SEVENTEENTH QUARTERLY STATUS REPORT
COVERING THE PERIOD JULY 15, 1953, TO OCTOBER 31, 1953

on

A METALLURGICAL STUDY OF MOLYBDENUM

(Contract No. N9onr 82100, Task Order No. N9onr 82101) (Project NR 039-003)

to

OFFICE OF NAVAL RESEARCH
NAVY DEPARTMENT

October 31, 1953

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

Battelle Memorial Institute

505 KING AVENUE COLUMBUS 1, OHIO

April 24, 1954

Mr. J. J. Harwood
Head, Metallurgy Branch
Office of Naval Research
Washington 25, D. C.

Dear Mr. Harwood:

Contract No. N9onr 82100
Task Order No. N9onr 62101
Project No. NR 039-003

Enclosed is the Seventeenth Quarterly Status Report on research done under the above contract. This report covers the period from July 15, 1953, to October 31, 1953.

The technical achievements during this quarter are presented briefly in the summary, preceding the body of the report.

Very truly yours,

Harry B. Goodwin

HBG/NLC
Enc.

DISTRIBUTION LIST

Chief of Metallurgical Group
Aeronautical Research Laboratory
WCRRL
Wright-Patterson Air Force Base
Ohio
Attention Mr. J. B. Johnson

Metallurgical Branch
Materials Laboratory
Research Division
Wright Air Development Center
Wright-Patterson Air Force Base
Ohio
Attention Mr. I. Perlmutter

Wright Air Development Command
Wright-Patterson Air Force Base
Ohio
Attention Power Plant Laboratory

Office of Chief of Ordnance (ORDTB)
Department of the Army
The Pentagon
Washington 25, D. C.
Attention Mr. E. L. Hollady (2)

Ordnance Department
Springfield Armory
Springfield, Massachusetts
Attention Mr. H. P. Langston

Watertown Arsenal
Laboratory Division
Watertown, Massachusetts
Attention Mr. P. Kosting

Oak Ridge National Laboratory
Oak Ridge, Tennessee
Attention Metallurgical Division
Mr. W. D. Manly

Bureau of Aeronautics
Navy Department
Washington 25, D. C.
Attention Mr. N. E. Promisel
AE-41 (Room 1W68)

Bureau of Aeronautics
Navy Department
Washington 25, D. C.
Attention Technical Library, TD-41

Commanding Officer
Naval Air Materiel Center
Naval Base Station
Philadelphia, Pennsylvania
Attention Aeronautical Materials Lab.

Chief, Bureau of Ordnance
Navy Department
Washington 25, D. C.
Attention Re5

Bureau of Ordnance
Navy Department
Washington 25, D. C.
Attention Re9a (John S. Nachtman)

Officer in Charge
Office of Naval Research
Navy No. 100
Fleet Post Office
New York, New York (2)

Director
Office of Naval Research, Branch Office
The John Crerar Library Building
Tenth Floor, 86 E. Randolph St.
Chicago 1, Illinois
Attention Mr. J. A. Bryson (2)

Chief of Naval Research
Department of the Navy
Washington 25, D. C.
Attention Code 423 (2)

Director, Naval Research Laboratory
Washington 25, D. C.
Attention Code 3500, Metallurgy
Division

DISTRIBUTION LIST
(Continued)

Director, Naval Research Laboratory
Washington 25, D. C.
Attention Code 2020, Technical Library

Director, Naval Research Laboratory
Washington 25, D. C.
Attention Dr. O. T. Marzke

Metallurgical Process Branch
(Code 343)
Bureau of Ships
Navy Department
Washington 25, D. C.

Navy Liaison Officer for Guided Missiles
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

ONR London, c/o Fleet P. O.
Navy 100, New York, New York
For transmittal to
Armament Research Establishment
Metallurgical Branch
Ministry of Supply
Woolwich S. E. 18, England

Commander NAMTC
Pt. Mugu, California
Attention Engineering Department

Bethlehem Steel Company
Bethlehem, Pennsylvania
Attention Dr. John Marsh

British Joint Service Mission
P. O. Box 165
Ben Franklin Station
Washington D. C.
Attention Navy Staff (3)

Bureau of Mines
Albany, Oregon
Attention Dr. S. M. Shelton

National Bureau of Standards
Washington 25, D. C.
Attention Dr. A. Brenner
Chemistry Division

California Institute of Technology
Pasadena 4, California
Attention Professor Pol Duwez
Department of Metallurgy

Climax Molybdenum Corporation
500 Fifth Avenue
New York 18, New York
Attention Mr. Carl M. Loeb, Jr.
Vice President

Climax Molybdenum Corporation of Michigan
14410 Woodrow Wilson Avenue
Detroit 3, Michigan
Attention Mr. A. J. Herzig

Fansteel Metallurgy Company
North Chicago, Illinois
Attention Dr. L. F. Yntema
Director of Research

General Electric Research Laboratory at the Knolls
Schenectady, New York
Attention Mr. R. M. Parke (2)

Johns Hopkins University
Baltimore 18, Maryland
Attention Prof. R. B. Pond
Dept. of Mechanical Engineering

Massachusetts Institute of Technology
Department of Metallurgy
Cambridge 39, Massachusetts
Attention Professor John Wulff

DISTRIBUTION LIST
(Continued)

National Advisory Committee for Aeronautics
Lewis Flight Propulsion Laboratory
Cleveland, Ohio

National Advisory Committee for Aeronautics
1724 F Street, N. W.
Washington 25, D. C.

Chief, Office of Aeronautical Intelligence
National Advisory Committee for Aeronautics
Washington 25, D. C.
Attention Mr. Eugene B. Jackson

Ohio State University
Department of Metallurgy
Columbus 10, Ohio
Attention Dr. Rudolph Speiser

Westinghouse Research Laboratories
Metallurgical Department
East Pittsburgh, Pennsylvania
Attention Mr. Howard Scott
Manager, Metallurgical and Ceramic Department

Mr. R. M. Sawyer
Bureau of Ordnance (Re5e)
Department of the Navy
Washington 25, D. C.

Mr. W. W. Dyrkacz
Assoc. Director of Research
Allegheny Ludlum Steel Co.
Watervliet, New York

Mr. James D. Nisbet
Director of Research
Universal Cyclops Steel Corp.
Bridgeville, Pennsylvania

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

SEVENTEENTH QUARTERLY STATUS REPORT
COVERING THE PERIOD JULY 15, 1953, TO OCTOBER 31, 1953

on

A METALLURGICAL STUDY OF MOLYBDENUM
(Contract No. N9onr 82100, Task Order No. N9onr 82101)
(Project NR 039-003)

to

OFFICE OF NAVAL RESEARCH
NAVY DEPARTMENT

from

BATTELLE MEMORIAL INSTITUTE

October 31, 1953

SUMMARY

(H. B. Goodwin)

Further work has been done to determine the validity of the bend test as a means of measuring the ductility of molybdenum. The amount of scatter to be expected in bend test data at a given testing temperature was determined over a wide range of testing temperatures for commercial arc-cast molybdenum tested as follows:

(1) As-rolled, unnotched specimens taken transverse to the rolling direction

(2) As-rolled, unnotched specimens taken parallel to the rolling direction

(3) Recrystallized, unnotched specimens taken transverse to the rolling direction

(4) Recrystallized, unnotched specimens taken parallel to the rolling direction

(5) As-rolled, notched specimens taken transverse to the rolling direction

(6) As-rolled, notched specimens taken parallel to the rolling direction

Bend tests under Condition (1) were made at several different strain rates. In the previous report, similar tests on cast molybdenum were discussed. It was concluded there that the bend test gave reproducible ductility measurements, which could be used to compare experimental materials.

An attempt was made to prepare a maximum-purity molybdenum ingot larger than those prepared in the past by arc melting with direct current in low-pressure hydrogen. Fractographic examination showed that the ingot was less pure than small high-purity ingots made in the past.

Molybdenum which was arc melted in vacuum directly from powder, without the addition of carbon, proved less satisfactory than sintered molybdenum for use as a starting material for preparing high-purity ingots.

Further work has confirmed the inverse relationship between ductility and nitrogen content of cast molybdenum reported in the Sixteenth Quarterly Status Report.

A detailed fractographic study has been completed on all ingots to which carbon, nitrogen, and oxygen were added deliberately to study the effects of these elements on the room-temperature ductility of cast molybdenum. The ductility tests were reported in the previous report. It is now believed that carbides, nitrides, and oxides can be identified by means of the fractographic technique, and distinguished from one another, in most cases.

The effectiveness of additions of 0.5 to 1.0 per cent titanium in improving the room-temperature ductility of molybdenum has been confirmed by additional work. With titanium contents higher or lower than this range, the ductility was less.

Further study has been made of the "solid-state purification" process by which the nitrogen and oxygen contents of molybdenum are reduced to very low values by heating the metal in vacuum. It now appears that the usually beneficial effects of the treatment on ductility result not only from simple purification, but from a heat-treating effect as well. Different materials with the same final analyses can have very different ductilities, depending on the heating cycle used for the solid-state-purification treatment. Brittle samples can be made ductile and ductile samples made brittle by heat treatment alone, without measurable compositional changes.

STATISTICAL STUDY OF THE BEND TEST

(L. E. Olds and R. B. Fischer)

INTRODUCTION

As reported in the Sixteenth Quarterly Status Report (pages 6 to 11), the results of a large number of bend tests on commercial cast molybdenum were analyzed statistically. The purpose was to evaluate the validity of the bend test as a means of measuring ductility and to determine the scatter in bend data normally to be expected at each testing temperature.

This study indicated that, to compare the ductilities of various samples of cast molybdenum by the bend-test method used throughout this research program, it was desirable to define the transition temperature as the highest temperature at which a 2-degree bend (at fracture) is never exceeded. Transition temperatures so determined are "comparative" only, and have no engineering usefulness for design purposes. However, the determination of bend transition temperatures provides a good laboratory method for measuring the progress of the research to improve the ductility of cast molybdenum.

As noted in the previous report, it had been planned to extend the statistical study to wrought and wrought-and-recrystallized commercial molybdenum, as well as cast molybdenum. This has now been done.

Experimental Work

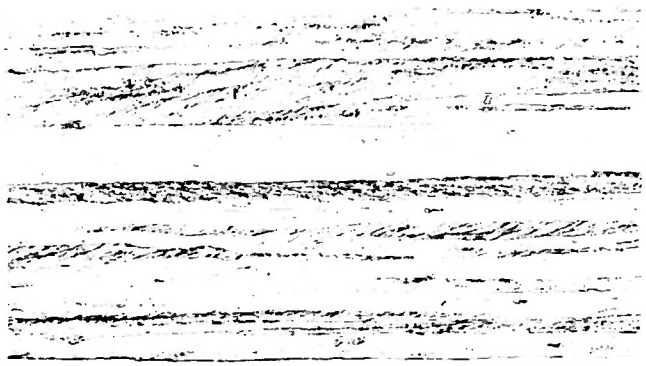
Climax arc-cast molybdenum that had been fabricated into plate was used for this study. This plate originated from Climax Heat 4-1188, which, as cast, contained 0.018 per cent carbon. The cast ingot had been given the following treatment prior to being sent to Battelle:

	Diameter, inches	Thickness, inches	Reduction in Thickness, per cent	Total Reduction in Thickness, per cent
As cast	7.5	--	--	--
Machined	6.5	--	--	--
Extruded at 2300 F	3.75	--	67	67
Machined	3.5	--	--	--
Forged at 2400 F		1.25	64	80
Recrystaliized, 1 hour at 2600 F	--	--	--	--
Rolled	--	0.21	83	97

The plate had been rolled in one direction only and its final dimensions were 0.21 inch in thickness by 5 inches in width.

At Battelle, the plate was stress relieved at 1200 F for 20 minutes prior to being machined into the standard bend-test specimens* used throughout the present research.

The microstructure of the stress-relieved fibered plate is shown in Figure 1. In addition to the fibered grains of molybdenum, a number of elongated inclusions of molybdenum carbide are present in the microstructure.



100X N10999

20 Minutes at 1200 F

FIGURE 1. MICROSTRUCTURE OF STRESS-RELIEVED CLIMAX PLATE

Etched in Murakami's Etchant

An extensive series of bend tests was made on specimens with a grain orientation such that the long axes of the elongated grains were transverse to the long axis of the specimen. In these tests, a very ductile specimen was considered to be one which bent 90 degrees without failure**, whereas a brittle specimen was considered to be one which fractured with no permanent bend. The bend angles were measured by fitting the broken specimens together and visually comparing the angle of bend with angles which were carefully drawn on paper.

Ten specimens were bent at each testing temperature, the temperature interval being 20 C for the temperature range of -60 C to +20 C, and 40 C for the temperature range of 20 C to 300 C. For this test, the deflection rate of the platen was 1 inch per minute. This deflection rate corresponds to a strain rate of about 0.038 in./in./sec in the outer fibers of the test specimen. The results of the tests are given in Table 1 at the end of this section, and graphs of the data are shown in Figures 3 and 5c.

*0.150 inch thick by 0.250 inch wide by 1 inch long. Length between supports: 0.625 inch.

**The largest bend angle that could be attained with the test jig was approximately 90°.

After the above tests were completed for transverse-grain-fibered specimens, a less extensive series of tests was made to investigate the effect of each of the following variables on the distribution of bend data at various testing temperatures:

(1) Type of microstructure, fibered or recrystallized

(2) Presence or absence of artificial notches in the specimens

(3) Grain orientation in fibered, recrystallized, and notched specimens

(4) Strain rate.

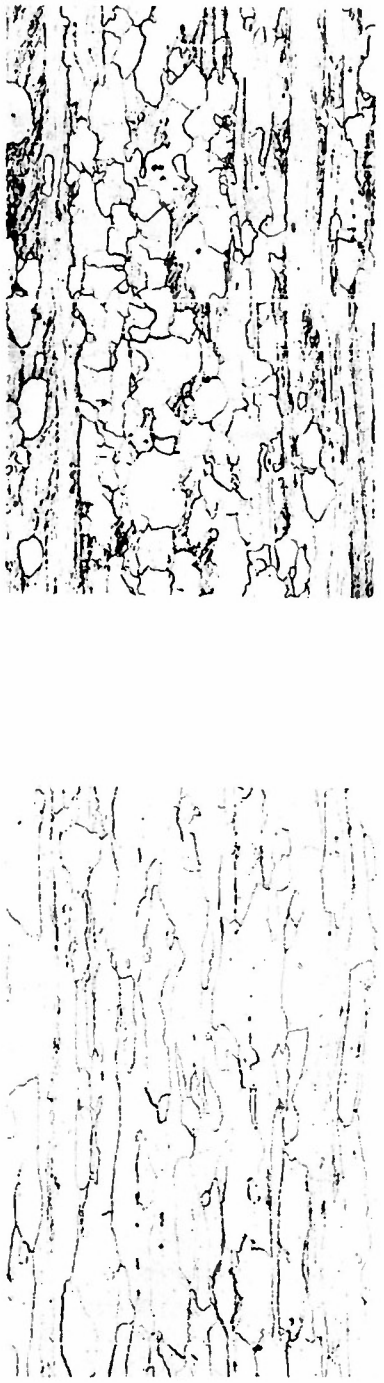
Effect of Recrystallizing the Fibered Microstructure

To determine the effect of recrystallization on the distribution of bend data, a piece of the same plate as used for the above tests was recrystallized by an annealing treatment.

To determine the annealing treatment that would produce the desired fine, uniformly recrystallized microstructure, a series of trial heat treatments was made. Test coupons were heated in vacuum at 2400 F for 5, 10, 15, and 20 minutes and at 2700 F for 10, 20, 30, 60, 120, and 180 minutes. Photomicrographs of some of these specimens are shown in Figure 2. From these photomicrographs, it may be seen that recrystallization initiated during the heat treatment of 5 minutes at 2400 F, but that complete recrystallization was not obtained until 2 hours at 2700 F. Such a lengthy heat treatment was not anticipated in view of the findings of Bechtold* that fabricated arc-cast molybdenum with 59 per cent cold reduction in area would be expected to be completely recrystallized after approximately a 3-minute heat treatment at 2400 F. Since Bechtold's work was done on molybdenum that had been heat treated in a hydrogen atmosphere, whereas the present heat treatments were made in vacuum, it appears that furnace atmosphere may have an important influence on the recrystallization behavior of molybdenum. Another possibility is that there were some differences between the metal studied by Bechtold and that used in this study that would account for the difference in findings.

For the present investigation, a recrystallization heat treatment of 2 hours at 2700 F was chosen in order to insure complete recrystallization. The microstructure of the molybdenum after this heat treatment is shown in Figure 2d.

*Bechtold, James H., "Recrystallization Data Applied to Control of Mechanical Properties of Molybdenum", ASM Preprint No. 15 (1953).



