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A STUDY OF
SELECT CERAMIC OXIDE COMPOSITIONS
AS HIGH TEMPERATURE (1600-2100° K)
THERMAL ENERGY STORAGE MATERIALS

FINAL REPORT
FEBRUARY 1962 TO FEBRUARY 1963

PREPARED FOR
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT NAS5-826
LEWIS RESEARCH CENTER

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ABSTRACT

An investigation of select ceramic oxide mixtures was conducted which included corrosion, materials testing and the development of a thermal conductance apparatus. This apparatus was designed to measure the thermal conductance of these oxide mixtures through their melting temperatures (as high as 2200°K).

The corrosion tests have shown that these oxide mixtures are chemically compatible with certain refractory metals. The combinations of materials studied and the test results are shown below:

			Satisfactory for
3BeO-2CaO (1685°K)	Mo	>	2500 hours
	Mo-Re	>	3500 hours
	W	>	2500 hours
	W-Re	>	1500 hours
Al_2O_3-4BeO-4MgO (1910°K)	Mo	to	1000 hours
	Mo-Re	to	500 hours
	W	>	1500 hours
	W-Re	>	1000 hours
	Re	>	1000 hours
Al_2O_3-4BeO-MgO (2020°K)	Mo	to	500 hours
	W	to	500 hours
3BeO-2MgO (2145°K)	W	>	1400 hours
	W-Re	>	1200 hours
	Re	>	1000 hours

All but a few of the failures in the containers have been caused by poor welds or excessive grain growth. Analyses show good chemical compatibility between oxide mixtures and the refractory metals. Corrosion rate calculations based on the limited data indicate 2-4 mils loss in 10,000 hours for the best combinations.

The thermal conductance apparatus was fabricated, installed and calibrated. Calibration data are presented. The first oxide specimen is being fabricated and will be tested in the follow-on effort. The oxide specimen container geometry is rather difficult to fabricate and requires techniques to insure no voids in the oxide melt as well as to keep parasitic heat losses to a minimum.

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I INTRODUCTION

1.1 A STUDY OF SELECT CERAMIC OXIDE COMPOSITIONS AS HIGH TEMPERATURE (1600-2100^{o}K) THERMAL ENERGY STORAGE MATERIALS

The work covered in this report is a study of fusible materials, and containers for such materials, suited for use as high temperature thermal energy storage (TES) materials. The application for these TES materials is a direct conversion solar thermionic electrical power system for use in space. These TES materials are expected to supplant other auxiliary power during occultation of an earth (or other planet) orbiting power system of this type.

1.2 PROGRAM OBJECTIVES AND BACKGROUND

The initial phase of this thermal energy storage program (December 1961 - December 1962) has provided useful data on thermal energy storage materials applicable for use in solar thermionic space power systems. Continued investigation was undertaken to establish means for efficiently utilizing stored thermal energy. Containment life requirements also indicated necessity for corrosion testing of long duration (thousands of hours). The complexities of preparing and handling these high melting materials and the associated health hazards were also given careful consideration in pursuing the objectives of this program.

More specifically, the program involved the following areas of study:

1.2.1 Life and Cycling Tests

1. Study of three (3) select oxide mixtures in six (6) metals under cycling conditions in vacuum. This study was later modified to include a fourth oxide and several substitutions in the metals group.

2. Develop corrosion rate data up to 3500 hours, which can be extrapolated to 10,000 hours.

3. Develop this data under cycling conditions.

1.2.2 Thermal Transfer Studies

1. Basic thermal conductance tests.

2. Design, development, fabrication and calibration of a vacuum thermal conductivity test fixture for item (1) above.

3. Correlation of experimental results with an analytical model.

1.2.3 Continued Materials Studies

1. Study compositions, purity control of the MgO-BeO mixture and effects on its properties.

2. Study preparation and handling techniques.

3. Screen alternate TES materials for desirable properties.

Major emphasis was placed on thermal transfer studies since this property was important for evaluation of these materials for space power systems applications. The thermal test fixture and its operation would also represent a noteworthy advance in high temperature vacuum technology. Corrosion testing was accepted as a necessary adjunct to any research and development program of this nature. Item C (Materials Studies) was given a low priority and represented inherent flexibility to allow for more immediate solution of problems as they might arise.

1.3 SUMMARY OF OVERALL PROGRAM ACCOMPLISHMENTS

This report is divided into two distinct parts for clarity of presentation. The first part (Section II) deals with corrosion test data. The second part (Section III) deals with the design, fabrication and calibration of the thermal conductance test fixture.

Corrosion tests have been completed and indicate that containment of various oxide-metal combinations is feasible up to one year. Extrapolated corrosion rates of 2 to 4 mils attack per 10,000 hours have been calculated from actual data taken from tests to 3500 hours. The data also indicated that the attack rate was linear. The 3BeO-2MgO oxide mixture melting at 2145°K appears to be the most stable of the mixtures studied. The best choices in container metals are W-Re and Re. Considering fabrication, rhenium is by far the best choice.

A thermal conductance apparatus was designed, fabricated and successfully calibrated. This apparatus will be used to determine thermal conductance of these oxide mixtures to temperatures above their melting points. Because the oxide conductance specimen was rather complex, it was not successfully fabricated within the program funding.

A follow-on program to continue both corrosion and conductance testing is currently underway. The corrosion tests are now concentrated on 3BeO-2MgO in rhenium and will run to 5,000 hours. Conductance specimens will be fabricated and tested as part of this follow-on effort. Thermal conductance measurements under static and transient conditions will be attempted on 3BeO-2CaO and 3BeO-2MgO. The former oxide mixture will be studied first because lower temperatures (1600 - 1750°K) are involved. The 3BeO-2MgO oxide will require testing to 2200°K.

II CORROSION TEST PROGRAM

2.1 SUMMARY OF CORROSION TEST RESULTS

Four oxide mixtures in various combinations with five potential container materials were tested. These combinations and test results are shown in Table 2-1 below.

TABLE 2-1. CORROSION TEST RESULTS

OXIDE	METAL	TEST TEMP. °K	HOURS TO FAILURE	THERMAL CYCLES
3BeO-2CaO	Mo	1645-1785	>2492 <3165	113
	Mo-50Re		3500 (N. F.)	135
	W		>2535 <3500	135
	W-25Re		>1484 <2029	69
Al_2O_3-4BeO-4MgO	Mo	1866-1977	> 192 < 814	50
	Mo-50Re		> 695 <1196	50
	W		1500 (N. F.)	46
	W-25Re		>1031 <1529	58
	Re		>1050 <1504	46
Al_2O_3-4BeO-MgO	Mo	2085-2195	>1196 <1484	58
	W	2200	<500	0
3BeO-2MgO	W	2085-2195	>1390 <1504	58
	W-25Re		1196 (N. F.)	50
	Re		1000 (N. F.)	20

N. F. - No Failure

Five capsules of each oxide-metal combination listed in Table 2-1 were tested. The intent was to develop test data at five time intervals. The data in Table 2-1 represents the best values obtained on all capsules. All but a very few of the capsules failed prior to the selected inspection times beyond 1000 hours.

Almost all failures were traceable to weld failures, in particular at heat affected zones. The Mo-Re and W-Re alloys were difficult to weld because of the poor quality material (the best obtainable). In some cases, excessive grain growth was apparent in pure Mo and W. Grain boundaries extending across the thickness of the capsule will be potential planes of weakness.

In several cases, attack on the outside capsule wall was also noted which was caused by the materials in contact or near-contact with the capsule walls. In no single instance was it possible to attribute failure to excessive corrosive reactions between oxide and container.

There are indications that internal pressures were developed in at least half of the capsules. This pressure is accountable as a result of two conditions: First, improper evacuation and outgassing of the capsule and oxide prior to sealing; second, expansion of the oxide on freezing - especially noticeable in the case of 3BeO-2CaO. These two possibilities would, in turn, aggravate weld structures and thereby result in capsule failure. The first condition (outgassing) was recognized as a problem early in the program and was resolved by modifying the preparation techniques. The second condition (thermal expansion) could possibly be resolved by directionally-controlled freezing or by use of expansion bellows. The BeO-MgO base mixtures show slight contraction on freezing and did not cause deformation of the capsule.

A technique to contain or limit leakage was also studied by using sponge zirconia as an absorbing material. Several tests indicated that this method could be used effectively.

Techniques to actually cast the oxides as a solid mass or ingot were also studied. A method to eliminate all void spaces is desirable since usual hot-press sintering contaminates the oxide with adsorbed or entrapped gases. Pressing was also done in graphite dies, followed by vacuum firing to remove any carbon. Several 10-inch capsules containing Al_2O_3-4BeO-4MgO were heated to above the oxide melting point and a considerable number of voids were found. It was concluded that careful freezing would be required to prepare a solid, pore-free, oxide body.

In conclusion, most failures appear to be the result of development of intergranular cracks, usually in or near weld areas. While the actual mechanism of crack formation is not completely understood, it is believed that factors such as grain growth, weld structure, mechanical stress resulting from the freezing and thawing of the oxide during cycling, and the grain boundary weakness inherent in these materials at very high temperatures all can contribute to failures. The observed inconsistency in capsule life of any one of the fourteen combinations of oxide and container material which have been tested suggests that material or fabrication variations do exert an important influence on individual capsule integrity.

2.2 EXPERIMENTATION

The objective of the corrosion test program was to determine the feasibility of long-life containment of thermal energy storage materials. The results of heats of fusion determinations and preliminary container compatibility tests for a group of oxide mixtures obtained under previous contract effort have been presented. *

In that early effort, the main requirement was that thermal energy storage materials provide energy (using heats of fusion) in the 1600°K to 2100°K range. An exploration of available pertinent data revealed that only the oxides were capable of meeting the required combination of melting point and high heat of fusion. Since no single oxide possessed this combination, it was found possible to obtain melting points in the desired range by combining select ceramic oxides in eutectic proportions as indicated by existing phase diagrams.

The heats of fusion were determined for some eighteen such oxide combinations. As was predicted, only those mixtures containing significant quantities of beryllium oxide exhibited significant heats of fusion on a weight basis. It also became apparent that, in general, the heat of fusion varied directly with melting point. Since power output and efficiency of thermionic converters varies directly with temperature, the high melting oxides were most attractive systems-wise.

The next basic systems requirement was that these thermal energy storage materials be compatible with suitable container materials for one year or better. The temperatures involved, together with materials used in thermionic converters, dictated that refractory metals be studied. Therefore, the oxides to be considered were selected on the basis of their thermodynamic stability relative to these metals. Previously, short time (500 hour) tests did verify thermodynamic predictions of good compatibility with these oxides and molyb-

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* E. F. Batutis, "Final Technical Report, Thermal Energy Storage Research and Development Program," 6 December 1960 to 1 December 1961, NASA Contract NAS5-826.

denum or tungsten. However, since space systems involve lifetimes of thousands of hours, it was necessary to develop long time corrosion data between molten oxide and refractory metal containers.

2.2.1 Program Outline

Four oxide mixtures (3BeO-2CaO, 3BeO-2MgO, Al_2O_3-4BeO-4MgO and Al_2O_3-4BeO-MgO were selected for testing with four container materials (Mo, Mo-50% Re, W and W-25% Re) to obtain data which would permit (1) the calculation of corrosion rate constants and (2) the reliable extrapolation of corrosion effects to 10,000 hours. The latter was to be supported by data taken at five test periods (100, 500, 1500, 2500 and 3500 hours) for each combination of TES material and container. The nominal test temperature was 50°K above the melting point of the oxide mixture. Since the thermal energy storage material would be cycled through its melting point, the corrosion samples were thermally cycled 50°K above and below their melting points.

The corrosion capsules evaluation after testing involved a detailed examination of both oxide and container material. In the case of oxide, spectrographic analyses were to determine the extent of container material dissolution in the oxide and X-ray techniques were used to establish changes in crystallographic or chemical structure of the TES material. Densities of the fused oxides were also measured. The corrosion effects of the TES materials on the container materials were analyzed by metallographic examination. The measurement of wall thickness after test was considered to be the most direct evidence of any corrosive attack. Microhardness readings were taken across a capsule section to provide evidence of any progressive compositional change. Spectrographic analyses of refractory metal containers were also used to detect oxide metallic elements (Al, Be, Ca, Mg) penetration. Program details are shown in Table 2-2.

TABLE 2-2. COMPATIBILITY TEST PROGRAM SUMMARY

TEST TEMP. RANGE, °K	TES MATERIAL	CONTAINER MATERIAL	TEST DURATION HOURS
1785-1645	3BeO-2CaO (1685°K)	Mo	100, 500, 1500, 2500, 3500
		Mo-50% Re	100, 500, 1500, 2500, 3500
		W	100, 500, 1500, 2500, 3500
		W-25% Re	100, 500, 1500, 2500, 3500
1977-1866	Al_2O_3-4BeO-4MgO (1910°K)	Mo	100, 500, 1500, 2500, 3500
		Mo-50% Re	100, 500, 1500, 2500, 3500
		W	100, 500, 1500, 2500, 3500
		W-25% Re	100, 500, 1500, 2500, 3500
		Re	500, 1500
2200-2087	3BeO-2MgO (2145°K)	W	100, 500, 1500, 2500, 3500
		W-25% Re	100, 500, 1500, 2500, 3500
		Re	1000
2200-2087	Al_2O_3-4BeO-MgO* (2020°K)	Mo	100, 500, 1500, 2500, 3500
		W**	500

* The Al_2O_3-4BeO-MgO which has a melting point of 2020°K was included in the high temperature cycling range although its melting point is below the minimum temperature in the cycle. In this particular case, the test was conducted with the oxide continuously molten.

** No cycling, held at 2273°K throughout test.

2.2.1.1 Materials Selection

Pertinent physical data of the oxides are presented in Table 2-3.

TABLE 2-3. PHYSICAL CHARACTERISTICS OF SELECTED OXIDE MIXTURES

OXIDE	MELTING POINT °K	DENSITY gm/cc	HEAT OF FUSION Watt-hrs/lb.	cal/gm
3BeO-2CaO	1685	3.05	117	221
Al_2O_3-4BeO-4MgO	1910	3.33	170	340
Al_2O_3-4BeO-MgO	2020	3.22	202	360
3BeO-2MgO	2145	3.23	265	500

The choice of possible container materials was rather limited because of test requirements. Because of earlier screening tests molybdenum was one logical choice for further lower temperature testing. The recently developed molybdenum alloy containing 50 weight percent rhenium was also included in order to take advantage of the reported improved welding characteristics and superior physical properties. Thermodynamic considerations indicated that rhenium should be chemically compatible with the oxide materials. With the higher melting oxide mixtures, it was apparent that the relatively high vapor pressure of molybdenum posed a problem for long-time use. For example, at 2100°K, a molybdenum surface would evaporate approximately 0.25 inch thickness in 10,000 hours. A tungsten surface, under similar conditions, would lose about 4×10^{-5} inches in thickness. At high converter cathode temperatures, tungsten is a more likely choice as a container material for TES. Also because of reported improved fabricability, a rhenium alloy of tungsten was included in the test program. Consideration was given to "doped" tungsten, a General Electric Co. proprietary alloy developed to inhibit gain growth in lamp filament wire. However, attempts to weld this material were unsuccessful. The doping material was sufficiently volatile at the melting point of tungsten to generate pressures during weldment which resulted in excessive weld porosity.

Later in the program, after the relatively thin walled (.020") molybdenum capsules had failed, .125" thick arc-cast molybdenum capsules containing Al_2O_3-4BeO-4MgO were included in order to evaluate the effects of capsule wall thickness on capsule life. These heavy walled molybdenum capsules were scheduled for 500, 1500, 2500, 3500 hours. Several additional capsules of W-Re and Re with Al_2O_3-4BeO-4MgO and 3BeO-2MgO were also added toward the end of the scheduled program. The rhenium was found to be much easier to fabricate reliably. One rhenium capsule was run at test conditions without any outer capsule and survived for over 1000 hours with no sign of leakage.

2.2.1.2 Test Capsule Components

TES Raw Materials - The oxide source materials were selected on the basis of maximum obtainable purity. The beryllium oxide was nuclear grade material, Brush Beryllium Co. VOX grade lot 100-W-186-B. The magnesium oxide and calcium carbonate were both certified reagent grade materials obtained from Fisher Scientific Co. The aluminum oxide was Linde Company's Type O. The analyses provided by the vendors are presented in Table 2-4.

TABLE 2-4. OXIDE SOURCE MATERIALS IMPURITY LEVELS (PPM)

IMPURITY	BeO	MgO	Al_2O_3	$CaCO_3$
Al	45	30	--	NR
B	< 1	NR	NR	NR
Ca	<30	500	NR	NR
Cd	NR	NR	NR	NR
Co	< 1	NR	NR	NR
Cr	6	NR	NR	NR
Cu	< 2	NR	NR	NR
Fe	20	100	20	10
Li	1	NR	NR	NR
Mg	30	--	NR	100
Mn	< 2	5	NR	NR
Na	5	5000	80	100
Ni	3	NR	NR	NR
Si	45	100	30	NR
K	NR	50	NR	100
Ba	NR	50	NR	100
Sr	NR	NR		1000

NR Not Reported

Calcium carbonate was selected as the source of calcium oxide in order to minimize the problems associated with rapid hydration of the oxide. Any prior hydration introduces weighing errors which prevent accurate preparation of a desired final composition.

Container Materials - The capsule materials were obtained as nominal 0.020 inch sheet stock. Stress-relieved, arc-melted molybdenum and tungsten sheet was specified. The molybdenum sheet was supplied by the Lamp Metals and Components Department of General Electric Co. The tungsten was obtained from Universal Cyclops Steel Company. The two rhenium alloys were produced by powder metallurgy techniques only. Since these are relatively new materials, a brief description of their processing history as provided by the supplier, Chase Brass and Copper Company, may be of interest. Both alloys were fabricated from powder metallurgy ingots approximately 0.135 inches thick. Rolling was done at temperatures below the recrystallization temperature; with process anneals at 1650°C in hydrogen after each 50% reduction in area. Both alloys were given a final anneal at finished size for 1/2 hour at 1650°C. These experimental alloys were available from this single source only and it was not possible to buy them to any rigid specification. The certified analyses of all materials used are presented in Table 2-5.

TABLE 2-5. CHEMICAL ANALYSIS OF THE CAPSULE MATERIALS (PPM EXCEPT AS NOTED)

MATERIAL	VENDOR IDENTIFICATION	C	Ca	Cr	Cu	Fe	H_2	Mg	Mn	Mo	N_2	Ni	O_2	Si	V	W	Re
Mo	Lot C 6150-B2	.021%	NR	NR	NR	NR	NR	NR	NR	99.9%	NR	NR	NR	NR	NR	NR	
W	Heat No. KC1120	14	NR	10	NR	15	1	NR	10	NR	1	1	8	20	10		
Mo-Re		NR	<1	ND	<1	<75	NR	<1	NR	52.29%	NR	ND	NR	<50	NR	NR	
W-Re		NR	< 1	ND	<1	<50	NR	<1	NR	<50	NR	ND	NR	<1	NR	74.62%	
Re		NR	< 1	ND	< 1	40	NR	<1	NR	38	NR	ND	NR	< 1	NR	NR	

NR - Not Reported ND - Not Detected

2.2.2 Corrosion Test Capsule Preparation

2.2.2.1 Capsule Design Considerations

Since some seventy-five capsules were required, specimen size was somewhat governed by available test equipment. Test conditions were also likely to produce some failures, and leakage of BeO as a part of the liquid would best involve small samples. A final limitation on specimen size was imposed by the cost of rhenium alloys (approximately $900/lb). Since this cost made it impractical to fabricate capsules from bar stock (minimum weld was desirable), 0.020 inch sheet stock was chosen (reasonable workability). This 20-mil thickness was then specified for all test materials in order to be consistent throughout.

One major disadvantage in this design was the number of weldments involved. The cylindrical geometry would require one seam weld and two circular welds on the ends. Fabrication difficulties were expected to be minimized by using low energy electron beam welding. Preliminary weld specimens looked satisfactory and the design was then considered satisfactory. As it turned out, weld procedures had to be modified. These modifications are described in the following section.

2.2.2.2 Capsule Fabrication

The 20-mil sheet was sheared warm in the case of tungsten and tungsten-25% rhenium alloy, to 2.35 inches x 0.75 inch strip. These strips were then formed by means of a die and mandrel into cylinders 0.75 inch diameter x 0.75 inch high. Here again, it was necessary to form tungsten at a temperature about 600°F and the rhenium alloy at a temperature about 350°F. This substantiated the reported lower brittle to ductile transition temperature of rhenium tungsten alloys. End caps were punched from molybdenum and molybdenum-50% rhenium alloy but it was necessary to elox machine caps of the more brittle tungsten and tungsten-rhenium alloys. The cap for the top of each capsule was also provided with a .020 in. hole. The need for this hole will be described later.

