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FINAL REPORT

MECHANICAL, OXIDATION, AND THERMAL PROPERTY DATA FOR SEVEN REFRACTORY METALS AND THEIR ALLOYS

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PREPARED FOR THE DEPARTMENT OF THE NAVY, BUREAU OF WEAPONS
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Lockheed

MISSILES and SPACE DIVISION

LOCKHEED AIRCRAFT CORPORATION • SUNNYVALE, CALIF.

FOREWORD

This is a report of mechanical, oxidation, and thermal property data for seven refractory metals and their alloys. The research was performed by LMSC for the Department of the Navy, Bureau of Weapons under Contract NOas-60-6119-c. This report is supplementary to an initial report issued by Stanford Research Institute on January, 1959 under SRI Project SU-2436.

Minor corrections have been made in this publication since the distribution of preprint copies on 2 October 1961.

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SECTION I

INTRODUCTION

The Bureau of Aeronautics supported a compilation of the mechanical properties and oxidation resistance of the refractory metals chromium, columbium, osmium, rhenium, tantalum, tungsten, vanadium and their alloys. The compilation was issued in January 1959 and covered research reported through July 1958. Extensive research on refractory metals has continued since that date as a result of the urgent requirement for materials with capabilities to operate at elevated temperatures. A supplementary compilation was authorized to make the original report current.

This supplement covers research reported from July 1958 to mid-1961 and includes some data from the original survey for convenient reference which has not been revised or replaced by new information. The major effort was directed to obtaining more recent property data which either appear more accurate or extend to higher test temperatures, and to obtaining data on newly developed alloys. The production of higher purity unalloyed metals and the development of new alloys along with the demand for specific design and fabrication information has resulted in a large volume of new data.

Properties of molybdenum and its alloys have been included in this survey as a separate section. Osmium, which was included in the initial survey, was omitted due to its severe limitations because of its scarcity, toxicity, and brittleness. Available tensile, creep, transition temperature, oxidation, thermal conductivity, and thermal expansion data are included in a separate section for each of the metals and their alloys and a summary section is provided for comparison of these properties for the seven metals and selected alloys.

Technical reports issued on government-supported research programs were found to provide more recent, up-to-date information than published literature; consequently most data were obtained from this source. Over 500 references were reviewed which is an indication of the research effort directed toward refractory metals. The number of documents related to each individual metal was 28 Cr, 140 Cb, 139 Mo, 5 Re, 71 Ta, 112 W, and 31 V, and indicates the research activity in each during the period covered by this report. Recent compilations or summaries, when available, were used as a basis for the individual sections. More recently published reports were reviewed in detail and pertinent data were included in this compilation.

In many cases, alloys for which data are presented in each section and in the summary are included because property data were available, and not because of an attempt to select the outstanding candidates. Property data of those alloys which have attained commercial production status were reported to the limits of available data. Many of the alloys reported here are in the early stages of development, and research-in-progress should lead to improvements and to new alloys. Thus, it should be kept in mind when using this supplement, that the relative order of merit of the different alloys may change, and new alloys will appear.

SECTION 2
SUMMARY

INTRODUCTION

Property data for the seven metals which are presented in detail in separate sections of this report are summarized in this section. The figures presented are intended to serve only as a general guide, as the properties are sensitive to variations in impurities, fabrication history, thermal treatments, and specific test conditions. Details regarding the known effects of these variables are discussed in the individual section.

The melting point, crystal structure, and density of the seven refractory metals are summarized in Table 2.1. The mechanical, oxidation, and thermal properties of these metals and/or their alloys are summarized in this section from comparable data presented in the sections for each metal.

Table 2.1

MELTING POINTS, CRYSTAL STRUCTURES, AND DENSITIES OF SEVEN REFRACTORY METALS

METAL	ATOMIC NO.	MELTING POINT		CRYSTAL STRUCTURE	DENSITY AT ROOM TEMPERATURE	
		°C	°F		g/cc	lb/cu in
Vanadium	23	1900	3450	BCC	6.1	0.220
Columbium	41	2468	4474	BCC	8.57	0.310
Tantalum	73	2996	5425	BCC	16.6	0.600
Chromium	24	1900	3450	BCC	7.2	0.260
Molybdenum	42	2610	4730	BCC	10.22	0.369
Tungsten	74	3410	6170	BCC	19.3	0.697
Rhenium	75	3180	5760	HCP	21.04	0.759

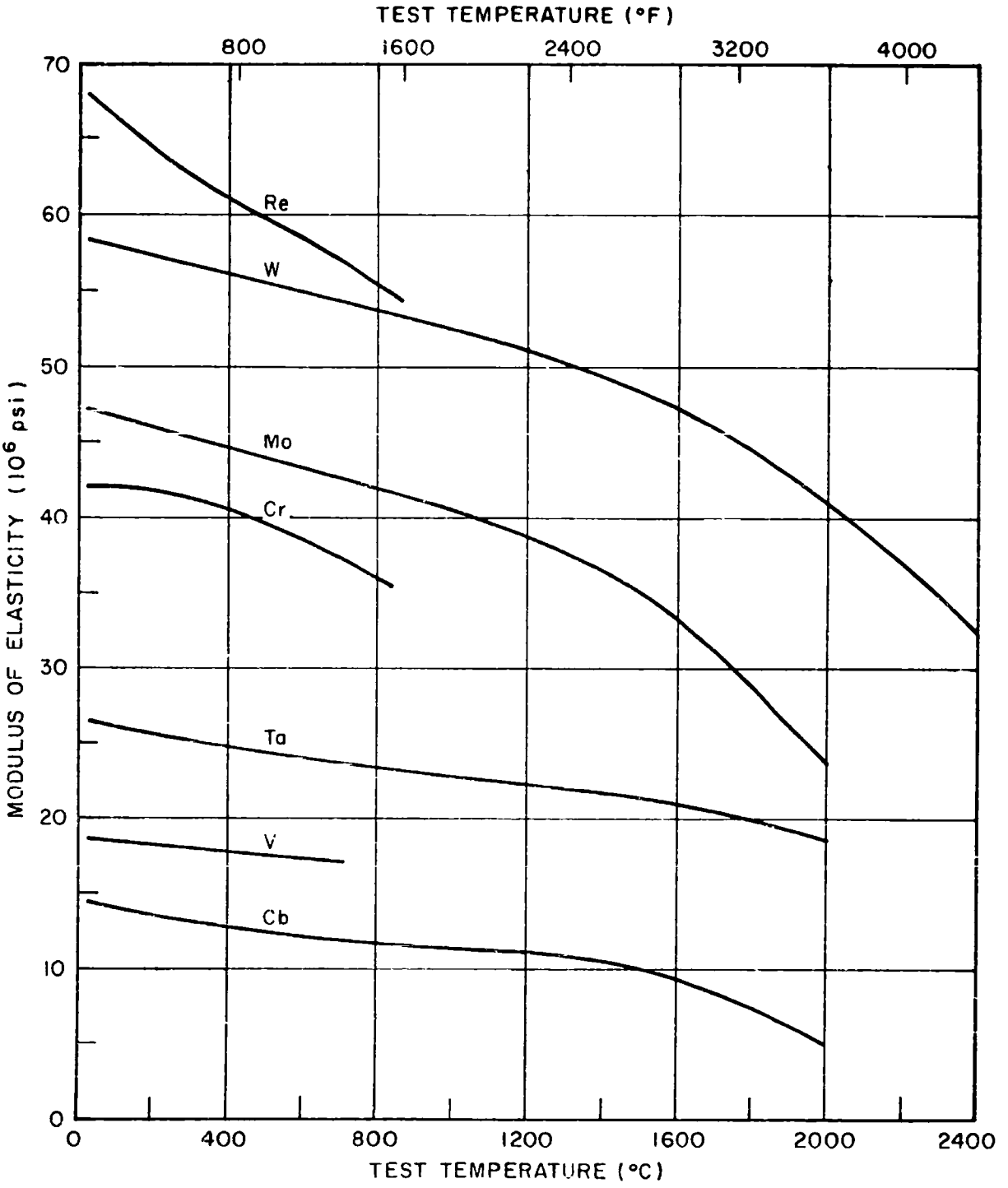


FIG. 2.1

MODULUS OF ELASTICITY VS TEST TEMPERATURE
FOR SEVEN REFRACTORY METALS

MECHANICAL PROPERTIES

Tensile Properties of the Unalloyed Metals

The effect of temperature on the modulus of elasticity of the seven metals is shown in Fig. 2.1. The data for four metals (Cb, Ta, Mo, and W) have now been evaluated to 2000° C, whereas three years ago, these data were only available up to 1000° C.

Comparison of the tensile properties of the metals in the recrystallized condition is presented in two sets of figures. Figures 2.2 through 2.5 include data between -200 and 1000°C, and Figs. 2.6 through 2.8 include data between 800 and 3000°C. The data for the lower temperature range with the exception of that for Ta were taken from the initial survey report since the values at low temperatures have not changed appreciably. Tantalum data presented in Figs. 2.6 through 2.8 are from recent evaluations of electron beam melted material.

The effect of temperature on the elongation and reduction-in-area between -200 and 1000°C is given in Figs. 2.4 and 2.5. The reduction in area versus temperature curves are very sensitive indicators of the transition from ductile to brittle behavior. The curves given in Fig. 2.5 show that both Ta and V are ductile below -195°C, and Cb below -100°C. These three metals are all in Group VA of the periodic table. Tungsten shows the highest transition temperature (around 340°C) as indicated by the data in Fig. 2.5, and Mo a transition temperature around room temperature. No reduction in area data were reported for recrystallized Cr; however, the elongation data indicate a transition temperature of around 330°C. The latter three metals are in group VIA in the periodic table. The transition temperatures for the different metals are summarized in Table 2.2, in order of increasing transition temperature.

Table 2.2

TRANSITION TEMPERATURES OF THE DIFFERENT METALS

Values based upon data of Figs. 2.4 and 2.5

METAL	TRANSITION TEMPERATURE	
	°C	°F
Ta	<-195	<-320
V	<-195	<-320
Cb	-120	-185
Mo	30	85
Cr	330	625
W	340	645

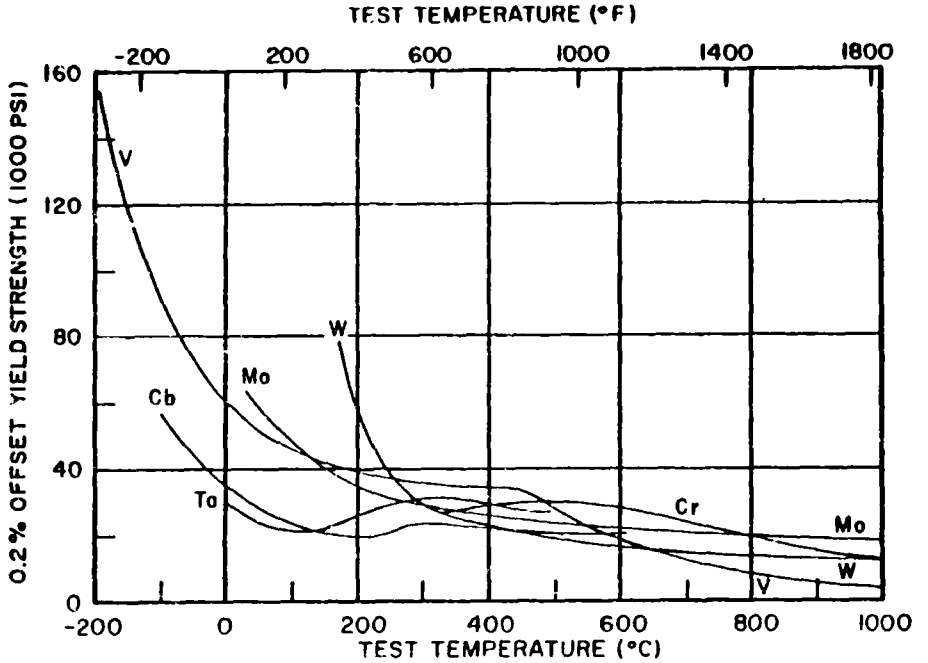


FIG. 2.2

YIELD STRENGTH OF SIX REFRACTORY METALS FROM -200 TO 1000°C

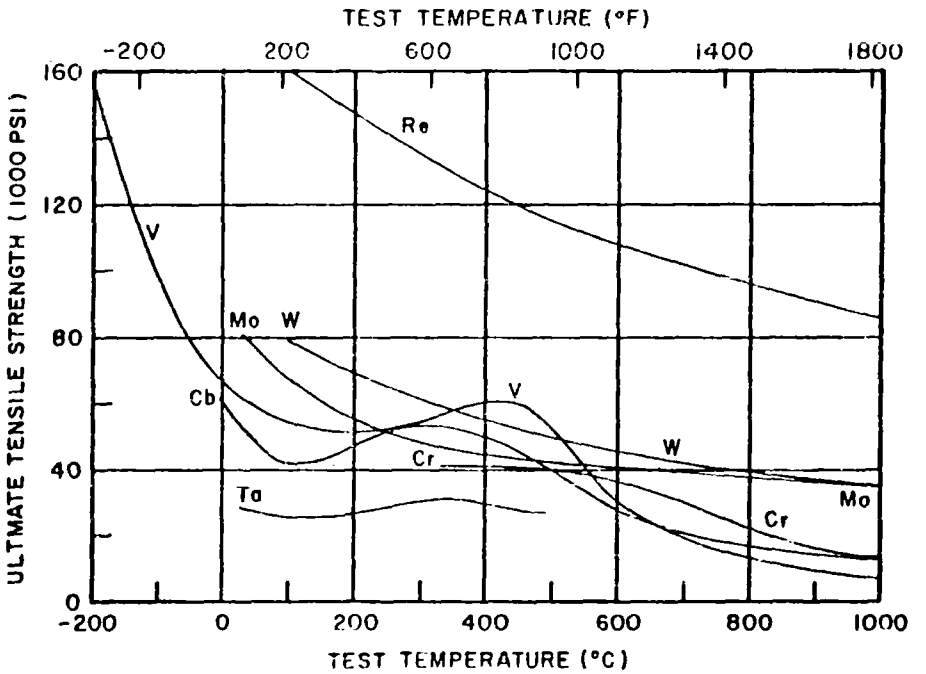


FIG. 2.3

ULTIMATE TENSILE STRENGTH OF SEVEN REFRACTORY METALS FROM -200 TO 1000°C

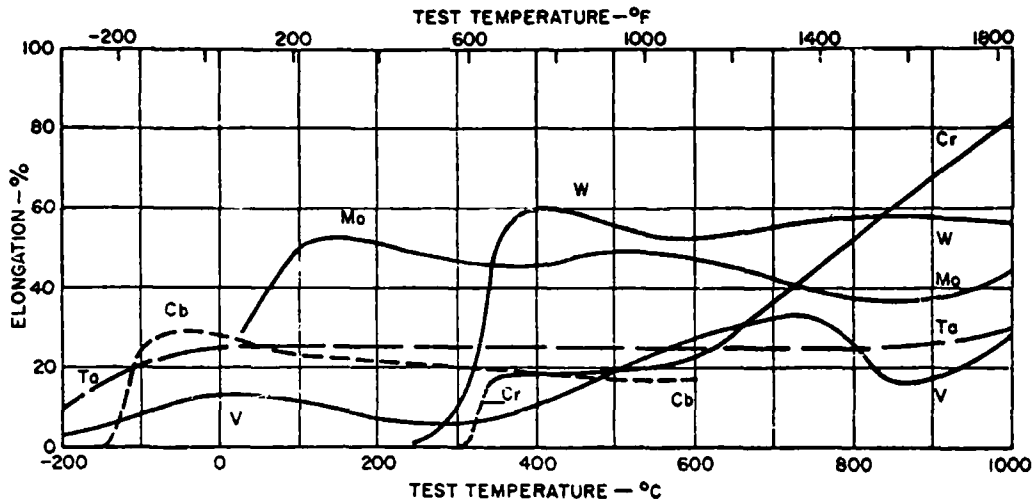


FIG. 2.4

ELONGATION VERSUS TEST TEMPERATURE FOR SIX REFRACTORY METALS FROM -200 to 1000°C

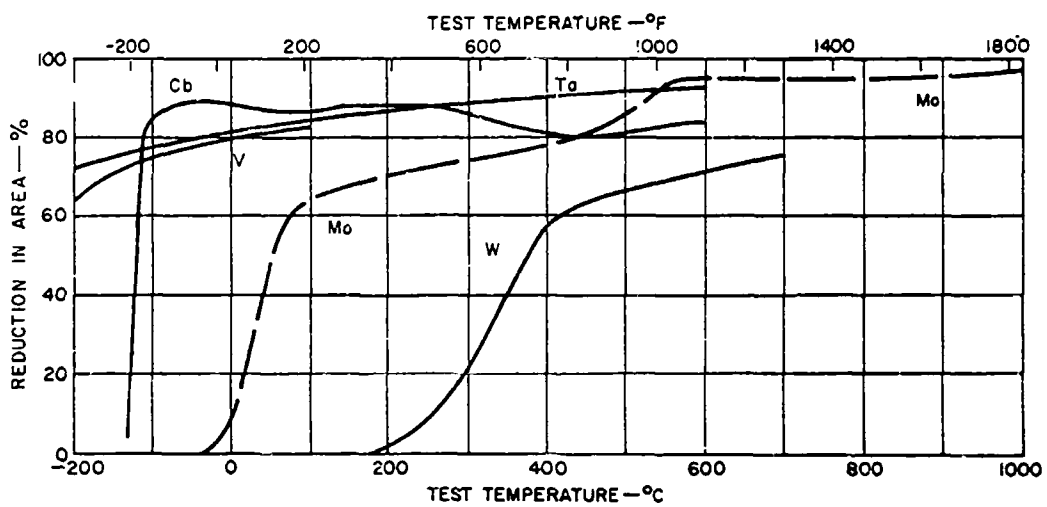


FIG. 2.5

REDUCTION IN AREA VERSUS TEST TEMPERATURE FOR FIVE REFRACTORY METALS FROM -200 to 1000°C

The yield strength and ultimate tensile strength above 800°C for the seven metals are given in Figs. 2.6 and 2.7 for recrystallized material. Vanadium is shown to have the lowest strength and Re the highest up to about 2000°C. Above 2000°C, W and Re appear to have about equal values of ultimate tensile strength. The ultimate tensile strength values for W are presented in three curves from different investigations covering different temperature ranges. These three sets of data serve to point out again the differences which are commonly observed for different materials and test conditions.

Elongation values for the seven unalloyed metals tested above 800°C are given in Fig. 2.8. Sufficient reduction in area data were not available at these temperatures to make a meaningful summary curve. The transition temperature at which ductile to brittle behavior occurs for recrystallized material is sensitive to a number of factors and any specific transition data apply only to one set of conditions. The factors which have been shown to affect the transition temperature or its determination include the following:

- impurity content and distribution of both interstitial and metallic elements
- microstructure as produced by fabrication and/or thermal treatment
- the stress system as induced by tension, compression, torsion, bend, impact, and hardness tests
- the strain rate of the test procedure
- the surface condition of the test specimen (mechanical and chemical)

Thus the transition data as obtained from Figs. 2.4 and 2.5 are only presented as a general guide. For a discussion of the effect of the various factors on the ductile-brittle behavior reference should be made to the separate sections of this report.

Tensile Properties of Selected Alloys

The yield strength and ultimate tensile strength for a number of refractory alloys are presented in Fig. 2.9 and 2.10 for test temperatures above 800°C. One or two alloys were selected for each base metal. These selections were made primarily on the basis of the highest strength properties, and do not necessarily represent the "best" alloy on an overall basis considering fabricability and oxidation resistance in addition to strength. Any one alloy might be chosen as best for a specific application.

Most of these data were obtained on wrought alloys, and it should be noted that different worked states existed between the different alloys. Also, the yield strength values should be considered as only approximate as different determination methods were used by different investigators. A detailed discussion will not be given here but can be found in the individual sections in the main body of the report.

Figure 2.10, however, does give a general idea of the relative strengths of the different alloys, and Fig. 2.11 adjusts these alloy data for density. On a strength – density basis, alloy V-5Ti-20Cb has the highest value below about 1100°C (2010°F). Alloy TZM is superior from 1100°C to about 1400°C (2550°F). From 1500 to 1700°C (2730 to 3090° F) W-10Mo is highest, and at temperatures above 1700° C, the W-2ThO_2 has the highest strength – density value.

Stress-Rupture Properties of the Unalloyed Metals

Stress-rupture properties for W, Mo, Ta, Cr, and Cb all in the recrystallized condition are summarized in Fig. 2.12 for temperatures between 800 to 1400°C (1470 to 2550° F).

Tantalum is shown to have low stress-rupture strength in comparison to Cr and Cb which have much lower melting points. However, the Ta used to obtain the data shown was high purity EB melted material and less pure material exhibited higher strength as is shown in the Ta section of this report. Similarly, the strength of Cb shown in the figure is below that of Cr except in the highest temperature long-time tests, probably as a result of the relative purity of the two materials

Stress-Rupture Properties of Alloys

Stress-rupture data for five alloys at 2000°F (1090°C) are summarized in Fig. 2.13 and in the density-adjusted curves of Fig. 2.14. In both cases, the TZM alloy had the highest strength values and the V-5Ti-20Cb - 0.25C the lowest. This is a relatively low temperature for refractory alloy application but it was the only temperature at which this number of alloys could be compared over a rupture time from 1 to 100 hours. Even at this temperature, in some cases it was necessary to extrapolate data from shorter time tests.

A general summary of stress rupture data for nine alloys adjusted for density is presented in Fig. 2.15 for tests ranging from 1600 to 3000°F. For all three rupture life values, 1, 10, and 100 hours, the TZM alloy exhibited the highest stress-density values up to 2400°F. At the higher temperatures, 2500 to 2700°F, only data for W alloys were available.

OXIDATION PROPERTIES

Oxidation Properties of the Unalloyed Metals

All of the metals under consideration, with the exception of Cr, have poor oxidation resistance. This is a major problem and is a serious limitation to the use of these refractory metals at elevated temperatures in an oxidizing atmosphere.

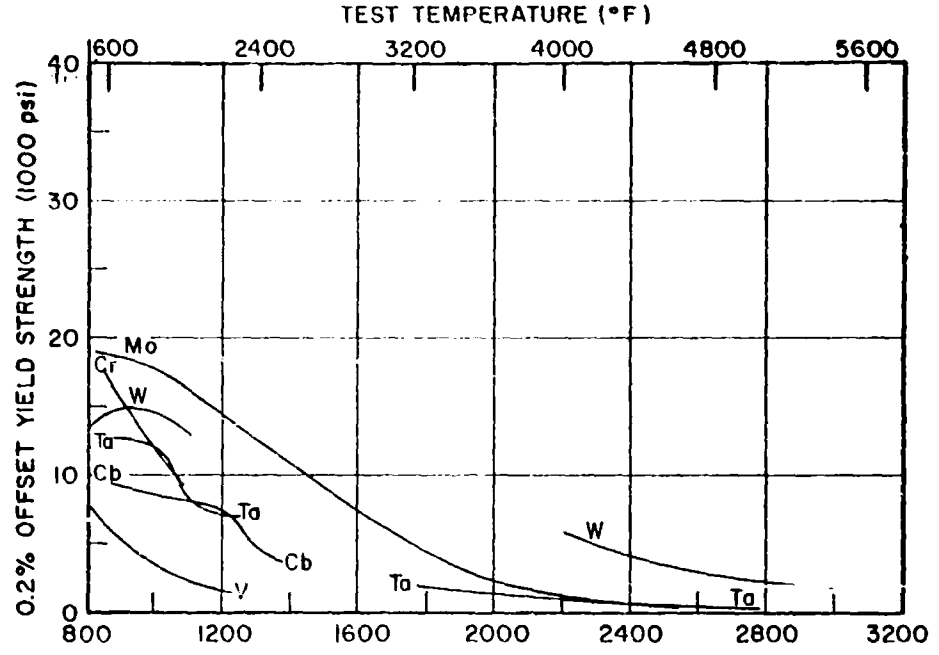


FIG. 2.6

YIELD STRENGTH OF SIX REFRACTORY METALS FROM 800 TO 3000°C

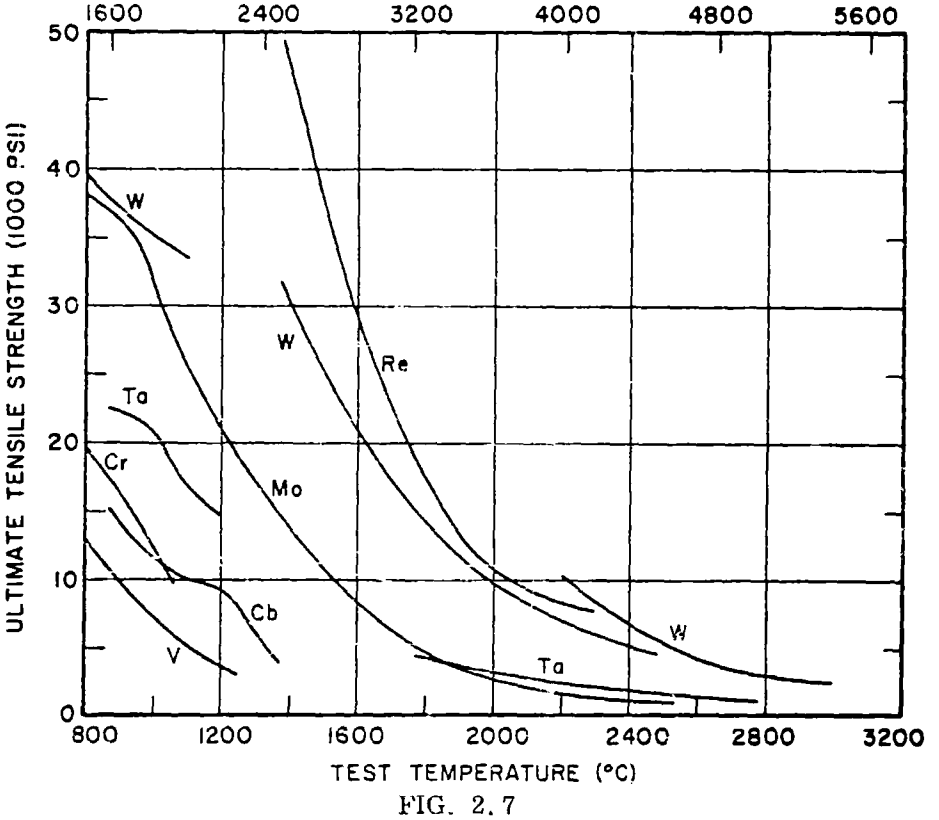


FIG. 2.7

ULTIMATE TENSILE STRENGTH OF SEVEN REFRACTORY METALS FROM 800 TO 3000°C

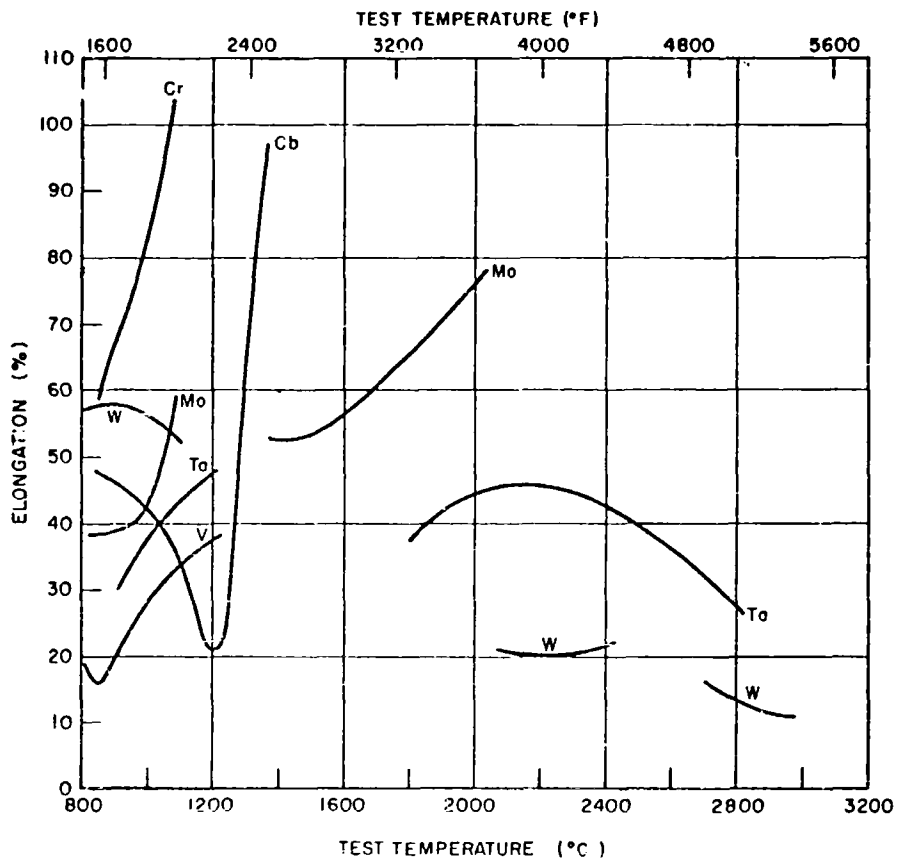


FIG. 2.8

ELONGATION OF SIX REFRACTORY METALS FROM 800 TO 3000 °C

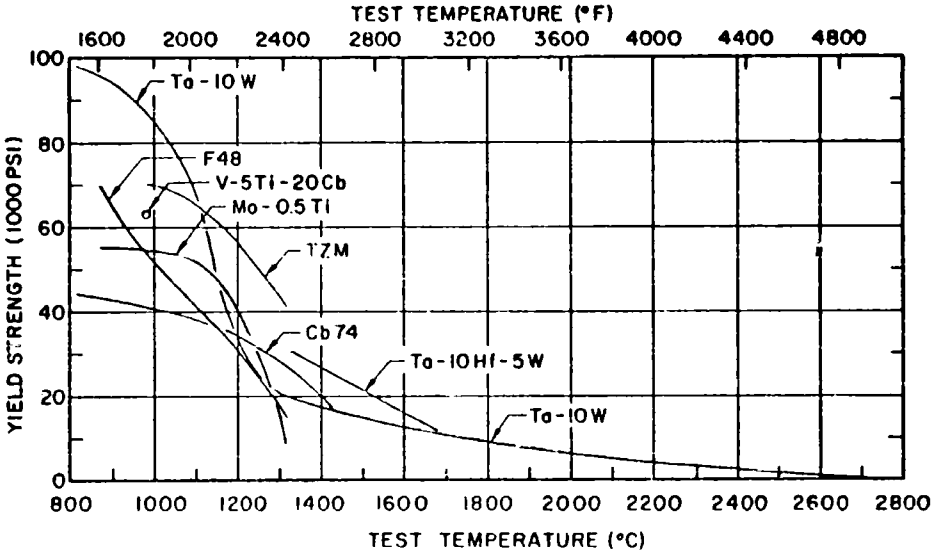


FIG. 2.9

YIELD STRENGTH VS TEMPERATURE OF SELECTED REFRACTORY ALLOYS

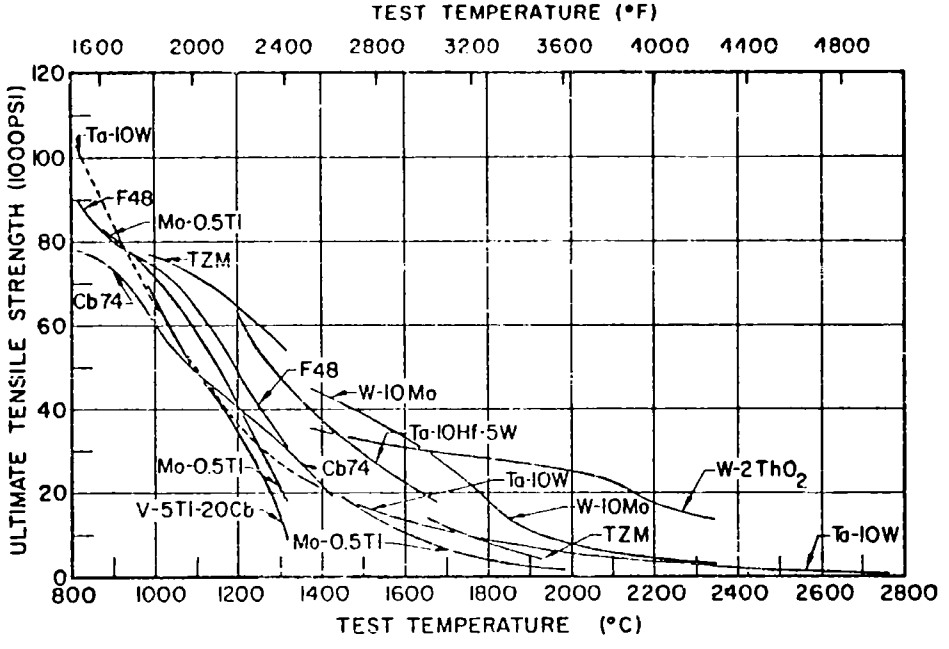


FIG. 2.10

ULTIMATE TENSILE STRENGTH VS TEMPERATURE OF SELECTED REFRACTORY ALLOYS

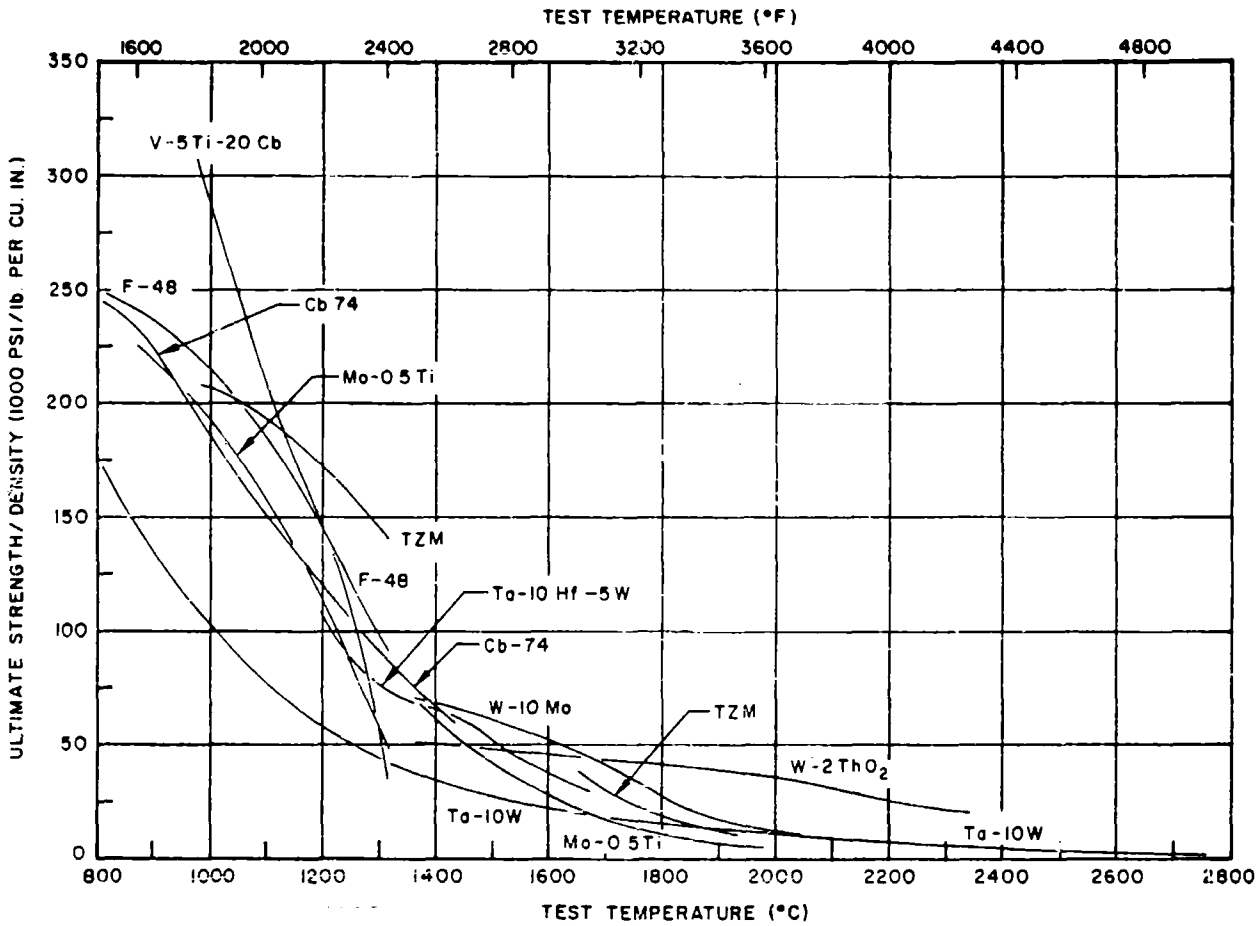


FIG. 2.11

ULTIMATE TENSILE STRENGTH – DENSITY RATIO VS. TEST TEMPERATURE FOR SELECTED REFRACTORY ALLOYS

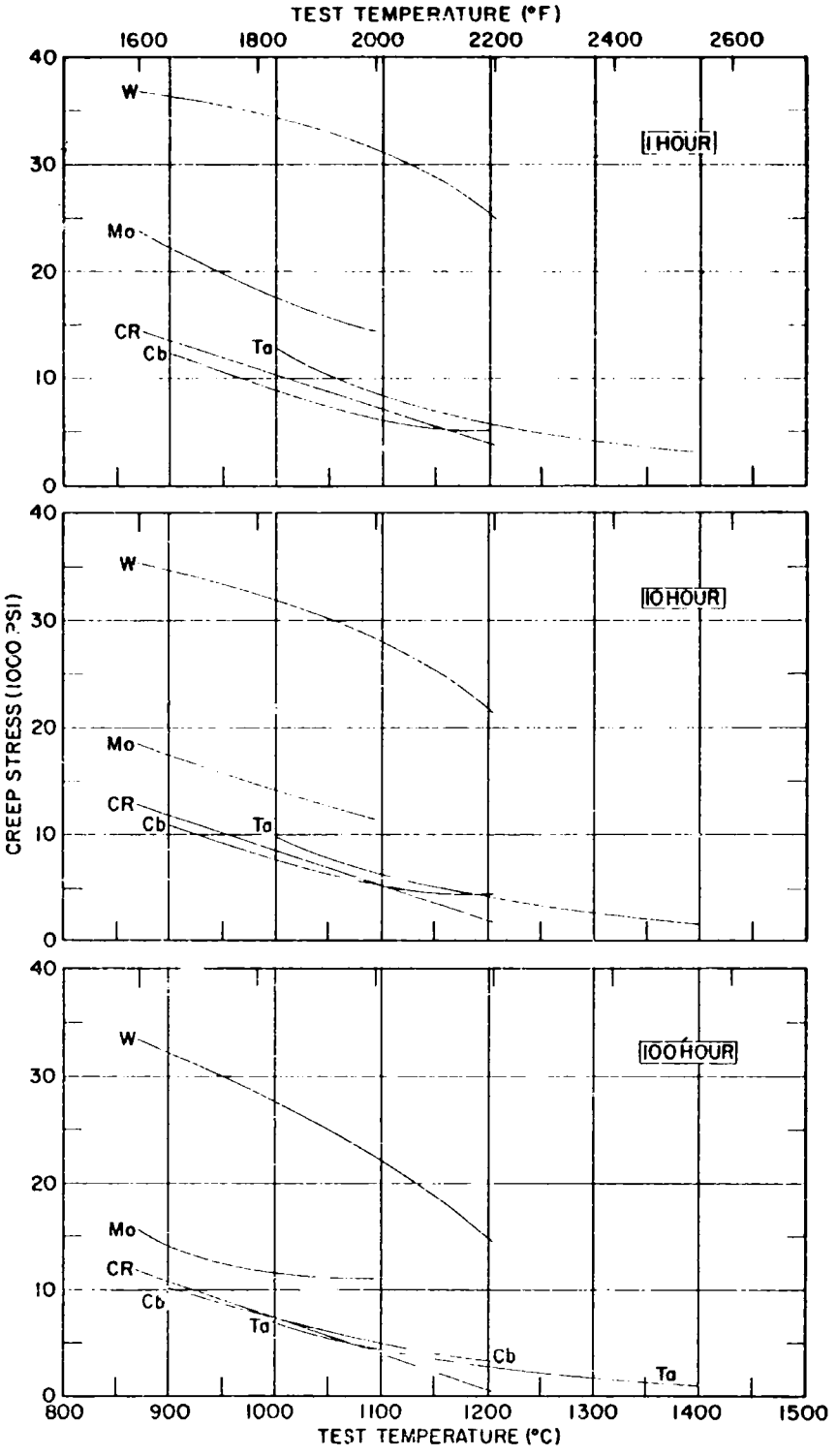


FIG. 2.12

1, 10, and 100 HR RUPTURE STRENGTH VS TEST TEMPERATURE FOR 5 REFRACTORY METALS

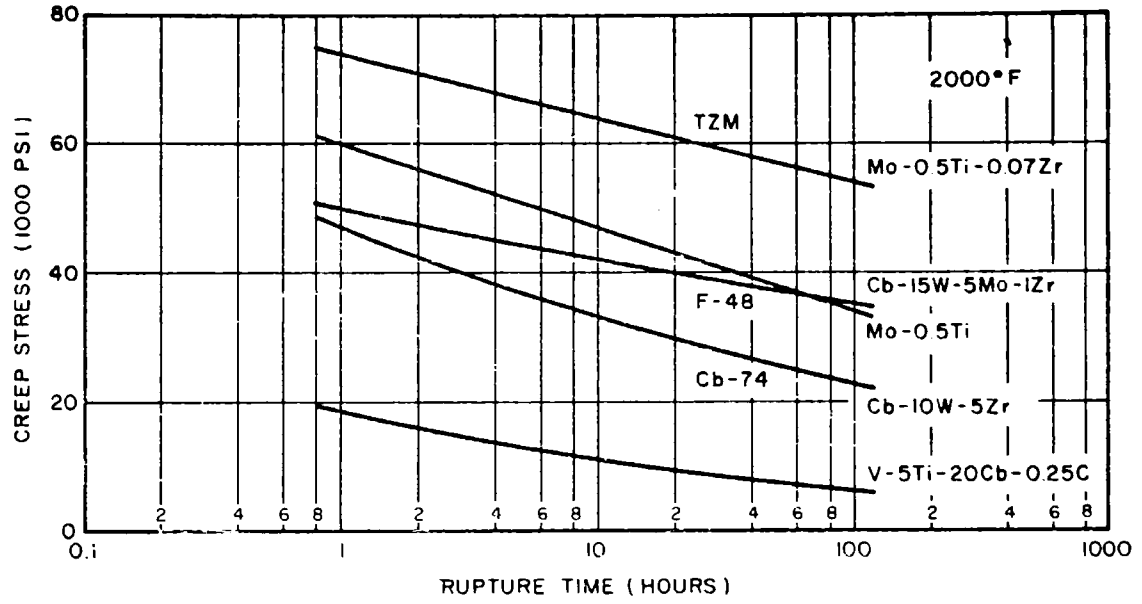


FIG. 2.13

CREEP STRESS VS RUPTURE TIME FOR VARIOUS ALLOYS TESTED AT 1090°C (2000°F)

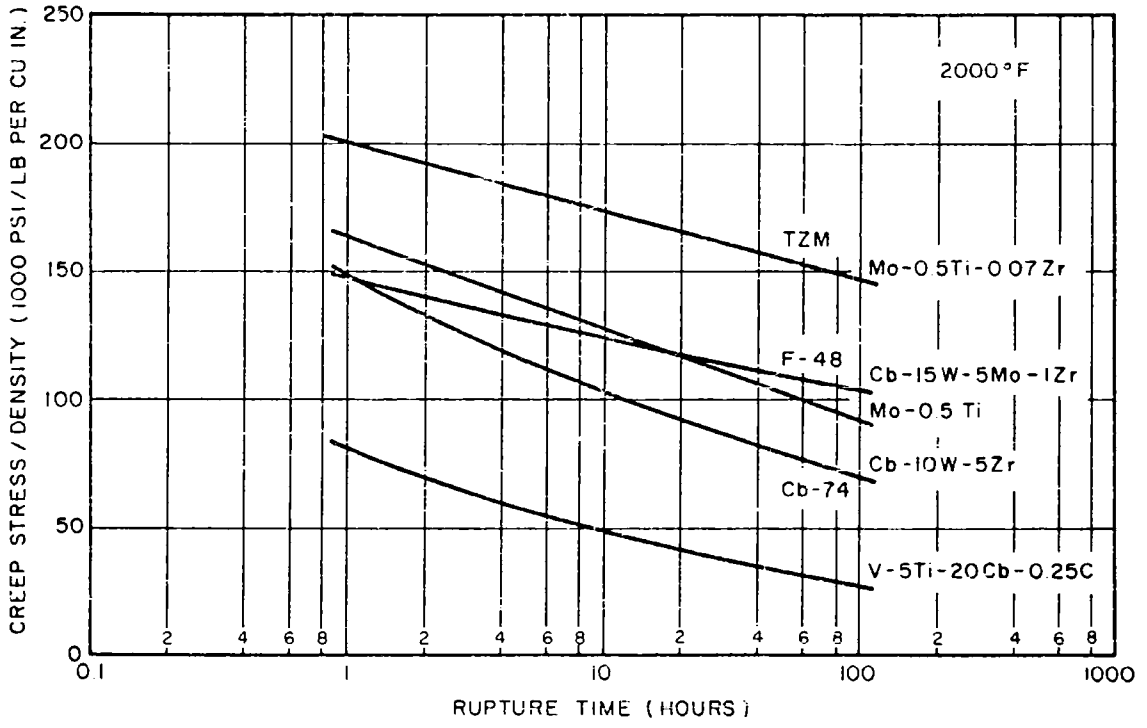


FIG. 2.14

CREEP STRESS – DENSITY RATIO VS RUPTURE TIME FOR VARIOUS ALLOYS TESTED AT 1090°C (2000°F)

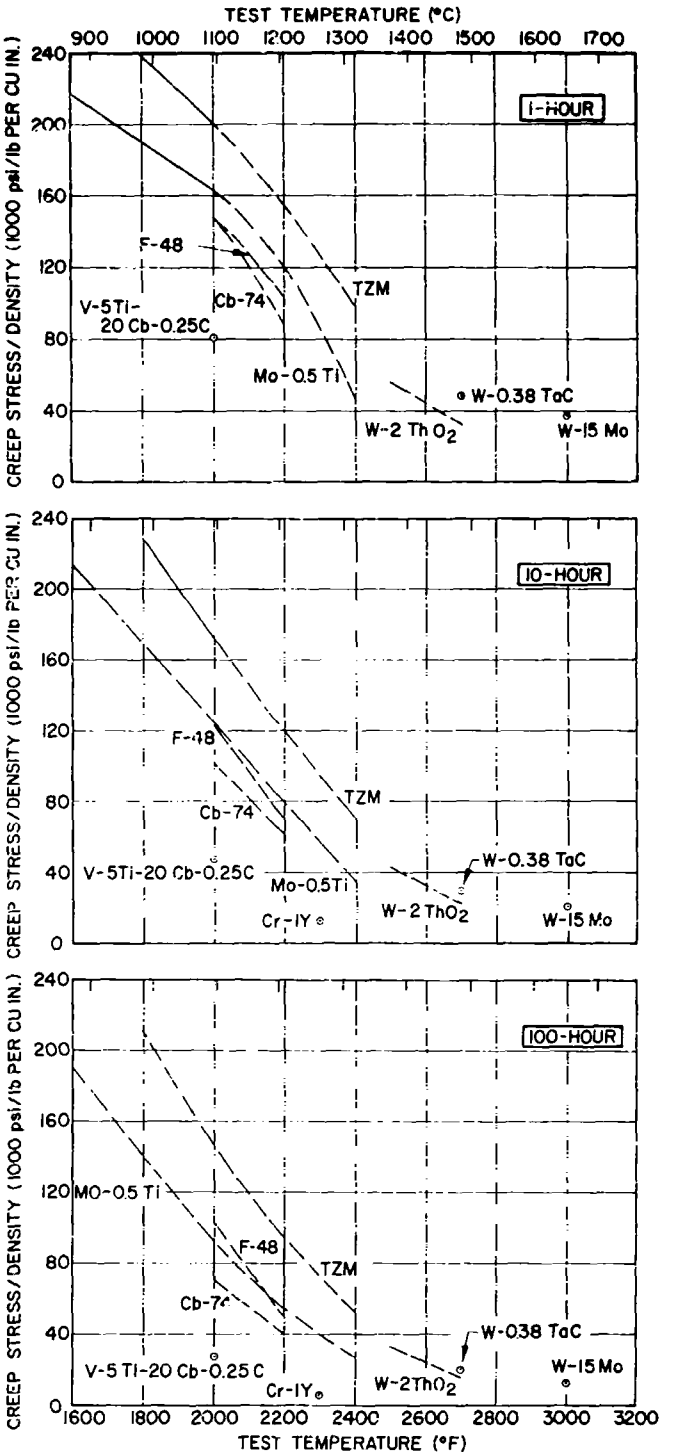


FIG. 2.15

CREEP STRESS--DENSITY RATIO FOR 1, 10, and 100 RUPTURE LIFE FOR SELECTED ALLOYS FROM 1600 TO 3000°F

Table 2.3 lists the metals and their major oxide in order of increasing stability of the oxides. The oxide of Re, Re_2O_7, is the least stable with a melting point of 297°C (565°F) and a boiling point of 363°F (685°F). Thus, the high strength of Re at elevated temperatures can only be utilized in a protective atmosphere. The V oxide, V_2O_5, melts at 675°C (1270°F), and therefore V can not be used much above 650°C in an oxidizing atmosphere. Molybdenum is the next in order; it oxidizes catastrophically above about 800°C (1470°F), due to the volatility of MoO_3. The other 4 metals W, Cb, Ta, and Cr, appear to be less critically limited in this respect. WO_3 is substantially novolatile below 1000°C (1830°F) and Cb_2O_5 and Ta_2O_5 have been found nonvolatile below 1370°C (2500°F).

Table 2.3

STABILITY OF REFRACTORY METAL OXIDES

METAL	OXIDE	STABILITY OF OXIDE
Re	Re_2O_7	Melts at 296°C (565°F); boils at 363°C (685°F)
V	V_2O_5	Melts at 675°C (1270°F)
Mo	MoO_3	Volatile above 795°C (1465°F)
W	WO_3	Volatile above 1000°C (1830°F)
Cb	Cb_2O_5	Nonvolatile below 1370°C (2500°F)
Ta	Ta_2O_5	Nonvolatile below 1370°C (2500°F)
Cr	Cr_2O_3	Melts at 2440°C (4424°F) (Metal volatile above 1000°C; 1830°F)

The results of oxidation studies on a particular metal by different investigators often differ by a factor of 10 or more in terms of the rate of oxidation at a given temperature and oxygen pressure. This variation is apparently due to variations in test procedures, and in purity and condition of the test material. For comparison of the oxidation rates of different metals there would therefore be merit in comparing the results as reported by one investigator, if possible. Gulbransen and Andrew, and Gulbransen and Wysong, have conducted oxidation studies on Cr, Cb, Mo, Ta, V, and W, all in oxygen at 0.1 atmosphere pressure, using similar test procedures. Their results on these metals are summarized in Fig. 2.16 in terms of rate of weight gain vs. test temperature. The results of other investigators are also included in Fig. 2.16 especially at the higher test temperatures for Cb, Ta, and W. The test conditions for the different investigations are indicated in the box in Fig. 2.16. The rate of weight gain was determined by taking the average weight gain over the indicated time period.

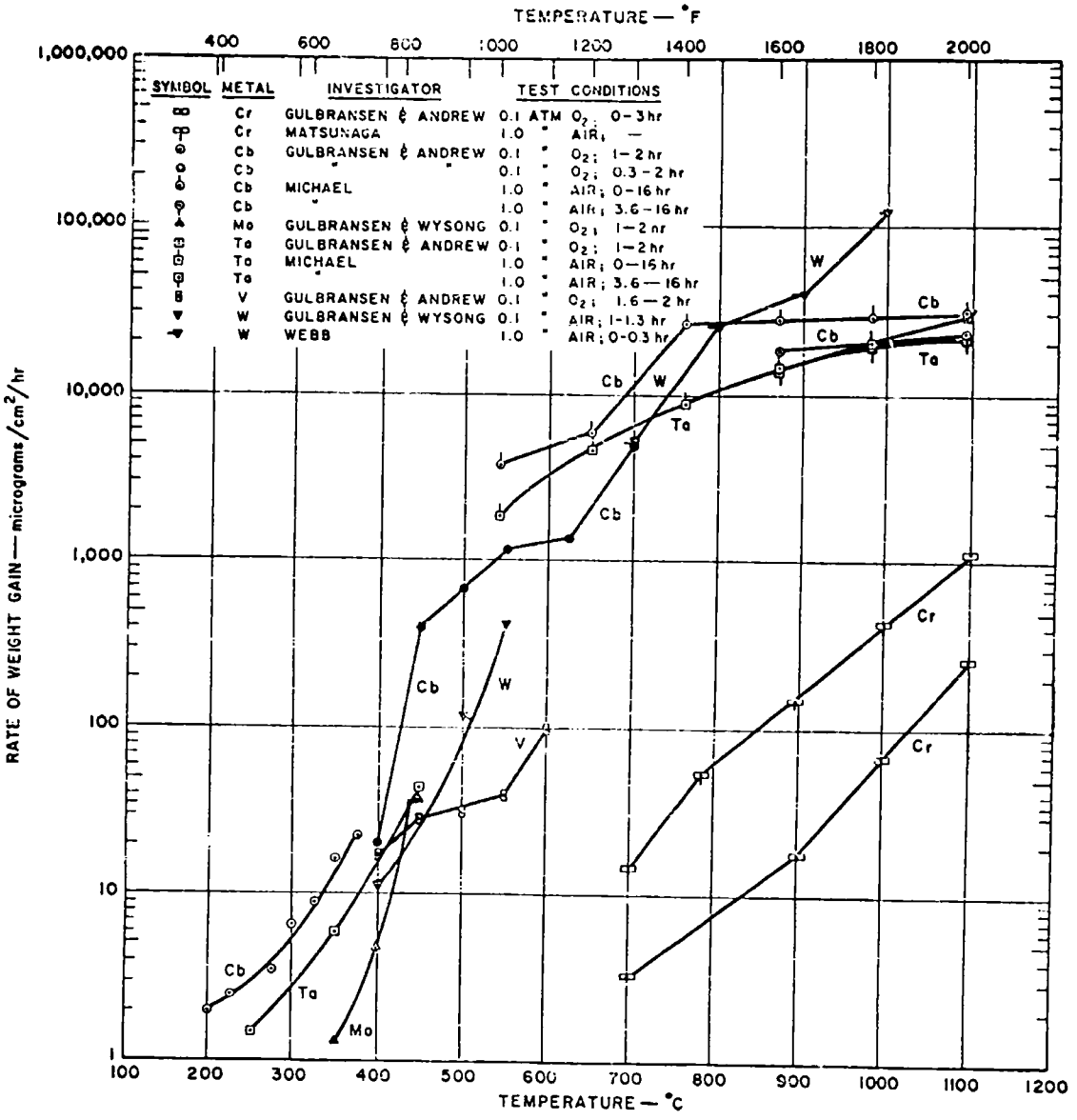


FIG. 2.16

COMPARATIVE RATES OF OXIDATION AS A FUNCTION OF TEMPERATURE

A parabolic rate law was found to apply at the lower temperatures for short time tests, for all six metals. A linear rate was approached in some cases when the tests were continued for a longer time.

As the temperature was increased, the parabolic portion became of shorter duration until in some cases a linear rate law apparently applied from the start of the test. Reference should be made to the separate sections of the initial survey report for a more detailed discussion.

The data for V in Fig. 2.16 indicate a relatively low rate of oxidation up to 600°C (1110°F); however, much above this temperature the rate was observed to increase greatly due to the low melting point of V_2O_5. Gulbransen and Wysong did not extend their study on Mo above 450°C (840°F). Weight gain measurements are unreliable at temperatures where a high vapor pressure for the oxide, MoO_3, exists. It is evident that at temperatures much above 800°C (1470°F) the only metals of the original eight which are of interest from an oxidation resistance standpoint are Cr, Ta, Cb, and W.

Comparative oxidation data of these four metals in terms of displacement of metal interface during oxidation in air at 2000°F are given in Fig. 2.17. This type of measurement has much to recommend it from the application viewpoint, as it gives a clear indication of how much parent metal has been oxidized, and occurrence of possible volatility or spalling of the oxide does not pose a problem in interpreting the results as it might in the case of weight gain measurements. The data presented in Fig. 2.17 for Cb, Ta, W, and Mo were reported by Michael from tests conducted in air. The dashed curve for Cr is based upon one 20-hour test, also in air, conducted at Stanford Research Institute. The results of these tests indicate that Mo oxidized about 6 times faster than W, and W about 3 times faster than either Cb or Ta.

Oxidation Properties of Alloys

The oxidation behavior of the attractive alloys have not been extensively investigated as discussed in the individual sections. The attractive alloys from a strength or fabricability standpoint do not have exceptional oxidation resistance. High temperature applications of refractory metal alloys above 2500°F, for long time service will require protective coating systems or inert atmosphere protection. A survey of protection systems for the refractory metals and their alloys is in preparation at DMIC and will soon be available as a DMIC report.

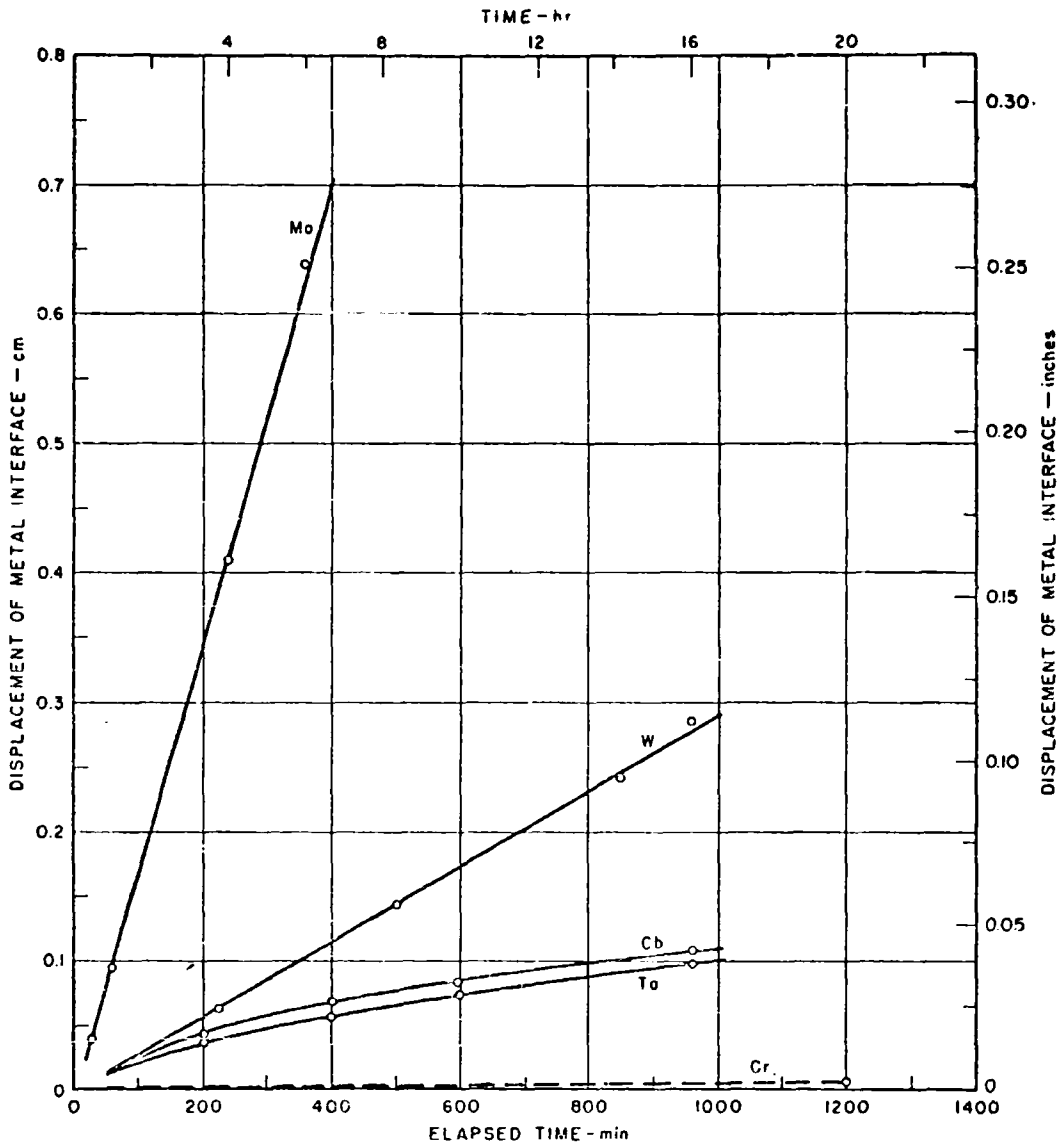


FIG. 2.17

COMPARATIVE RESISTANCE TO OXIDATION IN TERMS OF DISPLACEMENT OF METAL INTERFACE DURING OXIDATION IN AIR AT 1090 C (2000 F)

THERMAL PROPERTIES

Thermal Conductivity

The thermal conductivity data as a function of temperature for Cb, Cr, Mo, Ta, V, and W are summarized in Fig. 2.18, along with one value for Re at room temperature

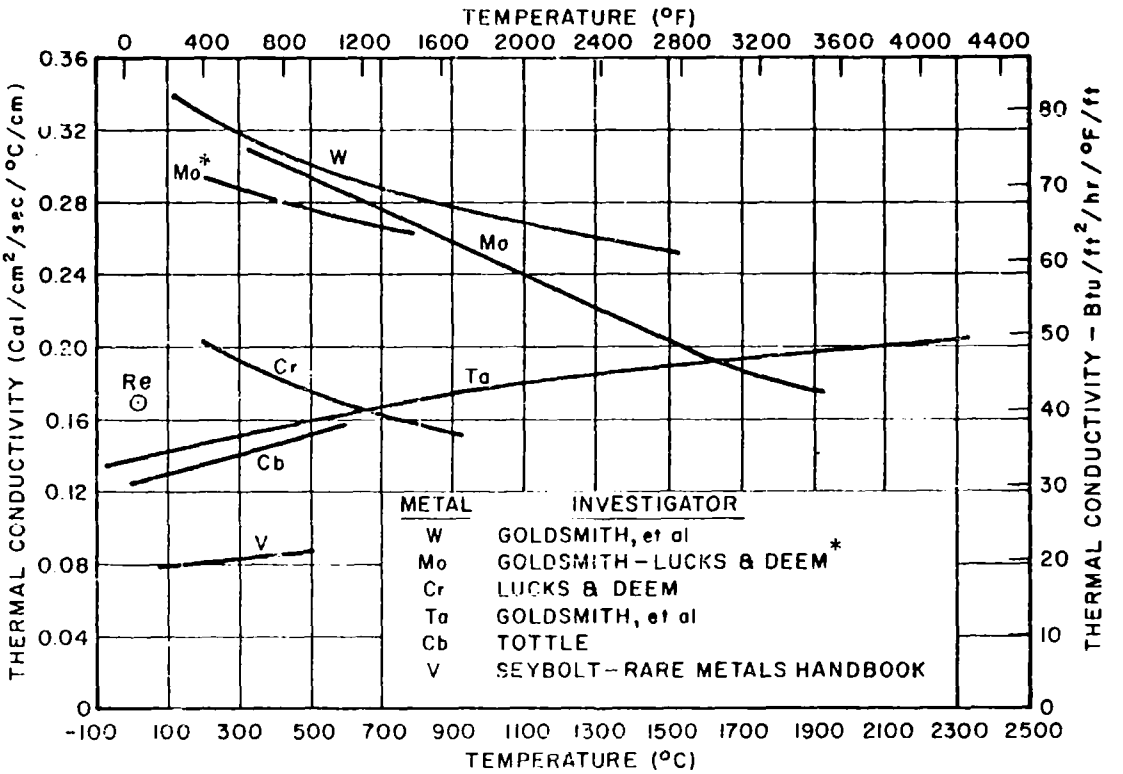


FIG. 2.18

THERMAL CONDUCTIVITY AS A FUNCTION OF TEMPERATURE

Thermal Expansion

The linear thermal expansion data as a function of temperature for Cr, Cb, Mo, Re, Ta, W, and V are summarized in Fig. 2.19.

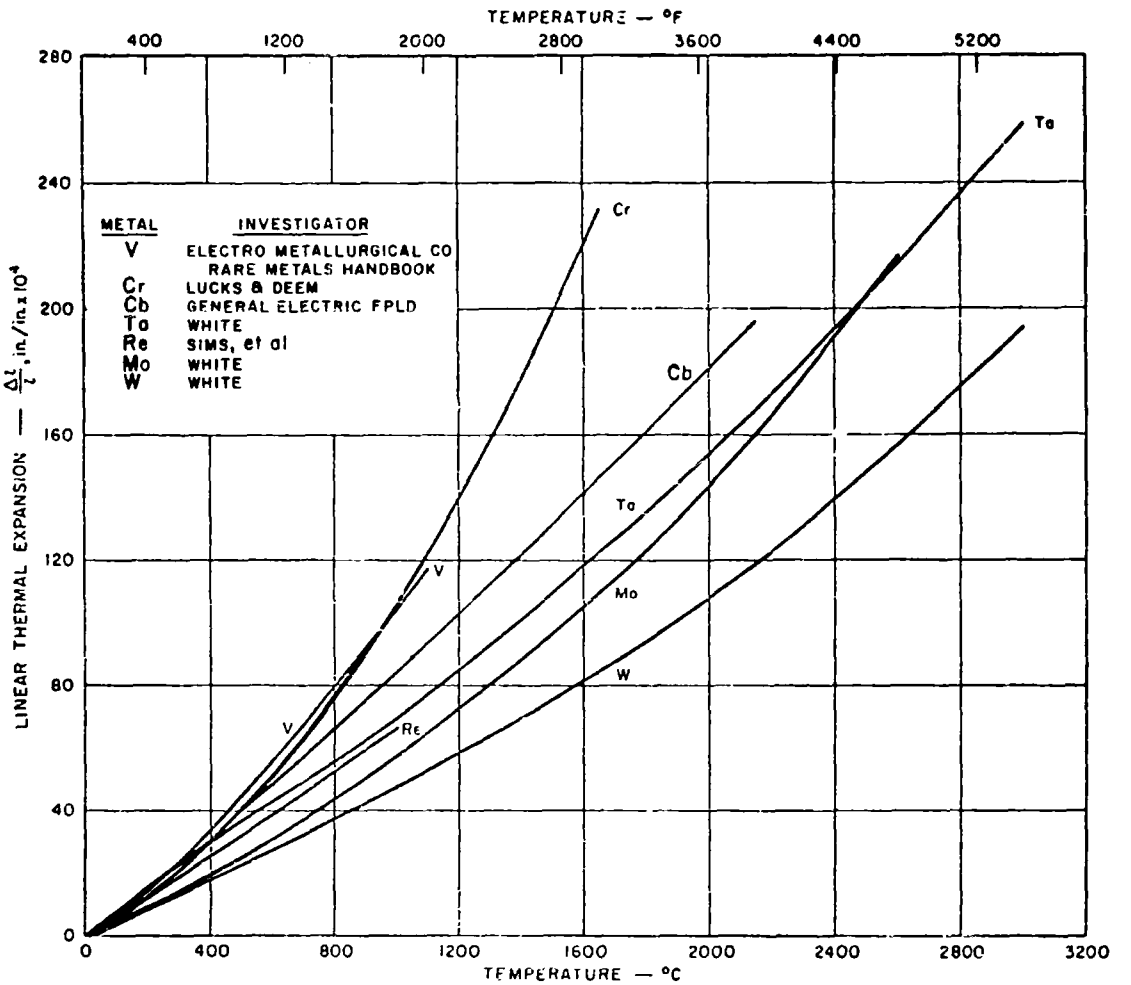


FIG. 2.19

THERMAL EXPANSION AS A FUNCTION OF TEMPERATURE

SECTION 3

CHROMIUM

INTRODUCTION

The properties which have made chromium attractive for elevated temperature applications are its melting point of 1880°C (3410°F), which is about 400°C (750°F) above that of nickel or cobalt; its relatively good oxidation resistance; and its low density. In addition, its abundance enhances its degree of usefulness.

Much of the past interest in Cr has been based upon the potential development of a Cr-base alloy for structural applications in the temperature range 1800 to 2100°F. To date, one of the major drawbacks in realizing the objective has been the lack of sufficient ductility at room temperature and, thus, of sufficient mechanical and thermal shock resistance for use in such applications as blades and vanes in gas turbine engines.

Because of this factor and the substantial strides made in the more refractory alloy systems, such as Cb and Mo base alloys, the rate of activity on Cr-base alloys has decreased substantially during the past three years. Currently, government supported work on Cr-base alloys is in progress in two laboratories, and recent developments resulting in a lower cost high-purity chromium starting material may lead to potentially useful alloys. The more recent studies have been directed primarily toward a better understanding of the factors which affect the ductile-brittle behavior of Cr, such as impurities and thermal-mechanical treatments.

The chromium section in the original compilation[1] contains a detailed summary of earlier property data on chromium. In addition, an excellent review which covers the preparation and properties of high-purity chromium was published in 1959 by Edwards, Nish, and Wain.[2]

MECHANICAL PROPERTIES

Edwards, Nish, and Wain[2] outline the attractive electrolytic and halide decomposition methods of production of Cr, and include the range of impurities experienced in commercial and high-purity methods. Impurity ranges for iodide and the various electrolytic processes are shown in Table 3.1 (reproduced from the SRI report),[1] to which the analysis range for chromic acid/sulphate bath electrolized material is added under the heading "Electrolytic-High Purity." The data indicate that the cheaper "high-purity" electrolytic process can produce material comparable to the iodide process, with the exception that the iodide material contains less oxygen, by a factor of 50 to 100 times.

Table 3.1

IMPURITIES IN CHROMIUM METAL,[1,2] ppm

ELEMENT	ELECTROLYTIC (Commercial)	ELECTROLYTIC* (H_2 Reduced)	IODIDE†	ELECTROLYTIC (High-Purity)
O	5400 to 6000	88 to 300	4 to 6	100-200
H	–	1 to 9	1	–
N	70 to 110	28 to 200	5	3-5
C	30 to 100	5 to 100	10 to 40	0.1 - 10□
S	130 to 280	70 to 160	3	0.1 - 10□
P	–	–	1.4§	–
Si	10 to 100	40	Not detected	<0.2
Fe	200 to 600	200	Not detected	0.6
Cu	50	50	1 - 2	<0.1
Sb	--	10 to 100	Not detected	–
Pb				0.7
Al				<0.2
Ag, Mg, Mn				ea. <0.1
Sn				0.1 - 10□

*Supplier's Analysis

†Battelle analysis

§By neutron-activation analysis at Oak Ridge

□Uncertain-probable values

Allen, Maykuth, and Jaffee[3] have presented additional analyses of Iodide Chromium and a typical impurity analysis for Cr produced by electrolysis of fused Cr salts. The impurity content of fused-salt Cr, as-grown iodide-Cr crystals, two arc-melted and fabricated rods, and six alloys with intentional interstitial additions are shown in Table 3.2. The typical fused-salt analysis indicates higher Fe and Ni impurity but about the same O and N content as the material produced by the electrolytic processes presented in Table 3.1. It is also interesting to note the increase in C, O, N, and H content during arc-melting and fabrication of the bars I Cr-1 and I Cr-2. The C, O, N, and S alloys are discussed in the ductile-brittle transition and recrystallization sections.

Table 3.2

IMPURITY ANALYSES OF CHROMIUM AND CHROMIUM IN INTERSTITIAL ALLOYS[3]

ALLOY	PARTS PER MILLION BY WEIGHT														
	INTERSTITIALS					METALLIC									
	C	O	N	H	S	Fe	Ni	V	Si	Cu	Mg	Ca	Al	Ti	Mo
FSCr-1	80[a]	150[a]	4	0.6[a]	20[a]	5000	3000	<100	~30	<10	<10	<10	<30	~50	<30
As-received iodide chromium crystals	37	5	<3	<0.2	10[a]	20	2	3	--	1	1	2	1	--	--
ICr-1	48	32	14	<0.8	6	--	--	--	--	--	--	--	--	--	--
ICr-2	44	24	10	<0.7	9	<30	<30	<100	<30	<10	<10	10	<30	<50	<30
C-1	150	27	10	<0.7	13	--	--	--	--	--	--	--	--	--	--
O-1	40	128	13	<0.6	11	--	--	--	--	--	--	--	--	--	--
O-3	54	545	12	1	9	--	--	--	--	--	--	--	--	--	--
N-1	--	--	145	--	--	--	--	--	--	--	--	--	--	--	--
N-2	--	--	80	--	--	--	--	--	--	--	--	--	--	--	--
S-1	83	62	25	<0.5	90	--	--	--	--	--	--	--	--	--	--

(a) Typical values

Tensile Properties of Chromium

Allen, Maykuth, and Jaffee[3] determined the tensile properties of unalloyed Cr from -70 to 500 C incidental to a program concerned with the tensile transition temperature of Cr. The results are presented in the ductile-brittle behavior section of this report. No new data have been reported during the past three years which would add to the room and elevated temperature tensile properties of Cr as presented in the SRI report previously cited. In that report, a more detailed review of these data is presented; a brief presentation of these data is contained in the Summary of this LMSC publication.

Compression Properties of Chromium

The yield strength and flow stress at 3 percent strain in compression are presented as a function of test temperature down to -195° C, as reported by Marcinkowski[4] in Fig. 3.1. The compression specimens, with a diameter of 0.200-0.250 in. x 0.400 in. long, were in the recrystallized state with a mean grain diameter of 0.095 mm.

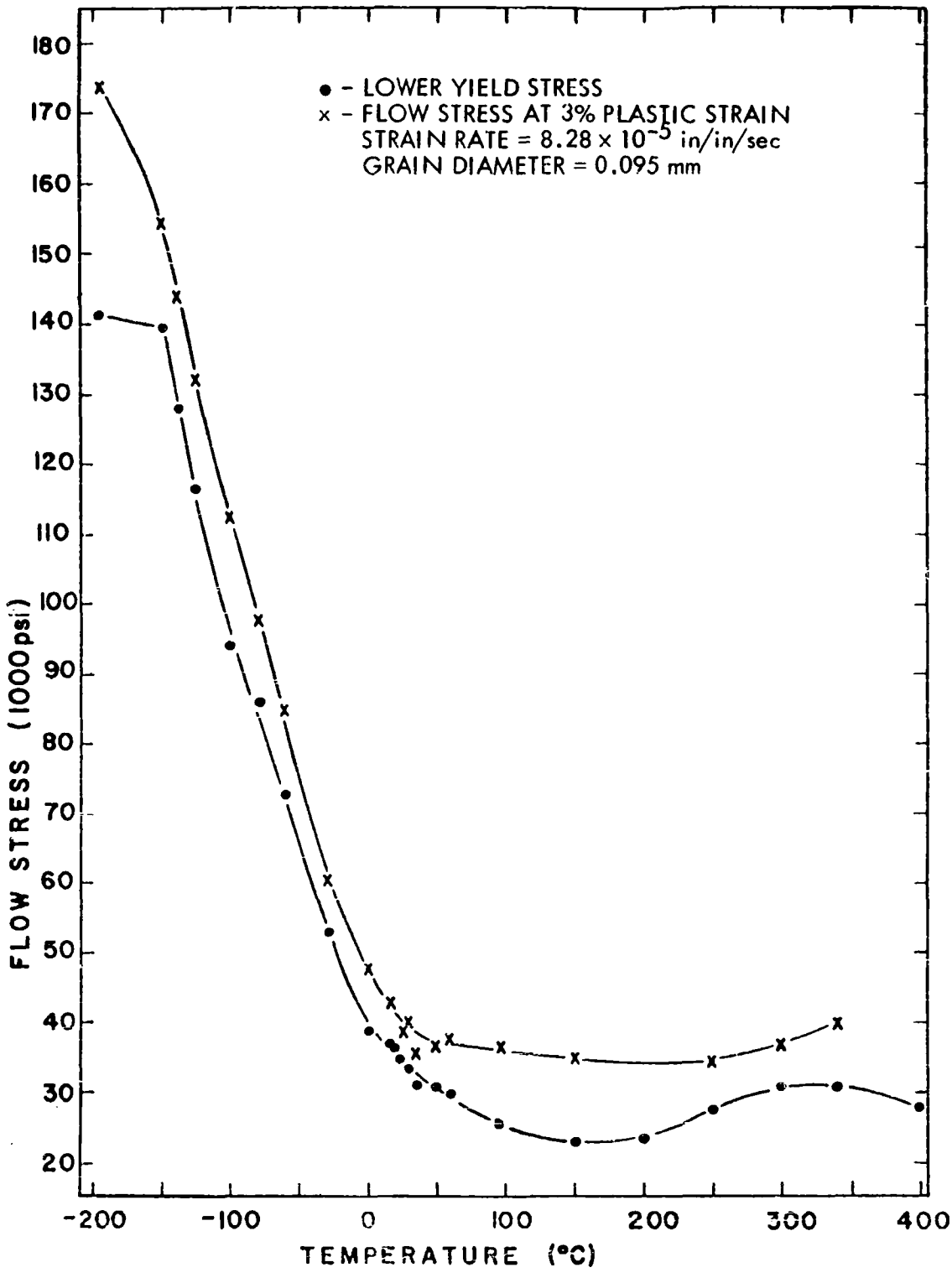


FIG. 3.1

YIELD STRENGTH AND FLOW STRESS IN COMPRESSION VS TEST TEMPERATURE FOR RECRYSTALLIZED CHROMIUM[4]

The starting material, H_2 reduced electrolytic powder, was arc-melted, swaged with intermediate anneals, machined, and recrystallized at 1250° C in 30 min. The final hot swaging operation was at 800° C and included 71 percent final reduction in area. All specimens were from one ingot.

These data show the rapid increase of yield stress with decreasing temperature in the temperature range where reliable tensile data have not been available because of brittle-tensile fracture. All specimens of the recrystallized material deformed by slip down to -150° C. The compressive yield stress is approximately the same as the tensile yield stress values previously reported in the temperature range 300° to 400° C where ductile-tensile and compression tests have been conducted. As shown in Fig. 3.2, the compressive yield stress was found to vary linearly as the reciprocal of the square root of the grain diameter. From the same investigation, the effect of strain rate on the yield stress over the same temperature range is shown in Fig. 3.3. In Fig. 3.3, the identical yield stress at both -150 and -195° C independent of strain rate where deformation occurred principally by twinning is of interest. Specimens which deformed by twinning exhibited microcracks associated with the twin lamellae. A specimen deformed 3 percent in compression at room temperature and subsequently strained an additional 2 percent at -195° C did not twin or evidence microcracks. Marcinkowski,[4] concluded that twins were not necessary for crack formation but that they were responsible for the cracks formed in chromium under compressive strains at low temperature.

Ductile-Brittle Behavior of Chromium

The specific causes of the low temperature brittle behavior of chromium, and the possible means of decreasing the temperature at which chromium undergoes a transition from ductile to brittle behavior continue to be of prime interest.

In a recent review, Edwards, Nish, and Wain[2] adequately covered the problem of brittleness of Cr as affected by impurities, surface condition, and worked structure. These authors arrived at the following conclusions:

(1) Brittleness in Cr is associated with the presence of small amounts of nitrogen

(2) Cr can tolerate more nitrogen in the cold-worked state than in the recrystallized state without becoming brittle, because of the increased density of dislocations and thus a lower number of nitrogen atoms per dislocation in the cold-worked material

(3) Thermal and mechanical treatments have been demonstrated to show promise of leading to more satisfactory ductility

For example, Weaver reported that prestraining a recrystallized material 3 percent at 400° F produced Cr with room temperature tensile properties of 66 percent elongation and 76 percent reduction in area.

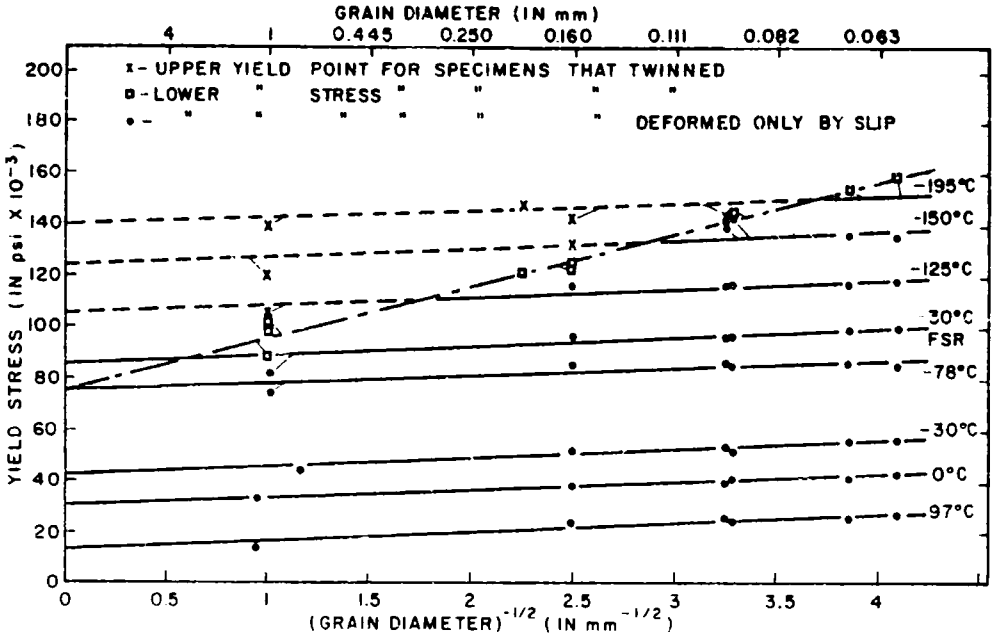


FIG. 3.2

YIELD STRESS IN COMPRESSION VERSUS RECIPROCAL SQUARE ROOT OF GRAIN DIAMETER FOR RECRYSTALLIZED CHROMIUM AT CONSTANT TEST TEMPERATURES BETWEEN -195 AND 97° C[4]

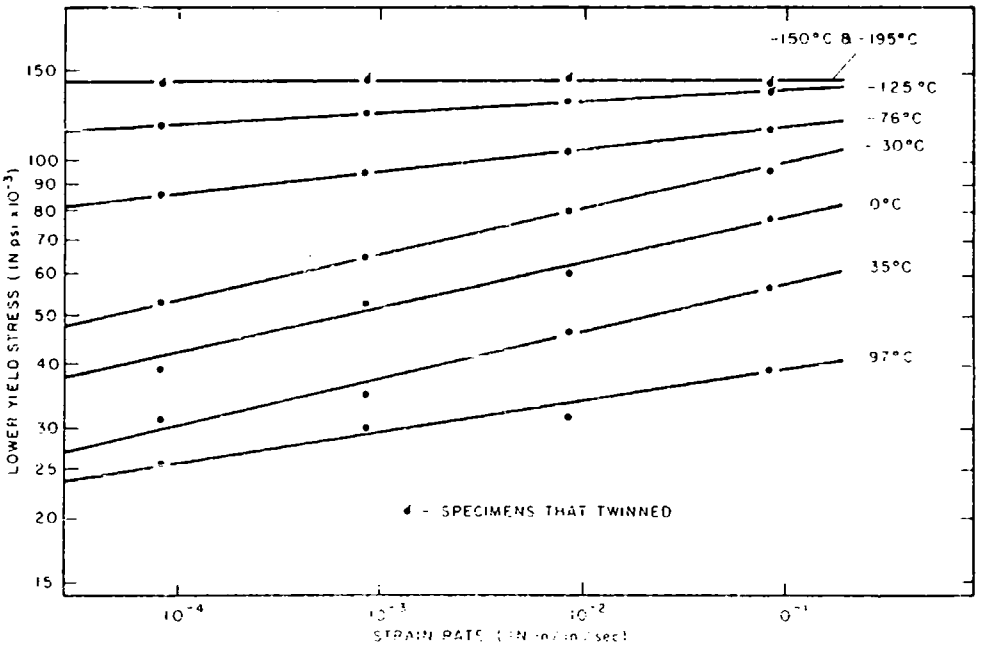


FIG. 3.3

YIELD STRESS IN COMPRESSION VS STRAIN RATE FOR CHROMIUM AT CONSTANT TEST TEMPERATURES BETWEEN -195 TO 97°C[4]

It should be pointed out that not all investigators agree as to the detrimental effects of nitrogen. Metcalfe, Spachner, and Rostaker[5] concluded from their studies that nitrogen is not responsible for brittleness of Cr, whether in solution or as a precipitate.

Henderson, Wain, and Johnstone[6] have continued investigations of the parameters which affect the ductile-to-brittle transition using high-purity electrolytic Cr. They reported that rolling temperatures in the range from 300 – 1050° C did not measurably change the bend transition temperature of wrought Cr. The wrought structure showed low bend transition temperatures, ranging from -70 to -93° C, without marked preferred orientation. The effect of deforming recrystallized sheet slightly above the transition temperature was also investigated. The results, summarized in Table 3.3, indicate that a three-percent reduction by rolling at 400° C lowered the bend transition temperature from 280 to 5° C. The table also indicates a further lowering of the transition temperature after re-annealing recrystallized and deformed specimens at 1100° C for 2 hours. However, the authors[6] state that the structure produced by prestraining and re-annealing was coarse grained, non-uniform and incompletely recrystallized as determined by X-ray examination. A narrow band along the central plane of the strips was fine grained and the outer layers evidenced grains about ten times larger than the recrystallized starting material, 0.1 to 0.2 mm, as a result of the non-uniform nature of the prestrain deformation.

Table 3.3

BEND TRANSITION TEMPERATURE OF RECRYSTALLIZED, DEFORMED, AND RE-ANNEALED CHROMIUM[6]

CONDITION	TRANSITION TEMPERATURE, °C	HARDNESS (D. P. H.)
Recrystallized	280	120 – 122
Recrystallized and deformed 3 percent at 400° C	5	134
Recrystallized and deformed; re-annealed 1100° C for 2 hours	0	102 – 124

The effect of strain rate on the bend transition temperature of wrought strip was also reported by these investigators.[6] As shown in Fig. 3.4, a 1000-fold increase in rate of loading from 2 x 10^{-3} to 2 in./min increased the transition temperature from -40 to +40° C.

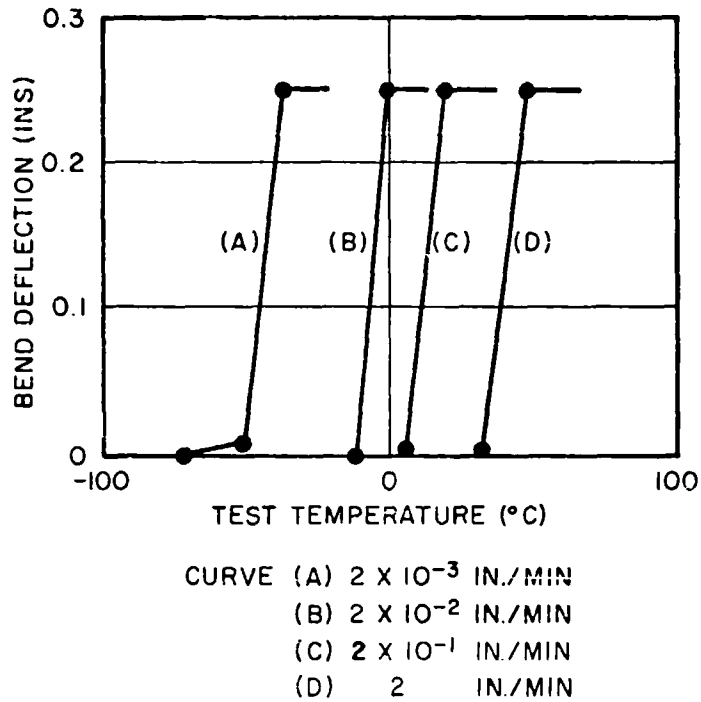


FIG. 3.4

EFFECT OF LOADING RATE ON THE BEND TRANSITION TEMPERATURE OF COLD-WORKED CHROMIUM [6]

Allen, Maykuth, and Jaffee[3] have recently investigated the influence of impurity elements, structure, and prestrain on the tensile transition temperature of Cr. The base material was iodide-Cr to which controlled additions of C, O, N, and S were made during arc melting. Button-head tensile specimens were prepared from 0.257 in. diameter swaged and ground rod with 1/8 in. in diameter x 1/2 in. long reduced gauge sections. Recrystallized specimens were reported to show average grain diameters between 0.013 and 0.030 mm after annealing at 1100° C for 1 hour. Typical tensile strength and ductility curves are shown in Fig. 3.5 from tests on an unalloyed Cr bar, ICr-2. The strength values are comparable to those previously reported[1] for recrystallized material. The tensile ductile-to-brittle transition temperatures are shown to be -10, 300, and 390° C, as represented by the temperature at which the reduction in area value was one half of the maximum value, for material in the wrought stress-relieved, recrystallized furnace-cooled, and recrystallized oil-quenched conditions, respectively. Similar curves for the impurity alloys and fused-salt Cr gave tensile

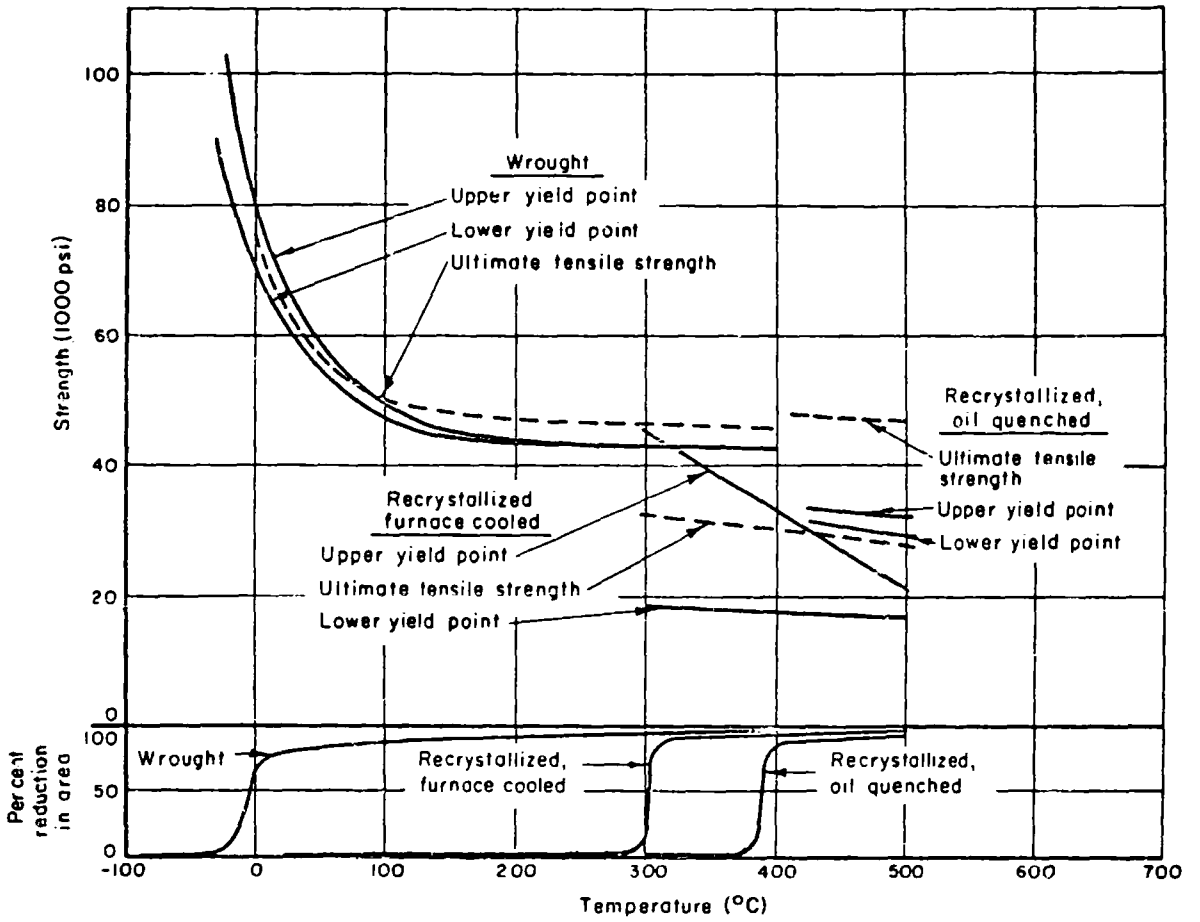


FIG. 3.5

TENSILE PROPERTIES OF UNALLOYED IODIDE CHROMIUM, ICr-2

transition temperatures as indicated in Table 3.4. The alloys containing N additions did not fabricate satisfactorily and their tensile properties were not reported. The table indicates an increase in the transition temperature for each type of impurity addition with the increase being more predominant in the recrystallized than in the wrought condition. Transition temperatures determined by bend, torsion, or compression tests have been reported[1] to be lower than those determined by tensile tests.

Table 3.4

TENSILE TRANSITION TEMPERATURE OF CHROMIUM AS AFFECTED BY PURITY AND STRUCTURE[3]

Impurity Content (weight percent)						Tensile Transition Temperature[(a)], °C		
						Wrought and Stress Relieved 1 Hr 800°C.	Recrystallized 1 Hr 1100 C	
Alloy	Carbon	Oxygen	Nitrogen	Sulfur	Total Metallics	Furnace Cooled	Oil Quenched	Furnace Cooled
Iodide Chromium								
ICr-2	0.0044	0.0024	0.0010	0.0009	<0.005	-10	390	300
C-1	0.015	0.0027	0.0010	0.0013	<0.005	(90)	500	470
O-1	0.0040	0.013	0.0013	0.0011	<0.005	20	590	400
O-2	0.0054	0.055	0.0012	0.0009	<0.005	30	600	390
S-1	0.0083	0.0062	0.0025	0.009	<0.005	150	550	(420)
Fused-Salt Chromium								
FSCr-1	0.008	0.015	0.0004	0.002	0.90	(170)	--	--

(a) Values in parentheses are estimated from data. Others are believed accurate to ±10°C.

Recrystallization Behavior

The effect of annealing temperature on the grain size produced in hydrogen purified electrolytic Cr was studied by Marcinkowski.[4] Results of the investigation are summarized in Table 3.5. The starting material was pressed and sintered, and consumable-arc melted to a 2 in. diameter ingot. The ingot was alternately swaged and hydrogen annealed to 0.50 in. diameter. Final reduction at 800° C produced specimens with a 71 percent warm-worked structure for the recrystallization study and compression tests. The grain size was determined metallographically, and the degree of recrystallization was evaluated by X-ray technique. The data indicates that heating at 1050° C or above resulted in complete recrystallization. Other work has

shown that 1100° C annealing was required for complete elimination of cold work as detectable by micro-focus examination.[2]

Table 3.5

RECRYSTALLIZED GRAIN SIZES PRODUCED BY ANNEALING CHROMIUM AT VARIOUS TEMPERATURES[4]

TEMPERATURE OF ANNEAL (° C)	DURATION OF ANNEAL (Min)	GRAIN DIAMETER (mm)	DEGREE OF RECRYSTALLIZATION
950	30	0.041	Incomplete
1050	30	0.060	Complete
1150	30	0.067	Complete
1250	30	0.095	Complete
1350	30	0.093	Complete
1450	30	0.162	Complete
1450	60	0.197	Complete
1600	120	≃1.00	Complete

Results of earlier investigations are summarized in Figs. 3.6 and 3.7, wherein recrystallization temperatures of 900 – 1000° C are indicated on the basis of hardness measurements. The somewhat lower recrystallization temperatures may be attributed to the lower rolling temperatures. The curves of Fig. 3.7 also indicate that higher rolling temperatures resulted in higher values of final recrystallized hardness.

Allen, et al.[3] observed the recrystallized grain size of Cr with several impurity contents after various annealing treatments. The compositions of the materials were given in Table 3.2 and the results of the annealing study are shown in Table 3.6 and Fig. 3.8. The material for the annealing studies had received final working of 75 to 70 percent reduction by swaging at 900° C. Alloys containing the O and C additions as well as the base I Cr-2 exhibited rapid grain growth above 1200° C. The O and C, as well as the N additions apparently had an inhibiting effect on the grain growth. The sulfur containing alloy was unique in that it inhibited even more rapid grain growth than the I Cr-2. The authors stated this was associated with the finely dispersed sulfide inclusions dissolving at the higher annealing temperatures. It is difficult to understand this observation, especially when noting from Table 3.4 that the S-1 alloy contained twice as much C, O, and N as I Cr-2. The fused-salt Cr, which was also studied, was reported to have a recrystallization temperature over 200° C higher than the I Cr-2 material due, apparently, to the high nickel (0.3 percent) and iron (0.5 percent) content. This material had a non-equiaxed grain structure after recrystallization, in contrast to all the other materials studied.

