75
12/22/65

MASTER

UNCLASSIFIED
GEMP-53A

Nuclear Materials & Propulsion Operation

**HIGH-TEMPERATURE MATERIALS PROGRAM
PROGRESS REPORT No. 53, Part A**

November 26, 1965

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

REPRODUCIBLE COPY

GENERAL **ELECTRIC**
ATOMIC PRODUCTS DIVISION

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, material, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, material, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission or his employment with such contractor.

Printed in USA. Price \$3.00. Available from the
Clearinghouse for Federal Scientific and
Technical Information,
National Bureau of Standards,
U. S. Department of Commerce,
5285 Port Royal Road,
Springfield, Virginia 22151

UNCLASSIFIED

GEMP-53A

UC-25 Metals, Ceramics
and Materials
TID-4500 (46th Ed.)

**HIGH-TEMPERATURE MATERIALS PROGRAM
PROGRESS REPORT No. 53, Part A**

November 26, 1965

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

**NUCLEAR MATERIALS and PROPULSION OPERATION
ATOMIC PRODUCTS DIVISION**

GENERAL ELECTRIC

Cincinnati, Ohio 45215

UNCLASSIFIED

DISTRIBUTION

EXTERNAL

AEC Headquarters

G. K. Dicker W. R. Voight
F. C. Schwenk G. W. Wensch
J. M. Simmons M. J. Whitman

AEC, CAO

C. L. Karl
J. F. Weissenberg

AEC, OROO

D. F. Cope (3)
D. S. Zachry, Jr.

AEC, SAN

Col. J. B. Radcliffe, Jr.
Argonne National Laboratory
R. Noland

Atomics International

S. C. Carniglia
C. E. Weber

Battelle-Northwest

F. W. Albaugh J. J. Cadwell

BMI

S. Paprocki

Chase Brass & Copper

J. Port

General Atomic

D. Ragone

Institute for Defense Analyses

R. C. Hamilton

Jet Propulsion Laboratory

J. Davis

LASL

R. D. Baker

Lawrence Radiation Laboratory

C. Cline A. J. Rothman

NASA Headquarters

J. J. Lynch B. Reznick

NASA, Lewis Research Center

J. W. Creagh T. P. Moffitt N. D. Sanders
T. A. Moss L. Rosenblum N. Saunders
H. Schwartz

ORNL

R. E. Blanco P. Patriarca (2)
W. R. Grimes

Universal-Cyclops Steel Corporation

L. M. Bianchi

Westinghouse Astronuclear Lab.

D. C. Goldberg

Wah Chang Corporation

S. Worchester

INTERNAL

W. G. Baxter	H. S. Edwards	J. W. Morfitt	F. O. Urban
J. R. Beeler	E. W. Filer	J. Moteff	G. R. VanHouten
J. C. Blake	P. N. Flagella	R. E. Motsinger	H. Wagner
B. Bonini	E. S. Funston	G. T. Muehlenkamp	J. F. White
H. C. Brassfield	G. F. Hamby	C. E. Niemeyer	V. C. Wilson, R&DC
R. W. Briskin	J. O. Hibbits	W. E. Niemuth	O. G. Woike
V. P. Calkins	A. N. Holden, APED (2)	G. W. Pomeroy	R. E. Wood
B. A. Chandler	L. D. Jordan	W. Z. Prickett	C. S. Wukusick
C. L. Chase (3)	F. Kingsbury	R. Reid	J. F. Young, APD
K. P. Cohen, APD	G. Kortan	F. C. Robertshaw	Library (10)
C. G. Collins	W. C. Kuhlman	E. J. Schmidt, ATS	
E. S. Collins	W. H. Long	H. R. Stephan	
J. F. Collins	J. E. McConnelee	R. E. Tallman	
P. K. Conn	L. R. McCreight, MSD	C. O. Tarr	
J. B. Conway (2)	J. A. McGurty	P. P. Turner	
E. B. Delson			

CONTENTS

	Page
1. Introduction and Summary	9
2. Oxidation-Resistant Fuel Element Materials Research (57001).....	11
3. High-Temperature Reactor Materials Research (57003)	33
4. High-Temperature Thermocouple and Electric Materials Research (57014) ...	53
5. Refractory-Metal Alloy Research and Development (57015).....	57
6. Appendix	81

FIGURES

	Page
2.1 – Photomicrographs of two fueled specimens showing conditions at the core – cladding interface after 7000 hours at 950°C in air	14
2.2 – Photomicrographs of two fueled specimens showing conditions at the core – cladding interface after 5100 hours at 1100°C in air	16
2.3 – Photomicrographs of 2541-clad chromium matrix fuel core specimens showing conditions at the core – cladding interface after 5100 hours at 1100°C in air	17
2.4 – Photomicrographs of two 2541-clad iron matrix fuel core specimens showing conditions at the core – cladding interface after 7000 hours at 1100°C in air	18
2.5 – Alpha surface activity as a function of time for 1541-clad unalloyed UO ₂ capsules tested in air at 750°, 950°, 1100°, and 1250°C	20
2.6 – Alpha surface activity as a function of time for 1541-clad Fe – 40UO ₂ capsules tested in air at 750°, 950°, 1100°, and 1250°C	20
2.7 – 1541-clad Fe – 25UO ₂ fuel element specimen ORFC-7 ready for installation in ORFC-2 test cartridge	22
2.8 – Weight gain of Fe-Cr-Al-Y alloys as a function of test time at 900°C and 1100°C in static air for times up to 10,000 hours	23
2.9 – Microstructures of 2541 alloy oxidized in air for 10,000 hours at 450° to 1100°C	24
2.10 – Microstructures of 1541 alloy oxidized in air for 10,000 hours at 450° to 1100°C	24
2.11 – Microstructures of 1540 alloy oxidized in air for 10,000 hours at 450° to 730°C	25
2.12 – Weight change of Fe – 15Cr – 4Al alloys containing 0 to 1 percent Y tested at 1100°C in air for 1000 hours	27
2.13 – Pre-oxidized and pre-strained specimens of 1041 alloy after testing in steam at 550°C for 1000 hours	28
2.14 – Photomicrographs of 1041 alloy pre-oxidized for 20 hours at 1000°C; pre-strained 0, 2, and 4 percent; and then exposed to 550°C steam for 1000 hours.....	30
2.15 – Photomicrograph of 1041 alloy tested in 550°C steam for 240 hours without pre-oxidation	31
2.16 – Hardness as a function of annealing time for various Fe-Cr-Al-Y alloys after irradiation to 9.25×10^{20} nvt	32
3.1 – Creep curves for tungsten sheet at various temperatures and stress in a hydrogen atmosphere.....	35
3.2 – Log-log plots of creep data for tungsten sheet at various temperatures and stress in a hydrogen atmosphere	36
3.3 – Tungsten sheet specimens after creep-rupture testing at 2000°C and 2.11 kg/mm ² in hydrogen	37

	Page
3.4 – Photomicrographs of wrought sintered tungsten from the Navy Sheet Rolling Program after creep rupture testing in hydrogen	38
3.5 – Photomicrographs of commercial tungsten sheet after creep-rupture testing in hydrogen	39
3.6 – Creep curves for 0.05-cm-thick W – 25Re sheet from various vendors at 2000°C and 2.11 kg/mm ² in hydrogen.....	41
3.7 – Log-log plot of creep data for 0.05-cm-thick W – 25Re sheet from various vendors at 2000°C and 2.11 kg/mm ² in hydrogen	42
3.8 – W – 25Re creep-rupture specimens fabricated from material from various sources tested at 2000°C and 2.11 kg/mm ² in hydrogen	43
3.9 – Comparison of how well various equation forms provide a fit for nickel data at 700°C	44
3.10 – Platinum data at 1350°K and 1.14 kg/mm ² analyzed in terms of the Andrade and hyperbolic sine equations	46
3.11 – Comparison showing excellent agreement between experimental creep data for arc-cast tungsten at 2400°C and 0.50 kg/mm ² and calculated creep curves	51
3.12 – Tensile strength of W – 25Re – 30Mo	52
4.1 – Hermetically sealed W – 5Re capsule after exposure to graphite for 1 hour at 2450°C in hydrogen	53
4.2 – Photograph showing the inner two-thirds of a cross section of Ta capsule containing HfO ₂ after exposure to a carbonaceous environment at 2450°C for 1 hour	55
4.3 – Performance of a Ta sheath and HfO ₂ -insulated W versus W – 25Re thermocouple in carbon and He and H ₂	55
5.1 – Effect of decreasing rhenium content in alloys with 10 percent molybdenum	58
5.2 – Influence of rhenium content on bend ductility of W-Re-Mo alloys held for 100 hours at 1200°, 1600°, 2000°, and 2400°C	61
5.3 – Angle of bend to fracture on W-Re-Mo alloys after holding for 100 hours at 1200°, 1600°, 2000°, and 2400°C	62
5.4 – Typical structures developed in as-processed (cold-worked plus 1400°C stress-relief) W-Re-Mo alloys	64
5.5 – As-processed structures of W – 27Re – 10Mo alloys with low and high carbon levels	65
5.6 – Structures observed in W-Re-Mo alloys held for 100 hours at 2400°C in hydrogen	67
5.7 – Typical structures of W – 25Re – 30Mo, W – 30Re – 30Mo, and W – 30Re alloys	68
5.8 – Influence of thermal and working history on structures of Mo-Re-W alloys	71
5.9 – Pressed and sintered compacts of purified molybdenum prior to working to sheet	72
5.10 – Tube extrusion blank of purified molybdenum	72
5.11 – Cross section of unalloyed molybdenum compact treated for 624 hours at 1000°C in wet hydrogen (dewpoint 5°C) before sintering at 2510°C in dry hydrogen.....	74
5.12 – W – 25Re – 30Mo sheet equivalent to 2 square feet of 0.05-cm-thick by 9-cm-wide by 33-cm-long material processed for radiation damage control studies	75

	Page
5.13 – W-Re-Mo tubes machined in primary extrusion form with molybdenum core and outer container material retained	75
5.14 – Cluster extrusion assembly showing tube positions prior to secondary extrusion.....	76
5.15 – Cluster extrusion container with threaded closure plugs	76
5.16 – W – 25Re – 30Mo tube prepared for evaluation in test assemblies	77
5.17 – Product of a secondary extrusion of W – 5Re alloy	77
5.18 – A W – 25Re heavy-walled tube and rolled plates furnished to ORNL.....	78
5.19 – Tensile test pieces prepared from extruded NMP-256 alloy.....	80

TABLES

	Page
2.1 – Status of continuing 10,000-hour test program of Fe-Cr-Al-Y-clad fueled specimens	12
2.2 – Results of periodic analyses for surface uranium concentration on Fe-Cr-Al-Y-clad fueled specimens tested at 950°C and 1100°C in air	13
2.3 – Summary of metallographic analysis of thermal stability test specimens ..	15
2.4 – Fission product release from in-pile specimen LTFC-2 of 1541-clad Fe – 40UO ₂ at 950°C	21
2.5 – Results of metallographic analyses of Fe-Cr-Al-Y alloys after 10,000-hour oxidation testing.....	26
2.6 – Fe-Cr-Al-Y alloys irradiated in ETR test GEFP2-220	29
2.7 – Effects of irradiation on ductile-to-brittle transition temperatures of Fe-Cr-Al-Y alloys	29
3.1 – Chemical analysis of as-received, unalloyed tungsten sheet	34
3.2 – Creep-rupture results for tungsten sheet in hydrogen	40
3.3 – Creep-rupture results for W – 25Re from various vendors at 2000°C and 2.11 kg/mm ² in hydrogen	41
3.4 – Effect of n in t ^{1/n} term of Andrade equation on the sum of the squares of the residuals	45
3.5 – A comparison of the degree of representation afforded by various creep equations for the data for arc-cast tungsten at 2400°C and 0.46 kg/mm ² ..	47
3.6 – Summary of least squares creep equation constants of arc-cast tungsten data at 2200°C to 2800°C analyzed in terms of the Cottrell-Aytenkin equation.....	48
3.7 – Summary of least squares creep equation constants for arc-cast tungsten data at 2200°C to 2800°C analyzed in terms of third degree polynomial in t ^{1/3}	48
3.8 – Summary of least squares creep equation constants for arc-cast tungsten data at 2200°C to 2800°C analyzed in terms of the Garofalo equation	49
3.9 – Summary of least squares creep equation constants for arc-cast tungsten data at 2200°C to 2800°C analyzed in terms of Andrade equation...	49

	Page
3.10 – Tensile strength of powder metallurgy W – 25Re – 30Mo	50
4.1 – Summary of evaluation of sheath materials tested at 2450°C in H ₂	54
5.1 – Chemical compositions of W-Re-Mo alloys.....	59
5.2 – Room-temperature bend-test results on W-Re-Mo sheet after holding at 1200 ^o , 1600 ^o , 2000 ^o , and 2400 ^o C	60
5.3 – Rockwell "A" hardness values for W-Re-Mo alloys after holding at 1200 ^o , 1600 ^o , 2000 ^o , and 2400 ^o C	63
5.4 – Precipitated sigma phase observed in W-Re-Mo alloys	65
5.5 – Nominal composition and impurity content of Mo-Re-W alloys fabricated to 0.05-cm-thick sheet	66
5.6 – Room-temperature bend test results for Mo-Re-W alloys held at 1200 ^o , 1600 ^o , 2000 ^o , and 2400 ^o C	70
5.7 – Impurity content of unalloyed Mo and Mo – 5Re alloy	73
5.8 – Tensile test results for extruded W – 25Re – 30Mo alloy	79

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

1. INTRODUCTION AND SUMMARY

Introduction

This report is the unclassified portion of the fifty-third in a series of monthly reports of the work in process on materials development for the Atomic Energy Commission under Contract AT(40-1)-2847.

Included is a summary of the work from August 15, 1965 to October 15, 1965, on four of the seventeen specific development programs in process. Three of the remaining programs are reported in the classified portion of this report, GEMP-53, Part B. The other ten programs are reported in alternate months.

Summary

OXIDATION-RESISTANT FUEL ELEMENT MATERIALS RESEARCH (57001)

Four Fe-Cr-Al-Y-clad fueled specimens have completed 10,000 hours at 950°C in air. Uranium was detected on the surface of the specimens after 8000 hours. A total of 36 specimens is continuing on test at temperatures of 750° to 1100°C.

The in-pile test (LTFC-2) of a Fe - 15Cr - 4Al - 1Y-clad Fe-UO₂ specimen was completed; it had accumulated 2000 hours at 950°C in flowing air. Fractional release of fission gases remained low throughout the test (R/B: 6×10^{-7} for Xe¹³³). An identical specimen (designated LTFC-3) was prepared for insertion in a higher flux, to be operated at 950°C for 3000 hours.

Examination of a series of Fe-Cr-Al-Y alloys after testing in air for 10,000 hours at 450° to 1100°C revealed that the Fe - 25Cr - 4Al - 1Y and Fe - 15Cr - 4Al - 1Y alloys have nearly identical oxidation resistance at all temperatures tested. The Fe - 15Cr - 4Al alloy (containing no yttrium) experienced oxide spalling and demonstrated generally poor oxidation resistance at 900°C and 1100°C.

HIGH-TEMPERATURE REACTOR MATERIALS REACTORS (57003)

Creep-rupture evaluations were performed at 1600°, 2000°, and 2400°C using six different sheets of powder metallurgy tungsten, four from the Naval Sheet Rolling Program and two from different commercial sources, and an arc-cast tungsten sheet from an Air Force program. The results at 1600°C were the most consistent, but even at this temperature, the time to rupture at 5.62 kg/mm² varied from 4.5 to 19.5 hours. The

larger variation at 2000°C and 2400°C was attributed to considerable differences in the resultant microstructure of the sheets tested at these temperatures.

Powder metallurgy and arc-cast W – 25Re sheet, obtained from a number of vendors, was creep-rupture tested at 2000°C and 2.11 kg/mm² in hydrogen. Each sheet exhibited different creep curves but when the data are plotted log-strain versus log-time, the creep curve shapes are similar for either the powder metallurgy material or arc-cast material but not for both. The arc-cast material was three times as ductile as the powder metallurgy material based on elongation at rupture.

The first-stage creep equation forms previously evaluated using data for lead at 14.5°C and recent GE-NMPO data for arc-cast tungsten at 2400°C were employed in an analysis of some published first-stage creep data for nickel at 700°C. In each case the degree of representation was found to be very good. Similarly, good results were obtained using data for Al, Pt, Ag, and Mo. Analyses were initiated to evaluate various expressions capable of describing the strain – time behavior for combined first- and second-stage creep data.

