to avoid misleading implications.

A. PREPARATION FOR METALLOGRAPHIC AND ELECTRON BEAM MICROPROBE EXAMINATION

The tested coupon stacks were marked with proper identification and then impregnated with epoxy. A vacuum was not used during impregnation to avoid pulling the epoxy unnecessarily into the interfaces. This casting was then machined to a 1-inch OD by conventional machining techniques and sectioned. The first stacks tested were sectioned by an abrasive cut-off wheel. It was felt that this produced an excessive amount of heat and later samples were sectioned by a band saw. The samples were then prepared for examination by grinding with water cooled silicon carbide abrasives (120, 240, 320, 400, 600 grit) and then rough polishing with diamond paste. Alumina was used for final polishing. Figure 11 shows prepared coupon stacks of the old and new type. A list of the etchants used for coupon stack preparation is given in Figure 12.

In order to obtain the maximum amount of information on each stack, the interfaces were etched in the order, molybdenum base, niobium base, tantalum base, and finally platinum base. The results of the compatibility evaluations will be presented in sections related to the primary structural materials.

Figure 11. Prepared Coupon Stacks

MATERIAL	ETCHANTS	COMMENTS
T-111	75 HNO ₃ 25 HF	Ref. LRHSC Topical Report 5 page 23
Ta-10W	75 HNO ₃ 25 HF	Etches Rapidly
Nb-1Zr	50 H ₂ O 30 HNO ₃ 10 HF	
Mo-50Re and TZM	360g potassium ferricyanide 36g NaOH 1000cc Distilled water	Ref. Metals Reference Book
Pt-20Rh	20% HCl saturated with NaCl 5.5 volts AC	Ref. Metals Reference Book

Figure 12. Etchants Used in Coupon Stack Preparation

B. T-111 (Ta-8W-2Hf) COMPATIBILITY

Interfaces of T-111 to platinized alumina, TZM, Cb-3015, Pt-20Rh, Mo-50Re, RPG, AXF-5Q type graphite and alumina were evaluated. The alumina was in the form of a plasma arc sprayed coating on T-111. T-111 interfaces with Pt-20Rh and TZM will be covered in those respective sections. The material used for T-111 coupons was 0.040-inch sheet that had been fully recrystallized. The as-received microstructure is shown in Figures 13a, b, c, and d. The average size is an ASTM 9. In a coupon stack, the view is always perpendicular to the sheet plane.

Interfaces of T-111 that were composed of the refractory metals Cb-3015, and Mo-50Re showed no adverse affects on either the T-111 or the adjacent material. Contact of the materials seems to have been excellent since diffusion bonding was observed in several cases. Figure 14 shows T-111 and Cb-3015 with diffusion bonded areas. Both materials are in the unetched condition. Previous coupon stack work (GFY 1968) had indicated a possible stability problem with the alumina diffusion barrier when used in a vacuum. The hypothesis was that the alumina could be reduced to its elements and the oxygen could diffuse into the T-111 and produce embrittlement. This year's program tested a 0.002 - 0.005-inch plasma arc sprayed coating of alumina on various substrates.

Figure 15a and 15b show the alumina coating after two test conditions. For this period the coating has acted as an effective diffusion barrier and there does not appear to be any deleterious effects to the T-111 substrate. After the 1000 hr., 2250 °F and the 75 hr., 2500 °F test, diffusion had occurred in several places along the interface. Reaction widths were from 0.001 to 0.005-inches and may have occurred at cracks in the coating. At these test conditions there is a very narrow reaction zone in the T-111 substrate that is too small for accurate microhardness determination. Since electron beam microprobe cannot accurately detect oxygen, the question of alumina vs. T-111 compatibility has not been unquestionably answered by this year's work.

The second area of T-111 compatibility testing involved interfaces of AXF-5Q graphite, reinforced pyrolytic graphite and platinized alumina. The two graphite types behave somewhat differently. The reaction widths, that

part of the T-111 that is visibly different from the rest of the material, is approximately twice as large with the AXF-5Q. At lower temperatures and times the reaction zone for both types of graphite is extremely small (Figures 16, 17, 18). However, these reactions become significant at 2250 °F for 1000 hours and 75 hours and 2500 °F. Figures 19, 20, 21 and 22 show the reaction that occurs between the graphite and T-111. The light etching leading edge of the reaction is continuous with AXF-5Q and discontinuous with RPG. The edge is no doubt composed of a tantalum carbide. Figure 23 shows a similar reaction in the Nb-1Zr with hardness indentations. Since carbide formation of the two elements is similar, both form a mono and dimetal carbide, this photomicrograph is indicative of the hardness in this area. The hardness of annealed T-111 generally varies between 210-275 DPH depending on the impurities, whereas the hardness of a TaC is greater than 1000 DPH. It should be noted that there is an apparent carbide formation to a significant extent in the T-111 grain boundaries. The depth of this formation is approximately 0.005 - 0.008-inch after 1000 hours at 2250 °F. Carbide formation in grain boundaries generally produces disastrous effects on the mechanical properties of a material, especially its impact properties. This phenomenon is dependent on grain size since grain boundary diffusion plays a significant role in the formation. The grain size that was used in the compatibility testing was significantly smaller than that normally used in T-111 capsules; ASTM 9 in contrast with approximately an ASTM 6 and these smaller grains would produce larger reaction areas than actual capsule material. It should be noted that very little grain growth has occurred in the T-111 after 1000 hours at 2250 °F.

The final interface that was examined was T-111 in contact with platinized alumina* that was arc plasma sprayed on a Pt-20Rh substrate. Figures 24a to 24e are photomicrographs of this interface.

