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GEMP-270A

MASTER

Nuclear Materials & Propulsion Operation

THIRD ANNUAL REPORT -
HIGH-TEMPERATURE MATERIALS
AND REACTOR COMPONENT
DEVELOPMENT PROGRAMS

Volume I-Materials

February 28, 1964

ADVANCED TECHNOLOGY SERVICES

GENERAL ELECTRIC

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United States Atomic Energy Commission

Contract No. AT(40-1)-2847

**NUCLEAR MATERIALS and PROPULSION OPERATION
ADVANCED TECHNOLOGY SERVICES**

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PREFACE

This report, GEMP-270A, is one of three volumes comprising the third annual report on the High-Temperature Materials and Reactor Component Development Programs being conducted by the General Electric Nuclear Materials and Propulsion Operation under Contract No. AT (40-1)-2847 of the Atomic Energy Commission.

Volumes I (GEMP-270A) and II (GEMP-270B) report the progress made from January 1, 1963 to January 31, 1964 on the unclassified and classified portions, respectively, of the materials program, and Volume III (GEMP-270C) reports the progress on that part of the contract covering instrumentation and controls. Some of these programs were terminated at the end of Fiscal Year 1963, others are continuations of Fiscal Year 1963 programs, and still others were initiated in Fiscal Year 1964. The status of each program is indicated in the more detailed breakdown of each volume given below.

This report also replaces the thirty-second bimonthly report on Ceramics and Chemistry for the period from November 15, 1963 to January 15, 1964, and the thirty-third report on Metallurgy covering the period from December 15, 1963 to February 15, 1964 except the 15 days in February. The next Ceramics and Chemistry bimonthly report, the thirty-fourth, will cover the period from February 1, 1964 to March 15, 1964. The thirty-fifth report, on Metallurgy, will cover the period from February 1, 1964 to April 15, 1964.

GEMP-270A

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2. Effects of Radiation on High-Temperature Alloys (continuation)
3. Radiation Effects in BeO (continuation)
4. Fission Gas Diffusion in Unfueled Ceramic Materials (initiated FY-64)
5. Fission Product Transport Processes in Refractory-Metal Fuel Systems (initiated FY-64)
6. Internal Conversion Ceramic Fuel Element Research (initiated FY-64)

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GEMP-270C

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CONVERSION TABLE

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

INTRODUCTION AND SUMMARY

This report, GEMP-270A, is one of three volumes of the third annual progress report on the high-temperature materials investigations and reactor components work conducted by GE-NMPO during Calendar Year 1963 under Contract No. AT(40-1)-2847. This volume covers six unclassified materials development programs: 1. materials for use as fueled and nonfueled, high-temperature (1000° to 3000°C) reactor components; 2. radiation effects on the time-, temperature-, and stress-dependent properties of selected high-temperature alloys and refractory metals; 3. radiation effects in BeO as a function of composition, grain size, density, porosity, and irradiation temperature and dosage; 4. the diffusion of fission gases (Kr, Xe, and I atoms) in ceramic oxides subsequent to their injection via ion bombardment; 5. the fission product transport processes in refractory-metal fuel systems at temperatures exceeding 1700°C; and 6. the chemistry involved in the use of a fertile material (thoria) in stabilized-fuel - BeO systems, and the development of such systems as internal conversion fuel elements.

Significant results achieved in these programs are as follows:

Creep-rupture tests were performed on some of the refractory metals and alloys to 2800°C in hydrogen and argon atmospheres for 1 to 1000 hours. Certain trends are apparent in the results obtained: (1) arc-cast materials have more consistent and reproducible stress-rupture strengths and linear creep rates (second stage) for different sources of various materials than the same materials fabricated by the powder metallurgy processes; (2) powder metallurgy materials, on the other hand, have greater stress-rupture and creep strengths than do the arc-cast materials; (3) the grain size of arc-cast materials heated above 2000°C is large (500 to 900 microns) whereas the grain size of powder metallurgy materials is usually relatively fine, although a duplex structure may be present.

An improved processing and fabrication procedure for W - 25Re sheet was developed which results in a homogeneous, sigma-free structure. In comparison to the commercial sheet, material produced by this technique exhibits superior stress-rupture and ductility characteristics at 2600°C in hydrogen.

At reactor ambient temperature, irradiation of recrystallized tungsten to a fast neutron dose of 2.5 to 3.2×10^{19} nvt reduced the creep rate by a factor of 2 and increased the stress-rupture life at 1100°C by a factor of 2.6. The elongation and the reduction in area were not affected by irradiation. Cold-worked tungsten was less affected by irradiation; the creep rate was reduced by a factor of 1.6, while the rupture life was increased by the same factor. A 1900°C anneal of an irradiated cold-worked specimen in a hydrogen atmosphere did not completely remove the irradiation-induced hardening when compared to a similarly annealed control specimen. Annealing the recrystallized tungsten at 1400°C for 1 hour prior to testing did not affect second-stage creep, but did eliminate the anomalous creep behavior in the primary stage of creep. Creep-rupture properties of Mo and W - 25Re sheet specimens (fast neutron dosage of 7 to 8×10^{18} nvt) tested at 980°C and 1100°C, respectively, were not significantly affected, although there was a slight, consistent reduction of creep rate.

The rupture life of A-286 specimens, containing about 0.010 percent boron and irradiated to a fast neutron dose of 5×10^{19} nvt, was within 25 percent of the control data. Specimens having only 0.0008-percent boron concentration, however, was reduced 500 percent, apparently due to increasing, stress-enhanced grain growth with decreasing boron content.

Expansion was found to be the principal effect of irradiation in BeO. In low-temperature irradiations, the expansion is made up of expansion components from the lattice and from cracks which form at grain boundaries as a result of the greater expansion of the crystallographic c-axis than the a-axis. Both the lattice expansion and expansion resulting from grain boundary cracking increase with increasing dosage; the expansion from grain boundary cracking being 2 to 3 times larger than the lattice expansion at dosages of approximately 4 to 10×10^{20} nvt. Grain size influences the expansion by its effect on the dosage at which grain-boundary cracks occur. In elevated-temperature irradiations, the expansion is smaller the higher the temperature. For dosages up to 1.5 to 10^{21} nvt, it can be approximated by the relationship:

$$\frac{\Delta V}{V} \cong \frac{K}{A} [1 - \exp(-At)]$$

where $\Delta V/V$ is the percentage increase in volume exclusive of grain-boundary separation, K is the defect production rate, A is the annealing rate, and t is the time of irradiation. Strength, elastic constants, and the thermal expansion of BeO are essentially unchanged if grain-boundary cracks are avoided. Once cracks have formed, the strength changes are slightly less severe in specimens of small grain size.

1. HIGH-TEMPERATURE REACTOR MATERIALS FABRICATION RESEARCH

(57003)

The object of this program is to develop and evaluate methods of preparing and joining refractory metals and alloys and other high-temperature materials for use as fueled and non-fueled, high-temperature (1000° to 3000°C) reactor components.

Work conducted during CY-63 included an extension* of stress-rupture and creep studies of some refractory metals to 2800°C for 100 hours and a 1000-hour test of molybdenum in hydrogen at 2200°C. A W-Re alloy development program was also conducted. Because of patent considerations, the development of refractory-metal braze alloys for Ta- and W-base metals conducted under this job is described in section 2.1 of GEMP-270B.

1.1 STRESS-RUPTURE AND CREEP STUDIES

Stress-rupture and creep studies at elevated temperatures were made on commercial molybdenum, molybdenum-TZM, tantalum, tungsten, rhenium, and W - 25Re[†] including GE-NMPO-processed W - 25Re material. These materials were tested in the as-received condition in sheet form ranging in thickness from 0.02 to 0.05 centimeter. Tests were conducted in hydrogen and argon atmospheres.

Test Procedure and Equipment Modifications

The basic equipment and test procedure used for these tests were described previously.[‡] Tests conducted during Calendar Year 1963 utilized improved test equipment and a modified testing procedure. Necessity for modifying the test procedure was determined when different results were obtained for tantalum tested in hydrogen and in argon atmospheres. The modification consisted of heating the specimen to 1000°C in vacuum (~1 micron) for 10 minutes prior to further heating and testing. This outgassing reduced the amount of contamination to the tantalum test samples. No difference in the rupture life of other materials such as molybdenum, rhenium, and W - 25Re was observed after adopting this procedure.

Three major modifications were incorporated in the equipment to improve its capabilities. First, the tungsten rod heating element was replaced with a tungsten split-tube heating element, shown in Figure 1.1. The overall dimensions of the new element were the same as those of the previous element. This sheet-type heating element appears to have a life capability of 500 hours at 2800°C or of >2000 hours at 2200°C in hydrogen; the rod-type heating element was limited to approximately 100 hours at 2800°C. Distortion of the rod-type element affected temperature uniformity of the test specimen. The second equipment modification

*Prior studies were made at 2800°C for 1 and 10 hours, as described in "Second Annual Report--High-Temperature Materials and Reactor Component Development Programs, Volume I--Materials," GE-NMPO, GEMP-177A, February 28, 1963, p. 15.

[†]Unless otherwise specified, all compositions are given in weight percent.

[‡]Ibid., p. 26.

Fig. 1.1 – Tungsten split-tube heating element for 2800°C stress-rupture and creep studies after operation in excess of 2000 hours at 2200°C in hydrogen of which 100 hours was at 2800°C (Neg. P63-6-6)

provided a continuous automatic measurement of elongation versus time. Continuous automatic measurements were achieved by installing a sensitive differential transducer below the load train with the core of the transducer fastened to a rod attached to the load pan.* The third modification consisted of automating the power equipment to control test temperatures to 2800°C. With the furnace element voltage used as a sensor, any change in the voltage was detected by a controller, and voltage adjustments were made automatically; constant voltage at the heating element resulted in a constant temperature control.

Stress-Rupture and Creep Test Results

Molybdenum - Molybdenum was extensively tested at temperatures from 1200° to 2400°C in hydrogen and argon atmospheres. Five different sources of molybdenum sheet were evaluated: (1) Mo-A, a powder metallurgy material, 0.02 centimeter thick; (2) Mo-A', a powder metallurgy material, 0.05 centimeter thick; (3) Mo-B, an arc-cast material, 0.02 centimeter thick; (4) Mo-B', an arc-cast sheet material, 0.05 centimeter thick; and (5) Mo-C, an arc-cast sheet material, 0.04 centimeter thick.

Creep-rupture tests in both hydrogen and argon atmospheres were performed at 2200°C on material from each source. Figure 1.2 gives the stress-rupture results, and Figure 1.3 shows the creep rates. As indicated in the figures, stress-rupture and creep results were similar for the three sources of arc-cast materials, whereas the results for the powder metallurgy materials were different from each other as well as different from the arc-cast material. Powder metallurgy material Mo-A' had a greater rupture life and was more creep-resistant in hydrogen than in argon. It also had the highest 10-hour stress-rupture strength and the lowest creep rate of the molybdenum material tested.

Fig. 1.2—Stress-rupture data for molybdenum at 2200°C

* "High-Temperature Materials Program Progress Report No. 25, Part A," GE-NMPO, GEMP-25A, July 31, 1963, p.7.

Fig. 1.3—Stress versus creep rate for molybdenum at 2200°C

Metallographic examination of samples from each source of material tested at 2200°C showed that the arc-cast materials in all cases consisted of huge grains, 500 to 800 microns in size. The powder metallurgy material Mo-A' consisted of basically huge grains, 400 to 700 microns, for test times exceeding one-half hour at 2200°C. The grain size of the powder metallurgy material Mo-A was relatively fine, 35 to 50 microns, for all samples tested (up to 80 hours at 2200°C). Since the grain structure of Mo-A remained fine, the metallography of Mo-A (powder metallurgy) as well as Mo-B (arc-cast) was studied for comparison in an effort to identify the grain-growth inhibitor in Mo-A. High magnification visual studies* showed that Mo-A contained a dispersed second phase, whereas Mo-B was single phase. This dispersed phase in powder metallurgy Mo-A possibly inhibited grain growth.

Creep-rupture tests of the three sources of arc-cast molybdenum yielded consistent and reproducible results at 2200°C in both hydrogen and argon. Additional tests were performed to obtain stress-rupture data for this material at temperatures from 1200°C to 2400°C for test times up to 80 hours in hydrogen. The results are presented in Figures 1.4 and 1.5. The stress-rupture data for the arc-cast molybdenum was used to determine the Larson-Miller curve shown in Figure 1.6. The constant in the Larson-Miller equation was determined by using a computer program; the curve is a least squares fit of the data.

Test equipment modifications, previously described, provided the capability to test at 2000°C to 2800°C for extended times. Several tests were conducted on arc-cast molybdenum for periods of 100 to 1000 hours at 2200°C in hydrogen. The results are presented in Figures 1.7 and 1.8.

Molybdenum Alloy (TZM) - The molybdenum alloy, TZM, is a commercial arc-cast material (Mo - 0.5Ti - 0.1Zr) developed to improve the strength of molybdenum primarily in the 900°C to 1400°C temperature range and to increase the recrystallization

*"High-Temperature Materials Program Progress Report No. 23, Part A," GE-NMPO, GEMP-23A, May 31, 1963, pp. 7, 11.

Fig. 1.4—Creep-rupture curves for arc-cast molybdenum tested at 1200°, 1600°, and 1800°C in hydrogen

GE-NMPO

Fig. 1.5—Creep-rupture curves for arc-cast molybdenum tested at 2000°C, 2200°C, and 2400°C in hydrogen

GE-NMPO

Fig. 1.6—Larson-Miller parameter for arc-cast molybdenum tested in hydrogen and argon at 1200° to 2400°C

temperature. This alloy was creep-rupture tested at 2000°C and 2200°C in a hydrogen atmosphere. The material used was commercial, 0.05-centimeter-thick, arc-cast sheet and was in the recrystallized condition.* The test results are given in Figures 1.9 and 1.10. For comparison, curves previously developed for pure arc-cast molybdenum are also given. These data and data from the literature indicate that additions of titanium and zirconium to molybdenum have a strengthening effect up to about 2000°C, but the effect is negligible at 2200°C. Based on total elongations of the samples at rupture, TZM exhibits about the same ductility as arc-cast molybdenum at these temperatures.

Tantalum - Stress-rupture and creep data were obtained for two sources of arc-cast tantalum, Ta(1) and Ta(2), at 2400°C and 2600°C and for powder metallurgy tantalum, Ta(3), at 2600°C in both hydrogen and argon atmospheres.

The stress-rupture test results initially reported† for arc-cast tantalum provided reasonably consistent data when testing was conducted in a hydrogen atmosphere at 2600°C. Tests in an argon atmosphere at 2600°C provided inconsistent results. These inconsistencies led to an investigation‡ of the effect of impurities in the test atmospheres.

Additional stress-rupture tests were performed with a 0.013-centimeter-thick tantalum foil surrounding the test sample to reduce or eliminate contamination. Tantalum foil was

*"High-Temperature Materials Program Progress Report No. 29, Part A," GE-NMPO, GEMP-29A, November 29, 1963, p. 11.

†"High-Temperature Materials Program Progress Report No. 19, Part A," GE-NMPO, GEMP-19A, January 25, 1963, p. 18.

‡"High-Temperature Materials Program Progress Report No. 25, Part A," GE-NMPO, GEMP-25A, July 31, 1963, p. 12.

Fig. 1.7—Stress-rupture data for arc-cast molybdenum at 2200°C in hydrogen and argon

Fig. 1.8—Creep data for arc-cast molybdenum at 2200°C in hydrogen and argon

Fig. 1.9—Stress-rupture data for molybdenum-TZM and arc-cast molybdenum at 2000°C and 2200°C in hydrogen

Fig. 1.10—Stress versus creep rate for molybdenum-TZM and arc-cast molybdenum at 2000°C and 2200°C in hydrogen

also placed around the outside of the furnace heating element, including the top and bottom ends. In addition, the furnace including the test specimen was outgassed by heating it under vacuum to approximately 1100°C for 10 minutes prior to filling with the test gas. Using the foil and the outgassing procedure decreased the sample contamination during testing (primarily oxygen and nitrogen) considerably but did not completely eliminate it.* Figures 1.11 and 1.12 show the results obtained with the Ta(2) material. As shown, good agreement was obtained in both hydrogen and argon atmospheres at 2400°C and 2600°C.

Fig. 1.11 – Stress-rupture data for powder metallurgy and arc-cast tantalum sheet at 2400°C and 2600°C

Fig. 1.12 – Linear creep rate versus stress for tantalum sheet at 2400°C and 2600°C

* Ibid., p. 15.

Powder metallurgy material, Ta(3), was also tested in hydrogen and argon and the results are shown in Figures 1.11 and 1.12. The Ta(3) material is stronger than the arc-cast material. The Ta(3) also shows a variation in strength depending on test atmosphere. The microstructure of a powder metallurgy tantalum sample after 6.67 hours at 2600°C in a hydrogen atmosphere is shown in Figure 1.13, and Figure 1.14 shows an arc-cast sample after 1.32 hours at 2600°C in hydrogen.

Fig. 1.13 - Microstructure of powder metallurgy tantalum Ta(3) after 6.67 hours at 0.21 kg/mm² and 2600°C in hydrogen

Rhenium - Commercial 0.05-centimeter-thick rhenium sheet was creep-rupture tested at 2600°C. The powder metallurgy material, reportedly sintered at approximately 2400°C in vacuum for 8 hours, was of relatively high purity with 25 ppm of oxygen, 1 ppm of hydrogen, and 2 ppm of nitrogen. Creep-rupture tests were performed at 2600°C in both hydrogen and argon with the results shown in Figures 1.15 and 1.16. Figure 1.17 is a photomicrograph of the material after 7.5 hours at 2600°C and 1.0 kg/mm² in hydrogen. The grain size is equiaxed and relatively fine (approximately 100 microns). Numerous voids are shown in conjunction with grain boundary separations.

Tungsten - Two sources, W(1) and W(2), of high-purity powder metallurgy tungsten were stress-rupture and creep tested at 1600°, 2200°, 2400°, and 2800°C in both hydrogen and argon atmospheres.*† No apparent contamination occurred during testing. The test results are shown in Figure 1.18. The data show that similar results are obtained in hydrogen and argon atmospheres at 2800°C for each material, but the results for each material, W(1) and W(2), differ. These results are similar to the stress-rupture results obtained with powder metallurgy molybdenum from different sources. The differences are probably related to the raw material processing variables employed by the vendors. The linear creep rate (second-stage creep) results also showed a difference between W(1) and W(2) at 2800°C, as indicated in Figure 1.19.

*"High-Temperature Materials Program Progress Report No. 23, Part A," GE-NMPO, GEMP-23A, May 31, 1963, p. 10.

†"High-Temperature Materials Program Progress Report No. 29, Part A," GE-NMPO, GEMP-29A, July 31, 1963, p. 19.

Neg. 3178

ETCHED
ELONGATION, 77.0%

100 X

Fig. 1.14—Microstructure of arc-cast tantalum Ta(2) after 1.32 hours at 0.14 kg/mm^2 and 2600°C in hydrogen

Fig. 1.15—Stress-rupture properties of powder metallurgy rhenium at 2600°C

Fig. 1.16—Stress versus creep rate for powder metallurgy rhenium at 2600°C

Neg. 3677

100 X

Fig. 1.17—Photomicrograph of rhenium tested at 2600°C and 1.0 kg/mm² stress for 7.5 hours in hydrogen

Fig. 1.18—Stress-rupture data for powder metallurgy tungsten at 2200°, 2400°, and 2800°C

Fig. 1.19—Initial stress versus linear creep rate for powder metallurgy tungsten at 1600°, 2200°, 2400°, and 2800°C

W - 25Re - Commercial W - 25Re sheet of relatively high purity (<0.01 wt % of Si, Al, Fe, Cu, Ca, Mg, and Ag) was obtained, and stress-rupture and creep testing were performed.* Figures 1.20 and 1.21 give the test results. The material was stronger and more creep resistant in a hydrogen atmosphere than in an argon atmosphere at 2400°C and 2600°C, but at 2200°C the results showed considerable scatter in both atmospheres with no apparent difference in magnitude between atmospheres.

As a result of the metallurgical investigations of the W-Re alloy system, a process was developed by GE-NMPO to give a high-quality homogeneous W - 25Re material. This work is reported in detail under "W - 25Re Alloy Development."

Six creep-rupture sheet samples, 0.05-centimeter-thick with a 2.54-centimeter gage length, were fabricated from the GE-NMPO-processed material and were creep-rupture tested at 2600°C. The stress-rupture and creep results are given in Figures 1.22 and 1.23 along with the results obtained for the commercial materials at 2600°C. The stress-rupture strength for the GE-NMPO material was greater, but the linear creep rate for the two sources of material was essentially the same in hydrogen. The total elongation of the commercial material at rupture was approximately 15 percent at 0.28 kg/mm² and 25 percent at 1.0 kg/mm² stress, whereas the GE-NMPO material was 30 percent at 0.42 kg/mm² to 100 percent at 0.9 kg/mm² stress. These data indicate that the GE-NMPO fabrication process improved the ductility of W - 25Re at 2600°C in both hydrogen and argon atmospheres.

Comparison of Test Data

Results of creep-rupture testing of the refractory metals and alloys at temperatures to 2800°C are summarized in Table 1.1 and Figures 1.24, 1.25, and 1.26. The curves are representative for the materials tested in a hydrogen atmosphere. Where different results were obtained in an argon atmosphere, these are included in the table but not in the figures.

Figure 1.26 shows a comparison of the linear creep rate of the various materials tested. Except for tungsten and rhenium, a linear slope of approximately 0.25 was obtained and resulted in a stress exponent of about 4.0 in the Weertman[†] creep equation. This is close to the stress relationship proposed by Weertman for dislocation climb as the mechanism of creep.

Monkman and Grant[‡] showed, in their studies of aluminum and some of its alloys, that an empirical relationship exists between rupture life and minimum creep rate that is independent of stress and temperature. Their relationship gives a straight line on a log-log plot of rupture life and minimum creep rate. The slope of these curves approaches unity in most cases.

With the use of the Monkman and Grant correlation method, similar curves were plotted for the refractory metals investigated in this program. Figure 1.27 shows these curves; all the materials except rhenium and W - 25Re have approximately the same slope. This figure suggests that the following general equation, Equation (1.1), applies to the curves:

$$\log t_R + m \log (\text{mcr}) = \log c \quad (1.1)$$

*"High-Temperature Materials Program Progress Report No. 27, Part A," GE-NMPO, GEMP-27A, September 30, 1963, p. 11.

†J. Weertman, "Internal Friction of Single Metal Crystals," *Journal of Applied Physics*, Vol. 26, 1955, p. 1213.

‡F. C. Monkman and N. J. Grant, "An Empirical Relationship Between Rupture and Life and Minimum Creep Rate in Creep Rupture Tests," *ASTM*, Vol. 56, 1956, p. 593.

Fig. 1.20 - Stress-rupture data for powder metallurgy W-25Re at 2200°, 2400°, and 2600°C

Fig. 1.21 - Linear creep rate data for powder metallurgy W-25Re at 2200°, 2400°, and 2600°C

Fig. 1.22 – Stress-rupture data for powder metallurgy W-25Re at 2600°C

Fig. 1.23 – Linear creep rate data for powder metallurgy W-25Re at 2600°C

TABLE 1.1
ISOCHRONAL STRESS-RUPTURE DATA FOR VARIOUS REFRACTORY METALS AND ALLOYS

Reference No. For Figures 1. 24, 1. 25 And 1. 26	Material	Temperature, °C	Number Of Tests	Test Range, hr	Atmosphere	Stress To Rupture, kg/mm ²	
						1 hour	10 hours
1	Molybdenum (Arc-cast - source C)	1200	15	0.4 - 12	H ₂	8.30	6.47
		1600	3	0.5 - 6.0	H ₂	2.46	1.62
		1800	7	0.6 - 10	H ₂	1.38	0.86
		2000	4	1.4 - 43	H ₂	0.83	0.51
		2200	80	0.2 - 1000	H ₂ and Ar	0.42	0.23
		2400	6	0.3 - 6.0	H ₂ and Ar	0.24	0.14
2	Molybdenum (Sintered - source A)	2200	21	0.2 - 80	H ₂ and Ar	0.89	0.32
3	Molybdenum (Sintered - source A')	2200	7	0.2 - 11	H ₂	0.70	0.52
4	Mo - 50Re (Sintered)	2200	16	1 - 10	H ₂ and Ar	0.77	0.51
5	Rhenium (Sintered)	2600	18	0.3 - 16	H ₂	2.28	0.97
		2800	12		H ₂	1.12	0.44
6	Tantalum (Arc-cast)	2400	8	1 - 11	H ₂ and Ar	0.22	0.12
		2600	12	1.0 - 14	H ₂ and Ar	0.14	0.07
7	Tantalum (Sintered)	2600	4	2.5 - 7.0	H ₂	0.55	0.17
		2600	4	1.0 - 13	Ar	0.36	0.15
8	Ta - 10W (Arc-cast)	2400	2	2.0 - 7.0	H ₂	1.18	0.65
		2600	30	1.0 - 11.0	H ₂ and Ar	0.74	0.39
		2800	17	1.0 - 10.0	H ₂ and Ar	0.42	0.22
9	Tungsten (Sintered - source 1)	1600	14	1.0 - 11.0	H ₂	8.79	6.66
		2800	5	0.2 - 11.0	H ₂ and Ar	0.87	0.71
10	Tungsten (Sintered - source 2)	2400	8	0.4 - 40.0	H ₂	1.44	0.89
		2400	6	0.6 - 22.0	Ar	1.20	0.81
		2800	11	0.4 - 100	H ₂ and Ar	0.76	0.53
11	W - 25Re (Sintered)	2400	5	0.6 - 6.0	H ₂	1.36	0.52
		2400	5	0.3 - 7.0	Ar	1.00	0.44
		2600	18	0.4 - 52	H ₂	0.84	0.43
		2600	11	0.2 - 4.0	Ar	0.58	0.31
12	TZM	2000	2	1.0 - 5.0	H ₂	1.12	0.70
		2200	3	1.7 - 6.0	H ₂	0.48	0.28

where

t_R = rupture time, hours

mcr = minimum true creep rate, percent per hour

m = slope

c = intercept

Table 1.2 lists the materials presented in Figure 1.27 along with the slopes and intercepts. As indicated, most of the slopes approximate unity. For unity slope, a more simplified equation is obtained:

$$\log t_R + \log (\text{mcr}) = \log c \quad (1.2)$$

Fig. 1.24 - One-hour isochronal stress-rupture data

Fig. 1.25 - Ten-hour isochronal stress-rupture data

Fig. 1.26—Stress versus linear creep rate data

TABLE 1.2

SLOPE (m) AND INTERCEPT (c) VALUES FOR THE EQUATION
 $\log t_R + m \log (mcr) = \log c$
 FOR SEVERAL METALS AND ALLOYS

Material	Test Temperature, °C	Slope, (m)	Intercept, (c)	Data Source
Molybdenum	1200 - 2400	0.99	1.35	GE-NMPO
Tantalum	2400 - 2600	0.94	1.39	GE-NMPO
Tungsten	1600	0.96	1.36	GE-NMPO
Aluminum	260 - 595	0.85	1.30	Monkman & Grant
Rhenium	2600	1.86	1.32	GE-NMPO
Rhenium	2800	1.22	0.83	GE-NMPO
Titanium	370 - 1090	0.87	1.00	Monkman & Grant
Ta - 10W	2400 - 2800	0.98	1.59	GE-NMPO
Mo - 50Re	2200	0.90	1.23	GE-NMPO
W - 25Re	2600	0.78	0.62	GE-NMPO
Monel	370 - 930	0.92	0.80	Monkman & Grant
Ferritic steels	425 - 705	0.85	0.56	Monkman & Grant
Austenitic stainless steel	540 - 815	0.93	0.89	Monkman & Grant
M 252	815	0.89	0.70	Monkman & Grant
Nimonic 80 and 90	705 - 815	0.77	0.48	Monkman & Grant
Inco 700	650 - 980	0.80	0.56	Monkman & Grant
S-816	650 - 1040	0.90	0.85	Monkman & Grant
S-590	650 - 1040	0.88	0.96	Monkman & Grant

Fig. 1.27—Rupture time versus minimum true creep rate of several refractory metals

Eliminating the logs in Equation (1.2) results in Equation (1.3):

$$t_R = \frac{c}{mcr} \quad (1.3)$$

Equation (1.3) suggests that the minimum creep rate is inversely proportional to the time to rupture. If the minimum creep rate is obtained in a relatively short time, the time to rupture may be predicted reasonably well.

