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FORMABILITY AND WELDABILITY
OF
VAPOR-DEPOSITED MOLYBDENUM

FINAL REPORT

31 October, 1952

by

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Amos Shaler
James Johnston
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Alfred Hofstatter
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by J. Wong and A.F. Hofstatter

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ABSTRACT

This report describes work done on the development of methods of working vapor-deposited molybdenum and of welding molybdenum produced either by this method or by existing arc-casting and powder-metallurgy processes. Some of the mechanical properties of all three kinds of molybdenum were measured. The element primarily responsible for embrittling molybdenum when it is heated above a temperature approximately equal to its recrystallization temperature is oxygen, the deleterious effect of which becomes serious at levels as low as 0.001%. The art of fractography was advanced by improvements in technique; it can serve to reveal and perhaps to analyse oxides and other impurities present in the metal in minute quantities.

The major contributions made by this study are: the development of a method of cold-working vapor-deposited molybdenum directly from the deposits, and the development of a new method of welding molybdenum. The welding method is applicable to arc-cast and to powder-metallurgy molybdenum, and probably also to the vapor-deposited metal.

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FORMABILITY AND WELDABILITY OF VAPOR-DEPOSITED MOLYBDENUM

I. Introduction

a. Purpose and Scope of the Investigation

The purpose of the investigation just concluded was to determine the applicability of vapor-deposited molybdenum in plumbing systems of the heat-exchanger type. Techniques were to be developed which could be used as bases for methods of forming sheet and thin-walled tube out of this material, and also for methods of welding or otherwise joining the metal so formed. The properties of the metal in the worked, annealed, and welded condition were to be investigated.

In deciding on the experimental approach to these problems, it was first necessary to investigate the published data concerning the properties of molybdenum available commercially. The strength, ductility, hardness, density, transition temperature, recrystallization, creep, and stress-rupture properties of arc-cast and powder-metallurgy molybdenum were found to be known, but this knowledge had been primarily obtained on bar stock and not on sheet. Since sheet made from these materials has internal flaws, the properties of sheet are not necessarily the same as those of bar. Accordingly the program had to include the establishment of norms for commercial molybdenum in sheet or tube form. Thereafter the working techniques for vapor-

deposited molybdenum could be developed, and the properties of the resulting sheet were studied. In welding, the published information was even scantier, for no systematic evaluation of the behavior of the metal under different welding conditions was found to exist. Various welding techniques were therefore systematically tried out on commercial molybdenum. None was found to be satisfactory. A wholly new welding method was then devised, and proved to be reasonably successful.

This report begins with a review of the published and otherwise reported information on commercial molybdenum. (Section Ib). In Section IIb, entitled Measured Properties of Commercial Molybdenum Sheet, the results of additional measurements made as a part of this investigation on commercial strip are reported, along with a description of the testing machine especially built for this work. Section IIa is an account of the development of the method of cold-rolling the vapor-deposited metal. In Section IIc are reported the properties of the resulting strip.

The next sections concern welding, the literature report on which is given in Section Ic in this Introduction. IIIa is an account of our investigation of conventional welding techniques. This study showed that no ductile welds can be expected from any of the common methods because in all these methods embrittlement stems from impurities existing in the metal. Section IIIb tells our reasons for this conclusion,

and describes our consequent development of the fractographic technique as a metallographic method of measuring the impurities present in the metal which lead to weld-embrittlement. In IIIc the new welding method is sketched, and the results obtained are given.

The report ends with general conclusions (Section IVa) and recommendations (IVb) concerning the usefulness of vapor-deposited molybdenum in high-temperature chemical-engineering applications.

A little over two man-years were spent on the project, but another project on a closely allied problem was under way in our laboratories at the same time, and some of the work on both projects was parallel. Accordingly some of the results given below represent more than the effort devoted exclusively to the present contract.

The project was supervised by Prof. John Wulff from the date the contract was awarded until 1 June 1952. After this date the assistant supervisor, Prof. Amos J. Shaler, became acting supervisor in Prof. Wulff's absence from this country. Graduate students engaged on a part-time basis primarily for this work were James Johnston and James Wong. Others who contributed were Alfred Hofstatter and William Hoffatt, undergraduate students, and Robert Rodgers, laboratory foreman.

b. Reported Mechanical Properties of Commercial Molybdenum Sheet.

Little information could be found on the properties of commercial sheet. Westinghouse Research Laboratories reports¹ indicate tensile strengths varying from 70,000 psi to 140,000 psi, depending on the degree of cold work, for cold-rolled sheet made from powder-metallurgy ingots. These specimens had a yield point 70-90% of their tensile strength, and showed elongations up to 25%. These figures are for specimens taken in the rolling direction, and it is expected that the metal is more brittle in the transverse direction.

Molybdenum sheet made from arc-cast ingots by Climax Molybdenum Company² has the set of as-rolled and after-annealing properties at various temperatures shown in Table I. The material was cold-rolled 60% from 0.052" to 0.020", and specimens 1/2" wide and 1" in gage length were cut both in the rolling direction and normal to it. The difference in properties is evident.

1. References are given together at the end of the report.

TABLE I

Properties of Molybdenum Sheet,
Arc-Cast, produced by Climax Molybdenum Co.

In Rolling Direction

<u>Annealing Temperature</u>	<u>Yield Point</u>	<u>Tensile Strength</u>	<u>% Elongation</u>
Cold Rolled	151,800	154,300	5
870° C	126,500	131,500	12
985	111,000	117,300	13
1090	74,400	88,800	29
1205	75,500	90,600	26

Normal to Rolling Direction

<u>Annealing Temperature</u>	<u>Yield Point</u>	<u>Tensile Strength</u>	<u>% Elongation</u>
870° C	130,200	132,100	3
985	-	123,400	2
1090	81,200	93,500	17
1205	82,800	91,100	17

The recrystallization temperature is evidently over 1000° C. It must also be noted that the Climax specimens were reported to exhibit the yield point phenomenon, to which we shall return below (Section IIa) in connection with our own measurements on commercial sheet.