100X a. 5 min at 2400 F N11000

100X b. 15 min at 2400 F N11001

100X c. 1 hour at 2700 F N11002

100X d. 2 hours at 2700 F N11003

Etched in Murakami's etchant

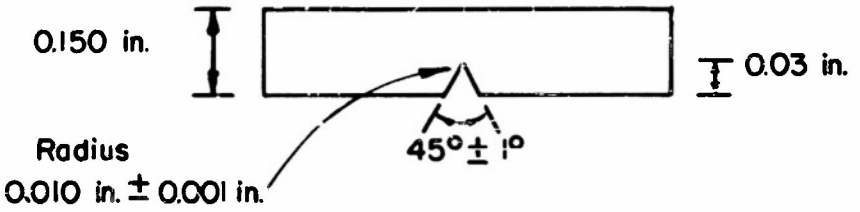
FIGURE 2. MICROSTRUCTURES OF ANNEALED CLIMAX PLATE

Bend-test specimens were cut from the recrystallized plate so that the long axes of the specimens were transverse to the rolling direction. The tests were made at temperature intervals of 25 C, and four specimens were tested at each temperature. The strain rate used in all the tests was about 0.038 in./in./sec. The results of these tests are given in Table 1 and Figure 5a.

Response of Molybdenum to Artificial Notches

The brittle behavior of commercial molybdenum may be the result of a phase in the microstructure of the metal which serves to concentrate applied stresses so that the fracture strength of the metal is exceeded locally. If such a stress raiser is naturally present in commercial molybdenum, the addition of an artificial notch would not be expected to have as great an effect on the distribution of bend data as it otherwise would.

To investigate the effect of artificial notches on bend ductility, specimens with a transverse grain orientation were tested after being notched as shown below.



This is the standard Izod-type V-notch, except for the notch depth. However, the ratio of notch depth to thickness of the specimens is the same as for the standard Izod specimens.

Test specimens were bent at temperature intervals of 50 C. Two specimens were bent at each temperature at strain rates of about 0.038 in./in./sec. The results of the tests are given in Table 1 and Figure 5c.

Effect of Grain Orientation

All of the tests described above were made on specimens cut from the plate transverse to the rolling direction. To determine the effect of grain orientation on the distribution of bend data, the tests on fibered, recrystallized, and notched molybdenum were repeated on specimens with

a grain orientation longitudinal to the specimen axis. (Specimen axes were parallel to the rolling direction.) The data for these tests are given in Table 1 and Figures 5b, 5d, and 5f.

Effect of Strain Rate

Fibered specimens with a transverse grain orientation were tested at different deflection rates in order to determine the effects of decreasing the strain rate. The deflection rates and the corresponding strain rates studied were as follows:

Platen Deflection Rate, in./min	Corresponding Strain Rate in Outer Fibers of Specimen, in./in./sec
1	0.038 (approx.)
0.1	0.0038 (approx.)
0.01	0.00038 (approx.)

For these tests, three specimens were tested at each temperature. The temperature interval was the same as that used in the tests for unnotched transverse-grain-fibered specimens, 20 C for the temperature range of -60 C to +20 C, and 40 C for the temperature range of 20 C to 140 C. Several additional specimens were tested at critical temperatures. The results of the tests are given in Table 1 and a graphical comparison of the effect of varying strain rate on the transition-temperature curve is shown in Figure 6.

Discussion

Selection of Criterion for Evaluating Transition Temperatures

All bend data for unnotched transverse-fibered molybdenum are plotted in Figure 3. Since ten specimens were tested at each temperature interval, it is felt that the curves in this figure represent approximately the limits of bend-data scatter in the transition zone. The distribution of bend data is quite similar to the distribution obtained from impact or tensile tests when testing metals over a temperature range in which a ductile-to-brittle transition occurs.

As was the case with cast molybdenum (page 9, Sixteenth Quarterly Status Report), several distinct zones of ductility may be noted from the graph of Figure 3. Zone 1 is a region of zero ductility, where all specimens would be expected to fracture without bending. Zone 2 is a region of low ductility, where minor amounts of bending often occur prior to fracture.

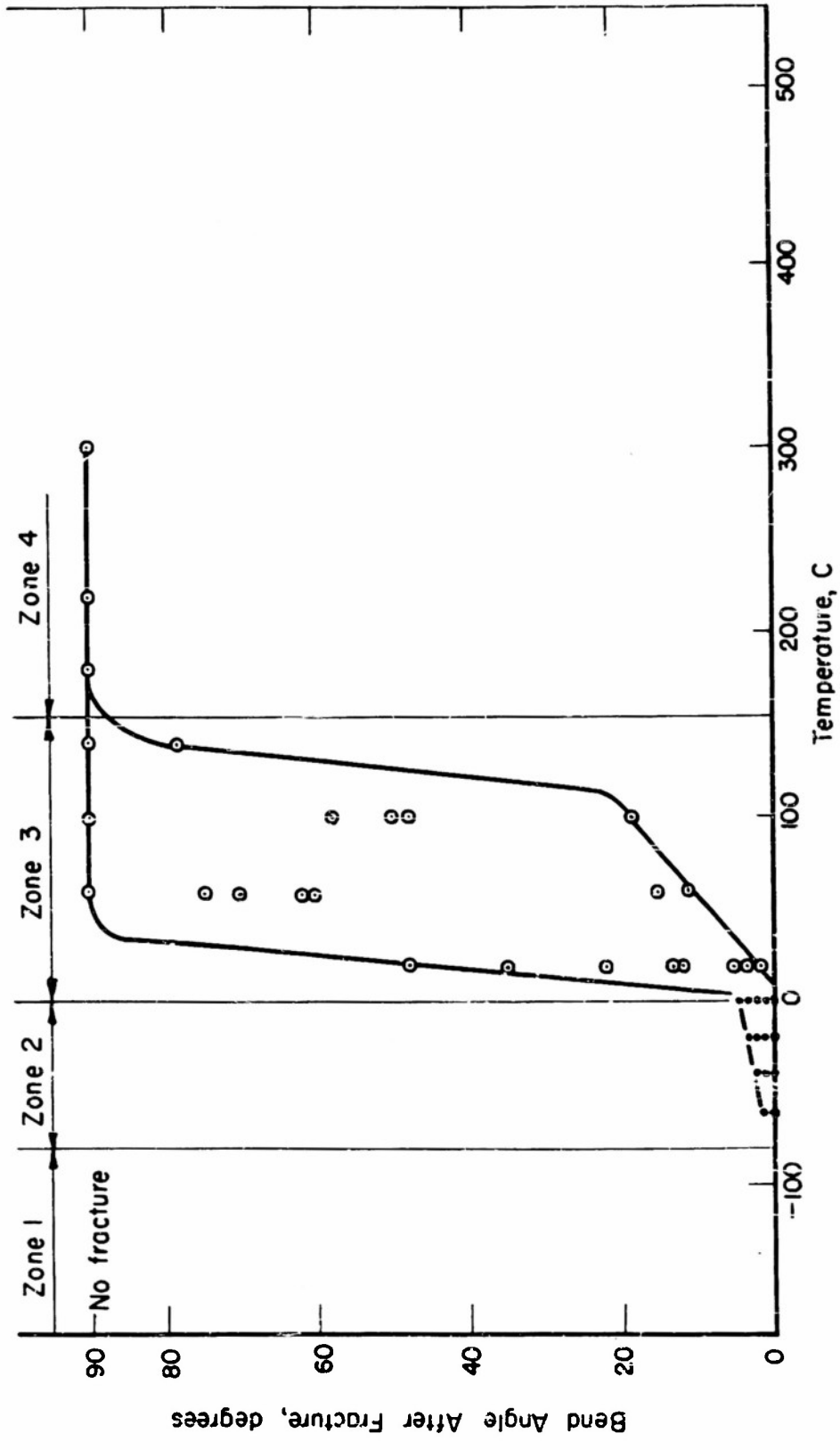


FIGURE 3. BEND-TEST DATA FOR FIBERED--MOLYBDENUM SPECIMENS WITH TRANSVERSE GRAIN ORIENTATION

Strain rate: 0.038 in./in./sec
Climax Heat No. 4-1188
0.018 per cent carbon

A-10165

Zone 3, the transition zone, in which a specimen may behave in either a brittle or a ductile manner, covers a wider temperature range than is usual when impact or tensile tests are used. Zone 4 is a region of completely ductile behavior, where all specimens would be expected to bend at least 90 degrees before fracture.

The selection of a proper criterion of ductility depends upon whether it is desired to compare experimental materials or to qualify a material for engineering usefulness. A criterion for comparing the ductilities of experimental materials should be well defined and should be capable of being easily determined, whereas the criterion for engineering usefulness of a material must insure that the material will have adequate ductility for the intended use.

For the comparison of various experimental materials, it appears to be most satisfactory to take the temperature of the "instep" in the upper curves of Figure 3 as the measure of ductility. This curve shows the maximum bend angle that can be expected at a given temperature. This "instep" appears to be rather definite, and it can be determined approximately with a limited number of specimens. From Figure 3, it may be seen that the "instep" occurs at the highest temperature at which a 4-degree bend angle was never exceeded. Although, in the Sixteenth Quarterly Status Report, a 2-degree bend angle was proposed as the criterion by which to evaluate the "instep" for cast molybdenum, it is now felt that 4-degrees is a more satisfactory criterion.

If sufficient data are available, it is possible to plot the probability of exceeding a given bend angle against the testing temperature. Such a plot for cast molybdenum was presented on page 11 of the Sixteenth Quarterly Status Report. The bend-test data for transverse-fibered, unnotched molybdenum have been analyzed in this manner and a graph of the probabilities of exceeding a bend angle of 0, 2, 4, 6, 30, or 90 degrees is shown in Figure 4. It may be seen from this figure that, for this particular material, the specimens must be at or above 140 C to insure that all specimens tested will bend through an angle of at least 30 degrees before fracturing. This temperature, although probably fairly accurate, undoubtedly would have to be modified slightly if more tests were made.

An insufficient number of tests were made with other types of specimens to allow approximate probability curves to be drawn.

Effects of Various Treatments on the Ductility of Molybdenum

The data from the various tests are compared graphically in Figures 5 and 6. In Figure 5c, the solid-line curves represent the outer limits of scatter in the bend data. These have been drawn as solid lines since it is felt that enough specimens were tested to locate the limits with reasonable certainty. For the other test series, only two to four specimens were tested

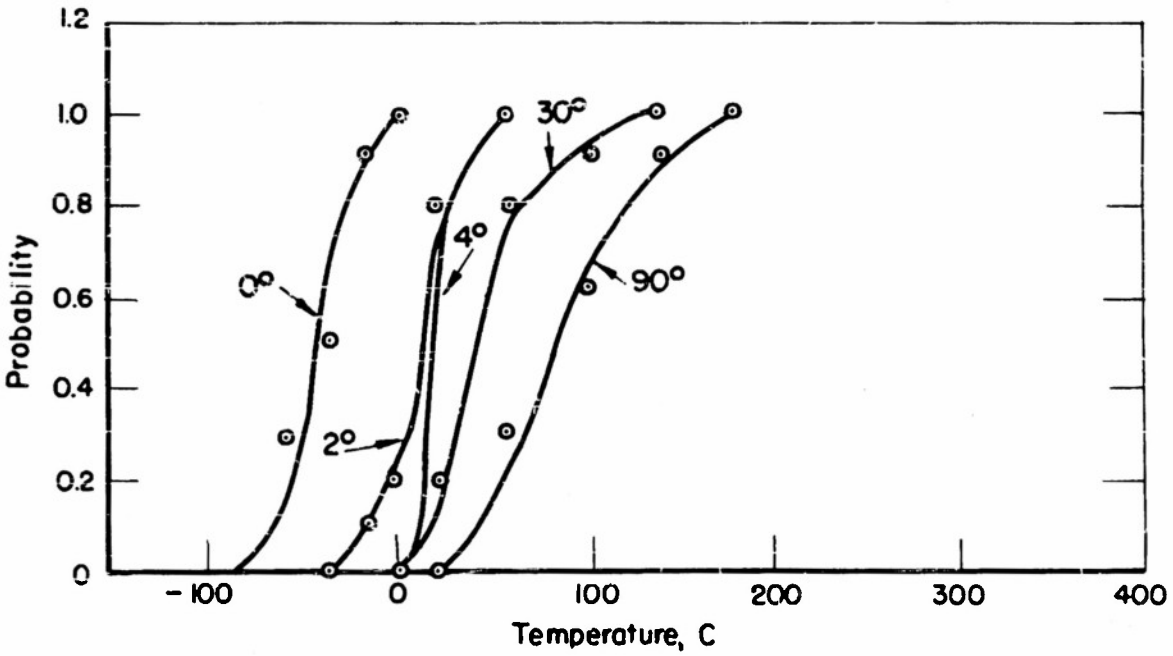


FIGURE 4. GRAPH OF PROBABILITY OF EXCEEDING A PARTICULAR BEND ANGLE AS A FUNCTION OF TEMPERATURE

Climax wrought molybdenum
0.018 per cent carbon

A-10166

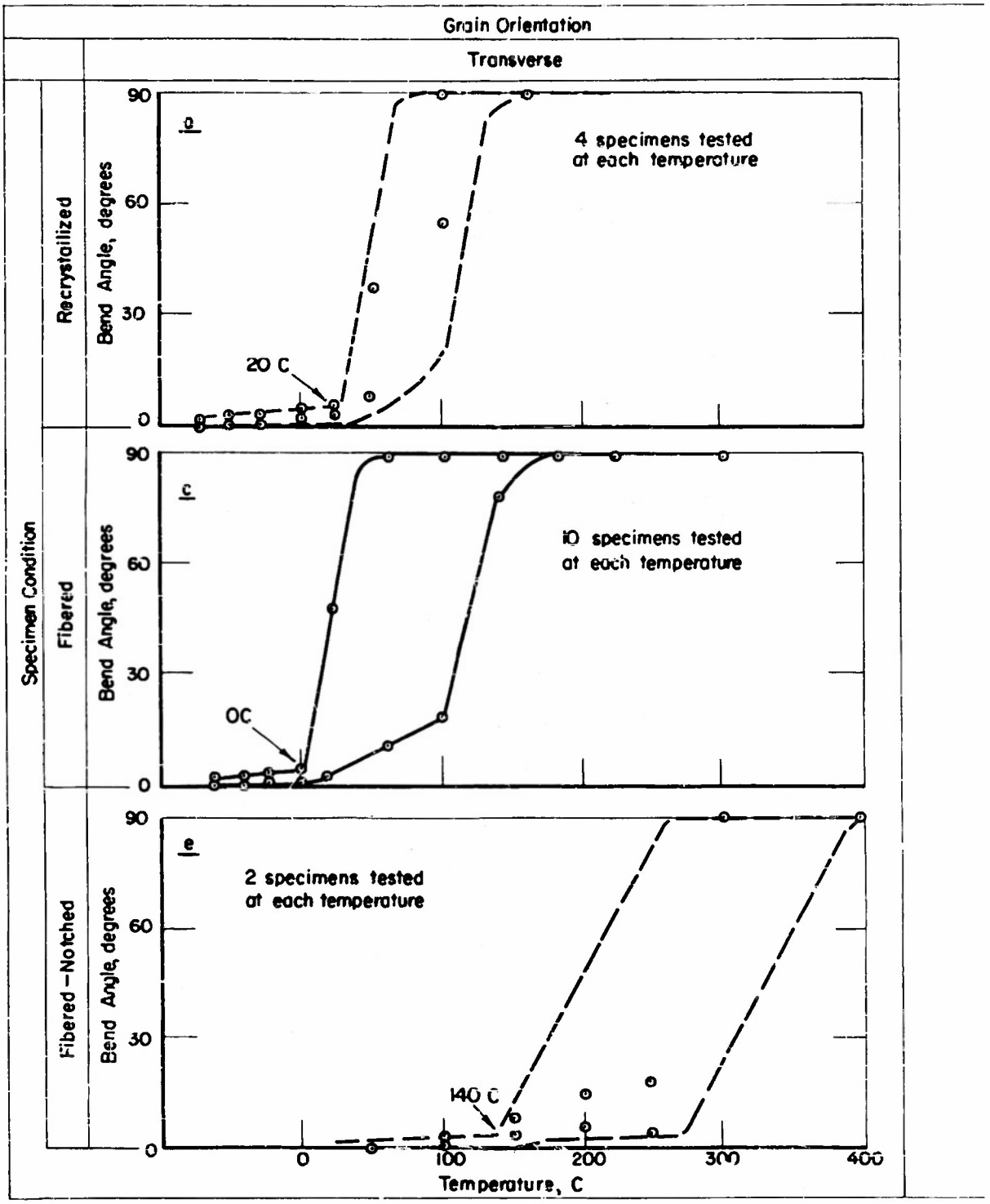


FIGURE 5. BEND-TEST TRANSITION-TEMPERATURE CURVES FOR WROUGHT MOLYBDENUM, ARC CAST
Strain rate: 0.038 in./in./sec
0.018 per cent carbon