1.2 W - 25Re ALLOY DEVELOPMENT

Since tungsten has, by a substantial margin, the highest melting point and the lowest vapor pressure of any metallic substance, its use in high-temperature environments has been extensively studied. However, the extreme brittleness at room temperature of all known forms of metallic tungsten, except the W-Re alloys, makes the potential of this material difficult to assess. The W - 25Re alloy appears to be adequately ductile (>22-degree bend before cracking), but commercial material is unsatisfactory since it is a two-phase material (Figure 1.28). In addition, when heated to about 3000°C, the structure deteriorates (Figure 1.29) because of an excess of interstitials. Attempts to weld this type of material yield unsatisfactory porous joints.

A development program to produce a homogeneous W-Re alloy of improved quality was initiated. Forty separate additions, each approximately 0.1 weight percent, of metals

NOTE ABSENCE
OF SIGMA PHASE

Neg. 3574

100 X

CROSS SECTION OF GE-NMPO-
PRODUCED W-25Re SHEET

Neg. 3366

100 X

SIGMA PHASE IN PURCHASED W-25Re SHEET
AS RECEIVED

Fig. 1.28—Comparison of commercial W-25Re and
GE-NMPO-produced W-25Re

Neg. 3944

100 X

GE-NMPO-PRODUCED SHEET

Neg. 3368

250 X

COMMERCIAL W-25Re

Fig. 1.29—Commercial W-25Re sheet and GE-NMPO-produced W-25Re after heating for 2 hours at 3000°C in hydrogen

4. Hot roll at 1300°C in hydrogen with small reductions and full reheats between each pass. Roll the normal starting thickness of 0.5 centimeter to ~0.06 centimeter in 20-percent reductions per pass.
5. Descale in a caustic bath (Virgo) and abrasive-belt-finish to a 0.06-centimeter thickness.

Sheets, 0.06 centimeter thick and 7.6 centimeters wide, were produced by this process. A typical sheet is shown in Figure 1.31. The GE-NMPO-produced sheet is compared to a commercially obtained sheet in Figure 1.28. Figure 1.29 compares the two materials after 3000°C recrystallization treatment. Stress-rupture testing at 2600°C of the GE-NMPO produced sheet is discussed in this section under "Stress Rupture and Creep Test Results." These data show significant strength and ductility improvements of this material relative to the commercial material.

Fig. 1.31 - A 0.06-centimeter-thick W-25Re sheet (Neg. P63-11-17)

Ten exploratory tube extrusions of W - 25Re alloy with variable processing factors were prepared as outlined in Table 1.3. Components for the tubing extrusions are shown in Figure 1.32. The results of this program were discussed with commercial vendors. In one case, a vendor's powder metal compact was sintered at 3000°C by GE-NMPO for subsequent tube fabrication at the vendor's plant. The resultant tube, 0.17 centimeter in outside diameter by 0.02-centimeter-thick wall, was metallurgically acceptable, although not satisfactory with respect to concentricity or smoothness of bore.

1.3 SUMMARY AND CONCLUSIONS

A significant number of creep-rupture tests was performed on some of the refractory metals and alloys to 2800°C in hydrogen and argon atmospheres for as long as 1000 hours. Certain trends are apparent in the results obtained:

1. The stress-rupture strengths and the linear second-stage creep rates obtained for arc-cast materials are more consistent and reproducible for different sources of the same material than are the results obtained from the same material fabricated by the powder metallurgy processes. This is particularly true of molybdenum and tantalum.
2. The stress-rupture and creep strengths of powder metallurgy materials is greater than that for the same material processed by arc-melting techniques.
3. The grain size of arc-melted materials exposed in the temperature range from 2000°C to 2800°C is always huge and ranges from 500 to 900 microns. The grain size of powder metallurgy materials is usually fine, although observed to be duplex at times.

An improved processing and fabrication procedure for W - 25Re sheet has been developed which results in a homogeneous (sigma-free) structure. This material has demonstrated

Neg. P63-11-3A

Neg. P63-11-26A

Fig. 1.32—Components for tubing extrusions. W-25Re as hollow sleeves fitted with molybdenum mandrel fillers for insertion into molybdenum extrusion cans.

TABLE 1.3
CONDITION AND DISPOSITION OF W - 25Re EXTRUSIONS^a

Lab No.	Starting Material	Pre-Extruded Size		Percent W - 25Re In Cross Section	Extrusion Ratio (Area)	Extruded Tube		Purpose Or Disposition Of Extruded Tube
		Outside Diameter, cm	Inside Diameter, cm			Outside Diameter, cm	Inside Diameter, cm	
1	Sintered Powders	6.22	4.18	21.4	9.3:1	2.010	1.420	Powder blank process and extrusion.
2	Sintered Powders	6.22	4.18	21.4	9.3:1	2.010	1.420	Powder blank - bore control in extrusion.
3	Sintered Powders	5.62	3.84	14.1	12:1 ^b	1.530	1.110	For swaging process development.
4	Sintered Powders	2.94	1.778	6.0	10:1	0.930	0.562	For swaging process development.
5	Sintered Powders	0.89	0.254	1.6	12:1 ^c	0.483	0.127	Direct extrude to drawing size.
6	Sintered Powders	2.60	0.74	6.7	12.5:1 ^c	0.740	0.153	For hot-rolling to drawing size.
7	Sintered Powders	6.22	4.20	21.4	15:1 ^c	1.630	1.120	Sent to vendor for draw development (not returned to date).
8	Sintered Powders	6.00	2.030	38.0	10:1	2.010	1.325	
9	Sintered Powders	4.58	3.28	10.9	9.3:1	1.530	1.090	For complete processing to small and intermediate tubes.
10	Arc-Cast Ingot	6.70	3.57	35.3	9.3:1 ^d	2.170	1.161	

^aAll extrusions as tubes - 1950°C extrusion temperature with glass lubricant.

^bDie wear reduced ratio from 15:1 originally planned.

^cDie wear reduced ratio shown which was originally planned.

^dDie wear very slight - not fully evaluated - estimated 8.5:1 reduction ratio.

superior stress-rupture and ductility characteristics compared to commercial W - 25Re sheet when tested in hydrogen at 2600°C.

1.4 PLANS AND RECOMMENDATIONS

The stress-rupture and creep studies of refractory metals and alloys will continue to 2800°C with the possibility of extending the tests to 3000°C, where applicable. Screening of materials of interest will be made in the 1- to 10-hour stress-rupture range. Creep-rupture tests will be performed on some materials in the 100- to 1000-hour range and the 1000- to 10,000-hour range. The temperature range of testing will be expanded to incorporate the intermediate range (1600° to 2000°C) for those materials exhibiting reproducible results. Tensile strength levels for the refractory metals and alloys versus temperature will also be established. More detailed studies of the mechanisms of creep will be made at elevated temperatures. The effect on the creep behavior of the materials as a result of temperature cycling at constant stress and at reduced stress after operation at elevated temperatures, will also be investigated.

Fabrication and extrusion studies on W - 25Re alloys will be continued to produce limited quantities of high-quality sheet and tubing for various application studies, including refractory-metal fuel elements. Other alloy systems, i. e., W-Mo-Re, will be investigated.

2. EFFECT OF RADIATION ON HIGH-TEMPERATURE REFRACTORY METALS AND ALLOYS

(57004)

The objective of this program is to determine the effect of radiation on the time-, temperature-, and stress-dependent properties of selected high-temperature alloys and refractory metals, to identify the causes of any observed changes in these properties, and to develop remedial measures.

2.1 REFRACTORY-METALS PROGRAM

A summary of the major experiments in the refractory metals and alloys radiation-effects program is presented in Table 2.1. Included in this tabulation are typical property changes caused by irradiation to various neutron dosages. The initial test program is based on the study of the effects of neutron irradiation on selected properties of tungsten and molybdenum and an alloy of each of these base materials. Other materials, such as niobium- and tantalum-base alloys, are to be considered in exploratory studies.

Most of the test data will be limited to creep-rupture, tensile, hardness, and resistivity measurements with a few studies on the effects of irradiation on other properties where deemed necessary to support any important observed phenomena. Theoretical studies include Monte Carlo computer experiments* on the primary damage state in neutron-irradiated BCC metals, and subsequent defect annealing with increasing temperatures.

The details and descriptions of some of the refractory-metal irradiation capsule designs, test facility designs, stress-rupture and hot hardness test equipment, and electrical resistivity measuring techniques are presented in an addendum to this section.

CREEP-RUPTURE, ELONGATION, AND TENSILE STRENGTH DATA

Tungsten Rod Material

A summary of creep-rupture tests on tungsten rods is shown in Tables 2.2 and 2.3. The data are presented in separate tables since it became evident early in this test sequence that there were differences in the rupture properties between specimens from two different tungsten rods. The test specimens were fabricated from rods, designated X and Y, of the same tungsten powder blend. The chemical analyses, microstructures, densities, and grain sizes indicated that both rods were essentially metallurgically identical, as reported later under the heading, "Materials and Structure Data." Specimens from rod X were fabricated by an outside vendor while the specimens from rod Y were fabricated at GE-NMPO. Rod Y showed a consistently higher rupture strength. The tests on control

*"High-Temperature Materials Program Progress Report No. 29, Part A," GE-NMPO, GEMP-29A, November 30, 1963, pp. 47-80.

TABLE 2.1
SUMMARY OF MAJOR EXPERIMENTS IN THE REFRACTORY METALS AND ALLOYS RADIATION EFFECTS PROGRAM

Exp. No.	Objective	Property	Test Specimen		Irradiation Conditions ^c		Post-Irradiation Heat Treatment		Test Conditions	Percent Change In Property ^d			Comments		
					Temp, °C	nvt, neutrons cm ⁻² Thermal (E _n ≥ 1 Mev)	Temp, °C	Time, hr		Creep-rate	Rupture life	Elongation			
1	To investigate the effects of neutron irradiation on the creep-rupture and tensile properties. To perform supporting studies on the effects of neutron irradiation on the hardness and resistivity properties.	Creep-rupture	W	Rod	MK137(PM)-Y	70	2.5x10 ¹⁹	5.3x10 ¹⁸		T, °C σ(kg/mm ²)	0	17	0	To be irradiated To be irradiated To be irradiated To be irradiated To be tested To be tested	
					MK137(PM)-Y	70	9.5x10 ¹⁹	2.5x10 ¹⁹		1100 20.40	-60	160	-7		
			MK137(PM)-X	70	4.1x10 ¹⁸	5.8x10 ¹⁷		1200 17.57	-	0	18				
			MK137(PM)-X	70	2.0x10 ¹⁹	3.7x10 ¹⁸		1200 17.57	-	10	4				
			MK137(PM)-X	70	2.0x10 ¹⁹	3.7x10 ¹⁸		1400 13.00	-	0	12				
			MK137(PM)-X	70	9.5x10 ¹⁹	2.5x10 ¹⁹		1400 13.00	-	10	19				
			MK137(PM)-J	70	3.0x10 ²⁰	6.0x10 ¹⁹									
			MK137(PM)-J	70	6.0x10 ²⁰	1.2x10 ²⁰									
			MK137(PM)-D	70	1.2x10 ²¹	2.4x10 ²⁰									
			MK137(PM)-J	1300											
			W	Sheet	PF(PM)	70	1.5x10 ²⁰	3.2x10 ¹⁹		1100 37.26	-30	60	8		
			W - 25Re	Sheet	RWS9(PM)-	70	5.5x10 ¹⁹	6.9x10 ¹⁸		1100 49.20	-20	9	-17		
			Mo	Sheet	KDM-515A(AC)	70	5.5x10 ¹⁹	6.9x10 ¹⁸		980 10.55	-2	10	14		
			Mo	Sheet	KDM-515A(AC)	70	3.1x10 ²⁰	4.0x10 ¹⁹							
			Mo-TZM	Sheet	ZM-974(AC)	70	3.1x10 ²⁰	4.0x10 ¹⁹							
			Tensile	W	Rod	MK142(PM)-B	70	2.8x10 ¹⁹	5.1x10 ¹⁸			Yield Strength	Tensile Strength		Elongation
		MK142(PM)-C				70	9.3x10 ¹⁹	1.7x10 ¹⁹						To be tested	
		Resistivity	W	Rod	MK142(PM)-D	70	2.5x10 ¹⁹	5.3x10 ¹⁸		T, °C	Resistivity			To be tested To be tested Material in warm-worked condition To be tested To be tested To be tested	
					MK142(PM)-D	70	1.0x10 ²⁰	1.3x10 ¹⁹		-196	105				
					MK142(PM)-D	70	1.2x10 ²⁰	3.3x10 ¹⁹		-196	142				
					MK142(PM)-D	70	1.2x10 ²⁰	3.3x10 ¹⁹		-196	304				
					MK142(PM)-D	1300	2.2x10 ²⁰	7.9x10 ¹⁹							
					MK142(PM)-D	1300	2.2x10 ²⁰	7.9x10 ¹⁹							
			W - 25Re	Rod	RWW5(PM)-A	70	1.0x10 ²⁰	1.3x10 ¹⁹		-196	11				
					RWW5(PM)-A	1300	2.2x10 ²⁰	7.9x10 ¹⁹							
			Mo	Rod	GEH(PM)-B	70	1.0x10 ²⁰	1.3x10 ¹⁹		-196	67				
					GEH(PM)-B	70	1.0x10 ²⁰	1.3x10 ¹⁹		-196	128				
			Mo-TZM	Rod	GEH(PM)-B	700	2.2x10 ²⁰	7.9x10 ¹⁹							
					ZM6003(AC)-5	70	9.5x10 ¹⁹	2.5x10 ¹⁹							
		Hardness	W	Sheet	ZM6003(AC)-5	700	2.2x10 ²⁰	7.9x10 ¹⁹							
		W - 25Re	Rod	RWW5(PM)-C	70	1.5x10 ²⁰	3.5x10 ¹⁹		T, °C Load	DPH Hardness			Single crystal To be tested To be tested To be tested		
	70			9.5x10 ¹⁹	2.5x10 ¹⁹		RT 500 g	8							
	70			9.5x10 ¹⁹	2.5x10 ¹⁹										
	70			9.5x10 ¹⁹	2.5x10 ¹⁹										
	70			9.5x10 ¹⁹	2.5x10 ¹⁹										

^aAll materials are in the recrystallized condition unless otherwise noted.

^bMaterial lot numbers are followed by parenthetical expressions denoting powder metallurgy (PM) or arc-cast (AC) processing. The last letter or number identifies the sheet or rod stock fabricated from the specified lot. Seven or more test specimens are generally machined from each sheet or rod stock.

^cThe listed irradiation conditions represent approximate values for specimens which were irradiated and represent target values for specimens to be irradiated. A summary of capsule irradiations, designations, and the number and type of specimens is given in Table 3.1, page 20, GEMP-31A.

^dProperty changes represent increases due to the indicated irradiations and test conditions when compared to a corresponding unirradiated test specimen. Negative values represent a decrease in the specified property.

TABLE 2.1 (Cont.)

SUMMARY OF MAJOR EXPERIMENTS IN THE REFRACTORY METALS AND ALLOYS RADIATION EFFECTS PROGRAM

Exp. No.	Objective	Property	Test Specimen			Irradiation Conditions ^c		Post-Irradiation Heat Treatment		Test Conditions	Percent Change In Property ^d			Comments				
			Material ^a	Type	Lot Number ^b	Temp, °C	nvt, neutrons cm ⁻² Thermal ($E_n \geq 1$ Mev)	Temp, °C	Time, hr		T, °C σ (kg/mm ²)	Creep-rate	Rupture life		Elongation			
3	To determine the influence of post-irradiation heat treatment on the creep-rupture and tensile properties. To perform supporting post-irradiation annealing studies on the resistivity and hardness properties and to make direct observations on the substructure.	Creep-rupture	W	Rod	MK137(PM)-Y	70	2.5x10 ¹⁹	5.3x10 ¹⁸	1100	1	1100 20.40	-27	13	4	Material in warm-worked condition Initial material in warm-worked condition but recrystallized due to heat treatment. To be irradiated To be irradiated To be irradiated			
					MK137(PM)-Y	70	9.5x10 ¹⁹	2.5x10 ¹⁹	1400	1	1100 20.40	-73	190	0				
			W	Sheet	PF(PM)	70	1.5x10 ¹⁹	3.2x10 ¹⁹	1100	3	1100 37.26	-40	52	-4				
					PF(PM)	70	1.5x10 ¹⁹	3.2x10 ¹⁹	1900	1	1100 18.63	-8	52	-4				
		Tensile	W	Rod	MK142(PM)-B	70	2.8x10 ¹⁹	5.1x10 ¹⁸				Yield Strength	Tensile Strength	Elongation	To be tested To be tested			
					MK142(PM)-C	70	9.3x10 ¹⁹	1.7x10 ¹⁹										
			Resistivity	W	Rod	MK142(PM)-D	70	2.5x10 ¹⁹	5.3x10 ¹⁸	650	1	T, °C	Resistivity				Material in warm-worked condition	
						MK142(PM)-D	70	1.0x10 ²⁰	1.3x10 ¹⁹	650	1	-196	8					
		MK142(PM)-D				70	1.2x10 ²⁰	3.3x10 ¹⁹	650	1	-196	18						
		MK142(PM)-D				70	1.2x10 ²⁰	3.3x10 ¹⁹	650	1	-196	76						
		W - 25Re		Rod	MK142(PM)-D	70	1.2x10 ²⁰	3.3x10 ¹⁹	1900	1	-196	10						
					RW5(PM)-A	70	1.0x10 ²⁰	1.3x10 ¹⁹	550	1	-196	1						
					Mo	Rod	GEH(PM)-BB	70	1.0x10 ²⁰	1.3x10 ¹⁹	450	1	-196	20				
					GEH(PM)-B		70	1.0x10 ²⁰	1.3x10 ¹⁹	450	1	-196	35					
		Hardness	W	Sheet		70	1.5x10 ²⁰	3.5x10 ¹⁹	650	1	T, °C Load	DPH Hardness				Single crystal		
						70	1.5x10 ²⁰	3.5x10 ¹⁹	650	1	650 500 g	60						
3	To investigate the influence of specimen configuration, purity level, structure and substructure on the post-irradiation creep-rupture and tensile properties. To perform supporting studies on the post-irradiation resistivity and hardness properties.	Creep-rupture	W												To be irradiated			
			Mo												To be irradiated			
		Tensile	W													To be irradiated		
			Mo													To be irradiated		
4	To determine the in-reactor creep properties of refractory metals and alloys.		W												In planning stage. Test conditions to be established when more data from experiments No. 1 and 2 are evaluated.			

TABLE 2.2
SUMMARY OF CREEP-RUPTURE TESTS ON TUNGSTEN SPECIMENS, ROD X MATERIAL

Specimen	Composition	Temperature, °C	Stress, kg/mm ²	Rupture Life, hours	Linear Creep Rate, sec ⁻¹	Elongation, percent in 2.54 cm	Reduction In Area, percent
89	Control	1400	12.30	4.15	-	25.2	65.5
92	Irradiated ORM-4 ^a	1400	12.30	3.95	-	26.4	54.5
95	Control	1400	13.01	2.60	-	23.0	63.6
90	Irradiated ORM-4	1400	13.01	2.55	-	24.2	64.7
96	Control	1400	13.36	1.90	-	28.3	87.7
85	Control	1200	16.87	5.00	1.1×10^{-5}	29.0	96.6
88	Control	1200	16.87	2.10	1.9×10^{-5}	26.9	96.4
91	Irradiated ORM-4	1200	16.87	2.10	2.3×10^{-5}	32.0	95.2
53	Irradiated ORM-5 ^b	1200	17.58	2.3	2.1×10^{-5}	28.0	94.8
84	Control	1100	19.34	5.85	7.0×10^{-6}	30.8	97.0
93	Irradiated ORM-4	1100	19.34	6.74	6.3×10^{-6}	31.5	95.7
52	Irradiated ORM-5	1100	19.34	5.65	7.7×10^{-6}	31.2	97.8
54	Irradiated ORM-8 ^c	1100	19.34	10.2	4.2×10^{-6}	30.3	96.3
86	Control	1100	20.35	1.25	3.5×10^{-5}	33.7	97.8
50	Irradiated ORM-5	1100	20.35	1.19	3.7×10^{-5}	32.9	97.7
55	Irradiated ORM-8	1100	20.35	2.83	2.0×10^{-5}	32.1	97.1
83	Control	1100	20.74	0.55	7.6×10^{-5}	36.2	98.0
82	Control	1100	21.66	0.15	22.8×10^{-5}	38.5	97.8

^aORM-4 irradiated at 5.8×10^{17} nvt ($E_n \geq 1$ Mev)

^bORM-5 irradiated at 3.7×10^{18} nvt ($E_n \geq 1$ Mev)

^cORM-8 irradiated at 2.5×10^{19} nvt ($E_n \geq 1$ Mev)

TABLE 2.3
SUMMARY OF CREEP-RUPTURE TESTS ON TUNGSTEN SPECIMENS, ROD Y MATERIAL

Specimen	Condition	Temperature, °C	Stress, kg/mm ²	Rupture Life, hours	Linear Creep Rate, sec ⁻¹	Elongation, percent in 2.54 cm	Reduction In Area, percent
22	Control	1400	12.30	6.30	1.0×10^{-6}	12.9	50.3
37	Control	1400	13.01	4.00	6.0×10^{-6}	15.4	55.2
38	Control	1400	13.01	4.00	2.3×10^{-6}	16.3	53.6
21	Irradiated ORM-6 ^a	1400	13.01	3.95	-	18.0	59.4
35	Irradiated ORM-8 ^b	1400	13.01	4.37	-	18.5	46.6
18	Control	1400	14.59	1.94	2.9×10^{-6}	18.8	86.8
41	Control	1400	15.12	0.75	-	22.7	87.5
43	Control	1100	20.74	2.21	1.76×10^{-5}	28.6	97.0
36	Control	1100	20.35	3.00	1.18×10^{-5}	26.6	97.2
29	Irradiated ORM-6	1100	20.35	3.47	1.23×10^{-5}	27.3	97.2
31	Irradiated ORM-8	1100	20.35	7.85	4.5×10^{-6}	24.9	96.6
44	Control	1100	19.69	7.31	5.5×10^{-6}	26.4	96.9
17	ORM-6 + annealed at 1100°C ^c	1100	20.35	3.59	1.18×10^{-5}	24.3	97.5
20	ORM-6 + annealed at 1400°C ^c	1100	20.35	2.55	1.37×10^{-5}	29.1	97.0
40	Control + annealed at 1400°C ^c	1100	20.35	2.27	1.76×10^{-5}	28.7	95.5
42	ORM-8 + annealed at 1400°C ^c	1100	20.35	6.74	5.7×10^{-6}	28.1	96.0
45	Control	1000	20.74		8.5×10^{-7}		
		1030			3.3×10^{-6}		
		1058			7.0×10^{-6}		
19	Irradiated ORM-6	1000	20.74		3.7×10^{-7}		
		1030			3.5×10^{-6}		
		1058			7.3×10^{-6}		
39	Irradiated ORM-8	1000	20.74		1.3×10^{-7}		
		1030			9.0×10^{-7}		
		1058			2.6×10^{-6}		
		1075			4.5×10^{-6}		
		1100			9.7×10^{-5}		

^aORM-6 irradiated at 3.7×10^{18} nvt ($E_n \geq 1$ Mev).

^bORM-8 irradiated at 2.5×10^{19} nvt ($E_n \geq 1$ Mev).

^cSpecimens were annealed without applied load for 1 hour in a H₂ atmosphere.

specimens at 12.30 kg/mm² and 13.00 kg/mm², for instance, show approximately a 50-percent longer rupture life for rod Y specimens. The reason for this consistent difference has not yet been identified. Some studies on the effect of surface electropolishing on the creep-rupture properties are discussed later in this section. Flat specimens from tungsten sheet were also creep-rupture tested; the results are given in Table 2.4.

In addition to the data on the control specimens, Tables 2.2, 2.3, and 2.4 present creep-rupture results for irradiated specimens from capsules ORM-4, ORM-5, ORM-6, ORM-8, and ORM-12. Preliminary tests on the effects of post-irradiation annealing treatments were also initiated with a few specimens.

TABLE 2.4
SUMMARY OF CREEP-RUPTURE TESTS ON TUNGSTEN^a AT 1100°C

Specimen No.	Condition	Stress, kg/mm ²	Rupture Life, hr	Linear Creep Rate, sec ⁻¹	Elongation, percent in 2.54 cm
201	Control	34.45	4.93	1.65×10^{-6}	7.0
206	ORM-12 ^b	34.45	8.89	1.4×10^{-6}	10.1
212	Control	35.86	3.59	2.78×10^{-6}	6.9
213	Control	35.86	3.26	2.55×10^{-6}	-
203	ORM-12	35.86	7.00	1.65×10^{-6}	8.5
202	Control	37.26	2.64	4.00×10^{-6}	7.5
207	ORM-12	37.26	4.20	2.80×10^{-6}	8.1
204	ORM-12 ^c	37.26	4.01	2.43×10^{-6}	7.2
214	Control ^d	17.58	8.69	7.40×10^{-6}	53.2
215	Control ^d	18.63	2.68	1.53×10^{-5}	39.7
205	ORM-12 ^d	18.63	4.08	1.41×10^{-5}	38.7

^aCold-worked 0.5 mm sheet; tested in cold-worked condition unless otherwise denoted. All tests were conducted in a hydrogen atmosphere.

^bORM-12 Capsule irradiated at reactor ambient temperatures in ORR F-2 facility to 3.2×10^{19} nvt, ($E_n \geq 1$ Mev).

^cIrradiated (ORM-12) plus annealed in hydrogen for 3 hours at 1100°C.

^dSpecimens annealed as a group at 1900°C for 1 hour in hydrogen prior to testing.