Finally, Bechtold and Scott³ have given figures for the temperature of transition from brittle to ductile fracture in molybdenum bar specimens. Although no similar measurements have been reported on sheet, their figures are reported here because the transition temperature, being near room temperature, is one of the most important factors in the usefulness and workability of this metal. These authors

compared the properties of Westinghouse powder-metallurgy metal and Climax arc-cast metal on the basis of specimens having had the same amount of working at the same strain rate, and annealed to the same grain size. The transition temperature lay from 15 to 45 degrees below room temperature in both cases, but could be raised for above it by introducing notches in the specimens or raising the strain rate.

These authors further report that metal made by both methods could be recrystallized at 1150° C after cold work. Since known analytical methods for determining oxygen in molybdenum are not sufficiently sensitive to reveal contents less than about 0.005%, and since as little as 0.001% oxygen can seriously raise both the recrystallization temperature and the transition temperature, the purity of molybdenum can best be expressed by noting these temperatures rather than the results of analyses.

Another criterion of impurity is the extent of the yield-point phenomenon in a body-centered cubic metal. For the powder-metallurgy metal (transition temperature -25° C) the separation between the upper and lower yield points was of the order of 10,000 psi at temperatures covering a wide range including the transition; whereas for the arc-cast metal (transition temperature +5° C), it was of the order of 2000 - 3000 psi. There seems to be no direct correlation here between the yield point spread and the transition temperature; perhaps an impurity other than oxygen may be

influencing one more than the other.

In summary, the mechanical properties reported for sheet molybdenum made from arc-cast and from powder-metallurgy ingots are similar and are in round numbers as follows:

Tensile strength after 60% cold work: 150,000 psi to 160,000 psi.

Tensile strength after recrystallization: 70,000 psi to 90,000 psi

Transition temperature: -25°C to $+5^{\circ}\text{C}$.

Elongation in 1", cold rolled: 2% - 5%

Elongation in 1", recrystallized: 15% - 25%

Elongation less in direction normal to rolling.

Recrystallization temperature: 1050°C to 1150°C .

Yield Point in all cases at 75% to 95% of tensile strength.

Upper-lower yield point separation: 2000 psi - 10,000 psi

c. Reported Welding Properties of Commercial Molybdenum Sheet

J. Heuschkel⁴ has reported on an investigation of welds in molybdenum made by the spot, seam, percussion, flash, and inert-gas **arc** processes. He reports that none of these methods can produce a high-strength ductile weldment. In addition, the procedures are not easy: in resistance-welding the high melting point of molybdenum leads to much electrode deformation, pick-up of molybdenum by the electrode, and

contamination of the molybdenum by the electrode metal. In inert-gas arc-welding, the difficulties are chiefly that non-porous welds can only result from use of special techniques such as multiple-pass welding. Percussion and flash welding are done on bars, but might be adapted to butt-joints in sheet; Heuschkel's report indicates, however, that special atmospheres must be used, and that ductility has not yet been obtained even in bars.

The problem of weld embrittlement is fundamental: in all processes in which the metal is heated above its recrystallization temperature (or melted), impurities already present in the metal or picked up during welding apparently segregate to the grain boundaries, where they behave in a deleterious manner. Inert or reducing atmospheres do not suffice to prevent embrittlement from impurities which are in the metal. It appears also that protective gases such as are used in industrial welding are not pure enough to prevent the slight additional atmospheric contamination that is sufficient to cause brittleness.

Other papers on welding tell the same tale.^{5,6,7,8,9} A report by Goodman¹⁰ describes molybdenum welding by the submerged-melt process, but fails to give the mechanical properties of the resulting joint.

In summary, previous reports indicate that conventional welding techniques not only do not, but cannot,

produce high-strength ductile welds.

Three approaches to the problem are under study: the first is the welding technique reported below (Section IIIc), in which the recrystallization temperature of the commercial molybdenum is not exceeded. Secondly, a study is being made at the Battelle Memorial Institute of alloying agents which, added to molybdenum, might prevent the occurrence of embrittlement when the metal is heated above the recrystallization temperature. The third approach is to produce molybdenum of sufficient purity in the first place, so that successful welds can be made under proper shielding atmospheres. As will be related below (Section IIIa), the purity requirements for such atmospheres turn out to be too stringent to be promising industrially.

II. The Experimental Work on Working and the Measurement of Properties

a. Working Vapor-Deposited Molybdenum

The technique of depositing molybdenum on the inside of graphite or metal tubes has been described by W.C. Childs, J. Cline, W. Kisner, and J. Wulff.¹¹ No new developments were involved in the production of specimens for the present study. Briefly, the technique consists of placing a graphite or metal tube of round, square or other cross-section into a Vycor reaction chamber arranged to be heated externally to approximately 900° C. Through the heated tube is passed at a closely controlled velocity a stream of gas consisting of approximately ten parts of purified hydrogen and one part of pure molybdenum pentachloride, at a total pressure of 20 to 40 millimeters. The reaction between these two occurs in the heated chamber in such a way that molybdenum metal is grown from the wall of the tube at a constant and uniform rate as high as 0.02 inch per hour, leaving a tubular, dense, mass of metal some 4 inches long, and as thick-walled as desired. By using multiple heaters, much longer tubular deposits of uniform thickness can be made, provided a close control of the many process variables is maintained, and provided no contaminants enter the gas stream.

By this technique, round tubes a few inches long

and approximately 1/2 inch in outside diameter were prepared for the experiments on the working properties of the deposit. Figure 1 shows the microstructure of the metal in such a tube. It is observed that the deposit is columnar. In this condition, the metal shows little ductility, although occasionally a thin deposit can be appreciably bent without cracking. If the columnar microstructure can be substantially deformed above or below the recrystallization temperature, the metal becomes ductile, and the ductility is maintained after recrystallization.

