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DEVELOPMENT OF A HIGH-TEMPERATURE VENTED RADIOISOTOPE CAPSULE

FINAL SUMMARY REPORT

AUGUST 1972

VOLUME 3

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PRELIMINARY COMPATIBILITY TESTING
OF CANDIDATE VENT AND CAPSULE MATERIALS

CONTRACT NO. AT(29-2)-2551

FOR
UNITED STATES ATOMIC ENERGY COMMISSION

TRW
SYSTEMS GROUP

ONE SPACE PARK • REDONDO BEACH • CALIFORNIA

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1. INTRODUCTION

Volume III of this final technical summary report describes the work performed by TRW for the Atomic Energy Commission (April 1969 to June 1970) on preliminary compatibility testing of the candidate materials of construction of the high temperature vented radioisotope capsule. This effort, performed under Contract AT(29-2)-2551, was aimed at determining, as a function of temperature and time, the extent of chemical/metallurgical interactions between contacting interfaces of materials systems which were candidates* for high temperature vented radioisotope heat source applications. Of particular interest were the noble metal/PAS** ceramic combinations which were representative of the venting systems, and the noble metal/PAS ceramic/refractory metal combinations which were representative of capsule cladding/diffusion barrier/strength member combinations. Although a high temperature vented radioisotope heat source system using the material combinations originally conceived on this program*** is not currently utilized for space application, this system is being actively investigated for artificial heart applications (Contract AT(04-3)-858).

Initial compatibility experiments yielded surprising and contrasting results. Combinations of the type tantalum alloy/PAS alumina/noble metal showed no evidence of gross interaction for time periods up to thirty days at 2600°F when the specimens were tested in a dynamic vacuum of 10^{-5} torr or better. On the other hand, when the same type of material combinations were tested in a static vacuum formed by electron beam welding the test specimen holder into a tantalum can (approximately 5×10^{-5} torr residual pressure in the can), a marked interaction between the material components was observed at test temperatures as low as 2200°F. The experimental evidence strongly suggested that in the case of the static environment (sealed can), the vapor phase transport of one or more chemical species

* In 1969.

** Plasma arc sprayed.

*** Noble metal/ceramic vent; noble metal liner and cladding; refractory strength member.

played a dominant role in the observed interactions. Since under actual capsule conditions the material interfaces of interest are either in a static or near static environment, it was of critical importance to determine the nature and extent of chemical interactions between the candidate material combinations which can take place in a static environment through the mechanisms of vapor phase transport. Therefore, a more detailed supplementary testing matrix was next conducted in order to isolate and pinpoint, as a function of temperature and time, those combinations of candidate materials which interact rapidly in a static environment via a vapor phase transport mechanism and those combinations of materials which do not react rapidly and hence remain useful candidates for the high temperature vented radioisotope capsule. A test matrix of forty experiments was performed, which covered the temperature range from 1600°F to 2600°F and exposure times from three to thirty days. Materials included in the matrix were:

Refractory Metals: Ta, Ta-10W, T-111 alloy, Mo, TZM

Noble Metals: Pt, Pt-10Rh

Plasma Arc Sprayed Ceramics: Al_2O_3 , Y_2O_3

In the following sections are presented detailed discussions of: (a) the initial compatibility experiments and (b) the subsequent more detailed experimental testing matrix.

2. INITIAL COMPATIBILITY STUDIES

2.1 TEST SPECIMENS

Test specimens consisted of 3/8-inch diameter, 0.040-inch thick discs arranged in a stacked configuration to provide contact between each combination of materials to be evaluated. The order of specimens in stacks prepared for testing at 2200°F was: FS-102 alumina, Pt-10Rh, platinized alumina, T-111 (Ta-9%W - 2.5%Hf), TRW-100 alumina, Pt-10Rh, yttria, Pt-10Rh, Pt-10Rh, platinized alumina, TZM (Mo-0.5%Ti - 0.08%Zr), Cb-1%Zr, platinized alumina, Pt-10Rh, platinized alumina. The order of specimens in the stacks prepared for testing at 2600°F was: FS-102 alumina, Pt-10Rh, platinized alumina, T-111, TRW-100 alumina, Pt-10Rh, yttria, Pt-10Rh, Pt-10Rh, platinized alumina, and TZM. The ceramic oxides were applied as 0.005-inch thick coatings to the Pt-10Rh discs by plasma arc spraying.

Semi-quantitative spectrographic analyses of the Pt-10Rh sheet used for the specimen discs were conducted independently by two different commercial laboratories. Results of these analyses are shown in Table 1. Spectrographic analyses of the ceramic powders used for spraying and of the ceramic coatings in the "as-sprayed" condition are given in Table 2.

Flat and parallel surfaces on the discs were attained by hand polishing to a metallographic finish (0.05 micron). Each disc was ultrasonically cleaned in trichloroethylene, dried and degassed at 2200°F in vacuum prior to assembly. Each stack of discs was contained in a molybdenum holder with threaded end caps. A sketch of the holder is shown in Figure 1. A photograph of a fabricated holder and typical stack of discs is shown in Figure 2. The specimen-holder assembly was placed in a tantalum can with tantalum chips for additional gettering of gaseous impurities and vacuum sealed by electron beam welding at a pressure of 5×10^{-5} torr.

TABLE 1. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSES OF
Pt-10Rh SHEET USED FOR COMPATIBILITY SPECIMEN DISCS

Element	Concentration (weight %)	
	Laboratory A	Laboratory B
Copper	0.00031	Not Detected
Iron	0.043	0.030
Lead	Not Detected	0.0003
Palladium	0.0063	0.025
Platinum	Major Constituent	Major Constituent
Rhodium	9.5	10.28
Silver	0.0034	0.008
Tin	Not Detected	0.0003
Other Elements	Not Detected	Not Detected

TABLE 2. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSES OF POWDERS USED FOR PLASMA ARC SPRAYING AND COATINGS IN THE AS-SPRAYED CONDITION

Material Element*	Concentration (weight %)							
	FS-102 Alumina		TRW-100 Alumina		Platinized Alumina		Yttria	
	Before PAS	After PAS	Before PAS	After PAS	Before PAS	After PAS	Before PAS	After PAS
Ag	- *	0.0022	-	0.0053	-	-	-	-
Al	Major Constituent	Major Constituent	Major Constituent	Major Constituent	Major Constituent	Major Constituent	-	0.064
Ca	-	0.0039	-	0.014	-	0.027	-	0.0056
Cr	-	0.0054	-	0.011	-	0.063	-	-
Cu	-	0.0057	0.0001	0.022	0.002	0.17	-	-
Fe	0.010	0.015	0.010	0.070	0.005	0.022	-	-
Ga	-	-	0.0005	0.0062	0.001	0.0058	-	-
Mg	-	0.0027	-	0.0076	-	0.033	-	-
Mn	-	0.0021	-	0.0054	-	0.023	-	-
Ni	-	<0.0005	-	0.0017	-	0.0059	-	-
Pt	-	0.057	-	0.045	1.0	0.41	-	-
Rh	-	0.048	-	0.041	-	<0.01	-	-
Si	0.010	0.015	0.010	0.12	0.10	0.42	-	<0.004
Ti	-	0.0048	-	0.0073	-	0.0040	-	-
Y	-	-	-	-	-	-	Major Constituent	Major Constituent
Zn	-	-	-	-	-	0.060	-	-
Zr	-	0.025	-	-	-	-	-	-

* All elements not tabulated were below limit of detectability

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SAMPLE HOLDER SCREW

1. Break all sharp edges 0.010

SAMPLE HOLDER BODY

2. All dimensions $\pm 1/64$ inch

SCALE: TWICE SIZE

Figure 1. Sample Holder

Figure 2. Specimen Holder with End Caps and Specimen Arrangement for 2600°F Compatibility Tests

Since the effective thermal expansion coefficient of the specimen stack is greater than that of the molybdenum holder, axial pressure develops during heating which serves to insure contact at the interfaces. This pressure is limited, however, to that which would cause yielding of the holder at the test temperature. Assuming a tensile yield strength of 12,000 psi for molybdenum at 2200°F, the axial compressive stress on the discs could not exceed 35,000 psi. According to reported data, this is insufficient to have an appreciable effect on rates of material interdiffusion.*

2.2 TESTING MATRIX

The original test plan called for evaluation of test assemblies subjected to thermal exposures of 2600°F for three days (Assembly #1); 2600°F for thirty days (Assembly #2); 2200°F for eighteen days (Assembly #3); 2200°F for 180 days (Assembly #4); and 2200°F for 540 days (Assembly #5). The first three of these thermal exposures were completed. However, due to results of the post test evaluation described in the next section, the extended duration 2200°F tests were not initiated but rather supplementary experiments were substituted.**

2.3 TESTING RESULTS

2.3.1 Specimen Assembly #1

Specimen assembly #1 was heated at 2600°F in a tantalum element resistance heated vacuum furnace for three days at a pressure of $\sim 5 \times 10^{-6}$ torr.

