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THE HIGH-TEMPERATURE COMPATIBILITY OF PROMETHIUM SESQUIOXIDE

H. T. Fullam

June 1970

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THE HIGH-TEMPERATURE COMPATIBILITY OF PROMETHIUM SESQUIOXIDE

By

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THE HIGH-TEMPERATURE COMPATIBILITY OF PROMETHIUM SESQUIOXIDE

H. T. Fullam

1. INTRODUCTION

A program to develop the technology of promethium has been underway at the Pacific Northwest Laboratory (PNL) for a number of years. This program has been supported by the Division of Isotopes Development. A major phase of the program has involved the preparation of high purity promethium sesquioxide (Pm_2O_3), determination of its chemical and physical properties, and development of potential applications for the oxide.

One major application for Pm_2O_3 involves its use as a fuel for radioisotope heat sources and a substantial effort at PNL has been directed at developing this use. Use of Pm_2O_3 as a heat source fuel requires an adequate knowledge of the compatibility of the oxide with containment materials at elevated temperatures. A study has been underway at PNL for several years to obtain this information. In the initial phase of the project a number of short-term scouting tests were carried out to select the optimum containment materials for long-term testing and to identify the factors which affect oxide-clad interaction. The results of the scouting studies were presented in interim report BNWL-327.(1)

Based on the results of the scouting studies, a series of long-term experiments was designed and carried out to evaluate Pm_2O_3 compatibility with nine selected metals and alloys at temperatures up to 2000 °C. This report presents the results of the long-term tests as well as summarizes the results of the entire Pm_2O_3 compatibility program at PNL.

2. SUMMARY

The long-term compatibility of Pm_2O_3 with nine different metals was evaluated at 1100 °C. The metals tested were 304L SS, Hastelloy X, Haynes 25, tantalum, rhenium, tungsten, Ta-10% W, W-25% Re and TZM. The tests lasted up to 2 yr. Sm_2O_3 was used as a stand-in in most of the tests. However, enough tests were run with Pm_2O_3 to verify that the results obtained with Sm_2O_3 were applicable to Pm_2O_3.

The data obtained in the tests show that:

- Oxide compatibility at 1100 °C is primarily dependent on oxide purity.
- A variety of metals can be used to contain Pm_2O_3 at 1100 °C provided the critical impurities (i.e., H_2O, C, organics) are removed from the oxide prior to use.
- From compatibility considerations alone, rhenium is the preferred containment material.
- Oxide-metal interaction is essentially independent of time at temperature. Couples tested for long periods of time (up to 2 yr) show the same amount of oxide-metal reaction as couples tested for much shorter time periods (1500 hr). Therefore, results obtained in the 2 yr tests can be safely extrapolated to much longer time periods.
- Sm_2O_3 makes a good stand-in for Pm_2O_3, and results obtained with Sm_2O_3 are completely applicable to Pm_2O_3.

A series of higher temperature compatibility tests was carried out with Sm_2O_3. Results obtained at 1550 °C and 2000 °C confirm those obtained at 1100 °C.

Potential users of Pm_2O_3 should not let fear of oxide compatibility problems deter their use of Pm_2O_3 at elevated temperatures. Provided the Pm_2O_3 is free of critical impurities, selection of a containment material can be based on factors other than oxide compatibility.

3. PRELIMINARY STUDIES

Early in the Pm_2O_3 compatibility program, a series of scouting studies was carried out to identify the factors which affect the rate of oxide-clad interaction and to select the best metals and alloys for long-term testing. These tests were carried at temperatures up to 1100 °C. The results of the scouting studies were reported in detail in BNWL-327(1) and are summarized briefly in this section.

Most of the scouting tests were made using Sm_2O_3 and Nd_2O_3 as stand-ins for Pm_2O_3. This was necessary because of an early-program shortage of high-purity Pm_2O_3 and because of the difficulty in carrying out a large number of tests with Pm_2O_3. It was felt that Sm_2O_3 and Nd_2O_3 should make excellent stand-ins for Pm_2O_3 because of the similar chemical and physical properties of adjacent rare earths. Sm_2O_3 was especially attractive as a stand-in because Pm_2O_3 always contains some Sm_2O_3 due to radioactive decay. Some scouting studies were carried out with Pm_2O_3, and the results obtained compare favorably with those obtained with the stand-ins.

Results of the scouting studies show that oxide purity is the most critical factor affecting the rate at which the oxides and containment materials interact. Commercial grades (99.9%) of Sm_2O_3 and Nd_2O_3 react quite rapidly with most metals and alloys at elevated temperatures. At 1100 °C, interaction rates of 5 mils and higher (in 1500 hr) were observed between Sm_2O_3 and most metals tested. Only rhenium and its alloys showed any appreciable resistance to attack by commercial grade oxides.

Experimental evidence obtained from the scouting studies showed that certain critical impurities in the oxide were the probable cause of the high interaction rates observed with commercial grade oxide. These critical impurities were found to be water, carbon monoxide, carbon dioxide, and impurities which can form CO or CO_2 (i.e., carbon, $CO_3^=$, and organic compounds). When these impurities were removed from the oxide prior to compatibility testing, the rates of oxide-metal interaction were reduced to much lower levels (see Table 1). The purification treatment developed for removing deleterious impurities consisted of heating the oxide in oxygen at 1100 °C for several hours and then heating in hydrogen at 1100 °C for a similar time period. The oxide was cooled to room temperature under argon and sealed in glass containers until needed. A possible explanation of why certain impurties so drastically affect rare earth oxide compatibility with metal is given in the appendix.

It was found that cycling the temperature also affected the oxide-metal interaction rates. When the test temperature was cycled between 700 and 1100 °C the interactions observed were substantially greater than those observed at a constant 1100 °C.

One major conclusion can be drawn from the results of the scouting studies. A variety of metals and alloys can be used to contain Pm_2O_3 at 1100 °C for periods up to 1500 hr, provided the oxide is specially purified. One can extrapolate the data to show that safe containment of the oxide is possible for much longer periods of time at 1100 °C. However, experimental verification is needed to assure potential oxide users the extrapolation is valid. The current experimental program was designed to provide this assurance.

TABLE 1. **Results of Compatibility Scouting Studies with Sm_2O_3 at 1100 °C**

Metal	Oxide Source[a]	Time, hr	Interaction Zone, mils
304L SS	1	1500	8
304L SS	2	1500	1
Haynes 25	1	840	5
Haynes 25	2	1500	1
Tantalum	1	840	>10
Tantalum	2	1500	2
Tungsten	1	840	5
Tungsten	2	840	<1
Rhenium	1	1500	0
Rhenium	2	1500	0
Platinum	1	840	>10
Platinum	2	840	>10
W-25% Re	1	1500	0.5
W-25% Re	2	1500	<1

(a) 1 - *Commercial Oxide*
2 - *Commercial Oxide Specially Purified*

4. EXPERIMENTAL PROGRAM

The basic objectives of the current Pm_2O_3 compatibility program were twofold:

- To obtain long-term experimental data on the compatibility of Pm_2O_3 with selected metals and alloys at 1100 °C.
- To obtain short-term compatibility data for Pm_2O_3 at temperatures up to 2000 °C.

This data would allow heat source users to design high integrity Pm_2O_3 sources for long-term high temperature use. The procedures used to obtain the required data are described in the following sections.

4.1 TEST PROGRAM

Nine different metals and alloys were selected for long-term compatibility testing at 1100 °C:

304L SS	Rhenium
Hastelloy X	TZM
Haynes 25	Ta-10% W
Tantalum	W-25% Re
Tungsten	

Hastelloy X and Haynes 25 were chosen as representatives of the nickel and cobalt base superalloys, and 304L was chosen as a typical stainless steel. The refractory metals were picked for their excellent shielding and high temperature properties. Rhenium and W-25% Re were selected because they showed the greatest resistance to oxide attack of any of the metals tested in the scouting studies. Program cost considerations limited the metals tested to those listed.

The testing conditions and schedules are presented in Tables 2 through 5. Most of the tests were carried out using Sm_2O_3 as a stand-in for Pm_2O_3. However, enough tests were run with Pm_2O_3 to show that the results obtained with the stand-in would be applicable to Pm_2O_3. While it would have been most desirable to carry out all of the tests with Pm_2O_3, the cost involved would have been prohibitive.

The high temperature tests (1550 and 2000 °C) were carried out with Sm_2O_3 only. This was necessary because furnaces for testing Pm_2O_3 couples above 1100 °C were not available.

In addition to the studies listed in Tables 2 to 5, a number of miscellaneous tests were carried out at various times during the program to evaluate specific factors. These included tests involving the use of hot pressed oxide pellets, slip cast oxide pellets, and oxide with specially added impurities.

TABLE 2. Pm_2O_3 *Test* Program at 1100 °C

Metal	Fabrication Method(a)	Test Period, hr	
		8,800	13,200
304L SS	PS	x	
304L SS	PI	x	
Hastelloy X	PS	x	
Hastelloy X	PI	x	
Haynes 25	PS	x	
Haynes 25	PI	x	
Tantalum	PS	x	x
Tantalum	PI	x	
Tungsten	PS	x	x
Rhenium	PS	x	x
Ta-10%W	PS	x	x
Ta-10%W	PI	x	
W-25% Re	PS	x	x
TZM	PS	x	

(a) PS - Capsule loaded with cold-pressed and sintered pellets

PI - Capsule loaded with cold-pressed and sintered pellets, then pneumatically impacted

TABLE 3. Sm_2O_3 Tests at 1100 °C

Metal	Fabrication Method[a]	Test Period, hr		
		4,300	8,800	17,600
304L SS	SP	2[b]	2	2
304L SS	PI	1	1	1
304L SS	PS		2	
Hastelloy X	SP	2	2	2
Hastelloy X	PI	1	1	1
Haynes 25	SP	2	2	2
Haynes 25	PI	1	1	1
Tantalum	SP	2	2	2
Tantalum	PI	1	1	1
Tantalum	PS		2	
Rhenium	SP	2	2	2
Rhenium	PI	1	1	1
Rhenium	PS		2	
Ta-10% W	SP	2	2	2
Ta-10% W	PI	1	1	1
Ta-10% W	PS		2	
W-25% Re	SP	2	2	2
W-25% Re	PI	1	1	1
TZM	SP	2	2	2
TZM	PI	1	1	1
TZM	PS		2	
				12,000
Tungsten	SP		2	2
Tungsten	PI		1	1

(a) SP - Oxide Step pressed into capsule
PI - Oxide step pressed into capsule - capsule pneumatically impacted
PS - Pressed and sintered oxide pellets

(b) Number of capsules tested at each set of conditions.

TABLE 4. Sm_2O_3 **Tests with Temperature Cycled Between 700 and 1100 °C - 24 hr Cycle**

Metal	Fabrication Method[(a)]	Test Period, hr 1,000	4,300	8,800
304L SS	SP	x	x	x
304L SS	PI	x	x	x
Hastelloy X	SP	x	x	x
Hastelloy X	PI	x	x	x
Haynes 25	SP	x	x	x
Haynes 25	PI	x	x	x
Tantalum	SP	x	x	x
Tantalum	PI	x	x	x
Rhenium	SP	x	x	x
Rhenium	PI	x	x	x
Ta-10% W	SP	x	x	x
Ta-10%W	PI	x	x	x
Tungsten	SP		x	
Tungsten	PI		x	
W-25% Re	SP	x	x	x
W-25% Re	PI	x	x	x
TZM	SP	x	x	x
TZM	PI	x	x	x

(a) SP - Oxide step pressed into capsule
PI - Oxide step pressed into capsule - capsule pneumatically impacted.

TABLE 5. **High Temperature Tests with Sm_2O_3**

Metal	Fabrication Method[(a)]	Test Period, hr 1,000	Test Period, hr 4,300
(A) Tests at 1550 °C			
Tantalum	SP	x	x
Tantalum	PI	x	x
Tungsten	SP	x	x
Tungsten	PI	x	x
Rhenium	SP	x	x
Rhenium	PI	x	x
Ta-10% W	SP	x	x
Ta-10% W	PI	x	x
W-25% Re	SP	x	x
W-25% Re	PI	x	x
TZM	SP	x	x
TZM	PI	x	x

Metal	Fabrication Method[(a)]	Test Period, hr 1,000	Test Period, hr 3,000
(B) Tests at 2000 °C			
Tantalum	SP	x	x
Tantalum	PI	x	x
Tungsten	SP	x	
Tungsten	PI	x	x
Rhenium	SP	x	x
Rhenium	PI	x	x
Ta-10% W	SP	x	x
Ta-10% W	PI	x	x
W-25% Re	SP	x	
W-25% Re	PI	x	x

(a) SP - Oxide step pressed into capsule
PI - Oxide step pressed into capsule - capsule pneumatically impacted

4.2 PREPARATION OF TEST COUPLES

In order to minimize the influence of fabrication techniques on the experimental results obtained, the method of preparing the test couples was standardized as far as possible. The basic steps in couple preparation were:

- Preparation of high purity oxide by a standarized process.
- Fabrication of the metal test capsule from bar stock or sheet obtained from a single source (and lot if possible).
- Loading of the oxide into the test capsule.
- Closure of the capsule by welding to form the completed couple.
- Pneumatic impaction (where required).
- Couple sealed in protective jacket, if necessary.

The completed couple was then ready for testing.

4.2.1 Oxide Preparation

As mentioned earlier, oxide purity has a pronounced influence on the rate of oxide-metal interaction. A special process designed to remove the critical impurities was used to prepare all of the oxide used in the program.

Samarium sesquioxide of 99.9% purity was obtained from the Lindsey Division of American Potash and Chemical Corporation. The oxide was dissolved in research grade nitric acid. The samarium was then precipitated from the solution as the oxalate by the addition of aqueous oxalic acid. The oxalate was filtered and washed thoroughly with distilled water. The oxalate cake was calcined to oxide at 1100 °C for 24 hr in a flowing oxygen atmosphere (in a quartz vessel). The system was then purged with argon, and the oxide heated for 16 hr at 1100 °C in an atmosphere of Ar-6% H. The oxide was cooled to room temperature under argon and transferred to glass containers.

The Sm_2O_3 was prepared in several batches, and these were thoroughly blended to ensure uniformity. Blending was done in a ball mill, and the product was stored in sealed glass jars until needed.

The promethium sesquioxide was prepared in a similar fashion except that the starting material was promethium solution from an ion exchange purification process.(2,3) This solution contained <1% cation impurities. The promethium was precipitated as the oxalate, and the oxalate was calcined in the same manner as the samarium oxalate. The Pm_2O_3 product was stored in metal cans. Preparation of the Pm_2O_3 was carried out in a lead-shielded glove box.

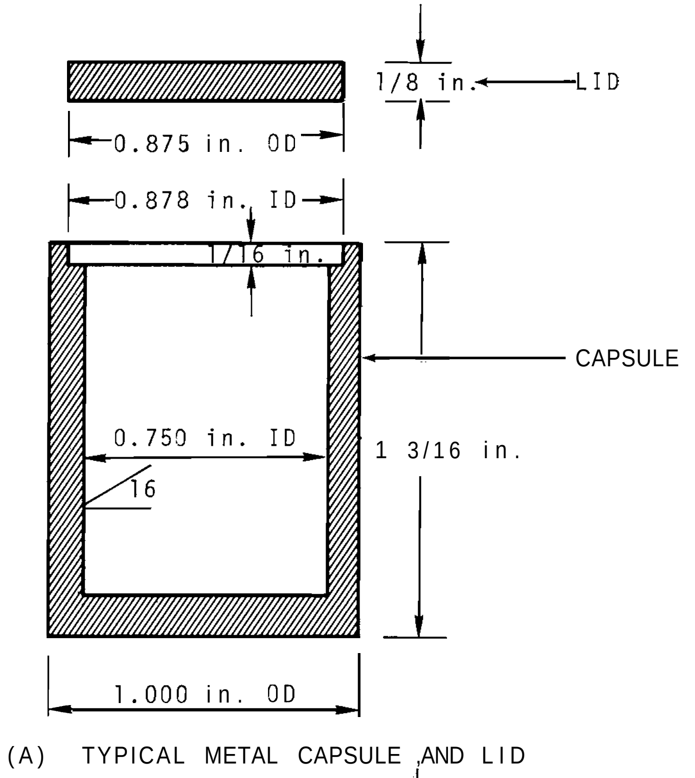
The Sm_2O_3 produced by the above treatment had the monoclinic crystal structure, as did the Pm_2O_3.

4.2.2 Capsule Fabrication

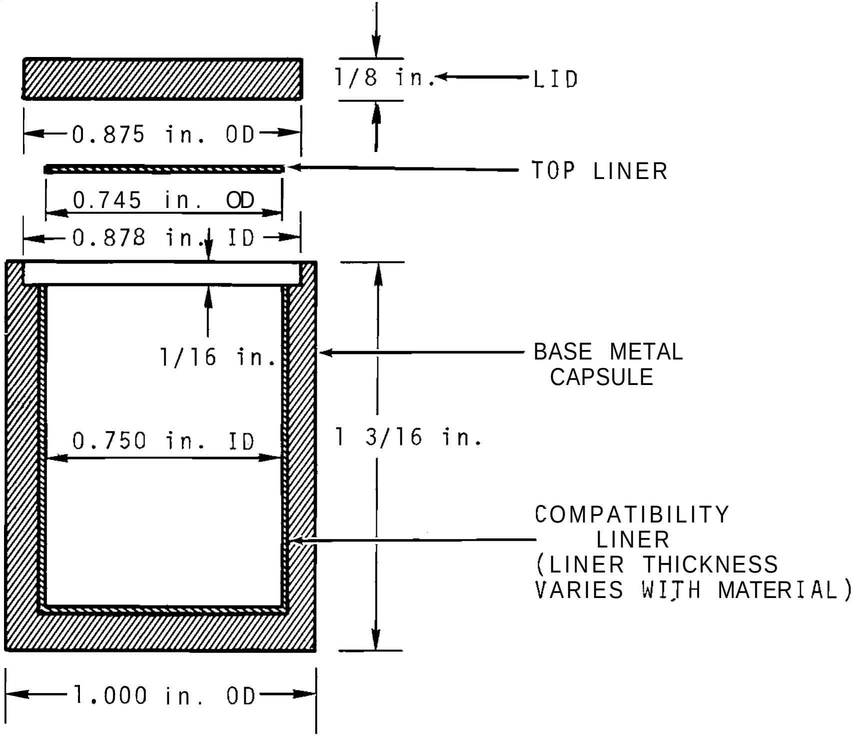
Nine different metals and alloys were evaluated in the program. For any given metal or alloy, all of the capsules required for the program were prepared from material obtained from a single supplier (and a single lot or heat if possible). The specifications for the metals tested are presented in the appendix.