The tensile strength for W – 25Re – 30Mo (at. %) was determined giving values of 130 kg/mm² at room temperature and 18 kg/mm² at 1600°C.

HIGH-TEMPERATURE THERMOCOUPLE AND ELECTRICAL MATERIALS RESEARCH (57014)

Studies of thermocouple sheathing materials show tantalum to be superior to W – 5Re, W – 25Re, W – 30Re – 30Mo, Mo, or Os for preventing degeneration of the emf signal as a function of time when exposed to carbonaceous environments at 2450°C.

In-pile testing to evaluate nuclear transmutation effects on the emf signal as a function of temperature for the W / W – 25Re thermocouple is in progress. Accumulated in-pile exposure time is now 7 weeks at 2×10^{14} nv thermal neutron flux.

REFRACTORY METAL ALLOY RESEARCH AND DEVELOPMENT (57015)

Seventeen W-Re-Mo alloys containing exceptionally low carbon and other impurities, were evaluated for bend ductility and hardness after holding for 2, 10, and 100 hours at 1200°, 1600°, 2000°, and 2400°C. Alloys with 30 percent molybdenum retained good ductility after holding at 1200°C. Comparisons with alloys containing more impurities indicate that carbon promotes sigma phase precipitation. Sigma phase in alloys with high carbon content dissolves readily at high temperature; i. e., carbon does not stabilize sigma phase. However, carbon and other impurities, when present in sufficient amounts, are believed to prevent grain growth in the alloys.

Mo-W-Re alloys with 25 percent rhenium were evaluated. Alloys of Mo – 15W – 25Re and Mo – 30W – 25Re retained high ductility in room temperature bends after holding for 100 hours at 1200°, 1600°, 2000°, and 2400°C. These alloys have been selected for further development. One alloy with 30 percent rhenium (Mo – 30W – 30Re) is being investigated for high strength requirements in the 1200°C range; tests to date indicate that this alloy undergoes age-hardening reactions in that temperature range.

Improved weldability and weld-ductility were obtained in unalloyed molybdenum treated for long times in hydrogen – water vapor atmospheres. Pore-free welds were not obtained, however, apparently due to high oxygen content in the treated metal.

In support of other programs, 1860 cm² of 0.05-cm-thick W – 25Re – 30Mo sheet was processed for radiation damage studies. Heavy-walled tubing and heavy end-closure stock of W – 25Re were produced for ORNL in a radioisotopic container application.

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 at temperatures up to 1250°C in air and 1100°C in steam for more than 5000 hours. The current objective is to complete the 10,000-hour laboratory evaluation of the compatibility of the Fe-Cr-Al-Y alloys with various forms of UO₂ at temperatures from 750° to 1250°C. A series of in-pile experiments is also being conducted to evaluate the burnup and fission product retention capabilities of these materials as a function of temperature.

10,000-Hour Laboratory Test Program

Two Fe-Cr-Al-Y alloys, designated 2541 and 1541,¹ have shown excellent resistance to air and steam corrosion at high temperatures. The 1541 alloy is a more recently developed cladding material which is less susceptible to sigma-phase embrittlement and has a lower ductile-to-brittle transition temperature (DBTT) than the 2541 alloy.

The specimens used in these tests are 10.5 mm in diameter by 25.4 mm in length, with 0.5-mm-thick cladding. The dispersion-type Fe - 40UO₂ fueled cores were sintered at 1200°C in hydrogen, machined to fit the cladding, assembled with end plates, sealed by electron-beam welding, and hot-gas-pressure bonded at 1100° to 1250°C under 700 kg/cm² helium pressure. Enough specimens are tested at each temperature to permit destructive evaluations at periodic intervals. Nondestructive analyses are made periodically during the tests by X-ray fluorescence or alpha counting of the cladding surface for uranium diffusion.

The status of the long-time test program is given in Table 2.1. Thirty-six specimens were on test at the end of the report period, representing nine different material systems or fuel forms. Eleven specimens completed scheduled test times of 2000, 5000, or 10,000 hours in good condition and were removed for metallographic examination and other analyses. The results of the X-ray fluorescence analyses that were made during testing are given in Table 2.2. Of the nine specimens containing UO₂ fuel, only three showed significant uranium concentration on the cladding surface at the termination of the test, and the first indications of uranium diffusion occurred in two of these only after several thousand hours of testing. Each of these three contained a different form of UO₂ fuel: agglom-

¹2541 alloy composition is Fe - 25Cr - 4Al - 1Y and 1541 alloy composition is Fe - 15Cr - 4Al - 1Y, expressed as weight percent.

TABLE 2.1
STATUS OF CONTINUING 10,000-HOUR TEST PROGRAM OF
Fe-Cr-Al-Y-CLAD FUELED SPECIMENS

Specimen	Cladding	Core Composition, vol %	Type Fuel ^a	Test Temperature, °C	Accumulated Test Time, hr
FAU-17	2541	Fe - 50UO ₂	KM-A	950	9250
FAU-36				950	9250
FAU-38				950	9250
FU-30	2541	Fe - 40UO ₂	AR	1100	8284
FAU-52	2541	Fe - 40UO ₂	GE-A	750	1855
FAU-53				750	1855
FAU-54				750	1855
FAU-55				950	1830
FAU-56				950	1830
FAU-57				950	1830
FAU-60				1100	1830
FAU-27	2541	Fe - 40UO ₂	KM-A	950	6500
FAU-22				1100	8195
FSU-26	2541	Fe - 40UO ₂	S-KM	750	1855
FSU-27				750	1855
FSU-28				790	1855
FSU-29				750	1855
FSU-22				950	1830
FSU-23				950	1830
FSU-24				950	1830
CAU-28	2541	Cr - 50UO ₂	KM-A	1100	8425
FCAU-6	2541	(Fe-25Cr)-40UO ₂	GE-A	750	1855
FCAU-7				750	1855
FCAU-8				750	1855
FCAU-9				950	1830
FCAU-10				950	1830
FCAU-12				950	1830
FCAU-13				1100	1830
FCSU-1	2541	(Fe-25Cr)-40UO ₂	S-KM	750	1855
FCSU-4				950	1830
FCSU-5				950	1830
FCSU-6				950	1830
FCSU-7				1100	1830
FCSU-8				1100	1830
FCSU-14				1100	1830
FUN-8	1541	Fe - 40UN	AR	950	9250

^aAR - As-received ceramic-grade UO₂ or UN of -325 mesh particle size;
GE-A - UO₂ agglomerated at GE-NMPO, -100/+200 mesh; KM-A - com-
mercially agglomerated UO₂, -100/+200 mesh; S-KM - UO₂ plasma-
spheroidized at GE-NMPO, -120/+200 mesh.

erated, plasma-arc spheroidized, or ceramic-grade powder. The plasma-arc spheroidized fuel had the highest and fastest uranium diffusion rate, reaching 4.2 percent after 5000 hours at 1100°C. Similar high uranium intensities were previously reported² for the specimens containing spheroidized fuel. The surface uranium concentrations remained below detectable limits (0.02% U) for the other six specimens containing UO₂ in various forms (Table 2.2).

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

TABLE 2.2
RESULTS OF PERIODIC ANALYSES FOR SURFACE URANIUM CONCENTRATION ON Fe-Cr-Al-Y-CLAD FUELED SPECIMENS
TESTED AT 950°C AND 1100°C IN AIR

Specimen No.	Cladding	Core Composition, vol. %	Fuel Form ^a	Test Temperature, °C	Surface Uranium Concentration, ^b %										
					Test Time, hours										
					500	1000	2000	2400	3000	4000	5000	6000	8000	9000	10,000
FAU-29	2541	Fe - 40UO ₂	GE-A	1100	—	—	—	ND	0.12	0.16	0.17	Terminated			
FAU-46	2541	Fe - 40UO ₂	GE-A	1100	—	ND	—	ND	ND	ND	ND	Terminated			
FAU-58	2541	Fe - 40UO ₂	GE-A	1100	ND	—	ND	Terminated							
FSU-11	2541	Fe - 40UO ₂	S-KM	1100	—	0.08	—	0.58	0.66	2.4	4.2	Terminated			
FSU-13	2541	Fe - 40UO ₂	S-KM	950	—	ND	—	ND	—	ND	ND	Terminated			
FSU-20	1541	Fe - 40UO ₂	S-KM	950	—	ND	—	ND	—	ND	0.03	Terminated			
FSU-25	2541	Fe - 40UO ₂	S-KM	950	ND	—	ND	Terminated							
FCAU-4	2541	(Fe - 25Cr) - 50UO ₂	GE-A	950	—	—	ND	—	—	—	ND	—	ND	0.04	ND
CU-26	2541	Cr - 50UO ₂	AR	950	—	—	ND	—	—	—	ND	—	0.03	0.10	0.11
CUN-5	2541	Cr - 40UN	AR	950	—	—	ND	—	—	—	—	ND	ND	0.03	0.06
FCUN-1	2541	(Fe - 25Cr) - 40UN	AR	950	—	—	ND	—	—	—	—	ND	ND	ND	ND

^aAR-As-received ceramic-grade UO₂ or UN of -325 mesh size.

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

S-KM - Spheroidized particles produced by plasma-arc fusion of commercially agglomerated UO₂, -140/+200 mesh size.

^bAnalysis for uranium on cladding surface by X-ray fluorescence technique; presence of uranium in amounts less than 0.02% cannot be detected.

The specimen containing 40 percent UN fuel in a chromium matrix and tested at 950°C showed no detectable surface uranium until 9000 hours. The surface of the (Fe - 25Cr) - 40UN specimen remained free of uranium throughout the 10,000-hour test. These limited data indicate that UN is at least as stable as UO₂ with Fe-Cr-Al-Y cladding at 950°C.

Studies of various fuel forms were continued as a part of the laboratory stability test program. As mentioned above, specimens containing plasma-arc spheroidized UO₂ prepared at GE-NMPO from agglomerated fuel particles had previously shown relatively high surface uranium intensities after 2500 to 2900 hours at 1100°C, although the spheroidized UO₂ had been expected to be a more stable fuel form. Fifteen new specimens containing spheroidized UO₂ particles were placed on test³ and have accumulated over 1800 hours at temperatures of 750°, 950°, and 1100°C. None has shown darkening of the cladding surface which is a reliable indication of uranium diffusion. This group of specimens will be analyzed by X-ray fluorescence after 2000 hours has been accumulated.

Electron microprobe analyses were performed on three spheroidized-fuel specimens shown metallographically in a previous report.⁴ These were identified as FSU-9, 2541-clad Fe - 40UO₂ and FSU-21, 1541-clad Fe - 40UO₂, both after 2500 hours at 950°C; and FSU-15, 1541-clad Fe - 40UO₂ after 2500 hours at 1100°C. No uranium was detected in the cladding of any of these specimens. The analyses of the two specimens tested at 950°C showed interdiffusion of iron and chromium to a depth of approximately 300 microns and aluminum diffusion into the core to a depth of 50 to 100 microns. Interdiffusion of these elements was complete in FSU-15 tested at the higher temperature. Major concentration peaks of aluminum occurred at the cladding surface in all specimens, and also at the core - cladding interface of FSU-9 and FSU-21. The average concentration of aluminum in the cladding of the specimens tested at 950°C was about 4 percent, whereas it was 1.5 percent in the specimen tested at 1100°C.

Metallographic examination was completed for nine specimens containing various fuels. The compositions, test conditions, and results are shown in Table 2.3. The microstructures of the core - cladding interfaces of two specimens tested for 7000 hours at 950°C are shown in Figure 2.1. These specimens contained ceramic-grade UO₂ clad with 2541 alloy or UN clad with 1541 alloy. Barriers of alumina about 2.5 microns thick had formed at the core - cladding interface in both specimens. The surface oxide layers were 2.5

³"High-Temperature Materials Program Progress Report No. 51, Part A," GE-NMPO, GEMP-51A, September 30, 1965, p. 15.

⁴Ibid., p. 16.

2541-clad Fe - 40UO₂ specimen FU-29
(Neg. 6292)

1541-clad (Fe - 25Cr) - 40UN specimen FCUN-5
(Neg. 6291)

Fig. 2.1 - Photomicrographs of two fueled specimens showing conditions at the core - cladding interface after 7000 hours at 950°C in air (250X)

TABLE 2.3
SUMMARY OF METALLOGRAPHIC ANALYSIS OF THERMAL STABILITY TEST SPECIMENS

Specimen No.	Cladding	Core Composition, vol %	Fuel Form ^a	Test Conditions		Surface Uranium Concentration, ^b %	Oxide Thickness, microns	
				Temperature, °C	Time, hr		Cladding Surface	Interface
FU-29	2541	Fe - 40UO ₂	AR	950	7000	<0.02	2.5	2.5
FCUN-5	1541	(Fe - 25Cr) - 40UN	AR	950	7000	<0.02	5.0	2.5
FU-32	2541	Fe - 40UO ₂	AR	1100	5100	<0.02	10.0	5.0
FCUN-3	1541	(Fe - 25Cr) - 40UN	AR	1100	5100	<0.02	22.8	7.3
CAU-27	2541	Cr - 50UO ₂	KM-A	1100	5100	1.25	12.6	nil
CUT-24	2541	Cr - 50(UO ₂ - 11ThO ₂)	GE-A	1100	5100	0.24	12.6	nil
FCAU-3	2541	(Fe - 25Cr) - 50UO ₂	KM-A	1100	7000	0.07	7.3	2.5
FAU-37	2541	Fe - 50UO ₂	KM-A	1100	7000	0.66	12.1	nil
FAU-28	2541	Fe - 40UO ₂	KM-A	950	5100	<0.02	7.9	1.8
FSU-19	1541	Fe - 40UO ₂	S-KM	950	3000	<0.02	5.1	nil
FSU-10	2541	Fe - 40UO ₂	S-KM	1100	2500	0.82	12.5	nil

^aAR - As-received ceramic-grade UO₂ or UN of -325 mesh size.

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

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

S-KM - Spheroidized particles produced by plasma-arc fusion of commercially agglomerated UO₂, -140/+200 mesh size.

^bAnalysis for uranium on cladding surface by X-ray fluorescence technique; presence of uranium in amounts less than 0.02% cannot be detected.

and 5.0 microns thick, respectively. The 1541 alloy cladding was internally oxidized in clusters. Both fuel cores showed fine porosity and some agglomeration of fuel.

The microstructures of two similar specimens tested at 1100°C for 5100 hours are shown in Figure 2.2. At this higher temperature, surface oxidation increased fourfold and the alumina barrier layer increased threefold. Intergranular oxidation occurred in the 2541 cladding of the Fe-UO₂ specimen both at the surface and at the interface. Oxidation was uniform throughout the 1541 cladding of the UN-bearing specimen, similar to the specimen tested at 950°C. An occasional large agglomerate of fuel was observed in the UO₂-bearing specimen and, to a lesser extent, in the UN specimen.

The microstructures of two specimens containing Cr - 50UO₂ cores tested at 1100°C for 5100 hours are shown in Figure 2.3. Both specimens had about 12.6 microns of surface oxidation but no interface barriers. X-ray fluorescence analyses indicated 0.24 percent uranium at the cladding surface and, in the case of the unstabilized UO₂ (CAU-27), particles of UO₂ were detected by electron microprobe analysis under the surface alumina layer. Fuel distribution was not good in either specimen.

Figure 2.4 presents photomicrographs of two 2541-clad Fe - 50UO₂ specimens after testing for 7000 hours at 1100°C in air. One of these (FCAU-3) had a core matrix of Fe - 25Cr rather than the usual iron-matrix core. X-ray fluorescence analyses showed uranium at the cladding surface of both of these specimens. A higher concentration (0.66% U) was found on the Fe - 50UO₂ specimen than on the (Fe - 25Cr) - 50UO₂ specimen (0.07% U). A fairly heavy oxide layer was observed on the cladding surfaces. The Fe - 50UO₂ specimen had more grain boundary oxidation at both the outer surface and at the core - cladding interface area.