The cylinders were completed by a butt type seam weld utilizing a low voltage electron beam welder. Initially the capsule ends were also welded by this means but because of the fit-up required by electron beam welding, these were more readily fabricated using a tungsten arc inert gas weld.

2.2.2.3 Test Capsule Assembly

After the side seam and bottom were welded, capsules were loaded with oxide compact. The top was then welded in place. It was found necessary to limit the oxide height to about 0.60 inch in order to avoid the possibility of its being melted and becoming involved in the molten weld metal. The specimen was then thoroughly outgassed in a vacuum furnace at 1300°C for 1 hour (via the 0.020 in. hole in the cap). This hole was then sealed under vacuum (10^{-4} torr) in the electron beam welder.

Since the test furnace vacuum chamber available could not be operated with a vacuum of less than 10^{-4} torr, some protection was required for the relatively thin walled test capsules for these long-time test periods. For this reason outer protective cans of molybdenum were provided. These cans were 0.800 inch in diameter by 0.800 inch high. This loose fit for the contained capsules was hoped to be sufficient for preventing diffusion bonding. As an added precaution, the inside of each molybdenum can was also flame sprayed with alumina to avoid this possibility. The outer can was also sealed under vacuum by electron beam welding.

These additional precautions later turned out to be more trouble than their worth. First of all, molybdenum vapor pressure at the higher temperatures was excessive. Alumina also appeared to attack the inner capsules from the outside in some cases. In rhenium capsules, molybdenum began to alloy with rhenium via vapor transport. Individual cases will be discussed in detail under test results.

2.2.2.4 Pre-Test Procedures

The 100 hour specimens were prepared and run first prior to fabrication of subsequent capsules. This was done in order to screen materials and to check the method of specimen preparation and testing. Upon completing this 100 hour test period, all capsules had bulged significantly and both the inner and outer capsules of eight of the ten specimens had failed. The evidence pointed to a relatively high internal pressure which was attributed to adsorbed gases and/or volatile materials in the oxide bodies. To check this, several test capsules were prepared and outgassed at 1560°K in a vacuum of 10^{-5} torr for one hour. This outgassing was done through the 0.020 inch diameter hole in the capsule top. Weight losses of approximately twenty milligrams were noted in all cases indicating that some volatile material had been present. These capsules were sealed and heated above the melting point of the contained oxide with no evidence of swelling. All subsequent capsule preparation included this outgassing step prior to sealing. The simultaneous outgassing of the outer capsules was also included as a part of this operation.

Methods for testing the capsule integrity were given serious consideration. Although a leak check would have been the most positive type of test, no feasible method could be devised which would provide results sufficiently positive to be of any value. All capsules were "zyglo" tested, a method which permits the detection of surface defects. In several cases, cracks were detected and subsequently repaired. This cracking was usually found in capsules made of pure tungsten.

During the course of the test program, it was decided to include pure rhenium among the capsule materials. Rhenium sheet was procured from Chase Brass and Copper Company. The fabrication of this material into capsules proved to be the most straightforward of any of the materials employed in the program. The rhenium showed excellent room temperature ductility and welded readily without subsequent embrittlement usually characteristic of molybdenum and tungsten. Two capsules containing the Al_2O_3-4BeO-4MgO oxide mixture were prepared and were included for test to 500 and 1500 hours. In addition, five heavy wall molybdenum capsules (0.125 inch) were loaded with this oxide directly and tested. These were designed to provide data relating to the effects of capsule wall thickness upon capsule life.

A group of capsules containing control samples of metal was also included in the test series. These capsules consisted of small specimens of each capsule material enclosed in the standard molybdenum protection capsule. Two sets were prepared; one set was run for 500 hours and one set for 3500 hours.

Late in the test period, additional capsules were fabricated and placed on test for 1000 hours. These included two tungsten-25% rhenium assemblies jacketed in molybdenum and one pure rhenium unjacketed capsule. Each contained the 3BeO-2MgO oxide mixture. These were added to the original test program schedule and were intended to be available for longer time corrosion testing in future work. At the end of the present program these capsules were run 1000 hours with no sign of failure.

2.2.2.5 Preparation of the Oxide Test Specimens

Earlier work utilized hot pressing of the oxide mixtures to obtain a high density body. In most cases, it was possible to obtain better than 90% of theoretical density using this technique.

With the exception of the 3BeO-2CaO, the compacts could be handled and stored in a normal manner. Difficulties were encountered, however, with calcia because of its relatively rapid hydration. High density bodies were found to completely deteriorate to powder after two weeks in ambient atmosphere.

Pertinent data of prepared hot pressed oxide bodies are presented in Table 2-6. It will be noted that the material balance in the 3BeO-2CaO analysis is not good. This is explained by the formation of calcium hydroxide during preparation and weighing of this sample prior to analysis. The presence of $Ca(OH)_2$ was found in every X-ray diffraction pattern of 3BeO-2CaO. In order to avoid this contamination, after 3BeO-2CaO was fired (to remove carbon) specimens were stored in a desiccator prior to loading into the capsules.

In order to minimize time and cost of hot-pressing the number of specimens required, a multi-cavity graphite die was used. Sixteen holes, 0.700 inch diameter, were drilled in a six inch diameter graphite block. These holes were then fitted with top and bottom rams making it possible to simultaneously press sixteen specimens. Each die cavity was loaded with individually blended and weighed charges. As mentioned earlier calcium carbonate was used to eliminate the weighing errors resulting from the hydration problem inherent in handling calcium oxide. The carbonate was allowed to decompose in situ during an early stage of the hot pressing operation. An induction heated hot pressing facility was used. Each batch of similar oxide composition was heated to 90% of the predicted melting temperature under 2500 psi for one-half hour.

Since all the oxide mixtures investigated contained beryllium oxide, special handling precautions were necessary. These materials were handled in an area specifically designed for beryllium and its compounds where regularly scheduled monitoring was required to detect possible beryllia contamination. The hot pressing facility itself was exhausted into a special filtered ventilating system.

Pressing in graphite resulted in a high carbon content surface on each compact. This carbon was removed by heating the compacts at 1000°C in air for twenty-four hours.

2.2.2.6 Test Furnace Description

The number of specimens, the variety of high temperatures required, the high vacuum required and the long-time test periods presented serious problems providing test facilities. This problem was solved by installing three induction coils in one large vacuum chamber. The coils, approximately six inches in diameter, were connected in parallel with external induction power controls effective on two coils (for the lower temperatures). These coils were powered by a 100 kilowatt, 3000 cycle motor generator set. The coils were lined with fused quartz cylinders, which in turn were lined with concentric 0.003 inch thick tungsten heat shields. The top and bottom of each furnace were also lined with multiple tungsten heat shields. Tungsten cylinders approximately 2 inches I.D. with 0.250 inch thick walls were stacked inside the radiation shields to act as susceptors. This provided a uniform heat zone two inches in diameter and six inches in height.

Figure 2-1, a picture taken through the top observation window with the furnace at temperature, indicates the general arrangement of the coils.

TABLE 2-6 DATA PERTAINING TO THE HOT PRESSED OXIDE BODIES

	DESIRED COMPOSITIONS (Wt. %)				ANALYZED COMPOSITION (Wt. %)				PHASES PRESENT (X-RAY DIFFRACTION)	DENSITY (gm/cc) THEORETICAL	DENSITY (gm/cc) ACTUAL
Oxide Mixture	BeO	MgO	Al_2O_3	CaO	BeO	MgO	Al_2O_3	CaO			
3BeO-2CaO	40.08			59.92	39.77			54.54	BeO, CaO, $Ca(OH)_2$	3.19	3.05
Al_2O_3-4BeO-4MgO	27.53	44.40	28.07		26.82	45.44	27.82		BeO-MgO-$2Al_2O_3$	3.56	3.33
Al_2O_3-4BeO-MgO	41.29	16.64	42.07		41.84	17.86	40.51		MgO-Al_2O_3	3.57	3.22
3BeO-2MgO	48.20	51.80			50.22	49.58			BeO, MgO	3.20	3.23

Spectrographic Summary - Elements Present as Impurities in Hot Pressed Oxide Mixtures (ppm)

	IMPURITIES																			
	B	Ba	Ca	Cd	Cr	Cu	Co	Fe	Li	Mo	Mn	Na	Ni	Pb	Si	Sn	Sr	Ti	K	Al
3BeO-2MgO	<3	<10	20	<3	<10	15	<10	40	<3	<10	<10	100	30	<10	80	<10	<10	<10	20	240
Al_2O_3-4BeO-4MgO	<3	<10	50	<3	<10	50	<10	80	<3	<10	<10	300	10	<10	1000	<10	<10	<20	50	-
3BeO-2CaO	<3	<10	--	<3	<10	4	<10	10	<3	<10	<10	40	<10	<10	20	<10	<150	< 2	20	360
Al_2O_3-4BeO-MgO	<3	<10	100	<3	<10	15	<10	40	10	<10	<10	200	<10	<10	60	<10	<10	< 2	50	-

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Note: Hot pressing has improved mixture purity.

Figure 2-1. Compatibility Test Furnace Arrangement

The capsules were stacked in their respective furnaces, which was not an ideal arrangement since a failure in one of the upper capsules resulted in the molten oxide contaminating the outer surfaces of those capsules below it. However, the outer molybdenum cans prevented direct contact of these leakages with the test capsules inside.

Temperatures were read with a calibrated optical pyrometer by sighting through a window in the chamber top. Readings were taken through a small hole in the top heat shield on a void space between capsules which provided approximate black body conditions. An initial temperature calibration was made using the melting points of nickel (1726°K), titanium (1940°K) and zirconium (2120°K) as standards for each of the three furnaces. At each calibration, the effect of the chamber window reduced the pyrometer reading by a nominal fifty degrees Kelvin. During test, each furnace was maintained within ± 10°K of temperature with any given power setting. These temperatures were reproducible throughout the test period as determined by periodic checks.

The installation of automatic temperature programming equipments to obtain the thermal cycling conditions was not possible to achieve economically. Manual variation of the power level was used, reducing the number of cycles to three (3) per day, or about fifteen (15) per week. The number of cycles for each capsule is shown in Tables 2-7 through 2-10.

2.2.2.7 Test Results

A. In-Test Evaluation

Capsule failures were noted by (1) external signs of leakage or (2) by capsule weight loss. All capsules were visually checked and weighed during every "down" period of the test furnaces. Weight loss measurements were uncertain for determining actual life of the inner capsules but were satisfactory for determining leaks. This was true because leakages were usually catastrophic in nature and the oxide usually passed through the outer molybdenum can as well. In only one case was a specimen which completed its scheduled test period apparently intact but found to have failed on sectioning. More positive means involving X-ray would have been desirable but were discarded as being too costly and time consuming. Subsequent tests will eliminate the outer capsule and visual check of oxide loss loss will be more reliable for leak detection.

Figures 2-2 through 2-5 present photographs of capsule cross sections as they appeared after removal from the furnace either because of excessive weight loss or at the completion of a scheduled test period. It will be noted that in the capsules which leaked, there is little or no oxide remaining and the capsule wall appears perfectly clean. Since the escape route from most capsules was through minute weld cracks, the oxides show low viscosity and excellent wetting characteristics. Capillarity can be the only explanation for the manner in which molten oxide completely escapes.

Tables 2-11 through 2-15 present a summary of capsule weight data. The tables indicate the weight change for each capsule when the test was terminated and the longest test time at which no significant weight change was noted. In the case of two tungsten-rhenium capsules containing the 3BeO-2MgO mixture, weight loss indicated failure but when these capsules were opened the inner capsules were still intact. In these cases the indicated weight loss resulted from evaporation of molybdenum from the outer capsule. This cause of weight loss was overlooked as a possibility, since calculations show that this amount of weight loss is reasonable to expect.

TABLE 2-7. SUMMARY OF RESULTS - MATERIALS COMPATIBILITY TESTS: 3BeO-2CaO

Melting Point 1685°K (2560°F)

Cycling Range 1650°K (2500°F) - 1750°K (2700°F)

Capsule No.	Capsule Material	Scheduled Test (hrs.)	Test Duration (hrs.)	Assembly Wt. Change (grams)	Remarks	Cycles
1	Mo	100	<24	----- Oxide Over Outside Capsule----		12
37	Mo	500	478	+0.100	No leaks	38
29	Mo	1500	1484	+0.445	No leaks	58
11	Mo	2500	>1820<2365	-7.293	Capsule empty	81
28	Mo	3500	>2492<3165	-7.710	Capsule empty	113
4	Mo-Re	100	100	+ .3178	No leaks	12
38	Mo-Re	500	500	+ .048	No leaks	38
30	Mo-Re	1500	1484	+ .264	No leaks	58
35	Mo-Re	2500	>2199<2492	-2.3128	Capsule Leaked	95
16	Mo-Re	3500	3500	- .361	No leaks	135
60	W	500	<500	+ .180	Inner capsule leaked	12
56	W	1500	1484	+ .278	No leaks	58
54	W	2500	>1484<2069	-6.712	Capsule empty	69
21	W	3500	>2535<3500	-5.998	Capsule empty	135
7	W-Re	100	<100	-5.521	Capsule leaked	12
48	W-Re	500	500	+ .234	No leaks	12
50	W-Re	1500	>1196<1484	-6.8118	Capsule leaked	58
49	W-Re	2500	>1484<2029	-7.229	Capsule empty	69

TABLE 2-8. SUMMARY OF RESULTS - MATERIALS COMPATIBILITY TESTS: Al_2O_3-4BeO-4MgO

Melting Point 1910°K (2985°F)

Cycling Range 1875°K (2900°F) - 1975°K (3100°F)

Capsule No.	Capsule Material	Scheduled Test (hrs.)	Test Duration (hrs.)	Assembly Wt. Change (grams)	Remarks	Cycles
2	Mo	100	100	-5.324	Capsule empty	12
55	Mo	500	500	+ .060	No melt	38
53	Mo	1500	< 478	-6.595	Capsule empty	38
52	Mo	2500	< 478	-9.666	Capsule empty	38
12	Mo	3500	> 192 < 814	-11.075	Capsule empty	50
5	Mo-Re	100	< 100	-10.423	Capsule empty	12
42	Mo-Re	500	< 478	+ .802	Inner capsule leaked	38
41	Mo-Re	1500	< 478	-8.288	Capsule empty	38
40	Mo-Re	2500	> 695 < 1196	-11.342	Capsule empty	50
17	Mo-Re	3500	> 192 < 814	-5.405	Capsule leaked	50
47	W	500	500	-1.7139	No leaks	12
46	W	1500	1500	-1.8460	No leaks	46
45	W	2500	> 1390 < 1500	-6.4718	Capsule empty	46
20	W	3500	> 192 < 814	-5.1382	Capsule empty	50
8	W-Re	100	< 24	-6.7321	Capsule leaked	12
43	W-Re	500	500	+ .435	No leaks	38
44	W-Re	1500	< 478	-8.571	Capsule empty	38
51	W-Re	2500	> 695 < 1196	-11.916	Capsule empty	50
15	W-Re	3500	> 1031 < 1529	-10.817	Capsule empty	58
61	Re	500	500	-1.41	No leaks	12
62	Re	1500	> 1050 < 1504	-8.668	Capsule empty	46
65	Heavy Mo (.125")	500	< 500	-8.561	Capsule empty	12
64	Heavy Mo	1500	< 500	-8.203	Capsule empty	12
63	Heavy Mo	2500	> 1050 < 1504	-11.8678	Capsule empty	46
67	Heavy Mo	3500	< 500	-10.284	Capsule empty	12

TABLE 2-9. SUMMARY OF RESULTS - MATERIALS COMPATIBILITY TESTS: 3BeO-2MgO

Melting Point 2145°K (3405°F)

Cycling Range 2085°K (3300°F) - 2195°K (3500°F)

Capsule No.	Capsule Materials	Scheduled Test (hrs.)	Test Duration (hrs.)	Assembly Wt. Change (grams)	Remarks	Cycles
10	W	100	< 100	-20.326	Capsule empty	6
36	W	500	< 500	-10.927	Capsule empty	12
39	W	1500	>1390 <1504	-14.7382	Capsule empty	58
33	W	2500	< 478	-11.6223	Capsule empty	38
19	W	3500	> 192 < 814	- 8.8551	Capsule empty	50
9	W-Re	100	< 100	-15.8529	Capsule empty	12
26	W-Re	500	478	- 0.383	No leaks	6
27	W-Re	1500	1196	- 4.973	No leaks*	50
25	W-Re	2500	1196	- 4.287	No leaks*	50
18	W-Re	3500	< 192	-10.217	Capsule empty	13
73	Re	Indefinite --- Currently has 1000 hour exposure ---			Available for further testing	
74	Re	Indefinite --- Currently has 1000 hour exposure ---			Available for further testing	
75	W-Re	Indefinite --- Currently has 1000 hour exposure ---			Available for further testing	

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* Removed from test because of weight loss. When opened capsules were found not to have leaked.

TABLE 2-10. SUMMARY OF RESULTS - COMPATIBILITY TESTS: Al_2O_3-4BeO-MgO

Melting Point 2020°K (3180°F)

Cycling Range 2085°K (3300°F - 2195°K (3500°F)

Capsule No.	Capsule Material	Scheduled Test (hrs.)	Test Duration (hrs.)	Assembly Wt. Change (grams)	Remarks	Cycles
3	Mo	100	< 100	- 5.324	Capsule leaked	12
34	Mo	500	478	- 1.682	No leaks	38
31	Mo	1500	>1196 <1484	- 2.9195	Capsule leaked	58
32	Mo	2500	>1196 <1484	-10.023	Capsule leaked	58
13	Mo	3500	< 192	-10.536	Capsule empty	13