Figure 1A shows the typical capsule design used in preparing the test couples. The capsules were normally machined from bar stock. Dimensional tolerances were held to ±0.001 in., and all machined surfaces were given a No. 16 finish.

For some of the metals to be tested, it was impractical to make the entire capsule from the test metal. In such cases, a capsule was machined from a base metal such as 304L SS or tantalum and lined with the metal to be tested (Figure 1B).



(A) TYPICAL METAL CAPSULE AND LID



(B) COMPOSITE CAPSULE WITH LINER

FIGURE 1. Metal Capsules Used in Fabricating Test Couples

The composite capsule design was used for rhenium and W-25% Re because of the cost involved in making the entire capsule from either metal. The tungsten test capsules were prepared in a similar fashion because of the difficulty and cost involved in preparing the capsules from bar stock. In preparing the composite capsules, the liner material was held in place by spot welding it to the base metal capsule.

For the Pm_2O_3 loaded capsules, the design was modified slightly by using a metal plug (of the same metal as the capsule) to occupy part of the space normally filled with oxide. This reduced the amount of oxide required per capsule from the 45 to 46 g used in the Sm_2O_3 couples to about 16 g in the Pm_2O_3 couples.

In carrying out any high temperature compatibility test it is highly desirable that only the materials to be tested be in contact. Excluding other material contact prevents any possible interaction with extraneous materials which might affect the results. The use of a composite capsule is, therefore, a poor choice in compatibility testing. However, the expense and difficulty involved in preparing capsules from rhenium, W-25% Re, and tungsten made it necessary to accept the compromise of composite capsules.

After fabrication and prior to loading, the capsules were cleaned in an ultrasonic bath using trichloroethylene, washed with alcohol, then with distilled water, and dried.

4.2.3 Capsule Loading

Two methods were used for loading oxide into the metal capsules. The first method involved inserting oxide pellets into the capsule. In the second method, the oxide was step pressed into the capsule at high pressures [60 to 70 tons per square in. (TSI)]. The first method was used in preparing the Pm_2O_3 couples and both methods were used in preparing the Sm_2O_3 couples.

The Pm_2O_3 pellets were prepared by cold pressing oxide at 50 to 70 TSI in a split sleeve die to give pellets of the required green density and diameter. The pellets were sintered in air at 1200 to 1400 °C to give the final required dimensions and density. The pellets were then inserted into the metal capsules. A detailed description of the preparation of the Pm_2O_3 couples is given in a separate report.(4)

Samarium sesquioxide pellets were prepared in several different ways. Some were prepared by cold pressing and sintering as were the Pm_2O_3 pellets. Others were prepared by hot pressing at 1500 to 1700 °C,(5) and still others were prepared by slip casting and sintering.(6)

When the oxide was step pressed into the metal capsule, the loading procedure was as follows:

> The capsule was pressed into a heavy-walled steel die. The capsule and die were placed in an argon atmosphere box which enclosed the ram of a hydraulic press. A small amount of oxide was placed in the capsule, and a close-fitting plunger was inserted on top of the oxide. A pressure of 60 TSI was applied to the plunger and held for 1 min. The pressure was released and the plunger removed. More oxide was added to the capsule and the entire operation repeated. This step-wise loading was continued until the capsule was filled to the desired level. When the capsule was full, the capsule lid was pressed in place and the capsule ejected from the die. The loaded capsule was then sealed in a glass container until ready for welding.

By pressing at 60 TSI, an oxide density of about 75% of theoretical was normally achieved in the capsule. Using the steel die to contain the capsule during the pressing operation held capsule wall distortion after loading to a maximum of 1 to 2 mils.

Step pressing resulted in good contact between the oxide and the metal surface. The use of oxide pellets, however, gave much poorer oxide-metal contact. As a result, one would expect greater oxide-metal interaction under a given set of conditions with the step-pressed couples than with the couples prepared using oxide pellets.

In all the loading operations, care was taken to reduce to a minimum oxide exposure to the atmosphere. This was necessary to prevent the oxide from picking up water or carbon dioxide.

4.2.4 Capsule Closure

After loading, the capsules were closed by electron beam welding the lids in place. Electron beam welding was used for two reasons:

- Good weld penetration could be achieved with all the metals and alloys under consideration.
- The high vacuum operation of the weld chamber during welding served to outgas the capsule and remove any traces of water vapor, carbon dioxide or carbon monoxide.

Figure 2 shows a number of Sm_2O_3 capsules after welding. Different capsule materials are labeled in the photograph. No difficulties were encountered in any of the welding operations.

The Pm_2O_3 capsules were welded in an electron beam welder specially designed to handle radioactive materials. A complete description of the operation is given in a separate report.(4)

4.2.5 Pneumatic Impaction of Test Couples

A number of test couples were pneumatically impacted prior to testing. This was done for two reasons: (1) to increase oxide-metal contact and (2) to increase oxide density. A description of the pneumatic impaction process is given in BNWL-1041.(7)

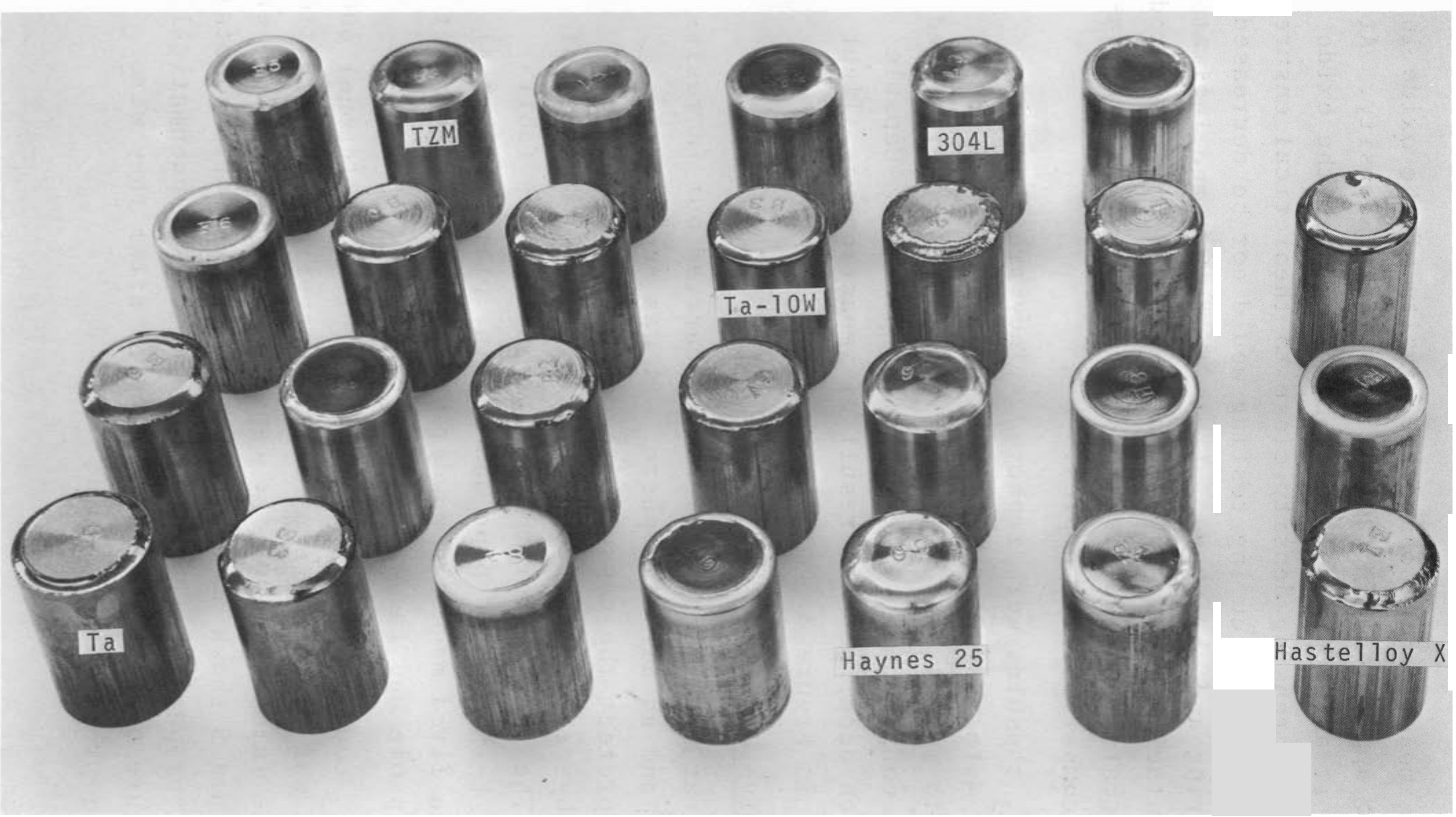


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FIGURE 2 Typical Samarium Sesquioxide Couples After Welding - Test Metals Labeled

Pneumatic impaction increased the density of the oxide in the capsules to approximately 100% of theoretical density. At the same time, it assured excellent contact between the oxide and the metal. Increasing density close to theoretical ensured that oxide-metal contact during testing would not be decreased by oxide sintering and shrinkage. It is felt that the intimate oxide-metal contact achieved by pneumatic impaction represented the most stringent test condition possible (at a given temperature) for the compatibility couples.

Five Pm_2O_3 capsules were impacted. They are shown in Figure 3. The metal capsules were sealed in jackets of 304L SS prior to impaction. The stainless steel jacket served to protect the couple during the impaction process. Capsule distortion which occurred as a result of impaction was slight as can be seen in Figure 3.

4.2.6 Protective Jackets

The tests at 1100 °C and lower were carried out in resistance furnaces and an air atmosphere. It was necessary, therefore, to protect the capsule from external oxidation. This was done by sealing the couples in protective jackets of Inconel 600. The jackets for the Sm_2O_3 couples were fabricated from 1-1/4-in. SCH 40 pipe and 1/8-in. plate (Figure 4). A layer of high-fired magnesia powder prevented direct contact between the capsule and the jacket.

Each Pm_2O_3 couple was sealed in two protective Inconel 600 jackets. This was to ensure against any potential contamination problems if the integrities of the capsule and inner jacket were breached. Figure 5 shows an exploded view of the various metal layers used in preparing a Pm_2O_3 capsule which was pneumatically impacted. Figure 6 shows the Pm_2O_3 couples after they were sealed in their protective jackets.

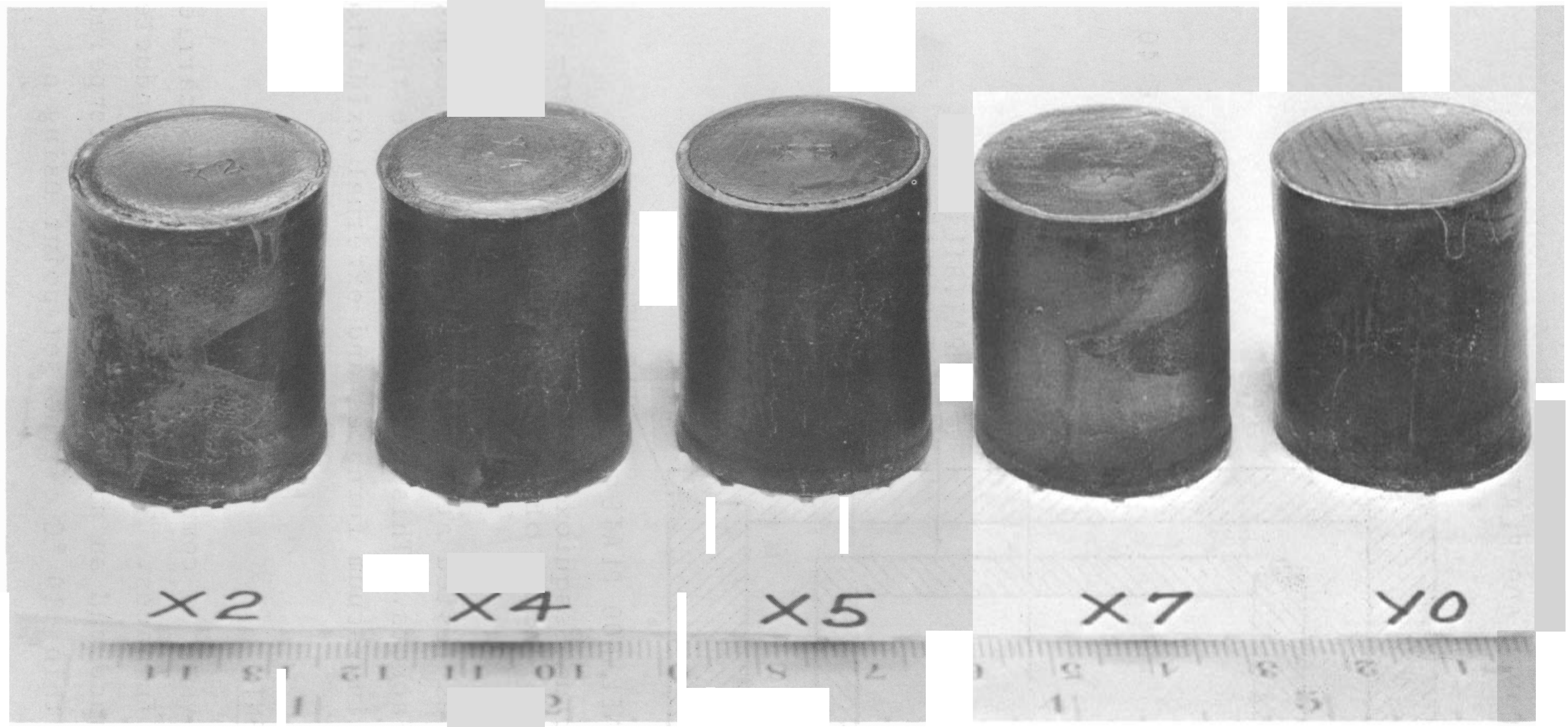

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FIGURE 3 Pneumatically Impacted Promethium Sesquioxide Couples

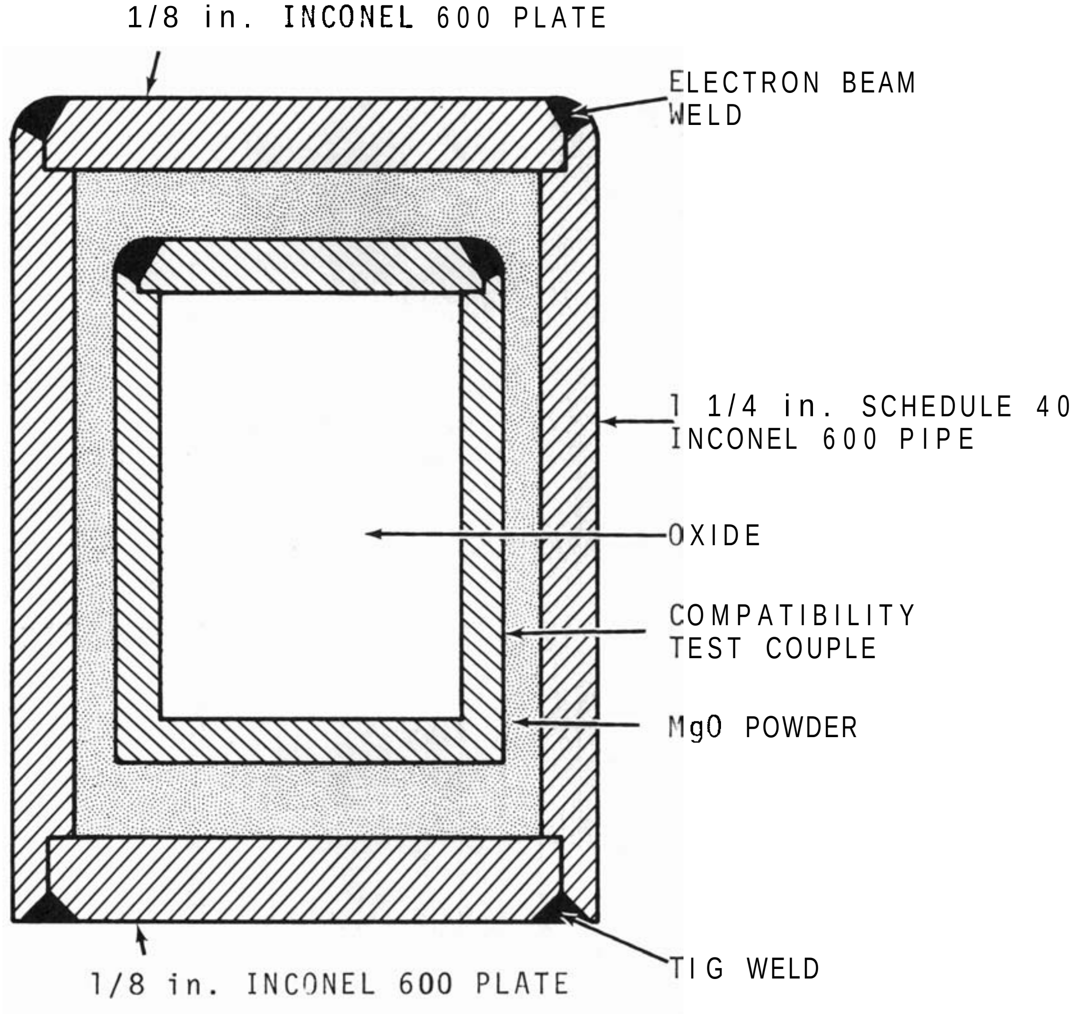

FIGURE 4. Samarium Sesquioxide Test Couple with Protective Jacket of Inconel 600

The Sm_2O_3 couples tested at 1550 and 2000 °C were exposed without protective jackets. This was possible because the couples were tested in vacuum furnaces and external oxidation was not a problem.