Uranium Diffusion Measurements by Alpha Counting

A series of specimens which contain enriched UO₂ either unalloyed or as agglomerated particles dispersed in an iron matrix has accumulated about 200 hours on test at temperatures from 750° to 1250°C in air. These specimens are clad with drawn tubing of 1541 alloy and are periodically monitored for uranium diffusion both by alpha counting techniques and by X-ray fluorescence analyses. The results of alpha counting are shown

2541-clad Fe - 40UO₂ specimen FU-32
(Neg. 6297)

1541-clad (Fe - 25Cr) - 40UN specimen FCUN-3
(Neg. 6295)

Fig. 2.2 - Photomicrographs of two fueled specimens showing conditions at the core - cladding interface after 5100 hours at 1100°C in air (100X)

Cr-50UO₂ specimen CAU-27 (Neg. 6296)

Cr-50(UO₂-11ThO₂) specimen CUT-24
(Neg. 6293)

Fig. 2.3—Photomicrographs of 2541-clad chromium matrix fuel core specimens showing conditions at the core-cladding interface after 5100 hours at 1100°C in air (100X)

(Fe-25Cr) - 50UO_2 specimen FCAU-3
(Neg. 6294)

Fe - 50UO_2 specimen FAU-37 (Neg. 6569)

Fig. 2.4 - Photomicrographs of two 2541-clad iron matrix core specimens showing conditions at the core-cladding interface after 7000 hours at 1100°C in air (100X)

in Figures 2.5 and 2.6. The specimens tested at 750°C and 950°C exhibited relatively low surface activity (2 to 6 counts/cm² - min, average) with unexplained peaks occurring after 30 hours and 125 hours of test time. The specimens tested at 1100°C and 1250°C have shown irregular increases of a generally linear character. At 1100°C the specimen containing the Fe - 40UO₂ core had much lower alpha activity on the surface than the specimen containing UO₂. Data at 1250°C were somewhat erratic but the count of both specimens was near 50 after 165 hours.

Testing of these specimens will continue and new specimens will be prepared to further define the behavior of these fuel systems.

In-Pile Test Program

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

1541-Clad Fe - 40UO₂ at 950°C (LTFC-2) - The in-pile test (LTFC-2)⁵ of a 1541-clad Fe - 40UO₂ specimen was completed. It was irradiated in the LITR for a total of 2000 hours at maximum indicated temperatures between 940° and 1000°C in a flowing air atmosphere (700 liters per minute). During the test, there were 18 thermal cycles caused by reactor shutdowns. The total burnup is calculated to be 1.3 percent based on 9×10^{19} fissions per cubic centimeter.

The effluent gas stream was sampled 19 times with carbon traps which were then analyzed for fission products. The data obtained are presented in Table 2.4. Fission gas release data obtained during the interval from 1083 to 1455 hours are not shown because of cross-contamination from another experiment which was operated during this interval and which shared the trapping station with this test.

Fission product release from this specimen was similar both in magnitude and mechanism to that observed in the LTFC-1 test which was operated at 1100°C for 1070 hours.⁶ The level of steady-state fission gas release from LTFC-2 remained low ($R/B = 4$ to 7×10^{-8} for Kr⁸⁷ and 2 to 6×10^{-7} for Xe¹³³) and essentially constant throughout the irradiation period. The release was slightly lower (a factor of 2 at most for Kr⁸⁷) than that from LTFC-1. The high Xe¹³³ release for traps C-1, -3, and -7 ($R/B = 1$ to 6×10^{-6}) taken shortly after thermal cycles indicates the presence of transient release conditions similar to those exhibited by LTFC-1 during its operation. In terms of half-lives of the various isotopes the steady-state release analysis suggests that diffusion, possibly through the surface oxide film, and recoil from fuel near the surface are the predominant release processes. Hot cell examination of the specimen will be performed during the next report period.

1541-Clad Fe - 40UO₂ at 950°C (LTFC-3) - The third in-pile test (LTFC-3), which is a duplicate of the LTFC-2 specimen, will be inserted in the LITR during the next report period. Revisions have been made in the air supply of the C-48 facility which will increase the coolant airflow to 1650 liters per minute, more than double that of the previous experiment. This will permit insertion of the cartridge into full flux (0.55×10^{13} nv); under these conditions the fueled specimen will experience a burnup of 3.2 percent during the scheduled 3000 hours of operation at 950°C.

⁵"High-Temperature Materials Program Progress Report No. 47, Part A," GE-NMPO, GEMP-47A, May 28, 1965, p. 18.

⁶"High-Temperature Materials Program Progress Report No. 49, Part A," GE-NMPO, GEMP-49A, July 28, 1965, pp. 18-19.

Fig. 2.5 - Alpha surface activity as a function of time for 1541-clad unalloyed UO_2 capsules tested in air at 750°, 950°, 1100°, and 1250°C

Fig. 2.6 - Alpha surface activity as a function of time for 1541-clad Fe-40 UO_2 capsules tested in air at 750°, 950°, 1100°, and 1250°C

TABLE 2.4
FISSION PRODUCT RELEASE FROM IN-PILE SPECIMEN LTFC-2 OF
1541-CLAD Fe - 40UO₂ AT 950°C

Trap No.	Cumulative Time At Temperature, hr	Fractional Release (R/B) ^a				
		Kr ⁸⁷	Kr ⁸⁸	Kr ^{85m}	Xe ¹³⁵	Kr ¹³³
C-1	13.7	5 x 10 ⁻⁸	9 x 10 ⁻⁸	1 x 10 ⁻⁷	6 x 10 ⁻⁸	3 x 10 ⁻⁶
Shutdown	20.4					
C-2	112.0	6 x 10 ⁻⁸	—	2 x 10 ⁻⁷	8 x 10 ⁻⁸	3 x 10 ⁻⁷
Shutdown	124.6					
C-3	161.7	7 x 10 ⁻⁸	6 x 10 ⁻⁸	2 x 10 ⁻⁷	9 x 10 ⁻⁸	6 x 10 ⁻⁶
C-4	279.4	5 x 10 ⁻⁸	6 x 10 ⁻⁸	2 x 10 ⁻⁷	1 x 10 ⁻⁷	2 x 10 ⁻⁷
Shutdown	316.5					
Shutdown	383.6					
C-5	446.2	4 x 10 ⁻⁸	5 x 10 ⁻⁸	1 x 10 ⁻⁷	1 x 10 ⁻⁷	3 x 10 ⁻⁷
C-6	591.4	4 x 10 ⁻⁸	5 x 10 ⁻⁸	1 x 10 ⁻⁷	1 x 10 ⁻⁷	4 x 10 ⁻⁷
Shutdown	607.3					
Shutdown	622.8					
Shutdown	698.4					
C-7	717.0	4 x 10 ⁻⁸	6 x 10 ⁻⁸	1 x 10 ⁻⁷	1 x 10 ⁻⁶	1 x 10 ⁻⁶
Shutdown	736.2					
Shutdown	804.4					
C-8	879.1	5 x 10 ⁻⁸	1 x 10 ⁻⁷	2 x 10 ⁻⁷	5 x 10 ⁻⁷	5 x 10 ⁻⁷
Shutdown	900.8					
Shutdown	1083.2					
C-9	1086.9	Data unreliable; cross-contamination ^b				
C-10	1209.4	Data unreliable; cross-contamination ^b				
Shutdown	1226.0					
C-11	1380.1	Data unreliable; cross-contamination ^b				
C-12	1431.8	Data unreliable; cross-contamination ^b				
C-13	1433.0	Data unreliable; cross-contamination ^b				
Shutdown	1455.6					
C-14	1586.8	5 x 10 ⁻⁸	8 x 10 ⁻⁸	2 x 10 ⁻⁷	2 x 10 ⁻⁷	6 x 10 ⁻⁷
C-15	1610.2	2 x 10 ⁻⁸	3 x 10 ⁻⁸	5 x 10 ⁻⁸	1 x 10 ⁻⁷	3 x 10 ⁻⁷
Shutdown	1611.3					
C-16	1726.9	7 x 10 ⁻⁸	1 x 10 ⁻⁷	2 x 10 ⁻⁷	2 x 10 ⁻⁷	3 x 10 ⁻⁷
Shutdown	1750.5					
C-17	1845.4	5 x 10 ⁻⁸	8 x 10 ⁻⁸	2 x 10 ⁻⁷	2 x 10 ⁻⁷	2 x 10 ⁻⁷
Shutdown	1863.9					
Shutdown	1876.1					
C-18	1906.6	5 x 10 ⁻⁸	8 x 10 ⁻⁸	1 x 10 ⁻⁷	1 x 10 ⁻⁷	2 x 10 ⁻⁷
C-19	1978.9	4 x 10 ⁻⁸	7 x 10 ⁻⁸	9 x 10 ⁻⁸	7 x 10 ⁻⁸	2 x 10 ⁻⁷
Shutdown	2000.5	End of Test				

^aFractional release is defined as the ratio of the rate of release of atoms from the specimen to the equilibrium production rate.

^bCross-contamination is believed to have come from a test in another LTR facility which was operated during this period and was connected to the LTFC-2 trapping system.

1541-Clad Fe - 25UO₂ at 750°C (ORFC-1) - A new series of six fuel element specimens of 1541-clad Fe - 25UO₂ was prepared for testing in the ORR under high burnup conditions. The cores were cold-pressed, sintered at 1200°C in H₂, autoclaved at 1100°C to densify (~98% T.D.) and machined to a final size of 12.6 mm OD, 10.6 mm ID, and 38 mm long. The cladding was chemically cleaned and the cores were cleaned ultrasonically in Freon-10. After assembling the core in the cladding and welding the end plugs, the specimens were outgassed through a vent hole by heating for 1 hour at 1100°C in vacuum. The vent hole was then sealed by EB welding and the six specimens were autoclaved at 1100°C in 700 kg/cm² helium pressure. All were well bonded.

After proof-testing for 16 hours at 1100°C in air, the specimens were machined to final size and inspected. The test specimen selected for the first experiment is shown in Figure 2.7. The cartridge was being assembled at the close of the report period; it is scheduled for insertion in the F-2 facility during the December shutdown of the ORR.

Fig. 2.7 – Typical 1541-clad Fe – 25UO₂ fuel element specimen as prepared for series of high-burnup tests in ORR (Neg. P65-10-4A)

ALLOY DEVELOPMENT

The objective of this portion of the work is to develop Fe-Cr-Al-Y alloys having improved structural properties without sacrificing oxidation or corrosion resistance.

Alloy Preparation

During this report period, a 200-kg heat (MS-51) of a 1541 alloy was melted and extruded into two rods, 3.2 cm diameter by 345 cm long; one rod 5.1 cm diameter by 120 cm long; and one rectangular sheet bar 1.9 cm by 7.6 cm by 190 cm long. This heat is large enough to serve as the reference alloy for future GE-NMPO programs and for a cooperative evaluation program with UKAEA (Harwell). A quantity of sheet stock, rods, and tubing blanks are being fabricated of this 1541 reference alloy.

AIR OXIDATION AND STEAM CORROSION STUDIES

Air Oxidation

A series of Fe-Cr-Al-Y alloys is being tested for oxidation resistance in air at 450°, 550°, 730°, 900°, and 1100°C for times up to 10,000 hours. The weight gain data accumulated to date for 900°C and 1100°C tests are shown in Figure 2.8. Specimens of three alloys completed 10,000 hours of testing time and were examined metallographically. The results are summarized in Table 2.5 and representative microstructures are shown in Figures 2.9 through 2.11. The two alloys containing yttrium (2541 and 1541) appear to have similar oxidation resistance at all temperatures. At 1100°C, internal oxidation of yttrium occurred to a depth of about 0.13 mm and the YFe₉ phase was depleted to a depth of 0.20 to 0.25 mm (Figures 2.9A and 2.10A). At 900°C (Figures 2.9B and 2.10B) internal oxidation occurred to a depth of about 0.15 mm but the depletion of the YFe₉ phase was not uniform.

At 730°C (Figures 2.9C, 2.10C, and 2.11A), the structures are similar to the normal pre-test condition except for the 1540 alloy which exhibits non-uniform oxide pitting. The

Fig. 2.8—Weight gain of Fe-Cr-Al-Y alloys as a function of test time at 900°C and 1100°C in static air for times up to 10,000 hours

Fig. 2.9 – Microstructures of 2541 alloy oxidized in air for 10,000 hours at 450° to 1100°C (250X; etchant, 10% oxalic acid)

Fig. 2.10 – Microstructures of 1541 alloy oxidized in air for 10,000 hours at 450° to 1100°C (250X; etchant, 10% oxalic acid)

A. 730°C (Neg. 6455)

B. 550°C (Neg. 6454)

C. 450°C (Neg. 6453)

Fig. 2.11 – Microstructures of 1540 alloy oxidized in air for 10,000 hours at 450° to 730°C (250X; etchant, 10% oxalic acid)

TABLE 2.5
RESULTS OF METALLOGRAPHIC ANALYSES OF Fe-Cr-Al-Y ALLOYS
AFTER 10,000-HOUR OXIDATION TESTING

Alloy	Heat	Test Temperature, °C	Weight Increase, mg/cm ²	Scale Thickness, ^a mm	Y Fe ₃ Depletion, ^a mm	Internal Oxidation, ^a mm	Hardness, DPH	
							Center	Edge
2541	36	Std ^b						200
		450	0.08	—	—	—	335	331
		550	0.08	—	—	—	362	359
		730	0.22	—	—	—	199	204
		900	0.81	0.025	—	0.15	190	190
		1100	2.85	0.15	0.2	0.13	173	168
1541	38	Std ^b						175
		450	0.13	—	—	—	226	215
		550	0.11	—	—	—	179	169
		730	0.22	—	—	—	171	172
		900	0.89	—	—	0.15	166	168
		1100	2.79	0.15	0.25	0.13	146	141
1540	230	Std ^b						165
		450	0.11	—	—	—	208	205
		550	0.11	—	—	—	160	159
		730	0.44	—	—	—	156	154

^aWhere no value is shown, the measurements were not significant.

^bControl specimen as annealed at 1000°C.

1540 alloy was not tested for extended times at 900°C and 1100°C because of oxide spalling and poor oxidation resistance. At 550°C (Figures 2.9D, 2.10D, and 2.11B), the only significant change is in the 2541 alloy which exhibited grain boundary precipitation. Sigma-phase precipitation occurs in this alloy at 550°C, which is responsible for the increase in hardness (see Table 2.5). Sigma-phase precipitation would not be expected in the alloys containing 15 percent chromium since according to the iron-chromium phase diagram this composition lies in the iron solid solution region at temperatures above 500°C.

At 450°C (Figures 2.9E, 2.10E, and 2.11C), alpha-prime precipitation occurred in all the alloys; the greatest amount was found in the 2541 alloy, which explains the increase in hardness (see Table 2.5).

The data indicate that the hardness decreased significantly during the 10,000-hour test at 1100°C. This was probably caused by aluminum depletion from the alloys through the formation of a surface layer of Al₂O₃. Hardness measurements were made near the surface and at the center of the specimens; in all cases, the values corresponded within a few points. This demonstrates that no subsurface or subscale hardening occurs as a result of the oxide formation.

Measurements of the bend ductility of these oxidation test specimens will be made to determine what changes occur with test time as a result of the oxidation and/or thermal treatments.

Another series of iron-base alloys containing 13 to 15 percent chromium, 4 to 7 percent aluminum, and 0 to 1 percent yttrium is being tested for air oxidation and steam corrosion resistance. The objectives of these tests are (1) to determine the minimum yttrium concentration required to maintain an adherent oxide film and (2) to evaluate the effects of various concentrations of aluminum and chromium on low-temperature structural stability. After 1000 hours of testing in air at 900°C and 1100°C, and in steam at 550°C, significant effects were noted only in the 1100°C air tests. As shown in Figure 2.12, the

Fig. 2.12 - Weight change of Fe-15Cr-4Al alloys containing 0 to 1 percent Y tested at 1100°C in air for 1000 hours

addition of only 0.1 weight percent yttrium to the 1540 alloy resulted in the formation of an adherent oxide at 1100°C, while the alloy without yttrium exhibited oxide spalling and weight loss. Similar spalling occurred on a 1560 alloy. The other three alloys which contain at least 0.2 percent yttrium exhibited adherent oxides. The weight gains were highest for the high-yttrium-content alloys, which is consistent with the data shown in Figure 2.8 for the 25-percent chromium alloys. After 1000 hours in 550°C steam, the alloys of this series all exhibited weight gains of 0.1 mg/cm² or less.

This series of alloys is also being aged at 450°C to determine the degree of hardening caused by alpha-prime precipitation. The data obtained to date are inconclusive, all the alloys exhibiting a small increase in hardness after 1000 hours.

The aging and corrosion evaluations will be continued to at least 2000 hours.

Steam Corrosion Studies

A group of experimental and commercial alloys is being tested in 730°C steam for times up to 10,000 hours. No additional data were obtained during this report period because the tests were interrupted during replacement of a superheater coil.