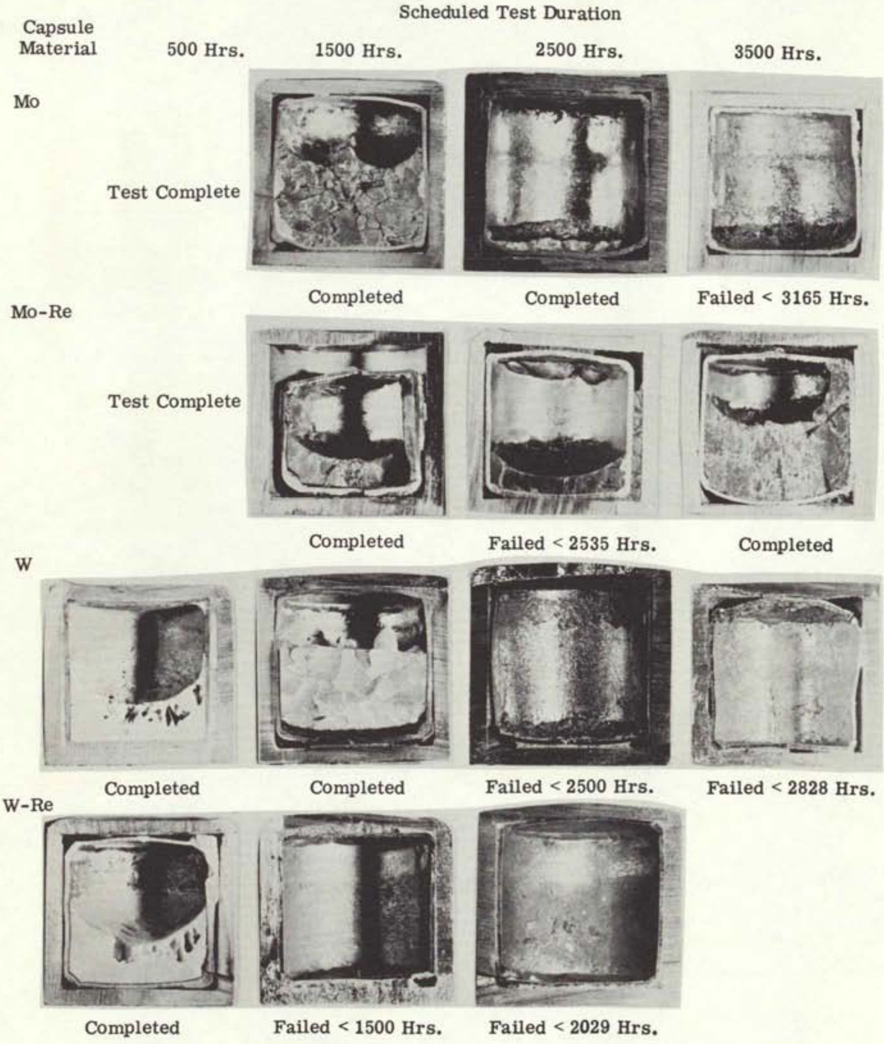

Figure 2-2. Cross Sections of 3BeO-2CaO Test Capsule Series

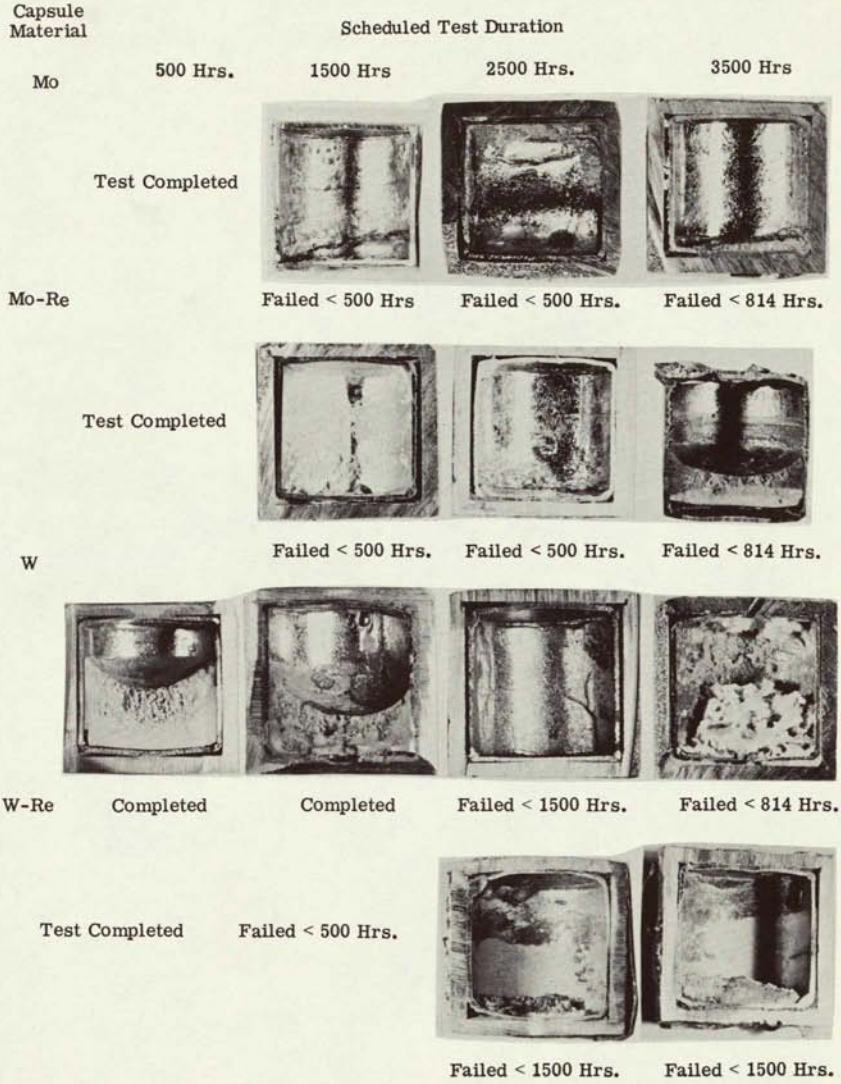

Figure 2-3. Cross Sections of Al_2O_3-4BeO-4MgO Test Capsule Series

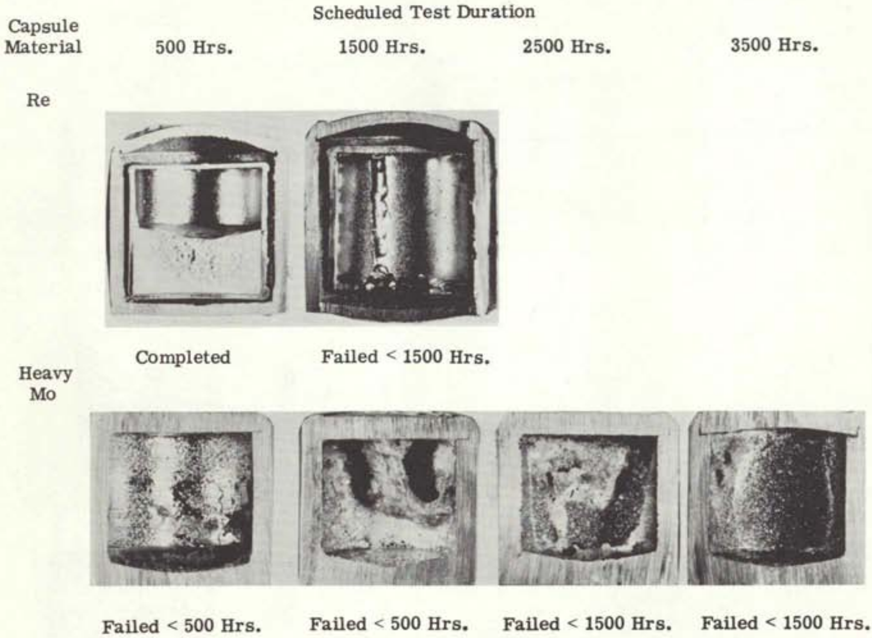

Figure 2-3. Cross Sections of Al_2O_3-4BeO-4MgO Test Capsule Series

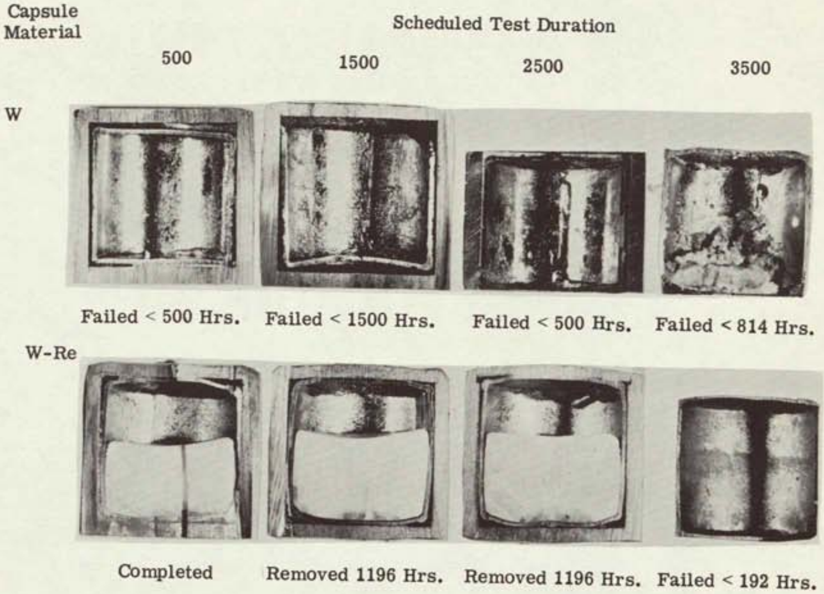

Figure 2-4. Cross Sections of 3BeO-2MgO Test Capsule Series

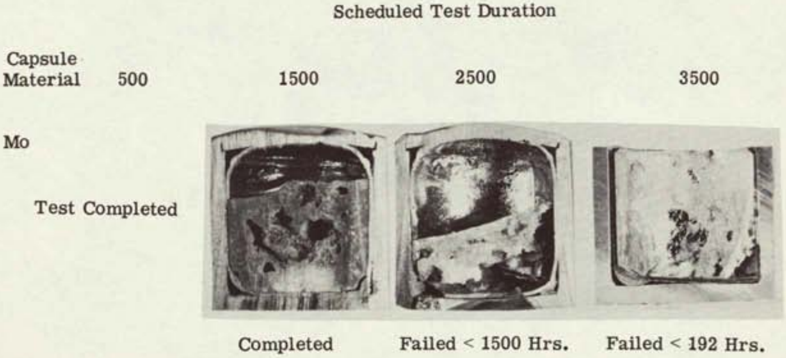

Figure 2-5. Cross Sections of Al_2O_3-4BeO-MgO Test Capsule Series

TABLE 2-11. CAPSULE WEIGHT DATA: 3BeO-2CaO

Oxide	Capsule Material	Oxide Wt. (gms.)	Initial Assembly Wt. (gms.)	Max. Time Wt. Duplicated (hrs.)	Termination of Test (hrs.)	Termination of Test (gms.)
3BeO-2CaO	Mo	11.1266	79.9440	< 24	24	test failed
	Mo	9.0461	76.6781	478	478	76.7781
	Mo	9.8812	77.0843	1484	1484	77.4450
	Mo	10.6367	74.6823	1820	2365	68.3122
	Mo	8.5106	75.3262	2492	3165	67.6160
	Mo-Re	10.0448	78.2946	100	100	78.6124
	Mo-Re	7.0622	74.7201	478	478	74.7688
	Mo-Re	3.5513	72.2203	1484	1484	72.4045
	Mo-Re	8.3183	73.2787	1484	2492	70.9659
	Mo-Re	11.3864	79.1054	3500	3500	78.9440
	W	8.2651	87.6138	500	500	87.7940
	W	8.3899	86.6633	1484	1484	86.9415
	W	8.3983	88.7098	1484	2069	80.4868
	W	7.5388	84.2359	2535	3510	78.2380
	W-Re	9.7282	87.8280	100	100	82.3075
	W-Re	6.0000	84.4195	500	500	84.6538
	W-Re	9.2851	83.5153	1196	1484	76.7035
	W-Re	8.2591	84.7759	1484	2029	77.5469

TABLE 2-12. CAPSULE WEIGHT DATA: Al_2O_3-4BeO-4MgO

Oxide	Capsule Material	Oxide Wt. (gms.)	Initial Assembly Wt. (gms.)	Max. Time Wt. Duplicated (hrs.)	Time and Wt. at Termination of Test (hrs.) (gms.)
Al_2O_3-4BeO-4MgO	Mo	11.4638	76.3014	100	100 - 76.6753
	Mo	10.0835	76.8227	< 500	500 - 77.1783
	Mo	10.3150	78.7830	< 478	478 - 72.1875
	Mo	10.6378	77.6167	< 478	478 - 67.9503
	Mo	10.4375	78.8828	192	814 - 67.7572
	Mo-Re	11.2295	81.9505	< 100	100 - 71.5277
	Mo-Re	9.7344	79.7485	478	478 - 80.5503
	Mo-Re	10.4010	81.3256	< 478	478 - 72.4973
	Mo-Re	10.6250	79.8663	695	1196 - 68.5240
	Mo-Re	11.8006	83.1084	192	814 - 77.7028
	W	9.1223	88.8019	500	500 - 87.0880
	W	9.1092	86.3910	1504	1504 - 84.5451
	W	5.5872	81.3159	1390	1504 - 74.8441
	W	10.8836	88.8697	192	814 - 83.7351
	W-Re	10.9511	86.4420	24	24 - 77.2637
	W-Re	8.7083	85.0443	< 500	<500 - 85.4778
	W-Re	8.7834	83.9500	478	478 - 75.3788
	W-Re	10.4146	87.5587	478	1196 - 75.6430
	W-Re	11.1259	88.6093	814	1529 - 77.7920
	Re	6.6343	80.1684	< 500	500 - 78.7576
	Re	6.8396	78.8194	789	1504 - 70.1510

TABLE 2-13. CAPSULE WEIGHT DATA: 3BeO-2MgO

Oxide	Capsule Material	Oxide Wt. (gms.)	Initial Assembly Wt. (gms.)	Max. Time Wt. Duplicated (hrs.)	Time and Wt. at Termination of Test (hrs.) (gms.)
3BeO-2MgO	W	11.0859	88.7162	< 100	100 - 68.3901
	W	10.3008	91.0252	< 500	500 - 80.0978
	W	9.3689	90.0986	784	1504 - 75.3604
	W	10.3447	89.3011	< 478	478 - 77.6788
	W	9.4088	90.4019	192	814 - 81.5468
	W-Re	11.9513	85.0397	100	100 - 69.1768
	W-Re	11.9832	88.9989	500	500 - 88.6155
	W-Re	11.9632	87.4397	<1196 see note	1196 - 82.4660
	W-Re	10.7963	87.1235	<1196	1196 - 81.8932
	W-Re	8.7191	84.5218	192	192 - 74.3047

TABLE 2-14. CAPSULE WEIGHT DATA: Al_2O_3-4BeO-MgO

Al_2O_3-4BeO-MgO	Mo	11.4638	76.3014	100	100 - 73.2449
	Mo	10.5111	80.8870	< 500	500 - 79.2048
	Mo	11.7823	79.8405	1196	1484 - 76.9210
	Mo	11.4579	77.6036	1196	1484 - 67.5810
	Mo	12.2562	80.6245	< 192	192 - 70.1287

Note: These capsules did not leak.

TABLE 2-15. CHARACTERISTICS OF OXIDE FROM SURVIVING CAPSULES

Capsule Material	Capsule No.	Test Duration	Color	Oxide Characteristics		Density (gm/cc)
				Solidification Geometry	Wetting Evidence	
3BeO-2CaO:						
Mo	37	478	Gray	Porous	Complete wetting	
Mo	29	1478	Black	High bulk density	Concave meniscus	2.67
Mo-Re	4	100	Black	High bulk density	Concave meniscus	
Mo-Re	38	478	Black	High bulk density	Concave meniscus	
Mo-Re	30	1484	Black	High bulk density	Concave meniscus	2.69
Mo-Re	16	3500	Black	High bulk density	Concave meniscus	2.72
W	60	500	White	Some porosity	Capsule completely wetted	3.11
W	56	1484	Tan	High bulk density	Capsule completely wetted	2.70
W-Re	7	100	White	Slight shrinkage	Capsule wetted	
W-Re	48	500	White	Some porosity	Concave meniscus	3.14
Al_2O_3-4BeO-4MgO						
Mo	2	100	White	Shrinkage pipe	Concave meniscus	
W	47	500	Greenish-White	Porous	Concave meniscus	3.22
W	46	1504	Gray	Porous	Concave meniscus	
W-Re	43	500	Greenish-White	Large pores	Concave meniscus	
Re	61	500	Gray	Porous	Did not wet	3.29
3BeO-2MgO:						
W-Re	26	500	White	Very dense	Convex meniscus	
W-Re	27	1196	White	Very dense	Convex meniscus	3.25
W-Re	25	1196	White	Very dense	Convex meniscus	
Al_2O_3-4BeO-MgO						
Mo	3	100	Gray	Dense	Concave meniscus	
Mo	34	500	Translucent	Dense	Capsule wetted	
Mo	31	1500	Brown	Porous	Capsule wetted	3.11

It can be seen from the capsule photographs that few capsules completed their scheduled test periods. These were the only capsules which provided oxide material for subsequent examination and analysis. Table 2-15 is a tabulation of the visual observations which could be made of those capsules which survived. In the case of 3BeO-2MgO in the tungsten-rhenium capsules there is evidence that the oxide had not wet the capsule wall. Since no tungsten capsule survived the test, it could not be determined whether this characteristic persists with other metals. The appearance of the oxide slugs is also an indication of volume changes on freezing. An extrusion ("pip") would indicate expansion. A void ("pipe") would indicate shrinkage. 3BeO-2CaO is an example of the former case and Al_2O_3-4BeO-4MgO is an example of the latter. The 3BeO-2MgO shows very little change with phase change. Wetting characteristics are observed by noting the meniscus angle at the wall. Note the difference in meniscuses of 3BeO-2CaO and 3BeO-2MgO.

B. Post-Test Oxide Analyses

With exception of the 3BeO-2CaO mixtures, it appears that the densities of the mixtures vary significantly from calculated and hot pressed densities (see Table 2-16). The measurements after fusion were difficult to make but it is noteworthy that 3BeO-2MgO is very near calculated density.

TABLE 2-16. DENSITIES OF TES OXIDES (Gm/cc)

	Calculated*	Hot-Pressed	Fused**
3BeO-2CaO	3.19	3.05	3.14
Al_2O_3-4BeO-4MgO	3.56	3.33	3.29
Al_2O_3-4BeO-MgO	3.57	3.22	3.11
3BeO-2MgO	3.20	3.23	3.25

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*Based on measured densities of BeO and CaO.

**Highest values only are reported since measurement used would tend to give low values.

The first three mixtures gave widely varying density values. Despite the fact that the samples were heated to 645°C prior to density determination, it is possible that the formation of calcium hydroxide or voids contributed to the density variations. Porosity contribution (low values) were minimized by crushing a sample into small pieces before density determinations were made using the pycnometer method. In view of the hydration problem, all determinations were made in carbon tetrachloride.

C. Spectrographic Analysis

Spectrographic analytical techniques were used to determine if container metals were present in the oxides. As explained previously, the number of specimens remaining were sparse. The results are presented in Table 2-17. Note that tungsten appears in the oxide in significant quantities and that molybdenum is also detectable. Rhenium, however, appears in very low concentrations. However, it should be pointed out that even the three (weight) percent tungsten found in the 1500 hour samples represents very

TABLE 2-17. RESULTS OF SPECTROGRAPHIC ANALYSES OF SEVERAL TEST CAPSULES AFTER LONG TIME COMPATIBILITY TESTS (IN WT. %)

Capsule No.	TES Material	Al	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Na	Si	Sr	Ti	W	Zr	K	Re
48	3BeO-2CaO 500 hrs. in W-Re	0.4	Hi	0.001	0.001	0.04	0.1	0.001	0.03	0.002	1.0	0.01	0.01	0.3	0.005	0.0002	0.03
60	3BeO-2CaO 500 hrs. in W	0.07	Hi	0.001	0.01	0.08	0.1	0.001	0.05	0.002	0.4	0.01	0.001	1.0	0.03	0.002	N.D.
56	3BeO-2CaO 1500 hrs. in W	0.05	Hi	0.001	0.001	0.06	0.1	0.001	0.005	0.002	0.1	0.01	N.D.	3.0	0.001	0.002	N.D.
30	3BeO-2CaO 1500 hrs. in Mo-Re	0.05	Hi	0.001	0.0005	0.06	0.05	0.001	0.2	0.002	0.02	0.01	0.001	N.D.	0.002	0.002	0.02
47	Al_2O_3-4BeO-4MgO 500 hrs. in W	Hi	0.04	0.001	0.001	0.1	Hi	0.001	0.02	0.01	0.5	N.D.	0.001	1.0	0.005	0.002	N.D.
61	Al_2O_3-4BeO-4MgO 500 hrs. in Re	Hi	0.02	0.001	0.0005	0.03	Hi	0.001	0.025	0.005	0.5	N.D.	N.D.	N.D.	0.001	0.002	0.05
27	3BeO-2MgO 1196 hrs. in W-Re	0.02	0.05	0.001	N.D.	0.07	Hi	0.001	0.005	0.007	0.02	N.D.	N.D.	0.2	0.001	0.002	N.D.
31	Al_2O_3-4BeO-MgO 1500 hrs. in Mo	Hi	0.02	0.001	0.001	0.10	Hi	0.001	0.4	0.005	0.3	N.D.	0.01	N.D.	0.001	0.003	N.D.

N.D. Not detected

little material removed from the capsule wall. Calculations based upon the weight of oxide present and the surface area of the capsule exposed to liquid oxide indicate that 3%W is equal to about 6×10^{-4} inch of W/1500 hours which extrapolates to about 0.004 inch/10,000 hours. From the limited data, it also appears that attack is linear with time: 1.0% at 500 hours and 3.0% at 1500 hours. It is unwise to extrapolate much beyond 1500 hours but these calculated values are of interest.

The Re and W-Re look especially attractive at higher temperatures with Al_2O_3-4BeO-4MgO and 3BeO-2MgO. The quantities of these metals in the oxides are about an order of magnitude lower for equivalent time periods.

D. Crystallographic Investigations

X-ray crystallographic investigations of hot pressed and fused oxides were conducted to determine the oxide compounds present. Results are tabulated in Tables 2-18 through 2-21. The patterns were obtained on an X-ray goniometer with the samples prepared by crushing the solid bodies and mounting the resulting powder on glass slides after mixing with Duco cement. The "D" spacings obtained from hot pressed and fused specimens together with those taken from the ASTM X-ray Powder Data File for the compounds present are presented in these tables. It was apparent that in the two binary mixtures, 3BeO-2CaO and 3BeO-2MgO, the two component oxides remain unchanged through both the hot pressing and melting operations. The calcium hydroxide pattern which is evident in the beryllia-calcia mixtures is the usual result of hydration which had taken place during sample preparation. The ternary alumina-beryllia-magnesia mixtures show formation of a compound in both hot pressed and fused material. This is a magnesia-alumina spinel (MgO-Al_2O_3) in 4BeO-MgO-Al_2O_3 mixture and a ternary compound (double spinel) in the 4BeO-4MgO-Al_2O_3 combination.