First attempts to work the deposit were performed directly in a swaging machine, without success. When the deposited tube was fitted over a mandrel and sheathed in a metallic envelope, some deformation became possible without cracking. But extensive deformation without cracking could not be obtained even at 500° C, no matter what material or design was used for sheath and mandrel (many of different yield strengths and rigidity were tried). The conclusion was soon reached and subsequently confirmed that at the extremely high strain-rates involved in swaging, the transition temperature of the columnar metal was raised to a high value. The difficulty of avoiding oxidation made swaging above 500° C undesirable. A method was then sought for working the metal at lower strain rates. One of the requirements was that specimens

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Fig.1 Microstructure of Vapor Plated Molybdenum. Mag. X200.

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could be made by vapor-deposition. Two methods were considered. First, deposits could be made up as tubes of rectangular cross-section, $1/2$ inch by $1/4$ inch in outside dimensions, and with as thick a wall as possible; these could then be sawed lengthwise into pairs of strips each $1/2$ inch wide and nearly $1/8$ inch thick. Lengths of about three inches of such strips could then be rolled at various temperatures after enveloping them in sheaths of various designs.

Secondly, sheathed tubular deposits of round cross-section could be rolled directly between a small roll inserted in the tube and a larger roll outside the tube. Considerable calculation is involved in designing a machine for this purpose, and much machine-shop time is required in its construction. As a result, it was not until after this contract expired that such a design was finally drawn up, and the construction of the machine is only now to be begun.

The first technique mentioned above is the simpler, and numerous specimens were made up accordingly. It was first found that the unsheathed deposit could not be rolled directly at room temperature. To roll the metal at elevated temperatures, sheathing is necessary to prevent contamination by oxygen from the atmosphere to the slight degree that would cause embrittlement and consequent edge-cracking. Several sheath designs were

tried, and the greatest success was obtained with that shown in Figure 2. The sheath is made of stainless steel; it envelops the molybdenum on all sides, and it is made air-tight by being completely welded by the atomic-hydrogen process. At first the sheathed molybdenum "sandwiches" were rolled at 450°C to 500°C with great success. Reductions between 50% and 87% were accomplished without cracking, oxidation, or adherence (cold welding) between the molybdenum and the sheath-metal. Passes of the order of 5% were used, and the "sandwich" was reheated after every pass. Other temperature sequences were then tried, and it became apparent that room-temperature rolling could be successful if a few passes were first made at 450° C. Finally it was found that the primary function of these early warm passes is to make perfect the three-dimensional constraint of the molybdenum by the sheath. This can be accomplished by a single light pass at about 450° C which does not reduce the molybdenum at all, but merely tightens the fit of the sheath. Thereafter the "sandwich" may be rolled cold. After the molybdenum has undergone some 50% reduction, the sheath may be cut away and the molybdenum strip may then be cold-rolled directly. Deformations greater than 90% have been obtained with no sign of cracking.

FIG. 2 - SHEATH FOR ROLLING MOLYBDENUM STRIPS. FULL SIZE.

b. Measured Properties of Commercial Molybdenum Sheet

In view of the paucity of data on commercial sheet (see Section Ib) and in view of the fact that the geometry of the tensile-test specimens, the rate of testing, the ambient temperature at the time of test, and possibly the surface finish of the specimens all influence the yield and tensile strengths and the ductility, it was deemed advisable to run control tests on strips of molybdenum made from arc-cast and powder metallurgy ingots simultaneously with all our tests on the rolled vapor-deposited material.

To make these tests, the small testing machine shown in Figure 3 was constructed. The application of load is done by an electric motor, running well under rated capacity, through an intermediary gear reducer and a multi-speed gear-and-worm train which actuates a single screw. A variety of approximately constant head speeds is thereby obtained. Jaws for the specimens are mounted on universal joints for self-alignment. The load is measured by means of an aluminum load-ring in series with the specimen. On the ring are mounted four strain gages, the signals from which are combined by an external Wheatstone bridge. The four-gage measuring method gives automatic temperature compensation and high sensitivity.

In the specially designed extensometer shown in Figure 4, a wide range of longitudinal elongation in a 1-inch gage length is converted into a range of

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Fig.3 Tensile Testing Apparatus.

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Fig.4 Strain Gauge Extensometer

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electronically measurable bending stresses in a pair of phosphor-bronze strips on either side of each of which is mounted a bakelite-type strain gage. These are connected in an external Wheatstone bridge, giving, as with the load ring, a high sensitivity and automatic temperature compensation, as well as automatic elimination of any reading that might be due to a bending moment in the specimen. The extensometer can be immersed in a constant temperature bath for transition-temperature measurements. The phosphor-bronze strips and strain gages on the extensometer are above the level of the heating or cooling liquid in the bath, as is the load ring. The constant-temperature bath is sealed to the bottom of the lower jaw to prevent loss of liquid without affecting the readings.

Specimens are accurately prepared by blanking them in a die from rolled 0.010-inch strip (as-rolled or annealed) to provide a reproducible 1-inch gage length with a width of 0.075 inch.

Signals from both the load ring and the extensometer are fed simultaneously into a Sanborn dual-channel recorder. By means of prior calibration the recorded curves are easily converted into stress-strain plots, from which values of elastic limit, yield points, elastic modulus, necking strain, ultimate stress, and final elongation can be obtained accurately at a series of fixed temperatures and strain rates. Figure 5 shows a typical record. A one-

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Fig.5 Load vs Elongation Record for Power Metallurgy Molybdenum.

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centimeter deflection on the record at maximum sensitivity is equivalent to a resistance change of 0.01% in each of the four arms of the two Wheatstone bridges, giving a sensitivity of 0.0025% per centimeter. Stress and strain sensitivities are accordingly 572 psi and .0014 respectively on the specimens.

