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ARC-CAST MOLYBDENUM BASE ALLOYS

SUMMARY REPORT

NR 039 002

BY

CLIMAX MOLYBDENUM COMPANY

OF MICHIGAN



CLIMAX MOLYBDENUM COMPANY OF MICHIGAN
14410 Woodrow Wilson
Detroit 38, Michigan

April 24, 1956

To Recipients of Summary Report on
Arc-Cast Molybdenum-Base Alloys:

Please make the changes indicated below on the copy of the Summary Report on Arc-Cast Molybdenum-Base Alloys, Contract N8onr-78700, recently mailed to you.

p. 66	Figure 54 should read Figure 45.
p. 224	Rupture time of 11 hours should read 1 hour.
p. 252	Paragraph 3, line 3, should read "is evident from Figure 179".
p. 258	Replace page 258 with the attached sheet.
p. 279	Paragraph 4, line 10, should read "identified as copper, about 0.0003" to 0.0005" thick, between the coating and"

Very truly yours,

CLIMAX MOLYBDENUM COMPANY OF MICHIGAN

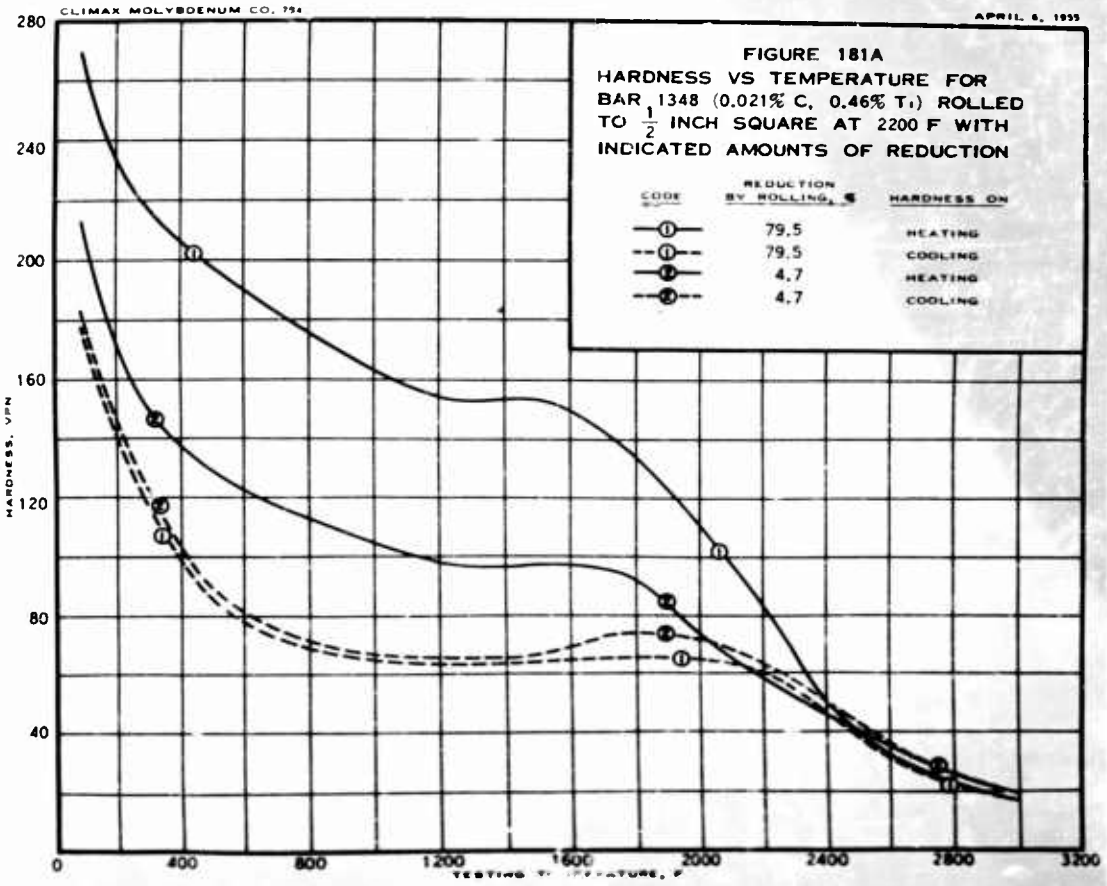
M. Semchyshen

M. Semchyshen

MS:wc

worked bars. The rapid change in hardness between 1800 and 2300 F is due to recrystallization during testing, and therefore the hardness on cooling is representative of a fully recrystallized structure. As the amount of strain hardening is decreased, recrystallization temperature increases, and, for reductions of 16% or less, only partial recrystallization occurs under the conditions of the hot hardness test. When the reductions are in the order of 5 to 10%, very little loss of hardness at room temperature occurs as a result of exposure at 3000 F.