TABLE 2-18. X-RAY CRYSTALLOGRAPHIC DATA FOR 3BeO-2CaO

Mixed Pwds. d Values	Hot Pressed d Values	Fused d Values	BeO d Values	CaO d Values	$Ca(OH)_2$ d Values
3.14	3.143				3.11
2.78	2.797	2.81		2.78	
2.65	2.652	2.65			2.63
2.41	2.423	2.44		2.40	
2.35	2.350	2.36	2.36		
2.20	2.201	2.20	2.20		
2.07	2.074	2.08	2.07		
1.94	1.935	1.93			1.93
1.80	1.804	1.80			1.80
1.70	1.701	1.71		1.70	
1.60	1.604	1.69	1.60		
1.49	1.488	1.49			1.48
1.45	1.455	1.45		1.45	
1.39	1.393	1.39		1.39	
1.35	1.352	1.35	1.35		
1.32	1.318				1.31
1.24	1.240	1.24	1.24		
1.15	1.149	1.15	1.15		
	1.106	1.11		1.10	
1.07	1.077	1.08		1.07	
0.982	0.983	0.984		0.982	
	0.913	0.928	0.913		
	0.824	0.814	0.820		

TABLE 2-19. X-RAY CRYSTALLOGRAPHIC DATA FOR Al_2O_3-4BeO-4MgO

Mixed Pwd. d Values	Hot Pressed d Values	Fused d Values	BeO d Values	MgO d Values	BeO-MgO-$2Al_2O_3$
		2.974			2.95
	2.876	2.931			2.86
	2.452	2.522			2.61
2.445	2.350	2.401		2.431	2.43
2.347	2.199	2.254	2.356		2.38
2.201	2.117	2.166	2.204		2.18
	2.069	2.122			2.05
2.117	2.029	2.056	2.076	2.106	1.93
	1.653	1.678			1.68
1.603	1.559	1.563	1.605		1.59
1.494	1.495	1.514		1.489	1.52
	1.433	1.451			1.48
1.351	1.349	1.371	1.354		
1.272	1.272	1.287		1.270	
1.238	1.236	1.230	1.242		
1.217	1.217	1.179		1.216	
1.150	1.168	1.158	1.150		
1.053	1.054	1.061		1.053	
	1.011	1.071			
0.942	0.942	0.945		0.942	
	0.903	0.916			
0.860	0.860	0.862		0.860	
		0.826			

TABLE 2-20. X-RAY CRYSTALLOGRAPHIC DATA FOR 3BeO-2MgO

Mixed Pwd. d Values	Hot Pressed d Values	Fused d Values	BeO d Values	MgO d Values
2.455	2.455	2.474		2.442
2.359	2.356	2.380	2.356	
2.206	2.206	2.222	2.204	
2.125	2.122	2.163		2.110
2.078	2.076	2.103	2.076	
1.658	1.658			
1.605	1.603	1.616	1.605	
1.497	1.495	1.506		1.491
1.354	1.352	1.361	1.354	
1.275	1.272	1.281		1.271
1.241	1.240	1.245	1.242	
1.220	1.218	1.225		1.216
1.172	1.170	1.175	1.170	
1.151	1.150	1.155	1.151	
1.130	1.130			
1.064	1.054	1.058		1.053
0.968	0.968	0.972		0.966
0.943	0.942	0.945		0.942
0.913	0.913	0.916	0.913	
0.861	0.866			0.860
0.821	0.820		0.820	

TABLE 2-21. X-RAY CRYSTALLOGRAPHIC DATA FOR Al_2O_3-4BeO-MgO

Mixed Pwd. d Values	Hot Pressed d Values	Fused d Values	BeO d Values	MgO d Values	MgO-Al_2O_3 d Values
	2.894	2.876			2.85
2.445	2.465	2.455		2.43	2.44
2.347	2.365	2.362			2.33
2.201	2.287	2.196	2.19	2.11	
2.117	2.085	2.076	2.06		
2.071	2.040	2.032			2.02
	1.661	1.653			
1.603	1.609	1.605	1.60		1.65
	1.566	1.559		1.50	1.55
1.494	1.437	1.431			1.43
	1.370	1.368			1.36
1.351	1.357	1.354	1.35		
1.272	1.274	1.278		1.27	1.28
1.238	1.244	1.234	1.24	1.22	1.23
1.150	1.170	1.172			1.16
	1.152	1.150			
	1.134	1.130			1.13
	1.082	1.079			1.08
1.053	1.054	1.051		1.05	1.05
	1.012	1.009			1.01

E. Capsule Wall Examination

Thickness Measurement and Hardness Data - All capsules were subjected to a detailed macroscopic and microscopic study. As can be seen from the photographs in Figures 2-2 through 2-5, the exact location of failure sites are not readily apparent. Longitudinal cross sections of each capsule were mounted for metallographic examination including the region which had been covered by liquid oxide during test. This permitted measurement of wall thickness and allowed a hardness profile to be obtained. These data are presented in Tables 2-22 through 2-25. The 500 hour control specimens are included but the 3500 hour controls are not. In the case of the latter series, diffusion bonding had taken place and interdiffusion had occurred to such an extent that the materials were no longer representative of the original compositions.

From the thickness measurements, no significant changes in wall dimensions resulted from exposure to the oxides. The variations noted are for the most part those which existed in the sheet material as received. There is also evidence, particularly in the case of the rhenium, the tungsten and the tungsten-rhenium alloy, that molybdenum from the outer capsule reacted with the test capsule. This would account for the apparent increase in thickness. This is most graphically evident in the case of the rhenium. Here the reaction layer is strongly evident with a narrow band of extremely hard and brittle material formed bounded by a molybdenum rich and rhenium rich layer on either side. In one 500 hour specimen, this hard brittle layer was nearly .004 inch below the outer capsule surface. After 1500 hours, this layer depth was .012 inch. In both cases, the intermetallic layer was about .002 inch thick. Of particular interest in this case is the fact that this reaction has taken place with no evidence of bonding between the two capsules. This could mean that molybdenum was transferred as a vapor.

Further evidence of this vapor transfer was presented by the rhenium control specimen which lay in the bottom of a molybdenum capsule. Here again extensive diffusion was noted through all surfaces of the rhenium despite the fact that the specimen had only one contacting surface. Again, there was no evidence of a diffusion bond having formed between contacting surfaces.

An explanation for the inconsistencies found in the Knoop micro-hardness values of the capsule materials is not readily apparent. The fact that the hardness impressions from which the numbers are derived are microscopic in character inherently results in a rather wide spread in hardness values. This reflects, to some extent, the effects of individual grain orientation, microscopic compositional variations as well as the more macroscopic effects of strains induced in the preparation of the sample.

A few generalized statements can be made, however, concerning the results obtained. With one or two exceptions, those materials which were exposed to the molten oxides for extended periods of time were less hard than in the as-received condition. This is as would be expected to result from recrystallization and the approach to complete equilibrium. It is also indicative of the absence of oxide contamination or penetration. This was also confirmed by spectrographically analyzing sections of capsule walls. No evidence of any of the metallic elements of the oxides (Al, Be , Ca, Mg) could be detected in the capsule walls.

TABLE 2-22. MICRO-HARDNESS AND THICKNESS FOR CONTAINER MATERIALS KNOOP HARDNESS NUMBERS 100 GRAM LOAD: MOLYBDENUM

								Thickness Inches
As-received		193	262	220	250	233		.020
1750°K Control 500 hrs.		210	210	205	210	221		.020
Containing 3BeO-2CaO								
100 hours	Inside	230	210	225	222	255	Outside	.020
500 hours		230	237	240	247	205		.020
1484 hours		186	202	200	187	180		.021
2365 hours		218	240	244	227	221		.020
3165 hours		215	215	209	210	195		.017
1975°K Control 500 hrs.		255	215	235	221	210		.020
Containing Al_2O_3-4BeO-4MgO								
100 hours	Inside	205	195	160	201	216	Outside	.020
500 hours		205	212	225	210	200		.021
478 hours		218	238	237	255	232		.020
478 hours		210	243	237	243	220		.020
814 hours		191	205	211	213	203		.020
2195°K Control 500 hrs.		230	245	210	205			.017
Containing Al_2O_3-4BeO-MgO								
100 hours	Inside	205	195	180	201	210	Outside	.022
478 hours		380	370	378	342	350		.020
1484 hours		180	184	180	172	183		.0185
1484 hours		191	197	186	187	179		.019
192 hours		340	335	340	332	305		.020

TABLE 2-23. MICRO-HARDNESS AND THICKNESS FOR CONTAINER MATERIALS KNOOP HARDNESS NUMBERS 100 GRAM LOAD: MOLYBDENUM-50% RHENIUM

								Thickness Inches
As-received		410	410	390	394	390		.016
1750°K Control 500 hrs.		205	200	205	210	200		.020
Containing 3BeO-2CaO								
100 hours	Inside	450	442	442	420	410	Outside	.020
478 hours		400	360	390	345	445		.020
1484 hours		386	378	372	350	400		.019
2492 hours		438	297	348	355	310		.021
3500 hours		350	345	355	338	295		.023
1975°K Control 500 hrs.		210	242	215	210	210		.020
Containing Al_2O_3-4BeO-4MgO								
100 hours	Inside	330	410	412	412	420	Outside	.018
478 hours		460	650	640	490	410		.016
478 hours		680	700	700	700	680		.020
1196 hours		197	202	190	199	200		.020
814 hours		482	395	350	426	372		.022

TABLE 2-24. MICRO-HARDNESS AND THICKNESS FOR CONTAINER MATERIALS KNOOP HARDNESS NUMBERS 100 GRAM LOAD: TUNGSTEN

								Thickness Inches
As-received		670	620	645	670			.020
1750°K Control 500 hrs.		552	537	540	550			.025
Containing 3BeO-2CaO								
500 hours	Inside	478	443	478	430	490	Outside	.026
1484 hours		510	560	520	500	460		.025
2069 hours		445	500	500	500	458		.024
3500 hours		405	410	410	420	420		.024
1975°K Control 500 hrs.		470	450	450	520			.019
Containing Al_2O_3-4BeO-4MgO								
500 hours	Inside	410	490	500	510	345	Outside	.025
1500 hours		415	300	305	335	348		.027
1500 hours		616	442	465	470	412		.025
814 hours		450	510	522	530	553		.024
2195°K Control 500 hrs.		570	711	790	630			.0165
Containing 3BeO-2MgO								
500 hours	Inside	426	430	426	415	400	Outside	.025
1500 hours		340	370	350	330	335		.0245
478 hours		383	382	397	360	360		.022
192 hours		467	470	440	429	448		.025

TABLE 2-25. MICRO-HARDNESS AND THICKNESS FOR CONTAINER MATERIALS
KNOOP HARDNESS NUMBERS 100 GRAM LOAD: TUNGSTEN-25% RHENIUM

								Thickness Inches
As-received		650	650	730	700			.019
1750°K control 500 hrs.		610	560	480	560			.0175
Containing 3BeO-2CaO								
100 hours	Inside	680	640	700	750	700	Outside	.019
500 hours		445	498	590	610	560		.019
1484 hours		511	572	572	503	540		.018
2029 hours		599	612	543	559	511		.020
1975°K control 500 hrs.		710	780	810	818	805		.021
Containing Al_2O_3-4BeO-4MgO								
24 hours	Inside	650	630	630	640	620	Outside	.020
500 hours		600	550	590	620	600		.018
478 hours		370	422	413	368	327		.022
1196 hours		550	550	640	460	429		.019
1529 hours		512	591	543	522	490		.018
2195°K control 500 hrs.		370	370	410	440			
Containing 3BeO-2MgO								
100 hours	Inside	550	575	575	520	510	Outside	.020
478 hours		540	522	495	570	397		.020
1196 hours		490	510	530	472	435		.0195
1196 hours		462	483	470	467	390		.019
192 hours		690	510	430	679	565		.021

TABLE 2-26. MICRO-HARDNESS AND THICKNESS FOR CONTAINER MATERIALS
KNOOP HARDNESS NUMBERS 100 GRAM LOAD: RHENIUM

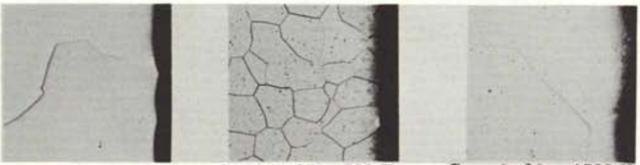
As-received		130	150	130	145	150		.020
1975°K control 500 hrs.		290	295	295	295	295		.017
Containing Al_2O_3-4BeO-4MgO								
500 hours	Inside	280	300	325	350	355	Outside	.025
1500 hours		363	382	390	410	369		.027

F. Metallography

Photomicrographs of the various capsule materials in the as-received condition; after 500 hour anneals at the various test temperatures, and after two oxide exposure periods are presented in Figures 2-6 through 2-10. As pointed out previously the specimen mounts include areas which had been continuously exposed to the oxide throughout the test. A complete set of all micrographs is presented in Appendix I.

As Received Material

3BeO-2CaO Test Temperature Range 1650°K - 1750°K

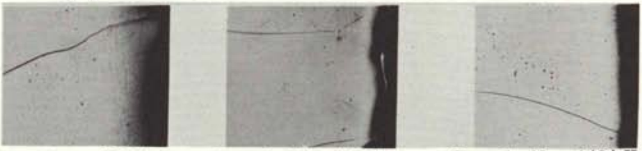


Control 500 Hrs. Capsule 37 500 Hrs. Capsule 29 1500 Hrs.

Al_2O_3-4BeO-4MgO Test Temperature Range 1875°K - 1975°K

Control 500 Hrs. Capsule 55 500 Hrs. Capsule 12 814 Hrs.

Al_2O_3-4BeO-MgO Test Temperature Range 2085°K - 2195°K



Control 500 Hrs. Capsule 34 500 Hrs. Capsule 32 1484 Hrs.

Figure 2-6. Microstructure of Molybdenum Capsules 250X

As Received Material

3BeO-2CaO Test Temperature Range 1650°K - 1750°K

Control 500 Hrs. Capsule 38 500 Hrs. Capsule 30 1484 Hrs.

Al_2O_3-4BeO-4MgO Test Temperature Range 1875°K - 1975°K

Control 500 Hrs. Capsule 42 478 Hrs. Capsule 40 1196 Hrs.

3BeO-2MgO Test Temperature Range 2085°K - 2195°K

Temperature Considered Excessive for Molybdenum Compatibility Test not Conducted

Capsule

Temperature Considered Excessive for Molybdenum Compatibility Tests not Conducted

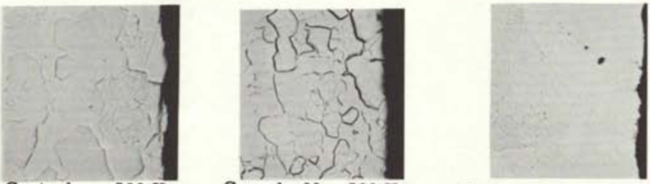
Capsule

Control 500 Hrs.

Figure 2-7. Microstructure of Molybdenum - 50% Rhenium Capsules 250X

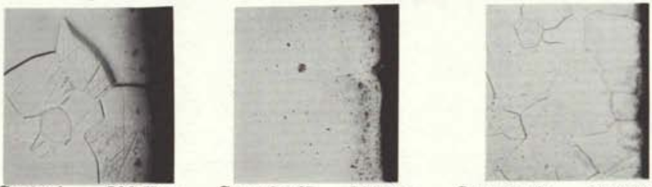
As Received Material

3BeO-2CaO Test Temperature Range 1650°K - 1750°K



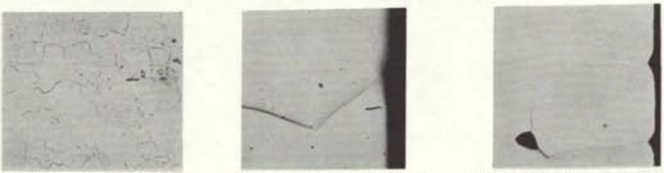
Control 500 Hrs. Capsule 60 500 Hrs. Capsule 56 1484 Hrs.

Al_2O_3-4BeO-4MgO Test Temperature Range 1875°K - 1975°K



Control 500 Hrs. Capsule 47 500 Hrs. Capsule 46 1500 Hrs.

3BeO-2MgO Test Temperature Range 2085°K - 2195°K



Control 500 Hrs. Capsule 36 500 Hrs. Capsule 39 1504 Hrs.

Figure 2-8. Microstructure of Tungsten Capsules 250X

As Received Material

3BeO-2CaO Test Temperature Range 1650°K - 1750°K

Control 500 Hrs. Capsule 48 500 Hrs. Capsule 50 1484 Hrs.

Al_2O_3-4BeO-4MgO Test Temperature Range 1875°K - 1910°K

Control 500 Hrs. Capsule 43 500 Hrs. Capsule 15 1529 Hrs.

3BeO-2MgO Test Temperature Range 2085°K - 2195°K

Control 500 Hrs. Capsule 26 500 Hrs. Capsule 27 1196 Hrs.

Figure 2-9. Microstructure of Tungsten - 25% Rhenium Capsules 250X

As Received Material
Al_2O_3-4BeO-4MgO

Control 500 Hrs. Capsule 61 500 Hrs. Capsule 62 1500 Hrs.

Figure 2-10. Microstructure of Rhenium Capsules 250X
(Polarized Light)

Note that in the case of the two rhenium alloys (Mo-Re, W-Re) there is evidence of a second phase, apparently an oxide. Although it is not readily apparent from the photomicrographs of the as-received material, this oxide is initially present in these materials in randomly distributed, isolated regions. This second phase can be seen in both the parent metal control and the two capsule specimens in the tungsten-rhenium - 3BeO-2CaO system in Figure 2-9. The stringer type distribution parallel to the rolling direction indicates that the oxide was occluded during metal strip processing. At the higher temperature this oxide contamination tends to coalesce in the grain boundaries. It is apparent that the best available rhenium alloys representative of present state of the art were not of optimum quality. Despite this contamination, however, rhenium and rhenium alloys appear most promising as container metals.

The following sections deal in more detail with the apparent behavior of each test combination, in order, through the micrographs:

Molybdenum (control): This metal, as received, shows the typical structure. After 500 hours at each of the three test temperatures, large grain structure is noted which is also typical. Some of these grain boundaries extend completely across the 0.020 in. thickness. These long boundaries present an ideal site for structural failure.

Molybdenum (3BeO-2CaO): After 500 hours, grain sizes have increased slightly and grain boundaries are more accented. Much larger grain sizes occur at 1500 hours, as would be expected. In this case the wall is showing signs of erosion especially at grain boundaries.

Molybdenum (Al_2O_3 - 4BeO-4MgO): At 500 hours, grain sizes are similar to the control specimens. There is no sign of attack at the wall. At 814 hours grain size has not increased significantly but the wall does appear to be slightly eroded at grain boundaries.

Molybdenum (Al_2O_3-4BeO-MgO): After 500 hours, little sign of attack or erosion is noted; grain sizes are typical. After 1484 hours, very large grains are present with continuous boundaries reaching completely across the wall. There is very little sign of preferential attack at grain boundaries as typified by "valleys" into the wall. It may be that this effect was erased as the grains grew.

From this study of molybdenum it would appear in general, that temperature effect on grain growth is a major problem. Some signs of attack are noted in some cases, but not nearly significant enough to indicate chemical incompatibility.

Molybdenum-Rhenium (control): This micrograph of as-received metal shows a relatively clean material. In many cases, occluded oxide is noted which appears as elongated patches parallel to the rolling direction. After 500 hours, increasing temperatures show drastic effects on the grain structure. There also appears to be considerable grain growth at the surface at 2195°K.

Molybdenum-Rhenium (3BeO-2CaO): These two micrographs after 500 and 1484 hours show the presence of another phase. The composition of this phase is not known but may be the beginnings of sigma phase regions. This could occur if the alloy was slightly off the 50-50 composition. Compatibility-wise, there does not appear to be any sign of attack by the oxide.

Molybdenum-Rhenium (Al_2O_3-4BeO-4MgO): Some attack at grain boundaries is noticeable after 1500 hours. Grain growth has also increased with the longer time. No sign of a second phase is seen in these samples.

Tungsten (Control): Grain growth is quite like that of molybdenum although not as pronounced. Increase in temperature speeds up this growth process.

Tungsten (3BeO-2 CaO): Grain growth or attack is not apparent after 500 hours. At 1500 hours, grain growth is as expected and the beginnings of attack at boundaries seem to be occurring. This attack is more evident at 2000 hours (see micrograph in Appendix I).

Tungsten (Al_2O_3-4BeO-4MgO): At 500 hours, a discoloration appears in the surface along with grain boundary attack. At 1500 hours, the metal has not changed much more than at 500 hours. This could indicate that some impurity reacts first and that reaction is limited after this first attack as the impurity is depleted.

Tungsten (3BeO-2MgO): Grain growth is quite aggravated in this case because of the high temperatures. Some corrosive attack is noticeable at grain boundaries after 1500 hours. This penetration is about 0.0002 inches in depth.