A-10167

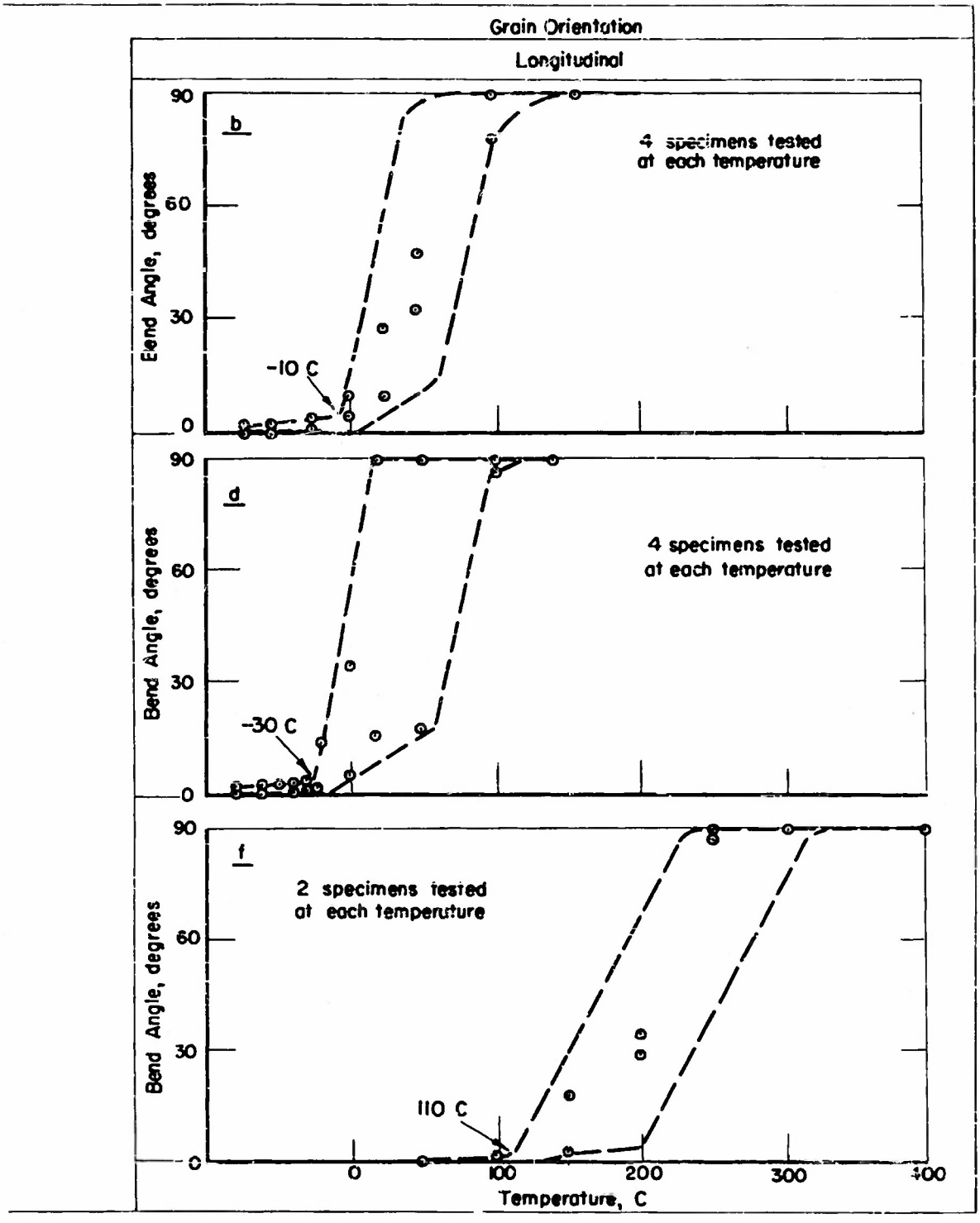


FIGURE 5. (CONTINUED)

A-10188

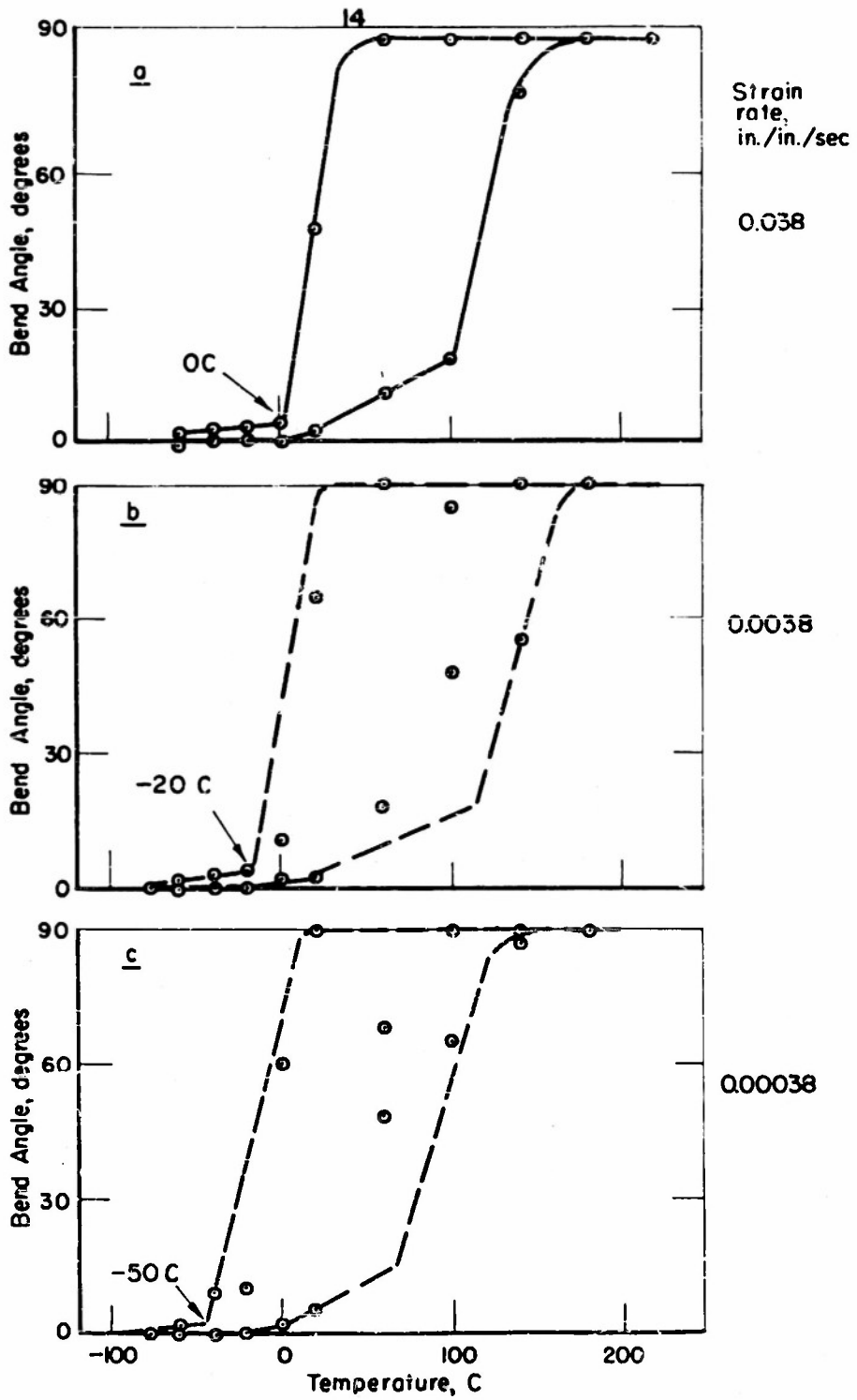


FIGURE 6. EFFECT OF STRAIN RATE ON BEND-TEST TRANSITION TEMPERATURES OF WROUGHT MOLYBDENUM, ARC CAST, FIBERED

C-10169

at each temperature; hence, the curves have been drawn as dotted lines to indicate that there is some uncertainty as to the limits.

From Figures 5 and 6, it is possible to compare the results of the tests on recrystallized molybdenum, unnotched fibered molybdenum, and notched fibered molybdenum, with both transverse and longitudinal grain orientations.

On the basis of the "insteps" in the curves of maximum bend angle plotted against test temperature, the following transition temperatures were obtained:

Material and Test Conditions	Strain Rate, in./in./sec	Transition Temperature, C	
		Transverse Grain Orientation	Longitudinal Grain Orientation
Recrystallized	0.038	20	-10
Fibered, unnotched	0.038	0	-30
Fibered, notched	0.038	140	110
Fibered, unnotched	0.038	0	--
Ditto	0.0038	-20	--
"	0.00038	-50	--
Cast (see preceding report)	0.038	80	--

These data support the following conclusions:

(1) Complete recrystallization of molybdenum (2 hours at 2700 F in vacuum) causes a small loss in ductility; the transition temperature is raised approximately 20 C for both transverse and longitudinal orientations.

(2) A notch of the geometry described in an earlier paragraph severely embrittles wrought molybdenum, since the transition temperature of the notched, fibered plate was approximately 140 C higher than that of unnotched fibered molybdenum. This was true both for the transverse and for the longitudinal grain orientations.

(3) The effect of grain orientation on the transition temperature is measurable. In every case, the transition temperatures for specimens with longitudinal grain orientation were 30 C lower than those for specimens with transverse grain orientation.

(4) A decrease in strain rate lowers the transition temperature of fibered molybdenum appreciably.

Further comparisons may be made between transverse unnotched fibered molybdenum and cast molybdenum, and between transverse notched fibered molybdenum and cast molybdenum.

A plot of the bend-test data on commercial cast molybdenum was shown on page 9 of the Sixteenth Quarterly Status Report. By comparing the curves of maximum and minimum bend angles versus test temperature for cast molybdenum with the similar curve for wrought fibered molybdenum (Figure 3 in the present report), it can be seen that the corresponding curves differ in shape. The maximum-bend-angle curve for wrought molybdenum rises sharply in the transition zone, whereas the curve for cast molybdenum does not show such a steep slope. The transition zone of wrought molybdenum is not so wide as the transition zone for the cast metal.

A sufficient number of specimens were tested for both types of molybdenum to allow approximate probability curves to be drawn. Although the present study is not intended to provide data useful for engineering-design purposes, it is interesting to note from the probability curves the temperatures at which these two materials begin to exhibit a degree of ductility that might be reasonable for useful applications. For example, the lowest temperatures above which specimens can always be expected to bend 30 degrees or more (approximately 8 to 10 per cent elongation in the outer fibers) would be as follows:

Cast commercial molybdenum	460 C
Transverse-fibered commercial molybdenum	140 C

The above temperatures might be changed slightly if more specimens were tested.

It is instructive to compare the results of the tests on notched fibered molybdenum with the results of the tests on unnotched cast molybdenum. Although only two specimens of the notched fibered molybdenum were tested for each temperature interval, it is believed that the curves in Figure 5e represent the approximate limits of scatter for this material. By comparing the curves in Figure 5e with the curves for cast molybdenum on page 9 of the Sixteenth Quarterly Status Report, it can be seen that the corresponding curves have approximately the same general shape. The similarity suggests that commercial carbon-deoxidized cast molybdenum may contain microconstituents which act as stress raisers in the same way as does an external notch. As pointed out on page 44 of the Fifteenth Quarterly Status Report, carbide particles at the grain boundaries of cast molybdenum often have such sharp geometric shapes that they might well act as stress raisers. It is possible that the low-temperature ductility of cast molybdenum would be enhanced considerably if these carbide particles were eliminated.

For unnotched wrought molybdenum, the curves of maximum bend angle versus test temperature are quite different in general shape than those for notched metal. In this respect, wrought molybdenum in both the fibered and the recrystallized conditions does not behave as though it were internally notched. This behavior may be the result of better distribution and shape of the carbide particles in the microstructures of these two types of molybdenum.

Conclusions. The results of the statistical study prove that the bend test is capable of showing real differences in ductility among various materials. The transition temperature must be carefully defined, of course. For the purposes of comparing one material with another, the temperature at which the instep of the curve of maximum bend angle versus test temperature occurs appears to be the most desirable temperature to use.

Future Work

The bend specimens from the various types of molybdenum used in this study will be examined to determine the mode and type of fracture that occurred. No other work is planned at present.

Data from which this section of the report was prepared are recorded in BMI Laboratory Record Book No. 7902, pages 43 to 44, 66 to 71, and 92 to 100; and Record Book No. 8573, pages 11 to 13.

TABLE 1. BEND-TEST DATA FOR MOLYBDENUM PLATE

Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees
Unnotched, Stress-Relieved, Specimen Orientation Transverse to Rolling Direction, 0.038-In./In./Sec Strain Rate								
-60	1		20	48		180	90	
	1			35			90	
	1			22			90	
	0			13			90	
	0			12			90	
	0			5			90	
	0			5			90	
	0			3			90	
	0			2			90	
	0			2			90	
		0.3			15			90
-40	2		60	90		220	90	
	1			90			90	
	1			90			90	
	1			75			90	
	1			70			90	
	0			62			90	
	0			60			90	
	0			60			90	
	0			15			90	
	0			11			90	
		0.6			62			90
-20	3		100	90		300	90	
	2			90			90	
	2			90			90	
	2			90			90	
	2			90			90	
	1			90			90	
	1			58			90	
	1			50			90	
	1			48			90	
	0			18			90	
		1.5			71.4			90
0	4		140	90				
	3			90				
	2			90				
	2			90				
	2			90				
	2			90				
	1			90				
	1			90				
	1			90				
	0	1.8		78	88.8			

TABLE 1. (Continued)

Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees
	Unnotched, Stress-Relieved, Specimen Orientation Transverse to Rolling Direction, 0.0038-In./In./Sec Strain Rate							
-77	0		0	11		100	85	
	0			2			48	
	0			2			48	
		0			5			60
-60	1		20	65		140	90	
	0			40			81	
	0			35			55	
		0.3		4				74
-40	1			2		180	90	
	1				29		90	
	0		60	90			90	
		0.7		81				90
-20	4			52				
	3			32				
	3			18				
	2				55			
	1							
	0							
		1.3						
	Unnotched, Stress-Relieved, Specimen Orientation Transverse to Rolling Direction, 0.00038-In./In./Sec Strain Rate							
-77	0		0	60		100	90	
	0			38			65	
	0			36			65	
		0		35				73
-60	1			28		140	90	
	0			2			90	
	0				33		88	
		0.3	20	90				89.3
-40	9			90		180	90	
	3			70			90	
	2			38			90	
	1			17				90
	0			6				
	0				52			
		2.5	60	68				
-20	10			62				
	4			48				
	2				59			
	2							
	2							
	0							
		3						

TABLE 1. (Continued)

Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees
			Unnotched, Stress-Relieved, Specimen Orientation Longitudinal to Rolling Direction, 0.038-In./In./Sec Strain Rate					
-78	2		-30	3		50	90	
	1			3			90	
	0			2			90	
	0			2			18	
		0.75			2.5			72
-60	2		-20	14		100	90	
	1			4			90	
	1			4			90	
	1			2			88	
		1.25			6			89.5
-50	2		0	35		140	90	
	2			7			90	
	2			6			90	
	2			5			90	
		2			14			90
-40	3		20	90				
	3			70				
	3			42				
	2			16				
	2				54			
	2							
	1							
		2.25						
			Unnotched, Recrystallized, Specimen Orientation Transverse to Rolling Direction, 0.038-In./In./Sec Strain Rate					
-75	1		0	4		100	90	
	1			4			90	
	0			4			80	
	0			2			55	
		0.5			3.5			79
-50	3		25	6		160	90	
	2			6			90	
	1			4			90	
	0			4			90	
		1.5			5			90
-25	3		50	38				
	2			28				
	2			22				
	2			8				
	1				24			
	1							
		2						

TABLE 1. (Continued)

Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees
			Unnotched, Recrystallized, Specimen Orientation Longitudinal to Rolling Direction, 0.038-In./In./Sec Strain Rate					
-75	2		0	10		100	80	
	1			10			90	
	0			6			90	
	0			4			78	
		0.75			7.5			87
-50	2		25	28		160	90	
	2			25			90	
	2			12			90	
	1			10			90	
		1.75			19			90
-25	6		50	48				
	4			38				
	4			38				
	4			32				
	4				39			
	2							
		4						
			Notched, Stress-Relieved, Specimen Orientation Transverse to Rolling Direction, 0.038-In./In./Sec Strain Rate					
50	0		250	18				
				6				
				6				
				4				
100	0				8.5			
	4		300	90				
		2.5		90				
					90			
150	4							
	8		400	90				
		5		90				
					90			
200	15							
	6							
		10.5						

TABLE 1. (Continued)

Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees	Temperature, C	Bend Angle, degrees	Average Bend Angle, degrees
Notched, Stress-Relieved, Specimen Orientation Longitudinal to Rolling Direction, 0.038-In./In./Sec Strain Rate								
50	0		250	90				
	0			88				
		0			89			
100	2		300	90				
	2			90				
		2			90			
150	18		400	90				
	4			90				
		11			90			
200	35							
	30							
		32.5						

STUDY OF HIGH-PURITY MOLYBDENUM PREPARED BY VACUUM FUSION

(G. W. P. Rengstorff, L. E. Olds, R. B. Fischer, and H. W. Lownie, Jr.)

Introduction

The preparation of molybdenum of the highest possible purity was undertaken originally with the following objectives in mind:

(1) To determine whether useful ductility in the cast and welded conditions could be achieved through purification

(2) To provide very pure molybdenum to which controlled amounts of impurities could be added individually during arc melting to determine their specific effects on the ductility of cast molybdenum

(3) To provide material that could be used to determine whether very pure molybdenum is embrittled by recrystallization in the same way as molybdenum of commercial purity.

The first two objectives have been essentially achieved. Work on the third is still in progress. For this work, larger quantities of high-purity molybdenum than were needed previously are desired because the ductility must be determined as cast, after fabrication, and after recrystallization at several different times and temperatures. Work has been carried on concurrently on (a) simplification of the multiple vacuum-melting process of preparing high-purity ingots, and (b) preparation of high-purity ingots larger than those that have been available heretofore.