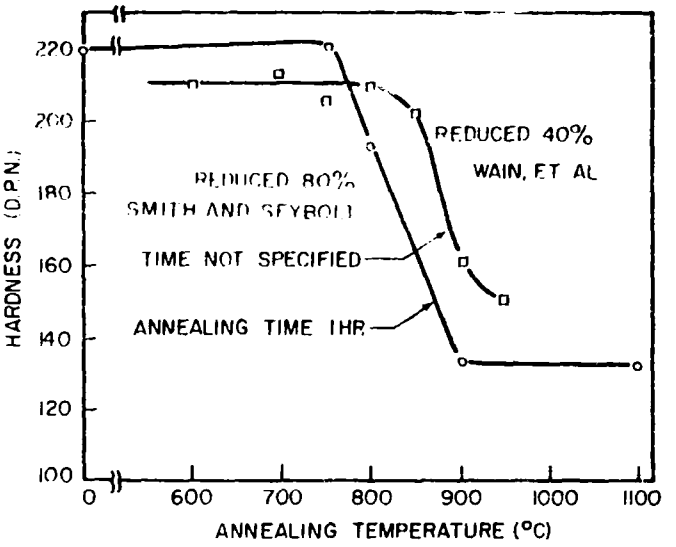


FIG. 3.6
HARDNESS OF CHROMIUM VS ANNEALING TEMPERATURE AFTER ROLLING 40% AND 80% AT 600°C

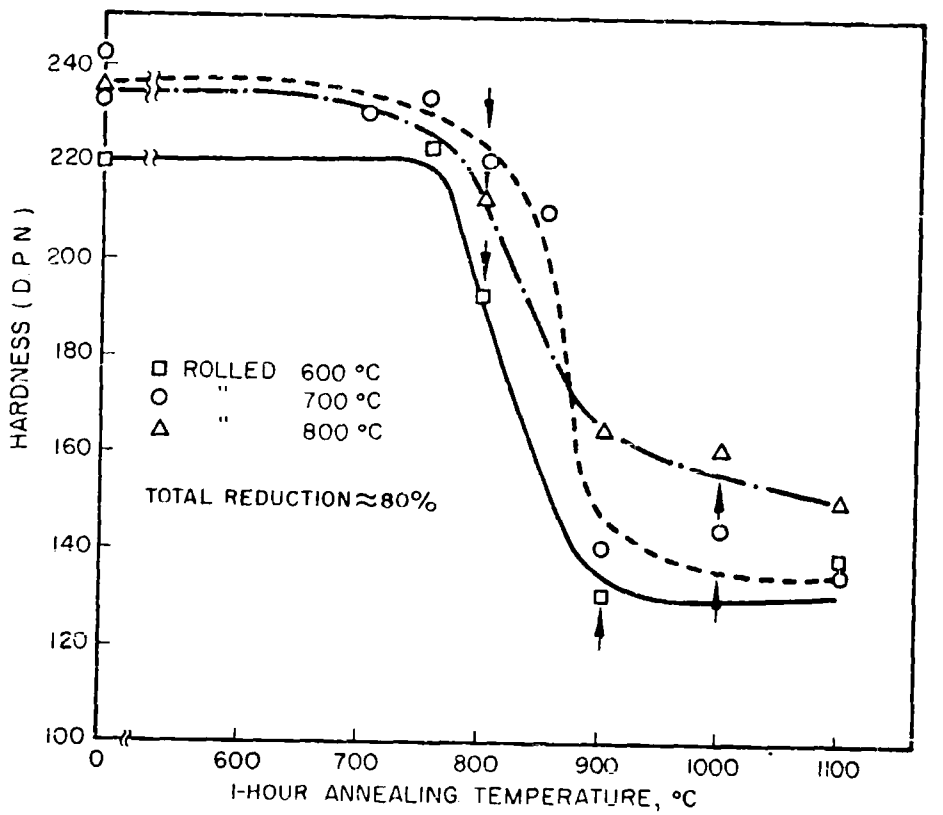


FIG. 3.7
HARDNESS OF IODIDE CHROMIUM VS ANNEALING TEMPERATURE AFTER ROLLING 80% AT 600, 700, AND 800°C[2] (Arrows indicate beginning and end of recrystallization)

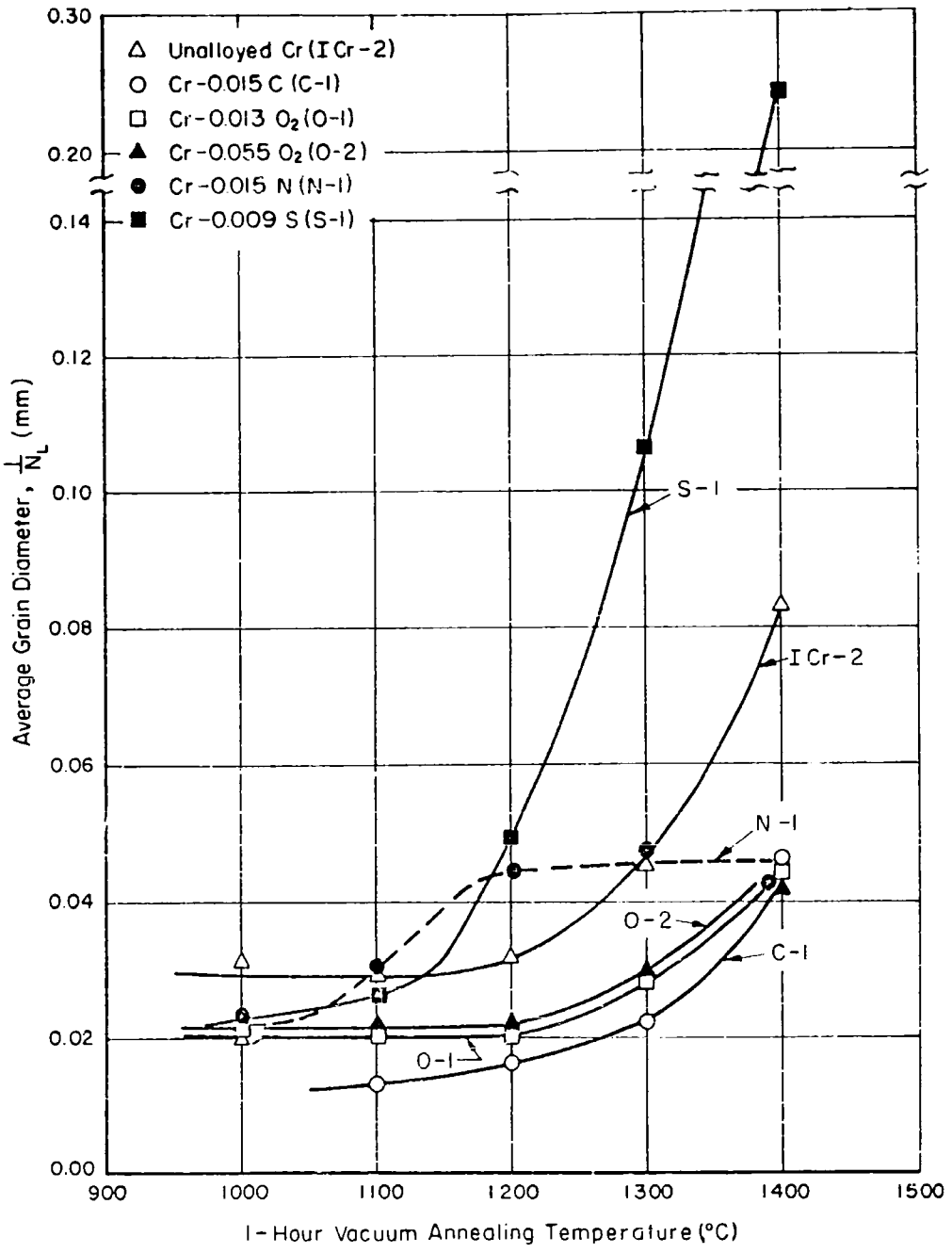


FIG. 3.8

GRAIN-GROWTH CHARACTERISTICS OF UNALLOYED IODIDE CHROMIUM AND FIVE IMPURITY ALLOYS WITH 75 TO 80 PERCENT HOT-COLD WORK BY SWAGING AT 900° C[3]

Table 3.6

GRAIN SIZES OF IODIDE CHROMIUM, FIVE IODIDE CHROMIUM-BASE IMPURITY ALLOYS, AND FUSED-SALT CHROMIUM AFTER ARC MELTING, FABRICATING, AND ANNEALING[3]

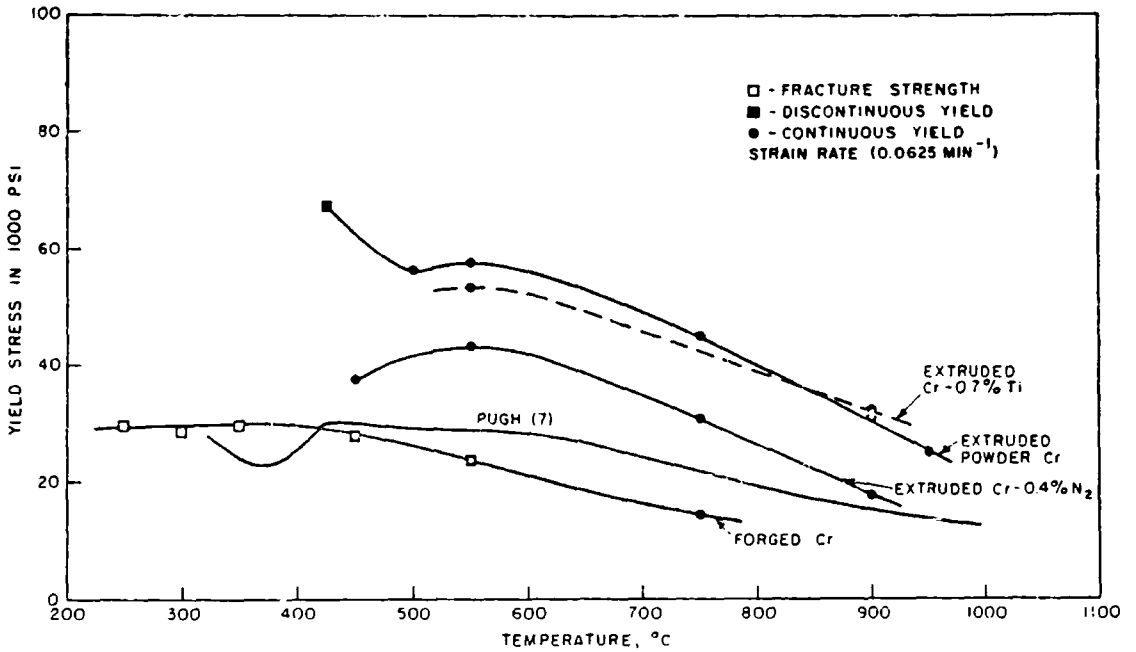
Alloy	Swaging Temperature, (°C)	Average Grain Diameter, $\frac{1}{NL}$, mm					
		As Arc Cast	Vacuum Annealed 1 Hr at Indicated Temperature, (°C)				
			1000	1100	1200	1300	1400
ICr-1	800	2.1	--	0.019	0.023	0.028	
ICr-1	900	2.1	--	0.025	0.028	0.031	0.125
ICr-2	900	3.2	0.031	0.029	0.032	0.045	0.083
C-1	900	1.8	--	0.013	0.016	0.022	0.046
O-1	900	1.2	0.021	0.020	0.020	0.028	0.043
O-2	900	0.9	0.020	0.022	0.022	0.029	0.042
N-1	900	1.1	0.020	0.030	0.044	0.047	0.042
S-1	900	0.9	0.022	0.026	0.049	0.106	0.243
FSCr-1	900	1.2	--	--	0.048[(a)]	0.049[(a)]	0.063[(a)]

(a) Elongated in swaging direction

Tensile Properties of Alloys

Few new tensile data on Cr-base alloys have been reported since the initial SRI survey report[1] was issued.

The yield strength and ultimate tensile strength for Cr-0.7Ti and Cr-0.4N_2 as reported by Metcalfe, at al.,[5] are presented in Fig. 3.9 as a function of temperature. The Cr-0.7Ti alloy gave about twice the strength values of those reported by Pugh[7] for recrystallized Cr over the temperature range 500 to 900° C. Over the same temperature range, the Cr-0.4N_2 alloy showed about a 50 percent increase in strength over Pugh's data. However, the strength values for the unalloyed extruded Cr were also about twice those reported by Pugh, or about equal to the curves for the Cr-0.7Ti alloy. The elongation values for the extruded Cr and Cr-0.4N_2 were about the same, whereas the values for Cr-0.7Ti were about 25 percent lower. The authors[5] stated that nitrogen appears to impart strength without any loss of ductility. However, the



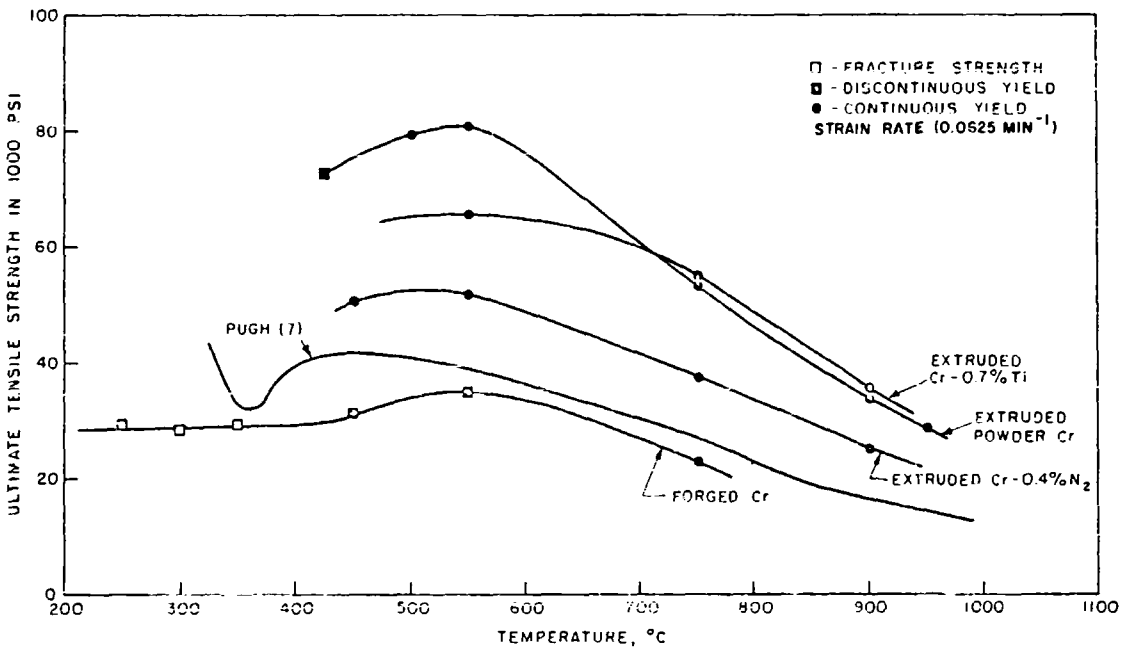


FIG. 3.9

YIELD AND ULTIMATE TENSILE STRENGTH OF CHROMIUM ALLOYS VS TEST TEMPERATURE[5]

Cr-0.4N_2 exhibited lower strength than the extruded powder Cr over the range of test temperatures studied.

Work at MIT by Levingston, et al.[8] on Cr-base alloys under Navy Contract NOas-60-5022-c, was summarized in a Final Report in December 1960. This work, which appears to be of considerable interest, is to be published in more detail. One alloy, Cr-1Cb-1Y was selected in this program for concentrated study. The tensile transition of this alloy in the recrystallized condition was reported to be 375° F, whereas after exposure to air at 1800° F for 100 hours the transition temperature increased to 575° F, reportedly due to a small amount of nitrogen dissolved into the surface of the test bar. From dynamic measurements, the modulus of elasticity for this alloy was reported to vary almost linearly from 41 x 10^6 psi for room temperature to 31 x 10^6 for 2000° F.

Klopp, Holden, and Jaffee[9] studied the ductility of Cr-Re alloys and found that Re additions to Cr inproved the fabricability and bend ductility. A Cr-39Re sheet produced by rolling at 1000° C from an as-cast ingot showed bend ductility of <1.5T at -196° C after vacuum annealing at 1200° C for 1 hour. The alloy was less ductile, >11.7T bend at room temperature, after hydrogen annealing for 1 hour at either 1300 or 1800° C. Chromium alloys containing Re near the solid solubility limit were shown by the authors[9] to exhibit the same ductility improvement over the unalloyed material as do W-Re and Mo-Re alloys.

Creep Properties of Chromium

The work reported by Pugh[7] remains the most extensive investigation concerning the stress rupture properties of unalloyed Cr. For convenient reference,these data are presented again in this report in Fig. 3.10 and Table 3.7.

Data from tensile creep tests conducted at 950° C in air has been reported by Wilms and Rea.[10] The test material was extruded from arc-cast ingots of high-purity electrolytic Cr with an average grain size of 0.05 mm. A typical rupture strength of 6.7 ksi at 185 hours was lower than the value of 8.6 ksi, interpolated from the data of Pugh shown in Fig. 3.10. The material used by Pugh in tests conducted in argon was recrystallized with an average grain size of 0.5 mm and contained more metallic and interstitial impurity. The lower purity and/or larger grain size may have contributed to the higher strength reported by Pugh.

Landau, Greenaway, and Edwards[11] have investigated the creep properties of wrought Cr in compression from 750 to 950° C. The results of these compression tests are not presented here as the data were not considered pertinent to this compilation.

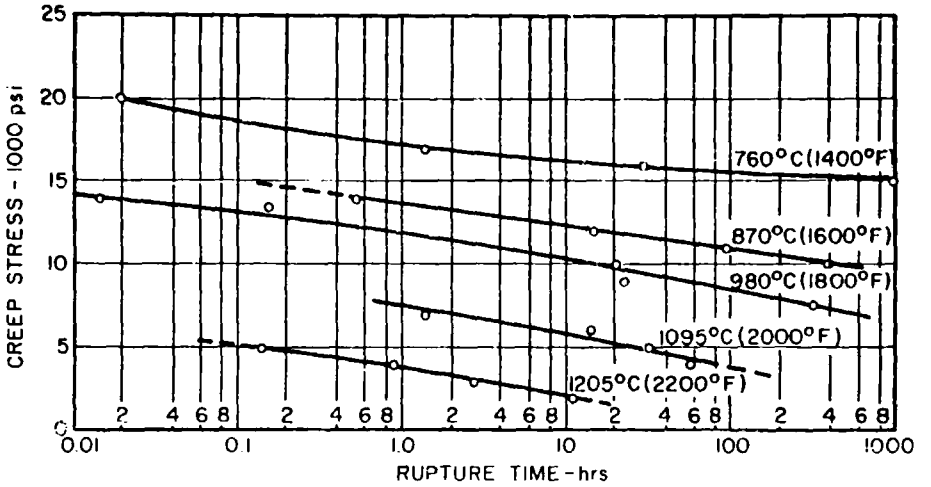


FIG. 3.10

CREEP STRESS VS RUPTURE TIME FOR CHROMIUM FOR VARIOUS TEST TEMPERATURES UP TO 1200°C [7]

Table 3.7

STRESS-RUPTURE DATA FOR UNALLOYED CHROMIUM[7]

TEMPERATURE (°F)	STRESS (1000 psi)	RUPTURE LIFE (hr)	TOTAL ELONGATION (%)
1400	20.00	0.02	40.4
1400	17.00	1.45	38.7
1400	16.00	31.10	29.9
1400	15.00	1122.23	13.7
1600	14.00	0.54	35.8
1600	12.00	15.02	12.8
1600	10.00	393.76	5.4
1800	14.00	0.015	31.8
1800	13.50	0.162	27.2
1800	10.00	20.91	12.2
1800	9.00	23.65	14.8
1800	7.50	131.86	20.2
2000	7.00	1.42	29.1
2000	6.00	14.39	19.1
2000	5.00	32.92	9.8
2000	4.00	50.73	10.9
2200	5.00	0.14	20.7
2200	4.00	0.89	19.1
2200	3.00	2.78	22.6
2200	2.00	10.95	22.2

Creep and Stress Rupture of Chromium Alloys

The results of eleven different investigations on creep and stress-rupture properties of numerous Cr-base alloys were summarized in the initial survey report.[1] Since that time, three studies on the creep properties of Cr-base alloys have been reported.

Levingston, et al.[8] reported preliminary stress-rupture data for the Cr-1Cb-1Y (added) alloy in both the recrystallized and warm-worked conditions. Their results are summarized in Table 3.8. The creep tests were apparently conducted in air; the grain size of the material was not reported.

Table 3.8

100-HOUR RUPTURE STRENGTH FOR Cr-1Cb-1Y ALLOY[8]

TEMPERATURE (° F)	CONDITIONS	
	RECRYSTALLIZED	WARM-WORKED
1500	37,000	45,000
1800	19,000	25,000
2000	9,500	—

Fox and McGurty[12] reported stress rupture data for three Cr-base alloys at 2300° F, apparently tested in air: Cr-1Y, Cr-8Ta-1Y, Cr-1Mo-0.5Cb-1Y. These results are given in Fig. 3.11 along with stress rupture data for Nichrome V and for unalloyed Cr, Cb, and Mo for comparison purposes. These Cr alloys were all found to be considerably weaker in stress rupture strength at 2300° F than either unalloyed Cb or Mo, but were considerably stronger than the 80Ni-20Cr alloy.

The effect of solid solution additions of W and Mo on the creep properties of Cr are under investigation by two groups in Australia. The work mentioned in the preceding section by Landau et al.[11] and Wilms and Rea[10] has not been reported in sufficient detail for comparison with the properties of alloys reported here, but the references were the only ones found concerning binary addition of W and Mo to Cr.

Fabrication

Edwards, et al.[2] reviewed the fabrication of unalloyed chromium. Cast Cr is fabricable using the necessary precautions of normal metalworking procedures such as forging, swaging, rolling, wire drawing, and machining. Studies of welding procedures have not been reported. The choice of primary working depends, in part, upon material purity, and working at elevated temperatures must be done in protective atmospheres to avoid interstitial contamination unless allowance is made for removal of the contaminated surface layer.

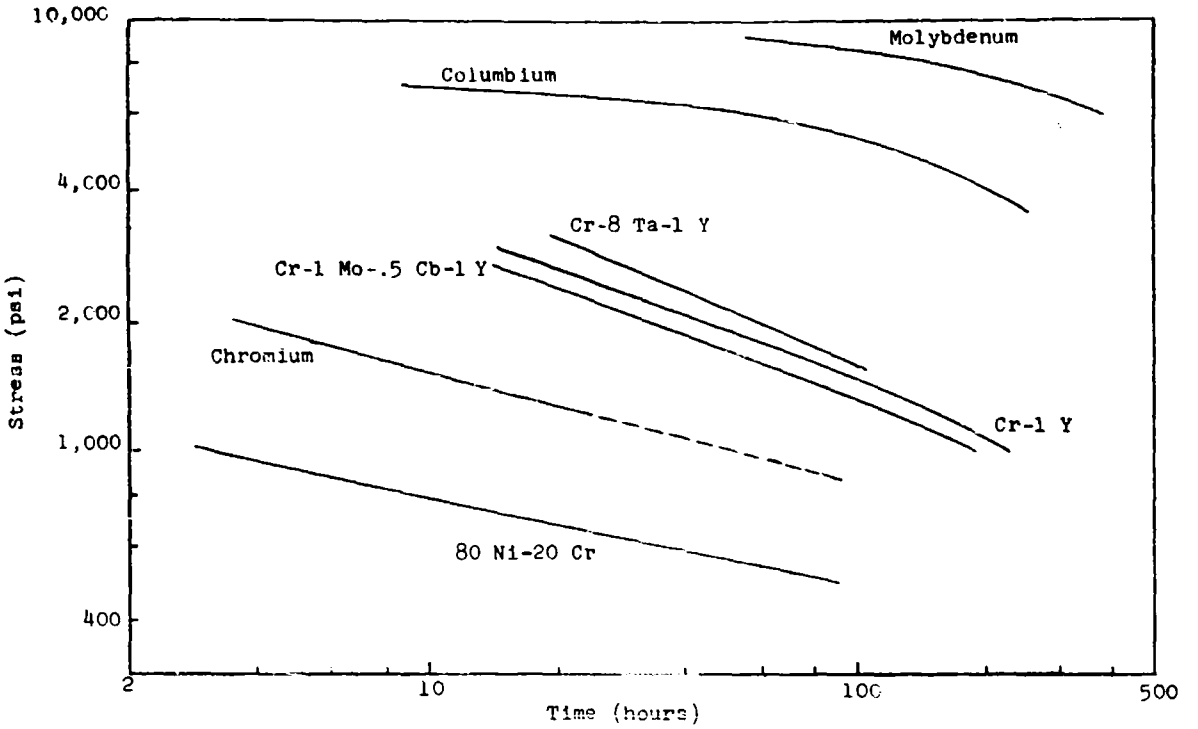


FIG. 3.11

STRESS-RUPTURE PROPERTIES OF CHROMIUM AND ALLOYS AT 2300°F COMPARED WITH COLUMBIUM, MOLYBDENUM, AND 80 NI-20 CR[12]

Reference to fabrication of the specific experimental alloys is contained in each of the reports previously cited for property data of the alloys.

OXIDATION PROPERTIES

Oxidation of Chromium

The oxidation resistance of unalloyed chromium was previously shown to be the best of the refractory metals included in this survey. Oxidation data for unalloyed Cr are included in the Summary of this report. The oxidation resistance of Cr is not, however, good enough for long time service requirements in oxidizing atmospheres at elevated temperatures and the need exists for improved oxidation resistance through alloying.

Oxidation of Chromium Alloys

Previously reported oxidation studies of a number of binary Cr alloys indicated that in the best alloys were still inferior to Nicrome V in air at 1800° F.

Levingston et al.[8] reported that the Cr-1Cb-1Y alloy showed an oxidation rate similar to Nichrome V in air at 1800° F, whereas at 2000° F, the oxidation rate of the Cr alloy in terms of weight gain was double that for Nichrome V, and the oxide tended to spall and continually expose new metal to oxidation rather than form a protective layer.

Fox and McGurty[12] have reported some interesting results on the effect of additions of Group III-A elements on the oxidation of chromium. These data are summarized in Table 3.9 in terms of weight gain and nitrogen absorption after 100 hours exposure at 2300° F. Binary additions of six separate elements were shown to improve the oxidation resistance of Cr by a factor of 20 or more.

THERMAL PROPERTIES

No additional data on thermal properties of Cr or Cr-base alloys have been reported during the last two years. Previously reported data are included in the Summary section of this report.

Table 3.9

EFFECT OF GROUP III-A ELEMENTS ON OXIDATION OF CHROMIUM IN AIR[12]

Element	Composition (w/o)		2300° F – 100 hr	
	Nominal	Actual	Weight Gain (mg/in^2)	N_2 Absorption* (ppm)
Unalloyed Chromium	–	–	185	16,500
Scandium	1	–	35	1240
Yttrium	1	0.66	8	160
Lanthanum	2	0.9	55	1820
Cerium	2	1.2	30	170
Praseodymium	2	1.7	8	30
Neodymium	2	0.75	8	280
Samarium	2	0.02	20	1040
Europium	1	<0.1	24	—
Gadolinium	2	1.85	8	230
Terbium	1	0.95	8	—
Dysprosium	2	0.75	15	1170
Holmium	2	1.26	15	150
Erbium	2	1.22	12	300
Thulium	2	0.16	90	1990
Ytterbium	2	0.03	45	1900
Lutetium	1	–	9	900

*Analysis for N_2 after oxidation test.

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SECTION 4

COLUMBIUM

INTRODUCTION

The following intrinsic properties make columbium advantageous for high-temperature applications:

- High melting point, 2468°C (4474° F)
- Density lower than the three other important refractory metals, 8.57 g/cc (0.31 lb/in.^{3})
- Low thermal neutron capture cross section
- Favorable resistance to liquid metal corrosion at moderate temperatures
- Ductility favorable to cold fabricability
- Adequate supply

In addition, the major oxide (Cb_2O_5) melts at a temperature 1500°C (2550° F), which is considerably above that of MoO_3 and above the sublimation point of the major oxide of W.

The oxidation resistance of Cb, however, is a disadvantage as attack occurs both by scaling at a linear rate and by oxygen penetration into the base metal. The scale formed is nonprotective because of the spalling or cracking tendency and the penetration of oxygen into the lattice tends to reduce fabricability. The low modulus of elasticity of Cb, 15 x 10^6 psi, is another disadvantage in certain applications which require stiffness.

The favorable attributes of columbium suggest its use in atomic reactors and air and space travel vehicles, in addition to the original use as an alloying element in high strength and stainless steels. Alloy development programs have improved both high-temperature strength and oxidation resistance to allow short-time use at temperatures up to 2500° F. If coating development programs are successful, the strength properties of Cb alloys may be utilized up to 3000° F.

The mechanical properties of unalloyed Cb have been evaluated up to 2500° F, and some alloys have been examined for tensile properties up to 4000° F. Some of the alloys are available commercially, but development of optimum consolidation and fabrication techniques are continuing. Most of the alloys are still in a laboratory or pilot production stage and only preliminary data have been reported for compositions which have evidenced attractive properties in the screening studies.

MECHANICAL PROPERTIES

The mechanical properties of unalloyed Cb presented in the SRI report[1] included tensile properties up to about 600°C, and limited creep data up to 1200°C. Additional data were also presented reporting ductile-brittle behavior, the effect of dissolved gases, the effect of cold work, and recrystallization behavior. Very limited data had been reported by mid 1958 on preliminary investigations of Cb alloys.

More recently, a number of reviews [2,3,4,5,6] have treated the properties of Cb and the more promising Cb alloys in detail. These reviews will serve as a basis for this section. More recent reports covering research on Cb and its alloys have been reviewed in detail, and results of interest are included in this compilation.

Tensile Properties of Columbium

Reported values for the modulus of elasticity of columbium at room temperature vary by approximately 19 percent from low to high. The variation of the modulus of elasticity with temperature as reported by several investigators [7,8,9,10,11,12] is summarized in Fig. 4.1. The description of the test material and the method of modulus determination used by these investigators are given in Table 4.1. The data shown in Fig. 4.1 suggest that the modulus of columbium may be sensitive to method of preparation, purity, and test condition. However, the available data are not sufficient to allow an evaluation of the effect of the individual variables.

The results presented in Fig. 4.1 are in general agreement in that the data of the different investigators show a similar decrease of modulus with temperature. The decrease of modulus with temperature is so slight when compared with the large variation reported by the different investigators, that the modulus value reported by Begley[7] for 900°C is above the room temperature value reported by Williams and Heal[10], Vaughn and Rose[11], or Brown and Armstrong[12].

The data of Brown and Armstrong[12] are of particular interest because of the temperature range covered. The values at all temperatures are the lowest of those reported. Begley[7] associated the difference in values between his two curves with contamination of the specimens during the tests conducted in air; and Wilcox and Huggins[8] described variation in room temperature modulus values associated with variation in H content and microstructure. An increase in H content from 10 to 780 ppm resulted in the appearance of a second phase and decreased the modulus at room temperature approximately 10 percent. These facts suggest possible reasons for the low values reported by Brown and Armstrong; however, the analysis and specimen conditions were not specified. Differences in measuring techniques indicated in the legend of Fig. 4.1 might also account for some variation in the modulus values.

In the curve from Brown and Armstrong[12], the modulus-temperature relation is shown to depart from linearity above about 1300°C. Similar behavior has been reported for other materials in a temperature region near 0.6 of the absolute melting temperature and has been associated with a grain boundary relaxation process which is sensitive to the frequency of imposed stress cycles.

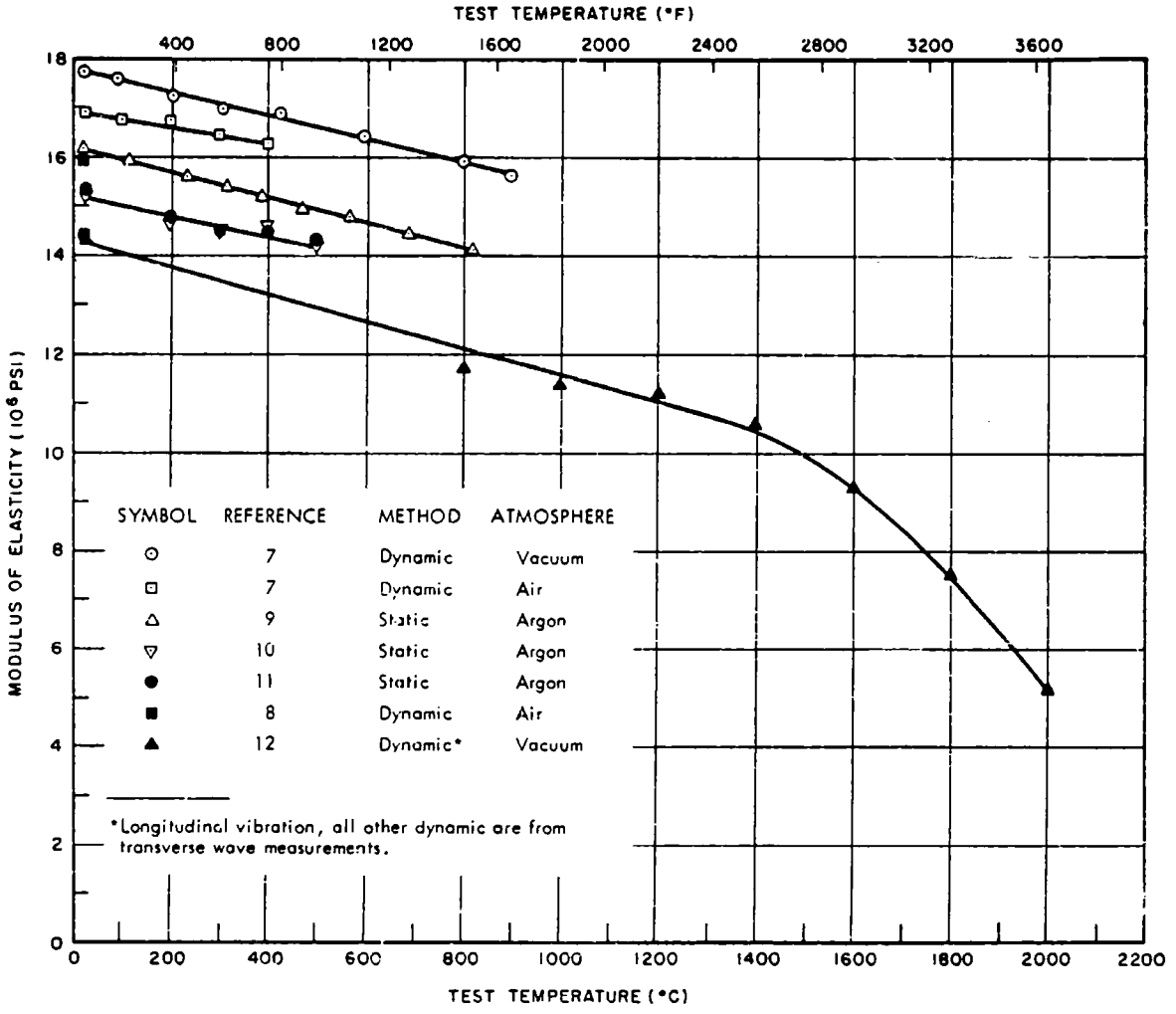

FIG. 4.1

MODULUS OF ELASTICITY OF COLUMBIUM VS TEST TEMPERATURE

Table 4.1

DESCRIPTION OF MATERIAL FOR MODULUS OF ELASTICITY DATA OF FIG. 4.1

Composition		Size (in.) Specimen	Grain Dia., (mm)	Mechanical and Heat Treatment
Element	Weight Percent			
			BEGLEY[7]	
O_2	0.019	0.060 in. Thick x 0.250 in.	0.06-0.07	Electron Beam Melted
N_2	0.026	Wide x 7 in. Long		Cold Rolled 90%
C	0.02			Recrystallized 2 Hr. at 1100°C in Vacuum of 5×10^{-5} mm Hg.
H_2*	0.0002			
Ta	0.07			
Zr	0.03			
Ti	0.014			
Fe	0.018			
			WILCOX and HUGGINS	
O_2	0.0117	1/4 in. Thick x 1/2 in.	0.04	Comml. arc-cast columbium (Fansteel)
N_2	0.0049	Wide x 3 in. Long		Received as 1/2 in. dia. Recrystallized Rod.
C	0.0050			Processing to achieve spec. size not specified
H_2	0.0010			Hydrogenated Matl.-annealed 7 Hr. at 650°C in
H_2**	0.0779			Dry Hydrogen
			LAVERTY and EVANS[9]	
O_2	0.0400	0.125 in. Thick x 1.0 in.		Electron Beam Melted
N_2	0.008	Wide x 8 in. Long with	0.1	Cold Rolled 95% to 0.14 in. Thick Sheet
C	0.0099	0.135 in. Thick x 0.500 in.		Recrystallized 2 Hrs. at 1260°C in Vac
H_2	0.0003	Wide x 3 in. Long gage		of 10^{-5} mm Hg
Ta	0.1100	Section		DPHN 92
Ti	0.0030			Tested at Elevated Temperatures in Argon
Fe	0.0030			
Cr	0.0030			
Ni	0.0040			
Si	0.0118			
B	0.00008			
			WILLIAMS and HEAL[10]	
O_2	0.001 to 0.015	.040 in. Thick x 1.25 in. gage length		Sintered - Forged - Resintered Powders
N_2	0.002 to 0.013			Sintered Bar Cold Rolled to Sheet, 0.125 in., Then annealed
C	0.001 to 0.02	Dimensions Hot	N.S.	
H_2	0.002 to 0.0004	Specified		Cold Rolled to 0.040 in. (68% thickness reduction)
Fe	0.03 to 0.05			Then annealed 1/2 Hr. at 1100°C in Vac 10^{-5} mm Hg
Si	.007 to .014			Tested in Rolling direction
			VAUGHN and ROSE[11]	
O_2	0.015	Not Specified	N.S.	5/8 in. dia Rod
N_2	0.005			Anneal to 1/2 Hr. 1100°C in Vac. 10^{-3} in Vac. 10^{-3} mm Hg
C	0.02			
H_2	0.0005			
Ta	0.35			
			BROWN and ARMSTRONG[12]	
Commercial Rod		1/4 in. dia x 4 in. Long	N.S.	Not Specified

It is apparent from the reported data, that for applications which require accurate knowledge of the modulus of elasticity, the modulus should be determined for the specific material used.

The effect of temperature on the tensile properties of columbium is presented in Figs. 4.2 and 4.3 showing the work of several investigators as summarized by Wessel, France, and Begley[6] over a temperature range of -269 to 1400°C (-450 to 2550°F). The chemical analyses, processing history and test conditions for the data presented in Figs. 4 2 and 4.3 are summarized in Table 4.2. As is evident from the data of Figs. 4.2 and 4.3, there is considerable variation in the tensile properties for columbium, as reported by the various investigators, which was in all cases in the recrystallized condition. Strain-ageing effects are particularly evident in the tempe ature range between 200 to 400°C.

Table 4.2

DESCRIPTION OF MATERIAL AND TEST CONDITIONS FOR TENSILE DATA OF FIGS 4 2 AND 4.3[5]

Curve No.	Chemistry (wt. %)				Grain Size (grains/mm^2)	Strain Rate (in./in./sec)	Type Specimen	Material Preparation
	C	O	N	H				
1	0.014	0.106	0.028	—	700	1 x 10^{-3}	Sheet 9.10 in. Thk.	Powder-Met. Recrystallized 2 hrs. at 1475°C in Vacuum
2	0.011	0.021	0.012	—	4	1 x 10^{-3}	Round 0.02 in. Dia. (Tested in air)	Powder-Met. Recrystallized 2 hrs.
3	0.070	0.010	0.05	0 02	8000	2 x 10^{-4}	Wire - 1 mm Dia.	Electron Beam Melted Recrystallized 1 hr. at 1075°C in Vacuum
4	0.01	0.007	—	--	5000	6.7 x 10^{-5}	Sheet 0.20 in. Thk.	Recrystallized 2 hrs. at 1200°C
5	0.016	0.029	0.011	0.000015	250	1 x 10^{-3}	Round 0.125 in. Dia. (Tested in Argon)	Electron Beam Melted Recrystallized 2 hrs. at 1200°C
6	0.03	0.04	0.025	0.001	—	--	Round	Arc-Melted Recrystallized
7	0.024	0.036	0.019	—	1000	1 x 10^{-3}	Round 0.178 in. Dia. (Tested in Vacuum)	Arc-Melted Recrystallized 4 hrs. at 1200°C in Vacuum
8	—	0.018 to 0.029	0.001 to 0.009	0.001	1500	—	Sheet 0.125 in. Thk.	Recrystallized 1/2 hr. at 1100°C in Vacuum
9	0.015	0.12	0.02	—	1500	—	Round 0.125 in. Dia.	Powder-Met. Recrystallized 1/4 hr. at 1700°C in Vacuum
10	—	—	Unknown	—	—	—	—	—

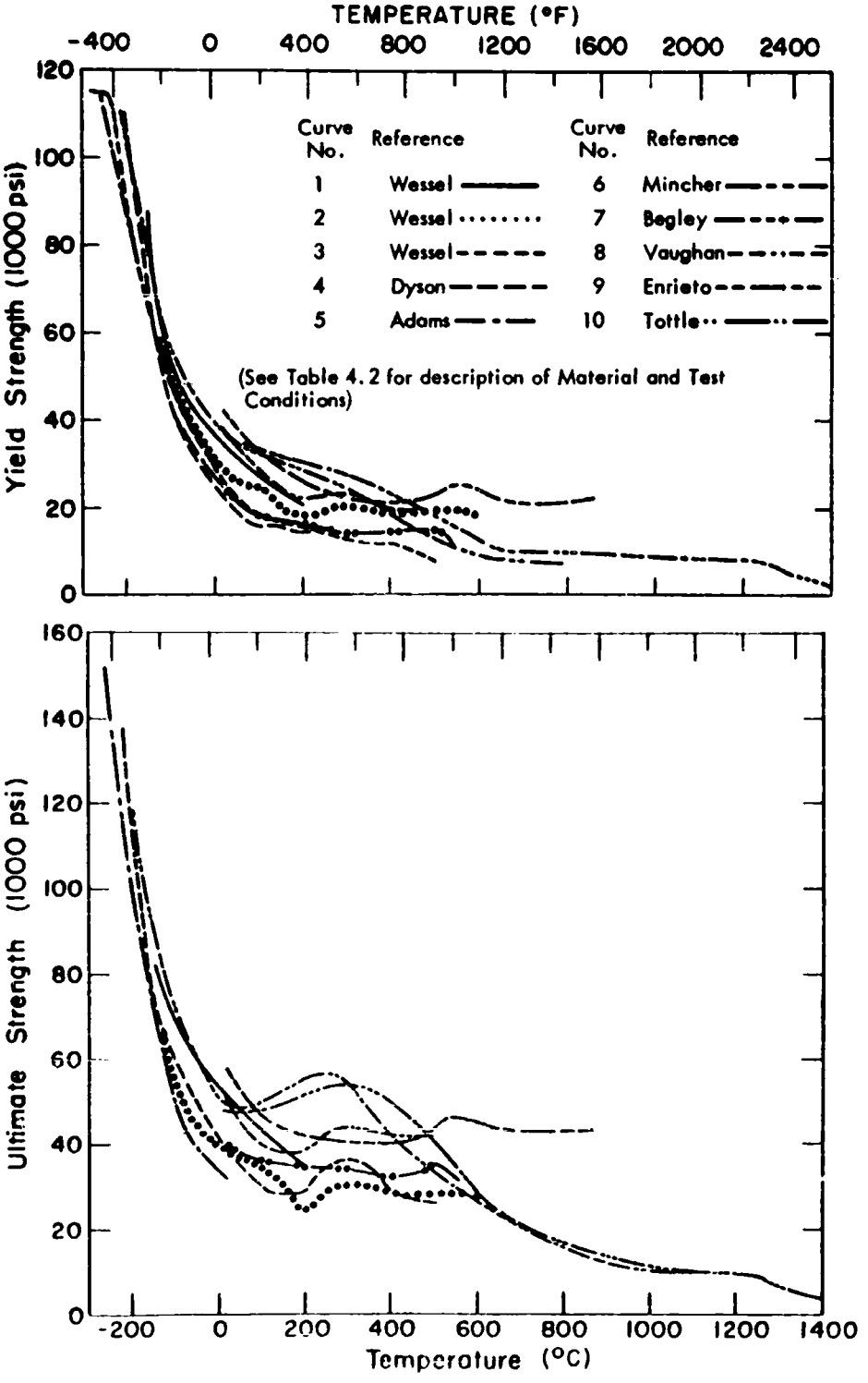

FIG. 4.2

YIELD STRENGTH AND ULTIMATE TENSILE STRENGTH OF COLUMBIUM VS TEST TEMPERATURE[5]

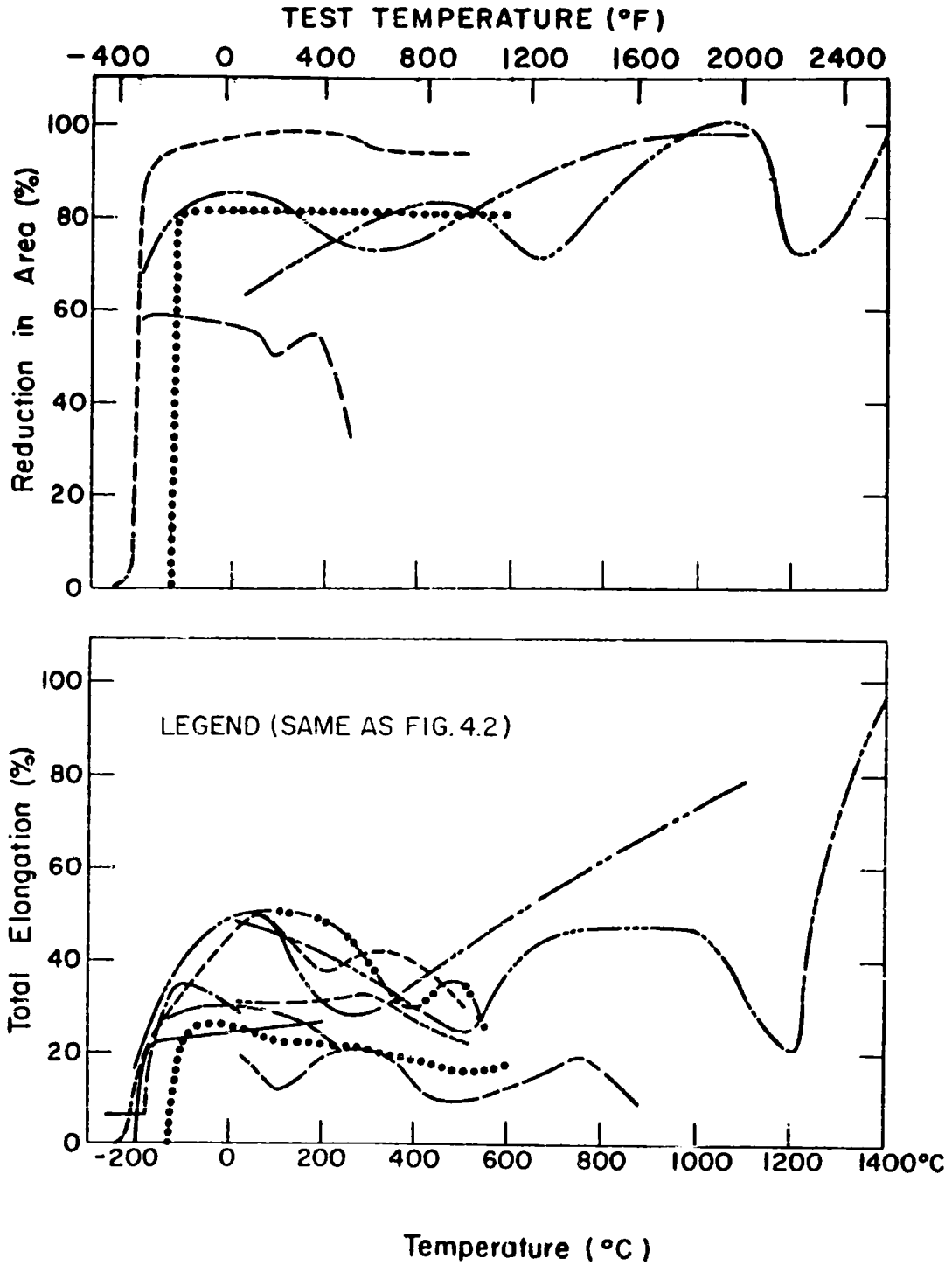

FIG. 4.3

ELONGATION AND REDUCTION-IN-AREA OF COLUMBIUM VS TEST TEMPERATURE[5]

Bartlett and Houck[3] summarized additional data on the effect of temperature on the ultimate tensile strength of Cb. Their summary is in agreement with the data shown in Figs. 4.2 and 4.3 but emphasizes uniformity of the strength above about 1100°C (2000°F) for material of varying purity, fabricating history, and test conditions.

A rapid increase in yield strength with decreasing temperature below room temperature can be seen for each set of plotted data. The rate of increase and the temperature range varied slightly with the purity of material and test condition. The transition from ductile-to-brittle behavior also occurred at different temperature ranges in separate investigations. This transition varied between -125 and -200°C as shown by the ductility data of Fig. 4.3.

Effect of Strain Rate and Grain Size on Tensile Properties of Columbium

Tankins and Maddin[13] have shown the combined effects of grain size, strain rate, and temperature on the yield strength of vacuum annealed columbium wires of 0.043 in. diameter which had been reduced 53 percent in area by cold swaging from 0.063 in. diameter. Table 4.3 summarizes their results for materials with the indicated grain sizes produced by annealing the 43-mil wires for 30 minutes at 1000°C, 1 hour at 1200, and 1 hour at 2000°C. The wires were heated by resistance and cut into sections of approximately equal grain size. The temperature gradient along the wire prohibited identification of a particular grain size with a particular temperature; however, the smallest grain size was associated with the 1000°C temperature and the largest, bamboo structure, with the 2000°C temperature.

Table 4.3

EFFECT OF STRAIN RATE AND GRAIN SIZE ON THE YIELD STRENGTH OF COLUMBIUM AT THREE TEMPERATURES[13]

YIELD STRESS, 1000 PSI AVERAGE VALUES

GRAIN SIZE	$\dot{\varepsilon}_1$ 1.67×10^{-4} TEMPERATURE			$\dot{\varepsilon}_2$ 6.67×10^{-4} TEMPERATURE			$\dot{\varepsilon}_3$ 6.6×10^{-3} TEMPERATURE			$\dot{\varepsilon}_4$ 3.3×10^{-2} TEMPERATURE		
	23°C	-50°C	-183°C	23°C	-50°C	-183°C	23°C	-50°C	-183°C	23°C	-50°C	-183°C
Bamboo Structure	9.3	15	69	11.2	19	77	16.5	28	88	21.5	32.6	95
80 Grains Per Inch	13.6	27	70	16.6	30	78	19	33	88	22	38	97
200 Grains Per Inch	19	34	84	24.8	40	92	28.5	50	102	36	60	112
400 Grains Per Inch	39	59	105	46	68	120	60	82	130	70	94	140

The following observations can be made from the table by comparing the yield strength of the three smallest grain sizes, 400, 200, and 80 grains per in., produced at the usual annealing temperatures for columbium, 1000-1200°C, over the temperature and strain-rate ranges used in the experiment.

1. The yield strength at room temperature increased by a factor of about 1.8 due to a 200-fold increase in strain rate for a constant grain size. The increase was only about 1.3 times at -183°C.

2. The yield strength at room temperature increased about 3 times with a five-fold decrease in grain size at each of the strain rates used. This grain size factor decreased to about 1.5 times at -183°C.

Ductile-Brittle Behavior of Columbium

Unalloyed Cb exhibited good tensile ductility down to temperatures around -125 to -200°C, as indicated in Fig. 4.3 where tensile elongation and reduction-in-area data are presented as a function of temperature.

Figure 4.4 contains impact transition data for unalloyed Cb in the following four conditions as reported by Begley and Platte:[14]

- Electron-beam melted and annealed
- Arc-melted
- Annealed and cold-worked
- Powder-metallurgy annealed

Table 4.4 summarizes the chemical composition, grain size, and hardness of these materials.

These data show the shift in impact transition temperature from about 100°C for arc-melted Cb to -100°C for E-B melted Cb. Even at 400°C, the powder metallurgy material had a lower impact value than arc-melted Cb exhibited below its transition temperature. The powder metallurgy specimens were thinner than the other specimens but the notch geometry was designed to allow direct comparison of impact energy with the other three test materials. It should be noted that the powder metallurgy material reported here contained 0.65 Zr, and therefore cannot truly be compared with the other three test materials which were unalloyed Cb. Of particular interest are the curves for arc-melted Cb in the recrystallized and cold-worked states. Cold work appears to have lowered the transition temperature slightly; however, the recrystallized material exhibited 2 to 3 times the impact strength of the cold-worked material at temperatures above 50°C, and appears to have a higher impact strength at even the lowest test temperature of -80°C.

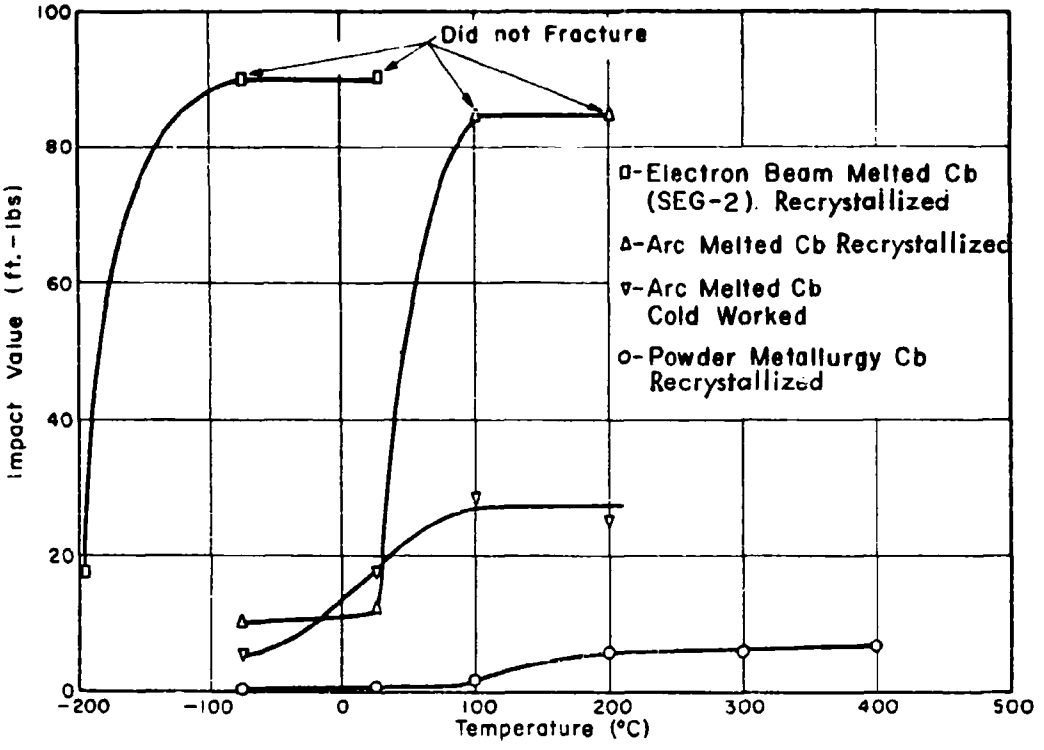

FIG. 4.4

IMPACT STRENGTH OF DIFFERENT GRADES OF COLUMBIUM VS TEST TEMPERATURE [14]

Table 4.4

CHEMICAL ANALYSIS, HARDNESS, AND GRAIN SIZE OF COLUMBIUM TEST MATERIALS FOR IMPACT PROPERTIES REPORTED IN FIG. 4.4[14]

Material	Specimen Type	Analysis-Weight Percent				Grain Size (ASTM No.)	VPN Hardness (30-kg load)	Condition
		H	O	N	C			
Arc-Melted Cb (VAM-17)	Modified Izod Type 1	0.0005	0.027	0.014	0.025	7	113	Recrystallized
Arc-Melted Cb (VAM-17)	Modified Izod Type 1	0.0005	0.027	0.014	0.025	-	190	Cold Worked
Electron-Beam Cb (SEG-2)	Modified Izod Type 1	0.0002	0.014	0.030	0.02	5-7	108	Recrystallized
Fansteel Bar* (2709) (Powder Met.)	Modified Izod	0.0009	0.065	0.022	0.022	3-4	145	Recrystallized

*Contained 0.65 percent Zr

Mincher and Sheely[15] also reported lower impact energy transition temperatures for E-B melted Cb than for arc-melted Cb from tests on recrystallized materials. The impact strength above the transition temperature was higher for both the E-B material, ~200 ft-lb, and the arc-melted material, 140 to 180 ft-lb, than comparable values reported by Begley and Platte of 85 to 90 ft-lb as shown in Fig. 4.4, although impurity contents were similar for each type of material used by each investigator. The transition temperature of the arc-melted material reported by Mincher and Sheely was about 80°C lower than for the arc-melted recrystallized material shown in Fig. 4.4.

Effect of Strain Rate on the Strain Aging Behavior

Wilhelm and Kattus[16] studied the effect of rate of straining on the magnitude of the strain-ageing peak by comparing the ultimate tensile strength of 0.030 in. thick sheet at four strain rates from room temperature to 1500°F (815°C). Their data are presented in Fig. 4.5 and indicate that no strain-aging peak was obtained at a strain rate of 0.2 per sec, whereas a very strong peak was obtained at a strain rate of about 10^{-4} per sec over a temperature range of 500 to about 1400°F (260 to 760°C). No grain size or processing history of the material was reported but the impurity content

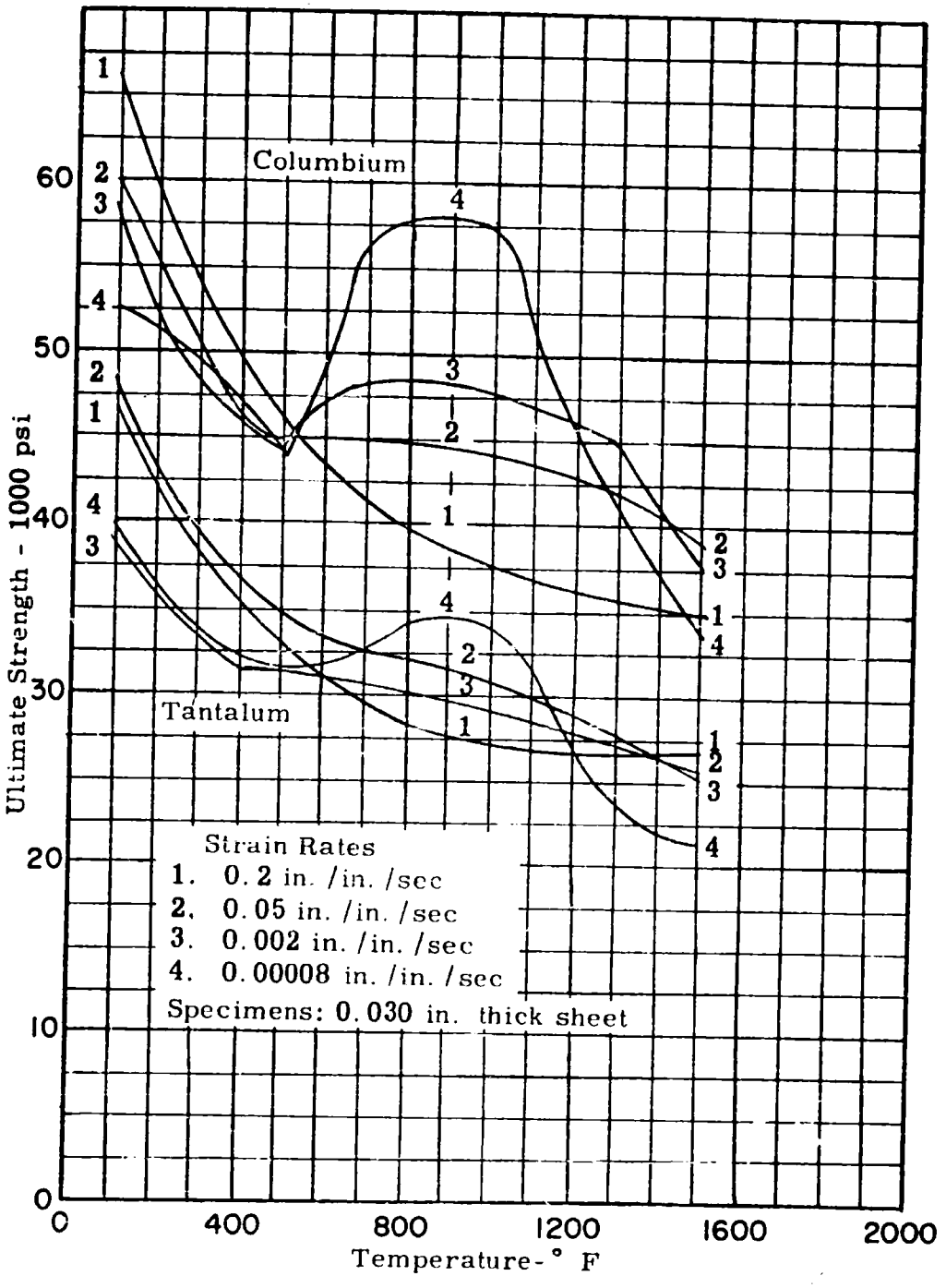

FIG. 4.5

EFFECT OF STRAIN AGEING ON THE TRANSVERSE ULTIMATE TENSILE STRENGTH OF COLUMBIUM AND TANTALUM [16]

was given as 50, 70, 1, and 60 parts per million of C, O, H, and N, respectively, with a trace of Zr. The strength of tantalum shown on the same plot appears low compared to that of columbium and the authors[16] suggest this may be due to history or purity of the two materials.

Mincher and Sheely[15] reported the ultimate tensile strength of arc-melted material to be insensitive to strain rate at 300°C (570°F), the temperature at which the strain ageing effect was observed to be most predominant. The strain-rate range used was from 0.00003 to 0.03 per sec. Figure 4.5 indicates less sensitivity of ultimate tensile strength to strain rate at this temperature. In this case, however, the strain-ageing peak was observed to be at about 900°F (480°C). The contrast cannot be explained on the basis of information furnished in the two reports, but does suggest the necessity of further investigation of strain-ageing phenomena in Cb.

Effect of Interstitial Impurities on the Mechanical Properties of Columbium

Enrietto, Sinclair, and Wert[17] evaluated the ultimate tensile strength of columbium from room temperature to 900°C in argon with the following three levels of oxygen content: 0.001, 0.02, and 0.43 percent. Their results, summarized in Fig. 4.6, indicate that a maximum in the strength occurred at 500°C for all three oxygen contents.

Similar peaks were observed by the same investigators[17] in fatigue-limit versus test-temperature curves as indicated in Fig. 4.7 for the same three materials tested in argon at 3450 cpm. The temperature at which the maximum fatigue strength was observed (400°C) was lower than that for the tensile test results (500°C). As can be seen in Fig. 4.8, the initial increase in oxygen content to 0.02 percent appeared to have the greatest effect on the increase in the peak tensile and fatigue strengths, and further oxygen additions appear to have little effect.

Regarding the effect of oxygen on levitation-melted material, Begley and France[18] made the following observations:

1. Oxygen additions from 0.0076 to 0.43 percent increased the as-cast hardness almost linearly from 62 to 350 VPN.

2. Cold fabricability was good up to 0.137 percent oxygen, but very poor above 0.137 percent.

3. Strain hardening was uniform for all oxygen contents up to 0.137 percent as measured by hardness increase with increase in reduction by cold rolling.

4. Oxygen additions of 0.121 percent broadened the recrystallization range of high purity Cb about 150°C after cold reduction of 75 percent.

Tensile yield strength and ductility comparisons were made on high-purity material produced by floating-zone, electron-beam, and arc-melted material of several ASTM

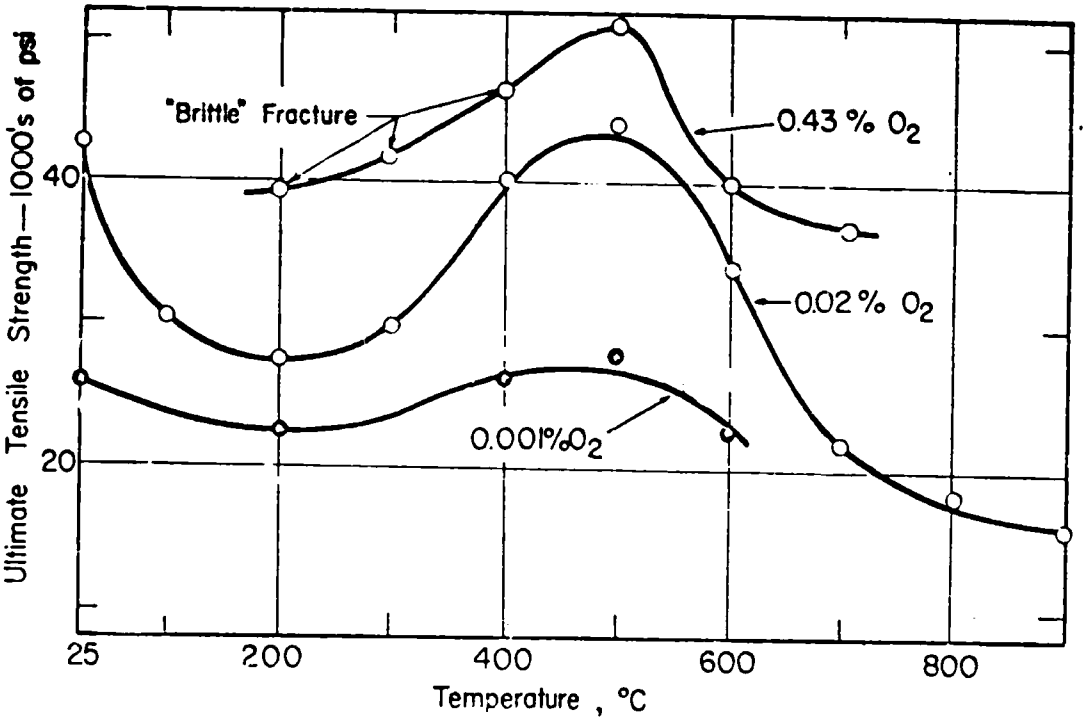

FIG. 4.6

ULTIMATE TENSILE STRENGTH OF COLUMBIUM VS TEST TEMPERATURE FOR VARIOUS OXYGEN CONTENTS [17]

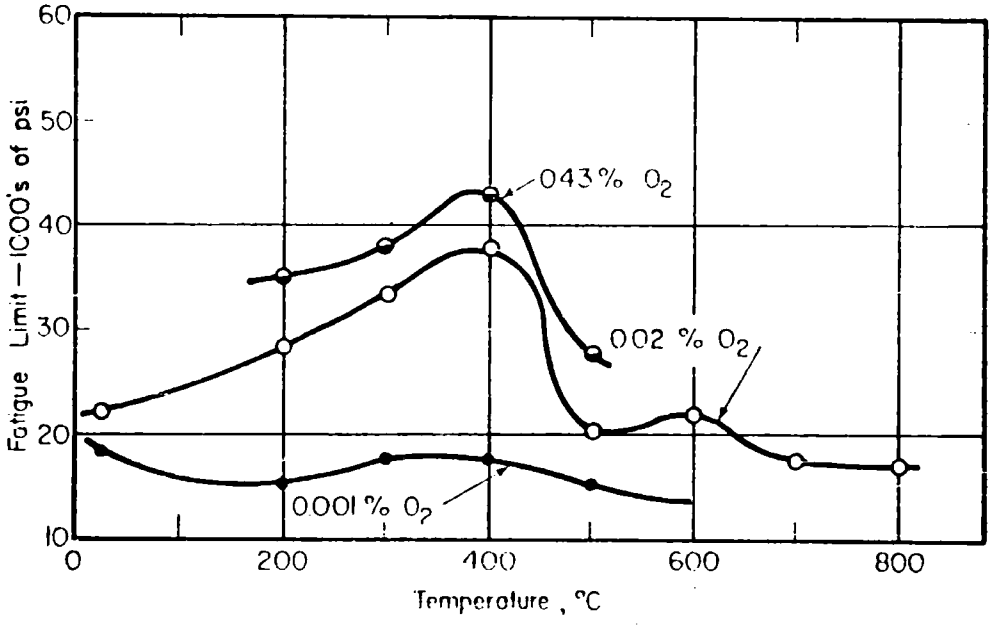

FIG. 4.7

FATIGUE LIMIT OF COLUMBIUM VS TEST TEMPERATURE FOR VARIOUS OXYGEN CONTENTS [17]

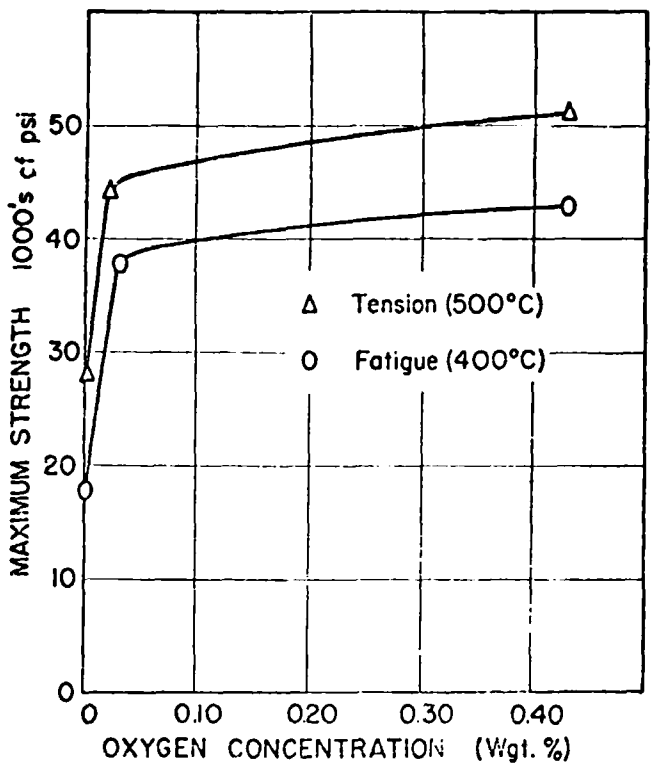

FIG. 4.8

MAXIMUM STRENGTH OF COLUMBIUM AT STRAIN AGEING PEAK VS OXYGEN CONCENTRATION [17]

grain sizes (>1, 2, and 5) all tested at the same strain rate (10^{-3}/sec), as levitation melted samples were too small for tensile test specimens. Yield strength increased with decreasing temperature from room temperature to -200°C at approximately the same rate for oxygen contents from 0.003 to 0.067. The yield strength at each temperature increased with increasing oxygen content. Brittle fracture occurred below about -125° C on samples of the highest oxygen content, 0.067. The ductility of 0.067 percent oxygen specimens as measured by reduction-in-area of tensile specimens dropped rapidly to a negligible amount near -100° C, whereas material with 0.007 and 0.020-percent oxygen exhibited greater than 60-percent reduction in area at -200° C which indicated that the ductile to brittle transition temperature for these materials was below -200° C.

These same investigators[18] observed similar effects of nitrogen content on the hardness, workability, strain hardening and recrystallization behavior of columbium during preliminary experiments that were not as extensive as those with oxygen. Small nitrogen additions were more effective hardeners than those of oxygen, and the recrystallization temperature range was broadened more with nitrogen additions than with oxygen additions.

Carbon additions to columbium up to 2.0 percent had little effect on hardness as reported by Begley and Lewis[19]. Samples containing up to 0.28 percent C were successfully forged at 1200° C, but higher carbon additions, which resulted in the appearance of carbide grain boundary networks, destroyed cold workability. For material containing Cb_2C particles, the tensile yield strength was not affected, but the tensile ductility was reduced in the temperature range -196° to 200° C.

Mincher and Sheely[15] have investigated in detail the effect of structure and purity on the tensile properties of Cb over the temperature range -196 to 1093°C. They describe the main strengthening mechanisms operative at three general temperature ranges to be as follows:

- Peierls-Nabarro lattice frictional resistance below room temperature
- Strain-ageing due to impurities from about 200-700°C
- Cold work from room temperature to about 500° C

The impurities responsible for strain ageing peaks in the ultimate tensile strength versus temperature curves were suggested to be O, C, and N at 300 , 500 , and 600°C, respectively. The O peak being more predominant and effective over a wide temperature range obscured the peaks at 500 and 600°C. The authors[15] correlated the temperatures at which the peaks occurred with diffusivities of the three interstitials which were equivalent (10^{-12} cm^2/sec) at 300 , 500 , and about 650°C for O, C, and N, respectively. The effect of cold work decreased rapidly with increasing temperature above 500°C, and the cold-worked material exhibited the same ultimate tensile strength at 1000°C as fully recrystallized material of the same origin, high-purity EB melted. The tensile strength versus temperature curves of Mincher and Sheely are similar to those shown in Fig. 4.2, and the reader is referred to their report for detailed description of their results.

McKinsey, et al.,[20] in a more recent report, have observed similar effects of interstitials on the strength properties of columbium. They reported a minimum in the strain-rate sensitivity versus temperature curve which corresponded to the maximum in the UTS versus temperature curves. They also showed a shift in the strain-ageing peak from 300 to between 700 -850°C associated with 5 atomic percent additions of either Ti, Zr, or V.

Wilcox and Huggins[8] correlated the strain-ageing behavior of Cb with interstitial hydrogen content using yield point return and dynamic modulus measurements. The activation energy calculated for the strain ageing process (10,500 cal/mole) was shown to agree closely with a reported activation energy for diffusion of H in Cb (9370 cal/mole). The authors[8] also observed that loss of room temperature ductility resulted from an increase in H content from 10 to 780 ppm which produced a hydride second phase which was observed microscopically.

Additional studies on the effects of impurities on columbium have been summarized in earlier survey reports[1,3] and are in general agreement with those described above.

Recrystallization Behavior of Cold-Worked Columbium

The effect of annealing treatment on cold-rolled columbium shown by the change in tensile properties was described in the original report from the work of Page. Savitskii, et al.,[21] investigated the annealing behavior of relatively impure columbium by observing the grain diameter produced at several annealing temperatures from 1000 to 2000°C on material deformed by cold rolling 2.5, 5, 7.5, 10, 20, 40, 60, 80, and 96 percent reduction in thickness. Fig. 4.9 shows that a critical degree of deformation existed between 5.0 and 7.5 percent which resulted in large grains at all annealing temperatures above about 1200°C. Grain coarsening occurred at deformations above 20 percent between 1450 and 1650°C. X-ray determination indicated that 7.5 percent deformation required an annealing temperature of 1200°C, and 60 percent required a temperature of 1025°C for the initiation of recrystallization. Increasing the deformation from 60 to 96 percent did not alter the initiation temperature.

Begley[7] conducted recrystallization studies on EB melted Cb after cold rolling 60, 80, and 95 percent. The start and completion of recrystallization was observed metallographically and by x-ray and hardness measurements after annealing for 0.1, 0.5, 1, 10, and 100 hours in vacuum at 700-1200° C. The results are comparable to those of Savitskii, et al.[21] Begley's study was in more detail but over a narrower annealing temperature range.

Tensile Properties of Columbium Alloys

During the past two-year period, the effect of binary and complex alloy additions to Cb has been extensively studied at Battelle, Du Pont, Fansteel, General Electric, Stauffer, Sylvania, Temescal, Wah Chang, and Westinghouse. The scope of several published alloy screening studies based primarily on mechanical properties are summarized in Table 4.5. Screening studies conducted on oxidation resistance and

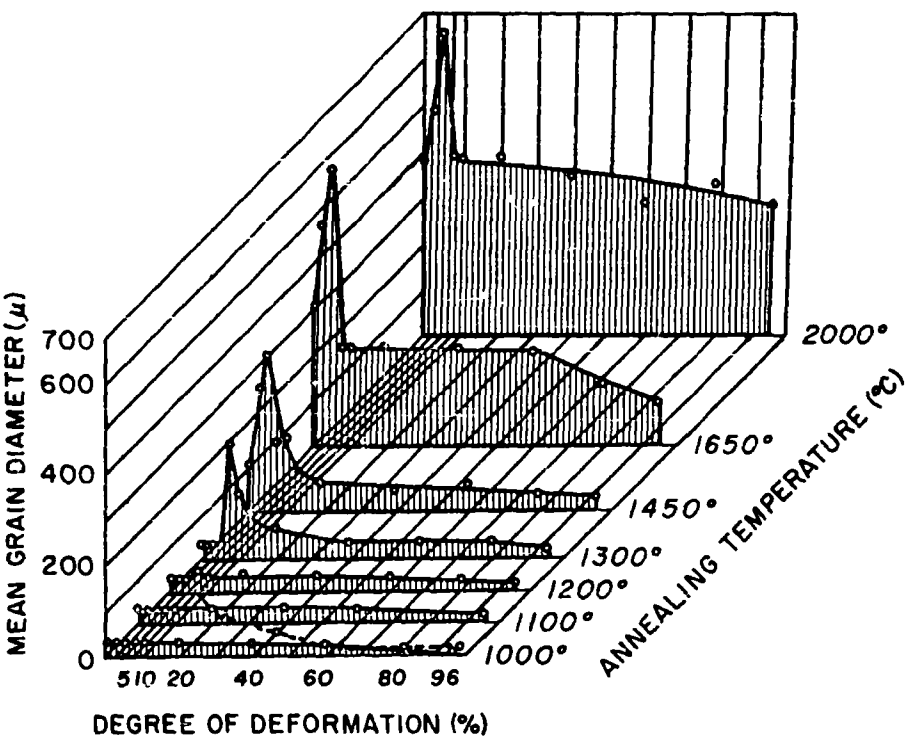

FIG. 4.9

RECRYSTALLIZATION DIAGRAM FOR COLUMBIUM [21]

Table 4.5

INVESTIGATIONS CONCERNED WITH COLUMBIUM ALLOY DEVELOPMENT

Alloy Addition		Properties Investigated	Reference
Binary	Ternary and Others		
Al Hf Mo Re Ti V W Y Zr	Hf - Mo Ti - Hf Ti - Mo Ti - Zr Ti - Zr - Hf	Fabrication, hardness, and tensile properties of fabricable alloys. Room temperature and 1093° C	Begley and Platte[14]
C Hf Ti V W Y	Hf - O Mo - Hf V - Al V - Mo V - Y V - Zr Ti - Zr - Hf V - Mo - Zr Ti - Zr - Hf - O	Same	Begley and Lewis[22]
Al Cr Mo W Zr	Mo - Hf V - W V - Zr V - Mo - Zr V - W - Zr	Same	Begley and Lewis[23]
Ce Cr Fe Mo Ni Pd Ti V Y Zr	Ti - Mo V - Al V - C V - Cr V - Fe V - Mo V - Ni V - Ti V - Zr Zr - Cr Zr - Fe Zr - Mo Zr - Ti +O, N, C modifications	Fabrication, Hardness, same Tensile at 1500F same creep and rupture properties to 750C (dilute alloy systems only for reactor applications)	Maykuth and Jaffee[24]
Mo Ti W		Hot Hardness, Elevated Temperature Tensile Creep Rupture and Recrystallization	Gemmel[25]
Ta	Ta - Mo Ta - W Ta - Mo - W	Impact Transition Temperature and Elevated Temperature Tensile	Smith, et. al[26]

weldability have not been included in the Table. The properties of the more promising alloys which have evolved from these programs have been treated in detail in three survey reports[2,3,4] and, therefore, will only be summarized in this compilation.

Alloys which have received attention beyond the screening studies are listed in Table 4.6 which also lists the nominal compositions and company designations. Several of the alloys have achieved commercial status and are available in rod and sheet form. The strengthening mechanisms most effective in these alloy systems are solid solution strengthening and/or dispersion strengthening. The strengthening effect of plastic deformation is maintained up to 2400° F for some of the alloys. The various alloys possess different degrees of short- or long-time strength at elevated temperatures, oxidation resistance, fabricability, and weldability. None of the alloys is superior by all criteria, and development work is continuing at all of the laboratories.

The modulus of elasticity of several Cb alloys as a function of test temperature is shown in Fig. 4.10. These data are based on strain measurements from tensile tests.

The reported data show an appreciable increase in the low temperature modulus value for Cb due to alloying. In the case of F-48, the increase was approximately 65 percent, whereas for F-50, the increase was slightly less. Alloy D-31 showed only a slight increase of about 15 percent over that for Cb, whereas the curve for D-41 falls about midway between the curves for unalloyed Cb and F-48. In general, additions of W and Mo appeared to increase the modulus, Ti additions appeared to result in a decrease, and Ta additions had little effect. As most metals show a gradual decrease in modulus with increasing temperatures, the curves of Fig. 4.10 showing a rapid drop above 1500° F should be questioned unless it can be demonstrated that only elastic and no plastic strain occurred during the evaluation of the modulus. It should be noted, however, that alloys with the highest combined W and Ta content had the highest modulus values above 2400° F.

The more attractive columbium alloys combine additions of W, Mo, Zr, V, Hf, Ti, and Ta. The first five elements contribute to strength through solid solution or dispersion strengthening mechanisms and the last two have been found to promote fabricability. Combinations of Ti and W with minor Mo and V additions impart the best oxidation resistance to columbium alloy systems without reducing fabricability.

The effect of V, Zr, Hf, Mo, and W additions on the 2000° F (1093° C) tensile properties of columbium is shown in Fig. 4.11 as reported by Begley.[14] All of the alloys were produced by non-consumable arc melting 100-150 gram buttons. Alloys of the first four additions were melted in a good vacuum furnace and had low gaseous impurity level (Series II alloys). The W alloys were reported to be contaminated during melting due to a poorly sealed furnace. Tungsten alloy specimens were produced by hot swaging in air at 1200° C to rod bars about 0.4375 in. in diameter, centerless grinding to a 0.375 in. diameter bar, then machining to a 0.200 in. x 1 in. gage section, and vacuum annealing at 1600° C for 1 hour wrapped in Cb foil. All other alloy specimens were hot forged at 1200° C in type 304 stainless steel jackets to 0.125-in.

Table 4.6

COLUMBIUM ALLOYS WITH POTENTIAL COMMERCIAL INTEREST

Company	Alloy Designation	Alloy Additions, Wt %						Other	Reference for Properties
		W	Mo	Ta	Ti	Zr	V		
DuPont	D-31			10	10				27
DuPont	D-41	20	6		10				4
Fansteel	FS80					0.75			28, 29
Fansteel	FS82			33		0.8			30
Fansteel	FS85	12		27		0.6			30
G.E.	F-48	15	5			1		0.06C 0.05O	31, 2
G. E.	F-50	15	5		5	1		0.06C 0.050O	31, 2
Haynes Stellite (UCM Co)	Cb 6	10			8				2
Haynes Stellite (UCM Co)	Cb 7	28			7				2
Haynes Stellite (UCM Co)	Cb 16	20			10		3		2
Haynes Stellite (UCM Co)	Cb 20	15			5	5			2
Haynes Stellite (UCM Co)	Cb 22						3	3A1	2, 29
Haynes Stellite (UCM Co)	Cb 24				7		3	3A1	2
Haynes Stellite (UCM Co)	Cb 65				7	0.8			2, 29
Haynes Stellite (UCM Co)	Cb 67				7	1	3	3A1	2
Haynes Stellite (UCM Co)	Cb 74	10				[illegible]			2, 29
Haynes Stellite (UCM Co)	Cb 84	20	3		7				4
Haynes Stellite (UCM Co)	Cb 85	20	3		7	1			4
Stauffer	SCb291	10		10					32
Stauffer	SCb278		10	10					32
Stauffer	SCb41	10	2	30		1			32
Stauffer	SCb61	10	2	10		1			32
Stauffer	15W-20Ta	15		20					33
Stauffer	20W-20Ta	20		20					34, 26
Temescal	22 Combinations	1.5-25	1-10	5-46		0-1			34, 26
Wah Chang	C-103				1	0.5		10 Hf	35
Westinghouse	NC155		5				5		22
Westinghouse	NC181		5			1	5		22

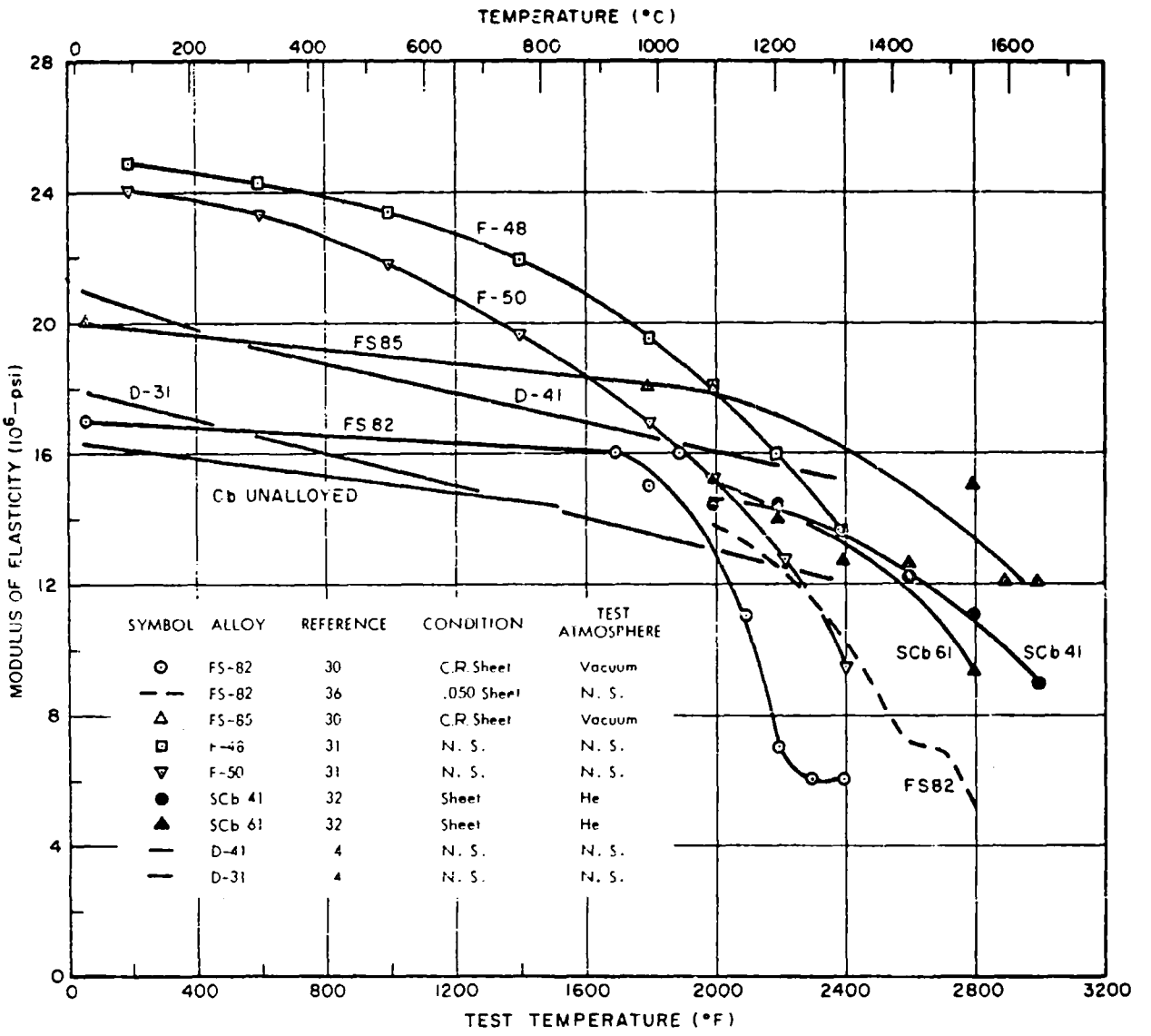

FIG. 4.10

MODULUS OF ELASTICITY VS TEST TEMPERATURE FOR EIGHT COLUMBIUM ALLOYS

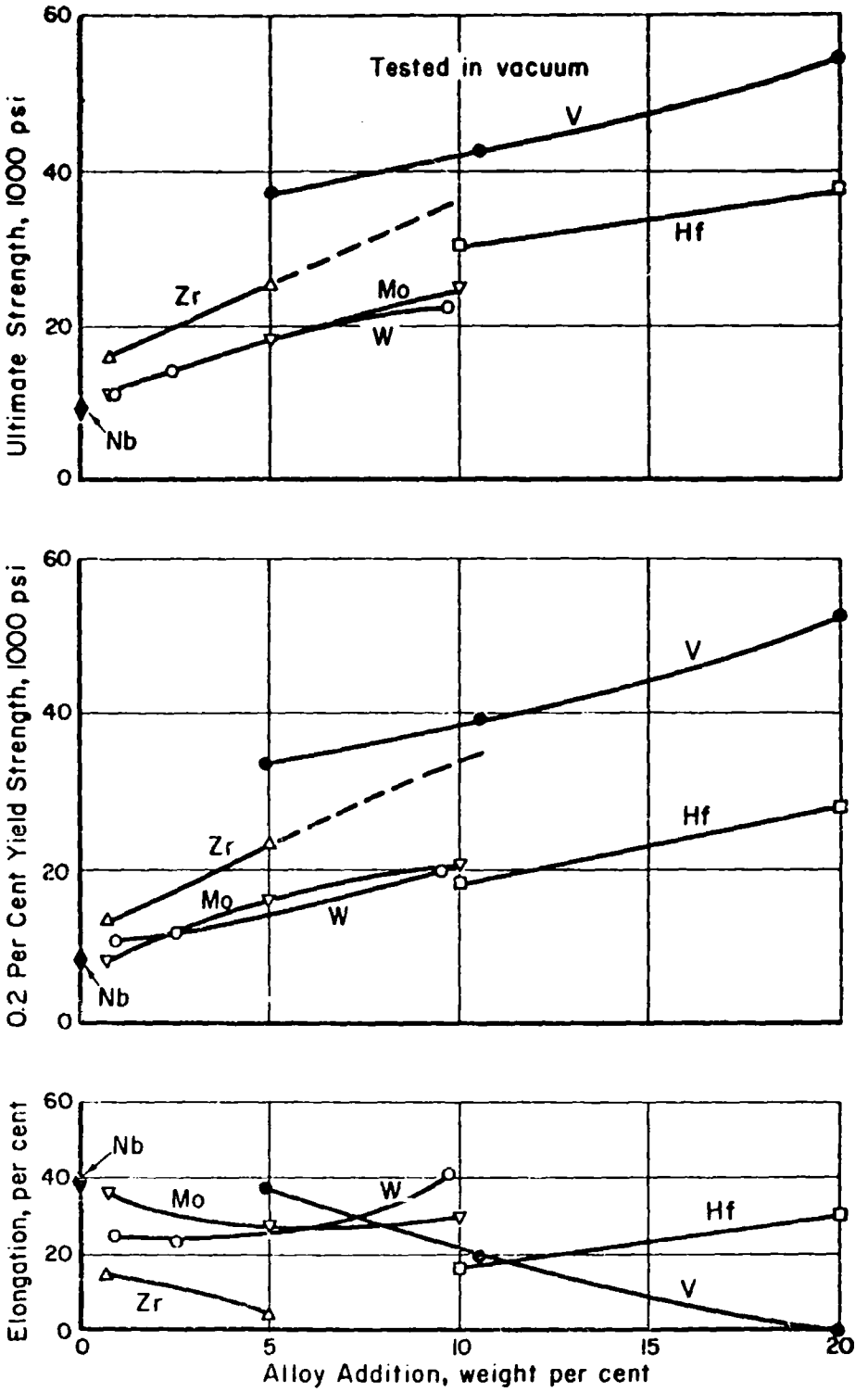

FIG. 4.11

TENSILE PROPERTIES OF RECRYSTALLIZED COLUMBIUM BINARY ALLOYS TESTED IN VACUUM AT 1093°C (2000°F) [14]

thick sheet bars, hot rolled to 0.060-in. thick sheet, unjacketed, pickled, and machined to 0.250-in. wide x 1-in. gage section and vacuum annealed at 1500° C for 1 hour wrapped in Cb foil. The elevated temperature testing was done in vacuum at a strain rate of 10^{-3}/sec.

This investigation showed V and Zr to be the most effective strengthening additions both at room temperature and 2000° F, but the ductility of both systems was low for the higher concentrations at the elevated temperature. The low ductility was associated with a grain boundary phase. These data are shown here to indicate the trends observed in this screening study. For a more complete review of alloying behavior in binary Cb systems, the reader is referred to the Westinghouse report[4] and the DMIC review. [3] The properties of the more complex Cb alloys are of greater interest to the user and will be emphasized in this survey.

The mechanical properties of alloys which have evolved to commercial, pilot production, or advanced laboratory status have been tested to established average values. The effect of temperature on the ultimate tensile strength of six alloys as presented by Bacon et al., [2] is shown in Fig. 4.12. The same relation is shown in Fig. 4.13 with an expanded temperature scale which allows better comparison of the alloys in the upper temperature region. Figure 4.13 also includes the strength properties of additional alloys which are of interest for high temperature service.

The mechanical and thermal history and test conditions as reported in the Crucible state-of-the-art survey[2] are listed in Table 4.7. A variety of methods for the preparation of the alloy samples and the use of various testing environments are presented in the table. Also indicated is a lack of information regarding configuration and rate of straining. The metallurgical state of each material resulting from individual mechanical and thermal treatments is different as would be expected, as each composition would display its optimum properties only after specific fabrication and heat treatment. Several of the data sheets submitted for the Crucible survey[2] included data from specimens with different processing than that indicated in Table 4.7. The change in properties with change in processing for each alloy has not been thoroughly defined by sufficient experiments; however, the survey[2] contains a more detailed review of the available data for a specific alloy.

The ultimate tensile strength at temperatures up to 4000° F of three Cb alloys as reported by Hall[33,37] are presented in Fig. 4.14. Data from the following tests are included for comparison:

- D-31 tested in air
- F-48 tested in vacuum in worked and worked and stress-relieved condition
- Cb-74 tested in vacuum in recrystallized condition

The curves for the Cb-W-Ta alloys indicate good retention of strength at elevated temperatures for alloys with large solid solution additions. For example, the Cb-20W-20Ta alloy is shown to be stronger at 2400° F than either F-48 or Cb-74 which are alloys containing both solid solution and dispersion strengthening alloy additions, but less solid solution content than the Cb-20W-20Ta alloy.

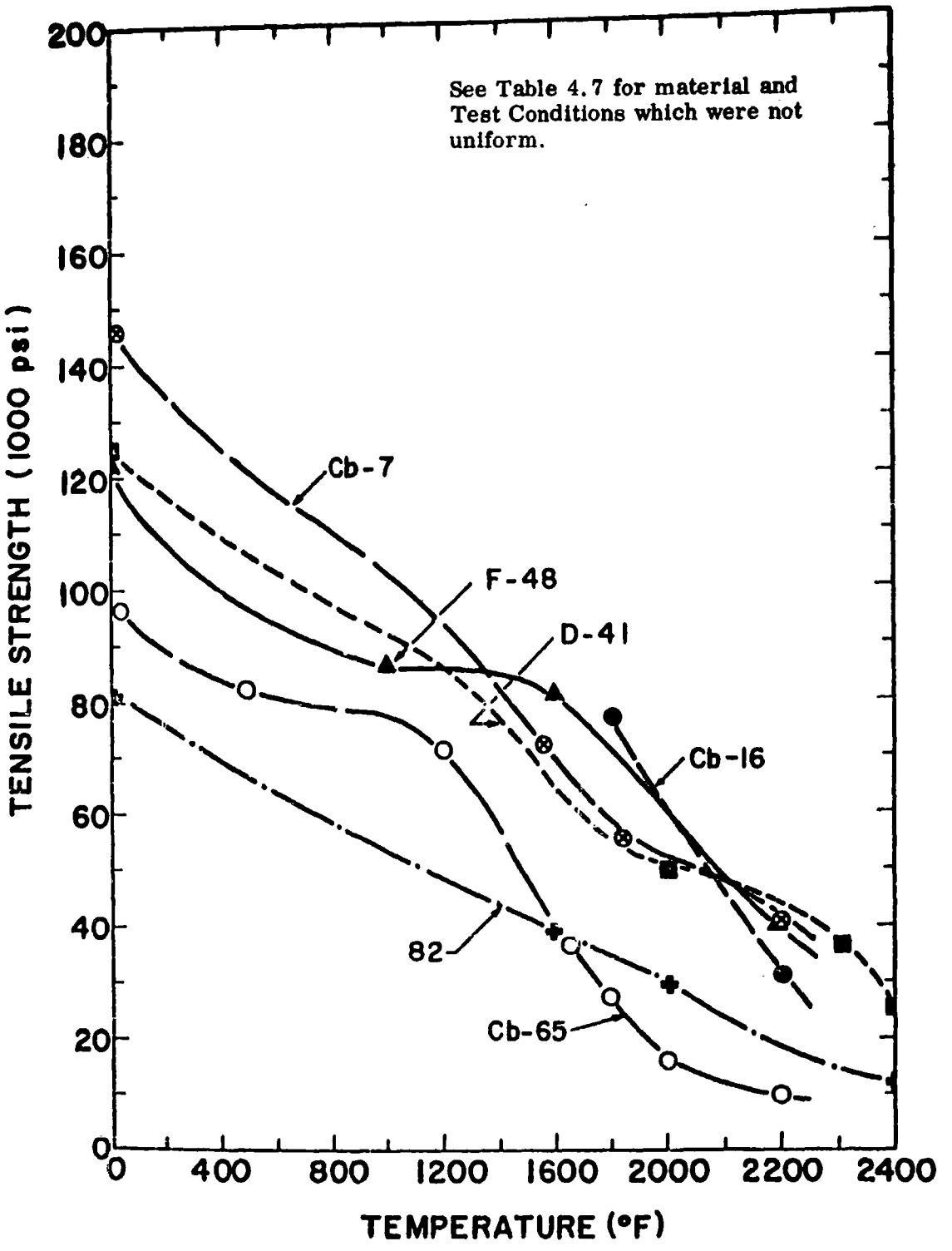

FIG. 4.12

ULTIMATE TENSILE STRENGTH FOR SIX COLUMBIUM ALLOYS BETWEEN ROOM TEMPERATURE AND 2400°F[2] (Note expended temperature scale from 2000 to 2400°F)

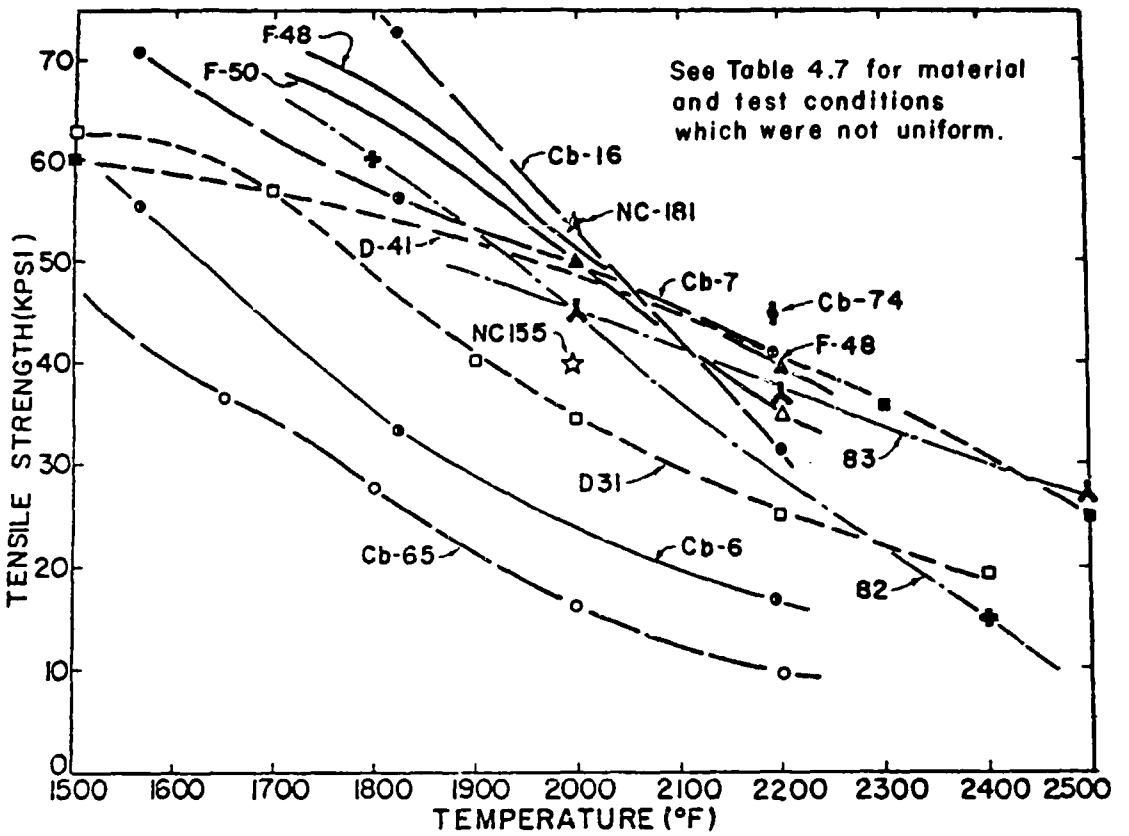

FIG. 4.13

ULTIMATE TENSILE STRENGTH FOR VARIOUS COLUMBIUM ALLOYS BETWEEN 1500 and 2500°F (815 and 1370°C) [2]

Table 4.7

DESCRIPTION OF MATERIAL AND TEST CONDITIONS FOR TENSILE DATA OF FIGS. 4.12 AND 4.13

Alloy Designation*		Consolidation Method	Primary Conversion Method	Secondary Conversion Method	Thermal Treatment	Specimen Size, in.	Strain Rate, min^{-1}	Test Atomsphere	Supplier
D-31	(a)	double Arc Melt to 4-1/2 in. dia ingot	extrude	N.S.	as extruded	N.S.	0.05	Air	Du Pont
D-41		same	extrude	N.S.	as extruded	N.S.	0.05	Air	Du Pont
FS82		same	hot forge 2700° F	R.T. value-as C.R. sheet 0.040 in. th. Elev. temp. values as swaged Rod	none	N.S.	N.S.	Air	Fansteel
FS83	(a)	N.S.	N.S.	N.S.		N.S.	N.S.	Argon	Fansteel
F-48		arc Melt to 5 in dia.	hot extrude in Mo can 2709° 3190° F	Roll to sheet stress relieved 2200° F. 1 hr with intermediate reheats		sheet			
F-50	(a)	Arc Melt to 6 in dia.	Similar to F-48	Extrude and Swage	none	N.S.	N.S.	Vac	G. E.
Cb-6		Arc Melt to 3-1/2 in. dia. Ingot	Forged 2100° F	Hot Roll 2250° 1520° F Cold Roll Finish	none	N.S.	N.S.	Argon	U.C.M.
Cb-7		Arc Melt to 2-1/2 in. dia. Ingot	Impact extrude 2500° F	Swage 2200° F from 1/2 in. to 3/8 in. dia.	none	Bar	0.02	Vac	U.C.M.
CB-16		same	Extrude 2700 to 2900° F. Ratio 3 or 4:1	none	none	N.S.	0.005	Argon	U.C.M.
Cb-65		Arc Melt to 3-1/2 in. dia. Ingot	Extrude 2300° F 2-1/2-2 in. dia.	Hot Roll to gothic 2000° F Cold Swage to 3/8 in dia. (88% C.W.)	none	Bar	0.02	Argon	U.C.M.
Cb-74	(a)	Arc Melt to 2-1/2 in. dia. Ingot	Impact extrude at 2550° F	none	none	N.S.	0.02	Vac.	U.C.M.
NC 155	(a)	Arc Melt 150 gm Button	Hot Forge	none	1 hr 2732° F Rexl	N.S.	N.S.	N.S.	Westinghouse
NC 181	(a)	same	same	none	same	N.S.	N.S.	N.S.	Westinghouse

(a) Data given in Fig. 4.13 only; data for all others given on Figs. 4.12 and 4.13.