With this apparatus, the following measurements have been made so far on commercial strip; all were at 23° C and at a strain rate of .00106 per second.

Arc-cast molybdenum, as received: tensile strength 174,000 psi; elongation 2% in one inch.

Arc-cast molybdenum, recrystallized 1 hour at 1050° C in dry hydrogen: tensile strength 71,600 psi; elongation 23.4% in one inch; upper yield point 57,000 psi; lower 54,300 psi. It may be noted that these figures are slightly lower than the ones reported by Climax Molybdenum Company (see Section Ib). Evidently our specimens were cold rolled more drastically and more thoroughly annealed.

Powder-metallurgy molybdenum, recrystallized 1 hour at 1050° C in dry hydrogen: tensile strength 71,500 psi; elongation 18.1% in one inch; upper yield point 56,200 psi; lower yield point 54,900 psi.

As will be detailed in the next section, the vapor-deposited metal does strain-harden as much as the commercial metal; its annealed properties are similar, but no yield

point is observed at room temperature and at the strain-rates used here.

No measurements were made on the recrystallization of the commercial metal, since the data reproduced in Table I are sufficient to indicate a temperature in excess of 1000° C. According to the Metals Handbook, "pure" molybdenum recrystallizes at 900° C. As will be shown below, the vapor-deposited metal recrystallizes at slightly over 850° C.

c. Measured Mechanical Properties of Rolled Vapor-Deposited Strip

A study was made of the molybdenum strip, rolled as detailed in Section IIa, to determine its recrystallization temperature, an index of its purity. The recrystallization temperature is defined as that at which the microstructure of the strained metal is completely replaced by new grains. It depends not only on purity, but also on the time during which recrystallization is allowed to proceed, the amount and temperature of prior plastic deformation, and the original grain size.

The first series of specimens were cut from strips rolled entirely in stainless-steel envelopes and at 450-500° C, the sandwich being reheated after each pass. The rolling was done on a two-high ten-inch roll-stand (through the courtesy of the Watertown Arsenal).

Recrystallization was carried out in an electric tube-furnace in which the temperature could be controlled to a constancy of 2°C . An atmosphere of hydrogen was provided, the gas being passed over copper gauze at 520°C and through a dry-ice trap. The furnace tube and boat were of zirconia. All runs were of two hours duration, after which the specimens were allowed to cool in a cold portion of the tube.

After the heat-treatment, all the specimens were polished metallographically, the final polish being done with diamond dust suspended in kerosene. Etching was with Coons' reagent (one part each by weight of potassium hydroxide and potassium ferricyanide in twenty parts of water); etching time was 25 seconds. Figure 6 shows the results for two extreme grain sizes (the two sides of each specimen had structures as shown in Figure 7. Figures 8 and 9 show cold-worked and fully recrystallized structures.

An extrapolation of the data of Figure 6 indicates an ultimate (100% reduction) recrystallization temperature of 868°C , lower by 30° than any previously reported.

The study of the influence of temperature of rolling on the recrystallization temperature was not completed -- no values have yet been obtained for the strips rolled entirely at room-temperature.

A few stress-strain curves have been measured for the vapor-deposited rolled strips.

FIG. 6 - PERCENT REDUCTION OF AREA VS RECRYSTALLIZATION TEMPERATURE FOR FINE AND COARSE GRAIN VAPOR PLATED MOLYBDENUM ANNEALED IN HYDROGEN FOR TWO HOURS.

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Fig.8 Cold Rolled Vapor Plated Molybdenum.
78% Red. in Area. Mag. X200.

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Fig.9 Fully Recrystallized Vapor Plated Molybdenum.
Two hours at 1057°C in Dry Hydrogen. Mag. X200.

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In the worked condition (87.5% reduction of area) the tensile strength was 35,300 psi, much lower than the 174,000 psi value found for arc-cast metal rolled to the same extent. Elongation was 2% on both metals. After recrystallization in dry hydrogen at 1050° C, the tensile strength of the vapor-deposited metal was 68,400 psi, comparing favorably with the 71,600 psi for arc-cast and the 71,500 psi for powder-metallurgy molybdenum. The elongation of these specimens was 19% (vapor), 23.4% (arc), and 18% (powder). The spread here is due to grain-size differences, the temperature of recrystallization being greatly excessive for the vapor-deposited metal. Measurements with specimens recrystallized to the same grain size (and therefore at different temperatures) were not completed.

Figure 10, a comparison of stress-strain recordings for vapor-deposited and for arc-cast metal, emphasizes the absence of a yield point in the former. This is additional evidence of its high purity.

Preparations are being made for running series of measurements of this kind at various temperatures from room-temperature down to that of liquid air, to provide information on the transition temperature of the vapor-deposited metal. These measurements will be available in the very near future.

Permagraph

CHART NO. 221

SANBORN Recording Permagraph

CHART NO. 221

Fig. 10a Arc-cast Molybdenum

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SANBORN *Recording Paper*

CHART NO. 221

LOAD

ELONGATION

Fig.10b Vapor Plated Molybdenum

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III. The Welding of Molybdenum

a. Experiments Using Conventional Techniques

Much of the work of evaluating conventional methods of welding molybdenum was done on the companion project, and was reported in detail in the Annual Report #1, Contract No. AF 33(038)-23281 Task II, entitled Research and Development of Molybdenum Welding, to Flight Research Laboratory, WCRRL, Wright Patterson Air Force Base, Ohio. Only the main results are repeated here.

The approach used was (1) to make and test fusion-welds accomplished in increasingly pure atmospheres, (2) to investigate the influence of impurities in the welding atmosphere by making deliberate additions of oxygen and nitrogen, (3) to make a fractographic study of the embrittling factors, and (4) to compare arc-cast and powder-processed molybdenum with regards to weldability by fusion processes.