Simplification of the Method for Preparing High-Purity-Molybdenum Ingots

The purification of molybdenum has been achieved by multiple melting in vacuum, by means of semi-inert, water-cooled electrodes. However, as pointed out in the Sixteenth Quarterly Status Report, page 18, the method is slow, because only about 2 pounds can be melted in the first melt, and only 1 pound on successive melts*. It was thought that the total number of melts necessary to prepare a given quantity of high-purity molybdenum might be

*The factor which limits the amount of molybdenum that can be melted at one time is the life of the electrode tip. The tip lasts longer on the first melt, apparently because more gas is evolved from the molybdenum on that melt than on later melts.

reduced greatly if the first melt were made by the consumable-electrode technique; much larger quantities can be melted by this process than can be melted by using semi-inert electrodes.

For a trial of the method, the Climax Molybdenum Company kindly consented to undertake to make the first melt using the consumable-electrode principle. As reported in the Sixteenth Quarterly Status Report, page 19, Climax melted a 5/8-inch-diameter molybdenum rod obtained from the Westinghouse Electric Corporation. The Climax ingot was as low in oxygen as is molybdenum melted once with a semi-inert electrode, but it contained 0.005 per cent carbon, as did the rod from which it was made. Consequently, an ingot made by remelting part of the Climax ingot by means of a semi-inert electrode was not so ductile as the high-purity molybdenum made in the past, with its normal carbon content of 0.002 to 0.003 per cent. Discussions with Westinghouse have shown that it is unlikely that rod can be obtained with the low carbon content necessary. With the equipment and process used by Westinghouse, heating and working of the sintered bar into rod invariably increases the carbon content.

Because it was unlikely that sufficiently pure bar could be obtained, the possibility of using an ingot made directly from powder was considered. The Climax Molybdenum Company, which has equipment for melting ingots directly from powder, again kindly cooperated and melted an ingot from powder that had been specially handled to minimize contact with air from the time the powder was prepared until it was melted. This powder was melted by Climax in vacuum without carbon additions. Although this ingot was apparently low in carbon content, there was an appreciable amount of oxide on the grain surfaces. It was not possible to remove this oxide by melting just once with the usual vacuum melting procedure.

Although a vacuum remelting treatment improved the ductility of the Climax ingot which was melted from Westinghouse rod, a second remelt resulted in some loss in ductility. Because it may be possible to overcome this difficulty by closer control of the remelting operation, it would be desirable to repeat the entire experiment if low-carbon arc-melted bar stock could be obtained commercially. Such material is not available at present, so a new lot of sintered molybdenum bar has been ordered for use as melting stock. High-purity-molybdenum ingots will be made from this material.

Preparation and Testing of Large High-Purity Ingot

Melting Procedure

Even in the most carefully controlled melting procedures, there are minor uncontrolled differences in composition and ductility between one high-purity ingot and another. Therefore, in the study of the effect of recrystallization on the ductility of high-purity molybdenum, it is desirable to study metal from the same ingot in the cast, fabricated, and recrystallized conditions. For this purpose, ingots weighing 3 to 5 pounds would be

needed, instead of the 1-pound ingots previously used in the studies of cast molybdenum.

Previous reports have described a number of unsuccessful attempts to prepare 3 to 5-pound high-purity-molybdenum ingots. In every case, either the desired size could not be achieved, or the ingots were less pure than the small high-purity ingots produced in the past.

In the Sixteenth Quarterly Status Report, it was stated that one more attempt would be made to prepare a larger ingot. If that failed, the studies of the recrystallization of high-purity molybdenum would be carried out on small high-purity ingots made as in the past.

Another attempt to prepare a large ingot has now been made. The melting stock was molybdenum that had been melted in vacuum from Westinghouse rod at the Climax Molybdenum Company. This melting stock was crushed to the usual minus 6 plus 20-mesh size. The large ingot was melted at Battelle by direct current in hydrogen at 28 mm of mercury, the lowest pressure at which a stable arc could be maintained. Although an alternating-current arc can be maintained in vacuum, the direct-current arc is stable only in the presence of a gas. The use of an atmosphere introduces the possibility that the melt may be contaminated by impurities in the gas. However, when direct current is used, large ingots can be made.* The hydrogen was the purest commercially obtainable**, and the gas pressure was kept low in order to keep contamination of the melt by impurities in the gas at a minimum. A water-cooled electrode with a molybdenum electrode tip was used. The electrode tip was cut from the same Climax ingot as that from which the melting stock was obtained.

Analysis of Large Ingot

The large ingot, B66A, was analyzed for oxygen and hydrogen by the vacuum-fusion method, with the following results:

	Amount Present, weight per cent
Oxygen	0.0002 ± 0.0001
Hydrogen	0.00006 ± 0.00002

On the basis of this analysis, the ingot would be considered as equal in purity to the average small high-purity ingot made in the past.

*Arc melting molybdenum with direct current allows a greater portion of the heat to enter the molten bath than enters the electrode. Therefore, the electrode can be truly inert, and any size of ingot can be obtained. On the other hand, when alternating current is used, the heat is distributed evenly between electrode and melt, and the electrode tip is gradually melted away. Therefore, in this case, the size of the final ingot is limited by the life of the electrode tip.

**The hydrogen was of a special quality obtained from the Rare Gas Division of Linde Air Products Company.

Fractographic Examination of the Ingot

An examination of grain surfaces on a fractured specimen from the large ingot showed that molybdenum oxide and molybdenum carbide were present. The oxide was present in relatively minor amounts. In contrast, the carbide phase was uniformly distributed over all the grain surfaces. Therefore, the ingot was not so pure as was desired.

Ductility Tests on the Ingot

Ingot B66A was evaluated for ductility by the usual bend test. Bend test specimens were machined from a 1/4-inch slab cut from the middle of the ingot. The specimens were cut so that the columnar grains of the ingot were transverse to the long axis of the specimen. The tests were performed at a deflection rate of 1 in./min. The strain rate in the outer fibers was 0.038 in./in./sec. The following results were obtained:

Test Temperature, C	Bend Angle, degrees	Load, pounds
20	0	100
60	0	100
80	0	375
120	0	225
120	10	400
160	2	175
160	6	300
200	38	950

On the basis of these results, the comparative transition temperature* of this ingot is approximately 120 C.

Discussion

Although the reported oxygen content of this ingot was low, the ingot was comparatively brittle in the bend test. It is not felt that the residual carbon content contributed greatly to the brittleness, because molybdenum ingots with carbon contents of about 0.005 per cent** would normally be expected to have a comparative transition temperature of approximately -20 C***. Because there is a small amount of molybdenum oxide in the

*See page 8 of this report.

**This is the analysis of the melting stock. No carbon analysis of the ingot was made, but it is not expected that it would have been changed by melting.

***See page 12 of the Fourteenth Quarterly Status Report.

microstructure, it is reasonable to conclude that the major cause of the brittleness of this ingot is the presence of oxygen. The low reported oxygen content of the ingot (2 ppm) supports the hypothesis proposed on page 38 of the Sixteenth Quarterly Status Report, that the critical oxygen content for embrittlement of coarse-grained cast molybdenum is in the vicinity of 0.0002 per cent.

It will be recalled that carbide, but not oxide, was present at the grain boundaries of a previous ingot melted in vacuum from this same melting stock.

Attempts to prepare a 3 to 5-pound high-purity ingot will be abandoned, and smaller ingots will be used for the remaining studies involving high-purity molybdenum. The preparation of a large high-purity ingot is definitely not an unsolvable problem, but additional effort does not seem justified within the present program.

Future Work

The future work for this phase of the project remains essentially the same as outlined previously. No further attempts will be made to produce large high-purity ingots. Instead, a number of carefully prepared 1-pound ingots will be fabricated, recrystallized, and tested for ductility.

Data from which this section of the report was prepared are recorded in BMI Laboratory Record Book No. 7902, pages 80 and 100, Record Book No. 8057, pages 30 to 75, and Record Book No. 8251, pages 12 to 38.

EFFECT OF IMPURITIES ON THE DUCTILITY OF CAST MOLYBDENUM

(G. W. P. Rengstorff, L. E. Olds, R. B. Fischer, and H. W. Lownie, Jr.)

Introduction

In the Sixteenth Quarterly Status Report, page 32, a series of experiments was discussed in which various amounts of nitrogen were added to otherwise high-purity cast molybdenum with the objective of determining the effect of nitrogen on ductility. The nitrogen was added by arc melting molybdenum in low-pressure nitrogen. The nitrogen content of the metal varies with the pressure of nitrogen in which the metal is melted. Ductility was measured by determining the bend transition temperature in the manner described in previous reports.

At the time of the Sixteenth Quarterly Status Report, all of the scheduled nitrogen-containing ingots had been prepared and all but two had been bend tested. The testing of the two remaining ingots has now been completed. These ingots were prepared in the same manner as were previous nitrogen-bearing ingots, except that the final melting was performed in an atmosphere of flowing nitrogen, instead of in a static atmosphere. It was felt that the ingots would be more uniform in nitrogen content if the pressure inside the furnace shell were held constant. One ingot was melted in nitrogen at a pressure of 1 micron, and the other at 6 microns.

Analyses of Ingots

The ingots were analyzed by the vacuum-fusion method for oxygen, hydrogen, and nitrogen, and also by the diffusion-extraction method for nitrogen*. The following results were reported.

Ingot	Partial Pressure of Nitrogen During Melting, microns	Sample Weight, grams	Amount Present, weight per cent			
			Vacuum-Fusion Analysis			Diffusion-Extraction Analysis
			O_2	H_2	N_2	N_2
B57D	1	10-1/2	0.00021	0.000012	0.00067	0.00020
B58D	6	10	0.00017	0.000010	<0.00006	0.00051
Reported sensitivity for 10-gram sample			±0.00005	0.00005	0.00006	0.00006

*See page 76 of the Sixteenth Quarterly Status Report for description of this analytical method and the reason for adopting it.

The reported contents of the gaseous elements are low. There is good correlation between the partial pressure of nitrogen during melting and the nitrogen content of the ingots as determined by the diffusion-extraction method; an increase in the nitrogen pressure resulted in an increase in nitrogen content. However, the higher nitrogen content of Ingot B57D obtained by the vacuum-fusion analysis may indicate either heterogeneity in the ingot or an error in the analysis, since this method of analysis is not expected to give a higher value than is obtained by the diffusion-extraction method.

Ductility Tests of Nitrogen-Containing Ingots

The data from the bend tests made on the ingots are given in Table 2 and in Figure 7.

From Figure 7, it may be seen that the number of tests made at lower temperatures was not sufficient for an accurate determination of a transition temperature. However, the results do indicate that Ingot B58D is more brittle than Ingot B57D. Since the comparative transition temperatures of these ingots were not obtained, it is not possible to compare them with the previous nitrogen-containing ingots.

Fractographic Examination of the Ingots

A preliminary examination of the grain surfaces in these ingots has been made, and small particles of a second phase were observed on the grain surfaces of both ingots. This phase is believed to be the same as was found in ingots previously melted in nitrogen.

Future Work

With the exception of hardness measurements and additional fractographic studies, no further work on the effect of impurities on the ductility of cast molybdenum is planned.

Data from which this section of the report was prepared are recorded in BMI Laboratory Record Book No. 7902, pages 72 to 75.

TABLE 2. BEND-TEST DATA FOR INGOTS MELTED IN FLOWING NITROGEN

Note: Transverse Grain Orientation
Deflection Rate - 1 in./min
Strain Rate - 0.038 in./in./sec

Test Temperature, C	Bend Angle, degrees	Load, pounds	Test Temperature, C	Bend Angle, degrees	Load, pounds
Ingot B57D, 1 Micron N_2			Ingot B58D, 6 Microns N_2		
160	20	580	350	8	180
160	6	350	300	25	700
120	2	400	300	18	400
120	0	250	250	22	400
120	0	150	200	0	250
120	0	125	200	68	1275
120	40	960	200	0	125
120	35	900	160	9	320
60	14	750	160	10	450
60	4	450	150	0	150
20	18	1200	150	2	200
			140	14	700
20	2	550	120	10	750
20	0	200	120	0	200
-20	0	500	120	2	380
-20	0	200	120	1	250
			120	0	250
			120	2	100
			20	0	50

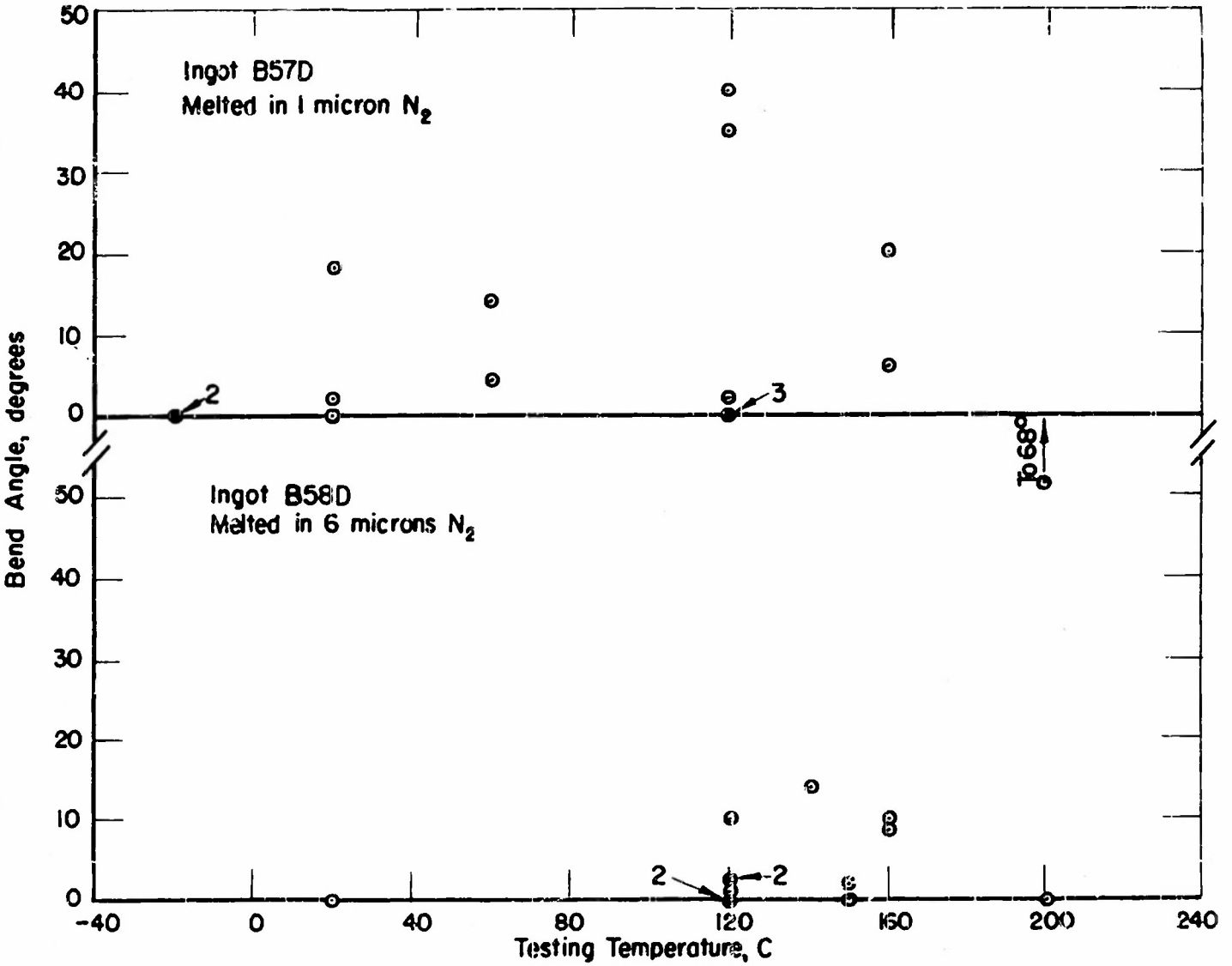


FIGURE 7. BEND-TEST DATA FOR CAST MOLYBDENUM MELTED IN FLOWING NITROGEN
Transverse grain orientation
Strain rate: 0.038 in./in./sec

A-10170

FRACTOGRAPHIC STUDY OF MOLYBDENUM

(L. E. Olds and R. B. Fischer)

Introduction

One phase of the research has been directed toward determining the relation between the impurity content, the mechanical properties, and the microstructure of molybdenum. One of the chief problems is the identification of very minute traces of excess phases. Since excess phases are often concentrated at grain boundaries or cleavage planes, examination of fracture surfaces is often preferable to examination of polished sections for studying microstructure. Some of the typical configurations seen both on polished and on fractured surfaces have been catalogued in past reports, and etching techniques for identifying them have been described.

One way to identify excess phases with specific impurities is to prepare a series of samples with increasing amounts of the impurity element in question. If the amount of a given excess phase increases in proportion to the impurity content, it can be assumed that the two are related.

Several series of ingots were prepared in the past with deliberate additions (singly) of various amounts of carbon, nitrogen, oxygen, and sulfur to otherwise high-purity molybdenum, for the purpose of determining the effects of these elements on the ductility of cast molybdenum. The fractures of these ingots have now been studied to determine whether any of the observed phases could be related to the amounts of these elements present in the ingots.

Experimental Work

Ingot Compositions

The ingots that have been examined in the present study are listed in Table 3, along with references to previous reports in which their preparation and testing are described.