Tungsten-Rhenium (Control): As received, this alloy usually shows striations of foreign material (probably ReO_2). This material lies along the rolling direction. The 500 hour control specimen shows a large quantity of this material and usually with heat treatment these randomly dispersed impurities begin to agglomerate in pockets between grain boundaries. This appears to be a fusing or melting process, since ReO_2 melts at 1475°K. Except for this phenomenon the grain growth seems to be less extensive than Mo or W over the same time period. The W-Re also shows good ductility after 500 hours.

Tungsten-Rhenium (3BeO-2CaO): The impurity described appears to behave like that in the control specimen after 500 hours. There is no sign of surface attack by 3BeO-2CaO. After 1500 hours, there appears to be an inter-granular penetration in the surface about 0.001 inch deep.

Tungsten-Rhenium (Al_2O_3-4BeO-4MgO): After 500 hours, the occluded impurity has taken a nearly cubical shape. Some attack is noticeable at the surface. There is considerable penetration after 1500 hours at one isolated spot. This capsule also shows a 50% or more penetration from the outside. Between the molybdenum outer capsule and the test capsules, large amounts of sloughed-off metal are evident. It is entirely conceivable that this capsule failed by virtue of this outside attack.

Tungsten-Rhenium (3BeO-2MgO): The metal looks very good after 500 hours but all welds were filled with large bubbles. After 1196 hours the metal still looks very good but alloying with molybdenum is beginning to appear on the outside wall. The welds in the 1500 hour capsule also show characteristic bubbles.

Rhenium (Control): As received and after 500 hours there does not seem to be much change. These polarized photographs markedly accent the crystalline structure. There appears to be very little change in structure and there are no signs of chemical attack. This metal shows pore-free welds and rhenium was the easiest to fabricate into capsules. Rhenium is a very attractive metal for this application as far as fabricability is concerned.

2.3 CONCLUSIONS AND RECOMMENDATIONS

The corrosion test study has indicated that the select ceramic oxides under study can be contained for periods of at least 1500 hours. Although many of the test capsules have failed, there are no definite indications that chemical compatibility is a problem up to 1500 hours and, in several cases, up to 3000 hours. The failure mechanisms seem to be a function of micro-cracking which appears near welds and that factors such as grain growth and re-crystallization are not grossly contributing. Stresses on weld joints because of internal pressures and cycling temperature may enhance the cracking process. There is also a possibility that an oxide mixture which expands on freezing (3BeO-2CaO, Al_2O_3-4BeO-4MgO and Al_2O_3-4BeO-MgO) may aggravate cracking by a "ratcheting" process during thermal cycling (freeze-fuse cycling).

From a fabricability stand-point, rhenium and the rhenium alloys of tungsten and molybdenum are best. These metals are expensive and need to be improved quality-wise, especially Mo-Re and W-Re. Impurity occlusions have been producing porous weldments of these oxides.

The ceramic oxides studied did not aggravate grain growth or hardness in the metals chosen. Spectrographic analyses of the metal capsules did not indicate any penetration of the oxide components into these metals.

The oxide mixtures containing Al_2O_3 show the formation of $MgAl_2O_4$ (spinel) and $BeAl_2O_4$. The effect of these compounds on chemical stability were not possible to ascertain in this study. The 3BeO-2MgO did not appear to wet W-Re and showed little density change with phase change. A photomicrograph of this oxide shows an interesting crystal structure indicating a composition very near the eutectic (Figure 2-11). The unusual crystalline patterns present are accented by the cutting direction.

On the basis of the limited results available, the following recommendations are made:

1. The 3BeO-2MgO in rhenium represents the best combination and should be studied for long-time compatibility.

2. Physical property data on 3BeO-2MgO especially thermal conductivity, should be obtained.

3. Compositions containing BeO and MgO should be investigated for additional oxide mixtures as ternaries or quartenaries which could be used for thermal energy storage.

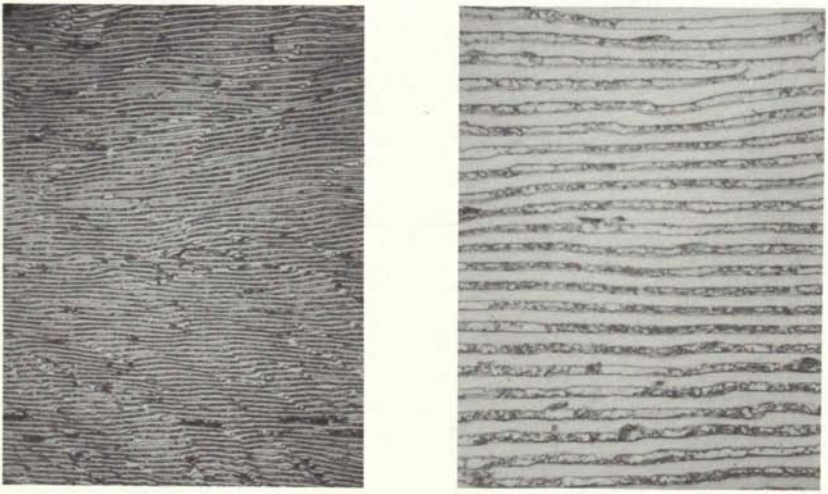
4. The 3BeO-2MgO phase diagram should be determined especially near the eutectic to better ascertain the eutectic point.

MATRIX

REMOVED 1196 HRS.

29.2 X

LAMELLAR EUTECTIC PHASE



(a) 154 X

(b) 625 X

Figure 2-11. Micrographs of 3BeO-2MgO Structure After Test

III THERMAL CONDUCTANCE APPARATUS

The primary objective of this phase of the program was to obtain data useful for heat transfer calculations involving the TES oxides. This effort involved design, fabrication and calibration of a suitable test fixture for measurement of thermal conductance. The experimental philosophy was to obtain basic thermal conductance data which could be utilized to correlate with an analytical model.

A device was designed to measure thermal conductivity, and possibly to separate out the heat transferred by photons from that by molecular or phonon conduction. Free convection and non-uniform temperature effects were also made negligible in this design. A device which measures pure conductance does not have to separate out these effects and is often based on a defined geometry. The conductance device described in this report is designed to hold free convection effects to a minimum or experimentally separable, value and will also allow separation of photon transfer from the other transfer mechanisms provided this transfer is a very significant part of the total thermal conductance. While some two-dimensional heat transfer effects can be expected in the test samples investigated with this device, these effects will have their practical counterparts in the intended application. In view of these considerations, the General Electric Company proceeded to carry out the design and construction of this thermal conductance apparatus.

3.1 MAJOR APPARATUS CHARACTERISTICS AND SPECIFICATIONS

3.1.1 Physical Characteristics

The nickel-plated steel apparatus case is 14 inches in diameter and 10 inches high excluding small local protusions. (See Figures 3-1 and 3-2.) The removable internal section is 11-1/4 inches in diameter and 7-1/2 inches high, consisting of about 100 dimpled tantalum and molybdenum radiation shields with their associated supporting structure. This section contains only refractory materials and encloses the electrical heater assembly.

The heater assembly consists of a tantalum heater, tungsten leads, thoria and tungsten standoff units, and a tantalum-tungsten support structure. The heater is supported by three electrical leads that provide for two separately controlled electrical circuits covering a total heated section having a 6-inch diameter. The top shielding is hung from stiffened plates located in colder sections of the top shielding structure while the side shields are hung on brackets that are in turn attached to colder stiffened structural members. The top, side and bottom shield assemblies have stepped clearances to reduce heat leakage and allow separate handling.

All thermocouples are W-5% Re versus W-26% Re insulated with specially prepared 99.9% pure thoria beads. The 3-feet long thermocouples installed in the radiation shielding structure have a standard calibration as submitted by the Hoskins Manufacturing Company, while the 4-feet long thermocouples for the test sample container are specially calibrated.

Heat is transported by radiation to the top of the 4-1/4 inch diameter test sample container. The test material is to be located between two 1/4-inch thick horizontal discs, separated by a 3/8-inch and 3/4-inch thickness of oxide respectively, using a 0.010-inch cylindrical wall. A maximum sample container having a height of 3 inches exclusive of the centrally located expansion reservoir, is allowable and a maximum container diameter of 6-1/2 inches is permissible in the future, provided the bottom shielding is redesigned.

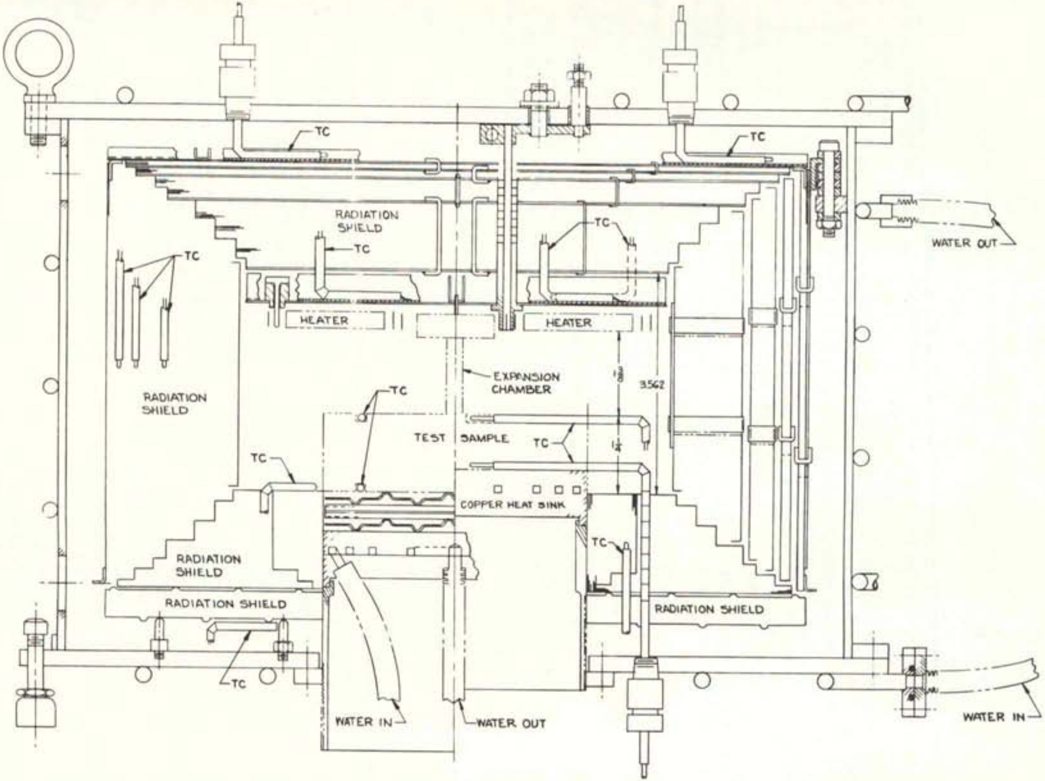


Figure 3-1. Thermal Test Fixture

Figure 3-2. View of Component Parts. (Bolts in Top Shielding Electrical Lead Holes are Temporary).

The heat is rejected from the bottom of the sample container through a desired number of radiation shields to a water-cooled copper heat sink. The heat sink has its own water circuit and is supported on a vertically adjustable stand.

The stiffened side wall outer structure of the radiation shielding supports the top and side shielding and is, in turn, supported at three points from the outer case. The bottom shielding rests on ten rounded pins attached to the base plate. The top plate supports the electrical heater assembly through the electrical leads. One water circuit removes the heat transferred to the entire outer enclosure excluding that transferred to the copper heat sink. The difference between the heat removed by both water circuits and that added electrically results in the heat balance for this apparatus. The heat removed by the copper heat sink divided by the measured temperature difference between the top and bottom plates of the sample container will yield the thermal conductance of the contained test material.

3.1.2 Major Specifications

3.1.2.1 Maximum Operating Pressure in Apparatus at Temperature of 10^{-3} Torr.

Pressures exceeding this value would result in tantalum embrittlement due to getter action and thermal conduction losses increase via convection. Pressures lower than 10^{-4} or 10^{-5} are not desirable due to possible vapor phase reaction above 1800°C between thoria and tantalum. At a pressure of 10^{-4} torr, molybdenum (sample container reservoir) could not be used above 1800°C and preferably not above 1700°C because of molybdenum vapor phase contamination.

3.1.2.2 Maximum Tantalum Heater Temperature of 1900° to 2000°C

While a safe operating heater temperature is closer to 1700°C, the above maximum temperatures were kept in mind in the design. Operating temperatures are possible between 2000°C and 2200°C but tantalum heater failure and/or excessive ground current leakage are expected in this range and insufficient tantalum creep data at high temperature renders any prediction at these temperatures questionable.

3.1.2.3 Maximum Heater Power Input of 1.9 KW on Center Coil and 1.1 KW on Outside Coil

The above input values are calculated to occur at 70 V and 59 V respectively. For the expected range of test material properties and initial test container sizes, a further increase in heater power will cause excessive filament temperature. For higher than expected test material conductivities, the power input can be increased until the monitored heater temperature reaches the maximum desired heater temperature. Should the increase in power input exceed 50% of the values given above, without reaching the maximum desired monitored heater temperature, then failure of the electrical leads will become likely. The indicated maximum power input values imply a maximum test container input heat flux of 90,000 BTU/hr-ft^2.

3.1.2.4 Minimum Suggested Test Container Temperature Difference of 100°C

As this temperature difference is decreased below this value, the ± 5°C thermocouples calibration will result in lower experimental accuracy. Considering minimum practical accuracy limits in all measurements, the conductance measurement will have minimum error limits of about ± 6%, at 90,000 BTU/hr-ft^2 and 300°C temperature difference, to ± 14% at 20,000 BTU/hr-ft and 100°C temperature difference. These error limits do not consider the possibility of free convection effects or two-dimensional heat flow.

3.2 CALIBRATION TEST RESULTS

Detailed consideration of this apparatus and its design and construction have been presented earlier in an interim report[1]. The following discussion will deal mainly with apparatus calibration and specimen preparation. A schematic of the overall test fixture is presented in Figure 3-3.

Calibration of the test apparatus proved out several design points. First, the apparatus was shown to be reliable from the materials compatibility standpoint. Second, a heat balance within 10% was found at each of the various heat fluxes. Third, the system did not out-gas appreciably at temperature, and vacuum of 4 x 10^{-6} torr was held at test conditions. Fourth, the thermal flux (heater input) was easily controlled.

Calibration tests were made using a solid molybdenum block whose geometry [illegible] ~~was exactly like~~ that of the intended oxide test specimen. (See Figure 3-4.) During the first several test runs there was a heater failure which was mechanical in nature. This problem was eliminated and subsequent runs were made with no further difficulty. The overall apparatus performance was satisfactory. Heat losses were about 50% higher than estimated in design calculation. The measured molybdenum conductivity of the calibration specimen was sufficiently close (± 50%) to published values. This agreement within ± 50% of the reported conductivity for molybdenum is good, considering that the device is designed to measure low conductivity materials (with higher ΔT). The conservative heater design has provided the temperatures and fluxes required (assuming parasitic heat losses do not increase significantly). Tables 3-1 and 3-2 include various calculated data as per the following typical heat transfer equations:

$$K = \frac{Q_s \Delta x}{A \Delta T}$$

where:

Q_s = heat flux to sink in watts

Δx = thickness, cm

A = area in cm^2

ΔT = temperature drop in specimen, $^{\circ}$C

K = watts-cm^{-1} - $^{\circ}$C^{-1}

In molybdenum calibration specimen:

Δx = 2.69 cm

A = 91.33 cm^2

$\frac{\Delta x}{A}$ = 0.0295 cm^{-1}

So,

$$K = \frac{0.0295}{\text{cm}} \left[\frac{Q(\text{watts})}{\Delta T\ (^{\circ}\text{C})}\right]$$

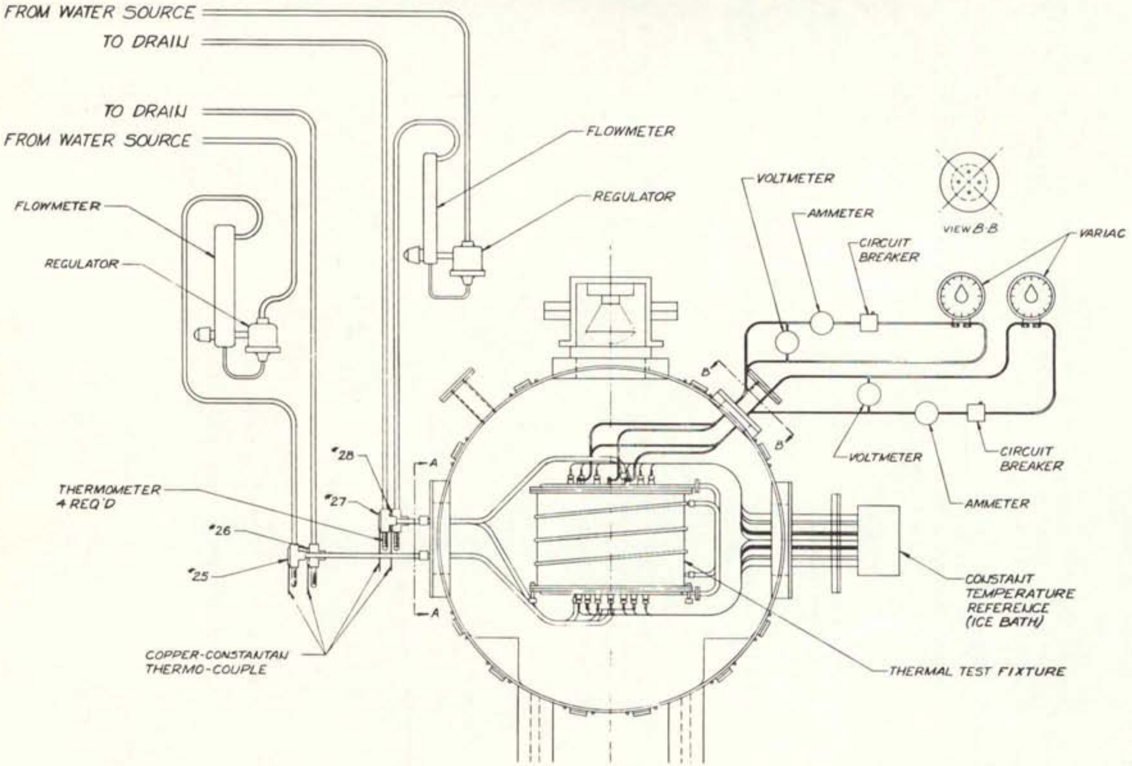


Figure 3-3. Schematic Diagram of Test Fixture

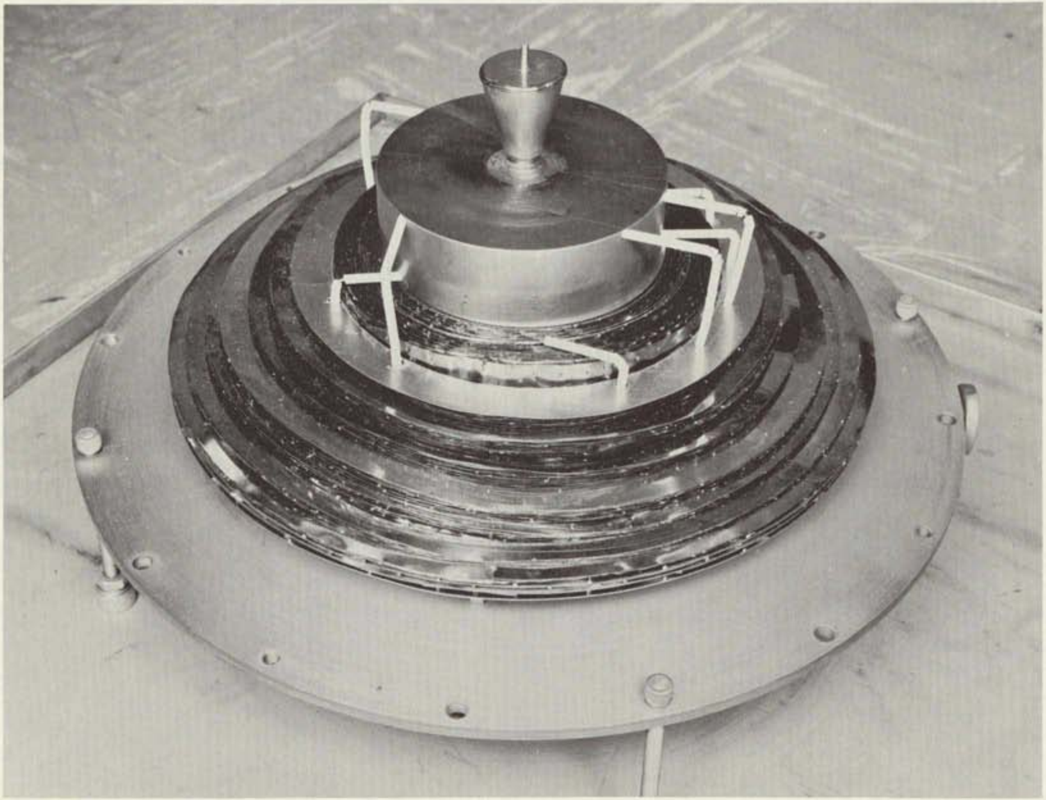


Figure 3-4. Calibration Specimen on Heat Sink Showing Thermocouple Placement

TABLE 3-1. EXPERIMENTAL CONDUCTIVITY DATA AND CALCULATED VALUES

RUN	HEAT ABSORBED BY SINK (WATTS)	AVERAGE Δ T* (°C) ACROSS BLOCK	EXPERIMENTAL CONDUCTIVITY	% DIFFERENCE $K_o = 1.00 \frac{\text{WATTS}}{\text{CM-}^\circ\text{C}}$
1	304	16.0	0.56	44 low
2	445	12.0	1.09	9 high
3	690	23.0	0.88	12 low
4	699	29.2	0.71	29 high
5	798	15.8	1.49	49 high
6	863	16.8	1.51	51 high

---

*Average of four (4) differential thermocouples.