*Composition of alloys are given in Table 4.6 except for FS 83 which was not specified. FS 83 was a W modification of FS 82 and has been replaced by FS 85

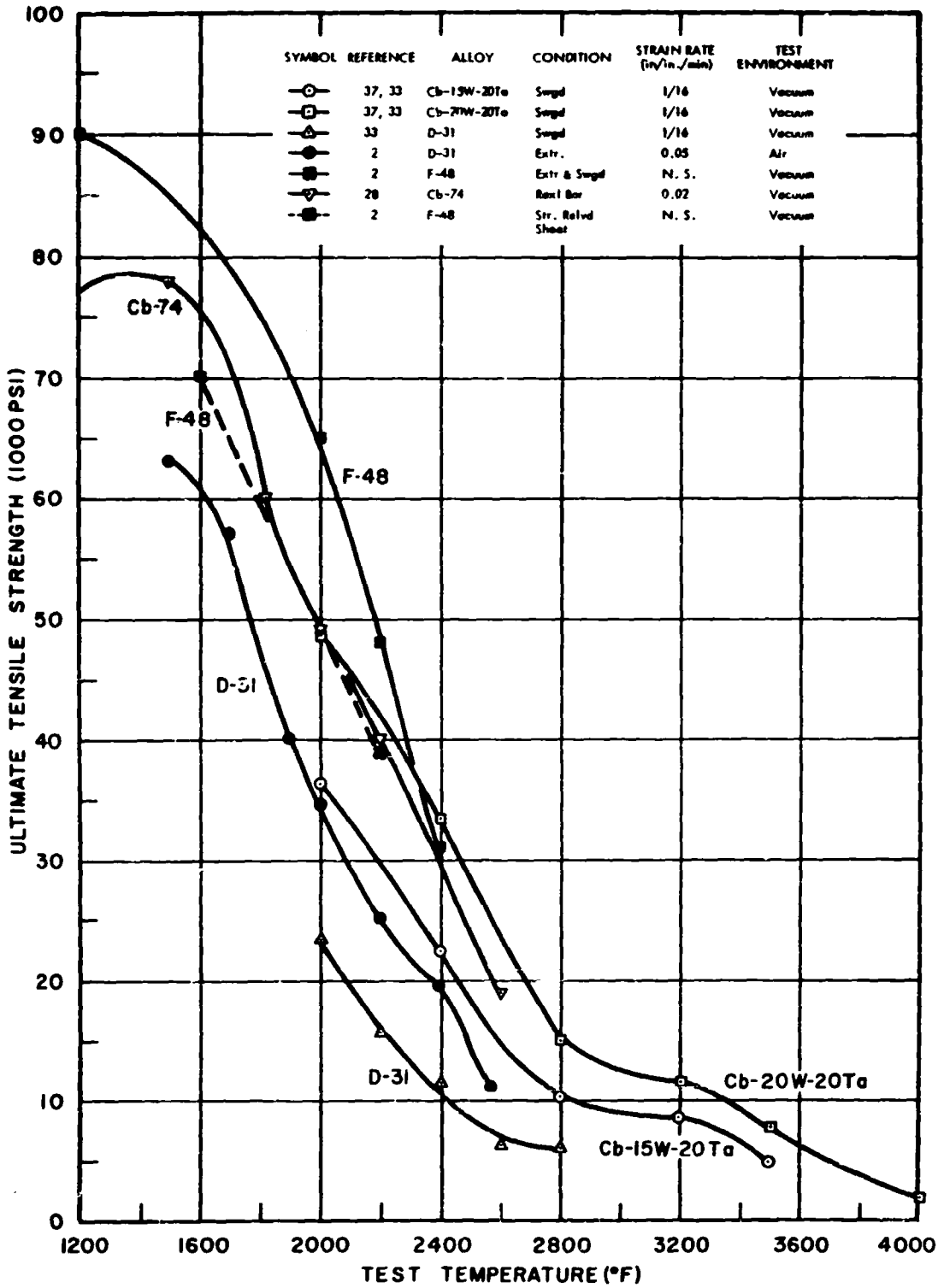

FIG 4.14

ULTIMATE TENSILE STRENGTH FOR SELECTED COLUMBIUM ALLOYS BETWEEN 1200 AND 4000° F

The strengthening mechanisms of Cb-74 (Cb-10W-5Zr) have not been clearly established, but the higher Zr content of Cb-74 apparently provides high temperature strengthening equal to the higher W and added Mo content of F-48 (Cb-15W-5Mo-1Zr). The recrystallized Cb-74 is shown to be equivalent in strength between 1600 and 2200°F to the stress relieved (2500°F, 1 hr) F-48 and about equal to as-worked F-48 at 2400°F and above. The one hour recrystallization temperature of Cb-74 and F-48 are reported [29, 32] to be 2600 and 3200°F respectively. Judging from the decrease in strength of F-48 after a stress relief anneal at 2500°F, the strength of Cb-74 would probably exceed that of F-48 up to 2600°F if both materials were tested in the completely recrystallized condition. Both Cb-74 and D-31 exhibited excellent room temperature ductility in the recrystallized condition.

Ductility as measured by elongation and reduction-of-area was better at all temperatures for tests conducted in vacuum, 61 percent and 90 percent at 2400°F, than for tests conducted in air, 8 percent and 11 percent at 2400°F. Results of tests conducted in vacuum on D-31 0.020 in. thick sheet material in the stress-relieved condition at Boeing [38] gave tensile strength values comparable to the air tests reported by Bacon et al.,[2] at 2000 and 2500°F. The true effect of environment on tensile test results of D-31 cannot be clearly evaluated by the few data available because of the variable specimen preparations involved.

The effect of the test environment on the strength value of FS 82 at 2000°F was indicated in the data sheets appended to the Crucible Report [2] on materials of identical preparation, where a strength of 29,600 psi and elongation of 2 percent are shown for a test in air, but a strength of 44,700 psi (50 percent increase) and elongation of 8 percent are shown for a test in argon. In this case, the strength of FS 82 was reported to be lower when evaluated in air in contrast to the environment effect for D-31 shown on Fig. 4.14.

Recent data on the ultimate tensile strength of FS 82 and FS 85 were reported by Gentry and Michael.[30] Their results on material in the as-cold-rolled and in the cold-rolled and recrystallized conditions are presented in Fig. 4.15.

The two curves for FS-82, cold-rolled 50 percent and cold-rolled 50 percent and recrystallized, exhibit the normal trend of strengthening by cold work. The strengthening effect was appreciable up to test temperatures of about 2000°F, above which the strength of the wrought material decreased rapidly. Above about 2400°F, the effect of cold work was nil and the two curves fall almost together.

In the case of the four curves for FS-85, however, the data are not so easily explained except for the two curves representing the 94 percent cold-rolled and the 94 percent cold-rolled and recrystallized conditions. Here again the strengthening effect of cold work is evident and persists to somewhat higher temperatures than for the FS-82 alloy. Also, the FS-85 alloy maintained high temperature strength better than FS-82; and, above 2600°F, had about twice the value of ultimate tensile strength compared with FS-82.

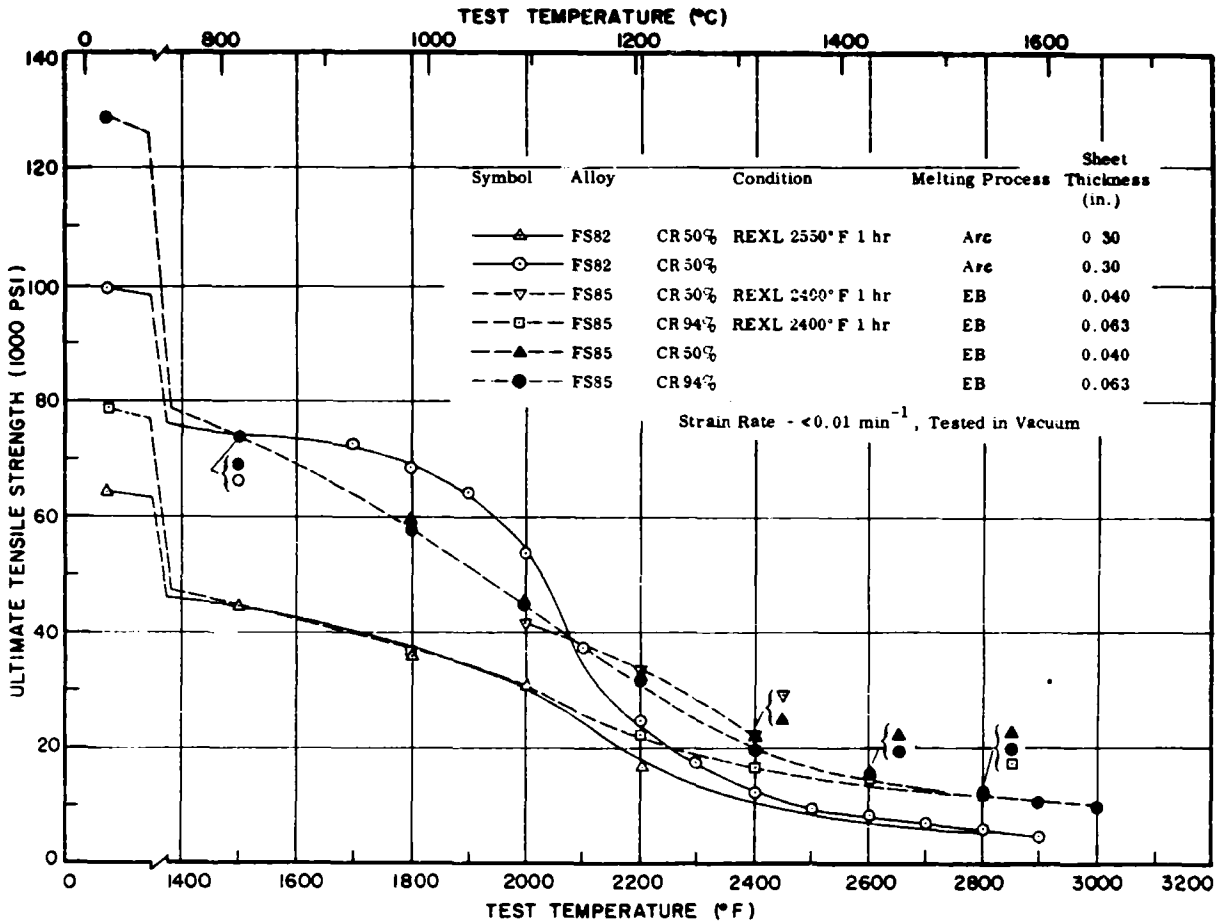

FIG. 4.15

ULTIMATE TENSILE STRENGTH OF FS 82 AND FS 85 FROM 1500 TO 3000° F (815–1650° C)[30]

The following conditions for the data on FS-85 appear to be anomolous:

(1) The curves representing the 50 percent cold-worked and 94 percent cold-worked conditions superimpose over their entire joint test temperature range, 1800 to 2800°F. Since the effect of cold-work is still apparent above 2400°F for this alloy, the 94 percent cold-worked material would be expected to have a relatively higher curve, at least up to 2400°F.

(2) The curve for 50 percent cold-worked and recrystallized FS-85 is much higher than that for the 94 percent cold-worked and recrystallized material. The tensile strength of fully recrystallized material would not be expected to be strongly dependent upon prior deformation.

(3) The curves for the 50 percent cold-worked and 50 percent cold-worked and recrystallized FS-85 almost superimpose over their common test temperature range, 2000 to 2400°F. The 50 percent cold-worked and recrystallized material would be expected to have an appreciably lower strength.

Two of these conditions indicate that the curve representing the 50 percent cold-rolled and recrystallized FS 85 may be erroneously high.

The relation between curves for FS-82 and FS-85 for both the 50 percent cold-rolled and recrystallized conditions is also difficult to explain. The FS-82 is shown to have higher strength between 1500 and 2100°F than FS-85 in the 50 percent cold-rolled condition and equal strength in the recrystallized condition even though the room temperature strength of FS-85 is superior in both conditions as would be expected from the large W content of FS-85. The higher impurity content of the arc-melted FS-82 would not be expected to strengthen FS-82 as much as the W content of the FS-85. Additional data on these alloys may clarify some of the above questions.

Creep and Stress Rupture Properties of Columbium

The stress-rupture properties of unalloyed Cb are presented in Fig. 4.16 as reported by Gemmel,[25] and in Fig. 4.17 as reported by Bechtold et al.[5] The latter is a summary of work by Begley[7] and Mincher and Sheely,[39] whose work was not found reported in the open literature. Table 4.8 includes the reported chemistry and history of the test materials. The high-purity material used by Gemmel had less metallic impurity, about the same interstitial impurity, and a larger grain size than that used by Begley[7]. Gemmel's material evidenced higher rupture strength values at 1650 and 1800°F than that of Begley which may reflect an effect of the larger grain size. Both investigators observed a slight hardness increase after test, and Begley reported a decrease in strain rate for long time creep tests which may indicate that contamination during testing accounted for some of the variation in rupture properties between the two sets of data. The data of Mincher and Sheeley[39] indicate a 100 hour rupture strength at 1500°F about the same as that of Gemmel at 1650°F even though the reported interstitial content is higher.

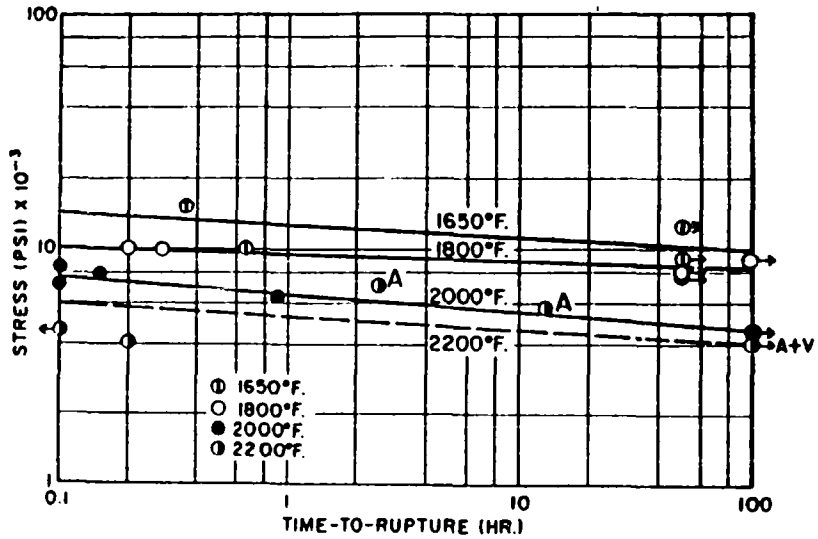

FIG. 4.16

CREEP STRESS VS RUPTURE TIME FOR COLUMBIUM AT 1650, 1800, 2000, AND 2200°F [25]

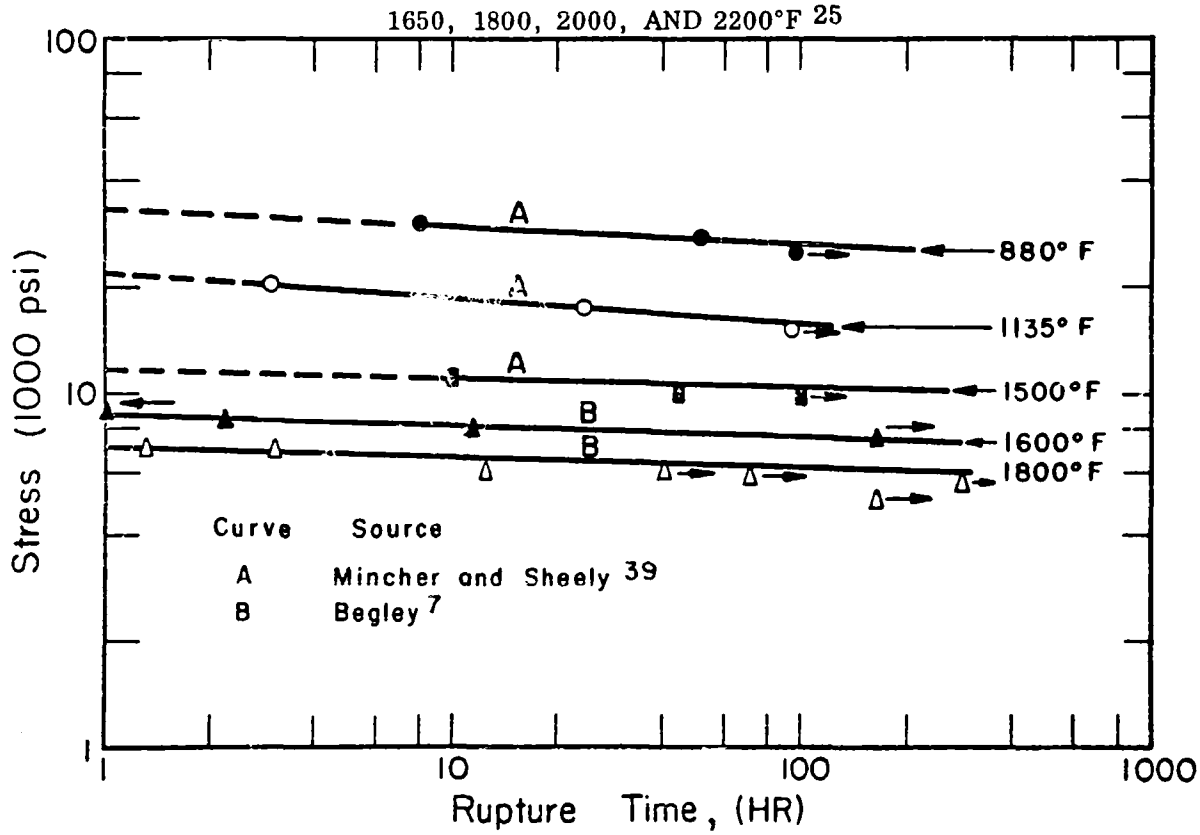

FIG. 4.17

CREEP STRESS VS RUPTURE TIME FOR COLUMBIUM AT 830, 1135, 1500, 1600, and 1800°F [5]

Table 4.8
DESCRIPTION OF MATERIAL AND TEST CONDITIONS FOR CREEP DATA OF FIG. 4.16 and 4.17

Reported Impurity: ppm					Process history	Test atmosphere	grain size mm	Spec. size in.	Ref.
O	N	C	H	Other					
140	130	27		Ta 1930 Zr < 300 Ti 20 Fe 20	Elect. Beam Melted Cold forged rolled, and swaged from 3 in dia to 3.8 in dia. Recrystallized – 2 hr at 1050C (1920F) in	vac 10^{-5} to 10^{-3} mm	0.06	0.198 dia x 1	Begley[7]
300	400	200	10		arc melted				Mincher & Sheely[39] after Bechtold, et al.[5]
166	40	28		Ta 300 Cr 30 Ni 30 Fe 60	arc melted, skull cast, cold swaged 50 percent reduction, recrystallized-16 1/2 hr at 1400C (2550F)	vac 10 mm	0.1 to 0.3	0.160 dia	Gemmel[25]

The creep properties of unalloyed Cb in terms of stress required to produce a specified strain at a given time and temperature have not been well established. Williams and Heal[10] have reported some creep properties at 400, 500 and 600°C from tests conducted in purified argon on material specified only as production columbium. The results are not shown because lack of material and test specifications made it impossible to evaluate or correlate the data.

Creep and Stress Rupture Properties of Columbium Alloys

Few data on the creep resistance of commercially attractive Cb alloys have appeared in the literature. The stress to produce 2 percent creep strain in one hour at several temperatures is indicated in Fig. 4.18. The three alloys reported show the same relative creep resistance at 2000°F as they did on the basis of tensile strength shown in Fig. 4.13. Unfortunately these data are very poorly documented as to material condition and test conditions.

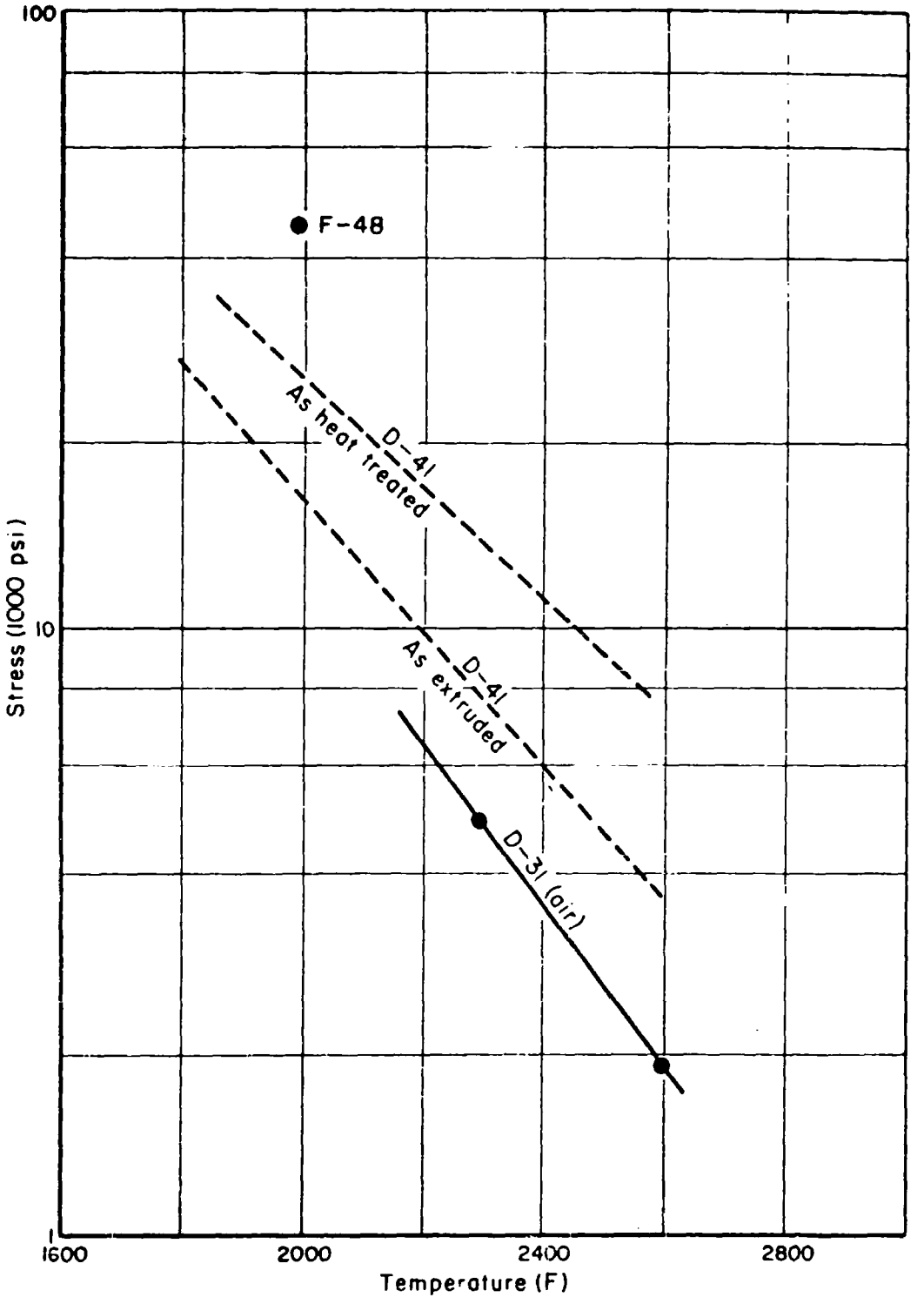

FIG. 4.18

STRESS FOR 2 PERCENT CREEP STRAIN IN ONE HOUR FOR THREE COLUMBIUM ALLOYS BETWEEN 1800 to 2600°F[2]

The stress-rupture properties of several attractive Cb alloys, at 2000 and 2200°F are shown in Fig. 4.19 and 4.20, respectively. Alloy F-48 is shown to exhibit higher rupture strengths at both temperatures than the other alloys reported. Additional tests should be conducted on each of the alloys under similar testing conditions before final judgement is made of the relative merit of the various alloys presented as the stress rupture properties are extremely sensitive to composition, fabrication, and test variables. For example, Guernsey and Carson[40] report times to rupture of 5.3, 66.7, and 100 hour at 2200°F and a stress of 24,000 psi for F-48 stress-relieved extrusions produced from ingots prepared by three consolidation processes: electron-beam melting, powder metallurgy, and electron-beam melting plus vacuum-arc remelting, respectively. These values differ considerable from the 10 hour rupture life at 24,000 psi shown by the curve for F-48 in Fig. 4.20. According to the authors,[40] no obvious explanation for the wide variation was evident, but an observation of surface contamination of specimens from long time tests in vacuum suggests a sensitivity of this alloy to chemical change and resulting mechanical property change during testing.

A comparison of the strength of F-48 and F-50 gives an indication of the effect of Ti additions on the elevated temperature strength of these alloys. The two nominal compositions vary only in the Ti content; F-50 contains 5 percent Ti and F-48 none. However, F-50 is shown to fail in 10 hours under a creep stress of 27,000 psi at 2000°F, whereas F-48 is shown to have at least a 1000 hour life under the same stress and temperature conditions. The Ti additions, however, have been shown to improve the oxidation resistance.

A similar effect of Ti addition on creep strength can be observed from a comparison between F-48 and D-41 alloys in Fig. 4.19. The D-41 composition contains more solid solution strengthening elements W and Mo, 10 percent Ti, and no Zr. The combination of Ti addition and deletion of the dispersion strengthening agent Zr apparently accounts for the lower strength of D-41.

The effect of test material preparation may be observed by comparing the strength of FS 82 determined from rod and sheet specimens shown in Fig. 4.19. The stress-relieved sheet specimen tested at 19,000 psi in vacuum failed in 1 hour, whereas a swaged bar specimen tested in argon would fail at about 60 hours at the same stress, judging from interpolation of the curve shown for the bar specimens. It is also interesting to observe the similarity in strength of FS 80 and FS 82 as indicated by the curves determined from bar specimens of each material. Both alloys contain the same nominal Zr content; however FS 82 contains about 33 percent Ta, whereas FS 80 contains no additional strengthening additions.

The rupture strength of the recrystallized Cb 16 alloy shown on Fig. 4.20 is greater than the as-worked material. Recrystallization of this alloy after extrusion and swaging at 2100 – 2200°F to produce a 45 percent hot work reduction is reported[2] to be complete after annealing at 2550°F for 30 min. The 30 min anneal at 2912°F given the specimens used for the Cb-16 data of Fig. 4.20, resulted in grain growth and elevated temperature strength improvement according to Bacon, et al.,[2] from

LEGEND FOR FIG. 4.19

Symbol	Alloy	Reference	Material	Material Condition	Heat Treatment	Test Atmosphere
○	F-48	31	Bar	Extr., Swgd, Str. Relvd	2,000°F	Vacuum
□	D-41	4	Bar	Extr & Swgd	2,350°F 16 hr	Vacuum
△	D-41	4	Bar	Extr & Coated	2,000°F 1 hr	Air
●	D-31	4, 2	Sheet 0.060 in.	Str. Relvd	1,750°F	Vacuum
■	FS-82	4, 2	Bar	Swgd	None	Argon
▲	FS-82	4	Sheet 0.070 in.	Str. Relvd	N. S.	Vacuum
▽	FS-80	2	Bar	Extr	None	Argon
▼	F-50	31	Bar	Extr, Swgd Str. Relvd	2,000°F	Vacuum
○	Cb-65	2	Bar	Swgd-Ann	2,600°F 1 hr	Vacuum
◇	FS-85	30	Sheet	Cold Rolled 94%	---	---
◆	Cb-74	28	Bar	Rexl	2,600°F 1 hr	Vacuum

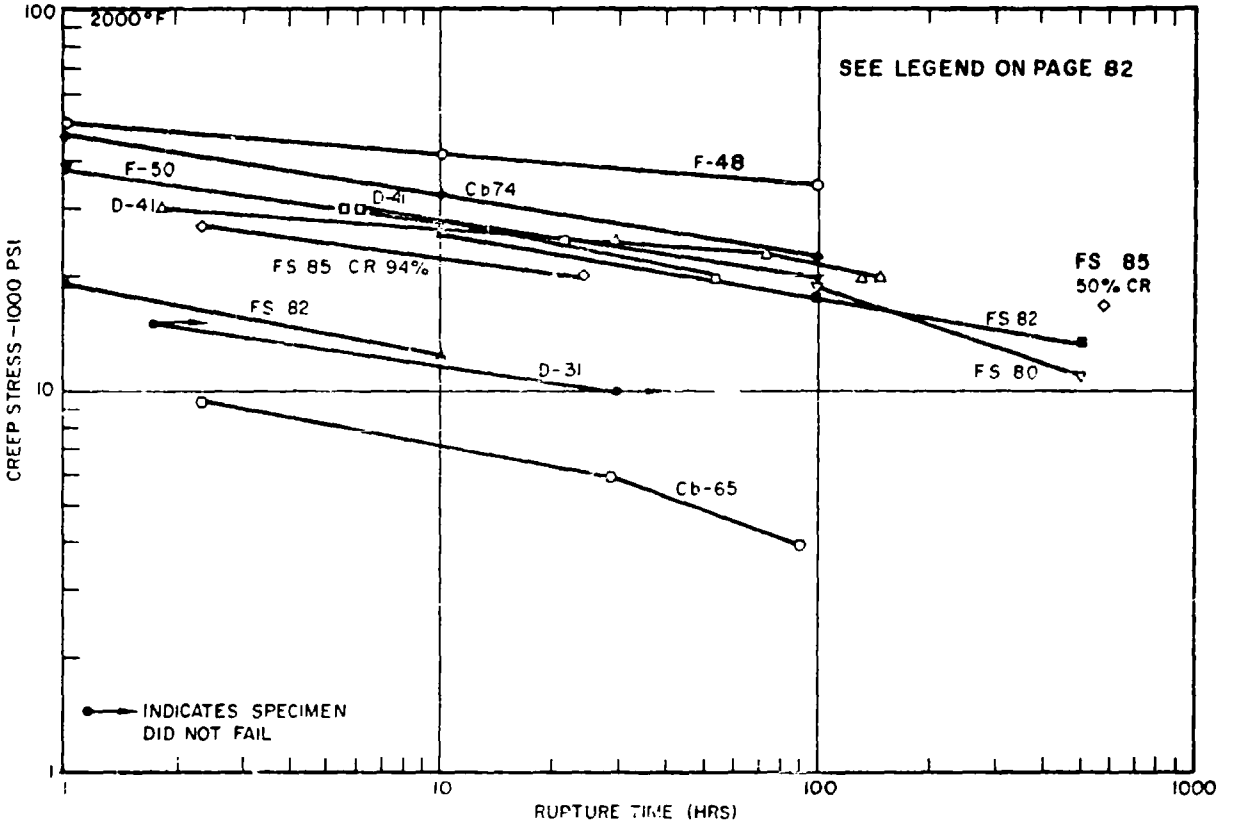

FIG. 4.19

CREEP STRESS VERSUS RUPTURE TIME FOR
SELECTED COLUMBIUM ALLOYS AT 2000° F

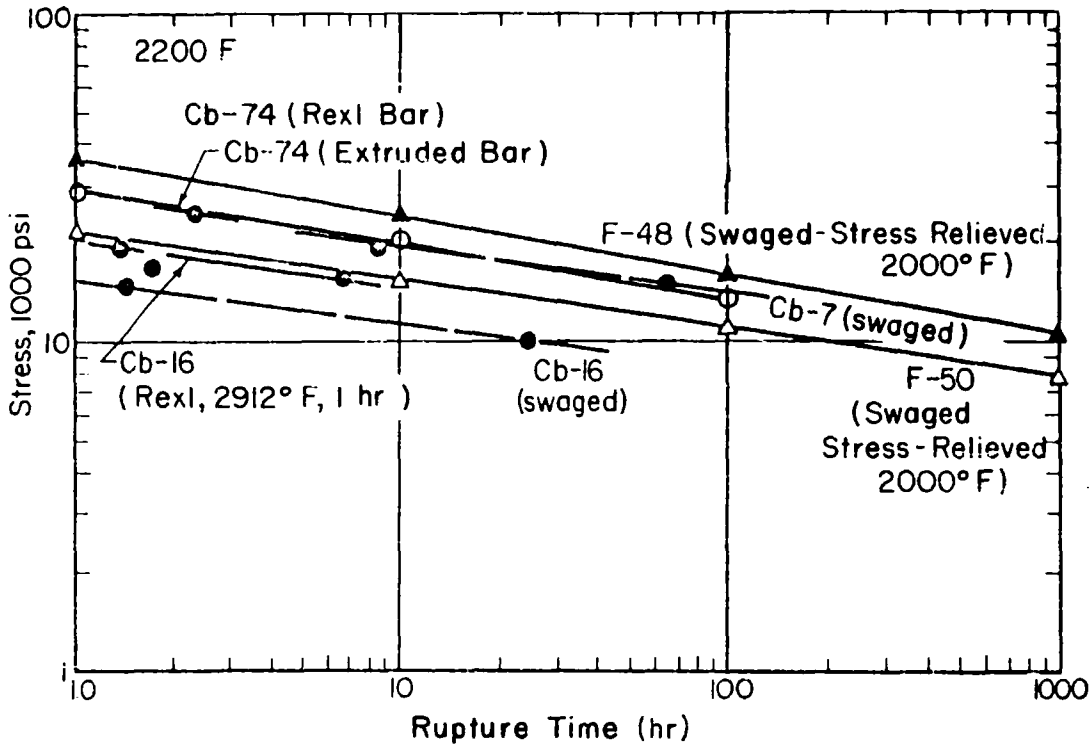

FIG. 4.20

CREEP STRESS VS RUPTURE TIME FOR SELECTED COLUMBIUM ALLOYS AT 2200° F[2,28]

observations made in unpublished work. Improvement in elevated temperature, strength by recrystallization is accompanied, however, by a reduction in the low temperature ductility.

Recent data from the work of McKinsey, et al.[28] has been added to Figs. 4.19 and 4.20 to show the comparison between Cb-74 and F-48 in more detail. The Cb-74 alloy is shown to have rupture strength superior to all alloys except F-48 at both temperatures. F-48 shows a 100-hour rupture strength advantage of 12,500 psi and a 1-hour rupture strength advantage of only 3,000 psi at 2000°F. The advantage of F-48 for the same two strength comparisons are shown to be approximately 3,000 and 6,500 psi at 2200°F. The F-48 material data on the two figures are from stress relieved bar material, whereas the Cb-74 data are from recrystallized bar material as indicated in the legend of Fig. 4.19. The Cb-74 data were obtained from interpolation of data from five tests at each temperature and are shown to agree well with the one point shown from earlier work reported by Bacon, et al.[2]

The stress rupture data presented are from tests on experimental lots of material and the reader must be aware that the results should not be used for design criteria. Use of the data for comparison of the alloys may also be misleading as the chemical and metallurgical state of the test specimens as well as the test conditions exert a strong influence on measured properties.

Fabrication of Columbium Alloys

Three Air Force contracts support large efforts to determine the manufacturing methods for production of forgings[2], sheet,[2] and extrusions[4]. Considerable privately sponsored effort is also being expended. Until results of these programs have been reported in summary form, a description of the fabricability of attractive columbium alloys would not add to judgements possible from consideration of the tensile and creep data previously discussed.

OXIDATION PROPERTIES

Oxidation of Columbium

The oxidation behaviour of columbium at elevated temperatures was reviewed in the original SRI report[1]. The absorption of oxygen into the metal and the build-up of a non-protective, spalling type oxide layer compounds the difficulty of comparing the oxidation rate of columbium to other metals by the normal criteria of weight gain, scale thickness, or weight loss. A discussion of the oxidation behavior of the pure metal would serve no purpose here except to re-emphasize the fact that columbium requires protection when used at elevated temperatures in an oxidizing environment. However, since the oxide of columbium is not volatile and has a relatively high melting point, alloying is effective in reducing penetration of oxygen into the substrate and decreasing the spalling tendency of the oxides, and shows promise for increasing the

utility of Cb for elevated temperature service. Although coatings will undoubtedly be required for long time service, their performance is enhanced when used over a substrate with improved oxidation resistance.

Oxidation of Columbium Alloys

A recent survey[2] by Crucible Steel Company in conjunction with Union Carbide Metals Company includes the oxidation behavior of a number of advanced columbium alloys. The results are summarized in this report.

Terms used in the presentation are defined as follows:

(1) Metal Penetration: depth of gaseous impurity, O and/or N, penetration into the metal below the oxide-metal interface as measured by microhardness traverse on cross section or by observation of birefringent effects on etched metallographic cross sections.

(2) Metal Loss: Metal converted to oxide as measured by removal of the oxide layer and comparing the pre- and post-oxidation weight.

A comparison of alloys initially chosen for their strength and fabricability (Figs. 4.21 and 4.22) are compared on the basis of metal loss and contamination rates from 1800 – 2400°F (982-1315°C) and on the degree of scaling and contamination during oxidation at 2200°F. The Cb-7 alloy (28 W-7 Ti) appeared to resist impurity penetration better than the other alloys and showed about a 100-fold improvement over unalloyed columbium at 2200°F. On the other hand, Cb-16 (20W-10Ti- 3V) appeared to resist scaling better than the other alloys. The three best alloys in each comparison contain combinations of W, and Ti. Strength advantages of some of the other alloys over the oxidation resistant compositions places their potential usefulness over that of the most oxidation resistant alloys, especially since coatings or environment changes must be considered for even the most oxidation resistant systems for long-time or cyclic use at elevated temperatures.

Coatings for Oxidation Protection of Columbium Alloys

The potential benefits of two experimental coatings are indicated in Table 4.9. These coating systems are proprietary. The Union Carbide coating was evaluated on unalloyed Cb but the base material used in the GE tests was not specified. Also, the criterion used to designate "failure" was not specified.

Many other coating systems are under study by both alloy developers and coating manufacturers or applicators. A DMIC report in preparation, reviewing the current status of coatings for refractory metals will appear soon.

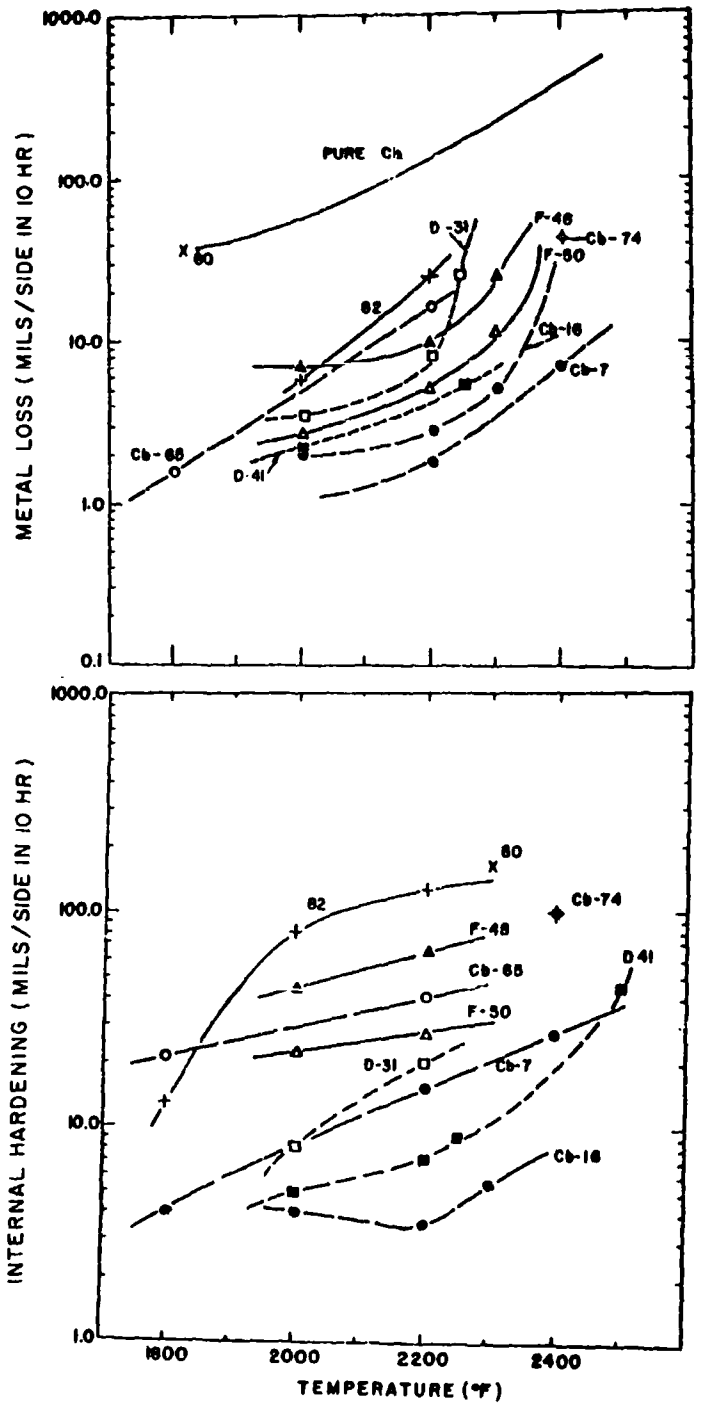

FIG. 4.21

METAL LOSS AND INTERNAL HARDENING FOR VARIOUS COLUMBIUM ALLOYS AFTER TEN HOURS EXPOSURE IN AIR UP TO 2400° F[2]

Table 4.9

RESULTS OF EVALUATION TESTS UP TO 2700°F
ON TWO EXPERIMENTAL COATINGS FOR COLUMBIUM

Thickness	Propriatory Coating General Electric Flight Propulsion Laboratory (7 to 9 mils)	Duplex Coating* Union Carbide Metals Co. (4) (7 to 9 mils)
Life to failure 2100°F**	–	1000 hours
Life to failure 2200°F**	500 hours	800 hours
Life to failure 2500°F**	100 hours	–
Life to failure 2730°F**	–	10 to 80 hours
Resistance to thermal shock	500 cycles 2300-1000°F at 0.5 cycles/hr. No failure	30 water quenches from 2100°F before failure
Behavior under stress	Good	Capable of withstanding creep rates of 0.1/in./in./hr. for hundreds of hours as low as 2000°F(***)
Resistance to Cont-tamination	–	No contamination of pure columbium after 1000 hr. at 2100 or 800 hr. at 2300°F
Self-healing properties	30 mil hole, no catastrophic failure after 45 hr. 2300°F	30 mil hole, no failure after 140 hr. 2100°F

* All data on "endless" cylindrical specimens of unalloyed columbium.
** Under static exposure in air.
*** Specified creep rate or creep time should be verified.

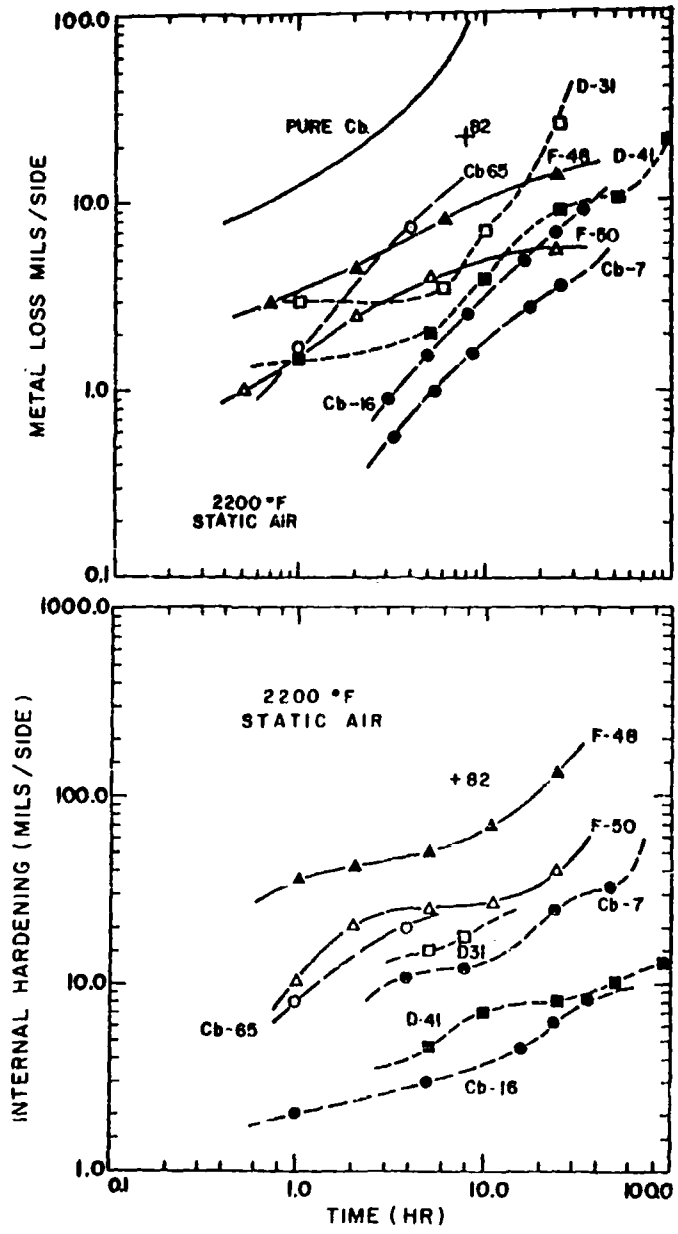

FIG. 4.22

METAL LOSS AND INTERNAL HARDENING FOR VARIOUS COLUMBIUM ALLOYS AS A FUNCTION OF TIME IN AIR AT 2200° F[2]

THERMAL PROPERTIES

Thermal Conductivity

Available thermal conductivity data for columbium and the D-31 alloy are presented in Fig. 4.23. The data of Tottle[41] was shown in the original SRI report[1] and is reproduced here for comparison. Tottle's data was obtained from longitudinal heat transfer studies on cylindrical rod, whereas the data of Fieldhouse, et al.,[42] was produced from radial heat transfer studies on stacked flat discs. The temperatures recorded are the mean values between the hot and cold surfaces at each temperature interval used for measurement. No explanation of the disagreement in the two sets of data could be made from the reported experimental material or technique. No additional experimental thermal conductivity data were found for Cb alloys.

Thermal Expansion

The thermal expansion of Cb and the D-31 Cb alloy are shown in Fig. 4.24 from determinations made by four different investigators. The data of Tottle[41] is included for comparison with the more recent data. The data for Cb from different investigators agree well at temperatures where comparison is possible with the exception of the deviation shown for data of Fieldhouse, et al.,[42] between 2000 and 2800°F. The linear thermal expansion of alloy D-31 was found to be nearly identical to that for unalloyed Cb. No additional data for Cb alloys was found.

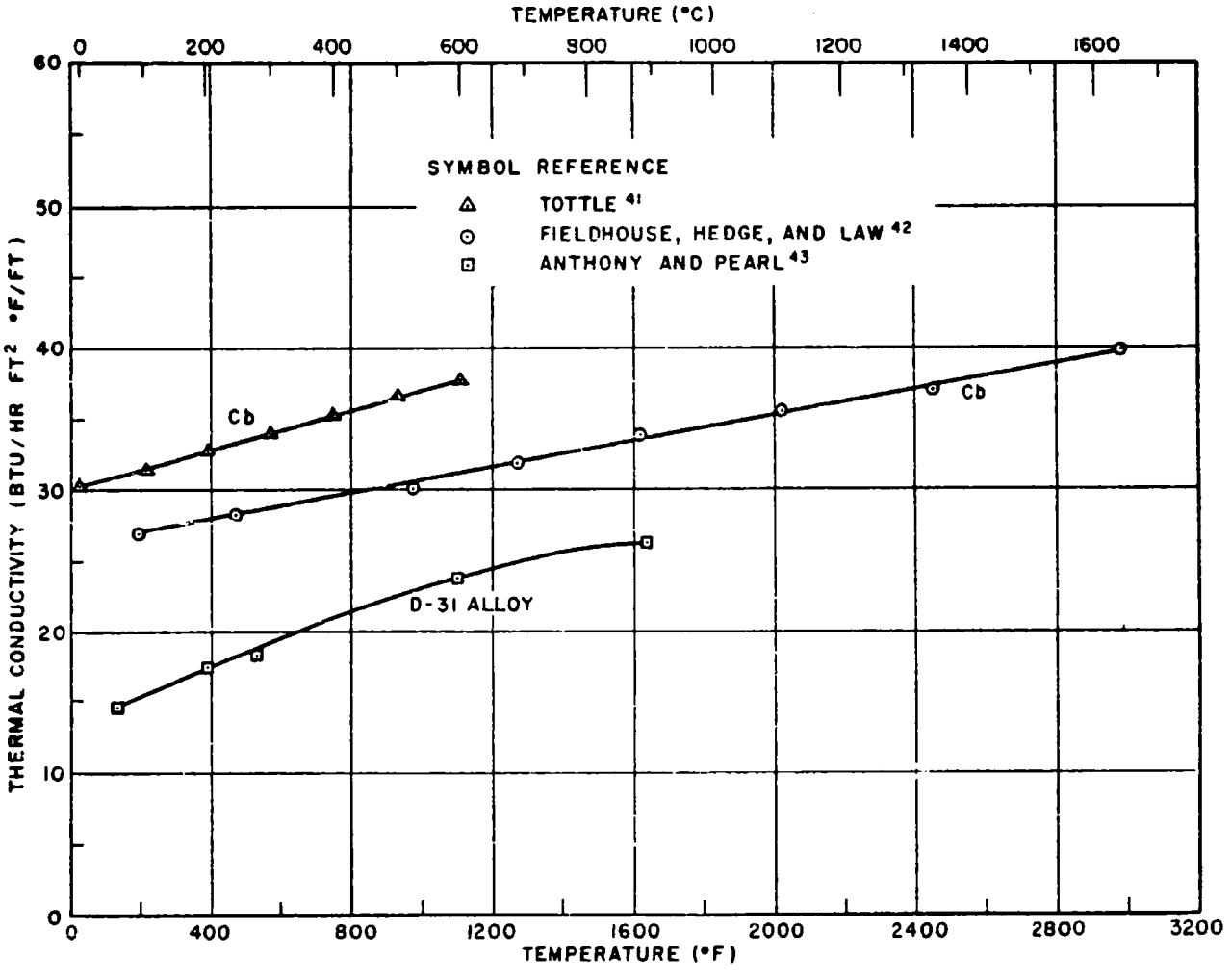

FIG. 4.23

THERMAL CONDUCTIVITY OF COLUMBIUM AND D-31 ALLOY
FROM ROOM TEMPERATURE TO 3000° F

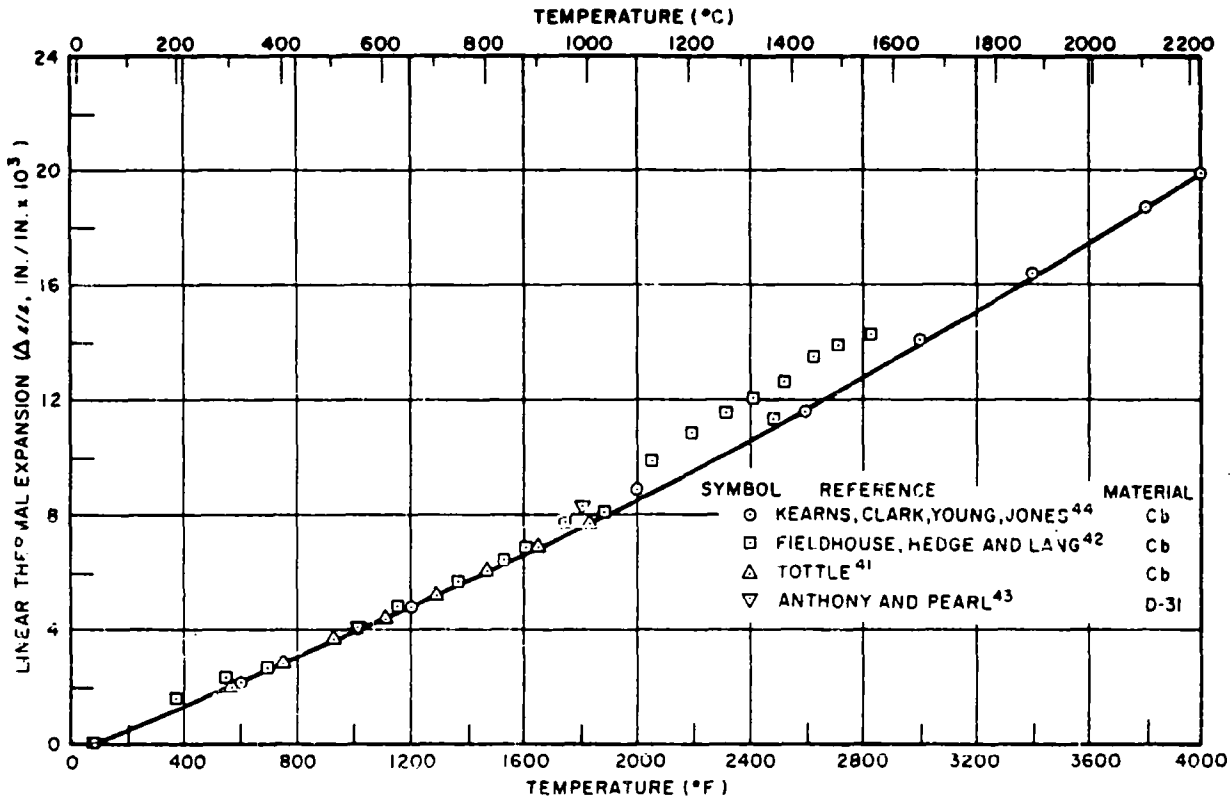

FIG. 4.24

THERMAL EXPANSION OF COLUMBIUM AND D-31 ALLOY
FROM ROOM TEMPERATURE TO 4000° F

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SECTION 5

MOLYBDENUM

INTRODUCTION

Properties which make molybdenum attractive for elevated temperature applications may be listed as follows:

- High melting point, 2610°C (4730°F)
- Low density, 10.22 g/cc (0.369 lb/cu in.), below Ta, W and Re
- High elastic modulus, second only to W and Re
- Excellent strength-to-density ratio at elevated temperatures with small alloy additions
- High thermal and electrical conductivity and low thermal expansion

In addition to these properties, the relative abundance, and highly developed technology of Mo are also in its favor.

The oxidation behavior of Mo, however, is a serious disadvantage for use at elevated temperatures. Above 500°C (932°F), MoO_3 begins to sublime and at 600°C (1110°F), the volatilization is significant. The existence of molten MoO_3 at temperatures above about 800°C leads to catastrophic oxidation in ordinary atmospheres. Another disadvantage is the low temperature ductility of Mo which is poor compared with many high strength steels and the three refractory metals with good ductility (Ta, Cb, and V).

Cladding and/or coating systems are being developed which show promise to partially overcome the first disadvantage, and improved consolidation and fabrication processes have been reported to improve the low temperature ductility.

The excellent retention of strength at elevated temperatures exhibited by Mo and its alloys has led to their use in the rocket, missile, and spacecraft industries.

The production, properties, and uses of molybdenum have been described by Archer in the 2nd Edition of the "Rare Metals Handbook" and by several authors in the ASM book[1] "The Metal Molybdenum." The recent DMIC Report[3], which was used as a primary reference for this section, reviews the latest reported mechanical

property and oxidation data for Mo and its more attractive alloys. The DMIC review serves as a good reference on the physical properties of Mo and Mo alloys, which are not within the intended scope of this compilation.

MECHANICAL PROPERTIES

Tensile properties of molybdenum have been reported in greater quantity than for any of the other refractory metals. The availability of molybdenum and its attractive elevated temperature properties have stimulated investigations, during the last twelve years, to improve and utilize its mechanical properties. Since these properties are usually sensitive to purity and processing history of the material, and testing conditions such as specimen configuration, strain rate, and stress system, reported tensile properties apply only for a given material tested under specified conditions.

Tensile Properties of Molybdenum

The modulus of elasticity of molybdenum at temperatures from 20 to 2600°C (70 to 4700°F) is presented in Fig. 5.1 as determined by five investigators. The values shown near room temperature are in good agreement, but above 800°C the data of different investigators disagree by as much as a factor of 4 from low to high. Koster[4] determined the effect of temperature on the modulus of Ta and W, and the curves were shown to agree well with results reported by other investigators for those metals. No material or test conditions were specified by Koster. The dynamic data shown by Freeman and Briggs[5] and Brown and Armstrong[6] indicate a decrease of modulus with increasing temperature similar to Koster's data and the values agree well at equal temperatures. The static tests by Barr and Semchyshen[7] were conducted at a slow and slightly variable strain rate, ~0.005 per min., and the authors suggest that slight variations in strain rate may have had a measurable effect on the modulus measurement. The data from duplicate tests at all but 2400°F gave almost identical values but the slow strain rate at elevated temperatures most likely allowed plastic strain to occur and resulted in low apparent modulus values. The three data points on the curve by Preston, Roe and Kattus[8] at 1650, 2070, and 2204°C were average values of 14, 12, and 7 tests, respectively. The modulus values varied from 7.2 to 29.0, 2.43 to 6.2, and 0.15 to 0.34 x 10^6 psi at the three respective temperatures, which is indicative of the difficulty inherent in modulus determination using static methods in the temperature range where appreciable plastic strain occurs. The stress strain curves used by Glazier, et al.[9] for modulus determinations were non-linear in the "elastic" region and judgment of the best fit between the modulus line and the data points allowed for doubt in the chosen modulus value.

Tentative specifications are shown in Table 5.1 for the chemical composition of molybdenum forging, sheet, rod, wire and bar materials as proposed by ASTM[10]. The limits of purity were established on the basis of compositions attained in commercial production. Improved purity has resulted from pilot production of tin reduced MoS and laboratory production of calcium reduced and electron beam consolidated material. These investigations,[11,12] however, have not produced sufficient material to establish practical purity limits.

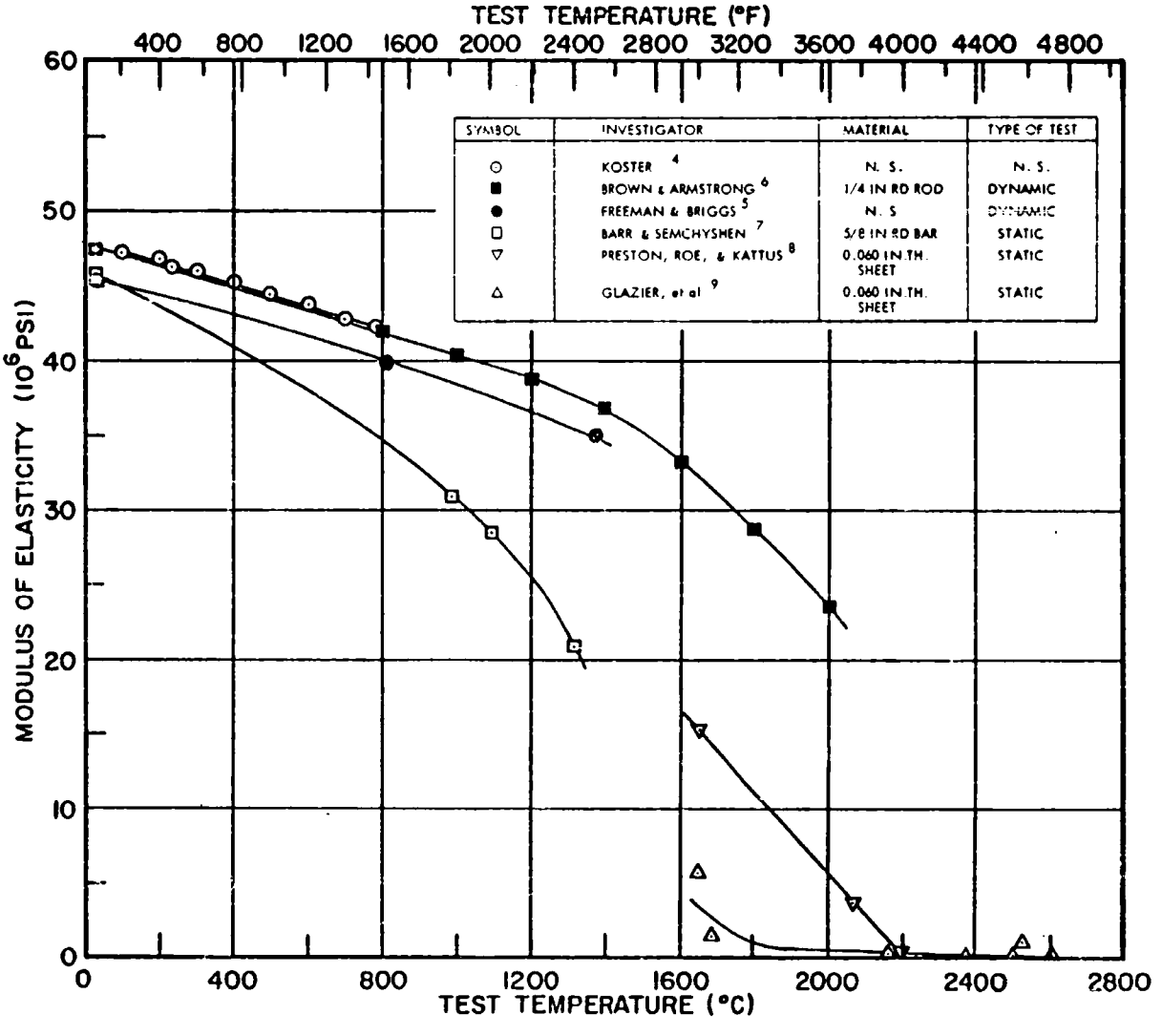


FIG. 5.1

MODULUS OF ELASTICITY OF MOLYBDENUM VERSUS TEMPERATURE

Table 5.1

ASTM TENTATIVE CHEMICAL COMPOSITION
OF COMMERCIAL MOLYBDENUM[10]

ELEMENT	ARC-CAST Mo (percent	POWDER METALLURGY Mo (percent)
C	0.010-0.040	0.010 max.
$O_{,max}$	0.0030	0.0070
$N_{,max}$	0.0010	0.0020
Fe, max.	0.020	0.020
Ni, max	0.010	0.010
Ti	–	–
Mo, (By Difference)	99.90	99.90

The minimum or range of tensile properties for rod, bar, wire and sheet molybdenum suggested in the ASTM tentative specification[10] are listed in Table 5.2. The properties specified are to be determined from test specimens produced and tested in accordance with ASTM tentative test procedures E-8 and E151-597 using a strain rate of 0.002-0.005 per min. through 0.6 percent offset and 0.02 to 0.05 per min. to fracture. No mechanical property specifications have been issued for forged material because of the many variations in size and processing techniques.

Room temperature tensile properties of commercially available rod and sheet are presented in Table 5.3 from the report by Houck[3]. The reported properties meet the requirements shown in Table 5.2 with the exception that the transverse properties of recrystallized sheet are slightly below the minimum requirements. The results show excellent ductility compared with the minimum specifications. It should be noted also that the strain rates used were slightly below the range proposed in the ASTM tentative specifications. The stress-relief and recrystallization treatments given the 5/8 in. rod material consisted of 1 hr heating at 1800 and 2150° F, respectively. Final reduction of the bar or sheet or thermal treatment of the sheet specimens were not specified in the test data presented[2]. The recrystallization treatment reduced the yield and ultimate strength of the rod material about 1/3 the value of the wrought or stress-relieved specimens with no appreciable change in the elongation.

The lower limit of elongation of the sheet specimens tested in the transverse direction is below the values for tests in the parallel direction. The decreased ductility in the transverse direction is associated with the directionality of tensile properties of wrought and recrystallized molybdenum sheet. Houck[3] has reviewed the factors responsible for mechanical property variations, and a summary will be presented in the following subsections.

Elevated Temperature Tensile Properties

A summary of the elevated temperature tensile properties of unalloyed Mo as prepared by Bectold, Wessel, and France[13] is reproduced in Fig. 5.2. Known material and test conditions related to these data are presented in Table 5.4. The data indicate the magnitude of variation in tensile property values from tests conducted under several conditions on materials of varying purity and thermal-mechanical history. Both strength and ductility properties show the greatest variation near room temperature where a slight increase in temperature produces a large decrease in strength and correspondingly large increase in ductility. This is, of course, due to variations in the ductile-brittle transition temperature as related to variations in material and test conditions.

The compression test curve indicates the same yield strength-temperature dependence as do the tensile yield strength curves. The lower strength exhibited by the compression curve below room temperature may be attributed to the lower carbon content. Alers, Armstrong, and Bechtold[14] observed that material of the purity used for the compression tests exhibited a sharp yield point only below -150° C, whereas less pure material yielded abruptly below 400° C. The less pure material, however, had a finer grain size (1000 grains per square mm).

Table 5.2

ASTM TENTATIVE SPECIFICATIONS FOR MOLYBDENUM ROD, BAR, WIRE AND SHEET PRODUCTS[10]

Diameter (in.)	Tensile Strength Minimum or Range (1000 psi)	Minimum Yield Strength 0.2% Offset (1000 psi)	Minimum Elongation in 2 in. (percent)	VHN (10 Kg)	Bend Test Radius (c)
	STRESS RELIEVED BAR, ROD, OR WIRE				
3/16 - 7/8	90	75	18	230-280	
7/8 - 1-1/8	85	70	15	225-270	
1-1/8 - 1-7/8	75	65	10	215-260	
1-7/8 - 2-7/8	70	60	10	210-250	
2-7/8 - 3-1/2	65	55	10	205-240	
	RECRYSTALLIZED BAR, ROD, OR WIRE				
2	60	35	20	200 Max.	
2 - 3-1/2	55	25	20	200 Max.	
		SHEET			
A[a]	60-85	45	5[b] 10		-[d]
B	85-110	70	5 10		T
C	110-135	90	3 5		T
D	135-160	110	2 5		T

[a] Denotes Temper as determined by post-working thermal treatment, Treatments ABCD are not specified.

[b] Low and high values are for sheet below and above 0.020 in. thick respectively.

[c] For sheet 0.065 in. thick and under.

[d] Recrystallized or lightly worked material not recommended for room temperature forming.

Table 5.3

ROOM TEMPERATURE TENSILE PROPERTIES
OF COMMERCIALLY AVAILABLE MOLYBDENUM [3]

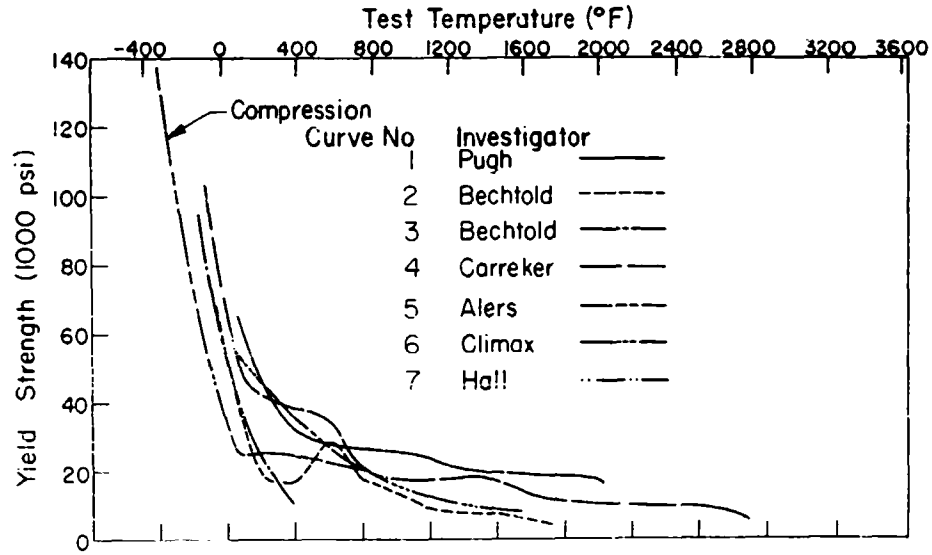
Thermal Treatment	Tensile Strength (psi)	Yield Strength (psi)	Elongation (per cent)	Reduction of Area (per cent)
5/8-Inch Rod				
As rolled	102,000	78,800	40	61.1
Stress relieved	97,200	82,900	42	69
Recrystallized	68,200	55,900[a]	42	37.8
1/12-Inch Sheet				
Stress relieved[b]	91,300-105,500	79,700-90,800[a]	20-27	–
Stress relieved[c]	91,500-106,200	82,700-95,800[a]	16-24	–
Recrystallized[b]	62,200-66,500	45,500-61,300[a]	40-58	–
Recrystallized[c]	58,200-66,000	43,700-58,500[a]	16-58	–

[a] Yield strength based on drop in load, others on 0.1 percent offset.

[b] Parallel to rolling direction.

[c] Transverse to rolling direction.

[d] Strain rates, 0.005 and 0.01 per min in elastic and plastic ranges, respectively.



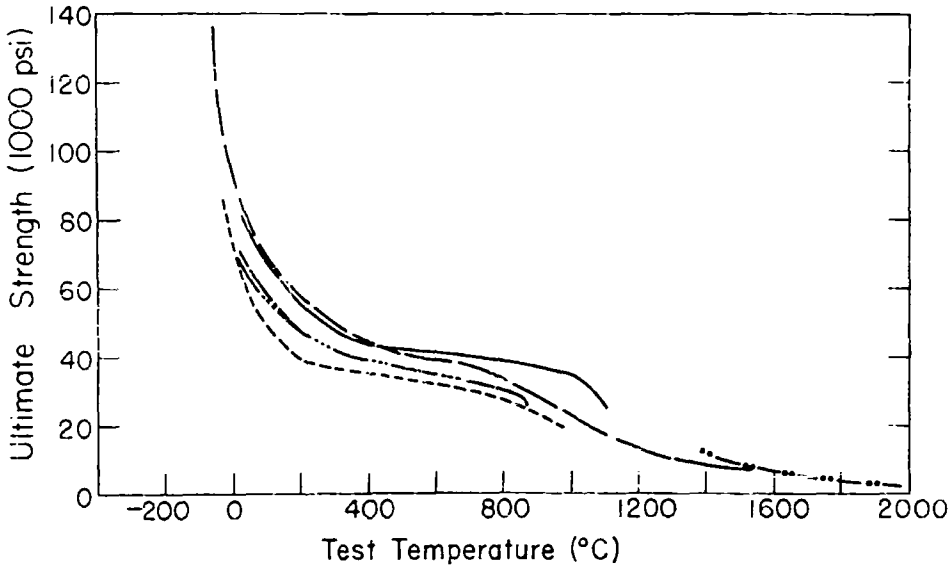


FIG. 5.2

TENSILE PROPERTIES OF RECRYSTALLIZED MOLYBDENUM AT TEMPERATURES FROM -200 TO 2000°C[3]

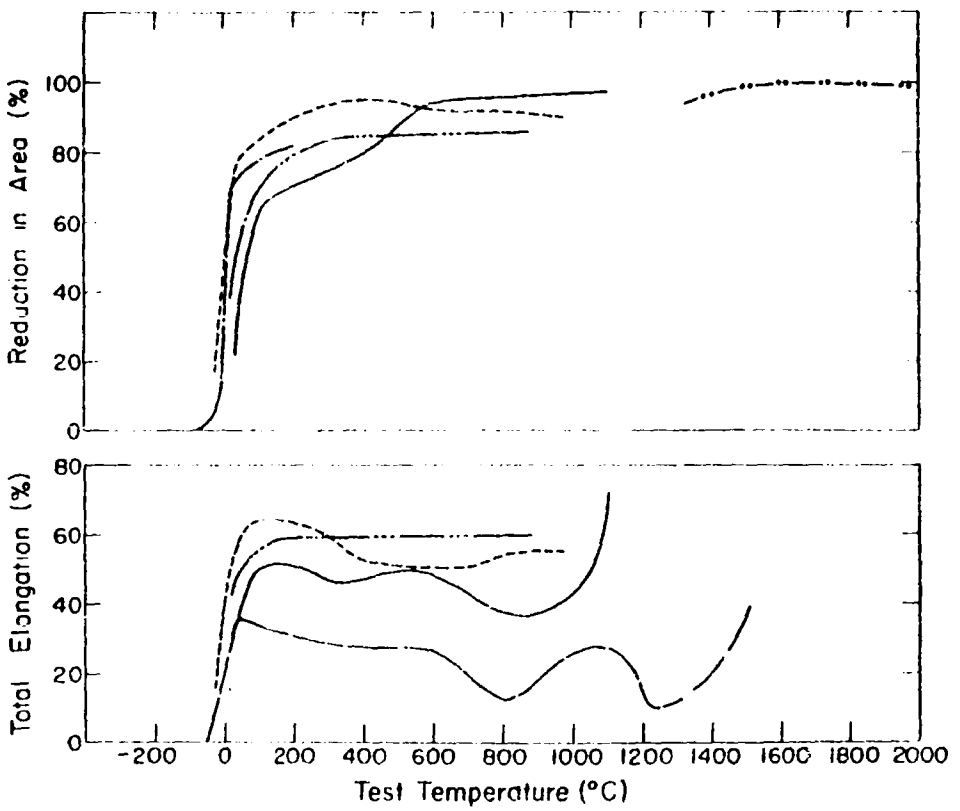

Reduction in Area (%)
100
80
60
40
20
0
Total Elongation (%)
80
60
40
20
0
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Test Temperature (°C)

FIG. 5.2

(CONT'D)

Table 5.4

MATERIAL AND TEST CONDITIONS FOR TENSILE DATA PRESENTED IN FIG. 5.2

CURVE No.	CHEMISTRY (wt. percent)				GRAIN SIZE GRAINS/mm^2	STRAIN RATE in./in./sec.	TYPE SPECIMEN	MATERIAL PREPARATION
	C	O	N	H				
1	0.05	0.003	0.001	.0003	500	3.3×10^{-3}	Round 0.160 in. Dia. (Tested in Vacuum)	Arc-Melted Recrystallized 4 hrs. at 1400° C
7	0.036	-	-	-	-	-	Round 0.250 in. Dia.	Powder-Met. Recrystallized 1/2 hr. at 2100° C in Vacuum
3	0.031	0.0002	0.0056	-	1100	2.8×10^{-4}	Round 0.252 in. Dia.	Arc-Melted Recrystallized 1/2 hr. at 1150° C
2	0.014	0.0017	0.0056	-	900	2.8×10^{-4}	Round 0.252 in. Dia.	Arc-Melted Recrystallized 1 hr. at 1150° C
5	0.0007	0.008	0.006	-	500	2.8×10^{-4}	Round 0.20 in. Dia.	Powder-Met. - Recry. 4 hrs. at 2100° C
4	0.010	0.003	-	-	2500	-	Wire 0.30 in. Dia.	Arc-Melted Recrystallized 2 hrs at 1100° C in H_2 Recrystallized 2 hrs. at 1375° C in H_2
6	Not specified by referenced author[13]							

Additional elevated temperature tensile property data are presented in Fig. 5.3 which gives comparisons between electron-beam melted and arc-cast material, sheet and bar material of commercial arc-cast quality, and strength properties between 3500 and 3700° F under two different test conditions. The curve from Pugh's investigation[15] is repeated in Fig. 5.3 for orientation with Fig. 5.2, and the data from Hall et al.[16] for comparison with that from Glazier, et al.[9] Material and test conditions for the tensile data presented in Fig. 5.3 are summarized in Table 5.5.

The electron-beam melted material is shown to have lower strength than the arc-cast specimens in the test temperature range from room temperature to about 200° F. The ductility of the E-B material is also below that of any of the arc-cast samples included in the figure. Semchyshen and Barr[17] reported the same comparison between the E-B melted material and fine grained arc-cast material tested under the same condition. The E-B melted specimens had larger grain sizes than the arc-melted material. The authors[17] also observed that E-B melting per se did not improve purity, but that a deoxidizing additive such as C was required for reduction of the oxygen content.

The commercial sheet material tested by Imgram et al.[18] evidenced larger variation of strength properties at all temperatures than did bar material produced by commercial practice. Fabrication to sheet and bar naturally require different reduction procedures; this inherent difference coupled with the difference in chemistry and recrystallization treatments shown in Table 5.5 probably account for the difference in strength at 200° F and the slight difference in transition temperatures indicated by the elongation curves.

Curves from tests on bar and sheet stock above 2500° F were obtained from specimens in the as-worked condition. Hall, Sikora and Ault[16] reported little difference in strength or ductility between recrystallized or worked material at the high test temperatures used. Tests conducted by Glazier et al.[9] employed higher strain rates than those conducted by Hall et al.[16] Glazier's sheet specimens were loaded by allowing lead shot to fall into a beaker at controlled rates. The authors[9] reported that variations in the loading rate from 5 to 295 psi per sec had little effect on the strength properties. Hall used a screw type tensile machine to test bar material and controlled the crosshead travel rate at 1/16 in. per min. The heating systems and test temperature holding times were also different in the two investigations. Glazier heated the specimen by self-resistance, held the specimen at temperature for only 5 to 10 seconds, and completed the entire test from start of heating to moment of fracture in an average time of 56 seconds, range 21 to 173 seconds. Hall heated his specimens by radiation from an inductively heated tantalum susceptor, held the specimen at temperature for 15 minutes after an average one-hr heat-up time, and loaded the specimen to fracture at a crosshead speed of 1/16 in. per min which resulted in a total loading time of between 3 and 12 minutes. Specimens from both investigations showed recrystallized structure after the tensile tests. Total elongation measurements on the resistively heated samples were difficult to obtain because of melting of the fracture surfaces at the instant of fracture, and the values reported must be judged with knowledge of the temperature gradient inherent in this type of heating especially after initiation of necking.

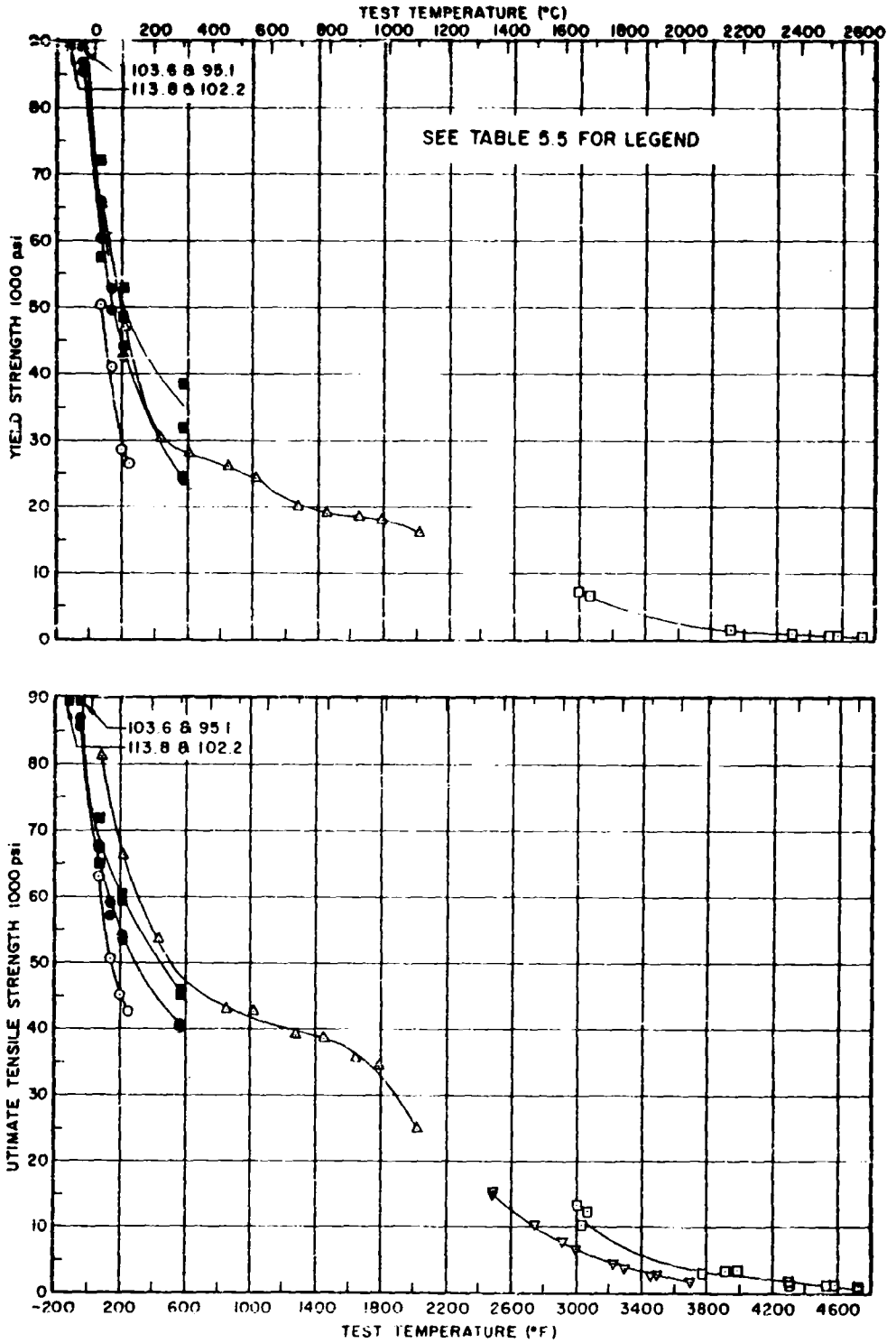


FIG. 5.3

TENSILE PROPERTIES OF WROUGHT AND RECRYSTALLIZED MOLYBDENUM OF TEMPERATURES FROM -100 TO 4700° F (-75 to 2600° C)

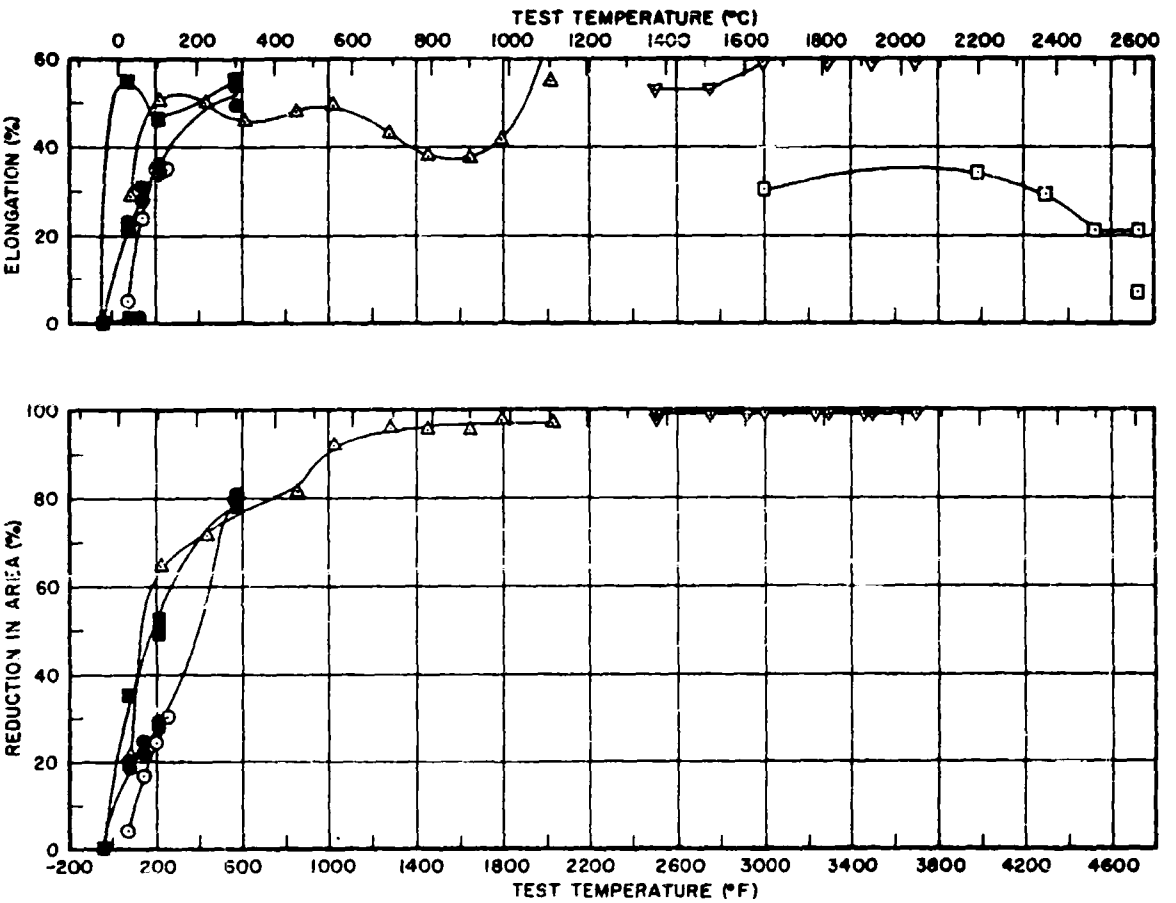

TEST TEMPERATURE (°C)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
ELONGATION (%)
60
40
20
0
REDUCTION IN AREA (%)
100
80
60
40
20
0
-200
200
600
1000
1400
1800
2200
2600
3000
3400
3800
4200
4600
TEST TEMPERATURE (°F)

FIG. 5.3

(CONT'D)

Table 5.5

MATERIAL AND TEST CONDITIONS FOR DATA PRESENTED IN FIG. 5.3

SYMBOL	REFERENCE	IMPURITY (Wt. Percent)					GRAIN SIZE ($Grain\text{-}mm^2$)	STRAIN RATE (min^{-1})	SPECIMEN GAGE SIZE (in.)	MATERIAL PREPARATION
		C	O	N	H	Metallic				
○	Semchyshen and Barr[17]	0.003	0.0002	-	0.00003	0.009[a] Ti	12	5×10^{-4}	1.4 dia. x 1 Lg	Electron Beam Melted Roll at 2000° F to 1.2 in. sq. Recl 2100° F (1 Hr.)
□	Glasier, et. al.[9]	0.04[b]	0.035[b]	-	-	Fe 0.19	N.S.	(d)	0.06th. x 0.250 wide x 2.-. Lg.	Arc-cast Mat. Rolled to Size
△	Pugh[13]	0.04	0.003	0.001	0.0003	-	900	2×10^{-1}	0.160 dia. x 1 Lg.	Arc Cast Extruded 3000° F Swaged 1830° F 38% Total Reduction Recrystallized 4 Hr. at 2550° F
▽	Hall, Sikora and Ault[16]	0.076[c]	-	-	-	-	N.S.	1.16-in.[e]	0.250 dia. x 1 or 1-1/2 Lg	Arc-cast Extruded at 2200° F Rolled to 1.2-in. Dia. at 2200° F
●	Imgram, et. al.[15]	0.092	0.0022	0.001	6×10^{-5}	17 Metallic 0.251	970	0.02 in.[e]	0.212 dia. x 1	Arc-cast Swaged at 1110° F Recrystallized 1 Hr. 2440° F
■	Imgram, et. al.[15]	0.026	0.0009	0.021	6×10^{-5}	17 Metallic 0.151	400	0.02 in.	0.065th x 0.250 Wide x 1 Lg.	Arc-cast Rolled at 1110° F Recrystallized 15 min. 2350° F

NOTES: N.S - Not Specified
(a) - Limit of Detection
(b) - Maximum
(c) - Nominal
(d) - Loading Rate Varied from 5 to 295 psi per second
(e) - Cross-Head Rate

Although ultimate strength values are shown to vary by a factor of two at some test temperatures, the absolute differences are small at the high test temperatures and both types of tests simulate environments in which molybdenum might be used.

Effect of Dissolved Gases

Studies concerning the effect of dissolved gases on the mechanical properties of molybdenum have been directed toward the ductility properties. Therefore the comments included in this section are pertinent also to the section on ductile-brittle behavior. The summaries by Spacil and Wulff[19] and Bechtold,Wessel,and France[13] adequately describe the difficulty in separating the effects of individual gases from each other as well as from those of grain size and strain hardening. The summaries agree that contamination by O, N, and C lower ductility and fracture stress of unalloyed recrystallized Mo, that the effects are not additive, and that the deleterious effects can be partially overcome by proper thermal-mechanical treatments and/or alloying which reduce grain size.

Ductile-Brittle Behavior of Molybdenum

The ductile-to-brittle transition temperature of molybdenum is dependent on impurities, processing, and testing conditions. A value given without specification of these variables is meaningless. For example, the temperature at which molybdenum goes through a transition from ductile to brittle behavior may vary from 900 to -100° F for different combinations of purity, worked state, and test condition.

Impurity effects on the bend-transition temperature are indicated in Fig. 5.4 from the experiments of Olds & Rengstorff[20]. The data must be considered qualitative since intentional additions of one interstitial element produced changes in the content and/or effect of others. As an example, the 0.033 percent nitrogen specimens contained more oxygen (0.0015 percent) than any of the oxygen specimens and yet had a lower transition temperature than the oxygen doped material. The transition temperatures reported are the maximum temperatures at which a four-deg bend was not exceeded regardless of the number of tests conducted at those temperatures. The bend tests were made on 0.150-in. thick x 0.250-in. wide specimens supported between centers 0.625 in. apart at a loading rate of 1 in. per minute or calculated outer fiber strain rate of about 2 per minute. The specimens were machined from arc-cast ingots and tested with a ground unnotched surface. Figure 5.4 shows the relative effects of three interstitial impurities studied; oxygen is shown to be most detrimental to ductility, with nitrogen less detrimental and carbon least.

The effects of small metallic impurities has not been as well studied as the effects of non-metallic impurities. Small additions of strong deoxidizers which alter the oxide film at grain boundaries promote ductility. Only Re additions in large quantities have been reported[21] to improve low temperature ductility.

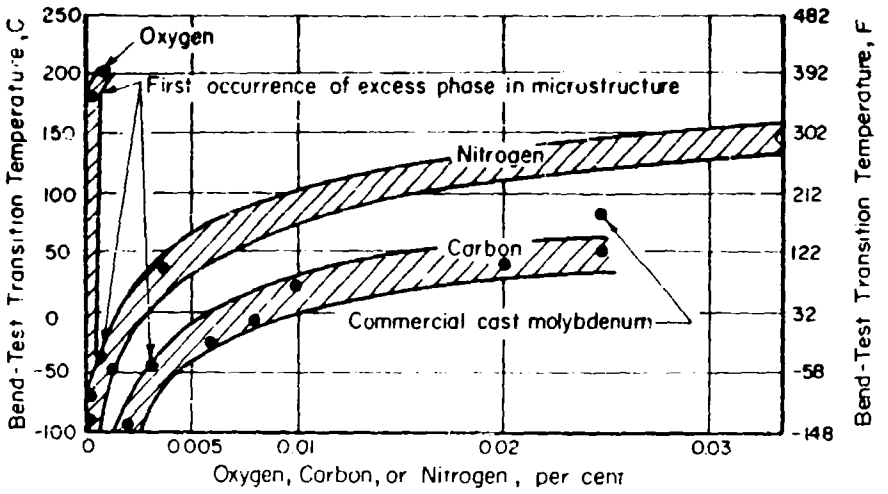


FIG. 5.4

EFFECT OF OXYGEN, CARBON, AND NITROGEN ON THE BEND TRANSITION TEMPERATURE OF MOLYBDENUM(20)

Bechtold and Wessel[22] have discussed in detail the ductile-to-brittle transition of molybdenum as affected by processing variables. They have shown that work hardening decreases the transition temperature of commercial purity Mo but that deformation up to 90 percent reduction in area has little effect on the transition temperature of fine-grained high-purity material. The grain size produced by mechanical and thermal processing procedures was suggested to be the critical parameter affecting ductile-brittle behavior. Tensile transition temperature determinations showed coarse grain material (ASTM No. 3-4) to have a broad transition temperature range considerably higher than the narrow range of smaller grain size material (ASTM Nos. 5.9 and 7.8). The temperatures at which the maximum tensile reductions in area were reduced 50 percent were 100, -15, and -25°C for the three grain sizes mentioned.

The effect of thermal treatments on the transition temperature of 1/16-in. thick commercial Mo sheet is shown in Fig. 5.5 as reported by Climax Molybdenum Co.[2]. If the transition temperature is defined as that temperature at which the material can sustain a 20° bend the reported data would show a transition temperature range for the stress-relieved material from about -25 to 105° F and for the recrystallized material

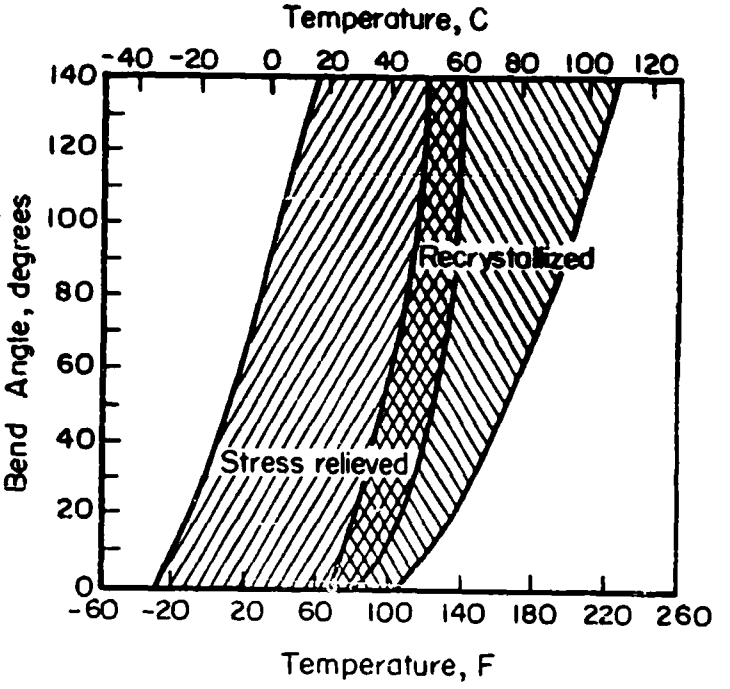


FIG. 5.5

BEND ANGLE VERSUS TEST TEMPERATURE FOR STRESS-RELIEVED AND RECRYSTALLIZED ARC-CAST MOLYBDENUM SHEET

from about 80 to 135° F. The overlap of the two ranges is associated with a critical grain size or purity which would allow fine grained recrystallized material to exhibit a lower transition temperature than wrought stress-relieved material which had experienced processing procedures less than optimum for maximum ductility. The curve indicates scatter commonly found in bend test data. Belk et al.,[23] recorded the scatter obtained in bend transition temperature data as shown in Fig. 5.6 from an investigation concerned with the change of ductility and toughness with rolling temperature. Figure 5.7 indicates the effect of different initial and final rolling temperatures on the impact strength of molybdenum over the transition temperature range. Figure 5.7 shows data from as-rolled specimens in most cases with wide transition temperature ranges, whereas data from recrystallized material shown in Fig. 5.8 indicate a narrower transition temperature range generally occurring at higher temperatures than for the as-rolled material. The maximum capacity of the impact tester used in this investigation was 10 ft.-lb.

The data presented in Fig. 5-7 were chosen to emphasize some of the controllable variables affecting the ductility of Mo rather than to present absolute values. For more complete details of experimental results, the reader is referred to the review by Houck[3]; and for theoretical considerations, to the analysis by Bechtold and Wessel[22]; and to the

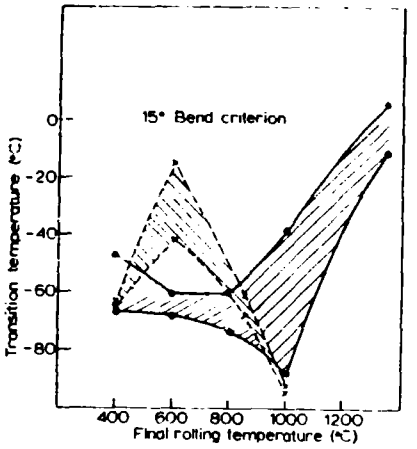


FIG. 5.6

VARIATION OF SLOW-BEND TRANSITION TEMPERATURE WITH ROLLING TEMPERATURE. X- - -X INITIALLY ROLLED 1000° C; 0- - -0 INITIALLY ROLLED 1350° C [23]

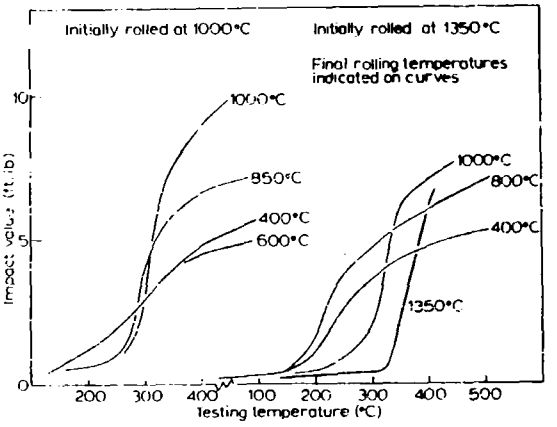


FIG. 5.7

EFFECT OF ROLLING TEMPERATURE ON V-NOTCH IMPACT STRENGTH OF AS-ROLLED MOLYBDENUM[23]

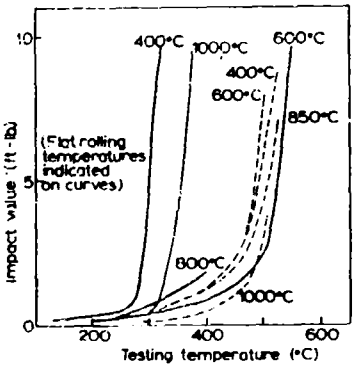


FIG. 5.8

EFFECT OF ROLLING TEMPERATURE ON THE V-NOTCH IMPACT STRENGTH OF RECRYSTALLIZED MOLYBDENUM[23]

references included in these two references. In summary, the transition from ductile to brittle behavior occurs in molybdenum near room temperature for most commercial products when subjected to average strain rate tests but may occur as high as 900° F in impure, coarse-grained, notched impact specimens or lower than -100° F in high-purity, fine-grained, polished bend specimens tested at a slow rate of deflection.