4.3 TESTING EQUIPMENT

Testing of the various compatibility couples was carried out in a variety of furnaces. The Pm_2O_3 tests were conducted in a resistance furnace and an air atmosphere. The temperature was controlled to within ±10 °C of the set point using a

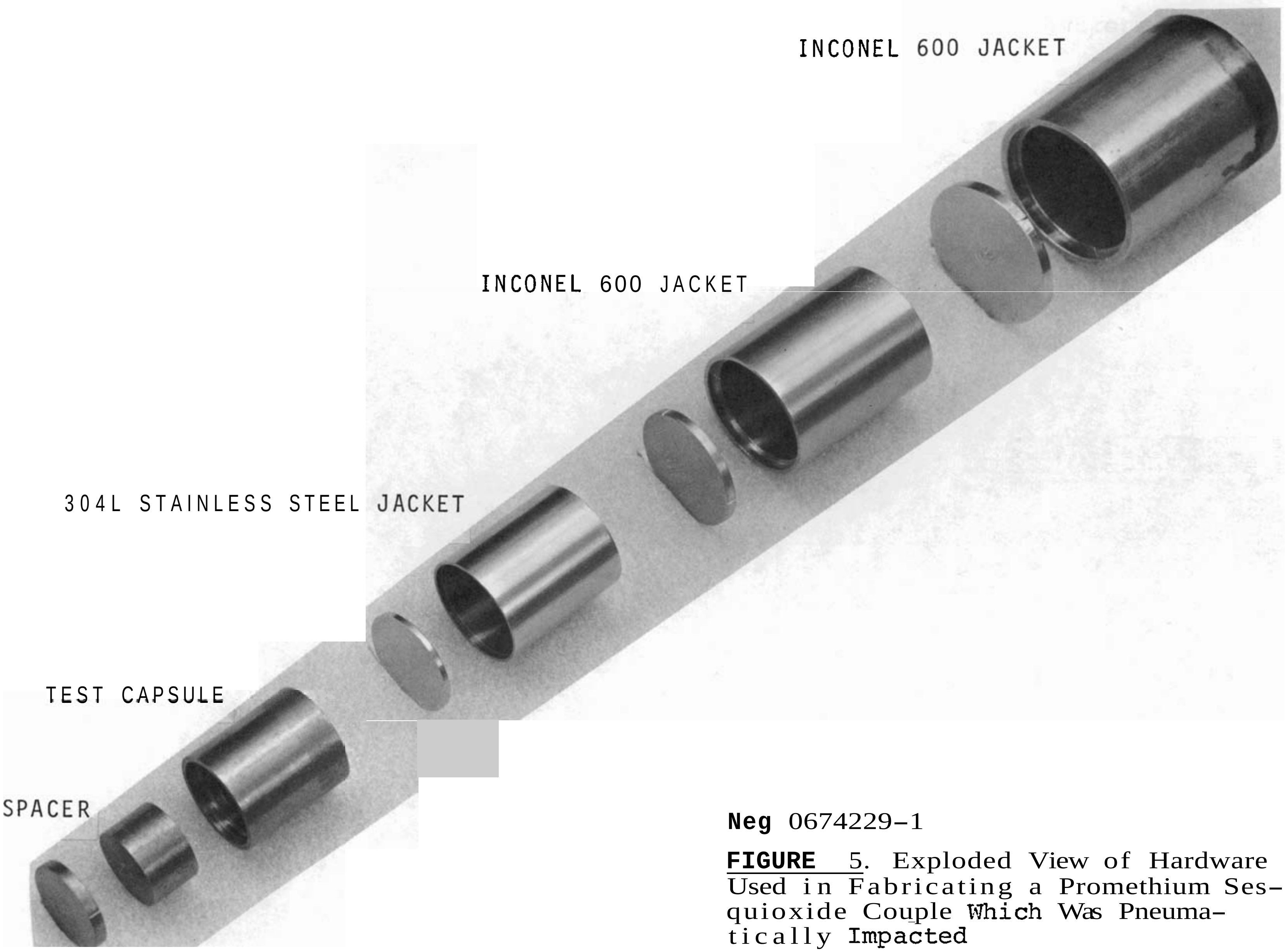

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FIGURE 5. Exploded View of Hardware Used in Fabricating a Promethium Sesquioxide Couple Which Was Pneumatically Impacted

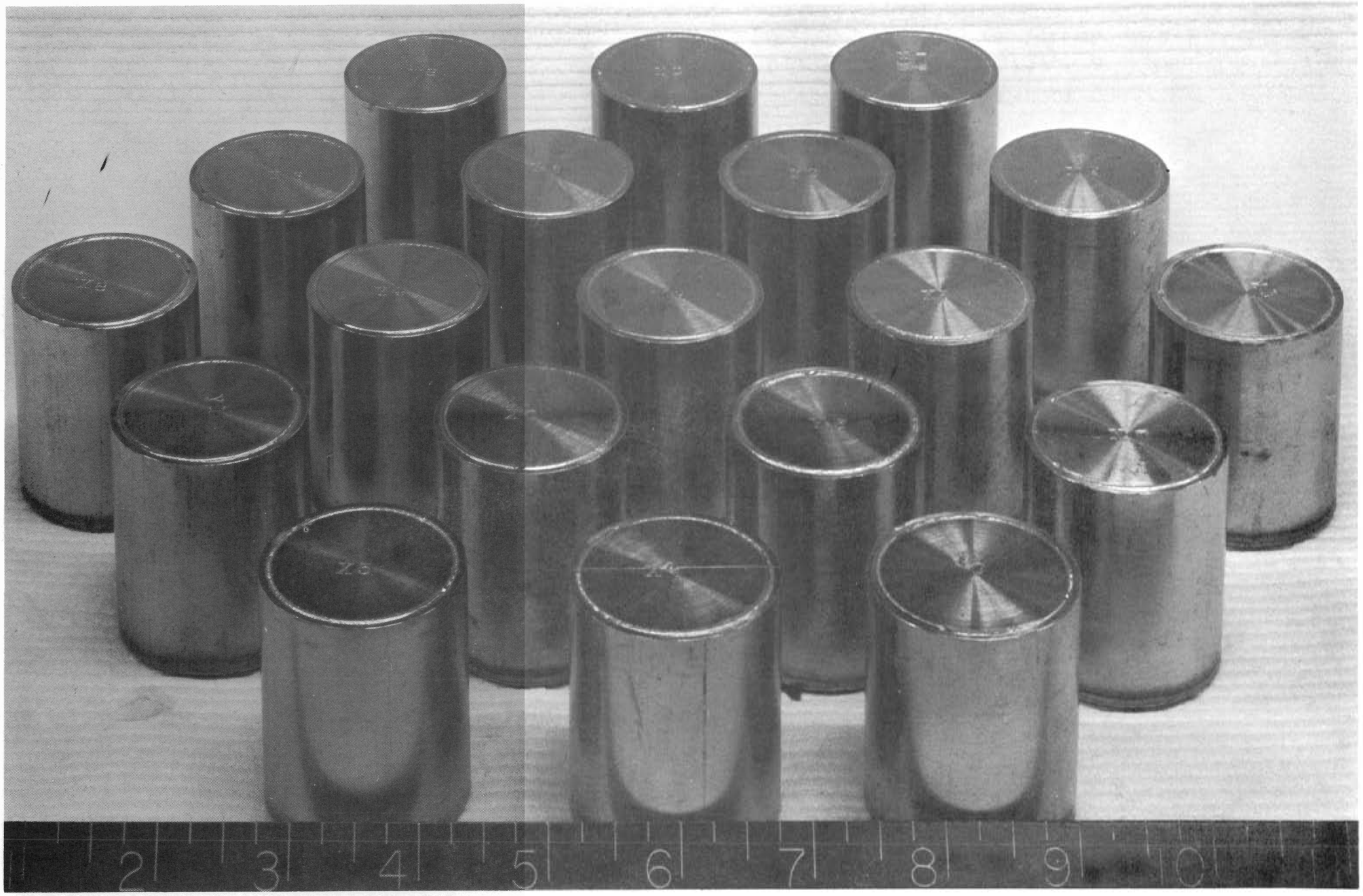

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FIGURE 6. Promethium Sesquioxide Couples Sealed in Protective Jackets of Inconel 600

proportioning controller and a Chromel-Alumel thermocouple. The temperature profile within the furnace chamber showed a maximum variation of 20 °C. Reliability of the equipment was very good, and only one loss of power was encountered during the 18-month test schedule (due to a thermocouple failure). For safety considerations, the furnace was equipped with a variable transformer which limited the power input to the furnace. The maximum power setting was such that the furnace temperature (in case of controller failure) could not exceed 1100 °C. The tests were carried out in a radiochemical facility equipped for remote operation.

The Sm_2O_3 tests at 1100 °C were conducted in a large resistance furnace. An air atmosphere was maintained in the chamber of the furnace. The temperature was maintained within ±10 °C using a proportioning controller and a Chromel-Alumel thermocouple. The temperature profile of the furnace showed a maximum variation of 15 °C from the control temperature of 1100 °C. Operationally, the furnace was less reliable than the furnace used for the Pm_2O_3 tests. Four power losses were encountered during the 2-year test schedule. One was caused by a burned out thermocouple and the other three resulted from heating element failure.

Tests with Sm_2O_3 in which the temperature was cycled between 700 and 1100 °C were carried out in a furnace identical to the one used for the 1100 °C Sm_2O_3 tests. The furnace was instrumented so that the power was turned off when the furnace temperature reached 1100 °C and came back on when the temperature dropped to 700 °C. Heat-up and cool-down rates of the furnace were such that 24 hr were required for one temperature cycle. Reliability of the furnace was poor and three power losses occurred during the 12-month test schedule: two due to heating element failure and one due to thermocouple failure.

The high-temperature tests with Sm_2O_3 were carried out in two resistance-heated vacuum furnaces (Figure 7). The 1550 °C

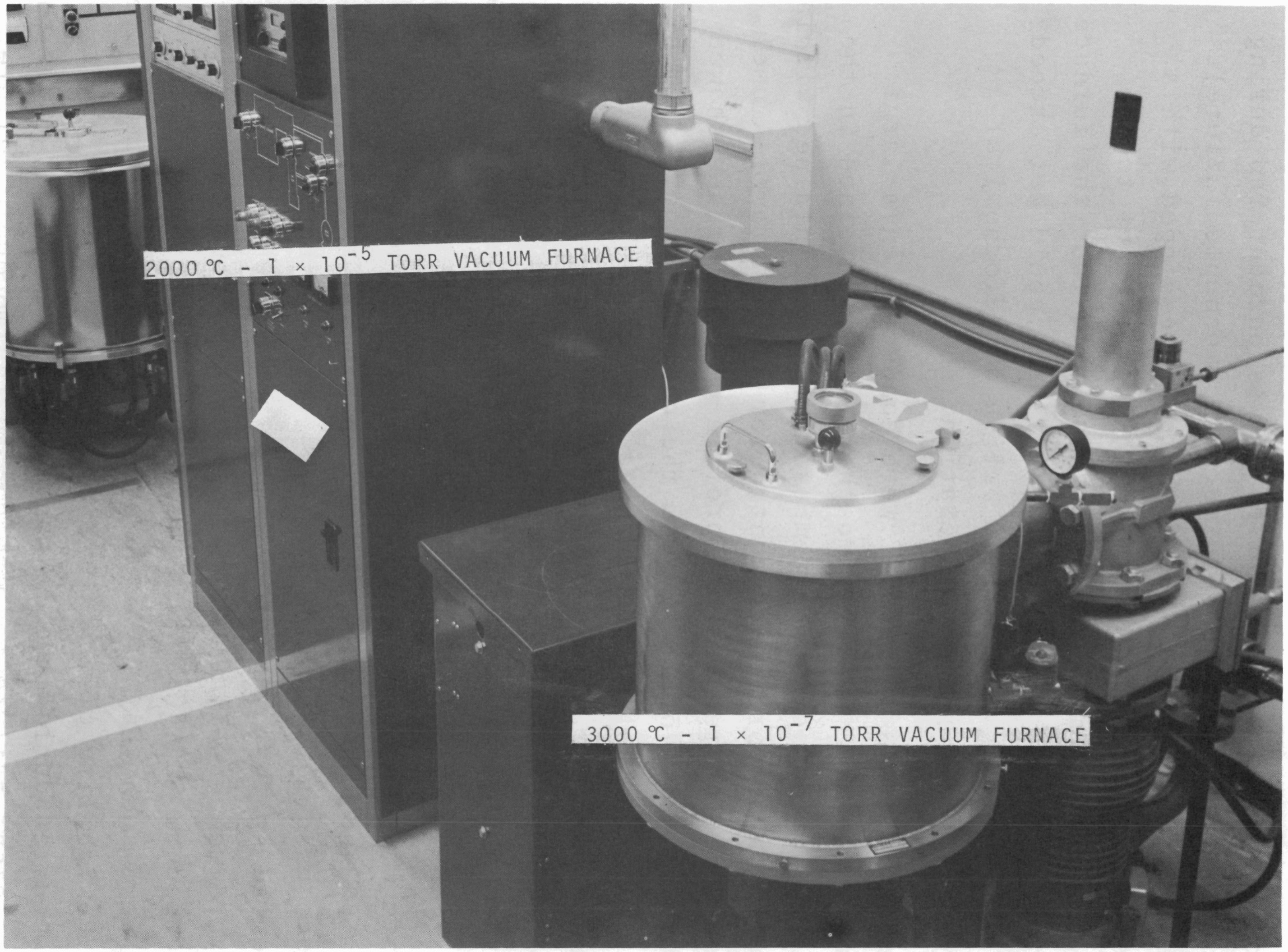

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FIGURE 7. High Temperature Vacuum Furnaces Used for Testing Samarium Sesquioxide Couples

tests were conducted in a furnace equipped with tantalum heating elements. The furnace had a maximum temperature capability of 2000 °C and was controlled within ±10 of the set point with a W/W-26% Re thermocouple. The temperature was checked periodically with an optical pyrometer. Chamber pressure was approximately 1 × 10^{-5} Torr. Furnace reliability was excellent, and no power losses occurred during the 1000 and 4300-hr tests.

The 2000 °C Sm_2O_3 tests were carried out in a furnace equipped with tungsten heating elements. Maximum temperature capability of the furnace was 3000 °C and chamber operating pressure was 2 × 10^{-7} Torr. The temperature was controlled within +25 °C of the set point by limiting the power input to the furnace. The temperature was monitored with an optical pyrometer. Furnace reliability was poor and several power losses occurred during the 1000 and 3000 hr tests.

4.4 COUPLE ANALYSIS AND EVALUATION

At the conclusion of a test the couple was cooled to room temperature; the protective jacket, if any, was removed. The test couple was then sectioned with an abrasive saw as shown below. Water-cooled, rubber-bonded silicon carbide cut-off

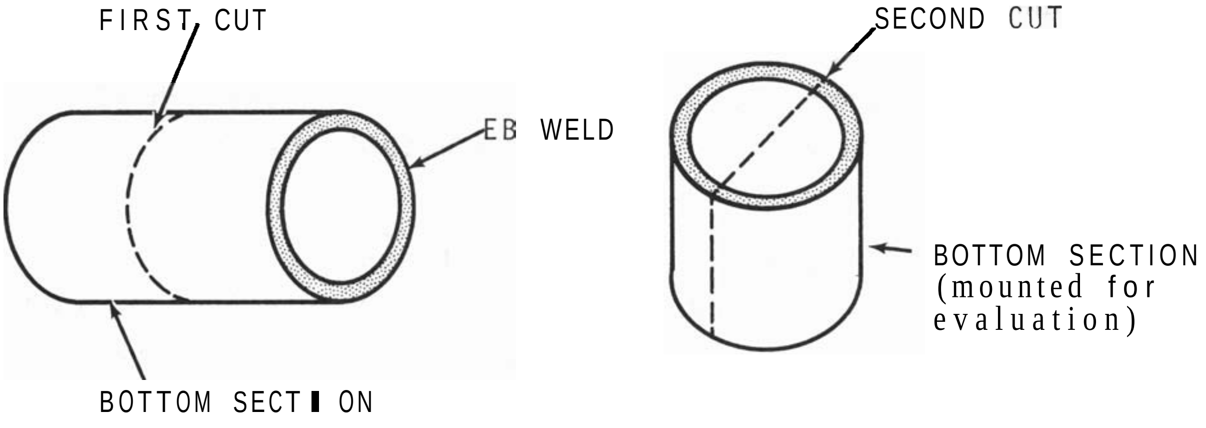


FIGURE 8. Sectioning of Test Couple for Evaluation

blades were used for the sectioning. Jacket removal and sectioning of the Pm_2O_3 tests couples was accomplished in a lead-shielded glove box.