Upon removal from the sealed tantalum can after the thermal exposure, the assembly was mounted and longitudinally cross sectioned through its midplane. The sectioned surface was ground and polished in preparation for metallographic and electron microprobe analyses. Although extreme care was taken during handling and the mounting epoxy was applied by vacuum impregnation prior to sectioning, some separation between each ceramic coated Pt-10Rh disc and the adjacent refractory metal disc was observed. This is believed to have occurred during cooling from the test temperature. Thermal contraction is greater for the specimens than for the holder resulting in removal of the axial compressive force maintained during the test.

* Grifalco, L. A., "Diffusion in Solids at High Pressures," presented at AIME Annual Meeting, February 1963.

** A detailed plan for the supplementary compatibility tests was prepared and submitted to the Atomic Energy Commission as TRW Document No. TRW(A)-11069-039, 4 November 1969. A complete discussion of the results of the supplementary compatibility tests is presented in Section 3 of this report.

Metallographic examination and electron microprobe analysis was conducted on the sectioned stack. Results of these analyses are:

- A narrow longitudinal reaction zone appeared along one edge of the entire stack affecting all discs and ceramic coatings. A portion of this zone is shown in Figure 3. The extent of attack was greatest at the edges of the Pt-10 Rh discs. Along the edges of the Pt-10Rh and T-111 discs the zone contained tantalum, aluminum, platinum, and rhodium. The reaction zone along the edge of the TZM disc contained tantalum, aluminum, platinum, rhodium, and molybdenum.
- Both platinized alumina and TRW-100 alumina in contact with Pt-10Rh on one side and T-111 on the other side exhibited evidence of reaction. A discontinuous metallic phase was found dispersed throughout the pores of these ceramic coatings. The phase contained tantalum, platinum, rhodium (very small quantities), and aluminum. No tungsten or hafnium was detected within the metallic phase (limit of detectability 500 ppm). A photomicrograph of a typical region of the affected platinized alumina between Pt-10Rh and T-111 is shown in Figure 4. The distribution of platinum, tantalum and aluminum throughout this region as shown by an electron beam scanning oscilloscope photograph is shown in Figure 5. Lighter areas correspond to a higher concentration of the element.
- No noticeable reaction occurred at the interfaces between Pt-10Rh and FS-102 alumina, Pt-10Rh and platinized alumina, Pt-10Rh and yttria, or TZM and platinized alumina. In all these interfaces, the ceramic oxide was not in contact with T-111. A photomicrograph of the Pt-10Rh/FS-102 alumina interface is shown in Figure 6, of the Pt-10Rh/yttria interface in Figure 7, of the Pt-10Rh/platinized alumina and TZM/platinized alumina interface in Figure 8.

2.3.2 Specimen Assemblies #2 and 2a

Due to the presence of aluminum and tantalum along the specimen edges, constituents of the T-111 were suspected of reacting with alumina, resulting in formation of liquid phase reaction products. In an attempt to prevent liquid phase formation in the thirty-day, 2600°F test, the T-111 disc was removed from assembly #2. A separate molybdenum holder was fabricated to contain the Pt-10Rh/platinized alumina/T-111 interface. This assembly designated 2a, was not sealed in a tantalum can but wrapped in tantalum foil without sealing. The molybdenum holder containing the stack of remaining disc specimens of assembly #2 was sealed in a tantalum can as before by electron beam welding at a pressure of about 5×10^{-5} torr. Both assemblies (#2 and #2a) were heated at 2600°F for thirty days in the same vacuum furnace.

After thermal exposure, both stacks were longitudinally cross-sectioned through their midplanes. Metallographic and electron microprobe analyses were conducted at the interfaces and other areas of interest. Results of the analyses are as follows:

Figure 3. Portion of Longitudinal Reaction Zone Along Edge of Sectioned Stack of Discs After Three Days at 2600°F (40X Magnification)

Figure 4. Photomicrograph of Cross Section through
Platinized Alumina Between Pt-10Rh and T-111
After Three Days at 2600°F (400X Magnification)

Figure 5. Intensity Distribution of Platinum, Tantalum and Alumina Characteristic X-ray Wavelengths Across Region of Platinized Alumina Shown in Figure 4 (400X Magnification)

Figure 6. Photomicrograph of Cross Section through Pt-10Rh/FS-102 Alumina Interface After Three Days at 2600°F (400X Magnification)

Figure 7. Photomicrograph of Cross Section Through Pt-10Rh/Yttria Interface After Three Days at 2600°F (400X Magnification)

Figure 8. Photomicrograph of Cross Section Through Pt-10Rh/Platinized Alumina and TZM/Platinized Alumina Interfaces After Three Days at 2600°F (400X Magnification)

- Regions of severe reaction are present along the edges of all Pt-10Rh discs in stack 2. A photomicrograph of an area along the edge of the discs is shown in Figure 9. The reaction products consists of two to four layered zones, the number of layers varying with location. All zones contain aluminum, tantalum* platinum, and rhodium. The aluminum concentration decreases and platinum increases in successive zones in a direction from the outer edge toward the center of the disc.
- No visible reaction occurred within the Pt-10Rh/yttria interface. A photomicrograph of this interface is shown in Figure 10.
- Reactions occurred within all alumina coatings applied to Pt-10Rh substrates which were contained in the sealed tantalum can during the thermal exposure (assembly #2). A photomicrograph of the Pt-10Rh/FS-102 alumina interface is shown in Figure 11, of the Pt-10Rh/TRW-100 alumina interface in Figure 12, of the Pt-10Rh/platinized alumina interface in Figure 13, and of the Pt-10Rh/platinized alumina/TZM interface in Figure 14. The metallic phases in all the above photomicrographs contain aluminum, tantalum, and platinum. In each case, the quantity of metallic constituents in the ceramic coating is greatest close to the edge of the stack and lowest at the center.
- No visible reaction occurred at the Pt-10Rh/platinized alumina/T-111 interface exposed to dynamic vacuum in assembly #2a during thermal exposure. A photomicrograph of this interface is shown in Figure 15.

2.3.3 Specimen Assembly #3

Assembly #3 was heated for eighteen days at 2200°F in a mullite tube vacuum chamber in a silicon carbide element resistance furnace. The pressure in the mullite chamber was maintained at or below 1×10^{-5} torr during the thermal exposure. The assembly was removed from the sealed tantalum can, mounted and longitudinally cross-sectioned through its midplane. Sectioned surfaces were ground and polished for metallographic and electron microprobe analyses. Results of these analyses are:

- Regions of reaction are visible along the edges of all Pt-10Rh discs in the stack. A photomicrograph of a cross-section through the edge of one of the discs is shown in Figure 16. Two distinct zones of reaction products are evident. The outer zone (closest to the holder wall) consists of high concentrations of aluminum with lower quantities of tantalum, platinum, and rhodium. The inner zone (closest to the Pt-10Rh disc) consists primarily of platinum and tantalum, with small quantities of aluminum and rhodium. In addition, the reaction zones at the edges of the Pt-10Rh disc adjacent to the Cb-1%Zr contained some columbium.

*Note that there were no T-111 discs in this stack. The only source of tantalum was the electron beam welded tantalum can which contained the specimen holder.