Effect of Deformation

Semchyshen, Barr, and McArdle[24] investigated the change of tensile properties at room temperature and 1800° F after reductions of 10 to 90 percent at temperatures of 2200 and 3000° F. Carbon analysis, 0.008 percent, only was reported for the 9 in. diameter arc-cast ingot but evidence of grain boundary oxides was observed in the unalloyed microstructures, indicating measurable oxygen content. The arc-cast ingot was consolidated in accordance with commercial practice and reduction of the ingot to 5/8 in. diameter bar varied from commercial practice only in that amounts of reduction were accurately varied and controlled in order to measure their effect on hardness, grain size, and tensile strength and ductility.

The cast ingot was cropped and machined to 7.3 in. diameter and extruded at 2300° F to 4-1/2 in. diameter, 2.6:1 ratio. The surface of the extrusion required no further machining except for cropping to remove the end burst. The extrusion was recrystallized at 2600° F in 1 hr. It was then rolled at 2200° F to a 2 in. diameter bar, which resulted in an 80 percent reduction. The 2 in. diameter bar was recrystallized at 2500°F in 1 hr, and rolled at 2200°F to 21/32, 11/16, 3/4, and 15/16 in. diameter resulting in 89 to 78 percent reduction in area. The intermediate size rods were all recrystallized at 2500°F in 1 hr, then finally rolled to 5/8 in. diameter which resulted in final nominal reductions of 10, 15, 30, 55, and 90 percent.

Tensile properties at room temperature and 1800° F are presented in Fig. 5.9 for material in the as-rolled condition after reductions at 2200 and 3000° F as indicated. Tensile tests were conducted in an argon-10 percent hydrogen atmosphere on specimens with 1/4 in. diameter by 1-1/4 in. long reduced sections. A one inch gage section was used for total elongation measurements, strains were recorded autographically from movement of extension arms attached to the specimen shoulders, and strain rates were 5×10^{-4} and 1×10^{-2} per min. through yielding and to failure, respectively. Yield strength is not plotted in this text although it was tabulated in the original report[24] and was shown to exhibit the same trends as the ultimate tensile strength. Each point plotted is the result of a single tensile test.

The strength at room temperature of material rolled at 3000° F is shown to be slightly higher than for bars rolled at 2200° F up to reductions of 30 percent but considerably lower for 55 to 90 percent reductions. The same observations were made by the authors using hardness as a criterion. The same relation is shown to exist for specimens tested at 1800° F. The authors[24] point out that recrystallization takes place during extreme deformation at the higher rolling temperature and results in lower strength at both room temperature and 1800° F.

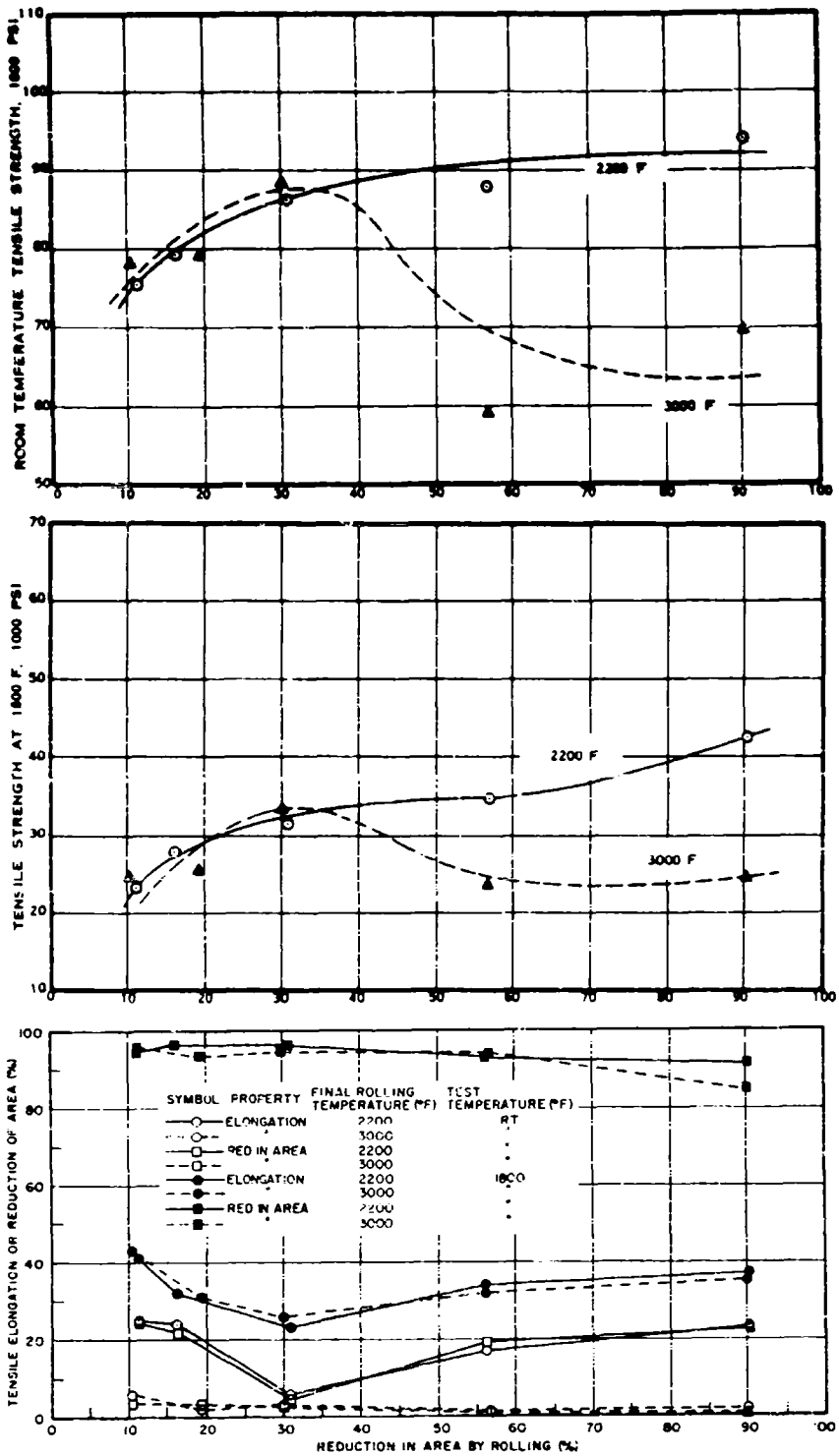


FIG. 5.9

TENSILE PROPERTIES OF AS-ROLLED MOLYBDENUM AT ROOM TEMPERATURE AND 1800°F VS AMOUNT OF REDUCTION BY ROLLING AT 2200 AND 3000°F [24]

Ductility was also found to be sensitive to processing procedure as shown in Fig. 5.9. Room temperature elongation and reduction of area both exhibit minima after 30 percent reduction at 2200° F as shown by the solid lines and open symbols. The same room temperature properties are extremely low after all reductions at 3000° F. The room temperature ductility for the nominal 10 percent reduction at either rolling temperature was found to be as good or better than for higher reduction. This last observation can also be made for the 1800° F curves although ductility is high at that testing temperature for all thermal mechanical treatments used in the investigation. A minimum in elongation at 30 percent reduction existed at the 1800° F test temperature for each rolling temperature.

The authors[24] have presented data valuable to processors and users. Additional data covering a wider working temperature range, smaller reduction increments, and including stress-relieved and recrystallized conditions would be of value.

Houck[3] cites room temperature tensile strength greater than 300,000 psi for wire drawn to 0.004 in. diameter. Bechtold[25] reported a decrease in the upper yield point from 92,000 to 53,000 psi after recrystallization of arc-cast Mo which had been rolled to 35 percent reduction at 1050 to 930° C (1930-1750° F). Hardness or bend ductility measurements only have been made in most other studies of the effect of cold work. The above discussion emphasizes that hardness or bend measurements do not present a complete picture of the effects of thermal mechanical treatments on the properties of molybdenum.

Recrystallization Behavior

A number of studies have been directed toward raising the recrystallization temperature and thus increasing the stability and strength of the worked structure at elevated temperatures. The recrystallization temperature is, of course, time dependent and is sensitive to purity, amount and temperature of working, and concurrent straining during annealing.

Semchyshen, Barr and McArdle[24] reported the minimum temperature for complete metallographically observed recrystallization in one hour of Mo and three commercial alloys after warm working at 2200 and 3000° F to nominal reductions in thickness of 10, 15, 30, 55, and 90 percent. Details of the material processing were presented in the ductile-brittle behavior section. The results are summarized in Figs. 5.10, 5.11, and 5.12.

The lower curve of Fig. 5.10 gives the recrystallization temperature of unalloyed Mo as a function of reductions of 10 to 90 percent by rolling at 2200° F. The addition of 0.50 percent Ti or 0.059 percent Zr increased the recrystallization temperature of Mo as indicated by curves 2 and 3 in Fig. 5.10. The effect of either of these additions was found to be approximately equal up to about a 60 percent reduction. For greater reductions, the 0.059 percent Zr addition appeared to be more effective than the 0.50 percent Ti. Both of the above additions together resulted in an appreciably higher recrystallization temperature as indicated by the upper curve. In fact, the increase over the unalloyed Mo was found to be considerably greater than a simple additive effect of the two separate additions over most of the rolling range studied.

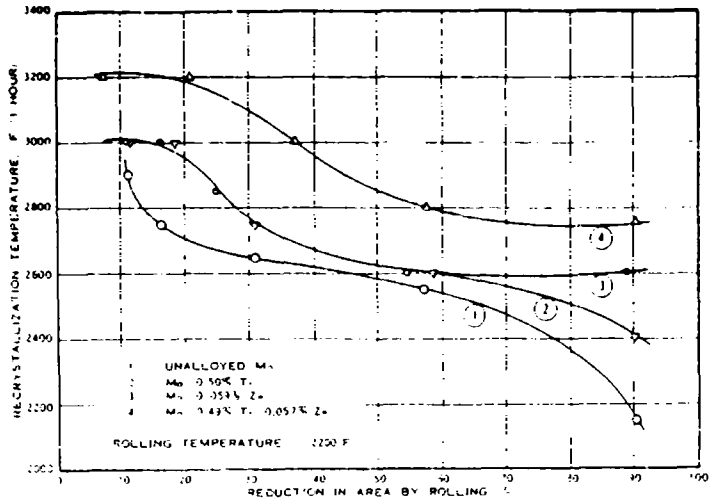


FIG. 5.10

RECRYSTALLIZATION TEMPERATURES VERSUS REDUCTION FOR INDICATED MATERIALS ROLLED TO 5/8-IN. ROUND BARS AT 2200° F

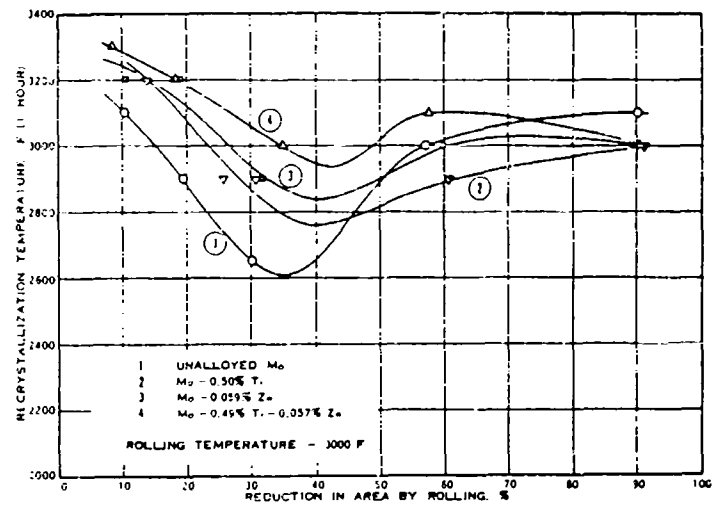


FIG. 5.11

RECRYSTALLIZATION TEMPERATURES VERSUS REDUCTION FOR INDICATED MATERIALS ROLLED TO 5/8-IN. ROUND BARS AT 3000° F[24]

SYMBOL	MATERIAL	FINAL ROLLING TEMPERATURE, °F
—⊙—	UNALLOYED Mo	2200
- -●- -	UNALLOYED Mo	3000
—□—	Mo-0.5 Ti	2200
- -■- -	Mo-0.5 Ti	3000
—△—	Mo-0.059 Zr	2200
- -▲- -	Mo-0.059 Zr	3000
—⊙—	Mo-0.5 Ti-0.057 Zr	2200
- -●- -	Mo-0.5 Ti-0.057 Zr	3000

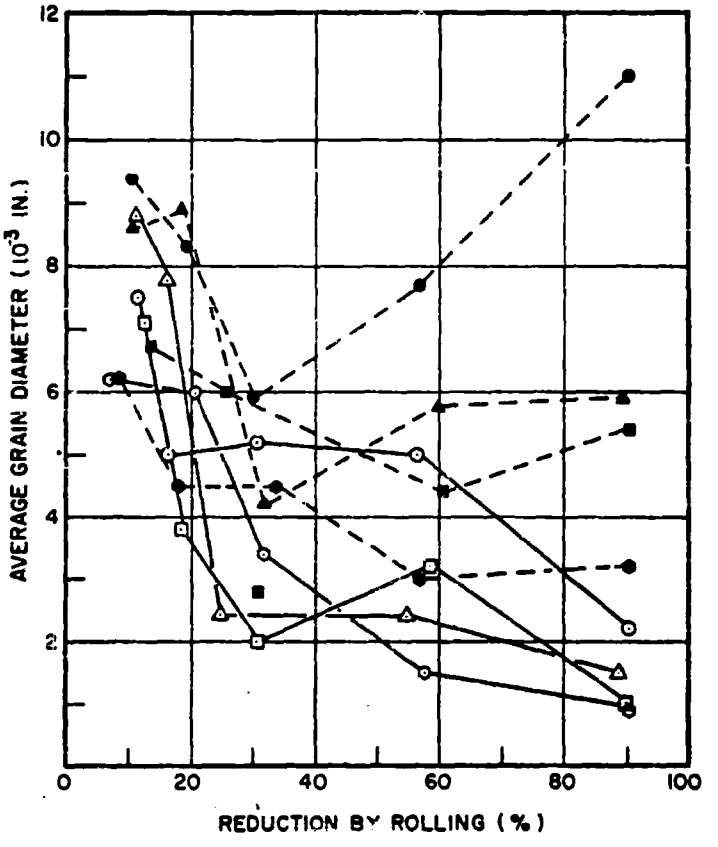


FIG. 5.12

GRAIN SIZE OF MOLYBDENUM AND THREE ALLOYS AS AFFECTED BY AMOUNT OF DEFORMATION AT 2200 AND 3000° F[24]

The effect of rolling at 3000° F on the recrystallization temperature of the same materials is given in Fig. 5.11. In general, the effect of the higher rolling temperature was to increase the recrystallization temperature of the unalloyed and alloyed materials. This statement holds true with two exceptions: (1) unalloyed Mo between about 30 to 40 percent reduction; and (2) the Mo-0.49Ti-0.057Zr alloy between about 20 to 40 percent reduction.

The substantially higher recrystallization temperature for all materials for reductions above about 50 percent by rolling at 3000° F, as compared to the 2200° F rolling treatment was attributed to the recrystallization taking place during rolling at the higher temperature of 3000° F. Thus the degree of worked structure is not accurately represented by the abscissa of Fig. 5.11. At 90 percent reduction, the three alloys probably have worked structures almost equivalent to from 25 to 35 percent rolling at 3000° F, and the unalloyed Mo a worked structure about equivalent to a 10 percent reduction, due to recrystallization occurring during the rolling treatment.

Figure 5.12 is a plot of grain sizes measured for the specimens after the reductions shown and the minimum temperature required for complete recrystallization in one hr. as shown in Figs. 5.10 and 5.11. The unalloyed specimens exhibited larger grain sizes than any of the alloys after both rolling treatments, and the ternary alloy appeared to have generally smaller grain sizes than the binaries. Also, the 3000° F rolling treatment and related heat treatments shown by the closed symbols and dashed lines in general resulted in larger grain sizes for all specimens and amounts of deformation than the 2200° F reduction procedures shown by the open symbols and solid curves.

Ward and Browning,[26] from observations of hardness, micrographs, and X-ray patterns, reported 100 percent recrystallization in 10 hr at 1100° C (2020° F) after 70 percent reduction at 950° C (1750° F) for unalloyed Mo of 0.008 C content. Complete recrystallization was attained after 1 hr. at 1200 and 1245° C (2190 and 2270° F) for specimens reduced 60 and 36 percent, respectively at 950° C. These recrystallization temperatures are considerably lower than those indicated in Figs. 5.10 and 5.11 for similar rolling reductions at the higher working temperatures, 2200 or 3000° F.

Ward and Browning[26] also observed that the grains were not equi-axed and that the grains had longer axes along a parallel rather than along a perpendicular traverse of a longitudinal cross section of the specimens. The ratio between the two grain size measurements was constant at about 1.4 for reductions in thickness between 35 and 70 percent at 950° C. The X-ray studies revealed considerable stress relief after 1 hr at 600° C, and complete stress relief after 1 hr at 600° C.

In summary, the recrystallization temperature for unalloyed molybdenum may be found reported in the literature from 1600 to 3100° F, depending upon material purity, the amount and temperature of prior deformation, and the time of the recrystallization treatment.

Effect of Strain Rate

The effect of strain rate on the stress-strain curves of 0.030 in. diameter Mo wire at 25°C is shown in Fig. 5.13 from data of Carreker and Guard.[28] The specimens were from commercial purity arc-cast carbon deoxidized ingots with a recrystallized structure, 0.018 mm grain diameter, resulting from 50 percent final cold reduction by swaging followed by 2 hr anneal at 1100°C (2010°F). The curves show abrupt yielding, followed by an irregular stress-strain behavior before strain hardening and necking become evident. The effect of strain rate on the upper and lower yield stresses, the ultimate tensile stress and true stress at 10 percent elongation are shown more clearly in Fig. 5.14. The logarithm of the upper and lower yield stress is shown to increase linearly with the logarithm of the strain rate over the entire range examined, whereas the logarithm of the ultimate tensile strength and flow stress at 10-percent strain increase in a non-linear manner.

Bechtold and Wessel[22] found a similar effect of strain rate on yield strength from 0-200°C. The effect of strain rate was found to be less at 300°C as indicated in Fig. 5.15, apparently associated to a strain-ageing effect. The effect of strain rate on ductility is magnified in the temperature region associated with transition from ductile to brittle behavior. For example, the figure indicates brittle failure for a test at room temperature using a strain rate of 1.02 per min., but ductile failure, about 80 percent reduction in area, using a strain rate of 0.017 per min.

Preston, Roe, and Kattus[8] have shown a three to five-fold increase in the 0.2 percent offset yield and ultimate tensile strength of Mo sheet between 3000 and 4000°F with an increase in strain rate from 0.003 to 6 per min. The specimens were heated to the test temperature rapidly, approximately 20 sec, held at test temperature for either 10 or 90 sec, and strained at controlled loading rates to failure. Total elongation at failure was highest at the faster strain rate for both holding times at 3750°F. For additional details of these tests the reader is referred to the original report[8].

Tensile Properties of Molybdenum Alloys

Screening studies[29, 30, 31, 32] concerning the effect of alloy additions on the mechanical properties of molybdenum have shown improvements due to solid solution, dispersion and/or precipitation strengthening, and alteration of the ductile to brittle behavior. The amount of alloy addition has usually been restricted by fabricability rather than by the limit of solid solubility[31]. To date, most wrought Mo alloys contain small alloying additions and are further strengthened by strain hardening. In order to retain this latter type of strengthening at elevated temperatures more promising alloy systems have been selected to increase the recrystallization or melting temperature over that of unalloyed molybdenum.

The marginal low temperature ductility of commercially produced unalloyed Mo has resulted in a search for alloy additives which lower the ductile-to-brittle transition temperature, in addition to strengthening the matrix. Fortuitously the Mo-Ti alloys have maximum tensile strength, creep strength, and bend ductility at the Mo-0.5Ti

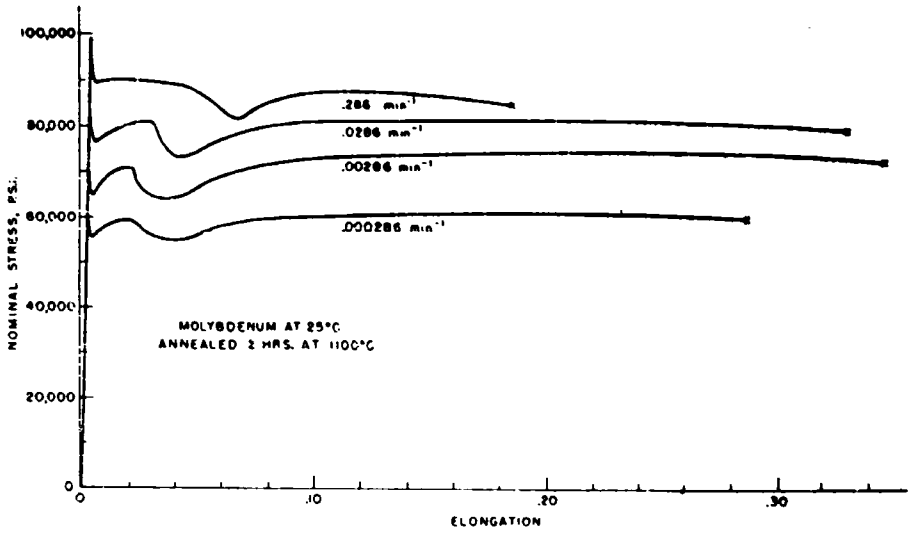


FIG. 5.13

STRESS-STRAIN CURVES FOR 0.030 INCH RECRYSTALLIZED MOLYBDENUM WIRE AT ROOM TEMPERATURE FOR VARIOUS STRAIN RATES [28]

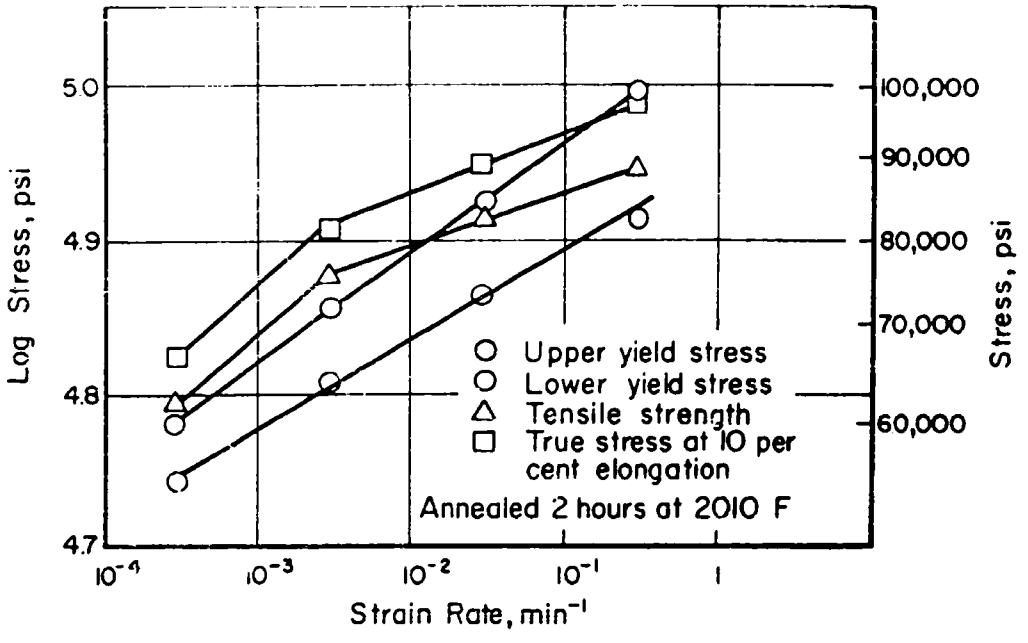


FIG. 5.14

TENSILE STRENGTH PROPERTIES OF ARC-CAST MOLYBDENUM AT 77° F AS A FUNCTION OF STRAIN RATE[28]

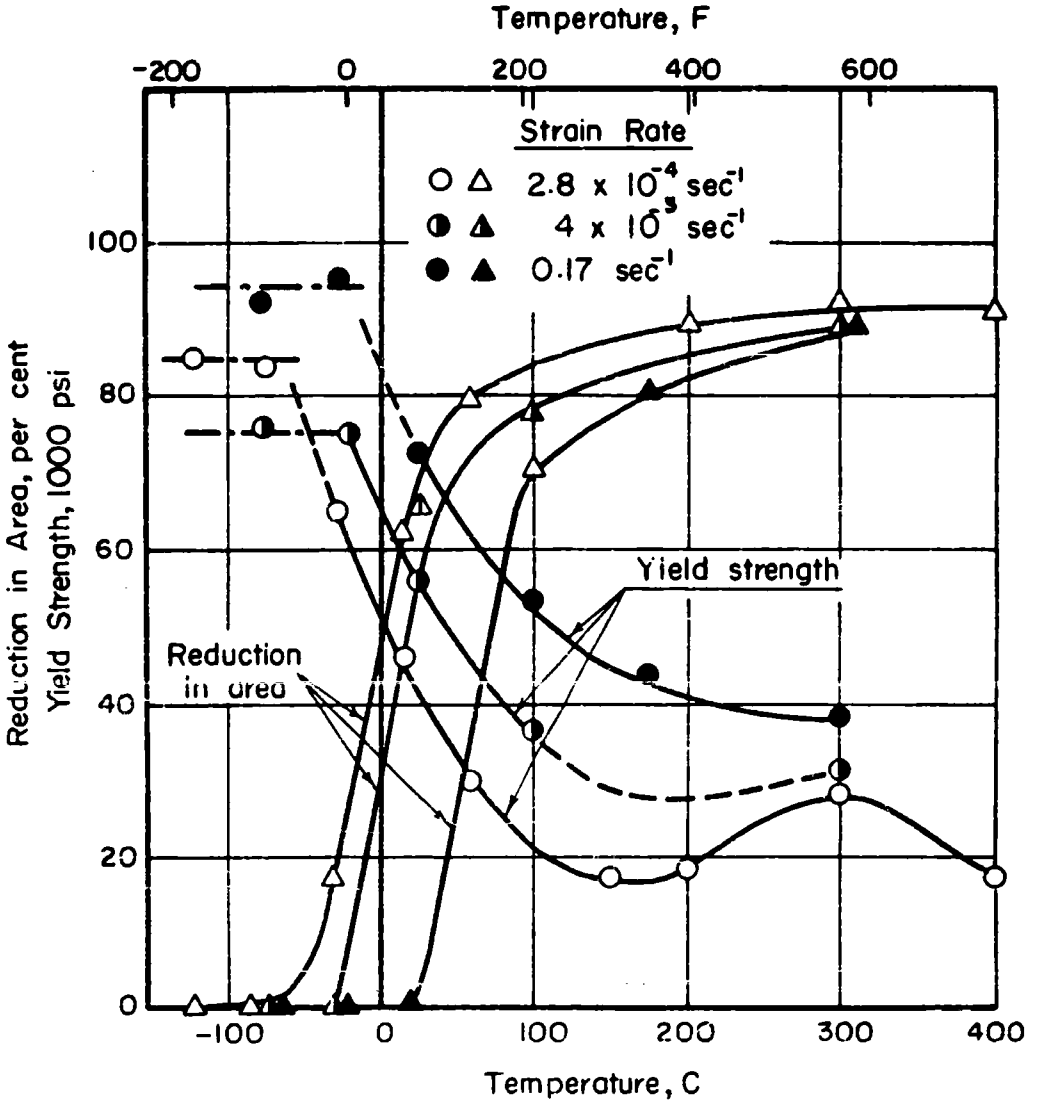


FIG. 5.15

EFFECTS OF TEMPERATURE AND STRAIN RATE ON THE DUCTILITY, YIELD STRENGTH AND BRITTLE-FRACTURE STRENGTH OF ANNEALED MOLYBDENUM[22]

composition as indicated in Figs. 5.16 and 5.17 as reported by Semchyshen[31], and Olds and Rengstorff[32]. Due partially to these circumstances, the Mo-0.5Ti alloy has become a popular commercial alloy. The following discussion will be concerned primarily with six alloys with attractive properties rather than with results of the screening studies. Twelve years of Mo alloy research has established the commercial potential of the six alloys chosen for discussion, the first three of which are available commercially. The six alloys have the following nominal alloy additions:

0.5 Ti
0.5 Ti – 0.08 Zr (TZM)
30 W
0.5 Zr
0.05 Zr
1.25 Ti – 0.15 Zr – 0.15 C, (TZC).

The carbon and oxygen contents of each alloy affect the properties but are not usually specified in the nominal compositions except in the case of TZC.

Comparison of the alloys on an ultimate tensile strength basis from room temperature to 2400° F is shown in Fig. 5.18 and 5.19 as prepared by Houck[3] from available data on specimens in both the stress relieved and recrystallized condition. Molybdenum alloys are mostly used in the stress-relieved condition to take advantage of the improved strength and low-temperature ductility of material in that condition compared to that of recrystallized material. In Fig. 5.18, which shows different alloys in the stress-relieved condition, TZM alloy is shown to have better strength at all test temperatures for which data were reported than the other alloys. The portion of the curves joining the room temperature data and the first elevated temperature values must be regarded as only approximate. However, these alloys are primarily intended for use in the upper temperature range where sufficient data points exist. In the intermediate temperature range, the indicated curves may be appreciably modified due to strain-ageing effects. The strength of TZM is shown to be only about 15 percent greater than unalloyed Mo at room temperature but more than four times greater at 2400° F, which is above the recrystallization temperature of moderately worked Mo and below that of the alloy. The indicated tensile strength superiority of TZM over 0.5 Ti at 2400° F of about three times is of particular interest because of the small but important difference in composition between the two alloys. The slight short time tensile strength advantage of Mo-30 W over unalloyed Mo would obviate its substitution for the lighter Mo alloys in the indicated test temperature range because of its 17 percent higher density. However, its high solidus temperature of about 5115° F is attractive for parts exposed to rocket exhaust, and its creep rupture strength may make it attractive for use at lower temperatures for long time applications. The recorded data are from several investigations. Attention is called to the effects due to possible differences in impurities, test conditions, and specimen preparation when reported tensile property values are judged. Higher and lower values of tensile strength may be found in report literature from tests conducted under different conditions, but those presented are typical.

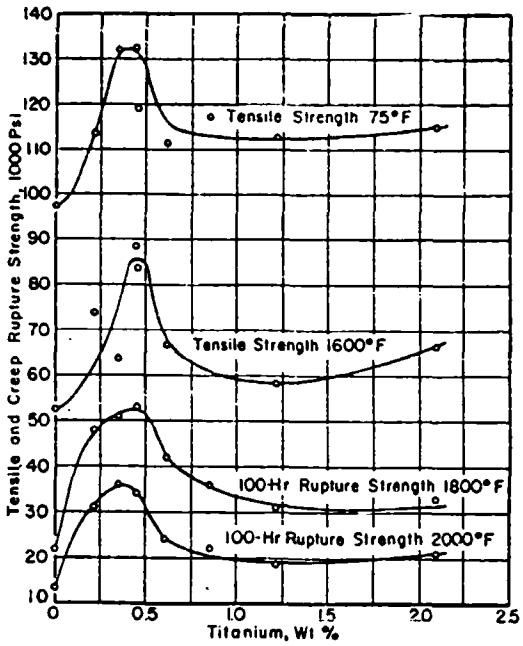


FIG. 5.16

EFFECT OF TITANIUM CONTENT ON THE TENSILE AND CREEP-RUPTURE STRENGTHS OF 5/8-IN. ROLLED ROUNDS OF MOLYBDENUM-TITANIUM ALLOYS IN STRESS-RELIEVED CONDITION[31]

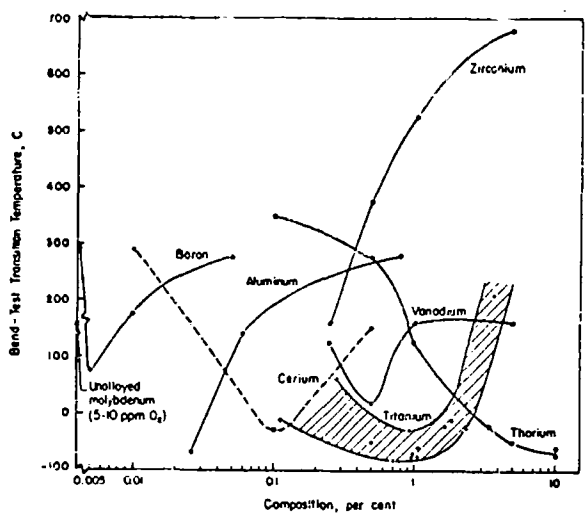


FIG. 5.17

BEND TRANSITION TEMPERATURE OF CAST MOLYBDENUM AS INFLUENCED BY VARIOUS ALLOY ADDITIONS [32]

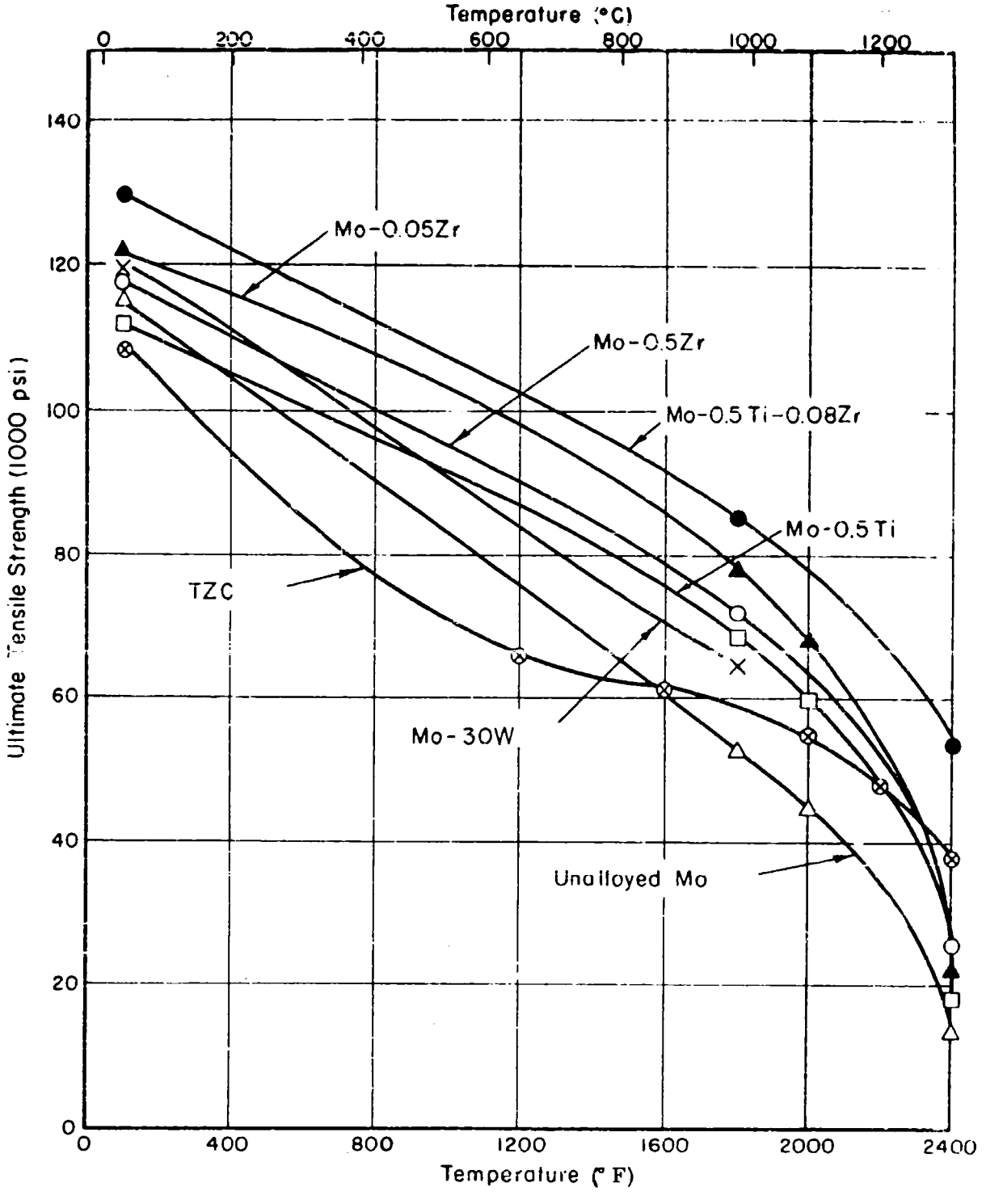


FIG. 5.18

ULTIMATE TENSILE STRENGTH BETWEEN 75 AND 2400° F
SELECTED MOLYBDENUM-BASE ALLOY BAR STOCK IN
THE STRESS-RELIEVED CONDITION[3]

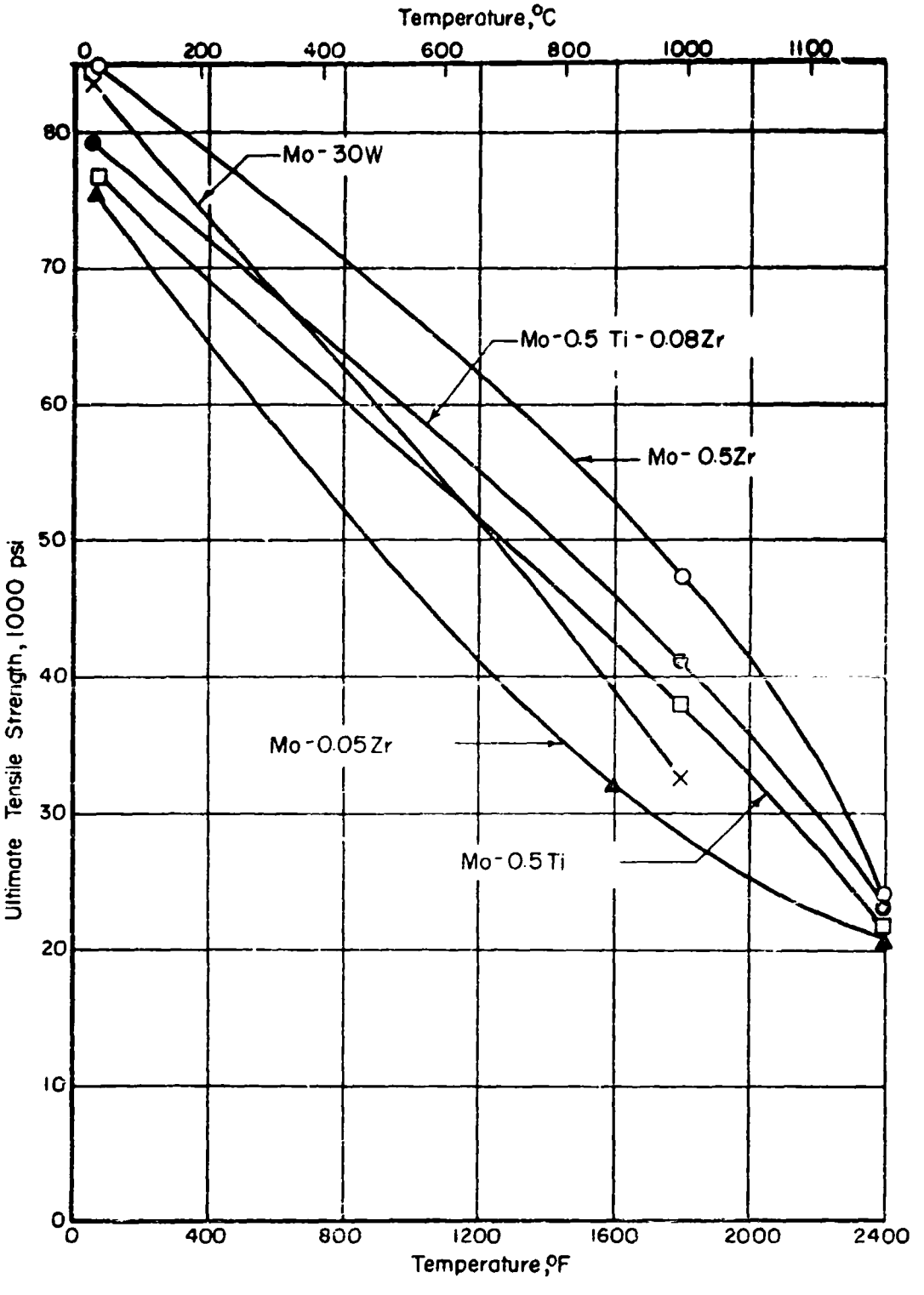


FIG. 5.19
ULTIMATE TENSILE STRENGTH BETWEEN 75 AND 2400° F
FOR SELECTED MOLYBDENUM-BASE ALLOY BAR STOCK
IN THE RECRYSTALLIZED CONDITION[3]

The ultimate tensile strength of five important Mo alloys at temperature up to 2400° F in the recrystallized condition is shown in Fig. 5.19. The increased strength as a result of the prior strain hardening is lost due to the recrystallization treatments as may be observed by comparing Fig. 5.18 and 5.19. Recrystallized unalloyed Mo has about the same strength at 2400° F as the stress-relieved material at 2400° F shown in Fig. 5.18. The strength of recrystallized Mo-0.5 Zr is shown to be higher than recrystallized TZM at all test temperatures which is reverse to the comparison in the stress-relieved condition.

The available data for strength of Mo alloys above 2000° F are shown in Fig. 5.20. The strength advantage of Mo-50 W above 2800° F is apparent and is partly due to its high melting point, reported[33] at 5250° F, about 500° F above that of unalloyed Mo. Limited commercial production of this alloy is primarily used as wire products in the electronic tube industry. Its fabricability is better than that of tungsten, and the data shown in the figure from sheet and bar specimens were obtained to investigate the alloy's possible use in other high temperature applications. Ductility as measured by tensile reduction-in-area was reported[37] to be lower for Mo-50 W, 68, 43, and 16 percent at 2500, 3000, and 3500° F, than for TZC 78, 92 and 99 percent, or TZM, 94, 99 and 99, at the same test temperatures.

The latter two alloys, TZC and TZM, have higher recrystallization temperatures than Mo-0.5 Ti and exhibit better strength from 2000 to 3000° F than Mo-0.5 Ti. The tests on TZC and TZM conducted under similar conditions in one laboratory[37] show the same strength at 2500° F for the two alloys but a superior strength for TZC between 2500 and 3500° F. In contrast, the data of Fig. 5.18 showed TZM to be stronger than TZC from 1800 to 2400° F and also at room temperature.

The data[35] from sheet and bar specimens of the Mo-0.5 Ti alloy shown by the vertically and horizontally half-shaded circle symbols indicate the effect of strain rate on results of tests at high temperatues. Tests on both bar and sheet material gave lowest values for slow strain rates (0.002 per min) than for faster rates (0.2 per min). No conclusion regarding the comparisons between relative strength of Mo-0.5 Ti sheet and bar material should be made from the few data presented, but the magnitude of variation in reported strength of Mo-0.5 Ti at 3000° F is indicated by comparison between the low (2700 psi) and high (9800 psi) values. Also, the variation between the strength at 2000° F of TZM and Mo-0.5 Ti sheet indicated in Fig. 5.20 and of bar material indicated in Fig. 5.18 emphasizes the importance of identification of material and test conditions to make accurate use of design data.

Effect of Impurities on Molybdenum Alloys

The combined effects of alloy addition and strain hardening on the mechanical properties of Mo alloys tend to mask or alter the effects of impurities. Ingram et al.[18] reported a lower ductility transition temperature for the Mo-0.5 Ti alloy than for unalloyed Mo, and associated the behavior with the interaction between the Ti and residual impurities. Semchyshen, McArdle, and Barr[29] and Chang[38] studied the effect of small carbon content changes on the strength and ductility of Mo alloys containing Ti and/or Zr.

SYMBOL	REFERENCE	MATERIAL	MATERIAL CONDITION	SPECIMEN GAUGE SIZE (IN.)	STRAIN RATE IN/IN/MIN
	Hall & Sikora[34]	Mo - 0.5Ti	Rex/3800°F - 30 Min	.250 dia x 3 1/2 Lg	1/16[a]
	Hall & Sikora[34]	Mo - 0.5Ti	As Wrought	.250 dia x 3 1/2 Lg	1/16[a]
	Kattus, Preston & Lessley[35]	Mo - 0.5Ti	Rex/2900°F - 35 Min	0.060Th x .5W x 2 Lg	1/16[a]
	Kattus, Preston & Lessley[35]	Mo - 0.5Ti	Rex/2900°F - 35 Min	0.060Th x .5W x 2 Lg	0.2
	Kattus, Preston & Lessley[35]	Mo - 0.5Ti	Rex/2900°F - 35 Min	3/8 dia x 2 Lg	0.002
	Kattus, Preston & Lessley[35]	Mo - 0.5Ti	Rex/2900°F - 35 Min	3/8 dia x 2 Lg	0.2
	Bauer[36]	Mo - 0.5Ti	Stress Relieved	0.015 - 0.040 Th x 0.2 5W x 1 Lg	0.005 & 0.1
	Hall & Sikora[34]	TZM	As Wrought	0.250 dia x 3 1/2 Lg	1/16[a]
	Hall[37]	TZM	As Wrought	0.250 dia x 1 Lg	1/16[a]
	Bauer[36]	TZM	Coil Rolled	0.015 - 0.040Th x 0.25 W x 1 Lg	0.005 & 0.1
	Hall[37]	TZC	As Wrought	0.250 dia x 1 Lg	1/16[a]
	Hall[37]	Mo - 50W	Sintered and Wrought	0.250 dia x 1 Lg	1/16[a]
	Bauer[36]	Mo - 50W	Stress Relieved	0.030Th x 0.25W x 1 Lg	0.005 & 0.1

(a) Crosshead Travel Rate (In/Min)

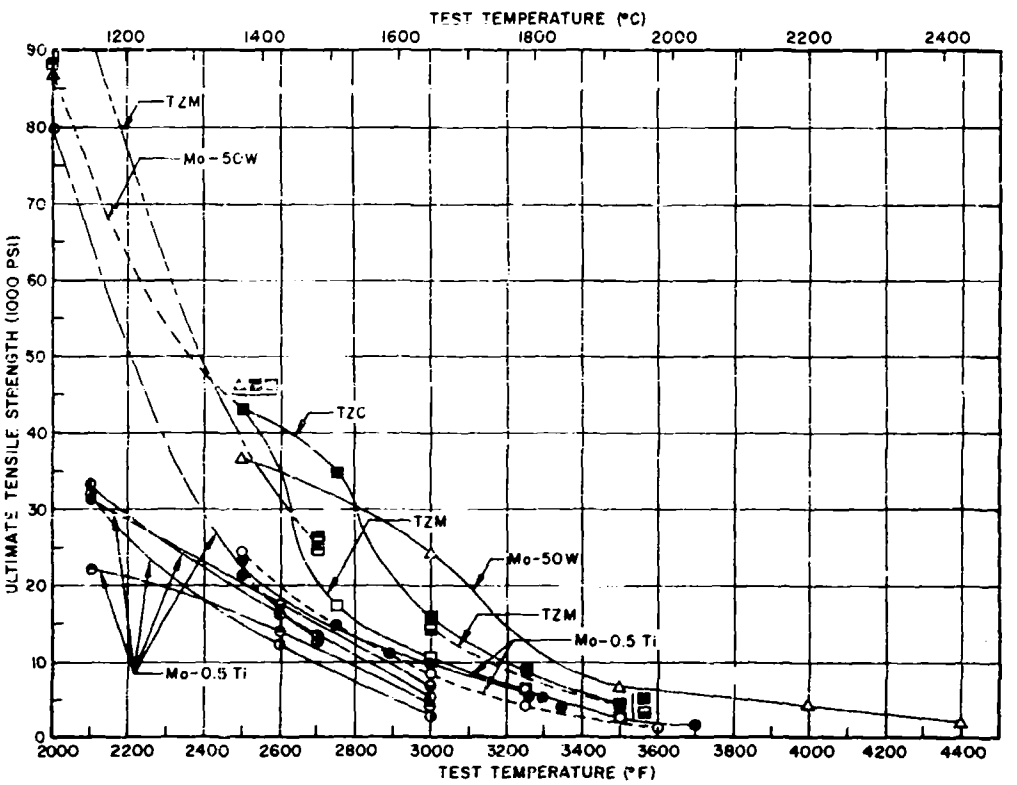


FIG. 5.20

ULTIMATE TENSILE STRENGTH OF MOLYBDENUM ALLOYS ABOVE 2000°F

Both investigations agreed that different interaction between Ti and Zr with residual carbon existed in that Ti containing alloys exhibited a finely dispersed second phase whereas Zr alloys displayed massive, striated carbide agglomerates which had less effect on mechanical properties than the finely divided TiC phase. Chang[38] correlated the difference with total metal to carbon atom ratio. The most consistent effect of carbon additions to sheet material was an observed decrease in tensile ductility and an increase in recrystallization temperature. Analysis of the sheet stock used in the Climax investigation[29] showed higher Ti and/or Zr contents near the surface than at the mid-section and removal of surface layers, 4 to 16-mils thick, resulted in lower bend ductility temperatures. The surface removal had a larger effect on ductility than identified carbon content effects.

Published results on the effect of O, N, and H on the mechanical properties of Mo alloys were not found.

Effect of Cold Work on Molybdenum Alloys

As in the case of unalloyed Mo, the investigation by Semchyshen, Barr, and McArdle[24] will be used to illustrate the effect of deformation on the ultimate tensile strength of Mo alloys. The effect of rolling at 2200 and 3000° F on the ultimate tensile strength at room temperature and 1800° F on three alloys, Mo-0.5Ti, Mo-0.06Zr, and TZM (Mo-0.5 Ti-0.08 Zr nominal) is shown in Figs. 5.21, 5.22, and 5.23. The fabrication and thermal treatment procedures were the same as previously described for the unalloyed Mo.

According to the figures, maximum strengthening of all three alloys was obtained by rolling at 2200° F to 90 percent reduction. Increasing the reduction by rolling at 2200° F from 10 to 90 percent caused an additional increase in the room temperature strength for Mo-0.5 Ti of 27 percent, Mo-0.06 Zr of 38 percent, and TZM of 46 percent. Similar reductions caused the tensile strengths at 1800° F to be increased 65, 67, and 72 percent for the alloys in the same order. Rolling at 3000° F produced maximum increases in room temperature strength of 24, 35, and 17 percent, and 1800° F strength of 27, 8, and 38 percent for the alloys in the same order. However, the maximum in strength occur at 30 percent reductions by rolling at 3000° F in Mo-0.5 Ti and Mo-0.06 Zr, and at 90 percent in TZM.

The strength at 1800° F was found to increase a greater percentage than room temperature strength as a result of rolling at both 2200 and 3000° F, with the exception of the 0.06 percent Zr alloy rolled at 3000° F. These observations have all been made by comparing the strength after 10 percent nominal deformation with the maximum strength, which occurred either at 30 or 90 percent nominal, since no tensile tests were reported on the recrystallized materials prior to final reduction to 5/8 in. diameter bar stock. Higher hardnesses, strengths and recrystallization temperatures were observed by the authors[24] for the TZM alloy than for the other two alloys or unalloyed material within the range of deformation variables studied.

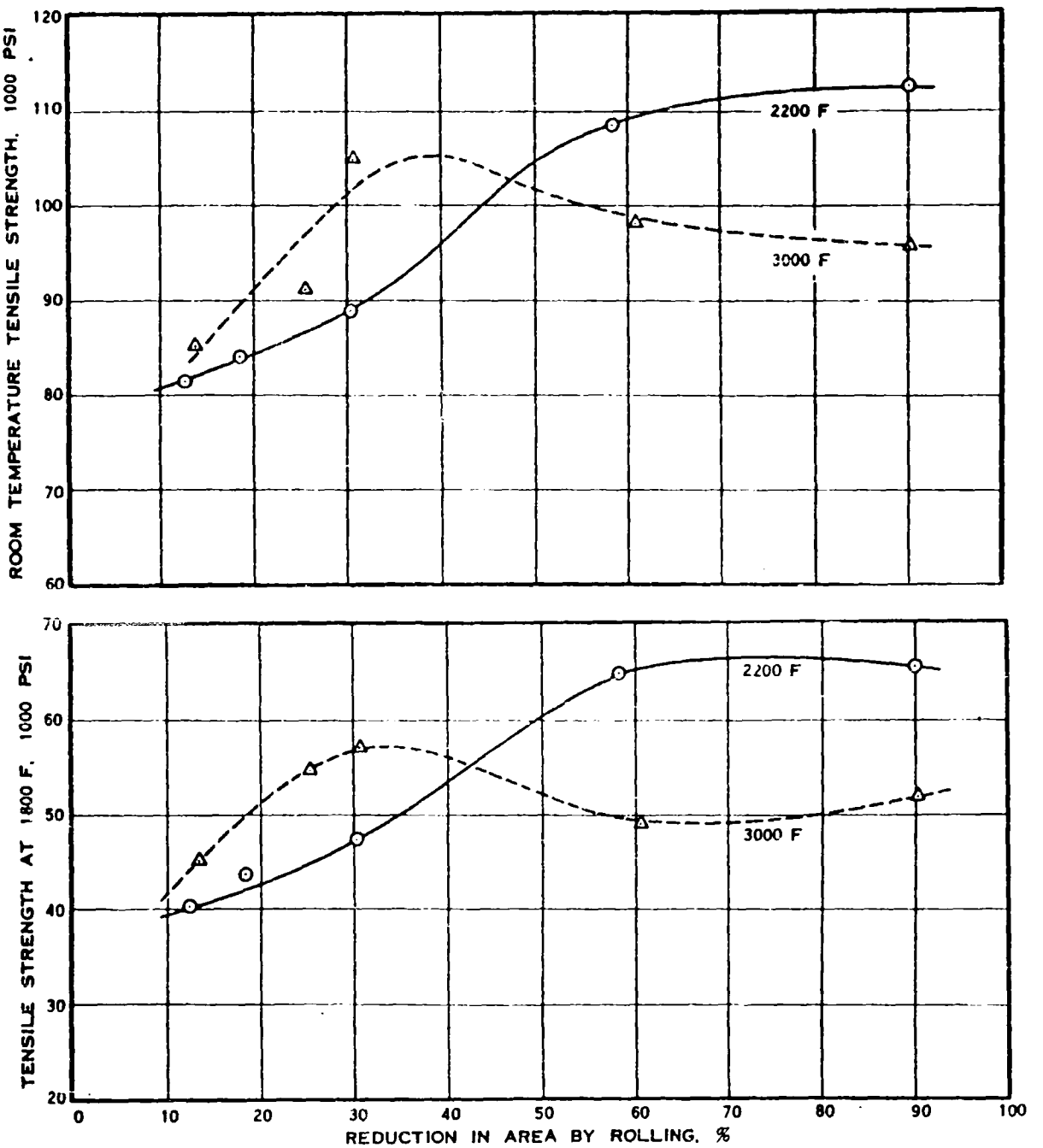


FIG. 5.21

TENSILE STRENGTH AT ROOM TEMPERATURE AND 1800°F OF Mo-0.5Ti ALLOY AFTER DEFORMATION BY ROLLING AT 2200 AND 3000°F[24]

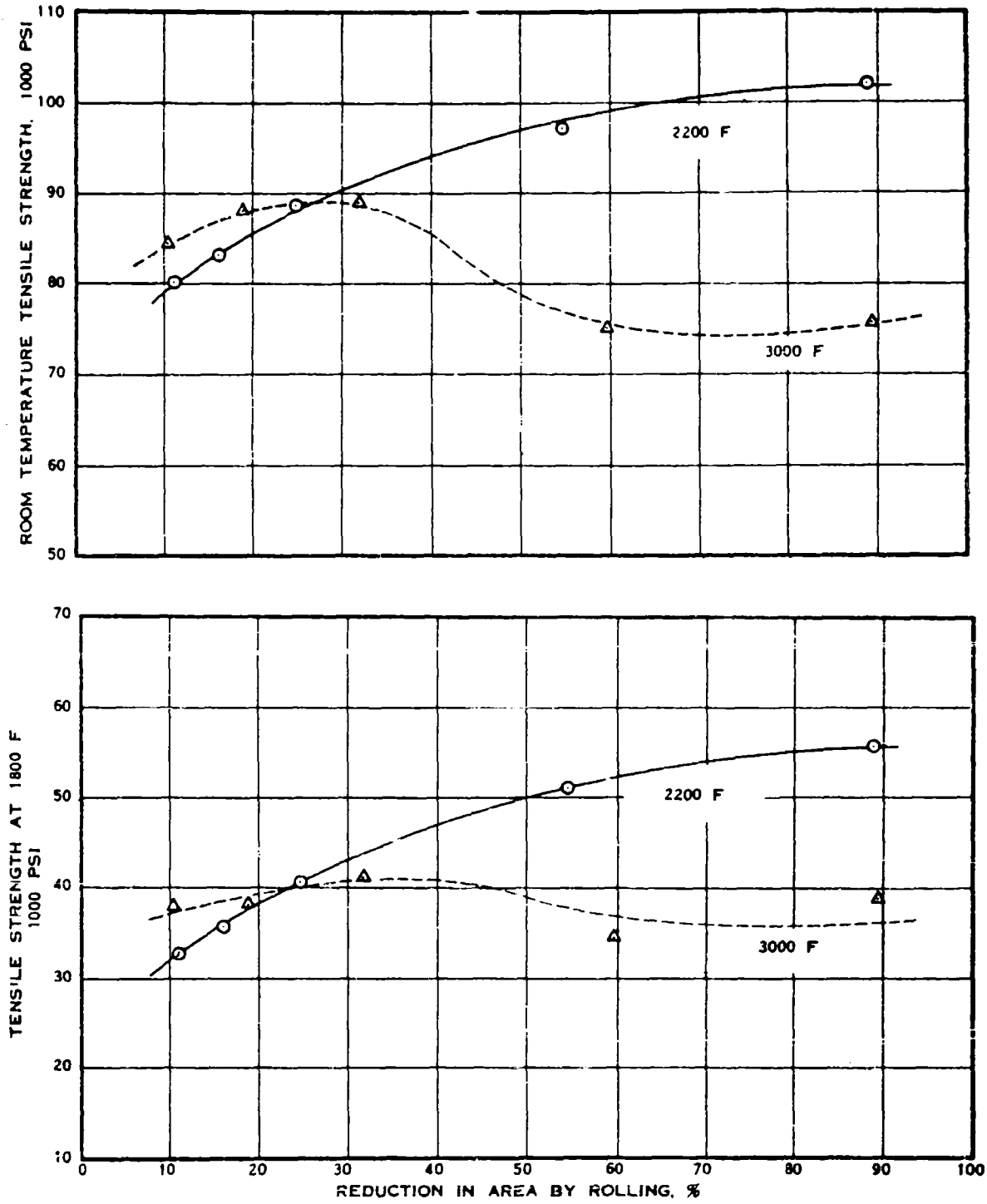


FIG. 5.22

TENSILE STRENGTH AT ROOM TEMPERATURE AND 1800°F OF Mo-0.06Zr ALLOY AFTER DEFORMATION BY ROLLING AT 2200 AND 3000° F[24]

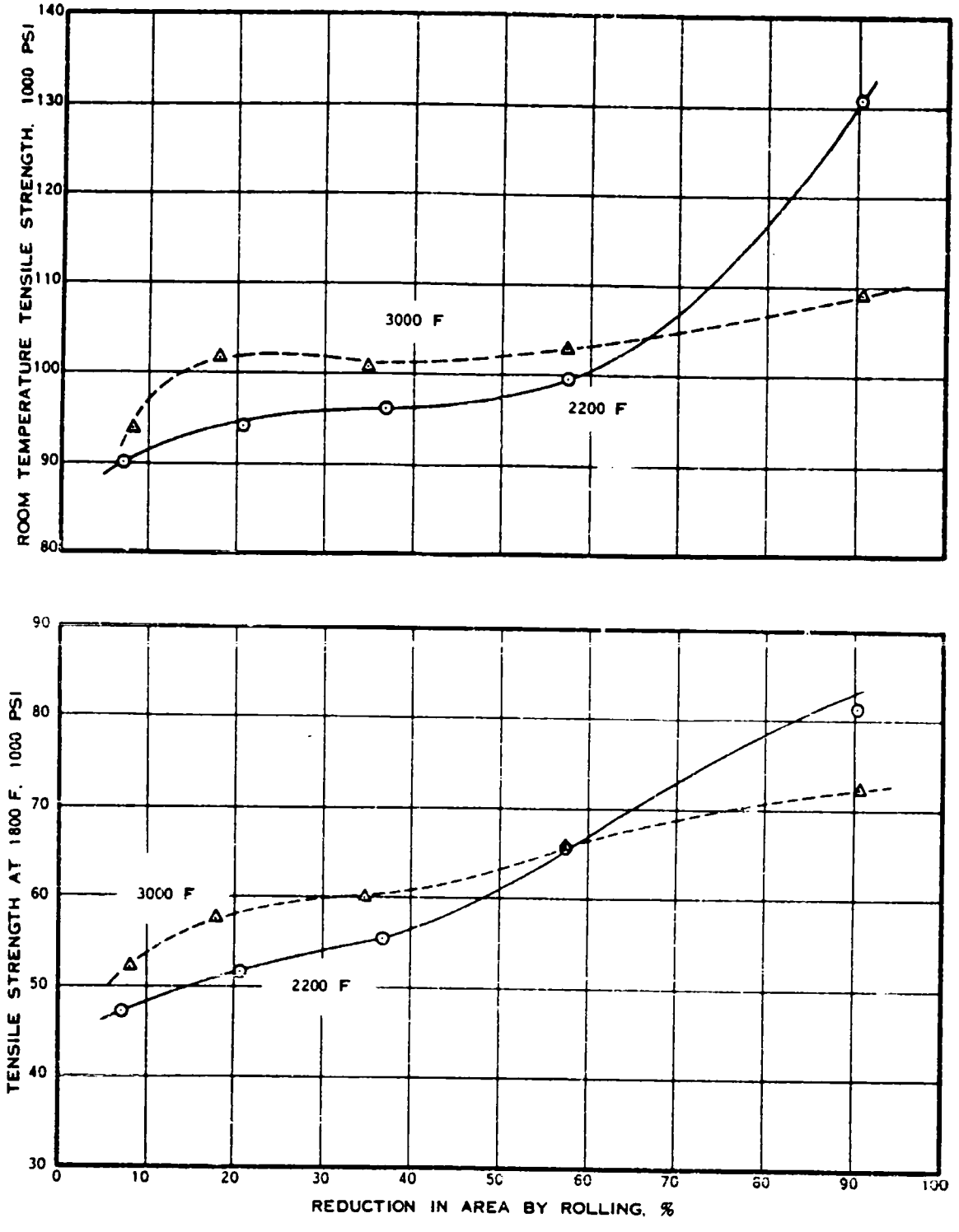


FIG. 5.23

TENSILE STRENGTH AT ROOM TEMPERATURE AND 1800° F OF Mo-0.5Ti-0.06Zr ALLOY (TZM) AFTER DEFORMATION BY ROLLING AT 2200 AND 3000° F[24]

Additional investigations[27, 3, 39] concerning the effect of hot-cold work on the tensile properties of Mo alloys used different approaches to the study. These investigations are described only briefly in this summary. Test conditions are given in detail in the references cited.

Barr, Semchyshen, and Perlmutter[27] observed: (1) forging of Mo-0.5 Ti alloy developed higher strain hardening than rolling, (2) as-wrought hardness was higher for higher forging or rolling temperatures in the range 1800-2400° F; and (3) higher strength and ductility properties resulted from material strained and stress relieved to a given hardness than from material in the fully strained condition with the same hardness.

Houck[3] summarized earlier data from work by Semchyshen and Barr[40] which showed the same percentage increase in strength (37 percent) between Mo-0.5 Ti bars rolled at 1800° F to 5 and 82 percent reductions as reported above[24] for bars rolled at 2200° F. This would indicate little temperature effect on as-rolled strength in contrast to the earlier reported results.[27] No strength for reductions at 1800° F were given for the range 35 to 82 percent so it is not known as to how the strength increased with amount of straining in that range.

Taebel[39] observed little change in properties of Mo-0.5 Ti alloy over the range of extrusion reduction ratios of 2:1 to 5:1 at extrusion temperatures from 2000 to 3000° F, but suggested that extrusion temperatures below 2000° F might result in increased tensile strength.

Recrystallization Behavior of Molybdenum Alloys

Alloy recrystallization behavior was introduced in the section concerning recrystallization of unalloyed Mo and the recrystallization temperatures of three alloys after different amounts of deformation at 2200 and 3000° F were shown in Figs. 5.10 and 5.11 with resulting grain sizes shown in Fig. 5.12. Houck[3] summarized earlier reported recrystallization temperatures of the same alloys plus two additional alloys as shown in Table 5.6 and Fig. 5.24. Recrystallization temperatures indicated in the table agree with temperatures shown in Fig. 5.10 for unalloyed Mo and Mo-0.5Ti but are lower than Mo-0.05Zr and TZM for material reduced 90 percent nominally at 2200° F. The 100 percent one-hour recrystallization temperatures indicated in Fig. 5.24 are higher than those for comparable alloys shown in Fig. 5.10. Recrystallization temperatures for the Mo-30W were not determined, but Semchyshen and Barr[40] have reported one-hour recrystallization temperatures between 3000 and 3400° F for Mo-W-Zr alloys containing nominally 25W and 0.1Zr from studies still in progress.

Ductile-Brittle Behavior of Molybdenum Alloys

Tensile ductility of three recrystallized Mo alloys as measured by reduction-in-area is presented in Fig. 5.25 as compiled by Houck.[3] The Mo-0.5 Ti alloy is shown to have the lowest transition temperature and the highest ductility immediately above the transition range. The TZM alloy, however, is reported[41] to have a lower transition

Table 5.6

RECRYSTALLIZATION TEMPERATURES OF MOLYBDENUM AND MOLYBDENUM ALLOYS[3]

Alloy	Recrystallization Temperature, °F*
Unalloyed Mo (0.01C)	2150
Mo-0.5 Ti	2450
Mo-0.5 Ti-0.08 Zr (TZM)	2600
Mo-0.5 Zr	2650
Mo-0.05 Zr	2450
Mo-1.25 Ti-0.15 Zr-0.15C (TZC)	2800

*Hardness determination of minimum temperature for recrystallization in 1 hr after hot-cold work, 75-97 percent reduction, at different temperatures and reduction processes.

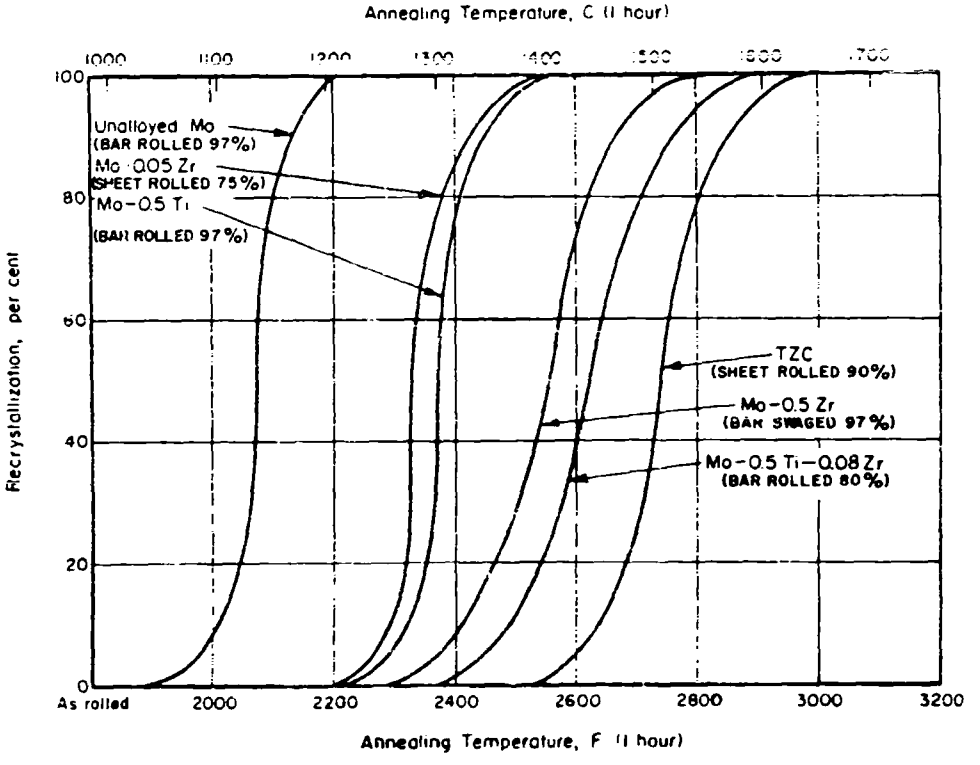


FIG. 5.24

RECRYSTALLIZATION OF MOLYBDENUM-BASE ALLOYS AFTER HOT-COLD WORKING AND ANNEALING[3]

temperature in bend tests than Mo-0.5Ti in either the stress-relieved or recrystallized conditions. Comparable values of the lowest temperature for a 2T, 130° transverse bend for TZM and Mo-0.5Ti were reported[41], respectively, as -50 and > 200° F in the stress-relieved condition and 40 and 75° F in the recrystallized condition. These tests were from one heat only of each alloy and are given for comparison only. The >200° F value for Mo-0.5Ti was from a 1T bend test. Houck[3] also summarized the transition behavior of notched and unnotched tensile specimens of Mo-0.5Ti from the investigation by Imgram, et al.[18] The results shown in Table 5.7 indicate lower transition temperatures for stress-relieved than for recrystallized material tested either in the notched or unnotched condition. The tensile transition temperatures reported in the table are those at which the reduction-in-area is approximately one-half its maximum value. Additional data concerning the tensile transition temperature in experimental alloys may be found in the report by Semchyshen, McArdle, and Barr.[30]

Available impact data shown in Fig. 5.26 present impact strength versus test temperature for Mo-0.45Ti alloy in the as-rolled, stress-relieved, and recrystallized conditions. The behavior is not simple; both the as-rolled and stress-relieved material start a rapid transition from ductile to brittle behavior at about 700° F, or about 100° F higher than for the recrystallized material. However, the shapes of the curves for as-rolled and stress-relieved materials are such that below 600° F, these materials have higher values of impact strength than the recrystallized materials.

These investigators[30] also have shown that room temperature embrittlement occurs in alloys exposed to temperatures of 1000° F or more above their recrystallization temperature where grain coarsening is facilitated.

Klopp et al. (Section 3, Ref. 9) conducted a detailed study on the effect of Re additions on the bend ductility of Mo. Their results showed that the 10T bend transition temperature of recrystallized Mo was decreased from 60° C to -40°C, -100, -150, -180, and ≤ -250°C as a result of additions of 10, 20, 25, 30, and 35 atomic percent Re, respectively.

Table 5.7

TENSILE TRANSITION TEMPERATURES FOR NOTCHED AND UNNOTCHED SPECIMENS OF Mo-0.5 Ti ALLOY[3]

Material	Condition	Specimen	Temperature Range of Testing, ° F	Reduction in Area Transition Temperature, ° F	Notch Sensitive at Temperature, °F
Mo-0.5 Ti (bar)	Wrought, stress relieved	Unnotched	-104 to 212	-58	≤32
		Notched		54	
	Recrystallized	Unnotched	-40 to 572	260	
		Notched		482	≤32
Mo-0.5Ti (sheet)	Wrought, stress relieved	Unnotched	-320 to 392	-104	≤ -76
		Notched		32	
	Recrystallized	Unnotched	-104 to 572	14	≤78
		Notched		347	

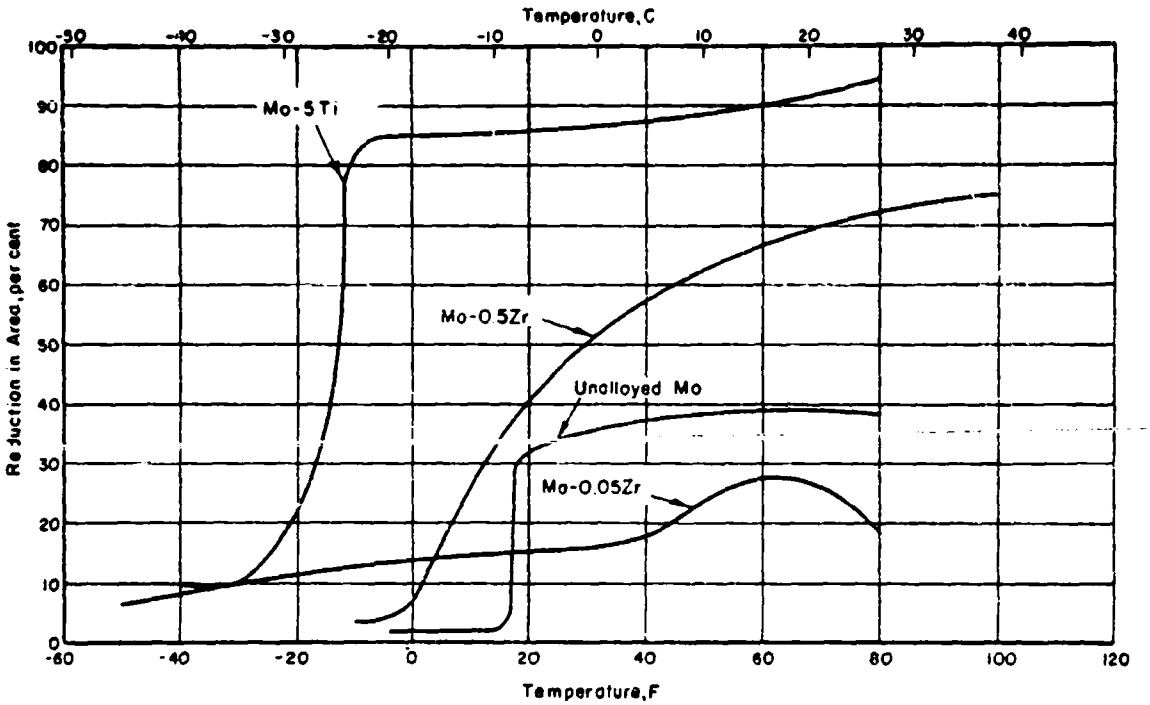


FIG. 5.25

REDUCTION IN AREA VERSUS TEST TEMPERATURE FOR MOLYBDENUM AND FOR THREE MOLYBDENUM ALLOYS IN THE RECRYSTALLIZED CONDITION[3]

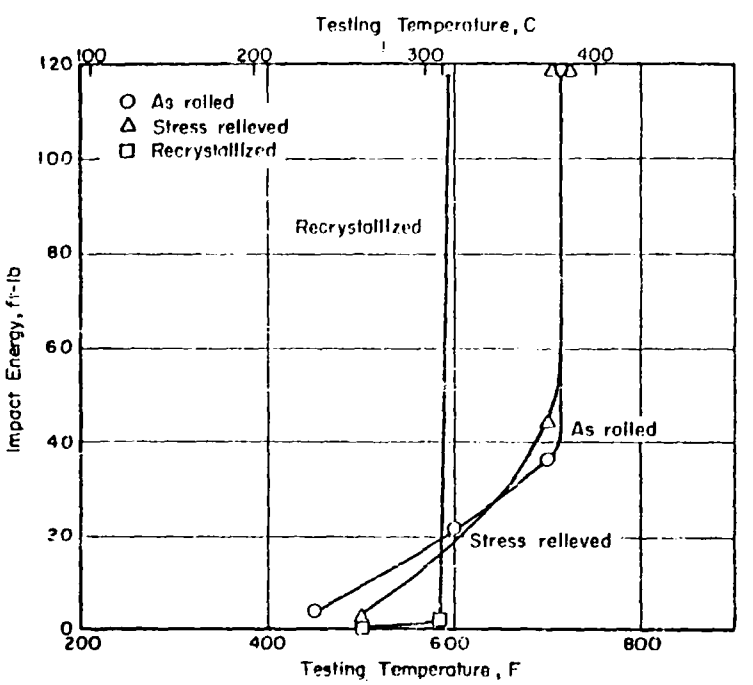


FIG. 5.26

IMPACT STRENGTH VS TEST TEMPERATURE FOR Mo-0.46Ti ALLOY IN THE AS-ROLLED, STRESS-RELIEVED, AND RECRYSTALLIZED CONDITION[3]

Creep and Stress-Rupture Behavior of Molybdenum

The resistance of unalloyed molybdenum to creep and rupture at elevated temperature has received intensive study. Pugh[15] reported considerable creep data at 1600, 1800, and 2000° F over a range of stresses from 9000 to 36000 psi and correlated the stress, temperature, and time parameters for material of one composition and thermal-mechanical fabrication history. Iannucci, et al.[42] prestrained specimens prior to creep deformation and observed an increase in creep resistance at 1000° C and 8000 psi as a function of prestrain.

Creep and stress-rupture data from commercially produced unalloyed molybdenum bar and sheet stock have been recently summarized by Houck[3]. Figures 5.27 through 5.33 are reproduced from that summary. Figure 5.27 presents stress-rupture data for stress-relieved and recrystallized bar stock from 1000 to 2000° F. The stress required to produce deformations from 0.2, to 10 percent and rupture at 1600, 1800, and 2000° F is shown in Figs. 5.28, 5.29, and 5.30, respectively. Minimum creep rate and stress-rupture data from 2900 to 4500° F are shown in Figs. 5.31 and 5.32 from short-time creep rupture studies on rod material produced by powder metallurgy techniques. Open and closed symbols in Fig. 5.31 represent engineering and true stresses for minimum creep rates. Figure 5.33 also summarizes short-time creep behavior at very high temperatures but on sheet specimens resistively heated rapidly to test temperature after loading at room temperature. Strain values indicated in Fig. 5.33 apparently refer to creep strain after reaching test temperature. Since the specimens were under load during the heating period, these values do not represent total strain.

Creep and Stress Rupture of Molybdenum Alloys

Data for commercial alloys reported subsequent to the DMIC survey by Houck[3] have not been found in the report literature. Available creep data were reported tabularly and graphically in that compilation with adequate reference citations. Stress-rupture data at 1600, 1800, 2000, and 2400° F for various Mo-alloys are reproduced in Figs. 5.34 through 5.37 with a summary of 100-hr. stress rupture strengths in the same temperature range shown in Fig. 5.38. All creep tests were conducted in vacuum. The data originated in the Climax Molybdenum Co. laboratories from 1955 through 1959 with the exception of the TZC properties reported in Fig. 5.38, which originated in a G. E. Co. laboratory. The three alloys which may be compared at 2000° F on a 100 hr. rupture stress basis in Fig. 5.38 exhibit increasing strength in the order Mo-0.5Ti, Mo-0.05Zr, Mo-0.5Ti-0.08Zr in the stress relieved condition, and Mo-0.05Zr, Mo-0.5Ti, Mo-0.5Ti-0.08Zr in the recrystallized condition.

The data of Figs. 5.34, 5.35, and 5.36 indicate that the stress-relieved Mo and Mo-alloys had roughly twice the stress-rupture strength of the recrystallized material at 1600, 1800, and 2000° F. There is not sufficient data to make this comparison at 2400° F with the exception of the data given in Fig. 5.38 for Mo-0.05Zr, where the 100-hour stress-rupture strength is seen to be equal for the stress-relieved and for the recrystallized condition.

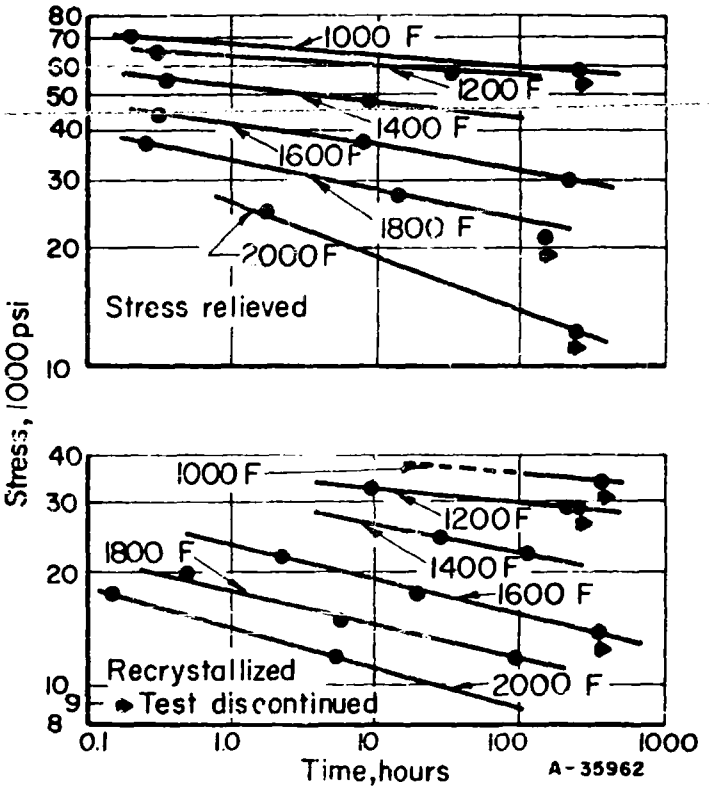


FIG. 5.27

STRESS-RUPTURE CURVES FOR ARC-CAST MOLYBDENUM, AS STRESS RELIEVED (1800 F−HOUR) OR RECRYSTALLIZED (2150 F−1 HOUR)[3]

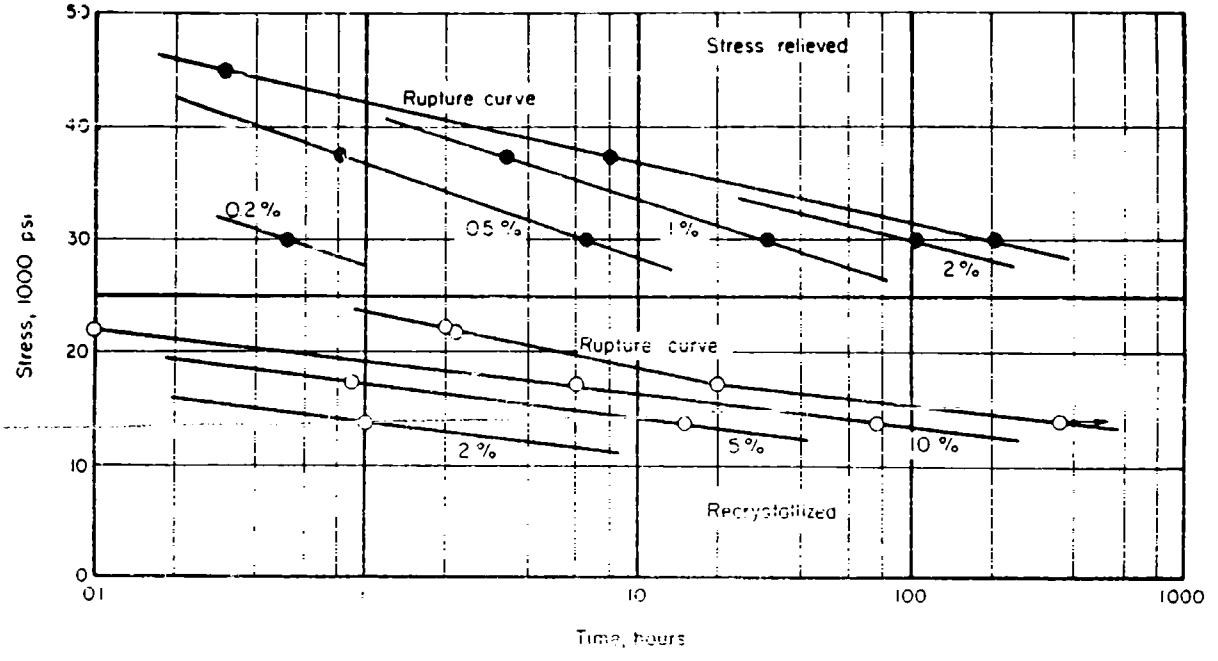


FIG. 5.28

CREEP STRESS VERSUS TIME FOR VARIOUS AMOUNTS OF TOTAL DEFORMATION FOR MOLYBDENUM (0.015 PER CENT C) TESTED IN VACUUM AT 1600 F[3]

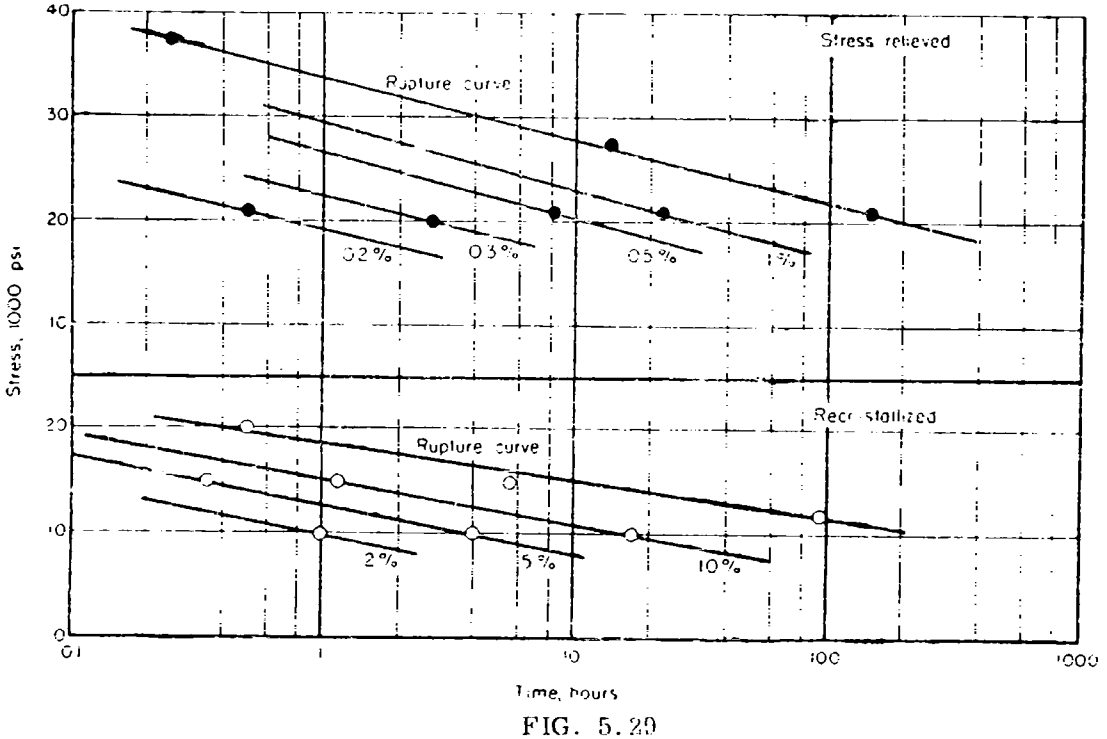


FIG. 5.29

CREEP STRESS VERSUS TIME FOR VARIOUS AMOUNTS OF TOTAL DEFORMATION FOR MOLYBDENUM (0.015 PER CENT C) TESTED IN VACUUM AT 1800 F[3]

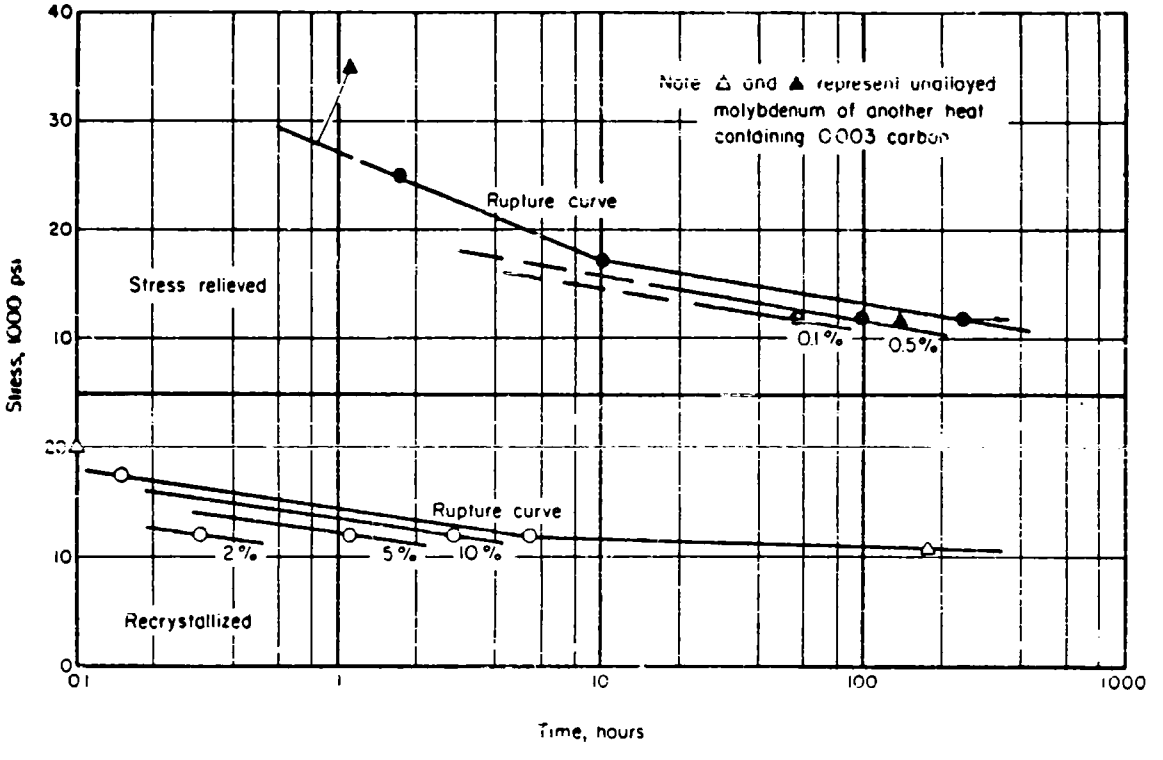


FIG. 5.30

CREEP STRESS VERSUS TIME FOR VARIOUS AMOUNTS OF TOTAL DEFORMATION FOR MOLYBDENUM (0.015 PER CENT C) TESTED IN VACUUM AT 2000 F[3]

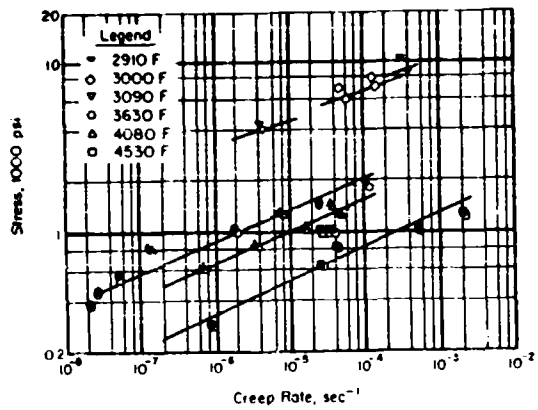


FIG. 5.31

SHORT-TIME CREEP PROPERTIES OF UNALLOYED POWDER-METALLURGY MOLYBDENUM[3]

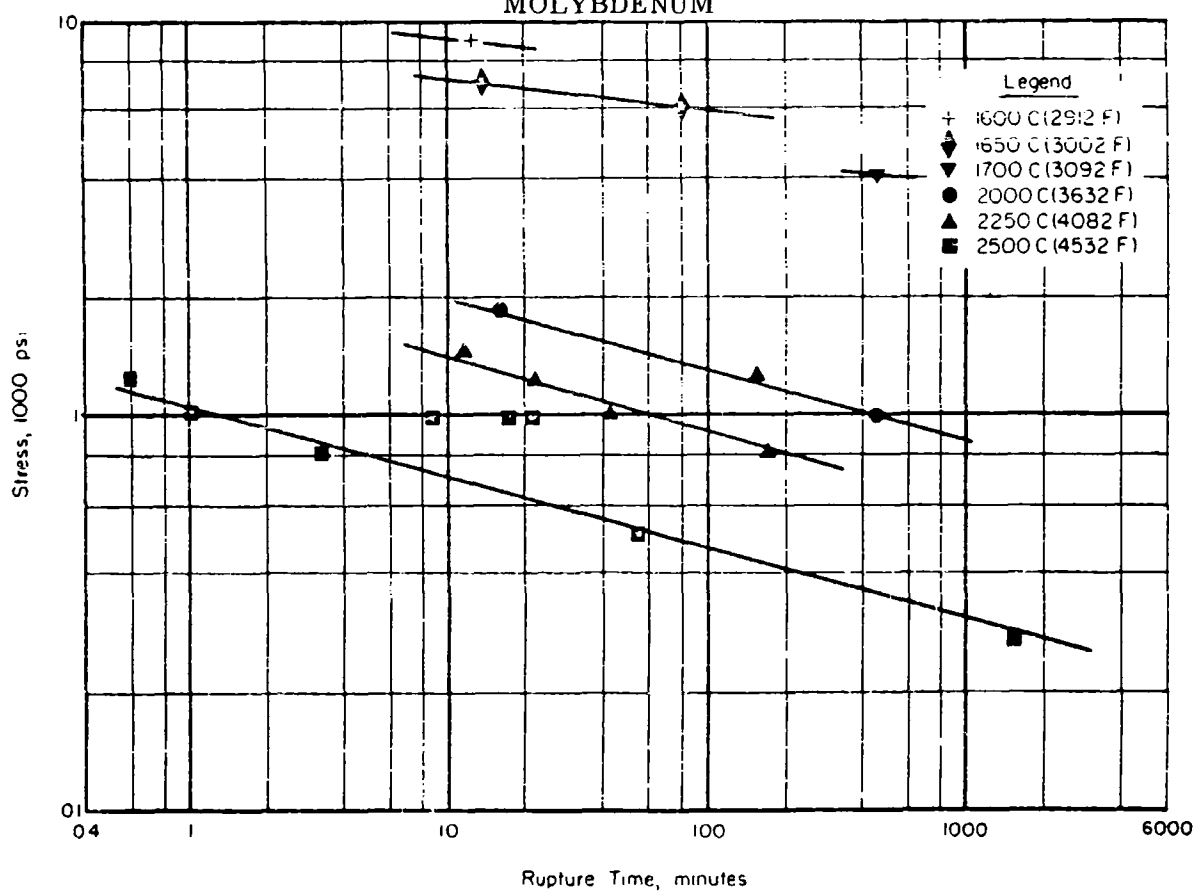


FIG. 5.32

SHORT-TIME STRESS-RUPTURE DATA FOR POWDER-METALLURGY MOLYBDENUM[3]

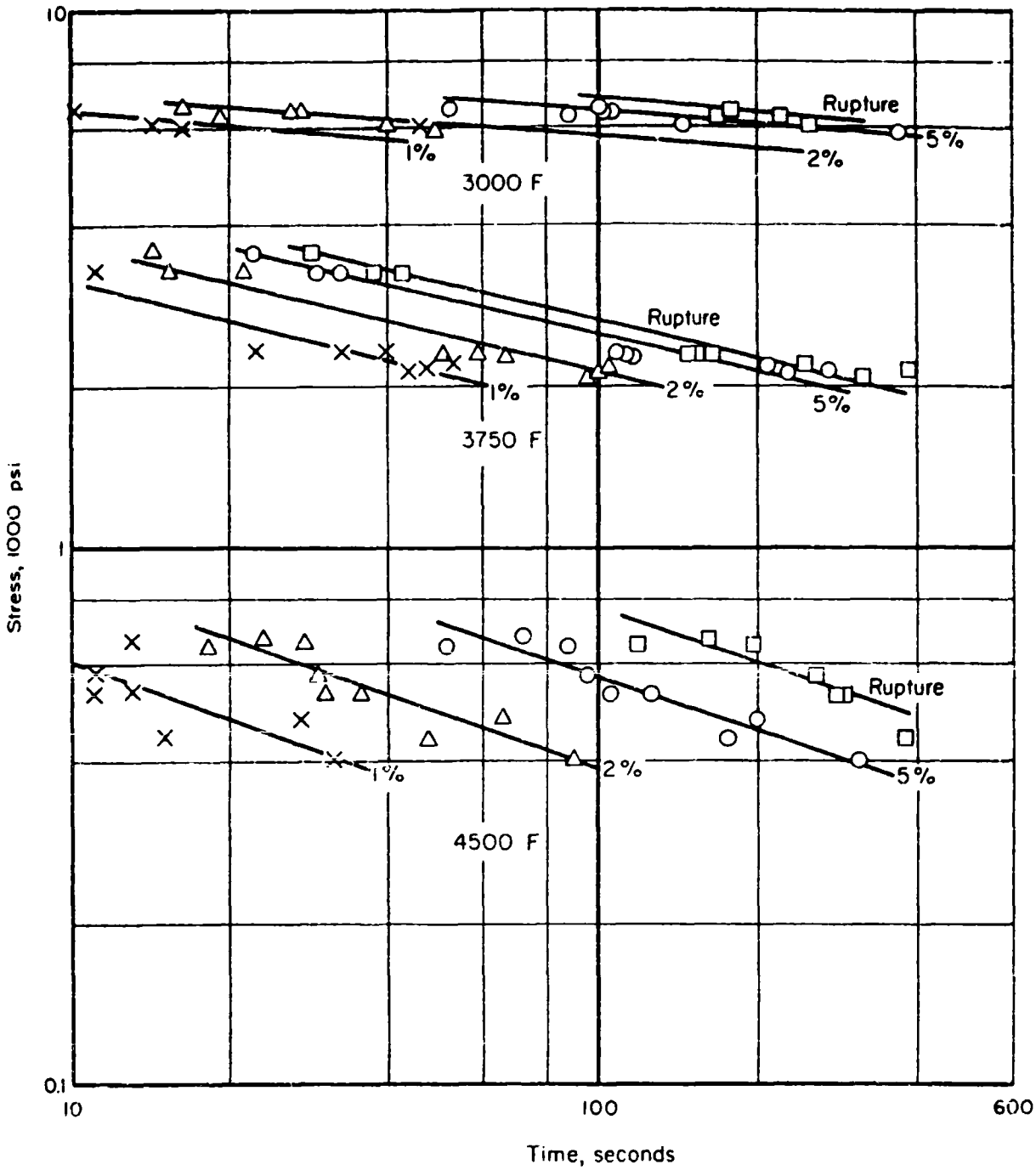


FIG. 5.33

CREEP STRESS VS TIME FOR VARIOUS VALUES OF CONSTANT CREEP STRAIN FOR ARC-CAST MO SHEET TESTED IN ARGON AT 3000, 3750 and 4500°F. [86]

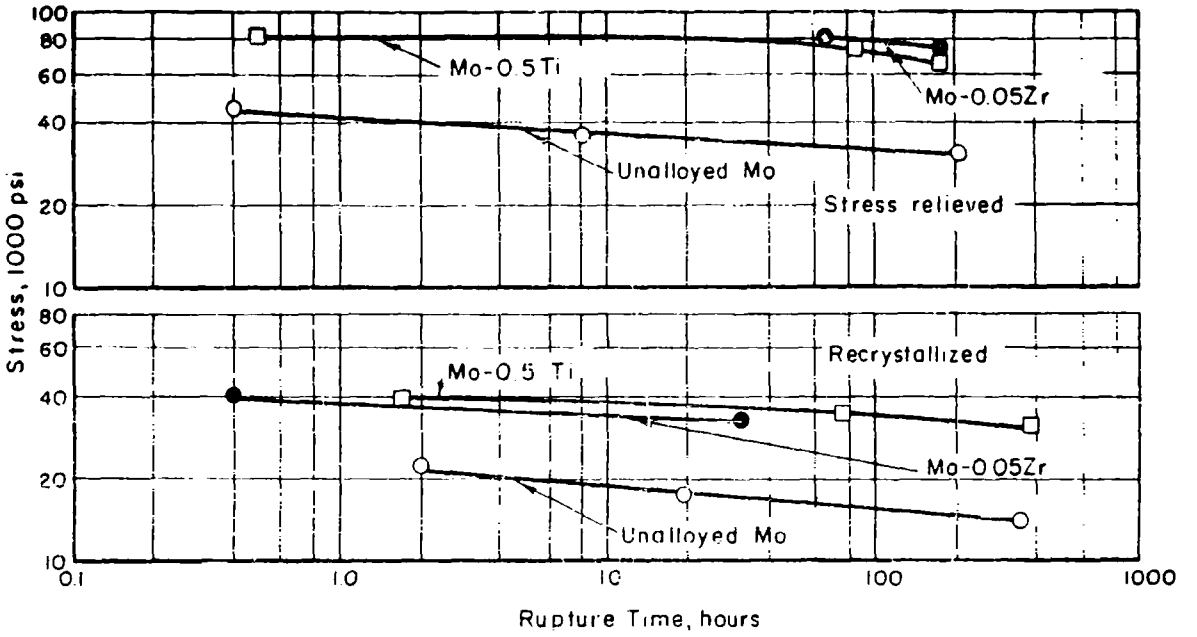


FIG. 5.34

STRESS-RUPTURE CURVES FOR SELECTED MOLYBDENUM-BASE ALLOYS TESTED IN THE RECRYSTALLIZED AND STRESS-RELIEVED CONDITIONS AT 1600 F[3]

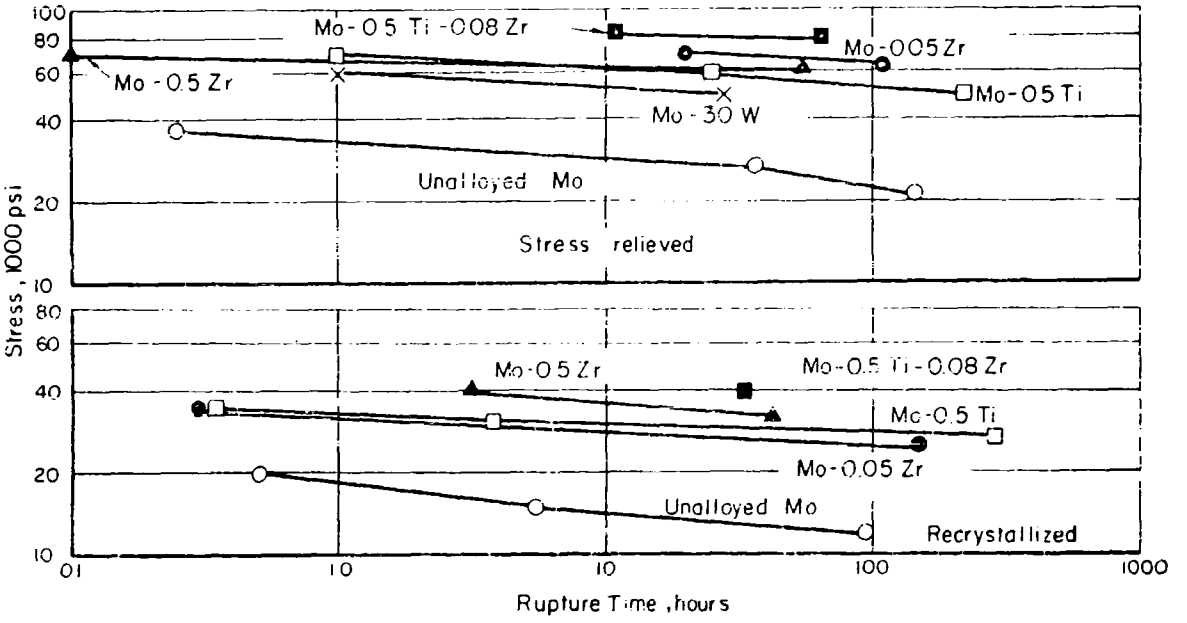


FIG. 5.35

STRESS-RUPTURE CURVES FOR SELECTED MOLYBDENUM ALLOYS TESTED IN THE RECRYSTALLIZED AND STRESS RELIEVED CONDITIONS 1800 F[3]

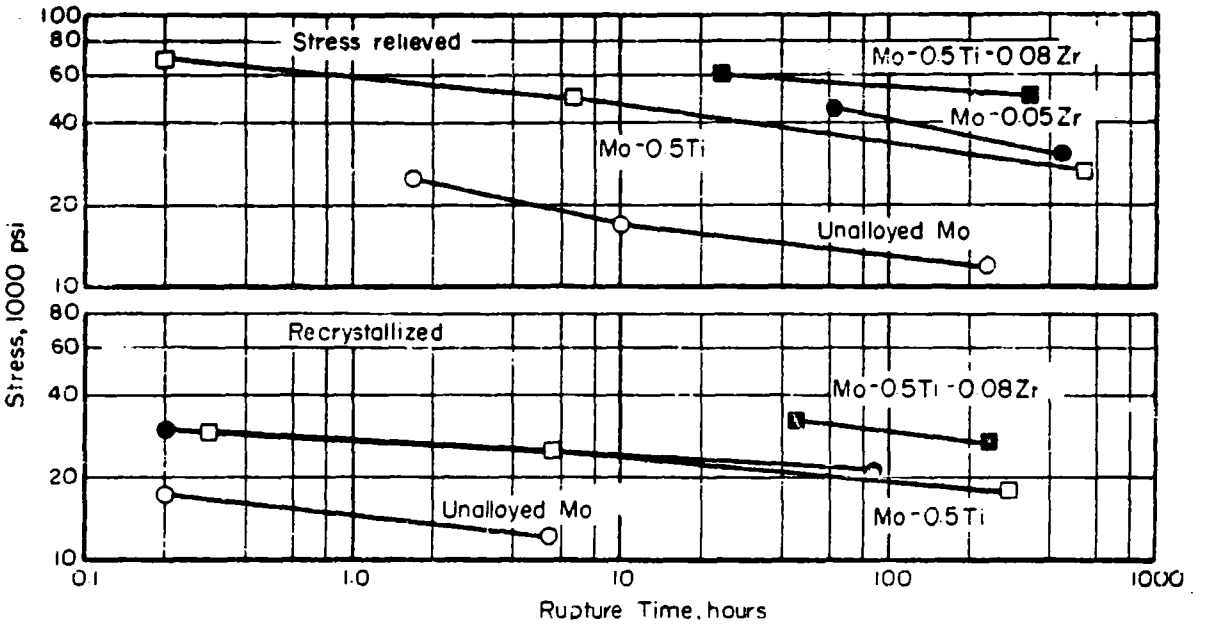


FIG. 5.36

STRESS-RUPTURE CURVES FOR SELECTED MOLYBDENUM ALLOYS TESTED IN THE RECRYSTALLIZED AND STRESS-RELIEVED CONDITIONS AT 2000 F[3]

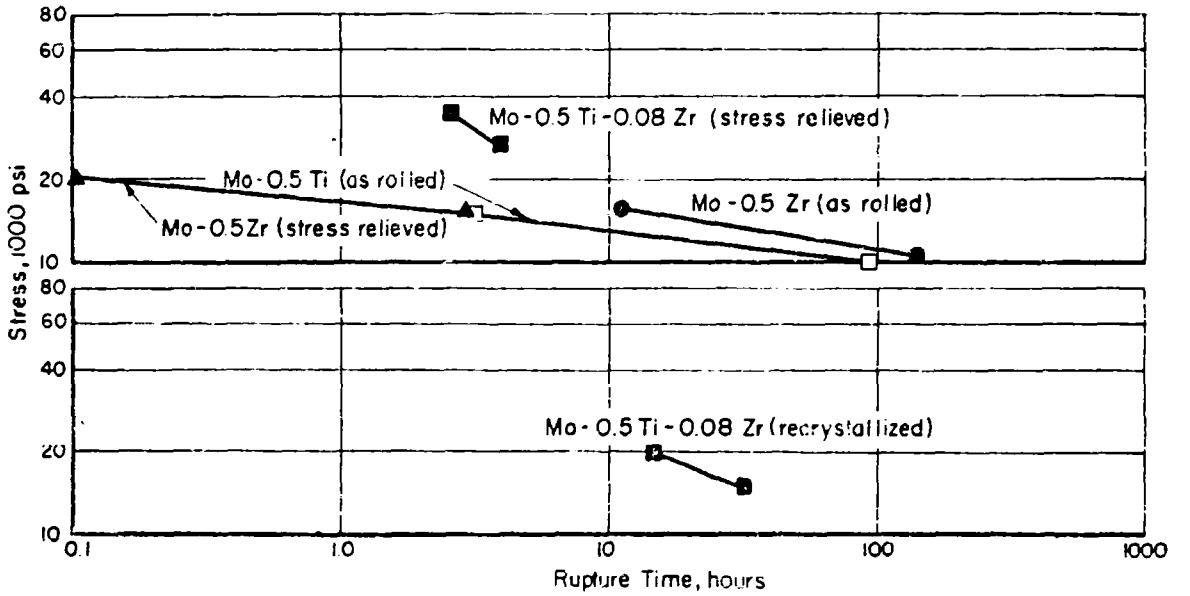


FIG. 5.37

STRESS-RUPTURE CURVES FOR SELECTED MOLYBDENUM ALLOYS TESTED IN VARIOUS CONDITIONS AT 2400 F[3]

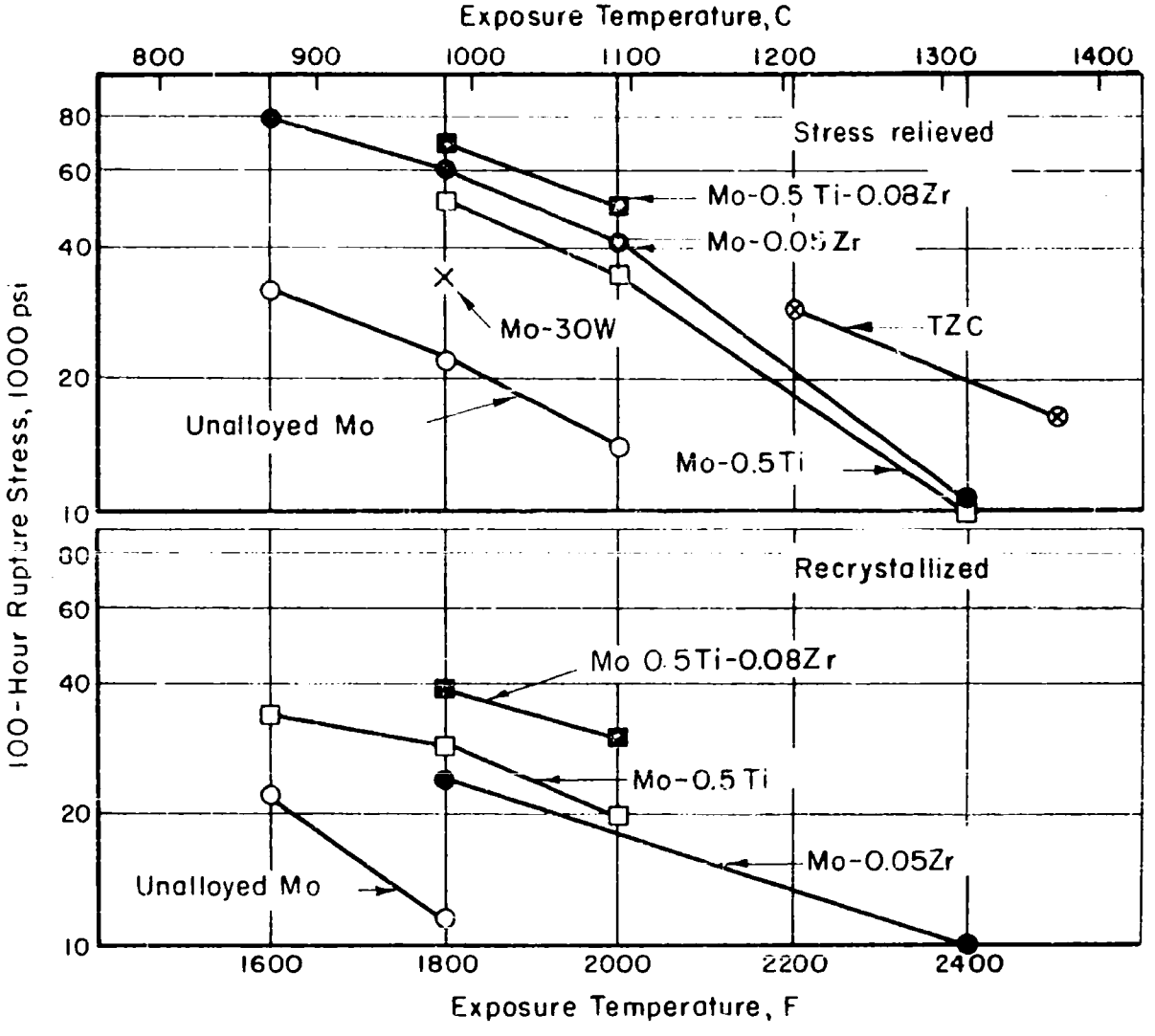


FIG. 5.38

100-HOUR RUPTURE STRENGTH OF SELECTED MOLYBDENUM ALLOYS IN THE STRESS-RELIEVED AND RECRYSTALLIZED CONDITION[3]

Further development of optimum processing procedures or control of impurities may result in a different order of strength between the various alloys.