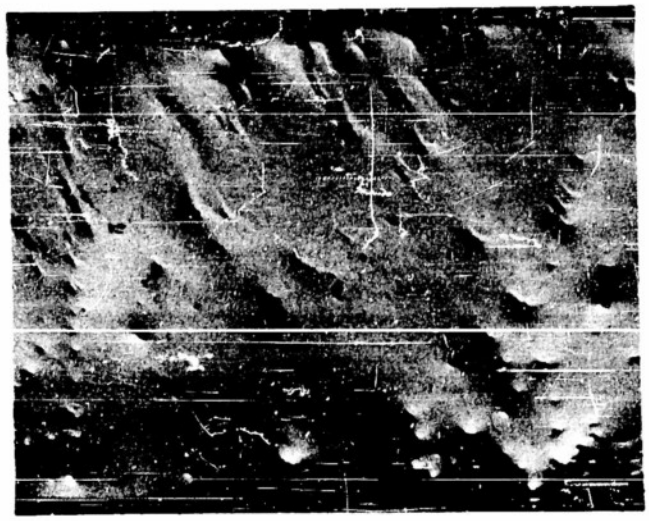
Fractographic Examination

Control Ingot (High-Purity Molybdenum). Typical grain surfaces from the high-purity control ingot (A8827C) are shown in Figure 8. The low-magnification fractograph (Figure 8a) shows the usual grain-surface

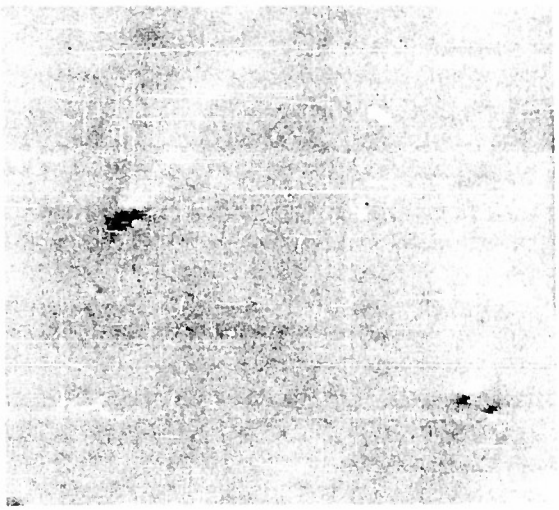
TABLE 3. SUMMARY OF INGOTS EXAMINED BY FRACTOGRAPHY

Ingot	Composition, weight per cent O_2	N_2	C	S	Preparation and Testing Reported
Control ingot (no added impurities)					Page 8, Fourteenth Quarterly Status Report
A8827C	0.00019	<0.00009*	0.002	0.002	
Carbon series					Page 8, Fourteenth Quarterly Status Report
A9139C	-	-	0.003	-	
A8809C	-	-	0.006	-	
A8810C	-	-	0.008	-	
A8811C	-	-	0.010	-	
A8812C	-	-	0.020	-	
A9147C	-	-	0.024	-	
Nitrogen series					Page 20, Fifteenth Quarterly Status Report
A9039C	-	0.0008*	-	-	
A9030C	-	0.0014*	-	-	
A9029C	-	0.0037*	-	-	
A9149C	-	0.033**	-	-	
Oxygen series					Page 34, Sixteenth Quarterly Status Report
A9457C	0.0001	-	-	-	
A9456C	0.0002	-	-	-	
A9458C	0.0006	-	-	-	

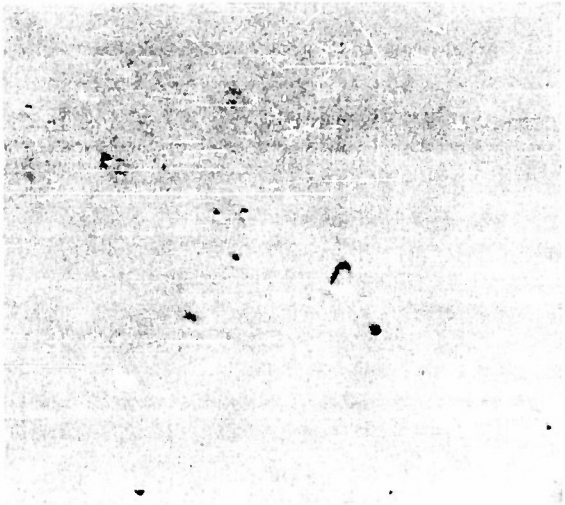
*By diffusion-extraction method.
**By Kjeldahl method.



100X a. N3000



2000X b. N4941



2000X c. N4942

Unetched

FIGURE 8. FRACTOGRAPHS OF GRAIN SURFACES IN HIGH-PURITY MOLYBDENUM (INGOT A8827C)

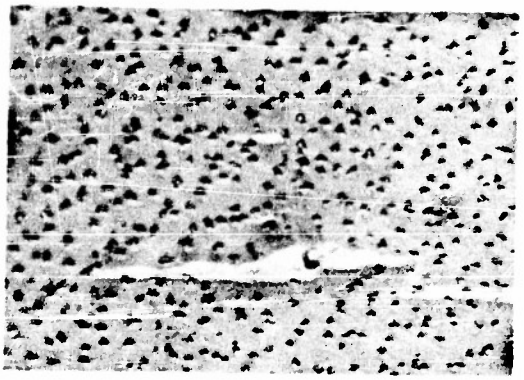
microporosity, which is always found in high-purity molybdenum, as well as in some of the other types of molybdenum. On most of the grain surfaces in this ingot, the light microscope is incapable of detecting any evidences of a second phase (Figure 8b). In a few areas, however, there are signs of some precipitation of excess phases (Figure 8c). The identity of the small particles in this fractograph is unknown.

Carbon Series. Grain surfaces in the ingots to which carbon had been added are shown in Figure 9. For each carbon content, a fractograph of low magnification is shown on the left side of the page and a fractograph of high magnification is shown on the right. From these figures, it may be seen that an increase in the carbon content results in a corresponding increase in the size of the carbide particles. In the ingot containing 0.003 per cent carbon, the grain surfaces are entirely covered with a uniform, fine precipitate which is believed to consist of carbide particles. From Figure 9a, it may be seen that these particles are extremely small and that they form a pattern which resembles the speckling observed in molybdenum containing small amounts of oxygen. When the carbon content is increased to 0.006 per cent, the carbide particles take on a needlelike form, and, as the carbon content is increased further, the particles begin to show additional markings which made them resemble feathers.

Nitrogen Series. Grain surfaces in the ingots melted in low-pressure nitrogen are shown in Figures 10, 11, and 12. From these fractographs, it may be seen that the amount of the precipitated phase increased as the amount of retained nitrogen increased. Therefore, the particles shown in these fractographs are believed to be a nitride of molybdenum. To provide more positive identification, the larger grain surfaces in the ingot containing 0.033 per cent nitrogen were examined by X-ray and electron-diffraction techniques. However, this work was unsuccessful in showing anything but the diffraction lines characteristic of molybdenum. An attempt was then made to concentrate the intergranular phase by lightly scraping a number of grain surfaces. Powdered specimens were then prepared and examined by X-ray diffraction. In the resulting pattern, the strongest lines were those of the molybdenum matrix. However, there were additional faint lines that could be attributed to the minor phase. This same family of faint lines was obtained from samples made from different scrapings. Although precise measurements could not be made on such faint lines, there was good agreement between these lines and the structure of gamma Mo_2N reported by Hagg* and there were obvious differences between this group of lines and the standard data for oxide and carbide. Thus, it appears that the phase observed in the ingots melted in nitrogen is Mo_2N.

* Hagg, G., Z. Phys. Chem., B7 (1930), 344.

100X Unetched 98184



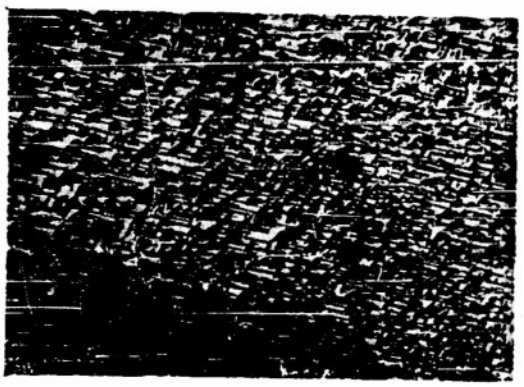
2000X Etched 98186

a. 0.003% C

100X Unetched N4931

2000X Etched N4932

b. 0.006% C



100X Unetched N4933

2000X Etched N4934

c. 0.008% C

Etchant: $(NH_4)_2HPO_4:H_2O_2$

FIGURE 9. FRACTOGRAPHS OF GRAIN SURFACES IN CAST MOLYBDENUM CONTAINING CARBON

100X Unetched N4935

2000X Etched N4936

d. 0.010% C

100X Unetched N4937

2000X Etched N4938

e. 0.020% C

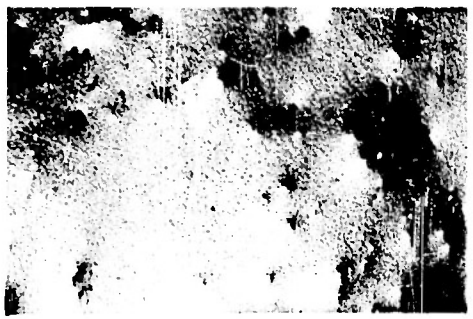
100X Unetched N4939

2000X Etched N4940

f. 0.024% C

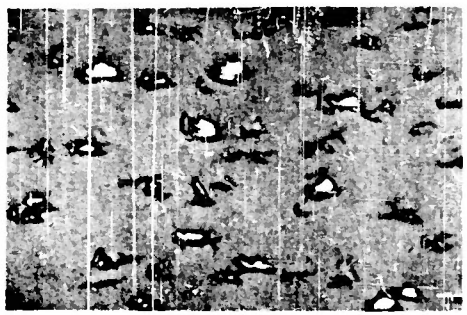
Etchant: $(NH_4)_2HPO_4$:H_2O_2

FIGURE 9. (Continued)

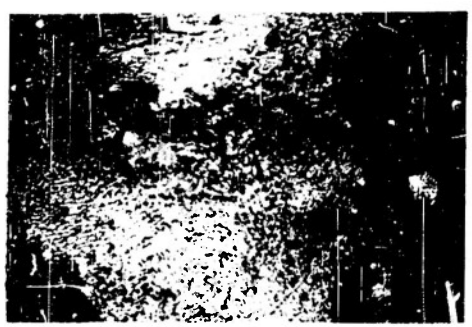


100X Etched N2980

500X Unetched N2981

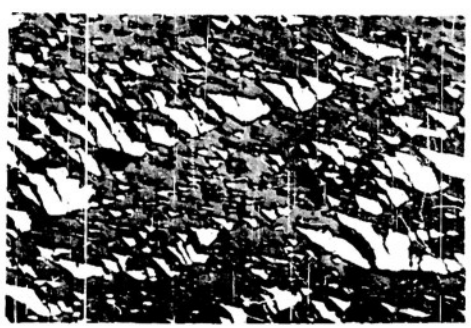


2000X Etched N2982



100X Etched N2977

500X Unetched N2978

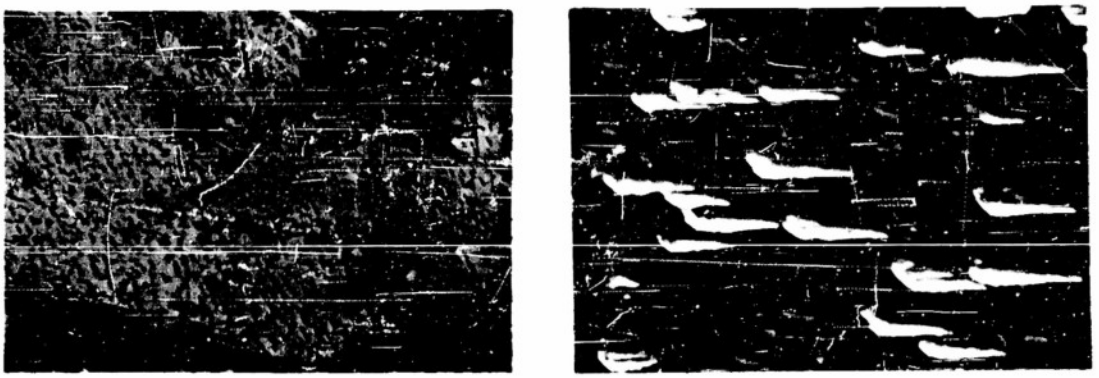


500X Etched N2979

0.0007% N_2

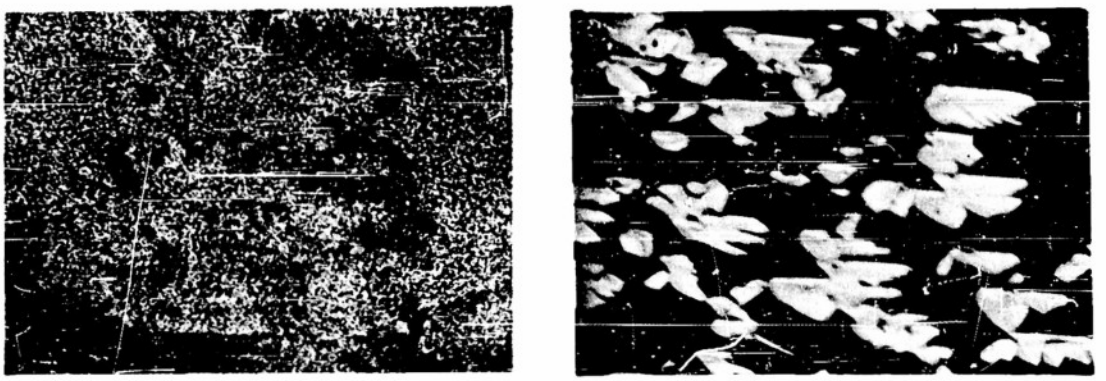
Etchant: $(NH_4)_2HPO_4 \cdot H_2O_2$

FIGURE 10. FRACTOGRAPHS OF GRAIN SURFACES IN CAST MOLYBDENUM MELTED IN 10 MICRONS PRESSURE OF NITROGEN



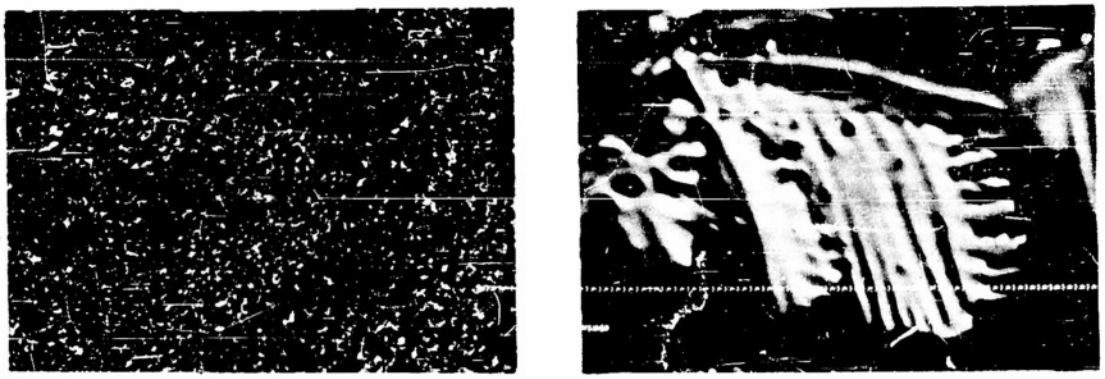
100X Unetched N2987 2000X Etched N2983

a. 0.0014% N_2



100X Unetched N2990 2000X Etched N3001

b. 0.0037% N_2



100X Unetched N2992 2000X Etched N2996

c. 0.033% N_2

Etchant: $(NH_4)_2HPO_4$:H_2O_2

FIGURE 11. FRACTOGRAPHS OF GRAIN SURFACES IN CAST MOLYBDENUM MELTED IN PARTIAL PRESSURES OF NITROGEN

Figure 10 shows the effect of etching the grain surfaces of molybdenum containing these nitride particles. The middle photographs represent an unetched specimen and the photographs on the right show the same area after etching. The etchant darkens the molybdenum, but the nitride phase remains light in color. From the fractographs in Figures 11 and 12, it may be seen that the Mo_2N particles often resemble carbide particles. However, the fractographic examination showed that the nitride particles usually formed as platelets at grain boundaries, in contrast to the usual needlelike formation of carbide particles.

Oxygen Series. Grain surfaces from the ingots containing oxygen are shown in Figure 13. In the fractographs, the oxide phase increases as the oxygen content of the ingots increases. This figure shows that the ingot containing 0.0001 per cent oxygen is comparable to high-purity molybdenum, since the grain surface is generally clean and free of precipitated phases. However, more porosity and distortion were present on the grain surfaces of this ingot than are usually observed in the high-purity ingots. A few tiny inclusions were found in some grain surfaces. Figure 13 shows a fractograph of one such inclusion, the identity of which is not known.

The ingot containing 0.0002 per cent oxygen has the speckled grain surfaces that are typical of molybdenum containing relatively small amounts of oxygen, as shown in Figure 13. An increase in oxygen content results in the formation of needles and larger platelets of oxide. The platelets in molybdenum containing 0.0006 per cent oxygen are shown in Figure 13.

One peculiarity associated with oxygen in molybdenum is shown in Figure 13. In this fractograph, there are distinctive markings associated with the pore holes. These markings appear to be characteristic of all molybdenum ingots that contain oxygen.

