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Nuclear Materials & Propulsion Operation

**HIGH-TEMPERATURE MATERIALS PROGRAM
PROGRESS REPORT No. 51, Part A**

September 30, 1965

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**HIGH-TEMPERATURE MATERIALS PROGRAM
PROGRESS REPORT No. 51, Part A**

September 30, 1965

United States Atomic Energy Commission Contract No. AT (40-1)-2847

**NUCLEAR MATERIALS and PROPULSION OPERATION
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CONVERSION TABLE

To Convert From	To	Multiply By
Atmospheres	Pounds/inch ²	14.7
Calories (mean)	Btu (mean)	0.00397
Calories/gram-°C	Btu/pound-°F	1.0
Calories/sec-cm-°C	Btu/hr-ft-°F	241.8
Calories/sec-cm ²	Btu/hr-ft ²	1.32 x 10 ⁴
Calories/sec-cm ² -°C	Btu/hr-ft ² -°F	7370
Centimeters	Feet	0.03281
	Inches	0.3937
Cubic centimeters	Cubic feet	3.531 x 10 ⁻⁵
	Cubic inches	0.06103
Grams	Pounds	0.002205
Grams/cm ³	Pounds/ft ³	62.43
Grams/cm ²	psi	0.01422
Kilograms	Pounds	2.205
Kilograms/cm ²	Atmospheres	0.9678
	Pounds/ft ²	2048
	Pounds/inch ²	14.22
Kilograms/mm ²	Pounds/inch ²	1422.32
Kilowatts	Btu/sec	0.948
Liters	Cubic feet	0.0353
Meters	Inches	39.37
Millimeters of mercury	Atmospheres	0.001316
Square centimeters	Square feet	0.001076
	Square inches	0.155
Torr	mm of Hg	1.0
	Atmospheres	0.001316
Watts/cm-°C	Btu/hr-ft-°F	57.8
Watt-seconds	Btu	0.000948
Watts/cm ² -°C	Btu/hr-ft ²	3170
Watts/cm ² -°C	Btu/hr-ft ² -°F	1760
Centimeters/sec	Feet/sec	0.03281
Meters/sec	Feet/sec	3.281

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1. INTRODUCTION AND SUMMARY

Introduction

This report, Volume A of GEMP-51, is the unclassified portion of the fifty-first in a series of monthly reports of the work in progress on the High-Temperature Materials Program for the Atomic Energy Commission under Contract AT(40-1)-2847 in which each task under the program is reported on a bimonthly basis.

The period covered by this report, June 15, 1965 to August 15, 1965, encompasses the transition from the FY-65 to the FY-66 programs. The schedule for the reporting of each FY-66 task is shown in the following breakdown for the monthly reports.

EVEN-NUMBERED REPORTS

Unclassified – GEMP-50A, -52A, etc.

1. Effect of Radiation on High-Temperature Metals and Alloys (57004)
(Continuation: formerly reported in odd-numbered reports)
2. Evaluations of the Plastic Fatigue Properties of Heat Resistant Alloys (57016)
(Initiated FY-66)
3. Effect of Radiation on Heat Resistant Metals and Alloys (57018)
(Initiated FY-66, formerly reported under task 57004)
4. Radiation Effects in BeO (57063)
(Continuation)
5. Fission Product Transport in Refractory Metals (57070)
(Continuation)
6. Physico-Chemical Studies of Clad UO_2 in Meltdown (57075)
(Initiated FY-66)
7. Physico-Chemical Studies of Fe-Cr-Al-Y-Clad Fuel Elements (57076)
(Initiated FY-66)

Classified – GEMP-50B, -52B, etc.

1. Burnup Capability of Y_2O_3 -Stabilized UO_2 and BeO-Stabilized Fuel Materials (57068)
(Continuation)
2. High-Temperature Studies of Substoichiometric Urania and Urania Solid Solutions (57071) (Continuation)
3. High-Temperature Research on Carbides for Fuel and Structural Application (57073)
(Continuation)

ODD-NUMBERED REPORTS

Unclassified – GEMP-51A, -53A, etc.

1. Oxidation Resistant Fuel Element Materials Research (57001)
(Continuation)
2. High-Temperature Reactor Materials Research (57003)
(Continuation)
3. High-Temperature Thermocouple and Electrical Materials Research (57014)
(Continuation)
4. Refractory-Metal Alloy Research and Development (57015)
(Initiated FY-66, formerly reported under task 57003)

Classified – GEMP-51B, -53B, etc.

1. Moderator (Fueled and Unfueled), Controls and Shield Materials Research (57002)
(Continuation)
2. Refractory-Metal Fuel Element Materials Research (57005)
(Continuation)
3. High-Temperature Materials Engineering Properties Evaluation (57017)
(Initiated FY-66)

Summary

OXIDATION RESISTANT FUEL ELEMENT MATERIALS RESEARCH (57001)

Laboratory testing of Fe-Cr-Al-Y-fueled specimens has exceeded 9500 hours at 950°C, and 7000 hours at 1100°C in air with virtually no uranium (<0.02%) detected on the cladding surface. A total of 57 specimens of various compositions continue on test at temperatures ranging from 750° to 1100°C.

The second in-pile test of a 1541-clad Fe-UO₂ specimen has been on test in the LITR for 565 hours at 950°C and is continuing satisfactorily. Fractional release of fission gases has not exceeded 10⁻⁷. Analysis of the fueled specimen from in-pile test LITFC-1 which operated for 1007 hours at 1100°C revealed no structural damage from irradiation. The diametric growth ranged from 0.2 to 0.7 percent.

Weight gain data for a series of Fe-Cr-Al-Y alloys were obtained at temperatures of 450°, 550°, 730°, 900°, and 1100°C in static air for more than 1 year (9000 hours). The lowest oxidation rates are shown by 2541 alloys containing 0.3 to 0.5 percent yttrium.

HIGH-TEMPERATURE REACTOR MATERIALS EVALUATIONS (57003)

Creep-rupture tests of arc-cast tungsten at 2000°C and 2200°C (62% and 67% of the absolute melting temperature, respectively) indicate a transition in the creep mechanism within this temperature range. Specimens annealed at 2400°C and tested at 2000°C are more creep resistant and have a greater rupture life than specimens annealed at 2000°C and tested at 2000°C. The reverse is shown for specimens tested at 2200°C.

Multi-temperature creep tests of arc-cast tungsten at constant stress (load) yield an apparent activation energy for creep of 160 kcal/mole. This is in reasonably good agreement with the quoted value of 140 kcal/mole for self-diffusion.

A creep-rupture test of arc-cast molybdenum was performed in vacuum at 1600°C with no apparent operational problems. In tests at 2000°C in vacuum, a metallic film was deposited on the furnace sight glass introducing serious error in the optical measurements of temperature.

Creep-rupture tests of W – 25Re – 30Mo (at. %) were performed at 1600°C and 2200°C. The results indicate a possible material structural change at 2200°C and 0.352 kg/mm² (low stress). This was not indicated for the other test conditions.

Along with the familiar Andrade and parabolic creep equations, two additional equation forms were found to yield excellent results in first-stage creep evaluations. Special least-squares computer programs were written to enable all the equation constants to be calculated.

Refinements in the radial heat flow technique which has been used in the past for measuring the thermal conductivity of ceramic materials have recently allowed measurements to be made for high conductivity materials. Data for molybdenum were obtained from 900° to 2000°C and are in excellent agreement with previously published data for molybdenum. This apparatus also proved useful in measuring the electrical resistivity of refractory metals from room temperature to 2300°C.

HIGH-TEMPERATURE THERMOCOUPLE AND ELECTRICAL MATERIALS RESEARCH (57014)

The thermoelectric properties of Cr – 20 Os and Mo – 10Ru – 10 Os were measured as a function of temperature; Cr – 20 Os was found to be a good negative thermoelement material.

The resistivity of BeO was shown to be much higher than that of ThO₂; its activation energy, however, is less than that of ThO₂, suggesting that impurities control its resistivity.

REFRACTORY-METAL ALLOY RESEARCH AND DEVELOPMENT (57015)

Studies of the effect of rhenium content of less than 25 percent in the W-Re-Mo system showed that the alloys containing 10 and 12.5 percent rhenium could not be processed using the techniques established for the NMP-256 alloy (W – 25Re – 30Mo) or the alloys containing 19, 21, 23 or 27 percent rhenium with 30 percent molybdenum content. Other alloys containing varying amounts of rhenium with molybdenum contents of 10 and 20 percent were partially processed.

Mo-W-Re alloys with high molybdenum contents were prepared and hot-rolled into sheet. Alloys containing 20, 25, and 30 percent rhenium were readily processed, but difficulty was encountered with alloys containing 5, 10, or 15 percent rhenium and 15 or 30 percent tungsten. Room-temperature bend tests were conducted on hot-rolled sheet (20 to 30 percent Re) which had been heated for 10 hours at 2000°C in hydrogen before bending. These alloys showed a high degree of ductility.

Sheet and tubing were also made from W – 3Re and W – 5Re alloys. Welds on sheet stock made from these binary systems were strong and non-porous.

Additions of 1, 2, or 5 percent rhenium to molybdenum reduced voids and porosities in the welds. Special purification techniques to remove oxygen, nitrogen, and carbon impurities in unalloyed and alloyed molybdenum result in an increase in ductility and an improvement in weldability.

Major emphasis is being placed on fabrication of W – 25Re – 30Mo (NMP-256) as plate, sheet, and seamless tubing. Over 100 sheets of sufficient size for use in fuel element fabrication were produced. The first lot of commercially produced W – 30Re – 30Mo tubing was inspected and found to be of good quality although not up to GE-NMPO standards.

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2. OXIDATION-RESISTANT FUEL ELEMENT MATERIALS RESEARCH

(57001)

The objective of this research is to develop and evaluate oxidation-resistant fuel element materials markedly superior to presently available fuel materials in terms of high-temperature capabilities, long-time service (high burnup), and containment of fission products in environments of steam, air, carbon dioxide, or other oxidizing coolants.

FUEL ELEMENT MATERIALS EVALUATIONS

Fuel element cladding alloys of the Fe-Cr-Al-Y compositions developed under this program have demonstrated excellent stability in air to 1250°C and in steam to 1100°C, for periods in excess of 5000 hours. Currently, a 10,000-hour laboratory test program is being conducted to evaluate the compatibility of Fe-Cr-Al-Y with various forms of UO₂ at temperatures of 750° to 1250°C. In addition, a series of in-pile experiments is being conducted to evaluate the fuel element materials in regard to high burnup and fission product retention as a function of temperature in the range of 750° to 1100°C.

10,000-Hour Laboratory Test Program

Both the 2541 alloy and the 1541¹ alloy have exhibited excellent resistance to air and steam corrosion at high temperatures. The 1541 composition is preferred for fuel element cladding applications because it is less susceptible to sigma phase embrittlement and has a lower ductile-to-brittle transition temperature (DBTT) than the 2541 alloy. The objective of the current laboratory test program is to demonstrate the time - temperature capabilities of 1541-clad Fe - 40UO₂ fuel element specimens in comparison with 2541-alloy-clad specimens at temperatures of 750°, 950°, and 1100°C in air for times in excess of 10,000 hours. Cylindrical specimens, 1.05 cm in diameter by 2.54 cm in length, were prepared using cladding in the form of tubing with 0.5 mm wall thickness. Dispersion type fueled cores of Fe - 40UO₂ were sintered at 1200°C in hydrogen, machined to fit into the cladding tubing, assembled with end plates, sealed by electron-beam welding, and hot-gas-pressure bonded at 1250°C under 700 kg/cm² helium pressure. A sufficient number of specimens is being tested at each condition to permit destructive evaluations at interim time periods. In addition, nondestructive analysis is being made periodically by X-ray fluorescence or alpha counting of the cladding surface for uranium diffusion.

The status of the long-time test program and the results of latest X-ray fluorescence analyses are given in Table 2.1. A total of 57 specimens were on test at the end of the report period, representing 17 different materials systems or fuel forms. One group of specimens containing UN has completed 9575 hours at 950°C and another group containing agglomerated UO₂ has completed 7000 hours at 1100°C in air with no uranium detected on the cladding surface by X-ray fluorescence.

¹The composition of the 1541 alloy is Fe - 15Cr - 4Al - 1Y, and that of the 2541 alloy is Fe - 25Cr - 4Al - 1Y; all compositions are in weight percent, unless otherwise noted.