The creep stress versus time curves for various degrees of total strain at 2000° F for the Mo-0.5Ti alloy in the stress relieved and recrystallized conditions are given in Fig. 5.39. As indicated earlier, creep properties are extremely sensitive to structural variations, and critical design requirements should be based upon creep tests on material in the same condition as that to be used in the application.

Creep data of interest for applications which include short heating and loading cycles at high temperatures are shown in Figs. 5.40 and 5.41 from tests on Mo-0.5Ti sheet specimens heated by resistance, from preliminary studies at Marquardt.

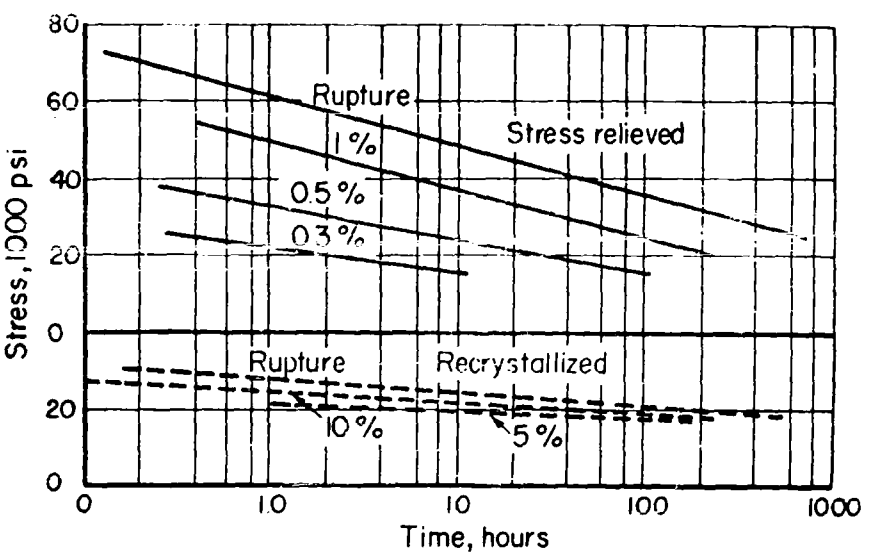


Fig. 5.39

STRESS-TIME CURVES FOR VARIOUS PERCENTAGES OF TOTAL DEFORMATION FOR THE Mo-0.5Ti ALLOY 2000° F[3]

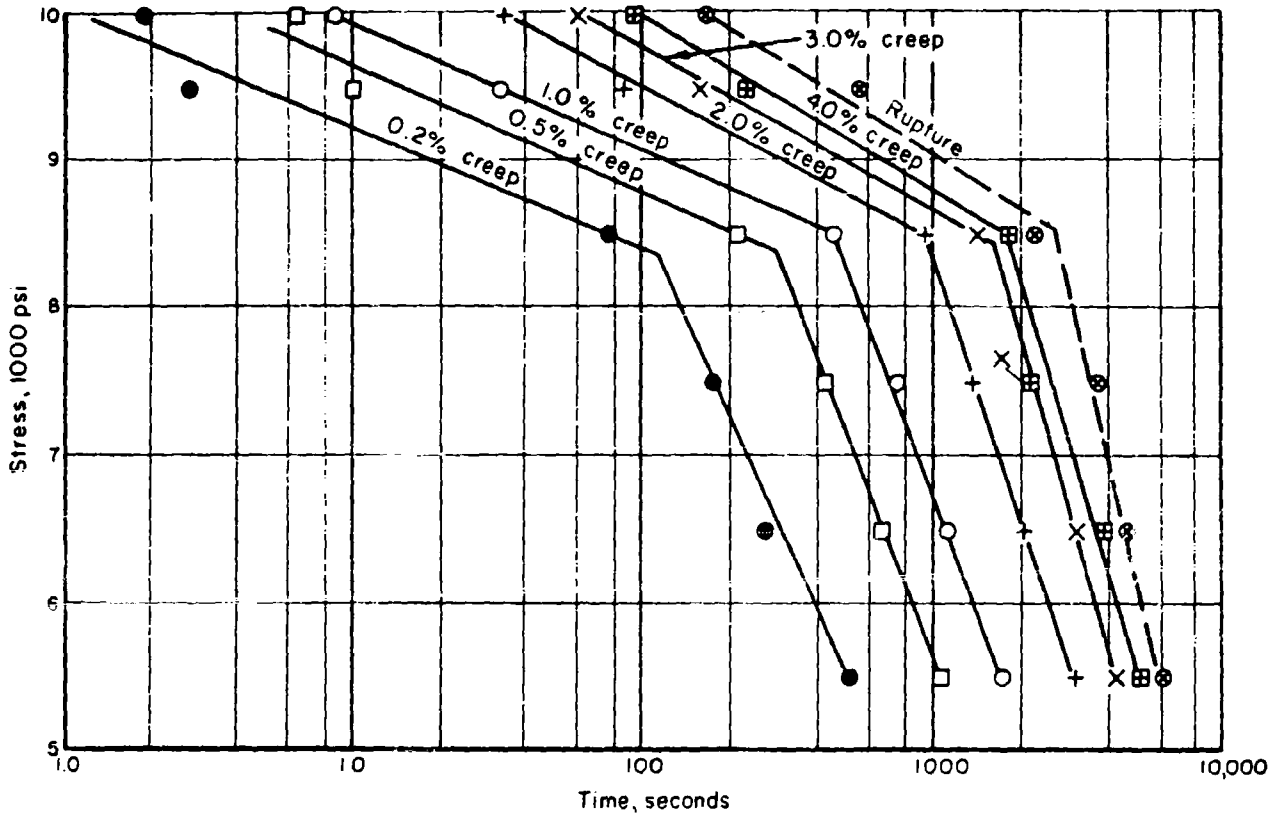


FIG. 5.40

SHORT-TIME CREEP PROPERTIES AT 2800°F FOR ARC-CAST Mo-0.5Ti ALLOY SHEET[3]

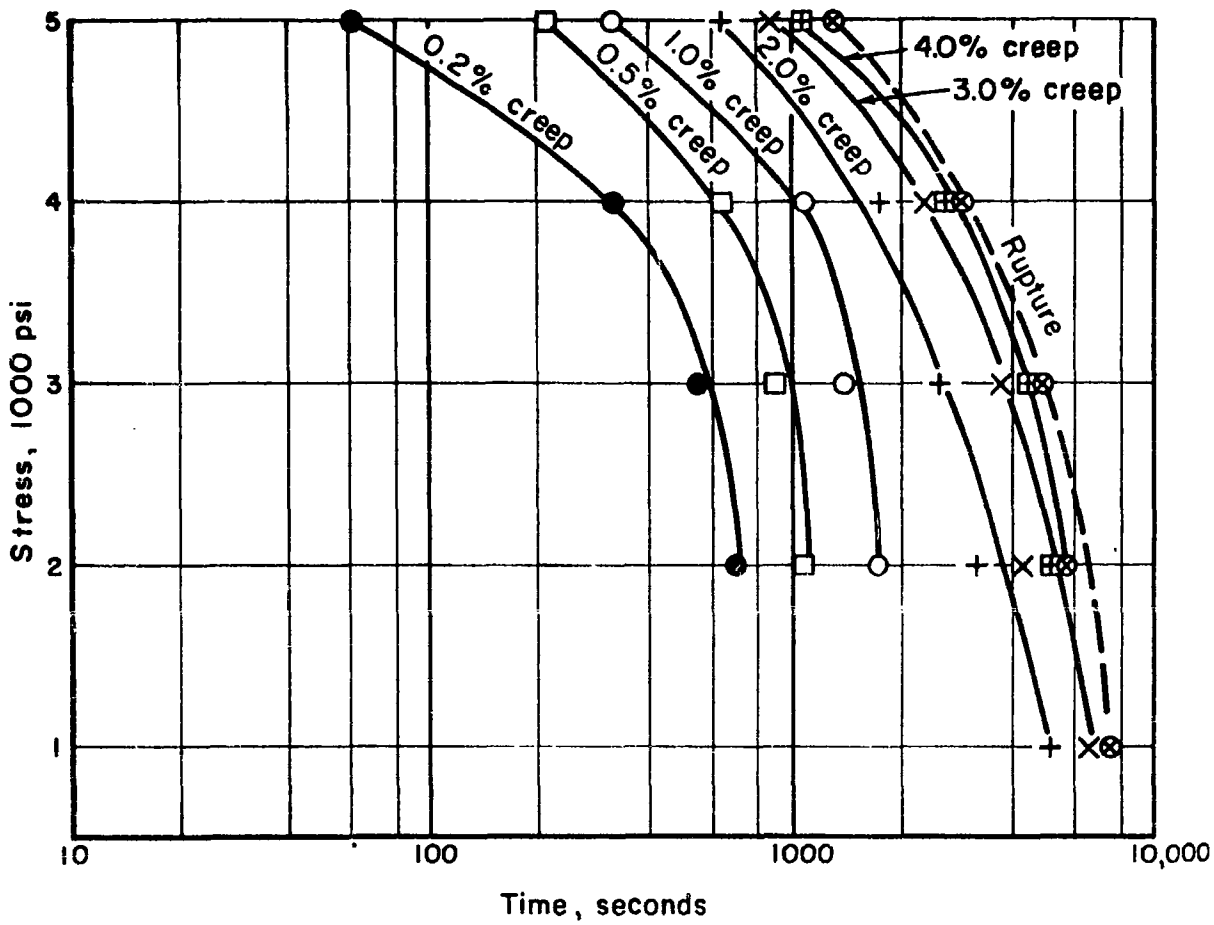


FIG. 5.41

SHORT-TIME CREEP PROPERTIES AT 3100° F FOR ARC-CAST Mo-0.5Ti ALLOY SHEET[3]

OXIDATION PROPERTIES

Commercial and attractive developmental alloys of Molybdenum exhibit about the same poor oxidation resistance as unalloyed molybdenum; their oxidation characteristics, therefore, will be discussed synonymously. Harwood[43] presented a summary of investigations of oxidation resistance which needs no further amplification even after more recent studies, and his discussion and appended references supplied the basis for the following remarks.

Above 500° C (932° F) at atmospheric air pressure the outer oxide layer, MoO_3 on molybdenum begins to volatilize and at about 770° C (1415° F) the rate of evaporation equals the rate of oxide formation. Because no protective intermediate oxide is formed the rate is linear. Above the melting point of MoO_3, about 815° C (1500° F), oxidation becomes catastrophic with molten MoO_3 dripping from the exposed surfaces until a temperature about 980° C is reached where evaporation is so rapid that the liquid oxide does not exist in contact with the metal surface. The rate at 1800° F is between 1500 and 4000 times as fast as the oxidation rate of Fe-Cr-Ni alloys designed for use at that temperature and at 1750° F is about 10 times faster than the oxidation of Armco Iron or 1025 steel.

An investigation in progress on tungsten[44], similar to one published recently, has indicated a reversal of oxidation rate of Mo at low oxygen pressures above the temperature, about 1600° C (3020° F), at which the oxide begins to dissociate. Final results of this investigation may suggest potential uses of unprotected Mo in low oxygen pressure environments at very high temperatures. Harwood[43] cites a reference which showed acceptable 100-hr life at 2000° F of uncoated Molybdenum in oxygen deficient turbine engine combustion gases.

The use of alloy additions as a means to improve molybdenum oxidation resistance has not been successful[43]. Some of the alloy additions investigated improved the resistance somewhat but the amount of additive necessary for protection exceeded the tolerance for fabricability.

The lack of success of protection by alloying has directed research effort toward protection by cladding and/or coating systems to utilize the high temperature strength of molybdenum and its alloys. Although these subjects are beyond the scope of this compilation, reference will be made to sources of information in addition to the review by Harwood[43] regarding these protection systems. Klopp,[45] in a recent review of coating development programs, cites an average life of 11 hr at 2700° F under cyclic oxidation for molybdenum protected by a proprietary coating, W-2, and lives on the order of 10 and 3 minutes at 2900° F and 3000° F, respectively, with W-2, Al-Si, and Al-Cr-Si coatings. Jaffee[46] reported that German studies involving treatment in a molten bath of Cu-Si have resulted in protection of molybdenum for 200 hr at 1600° C (2910° F). Detailed information concerning coating systems for the refractory metals will be contained in a DMIC report in publication.

THERMAL PROPERTIES

Thermal Conductivity

Thermal conductivity data from seven investigations on molybdenum have been compared and a best fit line chosen by Goldsmith, Waterman, and Hirschhorn[47]. This best fit line is presented in Fig. 5.42, along with other data from the work of Lucks and Deem[48], Rudkin[49], and Rasor and McClelland[50]. The reader is referred to the compilation by Goldsmith et al. for evaluation of the comparative data presented. Conductivity for the Mo-0.5Ti alloy is compared with the values for unalloyed material obtained by Lucks and Deem and Climax Molybdenum Co. in Fig. 5.43. The Climax data for unalloyed material agrees more closely with that of Lucks and Deem than with the average curve shown in Fig. 5.42. The alloy exhibited slightly lower conductivity than unalloyed Mo between room temperature and 1500° F.

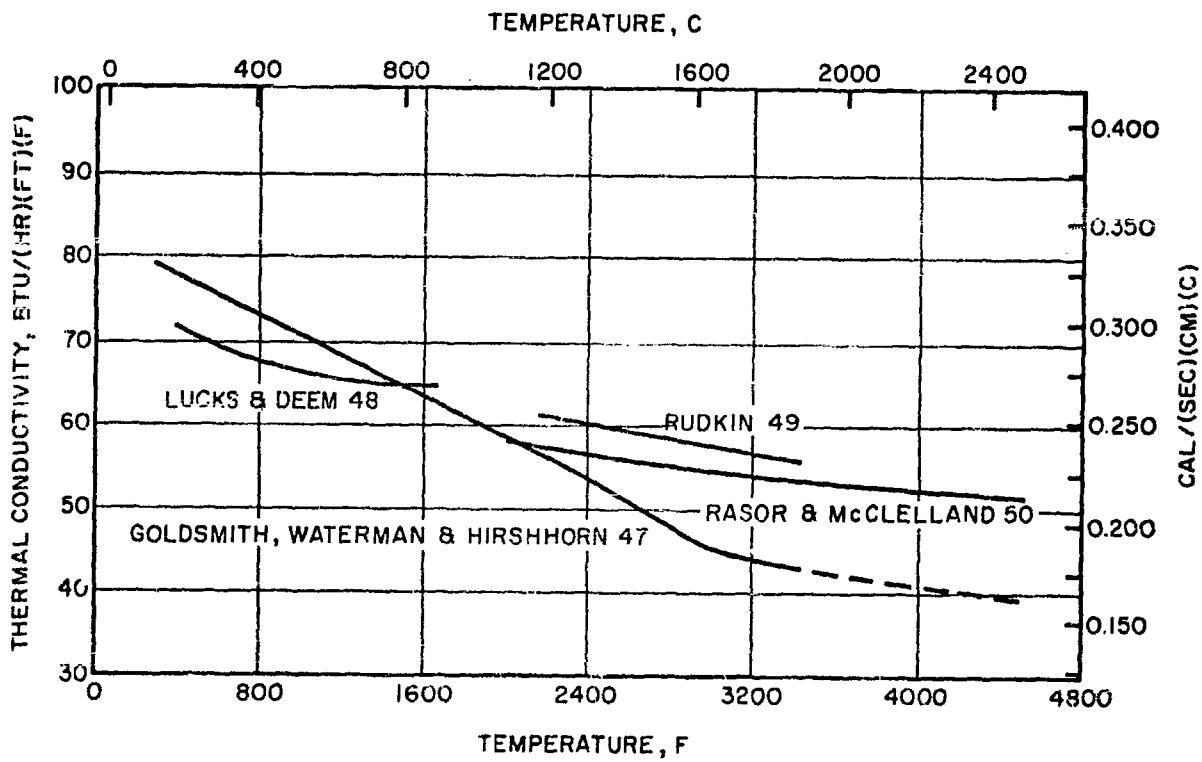


FIG. 5.42

THERMAL CONDUCTIVITY OF MOLYBDENUM VERSUS TEMPERATURE

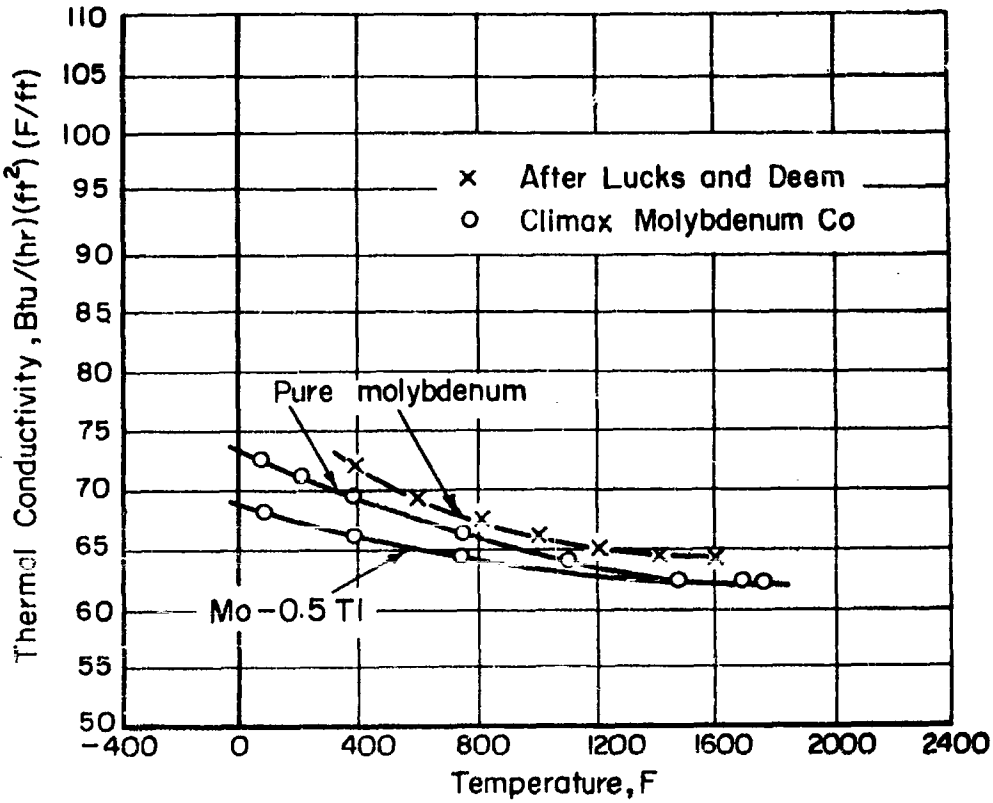


FIG. 5.43

THERMAL CONDUCTIVITY OF MOLYBDENUM AND OF Mo-0.5Ti ALLOY VERSUS TEMPERATURE[3]

Thermal Expansion

Values for linear thermal expansion of molybdenum, $\Delta l/l$, from eight investigations were plotted by Goldsmith, Waterman, and Hirschhorn[38]. The values of the various investigations were in excellent agreement along the entire temperature range. The average values from room temperature to near the melting point of unalloyed Mo are shown in Fig. 5.44 as prepared by Houck.[3] Data for the Mo-0.5Ti alloy from room temperature to 1832° F reported by Houck from Climax Molybdenum Co determinations were in excellent agreement with the curve of Fig. 5.44 for unalloyed Mo.

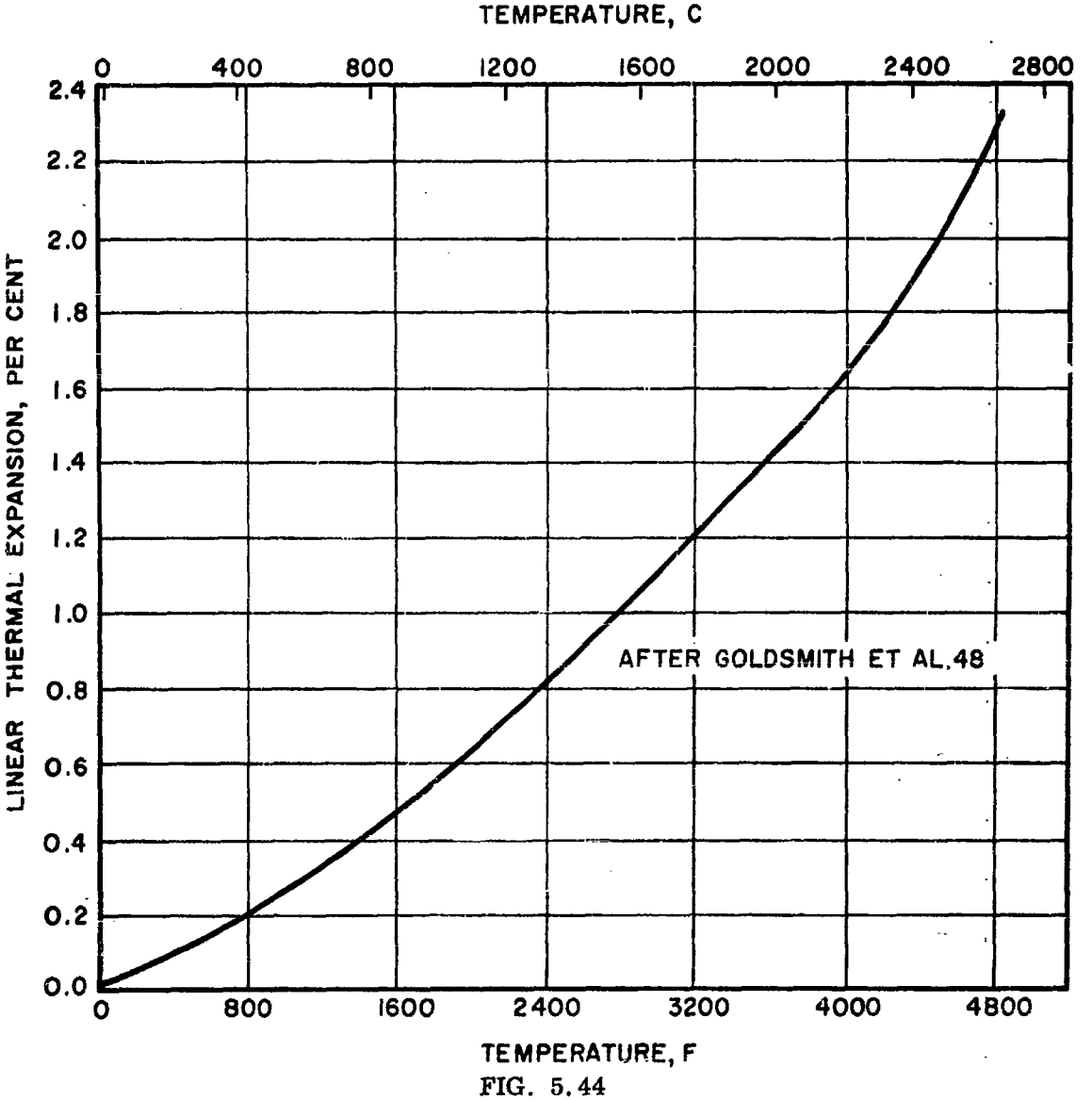


FIG. 5.44

THERMAL EXPANSION OF MOLYBDENUM VERSUS TEMPERATURE[3]

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SECTION 6

RHENIUM

INTRODUCTION

The properties which make rhenium potentially attractive for high temperature applications are listed below:

- High melting point of 3180°C (5760° F), second only to tungsten
- High strength at elevated temperatures, higher than any of the other refractory metals up to about 2000°C (3600° F), about twice that of W between room temperature and 1200°C (2190° F), both in the recrystallized condition
- High modulus of elasticity, 68 x 10^6 psi at room temperature, higher than any of the other metals included in this compilation
- Good room temperature ductility in the recrystallized condition

The use of Re is first restricted by its rather limited supply and, thus, its high cost. Chase Brass and Copper Co. has estimated that the potential production of Re could reach 20,000 to 30,000 pounds per year. Present cost of Re powder is $500 to $600 per pound, and wrought products such as wire and strip are about twice this amount.

An additional limitation of Re is its poor oxidation resistance. The oxide which forms (Re_2O_7) has a melting point of 297°C (570° F) and a boiling point of 363°C (685° F), which seriously limits the use of Re at elevated temperatures except in vacuum or in an inert atmosphere.

Applications for Re will be based on its high melting point and a combination of high temperature strength and low-temperature ductility. Applications will be limited by scarcity and cost and to its use in inert atmospheres. Currently, the largest application of Re is for thermocouples. Re versus W thermocouples have been reported[4] to be useful up to 2200°C (3990° F), and combinations of W - Re alloys such as 74W - 26Re versus 95W - 5Re couples to be useful up to 2750°C (4980° F). Future applications of Re appear likely in electronic tube structural elements where its high elevated temperature strength combined with room temperature ductility offer distinct advantages.

PROPERTY DATA

The original SRI survey report[1] covered the published property data on Re and Re alloys. These data included tensile, creep, effect of cold-work, recrystallization

behavior, oxidation, and thermal properties. Since that time, three review papers on rhenium have been published. [2,3,4] Data presented in these reviews were basically the same as had been reviewed in the SRI survey, with the exception of new data on the ductile-brittle bend behavior of W-Re and Mo-Re alloys.[5] These later data are discussed in the Tungsten and Molybdenum section of this report.

The property data previously reviewed[1] for Re is given in the Summary Section of this report.

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SECTION 7

TANTALUM

INTRODUCTION

The properties of tantalum of interest for high temperature applications are as follows:

- High melting point, 2996° C (5425° F)
- Moderately high modulus of elasticity, 27 × 10^6 psi
- Excellent low temperature ductility, tensile reduction in area as high as 80 percent at -250° C
- Useable strength at 1650° C (3000° F), ultimate tensile strength about 4000 psi
- Stability of major oxide Ta_2O_5, nonvolatile below 1370° C (2500° F)

In addition, simple tantalum alloys which are fabricable at room temperature have sufficient strength for structural applications above 2500° F.

The major disadvantages are the relatively high density, 16.6 g/cc (0.6lb/cu in.), poor resistance to oxygen contamination at even relatively low temperatures, 500° C (930° F), and relatively short supply with associated high cost.

The tantalum properties discussed in the original SRI compilation[1] were based on results from tests on material produced by one supplier by powder metallurgy consolidation. At least 11 suppliers now offer tantalum consolidated either by powder metallurgy, EB melting, and/or arc-melting techniques; many new data have been reported in the last two years. Recent data for Ta and Ta alloys have been reported by Battelle[2,3] and Westinghouse[4] and the laboratories for suppliers of tantalum alloys, Fansteel, National Research Corp., Stauffer, and Wah Chang. The readily available DMIC review by Schmidt[5] is a detailed report of data accumulated to mid 1960. The state-of-the-art-survey[6] prepared by Battelle for Wah Chang includes the most recent status of alloy development and production, and the chapter Tantalum in the second edition of the Rare Metals Handbook[7] includes excellent summaries of the production, fabrication, physical and mechanical properties, corrosion resistance and current uses of tantalum. This section is a summary of the status of tantalum and its alloys. The reader is referred to the recent surveys for details which could not be included without unnecessary expense of complete duplication of those available compilations. Many of the figures and tables included here have been reproduced from the surveys, and they will be so referenced.

MECHANICAL PROPERTIES

Tensile Properties of Tantalum

Production techniques of tantalum are sufficiently advanced to permit tentative limits of chemical composition to be established. An ASTM committee has proposed the limits shown in Table 7.1 from proposals by six tantalum suppliers. Unless impurity contents of specific test materials used to obtain the data reported herein vary appreciably from the values shown in the table, the composition will not be reported.

Room temperature tensile properties of tantalum are shown in Table 7.2. The range in ultimate tensile strength from 27,500 to 180,000 psi is indicative of the large effect of purity and thermal-mechanical history on the strength properties of Ta. Chemical analysis typical of EB-melted Ta is given in footnotes to the table; an indication of the effect of purity on the strength of Ta is shown by a comparison between the first three strengths cited and other strengths reported for less-pure recrystallized samples. The high-purity materials exhibited tensile strengths from 27,500 to 33,500 psi whereas the strength of less-pure recrystallized material was reported to range from 40,000 to 67,100 psi. The excellent room temperature ductility reported for all conditions except those of extreme deformation is a characteristic of Ta not common to the other refractory metals.

The modulus of elasticity of Ta from -196 to 900°C as determined dynamically by two investigators and summarized by Schmidt is shown in Fig. 7.1. The difference in values shown, about 6 percent maximum, cannot be explained by information included in the original reports and the departure from linearity at about 700°C in Begley's curve is probably due to experimental difficulties rather than a change in the modulus temperature dependency.

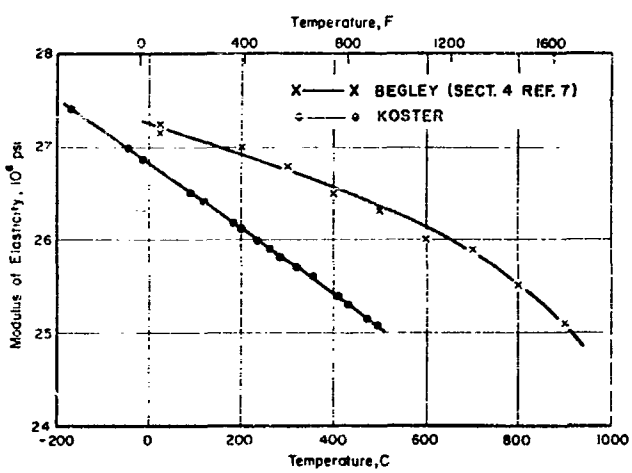

FIG. 7.1

THE MODULUS OF ELASTICITY OF TANTALUM FROM -196 TO 900°C[5]

TABLE 7.1

PROPOSED RECOMMENDATIONS FOR CHEMICAL SPECIFICATIONS FOR ROD, WIRE, INGOT, AND SHEET TANTALUM[5]

Impurity	Number of Proposals[(a)]	Maximum	Weight Percent		
			Minimum	Average	Limit Based on Average
Carbon	6	0.05	0.01	0.027	0.03
Oxygen	5	0.05	0.02	0.027	0.03
Nitrogen	5	0.025	0.005	0.014	0.015
Hydrogen	4	0.02	0.001	0.007	0.01
Columbium	5	0.10	0.02	0.044	0.05
Iron	6	0.03	0.003	0.015	0.02
Titanium	2	0.02	0.005	0.0125	0.01
Tungsten	1	—	—	0.01	0.01
Silicon	2	0.03	0.01	0.02	0.02
Nickel	3	0.02	0.001	0.013	0.02

(a) Proposals from Fansteel, Haynes Stellite, Kawecki Chemical, National Research, Pfaudler, and Radio Corporation.

Table 7.2

TENSILE PROPERTIES OF TANTALUM AT ROOM TEMPERATURE[5]

Condition	Ultimate Tensile Strength, 1000 psi	Yield Strength, 1000 psi	Elongation, per cent	Reduction in Area per cent
Recrystallized[(a)]	27.5	--	38	89
Recrystallized high-purity sheet (1 hr at 1200 C 0.040 inch thick) (b)	29.4	26.3	36	--
Recrystallized rod (1 hr at 2600 C) (c)	33.4	--	50	--
Recrystallized sheet	40.0/50.0	30.0/40.0	30/40	--
Recrystallized rod (1 hr at 1700 C) (d)	49.8	39.3	45	86
Annealed sheet (0.010 inch thick)	50.0	--	40	--
Cold-worked high-purity sheet (cold reduced 95%; 0.040 inch thick) (b)	60.5	49.0	--	--
Recrystallized sheet (0.010 inch thick) (e)	67.1	57.4	25	--
Annealed wire (0.002 inch diameter)	100.0	--	11	--
Cold-worked sheet	100.0/120.0	95.0/105.0	3	--
Cold-worked sheet (0.010 inch thick)	110.0	--	1	--
Hardened plate (0.010 inch thick)	145.0	--	18	--
As-drawn wire (0.002-inch diameter)	180.0	--	2	--

(a) Degassed; 0.01% C.
(b) Electron-beam-melted tantalum supplied by Temescal Metallurgical Corporation; 0.0016% O, 0.0010% N, 0.00014% H, 0.0030% C, 0.0003% Cr, 0.01-0.03% Cb, 0.003% Cu, 0.0008% Fe, 0.0003% Ni.
(c) From hydrogen-reduced powder; 99.95% Ta, traces of Ni, Fe, W, Cu, Ca, Si, Pb, Sn, Cr.
(d) Supplied by Fansteel Metallurgical Corporation; 0.01% N, 0.010% C, 450 grains/mm^2.
(e) Powder-metallurgy ingot supplied by Fansteel Metallurgical Corporation; 0.0056% O, 0.013% N, 0.02% C, 0.10% Cb, 0.01% W, 0.015% Fe, 512-1024 grains/mm^2.

The tensile properties of unalloyed recrystallized Ta are shown in Fig. 7.2; conditions of the test material and chemical analyses are given in Table 7.3. The first three investigations cited in Fig. 7.2 used powder-metallurgy Ta and the last used Ta produced by electron-beam melting. Bechtold[8] used bar type specimens; the other three investigators used sheet specimens. The ultimate tensile and yield strengths of EB-melted material reported by Schmidt[3] are considerably below the same properties for powder metallurgy specimens reported by the other three investigators in the temperature range from -196 to 500° C. On a percentage basis, the difference is particularly large between room temperature and 500° C. The maximum in the ultimate tensile strength vs temperature curve between 300 and 400° C which was ascribed to strain-ageing behavior by Pugh[9] is not as pronounced in the higher purity material used by Schmidt. Comparison of strength values above 1200° C is difficult because of the few data available at comparable test temperatures and also because of the different test conditions used. Both types of material exhibited measurable ductility at the lowest test temperature of -195° C. The ductility-temperature relation between room temperature and 500° C is complicated by strain-ageing behavior.

The range of ultimate tensile strength of Ta from 1000 to 2800°C as reported by five investigators and summarized by Schmidt[5] is shown in Fig. 7.3. The effect of strain rate at the high temperatures appears to overshadow the effect of impurity on the strength of Ta. For example, at all temperatures at which strength comparisons can be made between tests conducted at fast and slow strain rates there is a large variation in strength. EB-melted and powder-metallurgy material tested near 1700° C exhibit the same strength for tests conducted at about the same strain rate. The data points for arc-cast, and powder-metallurgy material, reported by Glazier et al.,[11] indicated a tendency toward lower strength for the higher purity arc-cast material. However, tests on the two materials at each temperature were conducted at different loading rates. Description of testing procedures used at very high temperatures are contained in the literature[1, 5, 12, 11, 13], and in the Mo section on tensile properties.

Ductile-Brittle Behavior of Tantalum

Tantalum has not been observed to undergo a transition from ductile-to-brittle behavior with decreasing temperatures as low as -250° C. Imgram, et al.,[14] have reported tensile reduction-in-area values of 80 percent for high purity notched tensile specimens tested at -250° C. A recent report by Adams and Iannucci[15] discusses the ductility of Ta at low temperatures as related to grain size and purity. Even these investigators have not reported brittle behavior of Ta, but they have observed cleavage on some coarse-grained samples tested at -78 and 23° C. A complete discussion of the ductile-brittle behavior from known literature references is contained in the compilation by Schmidt[5].

Effect of Dissolved Gases on Properties of Tantalum

A complete review of investigations concerned with the effect of interstitial elements on the properties of Ta may be found in the summary report by Schmidt[5]. A thorough investigation was conducted by the same author[2] into the reactions of Ta with oxygen, air, and nitrogen and the effect of these reactions on the surface hardness and microstructure of Ta. Schmidt also investigated the properties of Ta-O, Ta-N,

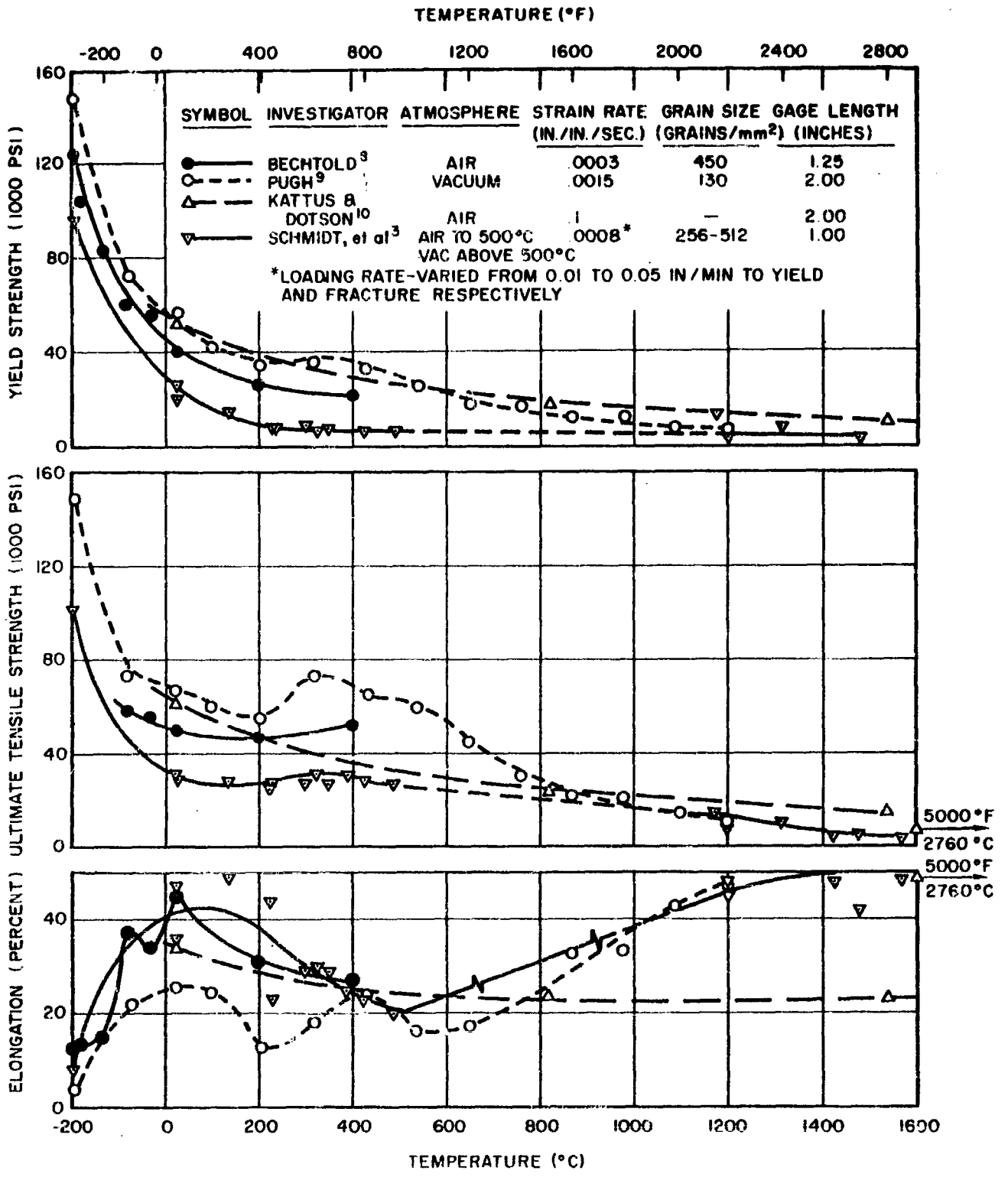

FIG. 7.2

TENSILE PROPERTIES OF TANTALUM AS A FUNCTION OF TEMPERATURE

Table 7.3

MATERIAL AND TEST CONDITIONS FOR TENSILE DATA PRESENTED IN FIG. 7.2

Impurity Element	Weight Percent	Data on Test Material
Bechtold[8]		
0	Not determined	Powder Metallurgy 0.300-inch diameter
N	0.01	swaged bar
C	0.010	Specimens annealed 1 hour
Ta	99.9 (estimated	at 1700°C in vacuum. Grain size – 450 grains/sq. mm.
Pugh[9]		
0_2	0.0056	Powder Metallurgy 0.010-inch sheet vacuum
N_2	0.013	annealed
C	0.02	Recrystallized grain size
Cb	0.10	approximately 130 grains/sq. mm.
W	0.01	
Fe	0.015	
Kattus, et al.[10]		
Commercially pure		Powder Metallurgy 0.064-inch sheet
Schmidt, et al.[3]		
0	0.0016	Electron Beam Melted ingot 2 in. dia 75 percent final cold reduction by rolling to 0.035 in thick sheet
N	0.0010	Recrystallized after 1 hr at 1200°C (2190°F)
H	0.00014	Specimen gauge size - 0.035 in. thick x 0.250 in. wide x 1 in. lg
Cb	0.01-0.03	256-512 grains/mm^2 (0.06-0.04 mm dia)
Cu	0.003	
Fe	0.008	
Ni	0.0003	

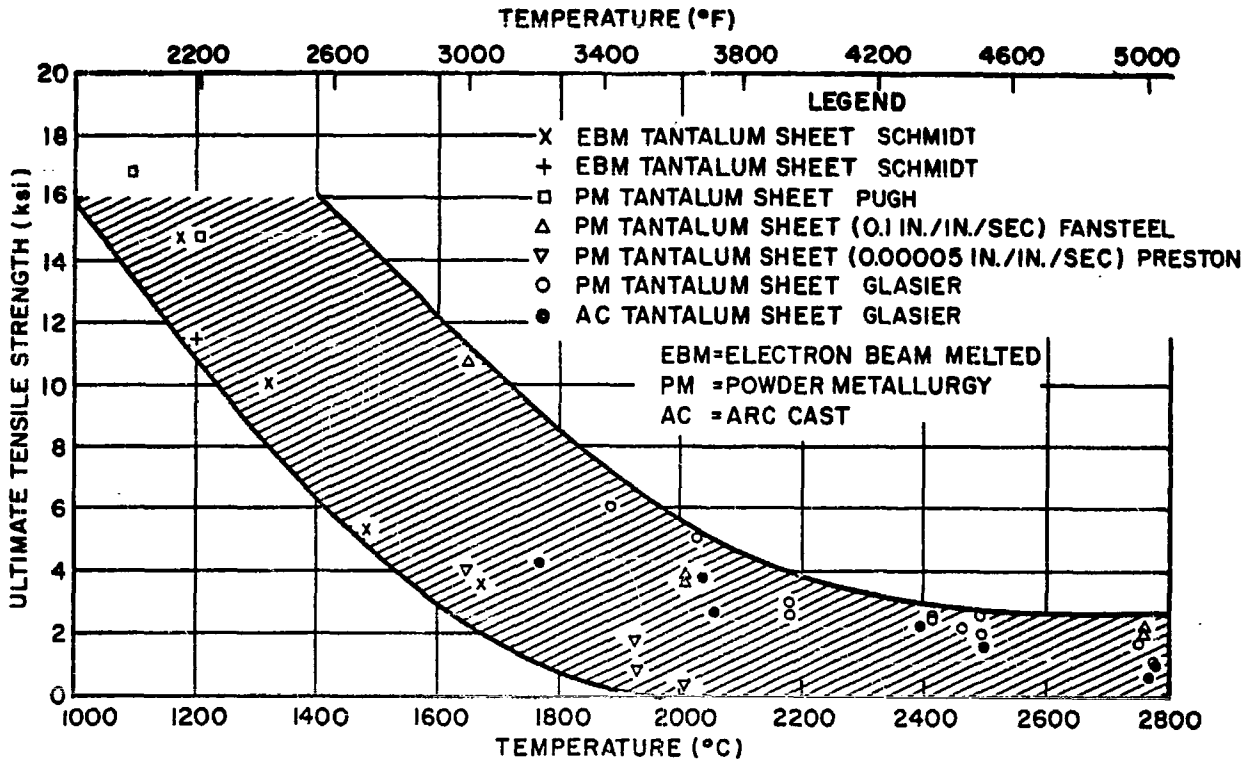

FIG. 7.3

ULTIMATE TENSILE STRENGTH OF TANTALUM SHEET
FROM 1000–2800°C[5]

and Ta-C alloys. Only an introduction to the subject will be given here and the reader is referred to either the summary report or the original work by Schmidt[5, 2]. The original work included fundamental considerations of diffusion coefficients of the interstitial elements as well as mechanical properties of the alloys.

Hardness data from which diffusion coefficients were calculated are given in Fig. 7.4 which indicates the depth of oxygen and/or nitrogen penetration from air reactions at 600°C and oxygen and nitrogen reactions at 1200°C. The data indicate a much higher reaction rate between oxygen and Ta surfaces than between nitrogen and Ta surfaces. The author[2] observed no nitride second phase in the specimens exposed to air. However, nitride surfaces were observed on specimens treated only in nitrogen. Little difference between the reaction between air and Ta and between oxygen and Ta was observed. The figure may be used to estimate the amount of surface that must be removed from Ta products heated in air during fabrication at the temperatures indicated. Figure 7.5 as presented by Schmidt[5] from work of Yancey also shows the effect of air heating on properties of very thin Ta sheet, 0.002-in. thick. This figure shows

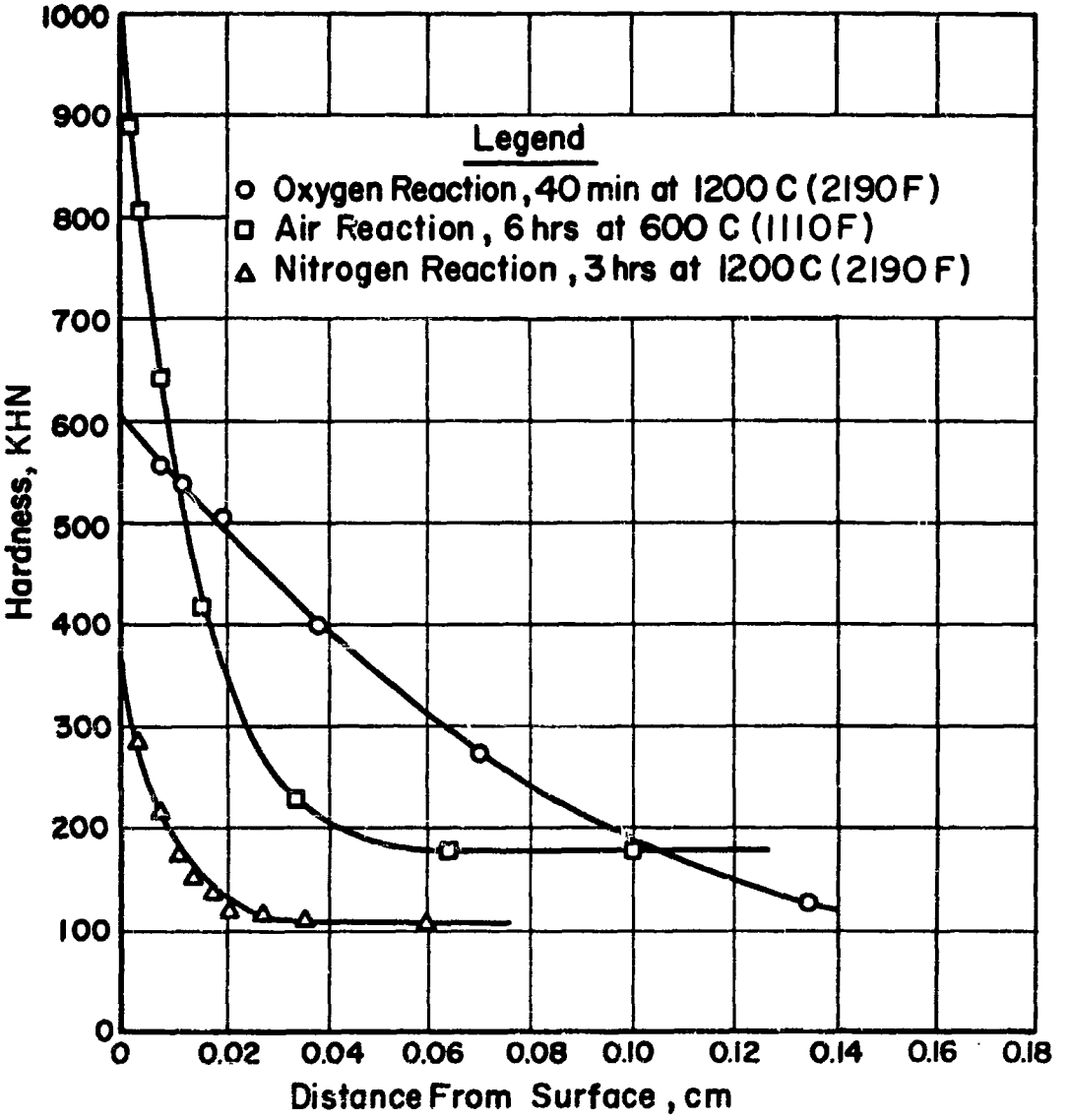

FIG. 7.4

HARDENING OF TANTALUM BY OXYGEN AND NITROGEN[2]

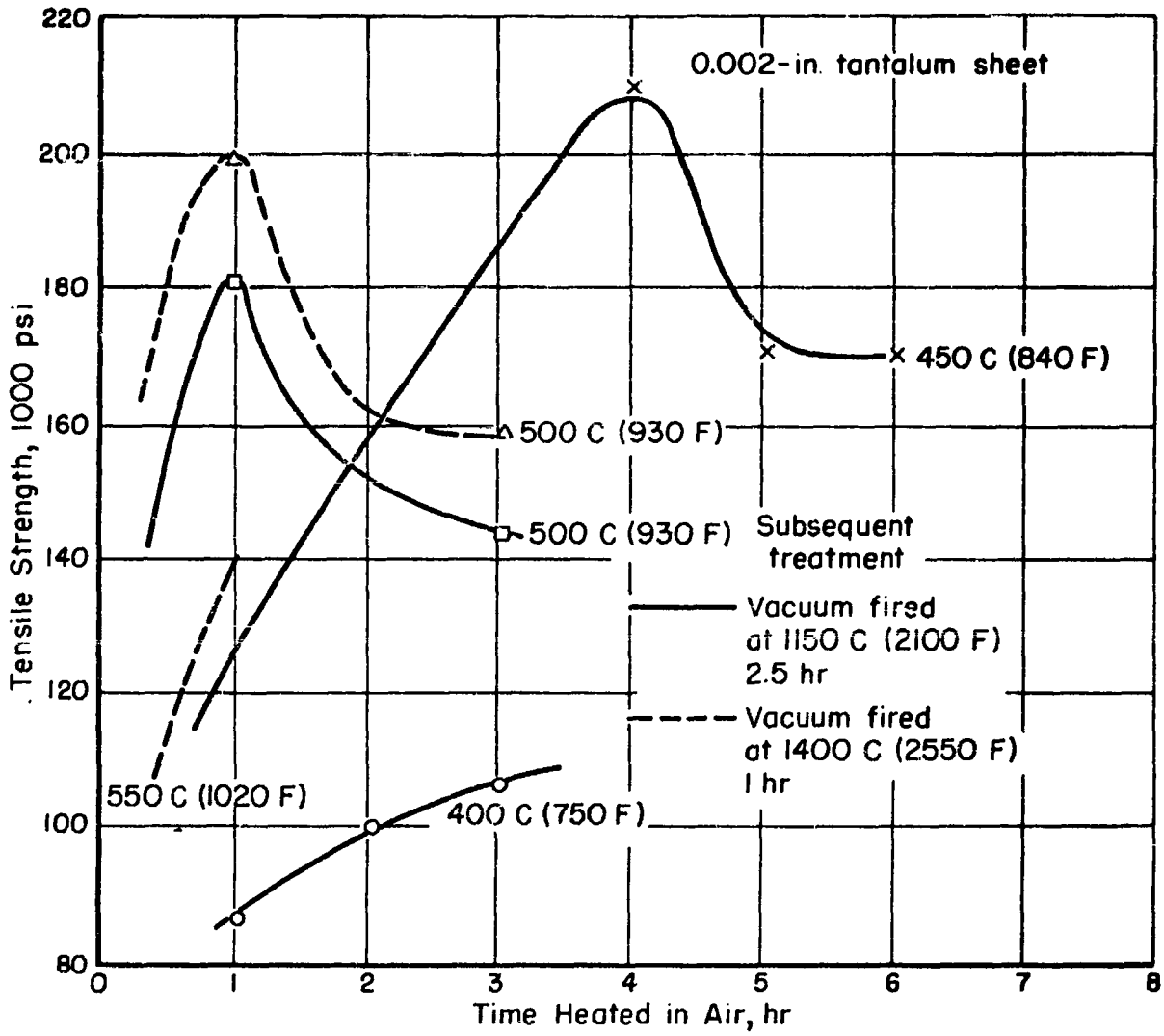

FIG. 7.5

ROOM TEMPERATURE TENSILE STRENGTH OF TANTALUM AFTER EXPOSURE IN AIR AT 400–550° C FOR PERIODS UP TO 6 HOURS[5]

that heating in air at even 400° C can increase the ultimate tensile strength of Ta sheet from 85,000 to over 100,000 psi, and heating at 450° C for four hours can increase the tensile strength to over 200,000 psi.

Schmidt[2] prepared alloys containing controlled amounts of oxygen, nitrogen and carbon. The ultimate tensile strength of the three alloys and a comparison of their strength with that of powder-metallurgy specimens tested by Yancey and EB-melted specimens tested by Schmidt are given in Fig. 7.6. The oxygen contents of the three alloys are given in parenthesis on the figure and the author concluded that the increase in strength of the three alloys over that of EB-melted Ta was directly proportional to the oxygen content rather than to the contents of carbon and nitrogen. He also proposed that the peak in the carbon alloy shown at about 450° C was the only peak which resulted from carbon interstitial content. From a consideration of the strain rate used in the tests (8.33×10^{-4}/sec) and diffusion coefficients, the author calculated that strain-aging peaks should be observed at 304, 474 and 582° C for oxygen, carbon and nitrogen, respectively. He found close agreement between his calculated values and values reported by other investigators. Tests reported in this investigation were not conducted at high enough temperatures to observe a possible nitrogen peak at 582° C. The yield strength values of the three alloys shown in Fig. 7.7 as tabulated by Schmidt[2] and summarized by Bechtold[16] show that the interstitials have less effect on the yield strength than on the ultimate tensile strength. Ductility of the alloys as measured by tensile elongation also decreased initially with increasing temperatures from room temperature to about 200° and then increased and evidenced a maximum at the same temperature, about 350° C, as the maximum in the strength-temperature curves. The tensile elongation from 25-500° C had a maximum of 27percent and a minimum of 10 percent.

The stress-rupture strength of interstitial alloys, as measured by creep tests at 750 and 1200° C was also affected by the interstitial elements, carbon, oxygen and nitrogen, as shown in Table 7.4 from the work of Schmidt[2]. Additions of carbon were found to increase the rupture strength at both temperatures. The improvement in creep resistance due to the C additions was larger at the higher temperatures and increased for the longer time tests. Some increase was shown also for the nitrogen alloys, but the increase was less at longer times and at the higher temperatures. The oxygen alloys showed only an increase at the very short time creep tests; for the longer creep testing times and higher temperature the increase was nil.

Effect of Cold Work on Tensile Properties of Tantalum

Most recent investigations concerning the effect of cold work on Ta have been concerned with the change in hardness with different amounts of cold reduction. The original SRI report[1] showed from the work of Myers that the ultimate tensile strength of tantalum increased from about 33,000 to 115,000 psi after 99 percent cold-reduction of powder-metallurgy produced material. Myers[1] work showed a decrease in room temperature elongation from about 80 percent to less than 5 percent after 95 percent cold reduction. Schmidt[2] from his investigation on high-purity tantalum reported

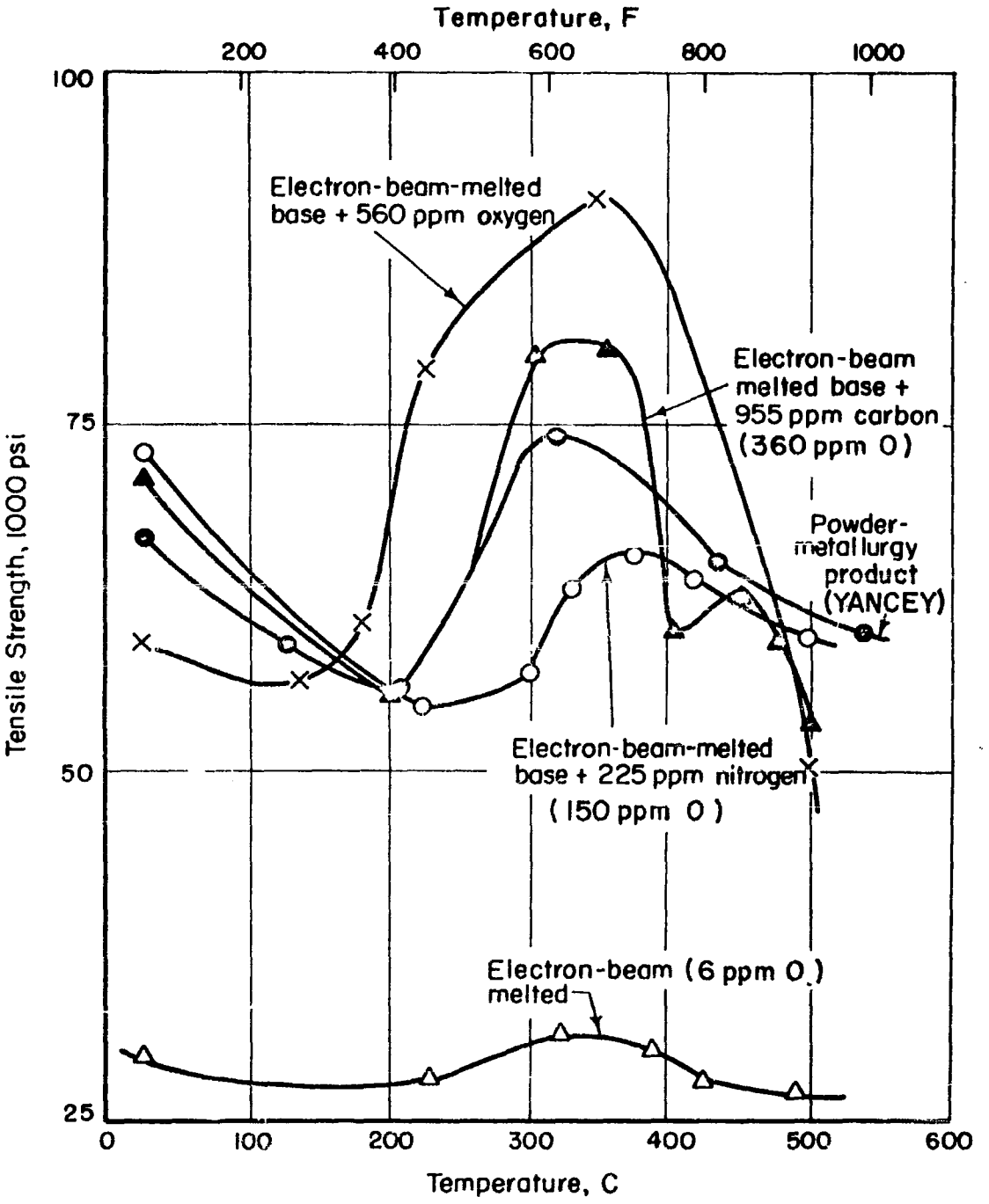

FIG. 7.6

ULTIMATE TENSILE STRENGTH OF TANTALUM FROM 25 TO 550° C AS INFLUENCED BY O, C, AND H ADDITIONS[5]

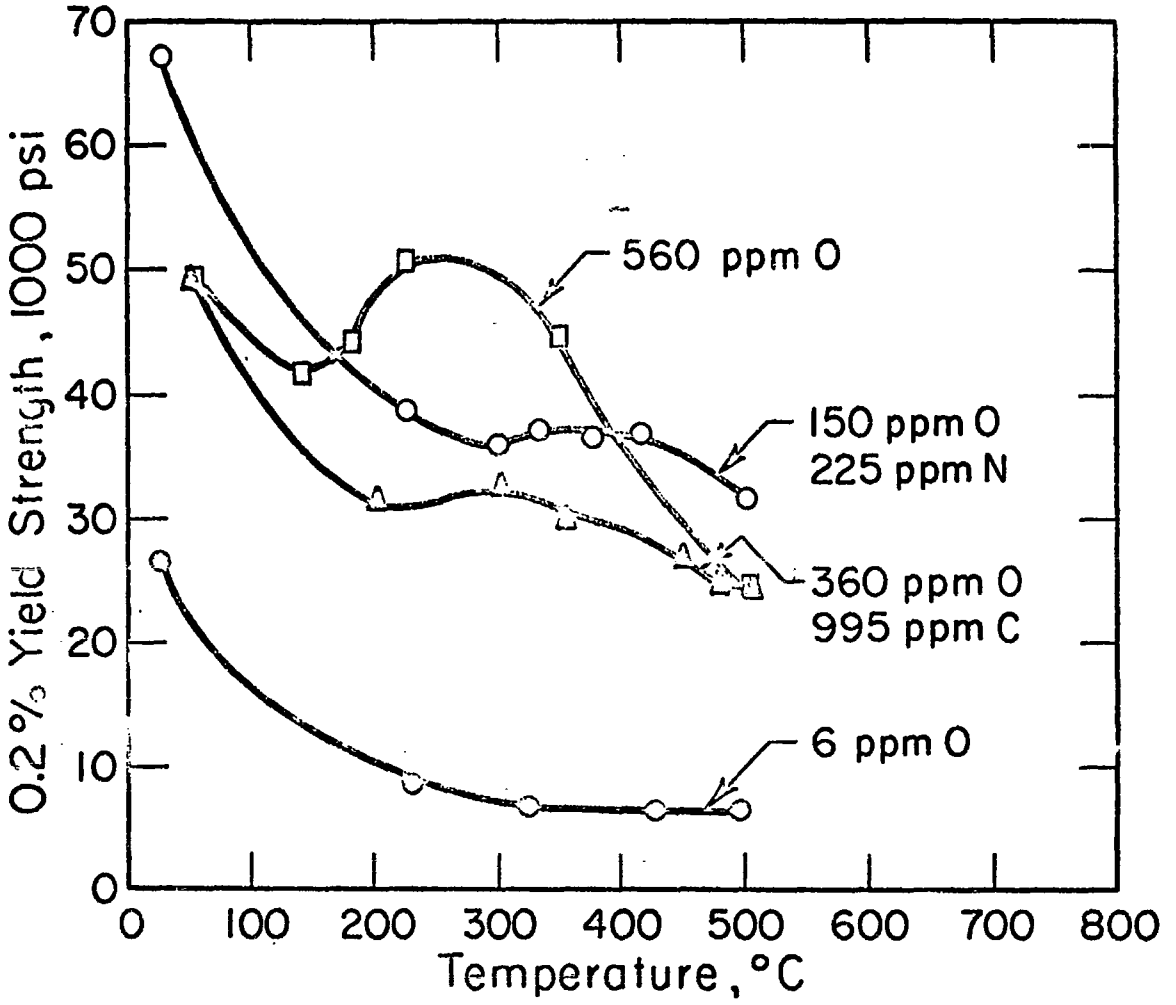

FIG. 7.7

YIELD STRENGTH OF TANTALUM FROM 25 TO 500°C
AS INFLUENCED BY O, N, AND C ADDITIONS[16]

Table 7.4

CREEP-RUPTURE STRENGTHS OF INTERSTITIAL-CONTAINING ALLOYS OF TANTALUM[2]

Temperature		Time	Composition				Strength Increase, percent(b)		
C	F	hours	Ta (a)	Ta-C (a)	Ta-N (a)	Ta-O (a)	Ta-C	Ta-N	Ta-O
750	1380	0.1	17.0	(29.0)(c)	25.0	22.5	71	47	32
		1.0	16.0	(28.0)	22.5	17.5	75	41	9
		10	15.0	(27.0)	19.5	15.0	80	30	0
		100	14.0	(26.0)	17.0	14.0	86	21	0
1200	2190	0.1	8.4	17.5	10.0	–	108	19	–
		1.0	6.1	14.5	7.2	8.6	138	18	24
		10	4.5	11.8	5.2	4.3	153	16	-4
		100	3.2	9.6	3.6	3.2	200	13	0

(a) Ta, high-purity
Ta-C, 955 ppm carbon
Ta-N, 225 ppm nitrogen
Ta-O, 560 ppm oxygen.

(b) In comparison with high-purity tantalum.

(c) Values in parentheses are estimated.

little difference between the as-cold-rolled hardnesses of material rolled without intermediate annealing from the as-cast ingot to reductions of 50, 75 or 95 percent. The as-cast ingot exhibited a hardness of 76 VHN. The hardness of material rolled directly from the as-cast ingot without intermediate annealing ranged from 150 to 156 VHN for the 50, 75, and 95 percent reductions; material of these reductions after final recrystallization at 1200°C showed hardnesses ranging from 70 to 80 VHN. A lower hardness, 129-138 VHN was shown for material cold-rolled 75 percent after intermediate annealing. The tensile properties of high-purity tantalum (Fig. 7.8) for material cold-rolled 95 percent and either stress relieved at 750°C for 15 minutes or recrystallized at 1200°C for 1 hour. The stress-relieved material had about twice the ultimate tensile strength at room temperature as the recrystallized material. Also of interest in the figure, is the lower ultimate tensile strength peak at about 350°C of the recrystallized material which suggests that the cold-worked material was more sensitive to strain aging. The tensile elongation of the wrought material was less than about 5 percent which is about the same as that shown by Myers for powder-metallurgy material reduced 95 percent.

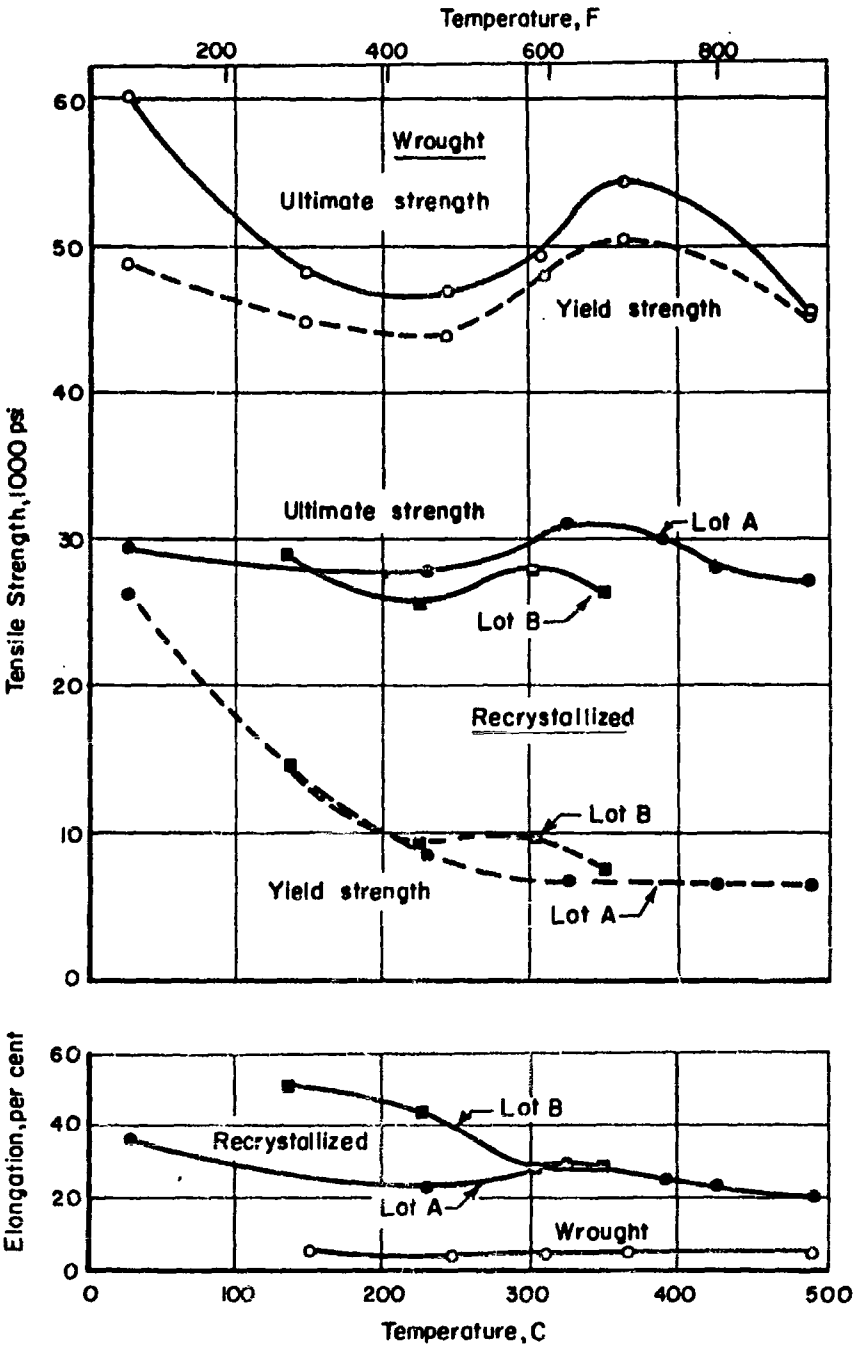

FIG. 7.8

TENSILE PROPERTIES OF HIGH-PURITY WROUGHT AND RECRYSTALLIZED TANTALUM SHEET FROM 25 TO 490°C[2]

Wrought: 95 percent cold rolled and stress relieved (750° C for 15 min)
Recrystallized: 1 hour 1200° C (2190° F) after 75 percent cold rolling with intermediate annealing

The directionality of tensile properties of Ta sheet is not an important consideration in the use of Ta as it is for some refractory metals as discussed by Schmidt[5].

Recrystallization Behavior of Tantalum

Table 7.5 indicates the temperature required for either 50 or 100 percent recrystallization of high-purity Ta cold-reduced 50, 75 or 95 percent directly from the as-cast ingot without intermediate annealing, and the same temperatures required for material cold-reduced 75 percent after intermediate annealing. The determinations were made both by metallographic examination and hardness measurements and were in agreement with one another. The table shows that a temperature of 1200° C (2190° F) is required for complete recrystallization in one hour for material reduced 75 percent, whether it is reduced 75 percent directly from the ingot or with an intermediate annealing treatment of 1200° C for one hour before the final reduction. However, the 50 percent recrystallization temperature was slightly lower for material rolled 75 percent from the ingot. It is interesting to note in the table that both 50 and 95 percent reductions required higher recrystallization temperatures for complete recrystallization in one hour than the 75 percent reduced material. Grain sizes resulting after one hour annealing treatments at 1200 to 1800° C on Ta cold-rolled 75 percent are shown in Table 7.6. A convenient relation between the amount of reduction, annealing temperature, and grain size is shown in Fig. 7.9 as prepared by Savitsky and reported by Schmidt.[5] The specimens were all annealed for one hour at the temperatures indicated. The material used for this investigation was prepared by arc-melting and was probably of lower purity than the electron-beam melted material used by Schmidt[2] in his investigation. The figure indicates a correspondingly higher recrystallization temperature for the less pure material and also a higher temperature required for grain coarsening. Fig. 7.9 indicates that temperatures above 1600° C were required before grain coarsening became evident. The table previously cited indicated that grain coarsening began to occur between 1400 and 1600° C; the grain size of the high purity Ta doubled in that temperature range, ASTM 4 (0.09 mm) to ASTM 2 (0.18 mm).

Preliminary results of an investigation by Lement, et al.[17] indicated that Ta wire produced by powder metallurgy techniques was completely recrystallized in only 10 minutes at 1200° C, as indicated by the data presented in Fig. 7.10. The authors[17] proposed that the increase in ultimate tensile strength above the annealing temperature of 1400° C was associated with the appearance of a second phase in the as-strained tensile specimen. The combined effects of strain rate and strain ageing on the tensile strength of Ta from 100 to 1500° F is shown in the columbium section (Fig. 4.5) from the work of Wilhelm and Kattus. The interstitial content of the Ta used was comparable to that of electron-beam melted Ta. The specimens contained <0.005 carbon, 0.0028 oxygen, 0.0001 hydrogen, and 0.0001 nitrogen. The figure indicated a decrease in the 100° F tensile strength from about 47,500 psi to approximately 40,000 psi with decreasing strain rates. However, at 900° F the order was reversed, i.e., a strain rate of about 0.005 per minute showed a tensile strength of 35,000 psi at 900° F and a strain rate of about 12 per minute showed a tensile strength of about 27,500 psi. The curves were drawn through data points obtained at temperatures of 400, 700, 900, 1100, 1300 and 1500° F. No information as to the metallurgical state of the material was given in the Wilhelm and Kattus report.

Table 7.5

RECRYSTALLIZATION BEHAVIOR OF HIGH-PURITY TANTALUM[2]

Condition	Temperature for Indicated Amount of Recrystallization in 1 Hour			
	50 Percent		100 Percent	
	°C	°F	°C	°F
Cold reduced 50 percent from as-cast ingot	1100	2010	1400	2550
Cold reduced 75 percent from as-cast ingot	1000	1830	1200	2190
Cold reduced 95 percent from as-cast ingot	900	1650	1300	2370
Cold reduced 75 percent after intermediate annealing	1050	1920	1200	2190

Table 7.6

RECRYSTALLIZED GRAIN SIZE OF TANTALUM[5]

1-Hour Annealing Temperature[(a)], °C	Average ASTM Grain Size[(b)]
1200	5-6
1300	4
1400	3-4
1425	3-4
1600	2
1700	1
1800	0-1

(a) Material cold rolled 75 percent after intermediate anneal.
(b) Obtained by comparison with ASTM grain-size chart at 100X.

The appearance of stress-strain curves at two different strain rates of commercially produced Ta is shown in Fig. 7.11. An approximate 100-fold increase in strain rate increased the yield strength from about 43,000 to 58,000 psi, the ultimate tensile strength from about 58,000 to 67,000 psi and had little effect on the total elongation.

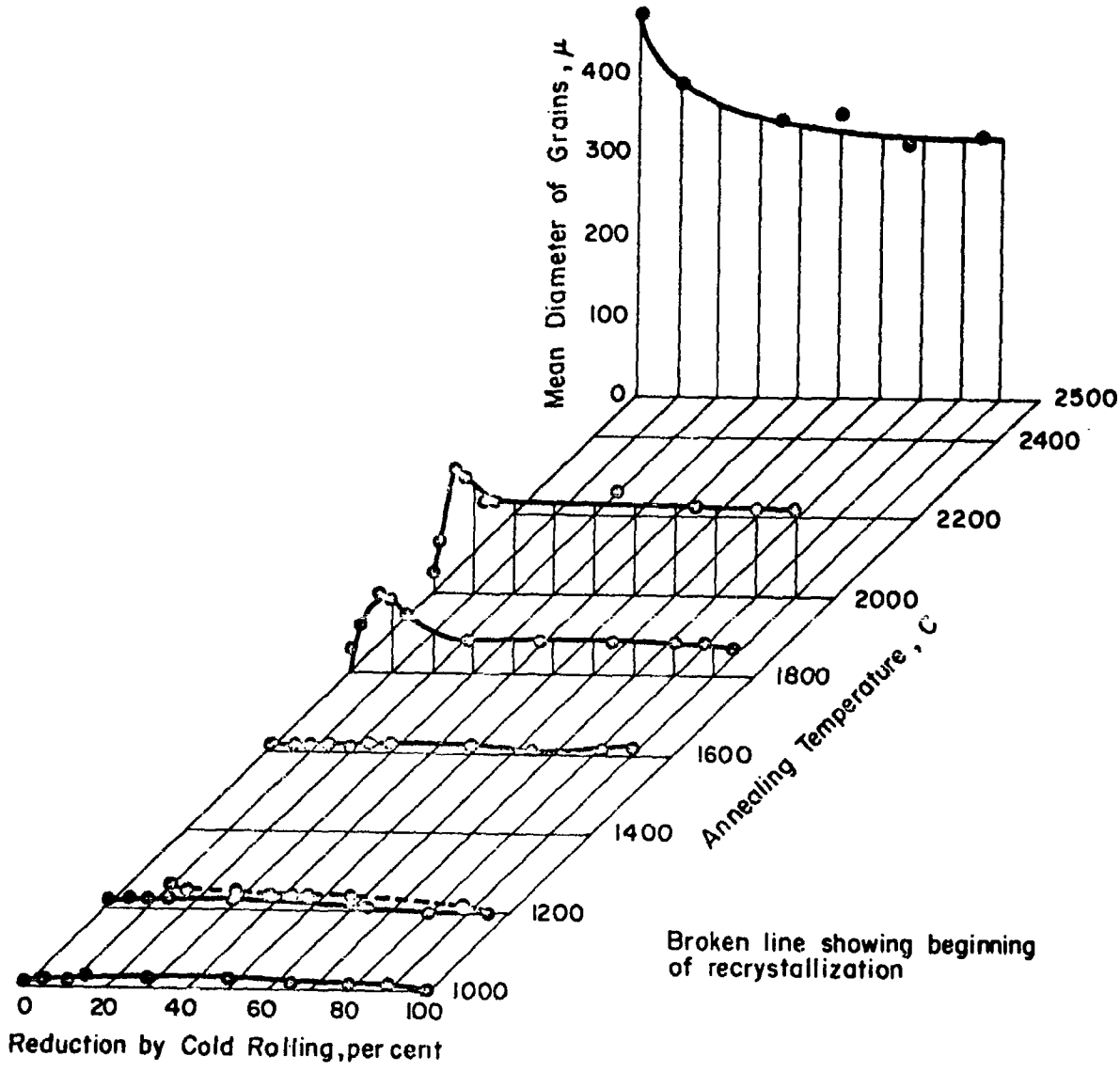

FIG. 7.9

ANNEALING TEMPERATURE VERSUS COLD REDUCTION AND RESULTING GRAIN SIZE[5]

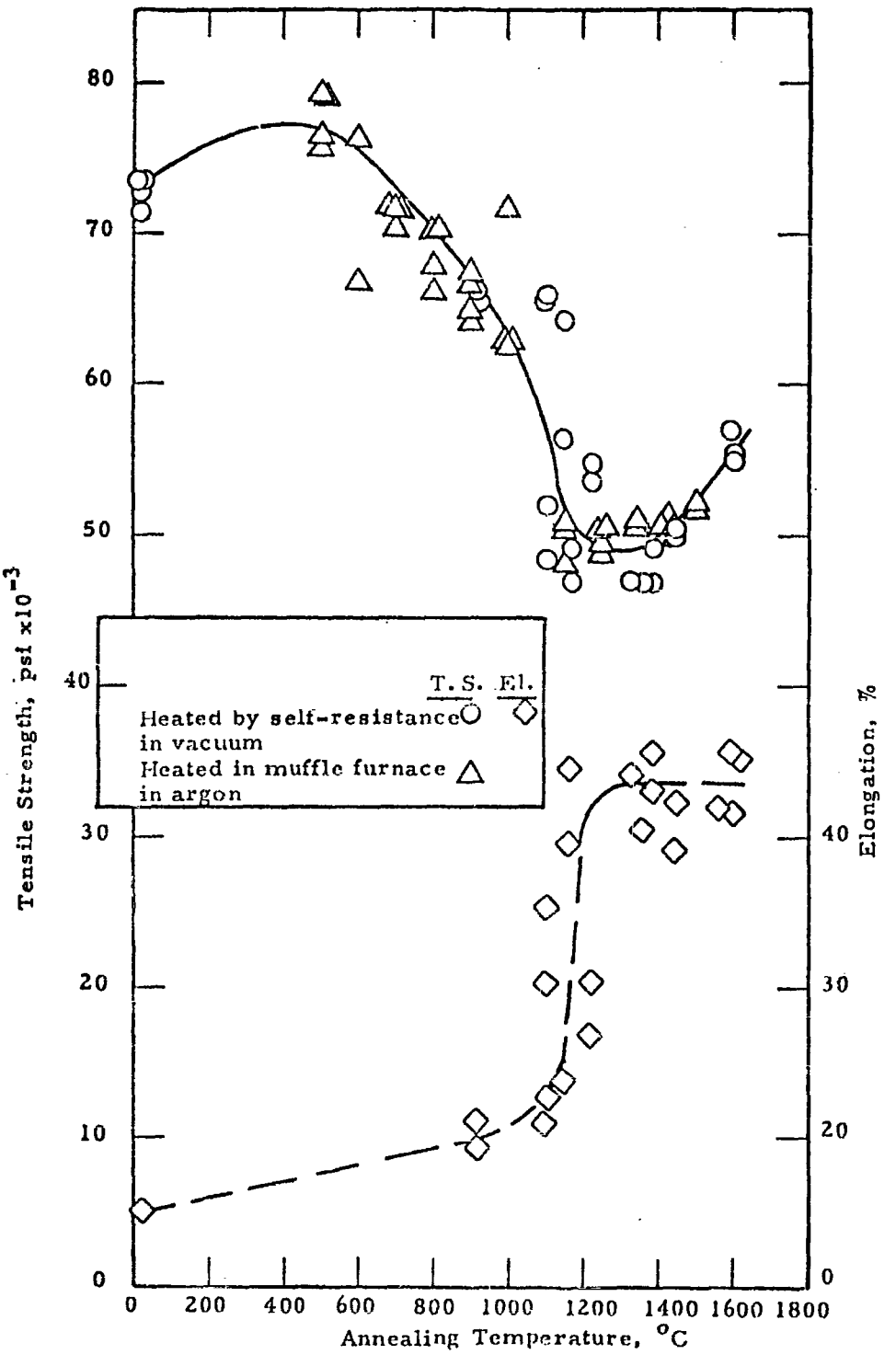

FIG. 7.10

ROOM TEMPERATURE TENSILE PROPERTIES OF 30-MIL TANTALUM WIRE AFTER TEN-MINUTE ANNEALING TREATMENTS UP TO 1600° C[17]

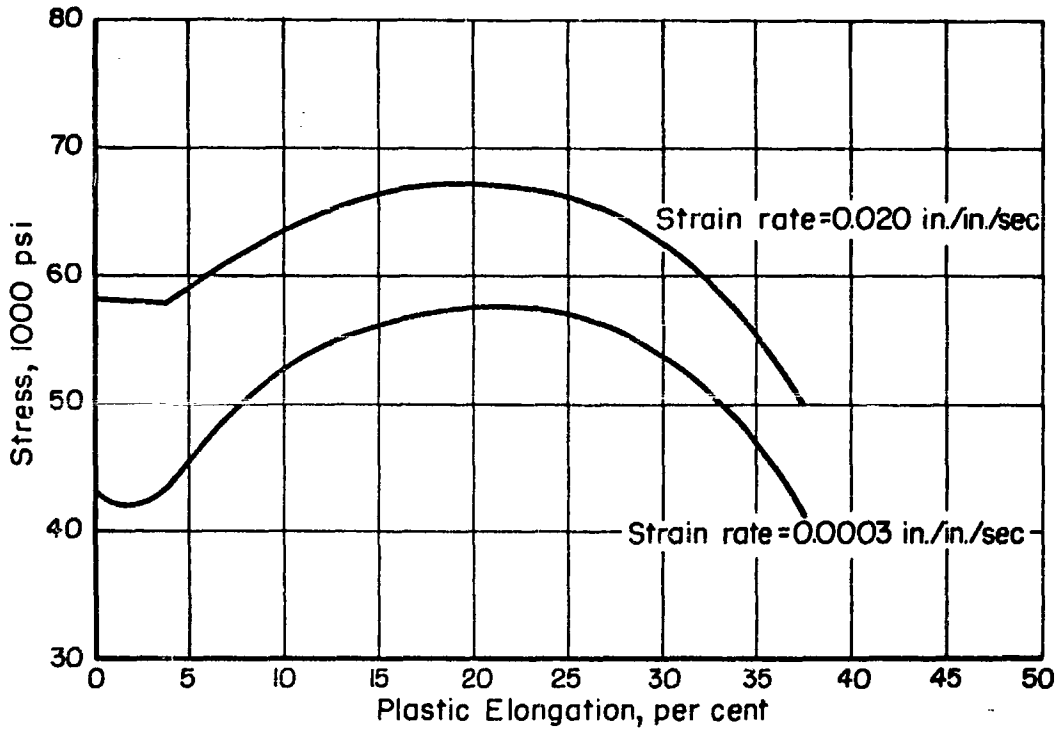

FIG. 7.11

STRESS-STRAIN CURVES OF COMMERCIAL TANTALUM AT ROOM TEMPERATURE AND TWO STRAIN RATES[5]

A 2000-fold increase in strain rate resulted in an increase in ultimate tensile strength from about 4,000 to 11,000 psi at 3,000° F, and resulted in a strength at 5,000° F about equal to the strength at 3,500° F as shown in Fig. 7.12 from a summary by Hall, et al.[13] from the work of Preston, Roe and Kattus[18]. The testing procedures used in this investigation are described in the section, Elevated Temperature Tensile Properties of Tantalum.