A comparison of the 1100°C test data of the specimens fabricated from rod Y material (Table 2.3) shows the following trends. The ORM-8 specimen (No. 31) which was irradiated for 240 hours to a neutron dosage of 2.5×10^{19} nvt ($E_n \geq 1$ Mev) showed a rupture life approximately 160 percent greater than the control specimen (No. 36) at a stress of 20.35 kg/mm². The ORM-6 specimen (No. 29) which was irradiated to a fast neutron dose of 3.7×10^{18} nvt and which was also tested at a stress of 20.35 kg/mm² showed only a slightly longer rupture life. Annealing an ORM-6 specimen (No. 17) at 1100°C in hydrogen for 1 hour before loading increased the stress-rupture life slightly. One-hour anneals at 1400°C in hydrogen were given to an ORM-6 (No. 20) and an ORM-8 (No. 42) specimen. Both exhibited shorter rupture life compared to their respective as-irradiated tests. A control specimen (No. 40) was similarly annealed at 1400°C and then creep-rupture tested. This specimen also exhibited a significant reduction in rupture life; the change being slightly greater than that observed with the ORM-6 specimen which was annealed at 1400°C. Although these specimens were originally recrystallized, the shorter rupture life of both is probably due to changes in the substructure. In the future, the specimens which are to be used in annealing studies will be subjected to additional pre-irradiation heat treatment at temperatures above 1700°C.

The elongation-versus-time plots of several specimens tested at a stress of 20.35 kg/mm² are shown in Figure 2.1. The initial slopes of both irradiated specimens show some hardening with increase in neutron dose. The shape of the creep curve for the specimen given the lower irradiation (3.7×10^{18} nvt) is similar to that of the control specimen, but

Fig. 2.1 — Elongation versus time for tungsten specimens (Rod Y) tested at a stress of 20.4 kg/mm² and a temperature of 1100°C in a hydrogen atmosphere

slightly displaced along the time axis. However, the specimen receiving the higher dose (2.5×10^{19} nvt) shows a pronounced difference in creep rate throughout the test.

The creep rate as a function of time is plotted in Figure 2.2 for the seven tungsten specimens (rod Y) which were tested at the same stress and temperature. The top set of curves shows the control data of a specimen in the as-received condition and also for a specimen which was annealed for 1 hour at 1400°C. The 1-hour anneal did not change the primary-stage creep rate, but did increase the secondary-stage creep rate by about 25 percent. There was a corresponding reduction in the rupture life due to the apparent softening of the material by this heat treatment at 1400°C.

For a relatively low irradiation (3.7×10^{18} nvt), the test specimen exhibited a slightly longer life although the second-stage creep rate did not appear to be significantly affected. The usual primary-stage creep rate, however, was delayed by about 10 minutes due to irradiation hardening of the material. Annealing a specimen for 1 hour at 1400°C eliminated this apparent incubation period, after a previous 1-hour anneal at 1100°C on another specimen had failed to eliminate it. The 1400°C anneal reduced the rupture life of the test specimen by about 25 percent of that of the as-irradiated specimen. This reduction is about the same as that observed for the control specimen when annealed at 1400°C.

For this low irradiation (3.7×10^{18} nvt), the creep rate shows a fairly rapid change with time during the first 10 minutes of test. The work-hardening of the stressed specimen then becomes the dominant mechanism which decreases the creep rate until the equilibrium rate of hardening and recovery is reached. The irradiation to this low neutron dose, however, did not reduce the minimum creep rate when compared to that of the corresponding control data. Although the creep rate did decrease during the first 2 minutes of test time, the rapid increase was again apparent for the next 8 minutes. This anomalous behavior during the first 10 minutes of testing is difficult to interpret at the present time,

Fig. 2.2 - Creep rate versus time for tungsten specimens (Rod Y) tested at a stress of 20.4 kg/mm^2 and a temperature of 1100°C in a hydrogen atmosphere

since after a 1-hour anneal at 1100°C, the radiation-induced increase in resistivity of tungsten is completely eliminated for the low irradiation, although about 4 percent of this increase still remains for the higher irradiation. Further studies, including transmission electron microscopy, are necessary to establish a reasonable interpretation of the initial creep rate behavior of this material.

Irradiation of the tungsten specimens to a higher neutron dose (2.5×10^{19} nvt) results in a factor of 2 decrease in the secondary-stage creep rate and a factor of 2.6 increase in the rupture life. The creep rate during the first 10 minutes of testing shows a pronounced decrease as though the material was work-hardened. The creep rate then shows a gradual increase up to about 1 hour of test time where the equilibrium rate of work hardening and recovery is reached. Irradiation to this higher dosage (2.5×10^{19} nvt) apparently forms either a sufficient number of larger vacancy clusters; or perhaps a second phase, resulting from trace impurities, yields a type of dispersion hardening. It is also possible that the peak observed in the creep rate at approximately 60 minutes, in the specimen receiving the high irradiation, corresponds to a similar mechanism yielding the peak at 10 minutes in the specimen which received the lower irradiation.

The 1400°C anneal for 1 hour does remove the anomalous initial-stage creep behavior, but does not dissociate the vacancy clusters (or second phases), which may be responsible for the observed factor of 2 reductions in the minimum creep rate. A reduction in rupture life, or more accurately, in the initiation of third-stage creep, was also observed. This earlier start of the third-stage creep is similar to that observed for the lower irradiation and for the control specimens when each were annealed at 1400°C.

Stress-rupture results of tests on rod Y specimens at 1400°C indicate that the ORM-6 specimen (No. 21) rupture life is nearly equal to that of the control specimen, but that the ORM-8 specimen (No. 35) exhibits a slightly longer rupture life. Testing an ORM-8 specimen at 1400°C results in about a 10-percent increase in rupture life compared to the 160-percent increase observed for the 1100°C test. This apparent annealing or reduction of radiation-induced strengthening of the tungsten will be further explored in future testing.

A plot of the logarithm of the creep rate as a function of the reciprocal absolute temperature for a given stress is shown in Figure 2.3. At 1000°C, the ORM-6 and ORM-8 irradiated specimens show a lower creep rate than the control data. A 30°C increase in test temperature appears to anneal out the factor of 2 difference between creep rates for the lower irradiation and the control specimen. A slight change is also noted at this temperature (1000°C) for the specimen which received the higher irradiation. The creep rate of the ORM-8 specimen is consistently lower at each temperature considered with the exception of the data point observed at 1100°C which does not appear to be valid. Further testing will be performed in this temperature range.

The difference in the effects of neutron irradiation on the creep as a function of time for a low- and a high-dose exposure is shown in Figure 2.4. At 1400°C the irradiated specimens tend to creep at the same rate as the control specimen. At about 80 minutes, the two irradiated specimens exhibit a slightly lower creep rate than the control specimen. The specimen receiving the higher dose (2.5×10^{19} nvt) retains the lower creep rate for the remainder of the test whereas the specimen receiving the lower dose (3.7×10^{18} nvt) appears to have lost the radiation-induced hardening at about 140 minutes of testing at temperature and stress. It appears that some significant radiation-induced defect(s) (or phase transformation) is occurring in the material when irradiated between 3.7×10^{18} nvt and 2.5×10^{19} nvt. Annealing the specimen at 1400°C for 1 hour and testing it at 1100°C failed to eliminate this effect of irradiation from the specimen receiving the higher dose, nor was it completely removed by testing at 1400°C under an applied stress.

Fig. 2.3—Natural logarithm of the creep rate as a function of temperature at a stress of 20.7 kg/mm^2

The creep-rupture test data on specimens from rod X material are listed in Table 2.2; the 1100°C and 1200°C data are plotted in Figure 2.5. Two ORM-8 irradiated specimens (Nos. 55 and 54) which were tested at 1100°C exhibited increases in rupture life of factors of 3.2 and 1.7, respectively, when compared to their respective control specimens. The ORM-5 specimens (Nos. 50, 52, and 53) creep tested at 1100°C and 1200°C , possessed rupture lives approximately equivalent to the control specimens. This suggests that these specimens were irradiated below the threshold for reactor ambient temperature radiation-induced strengthening.

A plot of the elongation-versus-time curves for the three irradiated specimens and the control specimen, tested at 1100°C and 19.3 kg/mm^2 , are given in Figure 2.6. The similarity in the curves for the ORM-5 and control specimen may be readily recognized. The lower creep rate and greater rupture life of the ORM-8 specimen are similar to those observed for specimens fabricated from the rod Y material.

Fig. 2.4—Elongation versus time for tungsten specimens (Rod Y) tested at a stress of 13.0 kg/mm² and a temperature of 1400°C.

Fig. 2.5—Stress-rupture strength of tungsten (Rod X) tested in hydrogen at 1100°C and 1200°C.

Fig. 2.6—Elongation versus time of tungsten specimens (Rod X) tested at a stress of 19.3 kg/mm^2 and a temperature of 1100°C in a hydrogen atmosphere

Elongation and Reduction in Area - Ductility indices, elongation, and reduction in area of tungsten show little spread in values. Rod Y specimens tested at 1100°C and 20.4 kg/mm^2 , for example, yielded elongation and reduction in area values which deviated only 2.4 and 1 percent, respectively, from the average values, although these specimens were tested under five conditions: control, control plus annealing at 1400°C , irradiated ORM-6 and ORM-8, irradiated ORM-6, and ORM-8 plus annealing at 1100°C or 1400°C .

Figure 2.7 is a histogram plot of the rod Y ductility indices versus the three test temperatures for various stress levels. This figure indicates that the ductility of recrystallized tungsten decreases with temperature at temperatures of 1400° , 1200° , and 1100°C , and that irradiation decreases the ductility only slightly at these three temperatures.

Tensile Tests - Tungsten rod tensile specimens were irradiated in capsules ORM-9 and ORM-10 to fast neutron dosages of approximately 5.1×10^{18} and 1.7×10^{19} nvt, respectively. These and corresponding control specimens were then given the various annealing heat treatments (shown in Table 2.5) in an argon atmosphere and will be tensile tested above the brittle-ductile transition temperature for this material. The purpose of this experiment is to study the irradiation hardening, any possible additional thermal hardening, and temperature at which the total hardening is completely annealed.

Electropolished Tungsten Rod Tests

Grinding of tungsten rod specimens produces a distorted or cold-worked surface layer. The effective thickness of this layer varies with the many process variables. Most of the work reported in the literature, however, deals with the effect of surface finish on the room-temperature properties of refractory metals, and very little is reported for this

Fig. 2.7 — Ductility indices for tungsten (Rod X) creep-rupture-tested specimens

effect on mechanical properties at elevated temperatures. Atkinson, et al.,* reported that as-ground tungsten single-crystal specimens at room temperature were brittle, while electropolished specimens were ductile. Other investigators have reported[†] on the effect of surface conditions on tensile and bend properties of polycrystalline tungsten. Wolf[§] determined by X-ray back-reflection investigation and room-temperature tensile tests on single-crystal tungsten specimens that an electrolytic diameter reduction of 0.051 millimeter was sufficient to remove the deformed surface layer. Stephan[†] reported that removal of 0.127 to 0.254 millimeter from the diameter was necessary to eliminate the effect of the distorted surface layer on room-temperature tensile properties of polycrystalline tungsten specimens.

*R. H. Atkinson, et al., "Physical Metallurgy of Tungsten and Tungsten-Base Alloys," WADD Technical Report No. 60-37, May 1960.

†J. R. Stephan, "Effect of Surface Condition on Ductile-To-Brittle Transition Temperature of Tungsten," Lewis Research Center, NASA TN D-676, February 1961.

‡J. R. Stephan, "An Exploratory Investigation of Some Factors Influencing the Room Temperature Ductility of Tungsten," Lewis Research Center, NASA TN D-304, August 1960.

§U. E. Wolff, "Orientation Dependence of the Tensile Properties of Tungsten Single Crystals at Room Temperature," General Electric Co., Cleveland, Ohio, Report LMC-62-191, July 2, 1962.

A series of creep-rupture tests at 1100°C was conducted on tungsten specimens with varying electrolytic diameter reductions. Electropolishing was accomplished with equipment and techniques previously described.* A summary of the tests is given in Table 2.6. Plots of the creep rates, rupture lives, and final elongations are shown in Figure 2.8. As may be noted, diameter reductions up to 0.203 millimeter did not yield any significant changes in the creep rates, although there appeared to be a 3-percent increase. The scatter in results from specimens having 0.203 to 0.229 millimeter reductions is believed to have been caused by misalignment. The split-collar grips designed for the larger diameter specimens were used for all tests. Note that all specimens with diameter reductions of less than 0.203 millimeter failed within 3.2 millimeters of the center of the gage length (44.5 mm). The final elongation of these same specimens varied from 12.5 to 13.7 millimeters which was within 5 percent of the average.

The rupture lives tend to show a decrease with the amount of surface removed by electropolishing consistent with the gradual increase noted in the corresponding creep rate. The

Fig. 2.8— Effect of electropolishing on creep-rupture properties of tungsten at 1100°C

*"High-Temperature Materials Program Progress Report No. 19, Part A," GE-NMPO, GEMP-19A, January 25, 1963, pp.24-25.

TABLE 2.5
ANNEALING HEAT TREATMENTS OF
TUNGSTEN TENSILE SPECIMENS

Specimen Identity			Heat Treatment, ^b °C
	Irradiated ^a		
Control	ORM-9	ORM-10	
64B	56B	65B	-
6C	-	7C	-
12C	57B	8C	146
66B	58B	9C	300
16C	59B	11C	435
68B	60B	13C	591
26C	61B	23C	743
70B	62B	24C	897
27C	63B	25C	1043
71B	64B		1210

^aFast neutron dose ($E_n \geq 1$ Mev);

ORM-9; 5.1×10^{18} nvt

ORM-10; 1.7×10^{19} nvt

^bOne hour anneals at indicated temperature in °C.

scatter in the rupture life data is probably due to the sensitivity of third-stage creep mechanisms to the specimen alignment and also to those grain boundaries exposed to the surface which may be affected to some degree by the electropolishing. A nominal spread of ± 18 percent is shown for the rupture lives of the electropolished specimens.

While surface conditions and finish can affect the results, it should be pointed out that the as-ground specimen data discussed earlier showed good reproducibility when tested at the same temperature and stress.

Tungsten Sheet Material

A summary of creep-rupture tests on sheet tungsten specimens is shown in Table 2.4, including control specimens and those irradiated specimens from capsule ORM-12.

Figure 2.9 presents a plot of the rupture life versus stress tests at 1100°C on cold-worked tungsten sheet material. The irradiation to a fast neutron dose of 3.2×10^{19} nvt increases the rupture life by a factor of about 1.6 when compared to corresponding control data. As expected, this radiation-induced hardening was not as significant as in the case of the recrystallized tungsten rod specimens where a factor of 2.6 increase in rupture life was observed at the same temperature for a fast neutron dose of 2.5×10^{19} nvt.

The creep rates of the tungsten specimens are shown in Figure 2.10. This plot, and the values shown in Table 2.4, indicate that all of the irradiated specimens possessed lower creep rates than did the control specimens. Irradiated specimen No. 204 was annealed in hydrogen for 3 hours at 1100°C before testing. Although the rupture life and the creep rate varied slightly in comparison to an as-irradiated specimen (No. 207), the differences are not considered significant. Irradiation reduced the creep rates of the cold-worked specimens by a factor of 1.6 compared to a factor of about 2 for the recrystallized tungsten rod at the same test temperature.

Elongation-versus-time plots of the two irradiated specimens and a control specimen, all tested at 37.26 kg/mm² and 1100°C, are shown in Figure 2.11. The 3-hour anneal of an irradiated specimen at 1100°C did not significantly change the creep curve.

One irradiated and two control specimens were annealed at 1900°C in hydrogen for 1 hour and then tested at 1100°C. The irradiated specimen tested at a stress of 18.63 kg/mm² possessed a longer rupture life and a slightly lower creep rate than the corresponding annealed control specimen. The elongation-versus-time plot of these specimens is

Fig. 2.9— Stress-rupture strength of tungsten sheet specimens tested at 1100°C in hydrogen

Fig. 2.10— Initial stress versus linear creep rate of tungsten sheet specimens tested at 1100°C in hydrogen

TABLE 2.6
CREEP-RUPTURE PROPERTIES OF ELECTROPOLISHED TUNGSTEN SPECIMENS^a

Specimen No.	Diameter Reduction By Electropolishing, mm	Rupture Life, hr	Linear Creep Rate, 10^{-5} sec^{-1}	Final Elongation, mm	Point Of Failure
276	none	2.58	3.05	12.8	Center of gage length ^b
277	none	2.78	2.93	12.5	Center of gage length
272	0.104	2.20	2.98	12.8	3.2 mm below center of gage length
271	0.168	2.61	3.09	13.7	3.2 mm below center of gage length
274	0.208	1.66	3.80	12.2	7.9 mm below center of gage length
273	0.213	1.93	3.21	11.4	6.4 mm below center of gage length
275	0.234	2.39	2.45	10.8	11.1 mm below center of gage length

^aTungsten specimens from recrystallized rod L tested at 1100°C and 20.36 kg/mm² in a hydrogen atmosphere.

^bGage length is 44.5 mm.

Fig. 2.11 — Elongation versus time for tungsten sheet specimens tested at 37.26 kg/mm² and 1100°C in hydrogen

shown in Figure 2.12. These data, although limited, indicate that all of the radiation-induced strengthening is not removed by the recrystallization anneal at 1900°C. A similar effect was observed in the tungsten resistivity tests discussed later in this report. Annealing the irradiated specimens at 1900°C, for example, did not completely remove the radiation-induced increases in resistivity, indicating that perhaps transmutations rather than vacancy clusters or precipitate phases are playing an important role in the change in properties due to irradiation. The third-stage creep appears to start at approximately the same elongation value for both specimens, with the irradiated specimen remaining in the third stage longer before fracturing.

Fig. 2.12—Elongation versus time for tungsten sheet specimens tested at 18.6 kg/mm² and 1100°C in hydrogen

1.50	1.00 x 10 ¹⁸	60.0	1.00	100000	1	600
8.50	6.01 x 10 ¹⁸	15.0	7.00	100000	1	100
	6.01 x 10 ¹⁸	20.0	7.00	100000	2	200
	6.01 x 10 ¹⁸	25.0	7.00	100000	3	300

Preliminary studies on the creep-rupture properties of W - 25Re were initiated at a relatively low neutron dose exposure. It is planned to irradiate these materials at doses up to 10²⁰ nvt. Figure 2.13 presents a stress-rupture plot of the 1100°C tests on W - 25Re sheet material. There appears to be little difference in rupture life between the control specimens and specimens irradiated at 6.9 x 10¹⁸ nvt. In the case of specimens from ingot No. 5, all data fell within 10 percent with the exception of one specimen.

Fig. 2.13 – Stress-rupture strength of W-25Re specimens in hydrogen at 1100°C

Creep rates of the W - 25Re specimens are shown in Figure 2.14. This plot and the values shown in Table 2.7 indicate that, with the exception of one specimen, the creep rate of the irradiated specimens was lower than the control specimens. In addition, there was a slight difference in both the control and irradiated data for specimens from ingots No. 1 and No. 5. Ingot No. 1 material appeared to have a consistently lower creep rate.

Control specimens from ingots No. 1 and No. 5 were examined metallographically to determine possible causes for the differences in creep rates. The microstructures are

TABLE 2.7

SUMMARY OF CREEP-RUPTURE TESTS ON W - 25Re SPECIMENS^a AT 1100°C

Specimen	Ingot Number	Condition	Stress, kg/mm ²	Rupture Life, hours	Linear Creep Rate, sec ⁻¹	Elongation, percent in 2.54 cm
561	5	Control	41.5 ^b	-	2.1 x 10 ⁻⁶	-
561	5	Control	43.6 ^b	-	4.8 x 10 ⁻⁶	(44.0)
563	5	Control	45.7	9.08	7.4 x 10 ⁻⁶	54.9
569	5	Control	45.7	8.40	7.4 x 10 ⁻⁶	52.1
566	5	ORM-13 ^c	45.7	9.08	6.6 x 10 ⁻⁶	41.0
568	5	ORM-13 ^c	45.7	10.11	6.5 x 10 ⁻⁶	55.1
575	1	Control	45.7	7.60	6.5 x 10 ⁻⁶	33.7
573	1	ORM-13 ^c	45.7	7.84	5.7 x 10 ⁻⁶	48.8
565	5	Control	47.5	6.92	9.8 x 10 ⁻⁶	53.5
560	5	ORM-13 ^c	47.5	6.73	9.7 x 10 ⁻⁶	30.7
564	5	Control	49.2	3.99	1.8 x 10 ⁻⁵	54.4
562	5	ORM-13 ^c	49.2	3.98	1.5 x 10 ⁻⁵	39.9
574	1	Control	49.2	3.84	1.6 x 10 ⁻⁵	41.1
581	1	ORM-13 ^c	49.2	4.56	1.2 x 10 ⁻⁵	39.1

^aSpecimens 0.051 cm (0.020 in.) sheet - powder batch RWS-9 - recrystallized.

^bTest restarted after 6 hours at lower stress levels.

^cORM-13; irradiated at 6.9×10^{18} nvt ($E_n \geq 1$ Mev).

Fig. 2.14 – Initial stress versus linear creep rate of W-25Re specimens tested in hydrogen at 1100°C

two-phase, with the primary and continuous matrix phase being a W-Re solid solution; the dispersed second phase is the rhenium-rich sigma phase. This phase appears as stringers resembling elongated voids, and as minute particles. Some of the stringers seem to partially contain small equiaxed grains. The sigma phase is apparently somewhat friable since it pulled out of the matrix where there were clusters. Both specimens showed a uniform grain size (average grain diameter of approximately 15 microns) except near the point of fracture. The specimen from ingot No. 1 appeared to contain approximately 50 percent more of the sigma phase. The larger concentration of the sigma phase in specimens from ingot No. 1 may account for the lower creep rate due to possible dispersion hardening. Although the mode of fracture, inter- or transgranular, could not be determined, high magnification of the fracture areas of specimens from ingot No. 1 revealed that the fracture had occurred through the sigma phase at several points.

Rhenium

Preliminary creep-rupture tests at 1100°C on recrystallized rhenium sheet specimens have shown this material to be stronger than the recrystallized tungsten rod specimens previously reported; however, the rhenium is considerably less ductile and has a shorter third-stage creep than the tungsten rod specimens. The elongation-versus-time plots of two specimens which were tested at a stress of 21.1 kg/mm² are shown in Figure 2.15. Based on this pair of tests, rhenium appears to be slightly strengthened by neutron irradiation to a dosage of about 6.9×10^{18} nvt ($E_n \geq 1$ Mev). Further testing is planned for this material.

Fig. 2.15—Elongation versus time for rhenium specimens tested at a stress of 21.1 kg/mm² and 1100°C in a hydrogen atmosphere

Molybdenum

Sixteen tests have been conducted to date on arc-cast molybdenum sheet at 870°, 980°, and 1093°C. A summary of the tests is shown in Table 2.8. Figure 2.16 presents a plot of creep rates versus stress for the three test temperatures. The solid lines represent the creep rates for control specimens of the as-received material. The vendor gave this material a recrystallization anneal at 1260°C for 15 minutes in a hydrogen atmosphere. Several specimens were further annealed at 1200°C for 1 hour in a hydrogen atmosphere at GE-NMPO and tested at 980°C. The results, as indicated by the dashed line, show an increase in the creep rate of about 30 percent. This additional annealing heat treatment, however, did not change the stress dependence at these test conditions.

The data from the two ORM-13 (6.9×10^{18} nvt, $E_n \geq 1$ Mev) irradiated specimens tested at 870°C indicated slight increases (averaging approximately 25 percent) in the creep rates compared to the control specimens. An ORM-13 specimen tested at 980°C showed no observable difference in the creep rate compared to the control specimen. The stress-rupture results are shown in Figure 2.17. Two of the three irradiated specimens showed rupture lives comparable to the control specimens. The specimens which were annealed at 1200°C had shorter rupture lives than the vendor-annealed material.

Fig. 2.16—Initial stress versus creep rate of molybdenum sheet specimens tested in hydrogen

PHYSICAL PROPERTY MEASUREMENTS

Resistivity Test Results

Tungsten - A 1-hour anneal at 980°C of a control sample, a sample irradiated to 5.3×10^{18} nvt, and a sample irradiated to 3.3×10^{19} nvt (Figure 2.18) showed that although the lower dose sample was completely annealed, the higher dose sample still showed some radiation-induced resistivity. No appreciable change was observed in the resistance of the control sample. The same three specimens were then annealed for 1 hour at 1630°C in argon. The resistance after this second anneal was not significantly changed although this temperature is approximately one-half the absolute melting temperature (T_m) of tungsten. Most of the effects of irradiation on materials are completely annealed at one-half T_m . A further anneal at 1900°C again did not remove the remaining 4 percent increment in resistivity of the irradiated specimen.

A second set of specimens was then annealed in smaller temperature steps starting at 300°C. These data are also plotted in Figure 2.18. Note that the recovery during the anneal

TABLE 2.8
SUMMARY OF CREEP-RUPTURE TESTS ON MOLYBDENUM

Specimen No.	Condition	Test Temperature, °C	Stress, kg/mm ²	Rupture Life, hr	Linear Creep Rate, sec ⁻¹	Elongation, percent in 2.54 cm
588	Control ^a	870	14.77	6.63	1.25×10^{-5}	60.6
589	Control ^a	870	15.47	3.55	2.20×10^{-5}	53.1
590	Control ^a	870	16.52	1.35	5.09×10^{-5}	49.2
585	ORM-13 ^b	870	15.47	3.38	2.55×10^{-5}	55.5
586	ORM-13 ^b	870	14.77	4.84	1.70×10^{-5}	57.5
891	Control ^a	980	11.25	2.49	3.13×10^{-5}	69.3
892	Control ^a	980	10.55	4.53	1.73×10^{-5}	69.7
893	Control ^a	980	9.84	8.18	0.9×10^{-5}	66.2
903	Control ^c	980	11.25	1.88	4.33×10^{-5}	62.7
904	Control ^c	980	10.55	3.02	2.40×10^{-5}	58.9
905	Control ^c	980	9.84	5.90	1.28×10^{-5}	65.6
591	Control ^a	980	10.55	4.26	1.80×10^{-5}	65.9
584	ORM-13 ^d	980				
587	ORM-13 ^b	980	10.55	4.85	1.72×10^{-5}	77.2
854	Control ^a	1093	7.73	3.07	2.73×10^{-5}	79.3
855	Control ^a	1093	7.03	6.92	1.10×10^{-5}	78.6

^a Arc-cast molybdenum sheet, 0.5 mm thick, recrystallized by vendor; tested as-received.

^b ORM-13; irradiated at 6.9×10^{18} nvt ($E_n \geq 1$ Mev).

^c As-received sheet annealed at 1200°C for 1 hour in hydrogen.

^d Invalid test - failed at pinned hole.

Fig. 2.17—Stress-rupture strength of molybdenum sheet specimens tested in hydrogen

Fig. 2.18— Isochronal recovery of recrystallized irradiated tungsten

takes place in various steps or stages similar to the data reported by Thompson* on tungsten wires. The step between 300° and 400°C is particularly pronounced and correlates well with Thompson's data; he attributes this annealing behavior to vacancy migration. In the specimen which received the higher dose, there appears to be another small short stage between 750° and 925°C. Although there may be a large number of variables in this higher temperature stage, it may represent the mobility of the same defect which might account for the decrease in creep rate observed in the irradiated tungsten creep-rupture specimens.

Normalizing the radiation-induced increase in resistivity data to unity for the as-irradiated specimens and plotting as a function of temperature (Figure 2.19) show that the specimen receiving the lower dosage (5.3×10^{18} nvt) exhibits a larger change in the 250° to 400°C region than the specimen receiving the higher dose (3.3×10^{19} nvt). For increasing temperatures, the samples anneal along parallel paths up to about 800°C. The radiation-induced increase in resistivity of the specimen receiving the lower dose is essentially annealed out at 950°C, but a small amount of the resistivity increment (approximately 4 percent) still remains in the specimen receiving the higher dose, even at 1630°C.