Even at the lower temperature conditions there is indication of either coating, cracking or diffusion through the coating. Electron beam microprobe results indicate that aluminum is still in the coating and has not diffused into the Pt-20Rh or the T-111. The area in Figure 24d (Area B) that is apparently metal and coating mixed shows an increase in tantalum as one proceeds toward

* Developed by TRW

the T-111 coupon and also a significant rhodium level, that indicates diffusion from the substrate. The determination of concentration in the reaction zones was not attempted. Area A of Figure 24d has the same characteristic appearance as a plain T-111 to Pt-20Rh diffusion couple. In that area hafnium is generally depleted and there appears to be a segregation of tungsten. The leading edge of the reaction contains a concentration gradient of platinum and virtually no rhodium. The second band apparently contains a platinum intermetallic compound since the platinum concentration through the band is constant. Rhodium does occur in the second band. The microprobe has shown that the platinized alumina coating is apparently stable and the only adverse phenomenon that occurs is equivalent to a T-111 vs. Pt-20Rh interface.

Average Grain Size ASTM 9

Figure 13a. As-Received T-111
View Perpendicular to the Rolling Plane

Average Grain Size ASTM 9

Figure 13b. As-Received T-111
View is Perpendicular to the Rolling Plane

Average Grain Size ASTM 9
Figure 13c. As-Received T-111
View Parallel to Rolling Plane

Average Grain Size ASTM 9
Figure 13d. As-Received T-111
View Parallel to Rolling Plane

Cb-3015

T-111
100 Hr, 2000 °F

Figure 14. Cb-3015 vs. T-111

Figure 15a. Al_2O_3 Plasma Sprayed on T-111 vs. Pt-20Rh

Figure 15b. Al_2O_3 Coated T-111 vs. Pt-20Rh
10 hrs., 2250 °F

AXF-5Q

Unetched T-111

10 Hrs. at
2250 °F

Figure 16. Unetched T-111 and AXF-5Q
Graphite Interface

10 Hrs. at
2250 °F

Figure 17. Unetched T-111 and RPG Interface

RPG

T-111
100 Hr. 2000 °F

Figure 18. RPG vs. T-111

Figure 19. T-111 vs. RPG
(From CS-25-2) 200X

Figure 20. T-111 vs. RPG
(From CS-25-2)

200 X

Figure 21. T-111 vs. AXF-5Q Graphite
From CS-27-2

Figure 22. T-111 vs. AXF-5Q Graphite
From CS-25-2

Figure 23. Nb-1Zr vs. AXF-5Q
From CS-25-2
Hardness Indentations, Vickers Indenter 100g load

Pt-20Rh

Platinized Alumina

T-111

100 Hr., 2000 °F

Figure 24a. Platinized Alumina Plasma Sprayed
on Pt-20Rh vs. T-111

Pt-20Rh

Platinized Alumina

T-111
100 Hr., 2000 °F

Figure 24b. Platinized Alumina Plasma Sprayed
on Pt-20Rh vs. T-111

Figure 24c. T-111 vs. Platinized Alumina
From CS-25-2

Figure 24d. T-111 vs. Platinized Alumina
From CS-27-2

Figure 24e. T-111 vs. Platinized Alumina
on a Pt-20Rh Substrate

From CS-27-2

Nb-1Zr

Ta-10W
100 Hr. 2000 °F

Figure 25. Nb-1Zr vs. Ta-10W

C. Nb-1Zr COMPATIBILITY

Nb-1Zr was tested and evaluated in contact with Ta-10W, TZM, Pt-20Rh, alumina, platinized alumina and AXF-5Q type graphite. The alumina and platinized alumina were plasma arc sprayed coatings on Nb-1Zr and Pt-20Rh respectively. The interface with TZM and Pt-20Rh will be dealt with in those respective sections.

The coupons of Nb-1Zr used for compatibility testing were machined from 1-inch bar with an average grain size of ASTM 6. Figures 25 and 26 show interfaces of Ta-10W and Nb-1Zr for 100 hours at 2000 °F and 10 hours at 2250 °F respectively. The interfaces seem to be completely compatible at these test conditions. Examination of samples tested at higher temperatures (CS-27-1; CS-25-1) revealed no observable reaction at this interface. After 1000 hours at 2250 °F the hardness at 0.002 inches from both sides of the interface is the same as the center portion of the coupon. The hardnesses were 215 and 89 DPH for Ta-10W and Nb-1Zr respectively, which indicates that very little diffusion has occurred. Figures 27a, b, c, show the interface of Nb-1Zr and the platinized alumina coating. After 400 hours at 2000 °F (CS-22-2) there was no apparent reaction with either the Pt-20Rh or the Nb-1Zr. However, after 1000 hours at 2250 °F and 75 hours at 2500 °F there are several areas where diffusion has occurred. The diffusion reaction has the same appearance as a Pt-20Rh to Nb-1Zr diffusion couple, with no other effects noted. It could not be determined whether the diffusion occurred through cracks in the coating or through the coating itself. Since this phenomenon was not observed after 400 hours at 2000 °F, it appears that some type of coating breakdown occurs at 2250 °F and above.