Future Work

All the ingots prepared for the ductility studies will be examined by fractography.

Data from which this section of the report was prepared are recorded in BMI Laboratory Record Book No. 6782, pages 84 to 93; and Record Book No. 7902, page 38.

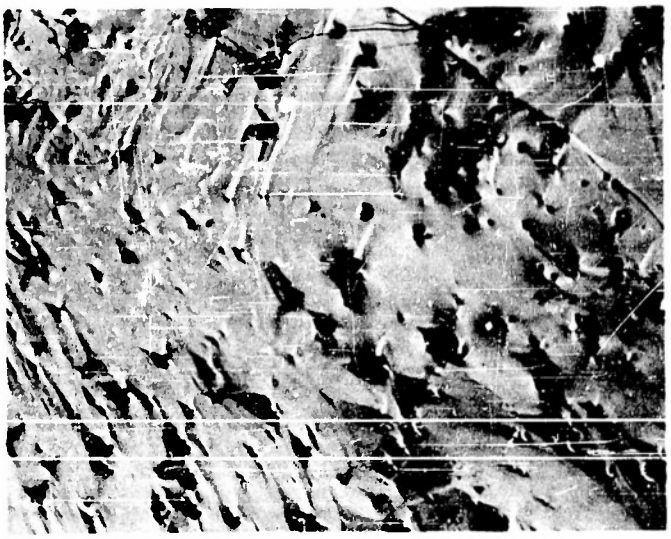
1000X Unetched N2998

1000X Etched N2999

1000X Etched N2997

Etchant: $(NH_4)_2HPO_4$: H_2O_2

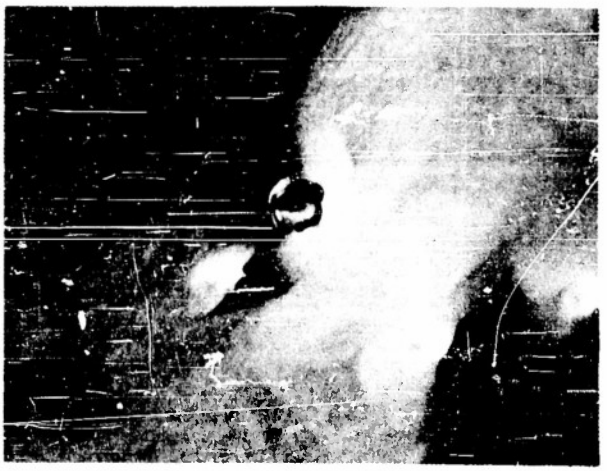
FIGURE 12. FRACTOGRAPHS OF GRAIN SURFACES OF CAST MOLYBDENUM MELTED IN 60,000 MICRONS PRESSURE OF NITROGEN



100X a. Unetched N10597

0.0001% O_2

2000X b. Unetched N10598

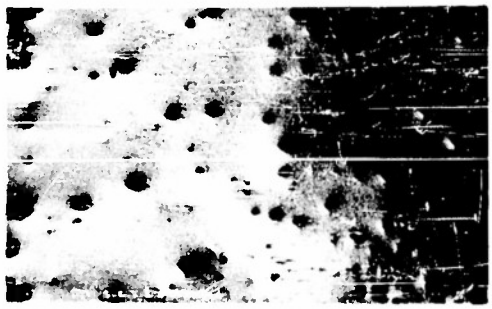


2000X c. Etched N10599

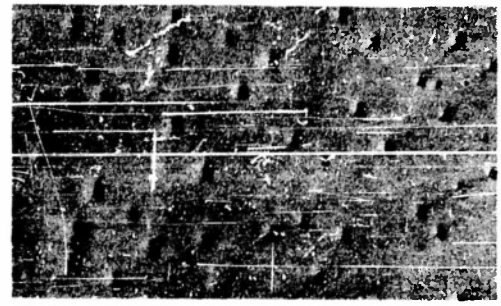
0.0001% O_2

$(NH_4)_2HPO_4$:H_2O_2

FIGURE 13. FRACTOGRAPHS OF GRAIN SURFACES IN CAST MOLYBDENUM MELTED IN PARTIAL PRESSURE OF OXYGEN

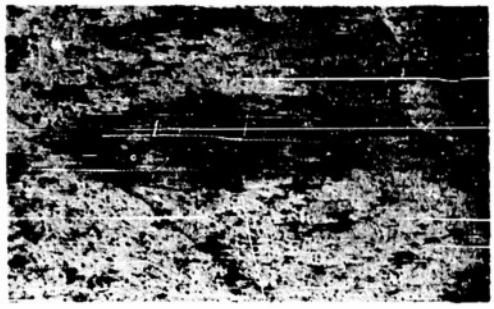


100X N10596

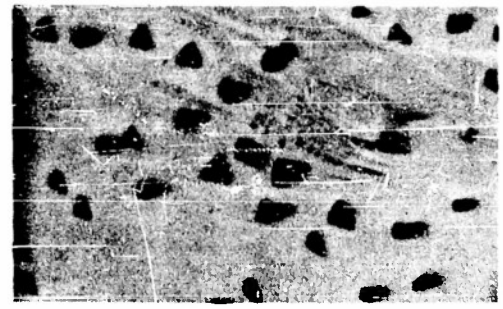


2000X N10600

d. 0.0002% O_2



100X N10595



2000X N10954

e. 0.0006% O_2

Unetched

FIGURE 13. (Continued)

EFFECT OF NEUTRALIZERS ON THE DUCTILITY OF CAST MOLYBDENUM

(G. W. P. Rengstorff, L. E. Olds,
R. B. Fischer, and H. W. Lownie, Jr.)

Introduction and Résumé of Past Work

It has been thoroughly established that oxygen, nitrogen, and carbon all affect the cold ductility of cast molybdenum adversely. Multiple melting in vacuum removes oxygen and nitrogen from molybdenum so effectively that a notable improvement in cold ductility results. Metal prepared by this method is useful in the laboratory for determining the effects of specific impurities. However, for cast molybdenum to have acceptable ductility, the purity requirements are so stringent that it seems unlikely the necessary purity can be achieved and maintained except on a laboratory scale.

Instead of purifying the molybdenum, it is possible to add certain elements that tie up the harmful impurities in nonharmful forms and thereby neutralize their effect. An investigation aimed at determining which elements are the best "neutralizers" for harmful impurities in molybdenum was reviewed and discussed in the Sixteenth Quarterly Status Report. Elements investigated as possible neutralizers have been primarily those with a strong tendency to form oxides, carbides, nitrides, or sulfides. It is hoped that neutralizer additions can be found which not only will impart ductility to cast molybdenum, but also will cause ductility to be retained after fabrication and recrystallization, and after welding.

The effects of adding small amounts of the following elements as possible neutralizers have been studied in a preliminary screening investigation described in past reports:

Group in Periodic Table	IIa	IIIa	IVa	IVb	Vb	VIb
Element	Be	B	Si	Ti	V	Cr
		Al		Zr	Cb	
				Th	Ta	

Those elements showing even slight promise are being investigated more thoroughly. Titanium and thorium showed considerable promise; therefore, considerable work has been carried out on molybdenum-titanium and molybdenum-thorium alloys. Vanadium and zirconium, although not so effective as titanium and thorium, showed some promise and are being studied further.

Vanadium and Zirconium as Possible Neutralizers for Impurities in Molybdenum

Melting Methods

During this quarter, new ingots were made with the following vanadium and zirconium additions:

Ingot	Vanadium, per cent	Ingot	Zirconium, per cent
B117	0.25	A9867	0.25
B118	0.5	A9866	0.5
B119	1.0	A9865	1.0
B120	5.0	A9864	5.0

These ingots were prepared under the following conditions:

(1) Ingots were arc melted, crushed, and remelted* to promote uniformity in the final ingot. For the same purpose, the alloying elements were added in the form of molybdenum-base master alloys containing 20 per cent vanadium or 15 per cent zirconium. When the ingots were broken with a hammer prior to crushing, it was noted that the fracture was intercrystalline (as in unalloyed molybdenum) until 5 per cent vanadium was added. It has been observed that a titanium content as low as 0.11 per cent changed the fracture from intercrystalline to transcrystalline. Therefore, vanadium apparently does not strengthen the grain boundaries of molybdenum as well as does titanium.

(2) The melting stock was as pure as is practicable. The molybdenum was purified by arc melting crushed, sintered molybdenum** under vacuum. The vanadium was the ductile grade produced by the Union Carbide and Carbon Corporation***. The zirconium had been purified by the iodide process****.

(3) Arc melting the master alloys and the final alloys was carried out in the most air-tight furnace available.

(4) Melting was carried out under helium so that a direct-current arc could be used readily. The ingots were melted more uniformly, therefore, and larger alloying additions could be made than with the inert-electrode vacuum-arc melting used to make the previous vanadium- and zirconium-containing alloys.

---

* The 5 per cent zirconium ingot (A9864) was not remelted. It cracked in the crucible during cooling, as did the 15 per cent zirconium master alloys.

** Obtained from the Westinghouse Electric Corporation.

*** Described by A. B. Kinzel in "Vanadium Metal - A New Article of Commerce," Metal Prog., 58, 315-321 (September, 1950).

**** Obtained from the Foote Mineral Company.

(5) Molybdenum was used for the electrode tip to prevent possible contamination by tungsten, from a tungsten electrode tip, or by other undesired impurities.

(6) The arc currents were comparatively low, usually 500 to 650 amperes, so that the electrode would have a long life. Therefore, the melting stock had to be fed in small increments and the arc played continually over the top of the ingot. Otherwise, the ingot would have contained a series of horizontal laps, because the molten pool was always shallow, never completely covering the top of the ingot.

(7) Each ingot weighed 250 grams.

Ductility Tests

The ductility of all the alloyed ingots was measured by the standard bend test used in previous work. For this test, 1/4-inch slabs were cut from the ingots and ground. The bend-test specimens were cut from the slabs in such a manner that the columnar grains of the ingot were transverse to the axis of the specimen. Most of the slabs from the ingots containing vanadium and zirconium cracked upon grinding. However, it was possible to prepare a few sound specimens from each ingot.

The specimens were all tested at a deflection rate of 1 in./min, which corresponds to a strain rate of 0.038 in./in./sec in the outer fibers of the specimen. The results of the tests are given in Tables 4 and 5 and Figures 14 and 15.

Because only a few tests were made on many of the ingots containing vanadium and zirconium, only a general approximation of the transition temperature can be given. The figures indicated on the graphs for the molybdenum-vanadium and the molybdenum-zirconium alloys represent approximate transition temperatures only.

The data plotted in Figure 14 indicate a lowering of the transition temperature for a vanadium addition of 0.5 per cent. Increasing the vanadium addition to 5 per cent appears to raise the transition temperature, but not nearly to the same extent as did the 5 per cent zirconium addition.

The data plotted in Figure 15 indicate a trend toward increased brittleness when the amount of zirconium was increased. Thus, if there is any lowering of the transition temperature of cast molybdenum by additions of zirconium up to 5 per cent, it must occur for a zirconium addition of less than 0.25 per cent.

TABLE 4. BEND-TEST DATA FOR MOLYBDENUM-VANADIUM-ALLOY INGOTS

Test Temperature, C	Bend Angle, degrees	Load, pounds	Test Temperature, C	Bend Angle, degrees	Load, pounds
Ingot B117 - 0.25% V Added			Ingot B118 - 0.5% V Added		
200	75	1650	300	90	1100
200	4	200	200	38	480
160	0	100	200	0	200
160	0	100	100	28	850
120	0	250	100	0	100
120	0	175	50	1	370
20	0	100	50	1	260
			50	16	810
			50	0	90
Ingot B119 - 1% V Added			Ingot B120 - 5% V Added		
300	32	500	450	57	850
250	4	200	300	28	900
			250	2	125
			250	18	700
			200	14	600
			120	2	500
			100	2	400
			100	1	250

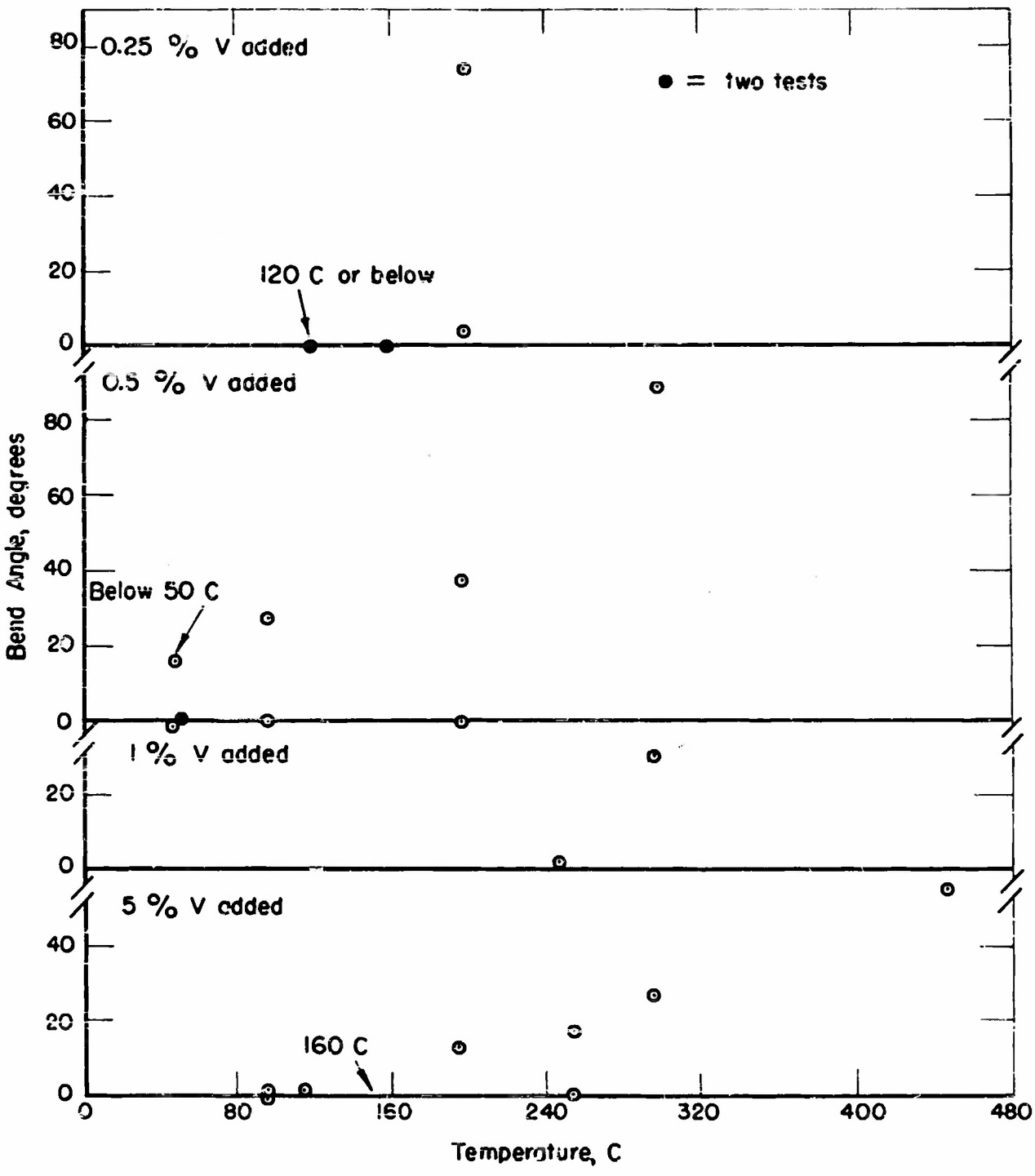


FIGURE 14. BEND-TEST DATA FOR CAST MOLYBDENUM-VANADIUM ALLOYS

Transverse grain orientation
Strain rate: 0.038 in./in./sec

A-10171

TABLE 5. BEND-TEST DATA FOR MOLYBDENUM-ZIRCONIUM-ALLOY INGOTS

Test Temperature, C	Bend Angle, degrees	Load, pounds	Test Temperature, C	Bend Angle, degrees	Load, pounds
Ingot A9867 - 1/4% Zr Added			Ingot A9866 - 1/2% Zr Added		
200	10	1250	330	0	650
180	0	250	330	0	150
180	6	525	330	0	100
160	4	420	200	0	200
160	2	320			
160	0	200			
160	0	200			
160	0	225			
Ingot A9865 - 1% Zr Added			Ingot A9864 - 5% Zr Added		
330	2	200	650	2	100
330	0	200	650	2	400
330	0	200	650	0	50
300	0	0	650	0	200
300	0	100	450	0	200
200	2	1050	450	2	480
20	0	300			