A more sensitive measure of the recovery can be obtained by calculating the slope of the isochronal annealing curve and plotting this as a function of temperature as shown in Figure 2.20. This curve was obtained by dividing the change in resistivity by the temperature increment and plotting the results as a function of temperature. From this plot, it is apparent that three zones (0.17, 0.22, and 0.31 T_m) of rapid recovery are present for the high dose material. The higher temperature recovery zone is not observed in the low-dose sample.

*M. W. Thompson, "The Damage and Recovery of Neutron Irradiated Tungsten," *Philosophical Magazine*, Vol. 5, 1960, pp.278-296.

Fig. 2.19 - Normalized isochronal recovery of recrystallized irradiated tungsten

Fig. 2.20 - Recovery spectrum of recrystallized irradiated tungsten

Tungsten - 25 Rhenium - The isochronal recovery of recrystallized irradiated W - 25Re is shown in Figure 2.21. The recovery spectrum shown in the same figure indicates that the peak occurs at about 225°C. Using a solidus temperature for W - 25Re of 3000°C, the observed peak occurs near $0.15 T_m$ which is in reasonable agreement with corresponding melting point correlation in pure metals.

Molybdenum - Isochronal resistivity recovery studies of irradiated molybdenum have been completed for annealing temperatures up to 1250°C. The material was irradiated at pile ambient temperature in capsule ORM-14 to a dose of approximately 1.3×10^{19} nvt, ($E_n \geq 1$ Mev). The samples were irradiated in the as-received (warm-rolled) condition and after a 1-hour annealing at 1175°C in hydrogen.

Fig. 2.21 - Isochronal recovery of recrystallized irradiated W-25Re

The change in resistivity as a function of annealing temperature is shown in Figure 2.22. Two rods, designated B and C, were made from the same powder blend, but not necessarily from the same ingot. The fabrication histories of the two rods were similar. The following observations were made, based on the data shown in Figure 2.22:

1. The relative increase in resistance due to irradiation is higher for the material which was annealed before irradiation. This confirms similar observations in tungsten.
2. The general recovery path is the same for the material irradiated in a warm-rolled or recrystallized condition.
3. The radiation-induced resistivity increase is completely removed in all samples after annealing above 750°C.

The slope of the isochronal curve as a function of annealing temperature is shown in Figure 2.23. The observed recovery peaks at 160°C ($0.15 T_m$) and at 620°C ($0.31 T_m$) are in good agreement with other reported values for BCC materials. The peak noted in

Fig. 2.22 – Isochronal recovery of irradiated molybdenum

RESISTIVITY AT -196°C, micro-ohm-cm

Fig. 2.23 — Recovery spectrum of warm-worked and irradiated molybdenum

the data from the warm-worked unirradiated specimens at $0.36 T_m$ coincides with the temperature region ($0.37 T_m$) in which stress relieving of worked material is performed and is lower than the conventional recrystallization temperature (0.41 to $0.51 T_m$).

Isochronal annealing of several irradiated specimens will be performed in a vacuum to determine whether any impurities from the argon gas may have been introduced into the samples. Future resistivity measurements will also include isothermal recovery studies on these same materials.

Hot Hardness Test Results

Tungsten - Work has been initiated on obtaining hardness data for irradiated tungsten specimens. A standard Kentron microhardness machine is being used. Samples are prepared according to standard metallographic procedures and finished by electropolishing with 2 percent NaOH. To bring out grain boundaries, the samples usually receive a light etching with Murakami's solution.

The most prominent difference noted is the appearance of the area immediately adjacent to the hardness impression. In the unirradiated condition, the area around the impression (Figure 2.24a) is unaffected except for some slight signs of disturbed metal. In the irradiated sample (Figure 2.24), however, evidence of extensive slip around the impression has been observed. These impressions were made with a 500-gram load. Similar observations were made with a 100-gram load; the impressions were confined to one grain.

Neg. 3143

MURAKAMI'S ETCH
a - UNIRRADIATED

600 X

Neg. 3144

MURAKAMI'S ETCH
b - IRRADIATED

600 X

Fig. 2.24 - Typical hardness impression in recrystallized unirradiated and irradiated tungsten - 500 gram load

Slip lines in irradiated BCC metals such as molybdenum have been observed by Bierlein, et al.,* and Radavich and Beib.†

Four tungsten single grains, approximately 0.05 centimeter thick, were irradiated at pile ambient temperature for 210 hours in capsule ORM-15 to an estimated fast neutron dose of approximately 3.5×10^{19} nvt. The large faces of two of the samples were identified by X-ray diffraction to be of (411) orientation. The orientation of the other two samples which were cut from a given grain was not determined. The hardness of all four grains (crystals) was determined before irradiation using a standard Kentron microhardness instrument with a 500-gram load and a DPH-type indenter. Preliminary measurements on one sample indicated that the irradiation increased the hardness by about 10 percent.

All room-temperature indentations on the unirradiated samples were symmetrical and showed no signs of deformation at a magnification of 500X. The room-temperature indentations on the irradiated sample tended to have one diagonal slightly longer (1-2 microns) than the other and also to have very definite localized deformation. The deformation around the indentations appears as observed for the polycrystalline material discussed above. Repolishing and etching eliminated the deformation marks, indicating that the deformation mechanism is slip rather than twinning.

Hot-hardness results on a single unirradiated crystal similar to that described above are shown in Figure 2.25. Note the difference in hardness as determined by measuring each

Fig. 2.25 – Hardness of tungsten as a function of temperature

*"Quarterly Progress Report: Irradiation Effects on Reactor Structural Materials, November 1962 – January 1963," GE-HAPO, HW-76635, February 15, 1963, pp. 7.84–7.86.

† Private communication with Dr. J. F. Radavich.

diagonal. This difference was investigated further since it was assumed to be due to either misalignment or to crystallographic orientation. Hardness traverses made at 90 degrees to the original data, however, retained the crystallographic dependence indicating that alignment was not responsible for the indentation diagonal differences.

Five indentations were made at each temperature starting at 1000°C and decreasing to room temperature in 200°C steps. All diagonal measurements were made at room temperature on the Kentron instrument. Reheating the sample to 1000°C, holding for 1 hour, cooling, and measuring the indentations again produced no appreciable relaxation or distortion. Indentations made on the sample reheated at 1000°C indicated hardness within 4 DPH units of those on the original run.

All indentations on unirradiated and irradiated material made at elevated temperatures showed signs of localized slip similar to that seen near room-temperature indentations of irradiated tungsten. The slip was barely evident near indentations made at 200°C, but became much more pronounced at the higher temperatures. No deformation was observed at magnifications up to 500X around any of the room-temperature indentations of the unirradiated tungsten.

For comparison, hot-hardness data obtained by other investigators*† were averaged and are presented in Figure 2.25. According to these investigators,‡ there is a possibility that some interstitial oxygen was present in their tests, since extrapolating some of their other data to zero alloying content gave a hardness of about 320 instead of the 390 DPH for unalloyed tungsten. This is in agreement with hardness values reported for electron-beam-melted single crystals and is consistent with the data obtained on the single crystal at GE-NMPO.

Materials and Structure Data

Tungsten - The preliminary investigation of the commercially pure sintered and swaged tungsten rods used for the preparation of tensile and creep-rupture specimens was completed. Two rod sizes were used, 0.343-centimeter-diameter rod for tensile specimens, and 0.508-centimeter-diameter rod for creep-rupture specimens. All material of a given size was fabricated by the same commercial producer from the same powder blend. Table 2.9 lists the chemical and spectrographic analyses of the rods, as well as the impurity levels.

Density measurements were made on samples from rods X and Y at 22.5°C. The density of rod X was 19.254 g/cm³ and that of rod Y was 19.202 g/cm³.

Samples of both size rods were examined metallographically. The as-received recrystallized microstructures are shown in Figures 2.26 and 2.27. The grains appear to be elongated in the direction of working. The average grain diameters as determined by lineal analysis are tabulated in Table 2.10.

2.2 HIGH-TEMPERATURE ALLOY PROGRAM

The objectives of three concluding experiments now in progress on the iron-base precipitation hardening alloy (A-286) and the nickel-base, solution-strengthened alloy (Hastelloy X) are to determine the effects of irradiation due to (1) long exposure times (approximately 2×10^{20} nvt, $E_n \geq 1$ Mev), (2) thermal neutrons, and (3) the presence of varying

*"Fundamental and Applied Research and Development in Metallurgy; High-Temperature Properties of Refractory Alloys," Nuclear Metals, Inc., NMI-1258, September 17, 1963, Figure 6, p. 48.

†"Fundamental and Applied Research and Development in Metallurgy; High-Temperature Properties of Refractory Alloys," Nuclear Metals, Inc., NMI-1253, May 20, 1963, Figure 12, p. 56.

‡Ibid., p. 16.

Neg. 1723

250 X

Fig. 2.26 – Microstructure of 0.343-centimeter-diameter tungsten rod

Neg. 1724

250 X

Fig. 2.27 – Microstructure of 0.508-centimeter-diameter tungsten rod

TABLE 2.9
TUNGSTEN MATERIAL ANALYSIS

Element	Composition, ppm				
	0.343-Centimeter Diameter Rod			0.508-Centimeter Diameter Rod	
	A	B	C	X	Y
B	< 3	< 3	< 3	< 3	< 3
Ba	< 5	< 5	< 5	< 5	< 5
Ca	<10	<10	<10	<10	<10
Cr	<10	<10	<10	<10	<10
Fe	20	20	20	20	20
Mo	10	10	10	30	30
Na	<10	<10	<10	<10	10
Si	10	10	10	10	10
K	<10	<10	<10	<10	10
Ce	<50	<50	<50	<50	<50
Th	<30	<30	<30	<30	<30
Al	15	15	15	15	10
C ^a	10	10	26	46	43
Sb	<10	<10	<10	<10	<10
O ₂ ^c	-	17	21	11	15
H ₂ ^c	-	1	1	1	1
N ₂ ^c	-	43	13	5	4

^aConductometric method.

^bPotassium iodate titration method.

^cVacuum fusion method.

TABLE 2.10
GRAIN SIZES OF AS-RECEIVED TUNGSTEN RODS

Diameter, centimeter	Rod	Lot Number	Average Grain Diameter, microns
0.508	X	MK-137	55
0.508	Y	MK-137	51
0.343	A	MK-142	38
0.343	B	MK-142	42
0.343	C	MK-142	43

amounts of boron that are normally found in these materials. Creep-rupture testing has been initiated on test specimens from this last experiment.

Status of Irradiations

A summary of irradiation data for the high-temperature alloy studies is presented in Table 2.11. Capsule 33MT-80 contains Hastelloy X and A-286 creep-rupture specimens and special samples of precipitates to be used in structure studies. This capsule was irradiated in the ETR at approximately 650°C for two cycles.

The last scheduled set of irradiations on the high-temperature alloys program will be used to determine the effect of neutron spectrum on creep-rupture properties of Hastelloy X and A-286. The twin cartridge assemblies 33MT-104A and 33MT-104B were irradiated in the ETR K-3 facility for 3895 megawatt-days (approximately 440 hours on test). These cartridges, one of which contains a 0.5-millimeter cadmium liner to reduce

TABLE 2.11
IRRADIATION DATA FOR HIGH-TEMPERATURE ALLOY PROGRAM

Capsule	Specimen Data			Irradiation Data					Temperature, °C
				Neutron Dose, nvt ^b					
	Material	Type ^a	Number	Facility	Exposure	Fast (E _n ≥ 1 Mev)	Thermal	Cooling	
33MT-80B	A-286	C-R	6	ETR-I-13	7204 MWD	8.3 x 10 ²⁰	1.1 x 10 ²¹	He-N ₂ -Air (~99% He)	650
	Hastelloy X	C-R	6		2 Cycles -				
	Precipitates	Powders ^c			54 and 55				
	Intermetallics	Discs ^c							
33MT-99	A-286 + 0.010B	C-R	7	ETR-K3	7910 MWD	4.9 x 10 ¹⁹	6.3 x 10 ²⁰	H ₂ O	80
	A-286 + 0.0043B	C-R	7		2 Cycles -				
	A-286 + 0.0008B	C-R	7		52 and 53				
	A-286 + 0.0065B ^d	C-R	7						
33MT-104A	A-286	C-R	6	ETR-K3	3895 MWD	2.4 x 10 ^{19e}	3.1 x 10 ^{20e}	He-Air	650
	Hastelloy X	C-R	6						
33MT-104B	A-286	C-R	6	ETR-K3	1 Cycle - 57				
	Hastelloy X	C-R	6						

^aC-R - creep-rupture specimen.

^bBased on Ni⁵⁸ (n, p) Co⁵⁸ and Co⁵⁹ (n, γ) Co⁶⁰ reactions.

^cMaterial to be used for structure studies of precipitation hardening alloys.

^dBoron-11 isotope - 98.6%.

^eEstimated dose.

the thermal-to-fast neutron flux ratio, were irradiated at a temperature of 650°C. Figure 2.28 shows the partial assembly of the 33MT-104B cartridge. In the foreground is the specimen train of six specimens with their machined jackets in place. The final cartridge is made up of three tubular assemblies. One tube contains the A-286 specimens; another tube contains the Hastelloy X specimens. The third tube in each cartridge contains dummy specimens (solid 0.95-cm rods) instrumented with eight thermocouples.

Capsule 33MT-99, containing 28 smooth creep-rupture specimens of A-286 alloy (with 0.00085 to 0.010 weight percent natural boron added), was irradiated in the ETR for two cycles.

Creep-Rupture Test Data (A-286)

Other investigators working with unirradiated specimens have determined that the trace quantities of boron normally found in precipitation-hardening alloys improved the ductility and creep-rupture properties. These properties were found by GE-NMPO to be significantly changed upon irradiation of the A-286 alloy, even to the relatively low fast-neutron dosage of about 10^{16} nvt. One possible cause of the low threshold for the irradiation-induced change in these properties is the effect of the irradiation on the particular enductilating role played by the presence of the boron in this type of alloy.

A special heat of the precipitation-hardening iron-base alloy (A-286) was split into three portions. Natural boron was added to give three heats ranging in boron concentrations from 0.00085 (Heat A) to 0.010 (Heat C) percent. Specimens of the three compositions were simultaneously irradiated at reactor ambient temperatures to a fast-neutron dosage of 4.9×10^{19} nvt, and were then creep-rupture tested at 660°C.

Testing of A-286 specimens from the 33MT-99 capsule (irradiated to 4.9×10^{19} nvt, $E_n \geq 1$ Mev) is now in progress. Test results on heats RV403-5A and RV403-5C are plotted in Figure 2.29 and listed in Table 2.12. The chemical analyses of these materials are presented in Table 2.13. Irradiated specimens from heat RV403-5A (0.00085 percent natural boron) show consistent and significant losses in rupture life and ductility. Heat RV403-5C (0.010 percent natural boron) did not exhibit significant changes in the rupture life when compared to the control data of both heats, although there was a significant reduction in the elongation. Figure 2.30 is a plot of the strain (ϵ) as a function of time for control and irradiated specimens from the two heats.

Because of a change in thermocouple calibration standards, a 10°C difference in temperature was being measured. Consequently, the data which were reported at 650°C were actually at 660°C, as indicated in Table 2.12. The few tests which were made with the new thermocouples installed were performed at 650°C. To correct rupture life to a common temperature of 660°C, a correction factor was applied.

The correction factor was obtained using the Dorn temperature-compensated time equation

$$\theta_r = F(\sigma) = t_r e^{-\Delta H/RT}$$

where ΔH is the activation energy for deformation (91,000 cal/mole),* t_r is the time to rupture, R is the gas constant, and T is the absolute temperature. Assuming that any stress dependence on temperature is small, the time to rupture at 660°C is reduced by a factor of 1.72 relative to 650°C.

*R. M. Goldhoff, "Comparison of Parameter Methods for Extrapolating High-Temperature Data," *Journal of Basic Engineering*, December 1959, p. 629.

Fig. 2.28 — High-temperature alloy irradiation capsule 33MT-104B (Neg. 63-6-24B)

Fig. 2.29— Stress-rupture strength of A-286 alloy specimens at 660°C

TABLE 2.12
STRESS-RUPTURE RESULTS ON A-286 SPECIMENS AT 660°C^a

Specimen	Heat ^b	Stress, kg/mm ²	Temperature, °C	Rupture Life, hr	Elongation, percent in 3.81 cm	Reduction In Area, percent
Controls						
147AS	RV403-5C	35.2	660	456.7	14.2	32.7
145AS	RV403-5C	38.7	660	191.9	10.5	31.8
144AS	RV403-5C	42.1	660	98.8	21.5	33.1
146AS	RV403-5C	49.2	660	15.7	12.3	33.4
112AS	RV403-5A	35.4	660	305.9	11.2	26.2
115AS	RV403-5A	35.2	650 (660)	647.6 (376.0) ^c	15.5	19.0
113AS	RV403-5A	38.7	660	194.5	7.7	19.1
111AS	RV403-5A	42.5	660	106.3	17.7	22.2
114AS	RV403-5A	49.2	660	23.3	17.3	25.2
Irradiated (33MT-99)^d						
140AS	RV403-5C	38.7	660	252.1	3.2	7.2
137AS	RV403-5C	42.7	660	76.9	2.3	-
143AS	RV403-5C	49.2	650 (660)	22.4 (13.0) ^c	3.1	7.3 -
106AS	RV403-5A	35.2	660	58.9	1.8	-
107AS	RV403-5A	38.7	650 (660)	46.4 (27.0) ^c	3.0	6.4
104AS	RV403-5A	42.2	660	18.0	1.9	~4.1
110AS	RV403-5A	49.2	650 (660)	4.6 (2.7) ^c	2.6	3.0

^aPreviously reported at 650°C.^bHeat RV403-5A contains 0.00085 percent natural boron.

Heat RV403-5C contains 0.010 percent natural boron.

^cTemperature corrected time based on an activation energy of 91,000 cal/mole.^dCapsule 33MT-99: 4.9×10^{19} nvt, ($E_n \geq 1$ Mev)
 6.3×10^{20} nvt, thermal

TABLE 2.13

CHEMICAL ANALYSIS OF A-286 SPECIAL HEATS^a

Heat	Analysis	Chemical Analysis, wt %													
		Fe	Ni	Cr	Ti	Mn	Mo	Si	Al	V	Co	C	S	P	B
RV 403-5A	Vendor	Balance	25.07	14.87	2.12	1.55	1.18	0.62	0.23	0.20	--	0.051	0.008	0.008	<0.001
	GE-NMPO	55.05	24.64	14.73	2.16	1.40	1.25	--	0.16	0.26	0.13	0.053	--	--	0.00085 ^b
RV 403-5B	Vendor	Balance	25.07	14.87	2.12	1.55	1.18	0.62	0.23	0.20	--	0.051	0.008	0.008	0.004
	GE-NMPO	54.77	24.75	14.73	2.22	1.45	1.25	--	0.21	0.27	0.14	0.048	--	--	0.00425 ^b
RV 403-5C	Vendor	Balance	25.07	14.87	2.12	1.55	1.18	0.62	0.23	0.20	--	0.051	0.008	0.008	0.0096
	GE-NMPO	54.88	24.56	14.80	2.22	1.40	1.35	--	0.20	0.26	0.15	0.032	--	--	0.010 ^b
RV 541	Vendor	Balance	25.50	14.73	2.17	1.57	1.25	0.61	0.30	0.30	--	0.040	0.011	0.008	0.006
	GE-NMPO	53.74	24.23	14.67	2.19	1.55	1.35	--	0.33	0.30	0.14	0.044	--	--	0.0065 ^b

^aMaterial Condition (Vendor, Allegheny Ludlum Steel Corporation)

Hot rolled, finished below 900°C; hot swaged, finished to 1/2-inch rod below 900°C; ASM 5737 (Vacuum Melting)

Heat treatment: 900°C - 2 hours - oil quench, 720°C - 16 hours - air cool, and 650°C - 16 hours - air cool

^bAverage of triplicate determinations.

Fig. 2.30—Strain versus time curves for boron-containing A-286 specimens at 650°C and 38.7 kg/mm²

Testing is continuing on the specimens containing the intermediate boron concentration (0.004 percent) and those from heat RV541. Preliminary observations of the effects of irradiation to these specimens indicate that the radiation-induced change in rupture life is not as great as in the case of the lower (0.00085) boron concentration.

Metallographic studies were started on two irradiated (4.9×10^{19} nvt, $E_n \geq 1$ Mev) and two unirradiated A-286 creep-rupture specimens containing 0.00085 and 0.010 percent of natural boron, respectively. The four specimens were tested at about 660°C and at a stress level of 38.7 kg/mm². The test results are listed in Table 2.12; curves showing the strain as a function of time appear in Figure 2.30.

Initial observations indicate that, although the unirradiated specimens had similar creep-rupture results, their microstructures were notably different, depending upon the boron concentration. The unirradiated specimens containing the high- and low-boron concentrations were tested for 192 and 195 hours, respectively. As indicated in Figures 2.31a and 2.31b, the grain sizes in the buttonhead portions of the specimens were similar. However, as shown in Figures 2.31c and 2.31d, the grain size increased considerably in the reduced section of the low-boron specimen but not in the high-boron specimen.

The irradiated specimens containing the low- and high-boron concentrations were tested for 46 and 252 hours, respectively. As shown in Figures 2.32a and 2.32b, the buttonhead

Neg. 3804 SPECIMEN NO. 113AS (0.00085% B) 100 X
BUTTON-HEAD

a

Neg. 3808 SPECIMEN NO. 145AS (0.010% B) 100 X
BUTTON-HEAD

b

Neg. 3806 SPECIMEN NO. 113AS 100 X
REDUCED SECTION

c

Neg. 3810 SPECIMEN NO. 145AS 100 X
REDUCED SECTION

d

Fig. 2.31 – Typical microstructure of unirradiated A-286 alloy

Neg. R-737

SPECIMEN NO. 107AS (0.00085% B)
BUTTON-HEAD

100 X

a

Neg. R-740

SPECIMEN NO. 140AS (0.010% B)
BUTTON-HEAD

100 X

b

Neg. R-742

SPECIMEN NO. 107AS
REDUCED SECTION

100 X

c

Neg. R-743

SPECIMEN NO. 140AS
REDUCED SECTION

100 X

d

Fig. 2.32 – Typical microstructure of irradiated A-286 alloy

grain size in the low-boron specimen is only slightly less than that in the high-boron specimen and both grain sizes are similar to those obtained in the buttonheads of the unirradiated specimens. Figures 2.32c and 2.32d corroborate the observations made on the unirradiated specimens in that the grain size in the stressed region (reduced section) of the low-boron specimen indicates some grain growth, which is not evident in the high-boron specimen.

These results suggest that a prominent role is played by the boron additions,* especially when the specimen is stressed. Microstructures will be further investigated with the electron microscope and the electron microprobe.

Fatigue Test Data

Some testing was performed to determine the effect of neutron irradiation on the fatigue strength of A-286. The fatigue equipment and test techniques employed were discussed previously.^{††}

Fifteen A-286 specimens have been tested at 650°C. Eight were irradiated in capsule MT-51 ($\sim 4 \times 10^{19}$ nvt, $E_n \geq 1$ Mev) at about 690°C for 64 hours. Five of the seven control specimens were heated in air at 690°C for 64 hours before testing to simulate reactor thermal conditions. The other two control specimens were tested in the as-machined condition. The results are presented in Table 2.14 and Figure 2.33. The data indicate irradiation strengthening as evidenced by increased fatigue life at stress levels of 42.2 and 52.8 kg/mm². The reason for the small difference in the data at 47.8 kg/mm² is not yet known.

Fig. 2.33 – Effect of irradiation on the fatigue strength of A-286 alloy at 650°C

*R. F. Decker, J. P. Rowe, and J. W. Freeman, "Relations of High-Temperature Properties of a Nickel-Base Precipitation-Hardening Alloy to Contamination By Crucibles," *High Temperature Materials*, John Wiley and Sons, Inc.; New York, 1959, pp. 388–406.

†"High-Temperature Materials Program Progress Report No. 7, Part A," GE-NMPO, GEMP-7A, January 15, 1962, pp. 46–49.

††"First Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume I—Materials," GE-NMPO, GEMP-106A, February 28, 1962, pp. 74–75.

TABLE 2.14
FATIGUE TEST RESULTS AT 650°C ON IRRADIATED AND
CONTROL SPECIMENS OF A-286 ALLOY

Specimen ^a	Type	Pre-Test Treatment	Stress,		Megacycles To Failure	Time To Failure, hr
			kg/mm ²	psi		
51AF	Control	64 hr at 690°C	42.2	60,000	21.6	43.1
55AF	Control	64 hr at 690°C	42.2	60,000	13.4	27.2
58AF	Control	As-machined	42.2	60,000	- ^b	0.45
42AF	Irradiated ^c	-	42.2	60,000	72.0	139.0
40AF	Irradiated	-	42.2	60,000	49.6	99.5
53AF	Control	64 hr at 690°C	47.8	68,000	3.6	7.1
59AF	Control	As-machined	47.8	68,000	3.4	7.0
38AF	Irradiated	-	47.8	68,000	4.3	8.7
39AF	Irradiated	-	47.8	68,000	5.7	11.5
45AF	Irradiated	-	47.8	68,000	4.0	8.1
54AF	Control	64 hr at 690°C	52.8	75,000	0.22	0.45
57AF	Control	64 hr at 690°C	52.8	75,000	0.16	0.35
46AF	Irradiated	-	52.8	75,000	1.2	2.4
41AF	Irradiated	-	52.8	75,000	1.4	2.9
43AF	Irradiated	-	52.8	75,000	b	0.4

^aAll specimens are from Heat B-15649 and all received the following heat treatment prior to finish machining:

900°C for 2 hours, oil quench
720°C for 16 hours, air cool
650°C for 16 hours, air cool

^bSpecimen failed abnormally at a location within the support vise where fretting had occurred.

^cIrradiated at $\sim 4 \times 10^{19}$ nvt ($E_n \geq 1$ Mev)

2.3 SUMMARY AND CONCLUSIONS

Creep-Rupture Tests

Tungsten - Irradiation of recrystallized tungsten rod to a dose greater than 4×10^{18} nvt ($E_n \geq 1$ Mev) tends to reduce creep rate and to increase stress-rupture life of specimens tested at 1100°C. Minimum second-stage creep rate was reduced by a factor of 2, and stress-rupture life was increased by a factor of 2.6 after irradiation to a fast neutron dose of 2.5×10^{19} nvt. The elongation and the reduction in area of control and irradiated specimens were quite similar when compared at the same temperature and stress.

Annealing at 1400°C for 1 hour prior to testing at 1100°C did not remove the defects causing irradiation hardening observed during second-stage creep, although this heat treatment did remove defects causing anomalous first-stage creep behavior. Annealing at 1100°C for 1 hour prior to testing did not remove radiation-induced hardening observed in the first-stage creep.

Comparison of creep rate results on recrystallized tungsten, specimens fabricated by grinding, and ground specimens having the diameter reduced electrolytically by 0.457 millimeter, shows that grinding does not significantly affect the creep rate at 1100°C. Third-stage creep, and consequently the rupture life, was affected more by the electro-polishing process.