Figure 9. Cross Section of Reaction Region at Edge of Pt-10Rh Discs After 30 Days at 2600°F in Static Vacuum (100X Magnification)

Figure 10. Cross Section through Pt-10Rh/Yttria Interface
After 30 Days at 2600°F in Static Vacuum
(400X Magnification)

Figure 11. Cross Section through Pt-10Rh/FS-102 Alumina
Interface After 30 Days at 2600°F in Static
Vacuum (400X Magnification)

Figure 12. Cross Section through Pt-10Rh/TRW-100 Alumina Interface After 30 Days at 2600°F in Static Vacuum (400X Magnification)

Figure 13. Cross Section through Pt-10Rh/Platinized Alumina Interface After 30 Days at 2600°F in Static Vacuum (400X Magnification)

TZM

Platinized
Alumina

Pt-10Rh

Figure 14. Cross Section through Pt-10Rh/Platinized Alumina/TZM Interface After 30 Days at 2600°F in Static Vacuum (400X Magnification)

T-111

Platinized
Alumina

Pt-10Rh

Figure 15. Cross Section through Pt-10Rh/Platinized Alumina/T-111 Interface After 30 Days at 2600°F in Dynamic Vacuum (400X Magnification)

Figure 16. Cross Section of Reaction Region at Edge of Pt-10Rh Disc After 18 Days at 2200°F in Static Vacuum (100X Magnification)

Figure 17. Cross Section through Pt-10Rh/Yttria Interface After 18 Days at 2200°F in Static Vacuum (400X Magnification)

- No visible reaction between materials was detected at any point along the Pt-10Rh/yttria interface. A photomicrograph at a typical location along the length of the cross section through this interface is shown in Figure 17.
- Reactions occurred within all alumina coatings applied to Pt-10Rh substrates. A photomicrograph of a cross-section through the Pt-10Rh/TRW-100 alumina/T-111 interface is shown in Figure 18. A metallic phase is dispersed through the alumina along the entire interface. This phase contains aluminum, tantalum, and platinum. Their concentrations vary considerably across the thickness of the alumina. The tantalum concentration is highest in the metallic areas close to the T-111 and decreases approaching the Pt-10Rh. The platinum concentration is lowest near the T-111 and increases approaching the Pt-10Rh. Grain boundary attack of the T-111 adjacent to the alumina left voids extending to a depth of 0.0015 inch at some locations.

A photomicrograph of a cross-section through the Pt-10Rh/platinized alumina/T-111 interface is shown in Figure 19. The appearance of and the elemental distribution through this interface is essentially identical to that for the Pt-10Rh/TRW-100 alumina/T-111 interface.

A photomicrograph of the Pt-10Rh/platinized alumina/Cb-1Zr interface is shown in Figure 20. Severe reaction is evident within the ceramic, particularly on the Cb-1Zr side. The metallic regions dispersed in the ceramic contain aluminum, columbium, tantalum, platinum, and rhodium. At some locations intermetallic compounds containing platinum had formed at the Cb-1Zr surface adjacent to the alumina.

A photomicrograph of a cross-section through the Pt-10Rh/FS-102 alumina interface is shown in Figure 21. Small quantities of a metallic phase are dispersed within the alumina, primarily near the Pt-10Rh. The quantity of dispersed metal is greatest near the edges and decreases towards the center of the interface. The metallic phase was found to contain aluminum, tantalum, platinum and rhodium. Although a molybdenum end cap was adjacent to the FS-102 alumina, no molybdenum was detected in the metallic phase or at any other location within the alumina.

A photomicrograph of a cross-section through the Pt-10Rh/ platinized alumina/TZM interface is shown in Figure 22. The appearance of and the elemental distribution across this interface is similar to that for the Pt-10Rh/FS-102/Mo end cap interface shown in Figure 21. Again, reaction was evident at the Pt-10Rh/FS-102 interface but not at the FS-102/TZM interface.

2.4 DISCUSSION OF RESULTS

Since substantial interaction occurred among the materials in all assemblies tested under static conditions, it was felt that no significant additional data could be extracted from the behavior of identical assemblies

Figure 18. Cross Section through Pt-10Rh/TRW-100 Alumina/T-111 Interface After 18 Days at 2200°F in Static Vacuum (400X Magnification)

Figure 19. Cross Section through Pt-10Rh/Platinized Alumina/T-111 Interface After 18 Days at 2200°F in Static Vacuum (400X Magnification)

Cb-1Zr

Platinized
Alumina

Pt-10Rh

Figure 20. Cross Section through Pt-10Rh/Platinized Alumina/Cb-Zr Interface After 18 Days at 2200°F in Static Vacuum (400X Magnification)

Molybdenum
End Cap

FS-102
Alumina

Pt-10Rh

Figure 21. Cross Section through Pt-10Rh/FS-102 Alumina Interface After 18 Days at 2200°F in Static Vacuum (400X Magnification)

Figure 22. Cross Section through Pt-10Rh/Platinized Alumina/TZM Interface After 18 Days at 2200°F in Static Vacuum (400X Magnification)

exposed to the same environmental conditions for longer time periods. Thermal exposure of assemblies prepared for 180-day 2200°F and 540-day 2200°F tests were therefore not initiated.

In all three test assemblies (eighteen-day 2200°F, three-day 2600°F, and thirty-day 2600°F) subjected to thermal exposure under static conditions, tantalum and aluminum were found in the reaction products at various locations within the stacks. Since one of these assemblies (thirty-day 2600°F) contained no tantalum in any specimen disc, the sole source of tantalum in the system was the outer can.

The test assembly containing the single Pt-10Rh/platinized alumina/T-111 interface (#2a) which was tested in a dynamic vacuum for thirty days at 2600°F exhibited no evidence of gross reaction. Compatibility tests conducted independently as part of the SNAP-29 program yielded similar results*. For the SNAP-29 tests, plasma arc sprayed alumina on a Pt-20Rh substrate was held in contact with Ta-10W for periods of time up to 180 days at temperatures between 1600°F and 2200°F. The configuration of the specimen-holder assemblies was similar to that used on the current program except that the holder material was tantalum instead of molybdenum. The specimens were not sealed in an evacuated container but placed in a vacuum furnace in which the pressure was dynamically maintained at 5×10^{-6} torr or less. No reaction could be detected at any of the Ta-10W/ Al_2O_3 /Pt-20Rh interfaces after thermal exposure under these environmental conditions.

Materials interaction observed thus appear to be related to the thermal exposure environment. Reactions occurred only when the specimen assembly was tested in a static environment (i.e., sealed in a can under vacuum). No reaction occurred in any test conducted in a dynamic vacuum (i.e., specimens contained in an unsealed holder placed in a vacuum chamber).

The experimental evidence obtained strongly suggests that the interactions occurring in a static environment were dependent on a vapor phase transport mechanism. One such mode of transfer for tantalum has been postulated. Residual oxygen in the EB welded container may react with tantalum to form volatile suboxides which diffuse through the volume of the container

* Carroll, D. F., Hewitt, W. B., Hoffman, H. M., and Schafer, C. E., "SNAP-29 Capsule Platinum-Rhodium Clad Development Program, Summary Report, March 1968 - March 1969, TRW10414-6003-RO-00, 6 June 1969.

and react with Al_2O_3 and/or platinum, releasing the oxygen for repetition of the cycle. In a dynamic vacuum, any volatile suboxide formed is likely to diffuse away from the reaction source and be pumped out of the system before it can accumulate to the extent necessary for reaction with Al_2O_3 or platinum.

Since the material interfaces of interest will be in a static or near static environment during capsule operation, it is of great importance to isolate the reaction mechanism and define temperature and time operational limits of specific materials combinations under static conditions. Supplemental compatibility tests were therefore designed to provide this information and were performed under a Phase I continuation study which is described in the next section of this report.

3. SUPPLEMENTARY COMPATIBILITY TESTS

As indicated above, in order to further pinpoint the nature and extent of major interactions which were observed in the initial static compatibility experiments an additional supplementary testing matrix was conducted. In the following sections the testing matrix and procedures, results and conclusions of this supplementary test program are presented.

3.1 EXPERIMENTAL MATRIX

Table 3 presents, in detail, the experimental testing matrix. The matrix shown in Table 3 is a selected matrix rather than a total matrix for all of the chosen test variables. The complete matrix would comprise 119 experiments and was beyond the scope of this effort. The selected matrix of 40 experiments, including five experiments the nature of which was determined as results were generated, was designed to pinpoint those combinations of materials or material elements which react in the static or sealed environment and to provide a semi-quantitative measurement of the extent or rate of reaction as a function of temperature and time.

Most of the tests were run in a nominal static vacuum of 5×10^{-5} torr, the static vacuum existing in an electron beam welded can. Several tests, however, Ta/Pt, Ta/Al₂O₃/Pt, Ta-10W/Al₂O₃/Pt-10Rh, and T-111/Al₂O₃/Pt-10Rh were duplicated in a TIG-welded can, sealed under a pressure of one atmosphere helium to alter the mean free path of the vapor species and to determine the influence of vapor phase transport on the interaction of the materials.