Tests of the welds were conducted on a bend-tester, described in the report mentioned above, taking care that the same grain-orientation, resulting from casting, was in the same position relative to the test-specimen axis in all tests.

Atomic-hydrogen weldments were made in air with carbon and wolfram electrodes on 1/4-inch arc-cast plate-stock machined from rounds, using filler-metal cut from

the same stock. The beads produced were neat though discolored, but the moduli of rupture never exceeded 35,000 psi. No ductility was observed. All specimens were porous, particularly those made with a carbon electrode.

Heliarc welding was done, using the same kind of specimens, in air with added helium, in helium, and in a very highly purified helium atmosphere. In all cases the specimens were clamped onto a water-cooled copper plate. Thoriated wolfram and graphite electrodes were used. With the former, in air with auxiliary helium streams, numerous variations of technique failed to prevent porosity, and strengths remained below 30,000 psi. With graphite electrodes, the strength rose to 45,000 psi, but no ductility was obtained.

With pure helium circulated through a box containing the specimens for 2 hours, heliarc welding gave a weld of 48,000 psi strength. When the circulation time was increased to 4 hours, a measurable deflection was obtained in the bend test, and the strength was 57,000 psi.

The third modification of the heliarc method consisted of using an arc-casting furnace. The metal parts were degassed by glow-discharge, and a titanium button was melted in the furnace to remove the last traces of residual gas. After taking these precautions, welds having bond-strengths of the order of 110,000 psi and

appreciable ductility were obtained. A tensile test gave a strength of 55,000 psi and an elongation of 3% of the weld zone in a specimen made in this manner.

The only specimens showing any ductility at all were these made under the extraordinary precautions noted above; these were also the only ones for which the fracture in bend or tensile test took place in the penetration zone and not in the deposit itself. The procedure for making these welds is hardly applicable to industrial production. But the results showed that embrittlement can be caused by the very slightest impurity.

b. Effects of Impurities on Brittleness of Molybdenum

To provide an indication of the nature and quantity of impurity which causes the embrittlement observed in the welded specimen described above, a series of arc-castings were made with increasing oxygen contents and with increasing nitrogen contents. These castings were not weldments in the strict sense of joining two pieces together, but they were made in a long slot in a water-cooled block, and were therefore similar to unconstrained weldments except for grain orientation and, to a minor extent, cooling rate. The impurity pick-up was controlled by introducing measured volumes of gases to the arc furnace.

The results of these experiments are given in

Figure 11 and in the photomicrographs and fractographs of Figures 12-19. These results convincingly demonstrate that the maximum allowable oxygen content in molybdenum to avoid brittleness is of the order of 0.001%, a value which poses a very difficult problem in analysis (in fact, no analytical method now in use is accurate enough to measure this impurity level).

At this point, a diversion from the main line of discussion is in order; the results of the fractographic examination will then be reviewed.

The art of making fractograms such as those pictured in Figures 14-19 has been exploited by Zappfe,¹² but had to be developed considerably further for the present study. Refinements in technique, in lighting, and the design of a new kind of stage (Figure 20), made possible these revealing photographs. The effort spent on this phase of our work was believed justified because it is probable that the fractographic technique can be used as a means of control of purity in molybdenum production. A set of standards of comparison is of course required, but since these cannot be sufficiently accurately analysed by any of the methods commonly in use, a study is under way to see if a method of analysis based on the separation of gaseous molybdenum pentachloride and oxytrichloride might be workable. Even though in all probability such an analytical technique

EFFECT OF OXYGEN ON DEFLECTION OF THE BEAM IN BEND TEST OF CAST MOLYBDENUM. HEAT #450

EFFECT OF OXYGEN ON BREAKING STRESS OF CAST MOLYBDENUM. HEAT #450

EFFECT OF NITROGEN ON DEFLECTION OF THE BEAM IN BEND TEST OF CAST MOLYBDENUM HEAT #450

EFFECT OF NITROGEN ON BREAKING STRESS IN BEND TEST OF CAST MOLYBDENUM HEAT #450

FIG. II EFFECTS OF IMPURITIES ON CAST MOLYBDENUM

Fig. 12

Weld Specimen I-A. Welded in Arc-Melting Chamber in Purified Helium.

Fig. 13

Cast Specimen 27-A. Vacuum Arc-Cast, Forged and Recast in Purified Helium.

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Fig. 14

500X Specimen 27-A. Vacuum Arc-Cast, Forged and Remelted in Purified Helium. Intergranular Fracture.

Fig. 15

1000X Specimen 27 - B. Same as in Fig. 14. But with .0004% O_2 added. Intergranular Fracture.

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Fig. 16
600X Intergranular fracture of Climax molybdenum, heat 465; 0.028% carbon.

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1000X Molybdenum Cast in a 5%N₂95% He Atmosphere.
Intergranular Fracture.

1000X Molybdenum Cast in a 5%N₂-95% He Atmosphere.
Intergranular Fracture.

40

Fig. 18
500X Specimen 27-A. Transgranular Cleavage.

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Fig. 19
400X Transgranular fracture of a very large grain in molybdenum
vapor-plate of Run T-16, plated June 5, 1952.

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Fig. 20
Fractographic Stage

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would be exceedingly laborious and not of wide industrial applicability, still it could provide the necessary standardization of specimens for fractographic classification. The considerable work involved in the development of these complementary methods of analysis is begun, but about two more man-years are estimated for completion.

We can now return to the discussion of the fractograms.

These photographs were selected as attempting to represent most closely the typical intergranular surface of each specimen. But it must be emphasized that each grain usually has an individual form or pattern different from that of adjoining grains, except at very low oxygen additions or very high oxygen additions. A marked transition could be observed between the fracture surfaces of specimens containing very low oxygen additions (less than 0.001%) and those with oxygen additions greater than 0.001%. The low-oxygen surfaces appeared broken up into chevrons or check marks similar to those observed by Zappfe. Additions higher than 0.001% were marked by the presence of continuous oxide inclusions in film or sheet form.