The effects of neutron irradiation are more pronounced in recrystallized material than in cold-worked material. For example, the creep rate of cold-worked irradiated ($3.2 \times$

10^{19} nvt) tungsten sheet was reduced by a factor of 1.6 when tested at 1100°C . The creep rate of recrystallized irradiated (2.5×10^{19} nvt) rod was reduced by a factor of 2 at the same temperature. The corresponding rupture life of the cold-worked irradiated material was increased by a factor of 1.6, and that of recrystallized material by a factor of 2.6. Annealing an irradiated cold-worked sheet specimen at 1900°C in a hydrogen atmosphere does not completely remove the irradiation-induced hardening when compared to a similarly annealed control specimen.

Tungsten - 25 Rhenium - Creep-rupture properties of W - 25Re sheet specimens irradiated to a dosage of approximately 7×10^{18} nvt ($E_n \geq 1$ Mev) and tested at 1100°C were not significantly affected, although there was a slight reduction in creep rate. Based on two tests, pure rhenium specimens irradiated to the same fast neutron dosage and creep-rupture-tested at 1100°C appear to be affected more than the W - 25Re specimens.

Molybdenum - Irradiation of molybdenum creep-rupture sheet specimens to a dose of approximately 7×10^{18} nvt ($E_n \geq 1$ Mev) did not significantly change the creep rate nor the rupture life when tested at 870°C and 980°C . The threshold of irradiation-induced changes apparently lies above this dosage level.

A-286 - Stress-rupture studies on A-286 containing various amounts of natural boron and irradiated to a dose of about 5×10^{19} nvt ($E_n \geq 1$ Mev) shows that the greatest radiation-induced changes occur in specimens containing the smallest amount of boron (0.00085 weight percent). The rupture life of specimens containing about 0.010 weight percent boron was within 25 percent of the control data, whereas the life of specimens having lower boron concentration was reduced 500 percent. The elongation of both groups of specimens was seriously reduced by the irradiation with the greater reduction occurring in the specimens containing the least amount of boron.

Optical microscopy studies of control and irradiated A-286 specimens indicate that a significant stress-enhanced grain growth results in the case of the unirradiated specimen containing the least amount of boron.

Fatigue

A-286 - Fatigue life of A-286 specimens irradiated to a dose of about 4×10^{19} nvt ($E_n \geq 1$ Mev) and tested at 650°C was increased by a factor of 3.3 at a stress of 42 kg/mm^2 and by a factor of 7 at a stress of 53 kg/mm^2 . The fatigue life at an intermediate stress of about 47 kg/mm^2 increased by only a factor of 1.2.

Resistivity Tests

Tungsten - Annealing studies on tungsten samples irradiated at pile-ambient temperature to a dose of $>10^{19}$ nvt ($E_n \geq 1$ Mev) indicate that recovery occurs in three stages with some radiation-induced increase still remaining (4 percent) after 1 hour at 1900°C . The three stages were observed at temperatures of 16, 22, and 31 percent of the absolute melting point (T_m) of tungsten. The recovery stage at 325°C ($0.16 T_m$) is in good agreement with Thompson's* value of 400°C and with the 350°C value reported for tungsten by Peacock and Johnson.† This peak is generally referred to as Stage III Recovery and is presently attributed to vacancy migration.*† The peak at $0.22 T_m$ is sometimes assumed to be caused by vacancy-solute pair dissociation from impurity atmospheres which may be locked to dislocations. Very little is known about the third peak which is observed at

*M. W. Thompson, loc. cit.

†D. E. Peacock and A. A. Johnson, "Stage III Recovery in Neutron Irradiated Molybdenum and Niobium," *Philosophical Magazine*, Vol. 8, April 1963, p. 563.

870°C ($0.31 T_m$). The radiation-induced increase in resistivity remaining even after the 1900°C annealing is probably due to transmutations.

Tungsten - 25 Rhenium - Samples of W - 25Re irradiated to a dose of 1.3×10^{19} nvt ($E_n \geq 1$ Mev) show recovery spectra with only one rapid recovery stage occurring at 225°C. Using a solidus temperature of 3000°C, this peak occurs at a homologous temperature of $0.15 T_m$ which is in good agreement with the melting point correlation of tungsten.

Molybdenum - Irradiating molybdenum samples to a dose of 1.3×10^{19} nvt ($E_n \geq 1$ Mev) increased the resistivity of recrystallized specimens by about 120 percent and that of the warm-worked specimens by about 80 percent. This same trend, in which the irradiation affects the recrystallized material more than the worked material, was noted in the tungsten resistivity and creep-rupture samples. The recovery peaks of irradiated molybdenum specimens occur at $0.15 T_m$ and $0.31 T_m$ which is consistent with correspondent data given above for tungsten and W - 25Re.

2.4 PLANS AND RECOMMENDATIONS

The post-irradiation creep-rupture testing of W, W - 25Re, Mo, and Mo-TZM specimens irradiated at reactor ambient temperatures in an inert atmosphere will continue. Specimens from similar materials will be irradiated at elevated temperatures in an inert atmosphere. Other refractory-metal alloys, such as Mo - 0.5Ti, Mo - 50Re, Ta, Ta - 10W, and Nb - 1Zr will be studied on an exploratory basis.

The effects of neutron irradiation on other properties, such as tensile strength, resistivity, hardness, and brittle-ductile transitions, will also be studied for some of these materials.

Theoretical studies on the neutron-induced defects in the base metals and also in the alloys will be evaluated by comparing: (1) activation energies for defect migration as determined by post-irradiation isochronal and isothermal annealing measurements, (2) substructure as observed by transmission electron microscopy, and (3) mechanical properties measured in the testing program.

Dosimetry studies related to refractory metals, including the influence of neutron spectrum, angular distribution, and material configuration, on the nature and the pattern of atom displacements in BCC metals will be continued.

ADDENDUM TO SECTION 2

"Effect of Radiation on High-Temperature Refractory Metals and Alloys"

CAPSULE DESIGNS

The initial reactor irradiations at ambient temperature were performed in capsules in which the test specimens were in contact with either static or flowing water. Figure 2A.1 shows photographs of capsule 33MT-112. In this design, the reactor coolant water flowed

Fig. 2A.1—Refractory-metal irradiation capsule 33MT-112 (Neg. P63-6-24G)

through the capsule along the specimen axis. Because of possible dissimilar metal reactions, high-flow-rate effects, or other corrosion phenomena, the specimens from this capsule were not suitable for subsequent creep-rupture testing. On the other hand, with the exception of a slight filming which could be removed by a dilute NaOH solution, earlier specimens irradiated in contact with water (in capsules ORM-1 through ORM-14, and 33MT-103) did not show any obvious corrosion. Nevertheless, to prevent any possible corrosion problem, capsules ORM-15 through ORM-19 were back-filled with helium gas and sealed before being irradiated.

The ORM-18 capsule assembly is shown in Figure 2A.2. Three types of specimens are shown. Figure 2A.2a shows one of the reduced-gage-section creep-rupture specimens produced by electropolishing 0.10-centimeter-diameter wire. Figure 2A.2b shows the larger type creep-rupture specimen with its heat transfer jacket and the standard resistivity and hardness specimen (0.32 centimeter in diameter and 5.72 centimeters long).

The first elevated-temperature capsule (33MT-113), containing five Mo, five Mo-TZM, ten W - 25Re, and twenty W resistivity and hardness specimens, was irradiated in the ETR for 4267 megawatt-days. Figure 2A.3 shows the four tubes of this capsule and the locations of the thermocouples, dosimeters, and specimens. Construction features of one of the tubes are shown in Figure 2A.4. The final assembly of the four tubes into the cartridge is shown in Figure 2A.5. The location of 8 of the 12 dosimeters can be seen in this photograph.

The design temperature for the W and W - 25Re specimens was 1300°C, and for the Mo and Mo-TZM, 700°C. The temperature of the specimens was controlled by the ratio

a. COMPONENTS OF CAPSULE ORM-18 (Neg. P64-1-7A)

Fig. 2A.2— Three types of creep-rupture specimens from irradiation capsule assembly ORM-18

b. SINGLE-STAGE HEAT TRANSFER CYLINDER WITH
CREEP-RUPTURE AND RESISTIVITY SPECIMENS (Neg. P64-1-7B)

c. HELIUM-FILLED FINAL ASSEMBLY (Neg. P64-1-7C)

Fig. 2A.3 - Specimen, thermocouple, and dosimeter locations of capsule 33MT-113

Fig. 2A.4 – Construction of one of the tubes of capsule 33MT-113 (Neg. P63-9-12A)

Fig. 2A.5 – Tube assembly of high-temperature refractory-metal irradiation capsule 33MT-113 (Neg. P63-9-12B)

of He-to-Ar gas mixture. A plot of the calculated temperature values at a power level of 175 megawatts versus the reactor core position is shown in Figure 2A.6.

Fig. 2A.6—Calculated temperatures versus core position of capsule 33MT-113

The second elevated-temperature capsule, designated 33MT-137, was designed and partially fabricated. This capsule will be used to irradiate twenty-four tungsten creep-rupture specimens at 1300°C to a fast neutron dose of approximately 10^{20} nvt.

REFRACTORY-METAL IRRADIATION TEST FACILITIES

Two test facilities of the type designed for testing refractory-metal-clad fuel specimens in the ETR are also being used for irradiation of refractory metals. Figure 2A.7 shows the loop and components of one of these two identical facilities. Major components are helium and argon gas supply stations, individual gas filters, dryers, rotameters, and temperature recorders located in the experiment control room. A 0.32-centimeter-diameter gas supply line extends from the control room to an auxiliary panel located in the reactor area. Parallel dryers and oxygen getters are located in the reactor area, as are the necessary valves and fittings for evacuation and purging the upstream portion of the system. The oxygen getter material is titanium metal which is operated at a peak temperature of 870°C. The ion chambers and gas exit lines are shielded and are located near the carbon trap, also in the reactor area. The gas exits into the off-gas system located in the reactor trench.

As in fuel tests, every precaution was taken to insure an ultraclean system. Each component, including the stainless steel tubing, was individually cleaned, purged with inert gas, and sealed prior to final assembly. After facility installation, the entire system was purged with gettered helium, and evacuated several times, a procedure which is followed each time a lead tube assembly is installed.

Fig. 2A.7 - Schematic of refractory-metal test facility

TEST EQUIPMENT

Modified Creep-Rupture Test Stands ($T > 850^{\circ}\text{C}$)

Two creep-rupture stands used in the FY-62 program were modified for use in the refractory-metal program. New high-temperature furnaces were installed on the stands. These furnaces, shown in Figures 2A. 8 and 2A. 9, have water-cooled walls and end plates. All joints or holes into the internal cavity are sealed with rubber O-rings. The furnaces employ a circular tungsten heating element of the type shown in Figure 2A. 10 and permit testing of sheet or round specimens in hydrogen, argon, or vacuum. The furnaces are capable of 1900°C operation with the present power supplies.

The tungsten grips and internal load rods extend into the heating element as shown in Figure 2A. 9. The components of the gripping and load-rod assembly for round specimens are shown in Figure 2A. 11. The accurately ground split-grip inserts mate with the radius under the head of the specimen and fit into a counterbore in the grip.

New Creep-Rupture Test Stand ($T < 950^{\circ}\text{C}$)

A new creep-rupture test stand was designed and fabricated for testing in the 700° to 950°C range. The stand utilizes a three-zone electric furnace with an Inconel muffle tube, which in this temperature range should give a better temperature profile along the specimen gage length than would the tungsten heating elements used in the higher-temperature furnace.

The direct-weight loading system was designed for a maximum load of 250 pounds. All weights are contained in a bottom load tank assembly. This assembly, together with static O-ring seals on the muffle tube, permits testing in hydrogen, inert atmosphere, or vacuum. The bottom load tank assembly also contains mechanisms for removing the loads and transducers. A schematic drawing of the new stand is shown in Figure 2A. 12; Figure 2A. 13 is a photograph of the complete assembly.

Hot-Hardness Test Furnace and Assembly

Hardness measurements at elevated temperatures may be made as a function of time by using the apparatus shown in Figure 2A. 14. The water-cooled molybdenum resistance-heated furnace is designed to operate in a vacuum, or in inert atmospheres, at temperatures up to 1650°C . The practical testing temperatures, however, might be limited by reactions between the indenter (diamond or sapphire) and the test specimen. The equipment incorporates most of the features of any standard microhardness machine. Ports for viewing the positioned test specimen and the loading platform are shown in the photograph. A chamber system is provided for loading and unloading specimens while at test temperature and under atmosphere. The upper recorder, shown in the photograph, indicates the applied load as a function of time, and the lower recorder indicates the specimen temperature.

The major components of the loading system are shown in Figure 2A. 15. The indenter and load column weighs 1000 grams and is suspended from an instrumented cantilever beam. As the indentation is being made on the sample, the cantilever beam is being unloaded, causing a deflection which is measured by strain gages attached to the beam. In this manner, the amount of load and the time of application can be recorded. The drive motor for the load column is also shown at the top of Figure 2A. 15. The dial gage shown below the drive motors is used when operating in various atmospheres. Lateral motion of the indenter and load column is obtained by a calibrated cam-operated drive mechanism. Rotational movement of the sample (not shown) gives an additional degree of movement so that any part of a flat specimen may be tested.

Fig. 2A.8—High-temperature furnace arrangement on lever-loaded creep-rupture stand (Neg. P63-3-1A)

Fig. 2A.9—Schematic drawing of high-temperature vertical furnace for testing refractory metals

Fig. 2A.10 – Tungsten heating element for high-temperature furnace (Neg. P63-1-27)

Fig. 2A.11 – Tungsten grip assembly and load rod for testing refractory metal creep-rupture specimens (Neg. P63-2-23A)

Fig. 2A.12—Schematic drawing of intermediate-temperature refractory-metal creep-rupture test stand

GE-NMPO

Fig. 2A.13—Furnace assembly for testing refractory metals at intermediate temperatures (Neg. P64-1-40A)

Fig. 2A.14— Hot-hardness testing furnace and associated equipment (Neg. P62-6-13F)

Fig. 2A.15 - Hot-hardness testing components (Neg. P63-3-25B)

Resistivity Equipment and Methods

Test equipment was assembled to measure the resistance of test specimens in a constant temperature bath. The technique consists of measuring the potential drop across the sample (unknown) and comparing it with the potential drop across a known precision standard resistance. Since the two resistors are connected in series, the current through each is equal and the resistance of the unknown can be calculated from the following relationship:

$$\frac{V_x}{R_x} = \frac{V_s}{R_s}$$

where

x = unknown
s = standard.

A Leeds and Northrup K-3 bridge is used to measure the potential drop. An oil bath maintained at a fixed temperature by controlled heaters is used to immerse the unknown and standard resistors. Liquid nitrogen is used for the low-temperature readings. The specimen fixture consists of copper bus bars connected to each end of the 5.72-centimeter-long samples for the current leads. The potential drop is measured near the center of the sample, contact being made with hardened steel knife edges placed 2.573 centimeters apart. The current through the system is usually about 2.9 amperes.

3. RADIATION EFFECTS IN BeO

(57063)

The objective of this program is to define the irradiation behavior of BeO in terms of the composition and microstructure variables that contribute to extended radiation stability, with emphasis being placed on variables that either promote loss of the helium gas formed by neutron absorption or enable the structure to retain the gas without undue property changes.

The experimental program consisted of two series of irradiation tests and pre- and post-irradiation examinations during Calendar Year 1963. The main irradiation series involved three compositions with grain sizes ranging from about 3 to 110 microns with densities of nominally 2.6, 2.75, and 2.9 g/cm³. Except for the high-dosage tests, the irradiations of this series were completed, and the post-irradiation measurements were approximately 70 percent complete. A further irradiation series was begun during the year. This series is intended to determine the influence of glass-phase additives on irradiation behavior. The initial measurements of this series were being made at the close of the report period.

The experimental results of this program established that the best irradiation stability is obtained with fine grain size (≤ 5 microns) materials. These materials exhibit both smaller expansion and greater strength retention than material of larger grain sizes in exposures up to approximately 1.8×10^{21} nvt (≥ 1 Mev). Expansion of the specimens, which results from expansion of the crystallographic lattice, grain-boundary cracks, defect clusters, and helium bubbles, depends upon both the irradiation temperature and the neutron flux. Under the proper temperature and flux conditions, grain-boundary cracking can be minimized so that strength is retained to higher dosages. The overall implications are that BeO in irradiation applications should be operated at temperatures greater than 700°C and preferably above 900°C at fluxes of 10^{14} nv (≥ 1 Mev); lower fluxes permit operation at slightly lower temperatures.

3.1 PROGRAM DESCRIPTION

The principal irradiation test series consisted of AOX-, UOX-, and Minox AAA-grade BeO specimens irradiated over a range of temperatures and dosages. The grain size of the test specimens ranged from about 3 to 110 microns with nominal densities of 2.6, 2.75, and 2.9 g/cm³. This grain size - density series is outlined in Figure 3.1; the test schedule and status are shown in Table 3.1.

The irradiation series involving glass-phase additives includes four compositions: 1-percent concentrations in UOX-grade BeO of the high-, medium-, and low-silica glasses listed in Table 3.2 and the 1-percent bentonite composition to be used in EBOR (Experimental Beryllium Oxide Reactor being built by General Atomics). The grain sizes of the specimens are nominal, ranging from 5 to 20 microns, and the density ranges from approximately 2.85 to 2.9 g/cm³. The planned irradiation conditions are outlined in Figure 3.2. In all cases, except the tests at approximately 100°C, specimens of this glass-phase

TABLE 3.1
IRRADIATION TEST SCHEDULE AND STATUS FOR BeO SPECIMENS OF GRAIN SIZE - DENSITY SERIES

Test No.	No. Of Specimens ^a	Temperature, °C	Dosage, ^b 10 ²⁰ nvt (≥1 Mev)	Irradiation ETR Cycle Dates		Facility	No. Of Cartridges	Status
				Start	End			
Tests at a flux of 1.5 to 4 x 10 ¹⁴ nv (≥1 Mev)								
33MT61	54	600	10.7 to 17.6	3-19-62	8-6-62	I-13	3	Completed
66MT50	366	1000	7.6 to 12.2	7-8-62	10-15-62	66	1	Completed
33MT76	81 ^c	100	1.0 to 6.9	7-8-62	8-6-62	I-13	1	Completed
33MT73	30	100	3.2 to 5.0	7-8-62	8-6-62	L-0	1	Completed
33MT75	108 ^d	100	0.8 to 2.6	7-8-62	8-6-62	E-5	3	Completed
33MT72	36	600	100	-	-	-	2	Cancelled
33MT82	24	300, 400, 500, 600	3.3 to 3.8	8-6-62	9-17-62	I-13	1	Completed
33MT68	54	1000	5.9 to 11.5	8-6-62	11-26-62	I-13	3	Completed
33MT59	18	1200	3.7 to 4.3	9-17-62	10-15-62	I-13	1	Completed
33MT89	108	100	0.5 to 1.2	9-17-62	10-15-62	E-5	3	Completed
66MT49	183	600	5.1 to 9.3	10-15-62	2-18-63	66	1	Completed
66MT49	183	800	9.3 to 12.2	10-15-62	2-18-63	66	1	Completed
33MT91	18	1200	3.1 to 3.6	10-15-62	11-26-62	I-13	1	Completed
33MT92	18	1200	(9 to 12)	11-26-62	2-18-63	I-13	1	Completed
66MT62	197 ^e	300	(2 to 3)	1-7-63	4-1-63	66	1	Cancelled
33MT64	54	1200	9.0 to 19.5	11-26-62	4-1-63	I-13	3	Completed
33MT95 ^f	36	1000	(30 to 50)	11-26-62	9-13-63	L-6	1	Completed
33MT95-2B ^g	18	1000	(30 to 50)	8-5-63	7-6-64	L-6	1	In Progress
33MT111	36	1000	(30 to 50)	10-28-63	5-25-64	I-13	1	In Progress
33MT105 ^h	72	1000	(7.5 to 15)	10-28-63	1-19-64	I-13	2	In Progress
Tests at a flux of ~6 x 10 ¹³ nv (≥1 Mev)								
33MT97	36	100	(1.9 to 2.4)	2-18-63	5-13-63	N-14	1	Completed
33MT83 ^g	18	700	1.8 to 2.8	3-16-63	6-24-63	E-5	1	Completed
33MT90 ^g	18	500	2.2 to 3.1	3-16-63	6-24-63	N-14	1	Completed
33MT98	36	300	(1.6 to 2.4)	6-24-63	9-13-63	E-5	1	Completed
33MT101	36	400	(2.0 to 2.8)	6-24-63	9-13-63	N-14	1	Completed
33MT127	36	>900	(~2)	Tentative		E-5	1	In Design
Tests at a flux of ~9 x 10 ¹³ nv (≥1 Mev)								
33MT96	36	1000	(1.5 to 2.3)	4-3-63	5-31-63	E-14	1	Failed
33MT106 ^g	36	600	(2.0 to 3.2)	8-5-63	10-28-63	E-14	1	Completed
33MT140 ^{g, i}	126	100	(1.5 to 2)	1-20-64	3-1-64	E-14, F-15	3	In Progress
33MT108 ^g	36	200-350	(2.0 to 2.8)	10-28-63	1-19-64	N-14	1	Completed
Tests at a flux of 2 to 4 x 10 ¹³ nv (≥1 Mev) (Tentative)								
33MT110	36	300-400	-	Tentative		F-15	-	-

^aSee Figure 3.1 for specimen compositions, grain sizes, densities, and program outline.

^bDosages enclosed in parentheses are estimated.

^cConsists of 18 full-length and sixty-three 2.54-cm specimens. The objective is to define the dosage required to initiate grain-boundary separation in irradiations at 100°C.

^d36 specimens to replace low dosage irradiation of composition series.

^eThis includes 14 specimens 8.9 cm long by 2.517 cm in diameter for thermal conductivity measurements.

^fReplacement for 33MT72.

^gThese tests include specimens containing glass-phase additives; see Figure 3.2 for program outline.

^hThese tests were run using the cartridges prepared for 33MT72.

ⁱFormerly designated 33MT107.

Compositions

1. AOX-grade BeO
2. UOX-grade BeO plus 0.5 wt % MgO
3. HPA-grade BeO

Grain size and density combinations

Density, g/cm ³	Grain size, microns
2.95 - 3.00	5, 20
2.90 - 2.95	5, 10, 20, 50, 80, 100
2.75 - 2.80	5, 10, 20, 50, 80
2.60 - 2.65	10, 20, 50, 80

(Not all of the listed combinations are used in all three compositions.)

GE-NMPO

Fig. 3.1 - Irradiation and measurement conditions of grain size - density series

GE-NMPO

Fig. 3.2 - Nominal irradiation conditions for BeO containing glass-phase additives

TABLE 3.2
COMPOSITION OF GLASSES TO BE
USED AS ADDITIVES IN BeO^a

Compound	Silica Glass Composition, wt %		
	High	Medium	Low
SiO ₂	82	53	30
Al ₂ O ₃	4	22	20
CaO	-	10	20
MgO	-	7	10
BeO	-	8	10
Na ₂ O	10	-	-
ZrO ₂	4	-	10

^aAdditives used in 1 weight percent concentration in UOX grade BeO. Specimen density 92 to 95 percent of theoretical density.

series were combined with tests of the grain size - density series. Three of these irradiations were completed and the remainder are in progress.

3.2 SPECIMEN DESCRIPTION

The specimens used in most of the irradiations were solid, right cylinders 8.9 centimeters long by 0.605 centimeter in diameter; in some of the high-dosage exposures, however, the length was reduced to 4.44 or 3.63 centimeters. The specimens were prepared principally by extrusion and sintering; a few were prepared by isostatic pressing and sintering. They were made from AOX-, UOX-, and HPA-grades of BeO and are briefly described below.

1. The AOX-grade BeO, supplied by Brush Beryllium Company, is a relatively low-purity material averaging about 1500 to 2000 ppm total impurities. The principal impurity elements, present in concentrations of 100 ppm or higher, are fluorine, sodium, silicon, carbon, and manganese. The size of the crystallites determined by X-ray analysis is about 400 Å.
2. The UOX-grade BeO is also supplied by the Brush Beryllium Company. Although the production process has not been described by the manufacturer, UOX is generally considered to be derived from the sulfate. The principal impurity elements are sulfur (400 to 1000 ppm), calcium (~100 ppm), and carbon (~100 ppm); the total impurity concentration ranges from 800 to 1500 ppm. The crystallite size ranges from 600 to 1000 Å; however, there is a small concentration of rod-like crystallites ranging up to 150 microns in length.
3. The HPA-grade BeO is a GE-NMPO designation for high-purity BeO derived from the basic acetate process. The material used in this program is obtained from the Mineral Concentrates and Chemical Company as beryllium hydroxide. After being calcined to BeO at 950°C, the material contains a total of 100 to 150 ppm of impurities and is comprised of crystallites about 1000 Å in diameter.

A more detailed description of these powders and the production and inspection processes was presented in the first annual report.* Observations with respect to purity, lattice constants, microstructure, porosity, and orientation of fabricated specimens are briefly summarized in the following paragraphs; further information may be found in the second annual report.†

*"First Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume I—Materials," GE-NMPO, GEMP-106A, February 28, 1962, pp. 76–88.

†"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume I—Materials," GE-NMPO, GEMP-177A, February 28, 1963, pp. 115–126.

Purity

In the as-sintered condition, there is comparatively little difference in the concentration of impurities in the various compositions studied. Table 3.3 lists the impurity concentrations for several different production runs on individual compositions that have been, or are being, examined in the program. In general, the concentrations of carbon, sulfur, and sodium are considerably reduced in processing, and there is an iron pickup of about 100 ppm.

TABLE 3.3
IMPURITY LEVELS IN BeO RODS OF SIX COMPOSITIONS
AFTER SINTERING

Impurity Element	Impurities, ppm					
	AOX (2) ^a	UOX (4) ^a	UOX+MgO (2) ^a	UOX+ZrO ₂ (4) ^a	HPA (2) ^a	HPA+MgO (2) ^a
C	115	160	125	186	145	86
F		20	20	10	15	20
P		27	23	16	25	22
S	15	23	60	26	35	30
Al	25	50	45	50	30	83
B	<3	<3	<3	<3	<3	<3
Ca	80	130	150	125	25	28
Cr	10	24	35	20	18	45
Fe	103	240	215	140	118	205
Li	<1	<1	<1	<1	<1	<1
Mg	110	80		72	85	
Mn		<10	20	<10	<10	<10
Na	25	17	10	15	25	12
Ni	33	35	33	30	<10	50
Si	83	90	95	113	125	180
Sr		<10	<10	<10	<10	<10
Zn		<20	<20	<20	<20	<20

^aNumber of determinations.

Lattice Constants

As summarized in the first annual report,* lattice constants measured on sintered specimens of the various compositions are essentially the same, $a = 2.698_0$ and $c = 4.378_0$.

Microstructure

With the exception of UOX-ZrO₂, all of the compositions appear to be single-phase materials in microscopic examination. Photomicrographs typical of the various densities and grain sizes[†] were presented in the previous annual report.[‡]

Porosity

The type and distribution of pores in various specimens is still under investigation. In specimens of 20-micron grain size or larger and densities ranging from 96 to 98 percent of theoretical, it was established that about 90 percent of the porosity is intragranular and of 1 to 2 microns in diameter. There are unusually large amounts of intergranular porosity in specimens of both the fine grain sizes (≤ 5 microns) and those to which resin was added

*"First Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume I—Materials," GE-NMPO, GEMP-106A, February 28, 1962, pp. 79–82.

[†]Grain sizes reported are calculated from lineal analysis of polished sections, as described in ASTM Method E112.