TABLE 2.1
STATUS OF Fe-Cr-Al-Y-CLAD FUELED SPECIMENS UNDERGOING THERMAL STABILITY TESTS IN AIR

Cladding	Core Composition, vol %	Type Fuel ^a	Specimen Number	Test Temperature, °C	Current Test Time, hr	Surface Uranium Concentration By X-ray Fluorescence, ^b %	Status ^c
2541	Fe - 50UO ₂	KM-A	FAU-17	950	7940	<0.02	
			FAU-36	950	7940	<0.02	
			FAU-38	950	7940	<0.02	
			FAU-16	1100	7655		Ruptured
			FAU-37	1100	7025	0.66	Completed
2541	Fe - 40UO ₂	AR	FU-29	950	7000	<0.02	Completed
			FU-30	1100	6974		
			FU-32	1100	5098	<0.02	Completed
2541	Fe - 40UO ₂	GE-A	FAU-52	750	520	<0.02	
			FAU-53	750	520	<0.02	
			FAU-54	750	520	<0.02	
			FAU-55	950	520	<0.02	
			FAU-56	950	520	<0.02	
			FAU-57	950	520	<0.02	
			FAU-58	1100	520	<0.02	
			FAU-60	1100	520	<0.02	
			FAU-46	1100	4100	<0.02	
2541	Fe - 40UO ₂	KM-A	FAU-29	950	5190		
			FAU-28	950	5100	<0.02	Completed
			FAU-22	1100	6885	0.17	
			FAU-29	1100	4190	0.16	
2541	Fe - 40UO ₂	S-KM	FSU-25	750	520	<0.02	
			FSU-26	750	520	<0.02	
			FSU-27	750	520	<0.02	
			FSU-28	750	520	<0.02	
			FSU-29	750	520	<0.02	
			FSU-13	950	4195	<0.02	
			FSU-22	950	520	<0.02	
			FSU-23	950	520	<0.02	
			FSU-24	950	520	<0.02	
			FSU-10	1100	2510	0.82	Completed
			FSU-11	1100	4115	2.40	
			FSU-12	1100	3270		Ruptured
1541	Fe - 40UO ₂	S-KM	FSU-19	950	3005	<0.02	Completed
			FSU-20	950	4195	<0.02	
			FSU-16	1100	2890		Ruptured
			FSU-17	1100	3270		Ruptured
2541	Cr - 50UO ₂	AR	CU-26	950	8940	0.10	
2541	Cr - 50UO ₂	KM-A	CAU-27	1100	5100	1.25	Completed
			CAU-28	1100	7115	0.60	
2541	Cr - 50(UO ₂ - 11ThO ₂)	GE-A	CUT-24	1100	5060	0.24	Completed
2541	(Fe - 25Cr) - 50UO ₂	KM-A	FCAU-4	950	8940	0.04	
			FCAU-3	1100	7000	0.07	Completed
2541	(Fe - 25Cr) - 40UO ₂	GE-A	FCAU-6	750	520	<0.02	
			FCAU-7	750	520	<0.02	
			FCAU-8	750	520	<0.02	
			FCAU-9	950	520	<0.02	
			FCAU-10	950	520	<0.02	
			FCAU-12	950	520	<0.02	
			FCAU-13	1100	520	<0.02	
2541	(Fe - 25Cr) - 40UO ₂	S-KM	FCSU-1	750	520	<0.02	
			FCSU-4	950	520	<0.02	
			FCSU-5	950	520	<0.02	
			FCSU-6	950	520	<0.02	
			FCSU-7	1100	520	<0.02	
			FCSU-8	1100	520	<0.02	
			FCSU-14	1100	520	<0.02	
1541	Fe - 40UN	AR	FUN-8	950	7940	<0.02	
2541	Cr - 40UN	AR	CUN-5	950	9575	0.03	
2541	(Fe - 25Cr) - 40UN	AR	FCUN-1	950	9575	<0.02	
			FCUN-3	1100	5100	1.10	Completed
1541	(Fe - 25Cr) - 40UN	AR	FCUN-5	950	7000	<0.02	Completed

^aAR - Ceramic-grade UO₂ or UN of -325 mesh particle size.

GE-A - UO₂ agglomerated at GE-NMPO, -100/+200 mesh.

KM-A - Commercial agglomerated UO₂, -100/+200 mesh.

S-NM - Commercial spheroidized UO₂.

S-KM - UO₂ plasma spheroidized at GE-NMPO, -140/+200 mesh.

^bAnalysis of cladding surface for uranium by X-ray fluorescence (penetration ~0.015 cm); presence of uranium in amounts less than 0.02 percent cannot be detected.

^cUnless otherwise noted, specimens are continuing on test satisfactorily.

Studies of various fuel forms are being conducted as part of the laboratory stability test program. Six specimens containing plasma-arc spheroidized UO_2 prepared at GE-NMPO from agglomerated fuel particles, as previously reported,² were showing relatively high uranium intensities after 2500 to 2900 hours at 1100°C . Three of these specimens ruptured after 2890 to 3270 hours, two were removed from test for analysis after 2510 hours, and one continues on test after 4115 hours. Since these specimens were expected to be more stable than the data show, more specimens are being tested to check the uranium intensities. Fifteen new specimens (Type S-KM in Table 2.1) were placed on test: six at 750°C , six at 950°C , and three at 1100°C . These specimens have accumulated 520 hours at temperature with none showing detectable uranium ($<0.02\%$) on the surface when analyzed by the X-ray fluorescence method.

Metallographic examination of three previously tested specimens containing the spheroidized UO_2 particles was completed. Three were tested for 2510 hours, two at 950°C and one at 1100°C . The interface areas between the core and cladding of these specimens are shown in Figure 2.1. The specimens tested at 950°C show a discontinuous layer of Al_2O_3 on parts of the fuel particles and at the interface of the core and the cladding, with finely scattered oxide particles in the grain boundaries of core and cladding matrices. The 1541-clad specimens tested at 950°C have an area containing a coarser precipitate which may be sigma. This phase is also present but not as well defined in the 2541-clad specimen. The exterior oxide layer on the 950°C specimens was less than 6 microns thick.

The specimen tested at 1100°C shows heavy intergranular oxidation of the cladding in the interface areas and at the surface. While greater internal oxidation occurred in this specimen, there is no oxide layer around the fuel particles or at the interface. The outer oxide layer was about 13 microns thick.

The two specimens tested at 950°C showed less than the 0.02 percent detectable uranium level on the surface when analyzed by X-ray fluorescence, while the specimen tested at 1100°C showed 3.1 percent uranium, which is much greater than the uranium diffusion measured for specimens containing agglomerated UO_2 particles. Electron-microprobe analysis of these specimens is being made to determine distribution of uranium and other major elements in the specimens.

A series of specimens was placed on test which contained either enriched UO_2 alone or as agglomerated particles dispersed in an iron matrix. These specimens were clad with drawn tubing of 1541 alloy and were autoclaved at 1100°C . They are being tested at temperatures of 750° to 1250°C in air. Periodic monitoring for uranium diffusion is being performed using both alpha counting techniques and X-ray fluorescence analysis. The status of this series of specimens and the results of uranium analyses are shown in Table 2.2. Although insufficient test time has been accumulated to indicate a trend, the alpha counts and X-ray fluorescence methods of analysis are in general agreement. X-ray fluorescence analysis is performed on a small area of the specimen while the alpha counting is performed over the whole surface of the specimens which may prevent detailed correlation of the two analytical techniques.

The alpha-count monitoring of specimens containing cores of UO_2 indicated a rapid increase in uranium on the surface, with the maximum count occurring at about 7 hours at 1250°C and at about 30 hours at 750°C and 950°C ; after reaching these peaks, the count rate returned to the level measured at the beginning of the tests. This trend is shown in Figure 2.2. The initial increases in alpha activity during the first 30 hours may be due to diffusion of uranium formed during the autoclaving operation at 1100°C . The subsequent reduction in alpha counts is attributed to the formation of the oxide films which restrict the alpha particles. For the specimen tested at 1250°C , the measured maximum alpha activity

²"High-Temperature Materials Program Progress Report No. 49, Part A," GE-NMPO, GEMP-49A, July 28, 1965, p. 13.

2541-clad specimen FSU-9
tested at 950°C
(Neg. 6171)

1541-clad specimen FSU-21
tested at 950°C
(Neg. 6172)

1541-clad specimen FSU-15
tested at 1100°C
(Neg. 6173)

Fig. 2.1—Photomicrographs of 1541- and 2541-alloy-clad Fe-40UO₂ specimens showing condition of interface areas after 2510 hours at 950°C or 1100°C in air. UO₂ in these specimens was plasma-arc spheroidized. (500X)

TABLE 2.2
URANIUM DIFFUSION THROUGH 1541 ALLOY CLADDING OF ENRICHED UO_2
SPECIMENS AS MEASURED BY X-RAY FLUORESCENCE AND
ALPHA COUNT TECHNIQUES

Specimen No.	Test Temperature, $^{\circ}\text{C}$	Current Test Time, hr	X-Ray Fluorescence Analysis, % U	Surface Alpha Activity, counts/cm ² -min
UO_2 Core				
EU-1	750	80	<0.02	<1
EU-2	750	80	<0.02	<1
EU-3	950	80	<0.02	2
EU-5	950	80	<0.02	<1
EU-4	1100	7	—	<1
EU-6	1100	7	—	9
EU-9	1250	77	<0.02	16
Fe - 40UO_2 Core				
FEAU-3	750	80	<0.02	<1
FEAU-4	950	80	<0.02	2
FEAU-5	950	80	<0.02	<1
FEAU-6	1100	7	—	<1
FEAU-7	1100	7	—	<1
FEAU-9	1250	77	0.04	28

Fig. 2.2—Alpha surface activity as a function of test time for 1541-alloy-clad enriched UO_2 capsules tested in air at 750°, 950°, and 1250°C

occurred at about 7 hours, dropped to a minimum after about 30 hours, and increased again after 77 hours. At the lower test temperatures, the alpha count continued to decrease after 30 hours.

Specimens containing 40 volume percent enriched UO_2 dispersed in an iron matrix showed less consistency in alpha activity than the specimens containing UO_2 cores and require longer time test data to establish a trend. Testing of these specimens will be continued and additional specimens containing enriched UO_2 will be fabricated to study the interactions of UO_2 , cladding, and matrix materials in more detail.

In an effort to obtain further correlation of the X-ray fluorescence technique and the alpha count method of detecting uranium at the cladding surface of a tested 1541-clad

Fe-UO₂ specimen, an experiment was performed by which chemical analyses for uranium were obtained for metal samples removed from the cladding. A prototype specimen of the in-pile design was tested for 4000 hours at 1100°C. During this test, brown rings appeared on the cladding near the ends of the fueled core after about 1800 hours; the rings gradually spread and darkened until the entire core area was affected. This is a normal indication of uranium diffusion through the cladding and blending with the alumina film. Such diffusion of uranium can be detected by X-ray fluorescence, but efforts to confirm it by metallographic or electron microprobe analyses have been unsuccessful.

Since the prototype specimen had a ground surface prior to testing it was possible to remove samples of the darkened surface by machining to definite depths. Samples were cut from parallel bands to depths of 0.025, 0.051, and 0.076 mm. Chemical analyses of these samples indicated uranium content of the 0.025 mm layer was 3.9 percent; of the 0.051 mm layer, 2.9 percent; and of the 0.076 mm layer, 2.2 percent. Since all three samples contained the surface oxide film, these data indicate the uranium tends to concentrate at the surface of the cladding. Further analysis of the fueled specimen by electron microprobe is planned in an effort to define the uranium concentration gradient through the cladding.

In-Pile Test Program

A series of in-pile tests of Fe-Cr-Al-Y-clad fuel element specimens is being conducted to demonstrate fission product retention capabilities as a function of temperature and burnup capabilities at elevated temperatures. These in-pile tests are currently being conducted in the LITR and preparations are being made for testing in the ORR.

2541-Clad Fe-UO₂ at 1100°C (LTFC-1) – The first in-pile test of a 2541-clad Fe – 40UO₂ specimen was operated for 1007 hours at maximum indicated temperatures of approximately 1100°C in flowing air. The specimen was subjected to 12 thermal cycles caused by reactor shutdowns. The burnup was calculated at 0.7 percent based on 4.8×10^{19} fissions per cubic centimeter. The results of analyses of a series of carbon traps indicated a low steady-state release of fission gases with R/B values for Xe¹³³ averaging 3×10^{-7} .

The cartridge was disassembled in the hot cell at GE-NMPO and the fuel element specimen was inspected. No significant changes in length were detected while the diametric growth ranged from 0.2 to 0.7 percent. The specimen appeared to be in excellent condition as shown in Figure 2.3. Based on data from three thermocouples located in the bore of the specimen, the temperature was about 960°C at the upstream end of the fueled core and 1100°C over most of the downstream half of the core section. The appearance of the specimen confirmed this temperature profile. The 1100°C area had a granular appearance which upon microscopic examination was found to be a result of shallow pitting and roughening of the surface as shown in Figure 2.4.

The specimen was cut into four pieces for metallographic examination of transverse and longitudinal sections. A typical transverse section of the 1100°C area is shown in Figure 2.5 which shows intergranular oxidation at the surface of the cladding and at the core – cladding interface similar to that observed on laboratory test specimens after several thousand hours at 1100°C. Oxide stringer penetration of the grain boundaries and subsequent spalling of the surface oxide resulted in roughening of the surface. Uniform distribution of UO₂ particles in the iron matrix was observed. No evidence of structural damage attributable to irradiation and the fission process was noted.