The majority of the test specimens were subjected to the most extreme conditions of 2600°F for thirty days so as to yield maximum information concerning the materials behavior at very high operating temperatures for long periods of time.

TABLE 3. TEST MATRIX - VENTED CAPSULE SUPPLEMENTAL COMPATIBILITY TEST

Coupon No.	Specimen Composition	1600°F		2000°F		2600°F		EB Weld 10 ⁻⁴ Torr	TIG Weld 1 Atm He
		3 Days	30 Days	3 Days	30 Days	3 Days	30 Days		
1	Pt-Al ₂ O ₃					X		X	
2	Ta-Al ₂ O ₃			X				X	
3	Ta-Al ₂ O ₃				X			X	
4	Ta-Al ₂ O ₃					X		X	
5	Ta-Al ₂ O ₃						X	X	
6	Ta-Pt	X						X	
7	Ta-Pt		X					X	
8	Ta-Pt			X				X	
9	Ta-Pt	Not in Physical Contact - Vapor Transport Only			X			X	
10	Ta-Pt					X		X	
11	Ta-Pt						X	X	
12	Ta-Pt						X		X
13	Ta/10W-Al ₂ O ₃						X	X	
14	Ta/10W-Y ₂ O ₃						X	X	
15	Ta-Al ₂ O ₃ -Pt	X						X	
16	Ta-Al ₂ O ₃ -Pt		X					X	
17	Ta-Al ₂ O ₃ -Pt			X				X	
18	Ta-Al ₂ O ₃ -Pt				X			X	
19	Ta-Al ₂ O ₃ -Pt					X		X	
20	Ta-Al ₂ O ₃ -Pt						X	X	
21	Ta-Al ₂ O ₃ -Pt						X		X
22	Ta-Y ₂ O ₃ -Pt				X			X	
23	Ta-Y ₂ O ₃ -Pt						X	X	
24	Ta/10W-Al ₂ O ₃ -Pt/10Rh						X	X	
25	Ta/10W-Al ₂ O ₃ -Pt/10Rh						X		X
26	Ta/10W-Y ₂ O ₃ -Pt/10Rh						X	X	
27	T-111-Al ₂ O ₃						X	X	
28	T-111-Al ₂ O ₃ -Pt/10Rh						X	X	
29	T-111-Al ₂ O ₃ -Pt/10Rh						X		X
30	Mo-Al ₂ O ₃						X	X	
31	Mo-Pt	Vapor Transport Only					X	X	
32	Mo-Al ₂ O ₃ -Pt						X	X	
33	Mo-Y ₂ O ₃ -Pt						X	X	
34	TZM-Al ₂ O ₃						X	X	
35	TZM-Al ₂ O ₃ -Pt/10Rh						X	X	
36	To be determined as results are generated.								
37									
38									
39									
40									

The first experiment in the Table 3 matrix (Pt/ Al_2O_3) is representative of the major elements present in the vent system. It was not anticipated that extensive reaction would take place in this system even under static conditions and hence only a single experiment at the highest temperature was planned. If reaction had been observed under these conditions, then other experiments would have been performed.

Experiments 2 through 5 (Ta/ Al_2O_3) looked at the binary system of major strength member element/diffusion barrier. This material system was also representative of the major elements present in the TRANSIT Pressure Relief Device (PRD). Since there is some thermodynamic potential for tantalum to partially reduce alumina at the higher temperatures, a submatrix of four experiments at the two highest temperatures was included for this combination.

Experiments 6 through 12 (Pt/Ta) were designed to provide basic data on what was thought to be the key source of vapor transport reaction in a sealed system. These experiments were performed in a manner such that the Ta and Pt were not in physical contact and reaction, if it took place, would be via a vapor phase mechanism. It was postulated that residual oxygen in the sealed system after EB welding would react with the tantalum to form a volatile suboxide which would diffuse across a gap to the platinum and react to form a Pt-Ta alloy, thereby releasing the oxygen for further repetition of the cycle.

Experiment 13 (Ta-10W/ Al_2O_3) was designed to show the effect of introducing tungsten into the pseudo-binary system Ta/ Al_2O_3 . The results of this experiment were compared to those of Experiments 2 through 5.

Experiment 14 (Ta-10W/ Y_2O_3) was designed to show the effect of substituting Y_2O_3 for Al_2O_3 in the pseudo-binary system tantalum alloy/ceramic oxide.

Experiments 15 through 21 (Ta/ Al_2O_3 /Pt) were representative of the primary ternary system of interest (strength member/diffusion barrier/

cladding). Results with this system were compared with results of the binary systems Ta/Pt, Ta/Al₂O₃ and Pt/Al₂O₃.

Experiments 22 and 23 (Ta/Y₂O₃/Pt) were designed to show the effect of substituting yttria for alumina in the ternary system strength member/diffusion barrier/noble metal cladding.

Experiments 24 and 25 (Ta-10W/Al₂O₃/Pt-10Rh) were designed to show the effects of alloying tungsten with tantalum and rhodium with platinum on the pseudo-ternary system Ta/Al₂O₃/Pt. The results of these experiments were compared with the results of Experiments 15 through 21.

Experiment 26 (Ta-10W/Y₂O₃/Pt-10Rh) substituted yttria for alumina in the ternary system tantalum alloy/ceramic barrier/platinum alloy.

Experiment 27 (T-111/Al₂O₃) substituted the tantalum-base alloy T-111 (containing hafnium) for tantalum or Ta-10W in the binary system tantalum alloy/ceramic oxide.

Experiments 28 and 29 (T-111/Al₂O₃/Pt-10Rh) substituted T-111 alloy for Ta-10W in the ternary system tantalum alloy/ceramic oxide barrier/platinum alloy. The results were compared with Experiments 25 and 26.

Experiment 30 (Mo/Al₂O₃) substituted molybdenum for tantalum in the binary couple refractory metal/ceramic oxide. The results of this experiment were compared with those of Experiments 2 through 5.

Experiment 31 (Mo/Pt) substituted molybdenum for tantalum in the binary couple refractory metal/noble metal. The results of this experiment were compared with those of Experiments 6 through 12.

Experiment 32 (Mo/Al₂O₃/Pt) substituted molybdenum for tantalum in the ternary system refractory metal/ceramic oxide barrier/noble metal. The results of this experiment were compared with those of Experiments 15 through 21.

Experiment 33 (Mo/Y₂O₃/Pt) substituted Y₂O₃ for Al₂O₃ in the ternary system molybdenum/ceramic oxide barrier/platinum. The results

of this experiment were compared with those of Experiment 32.

Experiment 34 (TZM/ Al_2O_3) substituted the molybdenum alloy TZM for pure molybdenum in the binary couple refractory metal/ceramic oxide.

Experiment 35 (TZM/ Al_2O_3 /Pt-10Rh) substituted the molybdenum alloy TZM and the platinum alloy Pt-10Rh for pure molybdenum and pure platinum in the ternary sandwich of Experiment 32.

Experiments 36 through 40 were supplemental tests whose character was determined as results of the other experiments were generated. Number 36 was a repeat of Experiment Number 1 to explain an anomalous result. Experiments 37 through 40 were all TIG welded and annealed for three days at 2600°F . Experiment 37 was a ternary system T-111/ Al_2O_3 /Pt-10Rh. Similarly, Experiment 38 was a ternary system TZM/ Al_2O_3 /Pt-10Rh. Experiments 39 and 40 were of the vapor transport type--Ta-10W versus Pt-10Rh and TZM versus Pt-10Rh, respectively.

3.2 SPECIMEN CONFIGURATION AND FABRICATION

A photograph of an exploded view of the specimen-holder assembly used for the binary material compatibility testing in which a refractory metal or alloy and ceramic oxide are the constituents is shown in Figure 23. The refractory metal or alloy specimens consisted of 3/8-inch diameter 0.040 discs machined from bar stock. Each disc was ground to obtain flat and parallel faces. For tests involving ceramic oxides, one surface was grit-blasted and plasma arc sprayed with a 0.005-inch thick coating of the appropriate ceramic oxide. The plasma arc sprayed surface was ground and polished and the disc ultrasonically cleaned in trichloroethylene prior to assembly.