[‡]"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume I—Materials," GE-NMPO, GEMP-177A, February 28, 1963, pp. 118–120.

during fabrication to control density. Further porosity measurements are being made in connection with measurements of helium release in irradiated specimens.

Orientation

Orientation measurements of the crystallographic axes in the finished specimens established that AOX- and HPA-grade BeO specimens are essentially randomly oriented irrespective of the method of processing. The UOX-grade BeO specimens are also essentially randomly oriented when they are fabricated by isostatic pressing; when fabricated by extrusion, however, they contain a considerable amount of c-axis orientation along the longitudinal axis of the specimen. This preferential orientation, which is of simple (001) fiber texture, increases in amount with increasing grain size of the specimens, as shown in Figure 3.3. It was established during Calendar Year 1963 that the amount of orientation was not significantly influenced by variation of specimen density.* Details of the measurement techniques, distribution, magnitude, and causes of this preferential orientation were presented previously.†

Physical and Mechanical Properties

A summary of the physical and mechanical property measurements completed on the specimens used in the irradiation tests, together with other pertinent BeO data, is presented in Table 3.4. Details of the data were summarized previously;‡ measurements on thermal expansion§ and on elastic constants at elevated temperatures•® were completed during this year.

3.3 RADIATION EFFECTS

Although several aspects of the behavior of irradiated BeO were described in previous reports, additional information in nearly all areas of investigation was obtained during Calendar Year 1963. Accordingly, this section presents an overall summary of the data obtained in this study.

The most important effect of irradiation in BeO is dimensional, and volume expansion, particularly since one of the aspects of expansion; i. e., grain boundary separation, appears to be the most significant factor influencing the changes in mechanical properties. It is convenient, therefore, to discuss expansion and the factors that influence it in low- and elevated-temperature irradiations, before describing the property changes. A tentative model of the kinetics of irradiation expansion is presented in a subsequent section.

Expansion in Low-Temperature Irradiations

In irradiations at approximately 100°C, BeO exhibits two nearly linear rates of dimensional and volume expansion with dosage. The smaller rate extends up to dosages of 1 to 2×10^{20} nvt (≥ 1 Mev). At this dosage, the volume expansion in specimens with grain sizes of 20 microns and less is 0.4 to 0.6 percent. At higher dosages, the expansion rate increases until the total volume increase becomes approximately 6 percent at a dosage of about 8×10^{20} nvt. The data in Figure 3.4 are typical of the observed changes.

*"High-Temperature Materials Program Progress Report No. 28, Part A," GE-NMPO, GEMP-28A, November 11, 1963, p. 8.

†"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume I—Materials," GE-NMPO, GEMP-177A, February 28, 1963, pp. 117–126.

‡Ibid., pp. 126–151.

§"High-Temperature Materials Program Progress Report No. 24, Part A," GE-NMPO, GEMP-24A, June 28, 1963, pp. 12–16.

•Ibid., pp. 9–12.

®"High-Temperature Materials Program Progress Report No. 28, Part A," GE-NMPO, GEMP-28A, November 11, 1963, pp. 8–12.

Fig. 3.3—Orientation as a function of grain size in UOX-MgO

Components of Low-Temperature Expansion

Expansion at low temperatures consists of crystal lattice expansion and cracks or voids at the grain boundaries.

Lattice Expansion - Crystal lattice expansion results from displacement of atoms by neutron collisions to form point defects and defect clusters. There are several important facets of the lattice expansion: (1) much of the expansion is comprised of clusters (Sabine, et al.;* Pryor, et al.[†]); (2) there are two rates of expansion with dosage, the higher rate occurring at dosages greater than approximately 1.7×10^{20} nvt (Hickman, Walker, Hemphill[‡]); and (3) the clusters are included in the lattice expansion.[‡] Lattice expansion and

*T. M. Sabine, A. W. Pryor, and B. S. Hickman, "The Scattering of Long Wavelength Neutrons by Irradiated Beryllium Oxide," *Philosophical Magazine*, Vol. 8, No. 85, 1963, p. 43.

[†]A. W. Pryor, R. J. Tainsh, and G. K. White, "Thermal Conductivity at Low Temperature of Neutron-Irradiated BeO," International Conference on Beryllium Oxide, Sydney, Australia, October 21–25, 1963.

[‡]B. S. Hickman, D. G. Walker, and R. Hemphill, "Comparison of Macroscopic and X-Ray Growth in Irradiated BeO Single Crystals," International Conference on Beryllium Oxide, Sydney, Australia, October 21–25, 1963.

TABLE 3.4
PHYSICAL AND MECHANICAL PROPERTIES OF UNIRRADIATED BeO

DYNAMIC ELASTIC CONSTANTS (20°C, 10 ⁶ kg/cm ² , porosity range 0.02-0.16)					References
Grain Size, microns	AOX (Extruded)		UOX-MgO (Extruded)		This table
	E ₀	A	E ₀	A	
Young's Modulus $E = E_0 \left[1 + \frac{AP}{1 - (A+1)P} \right]$ (Hasselman Equation)					D. P. H. Hasselman, <u>Journal American Ceramic Society</u> , 45, 9, 452-53, 1962.
5	3.87(55.09)*	-2.12	3.89(55.30)*	-1.99	
10	3.92(55.82)	-2.03	4.09(58.24)	-2.24	
20	4.01(57.07)	-2.22	4.21(59.91)	-2.16	
50	4.03(57.28)	-2.32	4.48(63.79)	-2.81	
Shear Modulus (Torsion) $G = G_0 \left[1 + \frac{AP}{1 - (A+1)P} \right]$ (Hasselman Equation)					D. P. H. Hasselman, <u>Journal American Ceramic Society</u> , 45, 9, 452-53, 1962.
	G ₀	A	G ₀	A	
5	1.47(20.93)*	-2.13	1.48(21.04)*	-2.00	
10	1.49(21.23)	-2.12	1.55(22.01)	-2.28	
20	1.52(21.61)	-2.20	1.60(22.75)	-2.28	
50	1.53(21.78)	-2.33	1.68(23.90)	-2.80	

Young's And Shear Moduli Versus Temperature, °C

Extruded AOX, 20°-1400°C, 5-50 micron grain size,
0.02-0.09 porosity

$$\% \Delta E \text{ from } 20^\circ\text{C} = 7.77 \times 10^{-3} (T-20) + 4.76 \times 10^{-7} (T-20)^2 + 1.23 \times 10^{-9} (T-20)^3$$

$$\% \Delta G \text{ from } 20^\circ\text{C} = 1.18 \times 10^{-2} (T-20) - 6.97 \times 10^{-6} (T-20)^2 + 4.90 \times 10^{-9} (T-20)^3$$

Symbols: E = Young's modulus, 10⁶ kg/cm²; E₀ = Young's modulus, 10⁶ kg/cm² at theoretical density of 3.01 g/cm³; G = shear modulus, 10⁶ kg/cm²; G₀ = shear modulus, 10⁶ kg/cm² at theoretical density of 3.01 g/cm³; P = fractional porosity; A = porosity coefficient; T = temperature, °C.

*Values in parenthesis refer to English system where E₀ = 10⁶ psi at theoretical density of 3.01 g/cm³ and G₀ = 10⁶ psi.

MODULUS OF RUPTURE

(4 point, 7.6 cm span, third point loading, 0.15 cm/min head travel)

$$S = kG^{-a} e^{-bP}$$

(10-100 micron grain size, 0.02-0.16 fractional porosity)

Temp., °C	AOX (extruded)			UOX-MgO (extruded)		
	k	a	b	k	a	b
20	9.98(142) [†]	0.50	2.51	6.17(87.7) [†]	0.35	2.19
300	9.98(142)	0.49	2.95	6.05(86.0)	0.31	3.79
500	7.94(113)	0.44	1.54	6.17(87.8)	0.31	3.57
800	5.32(76.7)	0.28	2.32	5.37(76.4)	0.23	2.85
1000	2.93(41.7)	0.15	1.52	4.50(64.0)	0.19	2.97
1200	1.68(23.9)	0.03	1.44	3.47(49.4)	0.11	4.25

Symbols: S = M/R, 10³ kg/cm²; G = grain size, microns; P = fractional porosity.

[†]Values in parenthesis refer to English system where S = M/R, 10³ psi.

THERMAL EXPANSION

Linear Coefficient, $\mu\text{cm/cm-}^\circ\text{C}$, AOX (extruded) 25°-1200°C
 $\alpha = 5.866 + 3.870 \times 10^{-3} (T-25) - 7.034 \times 10^{-7} (T-25)^2$

Percent Linear Expansion, AOX (extruded) 25°-1200°C
 $\% \text{ Exp.} = 5.866 \times 10^{-4} (T-25) + 3.870 \times 10^{-7} (T-25)^2 - 7.034 \times 10^{-11} (T-25)^3$

COMPRESSIVE CREEP AT 1200°C

(0-422 kg/cm², 5-100 micron grain size)

Creep Rate, $\mu\text{cm/cm-hr}^*$

Diffusion Coefficient, cm²/sec[†]

$$\text{AOX (extruded)} \dot{\epsilon} = 102.7 \times 10^{-7} \sigma / \mu^2$$

$$D = 1 \times 10^{14} \text{ cm}^2/\text{sec}$$

$$(\dot{\epsilon} = 7.22 \times 10^{-7} \sigma / \mu^2)^{\dagger}$$

$$\text{UOX-MgO (extruded)} \dot{\epsilon} = 58.7 \times 10^{-7} \sigma / \mu^2$$

$$D = 6 \times 10^{-15} \text{ cm}^2/\text{sec}$$

$$(\dot{\epsilon} = 4.13 \times 10^{-7} \sigma / \mu^2)^{\dagger}$$

Symbols: $\dot{\epsilon}$ = creep rate, $\mu\text{cm/cm-hr}$; σ = compressive stress, kg/cm²; μ = grain size, microns

[†]English system where $\dot{\epsilon}$ = creep rate, $\mu\text{in./in.-hr}$; σ = compressive stress, psi.

F. P. Knudsen, Journal American Ceramic Society, 42, 376-387, 1959.

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GEMP-177A^a

*GEMP-22A
[†]GEMP-177A^a

Fig. 3.4—Expansion of 20-micron grain size BeO, 2.9 g/cm³ density, irradiated at approximately 100°C

the microscopic expansion determined from hydrostatic density measurements on crushed specimens are compared to the macroscopic expansion in Figure 3.5. The indicated amount of lattice or microscopic expansion is about 3.3 percent at 10^{21} nvt (≥ 1 Mev).

Grain Boundary Separation - In addition to lattice expansion, macroscopic expansion of polycrystalline bodies is caused by the formation of grain-boundary cracks. These cracks

Fig. 3.5—Components of volume expansion in BeO irradiated at 100°C

form as a result of strain developed between grains of unlike orientation caused by the difference in expansion of the crystallographic axes. It is this aspect of irradiation behavior that leads to the friability and powdering of polycrystalline material in 100°C irradiations. The magnitude of the crack volume depends upon grain size and ranges up to two or three times that of the lattice expansion.

Influence of Grain Size and Density on Expansion

Although irradiation temperature is the most important factor influencing macroscopic expansion, both the grain size and density of the material have a measurable effect.

Grain Size Effects - The influence of grain sizes on expansion is most apparent in grain-boundary separation. Grain size influences the dosage (DGC) at which the cracking occurs. It is expected that DGC will be larger the smaller the grain size and in general, this trend is observed for grain sizes larger than 20 microns; the smaller grain sizes, however, appear to develop cracks at approximately the same dosage as the 20-micron materials. Data that illustrate this aspect of irradiation behavior are shown in Figure 3.6 in which the

Fig. 3.6--Hydrostatic density of BeO specimens of various grain sizes and bulk density irradiated at 100°C

changes in the apparent macroscopic density (ρ_{ma}) are plotted as a function of dosage. This apparent density is obtained by hydrostatic weighing of specimens in trichloroethylene which penetrates into the surface-connected voids; hence it approaches the density of the individual grains as the extent of cracking increases. As defined by this method, D_{GC} differs from the value obtained by X-ray methods. Walker, Mayer, and Hickman* have interpreted X-ray line broadening changes in irradiated material as indicative of D_{GC} . Measurements of changes in the lattice parameters on solid specimens have been similarly interpreted at GE-NMPO. In both cases, the determined D_{GC} values are higher than the values defined by the apparent density measurement. Since the latter measurements agree reasonably well with the changes in strength, they are considered the more pertinent values. The X-ray measurements appear to reflect an "average" condition and are somewhat less sensitive than density and strength measurements in detecting a limited number of cracks.

Density Effects - The influence of density on expansion also seems to be associated with grain-boundary cracking. As indicated by the 5-micron data in Figure 3.6, D_{GC} in materials of the same grain size is probably lower in specimens of lower density, and the macroscopic volume expansion is slightly larger.

Expansion at Elevated Temperatures

In elevated temperature irradiations, expansion is minimized by various annealing processes that reduce the number of defects. Up to temperatures of approximately 600°C, expansion appears similar to that in 100°C irradiations in that there are two rates of expansion with dosage. The point separating the two expansion regions is displaced to higher dosages at higher irradiation temperatures. Above 700°C, expansion appears to be approaching saturation. The data at 700° to 800°C are not clear on this point; however, for temperatures greater than 900°C, the expansion is either at saturation or increasing very slowly at dosages in the range from 1 to 1.5×10^{21} nvt. Data illustrative of these characteristics are shown in Figures 3.7 through 3.10 for irradiation at fluxes of 1 to 3.5×10^{14} nv (≥ 1 Mev).

Fig. 3.7— Volume expansion of AOX-grade BeO specimens, 20-micron grain size and 2.9 g/cm³ density, as a function of dosage and irradiation temperature

*D. G. Walker, R. M. Mayer, B. S. Hickman, "X-Ray Diffraction Studies of Irradiated Beryllium Oxide," International Conference on Beryllium Oxide, Sydney, Australia, October 21–25, 1963.

Fig. 3.8— Volume expansion of UOX-grade BeO specimens containing 0.5 percent MgO, 10-micron grain size and 2.9 g/cm³ density, as a function of irradiation temperature and dosage

Fig. 3.9— Volume expansion of UOX-grade BeO specimens containing 0.5 percent MgO, 20-micron grain size and 2.9 g/cm³ density, as a function of irradiation temperature and dosage

Fig. 3.10—Volume expansion of UOX-grade BeO specimens containing 0.5 percent MgO, 5-micron grain size and a range of densities, as a function of irradiation temperature and dosage

Figures 3.11 and 3.12 illustrate the macroscopic volume increase in different grain sizes for irradiation at 700°C to 900°C and approximately constant dosage of 1.5×10^{21} nvt. Total volume expansion under these conditions ranged from 0.7 to 2.0 percent. In both the AOX- and UOX-MgO-grade BeO specimens, there was a general trend to larger expansion with larger grain sizes. As shown in the figures, this trend is greater in AOX- than in UOX-MgO-grade BeO specimens. Expansion is also generally smaller in the lower density specimens of a given grain size; the effect being somewhat more consistent in the AOX-grade than in UOX-MgO-grade BeO specimens.

Components of Elevated-Temperature Expansion

The components of expansion in irradiations at elevated temperatures include lattice expansion, defect clusters, grain-boundary cracks, and helium bubbles. Although grain-boundary separation is similar, the expansion components from lattice expansion and cluster formation are significantly different from those which occur at low temperatures. Lattice expansion occurs almost solely in the c-axis, particularly at temperatures above 600°C. As indicated in Table 3.5, lattice expansion accounts for only a portion of the volume change after the grain-boundary separation component is eliminated. The excess expansion is attributed to growth of the clusters and to helium bubbles; the amount of expansion due to each of these factors can only be approximated at present.

Helium Bubbles - Bubbles formed from the helium generated in the $(n, 2n)$ and (n, α) reactions in beryllium appear to account for approximately 20 to 30 percent of the excess expansion. Helium bubbles have been observed in the grain boundaries of specimens irradiated at temperatures of 600°C and higher, and they possibly form at temperatures as low as 350°C to 400°C. At the lower temperatures, grain-boundary separation permits the gas to escape and fewer bubbles are formed.

Fig. 3.11—Volume expansion of UOX-0.5MgO (wt %) of different grain sizes and densities after irradiation to approximately 1.5×10^{21} nvt (≥ 1 Mev) at 700° to 900°C

Fig. 3.12—Volume expansion of AOX-grade BeO of different grain sizes and densities after irradiation to approximately 1.5×10^{21} nvt (≥ 1 Mev) at 700° to 900°C

TABLE 3.5
COMPONENTS OF VOLUME EXPANSION IN BeO IRRADIATED AT ELEVATED TEMPERATURES

Sample			Irradiation Conditions			Lattice Expansion			Macroscopic	True	Volume Increase Due To Porosity, ^b %	Surface-Connected Porosity, percent of total volume
Composition	Grain Size, microns	Density, g/cm ³	Temperature, °C	Flux 10 ¹⁴ nv (≥ 1 Mev)	Dosage, 10 ²⁰ nvt (≥ 1 Mev)	$\Delta a/a$, %	$\Delta c/c$, %	$\Delta V/V$, %	Volume Increase, %	Volume Increase, ^a %		
AOX	12	2.9	1000	2.0	2.4	~0	0.04	0.04	0.63	(0.4)	0.2	<0.1
AOX	20	2.9	1030	1.5	3.5	~0	0.04	0.04	0.72	(0.4)	0.3	<0.1
AOX	44	2.9	1000	1.7	4.1	~0	0.06	0.06	0.95	(0.7)	0.2	<0.1
AOX	17	2.9	800	1.9	8.6	0.04	0.25	0.33	2.0	(1.2)	0.8	2.7 ^c
AOX	17	2.9	600	1.8	8.3	0.07	0.81	0.95	2.9	(1.9)	1.0	3.6 ^c
UOX-MgO	20	2.9	970	1.6	3.8				0.60			
UOX-MgO	12	2.9	940	2.4	10.8				0.92			

^aValues are based on hydrostatic density of powder obtained by crushing specimens to size less than 10 microns and comparison to similar powder from the same or similar unirradiated specimens.

^bValues are the difference between macroscopic and true volume increases.

^cThese values indicate appreciable grain boundary cracking.

Figure 3.13 shows photomicrographs of fracture surfaces of a UOX-MgO-grade BeO specimen of 15-micron (nominally 20-micron) grain size. Figure 3.13a is somewhat unusual in that the voids in the "tight" grain boundary can be attributed to helium bubbles with reasonable confidence. Bubbles can be seen on a partially exposed grain surface and are apparent in this same grain boundary extending in both directions from the exposed area.

Figure 3.13b shows an area of the same specimen in which a pulled-out grain has exposed the surfaces of the six neighboring grains, all of which have extensive bubble colonies. The presence of bubbles on all of the faces is indicative of the absence of a high-order process of preferential segregation of gas along particular crystallographic orientations. It is possible, but not probable, that the surfaces are of the same orientation. The unusual bubbles in the surface parallel to the plane of the micrograph are the first observed of this particular shape. Although some of these may be pores, the curved shapes are not typical of normal porosity; rather, the dumbbell shapes indicate coalescence of smaller bubbles to form these large sizes and shapes.

The volume occupied by gas bubbles was estimated from Figure 3.13b, based on the grain surface located at the 6 o'clock position, to be about 0.5 cubic micron on this boundary surface of 21 square microns. The bubbles were assumed to be spheroids with major axes twice the minor axes. From these values, the volume of the bubbles in a 15-micron grain size material would be about 0.9 percent of the total volume, roughly twice the probable $(\Delta V/V)_{\text{He}}$ value for this specimen. A comparison of the bubble sizes in Figure 3.13 with those in Figure 3.14c indicates that the particular bubble surface used in this estimate would lead to an overestimate of the total bubble volume by an appreciable amount. Nevertheless, it appears possible that the bubble volume is in the right range to account for the $(\Delta V/V)_{\text{He}}$.

Photomicrographs of fracture surfaces of 5-, 11-, and 15-micron grain sizes of UOX-MgO-grade BeO specimens, shown in Figure 3.14, indicate that there is a significant difference in the bubble formation in the materials of different grain sizes. The number and sizes of the bubbles increases with increasing grain size. The presence of bubbles in the 5-micron grain size can be questioned; however, close examination discloses some surfaces that possibly contain small bubbles. Assuming that the gas has not escaped, the absence of the bubbles could account for the slightly smaller expansion of the 5-micron material. The difference in the expansion of 5- and 15-micron grain size specimens is about 0.2 percent. As an approximation, this difference may be ascribed to the different concentrations of bubbles and is probably a more realistic value than the bubble count procedure.

Clusters - Although the estimated volume of the helium bubbles is uncertain, it appears that large clusters account for at least part of the expansion in excess of that indicated by the lattice expansion. The clusters were observed in transmission microscopy studies that are in progress; their size and volume contributions are being investigated.

Property Changes

The property changes in irradiated BeO appear to be largely dependent upon the presence or absence of grain-boundary cracks. Properties examined include strength, elastic constants, and thermal expansion. Limited thermal conductivity data on specimens irradiated at approximately 100°C were presented in the previous annual report;* measurements on specimens irradiated at elevated temperatures are currently in progress.

*"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume I - Materials," GE-NMPO, GEMP-177A, February 28, 1963, pp. 167-170.

Neg. 724B

a

5000 X

Neg. 725E

b

5000 X

Fig. 3.13 — Photomicrographs of helium bubbles in fracture surface of UOX-MgO specimen of 15-micron grain size, 2.9 g/cm³ density, irradiated to $\sim 9 \times 10^{20}$ nvt (≥ 1 Mev) at 950°C

a - 5-MICRON GRAIN SIZE

Neg. 729A

5000 X

b - 11-MICRON GRAIN SIZE

Neg. 727E

5000 X

Neg. 725D

5000 X

c - 15-MICRON GRAIN SIZE

Fig. 3.14—Photomicrographs illustrating the progressive increase in the size and number of helium bubbles with increasing grain size. All specimens are UOX-MgO with a density of 2.9 g/cm^3 irradiated to $\sim 9 \times 10^{20} \text{ nvt}$ ($\sim 1 \text{ Mev}$) at 950°C .

Strength - The modulus-of-rupture strength is increased by irradiation at low dosages (or small expansion), followed by a marked decrease which accompanies grain-boundary separation. This trend is shown in Figure 3.15 in which the fraction of unirradiated strength is compared to the volume expansion.

Fig. 3.15 - Strength changes in AOX-grade BeO of 20-micron grain size, 2.9 g/cm^3 density, after irradiation to dosages up to 1.5×10^{21} nvt ($\geq 1 \text{ Mev}$) at temperatures from 100° to 1000°C

Several general aspects of the strength changes in BeO irradiated at elevated temperatures are apparent in the summaries shown in Figures 3.16 and 3.17. The data points represent the changes in the room-temperature modulus of rupture determined by 4-point loading over a 7.6-centimeter span for specimens irradiated at temperatures of about 600° to 950°C in the dosage range from 0.5 to 1.2×10^{21} nvt ($\geq 1 \text{ Mev}$). The curves indicate that there is a similar pattern of strength changes relative to length expansion for each grain size and density. In the randomly oriented AOX-grade BeO, there is no clear indication of a marked difference in the amount of expansion corresponding to grain-boundary separation in the different grain sizes. There is, however, a marked difference in strength-expansion relationship in the region involving grain-boundary cracking as indicated by the increasing slope of the curves with increasing grain size. The 5-micron grain size material retains greater strength at large expansion than do the larger grain sizes. Effects of density in a given grain size are not pronounced; however, specimens of higher density in the 5- and 10-micron grain sizes appear to undergo microcracking at somewhat larger expansions. The strength changes in the UOX-MgO-grade BeO specimens are similar to those in AOX-grade BeO specimens. Because of the preferred orientation in this composition, the curves are displaced to larger length expansion as the

Fig. 3.16— Modulus-of-rupture strength of randomly oriented AQX-grade BeO irradiated at 600° to 950°C to dosages of 0.5 to 1.2×10^{21} nvt (≥ 1 Mev) as a function of length expansion

Fig. 3.17— Modulus-of-rupture strength of UOX+0.5 wt % MgO composition of BeO irradiated at 600° to 950°C to dosages of 0.5 to 1.2×10^{21} nvt (≥ 1 Mev) as a function of length expansion

orientation increases with grain size and there is less variation of the slope for the different grain sizes.

Elevated temperature irradiation also increases the amount of expansion at which grain-boundary cracking occurs. Several types of specimens exhibit increased strength at length expansion ranging up to about 0.4 percent, which corresponds to a volume expansion of 1.2 percent in the randomly oriented material. In contrast, the strength decrease occurs in 100°C irradiations at 0.4 to 0.6 percent volume expansion.

The marked decrease of strength with very small increases in expansion appears to be a characteristic peculiar to specimens irradiated at elevated temperatures. In specimens irradiated at 100°C, the strength decrease appears less pronounced as indicated by the curve in Figure 3.16 for 5-micron AOX-grade BeO specimens irradiated at 100°C. This difference is attributed to interaction of the strains introduced by the anisotropy of the thermal and radiation expansion. In irradiations at elevated temperatures, the thermally induced strain is reduced as the temperature is raised and probably is completely absent at 1000° to 1200°C, the relaxation temperature. The radiation-induced strain accumulates during the exposure and may or may not cause grain boundary cracks at the irradiation temperature. On cooling, however, the thermally induced strain reappears, adds to the radiation strain, and leads to cracking. These considerations would appear to account for the greater slope of the strength-expansion curves of the larger grain sizes and for the lack of clear evidence within these exposure limits that the onset of grain boundary cracking is dependent on grain size.

Elastic Constants - The elastic constants measured by the resonant frequency method exhibit a small decrease that is consistent with the decrease in density up to the point at which grain-boundary cracking occurs. Once this occurs, reproducible readings of the resonant frequencies are difficult to achieve. It is concluded, therefore, that the elastic constants do not change under irradiation conditions that do not cause grain-boundary cracking.

Thermal Expansion - Thermal expansion measurements indicate essentially no effect of irradiation on the expansion coefficients. Specimens irradiated at both low and elevated temperatures were examined and, in all cases, the thermal expansion was within 1.5 percent of that found for unirradiated BeO of the same composition and grain size. Measurements were carried out in a sequence designed to avoid possible interferences from thermal annealing. Samples irradiated at 100°C were annealed in a dilatometer at temperatures up to 1200°C and the thermal expansion was calculated from the cooling curves. Samples irradiated at elevated temperatures were first given a standard thermal expansion test, both heating and cooling, up to the temperature of irradiation. No hysteresis was observed, indicating that no annealing occurred under these conditions. Thermal expansion was calculated from the cooling curves. No change in the thermal expansion was observed within the 1.5-percent reproducibility of the measurement.

Annealing Kinetics and Helium Diffusion

Concepts of the annealing kinetics during irradiation presented in the previous annual report* have been revised slightly in the light of evidence (1) that lattice parameters do not reflect the true expansion in elevated temperature irradiations and (2) the difference between the lattice and macroscopic expansion is not wholly attributable to helium bubbles. As discussed previously, thermal annealing during irradiation can apparently be described in terms of a first-order rate process involving radiation enhanced diffusion. For a first-order mechanism, the concentration, c , of displaced atoms as a function of time, t , is

*Ibid., p. 171.

given by $dc/dt = K - Ac$, where K is the rate of atomic displacements and A is the rate at which the atoms return to normal lattice sites. Integration yields:

$$c = \frac{K}{A} [1 - \exp(-At)] \quad (3.1)$$

Since one vacancy is produced for each displaced atom, the same equation applies to the concentration of vacancies with A now referring to the annealing rate for vacancies. Using this relationship, annealing rates were computed from the experimental data. The concentration, c , was based on the macroscopic volume increase observed in elevated temperature irradiations. The value of K in terms of fractional volume increase per second was obtained from the expansion data cited previously, 3.3 percent ($\Delta V/V$) per 10^{21} nvt, by the expression

$$K = 3.3 \times 10^{-23} \phi \quad (3.2)$$

where ϕ is the neutron flux in nv ($\geq 1 \text{ Mev}$).