1541-Clad Fe-UO₂ at 950°C (LTFC-2) – The second in-pile test of a 1541-alloy clad Fe – 40UO₂ specimen was inserted in the C-48 facility of the LITR in July and at the end of this report period had been operating at an average specimen temperature of 950°C for 565 hours. The cartridge design of this experiment is the same as that of LTFC-1 de-

Fig. 2.3—Specimen of 2541-alloy-clad Fe-40UO_2 from in-pile test LTFC-1 after 1007 hours at 1100°C . Arrow indicates direction of coolant airflow. (Neg. RML-2525)

Fig. 2.4—Magnified view of cladding surface of LTFC-1 specimen in 1100°C area showing shallow pitting resulting from intergranular oxidation (Neg. RML-2528, 6X)

Fig. 2.5—Photomicrograph of typical transverse section of outer cladding and core-cladding interface from 1100°C region of in-pile specimen LTFC-1 (Neg. R-1302, 100X)

scribed in a previous report.³ A higher airflow (850 liters per minute) than that of LTFC-1 is required to hold the specimen at the lower temperature of 950°C. The effluent air stream from the test is sampled periodically with carbon traps and analyzed for fission gases. Fractional release is low ($R/B = 4 \times 10^{-8}$ to 3×10^{-7}) with a half-life dependence which is indicative of recoil as the primary release mechanism. These data are generally comparable with the data obtained from test LTFC-1 for the same time period. This test will be continued for at least 1000 hours at 950°C.

Assembly of the third in-pile test cartridge is in progress. Like LTFC-2, it contains a 1541-alloy-clad Fe - 40UO₂ specimen and is scheduled to be tested in the LTR for 2000 hours at 950°C.

A new series of tests is being designed for operation in the F-2 facility of the ORR. These fuel specimens will be clad with drawn tubing of the 1541 alloy and will contain Fe - 40UO₂ cores. These tests will be conducted at temperatures of 750°, 950°, and 1100°C to a total burnup of about 15 percent. The first of these cartridges is scheduled for insertion in the ORR in late September.

ALLOY DEVELOPMENT

The objective of this portion of the work is to further the usefulness of Fe-Cr-Al-Y alloys for commercial reactor applications by improving the structural properties of the alloys at elevated temperatures without sacrificing oxidation or corrosion resistance. A secondary effort is concerned with obtaining data on the effects of radiation and composition on the ductile-to-brittle transition temperature of selected alloy compositions.

Alloy Properties - Impact Tests

Subsize notched-impact tests on Fe-Cr-Al-Y alloys performed at GE-NMPO indicated ductile-to-brittle transition temperatures between 100°C and 200°C, based on 50 percent of the absorbed energy.⁴ Recent tests performed at the Naval Research Laboratory⁵ using standard V-notch Charpy tests of material supplied by GE-NMPO indicate a DBTT for the 1541 alloy of approximately 150°C. The alloy after irradiation at ambient temperature (<120°C) to 1×10^{19} n/cm² exhibited a DBTT of approximately 210°C.

AIR OXIDATION AND STEAM CORROSION STUDIES

Air Oxidation

Oxidation tests of a series of Fe-Cr-Al-Y alloy compositions have been in progress for more than a year at temperatures of 450°, 550°, 730°, 900°, and 1100°C in static air. Weight change data for times up to 9000 hours at 900°C and 1100°C are shown in Figure 2.6. All the alloys exhibited similar weight gains except for the low yttrium alloys which continue to exhibit significantly lower oxidation rates. The data previously reported⁶ for the 1041 alloy at 1100°C were in error; the corrected data are shown in Figure 2.6.

As reported previously,⁷ a group of 14 alloys containing 13 to 15 percent chromium, 4 to 7 percent aluminum, and 0 to 1 percent yttrium was prepared to study optimum aluminum and yttrium contents. These are being evaluated for oxidation and steam corrosion resistance and aging behavior. After 200 hours, the data are inconclusive since

³"High-Temperature Materials Program Progress Report No. 47, Part A," GE-NMPO, GEMP-47A, May 28, 1965, p. 18.

⁴"High-Temperature Materials Program Progress Report No. 43, Part A," GE-NMPO, GEMP-43A, January 29, 1965, p. 17.

⁵L. E. Steele, J. R. Hawthorne, and H. E. Watson, "Irradiation Effect on Reactor Structural Materials," NRL Memo Report 1611, February 1 to April 30, 1965.

⁶"High-Temperature Materials Program Progress Report No. 49, Part A," GE-NMPO, GEMP-49A, July 28, 1965, p. 22.

⁷Ibid., p. 20.

Fig. 2.6 - Weight gain as a function of test time at 900°C and 1100°C in static air for Fe-Cr-Al-Y alloys for times up to 9000 hours

all the alloys exhibit similar behavior. Therefore, the tests for oxidation at 1100°C in air, steam corrosion at 550°C, and aging at 450°C are being continued for longer times.

Steam Corrosion Studies

Steam corrosion tests of Fe-Cr-Al-Y alloys are being conducted at 550°C and 730°C in low-pressure steam generated from deionized water. No additional data were obtained at 730°C because of a failure of the superheating coil in the test apparatus.

Previous work has shown that pre-oxidation in air at temperatures sufficiently high to form the protective oxide film greatly improves the corrosion resistance of Fe-Cr-Al-Y alloys in steam at lower temperatures. To determine the amount of strain that can be

imposed on the alloys without rupturing the protective oxide film, specimens of the 1041 alloy were pre-oxidized at 950°C, deformed by roll-forming to various radii, then tested in steam at 550°C. The weight change data after 600, 800, and 1064 hours are presented in Table 2.3. The approximate strain was calculated from the radius of curvature of the specimen. The data indicate that strains up to 4 percent may be tolerated without destroying the protective oxide film. The weight gains are somewhat higher for the specimens pre-oxidized for 1 hour than for those pre-oxidized for 20 and 100 hours. The tests will be terminated after 1000 hours and the specimens will be examined metallographically.

TABLE 2.3
WEIGHT GAIN DATA FOR PRE-OXIDIZED AND STRAINED
1041 ALLOY TESTED IN STEAM AT 550°C

Calculated Plastic Strain, %	Radius Of Curvature, cm	Pre-Oxidation Time At 980°C, hr	Weight Gain, mg/cm ²		
			600 hr	800 hr	1064 hr
0	—	1	-0.02	0.02	0.00
		20	-0.06	0.01	-0.02
		100	-0.05	-0.01	-0.02
1	7.6	1	0.13	0.10	0.17
		20	0.05	0.05	0.10
		100	-0.03	-0.03	0.06
2	3.8	1	0.15	0.15 ^a	—
		20	0.02	0.03 ^a	—
		100	0.06	0.00 ^a	—
3	2.5	1	0.15	0.17	0.22
		20	0.09	0.06	0.13
		100	0.07	0.06	0.06
4	1.9	1	0.26	0.18 ^a	—
		20	0.13	0.09 ^a	—
		100	0.08	0.06 ^a	—
5	1.3	1	Terminated after 200 hr because of excessive oxidation		
		20			
		100			

^a864-hour data.

In cooperative tests at Battelle-Northwest Laboratories, specimens of 1541 alloy (Heat MS-43) were tested for 10 days in a steam autoclave under a pressure of 34 atmospheres at 550°C. The surfaces of the specimens were treated in one of three ways: etched in phosphoric acid, etched in HNO₃-HF acid, or vapor-blasted, which is the standard test condition at GE-NMPO. The results given in Table 2.4 show that HNO₃-HF acid etch results in a weight gain more than 10 times that of specimens which were vapor-blasted.

TABLE 2.4
WEIGHT CHANGE DATA FOR 1541 ALLOY TESTED FOR
10 DAYS IN 550°C STEAM AT
BATTELLE-NORTHWEST LABORATORIES

Surface Treatment	Number Of Specimens	Average Weight Gain, mg/cm ²
As-received, vapor- blasted by GE-NMPO	10	0.07
Phosphoric acid pickle	5	0.16
HNO ₃ -HF pickle	5	0.80

These results confirm previous data which indicated that chemical treatment may preferentially leach aluminum from the alloys and destroy their corrosion-resistant properties. Testing of the vapor-blasted specimens for longer times will be continued at Battelle-Northwest Laboratories.

WORK PLANNED FOR NEXT PERIOD

Laboratory testing of Fe-Cr-Al-Y-clad fueled specimens for times up to 10,000 hours at 750°, 950°, and 1100°C in air will be continued. Specimens containing enriched UO₂ will also be tested in a study of uranium diffusion rates through 1541 alloy.

In-pile test LTFC-2 will be continued for at least 1000 hours in the LITR with periodic analyses for fission product release. The first of a series of high burnup tests (ORFC-1) will be prepared for insertion in the ORR late in the next report period.

The long-time corrosion testing of Fe-Cr-Al-Y alloys and selected commercial alloys in steam will continue. Studies of the effects of yttrium and aluminum contents on oxidation resistance and ductility of the Fe-Cr alloys will be continued. Evaluation of a series of Fe-Cr-Al-Y alloy compositions irradiated in the ETR will be continued to determine the effects of irradiation on ductile-to-brittle transition temperature.

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3. HIGH-TEMPERATURE REACTOR MATERIALS RESEARCH

(57003)

The purpose of this program is to measure and evaluate high-temperature physical and mechanical properties of commercially available and newly developed refractory materials being considered for use in fueled and non-fueled high-temperature (1000° to 3000°C) reactor applications.

MECHANICAL PROPERTY EVALUATIONS

Creep-Rupture Studies

Tungsten – Previous reports¹ presented the creep-rupture results obtained for 0.15-cm-thick arc-cast tungsten sheet from 1600° to 3000°C for rupture times from approximately 5 to 300 hours in hydrogen. Prior to testing, the specimens were annealed at the test temperature for 2 hours. Test results at temperatures of 2000°C and 2200°C showed indications of a transition in the stress dependency with respect to both rupture life and linear (secondary) creep rate. Additional 2000°C and 2200°C creep-rupture tests of specimens annealed at 2400°C confirmed this change. Annealing at the higher temperature provided a stable material structure for the test temperatures involved, and differences in creep rate are attributed to a change in the creep mechanism.

Figures 3.1 and 3.2 show the creep curves obtained for the same tungsten material exposed to different prior anneals. In tests at 2200°C, the 2400°C anneal caused the linear creep rate to increase and the rupture life to decrease (Figure 3.1), as expected; whereas at 2000°C, the 2400°C anneal caused the linear creep rate to decrease and the rupture life to increase (Figure 3.2). This result was not expected and indicates a change in the creep characteristics from 2200° to 2000°C. Additional tests at 2000°C and 2200°C but at different stresses revealed the same relationships.² This change is attributed to a change in the creep mechanism for tungsten occurring at approximately 60 percent (2000°C) of the absolute melting temperature. Attempts to identify the different mechanisms are being made.

Additional creep tests, of the same tungsten sheet, were performed at temperatures from 2000° to 2800°C in hydrogen to determine the apparent activation energy for creep. All specimens were annealed at 2800°C for 2 hours so that the starting material structure was constant. Each specimen was tested at constant stress (load), and the temperature was changed incrementally once the linear creep rate at each temperature had been observed. The incremental temperature change was 100°C and each temperature was repeated for the same specimen to evaluate the reproducibility of the creep rate for the same conditions. A summary of the results is given in Table 3.1.

A typical strain – time curve generated at a stress of 0.281 kg/mm² and temperatures of 2600°, 2700°, and 2800°C is presented in Figure 3.3 to show the effect of the changes

¹"High-Temperature Materials Program Progress Report No. 47, Part A," GE-NMPO, GEMP-47A, May 28, 1965, p. 27.

²"High-Temperature Materials Program Progress Report No. 49, Part A," GE-NMPO, GEMP-49A, July 28, 1965, p. 27.

Fig. 3.1 – Creep curves for arc-cast tungsten at 2200°C and 0.703 kg/mm² in hydrogen

Fig. 3.2 – Creep curves for arc-cast tungsten at 2000°C and 1.05 kg/mm² in hydrogen

TABLE 3.1
CREEP RATE DATA FROM MULTI-TEMPERATURE TESTS OF
ARC-CAST TUNGSTEN^a AT CONSTANT STRESS IN HYDROGEN^b

Specimen	Stress, kg/mm ²	Temperature, °C	Test Time, hr	Strain, cm/cm	Linear Creep Rate, min ⁻¹
W(3)-73	0.281	2800	1.75	0.0460	2.9 x 10 ⁻⁴
		2700	1.75	0.0094	9.0 x 10 ⁻⁵
		2600	4.50	0.0069	2.8 x 10 ⁻⁵
		2800	0.75	0.0130	2.9 x 10 ⁻⁴
		2700	1.55	0.0095	1.0 x 10 ⁻⁴
		2600	3.20	0.0064	3.3 x 10 ⁻⁵
		2800	1.00	0.0201	3.4 x 10 ⁻⁴
W(3)-74	0.457	2600	0.80	0.0317	3.6 x 10 ⁻⁴
		2500	1.60	0.0125	1.3 x 10 ⁻⁴
		2400	3.80	0.0095	4.2 x 10 ⁻⁵
		2600	0.60	0.0128	3.5 x 10 ⁻⁴
		2500	1.40	0.0106	1.1 x 10 ⁻⁴
		2400	4.80	0.0107	3.7 x 10 ⁻⁵
		2600	0.60	0.0137	3.5 x 10 ⁻⁴
W(3)-75	0.703	2400	1.20	0.0390	2.9 x 10 ⁻⁴
		2300	1.55	0.0097	1.0 x 10 ⁻⁴
		2200	6.75	0.0090	2.3 x 10 ⁻⁵
		2400	1.00	0.0152	2.6 x 10 ⁻⁴
		2300	2.50	0.0126	8.9 x 10 ⁻⁵
		2200	6.00	0.0082	2.4 x 10 ⁻⁵
		2400	0.90	0.0156	2.8 x 10 ⁻⁴
W(3)-76	1.20	2200	0.70	0.0530	4.0 x 10 ⁻⁴
		2100	2.00	0.0082	1.0 x 10 ⁻⁴
		2000	4.90	0.0058	2.0 x 10 ⁻⁵
		2200	0.70	0.0110	2.7 x 10 ⁻⁴
		2100	1.80	0.0070	6.6 x 10 ⁻⁵
		2000	4.00	0.0050	2.0 x 10 ⁻⁵
		2200	1.50	0.0270	2.9 x 10 ⁻⁴

^a0.15-cm-thick sheet with 0.64 x 2.54 cm gage section.