After sectioning, a portion of the couple was mounted, polished, and etched. The etched section was examined by microscope, and photomicrographs were obtained of the metal surface in contact with the oxide. All metallographic operations on the Pm_2O_3 couples were conducted in a shielded glove box. The mounted sections of a number of capsules were also analyzed by electron microprobe to measure the diffusion between couple components.

The extent of metal-oxide interaction was normally determined from the photomicrographs and electron microprobe analysis. In those couples where there was evidence of extensive interaction, attempts were made to identify the reaction products by X-ray diffraction.

5. RESULTS AND DISCUSSION

Metallographic examination and electron microprobe analysis were the primary tools used to measure oxide-metal interaction in the test couple. Photomicrographs were obtained of the areas of maximum oxide-metal reaction. Electron microprobe analysis was then performed on the same areas. Excellent agreement on couple interaction was achieved between metallographic and microprobe evaluation. Tables 6 through 13 present data representing the maximum attack observed in the various couples.

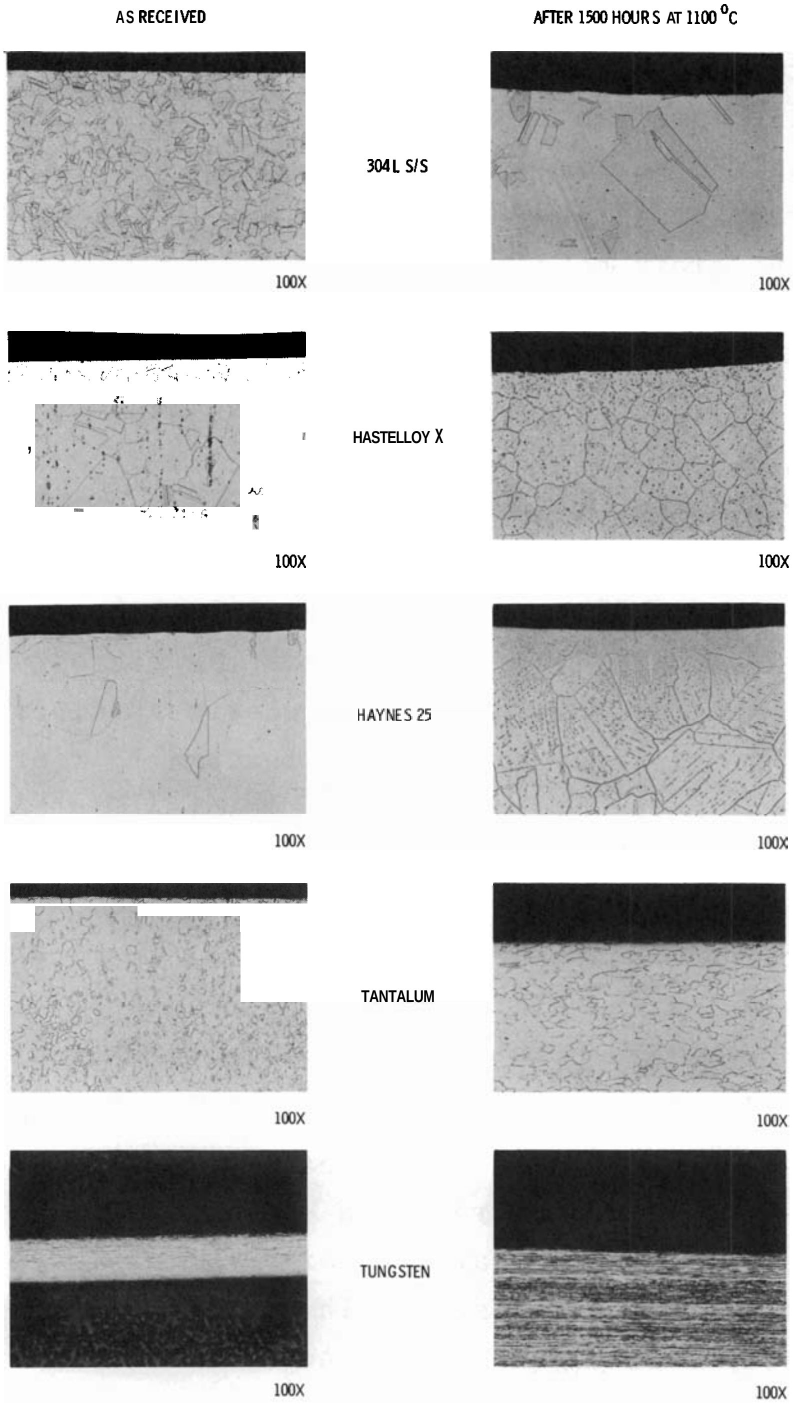
In those couple where extensive attack was observed, the previously-mentioned attempts to identify reaction products by X-ray diffraction were largely unsuccessful. This method was abandoned after several couples had been analyzed. The only reaction product definitely identified by X-ray diffraction was Ta_2O_3 which was found in $Ta\text{-}Sm_2O_3$ couples which had been temperature cycled.

It is possible for the oxide-metal components of the different couples to react in various ways. These include:

- Layer type corrosion of the metal surface. This primarily involves the formation of a metal oxide layer on the surface of the metal.
- Intergranular attack where diffusion of the oxide occurs along the grain boundaries.
- Alterations in the micro-structure of the metal phase of the couple.
- Void formation below the surface of the metal phase.
- Dissolution of the metal surface.

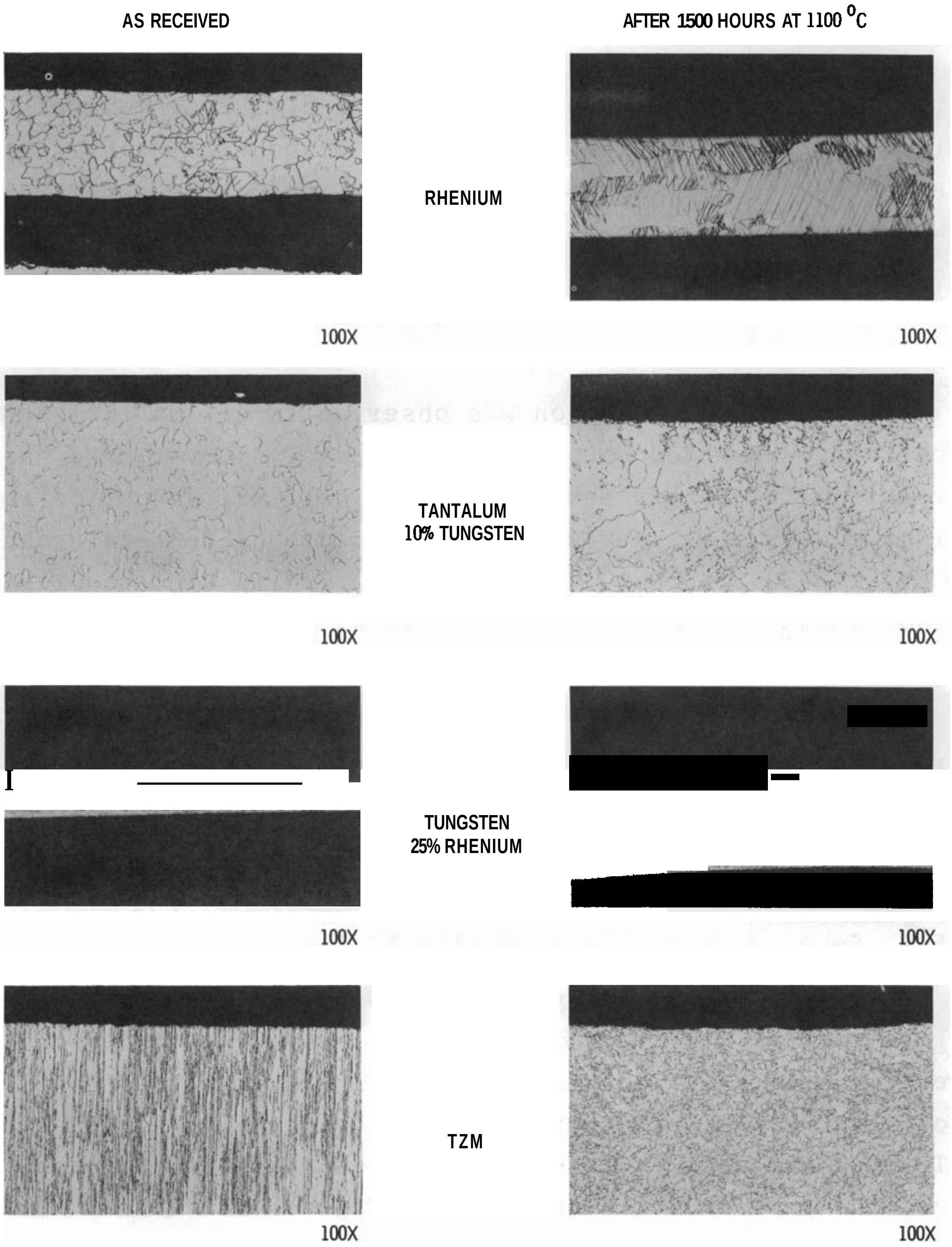
Each type of attack was observed in one or more of the test couples. In some of the couples, two or more types of reaction were present. It is difficult to obtain a quantitative measure of oxide metal interaction from the microprobe analysis and photomicrographs. The numerical values of oxide-metal reaction presented in Tables 6 through 13 represent qualitative estimates of the depth of metal affected by the oxide. Where very slight interaction was observed, an arbitrary value of <1 mil was assigned to the affected metal zone. Zero interaction was assumed when the metal surface of the couple was similar to reference metal specimens which had been heated to the test temperature without oxide present. Figure 9 shows photomicrographs of the reference metal specimens.

Pneumatic impaction involves heating the test couple to a relatively high temperature for a short period of time. There is the possibility that some oxide-metal reaction might occur during the impaction step. Therefore, Sm_2O_3 couples of each metal were sectioned and examined after impaction. No reaction was found to have occurred in most of the couples. Only the 304L SS-Sm_2O_3 and Ta-Sm_2O_3 couples showed a very slight reaction (<0.1 mils).



Neg 701736-8

FIGURE 9. Photomicrographs of Reference Metal Samples - As-Received from Vendor and After 1500 hr at 1100 °C



Neg 701736-7

FIGURE 9. (Contd)

5.1 Pm_2O_3 - METAL COMPATIBILITY AT 1100 °C

Tests at 1100 °C for periods up to 18 months showed very little reaction between Pm_2O_3 and any of the nine metals tested (see Table 6). Photomicrographs of a number of test capsules are presented in Figures 10 and 11. When oxide-metal reaction was found, it was primarily layer-type corrosion or solution attack. There was little evidence of void formation, intergranular attack or changes in the microstructure of the metal phase as a result of oxide attack.

Oxide-metal reaction was observed in all of the pneumatically impacted couples. In no case, however, did the reaction layer thickness exceed one-half mil. Most of the nonimpacted couples showed essentially zero oxide-metal reaction. Only the 304L SS-Pm_2O_3 and TZM-Pm_2O_3 nonimpacted couples showed some evidence of oxide attack. In each case, the attack was less than one-half mil.

The W-Pm_2O_3 couples showed no evidence of oxide-metal reaction, but some intergranular cracking of the tungsten foil was observed. However, this did not appear to be due to oxide attack. Tungsten foil in a dummy capsule (no oxide present) after heating to 1100 °C showed the same intergranular cracking.

5.2 Sm_2O_3 - METAL COMPATIBILITY AT 1100 °C

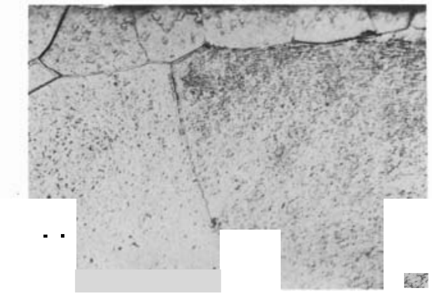
Tests with Sm_2O_3 at 1100 °C for periods up to 2 years gave results which were in good agreement with the results obtained with Pm_2O_3. In general, very little reaction was observed between the purified Sm_2O_3 and the nine test metals. This can be seen by referring to the data presented in Table 7 and the photomicrographs shown in Figures 12 and 13. The maximum interaction observed in any of the test couples was 2 mils (with Ta-Sm_2O_3). In most of the couples layer type corrosion or surface dissolution were the predominant type of attack.

TABLE 6. Metal-Pm_2O_3 Compatibility Data at 1100 °C

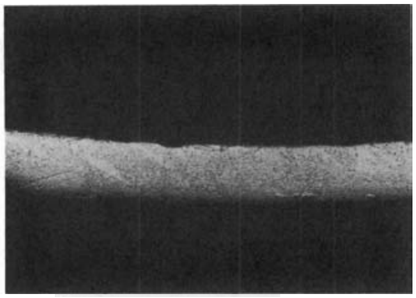
Metal	Fabrication Method[a]	Reaction Zone Thickness, mils 12 months	 18 months
304L SS	PS	<0.5	
304L SS	PI	<0.5	
Hastelloy X	PS	0	
Hastelloy X	PI	<0.5	
Haynes 25	PS	0	
Haynes 25	PI	<0.5	
Tantalum	PS	0	0
Tantalum	PI	<0.5	
Ta-10% W	PS	0	0
Ta-10% W	PI	0	
Tungsten	PS	0(b)	0(b)
Rhenium	PS	0	0
W-25% Re	PS	0	0
TZM	PS	0.5	

(a) PS - *Pressed and sintered pellets*
PI - *Pressed and sintered pellets-capsule pneumatically impacted*

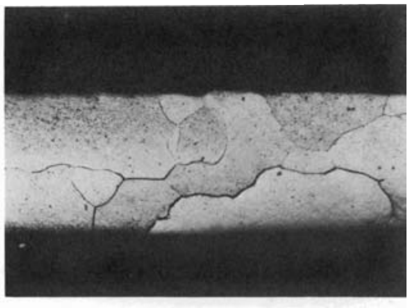
(b) *Some intergranular cracking observed*



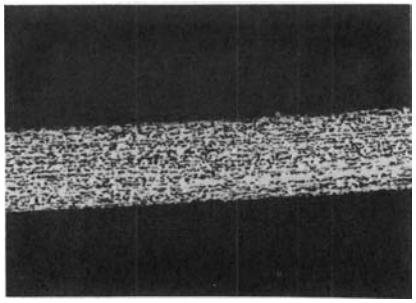
250X
TANTALUM



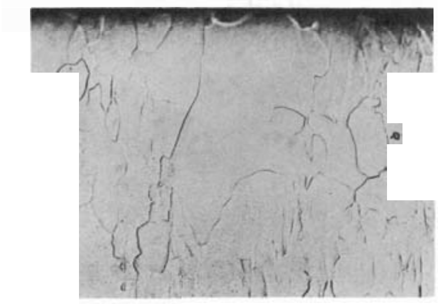
250X
RHENIUM



250X
TUNGSTEN



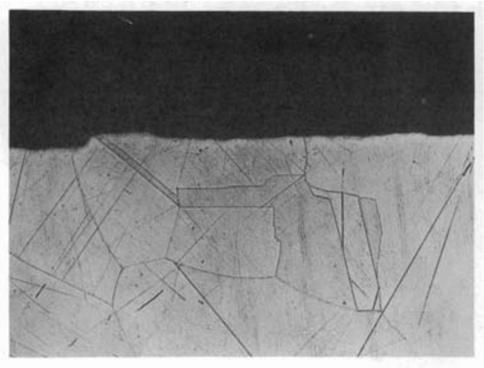
250X
TUNGSTEN-2% RHENIUM



250X
TANTALUM-10% TUNGSTEN

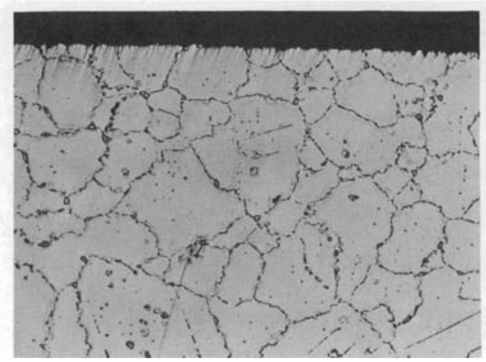
Neg 701736-2

FIGURE 10. Promethium Sesquioxide Couples Tested at 1100 °C for 18 Months



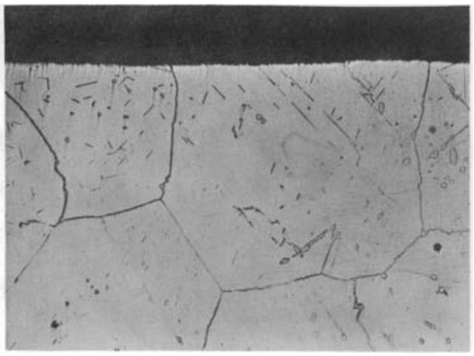
100X

304L S/S



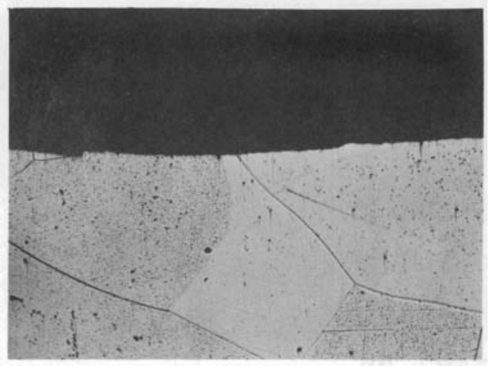
IOOX

HASTELLOY X



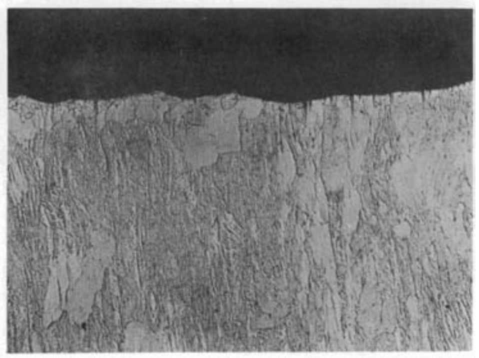
IOOX

HAYNES 25



IOOX

TANTALUM



IOOX

TANTALUM-10% TUNGSTEN

Neg 701736-4

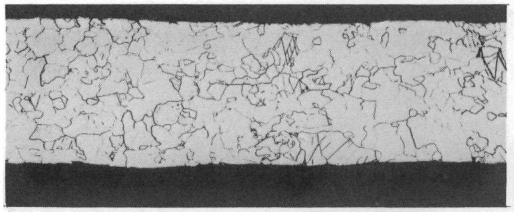
FIGURE 11. Pneumatically Impacted Promethium Sesquioxide Couples Tested at 1100 °C for 12 Months