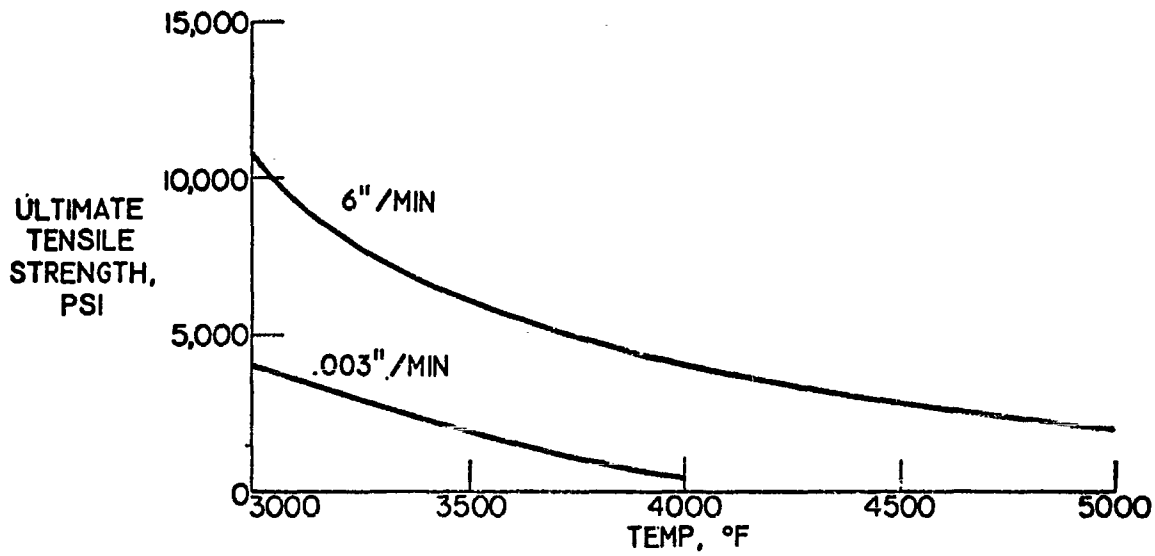

FIG. 7.12

ULTIMATE TENSILE STRENGTH OF TANTALUM ABOVE 3000° F AT TWO STRAIN RATES[13]

Tensile Properties of Tantalum Alloys

Room temperature modulus of elasticity values for Ta-W alloys were evaluated dynamically by Braun, et al.[19] and are summarized in Fig. 8.17 of the tungsten section.

The Ta-10W alloy was the first to attain commercial status, and is the only Ta alloy for which the modulus of elasticity as a function of test temperature has been reported. The modulus of elasticity of Ta-10W alloy sheet as determined from stress-strain measurements by four laboratories in a temperature range from room temperature to 5,000° F and reported by Torti[20] is shown in Fig. 7.13. Each reporting laboratory used different strain and/or loading rates and, as seen from the figure, the modulus values reported by each investigator are different, especially at the high temperatures where evaluation of purely elastic strains is difficult. The room temperature

values vary from < 21 to about 27 million psi; this large variation is probably attributable to measuring techniques rather than from different material conditions. Even the highest room temperature value, 26.7×10^6 psi, is below that reported for the Ta-10W alloy (see Fig. 8.17) of 33×10^6 psi. The difference in values using different experimental techniques was magnified at higher test temperatures. For example, at 3,000°F, the reported value at one laboratory varied from about 2 to 6 million psi and the range from low to highest value measured is 19 million psi. The data shown in Fig. 7.13 are of a preliminary nature and have not been finally summarized by Torti[20].

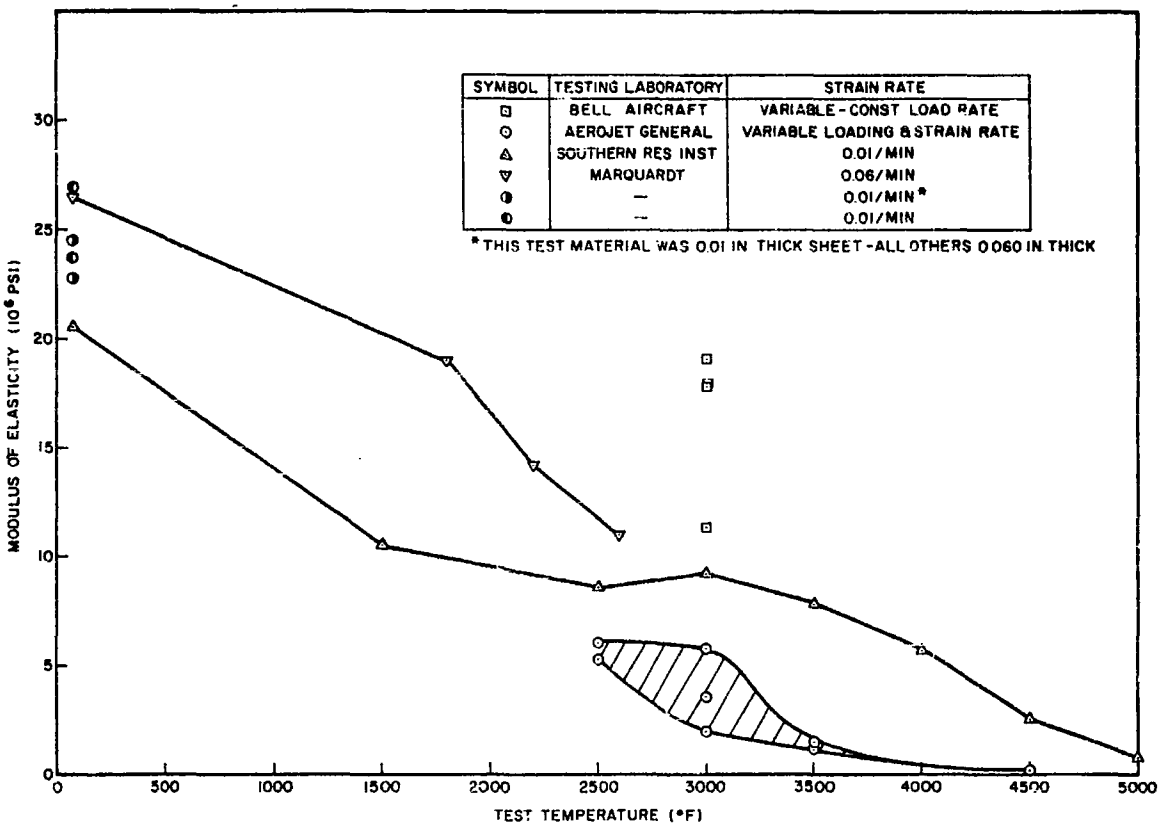

FIG. 7.13

MODULUS OF ELASTICITY OF TA-10W SHEET FROM 75 TO 5000°F AS DETERMINED FROM TENSILE TESTS[20]

A comprehensive study of the effect of alloy additions to tantalum has been in progress at Battelle Memorial Institute since May of 1958 under Air Force sponsorship. Results of screening studies and property evaluations of attractive alloys appear in two WADD technical reports[2,3]. Summaries of the work conducted at Battelle and other commercial laboratories are included in recent reports[5,6].

The screening studies included an investigation of the solid solubility limits, and the fabricability limits of eight binary alloy systems, and the effect of the binary additions on the strength and ductility properties of Ta. The binary alloys included additions of eight elements, Cb, Hf, Mo, Re, Ti, V, W and Zr. The choice of attractive binary alloys was followed by studies of the alloying behavior of ternary combinations of some of the same elements as well as ternary, quaternary and quinary additions involving Al, B, Be, Cr, Fe, La, Ni, Si, Y, and also interstitial additions of C and O.

The fabricability screening studies revealed that relatively large amounts of both substitutional and interstitial solutes could be added to Ta and still maintain reasonable fabricability, although with higher alloy additions, higher fabricating temperatures (up to 1600°C) were used. Screening studies also indicated that binary and ternary combination of Cb, Hf, Mo and W raised the recrystallization temperature of unalloyed Ta by as much as 500°C. Binary additions of Ti, V and Zr had little effect on the recrystallization temperature of Ta but ternary additions of Al and Cr to these binary combinations appeared to decrease the recrystallization temperature. The excellent ductility, characteristic of Ta, was maintained in most of the binary and ternary alloy combinations. Binary alloys containing up to 50Cb, 20Hf, 5Re, 40Ti, 15V, 10W and 10Zr were ductile in bend tests at both 25 and -196°C. Binary alloy additions of 5 to 7.5Mo, 15W and 5 and 20 to 40Zr were ductile at 25°C, but brittle at -196°C. Ternary additions of Al, Be, Cr, Mo and Si appeared to decrease the ductility of ternary combinations, whereas binary additions of Cb and Ti appeared to be the most ductile.

All binary and ternary alloys of Ta exhibited strength improvements over unalloyed Ta at room temperatures; the most effective binary additions were V and Hf. According to the most recent survey[6] the alloys which have evolved to commercial pilot development or advanced experimental stages are listed below in order of decreasing tensile strength at 2190°F.

Ta-10Hf-5W
Ta-30Cb-7.5V
Ta-20W
Ta-15W
Ta-10W modified
Ta-10W
Ta-7.5W

The order of merit on a high-temperature tensile strength basis may change upon development of optimum processing techniques for each of the alloys, and new alloy combinations will undoubtedly appear as refinements in alloying behavior are developed. The available recrystallization temperatures, strength, and oxidation properties of these alloys were summarized in the state-of-the-art survey prepared by DMIC for Wah Chang Corp. The tensile properties and recrystallization temperatures from that summary are given in Table 7.7. The property values for the Ta-10W alloy were from specimens in the as-worked condition, whereas the other alloys and unalloyed Ta were

Table 7.7

TENSILE PROPERTIES OF POTENTIAL TANTALUM ALLOY CANDIDATES[6]

Tensile Properties					
Alloy	Approximate Recrystallization Temperature F	Test Temperature F	Ultimate Tensile Strength 1000 psi	Yield Strength 0.2 Percent Offset 1000 psi	Strength-To-Weight Ratio, 1000 psi/lb/in^3
100 Ta[a]	2000-2300	2145	14.7	13.9	24.5
		2190	7.4	(3.8)[b]	12.3
		2190	11.4	—	19.0
		2400	10.0	8.4	16.7
		2600	4.6	—	7.67
		2700	5.3	(3.8)	8.84
		2860	3.3	—	5.50
		3040	3.6	—	6.00
Ta-7.5W[a]	2500-2700	—	—	—	—
Ta-10W[a]	2500-2800	1500	103.2	97.8	170
		2500	22.25	19.85	36.7
		3000	12.1	11.8	19.9
		3500	7.48	7.26	12.3
		4000	4.35	4.30	7.17
		4500	2.06	2.06	3.39
		5000	0.645	0.645	1.06
Ta-10W (Modified)[c]	—	—	—	—	—
Ta-15W	2600-2900	2190	47.5	32.5	77.4
Ta-20W	2800-3200	2190	49.6	45.1	80.3
Ta-30Cb-7.5V	2300-2500	2190	60.6	47.6	142
		2600	36.1	22.3	84.7
		3000	10.2	6.2	23.9
Ta-10Hf-5W	2500-2900	2190	63.8	—	108
		2415	41.4	30.6	70.3
		2605	37.0	25.0	62.8
		3045	17.8	12.1	30.2

(a) C = Commercial, others in advanced development stage.
(b) Values in parentheses are estimated.
(c) Strength data at moderate strain rates not available.

in the fully recrystallized condition. The Ta-15 and 20W and Ta-10Hf-5W alloys were reported to have good and all others to have excellent fabricability. The oxidation behavior of all of the alloys was shown to be similar to unalloyed Ta on a weight gain basis after exposure in air for 1 hr at 2190°F.

The tensile properties from room temperature to 5000 F of three attractive commercial Ta alloys are compared in Fig. 7.14 as compiled from data presented by Schmidt[3] and Torti.[20] The curves shown for the Ta-10W alloy identified by open circles are from data presented by Torti[20] as obtained by Southern Research Institute using extremely fast heating and loading rates on specimens which were in the as-wrought condition. The other three materials were tested in vacuum in the fully recrystallized condition by Schmidt.[3] The as-wrought Ta-10W alloy exhibited the highest strength up to 1500°F, as might be expected. Ductility of this alloy at room temperature, however, is the lowest of the alloys shown. The ultimate tensile strength and yield strength of the Ta-30Cb-7.5V alloy is shown to be higher than the Ta-10Hf-5W alloy at room temperature, about the same at 2200°F and slightly lower at 3000°F. The Ta-30Cb-7.5V alloy exhibited the highest ductility over the entire test temperature range of the three alloys. The recrystallized Ta-10W alloy tested at Battelle under the same conditions as the Ta-Cb-V, and Ta-Hf-W alloys exhibited lower strength at room temperature and 2190°F than the other two alloys. The ductility of the as-wrought material from 4000 to 5000°F was observed to decrease with increasing temperature and was possibly due to melting at the fractured surfaces, typical of tests using resistance type heating, which made total elongative measurements difficult after fracture.

Additional unpublished data[21,22] on tensile properties of as-wrought Ta-10W alloy have been made available for this compilation. Hall[21] reported the tensile properties of as-wrought bar and sheet material from 2200 to 4000° F. The 1/2-in. bar material which was prepared from electron-beam melted ingots exhibited measurably better strength and ductility at all test temperatures than the arc-cast wrought sheet material. The EB-bar material exhibited exceptional ductility from 2200 to 4000°F. The percent elongation increased from 30 to 94 percent in that temperature range and the reduction-in-area remained constant at 96 to 99 percent. The arc-cast sheet material exhibited poorer ductility from 3000 to 4000° F than the electron-beam melted as-wrought bar. The data submitted by Bauer[22] were obtained from as-cold-rolled 0.020-in. thick sheet. These data were obtained at slower heating rates and strain rates, 0.005 per minute, than the data shown for the as-wrought material in Fig. 7.14. However, the 0.020-in. sheet material exhibited exceptional strength at room temperature and up to 3000° F. The room temperature yield strength was 172,000 psi and the ultimate tensile strength 180,000 psi. At 1200°F the same property values were 132,000 and 143,000 psi respectively. From 2000 to 3000° F the data reported by Bauer[22] exhibited about the same yield and ultimate strengths as that shown in Fig. 7.14. Poor ductility was exhibited by this material up to and including 1200° F at which temperature the elongation was only 4 percent. However, from 2000 to 3000°F, the elongation increased from 13 to 58 percent.

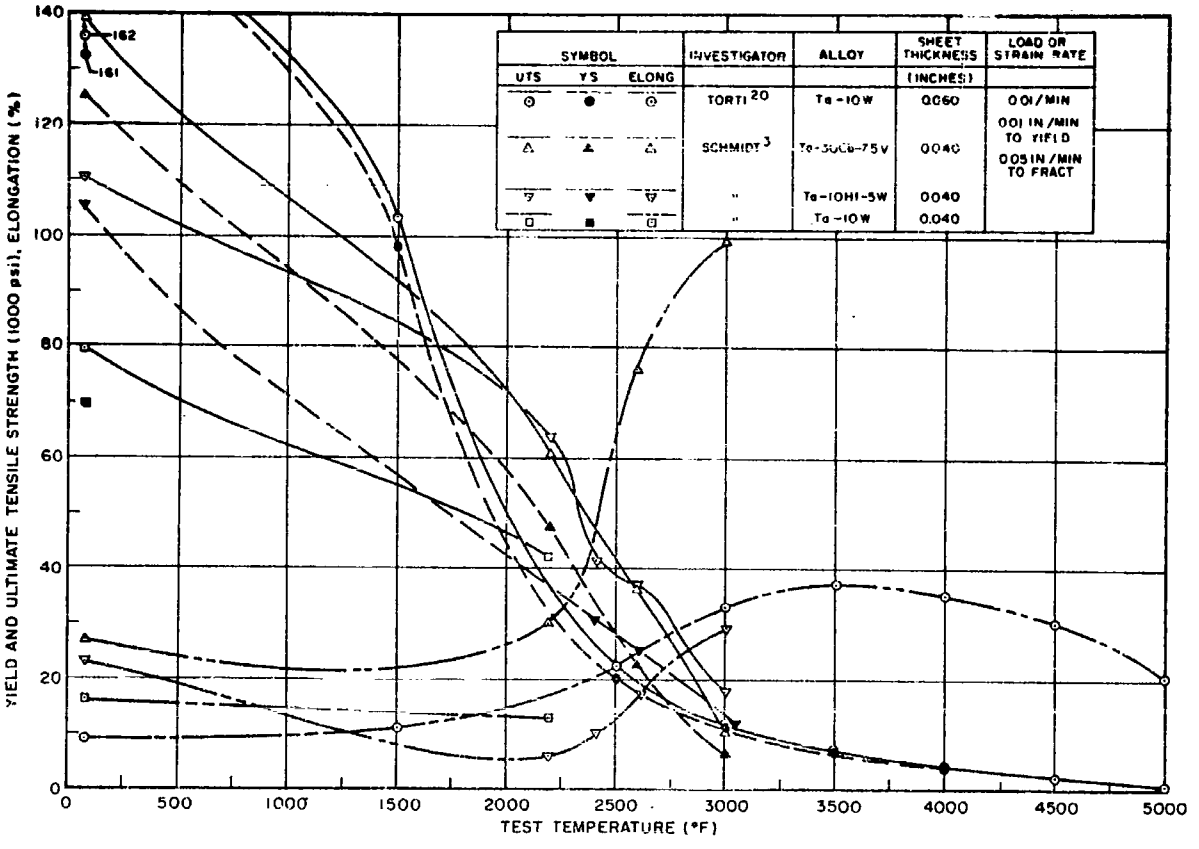

FIG. 7.14

TENSILE PROPERTIES OF COMMERCIAL AND ADVANCED EXPERIMENTAL TA ALLOY SHEET FROM ROOM TEMPERATURE TO 5000°F, TESTED IN VACUUM

Only preliminary data have been reported[6] for the Ta-10W modified alloys indicated in Table 7.7. The modifications consisted of small additions of Mo and Zr. As-wrought electron-beam-melted sheet material was reported to have an ultimate tensile strength at 3600°F of 13,000 psi, which compares to a value of about 6,000 psi from the curve in Fig. 7.14.

An order of merit rating for potential Ta alloy candidates for an extrusion program was presented in the Wah Chang report.[6] The comparison between unalloyed Ta and three important Ta alloys is given in Table 7.8.

An interim report of Ta alloy investigations in progress at the Westinghouse Research Laboratories for over two years has recently been issued by Field, et al.[4] Nine attractive alloys have evolved from the program but none have advanced sufficiently for accumulation of many property data. The tensile properties of arc-melted, stress-relieved sheet rolled to 95 percent reduction from extruded sheet bars are

Table 7.8

ORDER OF MERIT RATINGS FOR POTENTIAL TANTALUM ALLOY CANDIDATES[6]

Property	Order of Merit(a)			
	100Ta	Ta-10W	Ta-30Cb-7.5V	Ta-10Hf-5W
Development Stage	1	2	4	3
Primary Fabricability	1	2	2	3
Recrystallization Temperature	4	2	3	1
Ultimate Tensile Strength				
2200°F	4	1	3	2
2600°F	4	3	2	1
3000°F	4	2	3	1
Strength-to-Weight Ratio				
2200°F	3	2	1	2
2600°F	4	3	1	2
3000°F	4	3	2	1
Oxidation Resistance at 2190°F	4	2	3	1

(a) Rated in decreased order of merit, i.e., 1 most desirable; 4 least desirable.

Table 7.9

TENSILE PROPERTIES OF TANTALUM ALLOYS
95 Percent Reduction, Stress Relieved 1 Hour at 2000°F

Composition	Testing Temperature	Ultimate Tensile Strength	0.2 Percent Yield Strength	Elongation	Reduction in Area
(wt. %)	(°F)	(psi)	(psi)	(%)	(%)
Pure Ta	-320	162,000	162,000	5	54
	-100	109,000	109,000	21	74
	75	88,000	87,000	19	
	300	79,000	70,000	15	~100
	500	94,000	77,000	13	~100
	1000	81,000	65,000	13	40
	1500	63,000	60,000	15	~100
	2200	17,800	15,000	32	75
	2500	6,000	3,800	>61	—
Ta-2W-2Hf	-100	121,000	113,000	15	73
	75	110,000	105,000	16	64
	2200	52,000	48,000	16	41
	2500	24,800	20,700	37	65
	2700	16,400	14,400	51	~100
Ta-2W-4Hf	-320	156,000	153,000	21	60
	-100	124,000	118,000	16	65
	75	113,000	106,000	16	65
	2200	76,000	72,000	15	40
	2500	27,600	24,500	65	~100
	2700	20,500	19,500	106	~100
Ta-8W-2Hf	-320	190,000	184,000	18	44
	-100	150,000	146,000	17	64
	75	135,000	130,000	15	60
	2200	85,000	78,000	15	28
	2500	54,000	38,800	26	47
	2700	29,000	23,700	64	81
Ta-8W-4Hf	-320	205,000	204,000	11	16
	75	147,000	140,000	15	50
	2200	91,000	80,000	23	37
	2500	43,000	37,700	50	74
	2700	32,200	30,300	67	73
Ta-6W-6Hf*	2200	78,000	65,000	15	33
	2500	50,000	44,000	15	26

*Tested in the as-extruded and stress relieved condition.

shown in Table 7.9. The Ta-W-Hf alloys are shown to possess the highest strengths of the alloys tested at 2500 and 2700° F. The stress-relieved Ta-8W-2Hf, Ta-8W-4Hf, and Ta-6W-6Hf alloys exhibited better strength at 2500°F, 54,000, 43,000, and 50,000 psi, respectively, than the recrystallized Ta-30Cb-7.5V alloy strength at 2500° F shown in Fig. 7.14. Only the Ta-8W-4Hf stress-relieved alloy had better strength at 2700° F than the Ta-30Cb-7.5V alloy, 32,200 psi compared to 30,000 psi, and none of the highest strength alloys exhibited ductility at 2500 and 2700° F as good as the Ta-Cb-V alloy. The tensile results shown in Table 7.9 are preliminary data from single tests.

Creep and Stress Rupture Properties of Tantalum

The creep properties of high-purity Ta have been investigated at Battelle from room temperature to 1400° C.[2] The creep properties of powder metallurgy degassed, and arc-cast Ta have also been investigated at Battelle at 650° C (1200° F) under AEC sponsorship[23]. Both of these investigations have been summarized in the recent DMIC review.[5] A brief review of these data is given below in Figs. 7.15 through 7.19 and in Table 7.10.

Table 7.10

HARDNESS, CHEMICAL ANALYSES, AND CREEP STRENGTH FOR VARIOUS TYPES OF TANTALUM TESTED AT 1200° F IN A HELIUM ATMOSPHERE[23]

Tantalum	Grain Size (mm)	Chemical Analysis, ppm				Approximate Stress Required to Produce 0.5 Percent Deformation in Time Indicated, psi		
		Carbon	Hydrogen	Nitrogen	Oxygen	100 Hr	1000 Hr	10,000 Hr
Annealed, sintered	0.025	10	1.3-1.6	130-140	240-300	13,000	11,500	10,000
Annealed, arc cast	0.035	<10	<0.3	150	214	17,000	15,000	—
Thermally degassed, large grained, sintered	>1	<10	0.2	50	2	6,500	5,500	4,800
Annealed, sintered tantalum after exposure to sodium	0.025	10	5-6	130-270	15-36	—	12,500	—
Thermally degassed, fine-grained, sintered	0.025-0.035	20-30	0.7	20	10-16	—	16,000	12,000-14,000

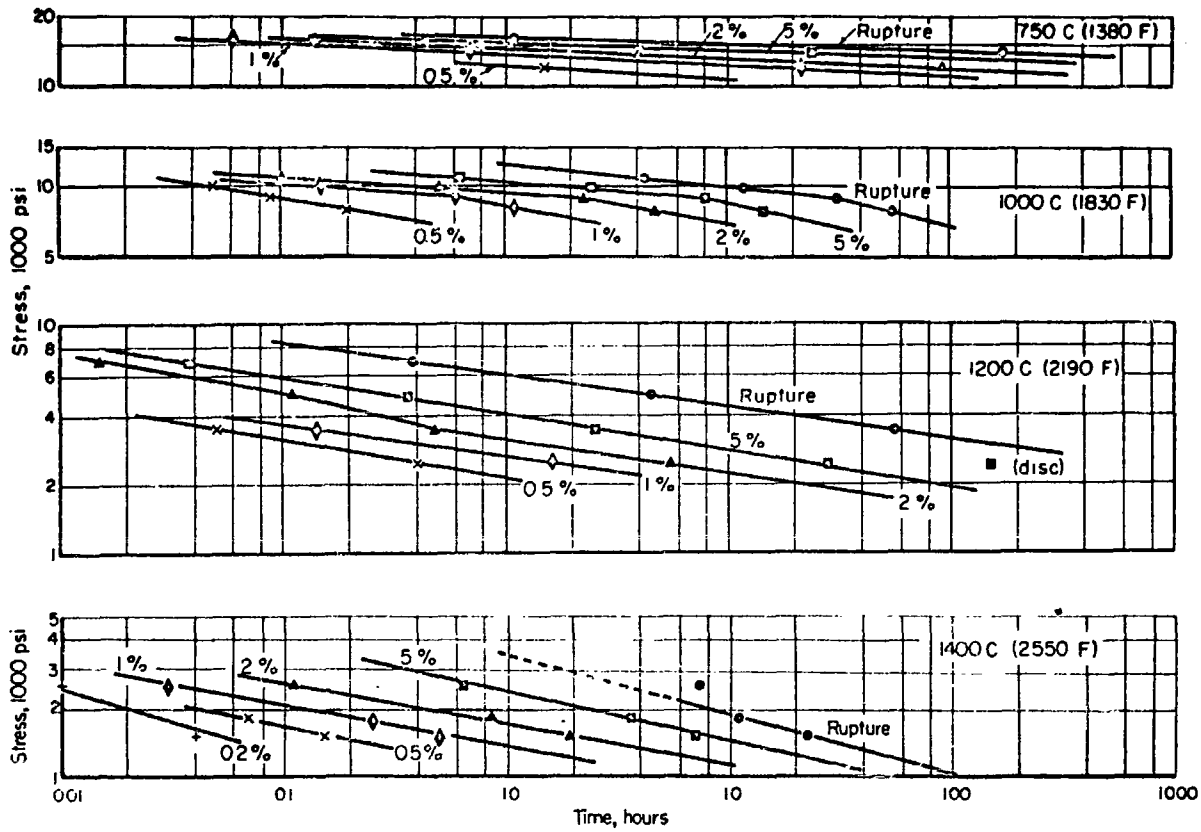

FIG. 7.15

STRESS VS. CREEP TIME FOR VARIOUS VALUES OF CONSTANT CREEP STRAIN FOR RECRYSTALLIZED HIGH-PURITY TANTALUM SHEET[5]

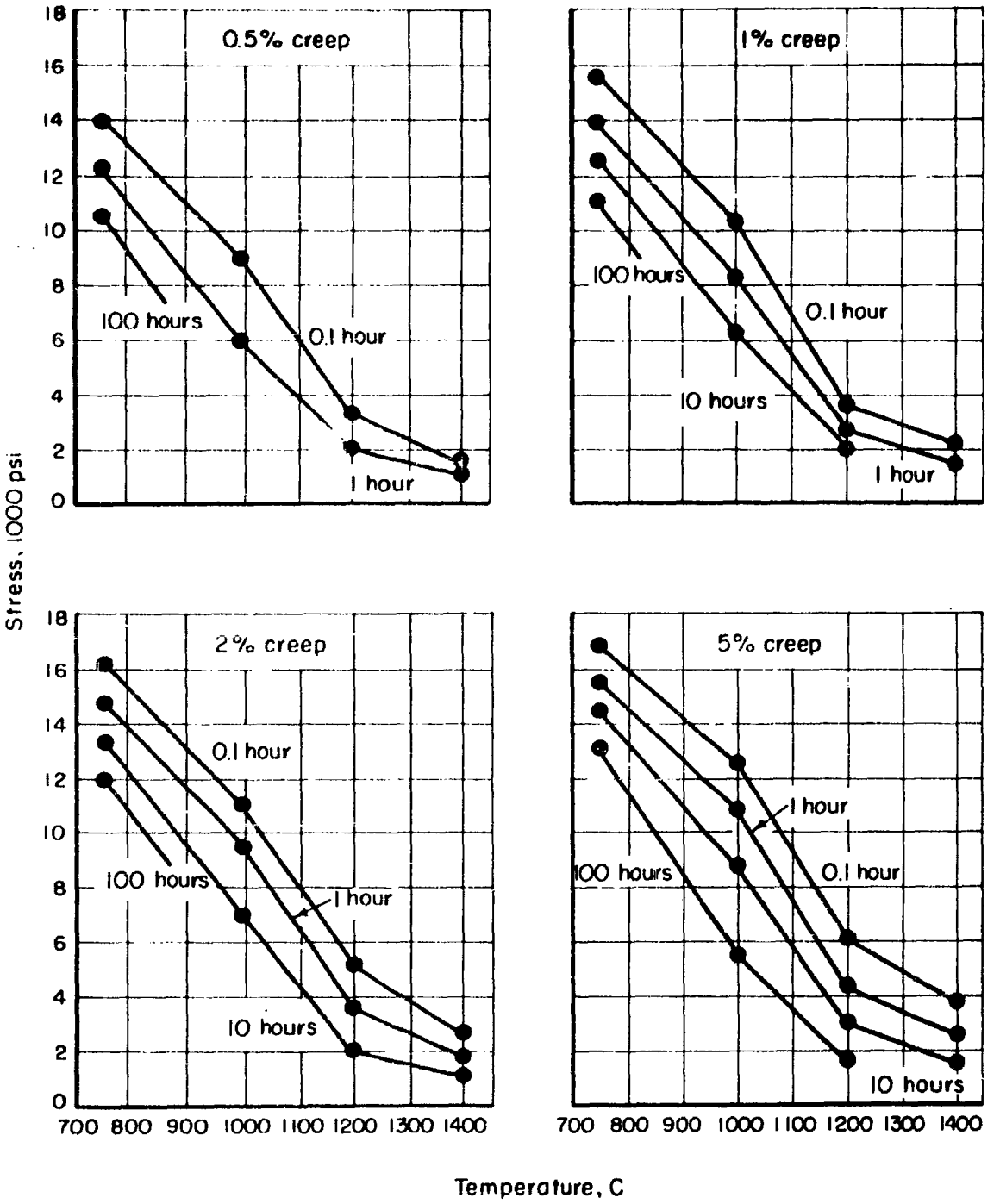

FIG. 7.16

EFFECT OF TEMPERATURE ON THE CREEP STRENGTH OF RECRYSTALLIZED HIGH-PURITY TANTALUM SHEET FOR CONSTANT VALUES OF CREEP TIME AND CREEP STRAIN[5]

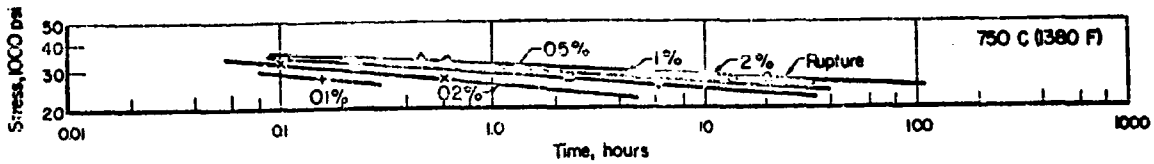

FIG. 7.17

CREEP AND RUPTURE CURVES FOR WROUGHT HIGH-PURITY TANTALUM SHEET[5] COLD ROLLED 95 PERCENT; STRESS RELIEVED AT 750°C(1380°F) FOR 1/4 HOUR.

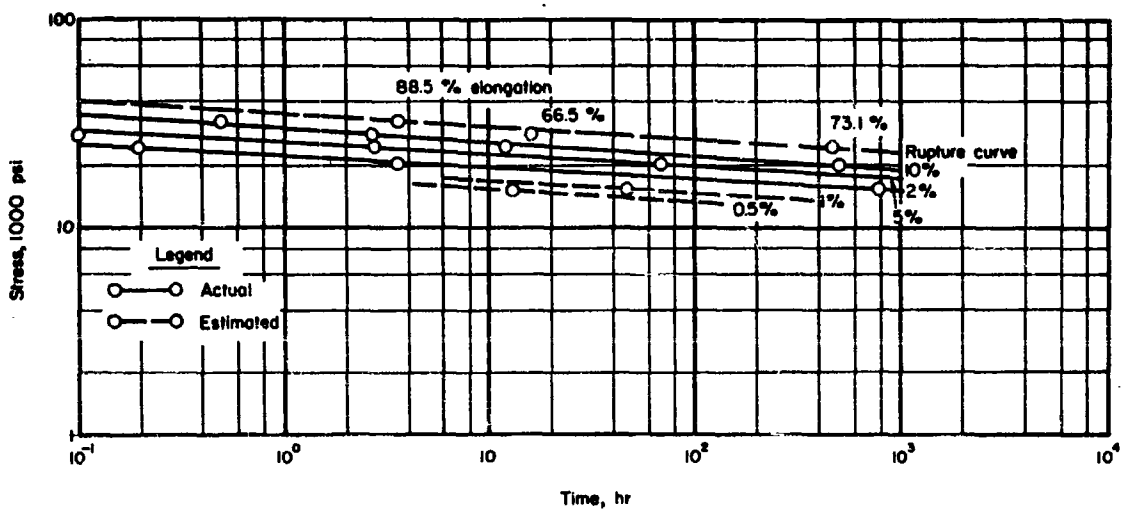

FIG. 7.18

CREEP DATA ON ANNEALED SINTERED TANTALUM SHEET TESTED AT 1200°F IN HELIUM[23]

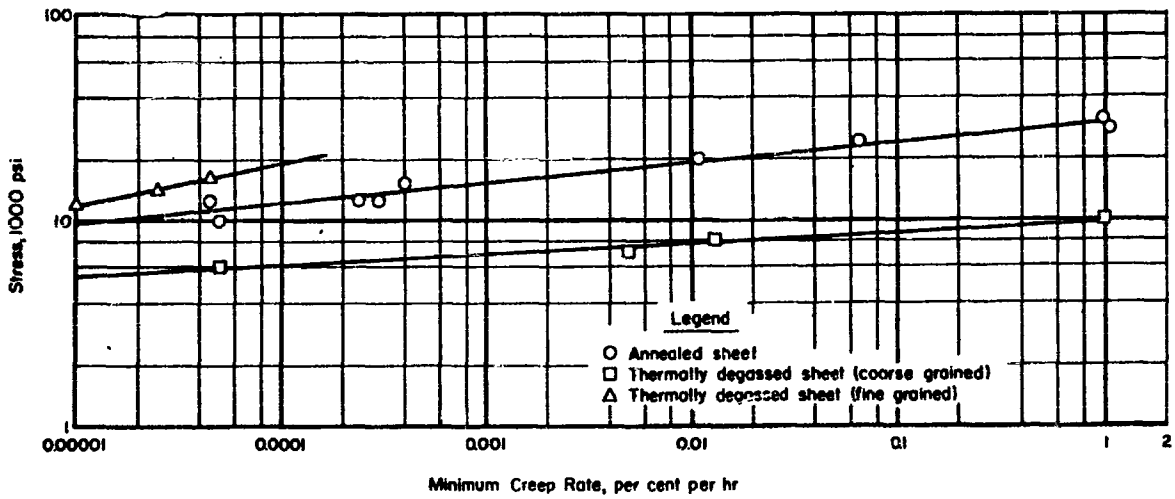

FIG. 7.19

STRESS VERSUS MINIMUM CREEP RATE FOR SINTERED TANTALUM TESTED AT 1200°F IN HELIUM[23]

The high-purity Ta sheet used to obtain the data shown in Figs. 7.15 and 7.16 was prepared by electron beam melting, and the typical chemical composition is shown in Table 7.2, under the section giving the tensile properties of electron-beam-melted Ta. The test material used for the creep test of Fig. 7.15 was given a recrystallization treatment of 1 hour at 1200° C which resulted in a recrystallized grain size from 0.04 to 0.06 mm. All tests were conducted in vacuum with the specimens wrapped in Ta foil to reduce contamination. However, the authors[2] reported some contamination was observed after testing at 1400° C. Figure 7.15 indicates the very low creep resistance of unalloyed Ta. For example, the 100-hour rupture strength at 750, 1000, 1200 and 1400° C was about 14,000, 6,000, 3,200 and 1,000 psi, respectively. The creep resistance as measured by time to specified amounts of creep strain is shown in Fig. 7.16 to have decreased more rapidly from 750 to 1200° C than between 1200 and 1400 °C. Figure 7.17 gives an indication of the effect of prior deformation on the rupture properties of Ta at 750° C. A comparison between Figs. 7.15 and 7.17 shows that the 100-hour rupture strength has been increased by prior cold deformation from about 14,000 to 25,000 psi.

The investigation by Drennan, et al.[23] included creep tests on Ta after various treatments described in Table 7.10. The annealing treatments consisted of heating for from 8 to 18 minutes at temperatures of 2600 to 2800 °F. The thermal degassing consisted of vacuum annealing at 4500 to 4800° F for five hours. The sodium exposure was intended to decrease the oxygen content of the sintered Ta without changing the grain size to observe the effect of oxygen on the creep resistance of Ta. The sodium exposure consisted of a treatment in flowing gettered sodium at 1200° F for thirty-three days. As a result of this treatment, the oxygen content was lowered from about 270 to 30 ppm. The fine-grain material was produced by fabrication and recrystallization treatments of the thermally degassed large-grained material. The Table indicates a reduction in grain size of about 40 times without an appreciable increase in interstitial content.

The authors[23] reported a substantial effect on creep resistance at 1200° F as a result of method of preparation, grain size, and treatments performed on the material. The annealed arc-cast Ta possessed somewhat higher creep resistance at 1200° F than did the annealed powder-metallurgy Ta. The fine-grained material exhibited better creep resistance than the coarse-grained material. Although the exposure to Na lowered the oxygen content of the annealed sintered material, the creep resistance was not changed appreciably. The summary of creep properties given by the authors in Table 7.10 was based on data of the type shown in Fig. 7.18 for annealed sintered sheet. The stresses for 0.5 percent deformation in 10,000 hours were extrapolated on the basis of minimum creep rate curves typical of those in Fig. 7.19.

Creep and Stress-Rupture Properties of Tantalum Alloys

Stress-rupture vs. creep-time curves for Ta and Ta-10W alloys from very short time tests are shown in Fig. 7.20. Donlevy and Hum[24] conducted tests on electron-beam melted Ta-10W alloy and also the modified Ta-10W alloy. The specimens were

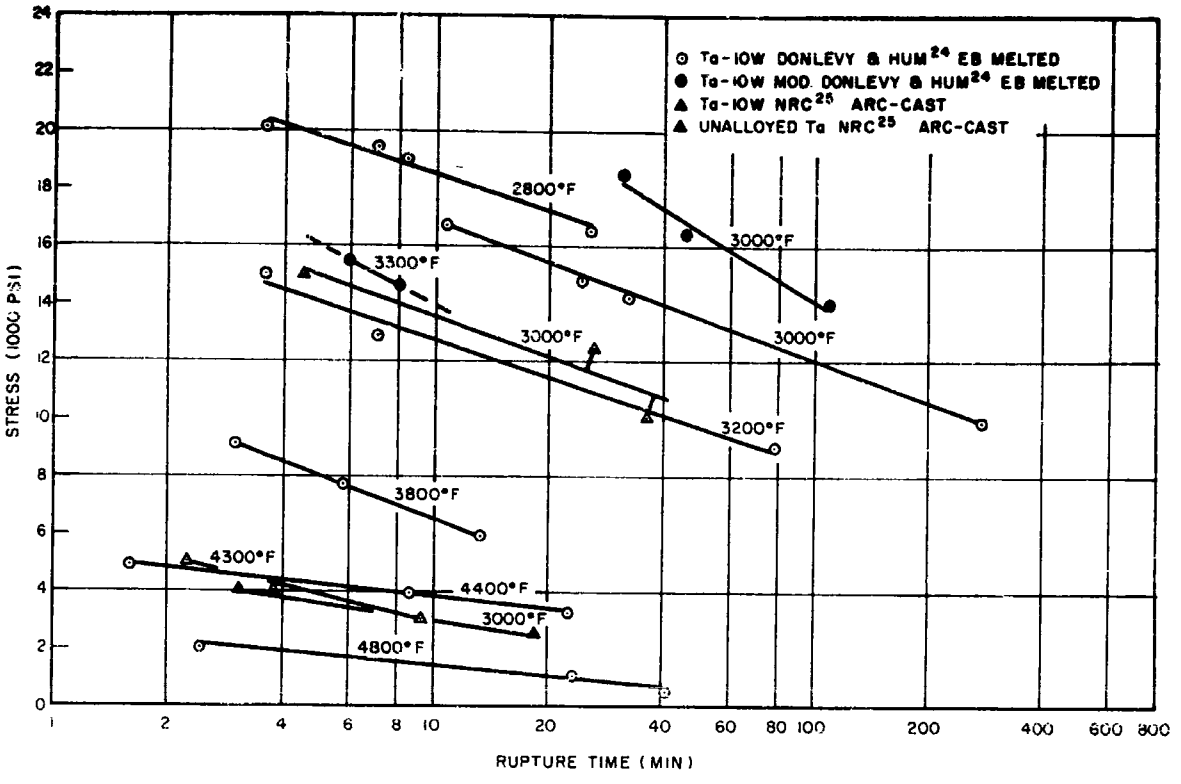

FIG. 7.20

SHORT-TIME RUPTURE STRENGTH OF TANTALUM AND THE TA-10W ALLOY FROM 2800 TO 4800° F

heated by an electron beam in a vacuum of 10^{-4} mm Hg or better. Only the total strain at fracture was recorded from these experiments. Very little information regarding test material or test conditions were given for the NRC data shown in the figure.

A comparison between the Ta-10W alloy and the unalloyed Ta tested by NRC[25] shows that at 3000° F the alloy was stronger by a factor of about 4 at the 10-minute rupture time. The EB-melted Ta-10W specimens tested by Donlevy and Hum[24] exhibited higher rupture strength at 3000° F than the arc-cast specimens tested at NRC.[25] The tests conducted at 4400 and 4300° F by the respective investigators had the same relation. The modified Ta-10W alloy which contains proprietary additions of Mo and Zr had the highest rupture strength in these short-time creep-rupture tests.

The creep-rupture properties of other attractive Ta alloys were not found reported in the literature.

OXIDATION PROPERTIES

Oxidation of Tantalum

Studies related to reactions of Ta with air, hydrogen, nitrogen, oxygen, dry carbon dioxide, hydrocarbons, sulfides, and water vapor are discussed in detail and referenced in the DIMC review[5]. The reactions of tantalum with oxygen and air were discussed in the original SRI review,[1] and a summary of these reactions is given in Figs. 7.21 and 7.22.

The air oxidation reaction rate is shown in Fig. 7.21 to occur parabolically at 500° C for times up to 16 hours at which time it transposes to a linear rate. The change from parabolic to linear behavior at 800° C is shown to occur very rapidly (less than 1 minute); above about 800° C, the linear rate is shown to increase rapidly with increasing temperature. Figure 7.22 shows the change in the one-hour weight gain at temperatures from 200 to 1200° C for either the Ta-air or Ta-oxygen reaction. Each symbol represents a different investigator and results from the different investigations agree well over the entire temperature range, especially when the oxygen atmospheres are normalized to the pressure of oxygen in one atmosphere of air.

Oxidation of Tantalum Alloys

Schmidt[3] has reported that the oxidation rate of the Ta-10W and Ta-10Hf-5W are about two-thirds that of unalloyed tantalum at 1200° C (2190° F) based on weight-gain measurements at one to two hour exposure times. The oxidation rate of a third attractive Ta alloy, Ta-30Cb-7.5V is roughly the same as that of unalloyed Ta. Rate of penetration of oxygen into the surface, has not been established for these alloys, but scaling rates have indicated that alloys developed to date will require protection from oxidation for continued use at elevated temperatures.

Screening studies[3] have indicated that Ti and ternary additions of Al, Cr, Si, and Be improve the oxidation and contamination resistance of Ta, but the attractive alloys from an oxidation resistance standpoint exhibit either reduced low temperature ductility, and/or lower recrystallization temperatures which suggest lower elevated temperature strength.

THERMAL PROPERTIES

Thermal Conductivity

Thermal conductivity data from four investigators were compiled by Goldsmith and Waterman[26] as shown in Fig. 7.23. Identification of the data symbols is given in Table 7.11. The data are the same as those reported in the SRI report[1] with the exception of the values below 200° K which are more recent. Glazier, et al.[11] have

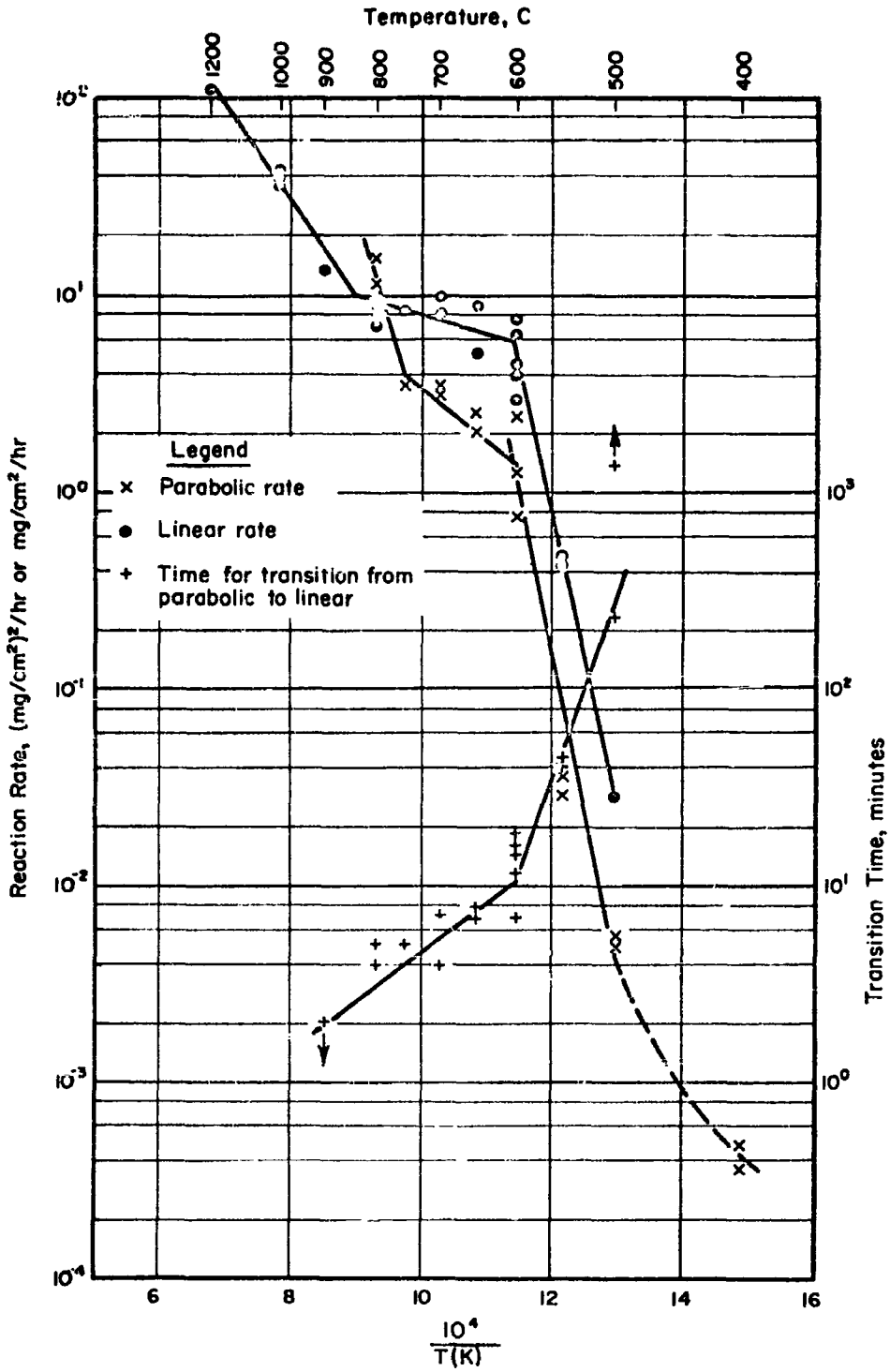

FIG. 7.21

RATE CONSTANTS AND TRANSITION TIMES FOR THE TA-AIR REACTION FROM 400 TO 1200°C[5]

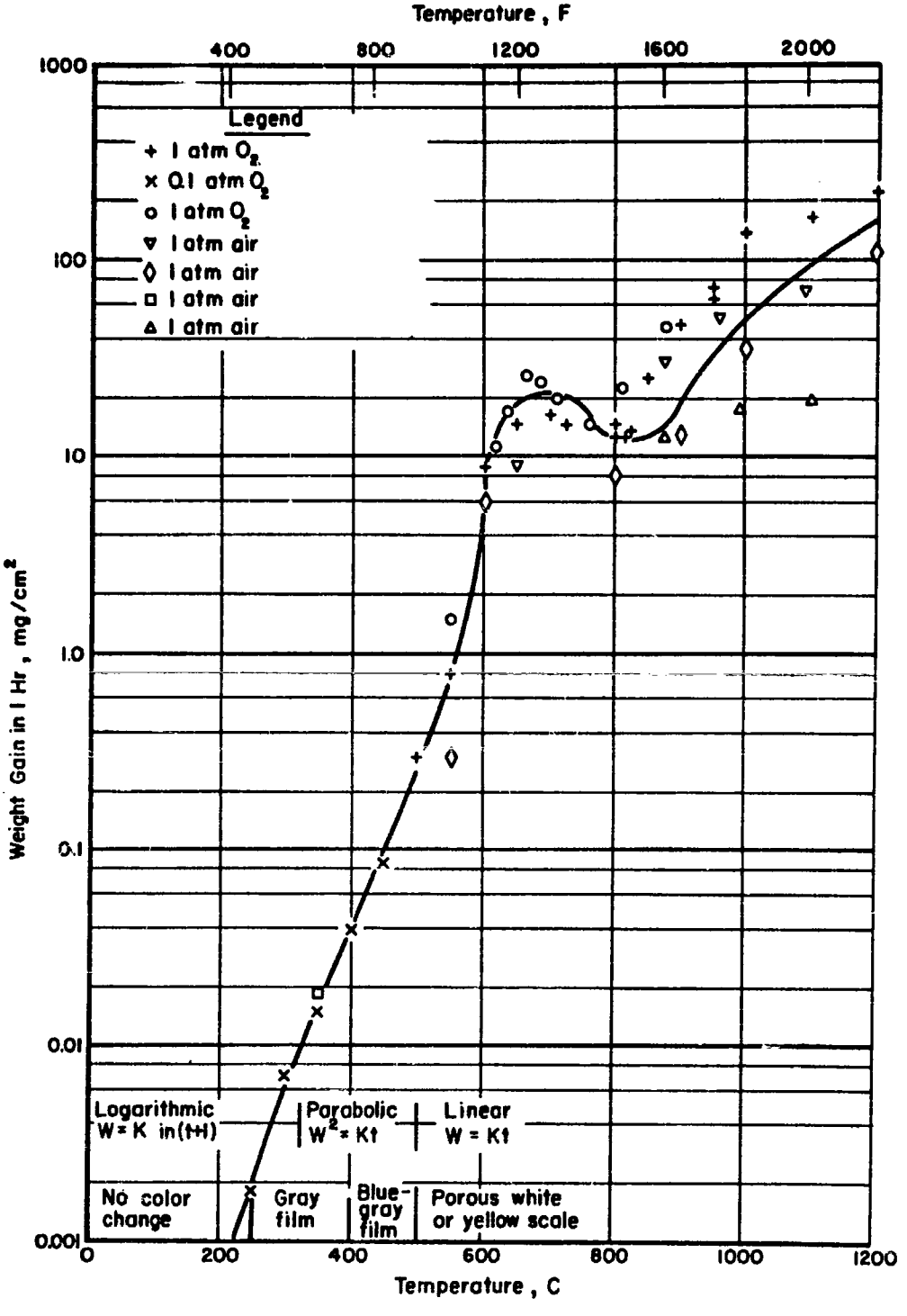

FIG. 7.22

WEIGHT GAIN OF TANTALUM FROM 200 TO 1200° C AFTER A 1-HOUR REACTION WITH OXYGEN OR AIR[5]

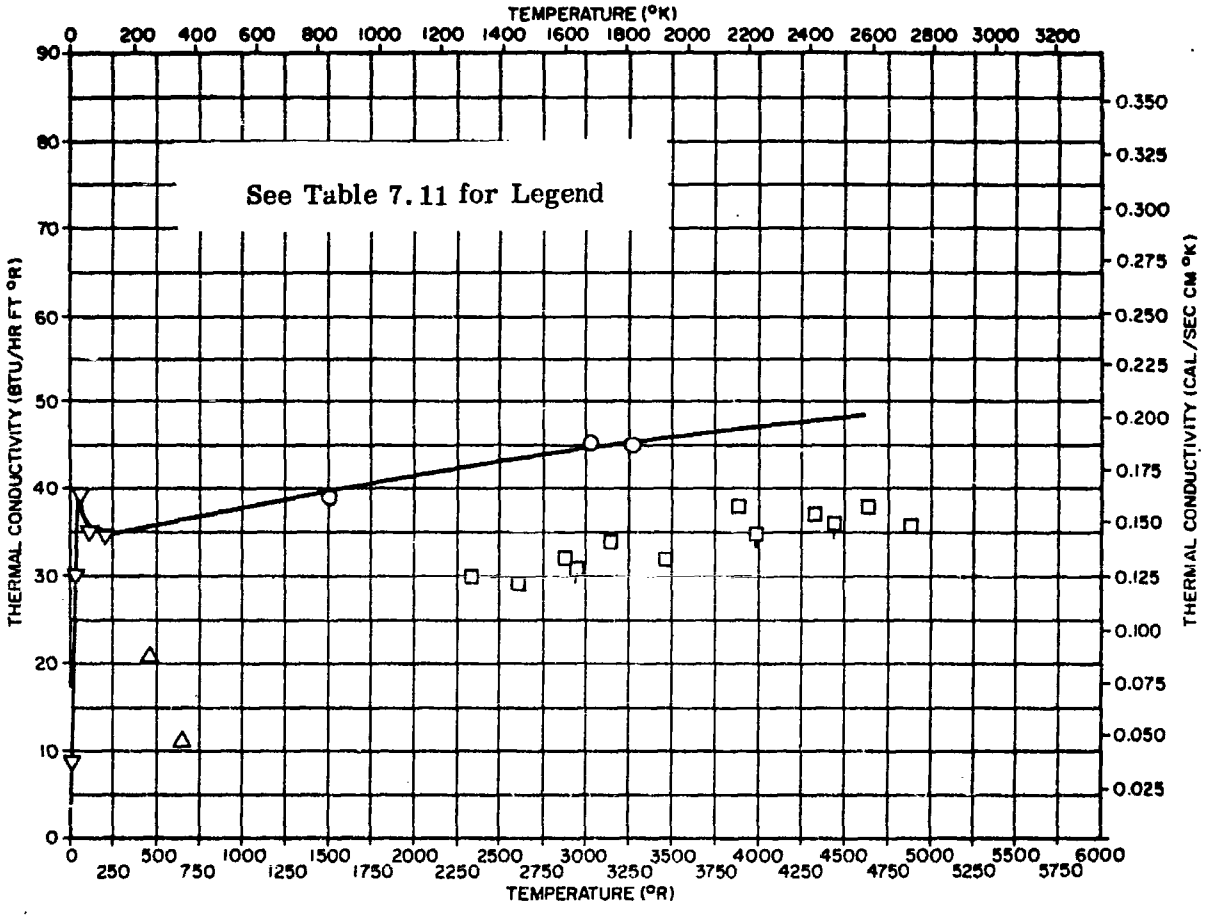

FIG. 7.23

THERMAL CONDUCTIVITY OF TANTALUM[26]

Table 7.11

LEGEND FOR FIG. 7.23 ON THERMAL CONDUCTIVITY OF TANTALUM[26]

Symbol	Investigator	Range, °R	Material Composition	Test Method	Remarks
○	Fieldhouse, I.B., Hedge, J.C. and Waterman, T.E.	1514-3275	Sintered. Before test: 0.052%N_2; traces of Ca, Cu, Mg. After test: 0.12%O_2; 0.044%N_2; 0.0061%H_2; traces of Al, Ca, Cu, Fe, Mg; p = 1029 lb_m/ft^3	Single flat plate; boiling liquid calorimeter	
△	Cox, Martha	492-672	99.9% pure	Temp. distribution along resistance heated wire	Sample aged at 1800°C and 2000°C for 2750 hr.
□	Rasor, N.S. and McClelland, J.D.	2360-4920	Sintered. Before test: 0.73%Cu; 0.73%Zr; 0.21%Fe; 0.05%Ni; 0.05%C; 0.97%Co; 0.03%Mn; 0.02%Si; 0.017%Al; 0.0047%Cr; 0.0033%Ca After test: 0.015%C; 0.013%Si; 0.0023%Cr; 0.0019%Cu p = 1040 lb_m/ft^3	Cylinder with radial heat flow inward; water calorimeter along axis	Swaged to given density. Letter from auth. indicates error in orig. ref. which gives p = 14.6 g/cm^3. corrected P = 16.66 g/cm^3 □: heating □: cooling
▽	Rosenberg, H.M	0-63	99.98% pure	Heat flow in rod in vacuum. Temp. gradient by differential gas thermometer. Temp. by gas thermometer	

reported thermal conductivity data for Ta and the Ta-10W alloy from 1700 to 3200° K; the values at 1700° K agree well with the data from Rasor and McClelland shown in Fig. 7.23, but both the alloy and the unalloyed material showed a decrease in conductivity with increasing temperature. Glazier, et al.[11] cite a reference by Zuikker which supports the temperature dependency exhibited in their experiment.

Thermal Expansion

The linear thermal expansion of Ta as determined by six investigators and summarized by Goldsmith and Waterman[26] is presented in Fig. 7.24 with a description of the test material and test conditions in Table 7.12.

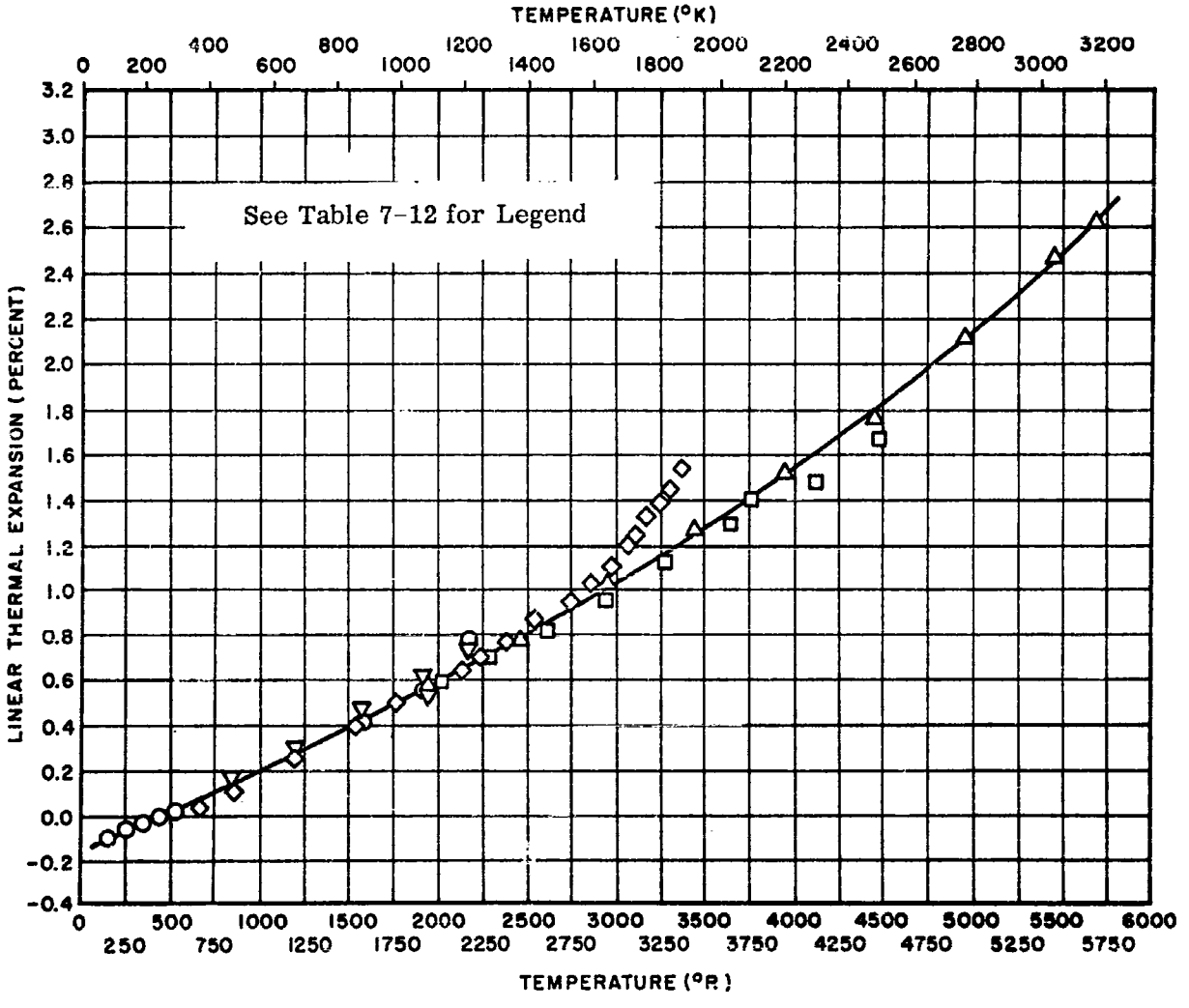

FIG. 7.24

LINEAR THERMAL EXPANSION OF TANTALUM[26]

Table 7.12

LEGEND FOR FIG. 7.24 ON THERMAL EXPANSION OF TANTALUM[26]

Symbol	Investigator	Range, °R	Material Composition	Test Method	Remarks
○	Nix, F.C. and MacNair, D.	165-542	99.9% pure; 0.01% Fe; 0.003% C	Interferometric dilatometer	
□	Edwards, J.W., Speiser, R. and Johnston, H.	524-4491	99.9% pure; principal impurities <0.03% ea. Fe, C	X-ray diffraction	Auth. est. accuracy ±2%
△	Rasor, N.S. and McClelland, J.D.	1960-5710	Before test: 0.73% ea. Cu, Zr; 0.21% Fe; 0.090% Ni; 0.080% C; 0.070% Cu, 0.030% Mn, 0.020% Si, 0.0047% Cr, 0.0033% Ca; no Ti After test: 0.0150% C; 0.013% Si; 0.0023% Cr; 0.0019% Cu; None of others; ρ = 1040 lb_m/ft^3	Telemicroscopes	Pressed, sintered, and swaged to given density. Data shown are smoothed; taken during second heating and cooling cycle. Letter from auth. indicates error in orig. ref. which gives ρ = 14.6 g/cm^3; corrected ρ = 16.66 g/cm^3
◇	Fieldhouse, I.B., Hedge, J.C., et al.	618-3369	Sintered: ρ = 950 lb_m/ft^3	Telemicroscopes sighting on wires suspended from sample	
▽	Bell, I.P. and Makin, S.M.	492-2184	"Murex" bar	Dilatometer	Meas. perpendicular to axis of bar
⬡	Ibid.	492-2184	"Heracus" bar	Same as above	Meas. parallel to axis of bar

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SECTION 8

TUNGSTEN

INTRODUCTION

The properties which make tungsten particularly attractive for high temperature applications are:

- melting point of 3410°C (6170°F), highest of all metals
- high modulus of elasticity, 58 x 10^6 psi, higher than that for columbium, molybdenum or tantalum
- abundance

The main problems in applying tungsten in structural applications are its high temperature for transition from ductile-to-brittle behavior and its relatively poor oxidation resistance. Another factor for which its outstanding high-temperature strength must compensate is its high density of 19.3 g/cc, which is higher than that of Cb, Mo or Ta.

At the time of the original survey[1] property data were found only for unalloyed tungsten. During the past three years, considerable tungsten-alloy data have been published from property evaluation studies, and from alloy screening and development programs.

Because of the importance and interest in ductile-brittle behavior of tungsten, considerable effort has been directed to this area. The sections dealing with ductile-brittle behavior of tungsten and tungsten alloys may appear inordinate. However, in the case of all properties, an attempt has been made to present only data which demonstrate some general behavior, or to present new data or evidence which will be of value to potential users or researchers. More studies which meet one of these criteria appear to have been reported in the area of ductile-brittle behavior than in the area of elevated temperature strength of tungsten alloys, for example.

Recent reviews on the properties of tungsten and tungsten alloys have been published by Barth,[2] the TAPCO Group of Thompson, Ramo Wooldridge,[3] and Maykuth, Barth, and Ogden.[4]

MECHANICAL PROPERTIES

At the time of the original survey,[1] available mechanical property data on unalloyed tungsten extended only to about 1200°C (2200°F), and no tensile or creep data were found in the literature on any tungsten alloys. In contrast to this, extensive work has been published during the past three years by a number of investigators extending tensile data to 3400°C (6150°F) and creep data to 2800°C (5070°F). Also, the elevated temperature properties of a number of tungsten alloys have been evaluated. Two reviews on the properties of tungsten and tungsten alloys have recently been published. One by Maykuth, Barth, and Ogden[4] of Battelle for Universal-Cyclops Steel Corporation on a tungsten sheet-rolling program for AMC, the other, by the Materials Department, TAPCO Group of Thompson, Ramo, Woolridge Company[3] on a tungsten forging development program for AMC. These reviews have served in part as the basis for this section. More recent reports have been reviewed, and data considered pertinent to this survey have been included in the general discussion.

Tensile Properties of Tungsten

The effect of temperature on the modulus of elasticity of tungsten is shown in Fig. 8.1. The previous report data which covered a temperature range from -150 to 1000°C have been extended by Brown and Armstrong[5] to 2400°C (4350°F). Brown and Armstrong evaluated the modulus dynamically in vacuum by measuring the fundamental resonant frequencies of rod samples approximately 4-in. long by 1/4-in. diameter. The earlier data by Koster, from dynamic measurements, is also given in Fig. 8.1 and it is seen to be in excellent agreement with the data of Brown and Armstrong in the overlapping temperature range. In neither case were the chemical analyses or material condition given.

The effect of temperature on the yield strength, ultimate tensile strength, elongation, and reduction-in-area of wrought tungsten is summarized in Fig. 8.2 from three investigations from tests conducted in either vacuum or in an argon atmosphere. The test material and test conditions for these data are summarized in Table 8.1.

The investigation by Union Carbide[8] provided data for both arc-cast and powder-metallurgy tungsten. In the case of the arc-cast tungsten, the yield strength and ultimate tensile strength decreased very rapidly with temperature from 25 to 300°C followed by a more gradual decrease to 1400°C. At 1400°C, the arc-cast tungsten was found to be stronger than the powder-metallurgy tungsten, probably due to a larger degree of cold work initially present or remaining. At 1650°C, both materials had about equal values of yield strength and equal values of ultimate tensile strength. At 1925°C, this was still true for the ultimate tensile strength; however, the yield strength of the powder-metallurgy tungsten was considerably above that of the arc-cast material (6200 psi versus 2500 psi).

Ductility data from this investigation[8] are of particular interest. For the arc-cast material, the elongation reached a maximum of about 30 percent at about 250°C, then decreased and remained at just above 10 percent up to a test temperature of 1375°C.

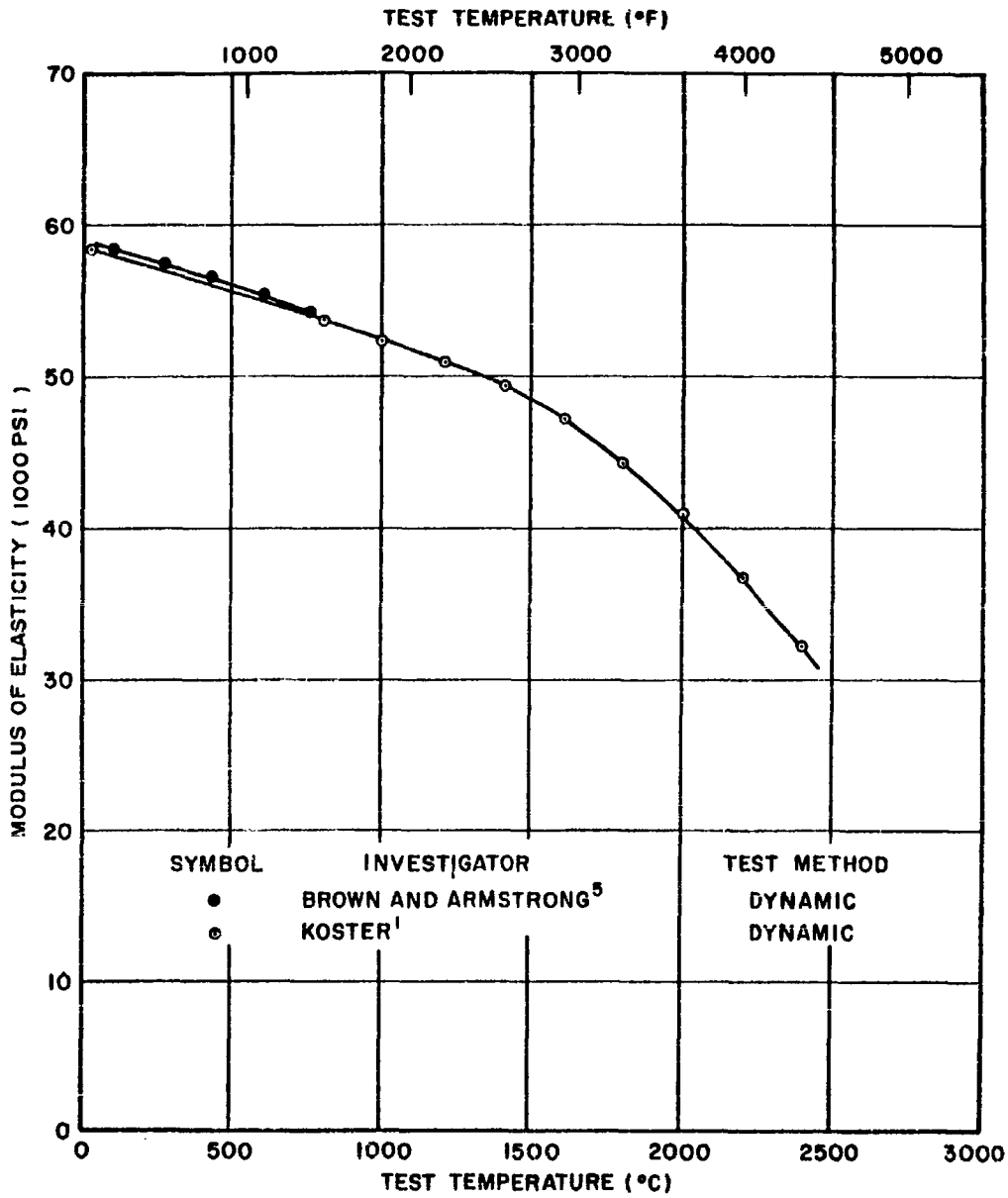


FIG. 8.1

MODULUS OF ELASTICITY OF TUNGSTEN VS TEMPERATURE

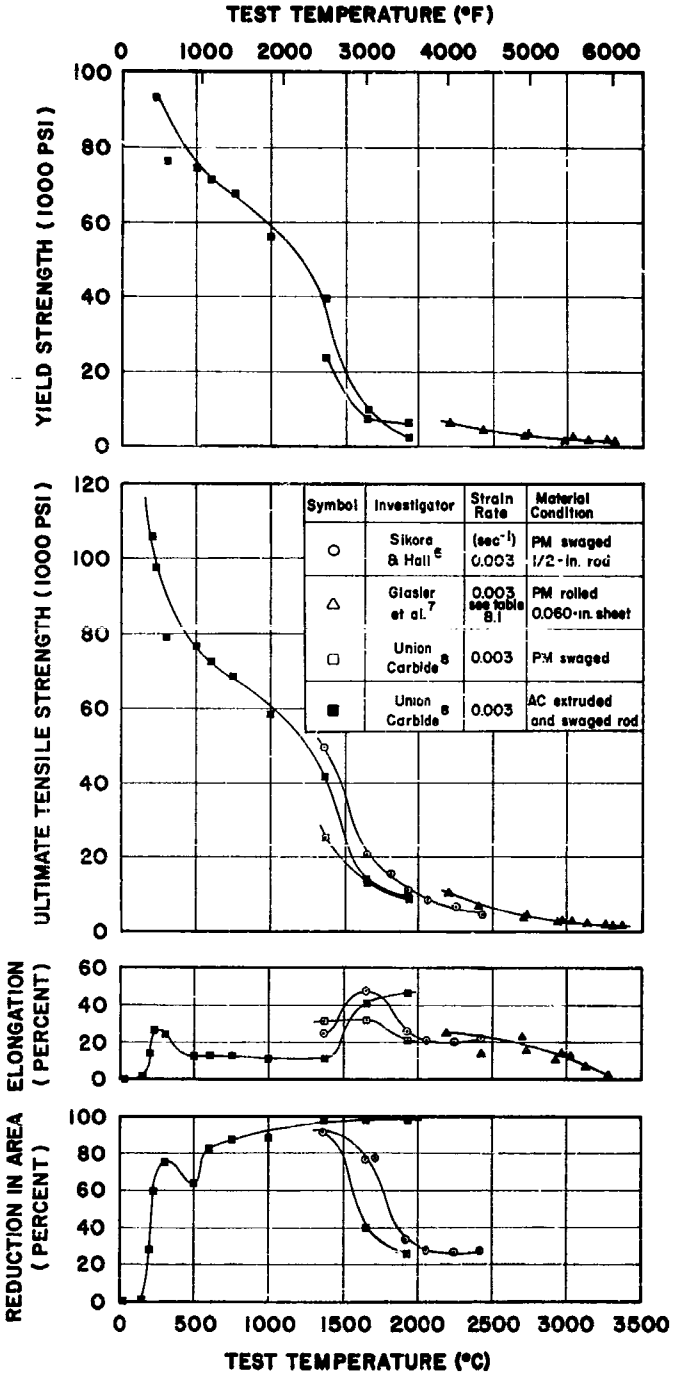


FIG. 8.2

TENSILE PROPERTIES OF WROUGHT TUNGSTEN FROM 25 TO 3400° C (75 TO 6150° F) IN AN INERT ATMOSPHERE

Table 8.1

CHEMICAL ANALYSIS AND TEST CONDITIONS FOR TENSILE DATA OF FIG. 8.2

ANALYSES		MATERIAL AND TEST CONDITIONS
ELEMENT	WEIGHT, PPM	
	UNION CARBIDE ARC-CAST MATERIAL[8]	
C O N H Si S P Fe Ni Cu	30 20 3 1 26 < 10 < 10 40 5 2	Impact extruded and swaged Test specimen had a 0.160 in. dia. by 1.00 in. long reduced section Tested in vacuum at a strain rate of 0.0003 per second Specimen heated by radiation from resistance heater
	UNION CARBIDE POWDER-METALLURGY MATERIAL[8]	
C O N H	70 40 30 3	Pressed, sintered and swaged 3/8 in. dia. rod from G.E. Test specimen and test procedures same as above for arc-cast material.
		GLAZIER[7]
O Fe Ni Ti Mo Others	60 40 50 50 400 270	Pressed, sintered, and rolled tungsten sheet 0.060-in. thick (Fansteel) Test specimen had a 1.00 in. gage length in a 0.250 in. wide by 1.81 in. long reduced section Specimen heated by self-resistance in an argon atmosphere Loading rates varied from 16 to 144 psi/sec
	SIKORA AND HALL[6]	
See Table 8.2 for Chemical Analyses		Swaged, pressed and sintered 1/2 in. dia. bars from five producers Test specimens were 0.250-in. dia. with an effective gage length of 1 in. Tests were conducted in vacuum and heated by radiation from a tantalum heater tube which was heated by induction

At the higher test temperatures of 1650 and 1950°C, the arc-cast material had elongation values above 40 percent. The reduction-in-area values for the arc-cast tungsten remained high over the entire test temperature range above the ductile-brittle transition temperature. In contrast to this, the elongation of powder metallurgy-tungsten decreased from 32 to 21 percent above 1650°C, and the reduction-in-area values for the powder-metallurgy tungsten were observed to decrease appreciably above 1500°C.

Tensile data covering the very high temperature range are presented in Fig. 8.2 as reported by Glazier, et al.[7] These data are for pressed and sintered 0.060-in. rolled tungsten sheet. The specimens were heated to test temperature by self resistance.

The data presented in Fig. 8.2 from Sikora and Hall[6] are average values from tests on tungsten from four producers (identified in Table 8.2, as ABCD). The data by Sikora and Hall cover an intermediate temperature range and are in general agreement with the lower and higher temperature data. These data for powder-metallurgy tungsten also show a drop in the reduction in area at test temperatures above about 1500°C; however, ductility is still quite good at 2400°C where the elongation is 20 percent and the reduction-in-area about 28 percent. It is not possible from available data to say whether or not this decrease in ductility exhibited by powder-metallurgy tungsten is a disadvantage as compared to the arc-cast tungsten. The entire stress-strain curves should be reviewed for both materials to determine the amount of strain which occurs before necking in each case.

Other tensile data for tungsten have been reported covering narrower temperature ranges and, in general, are in agreement with those presented in Fig. 8.2.

The data obtained by Sikora and Hall[6] for swaged, pressed and sintered tungsten bar from five producers are summarized in Fig. 8.3, as taken from DMIC Report No. 127.[2] The test conditions for these materials are given in Table 8.1; the chemical analysis in Table 8.2.

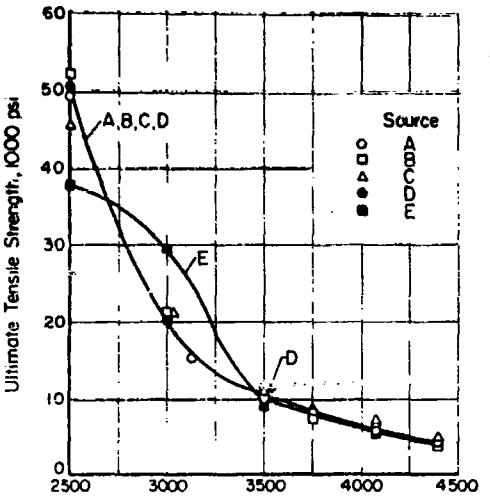
Table 8.2

CHEMICAL ANALYSIS OF MATERIAL FOR TENSILE DATA OF FIG. 8.3[2]

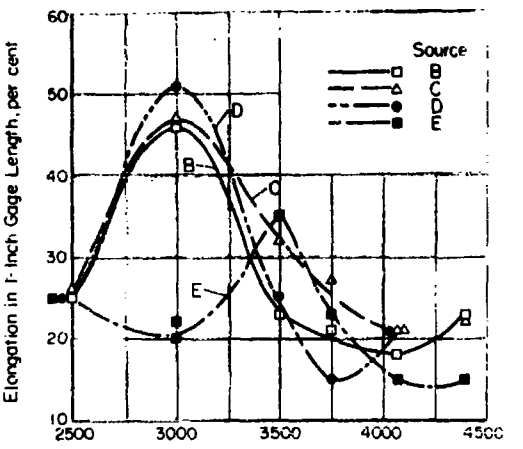
Source	Fe[(a)]	Mo[(a)]	Cr[(a)]	Si[(a)]	C[(b)]	O_2[(c)]	N_2[(d)]	H_2[(e)]
A	210	180	40	30	4	25	15	1
B	280	230	70	90	5	43	37	—
C	260	250	100	30	47	35	39	3
D	340	350	120	50	24	45	38	2
E	160	390	50	30	26	35	28	2

Impurity content, ppm by weight

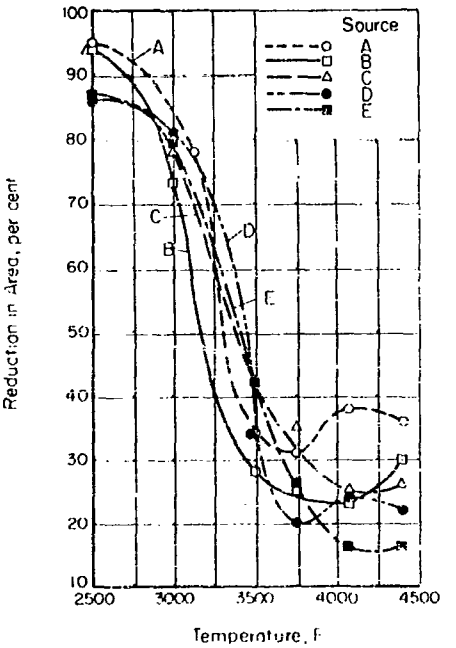
(a) Spectrograph
(b) Conductometric.
(c) LECO.
(d) Microkjeldahl plus colorimetric (Nessler's reagent).
(e) Combustion.



a. Tensile strength



b Total elongation at fracture



c Reduction in area at fracture

FIG. 8.3

TENSILE PROPERTIES FROM 2500 TO 4400° F OF TUNGSTEN BARS FROM FIVE PRODUCERS[2] AFTER SIKARA AND HALL[6]. (Note: See Table 8.2 for Description of Test Materials.)

The major point of interest in these data is the fact that the tungsten supplied by the five producers, for the most part, had similar tensile properties. The values of ultimate tensile strength versus temperature were almost identical for four of the materials; only the values for material E were lower at 2500° F and higher at 3000° F. The author suggested that this difference in behavior was probably due to less severe strain hardening of material E in the as-received condition, which resulted in a lower strength at 2500° F. The higher strength at 3000° F, in turn was probably due to a higher recrystallization temperature for material E than for the more severely worked materials.

Reduction-in-area values for the five materials and the elongation values (with the exception of material E) varied in a similar manner with increasing temperature. At 2500° F, all specimens were found to fracture with localized necking with values of reduction-in-area of 85 to 95 percent. The ductility decreased with increasing test temperature above 3000°F for materials A, B, C, & D and above 3500°F for Material E. Even at the highest temperatures, 4000 and 4500°F, all materials except material E had reduction-in-area and elongation values of 22 percent or greater.

It would be interesting to have information regarding the variations, if any, in the ductile-to-brittle behavior of these five materials from different producers. Also of interest would be elevated temperature creep properties. Appreciable variations would probably exist in the creep behavior as the different materials were reported to exhibit significant differences in grain size above 3500° F, and also in degree of porosity in the fracture region after tests at, and above, 2500° F.

Stress-strain curves for arc-melted tungsten between 25 and 1650° C are presented in Fig. 8.4 from the Union Carbide study.[8] The stress-strain curves indicate that the maximum load occurred, or necking began, after small strains for most temperatures up to and including 1375° C (2500° F).

The ultimate tensile strength for hot-pressed tungsten of two densities, 66 and 84 percent, as a function of test temperature up to 5000° F is shown in Fig. 8.5.[9] For most of the temperature range from 400 to 4000° F, the 84-percent dense tungsten had about double the strength of the 66-percent dense material.

The tensile notch sensitivity of wrought and recrystallized powder-metallurgy tungsten was investigated by Imgram, et al.[10] The chemical analysis of their test material was given as 10, 0.2, < 10, and 50 ppm of C, H, N, and O, respectively. Two material conditions were evaluated: (1) stress relieved one hour at 1200° C in argon, and (2) recrystallized one hour at 1600° C in argon, resulting in an average grain diameter of 0.076 mm.

The tensile specimens consisted of an unnotched bar with a 1-in. gage length in a reduced section 1-1/4 in. long by 0.212-in. diameter. The notched specimen had a reduced notched diameter of 0.212 in. with a theoretical stress-concentration factor of 3.0. The cross head speeds used were 0.02 in. per minute for the unnotched specimens and 0.005 in. per minute for the notched.

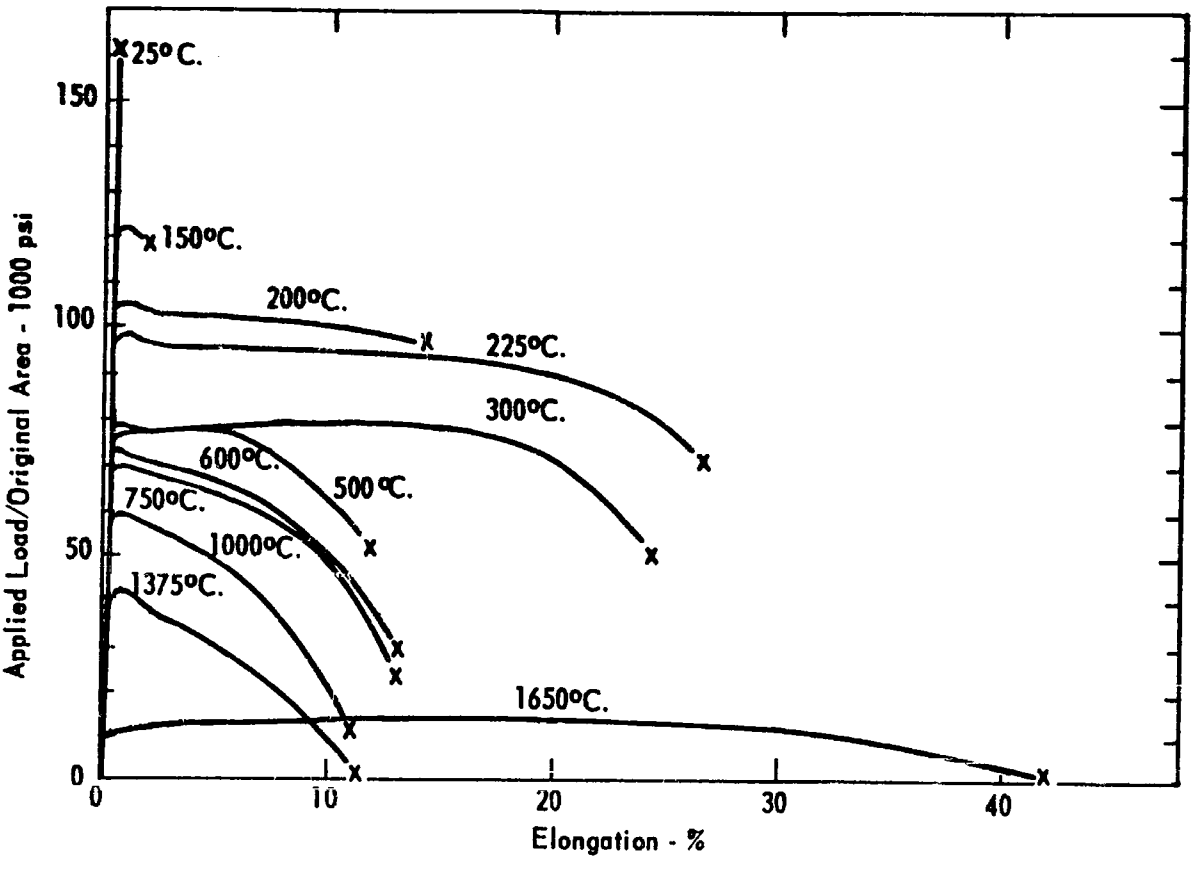


FIG. 8.4

STRESS-STRAIN CURVES FOR ARC-MELTED WROUGHT TUNGSTEN TESTED AT VARIOUS TEMPERATURES[8]

The stress-strain curves for the unnotched wrought and recrystallized material are presented in Fig. 8.6 for several test temperatures. It is interesting to note the absence of a yield point in the recrystallized material tested at 400, 500 and 600° C, whereas the 300° C curve exhibited a yield point. Also, it is interesting to note the degree of work hardening for the recrystallized material at all test temperatures. In contrast, the wrought material exhibited a yield point at both test temperatures shown, 250 and 300° C, and showed very little strain hardening.

The results for the notch-sensitivity study on tungsten are summarized in Fig. 8.7.[11] For the wrought-stress-relieved condition, the unnotched specimens showed a continual decrease in ultimate tensile strength with increasing test temperature, whereas the notched specimens showed an increase in notch strength (area at root of notch divided by maximum load) from 100 up to 250° C, followed by a decrease. The notched-to-unnotched strength ratio was greater than unity above a test temperature of about 175° C. The data for the recrystallized material presented in Fig. 8.7 show that the ultimate tensile strength for the unnotched specimens decreased over a

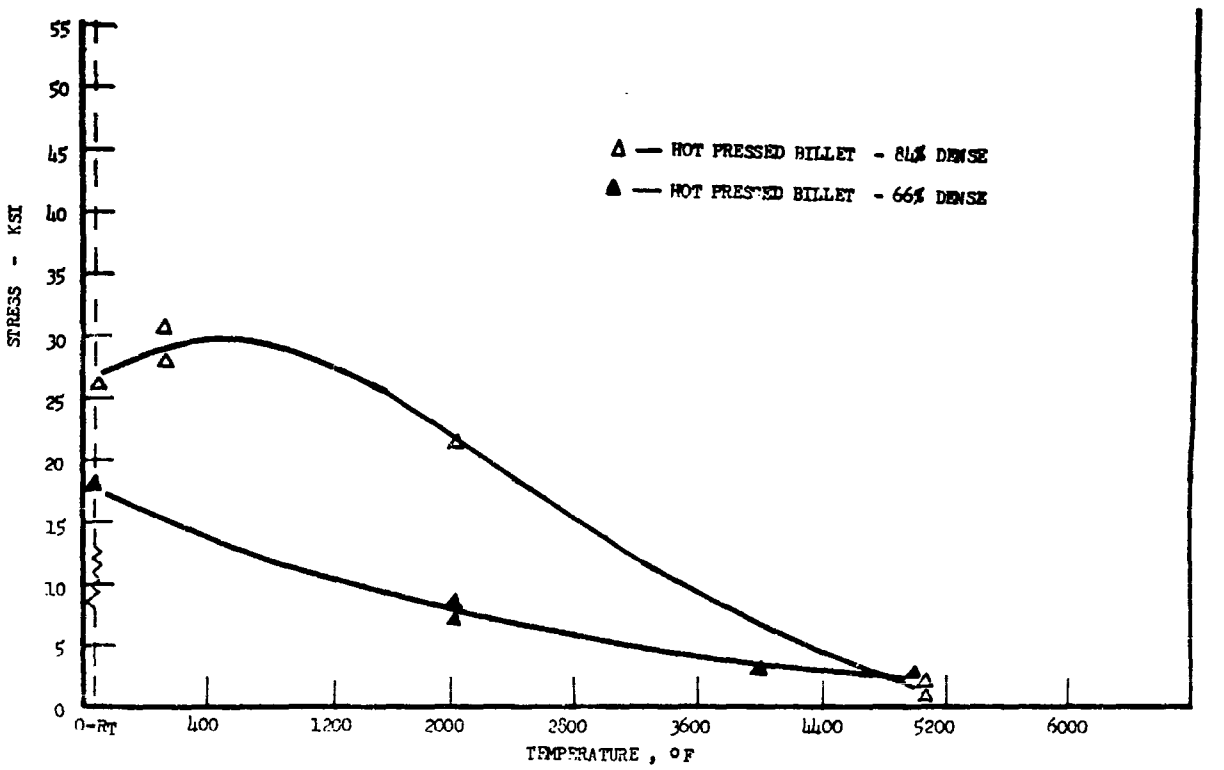


FIG. 8.5

ULTIMATE TENSILE STRENGTH FROM 75 TO 5100°F OF HOT PRESSED TUNGSTEN OF TWO DENSITIES [9]

temperature range of 300 to 600°C, whereas the notched specimens exhibited a peak in strength at about 500°C. In the recrystallized condition the notched-to-unnotched ratio exceeded unity above a test temperature of about 350°C.

Ductile-Brittle Behavior of Tungsten

Because of the serious nature of the low temperature brittleness of tungsten in structural applications, considerable effort has been directed during the past few years toward a better understanding of the ductile-brittle behavior of tungsten. The ductile-brittle transition temperature of tungsten is sensitive to the same factors which affect the transition temperature of other metals, and which have been discussed in some detail in the summary section of this report. Factors which are important include impurities, alloy additions, mechanical and thermal treatments, surface conditions, state of stress, and strain rate.

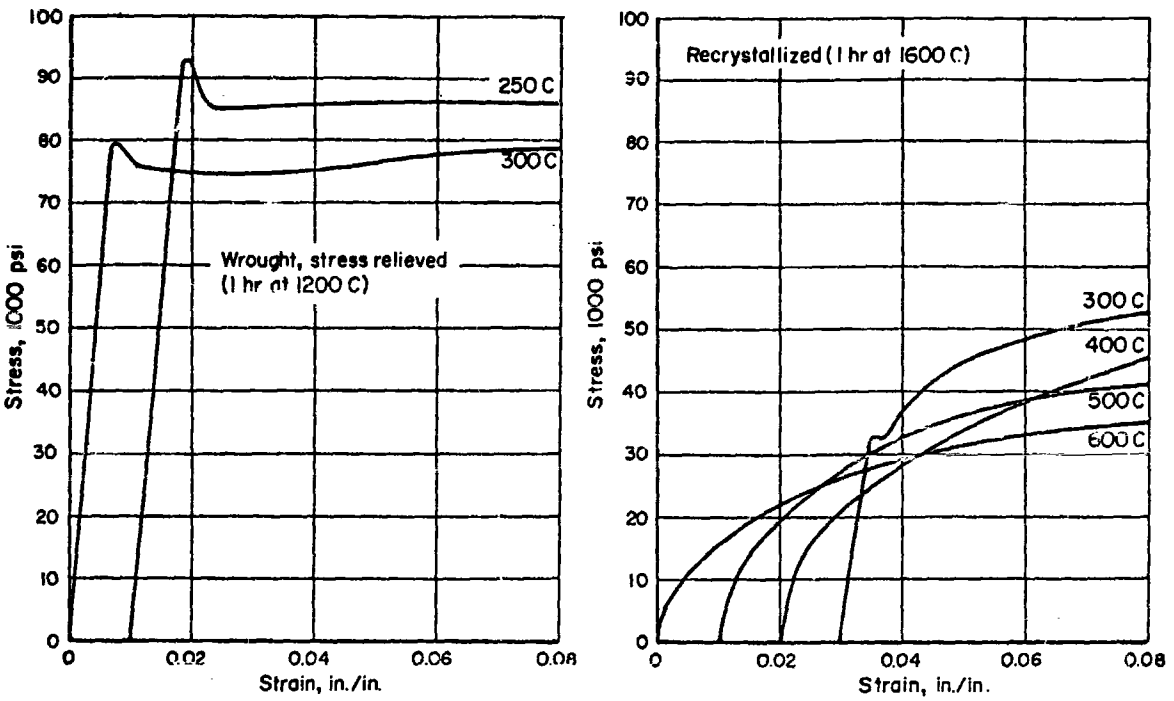


FIG. 8.6

STRESS-STRAIN CURVES FOR WROUGHT, STRESS-RELIEVED AND RECRYSTALLIZED TUNGSTEN BAR AT VARIOUS TEMPERATURES [10]

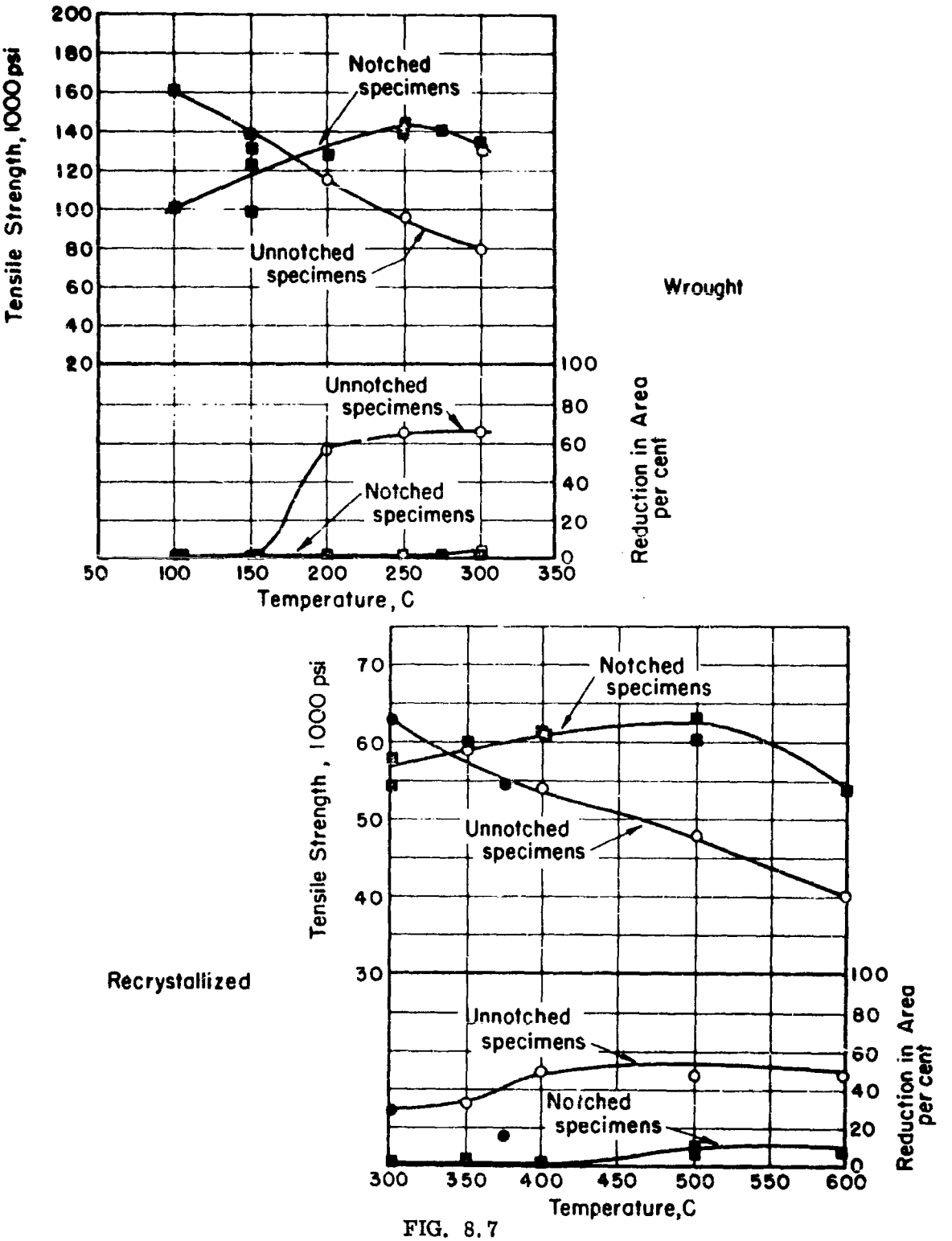


FIG. 8.7

TENSILE PROPERTIES OF NOTCHED AND UNNOTCHED SPECIMENS OF WROUGHT AND RECRYSTALLIZED TUNGSTEN [11]

The general effect of impurities is shown in Fig. 8.8 from the work of Atkinson,[12] where the curves represent three successively lower impurity levels. More recently,

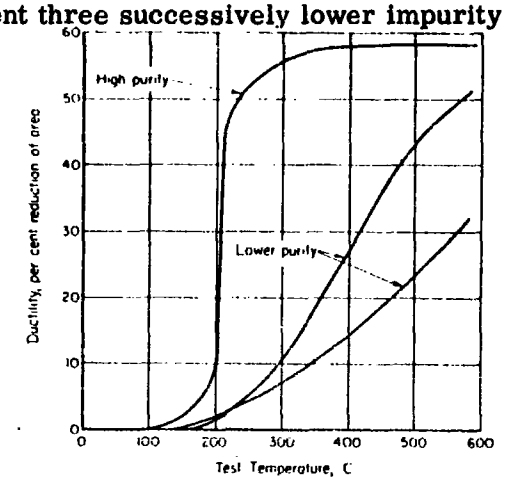


FIG. 8.8

TENSILE DUCTILITY IN THE DUCTILE-BRITTLE TEMPERATURE RANGE AS AFFECTED BY PURITY [2, 12]

Allen, Maykuth and Jaffee,[13] conducted an investigation on the effect of impurities on the recrystallization behavior and on the ductile-brittle behavior of tungsten. They investigated the effect on these two properties of interstitial elements in high-purity single crystal and polycrystalline tungsten, and the effect of refractory oxides, nitrides, and carbides in powder-metallurgy tungsten. The results of this study will be summarized under various subject headings in this section.