Similar results for the 0.46% titanium alloy, Figure 181A, indicate that reductions of 4.7 to 79.5% produce sufficient strain hardening in the material that it becomes fully recrystallized in the hot hardness test. On cooling, the hardness is identical with that of as-cast material. These results seem to be consistent with the recrystallization data presented in Figure 186, wherein the recrystallization temperature (and thus the effect of temperature during hardness testing) was less for the titanium alloy than for unalloyed molybdenum at the low reductions.



FC

SUMMARY REPORT

ARC-CAST MOLYBDENUM-BASE ALLOYS

Contract N8onr-78700, Task Order N8onr-78701
Project NR 039-002

to

Office of Naval Research
Navy Department

prepared by

M. Semchyshen and R. Q. Barr

Climax Molybdenum Company of Michigan

1955

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FOREWORD

The extraordinary properties of the metal aggregates employed in this age of metals are largely derived from compounded metal systems called alloys. The use of metals in alloys far surpasses the use of metals in the pure state. The alloying or blending of two or more metals to achieve a combination of properties not attainable in any one of the component metals is a device of metallurgical technology possessing almost unlimited possibilities. Literally, thousands of alloys have been developed and used in our metals age. An orderly presentation of the range of properties possessed by these many alloys reveals that a classification on the basis of the predominant metal component is possible and useful. In such a classification, it can be seen that while in broad generalization the character of the dominant metal or alloy base forecasts the character of an alloy system, specific properties and combinations of properties in that system can only be learned by experimentation or actual use.

To become a base for a system of alloys, a metal must meet certain requirements. First, it must be available in quantities commensurate with proposed use. Second, it must be amenable to the methods developed for compounding alloys. Third, the properties of its alloys must meet some new engineering requirement not fulfilled by existing materials. Finally, the metal must achieve commercial acceptance, which means that there can be no effective technical, economic, psychological, or political factors operating in a manner contrary to its exploitation.

The list of metals which have achieved the important role of alloy-base metals is not a particularly long one. The metals of antiquity would be copper, iron, tin, and lead, and the noble metals. The modern metals of the list would be cobalt, nickel, aluminum, zinc, and magnesium. Intensive development effort at the present time centers around the metals titanium, molybdenum, chromium, and zirconium. Of this group, it now appears that titanium- and molybdenum-base alloys will be established in the near future as metallic materials of construction.

The trend in the development of heat engines has been to require the service of metals at higher temperatures. This factor focused attention of molybdenum as a potential alloy base about 15 years ago. When, through the development of a feasible method of producing workable ingots of molybdenum, the limitations of section size were removed, investigation of the potential of molybdenum-base alloys became almost imperative. In the interest of national defense, the Office of Naval Research sponsored institutional and industrial research, beginning in 1949. Six years of development effort in the field, through the stages of research and pilot operations, have indicated that molybdenum-base alloys may now be added to the list of materials to serve our requirement of materials of construction for use in a temperature range beyond the realm of the older, classic alloys.

As measured against the vast amount of information which must be accumulated to establish the full potential of an alloy-base metal, the effort covered by this report is small. On the other hand, from the point of view that this research brings into the area of industrial development a system of alloys which materially broadens the range of properties obtainable in an already versatile metallic state, the Office of Naval Research should be congratulated on having sponsored this program.

Alvin J. Herzig
President
Climax Molybdenum Company of Michigan

SUMMARY REPORT

ARC-CAST MOLYBDENUM-BASE ALLOYS

Contract N8onr-78700, Task Order N8onr-78701
Project NR 039-002

INTRODUCTION

An understanding of the development of the field of molybdenum-base alloys must be founded on a knowledge of the technical character of the element molybdenum. Although molybdenum was filling a responsible position in the field of alloy steels as long as 25 years ago and although molybdenum, among the alloying elements commonly employed in the field of ferrous metallurgy, is the only one whose principal supply is in the United States, the element has never received much publicity at the popular level.

The metals iron, copper, tin, lead, aluminum, zinc, chromium, magnesium, and nickel are household words--these metals and their alloys being quite familiar to the general public. As a matter of fact, even rarer metals, such as cobalt, tungsten, and the noble metals, have achieved considerable notice because of the publicity given to their use, for example, tungsten filaments in incandescent lamps, Cobalt "60", and, of course, jewelry.