Failure of all oxygeniferous samples occurred predominantly intergranularly except after an impact blow. Impact caused the low-oxygen samples to fail principally by cleavage. An inclusion tentatively identified as

oxide was found on these transgranular cleavage facets; its typical appearance is shown in Figure 16.

Nitrogen additions caused intergranular failure, as is shown in Figure 17. The nitride was observed fractographically to predominate at 3-ray grain-boundary junctions. As the nitrogen content increased, the typical fractographic structure of the nitrides migrated further into grain boundaries and sometimes became disconnected from the grain-boundary junctions (Figure 17 lower).

All welded specimens failed by intergranular fracture. In the fracture surfaces of these, the dominant features are sheet or film, check marks or chevrons, and globular oxides as well as nitrides. Those weld specimens which exhibited ductility after welding in purified helium revealed only chevrons or check marks, indicative of very low oxygen contents.

c. New Cold-Welding Method, using Chlorine:

Although the methods described in Section IIIa, as well as the submerged-melt welding method and the spot-welding method, can all be utilized for joining molybdenum for the fabrication of articles not subjected to high stresses in service, they are not satisfactory for some of the purposes of interest to the sponsor of this contract; namely, for highly stressed articles.

Two different approaches to the problem exist. First, a more easily weldable metal can be produced. The fact that vapor-deposited molybdenum does not contain as much of the embrittling oxygen as do the powder-metallurgy and arc-cast products makes it probable that our material could be more easily welded. Another possible solution of the same kind is to try to introduce into the metal one or more alloying additions which can successfully compete with the molybdenum for oxygen, and thus render the latter less deleterious. The workers of Battelle Memorial Institute are engaged in trying to find such alloying additions, but to date there is no indication that they have achieved success. Whether or not either the vapor-deposited metal or an alloyed material will prove more easily weldable than the arc-cast or powder-metallurgy products, it is evident from the results reported in the previous section of this report that a very highly purified atmosphere will have to be maintained in the vicinity of the weld during welding.

We concluded therefore, that there was a greater probability of solving this problem by circumventing the embrittlement in another way; namely, by never raising the metal to the embrittling temperature during the process. Cold-welding has proved successful as a method of joining soft metals together, and for joining aluminum to steel. It has also been used extensively in

the manufacture of filled and clad sheet of various metals and alloys, but has not heretofore been applied to molybdenum or to any refractory metals.

Accordingly a new welding method has been developed, as a part of this contract, which embodies the following characteristics: (1) the temperature is maintained below 1000° C at all times, and (2) the surfaces to be joined are cleaned and kept clean to a high degree of perfection by forming with any oxygen present a compound more stable and more volatile than the molybdenum oxide.

To do this we preheat in chlorine gas the two halves of the specimen to be joined, and then weld them together in the resulting atmosphere at a temperature below the recrystallization temperature, using only moderate pressures.

The principal reactions are believed to be as follows:

The simultaneous formation of gaseous molybdenum pentachloride and oxychloride is necessary in order to mechanically entrain and carry away the molybdenum oxychloride. Neither of the products is dissociated or reduced during or prior to welding, so that any oxygen

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initially present in the metal or on its surface, or in the surrounding atmosphere, is effectively bound up and removed.

In order to make tensile measurements of completed welds, a jig was built for the purpose of holding pre-machined specimen-halves in alignment during welding. As shown in Figure 21 this equipment consists of a gas-tight water-cooled cylinder containing two water-cooled pistons, one of them insulated electrically from the cylinder.

Both pistons have alignment holes in them to receive the butt ends of the weld samples. A sight tube with window scraper enables the observer to measure temperatures. All parts are of monel metal for resistance to chlorine-gas corrosion. A transformer controlled by a variac permits the heating of a graphite sleeve placed around the specimen for the low temperature chlorination of the surfaces to be joined. A second transformer-variatic pair is used to heat the specimen itself for the second step, resistance butt-welding.

To carry out a welding operation in this apparatus, the following procedure is used.

The pre-machined specimen-halves are assembled in the butt-welding chamber with a graphite sleeve between the shank ends. The graphite sleeve has optical- and gas sighting holes drilled in it and performs the

ALL METAL PARTS OF MONEL METAL. MACHINING DONE AFTER ASSEMBLY FOR "PERFECT" ALIGNMENT.

FIG. 21 BUTT WELDING JIG

function of a heater while keeping the weld interfaces separated, as is shown in Figure 21. Tank chlorine is introduced either by flushing, or by evacuating and filling. The temperature of the graphite sleeve is raised until copious blue-brown clouds of gas may be seen coming off the weld interfaces. This temperature was found to be about 300° C by auxiliary measurements made with a thermocouple. The graphite sleeve is considerably hotter. Thermocouple measurements could not be long continued in chlorine gas and were finally abandoned after repeated attempts. The time of pre-chlorination is of considerable importance.

After prechlorination the graphite sleeve is cracked off by squeezing the two specimen-halves together, by applying a slight pressure to the top piston. The weld region is then heated by passing a current directly through the interface between the two pieces, now in contact. The current required for this step is previously calibrated to raise the temperature to 1000° C. Optical pyrometer readings cannot be taken for more than a few seconds because of the dense pentachloride clouds released. Thermocouple measurements cannot be made at all. The time is important during which the welding temperature is maintained before pressure is applied, and the manner is important in which the half-specimens are brought into contact (by repeated applications of light

pressure and subsequent separation, as in conventional upset-welding). The final step consists of applying to the top piston of the apparatus a load such that a pressure of some 65,000 psi is developed at the interface between the specimen-halves. A considerable deformation of the weld region ensues, as in upset welding (see Figure 22). After welding, the specimen is machined to a 0.200 inch diameter x 0.5 gage length using carbon tetrachloride as a cutting fluid. Carbon tetrachloride makes possible machining operations without the application of undue stresses to the specimens.