Allen, et al.[13] prepared a high-purity tungsten single crystal by electron-beam zone refining. The single crystals exhibited ductility at room temperature; however, polycrystalline tungsten specimens prepared from the high-purity zone-refined crystals exhibited a ductile-brittle bend transition temperature around 320°C, or only slightly below that for relatively impure powder-metallurgy sheet tungsten. The authors concluded that the presence of grain boundaries was more effective in shifting the ductile-brittle transition temperature than the added impurity elements, at least in the range that could be analytically detected.

The general effect of cold work on the ductile-brittle behavior of tungsten is presented in Fig. 8.9 from the work of Allen, et al.,[13] where bend ductility is presented for powder-metallurgy tungsten in the wrought and recrystallized condition. The wrought material had an appreciably lower transition temperature, about 150 to 200°C lower, than the recrystallized materials. The curves for the two recrystallized materials also indicate the effect of grain size. The material with the finer recrystallized grain size (600 to 650 grains/mm^2) had a transition temperature of about 40°C lower than that for the coarser grain material (250 grains/mm^2).

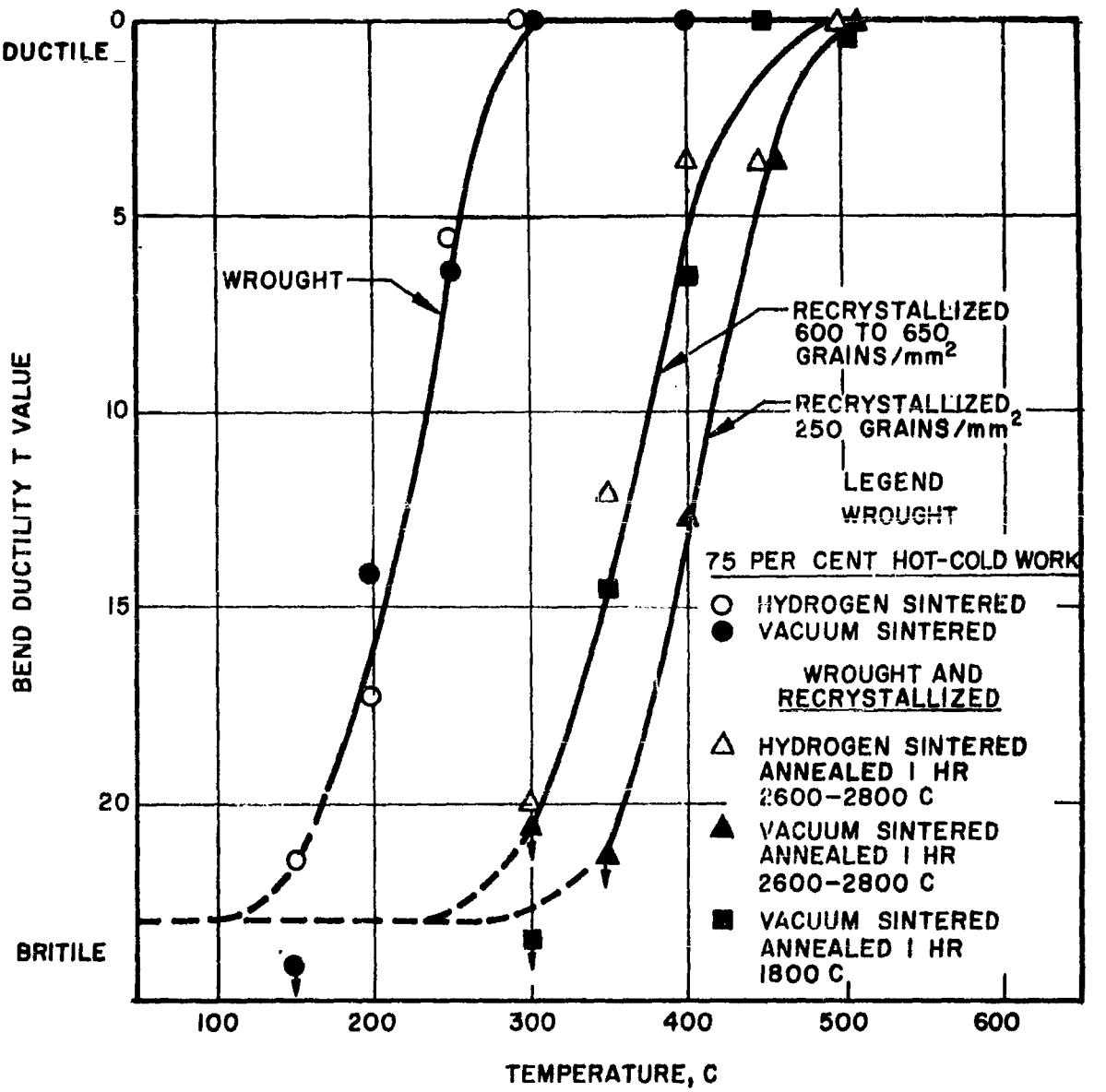


FIG. 8.9

BEND DUCTILITY OF WROUGHT AND RECRYSTALLIZED POWDER METALLURGY TUNGSTEN

The effect of strain rate on the ductile-to-brittle transition temperature of recrystallized powder-metallurgy tungsten was reported in a study by the Union Carbide Metals Company,[8] using strain rates of 0.008, 0.8 and 80 per minute, and on tensile specimens 0.113-in. diameter with an 0.250-in. gage length. An increase in the strain rate from 0.008 to 80 per minute was found to increase the tensile transition temperature about 200°C, from about 200 to 400°C. This magnitude of shift is about equal to that reported earlier by Magnusson and Baldwin[1] for swaged powder-metallurgy tungsten as a result of a 10^4 change in strain rate.

The results presented so far on the ductile-brittle behavior of tungsten have not demonstrated new effects but have been included primarily for general background. Several new investigations have recently been reported which are of interest; these will be discussed in detail.

The Union Carbide study[8] determined the effect of 1-hour annealing treatments at 1300, 1600 and 2100°C on the ductile-brittle behavior of swaged, powder-metallurgy tungsten. The tensile reduction-in-area as a function of test temperature for specimens treated at the different annealing temperatures is presented in Fig. 8.10. It would be interesting to have a transition curve for the as-swaged material; however, the available data are interesting in themselves. The authors[8] state that no visible microstructural change occurred up to the 1600°C annealing temperature. In any case, a progressive shift to higher transition temperatures occurred with increasing annealing temperatures. More work is needed in this area to clearly distinguish between the effect of recovery processes and recrystallization on the shift in transition temperature between cold-worked and fully recrystallized material to determine reasons for beneficial effects of cold work.

Figure 8.11 presents the yield strength and fracture stress corresponding to the data presented in Fig. 8.10. Fracture stress was defined as the load at fracture divided by the final area at fracture. The temperature at which the fracture stress becomes equal to yield strength is considered to be the lower limit of the ductile-brittle transition range. Although the yield strength was considerably higher after annealing at 1300°C than after annealing at 1600 or 2100°C, the fracture stress curve likewise was higher and the intersection of the yield strength and fracture strength curves occurred at a lower temperature for the 1300°C anneal resulting in a lower transition temperature. The intersection points for the 1600 and 2100°C annealing temperatures occurred at the same temperature in agreement with the identical lower limit of the ductile-brittle range for these two annealing temperatures as indicated in Fig. 8.10.

The effect of different fabrication histories on the tensile transition temperature of arc-cast tungsten was also evaluated in the Union Carbide study. The results are presented in Fig. 8.12 for three fabrication histories in terms of reduction-in-area versus test temperature. Direct swaging of arc-cast tungsten at 1700°C resulted in the highest transition temperature of the three conditions. This swaging temperature was reported to be about the lowest which could be used successfully without prior breakdown. It was possible to break down the cast structure by impact extrusion at 1600°C, which resulted in about a 70°C lower transition temperature. After breakdown

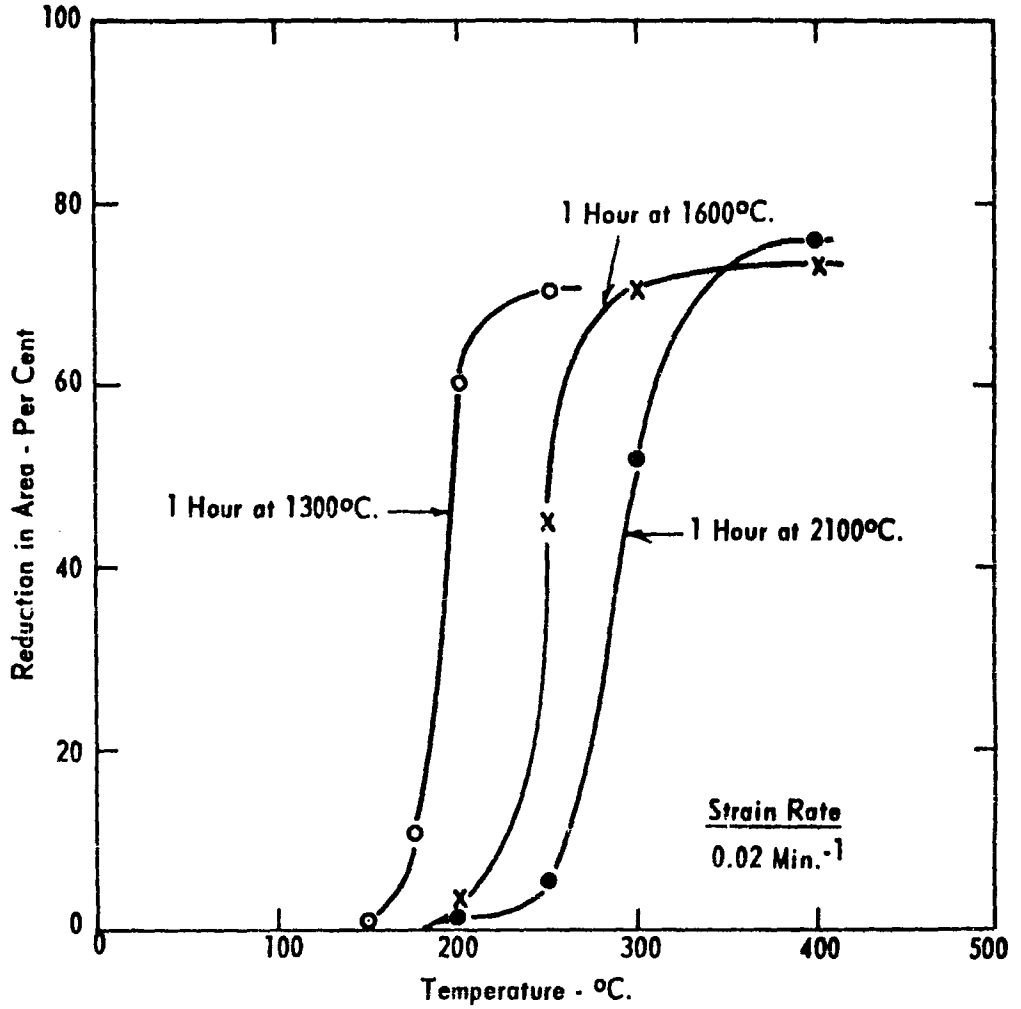


FIG. 8.10

DUCTILE-BRITTLE BEHAVIOR OF SWAGED POWDER-METALLURGY TUNGSTEN AS INFLUENCED BY VARIOUS ANNEALING TREATMENTS[8]

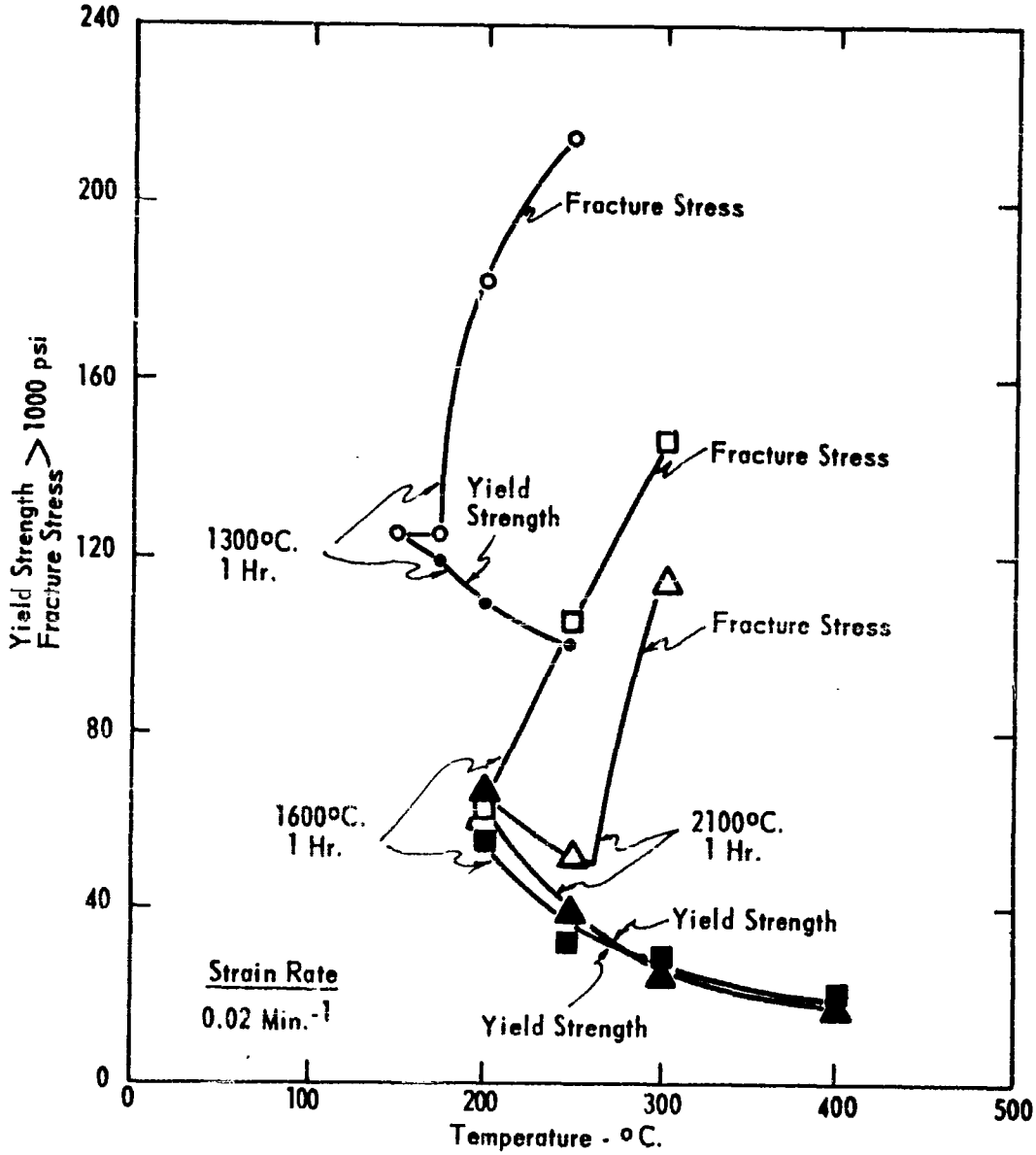


FIG. 8.11

YIELD STRENGTH AND FRACTURE STRESS OF SWAGED POWDER-METALLURGY TUNGSTEN AS INFLUENCED BY VARIOUS ANNEALING TREATMENTS[8]

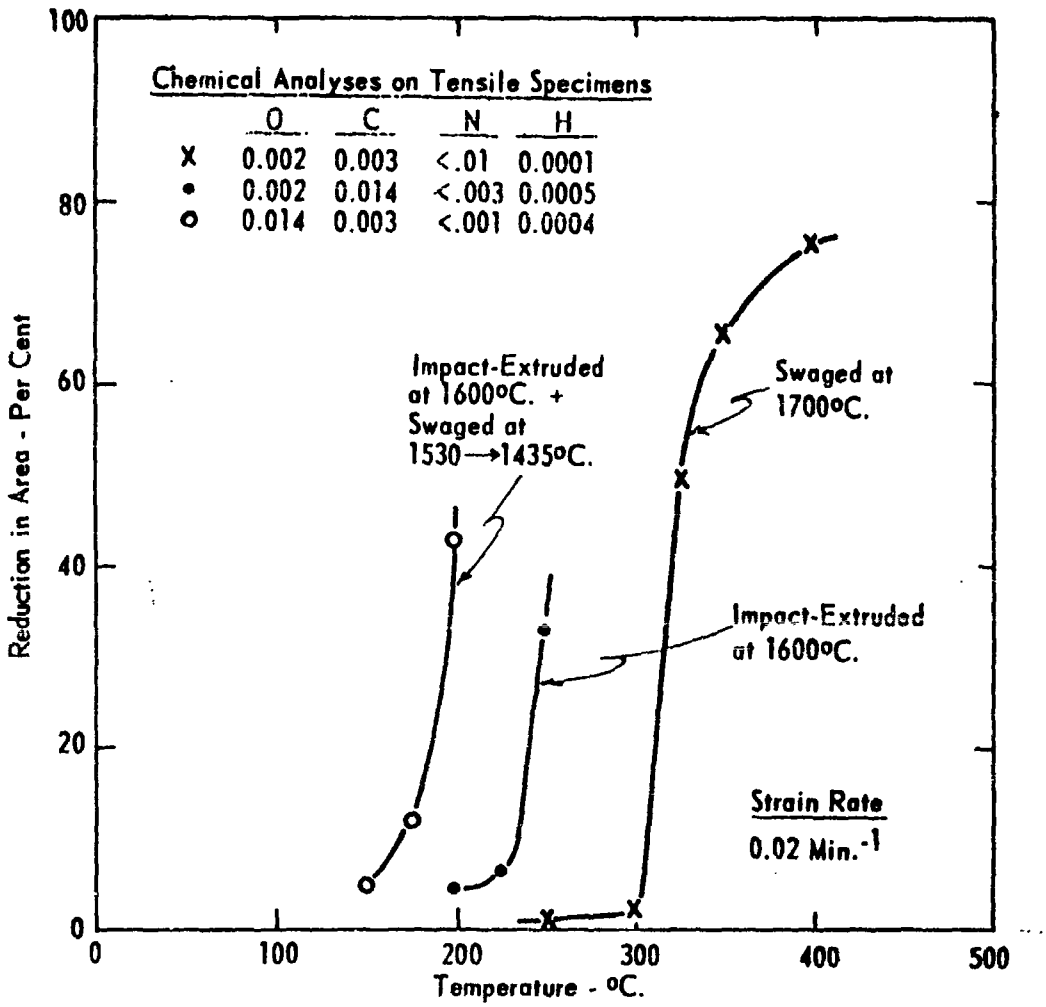


FIG. 8.12

EFFECT OF FABRICATION ON THE DUCTILE-TO-BRITTLE TRANSITION TEMPERATURE OF ARC-MELTED TUNGSTEN[8]

by impact extrusion at 1600° C, it was found possible to subsequently swage the material at still lower temperatures starting at 1530° C and finishing at 1435° C. This treatment resulted in a still lower transition temperature as indicated in Fig. 8.12. It would be interesting to have the transition temperature curve for the arc-melted tungsten used in this study in the recrystallized condition for comparison with the other curves of Fig. 8.12. Nevertheless, these data as well as those of Fig. 8.10 are interesting in that they emphasize the importance of thermal-mechanical treatments on ductile-brittle behavior of metals, and that more study in this area would be fruitful.

Stimulated by the findings of Sedlatschek and Thomas[14] which indicated the beneficial effects of electropolishing on the room-temperature ductility of tungsten, Stephens[15] investigated the effect of various surface conditions on the room-temperature bend ductility of tungsten. Preliminary studies were reported by Stephens[15] using 0.125-in. diameter sintered and swaged tungsten rods in the as-wrought condition. Stephens found that the room-temperature bend ductility increased with increasing depth of electropolishing. A sevenfold increase was obtained after a 0.005-in. reduction in diameter by electropolishing, as measured by bend angle before fracture. Removal of this amount of material by grinding rather than electropolishing did not produce any measureable increase in room-temperature ductility. Furthermore, specimens which were electropolished to produce good bend ductility and were subsequently scratched with emery paper experienced a large reduction in ductility.

Stephens[16] later reported the results of a more extensive study on the effect of different surface conditions on the ductile-brittle tensile transition temperature of recrystallized commercially pure powder-metallurgy tungsten. The results of this investigation are summarized in Fig. 8.13 in terms of reduction-in-area values. The button-head tensile specimens were recrystallized one hour at 1925° C (3500° F) in vacuum after grinding to the final dimensions with a reduced gage section of 0.170-in. diameter and 1.03-in. length. After recrystallization, all specimens were electropolished before being given other surface treatments. The term "mechanical worked" applies to three surface conditions: ground, ground and annealed, and ground and peened. The ground and annealed condition is on the low end and the ground and peened on the high end of the shaded area in Fig. 8.13. The electropolished surface condition had the lowest transition temperature. Oxidation of the surface for one hour at 1000° F was not found to be detrimental, while all other surface conditions studied raised the transition temperature above that for the electropolished surface.

Effect of Cold Work on the Tensile Properties of Tungsten

Data reported by Hall and Sikora[17] on both as-received wrought tungsten and recrystallized tungsten indicated that the effect of cold work was retained up to about 3000° F for their test conditions. At 2500° F, for example, the recrystallized material of Hall and Sikora had an ultimate tensile strength of 32,000 psi while the wrought material, had a value of 49,000 psi, whereas above 3000° F, both materials had about the same ultimate tensile strength. These data and earlier work by Pugh[1] giving ultimate tensile strength of both stress-relieved and recrystallized tungsten over a lower temperature range are summarized in Fig. 8.14.

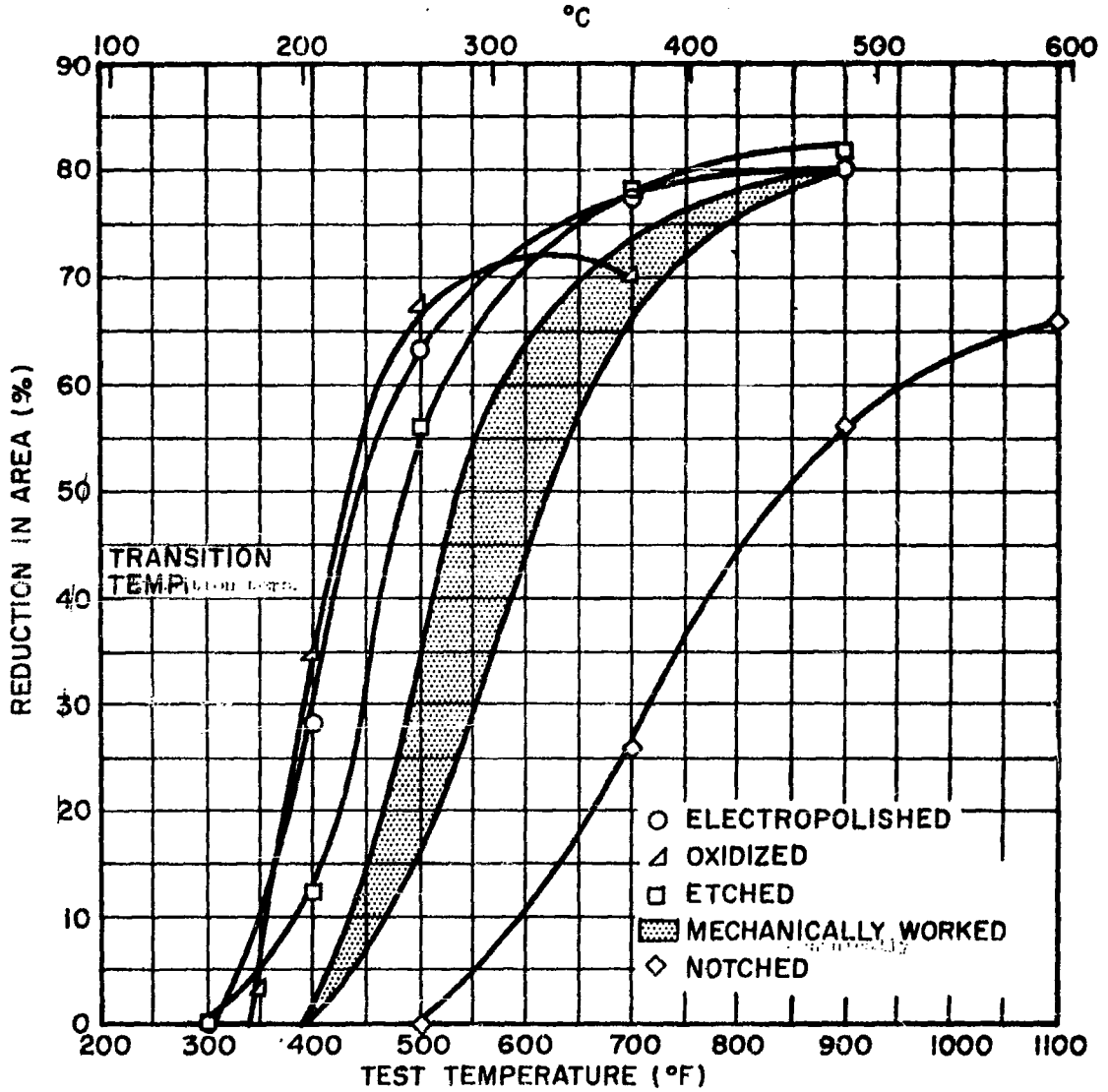


FIG. 8.13

DUCTILE-BRITTLE BEHAVIOR AS INFLUENCED BY VARIOUS SURFACE TREATMENTS [16]

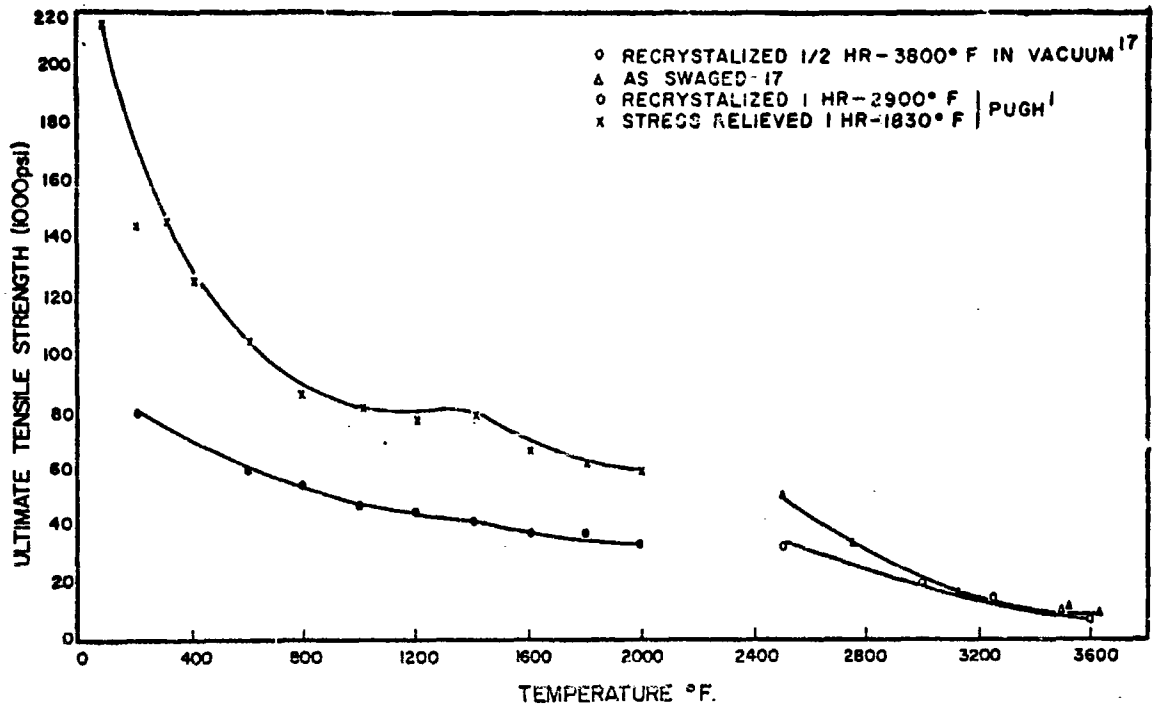


FIG. 8.14

TENSILE STRENGTH OF TUNGSTEN FROM 100 TO 3600° F IN THE RECRYSTALLIZED, STRESS-RELIEVED, AND WROUGHT CONDITIONS[3]

Recrystallization Behavior of Tungsten as Influenced by Impurities

Allen et al.[13] studied the effect of additions of carbon, oxygen, and nitrogen on the recrystallization behavior of high-purity single-crystal tungsten after 50-percent hot-cold work. Softening curves for the nitrogen-, oxygen-, and carbon-dosed and undosed single-crystal tungsten are presented in Fig. 8.15 along with data for sintered powder metallurgy tungsten. All test materials were hot-cold worked 50 percent at 1200° C with the exception of the undosed single crystal W which was worked 50 percent at 800° C. For the undosed tungsten crystal, recrystallization appeared to begin at about 1200° C and was complete at 1400° C. Thus, the high-purity tungsten recrystallized at a relatively low temperature over a narrow temperature range (200° C) as compared with the behavior of the sintered powder-metallurgy material. The numbers adjacent to the data points indicate percent recrystallization as determined metallographically. The authors[13] concluded that carbon in amounts of 100 to 200 ppm increased the recrystallization temperature of high-purity tungsten by about 100° C, whereas oxygen in amounts up to 40 ppm, and nitrogen up to 1.4 ppm had no significant effect.

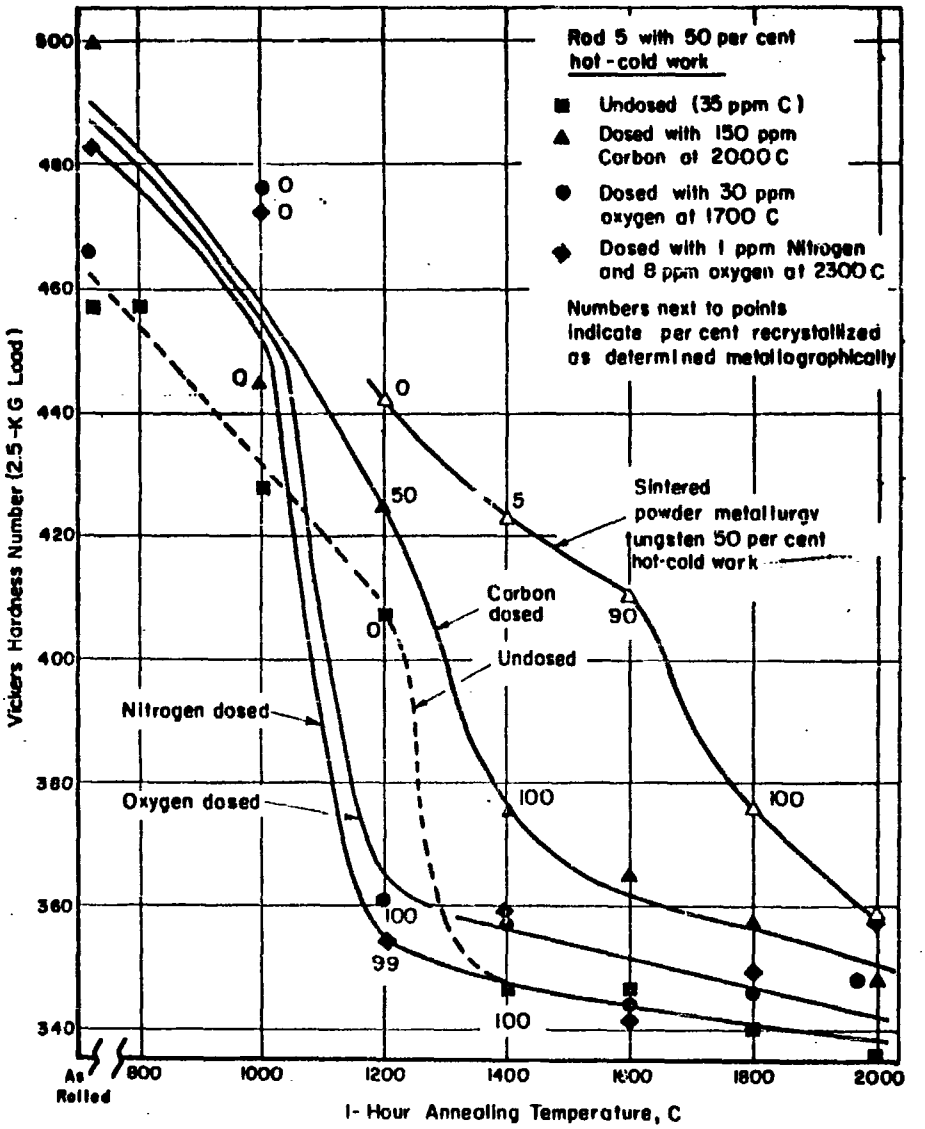


FIG. 8.15

SOFTENING CURVES FOR WROUGHT ELECTRON-BEAM-REFINED (5 PASSES) TUNGSTEN SINGLE CRYSTALS WITH AND WITHOUT INTERSTITIAL DOSING COMPARED WITH THAT OF SINTERED POWER-METALLURGY TUNGSTEN

It should be pointed out that hot-cold working the undosed tungsten 50 percent at 1200° C would have resulted in significantly less residual strain energy than the actual working of 50 percent at 800° C. In fact, the authors reported that for two samples having identical impurity content (both produced by 5-pass electron-beam refining) had different recrystallization temperature (1650 and 1300° C) as a result of different amounts of cold work, 35 percent and 50 percent reduction at 800° C, respectively. Presumably the higher recrystallization temperature was due to the lesser degree of cold work. Thus, it would be expected that the curve for the undosed tungsten in Fig. 8.15 would be shifted to a considerably higher recrystallization temperature for a material worked 50 percent at 1200° C rather than at 800° C. On the basis of this difference in worked state, it is difficult to conclude that carbon additions increased the recrystallization temperature of high-purity tungsten. In fact, it is possible that the softening curve for a material worked 50 percent at 1200° C would indicate that N and O additions decidedly lower the recrystallization temperature of tungsten.

Allen, et al.[13] also presented annealing data for unalloyed powder-metallurgy tungsten. These data, summarized in Fig. 8.16, indicate that vacuum-sintered material had a lower recrystallization temperature than hydrogen-sintered material by about 200° C. The lower recrystallization temperature of the vacuum-sintered material was explained on the basis of a probable higher purity of this material over the hydrogen-sintered material. The effect of amount of cold work is also shown in Fig. 8.16, where the 50 percent hot-cold worked material had a higher recrystallization temperature than material worked 75 percent by about 300° C in terms of the softening curves.

Tensile Properties of Tungsten Alloys

During the past several years more than a dozen separate investigations have been directed toward developing tungsten-base alloys and evaluating their high-temperature properties. These investigations are summarized in Table 8.3 by a description of the alloy systems and properties under study. The results of these studies, many of which are still in progress, will be presented separately under tensile, creep and oxidation properties. Tensile properties of some of the tungsten alloys which have been reported at temperatures above 2500° F are summarized at the end of this section in Fig. 8.22.

The only data found on modulus of elasticity of tungsten alloys are those presented in Fig. 8.17 for the room temperature modulus of W-Ta alloys. The elastic modulus of tungsten decreases almost linearally with the first 20 atomic percent tantalum additions, according to Fig. 8.17. No data for other tungsten alloys were found; however, small, solid-solution additions common to several attractive tungsten alloys would be expected to change the modulus of tungsten only slightly. It is surprising that more data are not available, as it would be relatively easy to determine at least the room-temperature modulus on alloy samples available in many past and current alloy development programs.

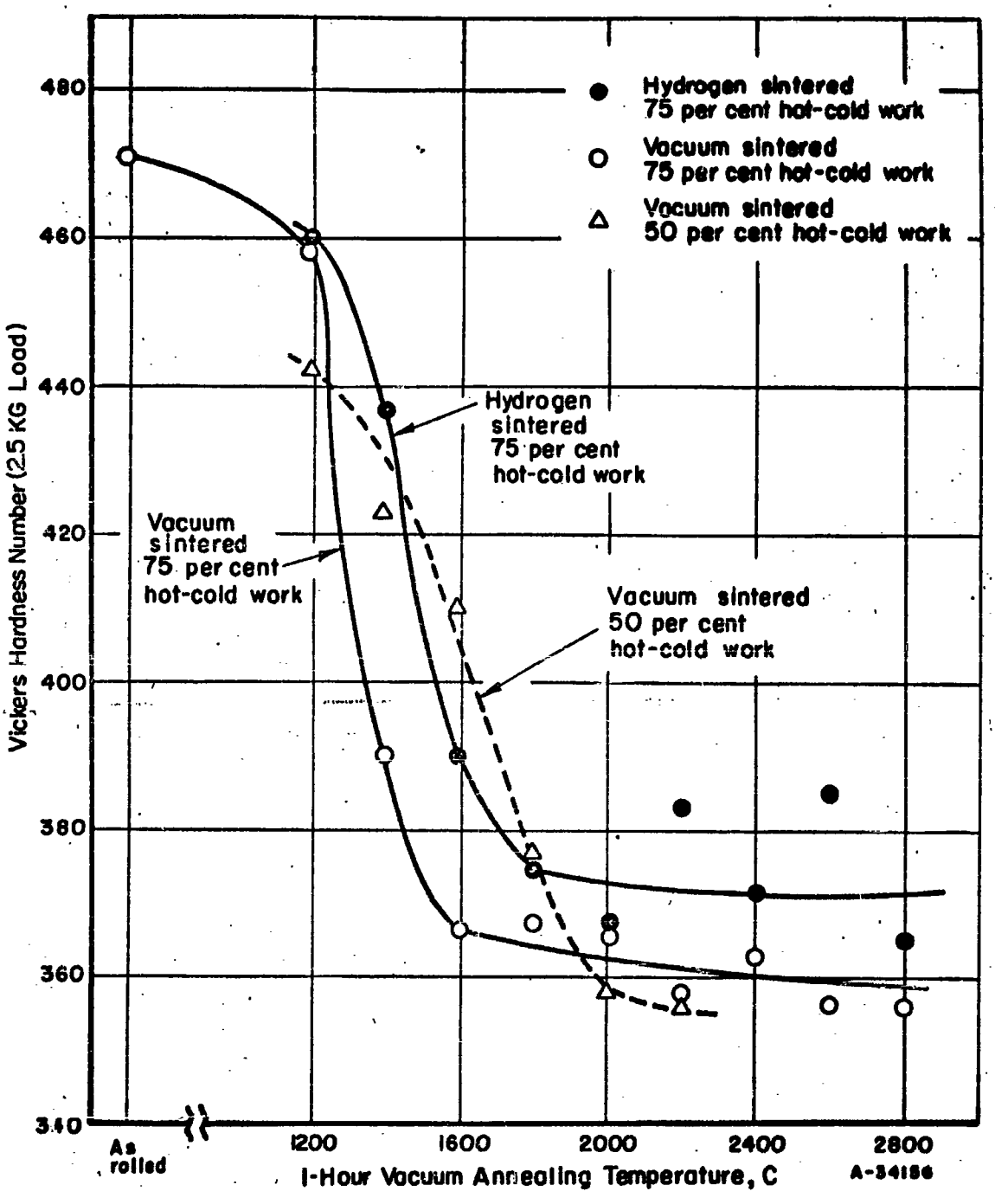


FIG. 8.16

SOFTENING CURVES FOR POWDER-METALLURGY TUNGSTEN[13]

Table 8.3

TUNGSTEN ALLOYS STUDIES

ALLOY SYSTEM	PROPERTIES STUDIED	INVESTIGATOR	REF.
W-Cb W-Ti W-Zr	Tensile, 3000 to 3500° F Oxidation at 1470 and 2190° F	UCMC Staff	8
W-Cb W-Ta-Cb	Hardness to 2900° F Oxidation at 2190° F	McKinsey, et al.	18
W-ThO_2	Recrystallization Temperature Tensile to 2700° F Creep to 2700° F (most data preliminary)	Atkinson, et al.	19
W-ThO_2 W-TaC W-HfO_2	Tensile to 3000° F Creep to 3000° F	Sell, et al.	20, 21
W-Hf W-Re W-Ta W-Re-Ta	Hardness to 2000° F (preliminary data)	Feild, et al.	22
W-Cb W-Co W-Hf W-Ta W-V W-Zr	Structure Lattice parameter Hardness to 3000° F Oxidation at 3000° F Forgeability	Semchyshen and Barr	23
W-ThO_2 W-Mo	Tensile to 4400° F Creep to 2200° F	Hall, et al.	24
W-Cb W-Ta W-Mo	Tensile to 4000° F	Foyle	25
W-Cb W-Mo	Forgeability Tensile to 4000° F Creep at 3000° F	Lake, et al.	26

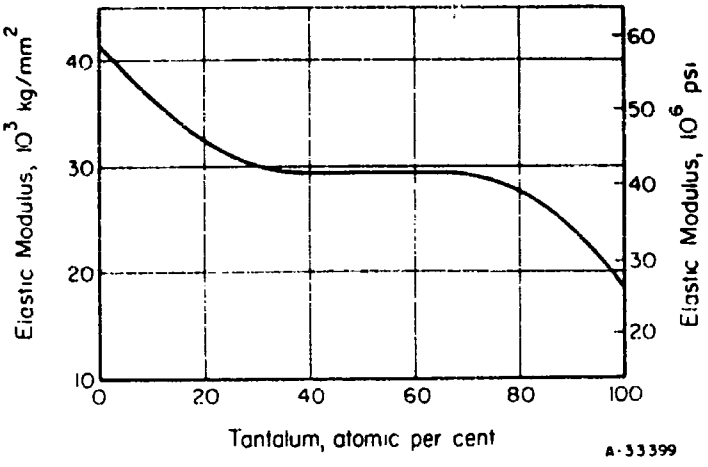


FIG. 8.17

ELASTIC MODULUS OF TUNGSTEN-TANTALUM ALLOYS[48]

The effect of binary additions of Cb, Ti and Zr on tensile properties of impact-extruded and swaged arc-melted tungsten at 1650 and 1925° C (3000 and 3500° F) was studied by the Union Carbide Metals Research Laboratories[8]. The results are summarized in Fig. 8.18 along with data for arc-melted and powder-metallurgy tungsten for comparison purposes. The actual alloy content with associated oxygen and carbon analyses are given in Table 8.4. The intended composition of the titanium alloy was 0.25; after melting, however, only 0.005 Ti remained. At 1650° C the Cb and Zr alloy additions significantly increased both the yield and ultimate tensile strength. At 1650° C, the W-0.57Cb alloy appeared to be the strongest alloy exhibiting strength values about four to five fold over those for the unalloyed material. The unalloyed tungsten and the W-0.005Ti alloy were found to be recrystallized after tensile testing at 1650° C,

TABLE 8.4

OXYGEN AND CARBON ANALYSES OF TUNGSTEN-BASE ALLOYS FOR DATA OF FIG. 8.18[13]

ALLOY	WEIGHT PER CENT	
	O	C
W-0.005Ti	0.009	0.003
W-0.12Zr	0.010	0.001
W-0.57Cb	0.004	0.001
W-0.88Cb	0.018	0.001

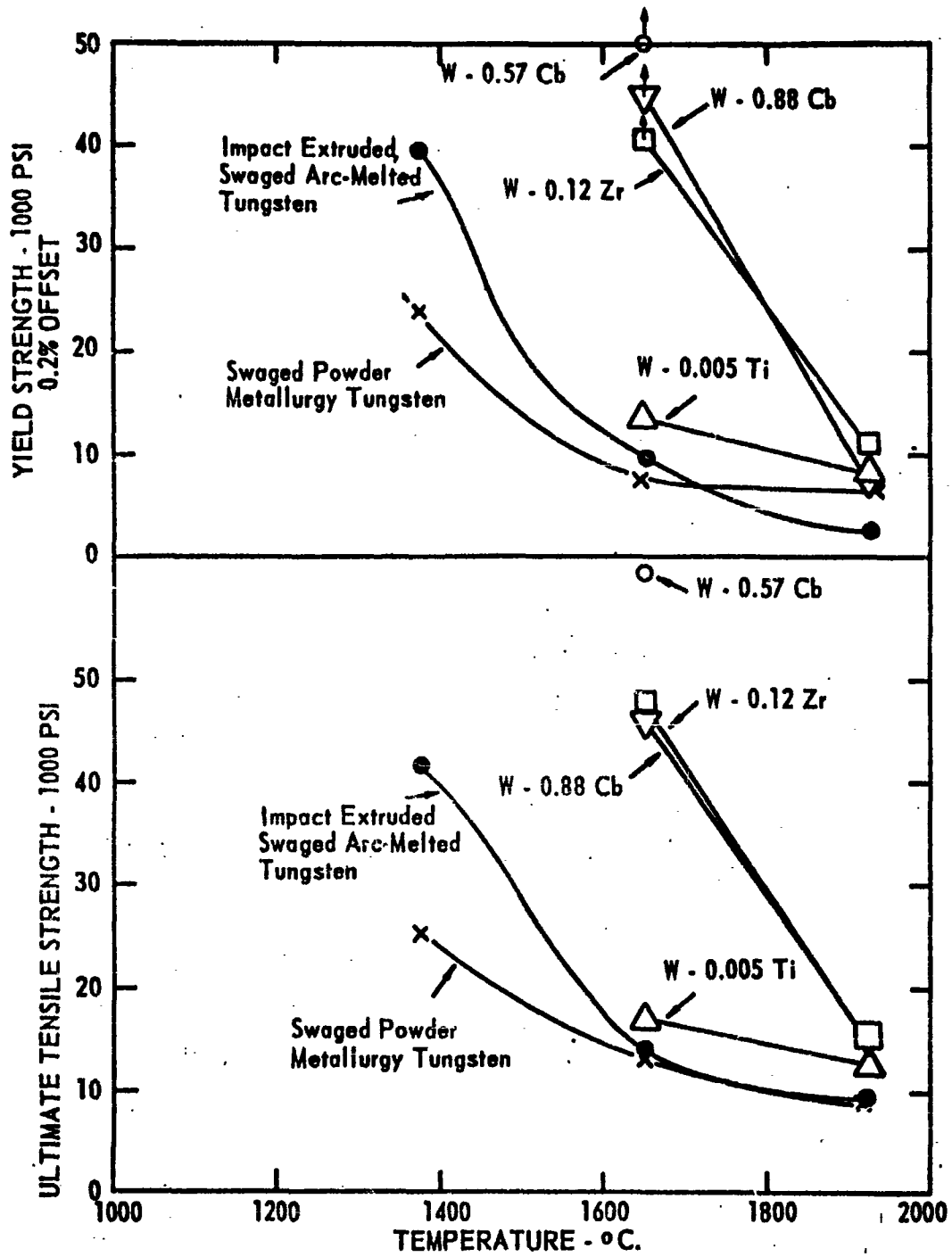


FIG. 8.18

YIELD STRENGTH AND ULTIMATE TENSILE STRENGTH FROM 1365 TO 1925° C OF TUNGSTEN ALLOYS COMPARED WITH UNALLOYED TUNGSTEN[8]

whereas the Cb and Zr alloys still retained some cold work. The authors[8] attributed the strengthening effect at 1650° C of Cb and Zr to higher recrystallization temperatures for these alloys. The W-0.57Cb alloy was not evaluated at 1925° C because of insufficient material; however, its reported ultimate tensile strength at 1650° C (3000° F); of 60,000 psi in the as-swaged condition is very attractive. Although the strength curves for the W-0.88Cb and W-0.12Zr alloys decreased rapidly above 1650° C, the ultimate tensile strength values of these alloys were still 60 to 80 percent greater than that for the unalloyed tungsten, at 1925° C. The yield strength values for these two alloys were 3 to 4 times greater than for the wrought arc-melted tungsten. The results presented on these alloys represent a preliminary study with only one test at each temperature, and thus require additional study and confirmation.

A more recent alloy study at Union Carbide reported by McKinsey, et al.[18], was directed toward evaluating arc-cast ternary alloys in the W-Ta-Cb system. The authors demonstrated that hot-hardness measurements were a reasonably reliable indication of the high-temperature tensile strength for the alloy system under study, and used hot-hardness measurements up to 2900° F in an initial screening study of the ternary field. Based upon the hot-hardness values, the ternary tungsten-base alloys listed in Table 8.5 were selected for tensile property evaluation. Tensile properties have not been reported as yet; however, the authors anticipate that some of these alloys will have ultimate tensile strengths in excess of 40,000 psi at 2900° F.

TABLE 8.5

TUNGSTEN ALLOYS SELECTED FOR TENSILE STRENGTH EVALUATION BY MCKINSEY, et al.[18]

WT. (%)			AT. (%)			APPROXIMATE VHN	
W	Ta	Cb	W	Ta	Cb	2700° F.	2900° F.
96	1	3	93	1	6	93	72
80	5	15	70	4	26	115	85
60	8	32	46	6	48	110	84
55	30	15	48	26	26	112	96

In an effort to confirm the earlier reported[3] high strength of the W-0.6Cb alloy, additional alloy test material was prepared[18] from a 4-in. diameter arc-melted ingot. The ingot was extruded at 3400° F at a 4 to 1 ratio, swaged from 1-3/8 in. diameter to 3/8 in. diameter at 3000° F. The tensile properties obtained for the W-0.58Cb alloy in the as-swaged condition are summarized in Fig. 8.19. The ultimate tensile strength at 3000° F at 39,400 psi is considerably below the 60,000 psi value reported earlier[7]; however, it is still about twice the value reported for swaged unalloyed tungsten rod.

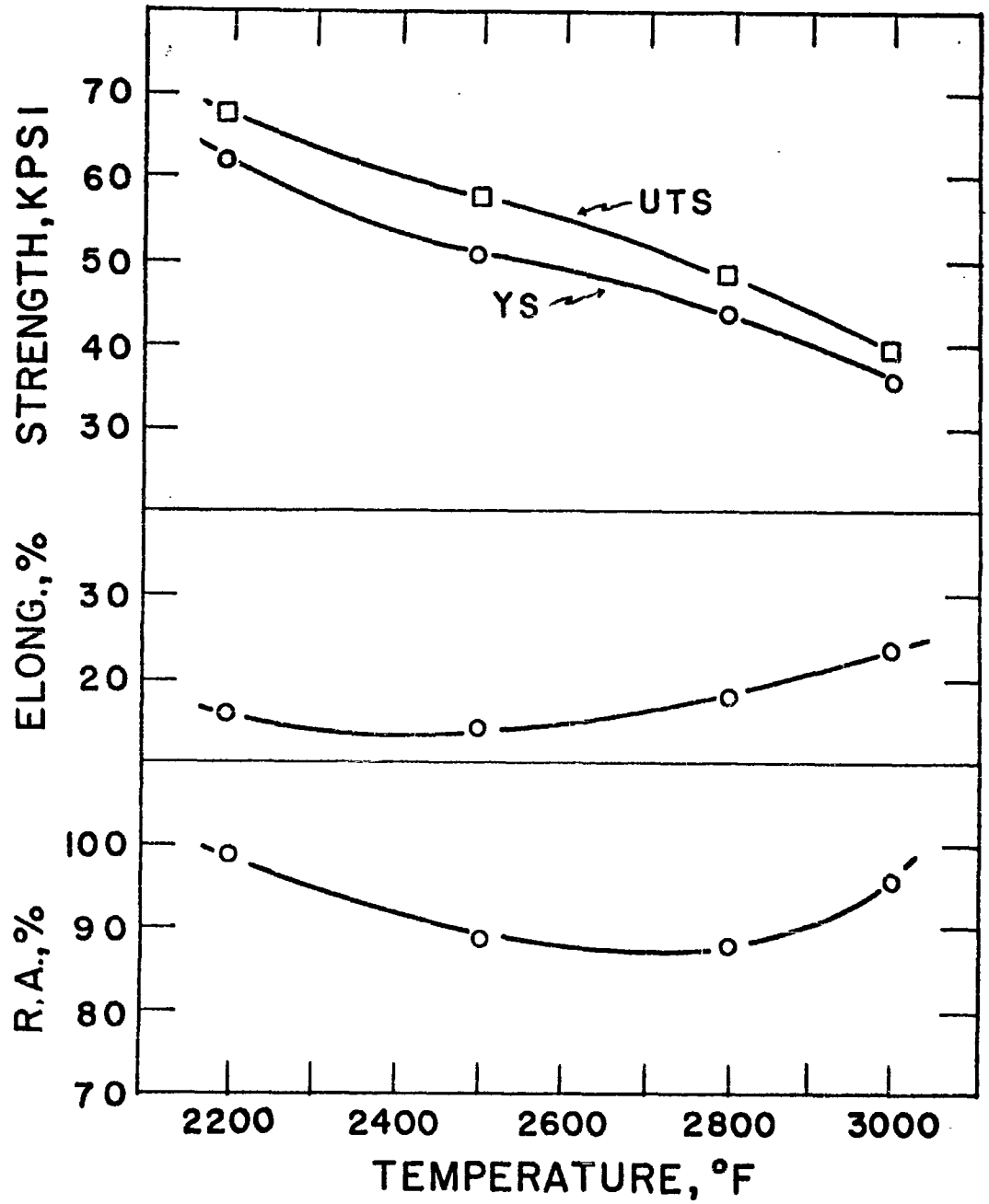


FIG. 8.19

TENSILE PROPERTIES OF SWAGED W-0.6Cb ALLOY FROM 2200 TO 3000° F[18]

Studies were initiated at the Westinghouse Lamp Division in early 1958 under Air Force support on the properties of tungsten and tungsten alloys, and initial results were reported by Atkinson, et al.[19] Tensile properties at 2500° F were evaluated for tungsten alloys containing 2, 4 and 5 percent ThO_2. The authors found the W-2ThO_2 alloy to be as good or better than those containing 4 and 5 percent ThO_2 and suggested that this was possibly due to better dispersion of the ThO_2, in the 2 percent alloy. These authors concluded that alloys in the W-ThO_2 system showed outstanding promise for high-temperature applications, having 3 to 4 times the yield strength and about two times the ultimate tensile strength of unalloyed tungsten at temperatures up to 2700° F.

Additional work at Westinghouse Lamp Division was recently presented in reports by Sell, et al.[20,21], on the effect of ThO_2, TaC, and HfO_2 additions on the tensile properties of tungsten. The authors evaluated tensile properties at 3000° F on a series of W-TaC alloys and found a peak strength at about 0.4 percent TaC. They considered their results not conclusive, however, as different processing conditions were used for the different alloys. The authors did conclude, however, that W-2ThO_2 alloy had about twice the strength of unalloyed tungsten up to 3000° F, and that the W-0.38TaC alloy had about 5 times the strength of the unalloyed tungsten base material at 2500° F. An addition of 0.5 percent HfO was found to increase the recrystallization temperature of tungsten by about 300 to 400°C, but initial tensile tests on the alloy did not indicate an appreciable gain in strength at 2700 or 3000° F.

A study at the Westinghouse Research Laboratories is being directed toward the development of tantalum and tungsten base alloys. A final report covering June 1958 through March 1961 was recently issued by Feild, at al.[22] Only preliminary data were available in this report on tungsten alloys. The effect of rhenium and rhenium plus tantalum additions on the hardness of tungsten up to 2000° F was determined. At 2000° F, the alloy W-8Re-4Ta had a hardness of 200 VHN as compared to a value of 72 for tungsten. Additions of Re and Re plus Ta resulted in a decrease in low temperature hardness of tungsten, which the authors suggested may indicate a shift in the ductile-brittle transition temperature to lower temperatures. This remains to be verified.

Semchyshen and Barr[23] recently issued a final report on an investigation of tungsten base alloys covering a period from June 1958 to December 1960. This study covered arc-cast W-binary alloys containing up to 11.7 Cb, 2.7 Co, 3.6 Hf, 18.1 Ta, 9.3 V and 3.8 Zr. The program evaluated structure, lattice parameter, hardness up to 3000° F, oxidation in air at 2000° F, and forgeability. The alloy additions in order of decreasing hardening at 1600° F, on a given weight percent basis, were listed by the authors as follows: Co, Zr, Hf, V, Cb and Ta. The same order existed at 3000° F, except for the vanadium alloys where hardness values were not obtained.

Tensile and creep data on tungsten and tungsten alloys have been reported by Hall, Sikora and Ault[24] at Lewis Research Center of NASA. The test specimens had a reduced section of 0.250 in. diameter by 1-in. gage length and were taken from swaged or rolled 1/2-in.-diameter bar. The test procedures have been adequately described in the section dealing with unalloyed properties.

Additional tungsten alloy studies of particular interest have been reported by Foyle[25] at the Lewis Research Center. The results of this study on the effect of binary additions of Mo, Cb, and Ta on the high-temperature tensile properties of arc-cast tungsten are presented in Figs. 8.20 and 8.21.

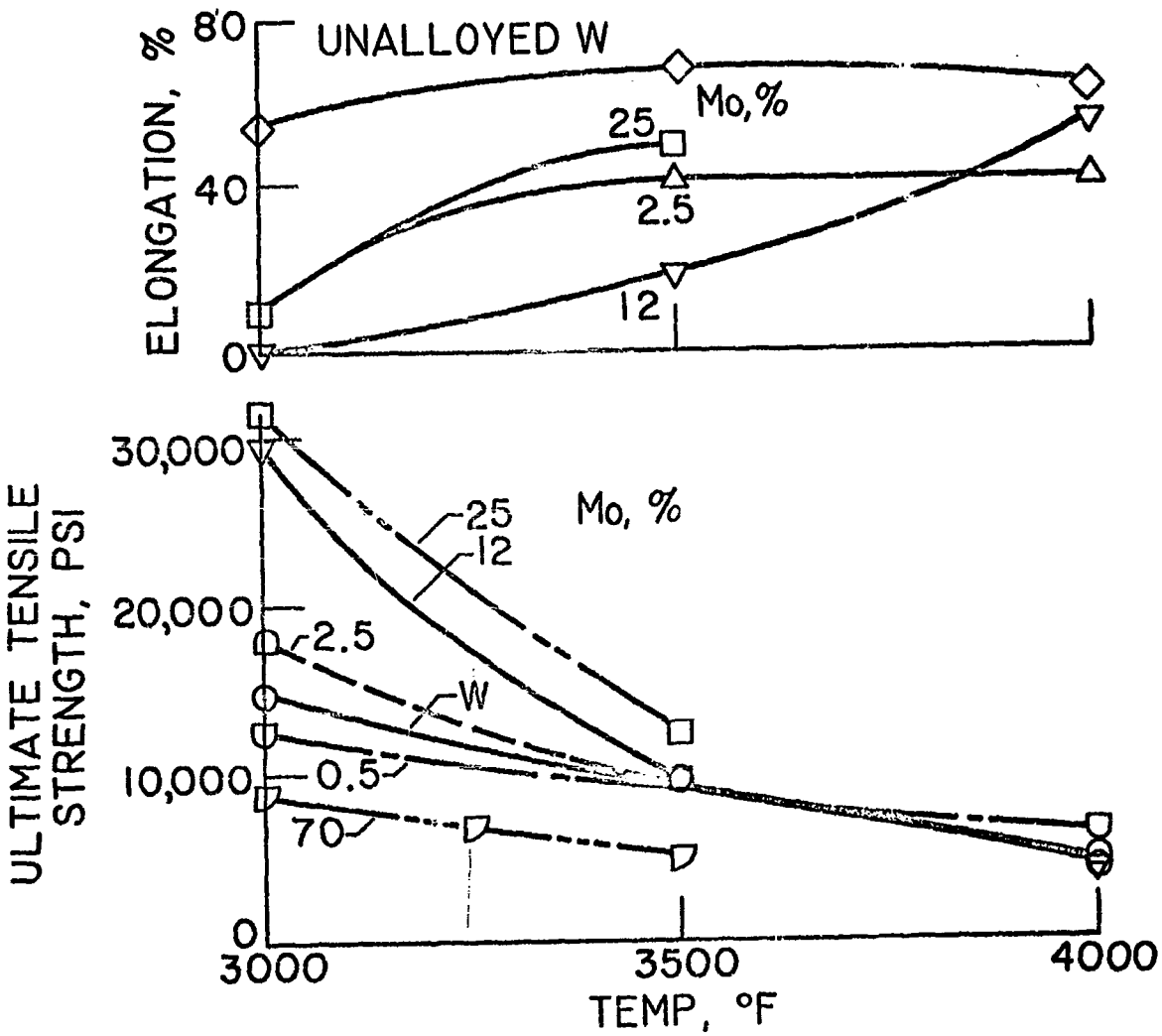


FIG. 8.20

TENSILE PROPERTIES OF TUNGSTEN-MOLYBDENUM ALLOYS FROM 3000 TO 4000° F[25]

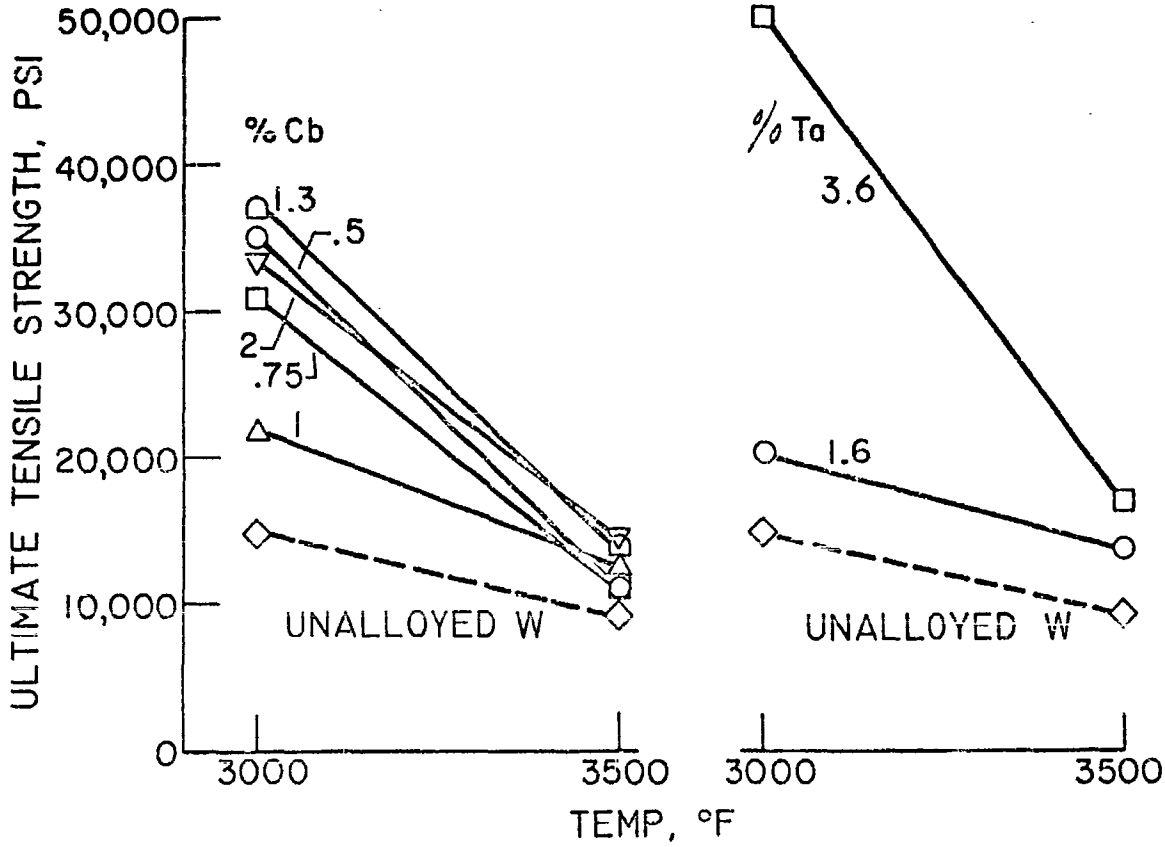


FIG. 8.21

TENSILE PROPERTIES OF TUNGSTEN-COLUMBIUM AND TUNGSTEN-TANTALUM ALLOYS FROM 3000 TO 3500° F[25]

The tensile specimens, ground from as-extruded bars, had a reduced section of 0.160-in. diameter with a 1-in. gage length. The tests were conducted in vacuum using a cross-head speed of 0.005 in. per minute up to 0.2 percent strain and then 0.05 in. per minute to fracture.

Fig. 8.20 summarizes tensile properties of the W-Mo alloys. Of the alloys evaluated, W-25Mo had the highest ultimate tensile strength at 3000° F, over twice that of unalloyed tungsten. At 3500° F, this alloy was only about 25-percent stronger than tungsten. The ultimate tensile strength of the W-Cb and W-Ta alloys at 3000 and 3500° F is given in Fig. 8.21. The W-1.3Cb alloy had a higher ultimate tensile strength at 3000° F than the best W-Mo alloy evaluated, and still maintained a slight advantage at 3500° F. The W-3.6Ta alloy had the highest yield and ultimate strength

at 3000° F and 3500° F of all the alloys evaluated. At 3000° F the W-3.6Ta alloy had a 0.2-percent offset yield strength of 31,200 psi and an ultimate tensile strength of 50,000 psi and at 3500° F these values were 9,000 and 16,900 psi.

The TAPCO Group of Thompson Ramo-Wooldridge[26] are conducting a tungsten forging development program for the Air Force. The W-15Mo alloy was selected as the initial alloy for the forging study, and tensile property data on specimens cut from forgings have been evaluated. In addition, tensile properties of three alloys, W-5Mo, W-15Mo, and W-0.52Cb, have been evaluated in the as-extruded condition. Tensile specimens had a 0.160-in. diameter by 0.500-in.-long reduced section in a 4-1/2-in.-long button-end specimen. The specimens were heated in vacuum by radiation from a tantalum resistance heater and tested at a strain rate of 0.0003 per second.

Tensile properties are summarized in Table 8.6 for the W-15Mo, W-0.52 Cb, and the W-5Mo alloys in the as-extruded condition, and in Table 8.7 for the W-15Mo alloy in both the as-forged and as-extruded conditions.

The values obtained in this study may be roughly compared with those obtained at NASA[25] for W-0.5Cb and W-12Mo alloys. The ultimate tensile strength values obtained by TAPCO at 3000 and 3500° F were slightly higher than the NASA values. However, the yield strength values obtained by TAPCO were about 50–100 percent higher than those reported by NASA. This could possibly be due to the slower strain rate used in the NASA study through the 0.2 percent offset yield strength. The greatest difference between the two sets of data was in ductility values for the W-Mo alloys. The NASA specimens exhibited much lower ductility at both 3000 and 3500° F than those tested by TAPCO.

A summary of the ultimate tensile strength of a number of tungsten alloys which have been evaluated at high temperatures is presented in Fig. 8.22 taken from Reference 4.

Ductile-Brittle Behavior of Tungsten Alloys

A number of studies have been conducted wherein data on the ductile-brittle transition temperature of tungsten alloys have been reported. With a few exceptions, these studies have been alloy screening investigations and not directed primarily to investigating ductile-brittle behavior. Variations of purity of the base metal and fabricating procedures would be expected to influence the ductile-brittle behavior of the alloy. In most cases however, variations in these parameters were not investigated.

A brief review of the reported transition temperature data for alloys will be given here primarily to indicate the general effects which have been observed. The details of processing and fabrication, although important, will not be presented in this review. If interested in greater detail, the reader is referred to the original references.

Table 8.6

TENSILE PROPERTIES OF ARC CAST AND EXTRUDED TUNGSTEN ALLOYS TESTED IN VACUUM AT 0.020 IN./MIN CROSSHEAD SPEED[26]

MATERIAL	TEMP. (° F)	U. T. S. (psi)	0.2 Y. S. (psi)	R. A. (%)	ELONGATION (%)
W-15Mo	3,000	36,000	34,500	78	27.8
	3,250	24,450	23,500	80	34.9
	3,500	11,190	8,060	95	85
	4,000	5,570	4,080	97	125
W-0.52Cb	3,000	38,210	35,075	80	32.6
	3,250	22,640	18,660	63.2	46.9
	3,500	13,040	7,710	64.7	55.6
	4,000	7,250	4,500	90	81.7
W-5Mo	3,000	30,840	29,850	83	28.7
	3,250	14,770	10,200	95	66.3
	3,500	10,450	5,630	97.9	89.8
	4,000	5,400	3,670	95	116

Table 8.7

HIGH TEMPERATURE TENSILE PROPERTIES
OF A UNIVERSAL FORGING OF THE W-15Mo ALLOY TESTED IN VACUUM
AT 0.020 IN./MIN CROSSHEAD SPEED[26]

SPECIMEN LOCATION	TEMP. (°F)	0.2 Y.S. (psi)	U.T.S. (psi)	R.A. (%)	ELONGATION (%)
Web	3,000	36,813	38,021	55	22.8
Thick Edge	3,000	42,964	43,718	68	20.7
As-Extruded*	3,000	34,500	36,000	78	27.8
Web	3,500	8,771	11,403	71	68.3
Thick Edge	3,500	7,920	10,496	92.5	98.6
As-Extruded*	3,500	8,060	11,190	95	85

*From Table 8.6

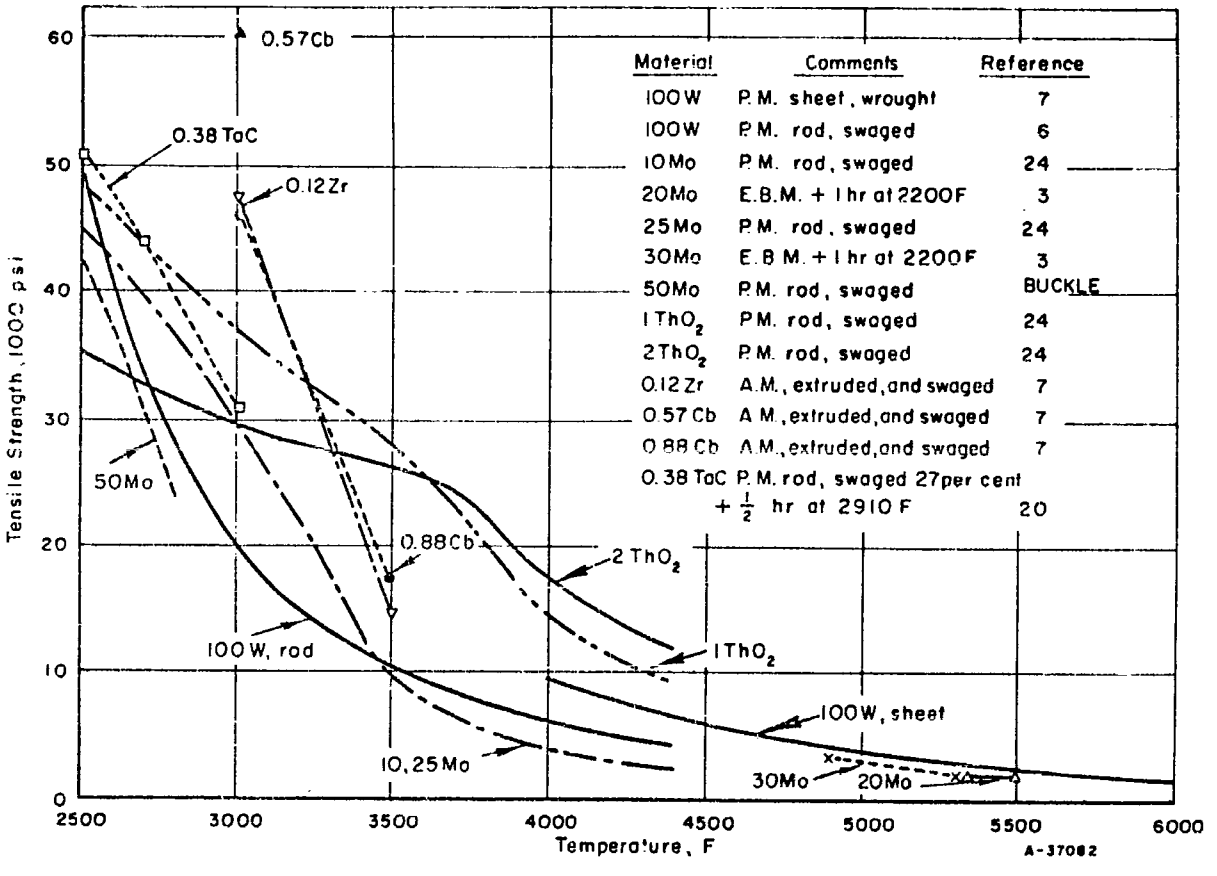


FIG. 8.22

EFFECT OF TEMPERATURE ON THE TENSILE STRENGTH OF TUNGSTEN ALLOYS

A series of studies on the ductile-brittle behavior of W-Re alloys has been conducted at Battelle. Bend data for the W-30Re alloy along with data for unalloyed tungsten, both in the recrystallized and wrought conditions are shown in Fig. 8.23[27].

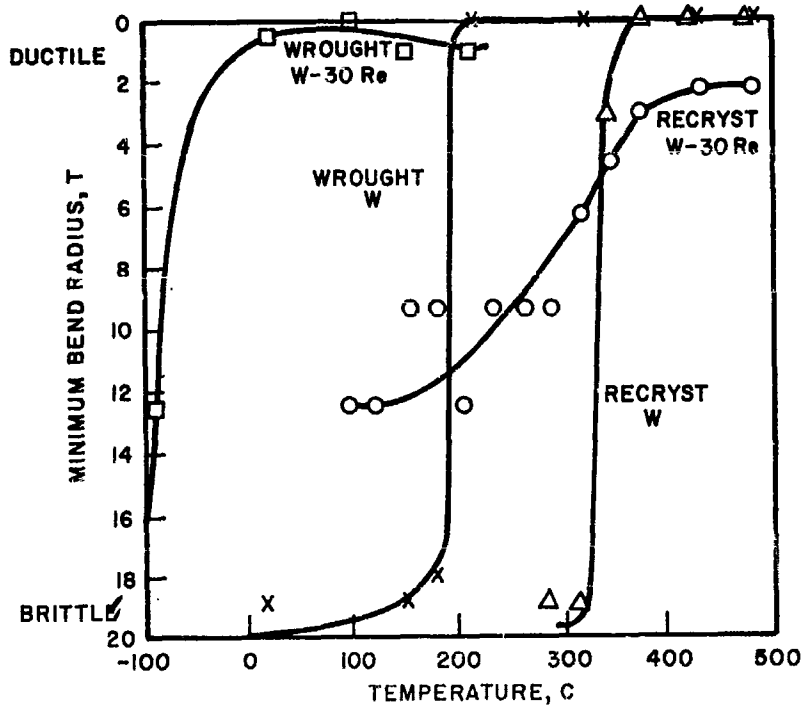


FIG. 8.23

BEND DUCTILITY OF TUNGSTEN AND W-30Re ALLOY IN BOTH THE WROUGHT AND RECRYSTALLIZED CONDITIONS[27]

The Re addition appeared to be much more effective in the wrought condition than in the recrystallized condition. If a minimum bend radius of 10T is taken as the ductile-brittle transition temperature, the Re additions lowered the transition temperature in the wrought condition almost 300°C, whereas in the recrystallized condition, the decrease was less than 100°C. The shape of the W-30Re curve is of interest in that it appears to be leveling off at 100°C and may actually extend to lower temperatures with appreciable ductility. Also, above about 350°C, the recrystallized alloy appeared to be less ductile than recrystallized tungsten.

Previous studies at Battelle indicated that arc-melted W-30Re alloy could be rolled at 1000°C from ingot into strip, whereas alloys containing 20 or less percent Re, or 35 or more percent Re were not fabricable. On the basis of these observations, Klopp, et al.[28] set out to investigate the ductility of alloys containing 20, 22, 24, 26 and 28 percent Re. Bend test results for these alloys are summarized in Fig. 8.24, for material rolled at 1000°C, recrystallized one hour at 1800°C, and water quenched to reduce possible sigma phase precipitation. The W-20Re alloy fractured during

fabrication at 1000° C and was therefore not evaluated. The bend ductility is given as the ratio of the bend radius to the specimen thickness, and the number given indicates the smallest value of this ratio at which no fracture occurred. The specimen thickness was not specified.

The results presented in Fig. 8.24 clearly indicate increased ductility with increasing Re additions from 22 to 28 percent. The W-30Re alloy actually exhibited less ductility than the alloys containing 24, 26 and 28 Re. The data for this alloy, however, given in Fig. 8.24 was taken from an earlier Battelle study.

The authors[28] concluded that the improved ductilities in the 22 to 30 percent Re alloys were associated with enhanced capacity for slip at low temperatures and low critical stresses for twinning, which appeared to be a function of Re content alone.

Allen, et al.[13] studied the effect of oxide, carbide, and nitride additions on the ductile-brittle bend transition temperature of both wrought and recrystallized powder-metallurgy tungsten. Certain additions were found effective in lowering the transition temperature of the wrought material. The most effective of these are listed in Table 8.8. None of the other oxides studied, which included SiO_2, MgO, HfO_2, Al_2O_3, and UO_2 had any significant effect on the transition temperature of the wrought material.

Table 8.8

EFFECT OF DISPERSOID ADDITIONS ON THE DUCTILE-BRITTLE BEND TRANSITION TEMPERATURE OF VACUUM-SINTERED WROUGHT TUNGSTEN[13]

ADDITION (wt%)	TRANSITION TEMPERATURE (° C)
None (100 W)	230
1 ThO_2 (Aqueous)	160
0.60 ZrO_2	150, 170 (a)
0.56 TiN	160
0.75 ZrN	150
1.50 TaC	170

(a) Two determinations

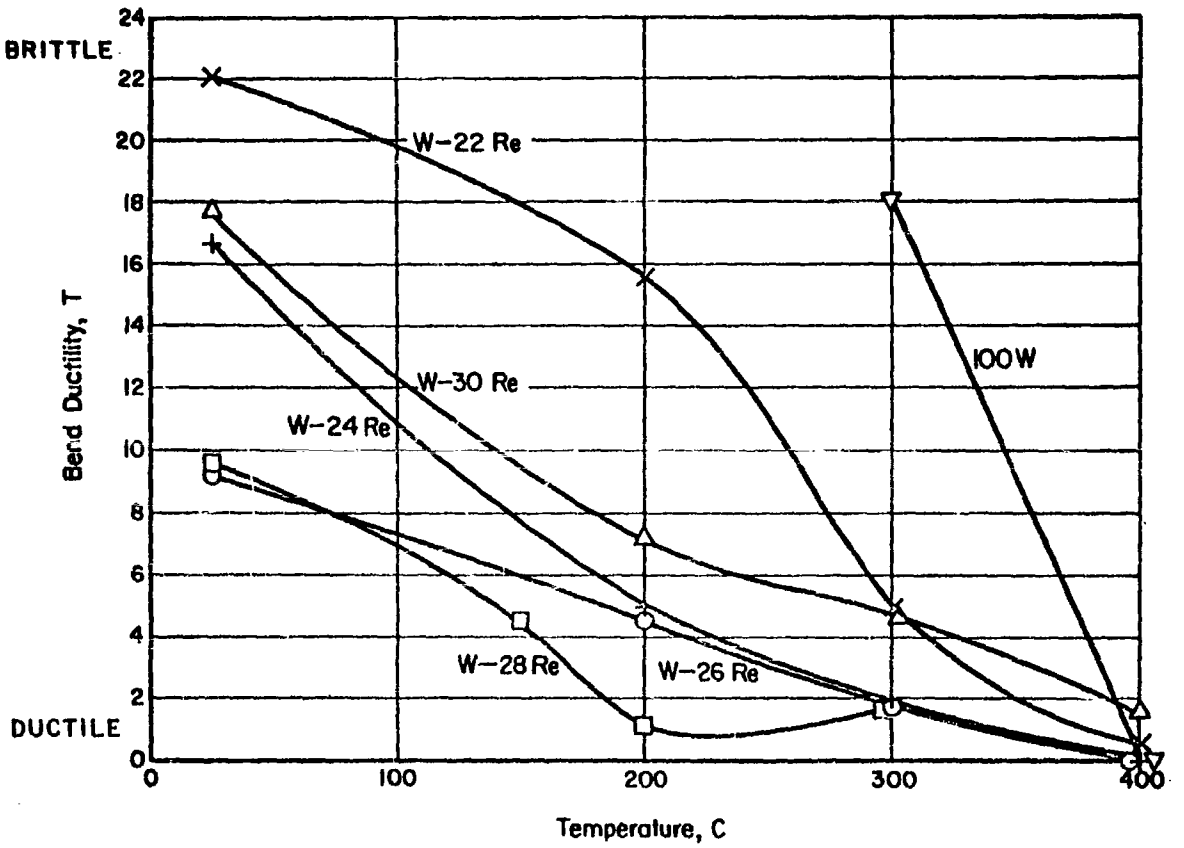


FIG. 8.24

BEND DUCTILITIES OF RECRYSTALLIZED TUNGSTEN AND TUNGSTEN-RHENIUM ALLOYS VERSUS TEMPERATURE[28]

The effect of the dispersoid additions on the ductile-brittle bend transition temperature of the recrystallized material is summarized in table 8.9.

Table 8.9

EFFECT OF DISPERSOID ADDITIONS ON THE DUCTILE-BRITTLE BEND TRANSITION TEMPERATURE OF VACUUM-SINTERED RECRYSTALLIZED TUNGSTEN[13]

ADDITION (wt%)	TRANSITION TEMPERATURE (°C)	RECRYSTALLIZED GRAM SIZE (GRAINS/mm^2)
None (100% W)	420	250
None (100% W)(a)	375	650
1.0 ThO_2 (Aqueous)	350	400
0.6 ZrO_2 (0.01μ)	380	500
0.6 ZrO_2 (1.9μ)	420	400
1.0 HfO_2 (1.3μ)	430	400
1.7 TaN	490	400
0.41 Al_2O_3	650	1950

(a) Hydrogen Sintered

An interesting comparison of bend test data for W-0.60 ZrO_2 alloy and unalloyed W is given in Fig. 8.25 for material in the wrought condition and after two recrystallization treatments. For all cases of identical wrought or recrystallization conditions it is apparent that the 0.60 ZrO_2 addition lowered the transition temperature about 40° C. The use of a higher recrystallization temperature resulted in a higher value for the transition temperature for both the alloy and unalloyed tungsten. This observation was suggested to be due to the larger resulting recrystallized grain size of the materials recrystallized at higher temperatures.

The ductile-brittle tensile transition temperature of several tungsten alloys was evaluated in the tungsten forging development program at TAPCO. Tensile transition data for the tungsten alloys containing 5, 11 and 15 percent Mo, and 0.52 percent Cb, all in the as-extruded condition are summarized in Table 8.10.[29] These transition data are based upon both reduction-in-area and elongation values above and below the transition temperature.

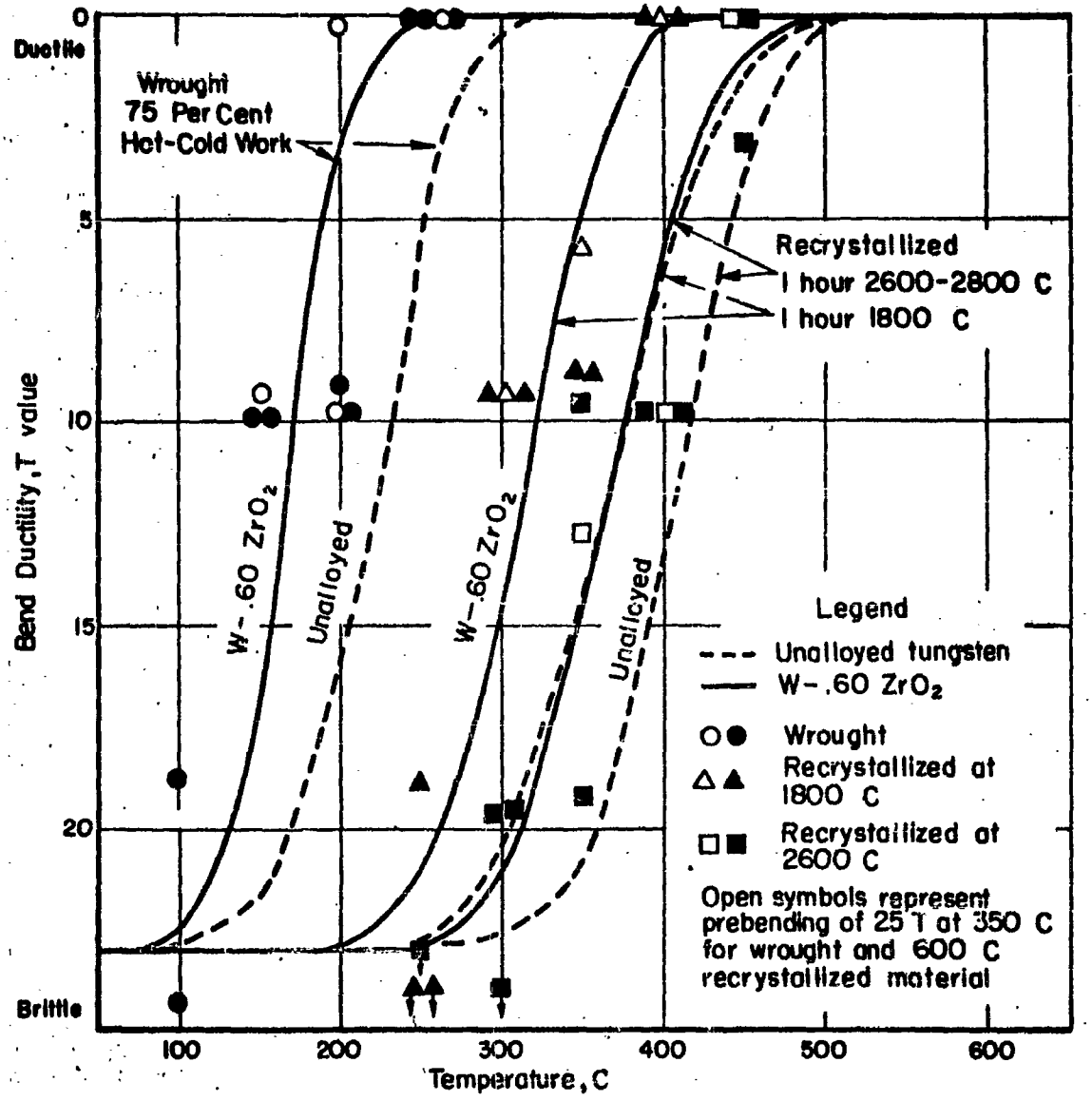


FIG. 8.25

BEND DUCTILE-BRITTLE TRANSITION BEHAVIOR OF VACUUM-SINTERED, WROUGHT, AND RECRYSTALLIZED W-0.60 ZrO_2 (0.01 μ PARTICLES), COMPARED WITH SIMILARLY FABRICATED VACUUM-SINTERED UNALLOYED TUNGSTEN [13]

Table 8.10

DUCTILE-BRITTLE TENSILE TRANSITION TEMPERATURES FOR AS-EXTRUDED TUNGSTEN ALLOYS AT 0.020 IN./MIN CROSSHEAD SPEED[29]

EXTRUSION NO.	ALLOY	TYPE	TRANSITION TEMPERATURE (° F)
1	85W-15Mo	Arc	480
2	85W-15Mo	Arc	500
3	85W-15Mo	Arc	590
3 (rerun)			555 (Average)
5	85W-15Mo	Arc	510
6	85W-15Mo	Powder	450
7	85W-15Mo	Powder	590
8	89W-11Mo	Co-refined Powder	300
10	95W-5Mo	Arc	390
11	W-.52 Cb	Arc	575

Additional data reported by TAPCO[26] on forged and stress relieved W-15Mo alloy showed the forced and stress relieved material to have a lower transition temperature than the as-extruded alloy by about 170°F.

Tensile transition data were reported by Atkinson[19] on the W-2ThO_2 alloy. The alloy cold-worked 80 percent and annealed one-half hour at 1500°C was reported to have a ductile-brittle tensile transition temperature about equal to the recrystallized base tungsten used in the study.

Creep Properties of Tungsten

Stress-rupture data for unalloyed tungsten reported by Pugh,[1] Atkinson[19] and Green[30] are summarized in Fig. 8.26 from reference 4.

Ref. No.	AUTHOR
1	Pugh
19	Atkinson
30	Green

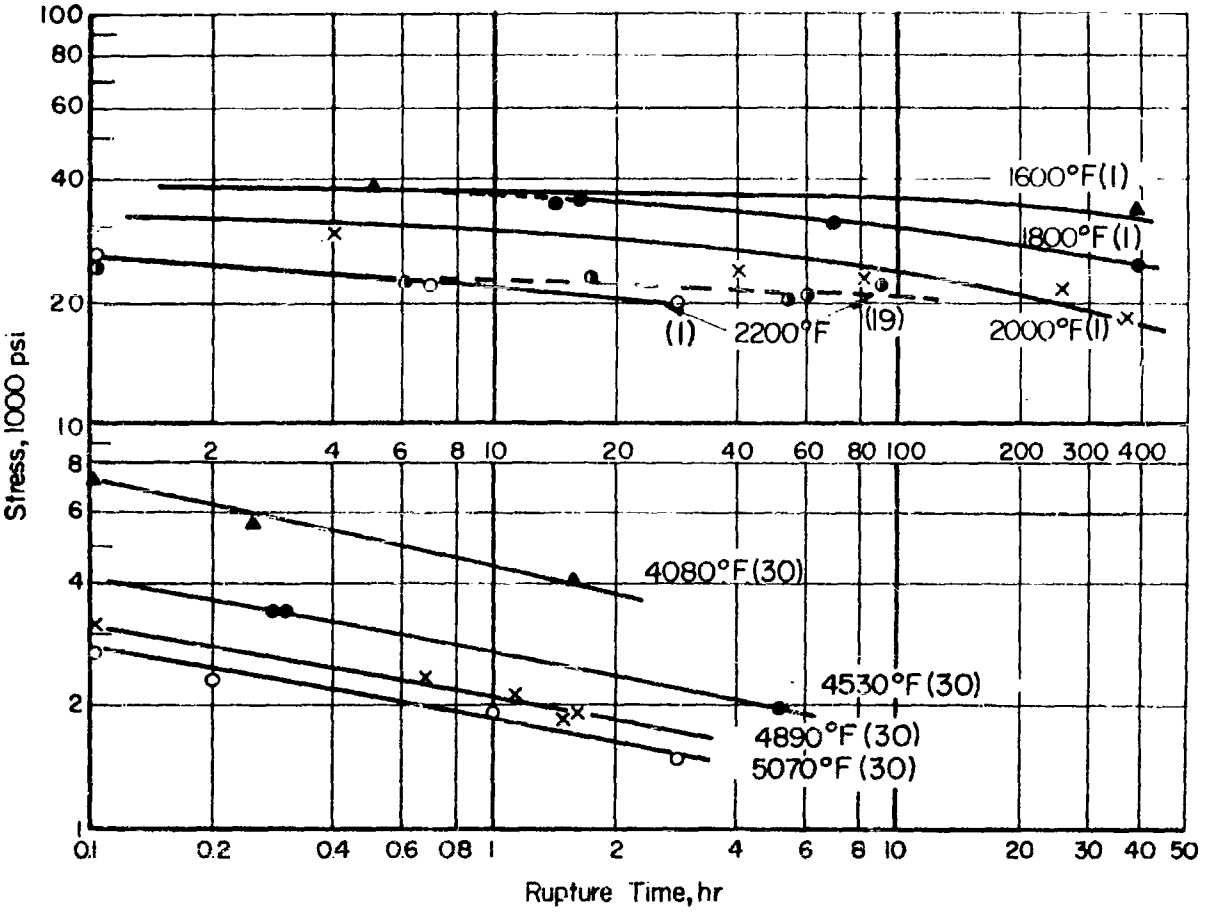


FIG. 8.26

CREEP STRESS VS. RUPTURE TIME FOR TUNGSTEN ROD TESTED IN INERT ATMOSPHERE[4]

The lower temperature data at 1600, 1800, 2000, and 2200° F by Pugh were presented in detail in the original survey report.[1] The tests by Pugh were conducted in a vacuum on tungsten rod material recrystallized one hour in hydrogen at 1590° C.

The creep tests reported by Atkinson at 2200° F were conducted in a vacuum or argon atmosphere on tungsten recrystallized 0.5 hours at 1500° C.

Green used commercial, powder-metallurgy, hot-swaged tungsten rod. The test specimens with a 1/4 in.-diameter by 3/4-in. gage length were heated by radiation from a cylindrical heater in a helium atmosphere.

More recent creep data reported by Sell, et al.[20] were conducted on recrystallized tungsten at an intermediate temperatures, 2700 and 3000°F, in vacuum. The reported stress-ruptured results are given in Fig. 8.27.

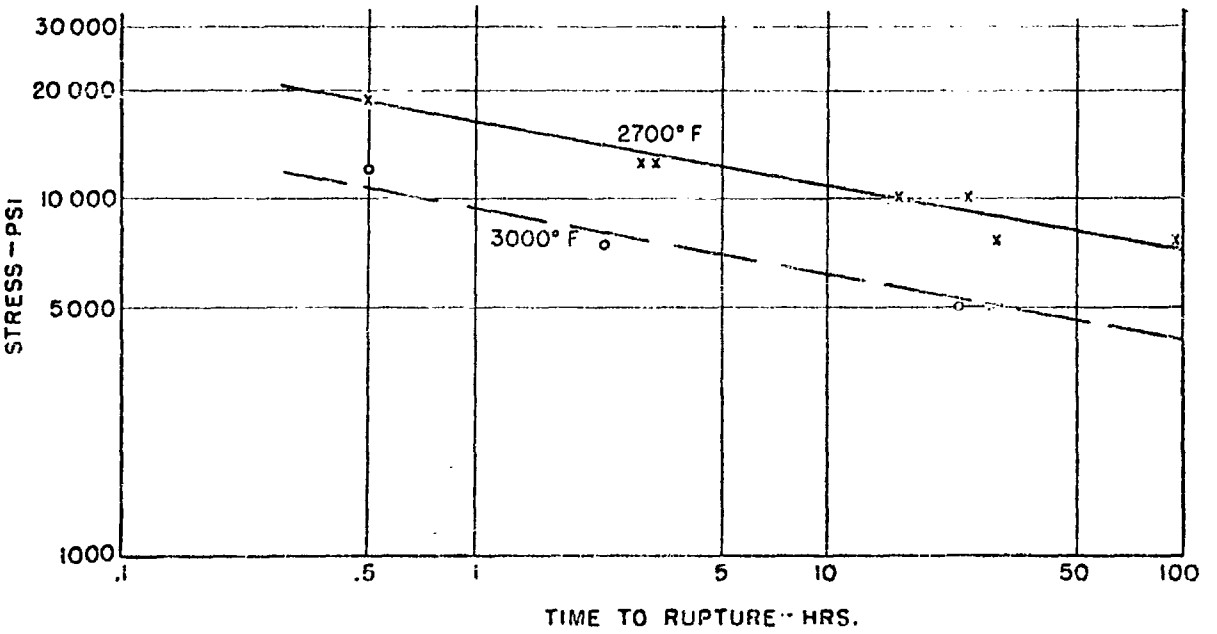


FIG. 8.27

CREEP STRESS VS RUPTURE TIME FOR RECRYSTALLIZED TUNGSTEN TESTED IN VACUUM [20]

Creep Properties of Tungsten Alloys

Creep data on W-ThO_2 alloys tested in vacuum are given in Fig. 8.28, as reported by Atkinson.[19] At 2500° F the W-2ThO_2 alloy was found to be more creep resistant in terms of rupture strength and in time to a 1 percent strain than either the 4 percent or 5 percent ThO_2 alloys.

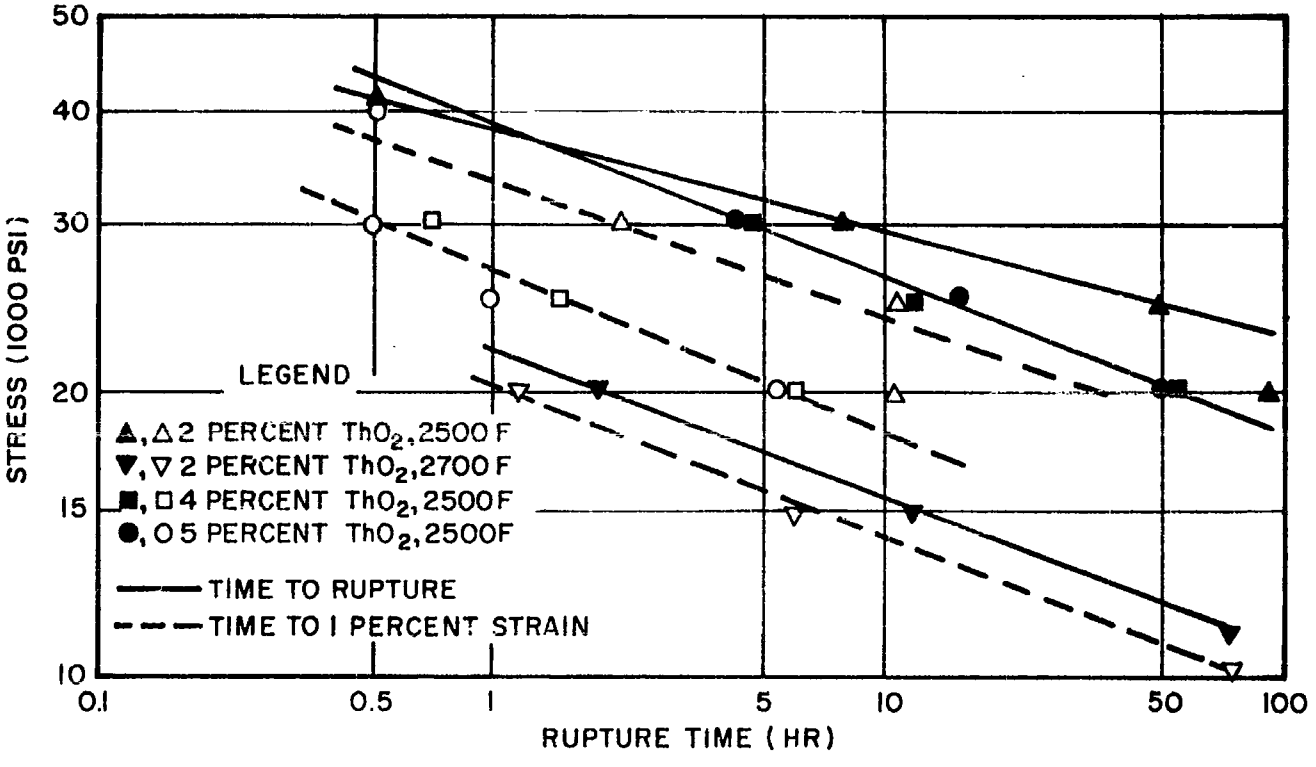


FIG. 8.28
CREEP STRESS VS RUPTURE TIME FOR THORIATED TUNGSTEN BAR ALLOYS(41) 4 AFTER 19

Creep properties for W-0.38TaC alloy tested in vacuum at 2700°F are given in Fig. 8.29 as reported by Sell, et al.[20] The rupture life of this alloy at 2700°F was roughly about seven times that for the W-2ThO_2 alloy at the same stress level.