Molybdenum, on the other hand, outside of a limited group of technologists, remains a relatively unknown entity. There seems to be very little doubt that one of the factors contributing to this lack of public knowledge or interest in the element is that one seldom, if ever, sees the metal or hears of its use in the relatively pure state. Molybdenum has no use parallel to that of the other metals, such as the use of "tin" cans, copper wire, lead pipe, aluminum foil, chromium plate, nickel coins, etc.

As an alloying element in steel, molybdenum makes three salient contributions. These are: (1) contribution to the characteristic of hardenability, which is the principal basis for the heat treatment of steel, (2) its capacity of introducing the characteristic of red hardness, in which it is nearly twice as effective as tungsten, and (3) its contribution to the increase in strength at elevated temperatures, attainable in the modern creep-resistant steels. Around these major attributes, there are secondary effects which have won for molybdenum an essential role in the products of the alloy iron and steel industry.

Although the consumption of molybdenum as an alloying element in steel increased rapidly in the past 25 years, the use of essentially pure metallic molybdenum centered primarily in the electrical industry, where the annual consumption of the metal was relatively small. Until recently, all the molybdenum consumed by the electrical industry was produced by powder metallurgy technique, which consists in compacting fine molybdenum powder under

high pressure and sintering the compact in an atmosphere of hydrogen at temperatures below the melting point of the compact. Some parts are made by compacting and sintering only, whereas other parts are machined from sections pressed and sintered as ingots and swaged and/or rolled to bars, rods, wire, or sheet.

A serious limitation of the powder metallurgy process as applied to molybdenum is that the maximum size of article that can be produced is relatively small. Furthermore, the mechanical properties developed by many of the powder metallurgy products were not characteristic of the base metal but were influenced by the presence of impurities and porosity. Despite the lack of consistent and reliable data on the pure metal, however, there has been considerable interest in molybdenum as an alloy base, because of its high melting point (4750 F); most alloys for elevated temperature service melt at temperatures below 3000 F.

To improve the quality of the product and to work with larger sections of molybdenum and thus to avoid the limitations of powder metallurgy, it appeared necessary to melt the metal. It was realized that molybdenum could not be melted and cast by conventional techniques, for several reasons. First, its high melting point precluded the use of any known crucible material. Second, because of its chemical activity at the melting point, molybdenum would have to be melted and cast in an inert atmosphere.

Since 1943 the Climax Molybdenum Company has been engaged continuously in a research program to establish a feasible method of producing large bodies of molybdenum which would be amenable to working with the equipment and by the methods available to the established metal industry. By 1948 it was established that the melting and casting of molybdenum in vacuum, with the electric arc to supply the heat, could be commercially feasible and that through such processing, larger sections having useful properties could be made available; there was evidence also that molybdenum-base alloys could develop elevated temperature strength superior to that of other commercial alloys.

Recognition of these facts in the Navy Department resulted in the contract under which the work described in this report was performed. Climax Molybdenum Company began performance under this contract in June 1949, and the contract has been extended every year since its initiation. The primary purpose of the contract was accelerated exploratory research in the field of molybdenum-base alloys, and its principal objective was the development of an alloy or series of alloys that could be used as engineering materials for high temperature service, for example, the turbine buckets for jet engines. The potential of such alloys for ordnance applications and for indirect defense applications such as die-casting dies, machine tools requiring extra rigidity, and electrodes for electric glass-melting furnaces was also recognized.

Specifically, the objectives of the contract were:

1. Classification of alloy systems of molybdenum according to solid solubility and the nature of the first excess phase developed in molybdenum-rich compositions, and establishment of certain phase diagrams.

2. Determination of mechanical properties of both cast and wrought molybdenum-base alloys over a wide temperature range, as a function of concentration of alloying elements.

3. Determination of the effects of alloy content on the rate of strain hardening of molybdenum and on recrystallization of the strain hardened metal.

4. Investigation of the effects of added elements on control of deleterious impurities such as oxygen in molybdenum produced by the arc-cast process, and the indirect effect of each element on the hot working characteristics of molybdenum.

5. Investigation of the effects of variations in the melting and casting process on hot plasticity.

6. The exploration of binary alloy systems of molybdenum which are amenable to heat treatment for the control of mechanical properties.

7. Development of hot working procedures for alloy ingots.

8. Investigation of the embrittlement resulting from exposure to high temperatures.

9. Investigation of the effect of variation in strain hardening on mechanical properties and the recrystallization temperature.