Annealing rates determined on this basis range from 10^{-8} to 10^{-6} per second for irradiation temperatures ranging from 600° to 1200°C . These data are summarized in Table 3.6.

TABLE 3.6
THERMAL ANNEALING RATES COMPUTED FROM EXPERIMENTAL DATA

Specimen Description			Irradiation Conditions		Temperature, $^\circ\text{C}$	Total Volume Increase, %	Annealing Rate, sec^{-1}
Composition	Grain Size, microns	Density, g/cm^3	Dosage, 10^{20} nvt ($\geq 1 \text{ Mev}$)	Flux, 10^{14} nv ($\geq 1 \text{ Mev}$)			
AOX	13	2.895	3.49	2.88	1070	0.58	1.30×10^{-6}
	19	2.770	4.02	1.70	1070	0.46	1.13×10^{-6}
	12	2.886	3.49	2.88	1007	0.63	1.11×10^{-6}
	13	2.887	2.61	2.16	992	0.52	0.919×10^{-6}
		2.904	9.24	2.05	890	1.16	0.530×10^{-6}
	13	2.895	2.61	2.16	766	0.71	0.327×10^{-6}
	10	2.901	3.00	0.649	700	0.46	0.389×10^{-6}
UOX-MgO	20	2.904	4.02	1.70	1040	0.46	1.14×10^{-6}
	20	2.904	5.05	2.14	1025	0.54	1.23×10^{-6}
	20	2.904	5.45	2.31	960	0.64	1.10×10^{-6}
	19	2.904	12.1	2.69	920	0.73	1.22×10^{-6}
	19	2.904	11.5	2.56	895	1.10	0.741×10^{-6}
	19	2.906	11.8	2.55	800	1.50	0.507×10^{-6}
	19	2.906	12.0	2.59	775	1.54	0.500×10^{-6}
	19	2.906	7.33	1.58	600	1.76	0.141×10^{-6}
	11	2.898	9.72	2.70	1016	0.79	1.12×10^{-6}
	12	2.901	9.62	2.14	920	0.86	0.789×10^{-6}
	12	2.901	9.58	2.12	800	1.31	0.469×10^{-6}
	12	2.901	8.66	1.92	750	1.38	0.375×10^{-6}
	12	2.901	7.01	1.51	600	1.61	0.161

As indicated in Figure 3.18, the annealing rates for the different compositions, irradiation temperatures, and fluxes fall along a common line within experimental accuracy. The annealing rates can be expressed by:

$$A = 6.3 \times 10^{-5} \exp(-10,400/RT) \quad (3.3)$$

where R is the molar gas constant $\text{cal/mole-}^\circ\text{K}$; and T is absolute temperature, $^\circ\text{K}$.

These results indicate that the annealing does follow first-order kinetics. It must be noted that basing the calculations on the macroscopic volume expansion limits the region

Fig. 3.18—Annealing rate during irradiation in 20-micron and 10-micron grain size BeO specimens with a density of 2.9 g/cm³.

of applicability of the equation to values of expansion that do not involve grain-boundary separation. The constant in the expression for K also may be questioned; however, its value may be varied appreciably with the only effect being to raise or lower the range of the magnitude of the annealing rate. On the other hand, the fit of the data to a common line over a range of temperatures suggests that the assumed kinetic relationship does apply.

These relationships describe the observed expansion in specimens of 20-micron grain size reasonably well (~20 percent) for the range of dosages investigated. They predict saturation of the expansion and significant differences in the expansion under different neutron fluxes, as indicated in Figures 3.19 and 3.20. The predicted expansion is, however, in only fair agreement with the observations of Keilholtz, Lee, Moore, and Hamner.* Their data for material of approximately 20-micron grain size, denoted by the solid lines in Figure 3.20, do not indicate saturation at high dosages. The disagreement has several possible explanation ranging from a need for revision of the equation constants to grain-boundary cracking induced by reactor shutdown (see comments under "Strength Changes"), and continued growth due to helium accumulation.

Helium Bubbles - Helium bubbles can account for continued expansion at high dosages. Since the accumulation of helium is governed by losses through diffusion, the diffusion path length is the critical factor influencing the expansion caused by helium. If the grain boundaries provide an essentially free escape path for helium, the diffusion path is limited to the grain dimensions and any contribution of the gas to expansion will depend on grain size. On the other hand, if diffusion through the grain boundaries is at a rate comparable to or slower than diffusion in the grains, the overall diffusion path approaches the macroscopic dimensions of the specimen. In this case, a significant difference will occur in the expansion (due to the helium) of specimens of different sizes. The occurrence of helium

*G. W. Keilholtz, J. E. Lee, R. E. Moore, and R. L. Hamner, "Behavior of BeO under Irradiation," Paper 3, International Conference on Beryllium Oxide, Sydney, Australia, October 21-25, 1963. To be published in mid-1964, *Journal of Nuclear Materials*.

Fig. 3.19—Estimated volume expansion exclusive of grain-boundary separation for randomly oriented BeO specimens of ~ 20 -micron grain size in exposures at low neutron flux

Fig. 3.20—Estimated volume expansion exclusive of grain-boundary separation for randomly oriented BeO specimens of ~ 20 -micron grain size in exposures at high neutron flux

bubbles in the grain boundaries of BeO indicates that the grain boundaries are not free escape paths; in general, however, diffusion of gases in ceramics is not found to be dependent on the macroscopic dimensions.

Data on the helium content in irradiated samples indicate that the grain boundaries are not free escape paths since greater helium loss occurs in specimens that exhibit grain-boundary separation. Also, there is no apparent dependence on grain size. The data listed in Table 3.7 show that up to 40 percent of the helium formed escapes in samples irradiated at temperatures of 600° to 1000°C and dosages of approximately 10^{21} nvt (≥ 1 Mev). The last two columns of the table list the apparent diffusion coefficient and diffusion rate calculated for the macroscopic dimensions case. Significantly, the fraction of helium retained is smaller (and the apparent diffusion rates are larger) in some of the samples irradiated at 600° to 800°C than in samples irradiated at higher temperatures. These particular results are attributed to escape of the helium as a result of grain-boundary separation which is more extensive at the low temperatures and in the larger grain sizes.

The apparent helium diffusion rates listed in Table 3.7 were computed for the macroscopic dimensions of the specimens using the complete diffusion relationship. Helium diffusion rates in the specimens were computed on the assumption that helium loss resulted from volume diffusion, i. e., that grain boundaries do not permit free escape of the gas. This assumption may be questioned for a sintered ceramic material such as BeO. Porosity of both the internal and surface-connected types and the porosity produced by irradiation expansion should influence volume diffusion. Nevertheless, normal materials are not highly pervious to gases except in special cases, and these considerations only lead to the expectation of considerable variation in the experimental data. Finally, the observation of helium bubbles is conclusive evidence that not all of the grain boundaries are escape paths.

The fraction, f_r , of helium formed that remains in a solid cylinder having a length large in comparison to the diameter is given by

$$f_r = \frac{4r^2}{Dt} \sum_{n=1}^{\infty} \frac{1 - e^{-\frac{D\alpha_n^2 t}{r^2}}}{\alpha_n^4} \quad (3.4)$$

where:

r is the radius of the cylinder in centimeters

D is the diffusion coefficient in cm^2/sec

t is time in seconds

α_n are the roots of the J_0 Bessel function.

To simplify the computations, a table of f_r values for Dt ranging from 10^{-5} to 10 was prepared. From a plot of Dt versus f_r , the apparent diffusion coefficient was then determined from the observed f_r and the known irradiation time and r^2 . The diffusion rates determined for the 800° to 1000°C irradiation temperatures of the specimens described in Table 3.7 are about 10^{-8} sec^{-1} , as listed in the next-to-last column of the table.

If the helium escape is a volume diffusion process, as assumed in the preceding paragraphs, the specimen size and geometry become highly important factors in the irradiation expansion of BeO. This size effect in cylindrical specimens is briefly outlined below.

The steady state, or saturation, concentration of helium, C_s , in cylindrical specimens is given by

$$C_s = \frac{S\phi r^2}{8D} \quad (3.5)$$

TABLE 3.7
HELIUM CONCENTRATION AND DIFFUSION IN IRRADIATED BeO

Composition	Grain Size, microns	Bulk Density, ^a g/cm ³	Open Porosity, ^a %	Irradiation Conditions			Helium			
				Temperature, °C	Time, sec x 10 ⁶	Dose 10 ²⁰ nvt (≥1 Mev)	Observed Concentration, cm ³ /g (NTP)	Fraction ^b Of Total Formed	Apparent ^c Diffusion Rate, sec ⁻¹	Apparent ^c Diffusion Coefficient, cm ² /sec
AOX	20	2.912	-	100	-	1.8	0.067	(100)	-	-
		2.864	-	930	4.5	10.6	0.24	0.62	1.7 x 10 ⁻⁸	1.6 x 10 ⁻⁹
		2.772	-	1000	2.36	5.6	0.15	0.73	1.5 x 10 ⁻⁸	1.4 x 10 ⁻⁹
		2.885	-	810	1.21	2.6	0.064	0.67	4.7 x 10 ⁻⁸	4.3 x 10 ⁻⁹
		2.742	-	890	4.5	9.2	0.22	0.65	1.4 x 10 ⁻⁸	1.3 x 10 ⁻⁹
	17	2.822	3.6	600	4.64	8.3	0.19	0.62	1.6 x 10 ⁻⁸	1.5 x 10 ⁻⁹
		2.842	2.7	800	4.64	8.6	0.27	0.86	1.8 x 10 ⁻⁹	1.7 x 10 ⁻¹⁰
	10	2.813	-	600	4.64	9.1	0.24	0.72	8.5 x 10 ⁻⁹	7.8 x 10 ⁻¹⁰
	12	2.824	-	800	4.64	11.0	0.26	0.64	1.5 x 10 ⁻⁸	1.4 x 10 ⁻⁹
		2.833	-	900	4.5	10.8	0.24	0.61	1.8 x 10 ⁻⁸	1.7 x 10 ⁻⁹
	10	2.882	0.2	1200	1.13	3.5	0.086	0.67	5.1 x 10 ⁻⁸	4.6 x 10 ⁻⁹
	3	2.756	-	900	4.5	10.6	0.23	0.59	2.1 x 10 ⁻⁸	1.9 x 10 ⁻⁹
	5	2.739	3.5	800	4.64	10.6	0.28	0.72	8.5 x 10 ⁻⁹	7.8 x 10 ⁻¹⁰
		2.725	6.5	600	4.64	9.2	0.21	0.62	1.6 x 10 ⁻⁸	1.5 x 10 ⁻⁹
	100	2.892	-	800	4.64	9.3	0.25	0.74	7.2 x 10 ⁻⁹	6.6 x 10 ⁻¹⁰
		2.931	1.3	900	4.5	9.7	0.24	0.68	1.2 x 10 ⁻⁸	1.1 x 10 ⁻⁹
UOX-MgO	10	2.860	1.8	800	4.64	11.1	0.28	0.69	1.1 x 10 ⁻⁹	9.8 x 10 ⁻¹⁰
		2.867	0.6	900	4.5	10.8	0.29	0.73	8.1 x 10 ⁻⁹	7.4 x 10 ⁻¹⁰

^aMeasured after irradiation. Open pore volume is expressed as percentage of bulk volume.

^bFormation rate is taken as 0.366 cm³ helium per gram of BeO per 10²¹ nvt (≥1 Mev).

^cComputations are based on bulk volume of sample.

where:

S is the helium production rate per neutron, $1.2 \times 10^{-21} \text{ cm}^3 \text{ He/cm}^3 \text{ BeO-n}$

r is specimen radius

ϕ is neutron flux in nv ($\geq 1 \text{ Mev}$).

For constant flux and temperature, C_g increases in proportion to the square of the radius of the cylinder. The curves of Figure 3.21 indicate the variation of C_g for diameters up to 2.5 centimeters for different neutron fluxes at an irradiation temperature of 1000°C . For a given helium production rate, i. e., constant flux, longer irradiation times are required to reach the equilibrium state in specimens of larger diameters; hence, specimen growth continues at higher dosages in larger specimens.

Fig. 3.21 – Maximum helium concentration in BeO cylinders of different diameters, assuming helium escape is a volume diffusion process

Actually, the saturation condition is not physically realistic for the larger diameters. At steady state conditions, the helium concentration at saturation varies from the center to the edge of the specimen as given by

$$C_r = \frac{S\phi}{4D} (a^2 - r^2) \quad (3.6)$$

where a is the specimen radius and r is the distance from the specimen center. The concentration at the center ($r = 0$) is thus $S\phi a^2/4D$, or twice the average concentration given by equation (3.5). This concentration gradient can result in intergrain stresses sufficient to cause grain-boundary separation and in macroscopic stresses sufficient to cause cracks along the length of the cylinder. Based on the 100°C irradiation data for AOX-grade BeO specimens of 20-micron grain size, the concentration is approximately $0.28 \text{ cm}^3 \text{ He/cm}^3 \text{ BeO}$ at the onset of grain-boundary separation. While this figure may not be applicable to

grain expansion in elevated temperature irradiations, it may be taken as a reasonable estimate for materials of 20-micron grain size. Thus, for the conditions indicated in Figure 3.21, only those specimens less than 0.3 centimeter in diameter might avoid grain-boundary separation completely. This size would, of course, increase for specimens of smaller grain size.

3.4 SUMMARY AND CONCLUSIONS

Expansion is the principal effect of irradiation in BeO. In low-temperature ($\sim 100^\circ\text{C}$) irradiations, the expansion in specimens of 3- to 20-micron grain sizes occurs at a rate of 0.2 to 0.3 percent $\Delta V/V$ per 10^{20} nvt (≥ 1 Mev) up to about 1.7×10^{20} nvt, and then increases to a rate of approximately 1 percent $\Delta V/V$ per 10^{20} nvt. It consists of volume components from lattice expansion and from cracks which form at grain boundaries as a result of greater expansion in the crystallographic c-axis than in the a-axis. The expansion due to grain-boundary cracks increases with increasing dosage and is 2 to 3 times as large as that from lattice expansion at dosages from approximately 4 to 10×10^{20} nvt.

Expansion is decreased in irradiations at elevated temperatures and is dependent on the neutron flux as well as the dosage. For dosages up to 1.5×10^{21} nvt, it can be approximated by the relationship:

$$\frac{\Delta V}{V} \cong \frac{K}{A} \left[1 - (\exp - At) \right] \quad (3.7)$$

where $\Delta V/V$ is the percentage increase in volume exclusive of grain-boundary separation, K is the defect production rate, A is the annealing rate, and t is the time of irradiation. For specimens of 20-micron grain size,

$$K = 3.3 \times 10^{-23} \phi \quad (3.8)$$

and

$$A = 6.3 \times 10^{-5} \exp(-10,400/RT) \quad (3.9)$$

where K and A are defined in terms of $\Delta V/V$ as above, ϕ is neutron flux in nv (≥ 1 Mev), R is the molar gas constant in cal/mole- $^\circ\text{K}$, and T is the absolute temperature, $^\circ\text{K}$.

These relationships appear to describe the expansion data for specimens of 20-micron grain size in this program within about 20 percent but predict somewhat less expansion than was observed by Kielholtz, et al., at dosages of 3 to 4×10^{21} nvt. Postulated causes of the continued expansion at high dosages include growth of clusters and formation of helium bubbles. Data at present are not conclusive; however, computations based on helium diffusion indicate that helium bubbles could account for continued growth at high temperatures and that their significance increases as the specimen size increases.

Grain-boundary cracking is influenced by the grain size and density of the material and by the irradiation temperature. It occurs at volume expansion in the range of approximately 0.4 to 1.2 percent. In 1000°C irradiations, cracking occurs at the highest dosages, approximately 1.5 to 2.5×10^{20} nvt, in specimens with grain sizes of 20 microns or less, and it appears to occur at lower dosages in a given grain size the lower the specimen density. In elevated-temperature irradiations, it occurs at higher dosages the higher the temperature.

Strength, elastic constants, and the thermal expansion of BeO are essentially unchanged if grain-boundary cracks are avoided. The strength changes once cracks have formed are less severe in specimens of small (< 5 microns) grain size.

3.5 PLANS AND RECOMMENDATIONS

The examination of specimens from all irradiation tests of the grain-size - density series will be completed. Particular emphasis will be placed on measurements leading to better definition of the contribution of clusters and helium bubbles to the volume expansion. Thermal conductivity data will be obtained on selected specimens for various irradiation temperatures and dosages.

Post-irradiation measurements will also be completed on the specimens containing glass-phase additives.

4. FISSION GAS DIFFUSION IN UNFUELED CERAMIC MATERIALS

(57069)

The objective of this program is to advance the basic knowledge of fission gas diffusion and radiation damage in unfueled ceramic materials.

This work is concerned with the diffusion of Kr, Xe, and I atoms in ceramic oxides (MgO, BeO, Al₂O₃, and ZrO₂) subsequent to their injection via ion bombardment. The diffusion characteristics of these heavy atoms are deduced by an analysis of the amount of diffusant remaining in a sample as a function of the time at constant temperature.

4.1 ION BOMBARDMENT STUDIES

Results from a preliminary study,* performed under Job 57067, are summarized as follows:

1. An approximately common activation energy (-90,000 kcal/mole) was obtained for krypton migration in polycrystals of BeO, Al₂O₃, and Y₂O₃-stabilized ZrO₂. This activation energy pertains to the temperature ranges 900° to 1200°C for BeO and 900° to 1100°C for both Al₂O₃ and stabilized ZrO₂.
2. A trend toward an increasing activation energy with increasing fractional release of krypton was observed. This particular behavior is qualitatively consistent with that characteristic of radiation-enhanced diffusion† in that the supersaturation of mobile point defects produced during krypton ion injection should decrease with time at an elevated temperature.
3. A larger krypton diffusion coefficient in Al₂O₃ and BeO than in stabilized ZrO₂ was indicated.

These results, however, are not necessarily characteristic of krypton diffusion in the bulk of the oxides considered because of deficiencies in the ion gun used for injection and, possibly, because of a rough specimen surface. Due to the construction of the bombardment apparatus used, the average ion beam energy and energy fluctuation about this average could not be measured. Furthermore, the beam current at the target was not known. Autoradiographs of bombarded samples showed that the portion of the target surface within the ion beam cross section was not uniformly bombarded. In addition, the target surface could have been contaminated.‡ These unfavorable conditions could have sufficiently perturbed the injected ion absorption distribution and the mode of krypton re-

*"High-Temperature Materials Program Progress Report No. 26, Part B," GE-NMPO, GEMP-26B, August 16, 1963, pp. 42-46.

†"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, pp. 118-125.

‡"High-Temperature Materials Program Progress Report No. 22, Part B," GE-NMPO, GEMP-22B, April 30, 1963, pp. 38-39.

lease at the surface from the conditions assumed in the diffusion calculation analysis of the data to vitiate the results. In short, the non-uniform beam intensity, variations in beam energy, and an initially rough surface probably combined to give an injected ion absorption distribution more skewed toward the incident surface than the computed distribution* for a monoenergetic, uniform beam, and a clean, smooth target surface. Because of this, it is highly probable that the diffusion coefficient was overestimated in the preliminary study and also that surface barrier effects were reflected in the activation energy results. Procedures were adopted, therefore, to improve the quality of the ion beam and the target surface and to separate volume and surface effects.

To improve ion beam quality, an ion gun (Figure 4.1) which will give a monoenergetic beam of singly charged ions with a uniform areal density was fabricated. This gun is similar to that developed by Carlston and Magnuson† and is characterized as possessing (1) a high gas efficiency, (2) a low gas consumption rate, and (3) an ion beam having an energy spread of 2 ± 1 eV and containing less than 3 percent impurities. The ion source of this gun uses magnetically confined oscillating electron bombardment of krypton gas to produce singly charged ions. This source is operated with the top plate, bottom plate, and negative side of the electron source filament at the desired ion accelerating potential. The ion source is shown in Figure 4.2.

Fig. 4.1 – Magnetically confined oscillating electron ion gun (Neg. P64-1-3)

*J. R. Beeler, Jr., and D. G. Besco, "Defect Configurations in Heavy Ion Bombarded BeO," Journal of Physical Society, Japan, Volume 18, Supplement III, 1963, p. 159.

†C. E. Carlston and G. D. Magnuson, "High Efficiency Low-Pressure Ion Source," Review of Scientific Instruments, Volume 33, 1962, p. 905.

Fig. 4.2—Magnetically confined, oscillating electron-bombardment ion source

Electrons are emitted from the filament and accelerated toward the anode cylinder which is biased approximately 45 volts, positive, with respect to the filament. The electrons are collimated into helical orbits by the axial magnetic field and oscillate between the top and bottom plates. During this oscillation they ionize krypton atoms via inelastic electron-atom collisions. Ultimately, these electrons are captured at the anode cavity wall after losing most of their energy in collisions.

The ions produced in the anode cavity are withdrawn by a grounded extractor and focused on the target by an Einzel lens. The beam cross section at the target is controlled by varying the potential difference between the two Einzel lens cylinders. Preliminary testing of the ion source was limited to magnetic field measurements of the anode spool pending the completion of an ion chamber manifold attachment for the vacuum system. Field strengths at the end of the anode spool of 210 Gauss are possible without overheating. The magnetic field was also found to be a linear function of the coil current.

Calibration of pressure manometers against a McLeod gage for use in krypton was completed. Krypton pressures of 10^{-3} Torr and higher were readily measured with a thermistor manometer using the electrical circuit suggested by Young.* The pressure range of the McLeod gage limits the calibration of the ion gage to pressures above 10^{-5} Torr.

4.2 SUMMARY AND CONCLUSIONS

Preliminary results of the diffusion coefficient and activation energy under Job 57067 are not necessarily characteristic of Krypton diffusion in the majority of the oxides considered because of non-uniform beam intensity, variations in beam energy, and, possibly, because

*Dushman and Lafferty, *Scientific Foundation of Vacuum Technique*, New York, J. Wiley, 1949, pp. 297-298.

of a rough specimen surface. For these reasons, it is highly probable that the diffusion coefficient was overestimated and also that surface barrier effects were reflected in activation energy results. Procedures were adapted to improve the quality of the ion beam and the target surface and to separate volume and surface effects. An improved ion gun was fabricated. Preliminary testing indicates the achievement of magnetic field strengths as high as 210 Gauss at the end of the anode spool without overheating and a magnetic field that is a linear function of the coil current. Calibration of pressure manometers was also completed to pressures above 10^{-5} Torr.

4.3 PLANS AND RECOMMENDATIONS

With the completion and preliminary checkout of the vacuum system, ion beam integrity will be checked by making autoradiographs, measuring atom ranges in bombarded aluminum using the method of Davies,* and determining the retarding potential required to annihilate the beam at the target. A Faraday cup, placed at the target position, can be used to measure the beam current. Ceramic targets will then be bombarded at room temperature with Kr^{85} and the back diffusion studied as a function of time at temperature. If necessary the target can be held at a low temperature by running liquid nitrogen through the hollow target holder. This is to be followed by studying the effect of target surface characteristics and bombardment-produced damage within the target on the transport of injected krypton.

*J. A. Davies et al., "A Radiochemical Technique for Studying Range Energy Relationships for Heavy Ions of Kev Energies in Aluminum," *Canadian Journal of Chemistry*, Vol. 38, 1960, pp.1526-1534.

5. FISSION PRODUCT TRANSPORT PROCESSES IN REFRACTORY-METAL FUEL SYSTEMS

(57070)

The purpose of this program is to study fission product transport processes in refractory metal fuel systems at temperatures exceeding 1700°C in inert or reducing atmospheres.

Because of their high-temperature capabilities, the refractory metals have good potential for use in reactors at elevated temperatures. As a part of the overall evaluation of these materials, diffusion and permeation studies of Kr⁸⁵ through Ta, W, Mo, Re, Nb, and alloys of these refractory metals are being conducted. This work is directed toward correlation of the parameters of time, temperature, diffusion path length, grain size, and impurities with the transport of fission gases through refractory metals.

5.1 DIFFUSION STUDIES

The diffusion of Kr⁸⁵ through Ta is the first system being studied. A brief literature search revealed needed information on the microstructural stability of the metal, and the problems associated with the introduction of the diffusive species into the metal.

While the effect of impurities in the structural stability of refractory metals is not yet completely understood, impurities are known to limit the growth of crystallites at temperatures above the recrystallization point; on the other hand, recrystallized pure refractory-metal samples reveal large, virtually single crystals.* In the present study, high-purity, arc-cast recrystallized Ta[†] is being used so that as many material variables as possible may be eliminated.

Tantalum, at intermediate and high temperatures, is an excellent scavenger for oxygen, nitrogen, and carbon dioxide, and is easily contaminated unless extreme precautions are taken. This problem is acute; for times in excess of 5 hours at partial pressures of 0.001 Torr for these gases, the impurity level of the sample increases and the advantages of starting with high-purity material are lost.

The literature search revealed that only limited work has been done on the diffusion of the noble gases in metals of any kind. The work that has been done indicates that the gas exists and diffuses in the metal as an activated atom or ion rather than as a free atom,[‡] and that a large amount of energy is required to dissolve the gas in a metal lattice.

The dissolution of noble gases in metals has only been observed under energetic conditions such as electrical discharge, or in the presence of ionizing radiation. If ions are a prerequisite for dissolution in a metal, the energy requirements for ionization of the noble

*"High-Temperature Materials Program Progress Report No. 28, Part A," GE-NMPO, GEMP-28A, November 11, 1963, p. 31.

[†]Impurities present: C, 50 ppm; O, 7 ppm; N, 15 ppm.

[‡]J. M. Tobin, "Mechanism of Volume Diffusion of Xenon and Krypton in Metals," Paper presented before ORNL Conference of Nuclear Reactor Chemistry, Gatlinburg, Tennessee, October 13, 1960.

gases at a metal surface (8 ev and higher)* appear to exceed those attainable from thermal kinetic energy in the temperature range of interest. The most promising technique for getting the gas into the metal lattice is by use of a glow discharge.†

The glow-discharge technique has obvious advantages compared with procedures involving in-pile irradiations. A discharge tube assembly was designed (Figure 5.1) to determine the optimum electrode spacing, pressure, and cathode temperature conditions for discharge.‡ High-purity, arc-cast Ta foil was employed as the anode and a 0.5-millimeter diameter Ta wire of the same purity level was used as the cathode. A variable a-c circuit was superimposed on the d-c electrode circuit in order to heat the cathode to the desired temperature of 2200°C. At a pressure of 0.5 to 2.0 Torr in a purified Kr atmosphere, and at a cathode temperature of 2200°C, a glow discharge was attainable at an electrode separation of 20 to 30 centimeters; the Kr ions were driven through a potential drop of 500 volts and yielded tube currents of 0.5 ampere and higher.