^bAll specimens annealed at 2800°C for 2 hours in hydrogen prior to test.

in temperature. Figure 3.4 shows these same data on an expanded time basis from which the linear creep rates for each temperature were determined. A summary of the results is presented in Figure 3.5 as linear creep rate versus reciprocal temperature based on the creep expression:

$$\dot{\epsilon} = A \sigma^n e^{\frac{-\Delta H}{RT}} \quad (3.1)$$

where

A, n, R, and e are constants

$\dot{\epsilon}$ is linear creep rate

σ is stress

T is temperature

ΔH is activation energy for creep

The slope of the lines in Figure 3.5 yields an apparent activation energy for creep of 160 kcal/mole. This value is the same as that reported by Green³ for tungsten at temper-

³W. V. Green, et al., "Short Time Creep-Rupture Behavior of Tungsten at High Temperature," *AIIME*, Vol. 215, 1959, p. 1057.

Fig. 3.3 – Multiple temperature creep curve of arc-cast tungsten

Fig. 3.4 – Expanded creep curves for arc-cast tungsten at 0.281 kg/mm² (see Figure 3.3)

Fig. 3.5 – Summary of creep rate versus reciprocal temperature for arc-cast tungsten (multi-temperature creep tests at constant load)

atures from 2250° to 2800°C. Dorn⁴ reports the activation energy for the self-diffusion of tungsten as 140 kcal/mole with the observation that the activation energies for self-diffusion and for high-temperature creep are equal. The value of 160 kcal/mole is therefore thought to represent a reliable value for the activation energy for high-temperature creep of tungsten.

Molybdenum – The major portion of the high-temperature creep-rupture tests performed to date on molybdenum have been performed in a hydrogen atmosphere with a few tests being performed in an argon atmosphere. A comparison of the results in the two atmospheres indicated that the creep-rupture characteristics were different for wrought sintered molybdenum and the same for arc-cast molybdenum.

During this report period, preliminary evaluations were performed in a vacuum to (1) determine the problems associated with testing in this environment and (2) evaluate the effect of the vacuum environment on the creep-rupture characteristics of the material.

A vacuum diffusion pump, normally used to evacuate the test chamber prior to testing in hydrogen, was used to evacuate the creep-rupture furnace for testing in vacuum. The system was capable of maintaining 3.5×10^{-5} Torr at 1600°C. At this temperature, an arc-cast molybdenum specimen was creep-rupture tested at a stress of 1.41 kg/mm². No operational problems were encountered for the test time involved (5.65 hours to rupture). A similar test of the same material was performed in a hydrogen atmosphere to determine if the two atmospheres would provide the same results. The two creep curves

⁴J. E. Dorn, "Creep and Recovery," *ASME*, 1956, p. 255.

obtained in these tests are presented in Figure 3.6. The results indicate that the linear creep rate in hydrogen is approximately twice that in vacuum. The time to rupture in vacuum is also greater by approximately 40 percent while the ductility is less on the basis of elongation at rupture.

Fig. 3.6 – Creep curves for arc-cast molybdenum at 1600°C and 1.41 kg/mm² in vacuum and hydrogen

The sharp change in slope of the creep curves rather than a gradual transition into third-stage creep is similar to that observed for arc-cast tungsten at approximately 60 percent of the absolute melting temperature.⁵ (1600°C is 65% of the absolute melting temperature for molybdenum.) This similar transition in the creep curve of tungsten is thought to be caused by a structural change in the material during testing. Therefore, the differences obtained for the two tests of molybdenum in hydrogen and vacuum at 1600°C are not necessarily the result of the environments. Additional work will be required to evaluate the effect of atmosphere.

An attempt was made to compare the creep-rupture results of arc-cast molybdenum in vacuum and hydrogen at the higher test temperature of 2000°C. While attempting to establish the test temperature in vacuum using an optical pyrometer, a thin film was observed on the furnace sight glass. This film prevented an accurate determination of temperature and the test was discontinued. Analysis of the film showed it to be tungsten and molybdenum which were apparently vaporized from a reaction of the test specimen and furnace heating element (tungsten).

On the basis of the above test results, the existing test equipment is capable of operating with a vacuum of 3.5×10^{-5} Torr at 1600°C. Operation at higher temperatures and/or higher vacuum will necessitate equipment modification.

⁵“High-Temperature Materials Program Progress Report No. 47, Part A,” GE-NMPO, GEMP-47A, May 28, 1965, p. 27.

W-Re-Mo Alloys – Previous reports^{6,7} presented the results of the creep-rupture testing of W-Re-Mo alloys (tungsten – rhenium from W – 26Re through W – 29Re with 0, 10, and 20 at. % molybdenum) at 1600°C and 2200°C. The tests are part of the evaluation for the materials fabricated at GE-NMPO under the Alloy Development Program.⁸

The creep-rupture results at 1600°C and 4.22 kg/mm² showed W – 26Re to be most creep resistant and have the greatest rupture life. Photomicrographs of the as-tested samples showed the grain size to decrease with increasing rhenium content and increase with increasing molybdenum content. The creep-rupture results at 2200°C and 0.56 kg/mm² showed the W – 27Re – 20Mo to be the most creep resistant and have the greatest rupture life.

Photomicrographs of the specimens after test are presented in Figure 3.7. No significant change in grain size is observed with increasing rhenium content but an increase in grain size is observed as the molybdenum content is increased. The grain size for the W – 27Re – 20Mo is considerably greater than any of the other specimens and may account for its better creep-rupture characteristics at 2200°C and 0.56 kg/mm². All specimens exhibit considerable grain boundary separation.

Creep-rupture tests of W – 25Re – 30Mo were performed during this report period using specimens from the same 0.025-cm-thick sheet. Table 3.2 gives the results obtained at 1600°C and 2200°C. Figures 3.8 and 3.9 present the creep curves obtained and show essentially no primary creep except for the test at 2200°C and 0.35 kg/mm². This may be due to a structural change (grain growth) or homogenization during the time at temperature. A metallographic evaluation will be performed.

TABLE 3.2
CREEP-RUPTURE RESULTS FOR W – 25Re – 30Mo^a SHEET IN HYDROGEN^b

Temperature, °C	Stress, kg/mm ²	Time To Indicated Elongation, hr							Elongation At Rupture, %	Linear Creep Rate, min ⁻¹	Hardness (DPH) ^c	
		0.5%	1%	2%	3%	5%	10%	Rupture			Before	After
1600	3.37	2.7	5.1	9.7	13.4	18.9	24.9	25.9	14	1.7×10^{-5}	420	398
1600	4.22	1.5	2.8	5.3	7.6	10.6	13.9	14.8	12	6.1×10^{-5}	405	398
2200	0.35	1.3	3.0	6.9	11.6	22.7	59.4	102	16	2.2×10^{-5}	437	437
2200	0.56	0.9	1.9	3.9	6.0	10.1	19.2	28.8	18	8.1×10^{-5}	412	400

^aAtomic percent.

^bSpecimens prepared from 0.025-cm-thick sheet; 0.025 x 0.6 x 2.54 cm gage section; specimens annealed for 2 hours at test temperature in hydrogen before test.

^c2.5-kg load.

Creep Analysis Techniques

Recent studies^{9,10} of the first-stage creep data have identified four equations which afford an accurate representation of transient strain – time behavior. These include the familiar Andrade and parabolic creep equations along with two additional equation forms which were found to yield excellent results in these first-stage creep evaluations. These newly proposed equations are:

$$\epsilon = a + bt^{1/3} + ct^{2/3} + dt \quad (3.2)$$

and

$$\epsilon = A + B \sinh (Ct^{1/3}) \quad (3.3)$$

⁶Ibid., p. 79.

⁷“High-Temperature Materials Program Progress Report No. 49, Part A,” GE-NMPO, GEMP-49A, July 28, 1965, p. 48.

⁸Formerly a part of this task; now Job 57015, “Refractory-Metal Alloy Research and Development.”

⁹“High-Temperature Materials Program Progress Report No. 47, Part A,” GE-NMPO, GEMP-47A, May 28, 1965, p. 34.

¹⁰“High-Temperature Materials Program Progress Report No. 49, Part A,” GE-NMPO, GEMP-49A, July 28, 1965, p. 41.

Fig. 3.7 - Photomicrographs of W-Re-Mo alloys (at. %) after creep-rupture testing at 2200°C and 0.56 kg/mm² in hydrogen showing grain size in microns, hardness in DPH, and rupture elongation in percent (250X)

Fig. 3.8 - Creep curves for W-25Re-30Mo at 1600°C in hydrogen

Fig. 3.9 - Creep curves for W-25Re-30Mo at 2200°C in hydrogen

The third degree polynomial in $t^{1/3}$ is particularly attractive since the first derivative approaches a constant value as time increases and hence offers the possibility of being used to express both first- and second-stage creep behavior in a single equation. In the case of the equation involving the hyperbolic sine this appears to be the first use of this function in expressing transient creep behavior.

Currently, all first-stage creep analyses involve fitting each of the above equations to a given set of data. Special least squares computer programs were written to enable all the equation constants to be calculated. Since these programs deal only with the original experimental data, unique solutions are obtained for the creep equation constants and hence the values are not influenced by the interpretation of the individual performing the analysis. Inasmuch as some of the previously employed techniques for creep analysis, especially those of Hazlett and Parker¹¹ and de Lacombe,¹² were so influenced, they have now all been abandoned in favor of the more rigorous solutions. Also abandoned was the approach involving the parabolic equation in which the exponent on time was assumed equal to 0.6. Now the non-linear regression analysis which is employed iterates until an exponent on time is identified for which the sum of the squares of the residuals is a minimum, thereby providing a parabolic expression representing the closest fit of the experimental data.

To date this standardized analysis procedure has been applied to the first-stage creep data for arc-cast tungsten at 2200°, 2400°, 2600°, and 2800°C and also to the creep data for lead at 14.5°C and 162°C reported by Andrade.¹³ These results are presented in Tables 3.3 through 3.6. In these tables, t_I represents the time values corresponding to

TABLE 3.3

CONSTANTS FOR USE WITH LEAD AND ARC-CAST TUNGSTEN DATA IN
ANDRADE CREEP EQUATION $[1 + \epsilon = \epsilon'_0 (1 + \beta t^{1/3}) e^{kt}]$

Material	Temperature, °C	Stress, kg/mm ²	t_I^a min.	ϵ'_0	β	k	$\mu^b \times 10^4$
Lead	14.5	1.67	550	39.149	1.429×10^{-2}	7.274×10^{-5}	140.0
	162	0.83	15	9.867	4.97×10^{-2}	1.011×10^{-2}	68.0
Tungsten	2200	0.703	468	1.0002	8.64×10^{-4}	1.337×10^{-5}	1.5
	2200	0.844	246	1.0009	1.192×10^{-3}	2.82×10^{-5}	1.4
	2200	1.05	180	1.0004	2.87×10^{-3}	7.04×10^{-5}	2.8
	2200	1.26	48	1.0017	3.95×10^{-3}	1.8×10^{-4}	1.4
	2200	1.41	45	1.0037	5.61×10^{-3}	2.9×10^{-4}	2.4
	2400	0.457	180	1.0007	1.024×10^{-3}	3.315×10^{-5}	1.2
	2400	0.562	210	1.0005	1.892×10^{-3}	5.605×10^{-5}	1.8
	2400	0.703	60	1.0017	3.0×10^{-3}	1.604×10^{-4}	1.9
	2400	0.844	54	1.0015	5.22×10^{-3}	2.95×10^{-4}	1.6
	2400	1.05	20	1.0018	9.52×10^{-3}	5.44×10^{-4}	3.0
	2600	0.281	300	1.0001	9.22×10^{-4}	3.59×10^{-5}	1.4
	2600	0.352	150	0.999	2.32×10^{-3}	8.04×10^{-5}	1.6
	2600	0.457	60	1.0004	2.8×10^{-3}	2.24×10^{-4}	2.4
	2600	0.562	21	1.0034	5.76×10^{-3}	6.75×10^{-4}	1.8
	2600	0.844	4.5	1.0138	8.24×10^{-3}	4.31×10^{-3}	1.9
	2800	0.176	1170	0.999	1.20×10^{-3}	1.45×10^{-5}	4.3
	2800	0.211	270	0.999	1.72×10^{-3}	4.99×10^{-5}	2.1
	2800	0.281	60	0.999	4.89×10^{-3}	1.57×10^{-4}	1.1
	2800	0.352	12	1.0035	7.64×10^{-3}	4.0×10^{-4}	2.1

^a t_I is the time corresponding to the end of the first stage of creep.