TABLE 7. Metal-Sm_2O_3 Compatibility Data at 1100 °C

Metal	Fabrication Method(a)	Reaction Zone Thickness, mils			
		1,500 hr	4,300 hr	8,800 hr	17,600 hr
304L SS	SP		<1	<1	<1
304L SS	PI	1	1	1	1
304L SS	PS			0	
Hastelloy X	SP		<1	1	<1
Hastelloy X	PI	<1	1	2	<1
Haynes 25	SP		<1	1	<1
Haynes 25	PI	1	<1	2	1
Tantalum	SP		1	2	1
Tantalum	PI	2	2	2	2
Tantalum	PS			0	
Rhenium	SP		0	0	0
Rhenium	PI	0	0	0	0
Rhenium	PS			0	
Ta-10% W	SP		<1	1	1
Ta-10% W	PI		<1	1	1
Ta-10% W	PS			<1	
W-25% Re	SP		<1	<1	<1
W-25% Re	PI	<1	<1	<1	<1
TZM	SP		<1	<1	<1
TZM	PI	<1	<1	<1	<1
TZM	PS			0	

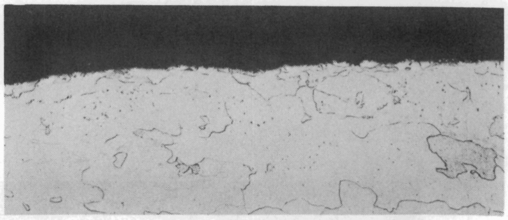
		1,500 hr	8,800 hr	12,000 hr
Tungsten	SP		<1	<1
Tungsten	PI	0	<1	<1

(a) SP - Oxide step pressed into capsule
PI - Oxide step pressed into capsule-capsule pneumatically impacted
PS - Capsule filled with pressed and sintered pellets



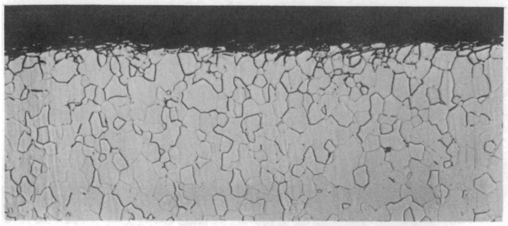
100X

RHENIUM
17,600 HOURS



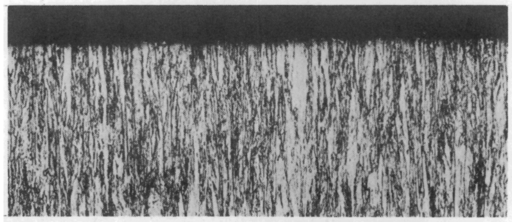
100X

TANTALUM
8800 HOURS



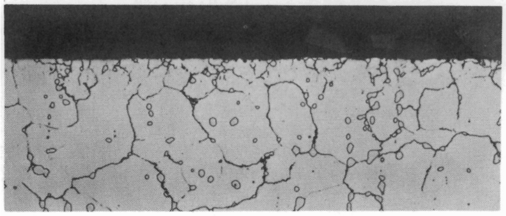
100X

TANTALUM-10% TUNGSTEN
17,600 HOURS



100X

TZM
17,600 HOURS

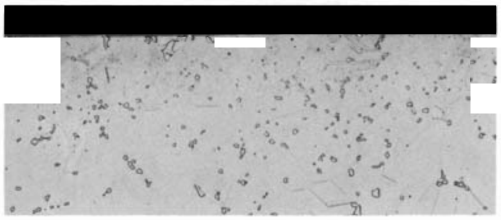


100X

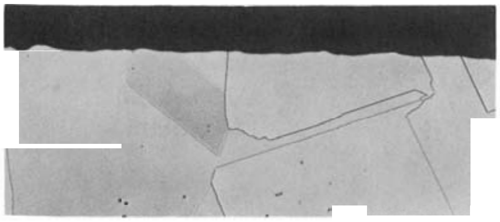
HASTELLOY X
17,600 HOURS

Neg 701736-5

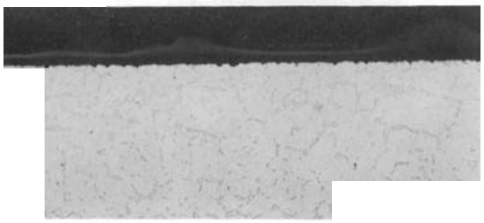
FIGURE 12. Photomicrographs of Samarium Sesquioxide Couples Tested at 1100 °C - Couples Pneumatically Impacte Prior to Testing



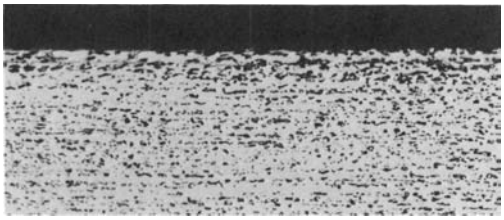
HAYNES 25
17,600 HOURS



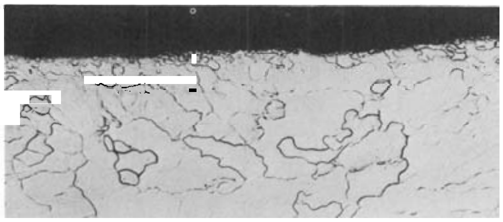
304L SIS
17,600 HOURS



HASTELLOY X
17,600 HOURS



TUNGSTEN-25% RHENIUM
17,600 HOURS



TANTALUM
8800 HOURS

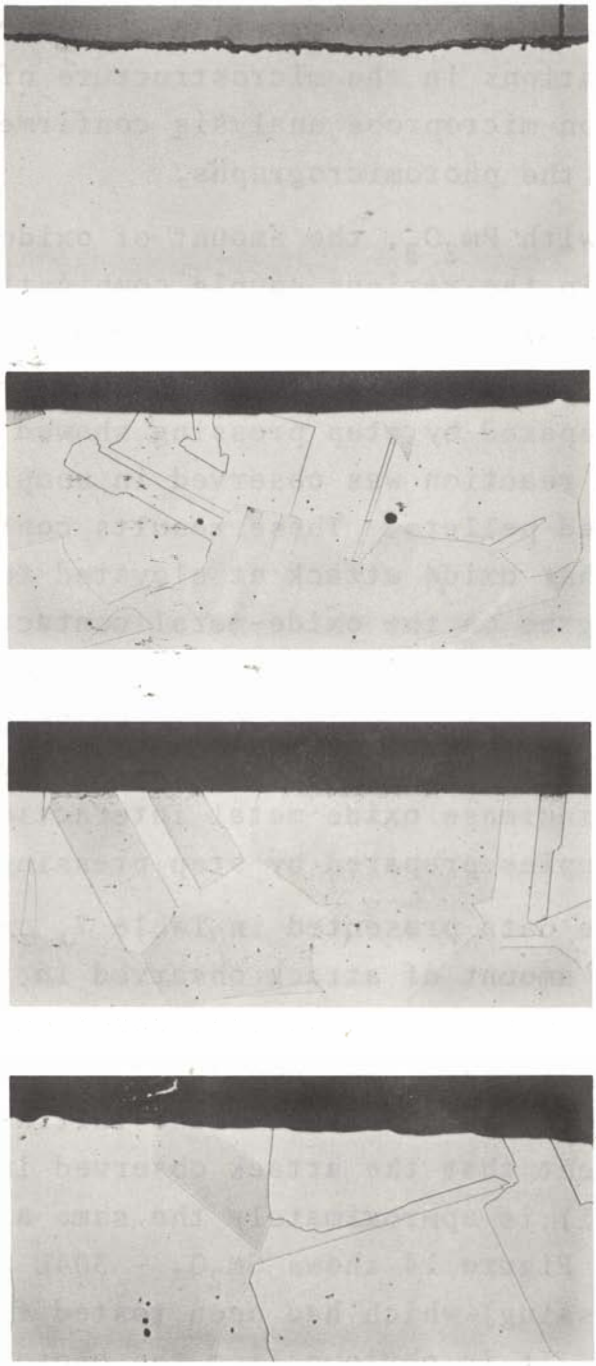
Neg 701736-6

FIGURE 13. Nonimpacted Samarium Sesquioxide Couples Tested at 1100 °C

There was little evidence of void formation, intergranular penetration, or alterations in the microstructure of the metal phases. Electron microprobe analysis confirmed the results obtained from the photomicrographs.

As was the case with Pm_2O_3, the amount of oxide-metal interaction observed in the various couple combinations depended on the method used to fabricate the couples. Couples prepared by pneumatic impaction showed the greatest oxide-metal reaction. Couples prepared by step pressing showed somewhat less reaction, and no reaction was observed in couples prepared using sintered pellets. These results confirm the original assumption that oxide attack at elevated temperatures depends to a large degree on the oxide-metal contact obtained in fabricating the couple. It is difficult to place a quantitative measure on the effect of oxide-metal contact on couple interaction. A qualitative estimate would be that pneumatic impaction appears to increase oxide metal interaction by about 50% as compared to couples prepared by step pressing.

In evaluating the data presented in Table 7, one fact becomes obvious. The amount of attack observed in the couples tested for 2 years is no greater than that observed in couples tested for 6 months or 1 year. And comparing the results of the current tests with those obtained in the initial scouting studies makes it evident that the attack observed in the 1500-hr tests (Table 1) is approximately the same as that found after 2 years. Figure 14 shows Sm_2O_3 - 304L SS couples (prepared by step pressing) which had been tested for 1500 to 17,600 hr at 1100 °C. It is obvious from the photomicrographs that the couple tested for 17,600 hr shows no more attack than the couple tested for 1500 hr. These results were completely unexpected. One would predict an increase in metal-oxide interaction with time, although the rate should decrease



1500 HOURS

4300 HOURS

8800 HOURS

17,600 HOURS

Neg 761843-1

FIGURE 14. Samarium Sesquioxide - 304L SS Couples, Prepared by Step Pressing, After Testing at 1100 °C (each at 100X)

as the reaction layer becomes thicker. Since this was not the case, it would appear that the reactions observed involved more than a simple reaction between the oxide and the metals. It is possible that the oxide-metal interactions observed are due to an impurity in the oxide, and the impurity is consumed in a relatively short time (<1500 hr).

As stated previously, there was good agreement between the results obtained with Sm_2O_3 and those obtained with Pm_2O_3. In fact, the Pm_2O_3 appears to be slightly less reactive to the test metals than Sm_2O_3. Therefore, Sm_2O_3 appears to be a good stand-in for Pm_2O_3 in compatibility testing, and the results obtained with Sm_2O_3 in the various test programs should be completely applicable to Pm_2O_3.

Based on all the tests at 1100 °C, rhenium appears to be the best metal to contain Pm_2O_3. No reaction was observed between rhenium and Pm_2O_3 or Sm_2O_3 in any of the 1100 °C tests. However, the results also show that any of the nine metals tested will do an adequate job of containing purified Pm_2O_3 at 1100 °C for periods up to 2 years.

5.3 THERMOCYCLING TESTS WITH Sm_2O_3

Tests with Sm_2O_3 in which the temperature was cycled daily between 700 and 1100 °C gave erratic and conflicting results. In the originally scheduled series of tests (see Table 4), which lasted up to 1 year, a number of couples showed extensive oxide-metal interaction. In addition, several of the capsules ruptured during testing so no valid measure of oxide-metal interaction could be made. Only rhenium and W-25% Re showed significant resistance to oxide attack during temperature cycling tests (see Table 8A).

Layer-type corrosion or surface dissolution was apparent in all the couples showing extensive attack. In addition, intergranular penetration and void formation was evident in several of the couples (see Figure 15). The superalloys, Hastelloy X and Haynes 25, appeared to be especially receptive to oxide attack during thermocycling.

The excessive amount of attack observed and the erratic nature of the results raised some question as to the validity of the results. Therefore, a second series of tests was run using Hastelloy X-Sm_2O_3 and Haynes 25-Sm_2O_3 couples. Six couples of each composition were prepared and tested for 1500 hr with the temperature cycled daily between 700 and 1100 °C. Extreme care was taken to insure that no impurities were introduced into the couples during fabrication. The results of the tests are presented in Table 8B. Very little oxide-metal interaction was observed in any of the couples. The average reaction of each set of six couples was less than 1 mil, with the maximum reaction zone thickness detected being 1 mil (see Figure 16).

The results of the second series of tests would seem to indicate that the initial tests were invalid. The erratic results of the first test and the fact that several of the capsules ruptured indicated that something was wrong with the test program. It may be that impurities (i.e., water-CO_2) were accidently introduced into the couples during fabrication, and the impurities affected the results obtained. Such a conclusion is substantiated by the fact that when impurities such as water and carbon were intentionally introduced into Sm_2O_3 test couples, the rate of oxide-metal interaction was greatly increased (see Section 5.5).

It is apparent that additional work is needed to adequately define the effect of temperature cycling on oxide-metal interaction. Time and budget considerations did not permit additional testing during the current program.

TABLE 8. Sm_2O_3-Metal **Compatibility with Temperature Cycled Daily Between 700 and 1100 °C**

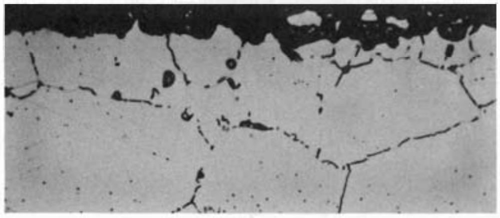
Metal	Fabrication Method(a)	Reaction Zone Thickness, mils 1,000 hr	 4,300 hr	 8,800 hr
(A) First Series of Tests				
304L SS	SP	1	3	R(b)
304L SS	PI	2	4	5
Hastelloy X	SP	2	5	R
Hastelloy X	PI	R(b)	5	5
Haynes 25	SP	5	10	R
Haynes 25	PI	5	15	5
Tantalum	SP	3	2	R
Tantalum	PI	R	2	4
Rhenium	SP	R	0	0
Rhenium	PI	R	<1	0
Ta-10% W	SP	0	5	R
Ta-10% W	PI	R	5	5
Tungsten	SP		5	
Tungsten	PI		2	
W-25% Re	SP	0	0	0
W-25% Re	PI	R	2	0
TZM	SP	R	<1	4
TZM	PI	0	2	3

Metal	Fabrication Method	Reaction Zone Thickness, mils 1,500 hr(c)
(B) Second Series of Tests		
Hastelloy X	PI	<1
Haynes 25	PI	<1

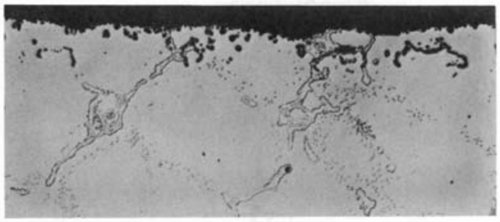
(a) *SP - Oxide step pressed into capsule*
PI - Oxide step pressed into capsule-capsule pneumatically impacted

(b) *R - Capsule ruptured*

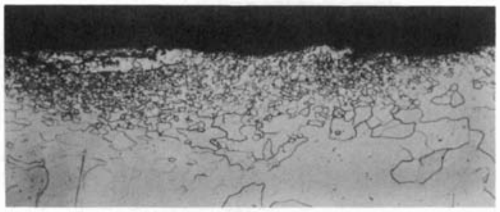
(c) *Average of six couples.*



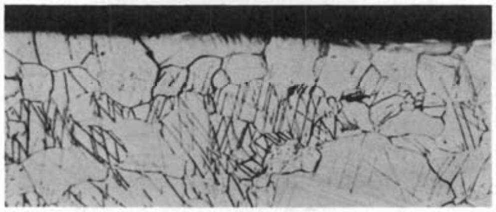
304L SIS - 500X
8800 HOURS
PNEUMATICALLY IMPACTED