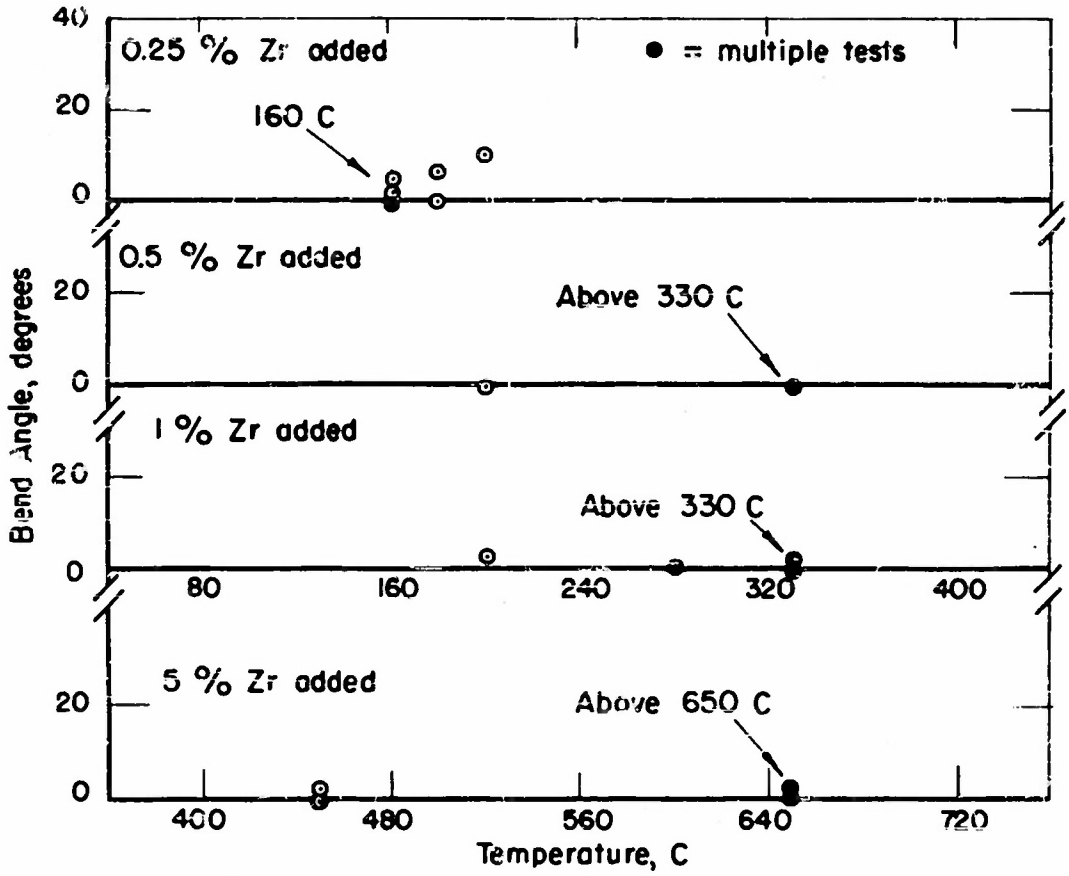


FIGURE 15. BEND-TEST DATA FOR CAST MOLYBDENUM-ZIRCONIUM ALLOYS

Transverse grain orientation
Strain rate: 0.038 in./in./sec

A-10172

Further Investigation of Titanium as a Neutralizer

So far, titanium has appeared to be the most promising neutralizer for the impurities in cast molybdenum. Consequently, a series of ingots with varying amounts of titanium has been prepared. These ingots will be used for determining the optimum amount of titanium to add to molybdenum for improved cold ductility. Most of the results of this work were given in the Sixteenth Quarterly Status Report. However, six new ingots were made during the present reporting period. Three of them (all with 1 per cent titanium added) were made larger than the others, so that a part of each could be fabricated and tested in the worked condition. At this writing, these three ingots have not been fabricated. All six ingots were made in the same manner as were the vanadium and zirconium alloys discussed previously. Iodide titanium was added in the form of a molybdenum-base, 20 per cent titanium master alloy. The ingots containing additions of titanium were analyzed spectrographically for titanium, with the following results:

	Titanium, weight per cent	
Ingot	Added	Retained
B126	0.8	0.7
B124	1.0	0.92
B125	1.0	0.96
B127	1.2	0.96
B123	1.0	1.02
B128	1.4	1.05

These analyses indicate that relatively little titanium was lost during melting. The titanium contents of these ingots all fall in the region 0.5 per cent to 1.25 per cent, where maximum ductility of the ingots would be anticipated*.

The ductilities of the ingots containing titanium were determined in the same manner as those of the ingots containing vanadium and zirconium. The bend data are shown in Table 6 and Figure 16.

The data plotted in Figure 16 show that most of the alloys containing titanium have a transition temperature of -70 C or below. The ingot containing 0.92 per cent titanium had a transition temperature of -40 C or lower. It is likely that, if additional specimens from this ingot had been tested below -40 C, the data would have indicated a transition temperature comparable to that of the other ingots. One of the ingots containing 0.96 per cent titanium cracked upon grinding, and only three sound specimens could be obtained for testing. Therefore, no transition temperature is reported for this ingot. None of the sound specimens from this ingot were ductile, however.

* See page 55 of the Sixteenth Quarterly Status Report.

A graph relating the transition temperature to titanium content is shown in Figure 17. In this graph, the open circles represent the ingots that were tested previously and reported on in the Sixteenth Quarterly Status Report, and the solid circles represent the recent ingots. From Figure 17, it may be seen that the points representing the recent ingots are in good agreement with previous work. Thus, it is felt that the good ductility of cast molybdenum containing approximately 1 per cent titanium is reproducible.

The testing of a series of molybdenum-titanium-alloy ingots prepared by the consumable-electrode, vacuum-melting technique was described on page 39 of the Fourteenth Quarterly Status Report. These ingots have now been analyzed spectrographically for titanium, and the following titanium contents are reported:

Ingot	Titanium, weight per cent		Comparative* Transition Temperature, C
	Added	Retained	
A9023A	0.5	0.27	-50
A9024A	1	0.19	-40
A9025A	3	1.35	50
A9026A	5	2.07	25

The results have been plotted in Figure 17 as squares. With the exception of the test data for the ingot containing 1.35 per cent titanium, the results are in good agreement with the data based on ingots melted in helium.

Future Work

Plans for future work on neutralizers for molybdenum include:

(1) Additional work on the molybdenum-titanium alloys to determine the effect of titanium on the ductility of the recrystallized alloys.

(2) A study of vacuum-melted molybdenum-titanium and molybdenum-thorium alloys made from highest purity melting stock. Smaller amounts of thorium will be used than were used in the previous thorium-containing ingots.

(3) A study of the effects of titanium and zirconium on molybdenum-thorium alloys.

* Data from which the comparative transition temperatures were determined are tabulated on page 40 of the Fourteenth Quarterly Status Report.

TABLE 6. BEND-TEST DATA FOR MOLYBDENUM-TITANIUM-ALLOY INGOTS

Test Temperature, C	Bend Angle, degrees	Load, pounds	Test Temperature, C	Bend Angle, degrees	Load, pounds
Ingot B126 - 0.7% Ti Added			Ingot B124 - 0.92% Ti Added		
25	5	1000	20	1	650
25	8	1040	20	4	800
-25	1	950	0	20	1500
-25	5	1200	0	16	1200
-50	6	1400	-25	3	1100
-50	1	500	-25	2	800
-50	6	1400	-25	2	800
-50	2	800	-25	5	1100
-75	5	1300	-25	2	900
-75	4	1400			
-75	1	950			
-75	4	1400			
Ingot B125 - 0.96% Ti Added			Ingot B127 - 0.96% Ti Added		
75	0	400	20	14	1300
20	0	400	20	8	1000
20	0	400	-25	3	800
			-25	6	1200
			-50	14	1500
			-50	2	700
			-50	10	1400
			-75	2	1200
			-75	2	1200
			-75	2	1200
Ingot B123 - 1.02% Ti Added			Ingot B128 - 1.05% Ti Added		
20	1	450	25	20	1200
20	38	1400	20	5	1000
-25	25	1500	20	25	1300
-25	6	1000	-25	2	1000
-75	2	500	-25	8	1300
-75	0	1000	-25	10	1500
-75	6	1500	-50	6	1400
			-50	1	1000
			-50	6	1400
			-75	2	1000
			-75	0	500
			-75	0	1000

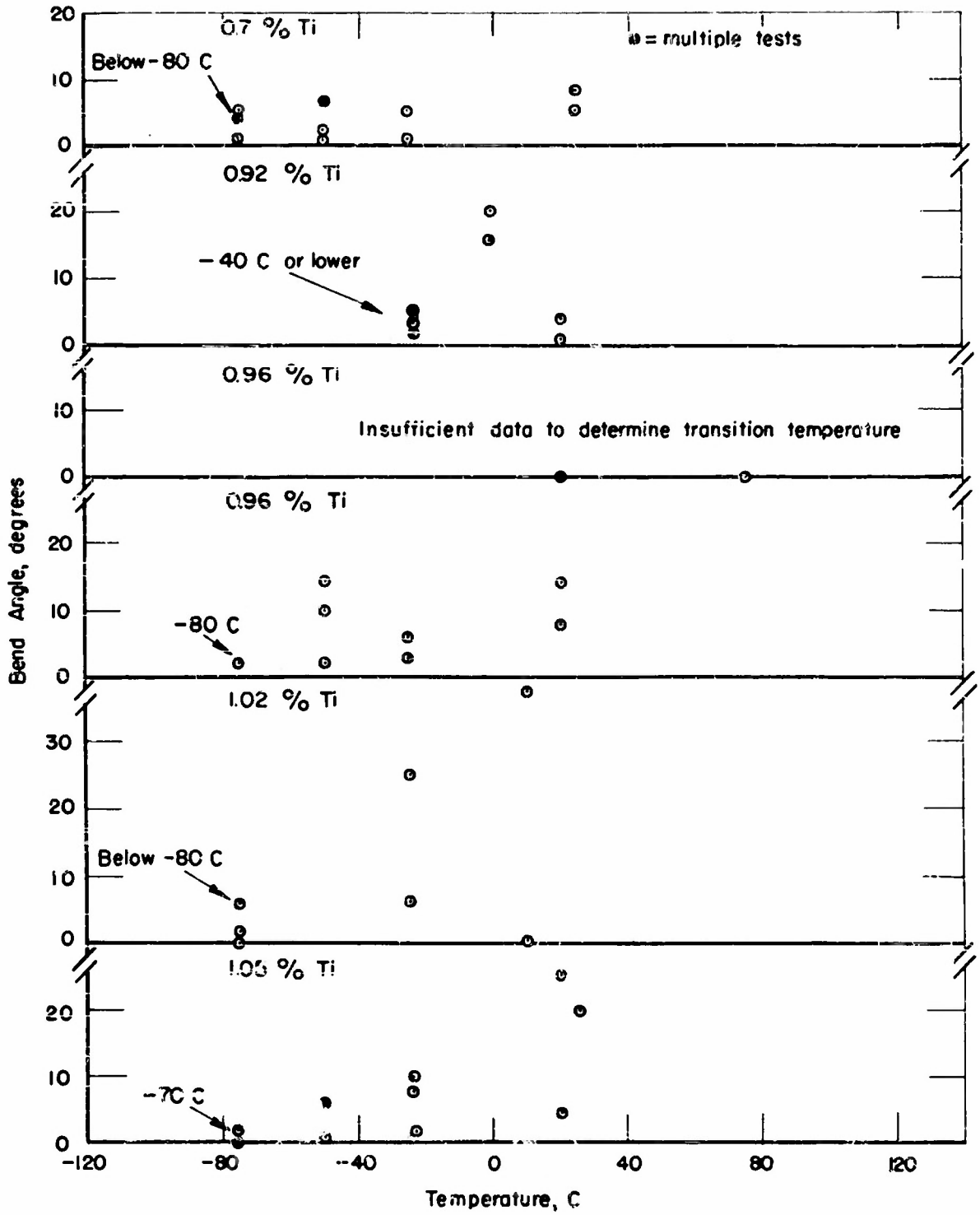


FIGURE 16. BEND-TEST DATA FOR CAST MOLYBDENUM-TITANIUM ALLOYS

Transverse grain orientation
Strain rate: 0.038 in./in./sec

G-10173

(4) An investigation of the effects of aluminum on the cold ductility of cast molybdenum.

(5) An investigation of the effects of boron on the cold ductility of cast molybdenum.

(6) An investigation of the effects of the individual rare-earth elements on the cold ductility of cast molybdenum. Elements which may be studied are cerium, lanthanum, and neodymium.

Formerly, studies of the welding of molybdenum that were supported by the Atomic Energy Commission were reported to the Office of Naval Research. As discussed in the Sixteenth Quarterly Status Report, much of that work is now classified and no longer will be covered in these reports. However, one unclassified portion of that study has as an objective the development of weldable molybdenum alloys. This study involves melting, working, and heat treating alloys, and is based on the ONR-supported investigation of neutralizers. The production and treatment of these alloys will be reported here.

Present plans call for an intensive investigation of the molybdenum-titanium alloys, mostly in the range of 0.5 to 2.0 per cent titanium. In connection with this work, a special arc-melting furnace is being built for use on both the ONR and the AEC investigations. Care is being taken to make this furnace more leak-tight than the furnace now used for melting under helium. The new furnace will be capable of producing larger ingots, perhaps up to 15 pounds.

The data from which this section of the report was prepared are recorded in BMI Laboratory Record Book No. 7902, pages 76 to 79; Record Book No. 8573, pages 4 to 7; Record Book No. 8057, pages 30 to 75; and Record Book No. 8251, pages 12 to 38.

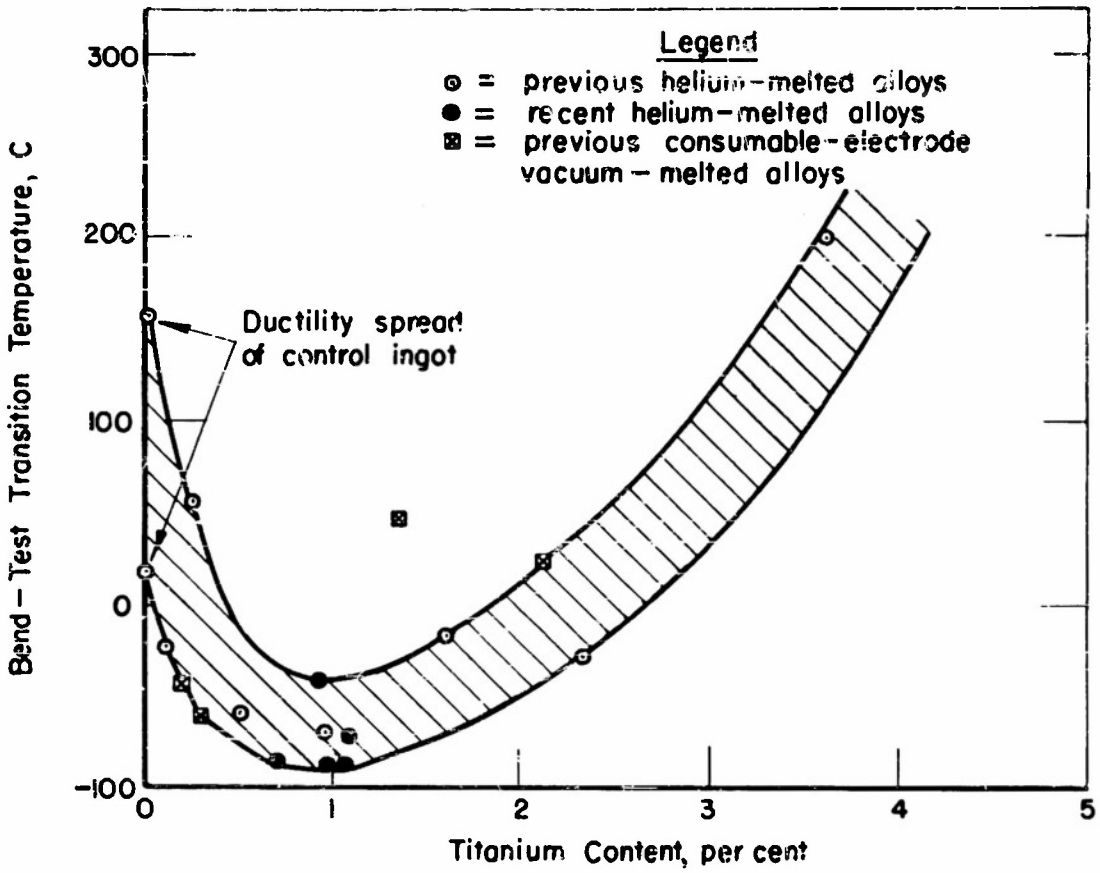


FIGURE 17. EFFECT OF TITANIUM ON BEND-TEST TRANSITION TEMPERATURE OF CAST MOLYBDENUM MELTED IN HELIUM

Transverse grain orientation
Strain rate: 0.038 in./in./sec

A-10174

A STUDY OF THE SOLID-STATE PURIFICATION OF MOLYBDENUM

(W. E. Few and G. K. Manning)

Introduction

In attempting to improve the ductility of molybdenum by purification, it has been found that oxygen and nitrogen can be effectively removed by heating thin sections of the metal in high vacuum. For example, analyses showed that heating 40-mil wires for one hour at 3800 F in a vacuum (0.05-micron residual pressure) reduced the oxygen content of the wire from the 20 to 70 parts per million typical of commercial sintered molybdenum to only 1 or 2 parts per million and reduced the nitrogen to about the same level. This process, termed "solid-state purification", usually greatly improves the room-temperature ductility of the material.

Because it was felt that a better fundamental understanding of brittleness in molybdenum might be gained thereby, the solid-state-purification process has been studied in some detail. The effects (or lack of effect) of a number of variables* on the mechanical properties of the treated molybdenum have been noted.

Past work has suggested that the effect of the process is not, as was at first supposed, one of simple purification. In other words, samples given different heating cycles may have very different mechanical properties, even if the final analyses are the same. This fact indicates that the distribution and form of residual impurities not removed by solid-state purification must be controlled by the heating cycle.