^b μ is the standard deviation weighted for the number of equation constants.

¹¹T. H. Hazlett and E. R. Parker, "Nature of the Creep Curve," *Journal of Metals*, Vol. 5, 1953, p. 318.

¹²J. de Lacombe, "A Method of Representing Creep Curves," *Rev. Metal.*, Vol. 36, 1939, p. 178.

¹³E. N. da C. Andrade, "On the Viscous Flow in Metals and Allied Phenomena," *Proceedings of the Royal Society*, Vol. 84, 1910, p. 1.

TABLE 3.4
CONSTANTS FOR USE WITH LEAD AND ARC-CAST TUNGSTEN DATA IN
HYPERBOLIC SINE CREEP EQUATION [$\epsilon = \epsilon_0 + A \sinh (Bt^{1/3})$]

Material	Temperature, °C	Stress, kg/mm ²	t_I^a min.	ϵ_0	A	B	$\mu^b \times 10^4$
Lead	14.5	1.67	550	39.143	3.201	0.176	150
	162	0.83	15	9.804	0.593	0.954	49
Tungsten	2200	0.703	468	-2.4×10^{-5}	4.0×10^{-3}	0.245	1.6
	2200	0.844	246	7.04×10^{-4}	4.13×10^{-3}	0.317	1.5
	2200	1.05	180	7.0×10^{-5}	9.45×10^{-3}	0.33	3.0
	2200	1.26	48	1.54×10^{-3}	9.0×10^{-3}	0.46	1.4
	2200	1.41	45	3.34×10^{-3}	1.23×10^{-2}	0.49	2.5
	2400	0.457	180	5.23×10^{-4}	3.15×10^{-3}	0.363	1.3
	2400	0.562	210	2.11×10^{-4}	6.03×10^{-3}	0.349	2.2
	2400	0.703	60	1.47×10^{-3}	6.67×10^{-3}	0.486	1.7
	2400	0.844	54	1.03×10^{-3}	1.14×10^{-2}	0.5	1.8
	2400	1.05	20	1.61×10^{-3}	1.81×10^{-2}	0.543	2.8
	2600	0.281	300	-2.49×10^{-4}	3.26×10^{-3}	0.36	1.8
	2600	0.352	150	-1.29×10^{-3}	6.8×10^{-3}	0.38	1.8
	2600	0.457	60	-1.67×10^{-4}	6.07×10^{-3}	0.55	2.5
	2600	0.562	21	2.93×10^{-3}	9.14×10^{-3}	0.7	2.3
	2600	0.844	4.5	1.19×10^{-2}	9.09×10^{-3}	1.26	2.1
	2800	0.176	1170	-1.49×10^{-3}	6.48×10^{-3}	0.214	5.4
	2800	0.211	270	-1.04×10^{-3}	5.92×10^{-3}	0.335	2.4
	2800	0.281	60	-1.08×10^{-3}	1.27×10^{-2}	0.4	1.2
	2800	0.352	12	3.37×10^{-3}	1.46×10^{-2}	0.53	2.1

t_I^a is the time corresponding to the end of the first stage of creep.

μ^b is the standard deviation weighted for the number of equation constants.

TABLE 3.5
CONSTANTS FOR USE WITH LEAD AND ARC-CAST TUNGSTEN DATA
IN PARABOLIC EQUATION ($\epsilon = \epsilon_0 + at^m$)

Material	Temperature, °C	Stress, kg/mm ²	t_I^a min.	ϵ_0	a	m	$\mu^b \times 10^4$
Lead	14.5	1.67	550	39.543	0.252	0.50	430
	162	0.83	15	10.219	0.259	0.86	180
Tungsten	2200	0.703	468	1.1×10^{-3}	2.35×10^{-4}	0.64	1.9
	2200	0.844	246	1.8×10^{-3}	4.13×10^{-4}	0.63	1.5
	2200	1.05	180	2.6×10^{-3}	1.07×10^{-3}	0.62	3.1
	2200	1.26	48	3.8×10^{-3}	2.13×10^{-3}	0.59	2.0
	2200	1.41	45	6.8×10^{-3}	2.95×10^{-3}	0.61	2.9
	2400	0.457	180	1.5×10^{-3}	3.52×10^{-4}	0.66	1.1
	2400	0.562	210	1.9×10^{-3}	6.63×10^{-4}	0.65	1.5
	2400	0.703	60	3.5×10^{-3}	1.42×10^{-3}	0.64	2.9
	2400	0.844	54	4.6×10^{-3}	2.55×10^{-3}	0.64	2.6
	2400	1.05	20	6.0×10^{-3}	5.94×10^{-3}	0.57	3.9
	2600	0.281	300	1.1×10^{-3}	2.34×10^{-4}	0.74	1.5
	2600	0.352	150	9.0×10^{-4}	8.21×10^{-4}	0.66	2.0
	2600	0.457	60	2.4×10^{-3}	1.18×10^{-3}	0.72	2.9
	2600	0.562	21	6.1×10^{-3}	3.7×10^{-3}	0.66	1.7
	2600	0.844	4.5	1.76×10^{-2}	8.9×10^{-3}	0.81	1.8
	2800	0.176	1170	3.0×10^{-4}	2.46×10^{-4}	0.67	1.5
	2800	0.211	270	9.0×10^{-4}	5.13×10^{-4}	0.68	3.0
	2800	0.281	60	1.7×10^{-3}	2.62×10^{-3}	0.56	1.4
	2800	0.352	12	5.9×10^{-3}	5.62×10^{-3}	0.51	2.2

t_I^a is the time corresponding to the end of the first stage of creep.

μ^b is the standard deviation weighted for the number of equation constants.

TABLE 3.6
CONSTANTS FOR USE WITH LEAD AND ARC-CAST TUNGSTEN DATA IN
THIRD DEGREE POLYNOMIAL IN $t^{1/3}$ ($\epsilon = a + bt^{1/3} + ct^{2/3} + dt$)

Material	Temperature, °C	Stress, kg/mm ²	t_I^a min.	a	b	c	d	$\mu^b \times 10^4$
Lead	14.5	1.67	550	39.205	0.508	1.07×10^{-2}	2.56×10^{-3}	74
	162	0.83	15	9.469	1.33	0.597	0.251	70
Tungsten	2200	0.703	468	3.0×10^{-4}	7.47×10^{-4}	3.38×10^{-5}	1.06×10^{-5}	1.5
	2200	0.844	246	1.19×10^{-3}	8.27×10^{-4}	1.13×10^{-4}	1.81×10^{-5}	1.3
	2200	1.05	180	1.07×10^{-3}	2.02×10^{-3}	2.85×10^{-4}	4.39×10^{-5}	2.8
	2200	1.26	48	1.33×10^{-3}	4.65×10^{-3}	-3.49×10^{-4}	2.37×10^{-4}	1.4
	2200	1.41	45	4.2×10^{-3}	4.85×10^{-3}	3.72×10^{-4}	2.44×10^{-4}	2.5
	2400	0.457	180	8.88×10^{-4}	7.67×10^{-4}	8.44×10^{-5}	2.52×10^{-5}	1.2
	2400	0.562	210	1.3×10^{-3}	8.27×10^{-4}	3.61×10^{-4}	2.15×10^{-5}	1.4
	2400	0.703	60	5.24×10^{-4}	4.9×10^{-3}	-9.03×10^{-4}	2.92×10^{-4}	1.7
	2400	0.844	54	1.56×10^{-3}	5.14×10^{-3}	1.36×10^{-5}	3.04×10^{-4}	1.7
	2400	1.05	20	-4×10^{-3}	2.06×10^{-2}	-6.61×10^{-3}	1.79×10^{-3}	2.3
	2600	0.281	300	5.06×10^{-4}	4.97×10^{-4}	1.24×10^{-4}	2.56×10^{-5}	1.3
	2600	0.352	150	-5.4×10^{-4}	1.8×10^{-3}	1.74×10^{-4}	6.38×10^{-5}	1.6
	2600	0.457	60	-1.7×10^{-4}	3.67×10^{-3}	-4.2×10^{-4}	2.88×10^{-4}	2.4
	2600	0.562	21	4.94×10^{-3}	2.57×10^{-3}	2.014×10^{-3}	3.06×10^{-4}	1.6
	2600	0.844	4.5	1.82×10^{-2}	-2.85×10^{-3}	9.11×10^{-3}	2.087×10^{-3}	2.0
	2800	0.176	1170	8.4×10^{-4}	-4.82×10^{-4}	3.49×10^{-4}	-5.58×10^{-6}	1.0
	2800	0.211	270	2.67×10^{-5}	9.53×10^{-4}	2.29×10^{-4}	3.06×10^{-5}	1.9
	2800	0.281	60	-2.6×10^{-4}	3.93×10^{-3}	4.27×10^{-4}	1.017×10^{-4}	1.0
	2800	0.352	12	2.2×10^{-3}	1.04×10^{-2}	-1.87×10^{-3}	8.12×10^{-4}	2.2

^a t_I is the time corresponding to the end of the first stage of creep.

^b μ is the standard deviation weighted for the number of equation constants.

the end of first-stage creep and the limit of applicability of the individual equations. Also given are values for μ , the standard deviation, to indicate the extent to which a given equation provides a fit for the experimental data. As can be seen, all four equations provide a very excellent representation of the data although, in general, the best fit is that obtained with the third degree polynomial and the Andrade equation.

A few examples of the effectiveness of the equation forms employed in these studies are presented in Figure 3.10. In each case the solid curves were calculated using the equations given in Tables 3.3 through 3.6, and the agreement with the experimental points is seen to be excellent.

Although the equations presented in Tables 3.3 through 3.6 were derived by submitting only those data within the first-stage portion of the creep curve to the computer, a logical question concerns how accurately these equations can be extrapolated in predicting the strain - time behavior in the second stage of creep. A few such evaluations were made with very interesting results. Time values well into the second and third stages of creep were used to calculate corresponding strain values. Two of the cases studied are shown in Figure 3.11. In both instances, the curve obtained is in very good agreement with the experimental data. Indeed, in the case of the Andrade equation, the agreement is outstanding inasmuch as behavior at times up to 6 hours is described quite accurately with an equation based on data covering only the first hour of the test. While this good agreement was not observed for every test condition in Tables 3.3 through 3.6, it does suggest that analyses made using both first- and second-stage creep data combined should be expected to yield acceptable results.

Fig. 3.10 – Effectiveness of various equation forms in representing data for
arc-cast tungsten at 2400°C and 0.84 kg/mm²

Fig. 3.11 – Comparison of experimental data with results obtained by extrapolating equations in Tables 3.3 to 3.6

PHYSICAL PROPERTY EVALUATIONS

Thermal Conductivity

The thermal conductivity of molybdenum from 900° to 2000°C was measured in a radial heat flow apparatus which has been described previously.¹⁴ The purpose of this work was to refine the radial heat flow technique to measure the thermal conductivity of refractory metals, which are good heat conductors. Because of the small thermal gradients involved in such cases, optical pyrometry was ruled out for temperature measurements. Instead, refractory-metal thermocouples (W / W – 26Re) were used to determine the temperatures and temperature gradients in the specimen. Special procedures had to be employed to eliminate relative errors between the two thermocouples. At temperatures above 2000°C, the relative error between thermocouples was exceptionally large and temperature gradient determinations were doubtful. Additional work is necessary to extend this capability to higher temperatures.

¹⁴A. D. Feith, "A Radial Heat Flow Apparatus for High Temperature Thermal Conductivity Measurements," GE-NMPO, GEMP-296, August 31, 1964.

Experimental data obtained in these tests were submitted to a least squares computer program to yield:

$$k = 0.99 - 1.376 \times 10^{-4}T \quad (3.4)$$

where

k is thermal conductivity in watt/cm-°C and T is temperature in °C. The standard deviation was found to be 0.053 watt/cm-°C. These results are shown in Figure 3.12 and compared to data reported in the literature.¹⁵⁻¹⁷

Fig. 3.12 – Thermal conductivity versus temperature for molybdenum

An attempt was made to study the effect of grain structure on the thermal conductivity of molybdenum. The results, based on a total of eight temperature cycles, indicate possible changes due to recrystallization but little or no change as a result of grain growth.

This work resulted in establishing a satisfactory procedure for measuring thermal conductivity values in the order of 1.0 watt/cm-°C in the temperature range from 900° to 2000°C using BeO-insulated W / W – 26Re thermocouples. This procedure may possibly be applied to other refractory metals and alloys provided that they are chemically compatible over this temperature range.