A second coating was evaluated with Nb-1Zr for compatibility and effectiveness as a diffusion barrier. The alumina coating was plasma arc sprayed on Nb-1Zr and tested in contact with Pt-20Rh. Although there is some distortion of the grain structure at the coating substrate interface, (Figure 28) there does not appear to be a reaction taking place. Other work⁽²⁾ performed in an inert atmosphere has shown that Nb-1Zr reacts with even high purity alumina to form

Figure 26. Nb-1Zr vs. Ta-10W
From CS-23-1

Figure 27a. Platinized Alumina Plasma Sprayed
on Pt-20Rh vs. Nb-1Zr

Nb_2Al and Nb_3Al after 500 hours at 1090°C (1994°F) and 1310°C (2390°F). The work at Al was carried out in vacuum and an observable reaction zone of approximately 0.001-inch was observed beneath the alumina coating in the substrate after 400 hours at 2000°F . Higher temperature data (CS-22-1) again shows a reaction layer in the substrate. There is apparent porosity beneath the coating that may be the Nb-Al compound. The nature of the reaction area was not investigated; however, the alumina did serve as an effective diffusion barrier throughout low temperature (2000°F) tests. The final interface that was evaluated in this section was that of Nb-1Zr and AXF-5Q type graphite. After 10 hours at 2250°F (Figure 29a, b) a narrow reaction area is apparent. This zone is observed for all test conditions and after 1000 hours at 2250°F the width is approximately 0.003 inches. The reaction zone is very hard and apparently brittle as evidenced by Figure 30. Evaluation of this photomicrograph shows cracks emanating from the indenter mark in the reaction zone. There does not appear to be any grain boundary carbide formation in Nb-1Zr as was observed in the T-111 interface. This could be partially due to the larger grain size of the Nb-1Zr.

Compatibility of Nb-1Zr with most of the materials tested appears excellent. However, its usefulness as a radioisotope structure member is limited because of the alloy's poor load carrying capacity at capsule operating temperatures.

(2) D. E. Fornwalt, R. R. Gourley, A. V. Manzione, "A Study of The Compatibility of Selected Refractory Metals With Various Ceramic Insulation Materials," AEC-AT-(30-1)2780.

Figure 27b. Nb-1Zr vs. Plasma Sprayed
Platinized Alumina
From CS-27-2 60X

Figure 27c. Nb-1Zr vs. Plasma Sprayed
Platinized Alumina
From CS-27-2 200X

Figure 28. Al_2O_3 Coated Nb-1Zr vs. Pt-20Rh
10 Hr., 2250 °F

Figure 29a. Nb-1Zr Vs. AXF-5Q, 10 Hr., 2250 °F

Arrows indicate
the same grain

Figure 29b. Nb-1Zr Vs. AXF-5Q, 10 Hr., 2250 °F

Figure 30. Nb-1Zr vs. AXF-5Q

From CS-25-2

Hardness Indentations, Vickers Indenter 100g load

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D. TZM (Mo-0.5 Ti-0.08 Zr-0.02C) COMPATIBILITY

TZM was the molybdenum base alloy that was tested in this year's compatibility program. TZM was tested and evaluated in contact with T-111, Ta-10W, Mo-50Re, Pt-20Rh, Nb-1Zr and graphite. It was also tested in contact with two emittance coatings, iron titanate and platinized alumina, and an alumina diffusion barrier. The Pt-20Rh interface will be discussed in that section.

Coupons of TZM were machined from 1-inch bar that had been stress relieved for 0.75 hours at 2350°F. The orientation of a coupon to the bar is such that a normal from a coupon face is parallel to the major axis of the bar. The microstructure of the as received material is shown in Figure 31a, b. The material certification indicated that the hardness is 279-287 DPH with a 10kg load.

The test evaluations revealed several unexpected phenomena with respect to the recrystallization of TZM. Table 1 identifies the condition of the TZM at various interfaces in the test program with representative photomicrographs. At 2000°F for 100 and 400 hours, there is no observable recrystallization of TZM at any of the interfaces. After 10 hours at 2250°F, a few recrystallized grains are apparent at the TZM to Nb-1Zr (Figure 38), Cb-3015 (Figure 40), Ta-10W (Figure 41), and T-111 interfaces, but none at the Mo-50Re interface. The most informative test in this area was CS-24-1 (100 hours - 2250°F). During this test a 0.030 inch coupon of TZM bounded by T-111 and Nb-1Zr completely recrystallized in the areas that were in contact but not in the tapered ends. Similarly, the TZM coupon of a TZM vs Ta-10W interface (Figure 41) was recrystallized to a depth of 0.015 inches. Again, as in CS-23-1, the Mo-50Re interface did not recrystallize.

It is concluded that the phenomenon observed is dependent upon contact of the refractory metals and is diffusion controlled.

It is well known that as little as 0.01% of a foreign element in solid solution can raise the recrystallization temperature of a material as much as several

hundred degrees. Zirconium (0.08% in TZM) has a marked elevating effect on the recrystallization temperature of molybdenum and is more potent than tungsten, tantalum, titanium and other metals that form solid solution with molybdenum and also have a larger atomic radius than molybdenum⁽³⁾. It has also been shown that the addition of carbon and one or more group IV-A elements to molybdenum greatly increases the recrystallization temperature⁽⁴⁾. From these considerations, the observed phenomenon is probably related to a zirconium, carbon and/or titanium depletion that occurs by diffusion in the TZM with the other refractory metal serving as a sink for the diffusing elements. CS-24-1 was examined for composition change with the electron beam microprobe. The microprobe showed no difference of the titanium level in the recrystallized and unrecrystallized section of the coupon. Also, the microprobe did not detect any titanium in the adjacent refractory coupon. Titanium depletion was shown to be the cause of similar recrystallization behavior with TZM in a fertile fissile salt atmosphere⁽⁵⁾.