Fig. 5.1 – Glow-discharge tube assembly (Neg. P63-11-6)

* N. M. Kornegay and H. S. Johnston, "Kinetics of Thermal Ionization; II. Xenon and Krypton," *Journal Chemical Physics*, Vol. 38, No. 9, 1963, p. 2242.

† "High-Temperature Materials Program Progress Report No. 28, Part A," GE-NMPO, GEMP-28A, November 11, 1963, p. 33.

‡ "High-Temperature Materials Program Progress Report No. 30, Part A," GE-NMPO, GEMP-30A, December 31, 1963, p. 29.

With this experimental arrangement, the pressure-rise rates were relatively low on occasion (0.001 Torr per hour), but were not sufficiently reproducible for reliable operation. To maintain the sample purity, a static system pressure of 5×10^{-4} Torr with no pressure rise in 2 hours (assuming the sample will absorb all the gas in the chamber), is necessary so that up to 2 hours of operation will not raise the impurity level in the sample significantly. Parts of the system were rebuilt and static pressures of 7×10^{-4} Torr are obtained after 2 hours; this pressure rise appears to be due to outgassing from parts of the apparatus which cannot be strongly heated.

The Kr carrier gas obtained was spectroscopic grade but the Kr^{85} tracer gas contained significant amounts (2 to 5%) of reactive contaminants (O, N, CO_2). A static gettering method is being employed in which a heated (800° to 1700°C) Ta foil is used to remove the impurities.*

5.2 PERMEATION STUDIES

A permeation technique is being employed to aid in the identification of Kr^{85} transport processes and to supplement the diffusion studies. Tantalum was selected as the initial material for the permeation study. A Ta specimen of high-purity, arc-cast material was fabricated and consists of an evacuated hollow right cylinder about 6 millimeters in diameter and 13 millimeters long, with a 0.5-millimeter wall thickness. The specimen was fabricated by electron-beam-welding Ta discs, 5 millimeters in diameter and 0.5 millimeter thick, in the ends of a short length of Ta tubing with an outside diameter of 6 millimeters.

In the present design, the Ta specimens can be soaked in a mixture of Kr containing Kr^{85} ; the amount of gas that permeates the specimen in various time intervals can be determined by both beta and gamma counting. To avoid the problem of complex data which may result from irreproducibility of specimen welds, a method is also being developed which would permit the continuous trapping and monitoring of the gas that permeates the specimen.

The external vacuum and storage system necessary for these operations has been designed and constructed. A tungsten resistance furnace was designed, built, and put into operation for heating the samples in a Kr environment; the furnace element is protected by a static argon atmosphere. Tests are presently in progress to determine the operating characteristics of the equipment prior to admitting the Kr^{85} into the system.

5.3 SUMMARY AND CONCLUSIONS

As a result of a literature survey of other noble gas - metal diffusion couples, a glow-discharge technique is being used to introduce Kr into refractory metals for the study of the diffusion of fission gas. A permeation technique is also being developed to supplement the basic diffusion studies. Arc-cast Ta was chosen for the initial diffusion and permeation work. The necessary equipment was constructed to maintain the purity of the sample in order to avoid as many indefinable variables as possible.

5.4 PLANS AND RECOMMENDATIONS

The feasibility of dissolving Kr in a hot Ta cathode under glow-discharge conditions will be determined. After the introduction of Kr^{85} into the cathode, the best methods of studying the diffusion in the material will be investigated. Studies on the permeation of Kr^{85} through various refractory metals other than Ta will be conducted.

*E. G. Zubler, "The Gettering Properties of Tantalum," *Journal Electrochemical Society*, Vol. 110, No. 10, 1963, p. 1072.

6. INTERNAL CONVERSION CERAMIC FUEL ELEMENT RESEARCH

(57072)

The objectives of this program are to study the chemistry involved in the use of a fertile material (thoria) in stabilized-fuel-BeO systems and to develop their capability as an internal conversion fuel element. In particular, the program includes research and development work on $\text{UO}_2\text{-ThO}_2$ and $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ systems that can be incorporated in BeO to result in an all-ceramic fuel element for gas cooled reactors having extended life at temperatures up to 1400°C .

An all-ceramic BeO fuel element has many nuclear, mechanical, chemical, and physical properties that may make it adaptable for use in advanced reactor concepts. Some advantages of using BeO fuel elements fueled with $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ solid solutions are:

1. High outlet gas temperatures leading to steam cycles comparable with those in use in the most modern conventional power systems.
2. Reaction of Y_2O_3 with $\text{UO}_2\text{-ThO}_2$ solid solutions in BeO results in a stable structure that precludes the formation of U_3O_8 with its inherent high volume change of 31 percent and gross fuel loss above 1200°C . Thus, air as well as pure or oxygen-contaminated He, CO_2 , and N_2 can be used as the reactor coolant if desired.
3. The addition of ThO_2 to $\text{UO}_2\text{-BeO}$ fuel elements can extend the reactor lifetime potential.
4. Dense BeO shows considerable resistance to the release of fission products from dispersion-type fuels; thus, fuel elements without metallic cladding may be practicable with a minimum of fission gas release.

6.1 INFLUENCE OF THORIA ON NUCLEAR LIFE

The influence of ThO_2 on reactor life* was studied to determine the amount of fertile material required and its effect on increasing the life of a BeO-moderated reactor. Figures 6.1 and 6.2 show the removable energy ratio as a function of reactor size and $\text{ThO}_2\text{-to-UO}_2$ ratio. These graphs indicate that adding ThO_2 to a homogeneously fueled $\text{UO}_2\text{-Y}_2\text{O}_3\text{-BeO}$ fuel element would have a significant effect on the lifetime or removable energy potential of a nuclear reactor. The magnitude of such an effect is a function of the relative ThO_2 content and the size of the reactor. Balancing the reactor size requirements against the increased life potential indicates that ThO_2 contents in the range of 1 to 3 moles per mole of UO_2 would be the most useful. As shown in Figures 6.1 and 6.2, the addition of 0.2 mole of ThO_2 per mole of UO_2 can extend reactor life only a few percent while the addition of 3 moles of ThO_2 per mole of UO_2 can almost triple the nuclear lifetime potential. The minimum burnup capability required to realize the nuclear lifetime potential

*R. J. Spera, "Influence of Thoria on the Nuclear Life Potential of a Beryllia Ceramic Reactor," GE-NMPO, TM 63-5-15, May 20, 1963.

Note:
Basis of comparison is an all urania
system having a 6.7 volume percent urania
content (20 weight percent) and a Y_2O_3 - UO_2
mole ratio of 0.55

Fig. 6.1 — Removable energy ratio, ThO_2 -to-all- UO_2 systems as a function of reactor size parameter and ThO_2 - UO_2 ratio (volume percent of UO_2 is constant)

ranges from 5.5×10^{20} fissions/ cm^3 for fuel elements containing 1 mole of ThO_2 to 12×10^{20} fissions/ cm^3 for fuel elements containing 3 moles of ThO_2 .

A second advantage of adding ThO_2 to BeO fuel elements is a smaller change in system reactivity for a given fuel burnup. As an example, when the total burnup is 6×10^{20} fissions/ cm^3 , the change in reactivity ($\Delta k/k$) for an all- UO_2 fuel is approximately -0.30 while it is only -0.027 for fuel containing 2 moles of ThO_2 per mole of UO_2 . This smaller reactivity change could decrease the total number of control elements required, lessen changes in the core spatial power distribution, and reduce the possibility of hot spot formations.

As shown in Figures 6.1 and 6.2, fuel elements containing ThO_2 have nuclear lifetime advantages only in reactor sizes exceeding $0.004 B^2/VF_s^2$. This value corresponds to a cylindrical reactor about 142 centimeters in length and diameter and having a solid volume fraction of 0.5; if the solid volume fraction is increased to 0.7, the reactor core diameter would be decreased to about 102 centimeters.

Fig. 6.2—Removable energy ratio, ThO_2 -to-all UO_2 systems as a function of reactor size parameter and ThO_2 - UO_2 ratio (volume percent of UO_2 is constant).

6.2 BASIC STUDIES OF THE UO_2 - ThO_2 - Y_2O_3 SYSTEM

Based on the above-mentioned considerations, current work is concentrated on fuels with UO_2 -to- ThO_2 mole ratios ranging from 1:1 to 1:3. The Y_2O_3 -to- UO_2 mole ratio is held constant at 0.55 for each composition in this study. Based on experience with stabilized oxide fuels, Y_2O_3 is required to preclude the formation of U_3O_8 with its inherent 31 percent volume expansion. To provide supporting information on phase relationships, vapor pressures, and comparative fuel retention data, additional compositions are being investigated; the binary and ternary compositions included in this study are shown in Figure 6.3. The compositions designated F-239 and F-240 with UO_2 -to- ThO_2 mole ratios of 1:15 are of interest for large BeO-base internal conversion reactors such as the German (AVR) pebble-bed reactor type.

Fuel Reaction Studies

Previous work showed that greater thermal stability in BeO-base stabilized fuel systems was attained if the fuel was added to the BeO as a well-crystallized homogeneous material. Available data on the phase relationships of oxide systems containing UO_2 ,

Fig. 6.3— $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ compositions for use as internal conversion fuels in an all-ceramic BeO reactor

ThO_2 , and Y_2O_3 are almost entirely concerned with their binaries. Face-centered cubic (FCC) solid solutions predominate in the $\text{UO}_2\text{-ThO}_2$, $\text{UO}_2\text{-Y}_2\text{O}_3$, and $\text{ThO}_2\text{-Y}_2\text{O}_3$ binary structures; therefore, it was expected that the $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ compositions under study would also form FCC solid solutions. Brief studies were made to determine the reaction conditions necessary for attaining homogeneous and well-crystallized $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ fuels.

The initial reaction studies were based on previous work wherein fuel additives had been prepared by reacting blended mixtures of -325 mesh powder in Y_2O_3 -stabilized ZrO_2 crucibles for 1 hour at 1850°C in air. Using this procedure, the $\text{UO}_2\text{-ThO}_2$ fuels (designated F-27 and F-76) and the $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ fuel compositions (designated F-227 through F-238) were reacted and then analyzed by X-ray diffraction and ceramographic techniques. The X-ray diffraction analysis revealed a FCC structure in each composition; however, more than half of the fuels also contained varying amounts of another FCC phase as well. Ceramographic examination revealed a phase, predominantly on the surface, that was identified by electron-microprobe analysis as a mixture of the oxides of yttrium and silicon. A typical fuel surface area contaminated by silica is shown in Figure 6.4a.

Contamination of $\text{UO}_2\text{-Y}_2\text{O}_3\text{-ZrO}_2$ compositions had occurred in an earlier program due to volatile calcium and silicon species traced to the calcia-stabilized ZrO_2 crucibles used as reaction containers. This contamination problem was eliminated by reacting these compositions in Y_2O_3 -stabilized ZrO_2 crucibles at temperatures no higher than 1850°C^* . The

*"First Annual Report—High-Temperature Materials and Reactor Component Development Programs; Volume II—Materials," GE-NMPO, GEMP-106B (CRD), February 28, 1962, p. 42.

a. REACTED IN Y_2O_3 -STABILIZED ZrO_2 FURNACE REFRACTORIES

b. REACTED IN BeO FURNACE REFRACTORIES

Fig. 6.4 – Typical microstructures of $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ fuel composition after reaction for 1 hour at 1850°C in air

$\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ compositions were reacted under these same conditions, but contamination still occurred. To eliminate contamination and obtain well-crystallized solid solutions, various time, temperature, and atmosphere parameters were investigated. Two methods of eliminating contamination were found. The $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ fuel additives could be reacted in Y_2O_3 -stabilized ZrO_2 refractories at 1675°C in air for periods in excess of 30 hours, or they could be reacted in air for 1 to 2 hours at 1850°C in high-purity BeO crucibles and furnace refractories (Figure 6.4b). Even though both methods yielded incompletely crystallized ternary fuels, no fuel contamination occurred. The $\text{UO}_2\text{-ThO}_2$ and $\text{UO}_2\text{-Y}_2\text{O}_3$ binary fuels reacted for 2 hours at 1850°C in BeO refractories formed single-phase FCC solid solutions; therefore, further work on reaction conditions is being concentrated on attaining well-crystallized ternary fuel structures leading to a study of phase relationships in the $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ system.

Phase Relationships in the $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3\text{-O}_2$ System

This portion of the program was essentially inactive during this report period in the interest of obtaining well-crystallized single-phase fuels for subsequent study of phase relationships.

6.3 FUEL RETENTION STUDIES

The various fuel compositions discussed above were incorporated in a BeO matrix for fuel retention studies prior to receiving analysis data showing silica contamination. These fuel additives had been comminuted to -500 mesh, blended with BeO to give 10 and 20 weight percent UO_2 loadings, pressed into discs, and sintered at 1675°C for 2 hours in hydrogen having a dewpoint of 0°C . Since experience had shown that minor quantities of contaminants such as silica or alumina may have no effect on fuel retention capability at temperatures below 1500°C , a fuel retention test on four 20BF-229 specimens (BeO fueled with F-229 additive to give 20 weight percent UO_2) was conducted at 1500°C to determine what effect contamination has on fuel retention. The results listed in Table 6.1 were obtained from fuels reacted at different times and temperatures in air or hydrogen atmospheres; three of the fuel additives became contaminated with silica or alumina during reaction while one fuel was essentially single phase and contamination-free.

After the fuel additives were blended with BeO and sintered in hydrogen, the X-ray diffraction patterns of all specimens were nearly identical; this was also true after the fuel retention test. Sintering for 2 hours at 1675°C in hydrogen may have volatilized the small amount of silica contamination from the fueled BeO. After 300 hours at 1500°C in moving air, the UO_2 loss (calculated from weight change data) ranged from 0.9 to 2.1 percent. Thus, it appears that variations in lattice parameters and silica and alumina contaminants have slight, if any, effect on fuel retention when tested for 300 hours at 1500°C . Based on these results, the fuel retention tests on BeO specimens fueled with binary and ternary $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ -containing compositions were continued as planned.

The fueled BeO specimens listed in Table 6.2 were tested in moving air at 1400°C and 1500°C to determine the composition or range of compositions on which additional studies of mechanical and physical properties, fuel retention, and irradiation tests would be conducted. The results of fuel retention tests (Table 6.2) show that BeO specimens fueled with F-227, F-228, and F-229 lose less than 1 percent UO_2 in 500 hours at 1400°C and less than 5 percent UO_2 in 300 hours at 1500°C . Variables such as fuel loading (10 and 20 weight percent UO_2 in BeO) and fuel processing (coprecipitation from aqueous solutions or as mechanical mixtures of oxides) appeared to have little or no effect on fuel retention of these specimens. As discussed previously,* minor variables in surface area,

*"High-Temperature Materials Program Progress Report No. 30, Part A," GE-NMPO, GEMP-30A, December 31, 1963, p. 32.

TABLE 6.1
EFFECT OF REACTION CONDITIONS ON FUEL PHASE AND FUEL
RETENTION OF BeO-CONTAINING F-229 FUEL ADDITIVES

F-229 Fuel Additive		Ceramographic Analysis	X-Ray Diffraction Analysis Of F-229 In BeO as-sintered ^a in H ₂	Fuel Retention Test Of 20BF-229 For 300 Hours At 1500°C	
Reaction Conditions	X-Ray Diffraction Analysis			UO ₂ Loss, wt % ^b	X-Ray Diffraction Analysis Of F-229 In BeO
1 hr at 1850°C in air, coprecipitated	Major-phase FCC, $a = 5.516 \text{ \AA}$ Minor-phase FCC, $a = 5.479 \text{ \AA}$	Two oxide phases (Si-contaminated)	FCC, $a = 5.500 \text{ \AA}$	2.1	FCC, $a = 5.48 \text{ \AA}$
1 hr at 1850°C in air, mechanical mixtures of oxides	Major-phase FCC, $a = 5.47 \text{ \AA}$ Trace-phase FCC, $a = 5.57 \text{ \AA}$	Two oxide phases (Si-contaminated)	FCC, $a = 5.495 \text{ \AA}$	0.9	FCC, $a = 5.48 \text{ \AA}$
42 hrs at 1675°C in air, mechanical mixtures of oxides	Single-phase FCC, $a = 5.470 \text{ \AA}$ (incompletely crystallized)	One oxide phase	FCC, $a = 5.500 \text{ \AA}$	1.0	FCC, $a = 5.48 \text{ \AA}$
42 hrs at 1675°C in H ₂ , mechanical mixtures of oxides	Major-phase FCC, $a = 5.49 \text{ \AA}$ (possible second phase)	Two oxide phases (Al-contaminated)	FCC, $a = 5.495 \text{ \AA}$	2.1	FCC, $a = 5.47 \text{ \AA}$

^aThe UOX-grade BeO contained 20 weight percent UC₂ added as the composition F-229 (29.3UO₂ - 57.3ThO₂ - 13.4Y₂O₃, in wt %).

Test specimens 1.27 centimeters in diameter by 0.3 centimeter thick, were sintered at 1675°C for 2 hours in hydrogen having a dewpoint of 0°C.

^bAll weight changes are assumed to result from oxidation of the UO₂ and volatilization as UO₃.

TABLE 6.2
FUEL RETENTION TEST RESULTS FROM BeO SPECIMENS^a FUELED
WITH BINARY AND TERNARY UO₂, ThO₂, AND Y₂O₃ COMPOSITIONS

Fuel Additive Designation	Fuel Compositions						UO ₂ Loss ^b During Fuel Retention Tests In Air, %			
	Wt %			Mole Ratio			500 hours at 1400°C		300 hours at 1500°C	
	UO ₂	ThO ₂	Y ₂ O ₃	UO ₂	ThO ₂	Y ₂ O ₃	10 wt % UO ₂	20 wt % UO ₂	10 wt % UO ₂	20 wt % UO ₂
F-27	50.6	49.4	-	1	1	0	2.6	0.4	-	2.8
F-76	68.5	-	31.5	1	0	0.55	1.2	0.7	0.6	1.4
F-227	41.0	40.1	18.9	1	1	0.55	0.3(0.6) ^c	0.7(0.6)	4.6(3.4)	2.8(1.5)
F-228	34.2	50.1	15.7	1	1.5	0.55	0.5	0.4	1.8	1.0
F-229	29.3	57.2	13.5	1	2	0.55	0.5(0.5)	0.7(0.5)	3.6(2.3)	2.1(0.9)
F-230	22.8	66.8	10.4	1	3	0.55	2.3(5.5)	2.3(6.1)	2.4(9.0)	4.2(12.3)
F-231	18.6	72.8	8.6	1	4	0.55	2.6(6.5)	-	6.9(12.5)	-
F-236	41.2	48.4	10.4	1	1.2	0.3	5.4	10.8	22.1	27.2
F-237	21.3	50.1	28.6	1	2.4	1.6	0.1	-	0.9	-

^aBeO specimens, approximately 1.27 centimeters in diameter and 0.3 centimeter thick were sintered in hydrogen having a dewpoint of 0°C for 2 hours at 1675°C to 97-98 percent of theoretical density.

^bUO₂ loss (in wt %) calculated from weight change data.

^cFuel loss in parentheses denote fuel additives processed as mechanical mixtures of the oxides. Numbers not in parentheses indicate fuel processed by coprecipitation as hydrous oxides. All fuel additives were reacted for 1 hour at 1850°C in air.

fuel particle size, density, and BeO grain size may account for the differences in fuel loss between these specimens. A comparison of UO₂ loss from specimens fueled with F-230 and F-231 shows that fuels processed as mechanical mixtures of oxides lost more UO₂ than coprecipitated fuels by an average factor of 2.7. Thus, if the UO₂ losses of BeO specimens fueled only with coprecipitated F-230 are considered, this composition appears to be sufficiently stable to warrant further investigation. The composition range of UO₂-to-ThO₂ mole ratios from 1:1 to 1:3 is being studied further in the form of extruded tubular fuel elements; the UO₂-to-Y₂O₃ mole ratio in these additives will remain at 1:0.55. For comparison, a UO₂-ThO₂ binary fuel (F-27) will be fabricated into BeO fuel elements.

6.4 TRANSPIRATION STUDIES

Vapor pressures of UO₃ over UO₂-ThO₂ and UO₂-ThO₂-Y₂O₃ compositions are being determined using a transpiration technique. This study will provide thermodynamic data and information on the relative effects of ThO₂ and Y₂O₃ in stabilizing UO₂ against high-temperature oxidation and consequent fuel loss. The principle, experimental procedure, and apparatus of the transpiration technique were described in an earlier report.* The binary and ternary UO₂, ThO₂, and Y₂O₃ fuel additives being studied were processed as mechanically mixed oxides and reacted for 1 hour in air at 1850°C using high-purity BeO refractories.

The vapor pressure measurements on two UO₂-ThO₂-Y₂O₃ compositions were completed at temperatures from 1200° to 1500°C, and the data are shown as an Arrhenius plot in Figure 6.5. The F-227 and F-231 compositions with UO₂-ThO₂-Y₂O₃ mole ratios of 1:1:0.55 and 1:4:0.55, respectively, have approximately the same slope as a UO₂-Y₂O₃ composition with a mole ratio of 1:0.55[†] (F-76). Since the UO₂-to-Y₂O₃ mole ratios of all three compositions are equal, it can be concluded that vaporization of UO₃ from the UO₂-ThO₂-Y₂O₃ compositions is independent of the ThO₂ content. Additional measurements are underway on UO₂-ThO₂ compositions with mole ratios of 1:1, 1:2, 1:3, and 1:4. When these measurements are completed, a least-squares fit of the data will be made, and the heat of vaporization and entropy of vaporization will be determined.

* M. Tetenbaum, "Volatility Studies on A.N.P. Fuel Materials," GE-ANPD, APEX-580, February 1959.

[†] "Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B (CRD), February 28, 1963, pp. 29-35.

Fig. 6.5—Vapor pressure of UO₃ for F-76, F-227, and F-231 compositions versus reciprocal temperature

6.5 SUMMARY AND CONCLUSIONS

Three component UO₂-ThO₂-Y₂O₃ fuels were found to be susceptible to silica contamination from Y₂O₃-stabilized ZrO₂ furnace refractories during reaction at 1850°C in air. Uncontaminated fuel additives, suitable for fuel retention studies, were prepared by reacting in the same refractories at 1675°C for periods in excess of 30 hours, or by substituting high-purity BeO furnace refractories for the Y₂O₃-stabilized ZrO₂ refractories and reacting for 1 hour at 1850°C. These reaction methods have not resulted in the desired well-crystallized material for the phase relationship studies.

A fuel retention test of BeO specimens fueled with F-229 (UO₂-ThO₂-Y₂O₃ mole ratio of 1:2:0.55) conducted for 300 hours at 1500°C in air showed essentially the same fuel loss from contaminated and uncontaminated fuel additives. It is postulated that the contaminants were volatilized by sintering in hydrogen at 1675°C.

Preliminary fuel retention tests show BeO specimens fueled with 10 and 20 weight percent UO₂ added as F-227, F-228, and F-229 (UO₂-ThO₂-Y₂O₃ mole ratio range from 1:1:0.55 to 1:2:0.55) lose less than 1 percent UO₂ in 500 hours at 1400°C and less than 5 percent UO₂ in 300 hours at 1500°C.

Vapor pressures of the F-227 and F-231 compositions ($\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ mole ratios of 1:1:0.55 and 1:4:0.55, respectively) are approximately the same as a $\text{UO}_2\text{-Y}_2\text{O}_3$ composition with a mole ratio of 1:0.55, indicating that the vapor pressure of UO_3 over $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ compositions is independent of the ThO_2 content.

6.6 PLANS AND RECOMMENDATIONS

Reaction studies on $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ compositions will be continued to determine the conditions necessary to attain a well-crystallized structure for X-ray diffraction determination of the phase relationships in the system.

Tubular fuel elements will be fabricated to compare $\text{BeO-UO}_2\text{-ThO}_2$ and $\text{BeO-UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ fuel systems on the basis of fuel retention capability in oxidizing or slightly oxidizing coolant gases (He , CO_2 , or N_2 containing up to 5 volume percent oxygen). The physical and mechanical properties of BeO -base fuel elements containing F-27, F-227, F-229, and F-230 ($\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ mole ratios of 1:1:0, 1:1:0.55, 1:2:0.55, and 1:3:0.55, respectively) as a function of fuel content, sintering temperature, and microstructure will be determined. As a result of this study, specific $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ compositions will be chosen for irradiation testing.

Compositions of $\text{UO}_2\text{-ThO}_2$ and $\text{UO}_2\text{-ThO}_2\text{-Y}_2\text{O}_3$ having ThO_2 -to- UO_2 mole ratios of approximately 15:1 will be processed and studied as internal conversion fuels in BeO for potential use in a variety of reactor applications.

APPENDIX

REPORTS ISSUED DURING CALENDAR YEAR 1963

PROGRESS REPORTS

GEMP-177A

Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume I - Materials, February 28, 1963.

GEMP-177B

Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials, February 28, 1963.

GEMP-177C

Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume III - Reactor Component Development, February 28, 1963.

METALLURGY

GEMP-19A and B

High-Temperature Materials Program Progress Report No. 19, January 25, 1963.

GEMP-21A and B

High-Temperature Materials Program Progress Report No. 21, April 23, 1963.

GEMP-23A and B

High-Temperature Materials Program Progress Report No. 23, May 31, 1963.

GEMP-25A and B

High-Temperature Materials Program Progress Report No. 25, July 31, 1963.

GEMP-27A and B

High-Temperature Materials Program Progress Report No. 27, September 30, 1963.

GEMP-29A and B

High-Temperature Materials Program Progress Report No. 29, November 30, 1963.

CERAMICS

GEMP-22A and B

High-Temperature Materials Program Progress Report No. 22, April 30, 1963.

GEMP-24A and B

High-Temperature Materials Program Progress Report No. 24, June 28, 1963.

GEMP-26A and B

High-Temperature Materials Program Progress Report No. 26, August 16, 1963.

GEMP-28A and B

High-Temperature Materials Program Progress Report No. 28, November 11, 1963.

GEMP-30A and B

High-Temperature Materials Program Progress Report No. 30, December 31, 1963.

INSTRUMENTATION AND CONTROLS

GEMP-76

Reactor Instrumentation and Control Progress Report No. 76, April 29, 1963.

GEMP-77

Reactor Instrumentation and Control Progress Report No. 77, May 31, 1963.

GEMP-78

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D. G. Besco and J. R. Beeler, Jr., "Computer Programs Describing Collision Cascades in Binary Materials, I: Square Planar Lattice," GE-NMPO, GEMP-192, February 1963.

E. C. Duderstadt and J. F. White, "The Sintering of BeO to Variable Densities and Grain Sizes," GE-NMPO, GEMP-219, September 1963.

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D. G. Besco and J. R. Beeler, Jr., "Computer Programs Describing Collision Cascades in Binary Materials, III: Body-Centered Cubic and Face-Centered Cubic Structures," GE-NMPO, GEMP-243, August 1963.

D. G. Besco and J. R. Beeler, Jr., "Computer Programs Describing Collision Cascades in Binary Materials, II: Wurtzite Structure," GE-NMPO, GEMP-200, February 1963.

J. A. Delaney, "Pseudo Infinite Lattices in a Digital Computer," GE-NMPO, GEMP-193, February 1963.

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INVENTION DISCLOSURES

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- L. H. Sjodahl and B. A. Chandler, "Single Crystal Elastic Constant of BeO from Polycrystalline Measurements," *J. Am. Ceram. Soc.*, Vol. 46, No. 7, 1963, pp. 351-352.
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