The stress-rupture properties of three as-extruded binary tungsten alloys, 5Mo, 15Mo, and 0.52Cb, tested at 3000°F in vacuum are presented in Fig. 8.30 as reported by Lake, et al.[26] The W-0.52Cb alloy had the highest stress-rupture strength of the three alloys. This alloy also exhibited a flatter curve than the other two alloys, its superiority thus increasing at the lower stresses and longer rupture times.

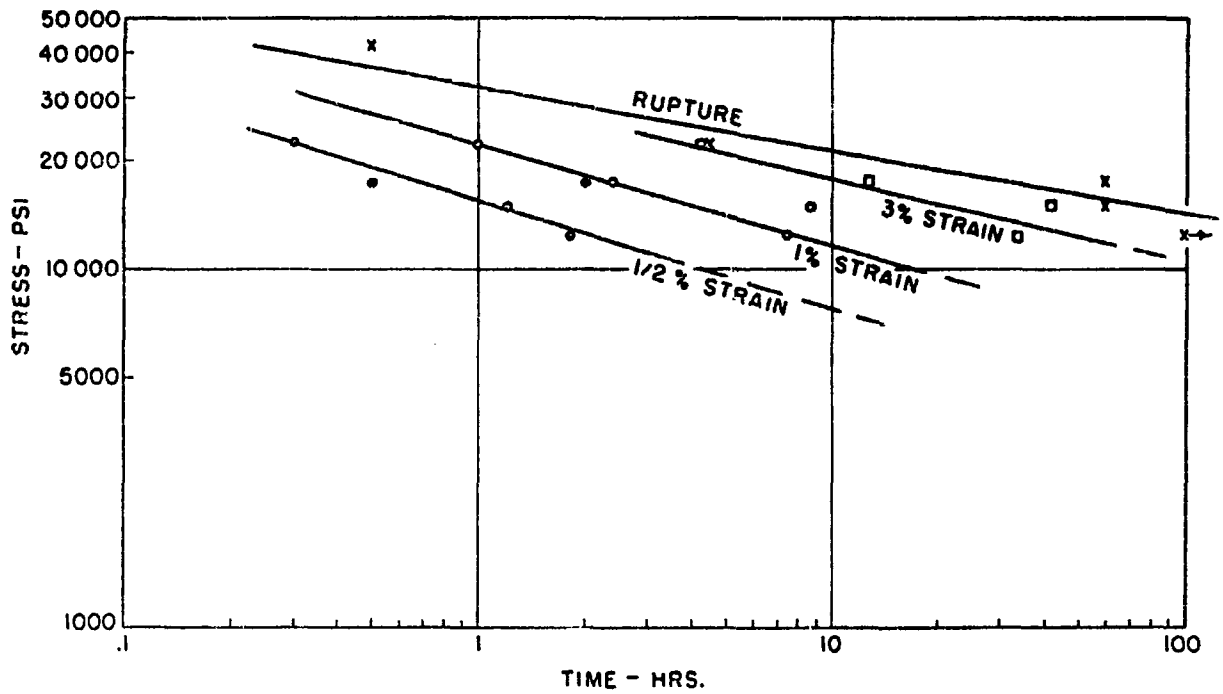


FIG. 8.29

CREEP PROPERTIES OF W+0.38% TaC ALLOY AT 2700° F

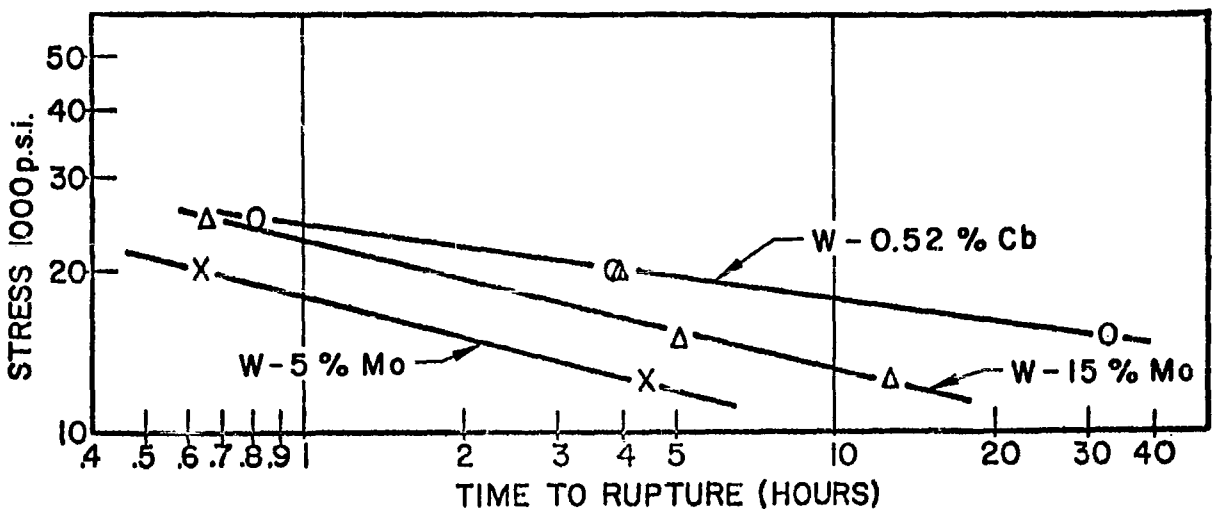


FIG. 8.30

CREEP STRESS VS. RUPTURE TIME FOR VARIOUS TUNGSTEN ALLOYS AT 3000° F[26]

Fabrication of Tungsten

No attempt can be made in this compilation to discuss the developments and current status of fabrication of tungsten and tungsten alloys. Appreciable strides have been made during the past few years in the fabrication of tungsten, and complex structural components are currently being manufactured for critical elevated temperature applications.

A number of reviews and surveys covering the consolidation and fabrication of tungsten are available. These include a state-of-the-art survey by Maykuth, Barth, and Ogden[4] related to the tungsten sheet rolling at Universal-Cyclops Steel Corp.; a state-of-the-art survey[3] by the Materials Department of TAPCO related to their tungsten forging development program, and an earlier review on the fabrication of tungsten by Barth.[31] Li presents a review in the 2nd edition of the Rare Metals Handbook[32] covering extraction, consolidation, fabrication, and applications of tungsten.

A number of government supported programs which deal with the fabrication of tungsten and W alloys are currently in progress. These are listed below:

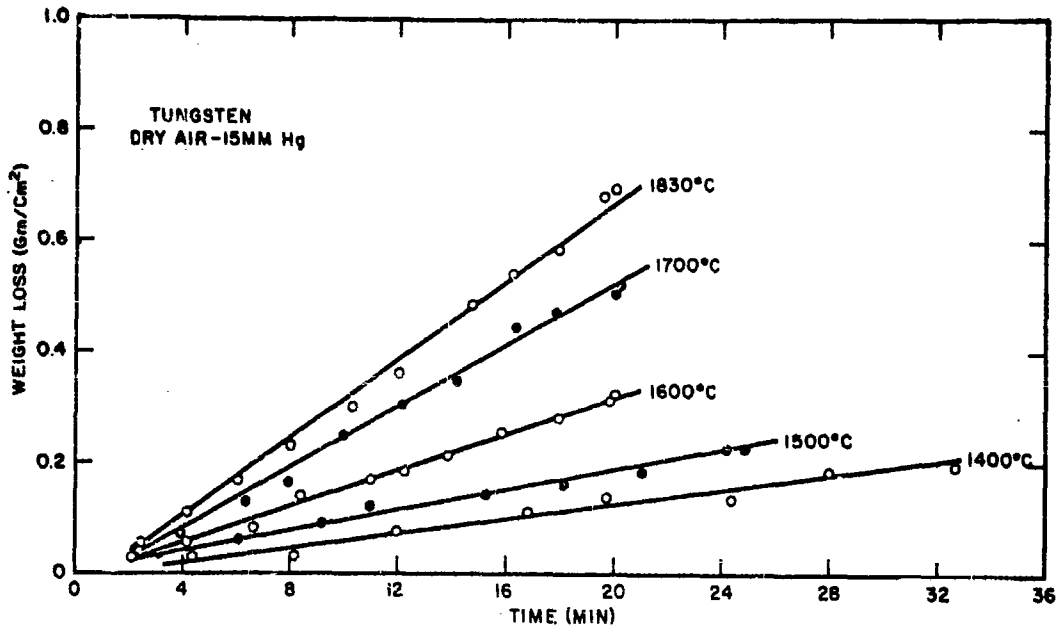
- "Tungsten Forging Development Program" with TAPCO group, Thompson Ramo Wooldridge Inc.[3, 37, 29, 26]
- "Tungsten Sheet Rolling Program" with Universal-Cyclops Steel Corp.[4]
- "Tungsten Sheet Rolling Program" with Fansteel Metallurgical Corp.[33, 34]
- "Development of Tungsten Sheet by Flo-turning" with Wah Chang Corporation under Contract No. AF33(600)-43034. No reports have as yet been issued on this contract.

OXIDATION PROPERTIES

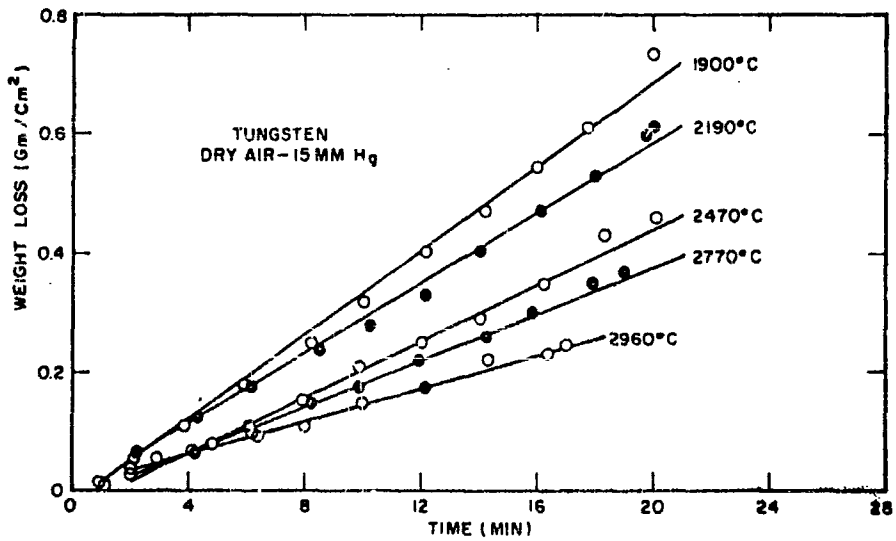
Oxidation of Tungsten

The oxidation behavior of tungsten was reviewed in detail in the original survey report.[1] Although more recent investigations have been reported on the oxidation of unalloyed tungsten, a detailed review would not add to the primary purpose of this survey. The general oxidation behavior observed for W is given in the summary section of this report.

One study by Perkins and Crooks[35] on unalloyed W is of particular interest, however, in that it extended to very high temperatures (3000° C) and showed a behavior pattern not previously demonstrated. Consideration of the possible oxidation behavior of metals at low pressures led the authors to conclude that at some high temperature the oxidation rate would actually decrease with increasing temperatures. Their results of oxidation tests in dry air at 15 mm Hg presented in Fig. 8.31 confirm this conclusion.



8.31A



8.31B

FIG. 8.31

OXIDATION RATE CURVES OF TUNGSTEN FROM 1400 TO 2960°C IN DRY AIR AT 15 mm Hg PRESSURE[35]

In Fig. 8.31a, the weight loss is seen to be linear with time and the rate was observed to increase with increasing temperature from 1400 to 1830°C. However, oxidation data from 1900 to 2960°C as presented in Fig. 8.31b show the reverse trend, and the rate was actually observed to decrease with increasing temperature in this temperature range. Oxidation tests conducted at 1, 5 and 15 mm Hg air pressure are summarized in Fig. 8.32. Indeed, under the given test conditions, the oxidation rate was found to increase rapidly with temperature above about 1200°C, reach a maximum and then decrease with increasing temperature. This behavior was attributed by the authors to be due to the dissociation of W oxide, and that at about 1750°C at low oxygen pressures the rate of dissociation becomes sufficient that the net rate of metal loss decreases with increasing temperature due to oxide dissociation. Results in flowing air would, of course, be expected to differ from those reported here for static conditions.

These results serve to point up the fact that the use of tungsten or other metals must be considered in terms of the actual operating environment, and that metals which have very poor oxidation resistance in normal atmospheric conditions may serve satisfactorily in very high temperature applications in high altitude or low pressure environments.

Oxidation of Tungsten Alloys

A number of isolated results have been reported on the oxidation of tungsten alloys in connection with alloy screening studies[19, 8, 23]. However, no significant improvements in oxidation resistance have been reported. In addition, most tests have been conducted in air around 2000°F, whereas anticipated applications for W alloys is at 2500°F or above. Thus, even if alloying additions are found which cause an appreciable improvement in oxidation resistance at 2000°F, they may be of no value at 2500°F or above.

Semmel[12] studied the effect of binary additions of Cb, Co, Cr, Mo, Ta, Ti, and V on the oxidation of tungsten, and found that Cb and Ta additions showed particular promise. The results of detailed studies on W-Cb alloys by Semmel[36] indicated that tungsten alloys containing from 2.5 to 10 percent Cb exhibited linear oxidation at 2000°F, whereas they exhibited parabolic oxidation at 2300°F, apparently due to sintering of the oxide at the higher temperatures. Alloys containing from 15 to 50 percent Cb exhibited parabolic oxidation at both 2000 and 2300°F. However, at 2400°F the oxide was found to evaporate. Oxidation data for W-Cb alloys at 2000 and 2300°F as reported by Semmel are presented in Fig. 8.33. At 2000°F, alloys containing 2.5 percent Cb or more had a lower oxidation rate than W. However, at 2300°F, only alloys containing 15 percent Cb or greater were found to have improved oxidation resistance.

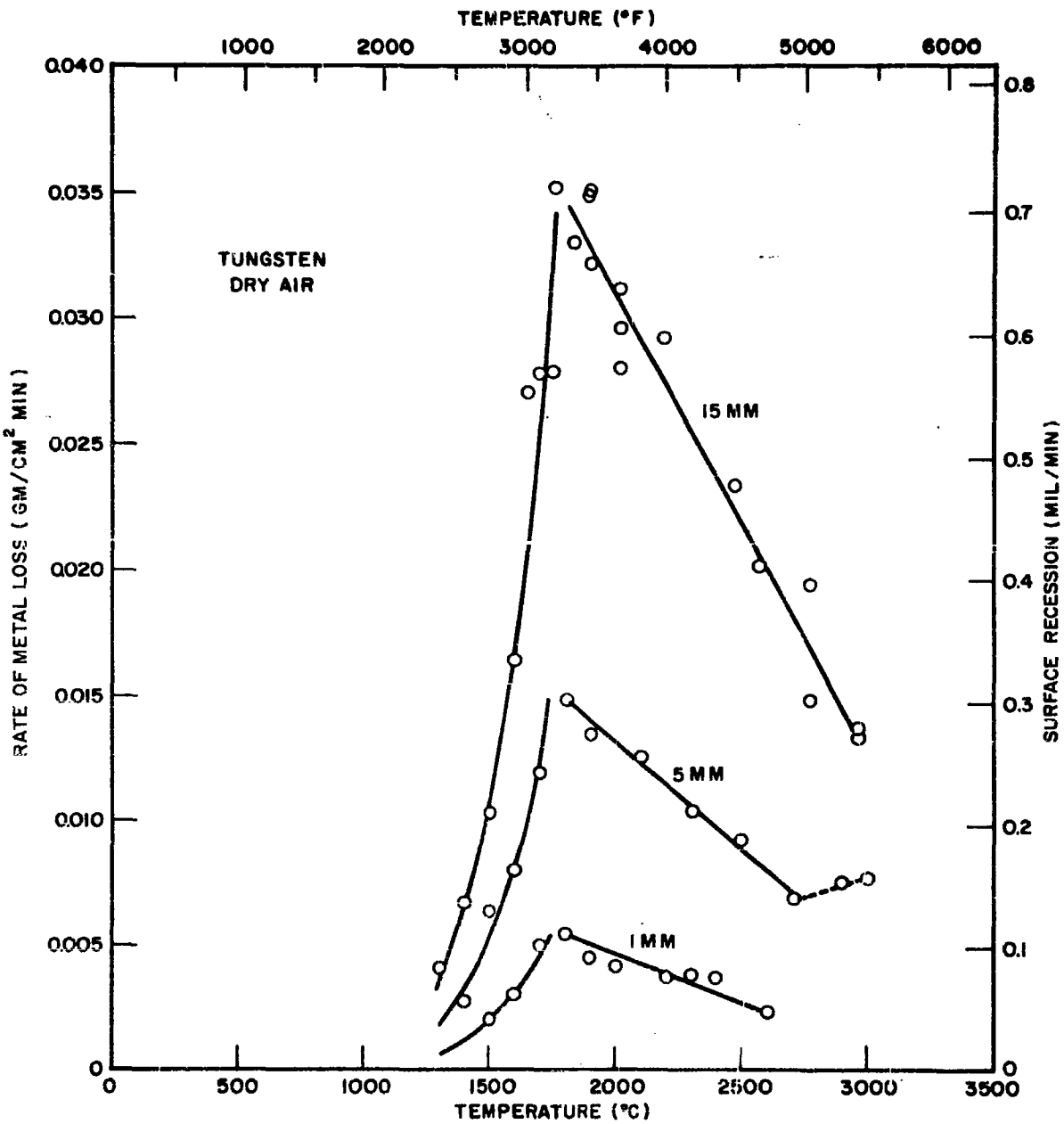
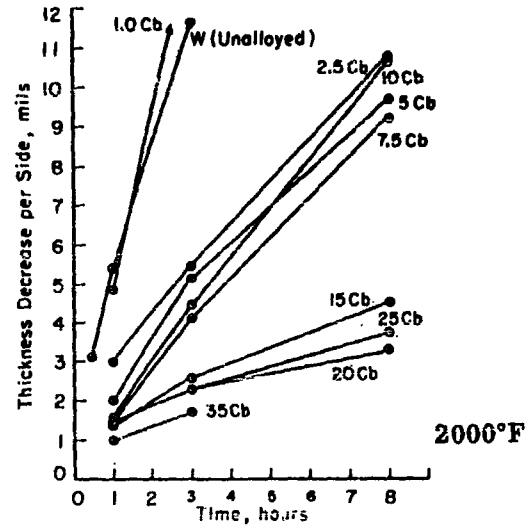


FIG. 8.32

OXIDATION RATE OF TUNGSTEN FROM 1400 TO 2960° C IN DRY AIR AT 1, 5, AND 15 MM PRESSURE[35]



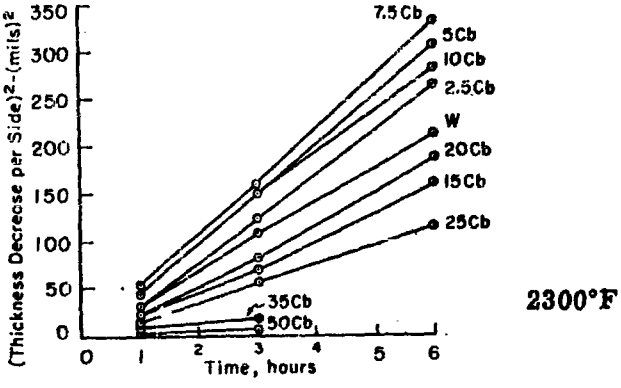


FIG. 8.33

OXIDATION RATE OF TUNGSTEN-COLUMBIUM ALLOYS AT 2000 AND 2300°F[36]

THERMAL PROPERTIES

Results of investigations of thermal conductivity of tungsten were reviewed in the original survey report.[1] More recently reported evaluations have not modified or extended the earlier work, and the reader is referred to the summary section of this report for these data.

The critical survey of the literature on thermal expansion of tungsten published by White in 1958 was reviewed and presented in the original survey report.[1] The thermal expansion vs. temperature curve based upon White's survey is presented in the summary section of this report.

Section 8

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Section 9

VANADIUM

INTRODUCTION

Vanadium first became of interest in France in 1896, when it was discovered that armor plate could be improved with small additions of the metal. Because of high production costs, the metal was relegated to alloy addition status until development of a refined calcium reduction process in 1950 allowed production in larger quantities. As a result of greater demand, improvements in the refining process, and increased production, the price of as-reduced vanadium has dropped from about $1,800 per lb. to between $30 and $50 per lb. since early 1950.

Current interest in vanadium arises from certain attractive properties which are listed below:

(1) Low density, 6.1 g/cc
(2) Corrosion resistance similar to titanium and chromium
(3) Good resistance to reaction with liquid metals proposed for reactor use
(4) Low thermal neutron absorption cross-section (4.98 barns per atom)
(5) Relatively high strength at intermediate temperatures in the range of usefulness of stainless steels or up to 500°C (930°F)
(6) Relative abundance, comparable to nickel and zinc

Limitations on the usefulness of vanadium are imposed by its melting point, 1900°C (3450°F), and the low melting point of its predominant oxide, V_2O_5, 675°C 1250°F. The melting point of the metal is below that of the other refractory metals discussed in this report with the exception of chromium. The oxide melts at a temperature below the oxides of other refractory metals except rhenium, and is corrosive to other metals at elevated temperatures.

The properties of unalloyed vanadium were reviewed in the SRI report[1], and little information has been added in the report literature in the last two years. This section, therefore, will primarily report results of alloy studies, as well as of additional studies concerning unalloyed material which contribute to previously reported data.

Dunn and Edlund[2] have reviewed the contemporary economic status of vanadium production. The most recently accepted values of physical and mechanical properties and the working of vanadium were also reviewed.

Early alloy development programs with vanadium as a base material involved the effect of additions of Al, Cr, Fe, Mo, Ni, Si, Ti and Zr. Titanium additions above 2.5 percent were shown to provide better strength with retention of ductility than the

other additions listed. Recent investigations have shown that ternary refractory metal additions of Cb, Mo, Ta, and W to a V-Ti binary base material produce alloys with attractive elevated temperature strength properties.

Studies at Armour Research Foundation [3, 4] have revealed alloys of vanadium which extend the potential of the base material to the 2000°F range. The alloys possess good formability, strength on a density corrected basis equivalent to some Mo alloys, and are weldable. Alloys have been developed which are competitive to Ti alloys in the 1000°F range, are useful for fuel element cladding in the 1200–1470 range, and are attractive for 2000°F service in applications requiring high-strength low-weight materials in a nonoxidizing atmosphere or in which oxidation protection can be attained.

MECHANICAL PROPERTIES

The development of apparatus to yield larger quantities of iodide-refined vanadium, described by Loomis and Carlson [5] and Carlson and Owen, [6] has allowed investigations of the behavior of the metal and its alloys with higher purity. The process virtually eliminates the N content, and the O and C contents are substantially reduced. In Table 9.1, from the work of Loomis and Carlson, [5] it is seen that lower interstitial content resulted from an experimental production of iodide-reduced material than from the commercially accepted Ca- reduction method. The typical analysis for iodide-reduced vanadium shown in Table 9.2 indicates that considerable improvement in purity has resulted from recent refinement of the iodide reduction process.

Table 9.1

ANALYSES OF THE TWO GRADES OF VANADIUM METAL [5]

Element	Iodide Reduced	Calcium Reduced
V	99.9+	99.7+
C	0.024	0.08
N	0.005	0.02
O	~0.01	0.02
H	0.001	0.006
Cr	<0.02	0.02
Fe	<0.02	0.02
Si	<0.02	0.02

Table 9-2

TYPICAL ANALYSIS OF IODIDE-REFINED VANADIUM* [6]

Element	Wt %	Element	Wt%
Ca	<0.002	Mg	<0.002
C	0.015	Ni	0.002
Cr	0.007	N	<0.0005
Cu	0.003	O	0.004
H	0.001	Si	<0.005
Fe	0.015	Ti	<0.002

*Not detected: Al, Ag, As, Au, B, Be, Bi, Cd, Ge, Hf, Hg, Mn, Mo, Na, Cb, P, Pb, Pt, Sb, Sn, Ta, Te, Tl, W, Zn, Zr.

According to the investigators, [6] the Fe and Cr impurity contents are the highest of the metallic impurities and result from the reaction between iodine and the reaction chamber material, Inconel. The final material is reported to be 99.95 percent vanadium, which is considerably better than that obtained from other commercially feasible production methods, e.g., alumino-thermic reduction of V_2O_5 or Mg reduction of VCl_3. Up to 4 pounds have been made in a single batch; however, cost estimates of scaled-up production by the iodide process have not been reported.

Tensile Properties of Vanadium

Several physical and mechanical properties of iodide vanadium at room temperature are given in Table 9.3, from Carlson and Owen [6]. No mechanical or thermal

Table 9.3

SOME PROPERTIES OF IODIDE REDUCED VANADIUM [6]

Property	Value
Melting point	1890° ± 10°
Lattice constant	3.026A ± 0.001
Yield point	17,000
Ultimate tensile strength	26,500 psi
Reduction in area	99 percent
Hardness	57 DPH (16 R_E)
Resistivity 20°C	25.5 μ ohm-cm

treatment of the test specimens were given in the report. The values of yield and ultimate tensile strengths are in fair agreement with the values previously reported for iodide vanadium of 16,700 psi yield strength (0.2 percent offset) and 31,600 psi ultimate tensile strength. The reported hardness, 57 DPH, is considerably below average values for Ca-reduced material, 135 VHN. Room temperature modulus values for this high-purity material will be most interesting since previously reported values varied from 17 to 22.5 $\times 10^6$ psi for material of several purity levels and methods of measurement. Comparison between the room temperature tensile properties of iodide- and Ca-reduced vanadium for material described in Table 9.1 is given below from Loomis and Carlson.[5]

Material	Yield Strength 0.2 Percent Offset, (psi)	Ultimate Tensile Strength (psi)	Elongation (Percent)	Reduction in Area, (Percent)	Hardness (R_A)	Grain Size (mm)
Iodide V Vanadium	13,200	28,700	38.3	95.0	21	0.20
Ca-Reduced Vanadium	23,000	37,600	33.7	36.7	38	0.04

The iodide vanadium specimens were produced by arc-melting deposited crystals to 3/4 in. diameter rod, followed by a 65 percent reduction by cold swaging to 7/16 in. diameter rod, and annealing at 1100°C for 48 hours. The Ca-reduced vanadium specimens were produced by arc-melting, 45 percent cold rolling, and recrystallizing at 900°C for 5 hours. Both recrystallization treatments were conducted in vacuo and resulted in 0.20 and 0.04 mm grain sizes for Iodide and Ca-reduced materials, respectively. The specimen size, 0.25 in. diameter × 1 in. gage long, was the same for each material, and all specimens were surface ground and hand polished before testing. Load and elongation values were recorded autographically using a strain rate of 10^{-4} sec^{-1}.

The annealing treatment given the iodide material resulted in large equiaxed grains with no sacrifice in ductility. The microstructure of the Ca-reduced material evidenced considerable impurity compared to the iodide material. The increased strength and decreased ductility exhibited by the Ca-reduced material was apparently a result of the higher impurity content.

Tensile Properties of Vanadium at Elevated Temperatures

The modulus of elasticity for vanadium is presented in Fig. 9.1 as a function of test temperature, as reported in three investigations [7, 8, 9] using dynamic measurements. Chemical analyses of the test materials are given in Table 9.4. The interstitial content of the two V materials used by Hill and Wilcox[7] was very similar, but analyses for metallic impurity were not reported. The structures of the two materials were dissimilar; the calcium-reduced material was as-wrought, whereas the aluminothermic specimens were recrystallized with no grain size specified. The modulus

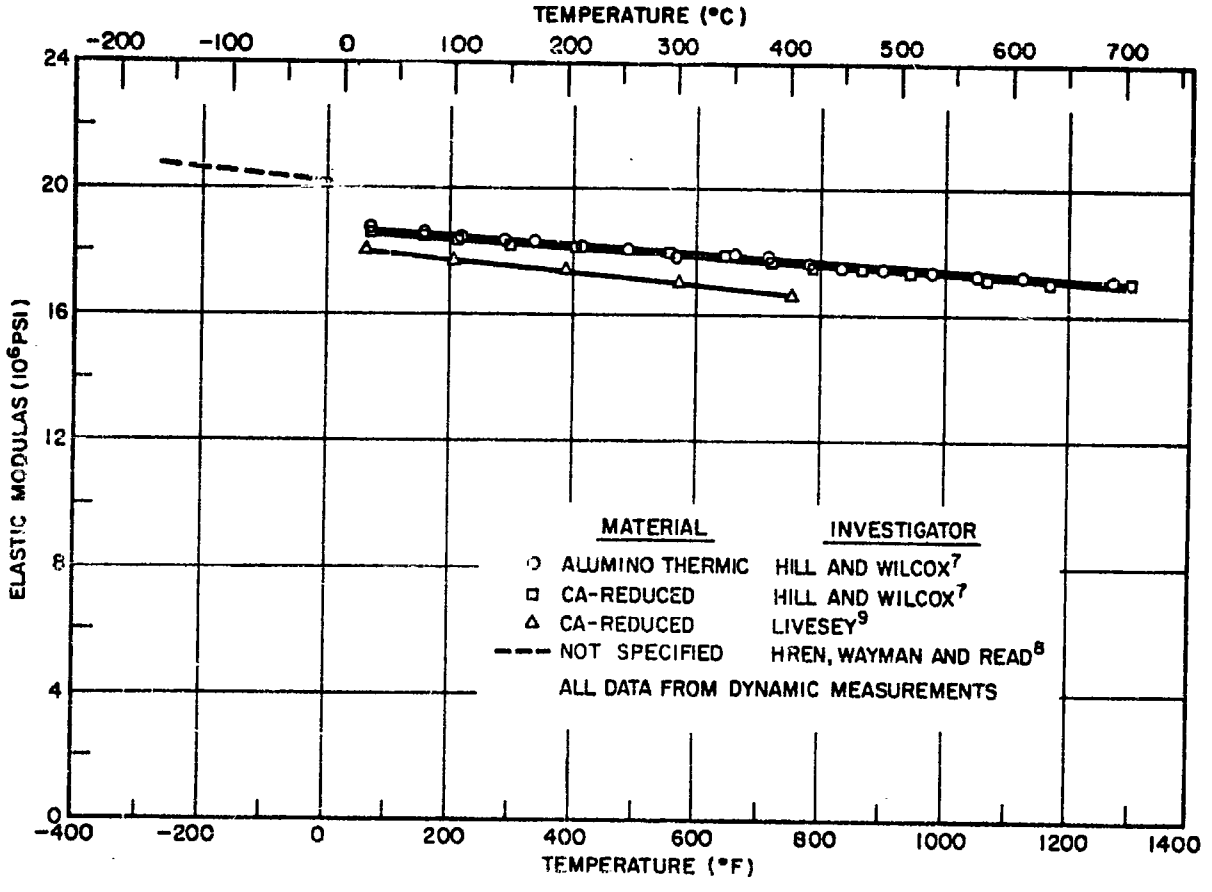

FIG. 9.1

MODULUS OF ELASTICITY OF VANADIUM VS TEST TEMPERATURE

decreased approximately 0.007 percent per °F (0.013 percent per °C), a behavior similar to other refractory metals. The agreement between modulus values of the two materials at all temperatures indicates little affect of impurity and structure on the modulus of vanadium as determined dynamically using a longitudinal vibration techniques.

Table 9.4

CHEMICAL ANALYSES OF VANADIUM USED FOR MODULUS DETERMINATIONS

REDUCTION METHOD	IMPURITY ANALYSIS (wt., percent)						INVESTIGATOR
	O	N	C	H	Fe	Si	
Alumino-Thermic	0.035	0.0058	0.025	0.0023			Hill & Wilcox[7]
Ca-Reduced	0.086	0.056	0.05	0.0032			Hill & Wilcox[7]
Not Specified	- - - - - - - - 99.7% Vanadium - -				- - - -	- - -	Hren, Wayman & Read[8]
Ca-Reduced	0.140	0.005	0.012	0.0002	0.130	0.027	Livesey[9]

Hren, et al.,[8] measured the modulus from -170° to 20°C (-274° to 70°F) of 99.7 percent pure as-annealed vanadium in an investigation concerning a proposed low temperature allotropy of vanadium. The method of measurement was similar to that of Hill and Wilcox. The decrease of modulus with increasing temperature was slightly greater, and the absolute value from extrapolation to 70°C was approximately 20×10^6 psi, about 1.4×10^6 psi (~7.5 percent) above the values presented by Hill &Wilcox.[7] Livesey[9] obtained a slope similar to that of Hren, et al., with a room temperature value slightly below that reported by Hill and Wilcox. The last results were also calculated from resonant frequency measurements but the rectangular bar specimen was vibrated in a free-free mode.

The effect of temperature on the tensile properties of vanadium has recently been reviewed by Wessel, et al.,[10] Comparison between materials of low purity as reported caslier by Pugh,[11, 12] and Ca-reduced and iodide refined materials recently tested by Clough[13] and Loomis and Carlson[5], is given in Fig. 9.2. The test materials are identified in Table 9.5. Unfortunately, the recent tests were not conducted at high enough temperatures to observe or confirm the strain ageing effect reported by Pugh at 400°C. However, the decrease of strength and increase of ductility at low temperatures with improved purity is striking. The work of Loomis and Carlson[5] is presented separately in Fig. 9.3 to compare in more detail the difference between the effect of temperature on the strength properties of two grades of vanadium. The shift in ductile-brittle transition temperature from -110°C for iodide material to approximately -70°C for the Ca-reduced material, and the more rapid increase in yield strength with decreasing temperature for the Ca-reduced material demonstrates the effect of purity on these properties. The rise in ductility with

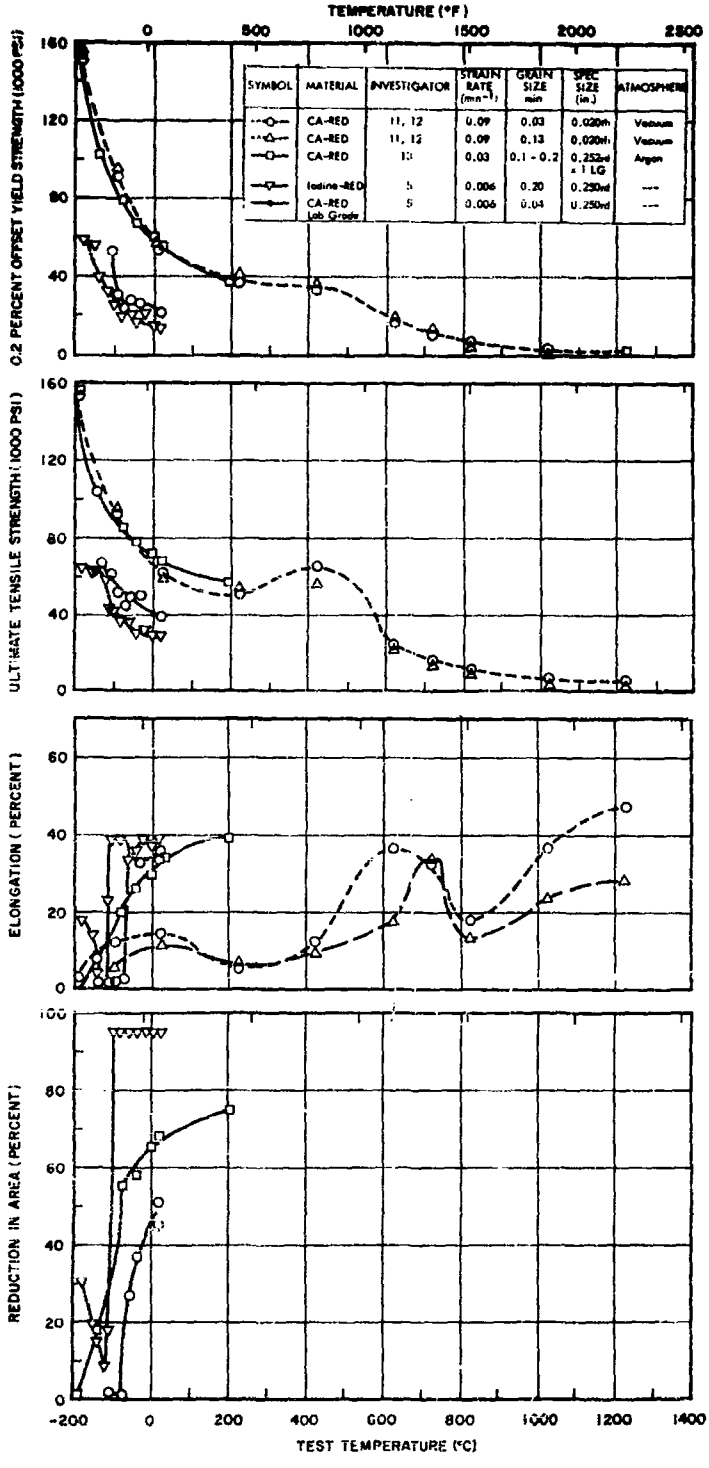

FIG. 9.2

TENSILE PROPERTIES OF RECRYSTALLIZED VANADIUM VS TEST TEMPERATURE

Table 9.5

IDENTIFICATION OF TENSILE TEST MATERIAL FOR DATA PRESENTED IN FIGS. 9.2 AND 9.3

MATERIAL PREPARATION	IMPURITY ANALYSIS (wt. percent)				INVESTIGATOR
	C	O	N	H	
Iodide Reduced, Recrystallized	0.024	0.010	0.005	0.001	Loomis and Carlson[5]
Ca-Reduced, Recrystallized	0.08	0.02	0.02	0.006	Loomis and Carlson[5]
Ca-Reduced Recrystallized 1 hr. at 1,000°C	0.09	0.057	0.070	0.004	Pugh[11, 12]
Ca-Reduced Recrystallized at 800°C	0.047	0.070	0.052	0.0043	Clough and Pavlovic[13]

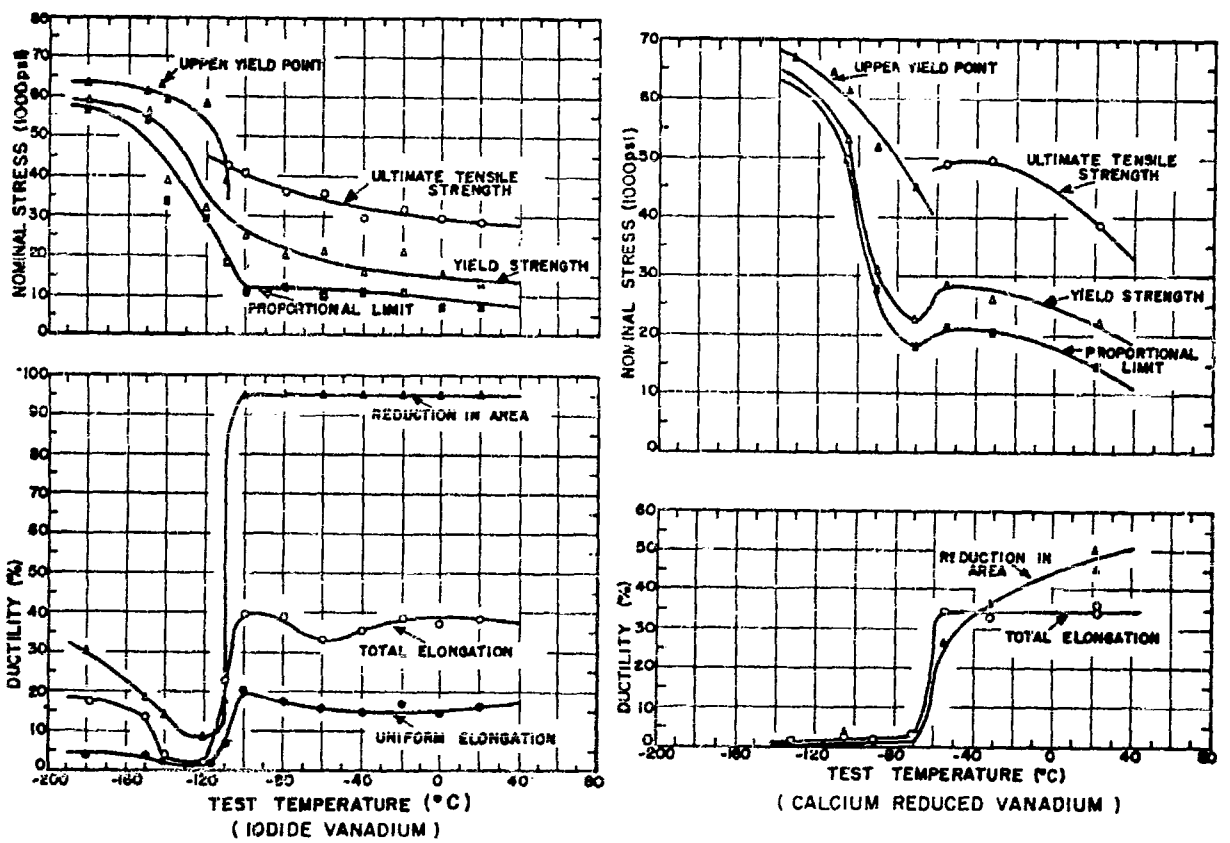

FIG. 9.3

TENSILE PROPERTIES OF IODIDE AND CALCIUM REDUCED RECRYSTALLIZED VANADIUM VS TEST TEMPERATURE[5]

decreasing temperature below -130°C was unexplained, but the observed ductility increase was confirmed by a reported change in mode of fracture to a shear type. The stress-strain curves shown in Fig. 9.4 also show the change in fracture behavior from -120° and -140°C to -150°C and below where considerable strain occurred after yielding.

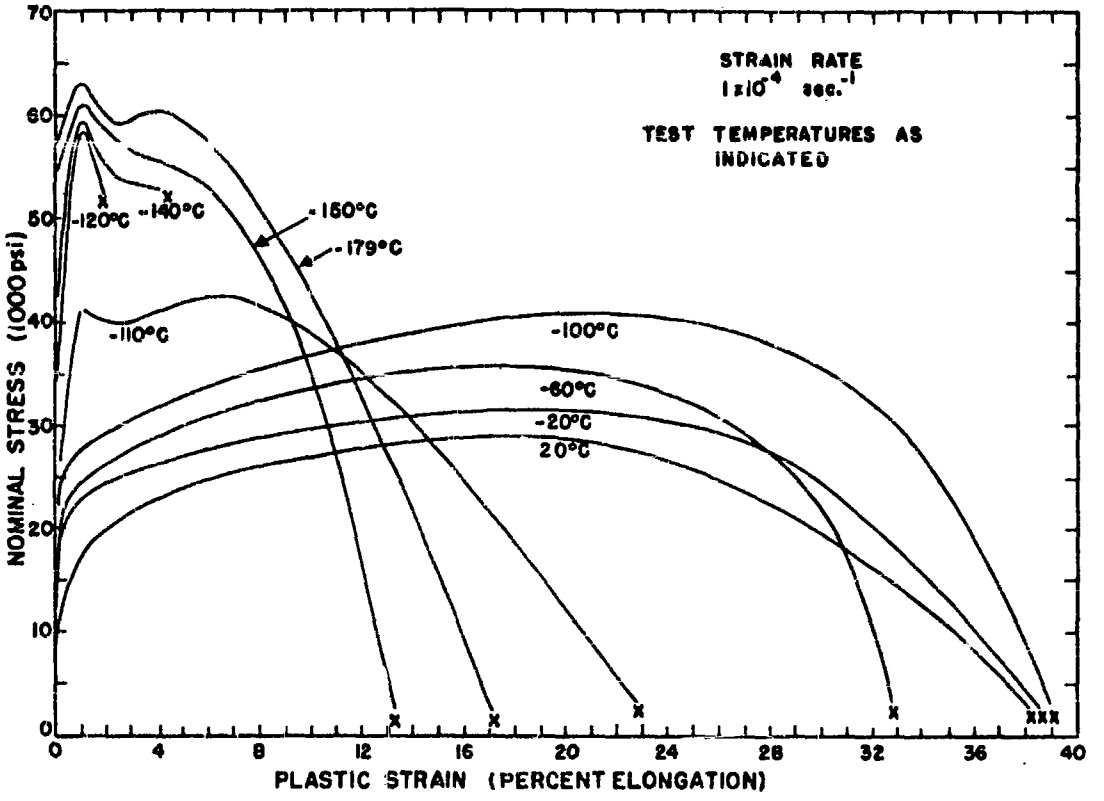

FIG. 9.4

STRESS-STRAIN CURVES FOR IODIDE VANADIUM FROM 20 TO -180°C[5]

Ductile-Brittle Behavior

The ductile-brittle transition temperature was determined by Loomis and Carlson[5] for the two materials discussed above. Tensile tests were used in the case of the iodide material, whereas in the case of the Ca-reduced material both bend tests and tension tests were used. The iodide material remained ductile down to -110°C ±10°C. Typical bend test data are plotted in Fig. 9.5 which shows the sudden drop in ductility between -60°C and -70°C exhibited by the Ca-reduced V. The maximum deflection of the test apparatus was 0.150 in.

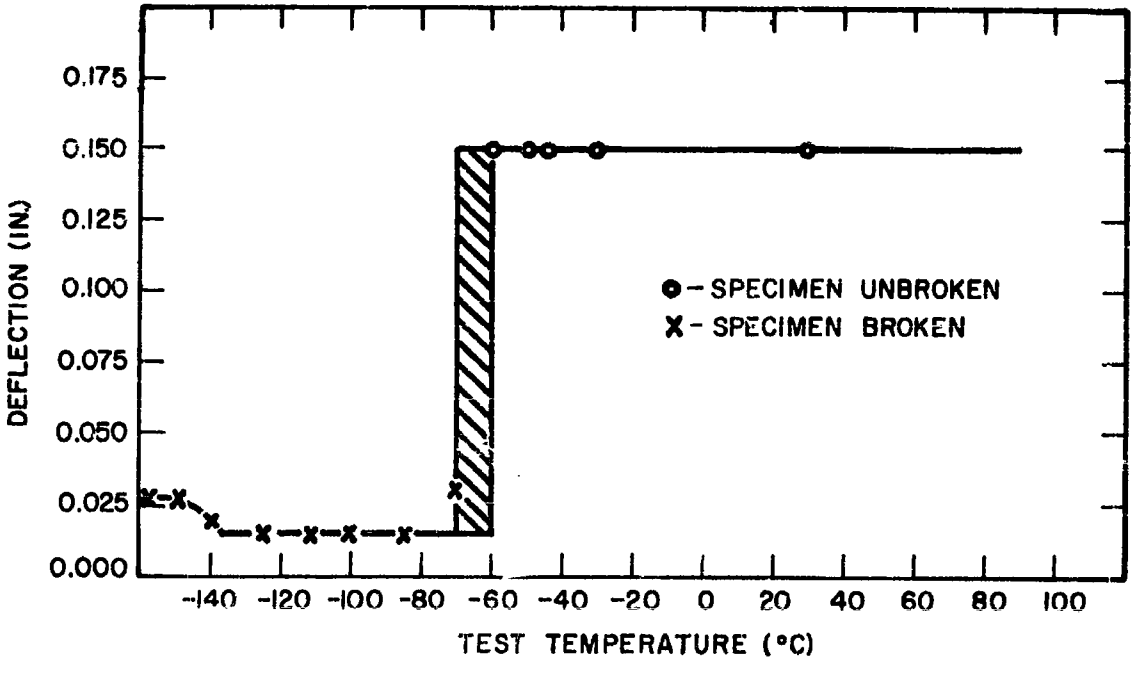

FIG. 9.5

BEND DUCTILITY FOR CALCIUM-REDUCED VANADIUM FROM -160 TO 25°C[5]

The effect of controlled interstitial additions on the ductile-brittle behavior of Ca-reduced V as reported by Loomis and Carlson[5] is shown graphically in Fig. 9.6. The minimum value for each curve is the transition temperature of the iodide material and the next highest are values for the Ca-reduced materials as produced with no intentional additions. The hydrogen curve is shown dotted above room temperature as the determinations were made by hand bending, or from data of another source. Small additions of H increased the transition temperature more than the other elements, and C additions had the least effect. The curves are presented to indicate a general trend rather than to present absolute values as a combination of elements may be more or less effective in altering the transition temperature.

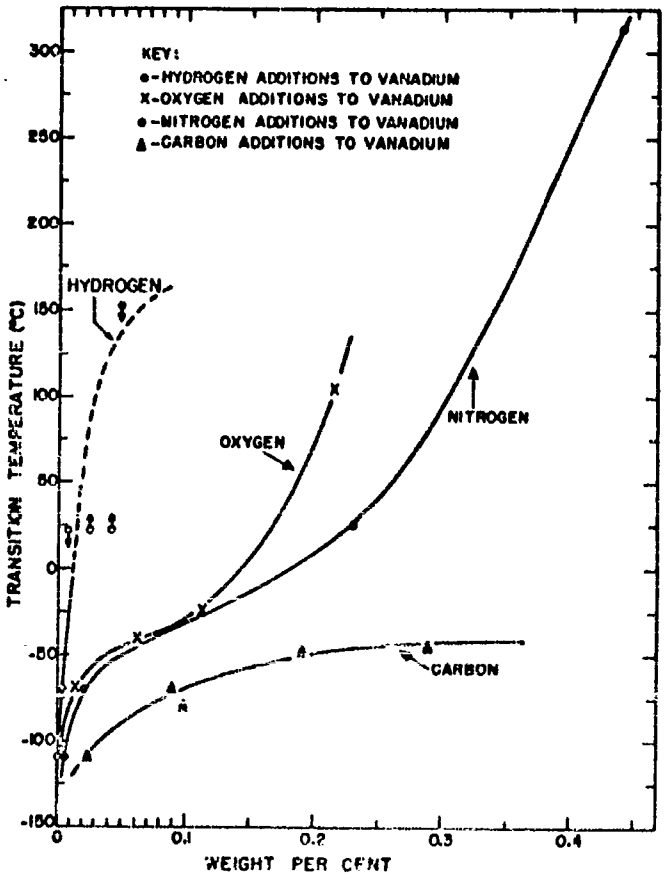

FIG. 9.6

BEND TRANSITION TEMPERATURE AS AFFECTED BY NONMETALLIC ADDITIONS TO VANADIUM[5]

Eustice and Carlson [14] observed a large effect of hydrogen on the embrittlement of V-Cb alloys although the effect decreased with Cb content above 50 percent.

Clough and Pavlovic [13] observed a ductile-brittle impact transition temperature of approximately 130°C using v-notch impact specimens of recrystallized Ca-reduced material with higher O, (0.48) and N, (0.047) low lower C, (0.045) and H, (0.0028) content than that of Loomis and Carlson. Their results are shown in Fig. 9.7. Impact values above 130°C were above 200 ft-lb, whereas below 130°C the fractures were completely brittle cleavage type and the absorbed energy was 16 to 18 ft-lb. Tensile tests on the same material, hot worked and recrystallized at 800°C showed ductile tensile failures at -78°C indicating the combined sensitivity to notches and strain rate shown by the impact tests. The tensile transition temperature reported by Loomis and Carlson[5] of -65 ±10°C was apparently higher than that indicated by Clough and Pavlovic as a result of different working and recrystallization heat treatment.

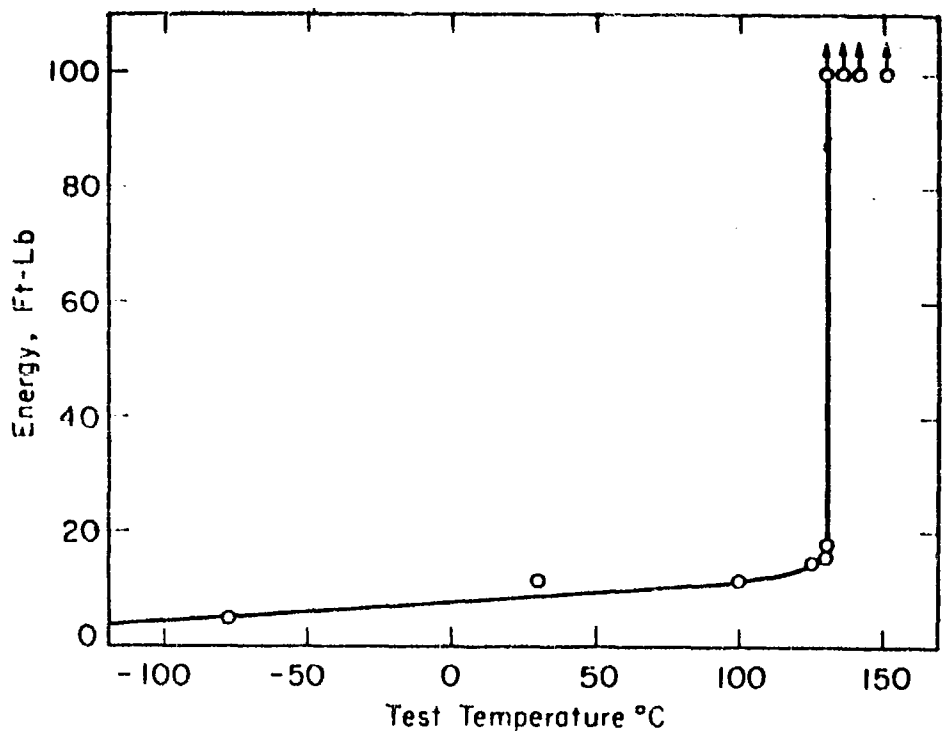

FIG. 9.7

CHARPY V-NOTCH/IMPACT STRENGTH VS TEST TEMPERATURE FOR RECRYSTALLIZED VANADIUM[13]

Tensile transition temperatures were determined for a series of binary alloys by Loomis and Carlson[5] and their results are shown in Fig. 9.8. Small additions of Cr, Mo, Ta, and Ti are shown to produce anomalous maxima and minima in the transition temperature curves. Titanium additions above 2.0 percent lowered the transition temperature below that of the base material and the authors[5] reported that microstructures of fractured specimens indicated increased solubility of interstitial impurities in the presence of Ti. Small additions of Zr and Th increased the transition temperature only slightly, whereas 4.0 percent Zr increased the minimum temperature for ductility about 375°C. Rostoker[15] has reported that small additions of Ti and Zr embrittled vanadium,but that additions of 5 percent Ti or 1 percent Zr improved ductility. However, Zr additions of 3 percent or more produced hot shortness.

Alloy additions of Y and rare-earth metals were also shown to improve the ductility of V by Lundin and Klodt.[16] The amount of cold reduction possible before cracking was used to measure ductility, and hardness measurements were used to evaluate the impurity scavenging effect; but no mechanical properties were reported.

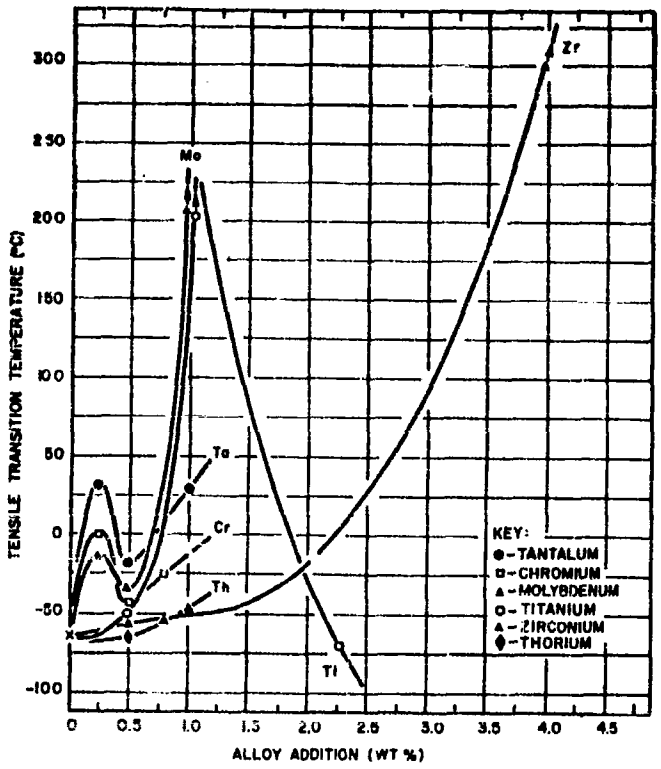

FIG. 9.8

TENSILE TRANSITION TEMPERATURE AS AFFECTED BY METALLIC ADDITIONS TO VANADIUM[5]

Recrystallization Behavior

Dunn and Edlund[2] (after Seybolt) reported the recrystallization temperature for vanadium to be between 700 −800°C (1292°−1472°F) for 70-percent, cold-rolled sheet. Reports were not found in recent literature concerning the effect of cold or hot work processes or impurity content on the recrystallization behavior of vanadium.

Tensile Properties of Vanadium Alloys

The modulus of elasticity of binary V-Ti alloys from room temperature to 1300°F is shown in Fig. 9.9 as determined by Hill and Wilcox[7] using a dynamic technique. The values for two grades of vanadium were discussed in a previous section and the values for two grades of Ti, iodide and Ti-75A, also shown in Fig. 9.9, were included for comparison with the alloys. The authors ascribed the difference in the behavior of the two grades to composition variations between the two materials described in Table 9.6. The authors[7] did not specify which type of Ti was used in preparing the alloys.

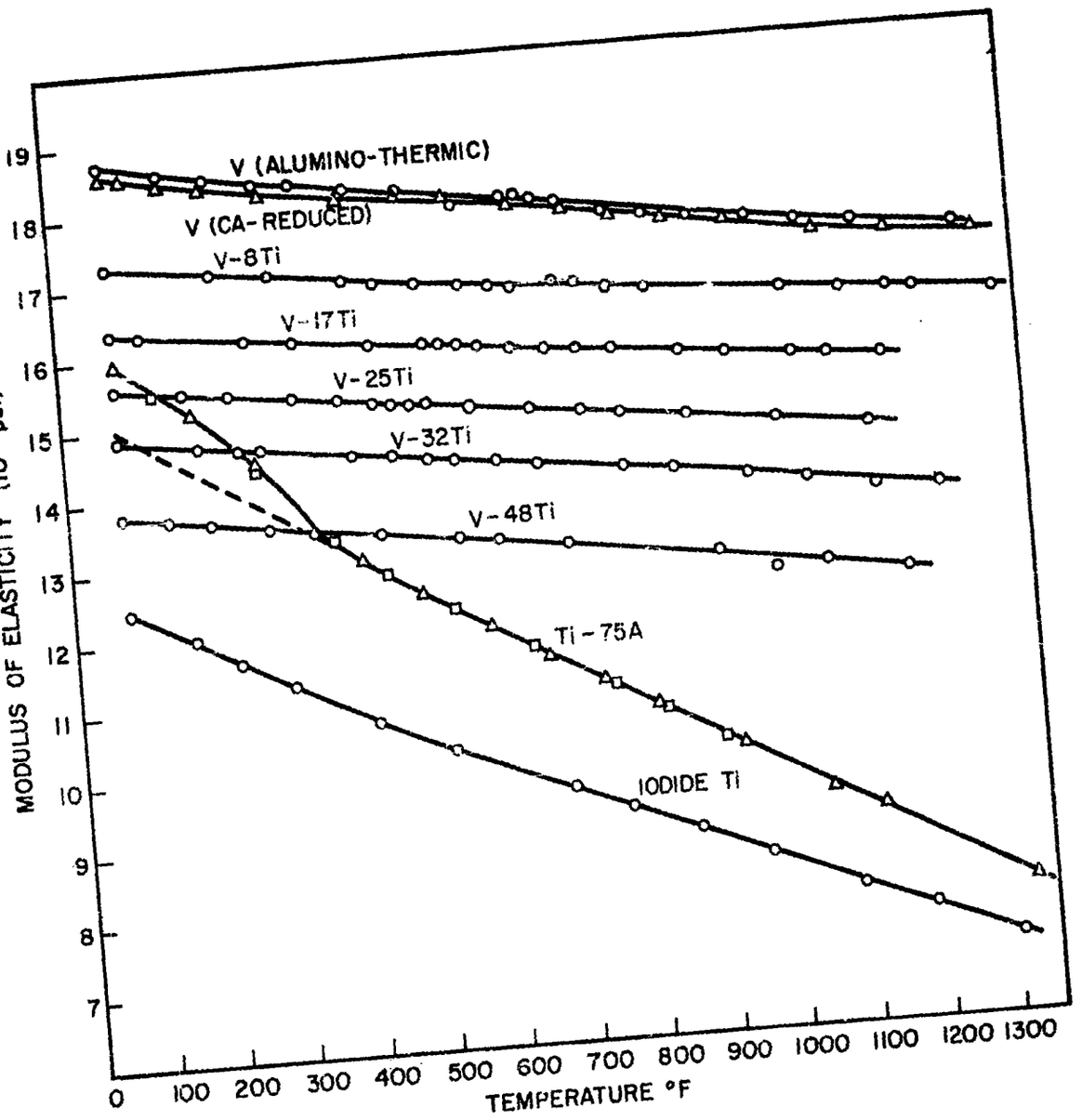

FIG. 9.9

MODULUS OF ELASTICITY OF VANADIUM, TITANIUM AND V-Ti ALLOYS FROM 70-1300°F[7]

Table 9.6

CHEMICAL ANALYSES OF MATERIAL USED FOR MODULUS EVALUATIONS[7]

MATERIAL	IMPURITY ANALYSIS (Wt. Percent)					
		O	N	C	H	Fe
Aluminothermic Vanadium	-	0.035 0.035	0.0058 0.0058	0.025 0.025	0.0023 0.0023	-
Calcium-reduced Vanadium	-	0.086	0.056	0.05	0.0032	-
V-8Ti	8.44	0.033	0.0028	0.04	0.0022	-
V-17Ti	16.85	0.044	0.0043	0.04	0.0051	-
V-25Ti		0.050	0.0036	0.04	0.0064	-
V-32Ti	32.02	0.047	0.0034	0.03	0.0065	-
V-48Ti	48.23	0.037	0.0032	0.03	0.0073	-
Iodide Ti*		0.01	0.005	0.03	0.009	0.02
Ti 75A		0.19	0.032	0.04	0.0321	0.12

* Chemical analysis not available -- values reported are considered typical.

At room temperature, the modulus value was found to decrease in a uniform manner with increasing Ti solute additions. In addition, the increase of the room temperature value with increasing temperature for each binary alloy followed approximately the same slope as the curve for unalloyed vanadium even though the unalloyed Ti modulus exhibits a stronger temperature dependency. All alloy specimens were in the recrystallized condition.

Investigators concerned with vanadium alloy development initially concentrated on the production and property determination of systems with Al, Cb, Co, Cr, Fe, Mn, Mo, Ni, Si, Ti, and Zr additions. Binary alloys containing Ti proved most ductile over a wide composition range and led to a study of ternary and more complex additions to the V-Ti base. Additions of Cr, Al, and Si were shown to be potent strengtheners, but ductility and fabricability were lower than desired.

Recent work by Rajala, et al.,[3, 4] with vanadium base material of higher purity has been directed toward alloys with major additions of the refractory metals Cb, Mo, Ta, and W to the V-Ti base material. Titanium additions of 2.5 percent or more were shown to improve room temperature ductility and fabricability; however, vanadium alloys made with higher purity vanadium did not require large additions of Ti for ductility, and reduction of Ti content to 5.0 percent increased the strength properties of V-Cb and V-Ta alloys at 1800°F. Tensile properties of alloys produced during the first year of this study at Armour[3] are summarized in Table 9.7. The alloys were prepared from materials of 99.8 percent purity or better by non-consumable arc melting in the form of 200-gram pancake ingots. The as-cast structures were altered first by hot press forging and warm rolling in a protective sheath at 2460°F–2515°F. Subsequent work, warm and cold rolling, was performed on un-canned sheet bar to produce 0.050-in. thick sheet. Some complex alloys were hot worked bare at higher temperatures because of the need for working temperatures above the melting point of practical canning materials. Contamination during exposure for short heating times was not deleterious judging from micro-hardness examination.

Sheet tensile and stress rupture specimens were 2-1/4 in. long with a gage section 1/4 in. wide × 3/4 in. long. Creep specimens were 4-3/4 in. long with 1/4 × 1.4 in. gage section. Results shown in Table 9.7 are from specimens annealed at 1830°F in 30 min. which completely recrystallized the single phase alloys, but only partially recrystallized alloys containing precipitates of a second phase. Continuous solid solution alloys were reported for the ternary additions of Cb, Mo and W to the V-Ti base but some precipitation was observed in V-50 Ta alloys after tensile tests at 1,800°F which evidenced brittleness. In every case, a ternary addition to a binary alloy or an increase in the ternary addition increased the tensile strength.

The tensile properties of the more attractive alloys are compared with the strength of some commercial super-alloys in Fig. 9.10 on the basis of ultimate tensile strength to density ratio. Stainless steels and Ti alloys are observed to lose strength rapidly above 1000°F. The V-50 Cb, and V-5Ti-20Cb alloys were superior to the super alloys shown above about 1500°F to 2000°F.

Work during the second year of the Armour alloy development program[4] emphasized optimizing the properties of the more attractive alloys developed during the first year. As columbium had been shown to be the most potent strengthener studied, modifications of the V–Cb system were studied intently. Alloys investigated are listed in Table 9.8 along with data related to fabricability. Optimum composition limits for Ti and Cb additions for maximum strength at 1800°F were determined to be 5 Ti and 20 Cb as indicated in Fig. 9.11 and 9.12. Substitution of Hf and Zr for the Ti component resulted in no increase in strength or recrystallization temperature. Quaternary additions of Mo, Si, Y, C, and B in small amounts increased the metallographically observed recrystallization temperature as shown in Table 9.9. The ultimate tensile strength at elevated temperature of the best vandium alloy developed to date is compared with commercially available Mo and Cb alloys in Fig. 9.13. On a strength-to-density basis, the V-5Ti-20 Cb alloy appears to be superior up to

Table 9.7

TENSILE PROPERTIES OF VANADIUM SHEET ALLOYS[3]
(Annealed 0.50 hr at 1830F (1000°C), Water Quenched)

ALLOY ADDITION (Wt percent)					ROOM TEMPERATURE			1200F (650C)			1800F (980C)		
Ti	Cb	Mo	Ta	W	Ultimate Tensile Strength (psi)	Yield Strength (psi)	Elong. (percent)	Ultimate Tensile Strength (psi)	Yield Strength (psi)	Elong. (percent)	Ultimate Tensile Strength (psi)	Yield Strength (psi)	Elong. (percent)
Unalloyed					58,000	50,000	16	30,000(f)			21,000(f)		
5					70,500	54,000	17						
10					73,500	65,900	29	46,700	34,800	32	35,800	34,000	36
20					86,900	77,800	22				37,000	34,500	40
		10			78,900	74,000	13	39,100	37,300		17,700	16,000	51
				10	78,200	73,600	9	37,900	34,900	13	19,100	15,200	2[a]
				20	103,000	102,600	0	71,300	58,600	11	26,700	23,500	14
	10				92,100	85,000	21	77,800	51,700		36,800	33,900	41
	20				107,000	105,500	6	81,700	61,200	13	55,100	41,500	22
	50				168,000	163,500	2	151,500	130,300	3	85,300	75,400	5
	50	(b)			216,000(c)	–	0	166,200	148,200	7			
	60				157,000	147,000	16	107,100	97,000	8(a)			
			10		89,200	85,500	11	53,500	42,200	10			
			20		103,000	89,000	3	65,000	57,000				
			50	(b)	216,000	160,000	4	154,500	143,000	7	42,100(c)		
5		5			71,800	55,500	25	54,600	42,800		32,900	29,600	19
10		5			89,700	82,700	22	68,900	47,000		34,600	32,400	28
10		10			91,200	79,400	13(a)	82,800	56,100	11	39,100	34,500	9
20		5			100,000	91,900	19	79,500	63,400		42,800	38,100	29
20		10			114,000	104,500	23	90,800	67,800	17	43,500	39,900	42
5		20			93,500	80,300	1				44,300	39,400	3
5	5				77,200	69,200	25	55,300	41,600		36,500	32,100	27
5	10				87,800	72,500	25	70,600	46,400		47,800	44,600	12
5	20				106,200	97,700	19	86,800	68,200		69,500	63,000	10(a)
10	5				84,200	70,400	27	67,600	50,000		39,700	35,000	39
10	10				94,400	77,500	21	71,900	60,700		52,700	48,500	6(a)
10	20				111,200	102,000	23	94,000	67,700	16	54,000	51,400	18
20	10				110,600	99,700	20	99,300	74,300	17	43,200	40,300	54
20	20				113,500	108,500	21	96,500	78,500	12	44,200	41,300	56
5	20	(d)			136,000	122,300	21	131,000	92,400	8(a)	37,200	34,200	74
5	20	(e)			187,000	178,200	3	147,500	116,200	6	46,900	36,800	18
5	20				111,000	106,000	14	90,000	71,900	12	46,100	37,800	18
5	40				129,000	112,700	20	97,900	84,200	7			
5			5		69,600	53,500	29	52,700	39,100		41,700	38,900	17
5			10		85,000	69,800	23	67,600	44,700		49,300	41,500	12
5			20		105,500	83,200	25	79,400	61,700		55,300	47,000	8
10			5		84,300	70,900	17	59,200	48,300		41,200	38,300	19
10			10		89,300	75,900	22	71,500	53,900		49,300	50,200	25
10			20		110,000	106,000	7	90,700	62,300	13	47,000	42,700	18
20			20		115,500	107,500	18	95,700	74,500	13	41,000	39,700	85
5				5	73,600	57,000	23	58,500	39,800		28,500	24,800	7(a)
5				10	85,900	76,500	23	74,300	51,200	17	39,300	36,600	13(a)
10				5	86,900	69,300	23	76,200	48,200		37,800	33,100	10
10				10	89,300	73,400	22	86,100	57,300	7	41,300	36,300	9
10				20	107,500	101,800	19	94,800	63,900	15	46,600	41,400	17
20				10	111,600	106,000	25	94,000	68,200	17	43,500	38,500	80
20				20	112,000	105,200	21	108,000	82,000	12	46,400	41,600	52
											2000F (1090C) Tensiles		
5	20										49,700		12
	20										35,400	32,100	85
	50										41,200	37,400	5

a – Broke near gage mark.
b – As rolled.
c – Brittle fracture, broke during elastic loading.
d – One percent Si added, annealed 2010F (1100C) 1/2 hr, water quenched.
e – One percent Si added, aged 100 hours at 1200 F.
f – Interpolated from plotted data.

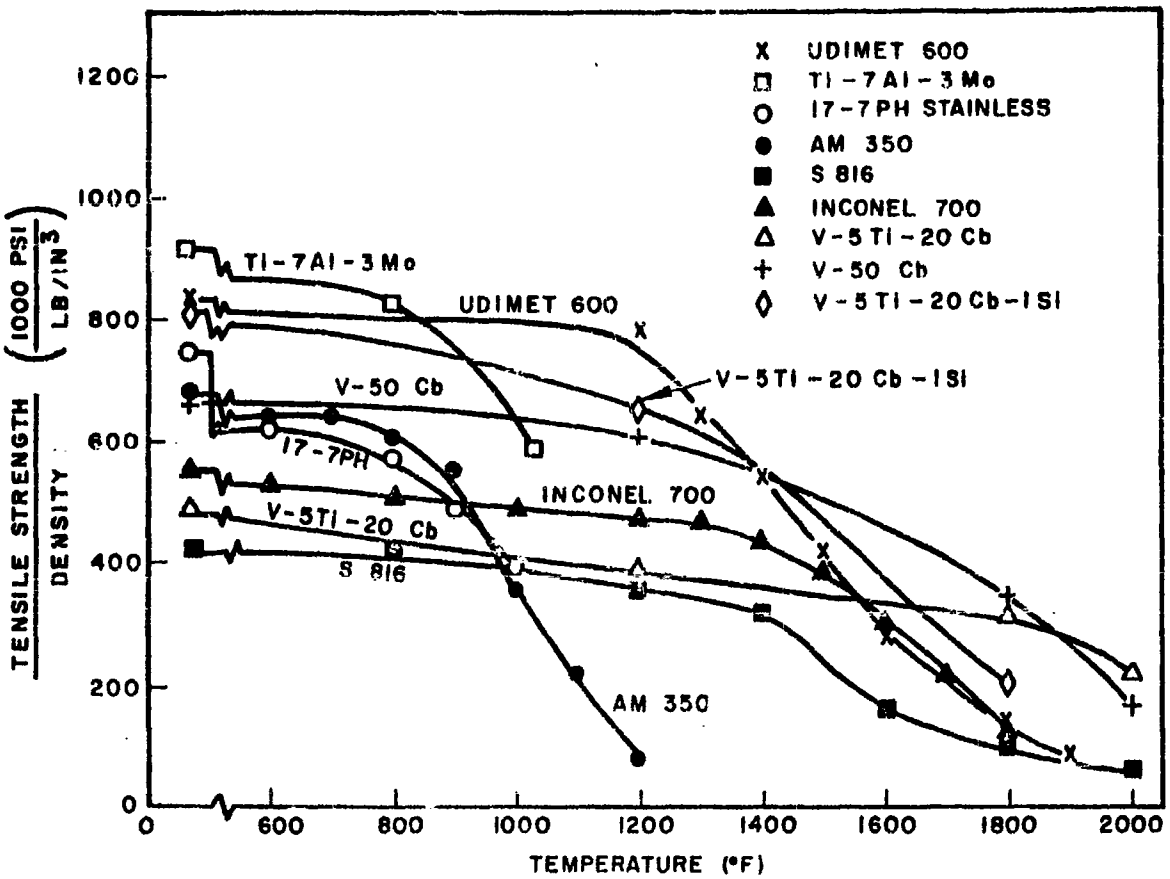

FIG. 9.10

ULTIMATE TENSILE STRENGTH-DENSITY RATIO VS TEMPERATURE FOR SELECTED VANADIUM AND SUPER ALLOYS[3]

Table 9.8

SUMMARY OF FABRICATION DATA ON SELECTED VANADIUM ALLOYS[4]

BASE ALLOY	ALLOY ADDITION				WORKING PROCESS[a]	BASE ALLOY	ALLOY ADDITION				WORKING PROCESS[a]
	Ti	Zr	Hf	Other			Ti	Zr	Hf	Other	
Solid Solution											
V-20Cb				0.25Y	HR	V-30Cb	–	–	–	–	HR-F
			1		CR		5				HR
			2		CR				2		HR
			4		CR		5			2.5 Mo	HR
	1				HR					5 Mo	HR
	2.5				HR	V-40Cb	–	–	–	–	HR
	5				CR				2		CR
	7.5				HR				4		CR
		0.5			CR		2.5				HR
		1.0			CR						
		2.0			HR	V-50Cb	–	–	–	–	CR
		5			HR-F		5				CR
	5			0.25Y	CR	V-60Cb	–	–	–	–	CR
	5			0.5	HR		5				CR
	5			5 Cr	HR-F		–	–	–	–	CR
	10			5 Cr	HR-F	V-70Cb	5				CR
						V-75Cb					CR
Age-Hardened											
V-2.5Ti				0.2Be	HR	V-10Cb	20			0.2Be	HR-F
				0.5Be	HR-F		20			0.5Si	HR
V-10Ti				0.2Be	HR		20			1.0Si	HR
				0.5Be	HR-F	V-20Cb	5			0.2Be	HR
							5			0.5Si	HR
							5			1.0Si	HR
Dispersion-Hardened											
V-20Cb			2	0.03C	HR	V-20Cb	5			0.50C	HR-F
			2	0.07C	HR			2		0.05C	HR
			2	0.10C	HR			2		0.10C	HR
	5			0.10C	HR			2		0.50C	HR-F
	5			0.25C	HR						
Solid Solution (10 lb ingots)											
V-20Cb	5[b]				c	–	5			0.5Y[b]	c
	5[d]				c	–	5			1.0Y[b]	c

a. HR – Hot worked at 2400°F, CR – Cold Rolled to sheet, F – Failed to fabricate

b. Vacuum induction melted

c. Upset press-forged at 2400°F

d. Consumable-electrode arc melted

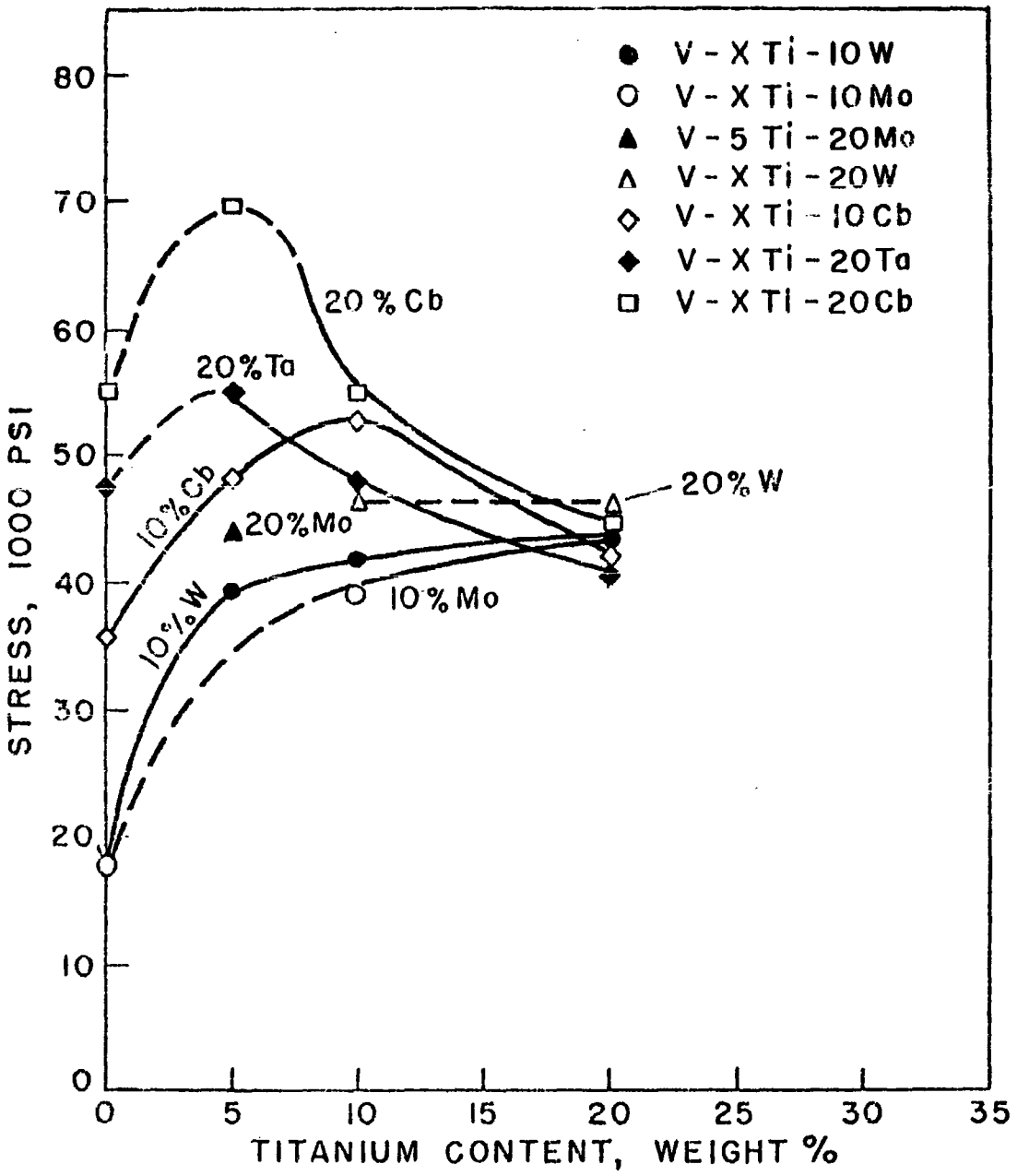

FIG. 9.11

EFFECT OF TITANIUM ADDITIONS ON THE ULTIMATE TENSILE STRENGTH OF VANADIUM ALLOYS AT 1000° F[4]

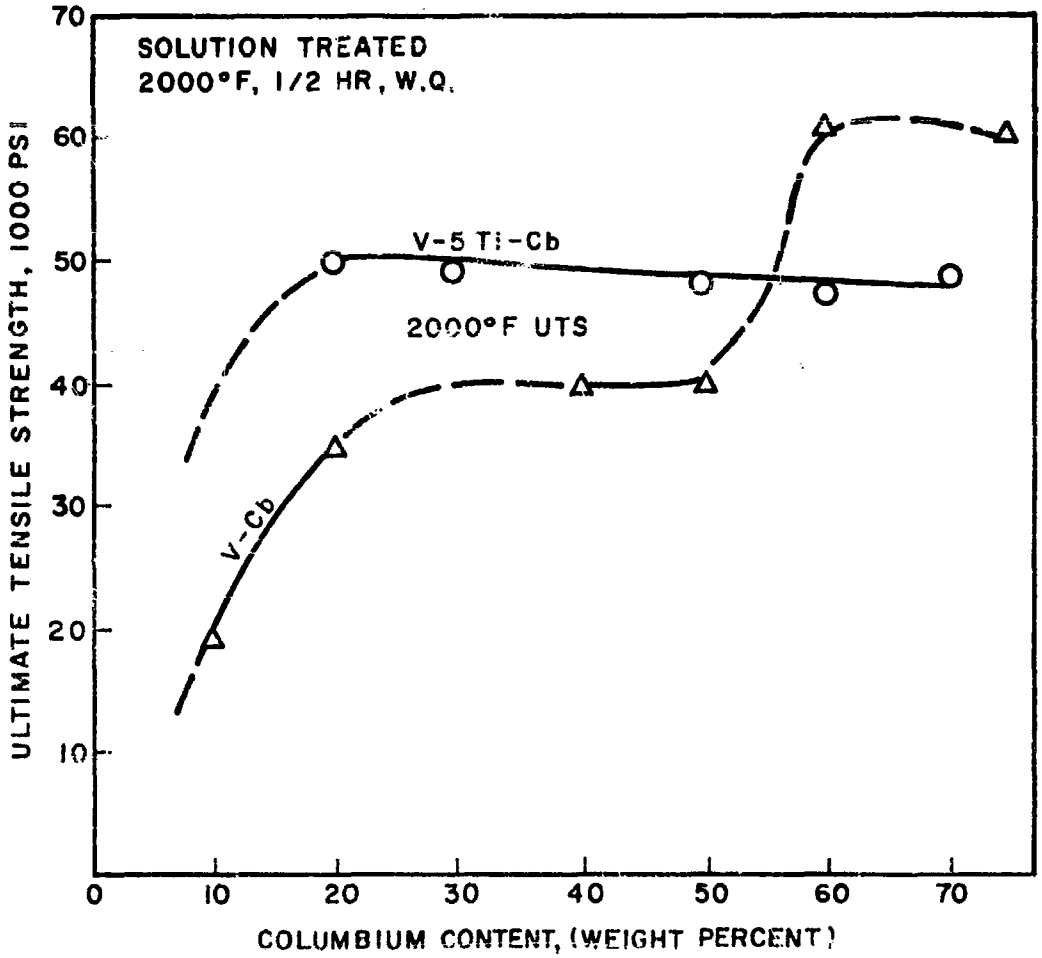

FIG. 9.12

EFFECT OF COLUMBIUM ADDITIONS ON THE ULTIMATE TENSILE STRENGTH OF VANADIUM AND THE V-5 Ti ALLOY AT 2000°F [4]

2000°F and competitive with the Mo and Cb alloys up to 2200°F, especially in view of the satisfactory fabricability and weldability of the vanadium alloy. It also should be noted that the V alloys were in the recrystallized condition, whereas the Cb and Mo alloys were all in the worked and stress-relieved condition. The alloy exhibited no degradation of room temperature ductility or strength when TIG welded, has over 19 percent room temperature elongation, and can be rolled at room temperature to 95 percent reduction in thickness. Preliminary age-hardening and dispersion strengthening have not produced improvement in short-time tensile strength of the V-5Ti-20 Cb alloy at 2000°F but additional studies are being conducted because of the apparent improvement in creep properties as discussed in the next section.

Table 9.9

RECRYSTALLIZATION TEMPERATURE OF VANADIUM ALLOYS[4]

ALLOY (w/o)	RECRYSTALLIZATION TEMP* (°F)
V	1525
V-20Cb	1800
V-50Cb	1800
V-2Hf-20Cb	1800
V-5Ti-20Cb	1800
V-5Ti-40Cb	2000
V-5Ti-20Cb-2.5Mo	2000
V-5Ti-20Cb-(0.5, 1.0)Si	2000
V-5Ti-20Cb-0.25Y	2000
V-2Zr-20Cb-0.1C	2200
V-5Ti-20Cb-0.25C	2200
V-5Ti-20Cb-0.1B	2400

*Minimum temperature at which 100 percent recrystallized microstructure was observed after 30 min using only the temperatures shown, 1800°, 2000°, 2200°, and 2400°F, for the alloy studies. Final reduction: ~60 percent either warm or cold depending upon alloy.

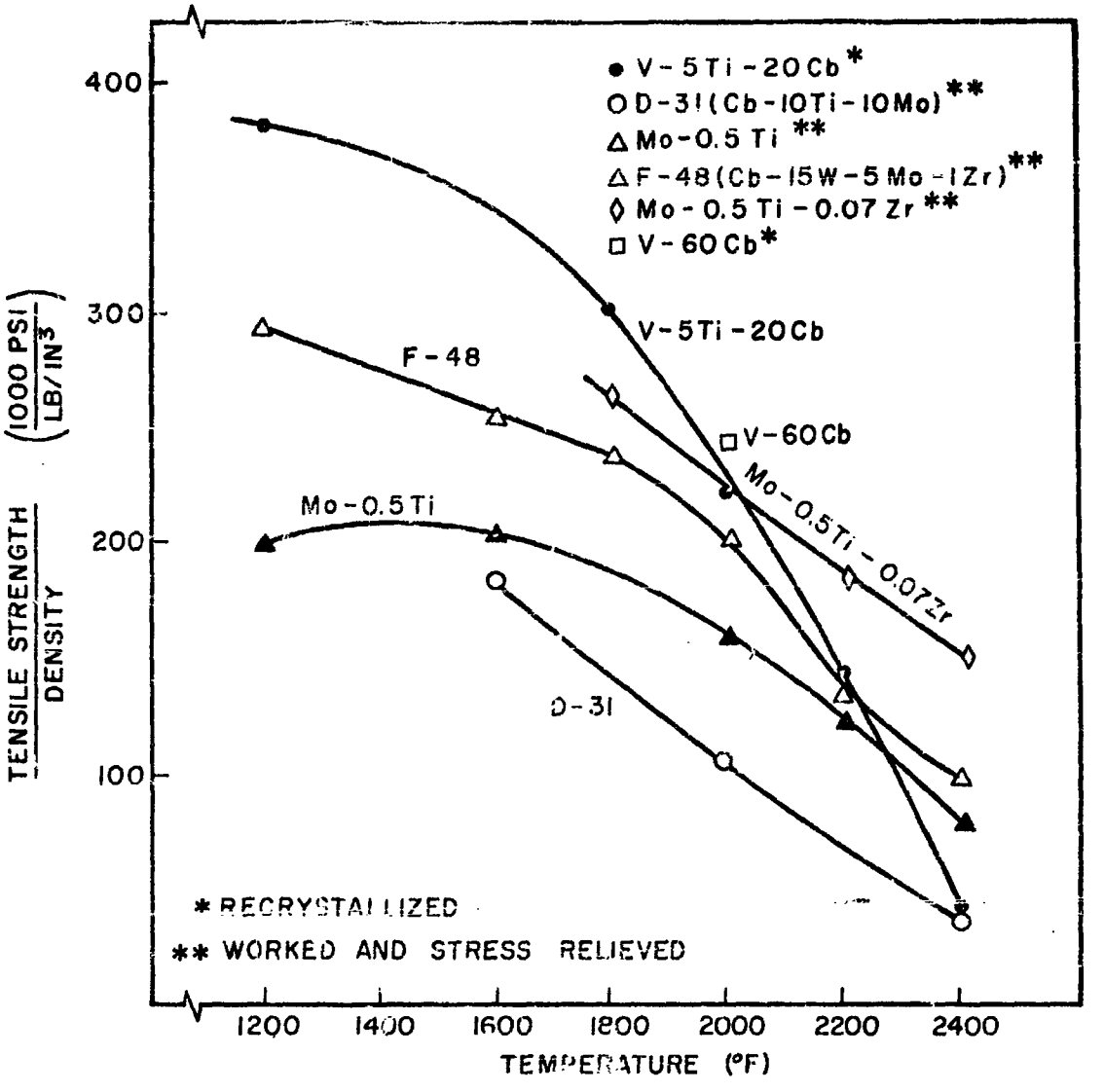

FIG. 9.13

ULTIMATE TENSILE STRENGTH-DENSITY RATIO OF VANADIUM, COLUMBIUM, AND MOLYBDENUM ALLOYS FROM 1200-2400° F[4]

Creep and Stress Rupture Properties of Vanadium Alloys

The short-time rupture strength of two vanadium alloys at 2000° F is compared with commercial Mo and Cb alloys in Fig. 9.14 as presented by Rajala, et al.[3] The vanadium alloys were tested in the recrystallized state and show superiority over the recrystallized Mo and Cb alloys on a strength to density basis. The reverse is true, however, if the recrystallized vanadium alloys are compared with the Mo and Cb alloys in the stress relieved condition. The annealing treatment, 1830° F for 30 min, given the vanadium alloys showed complete recrystallization of the cold-worked structure by metallographic analysis. The strengthening effect of deformation on vanadium alloys has not been reported.

The effect of 0.25 percent C additions on the stress-rupture strength of the basic V-5Ti-20Cb alloy at 2,000°F is shown in Fig. 9.15 and also summarized in Table 9.10. as reported by Rajala, et al.[4] The short time (1 hour) rupture strength of the basic alloy of 32,000 psi, is better than that for the carbon modification of 19,000 psi; however, the basic alloy failed in 17 hours at 2,500 psi compared to a 100-hour rupture strength of 6,000 psi for the 0.25 C modification. On a density corrected basis the 100 hour rupture strength of the V-5Ti-20Cb-0.25 C alloy, 26,300 psi per unit density, is about equal to that for D 31, a commercially developed columbium alloy, which has a density corrected strength value of 28,300 psi per unit density.

Additions of Y and B at levels which allowed fabricability resulted in short time 2,000°F rupture strengths similar to the C modification, as shown in Table 9.10. Longer time stress-rupture data for these alloys have not been reported.

Creep resistance of age-hardened V-5Ti-20Cb-Si alloys was investigated[4] and compared with a commercial high-strength alloy at 1,200°F, below the melting point of V_2O_5 (1,250°F). To date, however, this phase of the study has not produced any outstanding properties at 1200° F. Work is continuing on this program and additional data should be available by the end of the third year of the program, December 1961.

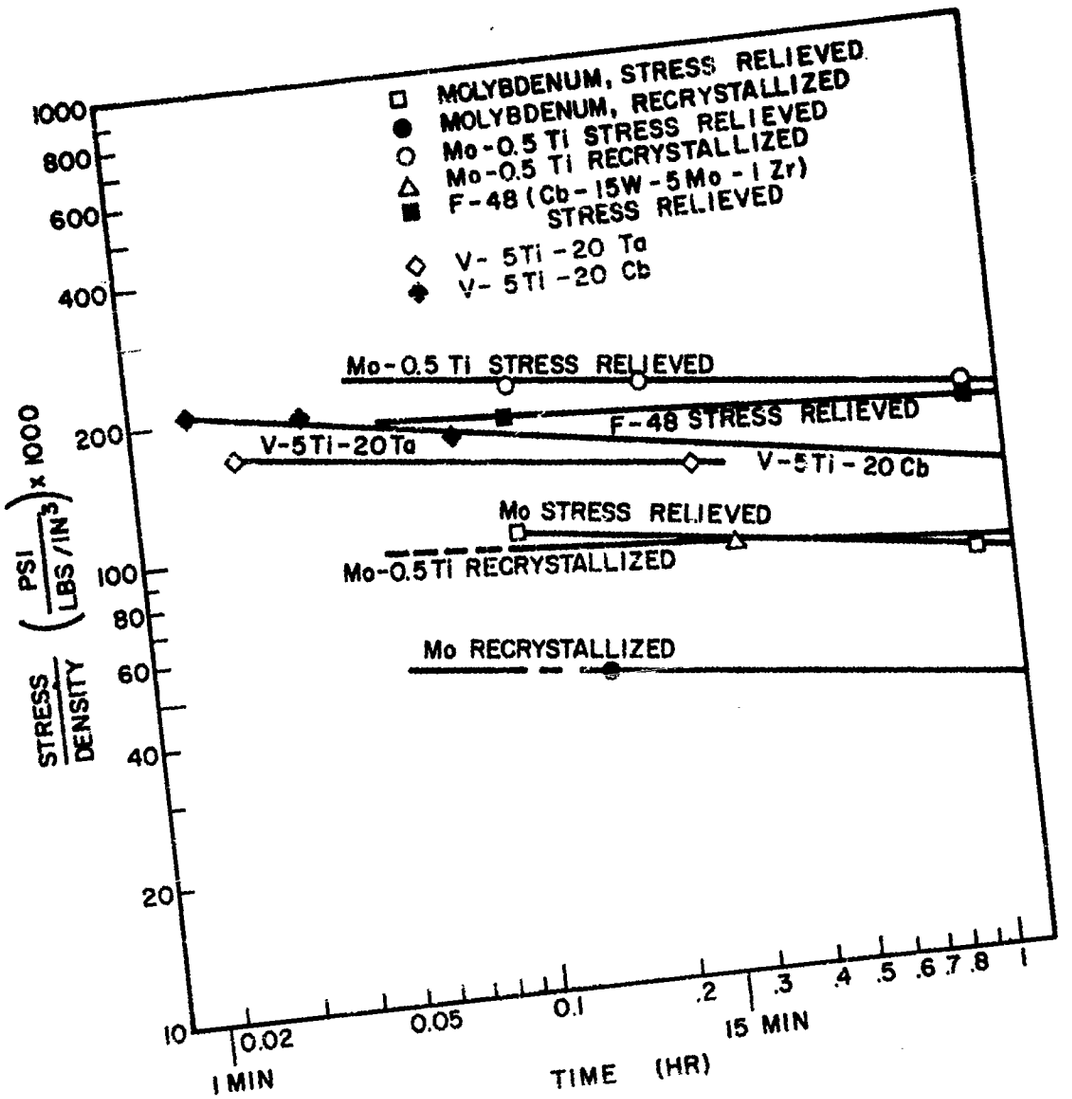

FIG. 9.14

STRESS-DENSITY VS RUPTURE TIME FOR SELECTED VANADIUM, COLUMBIUM, AND MOLYBDENUM ALLOYS AT 2000° F IN HELIUM

Table 9.10

STRESS RUPTURE DATA OF VANADIUM ALLOYS AT 2000°F IN HELIUM [4]

ALLOY ADDITION TO V-20CB BINARY (Wt percent)				1/2 HOUR HEAT TREATMENT (°F)	STRESS (psi)	TIME (hr)	ELONG. (percent)
Element							
Ti	ZR	Hf	Other				
5				2,000-WQ	46,000	0.0375	14
					40,000	0.075	18
					30,000	1.5	22
					20,000	2.1	16
					8500	4.1	20
					2500	17.8	45
5			0.25Y	2,400-WQ	20,000	1.4	22
5			0.1B	As cold rolled	20,000	1.1	44
				2,800-FQ-1 hr-2,000	20,000	1.4	22
	2		0.05C	2,800-FQ-1 hr-2,000	20,000	1.4	22
		2	0.1C	2,800-FQ-1 hr-2,000	10,000	4.1	95
		2	0.03C	2,800-FQ-1 hr-2,000	10,000	2.1	60
5			0.25C	2,800-FQ-1 hr-2,000	20,000	1.3	–
				2,800-FQ-1 hr-2,000	10,000	40.7	55
				2,800-FQ-1 hr-2,000	8000	21.7	64
				2,800-FQ-1 hr-2,000	6000	105.7	70
	2		0.1C	2,800-FQ-1 hr-2,000	20,000	0.9	19

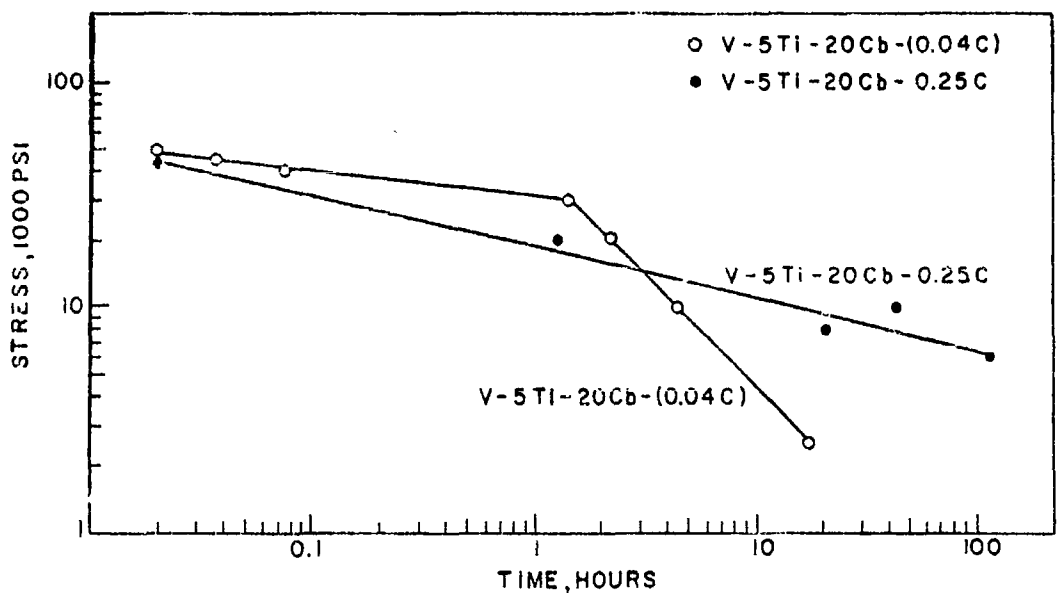

FIG. 9.15

EFFECT OF CARBON ADDITION ON THE STRESS VS RUPTURE TIME FOR V-5Ti-20Cb ALLOY AT 2000° F[4]

OXIDATION PROPERTIES

Oxidation Properties of Vanadium Alloys

The oxidation rate of the basic V-5Ti-20Cb alloy as determined by Rajala, et al.[4] is shown in Table 9-11. The oxidation resistance is not acceptable for service at the temperatures shown in the table, and coating studies have been initiated. Preliminary studies have shown promise, and work is continuing in an effort to develop coatings which will allow use of the strength properties of these fabricable alloys in ordinary atmospheres.

Table 9.11

OXIDATION DATA FOR V-5Ti-20Cb ALLOY[4]

TEMP (°F)	EXPOSURE (MIN.)	DEPTH OF SCALE (Mils/side)	DEPTH OF CONTAMINATION HARDENING* (Mils/side)	TOTAL OXIDATION (Mils/side)
1,800	15	7.5	2.0	9.5
	30	16.0	12.0	28.0
	60	22.0	26.0	48.0
1,900	15	8.0	4.0	12
	30	20	12	32
	60	24.0	28.0	52.0
2,000	15	13.5	4.0	17.5
	30	26.5	14.0	40.5
	60	30	32.0	62.0

*Depth to which hardness exceeds 250 VHN

THERMAL PROPERTIES

No additional data on the thermal properties of vanadium or its alloys have been reported in the last two years. The thermal conductivity and thermal expansion of vanadium are presented in Figs. 2.18 and 2.19, respectively, in the summary section of this report.

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