Stability of TZM appears to be a problem when in contact with other refractory metals. A significant loss of alloying elements from TZM would essentially leave a molybdenum structural member rather than the high strength alloy.

The second group of TZM compatibility evaluations considered coatings of iron titanate, platinized alumina and alumina. All coatings were plasma arc sprayed at Atomics International. Figure 60a, b, shows the platinized alumina coating in contact with TZM after 75 hours at 2500°F. The coating is continuous and there is no apparent effect on the TZM. Figure 39 shows the alumina coating after 10 hours at 2250°F. Examination of CS-27-1 and CS-25-1 reveals a continuous alumina coating that acted as an effective diffusion barrier with no apparent effect on the TZM substrate.

(3) E. Pipitz and R. Kieffer, Powder Met. Bull. 7, No. 2 (1955) 146/148.

(4) W. H. Chang, "A Study of the Influence of Heat Treatment on Microstructure and Properties of Refractory Alloys", ASD-TDR-62-211 (4-62)

(5) J. W. Kroger and A. P. Litman, "Compatibility of Moly-Base Alloy TZM With $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$ (68-20-11. 7-0.3 mole %) at 1100°C" ORNL-TM-2724.

The final coating to be evaluated was iron titanate. Previous compatibility work at AI has shown this coating to be incompatible with tantalum alloys. Low temperature testing revealed no unsatisfactory occurrences between the coating and TZM. However after 1000 hours at 2250°F and 75 hours at 2500°F, a peculiar band was noted on the TZM (Figures 53, 57, 58, and 59). The band is unrecrystallized even after 75 hours at 2500°F; a condition that has completely recrystallized all other TZM coupons in the stack. Wilcox has shown that wrought stress relieved TZM bar will completely recrystallize in one hour at 2534°F⁽⁶⁾. The unrecrystallized bands in both CS-27-2 and CS-25-2 continue to the end of the tapered coupon. As the coupons begin to separate, due to the taper, the width of the unrecrystallized zone decreases (Figure 59). The coating is not continuous and there appears to be very little iron titanate remaining in the interface. Apparently the coating has been transported as a vapor in the tapered section and by solid state diffusion in the flat section. The rate of vapor transport is considerable lower than solid state diffusion if one compares the width of the unrecrystallized bands. Electron beam microprobe data (Figure 61) shows the breakdown of the iron titanate. Back scattered electron differentiate between high and low atomic number elements. The back scattered electron photo in Figure 61 shows the position of the coating. Figure 61a and d indicate diffusion of iron and titanium respectively into the Pt-20Rh. The line profile (Figure 61c) of the area shows a significant iron increase in the Pt-20Rh to a depth of approximately 0.007 inches and virtually no iron remaining in the coating. A slight concentrate gradient of titanium is also shown by Figure 61e. This continues at a small level to a depth of approximately 0.003 inches. Apparently one or more elements has diffused into the TZM. Microhardnesses confirm this and the hardnesses are, 362 DPH in the unrecrystallized band, 264 DPH at 25 microns from the recrystallization interface and 185 DPH in the center of the coupon. The Pt-20Rh also shows a hardness increase as the center of

(6) B. A. Wilcox, Refractory Metal Alloys, Metallurgy and Technology, Plenum Press, New York (1968) p-26.

the coupon is approached. The iron titanate does not appear to be compatible with TZM at 2250°F or above. The amount of impurity pickup by the TZM is enough to significantly raise the hardness and quite possibly impair the mechanical properties. TZM should not be used either in intimate contact or in the proximity of iron titanate until the actual composition shift is determined and its effect on the mechanical properties of TZM are evaluated. The final area of TZM compatibility testing evaluated TZM against two reentry materials, AXF-5Q and RPG type graphites. A reaction layer is visible in the TZM vs. AXF-5Q interface after as little as 100 hours at 2000°F (Figure 37). The reaction at interface containing AXF-5Q are generally larger than those with RPG. This may be a function of density and contact of the graphite rather than real difference in reaction mechanism. After 1000 hours at 2250°F, the reaction zone for AXF-5Q vs. TZM and RPG vs. TZM are approximately 0.007 inches. After 75 hours at 2500°F, the TZM has been completely recrystallized and the reaction zones are 0.016 and 0.011 inches for AXF-5Q and RPG respectively.

In these reaction areas the hardnesses are between 1200-1550 DPH which is essentially the hardness of a pure Mo_2C . As can be seen in Figure 54, the carbide phase is extremely brittle.

It should be noted that after 1000 hours at 2250°F all the TZM recrystallized except for two areas. One was the band near the iron titanate that was discussed in the previous section and the second was the TZM in contact with two graphite coupons. The ends of this coupon that were not in contact with graphite did recrystallize. This indicates that carbon diffusion may be the cause of the "anomalous" recrystallization behavior of TZM.

The TZM evaluation have showed that this material in contact with other refractory metal produces unexpected and premature recrystallization of the TZM, probably from carbon or zirconium depletion of the matrix. Of the coatings, platinized alumina appears useful but iron titanate is unstable and produces significant hardness changes in the TZM. Finally, all reentry materials appear incompatible with TZM because of the extensive brittle carbide formation after only 1000 hours at 2250°F.