Electrical Resistivity

While the thermal conductivity measurements of molybdenum were being made it appeared possible to employ this same apparatus to measure the electrical resistivity of refractory metals. Such a capability has now been demonstrated from room temperature to 2300°C. A four-probe technique was employed in conjunction with a tubular molybdenum specimen made from the same raw material from which the thermal conductivity specimen was fabricated. Molybdenum wires were used as voltage probes to eliminate the possibility of a Peltier effect. The voltage drop was measured on a Leeds and Northrup-K2 potentiometer. Current was read on the same instrument by measuring the voltage drop across a precision 1-ohm resistor. The d-c power was supplied by three 1.5-volt batteries connected in parallel. A reversing switch was used so that readings could be taken in both directions of polarity.

¹⁵V. V. Lebedev, "Determination of the Coefficient of Thermal Conductivity for Metals in the High Temperature Range," *Physics of Metals and Metallurgy*, USSR, Vol. 10, 1960, pp. 31-34.

¹⁶R. L. Rudkin, W. J. Parker, R. J. Jenkins, "Measurements of the Thermal Properties of Metals at Elevated Temperatures," *Temperature, Its Measurements and Control in Science and Industry*, Vol. 3, Part 2, Reinhold, New York, 1962, p. 523.

¹⁷M. J. Wheeler, "Thermal Diffusivity at Incandescent Temperatures by a Modulated Electron Beam Technique," *British Journal of Applied Physics*, Vol. 16, 1965, p. 365.

The data obtained have been fitted to the following computer-derived equation:

$$\rho = 5.347 \times 10^{-6} + 2.563 \times 10^{-8}T + 1.637 \times 10^{-12}T^2 \quad (3.5)$$

where ρ is electrical resistivity in ohm-cm and T is temperature in $^{\circ}\text{C}$.

These data are presented in Figure 3.13 in comparison to other reported data for molybdenum.¹⁸⁻²⁰ In the present study no changes in resistivity were observed as a result of thermal cycling or microstructural changes.

Fig. 3.13 – Electrical resistivity versus temperature for molybdenum

Thermal conductivity and electrical resistivity of metals are related by the Wiedemann-Franz-Lorenz law which states that the product of these properties divided by the absolute temperature is a constant (2.45×10^{-8} watt-ohm/ $^{\circ}\text{K}^2$). This law assumes that all of the heat in a metal is transported by electrons and that the lattice component of thermal conductivity in electrical conductors is negligible. The deviation from this value is considered a measure of the effect of the lattice vibrations on the total thermal conductivity of the material. Figure 3.14 shows this ratio as a function of temperature derived from these data and compared to the work of Lebedev,²¹ Wheeler²² (modified using our ρ and his revised k values), and Osborn.²³

The Lorenz ratio derived from these data shows some temperature dependence but is in reasonable agreement with the data of other investigators except Osborn. Wheeler's

¹⁸Lebedev, loc. cit.

¹⁹Rudkin, et al., loc. cit.

²⁰R. P. Tye, "Preliminary Measurements on the Thermal and Electrical Conductivities of Mo, Nb, Ta, and W," *Niobium, Tantalum, Molybdenum, and Tungsten*, A. G. Quarell, Editor, Elsevier, Amsterdam, 1961.

²¹Lebedev, loc. cit.

²²Wheeler, loc. cit.

²³R. H. Osborn, "Thermal Conductivities of Tungsten and Molybdenum at Incandescent Temperatures," *J. Opt. Soc. A*, Vol. 31, 1941, p. 428.

Fig. 3.14—Lorenz ratio versus temperature for molybdenum

original report shows a lower value (2.1×10^{-8} watt-ohm/°K²) for the Lorenz ratio, which is constant over the entire temperature range.

A correlation between electrical resistivity and thermal conductivity is desirable because it enables one to calculate the thermal conductivity which is much easier to measure. An evaluation of the Lorenz ratio of each material studied may eventually lead to such a correlation and a better understanding of the mechanisms of thermal and electrical conduction in materials.

Thermal Expansion

A comprehensive topical²⁴ report has been published covering recent measurements of the thermal expansion characteristics of a number of refractory metals and alloys. Linear thermal expansion measurements in helium to 2500°C are reported for W, Re, Ta, Mo, Nb, W – 25Re, Ta – 10W, and Mo – 50Re. The data are compared to measurements obtained by a number of other sources. Also included is a discussion on the effect of gaseous impurities on the linear thermal expansion of Nb, Ta, and Ta – 10W.

WORK PLANNED FOR NEXT PERIOD

Additional creep tests of arc-cast tungsten will be performed to determine the apparent activation energy for creep between 1600° and 2000°C.

Creep-rupture comparisons of tungsten sheet from the Navy Sheet Rolling Program as well as other sources will be made at 1600°, 2000°, and 2400°C.

Analyses of first-stage creep data and an extension into second-stage creep will be performed.

Creep-rupture tests of W – 25Re obtained from various vendor sources as arc-cast and sintered materials will be performed.

²⁴J. B. Conway, "Properties of Some Refractory Metals, III – Thermal Expansion Characteristics of Tungsten, Rhenium, Tantalum, Molybdenum, Niobium, W – 25Re, Ta – 10W, and Mo – 50Re," GE-NMPO, GEMP-375, June 29, 1965.

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4. HIGH-TEMPERATURE THERMOCOUPLE AND ELECTRIC MATERIALS RESEARCH

(57014)

The objective of this program is to identify and establish the properties of reliable high-temperature thermocouple, electrical, and electronic materials to provide instrumentation and electrical components for long-life, high-temperature reactors and reactor experiments.

HIGH-TEMPERATURE THERMOELEMENT MATERIAL DEVELOPMENT

Development work was continued on metallic thermoelement materials that would have an adequate output and sensitivity and that would operate for at least 2 years at up to 1800°C in a thermal neutron flux of 10^{14} nv with only minor changes in thermoelectric signal. The thermoelectric outputs of two new alloys, Cr – 20 Os¹ and Mo – 10Ru – 10 Os (wt %), prepared by methods previously described,² were measured and are shown in Figure 4.1. The Cr – 20 Os shows an increasingly negative output with increased temperature. This very desirable characteristic would give a high output and sensitivity when used with Mo – 1Ru, a material which previously was determined to possess a good positive thermoelectric characteristic, as also shown in Figure 4.1. Although the Cr – 20 Os sample was single phase, long-time testing at temperatures up to 1800°C will be necessary to prove its stability, since metallographic analysis has indicated that a second phase tends to precipitate after long times at high temperatures.

The Mo – 10Ru – 10 Os (wt %) gave a fairly linear positive thermoelectric output; it is too low to provide sufficient sensitivity, however, and therefore cannot be seriously considered for thermocouple application.

HIGH-TEMPERATURE INSULATOR MATERIAL DEVELOPMENT

Good thermocouple performance at high temperatures depends not only on satisfactory thermoelement materials but also on maintaining high electrical resistance in the insulator material. The resistivity of two insulator materials, BeO and ThO₂, was reported previously.³ At high partial pressures of oxygen and high temperatures, the resistivity of BeO decreased rapidly with increasing pressure. Also, a high-temperature exposure increased the resistivity of BeO, especially in subsequent operation in the lower temperature regions. In an effort to determine the causes of resistivity changes after high-temperature exposure, a second series of resistivity measurements was conducted on a high-purity⁴ BeO sample; the results are shown (as Sample B) in Figure 4.2. Comparing these data with those of lower purity BeO (Sample A, 99+%) shows that the resistivities of both samples are similar at 1200°C and 1400°C. Above 1400°C, differences develop; these are more clearly shown in Figure 4.3 which is a plot of the log of resistivity versus

¹All compositions are nominal and are expressed in atomic percent unless otherwise noted.

²"High-Temperature Materials Program Progress Report No. 27, Part B," GE-NMPO, GEMP-27B, September 30, 1963, pp. 69–70.

³"High-Temperature Materials Program Progress Report No. 47, Part A," GE-NMPO, GEMP-47A, May 28, 1965, pp. 103–109.

⁴99.95% purity BeO, fabricated by Brush Beryllium Corporation.

Fig. 4.1 - Thermoelectric output of Cr - 20 Os and Mo - 10Ru - 10 Os (wt %) versus W - 25Re (wt %) commercial wire as a function of temperature

Fig. 4.2 - Resistivity of two samples of BeO as a function of temperature and oxygen pressure

Fig. 4.3—Resistivity of BeO and ThO₂ versus reciprocal temperature (oxygen partial pressures, 10⁻¹³ atmosphere)

reciprocal temperature at an oxygen partial pressure of 10⁻¹³ atmosphere. Sample B shows a linear relation from 1200°C to 2000°C while Sample A shows a break above 1400°C. After holding Sample A at 2000°C temperature, a repeat test at 1800°C indicated that the resistivity had increased almost to that of Sample B at 1800°C. This change has not yet been explained but will be studied further. The slope of the Sample B data indicates that BeO has an activation energy of 1.5 ev, which is lower than expected.

Previously reported⁵ ThO₂ electrical resistivity characteristics are also shown in Figure 4.3. From the slope of the plotted data, its activation energy was computed to be 3.6 ev. The low activation energy of BeO seems inconsistent with its relatively high resistivity; this strongly suggests that the conductivity found in these samples of BeO is caused by minute amounts of impurities. Therefore, it is possible that pure BeO has a higher electrical resistance than has thus far been measured. If the impurities could be removed, even better thermocouple performance might be expected than is now possible with presently available material.

THERMOCOUPLE ERRORS INDUCED BY THERMAL NEUTRONS

Work has shown that the operation of W / W - 25Re thermocouples is strongly affected by impurities formed through nuclear transmutation. Errors resulting from this transmutation have been empirically established.⁶ To verify these predicted errors, a reactor test was designed and is being fabricated; insertion is scheduled for December 1965. In this test, nine thermocouples will be subjected to 10¹⁴ nv thermal neutron flux for an extended period of time. The temperature of the hot junction will be controllable to 2000°C

⁵"High-Temperature Materials Program Progress Report No. 47, Part A," GE-NMPO, GEMP-47A, May 28, 1965, p. 104.

⁶"High-Temperature Materials Program Progress Report No. 43, Part A," GE-NMPO, GEMP-43A, January 29, 1965, p. 73.

so that periodic calibrations can be made. The thermoelectric outputs of the thermocouples will be compared with a reference thermocouple which can be mechanically removed from the flux field after each calibration is made.

Previous work⁷ had shown that the substitution of W - 1 Os for the tungsten leg in the W / W - 25Re thermocouple reduces the change in the emf output due to transmutation. To confirm these results, a billet of W - 1 Os was prepared and extruded to rods measuring 1 cm in diameter. These will be drawn to wire from which at least two of the nine test thermocouples will be made.

WORK PLANNED FOR NEXT PERIOD

Further studies will be performed on BeO in an effort to explain its low activation energy and effects of impurities on its electrical resistivity.

The electrical resistivity of HfO_2 as a function of temperature will be measured.

Development of low neutron cross-section materials for use as thermocouple materials in nuclear reactors will be continued.

The W - 1 Os alloy will be shipped to a qualified vendor to be drawn and stranded into thermocouple wire.

Preparation of an in-pile test to establish the effects of nuclear transmutation on thermoelectric output as a function of temperature will be continued.

⁷W. C. Kuhlman, "Evaluation of Thermo-Neutron Induced Errors in the W / W - 25Re Thermocouple," GE-NMPO, GE-TM 65-5-63, May 1963.

5. REFRACTORY-METAL ALLOY RESEARCH AND DEVELOPMENT

(57015)

The overall objective of this program is to advance the technology of refractory metals to permit early utilization of these materials in high-temperature reactors. Specifically, the program encompasses development of new refractory-metal alloys to improve the temperature and life capabilities of nuclear power plants.

The work reported herein is a continuation of the investigation previously reported under Task 57003. Beginning with this report, all work on refractory-metal alloy research and development will be reported under this new task number. The work is being performed in two major phases: (1) Alloy Development and (2) Fabrication Process Development.

ALLOY DEVELOPMENT

In alloy development, the areas of interest are designated on the W-Re-Mo ternary phase diagram shown in Figure 5.1. The particular compositional areas of interest on this diagram as well as other alloys include:

1. The ternary W-Re-Mo alloy region associated with W-25Re-30Mo¹ and W-30Re-30Mo. Alloys of lower rhenium and molybdenum content in conjunction with improved high-temperature properties are the objective of this work.
2. Ternary Mo-Re-W alloys with molybdenum rather than tungsten as the major constituent. Two alloy series containing 5 to 30 percent rhenium and 15 or 30 percent tungsten are being investigated. The objective of the work is to produce ductile high-strength molybdenum base alloys with lower rhenium content than in presently available Mo-Re commercial compositions.
3. Binary W-Re alloys (3 and 5 at. % rhenium). The objective of this work is to develop workable high-strength tungsten base alloys.
4. Unalloyed molybdenum and molybdenum with 1, 2, and 5 percent rhenium. The objective of this work is to establish processing procedures for producing weldable molybdenum and molybdenum alloys.

These regions or composition ranges are discussed individually herein.

TERNARY ALLOY SYSTEMS

W-Re-Mo

The immediate objective of this work is to determine the minimum amount of rhenium needed in the W-Re-Mo system to develop alloys having good ductility and fabricability. The particular region of interest is designated the NMP alloy region in the phase diagram (Figure 5.1). The molybdenum contents are 10, 20, or 30 percent. As rhenium concentrations are lowered, the percentage of tungsten is increased.