The holder, threaded cap, and end plate were fabricated from the same material as the specimen disc to avoid the introduction of additional constituents which may have affected chemical behavior of the binary material system. The function of the threaded end cap was to maintain axial pressure on the specimen during thermal exposure and thus prevent metal-ceramic separation at the interfaces due to spalling of the ceramic coating. The end plate of most assemblies was electron

Figure 23. Al_2O_3 -Coated Ta Disc Specimen With Ta Holder, Screw Cap, and End Plate

Figure 24. Uncoated Pt Disc Specimen with Ta Holder (Containing a Recession to Allow Vapor-Phase Transport) and the Screw Cap and End Plate

beam welded at a pressure of 5×10^{-5} torr or less, thereby providing a static vacuum environment within the holder. On some assemblies, the end plate was TIG welded in one atmosphere of helium to provide a helium environment within the holder. A similar specimen holder-assembly configuration shown in Figure 24 was employed for the refractory metal or alloy/platinum metal or alloy compatibility tests. A recess, however, was machined in the bottom of the holder to provide a gap between the platinum or platinum alloy disc and the refractory metal holder. This gap served to identify any reaction which occurred due to vapor phase transport.

For compatibility tests between platinum and ceramic oxides, a different configuration was utilized due to the high cost of the platinum. Previous experience at TRW showed that plasma arc sprayed ceramic oxide coatings on platinum substrates remained adherent during thermal cycling, so that the application of external pressure on the coating was unnecessary. The test configuration for these material combinations was two platinum discs joined with a circular electron beam weld near their peripheries after the application of 0.005-inch thick plasma arc sprayed ceramic oxide coating to one face of one disc. The weld was made at a pressure of 5×10^{-5} torr or less, so that the oxide was sealed under vacuum within the platinum enclosure.

A photograph of the specimen holder assembly used for the refractory metal or alloy/ceramic oxide/noble metal or alloy ternary material compatibility tests is shown in Figure 25. The configuration was similar to that which was used for the binary materials test. The differences were the increased depth of the cavity in the holder to accommodate both the refractory metal or refractory alloy disc and the platinum or platinum alloy disc coated on all sides with a ceramic oxide by plasma arc spraying. Complete coverage of the platinum or platinum alloy by the ceramic oxide prevented direct contact between the metallic materials.

3.3 EXPERIMENTAL EQUIPMENT

At 1600°F and 2000°F thermal exposures of the specimen assemblies

Figure 25. Al_2O_3 Coated Pt Disc and Uncoated Ta Disc Specimens with Ta Holder, Screw Cap and End Plate

were conducted in a mullite chamber in a silicon carbide element resistance furnace. The vacuum inside the chamber was maintained at or below a pressure of 5×10^{-5} torr during the test to prevent oxidation of the refractory metal holder.

The 2600°F thermal exposures were conducted in a tantalum element vacuum resistance furnace. The vacuum was maintained at or below a pressure of 1×10^{-6} torr during the test.

3.4 EXPERIMENTAL RESULTS

All samples were sectioned, polished, and examined metallographically. Most of the specimen capsules had been electron beam welded. A few were TIG-welded in 1 atm helium to determine if any differences would result. The great majority of samples were then carbon-coated to improve surface electrical conduction and analyzed quantitatively in the electron microprobe. Detailed microprobe analysis was not undertaken when only little or no additional information would result.

3.4.1 Platinum in Contact with Al_2O_3

A Pt/ Al_2O_3 couple, electron-beam welded at 10^{-4} torr, was found to have swelled during a 3-day anneal at 2600°F, but did not burst. Figure 26 is a photomacrograph of the specimen subsequent to the anneal and Figure 27 is a photomicrograph of the cross-section. Sectioning and detailed examination metallographically and with the electron microprobe failed to reveal any reaction.

The experiment was repeated and no swelling was observed. Likewise, nor was any reaction observed (Figures 28-30). The swelling of the original sample was probably due to entrapped gases.

3.4.2 Tantalum and Tantalum-Base Alloys in Contact with Al_2O_3 and Y_2O_3

Post-test evaluation of the respective 3-day anneals at 1600°F, 2000°F, and 2600°F by means of metallography and electron microprobe analysis indicated that there was no visible bulk reaction at these temperatures after 3 days between the tantalum metal and the plasma-arc-

Figure 26. Swelled Pt-Al₂O₃ Diffusion Couple. Welded Specimen did not Burst, but Plasma-Arc-Sprayed Al₂O₃ Separated from Pt

Figure 27. Photomicrograph of Swelled Specimen 400X

Figure 28. Edge View of Pt/Al₂O₃/Pt Sample After 3-Day, 2600°F Exposure
Note the absence of any swelling or bowing.

Figure 29. Cross Section of Disk Shown in Figure 13;
Bright Field (100X Magnification)
Note the absence of any reaction.

Figure 30. Enlarged View of Pt-Al₂O₃ Interface Shown in Figure 14; Bright Field (400X Magnification)

sprayed Al_2O_3 coating.* Figure 31 is a photomicrograph of a polished cross section of a specimen annealed at 2600°F.

Optical microscopy revealed no well-defined reaction zone between Ta and Al_2O_3 after 30-day anneals at 2000 and 2600°F (see Figures 32 and 33), although some surface cracking was apparent in the 2000°F experiment.* In many cases, separation between the metal and the plasma-arc-sprayed ceramic oxide was observed in samples which had been annealed for 30 days at 2600°F. Since all the capsules were screwed down very tightly prior to the annealing, it is believed that the separation is due to creep induced by thermal expansion. Consequently, the materials were believed to be in good contact during the anneal and became separated only on cooling. Reaction would promote adherence on cooling because of the strength of the chemical bonding and the thermal expansion gradient through the reaction zone.

After 30 days at 2600°F, isolated inclusions rich in tantalum were present within the Al_2O_3 . Their composition was approximately 15 w/o Ta. These inclusions were of submicron size, so that a quantitative determination of their composition was impossible. They were not optically differentiable from the Al_2O_3 , which indicates that the tantalum is present in the oxide form. Thermodynamic calculations show that approximately 1% Ta_2O_5 will be equilibrium with Al_2O_3 .

Larger inclusions were found when either Ta-10W or T-111 (Ta-8W-2Hf) replaced tantalum in contact with Al_2O_3 (Figures 34 and 35) for 30 days at 2600°F. The electron microprobe showed these to be pure tantalum.

Optical and electron microprobe analysis of a Ta-10W/ Y_2O_3 couple annealed for 30 days at 2600°F showed no visible reaction (Figure 36).

3.4.3 Tantalum or Molybdenum/Gap/Platinum

Reaction was found between samples of tantalum and platinum metal which were separated by a gap of 1/16". For the 3-day anneals, the reaction was particularly severe at 2600°F, where a reaction zone of over 130 μ was

* In the light of more recent work it is now considered likely that there was some oxygen uptake by the tantalum alloys. However, no testing for oxygen uptake was conducted in these experiments.

Figure 31. Ta-Al₂O₃; Three Days at 2600°F
Polarized Light, Green Filter,
Magnification 100X
Note the absense of any reaction
at the interface

Figure 32. Ta-Al₂O₃; Thirty Days at 2000°F
Bright Field (400X Magnification)

Figure 33. Ta-Al₂O₃; Thirty Days at 2600°F
Bright Field (400X Magnification)
Note the absence of any reaction
on either the Ta or the Al₂O₃ side.

Figure 34. Ta/10W-Al₂O₃; Thirty Days at 2600°F
Bright Field (400X magnification)

Note the two new phases in the
reaction zone.

Figure 35. T-111-Al₂O₃; Thirty Days at 2600°F
Bright Field (400X magnification)

Note the reaction zone formed on
the Al₂O₃ side.

Figure 36. Ta-10W/Y₂O₃; Thirty Days at 2600°F
Bright Field (400X Magnification)

found on the platinum side and none on the tantalum side. Figure 37 is a double electron microprobe trace of concentration-vs-distance for both platinum and tantalum in the platinum disk (3 days at 2600°F) showing the extensive matter transport, intermetallic compound formation, and atomic diffusion. After 3 days at 2000°F, only 14 μ of reaction was found on the Pt side and none was found on the Ta side. No reaction was observed after 3 days at 1600°F. In addition to the intermetallic compounds formed at the Pt-gap interface, substantial interdiffusion and intermetallic compound formation occurred in the area where the Pt disk was in direct contact with the Ta cap of the specimen holder.