TABLE 1
TZM RECRYSTALLIZATION BEHAVIOR

			<u>Figures</u>
CS-21-1	Pt (Al_2O_3) vs TZM	No Recrys. of TZM (May) A6-24	32
CS-21-1	Nb-1Zr vs TZM	No Recrys. of TZM	33
CS-21-1	Ta-10W vs TZM	No Recrys. of TZM	34
CS-21-1	T-111 vs TZM	No Recrys. of TZM	35
CS-21-1	Mo-50Re vs TZM	No Recrys. of TZM	36
CS-21-2	AXF-5Q vs TZM	No Recrys. of TZM	37
CS-23-1	Nb-1Zr vs TZM	A few grains have recrys; however, none on the tapered ends	38
CS-23-1	Al_2O_3 TZM vs Pt-20Rh	A few recrystallized grains	39
CS-23-1	Cb-3015 vs TZM	A few recrystallized grains	40
CS-23-1	Ta-10W vs TZM	A few recrystallized grains	41
CS-23-1	Mo-50Re vs TZM	No apparent recrys.	
CS-23-2	RPG vs TZM	No apparent recrys. Q11(A6-15)	42
CS-23-2	Pt(Al_2O_3) vs TZM	No apparent recrys.	43
CS-23-2	AXF-5Q vs TZM	No apparent recrys.	44
CS-24-1	Ta-10W vs TZM	Ends of coupon not recrys. Recrys. to about 0.015	45 46
CS-24-1	Nb-1Zr vs TZM vs T-111	Recrys. through coupon from both sides; ends not recrys.	47 48
CS-24-1	Mo-50Re vs TZM	No recrys.	49
CS-24-1	Pt-20Rh vs TZM	Narrow band below diffusion layer; recrys. band	50
CS-25-1	Al_2O_3 vs TZM	All coupons completely recrys.	
CS-25-2	AXF-5Q vs TZM	End completely recrys. reaction edge ≈ 0.007 Area between reaction is not recrystallized	51

TABLE 1
(continued)

			<u>Figures</u>
CS-25-2	RPG vs TZM	End completely recryst. Area between reaction is not recryst.	52
CS-25-2	Fe-TiO ₅ vs TZM	Band not recryst. Ends the same.	53
CS-27-1	TZM vs T-111	All TZM coupons completely recryst.	
CS-27-2	AXF-5Q vs TZM	TZM coupons entirely recryst.	54, 55
	RPG vs TZM	TZM coupons entirely recryst.	54, 56
	Fe-TiO ₅ vs TZM	Band not recryst. Ends the same	57, 58, 59
All other TZM coupons completely recrystallized.

Figure 3la. TZM in Stress Relieved Condition
Prior to Testing

Figure 3lb. TZM in Stress Relieved Condition
Prior to Testing

Figure 32. Platinized Alumina Plasma Sprayed on Pt-20Rh vs. TZM

Figure 33. TZM vs. Nb-1Zr

Ta-10W

TZM
100 Hr. 2000°F

Figure 34. Ta-10W vs. TZM

TZM

T-111
100 Hr. 2000 °F

Figure 35. TZM vs. T-111

TZM

Mo-50Re
100 Hr. 2000 °F

Figure 36. TZM vs. Mo-50Re

AXF-5Q

Reaction Zone

TZM
100 Hr. 2000 °F

Figure 37. AXF-5Q vs. TZM

TZM

Cb-3015
10 Hr. 2250 °F

200X

Figure 40. TZM vs. Cb-3015

Ta-10W

TZM
10 Hr. 2250 °F

200X

Figure 41. Ta-10W vs. TZM

Figure 42. TZM to RPG Interface

Figure 43. Interface of TZM and Platinized Alumina

Figure 44. TZM and AXF-5Q Type Graphite

Figure 45. As-Received TZM

Figure 46. TZM vs. Ta-10W
From CS-24-1

Figure 47. Nb-1Zr vs. TZM
From CS-24-1

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Figure 48. TZM vs. T-111
From CS-24-1

Figure 49. Mo-50Re vs. TZM

Figure 50. Pt-20Rh vs. TZM

From CS-24-1

Figure 51. TZM vs. AXF-5Q
From CS-25-2

Figure 52. TZM vs. RPG
From CS-25-2

Figure 53. FeTiO_5 vs. TZM
From CS-25-2

Figure 54. RPG vs. TZM vs. AXF-5Q
From CS-27-2

≈ 0.015-inches
of Carbide Phase

Figure 55. TZM vs. AXF-5Q
From CS-27-2

0.009 - 0.012-inches
of Carbide Phase

Figure 56. TZM vs. RPG
From CS-27-2

Figure 57. FeTiO_5 vs. TZM 200X
From CS-27-2

Figure 58. FeTiO_5 vs. TZM
From CS-27-2

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60X

Figure 59. TZM vs. Iron Titanate

0.003 on tapered section

0.005 - 0.006 on flat section

Figure 60a. TZM vs. Platinized Alumina
From CS-27-2

Figure 60b. TZM vs. Platinized Alumina
From CS-27-2

a. Fe

b. Pt

c. Back scattered electrons

d. Titanium

e. Each large division is 0.00086 in. or ~1 mil

Figure 61.
Electron Beam Microprobe Scans of
Iron Titanate on Pt 20Rh Against
TZM From CS-27-2

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E. Mo-50 WEIGHT PERCENT Re

Mo-50 wt % Re is included as a single section since the observations discussed are related to the material behavior itself rather than its interaction with other materials.