The most important part of the heating cycle was found, unexpectedly, to be the heat-up period. The rate at which the sample was heated to the treating temperature initially had a pronounced effect on its subsequent room-temperature ductility, a rapid heat-up being favorable to ductility. For example, changing the time required to heat the specimen to 3800 F from 45 minutes to 2 minutes changed the elongation in a tensile test from 3 to 5 per cent to 35 to 45 per cent. It is impossible to detect any consistent differences between ductile and brittle samples by metallographic, X-ray diffraction, or analytical techniques. However, there is some indication that ductile samples contain a second phase more often than brittle samples do.

In determining final room-temperature ductility, grain size, wire history, testing methods, and minor variations in furnace operation do not appear to be important variables in the solid-state-purification process.

*These variables were listed on page 61 of the Sixteenth Quarterly Status Report and include time, temperature, cooling rate, degree of vacuum, etc.

It was observed, however, that the type of heating element used had some effect on the ductility of the molybdenum. If a tantalum resistance element was used for heating, the specimens were less ductile than they were if a molybdenum heater was used. The reason is not yet known.

In early experiments with solid-state purification, before the effect of heating rate was realized, a heat-up time of 45 minutes followed by 1 hour at 3800 F was adopted as standard for treating 40 to 80-mil wire. The slow heat-up was adopted initially because gas was evolved from the specimens slowly and a better vacuum could be maintained by the pumps. After 1 hour at temperature, gas evolution usually had nearly stopped.

Molybdenum given the formerly standard 45-minute heat-up followed by 1 hour at 3800 F is not always, nor even usually, brittle, but the room-temperature ductility of such material is unpredictable and subject to wide variations. On the other hand, as stated in the Sixteenth Quarterly Status Report, specimens heated in 2 minutes were always ductile after 1 hour at 3800 F in high vacuum. During the current reporting period, further experiments have been made and so far all specimens heated in 2 minutes have been relatively ductile, without exception.

Experimental Work

Effect of Heating Rate on Room-Temperature Ductility

During the present reporting period, several experimental solid-state-purification treatments were made in which the temperature and time at temperature were held constant but the heat-up times were varied. Times between 1 minute and 3 hours were used to heat the samples to 3800 F.

When nearly instantaneous heating times were used, the specimens contained porosity and voids, as if gas had been released in the metal too rapidly to escape, and the subsequent room-temperature ductility of the wires was extremely low. This condition has not yet been fully explained.

For heating times of 2 minutes or over, the ductility varied inversely with heat time. This can be seen from Table 7, which summarizes this series of experiments. The specimens heated in 2 minutes were all ductile. Of those heated in 15 minutes, some were ductile and some were brittle. The specimens heated in longer times were nearly all more brittle. Enough experiments have been conducted by now to make it fairly certain that the effect of heating rate is real and the differences in ductility between slowly and rapidly heated specimens are not just coincidental.

Samples heated in 15 minutes had widely varying ductility. It appears that the ductility of samples heated at this intermediate rate is entirely unpredictable. Samples 153 and 153X were adjacent pieces from the same

TABLE 7. EFFECT OF HEATING RATE ON THE MECHANICAL PROPERTIES OF MOLYBDENUM WIRE HEAT TREATED AT 3800 F FOR 1 HOUR IN VACUUM

Wire Diameter = 0.040 Inch

Treatment	Heating Time, min	Ultimate Tensile Strength(1), psi(2)	Elongation in 2 Inches, per cent	Reduction in Area, per cent	Remarks(3)
165(4)	2	75,000-78,000	39-49	49-76	Excellent ductility
166B(4)	2	76,500-77,300	41-46	51-68	Excellent ductility
167(5)	2	42,400-71,900	42-60	60-99(5)	Some large grains; virtually testing a single crystal in tension
184(4)	2	78,900-79,200	37-42	68-74	Good ductility (2 min)
153(4)	15	75,000-76,500	32-44	41-68	15 min can produce material of either high or low ductility
153X(4)	15	66,700-69,700	6-13	10-14	Ditto
166A(4)	15	56,300-71,000	5-15	5-19	"
166X(4)	15	62,500-72,600	7-17	12-20	Unpredictable results
168(5)	45	42,200-46,800	9-26	20-50(5)	Some large grains; virtually testing a single crystal in tension
172(4)	45	63,300-70,300	5-10	7-16	Generally low for 45-minute heat-up
169(4)	90	61,700-67,200	9-15	12-20	Still low ductility, but no worse than 45-minute heat-up
170(4)	180	64,800-68,800	9-12	11-17	Ditto

(1) Range observed in testing 6 to 12 samples.

(2) All room-temperature tensile tests at a constant strain rate.

(3) All samples show approximately the same grain size. No significant variations here, unless noted.

(4) Fansteel Wire No. 22-40.

(5) Fansteel Wire No. 25-40. This lot shows a tendency to grow single crystals, thought to be caused by the high metallic-impurity content.

coil of wire, but approximately a month had elapsed between the time Sample 153 was heat treated and the time Sample 153X was heat treated. So far as is known, the heat treatments were identical. Variations in the wire, in the space of a few inches, seem very unlikely.

Metallographic examination showed that the more ductile of the two samples heated in 15 minutes (Sample 153) had very small particles of a second phase at the grain boundaries.

As was true in previous experiments, the brittle material produced in this series of experiments (Table 7) consistently failed in an intercrystalline manner, whereas the ductile material failed in a transcrystalline manner. It might be speculated that a nearly continuous submicroscopic grain-boundary film is formed on slow heating, and that the second phase noted in some of the ductile samples is the same material coalesced so that it forms discrete visible particles, rather than a continuous film. This structure would be less harmful to ductility. It may be speculated further that the same mechanism operates in ductile samples that do not show a second phase, but that the coalesced particles are submicroscopic.

Reversibility of Heat-Treating Effects

As the next step in the investigation, experiments were made to see whether brittle specimens that had been solid-state purified using a slow heating rate could be made ductile subsequently by a second treatment in which they were heated rapidly. The reverse procedure was also tried - that is, taking samples that were ductile after rapid heating and reheating them slowly to see whether they would become embrittled.

Table 8 shows the results of these experiments. It may be seen that brittle samples could be made ductile and ductile samples could be made brittle simply by controlling the heating rate and keeping the temperature and time at temperature constant. These results suggest, again, that the ductility differences are not the result of over-all compositional changes, but are, rather, the results of changes in distribution of impurities. The exact mechanism is not yet understood. It is not believed that the ductility of completely pure molybdenum would be affected by these heat treatments.

So far, it has been possible to demonstrate the reversibility of heat-treating effects in every case in which it was tried.

After their first heat treatment, several of the samples, Samples 167, 167A, 168, and 168A, were composed of a few large single crystals occupying the full cross section of the wires. The ductility even of these is affected by heating rate, and the effect is reversible.

TABLE 8. TENSILE-TEST DATA SHOWING CYCLIC NATURE OF HEATING-RATE EFFECTS

Treatment	Description of Treatment	Ultimate Tensile Strength, psi[1, 2]	Elongation in 2 Inches, per cent	Reduction in Area, per cent	Remarks
166A	15-min heat-up, 3800 F, 1 hr, vacuum	56,300-71,000	5-15	5-19	Tested 4 samples out of 16
166B	Reheated other 12 samples from 166A, 2-min heat-up, 3800 F, 1 hr, vacuum	76,500-77,300	41-46	51-68	Ductility now good; tested half the samples
166C	Reheated other 8 samples from 166B, 15-min heat-up, 3800 F, 1 hr, vacuum	45,500-69,000	1-12	6-12	Ductility now poor; all samples tested
165[3]	2-min heat-up, 3800 F, 1 hr, vacuum	75,000-78,000	39-49	49-76	Excellent ductility
165X[3]	15-min heat-up, 3800 F, 1 hr, vacuum	62,500-72,600	7-17	12-20	Tested 6 of 12 samples
165X-A	Reheated 6 remaining samples from 166X, 2-min heat-up, 3800 F, 1 hr, vacuum	73,600-76,500	39-48	59-69	Ductility completely recovered
167	2-min heat-up, 3800 F, 1 hr, vacuum	42,400-71,900	42-60	60-99	Single crystals in some samples[4]
167A	Reheated 6 samples from 167, 45-min heat-up, 3800 F, 1 hr, vacuum	24,200-49,200	2-15	3-15	Low ductility even in material with few boundaries
168	45-min heat-up, 3800 F, 1 hr, vacuum	42,200-46,800	9-26	20-50	Single crystals[4]
168A	Reheated 6 samples from 168, 2-min heat-up, 3800 F, 1 hr, vacuum	50,800-71,800	22-39	30-39	Ditto
169B	Reheated 169 (see Table 1), 2-min heat-up, 3800 F, 1 hr, vacuum	72,000-73,600	34-42	40-72	Originally low ductility after 1-1/2- and 3-hr heat-up cycles (see Table 1)
170B	Reheated 170 (see Table 1), 2-min heat-up, 3800 F, 1 hr, vacuum	71,200-72,000	39-47	41-61	Ditto

(1) Represents range observed in testing 4 to 12 samples.

(2) All room-temperature tensile tests.

(3) 165 and 165X means material for these samples has been cut alternately from adjacent sections of wire. Merely points out again that the wire itself is not to blame for inconsistencies.

(4) Inherent condition in this lot of wire Fansteel No. 25-40, to grow single crystals (see Table 1).

Treatments 165 and 165X were made on samples cut from adjacent locations in the original coil of wire. The fact that the two samples had greatly different ductilities after these treatments is additional evidence that differences in the samples are probably not the cause of most ductility differences between solid-state-purified wires.

Not only does material which has been solid-state purified at a rapid heat-up rate have a higher average ductility than material that has been heated slowly, but it is also more uniform. The ductility variation between samples treated together is much less for the rapid heating than it is for the slow heating rate.

Effect on Ductility of Varying Time at Temperature

In the previous experiments, time at temperature was held constant and the heat-up time was varied. The next step was to determine the effect of varying the time at temperature while holding the heating rate constant. Two series of experiments were made with the following objectives:

(1) To determine the time at temperature required to produce maximum ductility after a 2-minute heat-up.

(2) To determine whether samples given a 45-minute heat-up would be more apt to be ductile if held at temperature for periods much longer than the 1 hour which has been standard in previous experiments.

The results of these two series of experiments are shown in Table 9. They show that nearly maximum ductility was reached within 5 to 10 minutes at temperature after a 2-minute heat-up. Further work is needed to confirm these results and to establish the minimum time more specifically.

There is also an indication, from a single heat treatment, that, after 2-1/2 hours at a temperature, following a 45-minute heat-up, ductility is beginning to recover. Additional experiments will be required to confirm this. It is also planned to extend the experiments to times greater than 3 hours.

Effect of Using Tantalum Heater Element

In the Sixteenth Quarterly Status Report, evidence was presented to show that the ductility of the treated molybdenum tended to be lower when the heat-treating furnace was heated by means of a tantalum resistor, than when the furnace was heated by means of a molybdenum resistor, even though other conditions were the same.

TABLE 9. EFFECT OF HEATING-RATE VARIATIONS AND TIME OF SOLID-STATE-PURIFICATION TREATMENT AT 3800 F ON THE RESULTING ROOM-TEMPERATURE DUCTILITY

Treatment	Description of Treatment	Ultimate Tensile Strength, psi(1)	Elongation in 2 Inches, per cent	Reduction in Area, per cent	Remarks
186	2-min heat-up, 3800 F, 1/2 hr, vacuum	67,200-75,600	14-37	25-62	Improving ductility
196	2-min heat-up, 3800 F, 1/4 hr, vacuum	79,000-81,400	42-49	65-73	Maximum yet observed
185	45-min heat-up, 3800 F, 1/12 hr, vacuum	57,100-72,600	5-23	5-26	Relatively low ductility
172	45-min heat-up, 3800 F, 1 hr, vacuum	63,300-70,300	5-10	7-16	
174	45-min heat-up, 3800 F, 2-1/2 hr, vacuum	58,400-66,700	5-10	5-10	No improvement
176	45-min heat-up, 3800 F, 3 hr, vacuum	65,900-74,200	10-43	10-66	Starting to show improvement by longer times

(1) Range observed in testing 6 to 12 samples.

The reasons for this were not clear at that time, but some possible explanations were given. One possibility was that the molybdenum vapor given off from a molybdenum heater element might have been lowering the oxygen pressure in the furnace atmosphere by acting as an oxygen getter. Another possibility was that, since tantalum is a strong carbide former, the tantalum element was removing minute traces of carbonaceous vapors from the furnace atmosphere. Such vapors might originate from back-diffusion of pump oil. The carbon, when present, would act as a deoxidizer during the high-temperature treatment. In other words, ductility could result from either the presence of the molybdenum or the absence of tantalum. In order to explore some of these possibilities, or to eliminate them, additional experimental work was done.

Several experiments were performed to try to differentiate between the two mechanisms mentioned above. If molybdenum heater elements getter the residual furnace atmosphere, it should be possible to achieve the same effect by using a tantalum heater element, but maintaining a separately heated getter inside the furnace. If this is the case, high ductility should result. On the other hand, if ductility results from the absence of tantalum, rather than from the presence of molybdenum, then use of a tantalum element and a separate getter should produce metal of low ductility.

Solid-state-purification treatments were made using tantalum heating elements and molybdenum, titanium, and zirconium getters. These getters were in the form of resistance-heated wire filaments. The procedure was to heat the getter after the furnace chamber had been pumped down to ultimate vacuum, but before the heating power was turned on. The getter filament was not kept hot during actual heat treatment. For this series of experiments, the intermediate 15-minute heat-up time was used. Details of treatments and results are given in Table 10.

In general, the properties of the specimens so treated were about the same as those of specimens heated with tantalum elements without using an auxiliary getter. Room-temperature tensile elongations were in the range of 10 to 25 per cent, and reductions in area ranged from 20 to 26 per cent. These properties, although not extremely low, are far from the best obtained in the course of the solid-state-purification experiments.

One or two experiments were made using a tantalum heater and a rapid heat-up rate. The material was not especially ductile.

These few experiments are far from conclusive, and further work will have to be done. For one thing, it would be desirable to keep the getter hot during the entire heat treatment, instead of only before the treatment.

TABLE 10. EFFECT OF GETTERING TREATMENTS ON THE DUCTILITY OF MOLYBDENUM SOLID-STATE PURIFIED IN A TANTALUM HEATER TUBE

Treatment	Description of Gettering Treatment Prior to Standard 3800 F, 1 Hr Treatment[1,2]	Ultimate Tensile Strength, psi[3]	Elongation in 2 Inches, per cent	Reduction in Area, per cent	Remarks
157	Mo wire[4] fired to 3800 F for 3/4 hr	64,100-71,900	7-13	7-18	All samples were of the same grain size. No second phase was visible in the microstructure.
158	Mo wire fired to 3800 F for 1/3 hr	68,000-72,600	15-21	18-21	
159	Ti wire[4] fired to 2000 F for 1 hr	66,500-72,600	10-20	16-24	No apparent improvement in mechanical properties resulted from gettering treatments. Heating-time variable was not yet known to be important.
160	Ti wire fired to 2000 F for 2-1/2 hr	69,600-71,000	17-27	20-26	
161	Zr wire[4] fired to 2400 F for 1/12 hr	65,600-71,000	11-19	14-21	
162	Zr wire fired to 2400 F for 2-1/2 hr	65,600-71,000	10-21	16-23	

(1) 15-minute heat-up time used in all cases when tantalum element was heated up.
(2) Filament firing time varies in all cases because of burn-outs. Also, temperature fired to depends on maximum gas-absorption range.
(3) Range of properties observed in testing 12 samples.
(4) Ten to fifteen feet of 0.020-inch wire was used. This is about the maximum length that could be placed in the furnace and heated to temperature with the power supply available.

Discussion

So far, all solid-state-purified specimens that were heated to temperature in 2 minutes have been ductile, although those heated with tantalum heaters were not quite so ductile as those heated with molybdenum heaters. Samples heated in longer times have been brittle sometimes and ductile sometimes.

The effect of heating rate on ductility has been noted in wire supplied by two different manufacturers.

A reduction in oxygen content is the principal compositional change resulting from solid-state purification. From the work on cast molybdenum, it is known that oxygen has a more pronounced effect on the ductility of cast metal than does nitrogen or carbon. In the Eleventh Quarterly Status Report, some data on the detrimental effect of oxygen on molybdenum wire were presented. All this information, taken together, suggests that the ductility variations observed in solid-state-purified molybdenum are related to its residual oxygen content and to the way this oxygen is distributed. No conclusive proof can be offered at this time.

Future Work

During the next quarter, experimental work will be done to determine precisely the critical temperature zone through which it is necessary to heat rapidly. The limits of this zone may depend on composition. Also, it seems desirable to find out whether maximum ductility can be restored by holding for sufficiently long times at 3800 F after a slow heat-up.

With this new information added to that available, it is hoped that it will be possible to explain why molybdenum is sometimes ductile and sometimes brittle at room temperature, and why some welds are good and others are bad.

Data from which this section of the report was prepared are recorded in BMI Laboratory Record Book No. 7839, pages 79 to 100, and Record Book No. 8418, pages 1 to 20.

HBG:LEO:RBF:GWPR:HWL:WEF:GKM/NLC/js/hcl/vhh