Generally, the precise distance to which Ta penetrated on the Pt-gap side in each specimen was difficult to determine due to beveling of the interfaces during polishing. Electron microprobe analysis of the 3 day, 2000°F specimen showed a uniform composition of 12.6 w/o Ta (13.5 a/o) over the 14 μ reaction zone.

The 3 day, 2600°F specimen showed several intermetallic compounds in addition to terminal solid solutions of both Pt and Ta. All reaction, however, was confined to the Pt side. As can be seen from Figure 37, from the Pt-gap boundary, the 130 μ reaction zone consisted of a 10 μ wide Ta terminal solid solution extending from 0 to 25 a/o Pt, a phase 20 μ wide of composition Pt₃Ta₂, a phase 46 μ wide of composition Pt₃Ta, and a 54 μ wide terminal solid solution of 25 to 0 a/o Ta. No condensed oxide phases were found.

Although no reaction was found after 3 days at 1600°F, considerable reaction occurred after 30 days at the same temperature (Figures 38 and 39). At least four Pt-Ta phases are present on the Pt side but no reaction zone is present on the Ta side.

For the 30 day tests at 1600°F and 2000°F, the total penetration depths were approximately equal at 120 μ , but intermetallic compound formation was much greater at 2000°F. This indicates that the transport and reaction to form the intermetallic compounds proceeds at a much faster

Figure 37. Tantalum and Platinum Distribution in an Originally pure Platinum Disc After 3 Days Exposure at 2600°F to Tantalum Across a 1/16" Gap

Figure 38. Pt-Side of Ta-Pt Vapor Transport Couple;
Thirty Days at 1600°F Bright Field
(400X Magnification)

Note the extensive formation of
several Pt-Ta intermetallic compounds.

Figure 39. Ta-Side of Ta-Pt Vapor Transport Couple; Thirty Days at 1600°F Bright Field (400X Magnification)

Note the absence of any reaction zone.

rate than the ordinary diffusion of Ta into the Pt. At these temperatures, the intermetallic zone consisted almost exclusively of Pt_3Ta , with only a narrow band of Pt_2Ta at the interface. The zone measured 46μ in the $1600^{\circ}F$ sample and 65μ in the $2000^{\circ}F$ sample.

After 30 days at $2600^{\circ}F$, the entire Pt disk was impregnated with Ta. Ta entered from two opposite directions, by vapor transport across the gap and by solid state diffusion from the sample holder (Figure 40). There was no difference between the sample which was EB welded and that which had been TIG-welded. In each case, there was Ta all through the disk. The intermetallic zones consisted of approximately 60μ of Pt_2Ta followed by 50μ of Pt_3Ta . Apparently, the relative stability of Pt_2Ta is greater at $2600^{\circ}F$ than at the lower temperatures.

In contrast to severe vapor phase transport and reaction observed in the Ta-Pt system, no transport or reaction was observed metallographically or with the electron microprobe when Mo replaced Ta in a 3 day, $2600^{\circ}F$ test (Figures 41 and 42).

3.4.4 Tantalum or Tantalum-Base Alloys/ Al_2O_3 or Y_2O_3 /Pt or Pt-10Rh

In specimens where PAS Al_2O_3 was present as a diffusion barrier between the Ta and Pt, no reaction was observed after 3 day anneals at $1600^{\circ}F$ or $2000^{\circ}F$.

Considerable reaction occurred, however, in the Ta/ Al_2O_3 /Pt/ Al_2O_3 /Ta diffusion couple annealed for 3 days at $2600^{\circ}F$ (Figures 45 and 44). As can be seen in the photomicrographs, the Al_2O_3 barrier has been seriously attacked. Electron microprobe analysis shows that the zone which was once an integral Al_2O_3 diffusion barrier now contains several Pt-Ta-Al ternary intermetallic compounds including Pt_3Ta_2Al , in addition to free Al metal and several nonstoichiometric oxides containing the three metals.

Figure 40. Ta-Pt Vapor Phase Transport and Solid State Diffusion, 30 Days, 2600°F.

The apparent 0 Pt concentration at the interface is due to beveling.

Figure 41. Pt-Side of Mo-Pt Vapor Transport Couple; Thirty Days at 2600°F Bright Field (400X Magnification)

Note the absence of any reaction zone in contrast to the extensive formation of Pt-Ta intermetallic compounds in the Ta-Pt Vapor Transport Couple.

Figure 42. Mo-Side of Mo-Pt Vapor Transport Couple; Thirty Days at 2600°F Bright Field (400X Magnification)

Note the absence of any reaction.

Figure 43. Ta/Al₂O₃/Pt/Al₂O₃/Ta Couple; Three Days at 2600°F Polarized Light, Green Filter (Magnification 100X)

Substantial reaction has occurred. A good part of the Al₂O₃ has been consumed. Free Al metal and non-stoichiometric oxides containing Pt, Al, and Ta are present. Various Pt-Ta intermetallic compounds have formed on the Ta sides of the partially consumed diffusion barriers.

Figure 44. Enlarged Area of Reaction Zone Shown in
Figure 43 Polarized Light (400X Magnification)

On the Ta-rich sides, there are approximately 50μ of interaction including layered zones of the intermetallic compounds Pt_2Ta , Pt_3Ta_2 , $PtTa_3$, and the terminal solid solution. The solid solubility of Al in the Pt-Ta intermetallic compounds is only 2 w/o. On the Pt-rich sides, Pt_3Al is found with only 2.5 w/o Ta in solid solution. The Pt_3Al zone extends for only 12μ .

It is significant that very little Ta was found on the Pt side, while a substantial amount of Pt was found on the Ta side. In this experiment, the Al_2O_3 diffusion barriers have served qualitatively as stationary markers to show that diffusion is primarily in the direction $Pt \longrightarrow Ta$. Thus, it is seen that the diffusion of Ta into the Pt is much slower than the diffusion of Pt into the Ta in the presence of an Al_2O_3 diffusion barrier at $2600^{\circ}F$.

After 30 days at $1600^{\circ}F$, the reaction in a Ta/ Al_2O_3 /Pt couple was limited to isolated inclusions in the alumina of Ta-rich material. As in the tests where Ta was placed in contact with Al_2O_3 , the inclusions were of submicron size so that a quantitative determination of their composition was not possible.

A similar couple at $2000^{\circ}F$ maintained the integrity of its Al_2O_3 zone after 30 days, but metallic inclusions were present in the Al_2O_3 nearer to the Pt disk. These were of the composition 87 w/o Pt, 9 w/o Ta, and 4 w/o Al. A solid solution region containing Al was present in the Pt adjacent to the Al_2O_3 for a distance of 30μ . The maximum Al concentration within this region was 9 w/o.

The reaction after 30 days at $2600^{\circ}F$ was quite severe for Ta/ Al_2O_3 /Pt. Almost all the Al_2O_3 was consumed and a 250μ reaction zone formed (Figures 45 - 47). As can be seen from the photomicrographs, there was no discernible difference between the TIG-welded and the EB-welded specimens. Most of the atomic migration took place in the direction $Pt \longrightarrow Ta$, as can be seen by using the unconsumed Al_2O_3 as reference markers. There is no Ta within the Pt disk, but the

Figure 45. Ta/Al₂O₃/Pt/Al₂O₃/Ta; Thirty Days at 2600°F Bright Field, E.B. Welded (80X Magnification)

Severe reaction has occurred. Most of the Al₂O₃ has been consumed. Many intermetallic phases are present and much of the Ta has been converted to intermetallic.

Figure 46. Enlarged View of Al₂O₃ Region Shown in Figure 45; Bright Field (400X Magnification)

Figure 47. Ta/Al₂O₃ Pt/Al₂O₃/Ta TIG-Welded Under One Atm He;
Thirty Days at 2600°F Bright Field (100X Magnification)

The results are similar to those found for the EB-welded case. The voids may be due to a Kirkendall effect, whereby there is a net flux of atoms in the direction Pt → Ta.

disk has become a solid solution of Pt with approximately 3 w/o Al. In the region that was formerly Al_2O_3 , Al metal is present with about 3 w/o Pt and 3 w/o Ta in solution. In this region, the intermetallic compound Pt_2TaAl_3 was identified. On the Pt side, Pt_3Al is present with 2 w/o Ta in solid solution. On the Ta side, the intermetallic compounds Pt_3Ta , Pt_2Ta , Pt_2Ta_3 , and PtTa_3 are present in a layered structure.