The Mo-50 w/o Re used in this program was obtained from Cleveland Refractory Metals in the form of recrystallized sheet (Figure 62a, b). The phase diagram for the Mo-Re binary system is shown in Figure 63. From the phase diagram it is apparent that in equilibrium the Mo-50 wt % Re alloy will contain a rhenium rich chi (χ) phase and a molybdenum rich phase. However, as shown by Figure 62a, b, the microstructure is single phase and therefore not in equilibrium. At testing temperatures 2000°F (1093°C), 2250°F (1232°C), 2500°F (1371°C) the single phase containing approximately 70 w/o rhenium is stable, and the series of photomicrographs, Figures 64 through 76, show the appearance of a second phase after various test conditions. The phase can be seen as finely dispersed particles in the grain boundaries after 100 hours at 2000°F (Figure 66, 67) but not after 10 hours at 2250°F (Figure 64, 65). At longer times the phase continues to precipitate and coalesces in the grain boundaries (Figure 68-76). Photomicrographs were taken after several etching times to show the relationship of the phase to the grain boundaries. This was necessary because the second phase etched considerably faster than the matrix and is severely pitted by the time the grain boundaries are fully distinguished. The electron beam microprobe was used to identify the composition of the second phase in CS-27-1 (75 at 2500°F). Back scattered electron photographs (Figure 77a, b) from the sample at different magnifications show small areas that have a high concentration of rhenium. This is shown dramatically in Figure 77c where a sharp decline in the Mo line profile is accompanied by a significant rise in the rhenium level. Analysis showed the rhenium level of the phase to be between 63 and 71 weight percent Re, which indicates the phase is indeed sigma (refer to the phase diagram, Figure 63).

a.

b.

Figure 62. Mo-50 wt. % Re As-Received

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Generally a sigma phase is brittle and its occurrence in the grain boundaries could produce disastrous degradation of the impact and strength characteristics of the material. Mo-50 wt % Re has been noted for the occurrence of the sigma phase and the rhenium level is usually reduced in an effort to avoid its formation. This reduction of rhenium reduces the fabricability of the alloy but is felt to be a necessary trade-off to avoid sigma. It should be remembered that Mo-50 wt % Re was developed in the interest of fabricability rather than stable metallurgical structure and in view of the results obtained its use as a radioisotope containment vehicle would seem unwise until the aging characteristics found in this test program are fully investigated.

Figure 63. Molybdenum-Rhenium Phase Diagram

From Elliot, Constitution of Binary Alloys
McGraw Hill, N. Y. 1965 p. 629

Figure 64. Mo 50 wt. % Re
CS-23-1 (10 Hr. at 2250 °F)

Figure 65. Mo 50 wt. % Re
CS-23-1 (10 Hr. at 2250 °F)

Figure 66. 50 Mo wt. % Re
CS-21-1 (100 Hr. at 2000 °F)

Figure 67. Mo 50 wt. % Re
CS-21-1 (100 Hr. at 2000 °F)

Figure 68. Mo 50 wt. % Re
CS-24-1 (100 Hr. at 2250 °F)

Figure 69. Mo 50 wt. % Re
CS-24-1 (100 Hr. at 2250 °F)

Figure 70. Mo 50 wt. % Re
CS-24-1 (100 Hr. at 2250 °F)

Figure 71. Mo 50 wt. % Re
CS-25-1 (1000 Hr. at 2250 °F)

Figure 72. Mo 50 wt. % Re
CS-25-1 (1000 Hr. at 2250 °F)

Figure 73. Mo 50 wt. % Re
CS-25-1 (1000 Hr. at 2250 °F)

Figure 74. Mo 50 wt. % Re
CS-27-1 (75 Hr. at 2500 °F)

Figure 75. Mo 50 wt. % Re
CS-27-1 (75 Hr. at 2500 °F)

Figure 76. TZM vs. Mo-50 wt. % Re
From CS-27-1 (75 Hr. at 2500 °F)

Figure 77. Electron Beam Microprobe Data of Mo 50 wt % Re After Aging 75 hr at 2500°F

F. REENTRY MATERIALS VS EMITTANCE COATING COMPATIBILITY

Single capsules (Transit) placed in a heat shield have the emittance coating in contact with the reentry material in some places. Interfaces of AXF-5Q graphite with iron titanate and platinized alumina, and RPG graphite with platinized alumina, and RPG graphite with platinized alumina were tested to evaluate this condition.

In metallographic preparation some of the interface was lost and is shown as a grooved area (Figures 78 and 79).

The reentry materials appear compatible with the emittance coatings in all cases (Figure 80 to 83); however, after 75 hours at 2500°F, there is an apparent metallic area in the coating (Figure 83). The nature of this occurrence was not investigated.

G. Pt-20Rh COMPATIBILITY

A platinum base alloy of some type is necessary to protect the refractory metal components of a capsule against oxidation. Since some capsule designs or coating failures in others would place the Pt alloy in contact with the structural member, it is necessary to predict the interdiffusion distance and its effect on the refractory metals.

Although the Nb-1Zr and TZM vs. Pt-20Rh systems appear excellent for analysis, only their hardness measurements and interdiffusion distances will be noted. This section will be focused primarily on the Pt-20Rh vs. T-111 system.