As reported previously,⁷ specimens of the 1041 alloy were pre-oxidized in air, pre-stained, and then tested in 550°C steam for approximately 1000 hours. Some of the specimens are shown in Figure 2.13. In general, the surface darkening was caused by increased corrosion at cracks in the oxide film. Metallographic examination indicated

⁷"High-Temperature Materials Program Progress Report No. 51, Part A," GE-NMPO, GEMP-51A, September 30, 1965, p. 21.

Fig. 2.13 - Pre-oxidized and pre-strained specimens of 1041 alloy after testing in steam at 550°C for 1000 hours (Neg. P65-9-15)

that uniform strains up to about 2 percent can be tolerated by specimens pre-oxidized for 20 hours at 1000°C. At higher strains, cracking of the Al_2O_3 results in the formation of other oxides under the surface layer. Figure 2.14 shows the interface of the surface oxide and the metal in specimens strained 0, 2, and 4 percent. The condition of these structures is superior to that of a specimen of 1041 alloy which was not pre-oxidized before being exposed to steam at 550°C for only 240 hours (Figure 2.15).

Additional pre-oxidized specimens of 1041 alloy plastically strained 1 and 2 percent in tension are being tested in 730°C steam for extended times.

From the results thus far acquired under this program, it can be concluded that the optimum combination of alloy structural stability at low temperatures and steam corrosion resistance are achieved by a low-chromium alloy, pre-oxidized prior to steam exposure.

IRRADIATION EFFECTS

The effects of irradiation on the properties of the Fe-Cr-Al-Y alloys are being studied. Coupon type specimens of four alloy compositions were irradiated for 535 hours to 9.25×10^{20} nvt ($E_n \geq 1$ Mev) at ambient temperature in the ETR; this test was designated GEFP2-220. Alloy compositions are given in Table 2.6.

TABLE 2.6
Fe-Cr-Al-Y ALLOYS IRRADIATED IN ETR TEST GEFP2-220

Alloy	Heat No.	Chemical Analyses						
		wt %			ppm			
		Cr	Al	Y	C	P	Si	S
0561	M-236	4.71	6.51	0.39	73	3	30	20
1041	M-239	9.66	4.63	0.23	61	7	30	10
1541	MS-38	14.49	4.48	0.59	30	59	20	16
1541 FC	MS-41	15.36	4.44	0.43	31	91	85	14
2541	MS-36	25.57	4.30	0.41	48	58	28	11

After irradiation, the changes in ductility were measured by bending around a 2t radius. As shown in Table 2.7, all the alloys were capable of a full 90-degree bend at -79°C before irradiation. After irradiation, the transition temperature for the 1541 and 2541 alloys had increased to between -79°C and -54°C, while that of the 0561 and 1041 alloys remained below -79°C.

The alloys are being annealed at low temperatures to determine the influence of temperature on the radiation-induced changes in hardness and ductility. The initial hardness

TABLE 2.7
EFFECTS OF IRRADIATION ON
DUCTILE-TO-BRITTLE TRANSITION
TEMPERATURE OF Fe-Cr-Al-Y ALLOYS

Alloy	Ductile-To-Brittle Transition Temperature ^a	
	Unirradiated	Irradiated
0561	< -79°C	< -79°C
1041	< -79°C	< -79°C
1541	< -79°C	< -54°C > -79°C
1541 FC	< -79°C	< -54°C > -79°C
2541	< -79°C	< -54°C > -79°C

^a90-degree bend around a 2t radius.

Fig. 2.14—Photomicrographs of 1041 alloy pre-oxidized for 20 hours at 1000°C; pre-strained 0, 2, and 4 percent; and then exposed to 550°C steam for 1000 hours (750X; etchant, 10% oxalic acid)

Fig. 2.15—Photomicrograph of 1041 alloy tested in 550°C steam for 240 hours without pre-oxidation (Neg 5714, 250X)

data are shown in Figure 2.16. In general, the hardness dropped rapidly at 250°C and 300°C, in some cases to a level corresponding to the hardness of the control specimens.

The annealing study will be continued and further ductility evaluations will be made.

Cooperative Programs

A cooperative program was established between GE-NMPO and the UKAEA located at Harwell. The objective of the program is to evaluate the Fe-Cr-Al-Y alloys as fuel element claddings for CO₂-cooled reactors operating at temperatures up to 1000°C. GE-NMPO will provide 1541 and 1540 alloys in sheet, rod, and tube form. It will also provide sheets of experimental alloys, Fe - 28Cr and Fe - 28Cr - 1Y, for evaluation. The Harwell group will study four areas: (1) irradiation effects, (2) corrosion in CO₂, (3) fabrication techniques, and (4) fuel - cladding compatibility and other related problems.

The sheet and rod material will be shipped during the next report period.

WORK PLANNED FOR NEXT PERIOD

Laboratory testing of Fe-Cr-Al-Y-clad fueled specimens under the 10,000-hour test program will continue. A new series of 1541-clad Fe - 40UO₂ enriched specimens will be tested at 950°C and 1100°C as part of the study of diffusion gradients and surface uranium concentration.

In-pile test LTFC-3 will be inserted in the LITR to begin a 3000-hour test at 950°C in air. The first of a series of high burnup tests (ORFC-1) will be prepared for insertion in the ORR during the December shutdown.

The long-time corrosion testing of Fe-Cr-Al-Y alloys in air and steam will continue. A series of alloys with various yttrium and aluminum contents will be evaluated for oxidation resistance and ductility. Evaluations of a series of alloys irradiated in the ETR will continue, to determine the effects of irradiation on strength and ductility.

Fig. 2.16 - Hardness as a function of annealing time for various Fe-Cr-Al-Y alloys after irradiation to 9.25×10^{20} nvt

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 – To assist in evaluating the high-temperature mechanical properties of refractory metals under this program, four sheets of unalloyed, powder metallurgy tungsten, manufactured under the Bureau of Naval Weapons Refractory Metal Sheet Program (NSRP) (Contract No. 60-0621) were obtained through the Department of the Navy, Materials Division, Metals Branch.

The sheet identification information is as follows:

Sheet No.	Lot No.	Sheet Thickness, cm	Sheet Size, cm	Warm Work, %
1	A-5467	0.05	36 x 75	73
3-2	A-5467	0.05	48 x 85	98
5-2	A-5467	0.05	48 x 85	98
6	A-5467	0.025	47 x 65	Not available

A layout was made on each sheet identifying each tensile type specimen as to its location (longitudinal axis of specimens in the direction of rolling) and the section of the sheet used for chemical analysis. Each specimen was cut from the sheet by the electrical spark discharge method (Elox) and then the gage section surface-ground to the final dimension. The specimens were 7.6 cm long with a gage section 0.64 cm wide and 2.54 cm long and contained a 0.64-cm-diameter hole at each end for pinning to the load train members.

In addition to this material, tungsten sheet from three other sources was used for a comparative evaluation. Powder metallurgy tungsten sheet, 0.05 cm thick, was obtained commercially from two sources, and arc-cast tungsten sheet, 0.15 cm thick, was obtained from an Air Force Program (Contract AF 33(600)-41917). These materials were processed to specimens in the same manner as the NSRP material.

Chemical analyses for each sheet in the as-received condition are given in Table 3.1. Although no chemical data were obtained for commercial source 5, the analyses of the other sheets show the tungsten to be of high purity. As can be seen, the carbon content for the arc-cast sheet is higher than the others, as might be expected.

TABLE 3.1
CHEMICAL ANALYSIS OF AS-RECEIVED, UNALLOYED TUNGSTEN SHEET

Source	Source No.	Sheet	Sheet	Impurity Content, ppm											
		Thickness, cm	Fabrication Method	H ₂ ^a	O ₂	N ₂	C ^b	Si ^c	Al	Fe	Ti	Cu	Ni	Cr	Mo
NSRP	Sheet 1	0.05	PM ^d	2	10	0.8	28	<100	<100	100	ND	200	200	ND ^e	<50
NSRP	Sheet 3-2	0.05	PM	1	7.6	0.4	26	<100	<100	100	ND	<50	80	ND	<50
NSRP	Sheet 5-2	0.05	PM	0.4	8.4	1	25	<100	<100	100	ND	<50	<50	ND	<50
NSRP	Sheet 6	0.025	PM	3	22	12	26	<100	<100	300	ND	<50	<50	ND	<50
Commercial	5	0.05	PM	Not obtained											
Commercial	2	0.05	PM	2	32	3	18	<100	ND	<100	ND	ND	ND	ND	100 to 1000
Air Force	3	0.15	AC ^f	0.7	5.6	0.1	63	ND	ND	5 to 50	ND	<100	<100	<100	<100

^aVacuum fusion analysis.

^bConductometric analysis.

^cSemi-quantitative spectrographic analysis.

^dPowder metallurgy.

^eND – not detected; the following elements were analyzed for and not detected in each sample: Ta, V, Mn, Ca, Mg, Bi, Zr, Pb, Sn, Ag, Co, Sb, As, B, Zn, Ba, Sr, Na, K, Li, Cb, and Cd.

^fArc-cast.

Creep-rupture tests of specimens from each sheet of tungsten were performed in hydrogen at 1600°C and 5.62 kg/mm², 2000°C and 2.11 kg/mm², and 2400°C and 1.05 kg/mm². Prior to testing, the specimens were annealed for 2 hours at test temperature in hydrogen to minimize the structural change during testing. The test results are given in Table 3.2 and Figures 3.1 and 3.2. Figure 3.1 shows conventional strain – time plots to approximately 10 percent strain at each temperature, and in most cases shows the conventional primary (transient), secondary (linear), and tertiary stages of creep. At each temperature, the time to any given strain value varies considerably for the different sheets, apparently independent of processing history. At 1600°C and 5.62 kg/mm² the data are more consistent than at the other two temperatures. Less conventional type plots of the same tests with data approaching rupture are given in Figure 3.2 using logarithmic coordinates. The 1600°C test data show that each curve has essentially the same shape except for a uniform displacement. Results for the two sheets from the NSRP having the same amount of warm working (98%) also differ considerably at 2000°C and 2400°C. Results for the arc-cast tungsten show the material to be the least or next to the least creep resistant of the group evaluated.

The variation in the surface texture of the specimens after testing at 2000°C is shown in Figure 3.3. The arc-cast specimen (Source 3) shows considerable elongation.

Photomicrographs of each sheet specimen in the as-received condition and after testing at 1600°C, 2000°C, and 2400°C are shown in Figures 3.4 and 3.5. The as-received condition for each sheet displays the typically fibrous worked structure. The difference in warm working between sheet 1 and sheets 3-2 and 5-2, Figure 3.4, is easily observed. After the 1600°C tests, all sheets and sources, Figures 3.4 and 3.5, exhibit a similar recrystallized structure with small variations in grain size. The exception is source 3 material (arc-cast) which shows considerable grain growth. After the 2000°C tests, the sheets exhibit considerable differences with sheets 1 and 5-2, Figure 3.4, showing some grain growth, whereas sheet 3-2 and sheet 6 show considerable duplexing. Source 5, Figure 3.5, shows little grain growth whereas source 2 shows considerable duplexing. Source 3 shows huge grains typical of arc-cast material for this temperature. After the 2400°C tests, the observations are similar to those for the 2000°C tests but with additional grain growth.

Fig. 3.1 – Creep curves for tungsten sheet at various temperatures and stresses in a hydrogen atmosphere

Fig. 3.2—Log-log plots of creep data for tungsten sheet at various temperatures and stresses in a hydrogen atmosphere

Fig. 3.3 – Tungsten sheet specimens after creep-rupture testing at 2000°C and 2.11 kg/mm² in hydrogen

Fig. 3.4—Photomicrographs of wrought sintered tungsten from the Navy sheet rolling program after creep-rupture testing in hydrogen. Included are the rupture time, hours, and rupture elongation, percent (100X)

Fig. 3.5—Photomicrographs of commercial tungsten sheet after creep-rupture testing in hydrogen. Included are the rupture time, hours, and rupture elongation, percent (100X)

TABLE 3.2
CREEP-RUPTURE RESULTS FOR TUNGSTEN SHEET IN HYDROGEN^{a,b}

Material Source	Temperature, °C	Stress, kg/mm ²	Time To Indicated Strain, hours							Rupture Strain, %	Linear Creep Rate, min. ⁻¹
			0.5%	1%	2%	3%	5%	10%	Rupture		
NSRP 1	1600	5.62	—	0.04	0.28	0.75	1.77	4.57	9.47	30	3.0×10^{-4}
NSRP 3-2			0.02	0.16	0.72	1.47	3.12	7.10	13.4	32	2.0×10^{-4}
NSRP 5-2			0.08	0.40	1.34	2.57	5.00	10.0	16.8	29	1.4×10^{-4}
NSRP 6			0.02	0.13	0.62	1.30	2.73	6.35	12.4	32	2.3×10^{-4}
5			0.05	0.25	0.74	1.22	2.00	3.33	4.46	14	3.4×10^{-4}
2			—	0.04	0.30	0.77	2.07	5.83	19.5	63	2.1×10^{-4}
3			0.01	0.07	0.35	0.73	1.86	3.73	6.45	71	2.9×10^{-4}
NSRP 1	2000	2.11	0.90	2.20	4.75	7.35	11.6	18.1	23.2	24	6.3×10^{-5}
NSRP 3-2			1.26	2.15	2.95	3.43	4.35	6.66	11.2	33	6.8×10^{-5}
NSRP 5-2			2.00	4.00	8.80	13.1	20.8	33.3	42.3	26	3.8×10^{-5}
NSRP 6			—	0.02	0.08	0.25	0.96	3.60	5.03	16	3.0×10^{-5}
5			0.70	1.60	3.30	4.80	7.00	—	10.4	15	9.0×10^{-5}
2			0.47	1.13	2.00	2.18	2.36	2.91	5.74	36	1.2×10^{-4}
3			—	0.08	0.50	1.15	2.70	3.85	6.70	65	2.3×10^{-4}
NSRP 1	2400	1.05	0.07	0.17	0.40	0.74	2.00	6.00	7.62	26	1.9×10^{-4}
NSRP 3-2			0.03	0.11	0.42	1.02	2.60	—	4.39	18	2.1×10^{-4}
NSRP 5-2			—	—	—	—	—	0.02	0.41	43	5.3×10^{-3}
NSRP 6			0.39	0.86	1.92	2.70	4.00	5.25	5.30	11	1.5×10^{-4}
5			2.15	—	—	—	—	—	3.15	4	1.6×10^{-5}
2			0.02	0.10	0.38	0.68	1.32	2.72	4.22	19	5.3×10^{-4}
3			—	0.01	0.08	0.20	0.50	1.30	3.09	86	1.0×10^{-3}

^aAll specimens were annealed for 2 hours at test temperature in hydrogen prior to testing.

^b0.050-cm-thick sheet specimens with 0.64-cm-wide by 2.54-cm-long gage section.

The lack of reproducibility of the creep-rupture characteristics for unalloyed tungsten from different vendor sources as well as sheets from the same source at 1600°, 2000°, and 2400°C is evident from the above results. This difference may be related to small amounts of impurities affecting the grain structure and size. Since the arc-cast material exhibits considerable grain growth with huge grains at 2000°C, impurities may be inhibiting grain growth for the wrought sintered material. Some of the sheets exhibited considerable duplexing at 2000°C and the level of impurities may be inhibiting the grain growth locally, while other areas of the same sheet, without impurities, exhibit huge grains.

W - 25Re - Evaluations of commercial W - 25Re sheet purchased from all known vendor sources in 1964 was continued.¹ Seven different lots of 0.05-cm-thick sheet material from five commercial producers plus in-house material are being evaluated. One vendor supplied both arc-cast and powder metallurgy sheet. Another vendor manufactured only arc-cast sheet with the remaining vendors producing powder metallurgy sheet. Each lot of material was given a number with the prefix EV (EV-1, EV-2 --- EV-8). Lots EV-1 and EV-3 are arc-cast material; all the other lots are powder metallurgy material.

Creep-rupture studies were initiated with tests being performed in hydrogen at 2000°C and 2.11 kg/mm² using tensile type specimens with the longitudinal axis in the major rolling direction. Prior to the application of the load to give the desired stress, the specimens were annealed at 2000°C for 2 hours in hydrogen. The results are given in Table 3.3 and Figures 3.6 and 3.7. The conventional strain versus time curves are shown in Figure 3.6. The curves show a wide variation in time for any particular strain

¹"High-Temperature Materials Program Progress Report No. 47, Part A," GE-NMPO, GEMP-47A, May 28, 1965, p. 61.