EB-welded and TIG-welded couples of Ta-10W/ Al_2O_3 /Pt-10Rh and T-111/ Al_2O_3 /Pt-10Rh gave essentially identical results (Figures 48-51). The electron microprobe showed that a 315μ reaction zone formed. Many voids formed on the refractory alloy side and within the Pt-10Rh. Neither the W nor the Rh diffused very much, so the disk became enriched in Rh by virtue of the Pt diffusing out. The Pt-Rh ratio within the disk was approximately 3:1 with 3.8 w/o Al in solid solution. The Pt-Ta intermetallic compounds can accommodate up to 10 w/o W, providing the Pt:Ta ratio is less than 2. For Pt:Ta > 2, W is essentially insoluble. A thin zone or band containing precipitates high in W was present in the refractory. The composition of these precipitates was approximately (Pt, Rh) TaW, with the Pt and Rh in varying proportions.

Y_2O_3 proved to be inferior to Al_2O_3 as a diffusion barrier. After 30 days at 2000°F , a 200μ reaction zone occurred in a Ta/ Y_2O_3 /Pt couple (Figure 52). Quantities of Ta_2O_5 along with TaPt_3 and YPt_2 were found in the region that had been Y_2O_3 .

After 30 days at 2600°F , the reactions involving Y_2O_3 were far more severe (Figure 53). A 290μ Ta-Pt intermetallic zone was present on the Ta side. Large voids occurred in the Pt disk, which contained 8 w/o Y uniformly distributed. In addition to the compounds found at 2000°F , Ta_3Pt , TaPt , and TaPt_2 were present.

The attempt to use Y_2O_3 as a diffusion barrier between Ta-10W and Pt-10Rh at 2600°F resulted in total consumption of the Y_2O_3 , substantial void formation in the Pt disk, and the formation of several new phases

Figure 48. Ta-10W/ Al_2O_3 /Pt-10Rh/ Al_2O_3 /Ta; Thirty Days at 2600°F Bright Field (100X Magnification)
E.B. Welded

Figure 49. Same as Figure 48 but TIG-Welded (100X Magnification)

Figure 50. Same as Figure 48 but with T-111 as the Refractory Alloy (100X Magnification) E.B. Welded

Figure 51. Same as Figure 50 but TIG-Welded, 30% Polarized Light (100X Magnification)
The light polarization shows the unusual microstructure of the T-111.

Figure 52. Ta/Y₂O₃/Pt; Thirty Days at 2000°F Bright Field
(100X Magnification)
Reaction has occurred.

Figure 53. Ta/Y₂O₃/Pt/Y₂O₃/Ta; Thirty Days at 2600°F
Bright Field (80X Magnification)

The Pt has been essentially converted to intermetallic. The voids may be due to a Kirkendall effect whereby there is a net flux of atoms in the direction Pt → Ta.

in the Ta-10W. The void formation, which probably resulted from the diffusing out of the Pt was particularly severe. Figures 54 through 56 show the results of a 30 day anneal at 2600°F.

3.4.5 Molybdenum or TZM in Contact with Al_2O_3

Small inclusions were observed in Al_2O_3 which had been plasma-arc-sprayed onto Mo and TZM and annealed at 2600°F for 30 days. Their number and size were far less than were present in the Ta- Al_2O_3 experiment. They assayed at 10 w/o Mo.

3.4.6 Molybdenum or TZM/ Al_2O_3 or Y_2O_3 /Pt or Pt-10Rh

Mo/ Al_2O_3 /Pt and Mo/ Y_2O_3 /Pt showed less reaction after 30 days at 2600°F than did their Ta counterparts. Figures 57 and 58 are photomicrographs of these two systems. Figure 58 in conjunction with the electron microprobe shows a reaction zone approximately 400 μ across. The intermetallic compounds MoPt₂, MoPt, and MoPt₃ are present.

Three day and thirty day anneals at 2600°F of TZM/ Al_2O_3 /Pt-10Rh couples showed no strong evidence of reaction metallographically or with the electron microprobe (Figures 59-62). The plasma arc sprayed Al_2O_3 coating was applied to the Pt-10Rh in the three day test and to the refractory metals in the thirty day test. Since the capsules were screwed down tightly prior to the anneals, it is suspected that the materials were in intimate contact throughout the anneal, and separated only on cooling. The apparent absence of reaction, however, in the thirty day specimen is surprising.

3.4.7 Thermochemical Calculations

Thermodynamic calculations were made over the temperature range 1000° - 1800°K (1340° - 2780°F) by computer to estimate what species could be present at equilibrium in the solid, liquid, and gas phases for the systems Pt-Ta-O, Pt-Mo-O, and Pt-Ta-Al-O. Pt-Ta-O represents the conditions prevailing in the Pt-Ta vapor transport experiments, where an initial residual O₂ partial pressure of $\sim 10^{-4}$ torr exists in the EB-welded specimen holder. Likewise Pt-Mo-O represents the conditions of the Pt-Mo vapor transport experiment. Pt-Ta-Al-O represents the conditions prevailing in the Ta/ Al_2O_3 /Pt diffusion couples, where the efficacy of Al_2O_3 as a diffusion

Figure 54. Ta-10W/Y₂O₃/Pt-10Rh/Y₂O₃/Ta; Thirty Days at 2600°F Bright Field (100X Magnification)

Note the extensive reaction which has completely consumed the Y₂O₃. Several different phases are present in the material which was once Ta/10W. The extensive voids in the Pt-10Rh are probably due to a Kirkendall movement.

Figure 55. Enlarged View of Pt-Rh-Y-Ta Region Shown in Figure 54 Bright Field (400X Magnification)

Figure 56. Enlarged View of Pt-Rh-Y-Ta-W Region Shown in Figure 54 Bright Field (400X Magnification)

Figure 57. Mo/Al₂O₃/Pt; Thirty Days at 2600°F
Bright Field (100X Magnification)

Although the Al₂O₃ is partially consumed, a large amount remains.

Figure 58. Mo/Y₂O₃/Pt; Thirty Days at 2600°F Bright Field (100X Magnification)

Note the great amount of reaction which occurs when Al₂O₃ is replaced by Y₂O₃ as the diffusion barrier.

Figure 59. TZM/Al₂O₃/Pt-10Rh; Three Days at 2600°F, Bright Field (400X Magnification)

Note the absence of any apparent reaction.

Figure 60. Tz/ Al_2O_3 /Pt-10Rh/ Al_2O_3 /Mo; Thirty Days at 2600°F Bright Field (50X magnification)

Note the absence of any apparent reaction.

Figure 61. Enlarged View of TZM-Al₂O₃ Interface Shown in Figure 60 Bright Field (400X magnification)

Figure 62. Enlarged View of Pt Region Shown in Figure 60 opposite the TZM/Al₂O₃; Bright Field (400X magnification)

barrier was investigated. Since Y_2O_3 was generally inferior to Al_2O_3 in this respect, calculations of the thermodynamic properties of the yttrium-containing systems were not made.

The calculations were idealized in that the formation of intermetallic compounds was not considered due to the lack of thermodynamic data. This was a serious omission in the case of the oxide barrier diffusion couples, since extensive reduction of the oxides occurred by the formation of binary and ternary intermetallic compounds and the formation of solid solutions involving Al and Y metal.

The computer program used converts all input species to their dissociated, gaseous atomic states. It then calculates the configuration of species and gaseous, liquid, and solid phases present for the minimum system free energy, i.e. equilibrium. As long as excesses of all the input species, including the gaseous species, are present in the final configuration, the reported equilibrium concentration ratios of the formed species will correspond to the actual physical system at equilibrium.

For the Pt-Ta-Al-O system, the species considered as possibly present were:

Gas Phase: Al, AlO, AlO₂, Al₂O, Al₂O₂, O, O₂, O₃,
Pt, PtO, Ta, TaO, TaO₂

Liquid Phase: Al, Al₂O₃, Pt, Ta, Ta₂O₅

Solid Phase: Al, α Al₂O₃, γ Al₂O₃, Pt, Ta, Ta₂O₅

The calculations showed that, at 2600°F, 1% solid Ta₂O₅ would form by the reduction of Al₂O₃. The amount of Ta₂O₅ formed decreases with decreasing temperature.