Diffusion couples of Pt-20Rh to T-111, N-1Zr and TZM were tested and the interdiffusion distances measured. The results appear in Table 2. The Pt-20Rh used in the compatibility testing was obtained from Mathey Bishop and the as-received microstructure is shown in Figure 84. When the data for Pt-20Rh is compared to that of Pt-20Rh there are apparent inconsistencies. This arises because the Pt-20Rh data was obtained from previous coupon stacks where contact was sporadic due to variations in coupon and coating thicknesses. The

TABLE 2
Pt-Rh VS REFRACTORY METAL REACTION ZONES

Interface	100 Hrs. 2000°F	400 Hrs. 2000°F	1000 Hrs. 2000°F	10 Hrs 2250°F	100 Hrs. 2250°F	1000 Hrs. 2250°F	75 Hrs. 2500°F
T-111 to Pt-20Rh	0.0016	0.0025			0.0028	0.0072	0.0049
T-111 to Pt-10Rh							
Ta-10W to Pt-10Rh			0.0041			0.0046	
TZM to Pt-20Rh	0.0014	0.0026		0.0014	0.0028	0.0063	0.0031
Nb-1Zr to Pt-20Rh	0.0016	0.0026		0.0013	0.0025	0.0056	0.0043

Pt-20Rh data was obtained from interfaces in this year's program where the reaction zones were continuous for approximately 70% of the interface, Figures 85 to 90.

The reaction zones in the three materials, Nb-1Zr, T-111, and TZM are different but each system is consistent throughout the test program.

The phase diagrams for the binary Pt to Mo, Ta, and Cb systems are somewhat in question but all have several intermediate phases. Close metallographic examination of the diffusion couples revealed 5-6 different metallographically identifiable regions in the Nb-1Zr vs. Pt-20Rh system, four in the TZM and five in the T-111 system. Several of these areas are very small and boundaries can only be assigned somewhat subjectively.

Hardnesses were taken on CS-25-2 (1000 hours at 2250°F), since for this condition interdiffusion distances were the greatest. Figure 90 illustrates the general hardness behavior for the three systems and Table 3 gives the details of each system. The interdiffusion area in all cases is much harder than either the Pt-20Rh or the refractory metal. It is apparent that hard intermetallic compounds exist in these systems thus producing the hardness results obtained.

The electron beam microprobe was used to examine the T-111 to Pt-20Rh diffusion couple and approximate compositions of the various regions were assigned from this data (Table 4). Without the use of X-ray diffraction data it is somewhat pointless to speculate on the actual phases that exist and no effort was directed in this area since this subject is of more academic than practical interest.

TABLE 3
Pt-20Rh VS REFRACTORY METAL MICROHARDNESS

All hardnesses are reported in DPH and were obtained with a Leitz Miniload Hardness Tester and a 100g load except where noted.

System	Pt-20Rh	Region Nearest Pt-20Rh	Second	Third	Fourth	Hardness of Re- fractory Metal
Pt-20Rh vs. T-111	140	725	524	[*] 1172		210
Pt-20Rh vs. TZM	140	458	597			200
Pt-20Rh vs. Nb-1Z	130	580	560	908		89
NOTE: Left to right proceeds from the Pt-20Rh base metal through the various regions and finally into the refractory metal.						

* 25g load

TABLE 4
MICROPROBE DATA OF Pt-20Rh VS T-111 DIFFUSION COUPLE

	T-111	Second	Third	Fourth	Fifth	Sixth	Pt-20Rh
Ta	90	74.5	55	44	38	15	0
W	8	8	7.5	2	7.5	3.5	0
Pt	0	10	22	49	21	64.5	80
Rh	0	7	15	4.5	10	17.0	20
Hf	2	0.5	0.5	0.5	0.5	0	0
NOTE: Compositions of the various regions of the Pt-20Rh vs. T-111 diffusion couple.							

Analysis of the interdiffusion data was conducted for the various systems to determine time and temperature dependencies. The curve that best fits the data was a power function of the form $Y = Kt^B$, where Y is the interdiffusion distance, K is a rate constant, t = time, and B is a constant. The results of curve fitting by the method of least squares is given in Table 5.

TABLE 5
TIME DEPENDENCY OR INTERDIFFUSION
OF Pt-20Rh VS REFRACTORY METAL

	°F	K	B	
Pt-20Rh vs. T-111	2000	3.63×10^{-4}	0.32	2 Data Points
	2250	4.06×10^{-4}	0.42	2 Data Points
	2500	Cannot Determine		1 Data Point
Pt-20Rh vs. TZM	2000	1.79×10^{-4}	0.45	2 Data Points
	2250	6.62×10^{-4}	0.32	Calculated within $\pm 6.1\%$ of measured
	2500	Cannot Determine		1 Data Point
Pt-20Rh vs. Nb-1 Zr	2000	3.19×10^{-4}	0.35	2 Data Points
	2250	6.19×10^{-4}	0.32	Calculated within $\pm 5\%$ of measured
	2500	Cannot Determine		1 Data Point

$$Y = Kt^B$$

Y = Calculated thickness of interdiffusion

K = Rate constant

B = Time exponent

In order to determine a temperature correlation for the rate constant it was necessary to force the rate equations for the various temperatures into a particular time dependence. The results were for T-111 vs. Pt-20Rh.

$$Y = Kt^B$$

at 2000°F $Y = 2.81 \times 10^{-4} t^{0.37}$
 2250°F $Y = 5.36 \times 10^{-4} t^{0.37}$
 2500°F $Y = 0.9 \times 10^{-4} t^{0.37}$

The rate constant K was then determined as a function of temperature. It was expected that data would fit into the Arrhenius type equation, since this form usually accurately predicts the temperature dependence. The best fit of the three rate constants available was

$$K = C \exp \left(\frac{-Q}{RT} \right)$$

$$K = 0.495 \exp \frac{-18,486}{T}$$

$$T = \text{Temperature } ^\circ\text{R}$$

K = Rate constant
 C = Constant
 Q = Activation energy
 R = Gas constant
 T = Absolute temperature °R

The differences in rate constant calculated from this equation and those determined from constant temperature data is approximated $\pm 3\%$. A better fit of the data, however, was the power function $Y = 1.612 \times 10^{-27} T^{(-6.85)}$; this equation gives the rate constants within $\pm 1\%$. Using the functions $K = 1.61 \times 10^{-27} T^{(-6.85)}$ and $Y = Kt^{0.37}$ where Y = the interdiffusion distance, T = absolute temperature in °R, and t = time; the interdiffusion distances were calculated. The results are compared to the data obtained on this program and also with three low temperature data points obtained by TRW (Table 6).