10. Determination of the effects of alloying elements on the rate of oxidation of molybdenum at temperatures near 1800 F.

11. Preliminary investigation of protection against oxidation.

Melting Equipment

Prior to and simultaneously with performance of the contract, the engineering staff of the Climax Molybdenum Company of Michigan Research Laboratory continued its efforts to improve the apparatus for vacuum arc melting. In the initial experiments, molybdenum bars, produced by conventional powder metallurgy technique, were used as consumable electrodes which were melted by an

electric arc in vacuum, using a water-cooled copper shell as the crucible and mold.* This furnace comprised the first apparatus to produce a forgeable casting of molybdenum and is called the Bar Machine to distinguish it from machines which were developed later and which converted a powder charge to a cast ingot within a single evacuated chamber. The latter development has been identified as a Pressing-Sintering-Melting machine and will be referred to hereafter as a PSM unit. The first two PSM units were experimental in nature and served as stepping stones for PSM-3 and PSM-4, which are still in operation in the Research Laboratory.

PSM-3 is capable of converting a charge of molybdenum powder weighing 250 pounds to a casting approximately 6" diameter and 24" long. It was operated for the first time in December 1946.

PSM-4 was designed, constructed, and placed in operation in 1950, and has been in use almost continuously since December 1950 to provide molybdenum alloys for experimental and industrial applications with the ultimate aim of establishing a substantial market for these products.

Research Bar Machine. In 1948, a Research Bar Machine was designed and constructed for the primary purpose of producing high purity, experimental molybdenum-base alloy ingots for fundamental research and mechanical property determinations. In this machine (Figure 1), unalloyed, arc-cast molybdenum in the form of rolled bars 1/2" and 5/8" in diameter are arc melted, while alloying elements are added to the bath at a controlled rate from a tray vibrating beneath a vertical glass tube which contains the alloying element in finely divided form.

The apparatus is evacuated by two MC-500 diffusion pumps (Distillation Products, Inc.), each backed up with a VSD556 Kinney mechanical pump. The diffusion pumps are provided with cover plates which can be raised or lowered so that the system can be opened to the atmosphere or argon can be admitted without waiting for the pumps to cool. The consumable bar electrode is fed into the melting chamber by a chain which is driven by an electronically controlled, adjustable speed motor. The arc current employed is 60-cycle AC, and the potential is variable from 20 to 60 in steps of two volts.

The bar machine permits production of alloys in considerably wider composition ranges than has been possible in the powder machine, because well-deoxidized, rolled or swaged molybdenum bars are used as the consumable electrodes, and the alloying elements are added to the bath directly in the form of small grains, thus obviating the difficulties which result from forming an electrode of mixed powders of molybdenum and certain alloying elements. The low oxygen content of rolled or swaged electrodes simplifies the problem of deoxidation and permits the use of an argon atmosphere to retard volatilization of alloy additions having high vapor pressure at the melting temperature.

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* The water-cooled copper chamber in which the electrode is melted and which shapes the casting may be referred to as either a crucible or a mold, since it serves a dual purpose. In this report it will be referred to hereafter as a mold.