TABLE 3.3
 CREEP-RUPTURE RESULTS FOR W-25Re FROM VARIOUS VENDORS AT 2000°C
 AND 2.11 kg/mm² IN HYDROGEN^{a,b}

Vendor Source ^c	Time To Indicated Strain, hours								Rupture Strain, %	Linear Creep Rate, min. ⁻¹
	0.2%	0.5%	1%	2%	3%	5%	10%	Rupture		
EV-1	0.50	1.10	1.88	3.23	4.43	6.30	9.85	21.9	86	8.8×10^{-5}
EV-2	0.05	0.18	0.40	0.88	1.35	2.26	4.03	5.90	20	3.5×10^{-4}
EV-3	0.45	0.80	1.35	2.24	3.00	4.31	6.87	18.8 ^d	113 ^d	1.6×10^{-3}
EV-4	0.40	1.00	2.07	4.40	6.92	12.0	21.6	29.7	18	6.6×10^{-5}
EV-5	0.20	0.54	1.14	2.46	3.78	6.42	12.0	18.5	25	1.3×10^{-4}
EV-7	0.12	0.35	0.74	1.57	2.24	3.41	—	4.83	7	2.2×10^{-4}
EV-8	0.13	0.40	0.85	1.76	2.50	3.67	5.08	5.09	11	1.8×10^{-4}

^aAll specimens were annealed at 2000°C for 2 hours in hydrogen prior to test.

^b0.5-cm-thick sheet; 0.6-cm-wide by 2.54-cm-long gage length.

^cEV-1 and EV-3 arc-cast; all others powder metallurgy.

^dExtensive strain caused shutdown just prior to rupture.

Fig. 3.6 – Creep curves for 0.05-cm-thick W-25Re sheet from various vendors at 2000°C and 2.11 kg/mm² in hydrogen

Fig. 3.7 – Log-log plot of creep data for 0.05-cm-thick W – 25Re sheet from various vendors at 2000°C and 2.11 kg/mm² in hydrogen

value indicating no consistency of creep-rupture results for essentially the same alloy at the same test conditions. The arc-cast material (EV-1 and EV-3) showed more than 85 percent total strain at rupture with no evidence of secondary (linear) creep whereas the powder metallurgy material showed a maximum of 25 percent total strain and showed a detectable amount of first-stage creep.

The curves in Figure 3.7 are the same results presented on logarithmic coordinates. Except for the first few minutes of creep, all the powder metallurgy specimens exhibit a similar curve shape. Curves for the two arc-cast specimens are similar to each other but different from the powder metallurgy data. The significance of this difference between arc-cast and powder metallurgy material is not yet understood but metallurgical evaluations will be performed in an attempt to correlate the differences.

Figure 3.8 shows the specimens after test. The greater ductility at temperature of the arc-cast material (EV-1, EV-3) is obvious.

Creep Analysis Techniques

In recent reports^{2,3,4} it was indicated that first-stage creep data was being analyzed in terms of several different creep equation forms. Excellent results were achieved with

²Ibid., p. 34.

³"High-Temperature Materials Program Progress Report No. 49, Part A," GE-NMPO, GEMP-49A, July 28, 1965, p. 41.

⁴"High-Temperature Materials Program Progress Report No. 51, Part A," GE-NMPO, GEMP-51A, October 15, 1965, p. 68.

Fig. 3.8 – W – 25Re creep-rupture specimens fabricated from material from various sources tested at 2000°C and 2.11 kg/mm² in hydrogen (annealed 2 hours at 2000°C prior to test)

the Andrade one-third law equation, the parabolic creep law, a recently proposed⁵ hyperbolic sine creep equation, and third degree polynomials in $t^{1/2}$ and $t^{1/3}$. In equation form these are:

$$1 + \epsilon = \epsilon_0' (1 + \beta t^{1/3}) e^{kt} \quad (3.1)$$

$$\epsilon = \epsilon_0 + at^m \quad (3.2)$$

$$\epsilon = \epsilon_0 + a \sinh bt^{1/3} \quad (3.3)$$

$$\epsilon = a + bt^{1/2} + ct + dt^{3/2} \quad (3.4)$$

$$\epsilon = a + bt^{1/3} + ct^{2/3} + dt \quad (3.5)$$

It has been shown in the above studies that the data for lead⁶ at 14.5°C and recent GE-NMPO data for arc-cast tungsten at 2400°C can all be well represented by any of the above expressions although the best representation is, in general, afforded by the third degree polynomial in $t^{1/3}$.

During the present report period, these creep equations were employed in an analysis of some published first-stage creep data for nickel⁷ at 700°C. In each case the degree of representation, as expressed by the standard deviation, (μ), was found to be very good with the best fit, as expected, being obtained with the third degree polynomial in $t^{1/3}$. A summary of these results is presented in Figure 3.9 where the standard deviation

Fig. 3.9 – Comparison of how well various equation forms provide a fit for nickel data at 700°C

⁵J. B. Conway and M. J. Mullikin, "An Evaluation of Various First Stage Creep Equations," paper presented at AIME Meeting in Detroit, Michigan, October 1965.

⁶E. N. da C. Andrade, "On the Viscous Flow in Metals and Allied Phenomena," *Proceedings of the Royal Society*, Vol. 84, 1910, p. 1.

⁷E. R. Parker, "Modern Concepts of Flow and Fracture," *Transactions of American Society for Metals*, Vol. 50, 1958, p. 52.

(corrected for the number of creep equation constants) is plotted as a function of stress. At the lowest stress all equations give a very excellent fit and it is difficult to identify the expression which is most effective. At higher stresses, it is evident that the third degree polynomial in $t^{1/3}$ gives the best fit, although the third degree polynomial in $t^{1/2}$ and the parabolic equation yield excellent results. It can also be noted that the Andrade and the hyperbolic sine equations while somewhat less effective than the others still yield fairly acceptable correlations.

Similar analyses were made using data for Al, Pt, Ag, and Mo with the same type of results. All the equations used in these creep evaluations appear to be of fairly general utility in such representations of transient creep behavior. An example of the effectiveness of two of these equation forms is presented in Figure 3.10 for platinum data⁸ at 1350°K and 1.14 kg/mm².

A more detailed study of the Andrade and hyperbolic sine equation has led to the conclusion that better representations are obtainable with these expressions if the exponent on time is different from 1/3. One such result is shown in Table 3.4 from the analysis of the Andrade data for lead at 14.5°C.⁹ As can be seen, the sum of the squares of the residuals is found to decrease as the value of n in the $\beta t^{1/n}$ term of the Andrade equation is reduced below 3.0. At a value close to 2.7 the sum of the squares of the residuals reaches a minimum value indicating that a better representation of these particular data is obtained with the equation:

$$\ell = \ell_0 (1 + \beta t^{1/2.7}) e^{kt} \quad (3.6)$$

$$\ell = 39.266 (1 + 0.0118 t^{1/2.7}) e^{5.93 \times 10^{-5} t} \quad (3.7)$$

TABLE 3.4
EFFECT OF n IN $t^{1/n}$ TERM OF ANDRADE
EQUATION ON THE SUM OF THE SQUARES
OF THE RESIDUALS

n	ℓ_0	β	$k \times 10^5$	$\Sigma(R)^2$
3.1	39.1097	0.01516	7.63	3.57×10^{-3}
3.0	39.149	0.0143	7.27	2.37×10^{-3}
2.8	39.227	0.0126	6.42	7.69×10^{-4}
2.7	39.266	0.0118	5.93	5.22×10^{-4}
2.6	39.305	0.0109	5.38	7.61×10^{-4}
2.5	39.346	0.0101	4.79	1.59×10^{-3}

compared to the equation

$$\ell = 39.149 (1 + 0.0143 t^{1/3}) e^{7.27 \times 10^{-5} t} \quad (3.8)$$

using $n = 3$. Similarly, in the hyperbolic sine equation applied to these same lead data, a better representation is obtained when a term other than $t^{1/3}$ is employed. Computer studies have shown that the smallest value for the sum of the squares of the residuals is obtained when $n = 2.5$. In this case the best fit corresponds to:

$$\epsilon = 39.32 + 4.87 \sinh 0.085 t^{0.4} \quad (3.9)$$

compared to:

$$\epsilon = 39.149 + 3.16 \sinh 0.177 t^{1/3} \quad (3.10)$$

when $n = 3$ is employed. Since analyses of this type have not been very extensive as yet, the full significance of this characteristic cannot be stated. It would seem, however, that

⁸R. P. Carroker, Jr., "Plastic Flow of Platinum Wires," *Journal of Applied Physics*, Vol. 21, 1950, p. 1289.

⁹Andrade, loc. cit.

Fig. 3.10 – Platinum data at 1350°K and 1.14 kg/mm² analyzed in terms of the Andrade and hyperbolic sine equations

further studies are warranted and the effect of stress and temperature on the value of n should be evaluated in more detail.

Recently the Cottrell and Aytakin¹⁰ equation was added to the above list of creep equations employed in the analysis of strain – time behavior. This expression offers the possibility of being used in the analysis of transient creep or in the analysis of combined first- and second-stage creep data. Thus far the results obtained using this equation have been quite satisfactory and it appears to be very effective in providing accurate representation of creep behavior. For example, the summary of results given in Table 3.5 reveals that for the transient creep data for arc-cast tungsten at 2400°C and 0.46 kg/mm², the Cottrell-Aytakin equation yields as accurate a correlation as obtained with any other of the creep equations employed. It is seen to be just as effective in this case as the Andrade equation and the third degree polynomial in $t^{1/3}$. Also, as can be seen, this expression yields better results than the parabolic or hyperbolic sine expressions.

TABLE 3.5
A COMPARISON OF THE DEGREE OF REPRESENTATION AFFORDED BY
VARIOUS CREEP EQUATIONS FOR THE DATA FOR ARC-CAST TUNGSTEN
AT 2400°C AND 0.46 kg/mm²

		$\mu \times 10^4$
Andrade	$1 + \epsilon = 1.0007 (1 + 1.024 \times 10^{-3} t^{1/3}) 3.315 \times 10^{-5} t$	1.18
Hyperbolic Sine	$\epsilon = 5.23 \times 10^{-4} + 3.15 \times 10^{-3} \sinh 0.363 t^{1/3}$	1.27
Parabolic	$\epsilon = 1.5 \times 10^{-3} + 3.52 \times 10^{-4} t^{0.66}$	1.36
Third Degree – $t^{1/3}$	$\epsilon = 8.88 \times 10^{-4} + 7.67 \times 10^{-4} t^{1/3} + 8.44 \times 10^{-5} t^{2/3} + 2.52 \times 10^{-5} t$	1.19
Cottrell-Aytakin	$\epsilon = 6.9 \times 10^{-4} + 3.37 \times 10^{-5} t + 1.01 \times 10^{-3} t^{1/3}$	1.18

Analyses were initiated to evaluate various expressions capable of describing the strain – time behavior for combined first- and second-stage creep data. From the previous creep studies, the Cottrell-Aytakin equation and the third degree polynomial in $t^{1/3}$ both appear to possess this capability and have been included in this evaluation. Also the same capability is offered by the Garofalo¹¹ equation and hence a computer program has been written to permit calculation of the creep equation constants for this particular case. Since some preliminary analyses indicated that the Andrade equation might also be effective in this type of representation it too was included in this analysis. While the Andrade equation never really exhibits an exactly linear strain – time relationship, the slope changes beyond the transient region are so gradual that the representation of combined first- and second-stage creep data is a distinct possibility. To date, only the data for arc-cast tungsten have been analyzed but the results seem to be very encouraging. A summary of these results is presented in Tables 3.6 through 3.9 where the least squares creep equation constants are given along with the values for the standard deviation (μ), and t_{II} , the time to the end of the second stage of creep. In general, the correlations are seen to be excellent as evidenced by the low values of the standard deviation. It can also be concluded that the best representations of these data for arc-cast tungsten are afforded by the third degree polynomial in $t^{1/3}$. Also, for the purpose of expressing first- and

¹⁰A. H. Cottrell and V. Aytakin, "Andrade's Creep Law and the Flow of Zinc Crystals," *Nature*, Vol. 160, 1947, p. 328.

¹¹F. Garofalo, C. Richmond, W. F. Domis, and F. von Demmingen, "Strain-Time, Rate-Stress and Rate-Temperature Relations During Large Deformations in Creep," Joint International Conference on Creep, Book (I), Paper 30. 1963, p. 31.

TABLE 3.6

SUMMARY OF LEAST SQUARES CREEP EQUATION CONSTANTS FOR
ARC-CAST TUNGSTEN DATA AT 2200° TO 2800°C ANALYZED IN TERMS
OF THE COTTRELL-AYTEKIN EQUATION ($\epsilon = a + bt + ct^{1/3}$)

Temperature, °C	Stress, kg/mm ²	t_{II} , min	$a \times 10^4$	$b \times 10^5$	$c \times 10^4$	$\mu \times 10^4$
2200	0.70	3558	4.61	1.37	7.69	2.26
	0.84	2112	9.09	2.67	12.0	2.36
	1.05	609.0	8.69	7.62	26.3	4.18
	1.27	108.0	13.6	15.9	42.9	2.04
	1.41	180.0	44.8	31.6	51.3	4.01
2400	0.46	2124	6.65	2.81	11.0	2.99
	0.56	714	3.61	5.42	19.7	1.91
	0.70	370.8	22.8	17.2	26.4	3.77
	0.84	195	24.7	33.8	44.8	5.34
	1.05	84	55.6	86.2	61.5	5.69
2600	0.28	2880	3.53	3.57	8.59	4.07
	0.35	684	1.40	9.68	17.1	4.72
	0.46	180	-1.06	21.0	31.4	2.51
	0.56	144	57.1	77.4	40.0	7.17
	0.84	12	158	475	61.2	6.26
2800	0.18	3120	-24.0	1.04	16.9	17.1
	0.21	1326	-14.2	3.99	21.5	4.67
	0.28	261	2.32	19.0	41.2	3.75
	0.35	72	64.2	67.6	48.9	4.89

TABLE 3.7

SUMMARY OF LEAST SQUARES CREEP EQUATION CONSTANTS FOR ARC-CAST TUNGSTEN
DATA AT 2200° TO 2800°C ANALYZED IN TERMS OF THIRD DEGREE POLYNOMIAL IN $t^{1/3}$
($\epsilon = a + bt^{1/3} + ct^{2/3} + dt$)

Temperature, °C	Stress, kg/mm ²	t_{II} , min	$a \times 10^4$	$b \times 10^3$	$c \times 10^5$	$d \times 10^5$	$\mu \times 10^4$
2200	0.70	3558	-2.25	1.17	-5.57	1.59	1.82
	0.84	2112	5.26	1.47	-4.53	2.89	2.26
	1.05	609.0	-4.92	3.88	-29.7	9.65	3.77
	1.27	108.0	18.9	3.55	29.3	12.4	2.03
	1.41	180.0	21.8	7.88	-94.2	41.1	3.25
2400	0.46	2124	2.80	1.36	-4.40	3.02	2.92
	0.56	714	6.28	1.70	6.54	4.98	1.88
	0.70	370.8	5.24	4.55	-55.6	21.9	2.67
	0.84	195	-11.6	8.89	-150	48.8	3.42
	1.05	84	-17.0	16.6	-443	143	2.78
2600	0.28	2880	-6.17	1.47	-9.42	3.98	3.55
	0.35	684	-23.0	3.95	-54.6	13.5	2.62
	0.46	180	6.71	2.23	30.3	18.0	2.44
	0.56	144	1.97	11.3	-266	106	4.08
	0.84	12	34.2	32.9	-1825	868	5.29
2800	0.18	3120	36.9	(-4.10×10^{-5})	(2.54×10^{-4})	(-2.28×10^{-8})	16.0
	0.21	1326	-9.42	1.78	7.37	3.58	4.63
	0.28	261	-24.7	7.17	-95.7	27.8	2.10
	0.35	72	3.89	14.0	-401	121	2.18

TABLE 3.8

SUMMARY OF LEAST SQUARES CREEP EQUATION CONSTANTS FOR ARC-CAST
TUNGSTEN DATA AT 2200° TO 2800°C ANALYZED IN TERMS OF THE
GAROFALO EQUATION [$\epsilon = \epsilon_0 + \epsilon_t (1 - e^{-rt}) + \dot{\epsilon}_s t$]