Tensile testing of our specimens was done at a cross head speed of 0.04 inch per minute, at room temperature, in the special jig shown in Figure 23. This jig prevents a moment from being developed at the point of interest in the specimen.

The results of testing some of the sixty-one specimens welded in the apparatus described above are shown in Table II. The tensile strength of the unwelded material is 76,000 psi, and that of those specimens which fractured outside the weld is seen to be only slightly lower: very little loss of strength was caused in the metal near the weld. The ductility of the welds is not yet satisfactory; indications available show that the transition temperature has been raised to slightly above room temperature, but insufficient detail has been

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200X

50X

25X

Fig. 22
"Cold" weld specimen. Weld interface
in same direction as Flow lines.

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Fig. 23
As - Welded specimen and tensile testing jig

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obtained to date on this point. Neither is it yet known if slight modifications in procedure can bring the transition temperature back down to that of the starting material (a few degrees below room temperature). It is probable that if the metal has a lower transition temperature to begin with, room-temperature ductility could be achieved with the present welding procedure.

From the sample data shown in table, and other test results, we have so far established the following welding conditions:

- 1) Reduction of MoCl_x with H_2 does not appear to be useful.
- 2) A minimum prechlorination temperature of 300°C ($\sim 900^\circ \text{C}$ for the graphite sleeve) is necessary. Copious clouds of pentachloride are released at this temperature.
- 3) A maximum prechlorination temperature exists; it is about 500°C for satisfactory welding.
- 4) Accidental small air-leaks do not appear to make much difference in the results.
- 5) Contact pressure just prior to welding is of great importance. Low test results are believed to be due to trapped MoCl_x which becomes condensed on the joint surfaces after prechlorination and before the welding temperature is reached.

All failures of 75% joint efficiency and over are transgranular. Failures of less than about 60,000

psi have a peculiar burnished surface not recognizable as any common type of failure. Good welds do not reveal any sharp line of demarcation at the weld interface, as is shown in Figure 22.

It may be noted (only a few illustrative examples have been selected for Table II) that the tensile strengths are either 12,000 psi or under, or from 25,000 to 30,000 psi, or over 60,000 psi. There are but very few values outside these ranges. This result suggests that the first lot are failures, the last lot successes, and the intermediate lot are essentially successes, but that small regions of the weld-interface contain trapped reaction products. According to the theory of fracture a flat lenticular inclusion of this type, in a ductile metal, must be a region of stress concentration, the stress-concentrating factor being of the order of 3, in good agreement with our figures.

The proposed approach to further improvement of our welding process therefore is to eliminate these regions of trapped reaction products either by altering the design of the joint or by altering the technique of the welding step in the process.

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Table II
Welding Experiments

Run	<u>Prechlorination</u>		<u>Welding Experiments</u>			<u>Welding Cycle</u>		
	<u>Temperature of Graphite</u>	<u>Time</u>	<u>Remarks</u>	<u>Temperature</u>	<u>Hold time before weld</u>	<u>Gas</u>	<u>Remarks</u>	<u>Tensile Strength</u>
28	1025° C	8 min.	Evacuated and filled with chlorine	900°C	2 1/2 min.	H ₂		12,000 psi
25	1025°C	8 min.	" "	900°C	2 1/2 min.	H ₂	Accidentally pulled in some air	11,300 psi
30	1025°C	10 min.	" "	1000°C	2 1/2 min.	H ₂	Hydrogen line plugged up - welded with remaining chlorine	72,000 psi
33	1025°C	10 min.	Flowing Chlorine	240 volt (approx. 1000°C)	10 sec.	Cl ₂	Very light contact pressure	63,000 psi
35,	1030°C	12 min.	" "	240 volt	30 sec.	Cl ₂	" "	60,000 psi
36	<1025°C (~800°C)	10 min.	" "	240 volt	10 sec.	Cl ₂	Too cold during prechlorination	no weld
48	1125°C	10 min.	" "	240 volt	10 sec.	Cl ₂	Light contact pressure	26,000 psi
60	1000°C	10 min.	" "	240 volt	30 sec.	Cl ₂	Heavy contact pressure (10,000 psi)	28,000 psi

IV. CONCLUSIONS

a. Working Vapor-Deposited Molybdenum

The failure of swaging experiments designed to modify the columnar structure of vapor-deposits of molybdenum may be attributed to the excessive strain-rates encountered in this mode of working. Although it is probable that the transition temperature, below which the metal becomes brittle, is substantially lower in vapor-deposited molybdenum than in the arc-cast or powder-metallurgy product, it is nevertheless true that at high strain-rates or in the presence of highly stress-concentrating notches the metal may be expected to fail in a brittle manner above room-temperature. This behavior is consistent with the known behavior of body-centered cubic metals in general. Accordingly all methods that can be successfully utilized in cold-working the metal directly from its deposited form must be slow strain-rate operations. Since in addition the columnar deposit cannot withstand appreciable shear-strain until it has been subjected to some prior cold work, the methods available are limited to those which can deform a large area of the deposit at once: rolling, press forging in simple shapes, and perhaps a tube-modifying operation which is now under study, and in which the deposit is deformed between two rolls, one of which is inside the tube, one outside. The limitations of

this process depend directly on the rigidity of the internal roll. In addition, it is probable that a constraining envelope will continue to be required in the first passes of any cold deformation process. After some 50% deformation has been obtained, the metal can evidently be cold-worked easily by any slow-strain-rate method.

How well the vapor-deposited material can be hot-worked has not been determined in this study. Presumably it can be done at least as easily as with the molybdenum now commercially available. Further study alone can reveal whether the vapor-deposited product becomes embrittled during hot-working or during service at high temperatures.