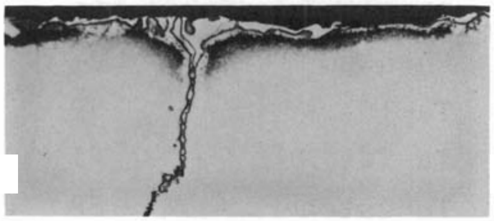
HASTELLOY X - 100X
4300 HOURS



TANTALUM - 100X
8800 HOURS



RHENIUM - 500X
8800 HOURS

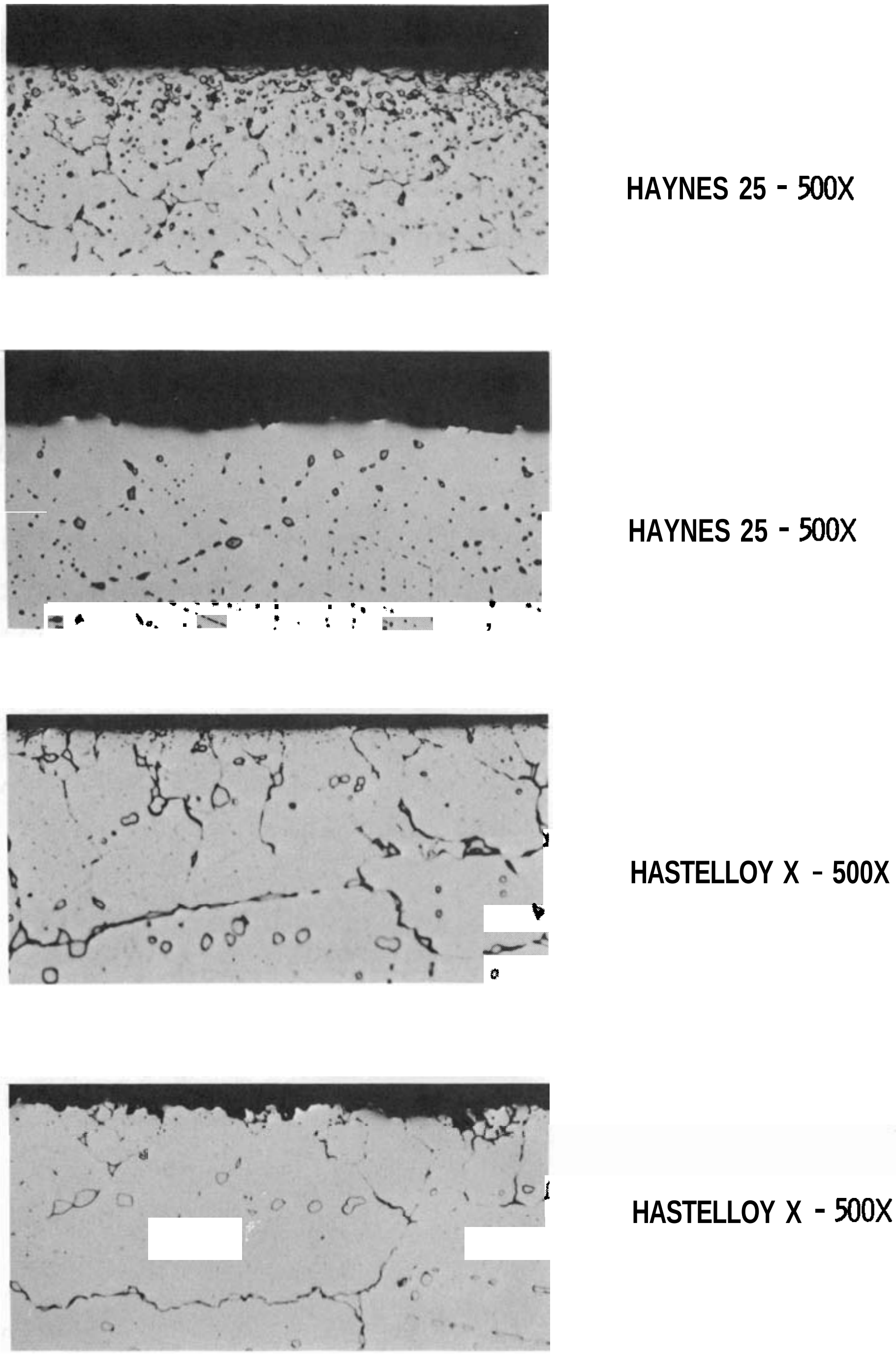


HAYNES 25 - 500X
4300 HOURS

TUNGSTEN - 25% RHENIUM-500X
4300 HOURS

Neg 701736-10

FIGURE 15. Samarium Sesquioxide Couples Which Had Been Cycled Daily Between 700 and 1100 °C - Initial Tests



Neg 701843-2

FIGURE 16. Sm_2O_3 - Hastelloy X and Sm_2O_3 - Haynes 25 Couples After Daily Cycling Between 700 and 1100 °C for 1500 hr - Repeat Tests

5.4 Sm_2O_3 - METAL COMPATIBILITY AT 1550 and 2000 °C

The Sm_2O_3-metal couples tested at 1550 °C for periods up to 4300 hr showed essentially the same type of interaction as was observed with couples tested at 1100 °C. Layer type corrosion and surface dissolution predominated with little evidence of intergranular attack or void formation. The amount of oxide-metal reaction found was generally low with a reaction layer thickness of 2 mils being the maximum observed in any of the test couples. The data for the 1550 °C tests are presented in Table 9. Photomicrographs of various test couples are shown in Figure 17.

Three to six couples of each composition were tested at 1550 °C for each time period. In general, the results for each set of couples were quite variable. The results presented in Table 9 are for the couples showing the maximum interaction. The average interaction for a set of couples was normally much less than the maximum reported. For example, six Ta-Sm_2O_3 couples were tested for 4300 hr. The interaction observed in each couple was as follows:

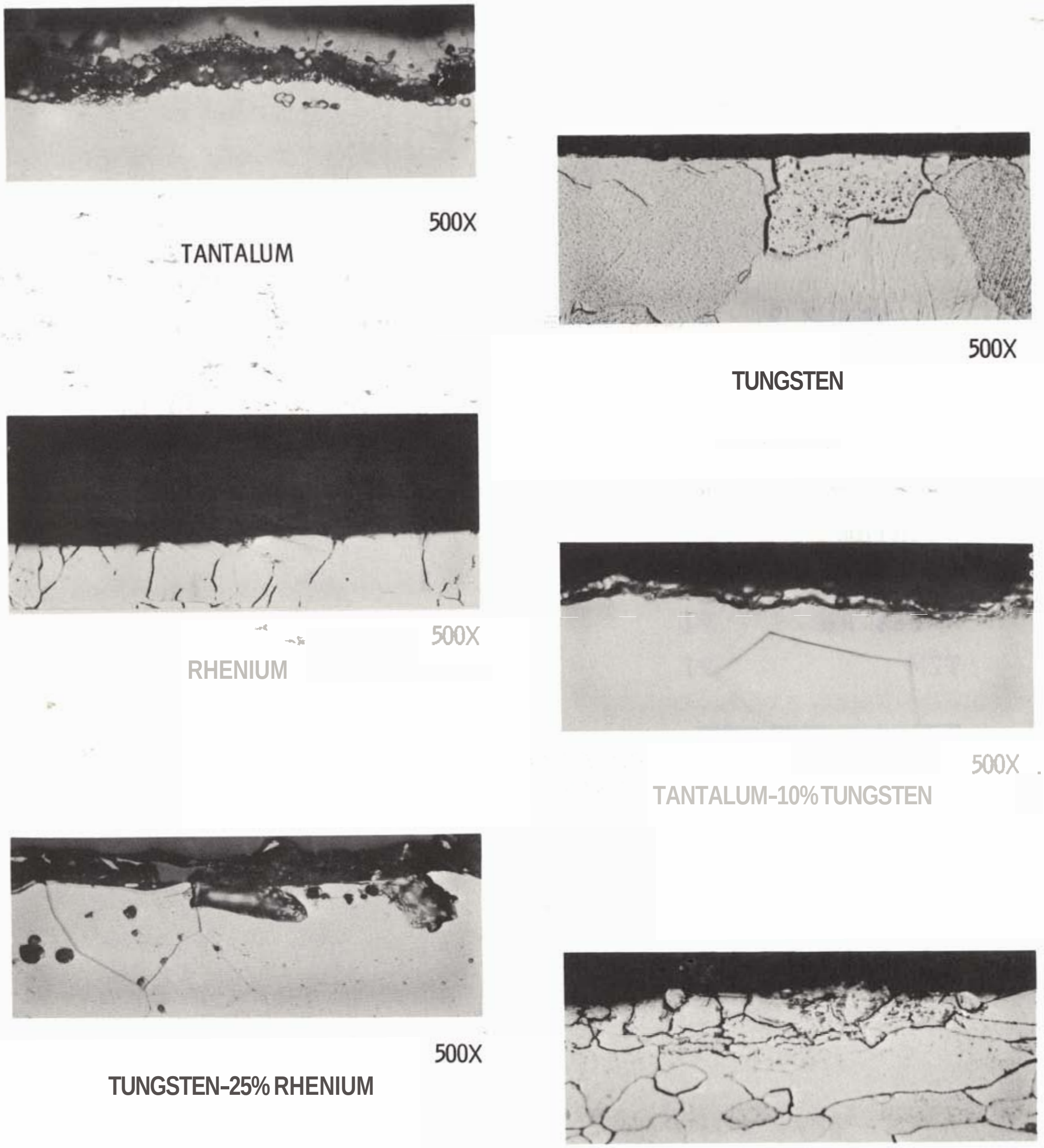
Couple	Reaction Layer, mils
1	0
2	<1
3	1
4	2
5	0
6	<1
Average	<1

Figure 18 shows some of the Ta-Sm_2O_3 couples. The variation in oxide attack is readily apparent. The other couple combinations showed a similar variation in data, except for the Re-Sm_2O_3 and W-Sm_2O_3 couples, none of which showed any interaction.

TABLE 9. Sm_2O_3-Metal **Compatibility at 1550 °C**

Metal	Fabrication Method[a]	Reaction Zone Thickness, mils	
		1,000 hr	4,300 hr
Tantalum	PI	2	2
Tungsten	PI	0	0
Rhenium	PI	0	0
Ta-10% W	PI	1	1
W-25% Re	PI	<1	1
TZM	PI	1	<1

(a) PI - Oxide step pressed into capsule-capsule pneumatically impacted.



500X

TANTALUM

500X

TUNGSTEN

500X

RHENIUM

500X

TANTALUM-10% TUNGSTEN

500X

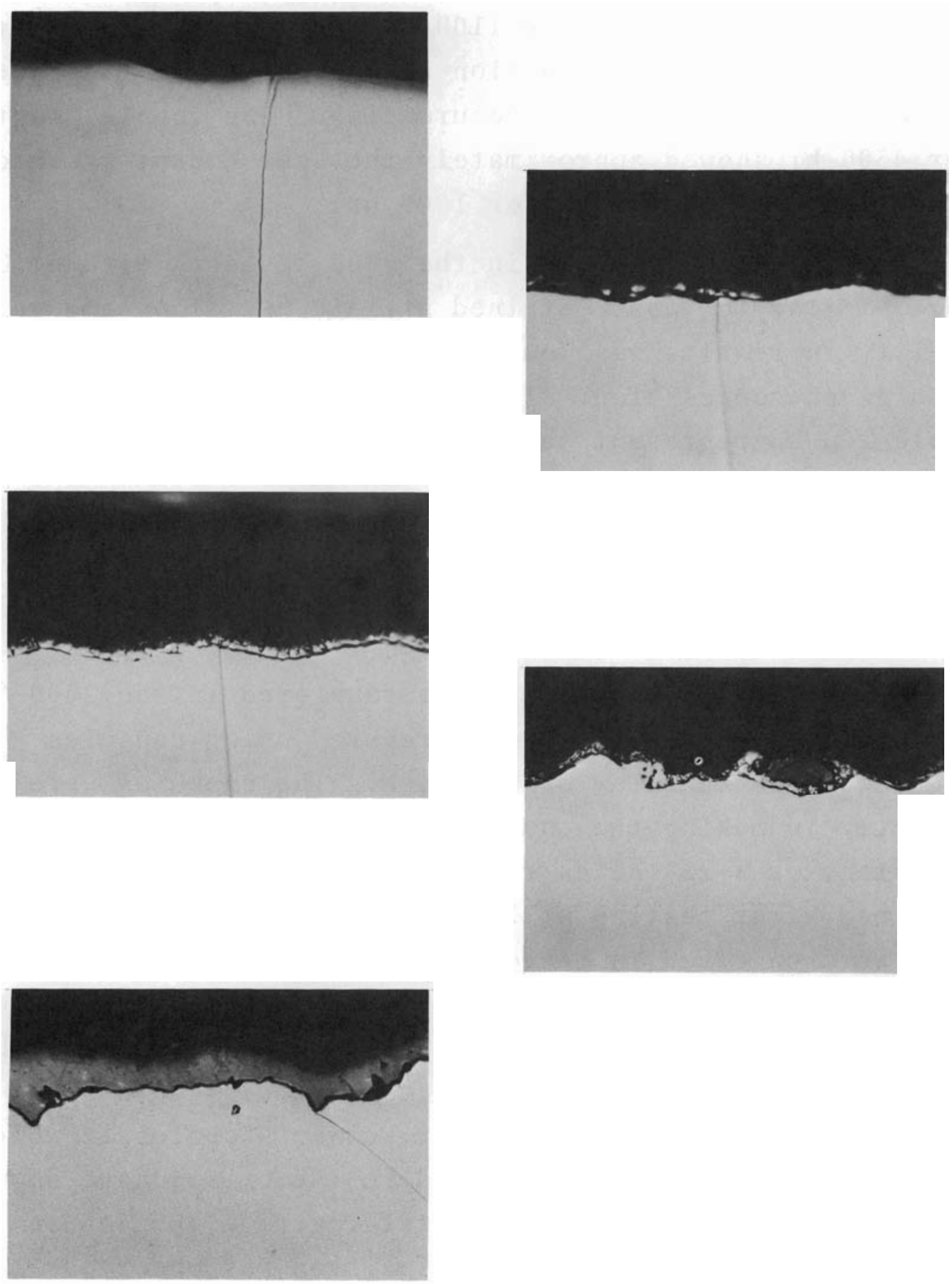
TUNGSTEN-25% RHENIUM

500X

TZM

Neg 701736-3

FIGURE 17. Samarium Sesquioxide Couples Tested at 1550 °C for 4300 hr



Neg 701736-9

FIGURE 18. Photomicrographs of Ta-Sm_2O_3 Couples, Tested for 4300 hr at 1550 °C, Showing Variations in Extent of Attack for Duplicate Couples Tested Under Identical Conditions (Each at 500X)

In agreement with the 1100 °C Sm_2O_3 test results, the extent of oxide-metal reaction at 1550 °C did not appear to increase with increased exposure time. The couples tested for 4300 hr showed approximately the same amount of oxide attack as couples tested for 1000 hr.

The results obtained in the 2000 °C tests with Sm_2O_3 were similar to those obtained at 1550 °C. The same variability in results was found in each set of couples (2 to 6) of a given composition. The 2000 °C data are presented in Table 10 and represent the maximum interaction observed for each couple composition.

At 2000 °C, the extent of metal-oxide reaction did appear to increase slightly with exposure time. The increase was so small, however, that it may be coincidental.

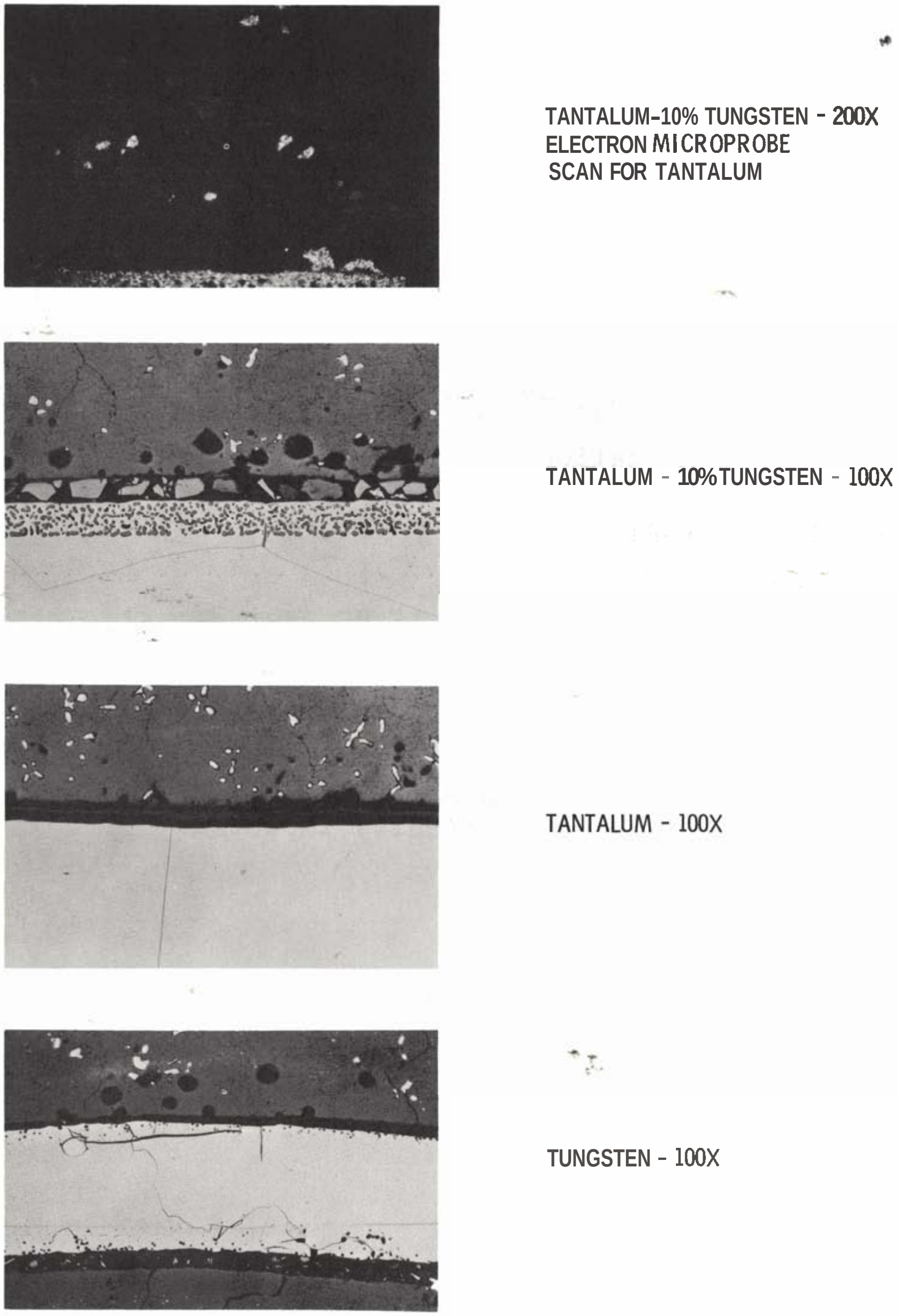
One potential problem was encountered in the 2000 °C tests. The test couples were prepared using capsules machined from tantalum or Ta-10%W. The capsules were used directly in making the couples, or were lined with rhenium, tungsten, or W-25%Re as required. When the couples were examined after testing at 2000 °C, extraneous discrete particles were observed in the oxide phase of some of the couples (see Figure 19). Electron microprobe analyses identified the particles to be tantalum. The mechanism by which the tantalum was dispersed as discrete particles throughout the oxide phase of the couple is not known. Couples in which tantalum particles were observed in the oxide phase showed no greater evidence of oxide-metal reaction than those couples in which no tantalum dispersion was observed. The tantalum dispersion was found in all the couple compositions tested, but not in all the couples of each composition.