NOTE: To convert watts-$(\text{cm-}^\circ\text{C})^{-1}$ to BTU-$(\text{hr ft }^\circ\text{F})^{-1}$ multiply by 57.78.

TABLE 3-2. HEAT BALANCE CALCULATIONS FROM DATA TAKEN DURING CALIBRATION

RUN	HEATER INPUT (KW)	HEAT ABSORBED BY SINK(KW)	HEAT ABSORBED BY SHELL(KW)	HEATER INPUT MINUS TOTAL HEAT ABSORBED(KW)	% OF HEATER INPUT UNACCOUNTED FOR
1	0.531	0.304	0,162	+.065	+12.2
2	0.674	0.445	0.266	-.037	- 5.5
3	1.026	0.690	0.361	-.025	- 2.4
4	1.026	0.699	0.380	-.053	- 5.2
5	1.126	0.798	0,409	-.081	- 7.2
6	1.204	0.863	0.426	-.085	- 7.0

The Q values were determined by water flow and temperature rise measurements in the heat sink. The ΔT measurements in the solid specimen were measured with W-Re thermocouples and were average values of four differential thermocouples. The small ΔT's found (as expected) were difficult to measure accurately and as a result the calculated thermal conductivity values fall in a ± 50% range of the reported values for molybdenum. Larger ΔT's could have been obtained at higher temperatures; however, heater temperatures would have been excessive.

After these calibration runs, the unit was partially dismantled to observe the condition of the interior. The thermocouples were all intact and the thoria insulators (thermocouple) showed no sign of attack. The tantalum heater was in excellent condition. The molybdenum calibration specimen was not affected or distorted in any way. Some vapor deposited copper was noted on shielding about two-thirds out from the hot zone. The source of this copper was probably from some spot welds made in the radiation shielding. All radiation shielding stacks are intact with no sign of sticking between shields. Overall, all components were in good condition and will not require any rework or replacement.

Another reason for this inspection was to determine the physical position and contact of the calibration specimen with respect to the heat sink. Poor contact was suspected because of the horizontal temperature distributions. This check showed that the calibration was squarely seated on the heat sink but flat contact was questionable. This latter point could easily cause thermal flux distortions leading to uneven temperature distributions.

One of the thermocouples in the calibration block was also found to be shorted about three inches from the thermocouple bead by a tantalum support wire which had slipped between two thoria insulators. This short seemed to cause this thermocouple to read low occasionally, and therefore was not a dependable thermocouple.

Several additional calibration runs are planned using the molybdenum specimen at new temperature and heat flux conditions. These runs will fully assess the overall performance of the apparatus. The new conditions will be produced by inserting sapphire spacers 0.020 inches thick between the calibration specimen and the heat sink. This will insure that all heat transfer to the heat sink is by radiation only.

3.3 CONDUCTIVITY TEST SPECIMEN

The fabrication of the oxide test specimen has not been possible because of serious difficulties. A great amount of effort has been concentrated on this problem without any significant success. The specimen parts are shown in Figure 3-5. One major problem involves weldment of the 10-mil cylindrical sheet to the 1/4-inch thick end plates. Many test weldments have been attempted using both low and high energy electron beam welding machines. Many of these welds looked satisfactory; however, minute leaks have been detected using helium leak testing. The leaks usually develop in the heat affected zone of the weldment. Electron beam welding also requires strict fixturing and manipulation to produce sound welds. The presence of the ceramic oxide block has also complicated fabrication procedures.

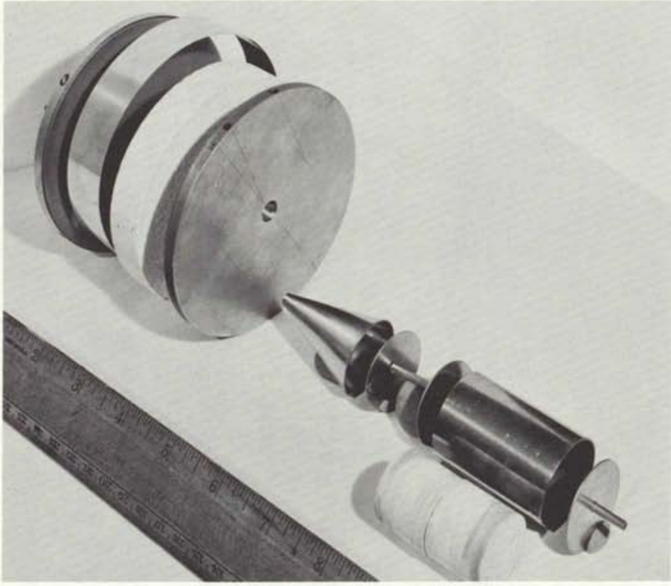


Figure 3-5. Conductivity Test Specimen Parts

Unfortunately, procedures beyond this point are also quite complex. It will be necessary to completely out-gas and then melt the oxide, after which X-ray photographs will be taken to inspect the specimen for any voids. The need for a void-free specimen is obvious. Final sealing of the specimen can only occur after this last inspection. Past experience has also shown that minute leaks usually allow all of the oxide to "creep" out of the container. This is due to its good wetting characteristics and to capillarity or surface tension. Because small leaks can be disastrous to the test equipment, special precautions will be taken to minimize potential damage.

Current plans call for a continuation of studies on 3BeO-2CaO until thermal conductance data is developed. Following those studies, the measurement of 3BeO-2MgO conductance will be attempted. In this case, the 3BeO-2MgO will have to be contained in rhenium or tungsten-rhenium alloy. This container should be easier to fabricate, but materials costs will be considerably higher since rhenium stock costs about $1,000 per pound.

3.4 CONCLUSIONS AND RECOMMENDATIONS

The apparatus has performed within design specifications for the most part. The side heat losses are somewhat higher than calculated but are not excessive. True performance will be best evaluated with an oxide test specimen. The test specimen fabrication has been difficult and is near completion. Test data on 3BeO-2CaO should be available early in the follow-on effort.

APPENDIX A

MICROGRAPHS

This section presents all micrographs taken of the container materials. They are classified as to oxide tested and then sub-divided according to the metal tested. Control specimens are shown where pertinent in the groupings. Each figure has notations which describe the test result interpretations as well as any pertinent observations or comments. Most of the micrographs show the surfaces which were in contact with the oxide. Others show particular sites of interest such as weld failures, large grain boundaries or unusual areas of localized reaction. Many of the specimens were difficult to polish without blemishes and to avoid long delay in polishing time, some scratches were acceptable as long as satisfactory examination could be made.

The presence of BeO also complicated preparation of these specimens. Care had to be taken to avoid any hazards to personnel and to prevent contamination of equipment and fixtures.

Some capsules have not been analyzed pending their continued testing in the current program. The results of these capsules will be published as an addendum to this report as these tests are completed.

GROUP 1

Oxide: 3BeO-2CaO (m. p. 1685°K)

Conditions: Cycled, 1650°K to 1750°K

Metals Tested:
Mo
Mo-Re
W
W-Re

Control Specimens Included in this Group

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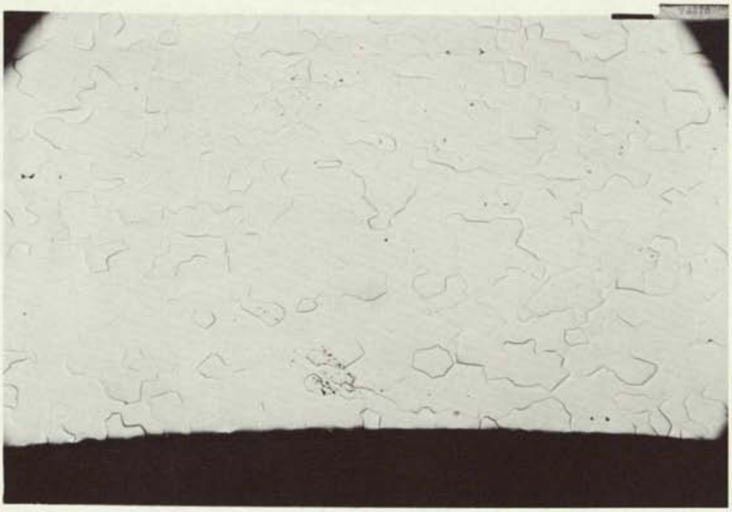

Figure A-1. Molybdenum as Received (250X)

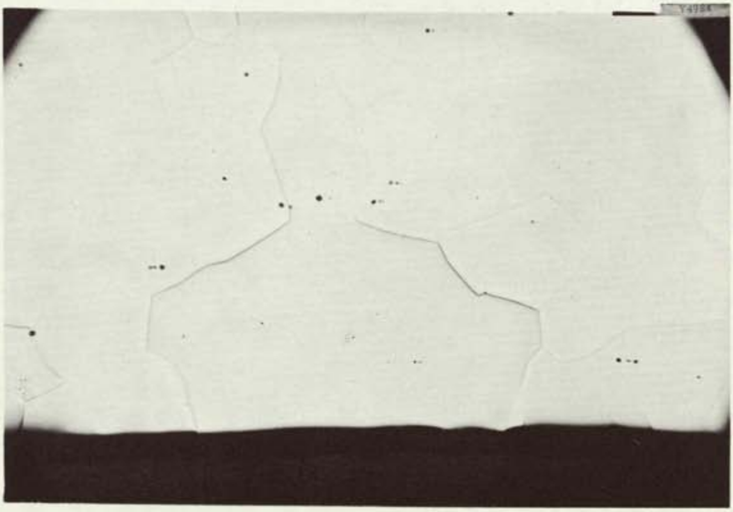

Figure A-2. Molybdenum Control Specimen After 500 Hours at 1750°K(250X)

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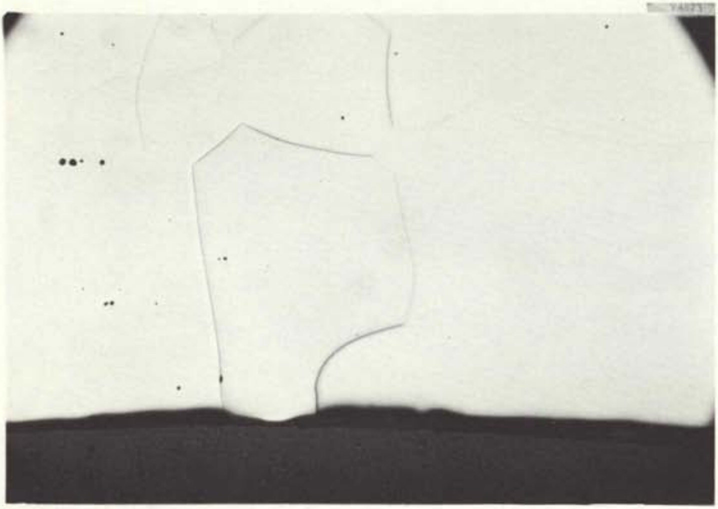

Figure A-3. Molybdenum Control Specimen After 500 Hours at 1975°K(250X)

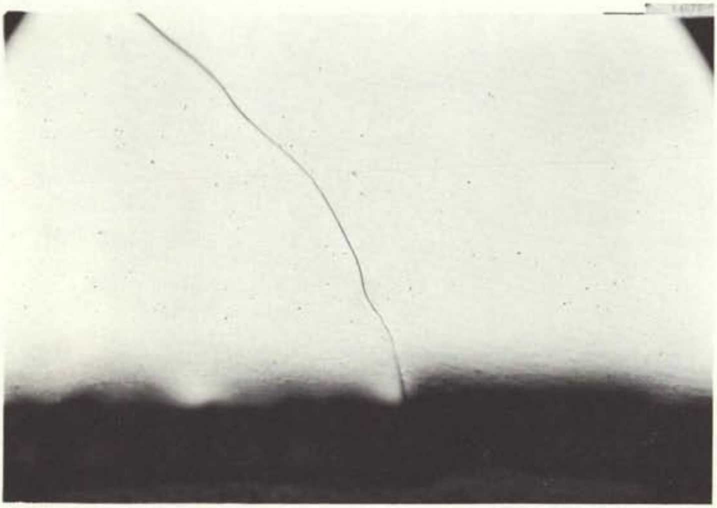

Figure A-4. Molybdenum Control Specimen After 500 Hours at 2195°K (250X) Shows extensive grain boundary

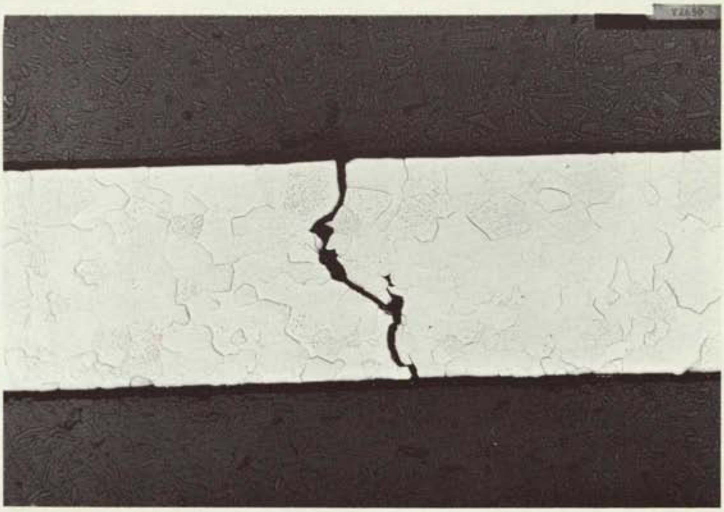

Figure A-5. Molybdenum with 3BeO-2CaO after 24 Hours (100X). Shows wall crack due to internal pressure (See text). Capsule No. 1

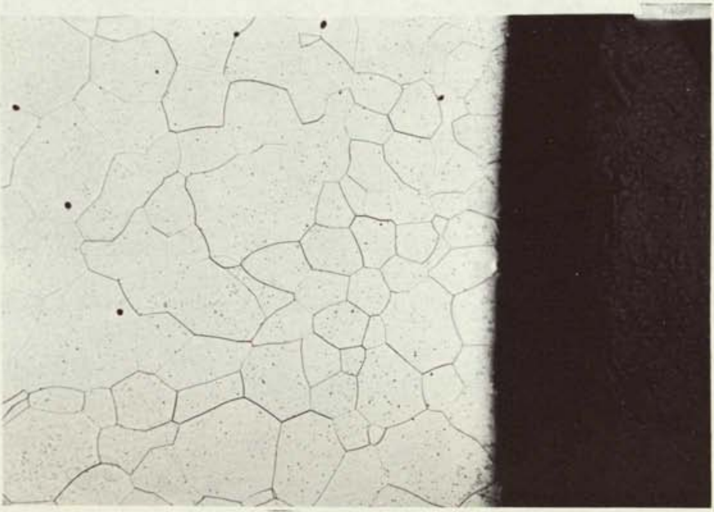

Figure A-6. Molybdenum With 3BeO-2CaO After 500 Hours (250X). Capsule No. 37. Did not leak

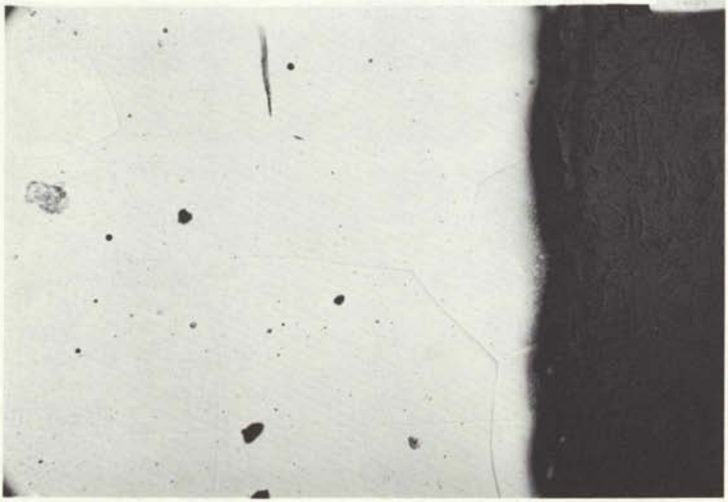

Figure A-7. Molybdenum With 3BeO-2CaO After 1484 Hours (250X). Capsule No. 29. Did not leak

GROUP 2

Oxide: Al_2O_3 - 4BeO - 4MgO (m.p. 1910°K)

Conditions: Cycled, 1875°K to 1975°K

Metals Tested:

Mo
Mo-Re
W
W-Re
Re

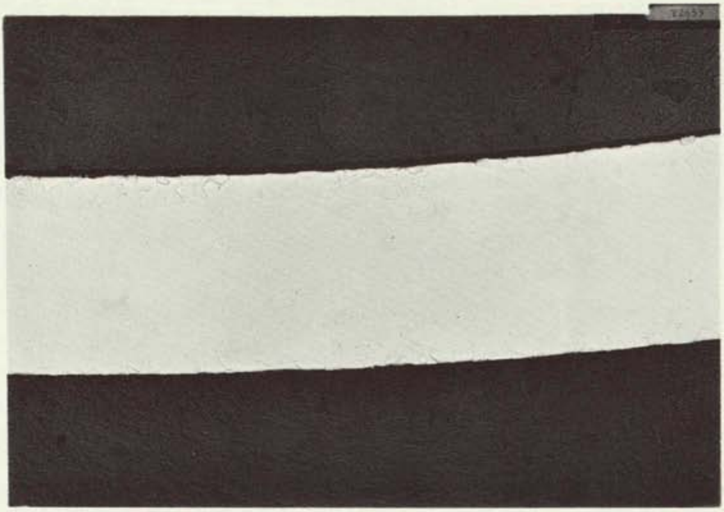

Figure A-8. Mo-Re as Received (100X)

Figure A-9. Mo-Re as Received (250X)

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Figure A-10. Mo-Re Control Specimen After 500 hrs at 1750°K (250X)

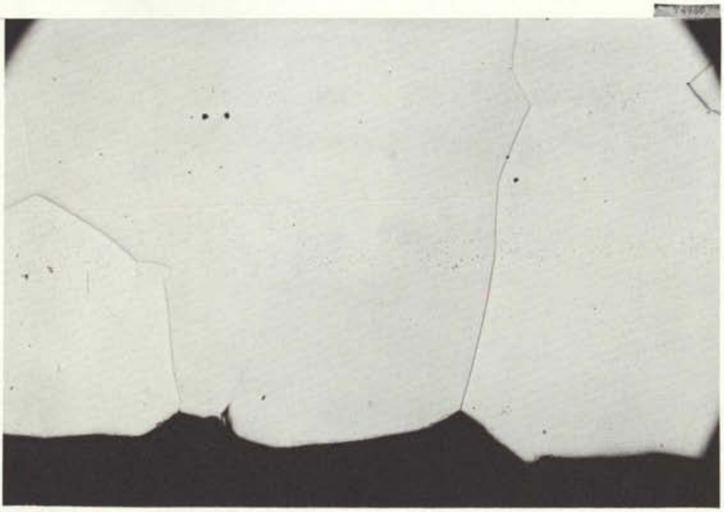

Figure A-11. Mo-Re Control Specimen After 500 Hrs at 2195°K (250X)