Temperature, °C	Stress, kg/mm ²	t_{II} , min	$\epsilon_0 \times 10^3$	$\epsilon_t \times 10^3$	$r \times 10^3$	$\dot{\epsilon}_s \times 10^5$	$\mu \times 10^4$
2200	0.70	3558	1.68	4.61	6.96	1.5	2.56
	0.84	2112	2.67	5.68	10.3	3.1	3.27
	1.05	609.0	3.60	8.54	29.3	0.5	3.89
	1.27	108.0	5.13	7.56	93.2	24.6	3.16
	1.41	180.0	8.70	10.4	89.5	40.0	4.04
2400	0.46	2124	2.06	5.15	12.6	3.2	3.66
	0.56	714	2.62	6.93	21.0	6.6	3.02
	0.70	370.8	4.67	6.79	56.2	20.1	3.99
	0.84	195	5.74	9.35	102	41.2	4.31
	1.05	84	8.21	9.95	291	105	4.24
2600	0.28	2880	1.52	4.56	9.27	3.8	3.49
	0.35	684	1.51	5.35	44.3	11.0	2.61
	0.46	180	3.33	6.74	48.3	25.3	3.34
	0.56	144	7.33	8.44	194	85.6	3.46
	0.84	12	17.7	5.71	1012	531	5.38
2800	0.18	3120	1.11	12.6	2.44	1.3	16.3
	0.21	1326	1.74	9.42	10.4	4.9	4.06
	0.28	261	3.67	9.25	77.6	24.7	3.01
	0.35	72	8.57	7.51	313	83.9	2.63

TABLE 3.9

SUMMARY OF LEAST SQUARES CREEP EQUATION CONSTANTS FOR
ARC-CAST TUNGSTEN DATA AT 2200° TO 2800°C ANALYZED IN
TERMS OF ANDRADE EQUATION [$1 + \epsilon = \epsilon_0' (1 + \beta t^{1/3}) e^{kt}$]

Temperature, °C	Stress, kg/mm ²	t_{II} , min	ϵ_0'	$\beta \times 10^3$	k	$\mu \times 10^4$
2200	0.70	3558	1.00	0.829	1.30×10^{-5}	1.90
	0.84	2112	1.00	1.29	2.52×10^{-5}	2.18
	1.05	609.0	1.00	2.75	7.17×10^{-5}	3.78
	1.27	108.0	1.00	4.32	1.53×10^{-4}	2.07
	1.41	180.0	1.004	5.45	2.90×10^{-4}	3.38
2400	0.46	2124	1.00	1.20	2.65×10^{-5}	2.98
	0.56	714	1.00	2.04	5.17×10^{-5}	1.99
	0.70	370.8	1.00	2.85	1.61×10^{-4}	2.94
	0.84	195	1.00	4.72	3.14×10^{-4}	4.14
	1.05	84	1.00	6.70	7.88×10^{-4}	4.90
2600	0.28	2880	1.00	1.09	3.28×10^{-5}	2.95
	0.35	684	1.00	1.88	9.11×10^{-5}	3.78
	0.46	180	1.00	3.26	2.00×10^{-4}	2.61
	0.56	144	1.00	5.00	6.92×10^{-4}	4.60
	0.84	12	1.01	7.40	4.33×10^{-3}	5.81
2800	0.18	3120	0.998	1.72	9.91×10^{-6}	17.3
	0.21	1326	0.998	2.26	3.75×10^{-5}	4.69
	0.28	261	1.00	4.31	1.78×10^{-4}	3.15
	0.35	72	1.01	5.24	6.29×10^{-4}	4.40

second-stage creep data by means of a single equation, the Andrade equation is seen to be just slightly inferior to the third degree polynomial in $t^{1/3}$, definitely better than the Cottrell-Aytenkin equation, and slightly superior to the Garofalo equation. This is a surprising result in view of what has been said above about the Andrade equation.

Illustrations of the excellence of the representations obtained with these equations are presented in Figure 3.11 for the arc-cast tungsten data at 2400°C and 0.56 kg/mm².

In a previously reported¹² analysis of the arc-cast tungsten data at 2400°C and 0.84 kg/mm², an equation of the form:

$$e = f + gt - h e^{-pt} \quad (3.11)$$

was proposed. It can be noted that this equation is quite similar to the Garofalo equation and hence, in view of the results shown in Table 3.8, this type of equation is to be expected in this particular case.

Tensile Strength

W – 25Re – 30Mo – Very little property data are presently available for the relatively new W-Re-Mo alloys. To help fill this void, the tensile strength of wrought powder metallurgy W – 25Re – 30Mo (at. %) was determined from room temperature to 1600°C. The results are given in Table 3.10 and Figure 3.12. Material extruded in rod form and ground to 0.32 cm diameter was tested in air at room temperature, 200°C, and 430°C in the as-extruded condition and after an anneal at 1450°C for 0.5 hour. As seen in Table 3.10, the ultimate and yield strengths for the two groups of tests were essentially the same.

TABLE 3.10
TENSILE STRENGTH OF POWDER METALLURGY W – 25Re – 30Mo

Form	Test Temperature, °C	Anneal		Ultimate Strength, kg/mm ²	Yield Strength (0.2% Offset), kg/mm ²	Rupture Elongation, ^a %
		Temperature, °C	Time, hr			
0.32-cm-dia rod ^b	RT	–	–	133.6	116.7	7
	RT	–	–	125.8	116.7	–
	200	–	–	111.8	92.5	19
	200	–	–	113.2	99.0	17
	430	–	–	96.3	73.5	17
	RT	1450	0.5	137.8	119.5	18
	200	1450	0.5	113.9	93.5	22
	430	1450	0.5	96.3	75.8	20
0.03-cm-thick sheet ^c	1000	1000	0.3	66.1	42.6 ^d	13
	1200	1200	0.3	49.7	42.7 ^d	19
	1400	1400	0.3	38.1	33.0 ^d	25
	1600	1600	0.3	16.4	13.0 ^d	12

^a2.54-cm gage length.

^bTested in air.

^cTested in H₂.

^dBased on total load train strain.

Tensile tests of W – 25Re – 30Mo from 1000°C to 1600°C were performed using specimens fabricated from 0.03-cm-thick sheet. The results of these tests are also given in Table 3.10 and Figure 3.12. The data appear to be consistent over the temperature range.

WORK PLANNED FOR NEXT PERIOD

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

¹²“High-Temperature Materials Program Progress Report No. 47, Part A,” GE-NMPO, GEMP-47A. May 28, 1965, p. 45.

Fig. 3.11 – Comparison showing excellent agreement between experimental creep data for arc-cast tungsten at 2400°C and 0.56 kg/mm² and calculated creep curves

Investigations of equation forms for describing the combined first and second stages of creep will be continued.

Additional creep tests of arc-cast tungsten will be performed in an attempt to determine the apparent activation energy for creep from 1600° to 2000°C.

Fig. 3.12 – Tensile strength of W – 25Re – 30Mo

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 reactor and reactor experiments.

DEVELOPMENT OF A THERMOCOUPLE SYSTEM FOR A CARBONACEOUS ENVIRONMENT

The proper selection of materials for a thermocouple to be used in carbonaceous environments becomes more difficult as the temperature increases. Carbon diffusion into the thermocouple can alter or destroy the electrical insulation and change the thermoelectric properties of the thermoelements. An investigation was made to identify sheathing materials which would provide the needed protection to HfO_2 -insulated W versus W - 25Re thermoelements. Previous work¹ on high-temperature electrical insulating materials had shown HfO_2 to be the best available material for electrical insulation at temperatures above the melting point of BeO. However, the good electrical insulation characteristics of HfO_2 can be rapidly destroyed if it becomes carburized.

In the search for a suitable sheathing material, various refractory metals and alloys were exposed to temperatures of 2450°C while in contact with graphite in a hydrogen atmosphere. Small hermetically sealed capsules containing a small rod of HfO_2 were enclosed in graphite as shown in Figure 4.1. If the HfO_2 rod becomes carburized inside

Fig. 4.1 - Hermetically sealed W - 5Re capsule after exposure to graphite for 1 hour at 2450°C in hydrogen (Neg P65-8-11B)

¹"High-Temperature Materials Program Progress Report No. 49, Part A," GE-NMPO, GEMP-49A, July 28, 1965, p. 79.

the capsule during test to the extent that the outside surface becomes electrically conductive, the metal or alloy sheathing tested was not considered to be a sufficient carbon barrier to give adequate protection for thermocouple application.

The materials evaluated and the results of the tests are summarized in Table 4.1. Rhenium, W – 30Re – 30Mo, W – 25Re, and Mo all melted during the test and of course are not suitable as sheathing materials at the test temperature. Tantalum proved to be the only material tested that prevented the carburization of the encapsulated HfO_2 . The slow diffusion of carbon through the Ta may be due to carbide phases developed in the Ta between the inner and outer surfaces. Figure 4.2 shows the microstructure of the inner two-thirds of the 0.25-mm-thick wall of the Ta capsule after testing in a carbonaceous environment. Two zones are apparent, a center layer tentatively identified as a Ta phase high in oxygen content, and a lighter phase tentatively identified as an alloy of Hf and Ta. The source of oxygen in the Ta is believed to result from the partial dissociation of HfO_2 .

TABLE 4.1
EVALUATION OF SHEATH MATERIALS TESTED AT 2450°C IN H_2

Sheath Materials	Wall Thickness, mm	Diffusion of carbon through sheath of small capsule as determined by its effect on HfO_2 after 1 hr at 2450°C in hydrogen
W (Vapor deposited)	0.25	No melting, but outer surface of HfO_2 carburized.
W – 5Re	0.25	No melting, but outer surface of HfO_2 carburized.
Re	0.5	Melting observed at 2450°C – no melting at 2400°C. Outer surface of HfO_2 carburized in 2400°C test.
Os	1.5	No melting, but outer surface of HfO_2 carburized.
W – 30Re – 30Mo	0.25	Melted.
W – 25Re	0.50	Melted.
Mo	0.25	Melted.
Ta	0.25	No melting or carburization of the HfO_2 .
Ta	0.05	No melting or carburization of the HfO_2 .

The effectiveness of Ta as a carbon barrier was ascertained by assembling a W / W – 25Re thermocouple, insulated with HfO_2 and sheathed with Ta. The probe was surrounded by a graphite block along its length with a black-body hole in the carbon block near the thermocouple junction. Figure 4.3 shows the performance curve of the thermocouple during a test in H_2 at 2400° to 2450°C. The thermocouple output was stable over the 1-hour period at 2450°C indicating no degeneration of the thermocouple. The temperature as indicated by the thermocouple was somewhat lower than the optically measured temperature at high temperatures. This may be due to a partial loss of electrical signal from the thermoelements caused by a decrease in resistivity of the HfO_2 insulators. The only questionable condition of the thermocouple after test was a somewhat electrically conductive coating found on the outside surface of the HfO_2 , but not enough to cause shorting of the thermoelements.

REACTOR TESTING OF THERMOCOUPLES

Two reactor tests of W versus W-Re thermocouples are in process. In one test, two capsules, each containing 1.84 meters of 0.25 mm OD W and W – 25Re stranded wires

Fig. 4.2 – Photograph showing the inner 2/3 of a cross section of Ta capsule containing HfO_2 after exposure to a carbonaceous environment at 2450°C for 1 hour (Neg. 8858, 500X)

Fig. 4.3 – Performance of a Ta sheath and HfO_2 -insulated W versus W-25Re thermocouple in carbon and He and H_2

are now being irradiated in the ORR reactor. Both capsules have experienced one reactor cycle of radiation equivalent to approximately 7 weeks at 2×10^{14} nv thermal flux. One capsule will be removed after completing the current cycle. The second capsule will be exposed for an additional 3 cycles. After removal from the reactor, the thermocouple wires will be matched to similar unirradiated wires and the thermoelectric differences measured as a function of temperature.

A second reactor test has been designed and is scheduled to be started early in CY-66. During this test, the thermoelectric changes of the W versus W - 25Re thermocouple due to nuclear transmutation will be constantly measured. Temperature will be referenced to an unirradiated thermocouple which will be inserted into the neutron flux area occupied by the test thermocouples. By comparing the differences in thermoelectric outputs of the reference and the thermocouple that receives continued neutron bombardment changes in emf, signals due to nuclear transmutation can constantly be monitored as a function of neutron dosage.

WORK PLANNED FOR NEXT PERIOD

Efforts to raise the temperature limitations on thermocouple systems operating in a carbonaceous environment will be continued.

5. REFRACTORY-METAL ALLOY RESEARCH AND DEVELOPMENT

(57015)

The overall objective of this program is to advance the technology of refractory metals, to permit the 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.

ALLOY DEVELOPMENT

Two ternary systems, W-Re-Mo and Mo-W-Re are being investigated. The alloy system W-Re-Mo is of special interest because it contains a range of alloy compositions having useful ductility in combination with high melting points, resistance to hydrogen embrittlement, and good high-temperature strength. Ternary Mo-W-Re alloys with molybdenum rather than tungsten as the major constituent are being studied with the objective of producing ductile high-strength alloys with lower rhenium content than in presently available Mo-Re commercial compositions.

W-Re-Mo

The immediate objective of alloy development work on the W-Re-Mo system is to determine the minimum amount of rhenium needed to retain useful ductility and fabricability. The work consists of lowering the rhenium content in alloys containing 10, 20, and 30 percent molybdenum^{1,2} to values below the 25 to 30 percent rhenium level studied in the previous work.

Billet Working – The W-Re-Mo alloys evaluated were processed to 0.05-cm-thick sheet using the procedure developed for W – 25Re – 30Mo alloy (NMP-256). As shown in Figure 5.1, alloys containing 18 to 27 percent rhenium in the 10 percent molybdenum level showed a marked reduction in workability as the rhenium content was decreased. Similar losses in workability were observed at the 20 and 30 percent molybdenum levels. The decrease in workability was primarily evidenced by edge-cracking in the warm-rolling (200°C) operation.

Chemical Compositions – The chemical compositions of the W-Re-Mo alloys processed to 0.05-cm-thick sheet are given in Table 5.1. As shown in the table, the chemically determined impurities (C-H₂-O₂-N₂) within the new alloys are exceptionally low. These alloys, therefore, provide a basis for measuring the influence of impurity on properties such as ductility and high-temperature strength through comparisons of the present series with similar alloys of higher impurity content. The new alloy compositions are also intended to verify the better creep resistance previously noted for the W – 26Re – 10Mo and W – 27Re – 20Mo alloys.^{3,4}

¹"High-Temperature Materials Program Progress Report No. 51, Part A," GE-NMPO, GEMP-51A, September 30, 1965, pp. 49–50.

²All compositions in atomic percent unless otherwise noted.

³"High-Temperature Materials Program Progress Report No. 47, Part A," GE-NMPO, GEMP-47A, May 28, 1965, p. 77.

⁴"High-Temperature Materials Program Progress Report No. 49, Part A," GE-NMPO, GEMP-49A, Jul 28, 1965, p. 52.

Fig. 5.1—Effect of decreasing rhenium content in alloys with 10 percent molybdenum. Edges of the sheet cracked in rolling with losses of material increasing as the rhenium content was lowered (Neg. P65-9-13, 1/8X)

TABLE 5.1
CHEMICAL COMPOSITIONS OF W-Re-Mo ALLOYS

NMP Alloy Designation	Nominal Composition, at. %			Impurity Content, ^a ppm			
	W	Re	Mo	C	N ₂	O ₂	H ₂
182	72	18	10	6	0.2	5.8	0.3
202	70	20	10	5	0.5	18.0	0.2
222	68	22	10	5	0.1	4.6	0.4
242	66	24	10	4	0.4	8.0	0.5
262	64	26	10	9	0.1	4.5	0.5
272	63	27	10	<3	0.5	7.7	0.4
184	62	18	20	<3	0.2	8.0	0.3
204	60	20	20	<3	1.0	19.0	0.3
224	58	22	20	—	—	—	—
244	56	24	20	13	1.0	4.2	0.3
264	54	26	20	9	0.6	5.4	0.5
274	53	27	20	<3	0.2	7.8	1.0
176	53	17	30	15	—	—	1.0
196	51	19	30	—	—	—	—
216	49	21	30	<3	0.3	8.4	0.8
236	47	23	30	4	0.4	11.0	0.2
276	43	27	30	19	0.2	6.8	0.5

^aCarbon by chromatographic method; gaseous impurities by vacuum fusion analysis. Carbon values <3 could not be detected by this method of analysis.