From these conclusions it follows that the art of making vapor-plated molybdenum has not yet reached the point where large components can be manufactured in one piece. But with the promise of the development of a successful sheet-welding method, such large components might soon presumably be made by joining smaller units together. Since the cold-worked metal is ductile and machinable (with carbon tetrachloride as a cutting fluid), joining can also be accomplished mechanically.

b. Welding Vapor-Deposited Molybdenum

For the reasons outlined in Section III, our effort has been concentrated on the development of a

method of welding which would be applicable both to vapor-deposited metal and to molybdenum available at present on the commercial market. It is believed that if the latter can be successfully welded, then a fortiori the process would also be applicable to the vapor-deposited product. Our study of the reasons for weld-embrittlement bears out this belief. So far, the newly developed welding process has not been tried on the vapor-deposited product because specimens of the shape and dimensions chosen for the welding experiments have not been easy to make in our existing vapor-deposition apparatus.

The new process of cold welding molybdenum after prechlorination has permitted us to produce the strongest welded joints yet reported for this metal. But the frequency of successes is still not satisfactory. Modifications in the shape of the mating surfaces are being studied in an effort to remove all patches of residual foreign material, presumably molybdenum chlorides, which act as stress-raisers in the joint. Although considerable work remains to be done both in perfecting our method of butt-welding and on the application of the new principle to spot-, seam-, and lap-welding, the process has been demonstrated capable of eventually being industrially successful.

V. RECOMMENDATIONS

A list can be made of the work still to be done.

It is:

1. Modification of the Initial Microstructure of Vapor-Deposits

In order to permit cold-working without the use of cumbersome and expensive envelopes, an equiaxed structure should be preferable to the columnar structure now produced. Two approaches exist: inhibiting the growth rate of the grains, and enhancing the rate of nucleation of new grains. Both approaches are under study in our laboratory.

2. Development of a Method of Making Seamless Thin-Walled Tube Directly from Tubular Deposits

The machine for wall-rolling such tubes is designed and is now under construction in our laboratory.

3. Measurement of the Transition Temperature of Cold-Worked and Annealed Vapor-Deposited Molybdenum

These measurements are now being made. From the results it is expected that more knowledge will be won concerning the causes of brittleness, so that the transition temperature can be lowered still further.

4. A Study of the Embrittlement of Vapor-Deposited Molybdenum in High Temperature Service

This study will indicate whether the vapor-deposited product needs protection against contamination

by certain types of atmospheres in such service. The work is planned but not begun.

5. A Study of the Corrosion-Resistance of Vapor-Deposited Molybdenum at Room Temperature and at Elevated Temperatures

Such a study will reveal the degree of necessity of forming protective coating on the metal in order to make it more useful in some classes of service, such as in plumbing systems.

6. Development of an Analytical Method for Oxygen in Molybdenum

Since the level of oxygen-content sufficient to be deleterious is below the range of accuracy of any existing technique, a new method is required. Preliminary study of a method based on our experience with molybdenum halides and oxyhalides is under way in our laboratory, as is the development of fractography as a possible analytical tool.

7. Development of Methods of Lap-Welding, Spot-Welding, and Seam-Welding Sheet Molybdenum

Using the principles found promising in butt-welding, this extension of our work is at the programming stage.

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8. Study of Alloying Elements of Possible Use in Making Commercial Molybdenum Weldable by Conventional Processes

Such a study is under way, according to information recently obtained, in another laboratory.

9. Study of Methods of Cladding Molybdenum for Protection Against High-Temperature Oxidation

Such a study is planned in our laboratory for the near future, and will make use of vapor-deposition processes, with which we are familiar. Other laboratories are also active in this field, but according to our information none to date have made successful use of vapor-deposition.

10. Development of a Method of Welding Molybdenum to Certain Other Metals and Alloys

The welding method developed for molybdenum might be extended to the joining of this metal to others to which it cannot now be brazed or welded.

SUMMARY

The report is divided into five parts. The first is an introduction in which is analysed the nature of the problems encountered in making plumbing components of vapor-deposited molybdenum. The literature pertinent to these problems is reviewed and it is concluded that additional information on commercially available metal is first required before making an evaluation of the comparative properties of vapor-deposited molybdenum. The measurements made to provide this information are reported. From the published data and from the measurements made it is concluded that the most important defect in commercial molybdenum is its transition from a ductile to a brittle state at a temperature at best only slightly below room temperature. It is raised by the presence of notches and also when deformation is carried out at rapid rates of strain. In welding by conventional fusion methods, this transition temperature is raised several hundred degrees by reason of the precipitation of oxides at the grain boundaries when the metal is solidified.

Molybdenum made by the hydrogen reduction of its gaseous pentachloride is a metal of high purity, judging from its recrystallization temperature (the lowest yet reported) and from the absence of a yield point in its tensile-test curve. No existing analytical

method is capable of accurately measuring the small oxygen contents (of the order of 0.001%) which seriously affect the properties of the metal. The art of fractography used in studies of precipitates in the metal was developed as a part of this contract to the point where it gives promise of becoming an analytical tool.

The vapor-deposited molybdenum may be extensively worked cold by rolling, but the initially columnar microstructure of the deposit makes it necessary to sheathe the workpiece during the first stage of cold-working.

Because the welding of the purest molybdenum by conventional processes would call for uneconomically pure neutral atmospheres, a new process was sought and found wherewith even the metal now on the market could be welded. The new process consists of prechlorinating at a low temperature the surfaces to be joined, and then effecting the joint by cold-welding at a temperature lower than the recrystallization or embrittlement temperature. The process, not yet developed to the industrial stage, has produced the strongest welds yet reported, in which, during testing, the eventual fracture occurs outside the weld zone. The ductility of these welds is still unsatisfactorily low.

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