For the Pt-Ta-O system (which represented the Pt-Ta vapor transport case), the species considered as possibly present were:

Gas Phase: O, O₂, O₃, Pt, PtO, Ta, TaO, TaO₂

Liquid Phase: Pt, Ta, Ta₂O₅

Solid Phase: Pt, Ta, Ta₂O₅

The condensed phases present, Ta, Pt and Ta_2O_5 , stayed relatively constant with temperature. Ta and Ta_2O_5 were in the ratio $Ta:Ta_2O_5 = 100:1$. Of the gas species, only Pt, TaO, and TaO_2 had partial pressures greater than 10^{-9} atm at the highest temperature. The ratio P_{Ta}/P_{Pt} decreased from 2.21×10^{-7} at $2780^\circ F$ to 1.96×10^{-12} at $1340^\circ F$. The respective partial pressures of Pt, TaO, and TaO_2 are plotted as a function of temperature in Figure 63.

For the Pt-Mo-O system (which represented the Pt-Mo vapor transport case), the species considered as possibly present were:

Gas Phase: Mo, MoO, MoO_2 , MoO_3 , O, O_2 , O_3 , Pt, PtO

Liquid Phase: Mo, MoO_3 , Pt

Solid Phase: Mo, MoO_2 , MoO_3 , Pt

As in the case of the Pt-Ta-O system, the condensed phases present, Pt, Mo, and MoO_2 , stayed relatively constant with temperature. Mo and MoO_2 were in the ratio $Mo:MoO_2 = 100:1$. The significant gaseous species present were MoO_2 and MoO_3 . At the highest temperatures, their partial pressures were generally a factor of 10^3 higher than those of the corresponding oxides in the Pt-Ta-O system. Figure 64 is a plot of the MoO_2 and MoO_3 partial pressures as a function of temperature.

Figure 63. Partial Pressures of Tantalum Oxides and Platinum

Figure 64. Partial Pressures of Molybdenum Oxides

4. CONCLUSIONS

1. There was no identified interaction (up to 3 days at 2600°F) in an isolated system containing Pt in contact with Al_2O_3 . Several 3 day anneals at 2600°F followed by detailed metallographic and electron microprobe analysis failed to disclose any oxide reduction or atomic diffusion.

2. Only for the longest annealing time and the highest temperature (30 days at 2600°F) was any gross reaction found when Al_2O_3 was plasma-arc-sprayed onto Ta. The reaction was limited to isolated inclusions rich in Ta to a maximum of 15 w/o. These inclusions were optically coherent, i.e., were optically indistinguishable, which leads to the conclusions that they may have been Ta_2O_5 .

Ta-10W or T-111 fared slightly worse than pure Ta when in contact with Al_2O_3 . The inclusions were larger and consisted of pure Ta. No visible reaction was observed in the Ta-10W/ Y_2O_3 couple after 30 days at 2600°F.

3. At all three test temperatures--1600°F, 2000°F, and 2600°F, extensive matter transport occurred over a 1/16" gap from a Ta disk toward a Pt disk. At least four Pt-Ta intermetallic compounds were found in the Pt disk along with both Pt and Ta terminal solid solutions.

These results are somewhat surprising for several reasons. The vapor pressures of Ta and Pt are 2.33×10^{-17} atm and 3.53×10^{-10} atm, respectively, at 2600°F, and certainly could not account for the observed matter transport. In addition, the vapor pressure of Pt is seven orders of magnitude higher than that of Ta, and yet all transport was from the Ta side to the Pt side. Two independent methods were used to calculate the respective Ta and Pt evaporation rates, the Langmuir methods, which assumes a flat-plate geometry, and an empirical equation. The calculated evaporation rates are shown in Table 4.

TABLE 4. EVAPORATION RATES OF Ta AND Pt AT 2600°F

	<u>LANGMUIR METHOD</u> (g/cm ² -sec)	<u>EMPIRICAL EQUATION</u> (g/cm ² -sec)	<u>VAPOR PRESSURE</u> (atm)
Ta	3.36×10^{-16}	4.07×10^{-16}	2.33×10^{-17}
Pt	3.80×10^{-9}	5.24×10^{-9}	2.53×10^{-10}

That the results of the two independent methods agree so closely indicates that they are good approximations to the actual values. In three days (2.6×10^5 sec) over an area of 1 cm^2 , only 10^{-10} g Ta would be expected to evaporate. This is orders of magnitude less than what was actually observed and, therefore, it is concluded that straight metal evaporation could not possibly account for the mass transport. Rather, it is postulated that an oxygen molecular shuttle is operating, where oxygen combines with Ta to form two gaseous species--TaO and TaO₂. These species then diffuse to the Pt side, where Ta-Pt intermetallic compounds are formed. The oxygen atoms are released to return to the Ta side and the process is repeated. The computer calculations identified and predicted the concentrations of all condensed and gaseous species present at thermodynamic equilibrium other than intermetallic compounds. The calculations showed that at 2600°F, the equilibrium vapor pressure ratios of TaO (g) to Ta (g) and TaO₂ (g) to Ta (g) in equilibrium with Ta (s) and the residual gas in the capsule (10^{-4} torr) are 5.6×10^6 and 9.6×10^6 , respectively.

If we assume that the kinetics of reaction at the respective Ta and Pt interfaces are instantaneous relative to the molecular motion across the void, then the transfer is governed solely by the speed with which the TaO and TaO₂ species are transferred. At equilibrium, there

will be a counterdiffusion of O vs TaO and TaO₂. To a good approximation, the kinetic theory of gases gives the interdiffusivity to be:

$$D_{AB} = 1.86 \times 10^{-3} \frac{\sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}}{p \sigma_{AB}^2} \text{ cm}^2/\text{sec}$$

Where

T = absolute temperature in ⁰K, M_A and M_B = respective molecular weights of the counterdiffusing species, p = pressure in atm, and σ_{AB} = mean molecular diameter in Å.

For an average molecular weight of 205 for the Ta oxides and σ_{AB} = 5.0Å, at 2600⁰F and 10⁻⁴ torr, D_{AB} = 3.07 x 10⁷ cm²/sec. For a linear concentration gradient over the 1/16" x 3/8" diameter gap space, the flux is 3.6 x 10⁻⁶ g Ta/sec, so that in 3 days (2.6 x 10⁵ sec), approximately 0.93g Ta could conceivably be transferred. In the 2600⁰F specimen annealed for 3 days, approximately 0.06g Ta is present in the 130μ reaction zone. The proposed molecular shuttle is a viable means of mass transport.

No mass transport occurred when Mo replaced Ta as the refractory metal in the vapor phase transport experiments. This is despite the fact that MoO₂ and MoO₃ have vapor pressures more than three orders of magnitude greater than those of TaO or TaO₂. Apparently, the free energy for the dissolution of Mo in Pt or the formation of the Pt-Mo intermetallic compounds is less than the free energy of the Mo oxides, so no reaction occurs and the molecular shuttle is not activated.

4. Al₂O₃ acts successfully as a diffusion barrier in tests up to 30 days at 1600⁰F and 2000⁰F. At 2600⁰F, however, the Al₂O₃ is rapidly reduced and binary and ternary intermetallic compounds involving Pt, Ta, and Al form. A 2-4 w/o uniform solid solution of Al in Pt is distributed throughout the disk. The remnants of the Al₂O₃ barrier acted as unmoving

markers and showed that the bulk diffusion is in the direction $\text{Pt} \rightarrow \text{Ta}$. The Pt-Ta solid solutions and intermetallic compounds form in the regions that were originally Ta, so that the Pt layer is not degraded by the Ta, but rather is merely decreased in thickness. When Ta alloys such as Ta-10W and T-111 are used instead of Ta as the refractory and the Pt is alloyed with Rh, neither the W nor the Rh diffuse to any great extent. The noble metal material thus becomes enriched in Rh by virtue of the Pt diffusing out.

Y_2O_3 is generally inferior to Al_2O_3 as a diffusion barrier for these systems. Y_2O_3 is reduced by Ta. There is a great amount of interdiffusion, which results in large Kirkendall voids within the noble metal disk.

5. Less reaction was observed when either Mo or TZM were used as the refractory with either Al_2O_3 or Y_2O_3 as the diffusion barrier. Again, Al_2O_3 was generally superior to Y_2O_3 .