Test Results — Room-temperature bend and Rockwell "A" hardness tests were conducted on the as-processed W-Re-Mo sheet, and on sheets held for 2, 10, and 100 hours at 1200^o, 1600^o, 2000^o, and 2400^oC. Bend test results are given in Table 5.2. In Figures 5.2a, b, and c, bend-test results after a 100-hour holding period are shown as a function of Re content; Figures 5.3a, b, and c show bend test results as a function of holding temperature. Several observations derived from the bend data appear useful as the basis for future work:

1. Holding for 100 hours at 1200^oC had no significant effect on the bend ductility of any of the alloys as would be expected since the alloys had been stress-relieved at 1400^oC prior to this lower temperature treatment.
2. In general, the ductility after 100 hours at 1600^o, 2000^o, and 2400^oC, temperatures above the 1400^oC stress-relieved temperature, is lowered regardless of molybdenum content. The loss of ductility is greater after the 1600^oC treatment with less ductility loss occurring at 2000^oC and 2400^oC.
3. In the series containing 10 and 20 percent molybdenum there are several alloys containing 24 or more percent Re which indicate good room temperature ductility after either the 2000^oC or 2400^oC 100-hour treatments.
4. Regardless of molybdenum content or holding time — temperature, the alloys show an increase in ductility with increasing rhenium content.

Because of the general interest in alloys suitable for service in the 1200^oC range, the ductility effect of additions of 30 percent molybdenum is considered noteworthy. Hardness values for specimens withstanding a 90-degree bend without fracture after holding for 100 hours at 1200^oC are identified in Table 5.3. The hardness values show no marked correlation between hardness and bend ductility. One additional observation of significance is the absence of changes in bend ductility and hardness with increased holding time for the majority of the alloys listed in Tables 5.2 and 5.3. This result indicates that the materials are probably stable at high temperatures, and will prove suitable for extended service life applica-

TABLE 5.2
ROOM-TEMPERATURE BEND-TEST RESULTS ON W-Re-Mo SHEET^a AFTER HOLDING AT 1200°, 1600°, 2000°, AND 2400°C

NMP Alloy Designation	Nominal Composition, at. % W Re Mo			As-Processed (1400°C-Stress- Relief)	Angle Of Bend To Fracture At 4T Bend Radius, degrees											
					Hours At 1200°C			Hours At 1600°C			Hours At 2000°C			Hours At 2400°C		
					In Hydrogen			In Hydrogen			In Hydrogen			In Hydrogen		
					2	10	100	2	10	100	2	10	100	2	10	100
182	72	18	10	15	15	15	20	5	5	10	15	15	10	5	5	5
202	70	20	10	15	20	15	15	15	10	15	15	15	15	15	15	10
222	68	22	10	30	40	40	40	15	20	15	20	25	20	25	15	35
242	66	24	10	90	90	90	90	40	40	30	35	35	30	30	40	40
262	64	26	10	40	35	30	30	45	40	30	40	60	40	40	40	70
272	63	27	10	20	20	20	20	50	50	25	60	80	90	50	55	30
184	62	18	20	20	50	20	30	10	10	10	10	10	10	15	15	15
204	60	20	20	20	20	15	20	10	10	10	10	10	10	10	10	20
224	58	22	20	—	—	—	—	—	—	—	—	—	—	—	—	—
244	56	24	20	50	50	30	50	20	30	25	25	30	35	25	25	80
264	54	26	20	60	30	30	40	40	25	30	35	50	40	40	50	60
274	53	27	20	60	30	60	90	40	45	35	40	75	50	45	55	65
176	53	17	30	20	10	20	10	15	10	15	20	15	20	15	20	20
196	51	19	30	—	—	—	—	—	—	—	—	—	—	—	—	—
216	49	21	30	90	40	90	90	15	15	15	15	15	20	20	15	25
236	47	23	30	90	40	90	90	20	25	35	20	30	25	15	20	30
276	43	27	30	90	90	90	90	45	35	55	50	50	55	45	45	50

^aAll sheet 0.05-cm-thick, using identical rolling procedures.

Alloys of constant 10 percent molybdenum content

Alloys of constant 20 percent molybdenum content

Alloys of constant 30 percent molybdenum content

Fig. 5.2—Influence of rhenium content on bend ductility of W-Re-Mo alloys held for 100 hours at 1200°, 1600°, 2000°, and 2400°C

Fig. 5.3 – Angle of bend to fracture on W-Re-Mo alloys after holding for 100 hours at 1200°, 1600°, 2000°, and 2400°C

TABLE 5.3

ROCKWELL "A" HARDNESS VALUES FOR W-Re-Mo ALLOYS AFTER HOLDING AT 1200°C, 1600°C, 2000°C, AND 2400°C^a

NMP Alloy Designation	Nominal Composition, at. %			As-Processed (1400°C-Stress-Relief)	Hours At 1200°C In Hydrogen			Hours At 1600°C In Hydrogen			Hours At 2000°C In Hydrogen			Hours At 2400°C In Hydrogen		
	W	Re	Mo		2	10	100	2	10	100	2	10	100	2	10	100
182	72	18	10	72.4	71.6	72.4	73.2	68.4	70.3	69.8	69.8	69.8	68.4	69.0	69.0	67.6
202	70	20	10	73.6	72.8	73.4	72.4	71.0	70.2	69.8	69.2	69.2	68.0	69.8	69.8	—
222	68	22	10	72.5	72.0	73.4	72.8	69.3	70.4	71.4	69.8	70.2	68.4	69.0	67.0	68.0
242	66	24	10	72.1	71.8	71.3	72.2 ^b	69.8	70.0	70.0	70.2	69.6	68.6	67.6	68.9	67.8
262	64	26	10	73.2	72.5	72.0	74.4	70.8	71.3	70.6	69.7	69.8	68.8	70.0	69.8	68.8
272	63	27	10	72.2	74.0	73.7	73.6	70.0	72.8	72.6	68.8	70.6	69.4	70.0	69.8	66.0
184	62	18	20	72.3	71.5	67.6	71.8	68.0	68.4	68.8	67.8	69.2	68.0	66.7	68.2	—
204	60	20	20	71.2	70.8	72.6	72.0	69.0	69.2	68.6	69.2	68.4	68.8	66.4	68.4	68.2
224	58	22	20	—	—	—	—	—	—	—	—	—	—	—	—	—
244	56	24	20	71.8	71.6	71.4	70.5	67.2	67.2	68.4	68.6	66.8	68.8	69.0	69.7	64.0
264	54	26	20	73.2	72.6	71.2	71.8	69.8	69.0	67.4	69.2	70.4	67.4	68.2	69.6	65.8
274	53	27	20	73.2	73.6	73.2	72.6 ^b	70.0	70.4	69.8	69.0	69.4	68.2	68.0	—	67.4
176	53	17	30	67.3	68.0	66.8	69.2	68.4	67.7	68.6	67.5	67.2	66.8	68.0	66.8	66.8
196	51	19	30	—	—	—	—	—	—	—	—	—	—	—	—	—
216	49	21	30	70.4	70.6	69.6	71.6 ^b	68.6	69.8	68.2	67.6	67.0	66.6	67.0	64.6	67.6
236	47	23	30	71.4	71.0	70.8	70.6 ^b	69.8	68.4	66.4	68.8	68.4	66.8	66.0	67.8	68.0
276	43	27	30	72.0	72.0	69.6	71.2 ^b	68.4	68.0	69.3	68.2	66.5	64.4	67.6	67.4	68.0

^aRockwell "A" Hardness is determined with a 60-kg load on a diamond brale compared to 150 kg for Rockwell "C" scale;

Rockwell value of 70 "A" approximates 39 "C," and 75 "A" is equivalent to 49 "C" scales. All tests on 0.05-cm-thick sheet.

^bHardness values for materials showing a 90° bend with fracture after holding 100 hours at 1200°C.

tions. Complete evaluation of these alloys must await results from creep-rupture tests requiring several months to obtain.

A metallographic examination was conducted on the bend-test specimens used to accumulate data shown in Table 5.2. Several major points of interest in this work were: (1) precipitants in relationship to composition, (2) grain size as a function of processing history, (3) grain size as a function of composition and holding temperature, and (4) comparison of newly completed materials versus older less pure materials. Materials available from work over the last two years were re-examined as a basis for detecting observable changes between compositions and/or purity levels for the recently prepared alloys.

As shown in Figure 5.4, the as-processed sheet (cold-worked + 1400°C stress-relief) showed a precipitation of W-Re-Mo sigma phase in the microstructure of the 26 and 27 percent rhenium alloys with 10 percent molybdenum content and the 27 percent rhenium with 20 percent molybdenum content. The tabulation of sigma phase occurrences in the alloys given in Table 5.4 confirms the effect of increasing molybdenum content in preventing the formation of sigma phase. Several non-positive observations of precipitants are noted as illustrated by the few scattered inclusions observed for the W - 26Re - 20Mo alloy shown in Figure 5.4. The alloys identified as containing precipitants are known to contain less than 9 ppm carbon content by chemical analysis.

Throughout the program, attention is being directed to obtaining high-purity alloys in terms of C-H₂-O₂-N₂ content because: (1) carbon is metallurgically recognized as a sigma-phase forming or promoting agent, and (2) all impurities are considered to contribute to loss of soundness (i. e., porosity) in welds. The influence of carbon content is shown in Figure 5.5 wherein a W - 27Re - 10Mo alloy containing 73 ppm carbon⁵ in the as-processed condition (1400°C stress-relief) is compared with a similar alloy with carbon content of <3 ppm. The higher carbon content alloy developed an excessive quantity of sigma phase constituent.

⁵"High-Temperature Materials Program Progress Report No. 47, Part A," GE NMPQ, GFMP-47A, May 28, 1965, Table 3.10, p. 78.

Fig. 5.4—Microstructure of W-Re-Mo alloys in as-processed condition, warm-rolled at 2000°C and stress-relieved at 1400°C, except as noted (as-polished, 150X)

TABLE 5.4
PRECIPITATED SIGMA PHASE OBSERVED IN W-Re-Mo ALLOYS

Nominal Composition, at. %	As- Processed ^a	Temperature At Which Specimen Was Held For 100 Hours In Hydrogen Atmosphere			
		1200°C	1600°C	2000°C	2400°C
W - 18Re - 10Mo	0	0	0	0	0
W - 20Re - 10Mo	0	0	0	0	0
W - 22Re - 10Mo	0	0	0	0	0
W - 24Re - 10Mo	T	0	0	0	0
W - 26Re - 10Mo	P	P	P	0	0
W - 27Re - 10Mo	P	P	P	0	0
W - 18Re - 20Mo	0	0	0	0	0
W - 20Re - 20Mo	0	0	0	0	0
W - 22Re - 20Mo	0	0	0	0	0
W - 24Re - 20Mo	0	0	0	0	0
W - 26Re - 20Mo	0	T	0	0	0
W - 27Re - 20Mo	0	P	P	0	0
W - 17Re - 30Mo	0	0	0	0	0
W - 19Re - 30Mo	0	0	0	0	0
W - 21Re - 30Mo	0	0	0	0	0
W - 23Re - 30Mo	0	0	0	0	0
W - 26Re - 30Mo	0	0	0	0	0
W - 27Re - 30Mo	0	0	0	0	0

^a0 = No precipitant

T = Trace or questionable precipitant

P = Definitely observed precipitant

<3 ppm carbon (Neg. 6579, 150X)

73 ppm carbon (Neg. 5531, 100X)

Fig. 5.5 - Microstructures of as-processed (warm-rolled and stress-relieved at 1400°C) W - 27Re - 10Mo alloy at low and high carbon levels (as-polished)

The precipitation of sigma phase in the high-rhenium content W-Re-Mo alloys is considered potentially beneficial. One obvious advantage of the presence of metallurgically controlled sigma phase, precipitated at moderate temperature, is to inhibit grain growth at high temperatures. However, carbon and/or other impurities are also believed to influence grain growth in W-Re-Mo alloys (powder metallurgy process alloys are usually fine-grained). For example, a W-26Re-10Mo alloy containing 9 ppm carbon was fine grained after holding for 100 hours at 2400°C, as shown in Figure 5.6 along with other alloys of this series, whereas a W-27Re-10Mo alloy of <3 ppm carbon showed excessive grain growth at 2400°C. The W-27Re-10Mo alloy (<3 ppm carbon) in the as-processed condition contained more sigma phase than the W-26Re-10Mo alloy with higher carbon content (Figure 5.5).

The W-25Re-30Mo and W-30Re-30Mo alloys selected for further development were the forerunners of the alloy series discussed above. Structures observed in these two alloys after holding at 1200°C, 1600°C, and 2000°C are shown for reference purposes in Figure 5.7. The structure of the W-25Re-30Mo is generally precipitant-free, and closely resembles the structure of W-25Re. In contrast, W-30Re-30Mo contains sigma phase unless heated above 1600°C. For comparison, W-30Re is also shown; this alloy tends to precipitate sigma phase in the temperature range above 1200°C.

Mo-W-Re

Chemical Composition – The objective of this work is to develop Mo-W-Re alloys with molybdenum as the major constituent. Two series of alloys of the Mo-W-Re type were processed to sheet. One series of alloys ranged in composition from 5 to 30Re content with a constant 15 percent tungsten; the other series was identical except that tungsten was present at a constant 30 percent level. The impurity content (C-H₂-O₂-N₂) determined for the alloys in the fully processed condition is given in Table 5.5.

TABLE 5.5
NOMINAL COMPOSITION AND IMPURITY CONTENT OF
Mo-W-Re ALLOYS FABRICATED TO
0.05-CM-THICK SHEET

NMP Alloy Number ^a	Nominal Composition, at. %			Impurity Content, ppm			
	Mo	W	Re	C	H ₂	O ₂	N ₂
4-13	65	15	20	30.0	0.1	15.0	0.7
5-12	60	15	25	11.0	0.1	12.0	0.4
6-11	55	15	30	7.2	0.5	15.0	1.0
3-11	55	30	15	25.0	0.5	4.1	0.2
4-10	50	30	20	6.6	0.1	13.0	1.0
5-09	45	30	25	16.0	0.2	10.0	0.6
6-08	40	30	30	19.0	0.1	5.8	0.8

^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.

Billet Fabrication – Hot-rolling experience with Mo-W-Re alloys was described previously to show no product yield from the alloys with 5, 10, or 15 percent rhenium content.⁶ Subsequently, the No. 3-11 alloy, Mo-30W-15Re, was hot-rolled by using light rolling reductions. This alloy and the Mo-15W-20Re and Mo-30W-20Re alloys were processed to 0.050-cm-thick sheet by warm-rolling from 425°C before each reduction.

⁶“High-Temperature Materials Program Progress Report No. 51, Part A,” GE-NMPO, GEMP-51A, September 30, 1965, p. 49.

W-18Re-20Mo, <3 ppm carbon
(Typical of W-26Re-20Mo and
W-27Re-20Mo)

W-20Re-20Mo, <3 ppm carbon
(Typical of W-22Re-20Mo)

Neg. 6578

W-26Re-10Mo, 9 ppm carbon
(Typical of lower Re alloys
to W-18Re-10Mo)

W-27Re-10Mo, <3 ppm carbon

Neg. 6570

Fig. 5.6 – Microstructures observed in W-Re-Mo alloys after 100 hours at 2400°C in hydrogen (as-polished, 150X)

A. W-30Re-30Mo, showing precipitation of sigma phase at 1200°C and 1600°C and solution of all precipitant at 2000°C

B. W-25Re-30Mo (Neg. 6587)

C. W-30Re (Neg. 6588)

Fig. 5.7 - Microstructures of W-25Re-30Mo, W-30Re-30Mo and W-30Re alloys after 100 hours at various temperatures (Murakami's etchant, 150X)

Also, the three alloys were stress-relieved at 1600°C (in vacuum) in comparison to 1400°C treatments for comparable alloys with 25 and 30 percent rhenium contents. The 25 and 30 percent rhenium content alloys were warm-rolled from 200°C. Cross sections of the finished sheet were examined metallographically; the observed structures are shown in Figure 5.8. The structures show that the 1600°C stress-relief treatment used for the alloys with 15 and 20 percent rhenium during cold-rolling was associated with grain coarsening in comparison to structures developed in materials processed with the 1400°C stress-relief. Also shown in Figure 5.8 are the structures, especially grain size, developed in the Mo-W-Re alloys during holding for 100 hours at 2400°C. Grain sizes are essentially not modified by the high-temperature treatment with the exception of grain coarsening developed in the Mo - 15W - 30Re alloy.