The capsule material of couples tested at 1550 and 2000 °C showed extensive grain growth. Figure 20 shows

TABLE 10. Sm_2O_3-Metal **Compatibility at 2000 °C**

Metal	Fabrication Method(a)	Reaction Zone Thickness, mils	
		1,000 hr	3,000 hr
Tantalum	PI	<1	1
Tungsten	PI	<1	1
Rhenium	PI	0	<1
Ta-10%W	PI	<1	2
W-25% Re	PI	<1	<1

(a) PI - Oxide step pressed into capsule-capsule pneumatically impacted.



TANTALUM-10% TUNGSTEN - 200X
ELECTRON MICROPROBE
SCAN FOR TANTALUM

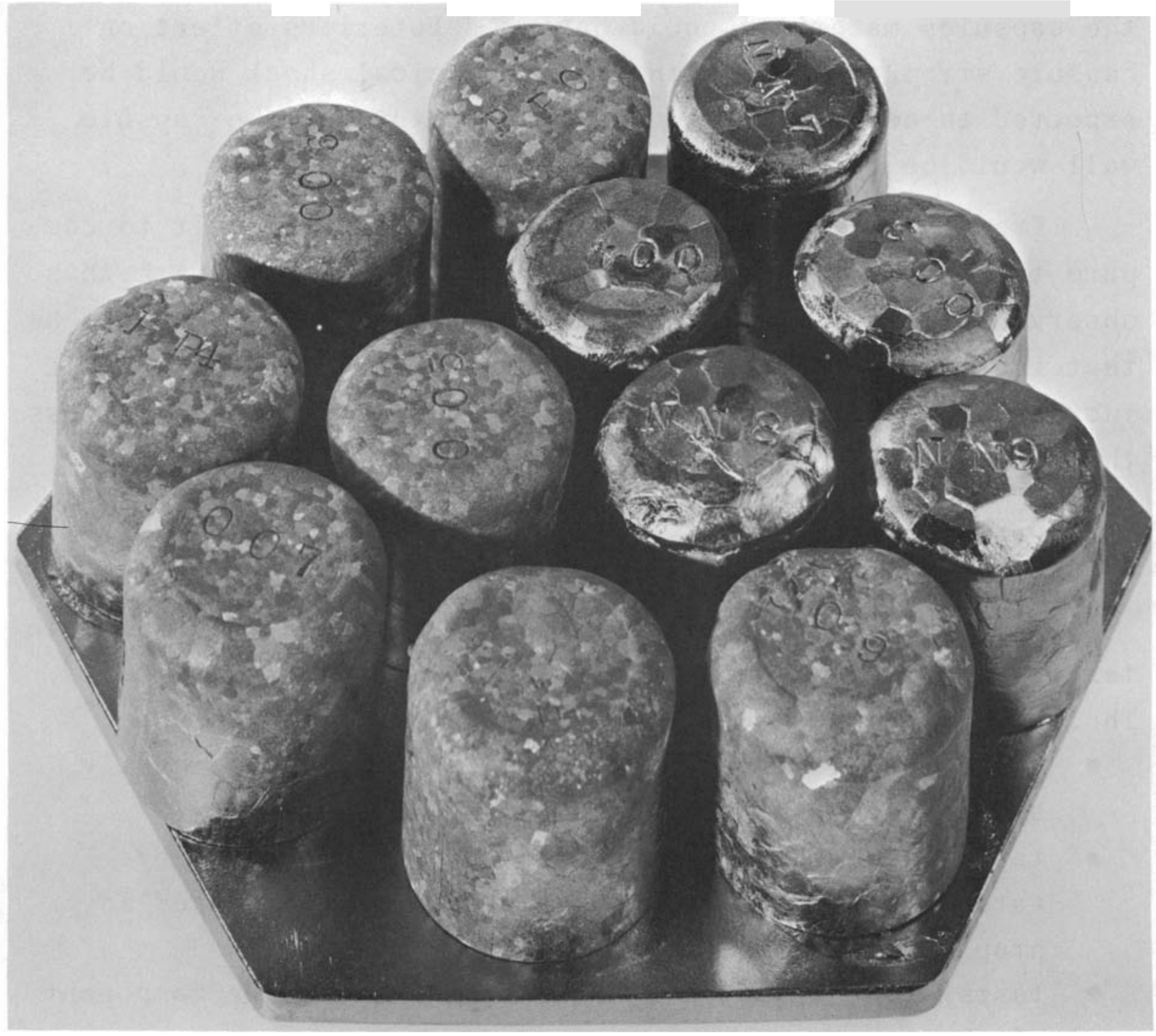
TANTALUM - 10% TUNGSTEN - 100X

TANTALUM - 100X

TUNGSTEN - 100X

Neg 701736-1

FIGURE 19. Samarium Sesquioxide Couples Tested for 3000 hr at 2000 °C, Showing Discrete Particles of Tantalum Dispersed Throughout the Oxide Phase



Neg 0691783-1

FIGURE 20. Tantalum and Ta-10% W Couples of Sm_2O_3 Tested at 2000 °C for 3000 hr - Before Sectioning

tantalum and Ta-10%W capsules after 3000 hr at 2000 °C. In addition to grain growth, some volatilization of metal from the capsule surface occurred. The extensive grain growth in the capsules materials could have a deleterious effect on capsule strength. Resistance to mechanical shock would be expected to be greatly reduced, and rupture of the capsule wall would be more likely in case of an accident.

From the limited data available, it is difficult to compare the interactions observed at 1550 and 2000 °C with those observed at 1100 °C. However a qualitative estimate would be that increasing the test temperature to 2000 °C from 1100 °C increases the reaction observed for identical couples by less than 50%.

5.5 MISCELLANEOUS Sm_2O_3 - METAL COMPATIBILITY TESTS AT 1100 °C

A variety of compatibility tests, not a part of the main testing program, were carried out at 1100 °C using Sm_2O_3. These included:

- tests in which specific impurities were intentionally added to the Sm_2O_3 prior to couple preparation,
- tests in which compacted oxide shapes, prepared by various methods (such as hot pressing), were used in preparing the test couples,
- tests using Sm_2O_3-Nd_2O_3 mixtures as the oxide component of the test couple.

All of the tests were carried out at 1100 °C and lasted for a period of 6 months. Only four metals (304L SS, tantalum, rhenium and Hastelloy X) were evaluated in the special tests.

The initial scouting studies showed that certain impurities (H_2O, CO_2, CO, etc.) appeared to accelerate oxide-metal interaction at 1100 °C. To confirm these results a series of tests was carried out in which water, carbon and oxalate were intentionally introduced into the test couples. Each impurity was added to the Sm_2O_3 in the amount of 0.01 wt%. Water was added in the form of hydrated samarium oxide ($Sm_2O_3 \cdot 3H_2O$). Carbon-containing couples were prepared by mixing graphite powder with the oxide. Oxalate was added by mixing samarium oxalate (which had been dried under argon at 250 °C) with the Sm_2O_3. The couples were prepared in the standard way by step pressing the oxide into the test capsule.

Extensive attack was observed in all the couples containing added impurities, except for the rhenium couples which showed no attack (see Table 11). Layer type corrosion and surface dissolution predominated, and in some of the couples the reaction layer thickness exceeded five mils. Each of the three impurities appeared to have about the same effect on oxide-metal interaction. Photomicrographs of various couples are shown in Figure 21.

Two important conclusions can be reached from the tests with impurities:

- To reduce oxide attack to a minimum, it is essential that critical impurities in the oxide such as water and carbon be reduced to as low a level as possible.
- Rhenium is the best material for containing Pm_2O_3 at elevated temperatures since it resists oxide attack even when narmful impurities are present.

In some cases it may be desirable to use Pm_2O_3 which has been compacted into shapes by special methods. For example, hot pressing can be used to form high density (>95% of theoretical) Pm_2O_3 pellets. It is desirable to know what effect the use of the specially compacted shapes might have an oxide-metal compatibility. Therefore, a series of tests was run using Sm_2O_3 pellets which had been prepared by

TABLE 11. The Effect of Impurities on Sm_2O_3-Metal Compatibility at 1100 °C

Metal	Impurity Added	Impurity in Oxide, wt%	Time, hr	Reaction Zone,[a] mils
304L SS	H_2O	0.01	4,300	4
Tantalum	H_2O	0.01	4,300	8
Rhenium	H_2O	0.01	4,300	0
Hastelloy X	H_2O	0.01	4,300	4
304L SS	carbon	0.01	4,300	3
Tantalum	carbon	0.01	4,300	5
Rhenium	carbon	0.01	4,300	0
Hastelloy X	carbon	0.01	4,300	5
304L SS	oxalate	0.01	4,300	5
Tantalum	oxalate	0.01	4,300	6
Rhenium	oxalate	0.01	4,300	0
Hastelloy X	oxalate	0.01	4,300	3

All couples were prepared by step pressing the oxide into the test capsule

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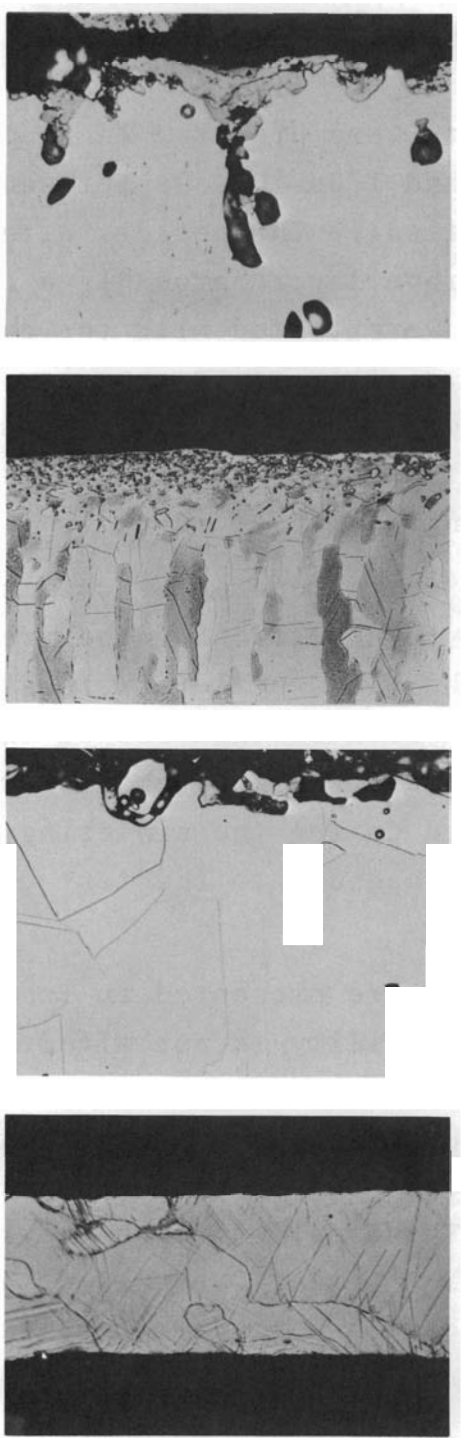
(a) *Average of two couples*



HASTELLOY X - 500X
OXALATE ADDED

TANTALUM - 100X
CARBON ADDED

304L SIS - 100X
CARBON ADDED

RHENIUM - 500X
WATER ADDED

Neg 701736-11

FIGURE 21. Samarium Sesquioxide Couples with Impurities Added-After Testing for 4300 hr at 1100 °C either hot pressing or slip casting. The metal component of each couple was 304L SS or tantalum.

The hot-pressed pellets were prepared in graphite dies at temperatures between 1500 and 1700 °C. Pellet density was greater than 95% of theoretical. The pellets after removal from the die had a thin carbon layer (probably a carbide) on the surface. Some pellets were tested with the carbon layer present. Others were tested after the carbon layer had been removed by firing the pellets in air at 1100 °C. The hot pressed pellets were inserted in the test capsules and the capsules closed in the standard manner.

The slip cast pellets were prepared by casting the Sm_2O_3 in a cylindrical shape and then sectioning the green cylinder to produce the pellets. The green pellets were sintered in air at 1400 °C to a density greater than 90% of theoretical. An organic acid (Daxad-23) was used in preparing the Sm_2O_3 slip. The acid was oxidized during the sintering step. The sintered pellets were then loaded into the test capsules and the capsules welded.

The results of the test are presented in Table 12. They show that oxide-metal compatibility is not affected by using the special pellets as long as the carbon is removed prior to couple preparation. The hot pressed pellets which had not been treated to remove the carbon from the pellet surface showed extensive attack. Those pellets with the carbon removed showed essentially zero oxide-metal interaction, as did the couple prepared from slip cast and sintered pellets.

Several oxide-304L SS couples were tested (at 1100 °C) in which the oxide phase was a mixture of Nd_2O_3 and Sm_2O_3. The results of the test show that the oxide mixtures exhibit essentially the same compatibility characteristics as the pure Sm_2O_3 (see Table 13).

TABLE 12. **Compatibility of Hot Pressed and Slip Cast Sm_2O_3 Pellets at 1100 °C**

Metal	Pellet Preparation	Time, hr	Reaction Zone, mils
304L SS	Hot Pressed	4,300	3
304L SS	Hot Pressed (C Removed)	4,300	0
304L SS	Slip Cast	4,300	0
Tantalum	Hot Pressed	4,300	6
Tantalum	Hot Pressed (C Removed)	4,300	0
Tantalum	Slip Cast	4,300	0

TABLE 13. **Compatibility of Sm_2O_3-Nd_2O_3 Mixtures at 1100 °C**

Metal	Composition of Oxide, wt%	Time, hr	Reaction Zone, mils
304L SS	100 Sm_2O_3	4,300	<1
304L SS	75 Sm-25 Nd	4,300	0
304L SS	50 Sm-50 Nd	4,300	<1
304L SS	25 Sm-75 Nd	4,300	<1
304L SS	100 Nd_2O_3	4,300	<1

All couples prepared by step-pressing oxide into test capsule.

6. CONCLUSIONS

Based on the results obtained in the current study, a number of important conclusions can be reached regarding the high temperature compatibility of Pm_2O_3 with metals and alloys.

- The purity of the oxide is the most critical factor affecting the high-temperature compatibility of Pm_2O_3. When impurities such as water, carbon or organics are present in the oxide, the interaction of the oxide with most metals and alloys is greatly accelerated. Only rhenium and the rhenium alloys appear unaffected by the presence of the impurities.
- A variety of metals and alloys can be used to contain Pm_2O_3 at temperatures up to 2000 °C, provided the critical impurities are removed from the oxide prior to use. This means that the selection of a containment material for a specific oxide application can be based on factors other than its oxide compatibility. A method for adequately purifying the oxide has been developed; it consists of firing the oxide in oxygen at 1100 °C followed by exposure to hydrogen at 1100 °C. Oxide given such a treatment exhibits a minimum of reaction with metals and alloys at temperatures up to 2000 °C.
- The reaction of purified Pm_2O_3 with containment metals appears to be relatively independent of time at temperature. Oxide couples tested for long periods of time (up to 2 years) show essentially the same amount of oxide-metal reaction as couples tested for much shorter times. These results were completely unexpected, and indicate that the mechanisms of oxide-metal interaction are not fully understood. If the reactions in question are simple oxide-metal reactions then they should continue with time, although at a decreasing rate as the reaction layer builds

up. Since the reaction apparently stops after a relatively short period of time ($\leq$1500 hr) it would seem that the reaction involves more than just the metal and the oxide. Apparently some impurity is involved in the reactions, and the impurity is consumed in a relatively short time. At this time, the reaction stops or the rate is reduced by orders of magnitude.

a Since the extent of oxide-metal reaction does not appear to increase with time (after 1500 hr), one can predict adequate Pm_2O_3 heat source cladding integrity for extremely long periods. Cladding failure due to oxide attack should not be a problem during the useful life of any Pm_2O_3 source.