The correlation of the calculated and observed distance is reasonably good and indicates that one could expect somewhat smaller interdiffusion distances

than previously thought; however, gross extrapolation (100 hours to 5 years) is still somewhat risky.

Discussion of Error

The rate and temperature dependencies that were derived have three areas where error could accumulate. Fortunately the method of testing and test evaluation tends to produce larger observed reaction areas than those that actually exist. High vacuum test operation necessitates a bake-out period and a gradual temperature ramp. This means that some diffusion occurs before the test actually begins and some after it is finished. Secondly, the coupon stack may not be sectioned exactly perpendicular to the interface. The observed reaction zone times the cosine of the cutting angle ($X \cos \Theta$) will give the actual thickness. However, this error is small since the cosine changes very little near 0° .

Finally, it should be noted that measurements made on the diffusion areas were all maximums rather than average values which would tend to exaggerate the reaction rates. The equations derived in this report should serve as a rule of thumb for predicting interdiffusion distances without losing sight of the fact that they are derived on the basis of five data points at three different temperatures.

TABLE 6
CALCULATED INTERDIFFUSION DISTANCES

Temp. °F	Time in Hours	K=Rate Constant	Calculated Inter- diffusion Distance	Measured Inter- diffusion Distance	Percent Difference	Is Calculated < or > Measured
1200	72	1.94×10^{-5}	0.94×10^{-4}	1.0×10^{-4}	6	< Less than
1550	72	7.14×10^{-5}	0.347×10^{-3}	0.4×10^{-3}	13.2	< Less than
1900	72	2.13×10^{-4}	1.036×10^{-3}	1.2×10^{-3}	13.3	< Less than
2000	100	2.82×10^{-4}	1.55×10^{-3}	1.56×10^{-3}	.64	< Less than
	400	2.82×10^{-4}	2.59×10^{-3}	2.85×10^{-3}	3.6	Greater than
2250	400	5.46×10^{-4}	3.0×10^{-3}	2.76×10^{-3}	8.7	Greater than
	1000	5.46×10^{-4}	7.03×10^{-3}	7.2×10^{-3}	2.2	< Less than
2500	75	9.97×10^{-4}	4.92×10^{-3}	4.9×10^{-3}	0.5	Greater than
TRW Data: 1200°F, 1550°F, 1900°F

Figure 78. Platinized Alumina and AXF-5Q
Graphite Interface

Figure 79. RPG to Platinized Alumina Interface

Figure 80. Iron Titanate Plasma Sprayed on Pt-20Rh vs. AXF-5Q

Figure 81. Platinized Alumina Plasma Sprayed
on Pt-20Rh vs. RPG

Figure 82. Iron Titanate Plasma Sprayed
on Pt-20Rh vs. AXF-5Q

Figure 83. Platinized Alumina Plasma Sprayed on Pt-20Rh vs. AX5-Q

Figure 84. Pt-20Rh As-Received

Figure 85. Pt-20Rh vs. TZM
From CS-24-1

Figure 86. CS-24-1 T-111 Top Pt-20Rh Bottom

Figure 87. CS-24-1 Pt-20Rh Top Nb-1Zr Bottom

Figure 88. Pt-20Rh vs. T-111

Figure 89. Pt-20Rh vs. Nb-1Zr

From CS-25-1

AI-AEC-12966

Figure 90. Hardness Indentations on
Pt-20Rh vs. T-111 Reaction Zone

IV. CONCLUSION

The major objectives of the compatibility program have been satisfied.

The various alternate materials were tested and evaluated and a rate equation for the Pt-20Rh vs. T-111 has been derived. The data indicates that a tantalum alloy capsule will operate successfully at the temperature intended with no loss of structural integrity.

Among the various alternate combinations of materials, only a few have questionable compatibility. TZM at or above 2250°F exhibits an instability with respect to recrystallization. It has **not** been conclusively determined the exact effect this behavior will have on the mechanical properties of the alloy.

The test evaluations indicate a potential problem with the reentry materials in contact with all structural members evaluated. The data shows that an excessive depth of the brittle carbide phase will form at these interfaces and possibly impair the functional characteristics (i. e., impact) of that component. After 1000 hours at 2250°F, the TZM vs. AXF-5Q interface showed carbide formations to a depth of 0.016 inches or 18% of a 0.090 inch structural member.

A second phase was observed in the grain boundaries of the Mo-50 wt. % Re alloy after as little as 100 hours at 2000°F. This phase continued to form and after 1000 hours at 2250°F there was a substantial amount of the phase present. The phase was tentatively identified as sigma from composition data; however, this needs to be verified and the aging effects on the mechanical properties evaluated.

The emittance coating, platinized alumina, proved to be stable in a hard vacuum and only very small reaction areas were observed. In contrast the iron titanate vs. TZM interfaces showed pronounced instability and hardness increases in the TZM indicate substantial impurity pickup. This occurs both in intimate contact and by vapor transport.

The tested coupon stacks still contain a substantial amount of information on the grain growth behavior of the major structural materials. Several areas might be investigated utilizing this year's coupon stacks; however, separation of variables may present a problem.