Test Results - Room-temperature bend tests were conducted on the 0.05-cm-thick sheet after processing which included a final 1400°C or 1600°C stress-relief treatment and following holding of specimens for 2, 10, and 100 hours at 1200°, 1600°, 2000°, and 2400°C in hydrogen. Bend-test results are given in Table 5.6. Several tentative conclusions derived from the bend-tests include:

1. At the 25 percent Re level, the Mo - 15W - 25Re and Mo - 30W - 25Re alloys withstand 90-degree temperature bend-tests following heating to 100 hours in the 1200° to 2400°C temperature range. These alloys are considered good subjects for property evaluation in the immediate future.
2. At the 30 percent rhenium level, the Mo - 15W - 30Re alloy showed good bend ductility after prolonged thermal treatment; whereas the Mo - 30W - 30Re alloy appeared to harden on holding in the 1200°C region. This reaction is in accord with precipitation of sigma phase as estimated from the W-Re-Mo phase diagram. This alloy may prove of interest as a creep-resistant material for service in the 1200°C temperature range by making use of the precipitation of sigma phase to strengthen the alloy.
3. Mo-W-Re alloys with less than 25 Re content were difficult to fabricate. As anticipated, the Mo - 15W - 20Re alloy (No. 4-13) was more ductile than the Mo - 30W - 20Re alloy (No. 4-10).

These alloys will require completion of creep tests for final evaluation.

Mo and Mo Alloys

The objective of this work is to establish processing procedures for producing weldable molybdenum and molybdenum alloys with useful room-temperature ductility after heating to high temperatures. Samples were prepared by powder metallurgy techniques which usually produce a product having a fine grain size after heating to high temperatures.

The early phases of this program disclosed that molybdenum powder compacts purified in wet hydrogen produced sheet in which welds were ductile and of fine grain size after heating to 2200°C.⁷ The welds, however, were not pore-free. Although a second purification treatment in wet hydrogen applied to rolled sheet gave some improvement in weld soundness,⁸ the welds still did not meet nuclear standards.

During this work period, unalloyed molybdenum was pressed into six compacts for rolling to sheet as shown in Figure 5.9, and a tube blank was processed to the shape shown in Figure 5.10. These green compacts and commercially produced powder metallurgy molybdenum sheet were purified by holding for 624 hours at 1000°C in a wet (dew-point 5°C) hydrogen atmosphere. The compacts were sintered at 2510°C in dry hydrogen following the purification treatment.

⁷"High-Temperature Materials Program Progress Report No. 49, Part A," GE-NMPO, GEMP-49A, July 28, 1965, p. 54.

⁸"High-Temperature Materials Program Progress Report No. 51, Part A," GE-NMPO, GEMP-51A, September 30, 1965, p. 53.

TABLE 5.6
ROOM-TEMPERATURE BEND TEST RESULTS FOR Mo-Re-W ALLOYS HELD AT 1200°, 1600°, 2000°, and 2400°C

NMP Alloy Number	Nominal Composition, at. %			Bend Results ^a Hot-Rolled To 0.10 cm Thick- ness, degrees	Bend Results ^b On Cold- Worked Sheet, degrees	Angle Of Bend To Fracture At 4T Bend Radius, degrees											
	Mo	Re	W			Hours at 1200°C In H ₂			Hours At 1600°C In H ₂			Hours At 2000°C In H ₂			Hours At 2400°C In H ₂		
						2	10	100	2	10	100	2	10	100	2	10	100
4-13	65	20	15	90	30	30	45	45	35	35	65	55	55	65	55	55	90
5-12	60	25	15	90	90	90	90	90	90	90	90	90	90	90	90	90	90
6-11	55	30	15	90	90	90	90	90	90	90	90	90	90	90	90	90	90
3-11	55	15	30	—	30	20	30	20	20	15	20	20	25	20	15	15	20
4-10	50	20	30	90	50	20	25	35	25	30	30	30	40	30	10	20	35
5-09	45	25	30	90	90	90	90	90	65	55	90	65	45	90	90	90	90
6-08	40	30	30	90	30	30	35	35	90	90	60	90	90	90	90	90	45

^aPreviously reported, "High-Temperature Materials Program Progress Report, No. 51, Part A," GE-NMPO, GEMP-51A, September 30, 1965, p. 51.

^bAlloys 4-13, 3-11, and 4-10 were stress-relieved at 1600°C in vacuum. Other compositions were stress-relieved at 1400°C in hydrogen.

Fig. 5.8 – Influence of thermal and working history on structures of Mo-W-Re alloys (as-polished, 150X)

Fig. 5.9 – Pressed and sintered compacts of purified molybdenum prior to working to sheet. The purification treatment consisted of holding the powder compact for 624 hours at 1000°C in wet hydrogen (dewpoint 5°C) prior to sintering at 2510°C in dry hydrogen (dewpoint -40°C). (Neg. P65-9-35)

Fig. 5.10 – Tube extrusion blank of purified molybdenum prepared as noted in Figure 5.9 (Neg. P65-9-36A)

Chemical analyses have been completed for impurities (C-H₂-O₂-N₂) in the compact treated for 624 hours (Specimen 15-1). These analyses also served as a check on material previously processed. The results of the analyses are given in Table 5.7. Several concluding factors that can be derived from the data are:

1. Wet hydrogen treatment lowers the carbon content of either rolled sheet or pressed powder compacts. For example, Specimen No. 1, which was not purified, had 23 ppm of carbon whereas Specimen No. 1, treated for 624 hours at 1000°C, shows a carbon level of only 12 ppm. In each of the remaining specimens (1a, 1b, 4, and M-7) the purification treatment also markedly reduced the carbon content.

TABLE 5.7
IMPURITY CONTENT OF UNALLOYED Mo AND Mo - 5Re ALLOY SHEET

Specimen Designation	Nominal Composition	Purification Treatment	Objective Of Chemical Analysis	Impurity Content, ppm			
				C	H ₂	O ₂	N ₂
1	Unalloyed Mo	None	Basic material	23.0	5.0	13.0	0.3
1a	Unalloyed Mo	324 hours at 1000°C in wet H ₂ ^a prior to sintering at 2510°C in dry H ₂	Purified Mo	20.0	0.1	54.0	0.3
1a-1	Unalloyed Mo	As 1a	Check on 1a analysis		1.0	118.0	0.4
1a-p	Unalloyed Mo	As 1a plus an additional 342 hours in wet H ₂ at 1450°C ^a	Doubly purified Mo	9.0	2.0	25.0	0.9
1b	Unalloyed Mo	324 hours at 1000°C in wet H ₂ ^a prior to sintering at 2510°C in dry H ₂	Purified Mo	13.0	49.0	119.0	0.2
1b-1	Unalloyed Mo	As 1b	Check on 1b analysis		0.2	105.0	0.4
1b-p	Unalloyed Mo	As 1b plus an additional 342 hours in wet H ₂ at 1450°C ^a	Doubly purified Mo	10.0	2.0	33.0	0.3
4	Mo - 5Re	324 hours at 1000°C in wet H ₂ ^a prior to sintering at 2510°C in dry H ₂	Purified Mo - 5Re	21.0	2.0	26.0	0.1
4-1	Mo - 5Re	As 4	Check on 4 analysis		0.8	26.0	3.0
4-p	Mo - 5Re	As 4 plus an additional 342 hours in wet H ₂ at 1450°C ^a	Doubly purified Mo - 5Re	13.0	9.0	19.0	0.3
M-7	Unalloyed Mo	Commercial sintered process sheet	As-received analysis	42.0	8.0	237.0	11.0
M-7a	Unalloyed Mo	As M-7 plus 624 hours at 1000°C in wet H ₂ ^a	Purification of M-7 sheet	9.0	6.0	108.0	45.0
15-1	Unalloyed Mo	624 hours at 1000°C in wet H ₂ ^a prior to sintering at 2510°C in dry H ₂	Purification of Mo compact	12.0	4.0	46.0	5.0

^aAll wet hydrogen treatments conducted in atmosphere of 5°C dewpoint.

2. The oxygen level of all specimens is higher than desired. A modification of the present treatment is planned to reduce oxygen in these materials. The present high oxygen level may be due either to solubility equilibria between the wet hydrogen and molybdenum or to entrapped oxygen. One possible reason for the high oxygen content was suggested by metallographic examination of a treated and sintered molybdenum compact. As shown in Figure 5.11, small voids believed to be nonrepresentative of the usual sintering voids were observed. These voids may contain entrapped molybdenum oxide.
3. Repeat analyses for C, H₂, O₂, and N₂ show discrepancies in the H₂ and O₂ contents which have not been resolved.

A simulated weld was used to observe weld porosity while avoiding contamination due to edge preparation prior to welding. As anticipated, in view of the high oxygen content of the treated molybdenum sheet, a definite porosity in electron-beam welds was observed. The simulated weld test pieces were subjected to a room-temperature bend (4T bend radius) transverse to the weld direction. Approximately 90 degrees of bend was required to crack the weld in each test piece representing treated material except the commercially produced M-7a sheet in which a 15-degree bend fractured the weld.

FABRICATION PROCESS DEVELOPMENT

Techniques for fabricating promising refractory-metal alloys are being developed concurrently with the alloy development program discussed above. In practice, the development program resolves into a series of trial runs aimed at establishing a suitable sequence of production parameters for each material.

Fig. 5.11 – Cross section of unalloyed molybdenum compact treated for 624 hours at 1000°C in wet hydrogen (dewpoint 5°C) before sintering at 2510°C in dry hydrogen. The small voids are not considered representative of the usual sintering void, and may contain entrapped molybdenum oxide. Light circles are outlines of molybdenum grains differing in orientation from matrix material. (Neg. 6567, 100X, Murakami's etchant)

Sheet Rolling

As shown in Figure 5.12, W – 25Re – 30Mo (NMP-256) sheet, 0.05-cm-thick by 9-cm-wide by 33-cm-long per sheet, was processed. The product will be applied on Job 57004, "Effect of Radiation on Refractory Metals and Alloys." Inspection of this sheet is not complete, but the impurity level is expected to approximate values shown in Table 5.1 for similarly processed W-Re-Mo alloys.

Tube Processing

Following extrusion of a large tube blank of W-Re-Mo alloy, a secondary hot-reduction by hot-rolling, hot-swaging, or secondary extrusion is required before drawing to small tubes. The secondary extrusion process prevents atmospheric contamination of the work piece which is protected by a sacrificial molybdenum container or billet. However, the length of rod or tube processed in a normal secondary extrusion is limited to a length of about 22 cm. A cluster or multiple extrusion technique is now being studied that will permit seven tubes to be processed in a single re-extrusion. As shown in Figure 5.13, tubes from several primary extrusions are prepared by machining the molybdenum container material to size. All sacrificial molybdenum core filler from the primary extrusion is left intact. Three tube blanks shown in Figure 5.13 contain small tungsten markers inserted in one end for identification after processing. The same tube blanks are shown positioned in an extrusion container in Figure 5.14, and the closure plugs for the billet assembly are shown in Figure 5.15.

Following secondary extrusion or other hot-working, the W-Re-Mo tubing is drawn using three to six reductions while heated to 425°C. This sequence appears useful in avoiding losses due to dimensional irregularities of the tubes in the initial drawing. Subsequently,

Fig. 5.12 - W-25Re-30Mo sheet equivalent to 1860 cm^2 of 0.05-cm-thick by 9-cm-wide by 33-cm-long processed for radiation effect studies (Neg. P65-10-11B, 1/5X)

Fig. 5.13 - W-Re-Mo tubes machined in primary extrusion form with molybdenum core and outer container material retained. Note tungsten marker rods inserted in three pieces on left. (Neg. P65-10-5C)

Fig. 5.14 – Cluster extrusion assembly showing tube positions prior to secondary extrusion (Neg. P65-10-5D)

Fig. 5.15 – Cluster extrusion container with threaded closure plugs. All material shown is molybdenum. (Neg. P65-10-5E)

all drawing is conducted with the tube blank heated to 200°C and retaining the molybdenum core filler material. Tubes prepared for use in test assemblies are shown in Figure 5.16. Each of the longer tubes will make one assembly with one spare part. Finishing of the tubes is awaiting selection of finishing procedures. One finishing operation consists of acid leaching to remove this core, and finishing by honing the interior to final size. This operation is followed by centerless grinding to remove excessive wall thickness.

Fig. 5.16 - W - 25Re - 30Mo tube prepared for evaluation in test assemblies. The longer tubes will make one assembly with one spare part. (Neg. P65-10-9)

Tube drawing techniques for drawing are established for W - 25Re - 30Mo alloy. In the immediate future, the techniques will be adapted to W - 30Re - 30Mo alloy.

In continuation of work on W - 5Re alloy tubing discussed in the preceding report,⁹ a tube of this material has been successfully drawn to 0.244 cm by 71 cm finished length, with a wall thickness of 0.25 cm. The starting material for the drawing of W - 5Re consisted of a re-extrusion conducted at 1950°C using a molybdenum container. The small final extrusion is shown in Figure 5.17.

Fig. 5.17 - Product of a secondary extrusion of W - 5Re alloy. After removing the "dog-bone," the material was warm-drawn to finished size (Neg. P65-9-24B)

In accord with the program plans to support refractory-metal alloy applications of interest to the AEC, a W - 25Re alloy extrusion of a tube and a solid bar was completed. The product as forwarded to ORNL is shown in Figure 5.18.

⁹Ibid.

Fig. 5.18 – A W-25Re heavy-walled tube and rolled plates furnished to ORNL. Rolled plates were processed from a solid bar included with the tube blank in the primary extrusion. The plates will be machined to end closures for the finished containers.
(Neg. P65-9-44, 1/2X)

Tube drawing operations for W – 25Re – 30Mo alloy (NMP-256) have periodically encountered high working loads in the first drawing stages. These operations normally are conducted with the material warmed to 200°C in hot oil. Unfortunately, operational experience is insufficient to permit identification of variables affecting drawing loads. To establish an engineering basis for the drawing work, a W – 25Re – 30Mo extrusion was ground to tensile test specimens of the type shown in Figure 5.19. Tensile tests were conducted using a slow and a moderate cross-head speed at 20°, 200°, and 400°C in the as-machined condition of the test pieces. Also, three machined test pieces were stress-relieved at 1400°C for 20 minutes in hydrogen, before testing at 20°, 200°, and 400°C. Tensile test results are given in Table 5.8. The tensile test results show a drop of approximately 18 percent in yield and tensile strength in heating from 20° to 200°C, and 37 percent in heating from 20° to 400°C. However, the tensile ductility rose from 3.6/7.2 percent to over 17 percent in heating from 20° to 200°C on the as-machined test pieces. The post-machining stress-relief treatment did not significantly influence strength properties, but the room-temperature (20°C) tensile elongation was 18.4 percent showing a large ductility recovery due to the stress-relief treatment over the 3.6/7.2 percent elongation of as-machined test pieces.

TABLE 5.8
TENSILE TEST RESULTS FOR EXTRUDED W – 25Re – 30Mo ALLOY

Lab. No.	Test Temperature, °C	Yield Strength (0.2% Offset), psi	Tensile Strength, psi	Elongation, % in 2.54-cm gage length
1	20 ^b	166,000	190,000	7.2
2	20 ^a	166,000	179,000	3.6
7	20 ^c	170,000	196,000	18.4
4	200 ^b	140,800	161,000	17.3
3	200 ^a	131,600	159,000	19.0
6	200 ^c	133,000	162,200	22.3
5	400 ^b	104,600	137,000	16.6
8	400 ^c	107,800	137,000	20.1

^aAs-machined – cross-head speed 0.006 inch per minute in test.

^bAs-machined – cross-head speed 0.003 inch per minute in test.

^cMachined + 1400°C stress-relief: cross-head speed 0.003 inch per minute in test.

WORK PLANNED FOR NEXT PERIOD

The W-Re-Mo and Mo-W-Re alloys processed to sheet in this work period are being prepared for creep-rupture testing. Effort will be made to complete stress-rupture tests at 2200°C for one series of alloys.

Processing of six sheets of purified molybdenum will continue, and additional evaluation of improved molybdenum will be made. In parallel with the sheet work, the first tube extruded from purified molybdenum will be subjected to hot working and tube drawing experiments. A series of exploration treatments to obtain a more detailed knowledge of equilibria in the Mo-H₂-H₂O system relative to dissolved oxide will be completed. Most thermodynamic data available on the Mo-O system emphasize the kinetics of forming volatile molybdenum oxide, whereas the dissolved oxygen-dissolved carbon equilibria with a wet hydrogen atmosphere is considered of major practical importance in improving molybdenum.

Work will continue on development of tube, plate, and sheet processing techniques.

Fig. 5.19 – Tensile test pieces prepared from extruded NMP-256 alloy
(Neg. P65-9-14B, 8X)

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
GEMP-51, A and B	June 15, 1965 - August 15, 1965	September 30, 1965
GEMP-52, A and B	July 15, 1965 - September 15, 1965	October 20, 1965

ATOMIC PRODUCTS DIVISION

GENERAL ELECTRIC