- Temperature cycling of a Pm_2O_3 source may have some affect on oxide-metal compatibility. Conflicting results were obtained during the program: some data indicated thermocycling had a pronounced effect on compatibility; other tests indicated thermocycling had no effect. For Pm_2O_3 applications where thermocycling occurs, additional testing should be carried out to determine its effect on compatibility.
- The results obtained show that Sm_2O_3 makes an excellent stand-in for Pm_2O_3 in compatibility studies. The results obtained with Sm_2O_3 are completely applicable to Pm_2O_3. In fact, they are probably on the conservative side since Pm_2O_3 couples showed slightly less oxide-metal reaction than Sm_2O_3 couples tested under similar conditions.

The over-riding conclusion to be reached from the Pm_2O_3 compatibility program can be summarized as follows: Potential users of Pm_2O_3 should not let fear of oxide compatibility problems deter them from using Pm_2O_3 in high-temperature applications. Any one of a number of metals and alloys can be used to contain the Pm_2O_3 at temperatures up to 2000 °C for long periods of time. Final selection of the containment material can be based primarily on factors other than oxide-metal compatibility.

ACKNOWLEDGEMENTS

The author is indebted to many co-workers at the Pacific Northwest Laboratory who collaborated in carrying out much of the experimental work reported. Special thanks are due L. J. Kirby and R. T. Allemann who performed many of the preliminary scouting studies, and to C. J. Mitchell, C. L. Nelson and J. H. Jarrett who carried out much of the long-term testing.

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APPENDIX

PROPOSED MECHANISM FOR OXIDE-METAL INTERACTION

The importance of the mechanism of interaction between promethium oxide and a metal cladding material was recognized at the inception of these compatibility studies. A knowledge of the mechanism was believed necessary to extrapolate valid interaction rates to long times or higher temperatures and to provide possible remedial actions for reducing or eliminating the extent of core-cladding interaction.

While screening possible cladding materials for inertness toward rare earth oxides, available thermodynamic data were used to establish standard free energy changes for reactions that might be expected to occur. Thus, for tantalum, the reaction

$$6\ Ta + 5\ Sm_2O_3 = 3\ Ta_2O_5 + 10\ Sm \qquad (1)$$

can be written. The estimated standard free energy of reaction at 298 °K is +680 kcal or about +45 kcal/g-atom 0, and at 1500 °C, the values are essentially the same. The large positive standard free energy change for the reaction, as written, strongly implies that the equilibrium will be largely to the left and that tantalum should not be oxidized to Ta_2O_5 nor Sm_2O_3 reduced to the metal.

However, the experiments with untreated oxide showed extensive attack of tantalum by the oxide. Possible explanations for the attack observed were:

- The oxide contained an oxidizing impurity (gaseous or gas-forming) as a result of process conditions, and this impurity was free to react with tantalum.
- Reaction (1) as written did not apply, and products other than Ta_2O_5 and samarium were formed.

- The activity coefficients for the products of reaction differed markedly from the value of unity usually ascribed to them.

(In a sense, the latter two explanations are quite similar: one implies formation of stoichiometric sub-oxides whereas, the other invokes an undefined nonstoichiometric material.)

To distinguish which (if any) of these mechanisms might predominate, residual gas was measured and found to be grossly insufficient to account for the extensive corrosion observed in the tantalum experiments. Therefore, it was hypothesized that either or both of the last two mechanisms apply. In other words the reaction, since it occurred, was "thermodynamically possible" and undoubtedly dependent upon the formation of reaction products other than those shown in Equation (1). Because the rate of attack was dependent upon the purity of the core material, it was further hypothesized that impurities catalyzed the reaction.

The implications of these hypotheses, if true, were quite serious with respect to long-term cladding integrity at elevated temperatures. Certainly some of the promethium oxide-metal couples are thermodynamically unstable, and kinetic factors will strongly influence the integrity of the interface. If kinetics is indeed the important factor, then catalytic effects become of vital interest, particularly at higher temperatures where rate processes accelerate. Also important are factors which might limit the extent of interaction, such as naturally occurring or applied diffusion barriers.

Impurities that might be expected in untreated Pm_2O_3 will include those present after the calcination process and those which might be introduced in subsequent treatment and handling of the oxide. The former group includes residual carbonate groups from incomplete oxalate calcination, carbon traces, H_2O, and (indirectly) oxidizing gases formed during heating of the oxide. Introduced impurities could include water or carbon dioxide adsorbed from the air.

The possibility that such impurities could catalyze a reaction was indicated by the lack of reaction in experiments where the impurity content was purposely lowered and by consideration of the following cyclic reaction sequences that provide a gas phase reactant for oxygen transfer. (In these systems SmO and TaO are arbitrarily assumed to be sub-oxide products. Other oxides could equally well have been chosen.)

$$Sm_2O_3 + C = 2\ SmO + CO \tag{2}$$

$$CO + Ta = TaO + C \tag{3}$$

or

$$Ta + H_2O = TaO + H_2 \tag{4}$$

$$Sm_2O_3 + H_2 = H_2O + 2\ SmO \tag{5}$$

or

$$Ta + CO_2 = TaO + CO \tag{6}$$

$$CO + Sm_2O_3 = 2\ SmO + CO_2 \tag{7}$$

Note that the net reaction in each case is

$$Sm_2O_3 + Ta = TaO + 2\ SmO \tag{8}$$

The "carriers" are not consumed, and if no diffusion barriers exist, reaction would continue until thermodynamic equilibrium was reached. It should be emphasized that such a catalytic effect could occur with relatively low impurity levels. In fact, impurity contents significant at higher temperatures may not be detectable by normal methods.

Several experiments and observations in the laboratory support the above hypotheses for explaining interactions detected for some metal-Sm_2O_3 couples. For example, the titanium-Sm_2O_3 couple was studied in some detail. Complete reduction of samarium sesquioxide by titanium is not favored at 1000 °C.

$$3\,Ti + 2\,Sm_2O_3 = 4\,Sm + 3\,TiO_2 (\Delta F^\circ_{1273} = +\,192\ \text{kcal}) \qquad (9)$$

The possibility for partial reduction of the sesquioxide to occur by the following reaction exists.

$$Ti + 2\,Sm_2O_3 = 4\,SmO + TiO_2 (\Delta F^\circ_{1273} = +\,8\ \text{kcal}) \qquad (10)$$

The more logical assumption, however, is that the sub-oxides of both samarium and titanium are formed.

$$2\,Ti + 3\,Sm_2O_3 = 6\,SmO + Ti_2O_3 (\Delta F^\circ_{1273} = -\,14\ \text{kcal}) \qquad (11)$$

Corrosion of titanium by samarium sesquioxide has been observed, and titanium sesquioxide identified by X-ray diffraction as one of the reaction products.

Generally solid-solid reactions of this type proceed relatively slowly. To test the validity of the hypothesis that gaseous impurities would catalyze the reaction, a series of experiments was carried out where trace amounts of gaseous impurities were placed in sealed tubes containing (in each tube) physically separated titanium and samarium sesquioxide (see Figure 22). The tubes were held at 1000 °C for varying periods

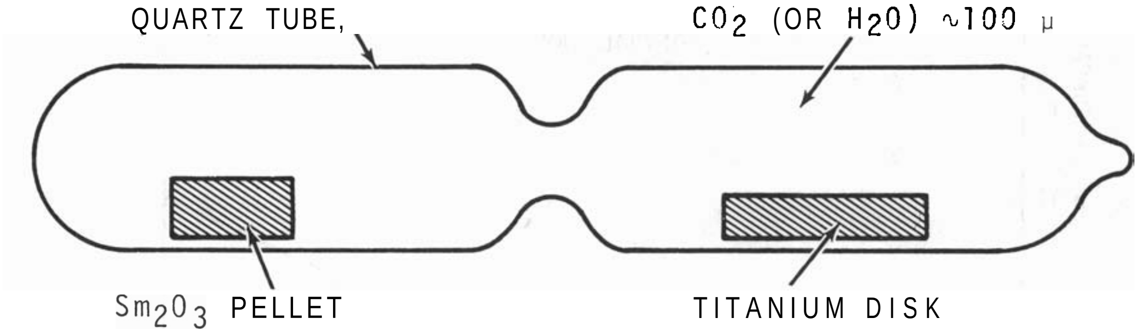

FIGURE 22. **Titanium-Samarium Sesquioxide Reaction System**

of time, and the weight change of titanium was determined as a function of time. Tests where minute amounts of CO_2, H_2O, or carbon (mixed with the Sm_2O_3) were added to the reaction tube showed a much greater reaction rate than where just titanium and samarium sesquioxide were present (Figure 23). The observed corrosion is believed to have proceeded by mechanisms similar to those described in Equations (2) through (7).

$$2\ Ti + 3\ CO_2 = Ti_2O_3 + 3\ CO \tag{12}$$

$$3\ CO + 3\ Sm_2O_3 = 6\ SmO + 3\ CO_2 \tag{7}$$

$$2\ Ti + 3\ H_2O = Ti_2O_3 + 3\ H_2 \tag{13}$$

$$3\ Sm_2O_3 + 3\ H_2 = 6\ SmO + 3\ H_2O \tag{5}$$

$$Sm_2O_3 + C = 2\ SmO + CO \tag{2}$$

The net reaction in each case is

$$2\ Ti + 3\ Sm_2O_3 = 6\ SmO + Ti_2O_3.$$

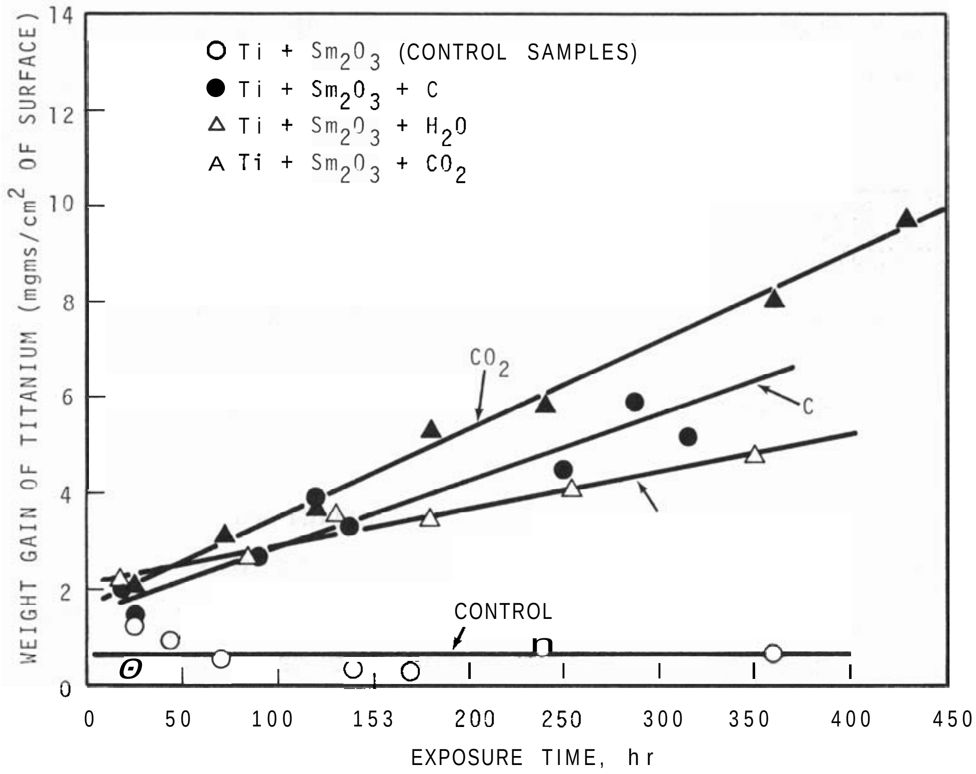

FIGURE 23. Reaction Between Titanium and Sm_2O_3 at 1000 °C Versus Reaction Time

The gaseous impurities serve as carriers for oxygen transfer, and the rate ofreactionbetween oxide and metal is greatly accelerated.

SPECIFICATIONS FOR TEST METALS

Haynes 25 Alloy Rod

Vendor - Union Carbide Corporation
Heat No. 186-5-1200 1 in. diameter × RL

Tensile Test at Room Temperature

Ultimate psi	0.2% Yield, psi	% Elongation in 4D, in.
138,050	63,250	64.0

Chemical Analysis

Element	%	Element	%
Cr	20.45	Ni	9.93
W	15.10	Mn	1.03
Fe	1.95	P	0.016
C	0.07	S	0.011
Si	0.07	Co	Balance

Hastelloy X Alloy Rod

Vendor - Union Carbide Corporation

Heat No. 260-6-2921 1 in. diameter × RL

Tensile Test at Room Temperature

Ultimate psi	0.2% Yield, psi	% Elongation in 4D, in.
120,100	56,950	64.0

Chemical Analysis

Element	%	Element	%
Cr	21.46	Ni	Balance
W	0.52	Mn	0.73
Fe	18.00	Mo	9.04
C	0.10	P	0.018
Si	0.19	S	0.003
Co	1.27		

Tantalum - 10% Tungsten Alloy Rod

Vendor - Norton Company

Heat No. 8175 1 in. diameter × RL

Hardness - Rockwell A 55.9 to 57.0

Chemical Analysis

Element	ppm	Element	ppm
O	27	Ca	<1
H	1	Fe	5
N	16	Mo	<10

Element	ppm	Element	ppm
C	26	Nb	<25
Al	<10	Ni	<1
Cr	<5	Ti	<5

W - 9.8%

Ta - Balance

Tantalum Rod

Vendor - Fansteel Metallurgical Corporation

Lot No. 69B 1879 1 in. diameter × RL

Chemical Analysis

Lot Analysis	
C	10 ppm
O	22 ppm
N	10- ppm
H	5- ppm
W	80 ppm
Nb	60 ppm
Zr	5- ppm
Mo	5- ppm
Ti	5- ppm
Fe	5- ppm
Ni	5- ppm
Si	5- ppm
Mn	5- ppm
Ca	5- ppm
Al	5- ppm
Cu	5- ppm
Sn	5- ppm
Cr	5- ppm
V	5- ppm
Co	5- ppm
Ta	Balance

TZM - Wrought Bar

Vendor - Climax Molybdenum Company of Michigan

Heat No. TZM 7949 1 in. diameter × RL

Structural Condition

Stress Relieved 3/4 hr at 2350 °F

Mechanical Properties

Ultimate, ksi	% Yield, ksi	Elongation % in 4D
120 - 123.7	104.1 - 105.3	28 - 31

Hardness, 10 kg
283 - 292 DPN

Chemical Analysis

Element	%	Element	%
Ti	0.45	Nb	0.0001
Zr	0.096	Fe	0.004
C	0.024	Ni	<0.001
O_2	0.0011	Si	<0.002
H_2	<0.0001	Mo	Balance

W-25% Re Sheet

Vendor - Chase Brass and Copper Company

Lot RWS-21 1 in. × 0.003 in. × RL

Starting Bar

(Powder Metallurgy)

Size - 5.0 in. long × 1.6 in. wide × 0.17 in thick

Density 97%

Sintered

Time - 3 hr at temperature

Temperature - 2550 °C

Atmosphere - Hydrogen

Rolling History

Bars crossed rolled warm to 2-1/2 in. wide, for a total reduction of approximately 25% where pieces were annealed for 1/2 hr in cracked ammonia at 1000 °C.

Bars turned end straight rolled, warm, for a total of 50% reduction. Pieces again annealed 1000 °C for 1/2 hr.

Bars continued to be straight rolled, warm, for another 50% reduction and again annealed same as above.

From 0.010 in. thick to final size pieces were cold rolled.

Pieces cut to final size and annealed at 1400 °C for 15 min in cracked ammonia atmosphere and shipped.

Chemical Analysis - Spectrographic

Element	ppm	Element	ppm
Al	<10	Mn	<1
Ca	<10	Mo	<50
Cr	5	Na	<5
Cu	<10	Ni	15
Fe	20	Si	<10
Mg	<1		

No other metals detected

W	74.80%
Re	25.17%

Rhenium Sheet

Vendor - Chase Brass and Copper Company
Lot No. RS-55 1 in. × 0.003 in. × RL

Starting Bar

(Powder Metallurgy)
Size 4.8 in. long × 1.6 in. wide × 0.18 in. thick
Density 93%

Sintered

Time - 3 hr at temperature
Temperature - 2550 °C
Atmosphere - Hydrogen

Rolling History

Rolled at room temperature. Crossed rolled to 2-1/8 in. wide with anneals at 1650 °C after every 10% reduction in cracked ammonia atmosphere.

Pieces now straight rolled to final sizes with anneals at 1650 °C after each 15% reduction in cracked ammonia atmosphere.

Material cut to size and annealed at 1650 °C for 15 min in cracked ammonia atmosphere.

Chemical Analysis

Spectrographic

Element	ppm	Element	ppm
Al	<1	Mn	1
Ca	<1	Mo	50
Cr	<1	Na	<1
Cu	<1	Ni	5
Fe	36	Si	<1
Mg	<1		

No other metals detected

Chemical

Fe 0.0050%

304L Stainless Steel Rod

Vendor - Allen-Fry Steel Company (Republic)
Heat No. 10356392 1 in. diameter × RL

Physical Properties

Yield, psi	Tensile, psi	Elongation, %	Reduction of Area, %
57,500	89,500	45.2	75.5

Chemical Analysis

Element	%	Element	%
C	0.027	Si	0.56
Mn	1.83	Cr	19.06
P	0.032	Ni	11.24
S	0.016		

Tungsten Sheet

Vendor - General Electric Company
Arc cast and rolled
No chemical analysis available.

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