¹All compositions in atomic percent unless otherwise noted.

GE-NMPO

Fig. 5.1 – Ternary phase diagram showing areas of interest in the W-Re-Mo system

Billet Fabrication – Twenty alloys were prepared by powder metallurgical processes and sintered in hydrogen in a tungsten resistance furnace. Thus far, the only data available are for the 30 percent molybdenum alloy. The compositions of these alloys, ranging from 60 to 43 percent tungsten and 10 to 27 percent rhenium, are shown in Table 5.1.

Billet Working – A marked change in both hot and cold workability was noted as the rhenium content of the alloys decreased below 20 percent. The alloys containing 21, 23, or 27 percent Re warm-rolled similarly to the W-25Re-30Mo alloy. However, the 19, 17, and 15 percent Re required initial lower hot-rolling reductions. The alloys having the lower rhenium content had to be warm-rolled at 420°C in contrast to 200°C for the higher Re alloys. In addition, the 15 and 17 Re alloys were recrystallized at the annealing temperature of 1650°C used between each warm-rolled pass.

Alloys of 10 and 12.5 percent rhenium content were difficult to process. For example, 88 light hot-rolling passes with a re-heating for each rolling pass were required compared to 53 similar operations for alloys with higher rhenium content. Both the 10 and 12.5 percent rhenium alloys were discarded due to edge cracking during warm-rolling from 420°C. Should complete evaluation of the successfully processed alloys show some potential for these lower rhenium materials, they will be evaluated using modified warm-rolling techniques.

TABLE 5.1
NOMINAL COMPOSITION OF W-Re-Mo ALLOYS

NMP Alloy Designation ^a	Nominal Composition, at. %			Nominal Composition, wt. %		
	W	Re	Mo	W	Re	Mo
106	60	10	30	69.9	11.8	18.3
126	57.5	12.5	30	67.0	14.8	18.2
156	55	15	30	64.1	17.7	18.2
176	53	17	30	61.7	20.1	18.2
196	51	19	30	59.4	22.4	18.2
216	49	21	30	57.0	24.8	18.2
236	47	23	30	54.7	27.1	18.2
276	43	27	30	50.0	31.8	18.2

^aThe first two digits of the NMP number give the Re content in atomic percent, and the last digit is multiplied by 5 to give atomic percent Mo.

Mo-W-Re

The alloys discussed in this program are shown in the lower left area of Figure 5.1 and include two alloy series at the 15 and 30 percent tungsten level. Alloys with high rhenium content are known to be very ductile. The objective of the present work is to produce ductile alloys containing less rhenium than the commercially available Mo - 35Re alloy.

Billet Fabrication – The compositions of the Mo-base alloys processed in this report are shown in Table 5.2. Alloys were prepared in billet form by the powder metallurgical process and sintered in a hydrogen furnace. Important aspects of the sintering cycle are given in Figure 5.2. The sintering process for 15 and 30 percent tungsten alloys was modified between series to avoid melting of unalloyed molybdenum (MP 2610°C). The overall processing and hot-rolling results for the alloys are also given. None of the alloys with 15 percent or less rhenium could be hot-rolled satisfactorily at 1450°C. Cold-rolling of the successfully hot-rolled sheets is in progress.

TABLE 5.2
NOMINAL COMPOSITIONS AND AS-SINTERED HARDNESS VALUES
OF Mo-W-Re ALLOYS

NMP Alloy Number ^a	Atomic Percent			Weight Percent			Rockwell "A" Hardness As-Sintered
	Mo	W	Re	Mo	W	Re	
1-16	80	15	5	67.53	24.26	8.19	54.5
2-15	75	15	10	60.89	23.34	15.75	55.0
3-14	70	15	15	54.74	22.48	22.77	60.5
4-13	65	15	20	49.03	21.68	29.28	61.8
5-12	60	15	25	43.71	20.94	35.34	63.8
6-11	55	15	30	38.74	20.24	40.01	64.4
1-13	65	30	5	49.17	43.49	7.34	55.2
2-12	60	30	10	43.82	41.99	14.17	57.6
3-11	55	30	15	38.84	40.60	20.60	60.8
4-10	50	30	20	34.17	39.29	26.53	61.4
5-09	45	30	25	29.79	38.06	32.13	65.6
6-08	40	30	30	25.68	36.91	37.39	66.8

^aAtomic percent of the Re and Mo content, respectively, is obtained by multiplying each number by 5. The hyphen between numbers distinguishes these alloys from NMP alloys of high W content; e. g., NMP-256.

Fig. 5.2 – Flow diagram for processing alloys with high-Mo content in Mo-W-Re system with 15 or 30 percent W and 5 to 30 percent Re content

Test Evaluation – Bend-test samples cut from the hot-rolled sheet were treated for 10 hours at 2000°C in hydrogen. Results of room-temperature bend tests (Table 5.3) showed the six hot-rolled alloys to be ductile. These results will be supplemented with tests on cold-reduced sheet.

BINARY ALLOY SYSTEM

W-Re

Tungsten, with small amounts of rhenium (3 to 5%) added as a ductilizer, is being evaluated for its capability of being processed as sheet or tubing. Whereas unalloyed tungsten is usually brittle in the stress-relieved condition, rhenium may provide the ductility needed for fabrication.

Billet Fabrication – The W – 3Re and W – 5Re alloys were compounded from high-purity powders and fabricated to sheet using the following procedures:

TABLE 5.3
ROOM-TEMPERATURE BEND-TEST
RESULTS FOR VARIOUS HOT-ROLLED
Mo-W-Re ALLOYS

NMP Alloy	Nominal Composition, at. %			Angle Of Bend To Fracture
	Mo	W	Re	
4-13	65	15	20	90°
5-12	60	15	25	90°
6-11	55	15	30	90°
4-10	50	30	20	90°
5-09	45	30	25	90°
6-08	40	30	30	90°

1. Blended metal powders were compacted at 14 kg/mm² and sintered for 3 hours at 3000°C in hydrogen. Rockwell "A" hardness value was 59.8.
2. One sintered compact of each alloy was hot-rolled to a thickness of 0.1 cm. A second compact of W - 5Re alloy was hot-rolled to a thickness of 0.038 cm. Each hot-rolled sheet was heated at 1400°C in hydrogen for 72 hours to remove oxygen absorbed from the air during hot-rolling operation. Rockwell "A" hardness of sheet after purification was 64.8.

Both the W - 3Re and W - 5Re hot-rolled sheet had good microstructures as shown in Figure 5.3. Cylindrical capsules measuring 1.25 cm OD by 2.0 cm long were formed from the 0.038-cm-thick hot-rolled W - 5Re sheet, using tooling heated to 540°C. The material was easily electron-beam welded and the welds were non-porous.

Following hot-rolling and treatment to reduce oxygen contamination absorbed during the hot-rolling, the 0.1-cm-thick W - 3Re and W - 5Re sheets were found to be low in carbon and gaseous impurities as shown in Table 5.4.

The first attempts to warm-roll the 0.1-cm-thick hot-rolled sheets of W - 3Re and W - 5Re alloy at 200°C and 400°C were unsuccessful. Cracks, starting at the sheet edges and rapidly traversing the sheet, occurred during warm-rolling. If initial reductions can be made at temperatures above 800°C, final finishing may be possible at lower temperatures.

Tube Fabrication - In addition to studying the sheet-rolling problems associated with W - 3Re and W - 5Re, the making of small tubing from these alloys was begun. Recently, two primary extrusions and two re-extrusions of tubular W - 5Re were started through processing.

The procedure followed for the W - 5Re extrusion is shown in the flow diagram in Figure 5.4. The first extrusion, designated D-31, was prepared as a sintered tube blank with

TABLE 5.4
CARBON AND GASEOUS
IMPURITIES IN W - 3Re AND
W - 5Re AFTER HOT-ROLLING

Alloy	Impurities, ppm			
	C	N ₂	O ₂	H ₂
W - 3Re	13.0	0.1	16	0.1
W - 5Re	17.2	10	13	0.1

W - 3Re (Neg. 6183)

W - 5Re (Neg. 6184)

Fig. 5.3—Microstructures of the cross section of hot-rolled and deoxidized W-Re sheet (Murakami's etchant, 100X)

Fig. 5.4 – Flow diagram for W – 5Re tube extrusion and tube processing

a molybdenum extrusion container similar to those shown in previous reports.² A section of the tube was machined from the primary extrusion with much of the molybdenum extrusion container retained around the embedded W – 5Re alloy as shown in Figure 5.5. This machined material was re-inserted into another molybdenum extrusion container and re-extruded. A similar procedure was followed for a second W – 5Re extrusion, designated D-32.

The W – 5Re tubing will be hot-drawn at 650°C. In the hot-drawing operation, the molybdenum filler of the extrusion is retained. The molybdenum filler will be removed after final drawing. A small hole electrochemically drilled through the length of the work piece will permit rapid removal of molybdenum by flushing with nitric acid.

Mo and Mo-Re

Work was continued on establishing procedures for producing weldable unalloyed molybdenum and molybdenum containing 1, 2, and 5 percent rhenium. The early phases of this work, described in the previous bimonthly report,³ showed that sheet prepared from molybdenum having low oxygen and carbon impurities exhibited greater weldability and ductility than the non-purified or the commercial arc-cast or powder process molybdenum, after being heated to high temperatures. Although the weldability of the sheet and the ductility of the welds were much better than with commercial powder process molybdenum, it was assumed that expected purity levels were not attained based on the number of voids detected in the welds by X-ray examination. This initial assumption was validated through chemical determination of impurities (Table 5.5).

²“High-Temperature Materials Development Program Progress Report No. 49, Part A,” GE-NMPO, GEMP-49A, July 28, 1965, Figure 3.32, p. 59.

³Ibid., p. 54.

Fig. 5.5 – Cross section of a W – 5Re extrusion after machining and prior to re-extrusion to a smaller size (Neg. 65-8-8B)

TABLE 5.5
RESULTS OF CHEMICAL ANALYSIS OF Mo AND Mo-Re SHEET

Laboratory No.	Nominal Composition	Processing Variable	Impurities, ppm				Voids In 5-cm Weld Revealed By X-ray
			C	N ₂	O ₂	H ₂	
1	Mo	Unpurified	23	5.0	13.0	0.3	Many
1a	Mo	Purified in sintering	20	0.1	54.0	0.3	3
1b	Mo	Purified in sintering	13	49.0	119.0	0.2	18
4	Mo – 5Re	Purified in sintering	21	2.0	26.0	0.1	20
1a-P	Mo	Same as 1a, 1b and 4 above plus 342 hours at 1450°C in wet hydrogen	9	^a	–	–	0
1b-P	Mo		10	–	–	–	1 (Small)
4-P	Mo – 5Re		13	–	–	–	1 (Small)

^aBlank columns indicate data not yet available.

Included in Table 5.5 are carbon impurities found after a second purification treating of hot-rolled sheet for 342 hours at 1450°C in hydrogen having a 5°C dew point. This treatment was intended to lower the carbon impurity level of the sheet prior to cold-working. The metallographically observable structural changes associated with lowering of the carbon concentration in unalloyed molybdenum are minor. The microstructure changes in molybdenum as a result of hydrogen purification treatments are shown in Figure 5.6. Metallographically, this sheet appears to be of better quality than indicated by the gaseous impurity analyses given in Table 5.5. These materials will be resubmitted for analyses. X-ray analysis was made of five centimeters of simulated electron-beam weld on the molybdenum and Mo - 5Re sheet treated to lower impurities after hot-rolling. Results are shown in the last column of Table 5.4. These data show a marked reduction in the number of voids in the welds. Presumably, weld voids form primarily as a result of formation of carbon-monoxide; lowering of carbon content tends to suppress this reaction giving a void-free weld.

The sheet purified following hot-rolling is now ready for cold-reduction. Additional sheet processing is now underway. Also the treating of commercial molybdenum sheet in conjunction with additional processing will be evaluated. Tubing of purified molybdenum will be scheduled for extrusion within the next report period.

FABRICATION PROCESS DEVELOPMENT

Techniques for fabricating promising refractory-metal alloys are being developed concurrently with the alloy development program discussed above. The work consists of developing methods of fabricating the selected alloys into sheet, plate, and tubing. The first alloys to be tested for fabricability are W - 25Re - 30Mo and W - 30Re - 30Mo (GE-NMPO designations, NMP-256 and NMP-306, respectively). These two alloys, widely used at GE-NMPO in high-temperature research activities, are readily available in sheet or plate and much of the preliminary development work has been accomplished. They are especially suited for fabrication development work because of their excellent room-temperature ductility after long-time exposure to high temperatures together with their strength and weldability characteristics.

SHEET ROLLING

One hundred pieces of NMP-256 alloy sheet, 0.05 cm to 0.10 cm in thickness, and 10 to 30 inches long were produced during this report period. In addition, small amounts of relatively thick plate were also produced by hot-rolling to size using extruded and press-forged NMP-256 alloy rods. Typical press-forged plates after hot-rolling are shown in Figure 5.7.