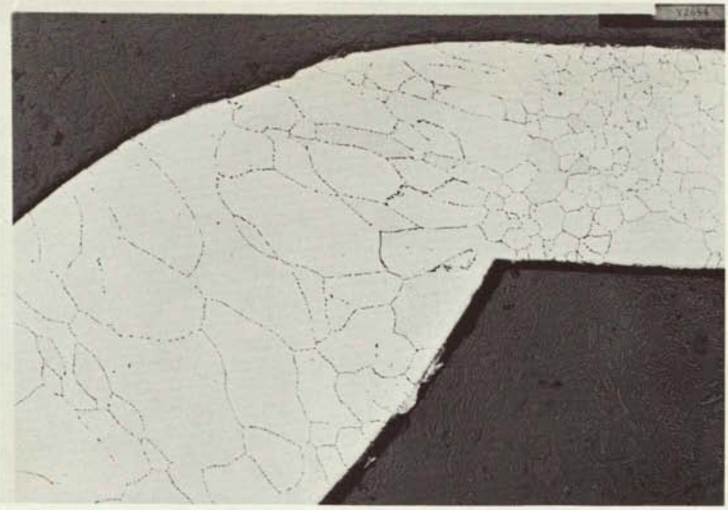

Figure A-12. Mo-Re with 3BeO-2CaO After 100 Hrs (100X). Sigma phase in grain boundaries. No leak. Capsule No. 4

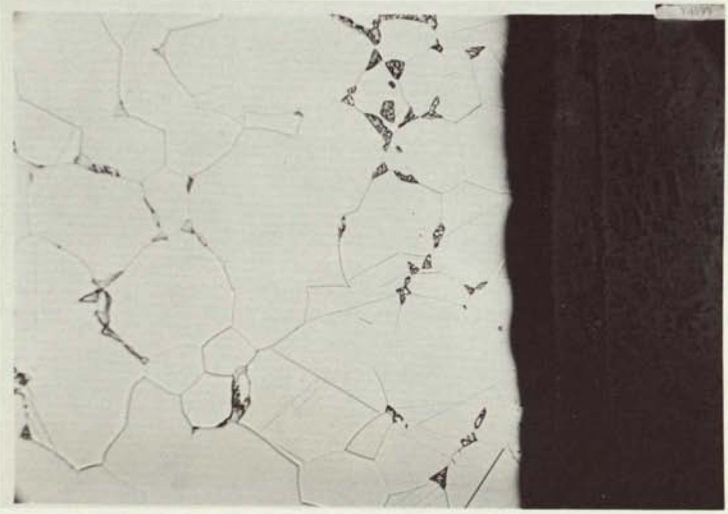

Figure A-13. Mo-Re with 3BeO-2CaO After 500 Hrs (250X). Sigma phase apparent. No leaks. Capsule No. 38

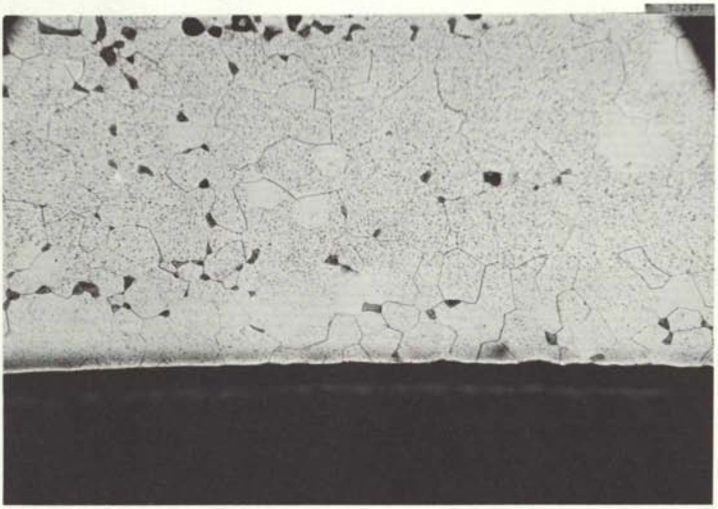

Figure A-14. Mo-Re With 3BeO-2CaO After 1484 Hrs (250X). Sigma phase apparent. No leaks. Capsule No. 30

GROUP 3

Oxide: 3BeO-2MgO (m. p. 2145°K)

Conditions: Cycled, 2085°K to 2195°K

Metals Tested:	W W-Re Re (not sectioned)

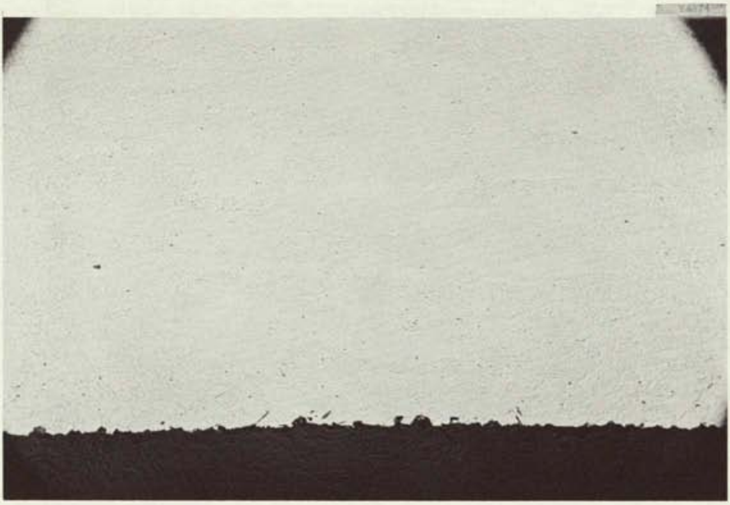

Figure A-15. Tungsten as Received (250X)

Figure A-16. Tungsten Control Specimen After 500 Hours at 1750°K(250X)

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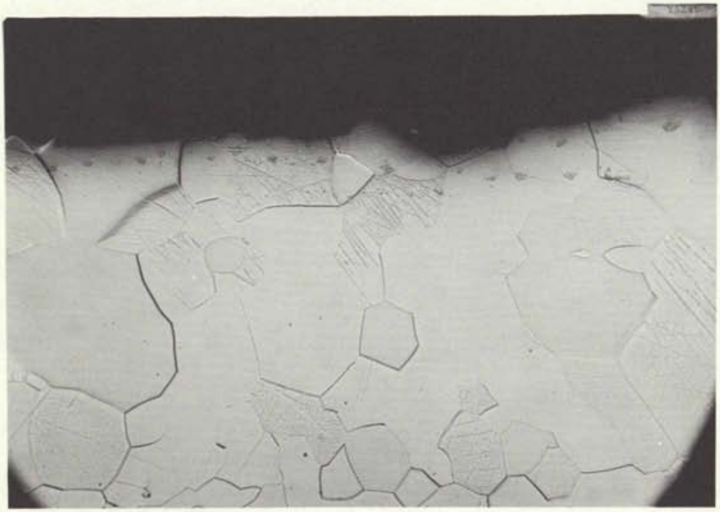

Figure A-17. Tungsten Control Specimen After 500 Hours at 1975°K. Increased grain size. (250X)

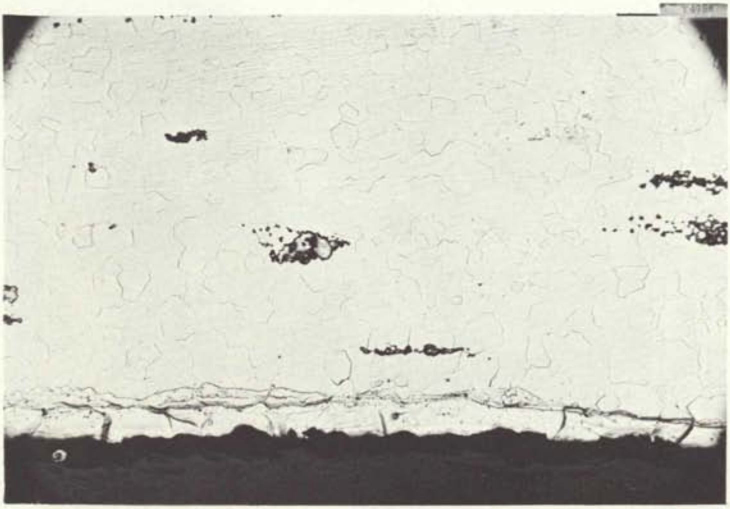

Figure A-18. Tungsten Control Specimen After 500 Hours at 2195°K(250X)

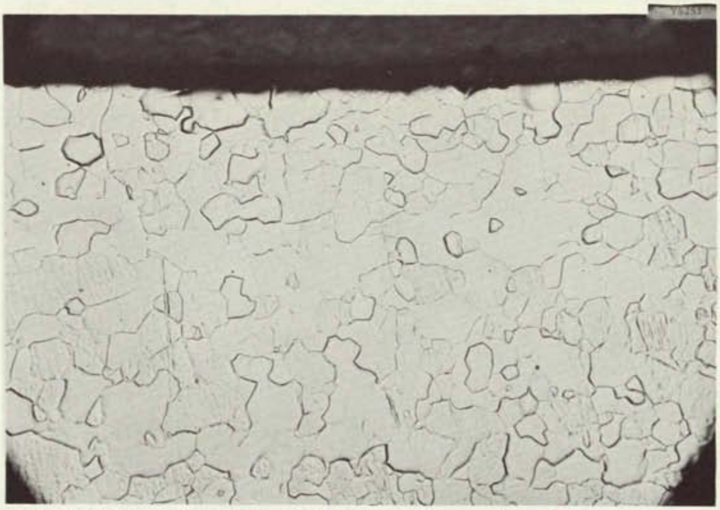

Figure A-19. W With 3BeO-2CaO After 500 Hours (250X). Capsule No. 60, leaked

Figure A-20. W With 3BeO-2CaO After 1484 Hours (250X). Capsule No. 56, did not leak. Increased grain size

Figure A-21. W With 3BeO-2CaO After 2069 Hours (250X). Capsule 54, leaked between 1500 and 2000 hours. Note large grains

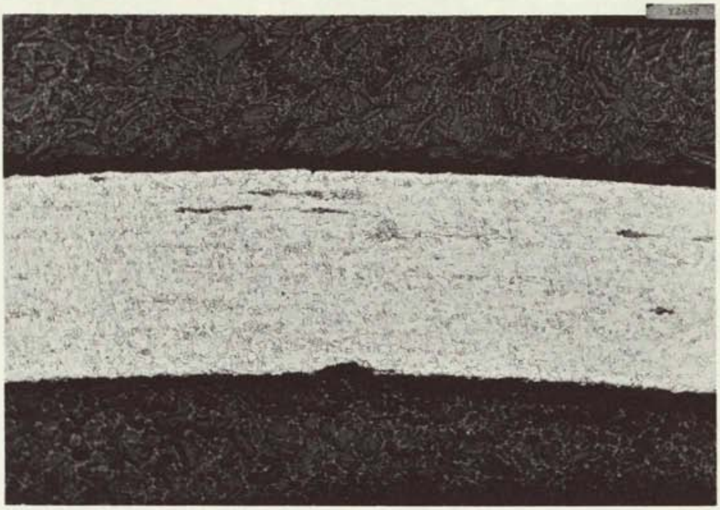

Figure A-22. W-Re As Received (100X) Note impurity occlusions

Figure A-23. W-Re, As Received (250X) Note occlusions

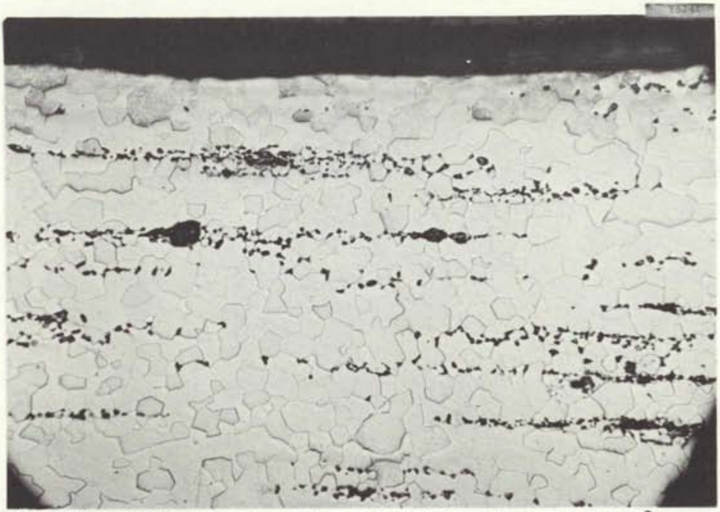

Figure A-24. W-Re Control Specimen (250X) After 500 Hours at 1750°K. Note extensive occluded striations

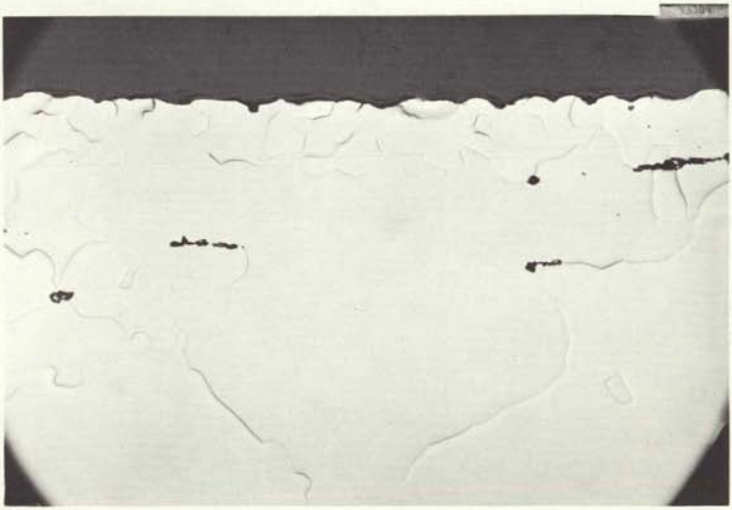

Figure A-25. W-Re Control Specimen (250X) After 500 Hours at 1975°K. Large grains and impurity occlusions

Figure A-26. W-Re Control Specimen (250X) Showing Extensive Attack By Al_2O_3 Present in This Capsule

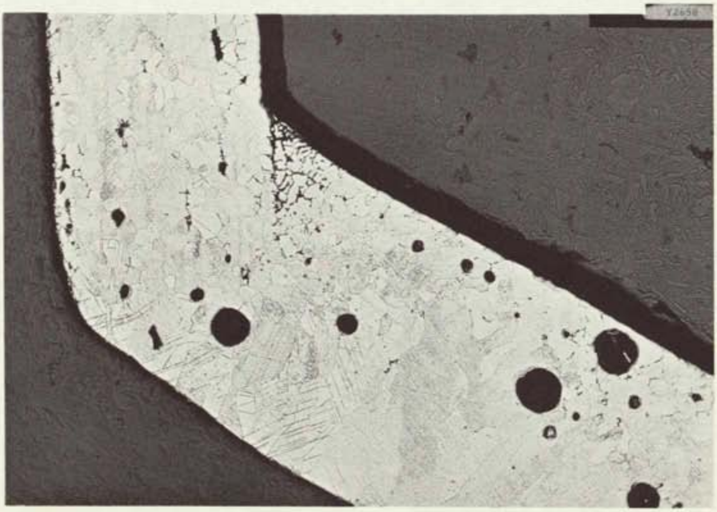

Figure A-27. W-Re With 3BeO-2CaO After 100 Hours (100X). Note porosity of weld zone. Capsule No. 7

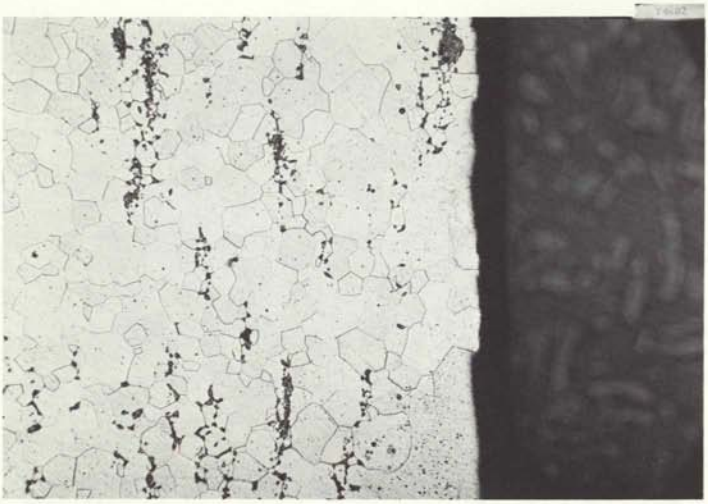

Figure A-28. W-Re With 3BeO-2CaO After 500 Hours (250X). Possible sigma phase and impurity. Capsule No. 48 did not leak

Figure A-29. W-Re With 3BeO-2CaO After 1484 Hours (250X). Capsule No. 50, leaked. Some sigma phase and impurity can be seen

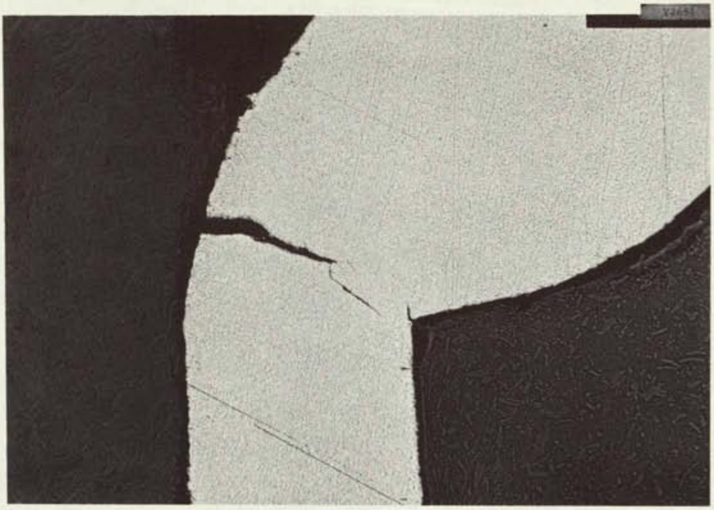

Figure A-30. Molybdenum With Al_2O_3-4BeO-4MgO After 100 Hours (100X). Capsule No. 2 failed due to internal pressure. Note extensive weld crack

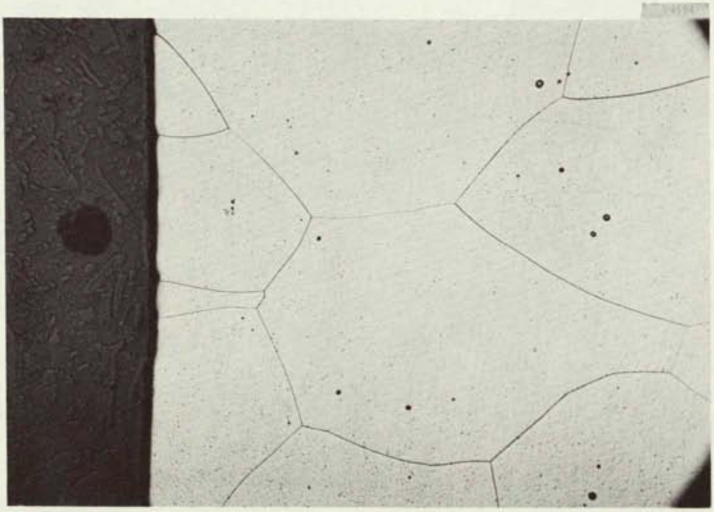

Figure A-31. Mo with Al_2O_3-4BeO-4MgO After 500 Hours (250X). Note extensive grain growth

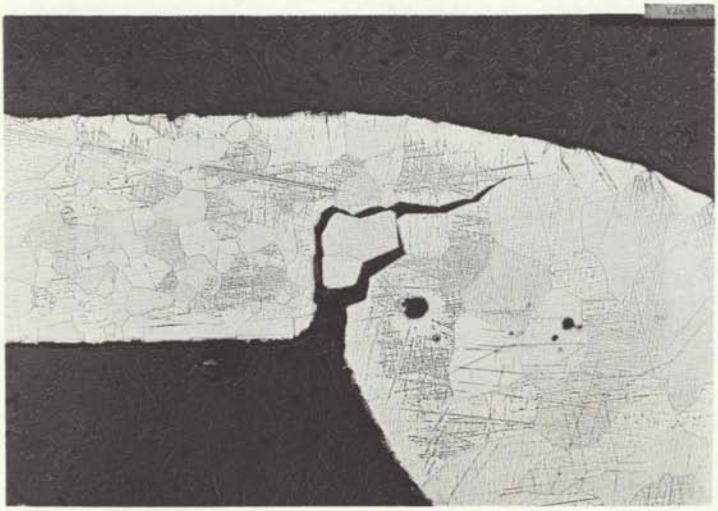

Figure A-32. Mo-Re With Al_2O_3-4BeO-4MgO After < 100 Hours (100X). Capsule No. 5, leaked. Shows weld crack and porosity in weld