Sheet development in the NMP-256 alloy consists of developing procedures to increase the size of finished sheet. The main problem area in this work is fabrication of metal powders into heavy rectangular sheet-bars that are free of pressing defects. Double-pressing, using floating dies, and rigid support plates in pre-sintering has produced satisfactory 600-gram compacts as shown in Figure 5.8. Compacts of NMP-256 alloy, W - 25Re alloy, and W - 30Re alloy were successfully hot-rolled. One piece of NMP-256 alloy sheet, 0.025 cm by 12.5 cm by 78 cm was completed. The cross section microstructure, typical of finished NMP-256 alloy sheet, is shown in Figure 5.9. Large sheets of W - 25Re and W - 30Re are being processed for comparison of working properties with those of NMP-256 alloy and for property measurements. The chemical determination of impurity constituents in the large sheet has not been completed. However, Table 5.6 gives the chemical analysis of smaller sheet previously fabricated.⁴

⁴Ibid., p. 57.

a. Unpurified Mo shown as 0.1 cm hot-rolled sheet.
Carbon content 23 ppm. (Neg. 6186)

b. Mo hot-rolled to 0.1 cm sheet – held at 1450°C
for 342 hours in hydrogen having a 5°C dew
point. Carbon content 20 ppm. (Neg. 6187)

c. Mo purified as (b) above, but additionally treated
in hydrogen – water vapor. Carbon content 9 ppm.
(Neg. 6190)

Fig. 5.6 – Comparison of the microstructure of unpurified molybdenum with
hot-rolled sheet after a purification treatment
(Murakami etchant, 250X)

Fig. 5.7 – Extruded, forged, and hot-rolled W – 25Re – 30Mo (NMP-256) alloy plates showing the lack of edge cracking after extreme metal working (Neg. P65-7-33)

TABLE 5.6
CHEMICAL ANALYSIS OF SMALL SHEETS
OF NMP ALLOYS

NMP Type	Nominal Composition	Impurity Content, ppm			
		C	N ₂	O ₂	H ₂
256	W – 25Re – 30Mo	4.3	1.0	21.0	0.3
306	W – 30Re – 30Mo	3.9	1.0	10.0	0.3

Fig. 5.8 – Compacted and sintered W – 25Re – 30Mo (NMP-256) metal-powder sheet rolling bar weighing 600 grams (Neg. P65-6-30)

Fig. 5.9 – Cross section showing the microstructure typical of 0.025-cm-thick NMP-256 alloy sheet. Sheet was stress-relieved 20 minutes at 1400°C in hydrogen following final cold-rolling. (Neg. 5913, Murakami's etchant, 100X)

TUBE DRAWING

Significant progress was made in drawing the NMP-256 alloy into small seamless tube. The processing procedure, currently in use, for small tubing is as follows:

1. Blend, isostatically press, and sinter tubular extrusion blanks from the metal powders.
2. Extrude the sintered extrusion blank in a molybdenum container and core mandrel to 1.33 cm OD with a reduction on an area basis of between 4:1 and 16:1. A slightly heavy wall thickness as compared to the finished wall thickness is desired as several surface cleanups and machining to true concentricity reduces the wall thickness in processing.
3. Hot-swage the extruded tube to approximately 0.62-cm OD with the original molybdenum core filler retained from the extrusion operation. The outer molybdenum container is removed chemically before swaging. Swaging yields a circular and straight tube drawing blank.
4. Mo - 50Re pull rods are welded into the swaged drawing blanks, and the tubes are drawn to cleanup size at 420°C in an argon atmosphere as shown in Figure 5.10.
5. Following the initial or smoothing draw, the welded pull rods are removed and a reduced section on the tube blank obtained by hot-swaging. Subsequent drawing is conducted at 200°C to the desired diameter for cleanup as shown in the lower portion of Figure 5.10.
6. Final tube drawing operations are based on a shop cleanup and mechanical dimensioning of the tubing. In this operation, the core is removed by drilling and circularity is obtained by honing the inside diameter. After positioning on a mandrel, the outer surface of the tube is ground concentric to the honed inner bore. At this point, the required ratio of outer diameter to inner diameter is established. The tubes are finished to size using carbide dies and carbide plug mandrels. Drawing to final size is conducted at 200°C with a 1400°C (H₂ atmosphere) stress-relief treatment between each reduction stage.

Fig. 5.10 - NMP-256 alloy tubes with Mo extrusion core material retained. Upper group shown has Mo - 50Re rods welded in to facilitate smoothing through drawing at 420°C. After removal of these rods, a section is reduced by swaging, and drawing continued at 200°C to the final size for shop cleanup as shown in the lower portion of this photograph. (Neg. P65-8-4)

TUBING EVALUATION

One commercial vendor has produced small seamless tubing of NMP-306 alloy (GE-NMPO tubing work is with NMP-256 alloy). Eddy-current measurements for wall thickness variations and wall defects, X-ray, dye penetrant (Zyglo), and leak-testing were used to ascertain tubing quality. A total length of approximately 5,670 cm of tubing was inspected and evaluated. On an 8-cm-length acceptance basis, the material was divided into the quality categories shown in Table 5.7.

TABLE 5.7
RESULTS OF INSPECTION OF NMP-306 ALLOYS

Wall Variation Measured By Eddy-Current Method, %	No. Of Acceptable 8-cm-long Tubes	Percent Of Total Tubing Acceptable As 8-cm-long Tubes
10	0	0.0
10 to 20	56	7.0
20 to 30	484	69.0
30 to 40	557	80.0
>40	—	Remainder

Preliminary chemical analysis of this tubing showed high carbon, sulphur, and iron contents probably present as surface contaminants. A study of thermal and purification treatments was completed on tubing determined to have 30 to 40 percent wall thickness defects. The results of metallographic examination of as-received tubing and after various heat treatments are shown in Figure 5.11. It is evident that surface contamination was present on the NMP-306 alloy tubes with the inner surfaces showing more contamination than the outer. By treating the tubing at 2000°C and 2400°C, the contaminant regions and general sigma-phase precipitant of the tubing was dissolved. However, large voids appear to have formed and were concentrated near the inner surface.

A sample from the section of tubing treated for 342 hours at 1450°C in hydrogen – water vapor (5°C dewpoint) to remove impurities is being analyzed. Some of the precipitant was removed by the treatment, and voids appear at the precipitant sites. A light-colored internal precipitant was observed which is indicative of the sigma phase in the W – 30Re – 30Mo alloy.

Room-temperature bend tests were conducted on the tubes treated to obtain the structures shown in Figure 5.11. Of these, the tubes given 2000°C treatment had the most bend ductility. The hydrogen – water vapor treatment gave the poorest bend results. These results cannot be considered conclusive at this time because the tubing was not uniform in quality, and production variables between the tubes used undoubtedly influenced test results. Fusion of a section of as-received tubing in an electron-beam welder showed low porosity in the fused metal. Low porosity indicates that reasonably nonporous welds can be expected when tubes are welded. All the above findings have been reviewed with representatives of the tube vendor.

WORK PLANNED FOR NEXT PERIOD

Processing of high tungsten alloys of the W-Re-Mo type now designated as NMP alloys will be continued in order to furnish test material for creep and ductility tests. Similarly, alloys with high molybdenum content will be processed as required for complete evaluation.

Sheets of W – 3Re and W – 5Re will be fabricated by processes intended to yield a highly worked structure. These sheets will be used for strength and bend ductility tests. Work will also be continued on extruding small diameter tubing.

(a) Tubes, representative of as-received structure after heating for 2 hours at 1400°C in H₂ (Neg. 6152, 100X)

(d) After fusion by electron-beam welder in a simulated weld. Lack of porosity is good. (Neg. 6151, 100X)

(b) After heating 2 hours at 2000°C much of the contamination near surfaces has been dissolved (Neg. 6155, 100X)

(c) After heating 2 hours at 2400°C in H₂. Note rounding of voids. (Neg. 6156, 100X)

(e) Treated 342 hours in H₂-H₂O mixture (5°C dew point) at 1450°C to remove C, O₂, S, and N. (Neg. 6195, 150X)

Fig. 5.11 – Transverse sections of NMP-306 tubing from commercial source after various thermal and purification treatments

Work will be continued to improve unalloyed molybdenum and molybdenum having low alloy additions. Concurrently, high-purity unalloyed molybdenum tube extrusion and drawing procedure development will be started.

The development of procedures required for fabrication of high quality seamless tubes of W – 25Re – 30Mo alloy will continue. Increased product yields, finalizing shop cleanup procedures, and selection of mandrel support will be the objectives of this program.

Work will be started in both Co- and Cr-base alloys intended for applications which would include oxidation resistance as a requirement.

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6. APPENDIX

The "High-Temperature Materials Program Progress Reports" previously issued in this series are listed below. The first two reports were each issued as one document, containing both the classified and unclassified portions. The subsequent reports were issued as two documents; part A, the unclassified portion and part B, the classified portion.

Report No.	Report Period	Publication Date
GEMP-1	May 1961 - June 30, 1961	July 15, 1961
GEMP-2	July 1, 1961 - July 31, 1961	August 15, 1961
GEMP-3, A and B	July 1, 1961 - August 31, 1961	September 15, 1961
GEMP-4, A and B	August 1, 1961 - September 30, 1961	October 15, 1961
GEMP-5, A and B	August 15, 1961 - October 15, 1961	November 15, 1961
GEMP-6, A and B	September 15, 1961 - November 15, 1961	December 15, 1961
GEMP-7, A and B	October 15, 1961 - December 15, 1961	January 15, 1962
GEMP-106, A and B (First Annual Report) Calendar Year 1961		February 28, 1962
GEMP-9, A and B	January 1, 1962 - February 15, 1962	March 30, 1962
GEMP-10, A and B	January 1, 1962 - March 15, 1962	April 16, 1962
GEMP-11, A and B	February 15, 1962 - April 15, 1962	May 15, 1962
GEMP-12, A and B	March 15, 1962 - May 15, 1962	June 15, 1962
GEMP-13, A and B	April 15, 1962 - June 15, 1962	July 31, 1962
GEMP-14, A and B	May 15, 1962 - July 15, 1962	August 15, 1962
GEMP-15, A and B	June 15, 1962 - August 15, 1962	September 14, 1962
GEMP-16, A and B	July 15, 1962 - September 15, 1962	October 15, 1962
GEMP-17, A and B	August 15, 1962 - October 15, 1962	November 15, 1962
GEMP-18, A and B	September 15, 1962 - November 15, 1962	December 14, 1962
GEMP-19, A and B	October 15, 1962 - December 15, 1962	January 25, 1963
GEMP-177, A and B (Second Annual Report) Calendar Year 1962		February 28, 1963
GEMP-21, A and B	January 1, 1963 - February 15, 1963	April 23, 1963
GEMP-22, A and B	January 1, 1963 - March 15, 1963	April 30, 1963
GEMP-23, A and B	February 15, 1963 - April 15, 1963	May 31, 1963
GEMP-24, A and B	March 15, 1963 - May 15, 1963	June 28, 1963
GEMP-25, A and B	April 15, 1963 - June 15, 1963	July 31, 1963
GEMP-26, A and B	May 15, 1963 - July 15, 1963	August 16, 1963
GEMP-27, A and B	June 15, 1963 - August 15, 1963	September 30, 1963
GEMP-28, A and B	July 15, 1963 - September 15, 1963	November 11, 1963
GEMP-29, A and B	August 15, 1963 - October 15, 1963	November 30, 1963
GEMP-30, A and B	September 15, 1963 - November 15, 1963	December 31, 1963

<u>Report No.</u>	<u>Report Period</u>	<u>Publication Date</u>
GEMP-31, A and B	October 15, 1963 - December 15, 1963	January 24, 1964
GEMP-270, A and B		
(Third Annual Report)	January 1, 1963 - January 31, 1964	February 28, 1964
GEMP-34, A and B	February 1, 1964 - March 15, 1964	April 15, 1964
GEMP-35, A and B	February 1, 1964 - April 15, 1964	May 28, 1964
GEMP-36, A and B	March 15, 1964 - May 15, 1964	June 19, 1964
GEMP-37, A and B	April 15, 1964 - June 15, 1964	July 31, 1964
GEMP-38, A and B	May 15, 1964 - July 15, 1964	August 19, 1964
GEMP-39, A and B	June 15, 1964 - August 15, 1964	September 30, 1964
GEMP-40, A and B	July 15, 1964 - September 15, 1964	October 15, 1964
GEMP-41, A and B	August 15, 1964 - October 15, 1964	November 30, 1964
GEMP-42, A and B	September 15, 1964 - November 15, 1964	December 18, 1964
GEMP-43, A and B	October 15, 1964 - December 15, 1964	January 29, 1965
GEMP-334, A and B		
(Fourth Annual Report)	January 1, 1964 - January 31, 1965	February 26, 1965
GEMP-46, A and B	February 1, 1965 - March 15, 1965	April 15, 1965
GEMP-47, A and B	February 1, 1965 - April 15, 1965	May 28, 1965
GEMP-48, A and B	March 15, 1965 - May 15, 1965	June 25, 1965
GEMP-49, A and B	April 15, 1965 - June 15, 1965	July 28, 1965
GEMP-50, A and B	May 15, 1965 - July 15, 1965	August 20, 1965

ATOMIC PRODUCTS DIVISION

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