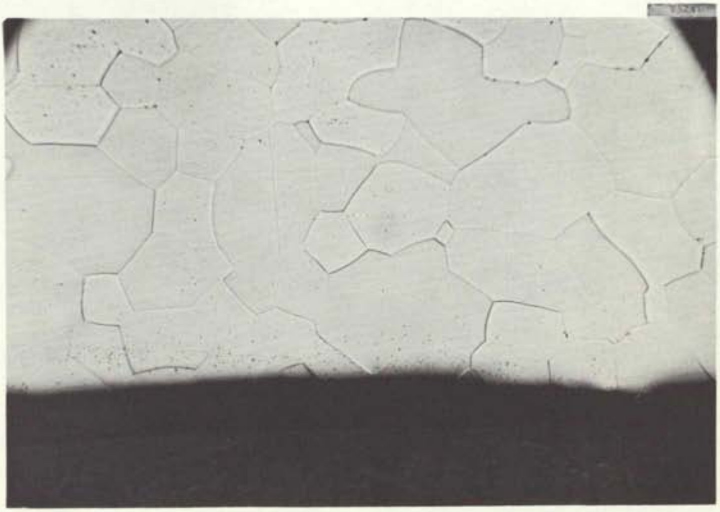

Figure A-33. Mo-Re With Al_2O_3-4BeO-4MgO After 500 Hours (250X). Capsule 42, leaked. Larger grains and some signs of sigma phase

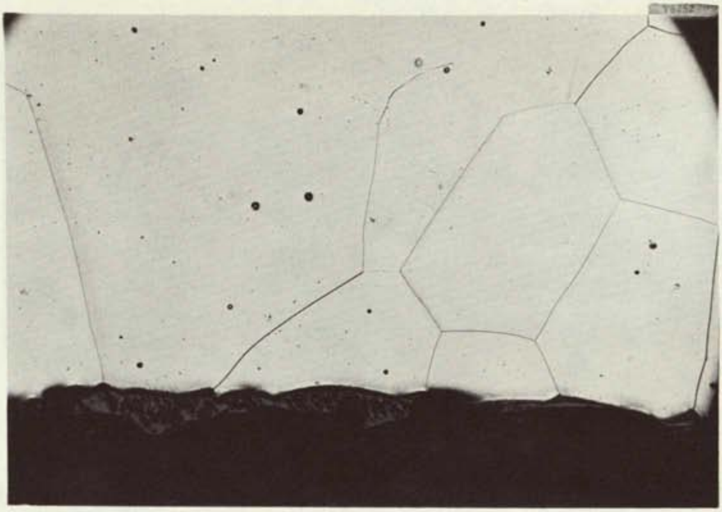

Figure A-34. Mo-Re with Al_2O_3-4BeO-4MgO After 1196 Hours (250X). Capsule 40, leaked. Large grains

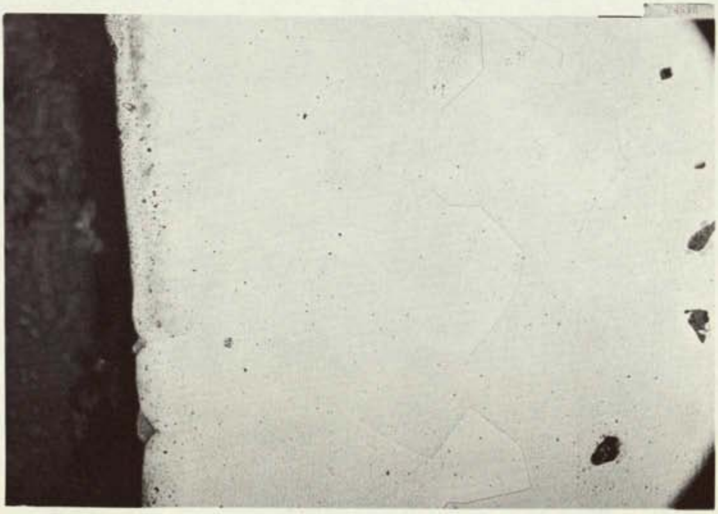

Figure A-35. W with Al_2O_3-4BeO-4MgO After 500 Hours (250X). No leaks. Capsule 47. Note penetration at wall also attack approaching from outside wall (See text)

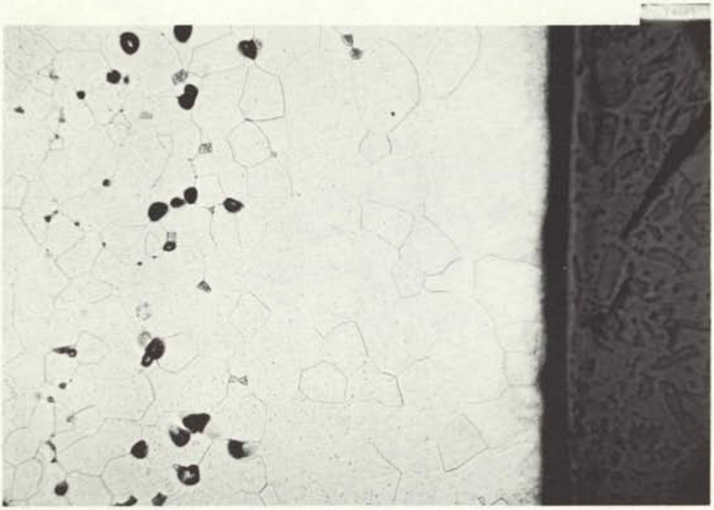

Figure A-36. W With Al_2O_3-4BeO-4MgO After 1500 Hours (250X). Capsule 46, no leaks. Attack from outside is shown at left

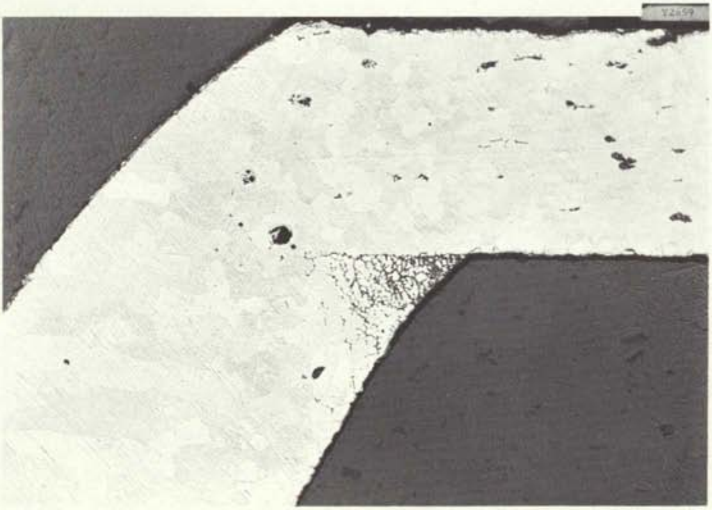

Figure A-37. W-Re With Al_2O_3-4BeO-4MgO After 100 Hours (100X). Failed due to internal pressure. Capsule No. 8. Note porosity in weld and impurities

Figure A-38. W-Re With Al_2O_3-4BeO-4MgO After 500 Hours (250X). Did not fail, Capsule No. 43. Note impurity or sigma phase

Figure A-39. W-Re With Al_2O_3-4BeO-4MgO After 1529 Hours. Leaked. Capsule No. 15. Apparent penetration into wall

Figure A-40. W-Re With Al_2O_3-4BeO-4MgO of Capsule No. 15 (See Figure 39). This attack was found in vapor region in an isolated spot

GROUP 4

Oxide: Al_2O_3-4BeO-4MgO (m.p. 2020°K)

Conditions: Cycled, 2085°K to 2195°K

Metals Tested: Mo

NOTE - These capsules were cycled but always above the melting point except during down times.

Figure A-41. Rhenium As Received (250X)

Figure A-42. Rhenium As Received (250X) Polarized

Figure A-43. Rhenium Control Specimen After 500 Hours at 1975°K. (250X). Polarized

Figure A-44. Re With Al_2O_3-4BeO-4MgO After 500 Hours. Did not leak. Capsule No. 61 (250X) Polarized.

Figure A-45. Re With Al_2O_3-4BeO-4MgO After 1504 Hours (250X). Capsule No. 62, leaked. No sign of attack. Polarized

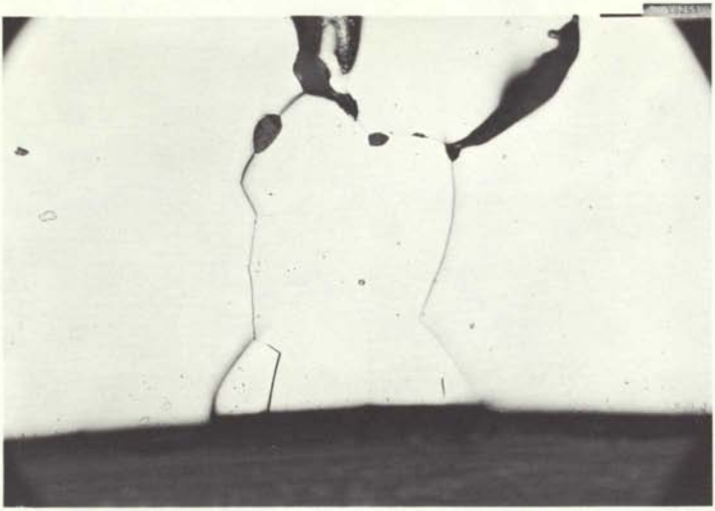

Figure A-46. W With 3BeO-2MgO After 500 Hours (250X). Capsule No. 36. Shows catastrophic attack from outside

Figure A-47. Same As Figure 46 Showing Outside Wall (250X)

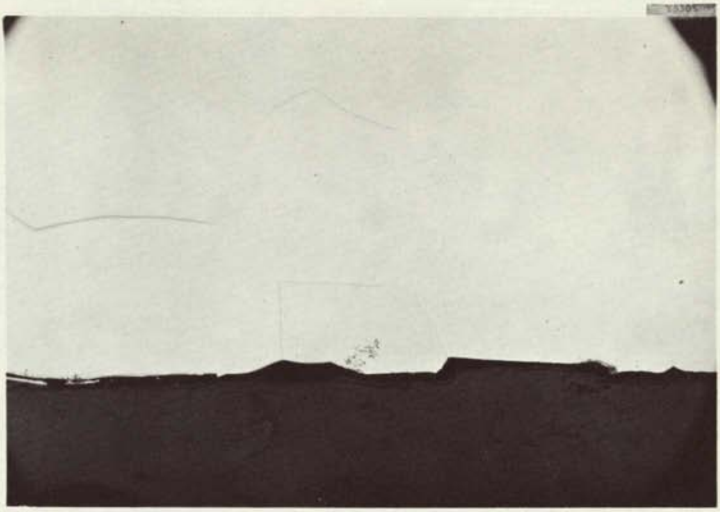

Figure A-48. W With 3BeO-2CaO After 1504 Hours (250X). Capsule 39, leaked

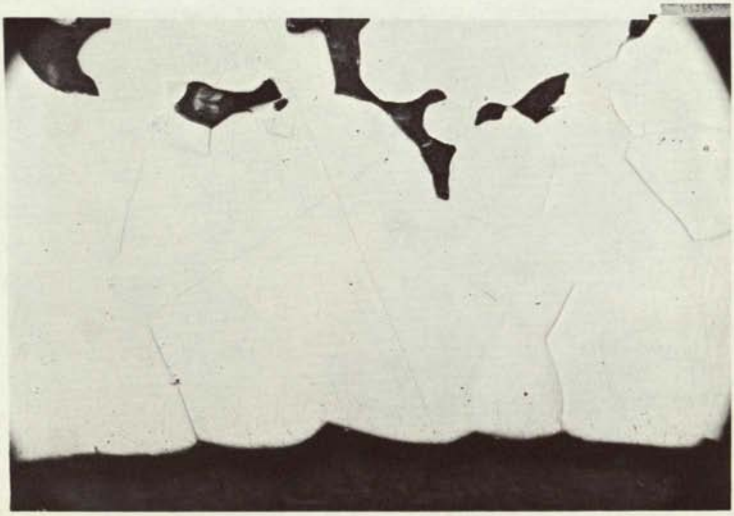

Figure A-49. Same As Figure 48 Showing Attack From Outside. Capsule 39. (250X)

Figure A-50. Same As Figures 48 and 49. Capsule No. 39 Showing Attack Of Outside Wall

Figure A-51. W-Re With 3BeO-2MgO After 100 Hours (100X). Note typical porous weld. Capsule No. 9 leaked due to internal pressure

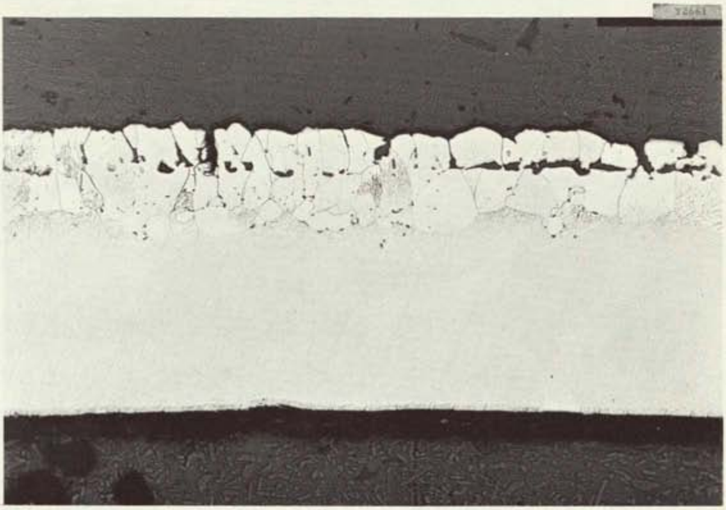

Figure A-52. Capsule No. 9 Same As Figure 51 Showing Beginnings of Attack From Outside After 100 Hours

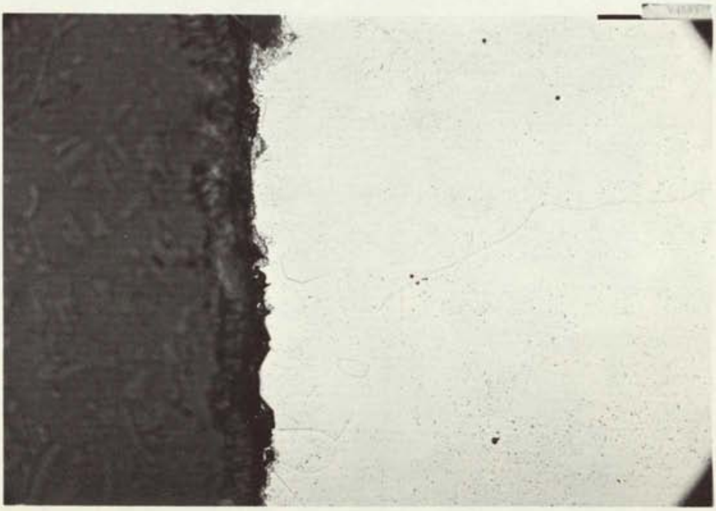

Figure A-53. W-Re With 3BeO-2MgO After 500 Hours (250X). Capsule 26, did not leak. Large grains

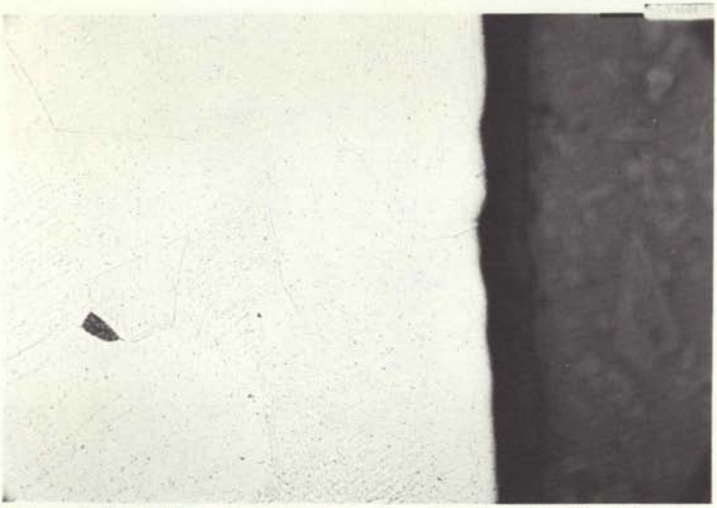

Figure A-54. W-Re With 3BeO-2MgO After 1196 Hours (250X). Did not leak, Capsule No. 27. Large grains

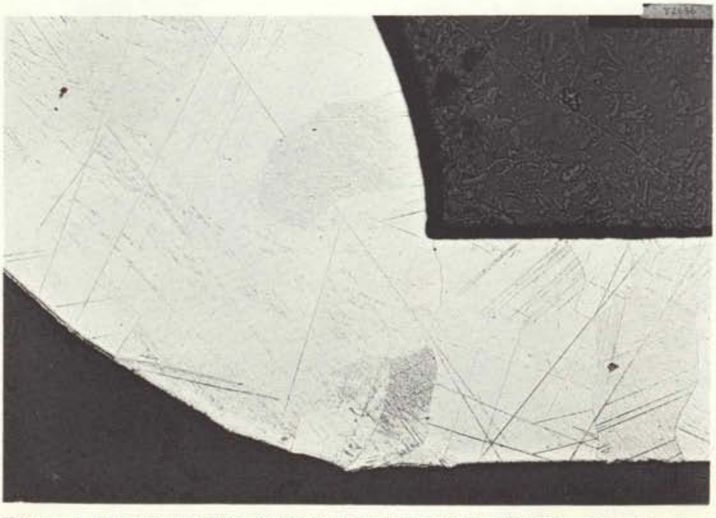

Figure A-55. Mo-Re With 3BeO-2MgO After 100 Hrs (100X). Capsule failed due to internal pressure

Figure A-56. Mo With Al_2O_3-4BeO-MgO After 100 Hours (100X). Note extensive grain growth

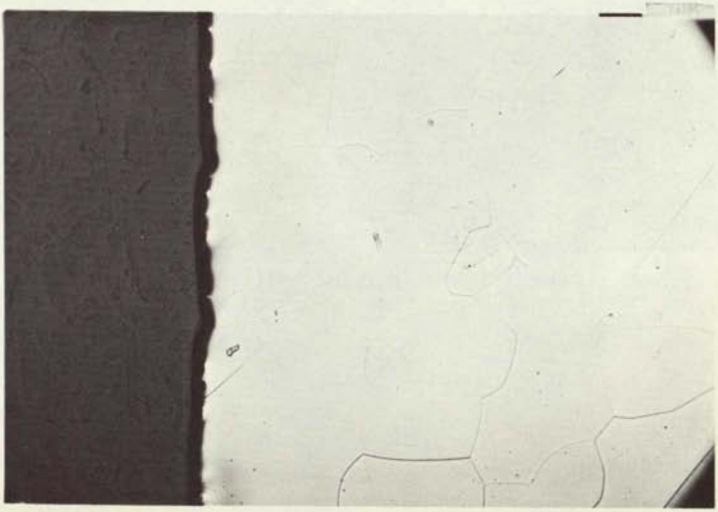

Figure A-57. Mo With Al_2O_3-4BeO-MgO After 500 Hours (250X). No leaks. Capsule No. 57. Note large grains.

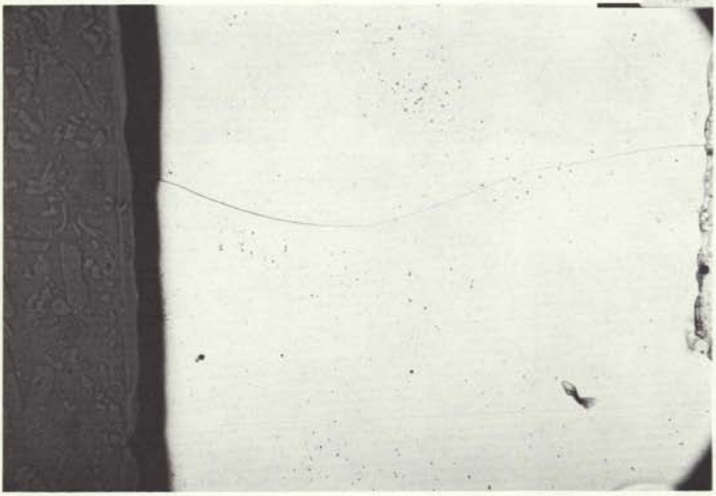

Figure A-58. Mo With Al_2O_3-4BeO-MgO After 1484 Hours. Capsule No. 32 leaked. Note grain boundary extending completely across wall(250X)

N65 19932

A STUDY OF SELECT CERAMIC OXIDE COMPOSITIONS AS HIGH TEMPERATURE (1600-2100° K) THERMAL ENERGY STORAGE MATERIALS

FINAL REPORT
FEBRUARY 1962 TO FEBRUARY 1963

PREPARED FOR
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT NAS5-826
LEWIS RESEARCH CENTER

GENERAL ELECTRIC
MISSILE AND SPACE DIVISION

APPENDIX A

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