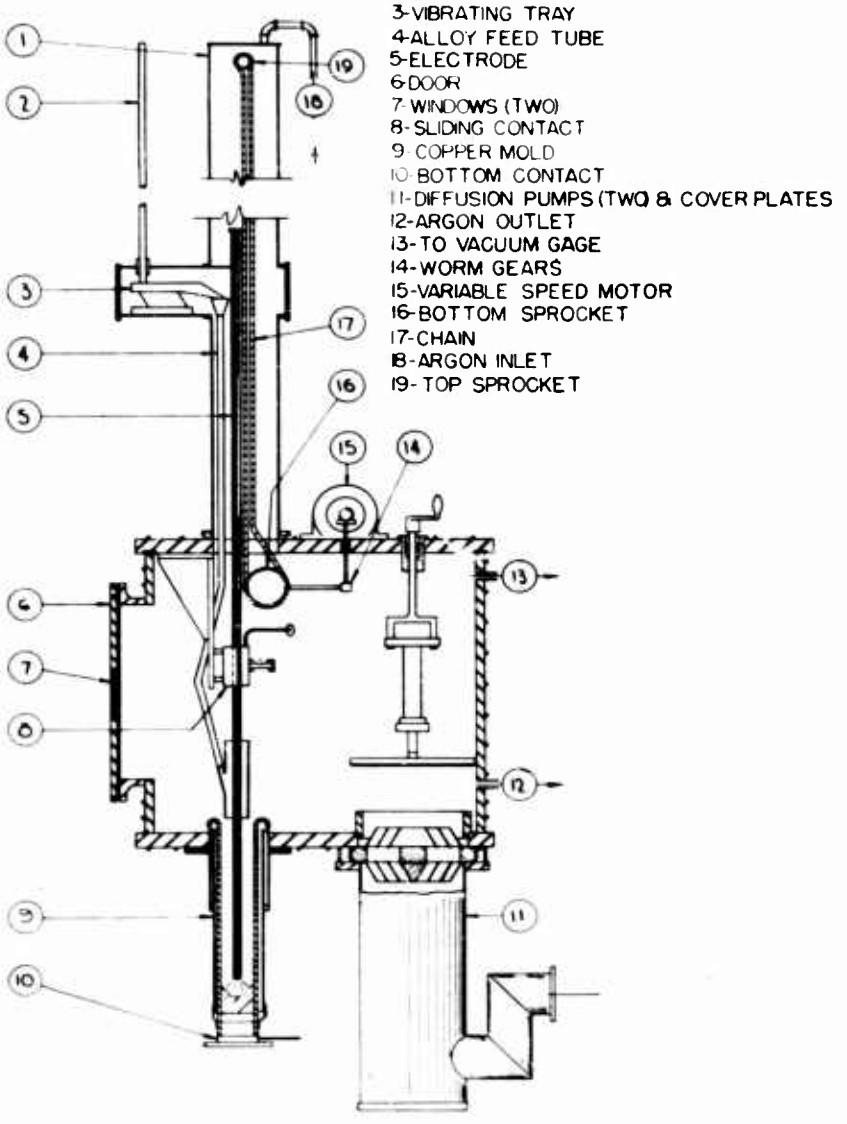


FIGURE 1 – ALLOY MELTING FURNACE
(P725)

In the course of this investigation, most of the alloys produced in the bar machine were melted in argon atmosphere. Before argon was admitted, the system was evacuated to 0.5 to 1.0 micron pressure. The argon was passed over titanium turnings at 1500 F and magnesium chips at 1100-1200 F and was slowly admitted to the melting chamber. It was recirculated through the purifying train before and during melting.

The rate of addition of alloying element was controlled by adjusting the current supplied to the electrical vibrator used for feeding and by adjusting the space between the end of the glass tube and the vibrating tray. Before evacuation of the furnace, the feed rate was calibrated by collecting and weighing the amount fed in known time intervals for various current settings. For heats in which the alloy content varied from zero to maximum over the length of the casting, the current to the vibrator was gradually increased to produce an increasing rate of feed.

The power required for melting depended on the atmosphere. For 5/8" diameter electrodes, melting in argon required from 2200 to 2700 amperes at 25 to 32 volts, whereas melting in vacuum required 1700 to 2000 amperes at 30 to 35 volts. These values varied only slightly with the nature of the added element.

Pressing-Sintering-Melting Units. The essential difference between PSM-3 and PSM-4 is the size of the machines and the size of the ingots they produce. Although PSM-3 was placed in use first, the operation of the newer, larger unit will be described, as it embodies the principal features of the earlier machine.

A diagram of PSM-4 is shown in Figure 2. The conversion of molybdenum powder to cast ingots is a batch-type process. A single charge (1) is loaded into a hopper (2) which is assembled to the main chamber (28) of the machine with a vacuum seal. A water-cooled copper mold (25) is also assembled to the main chamber with a vacuum seal. The entire system is pumped down to the desired vacuum. The charge from the hopper is fed horizontally (8) to the electrode-forming mechanism (11)(18) in which compacts (17) are formed consecutively one on top of the other. The compacts are hexagonal in cross-section (21), 2-1/8" across flats, and vary from 1/4" to 1-1/4", depending upon the feed rate. The electrode (21) which is built up from these compacts moves downward through two sets of electrical contacts or "shoes" (19). The distance between these sets of shoes is referred to as the "sinter zone" because an alternating current is passed through this length of electrode to sinter the powder, particularly at the joints between adjacent compacts. It is necessary to form a bond, or weld, sufficiently strong to support the length of electrode which extends to the bottom of the mold (or crucible) before the arc starts at the beginning of a heat. For molybdenum, this length of the electrode is approximately 60" long and weighs approximately 50 pounds.

After it leaves the sinter zone, a given section of the electrode moves downward into the cavity of the mold. The lower set of contacts or shoes supplies one side of the AC arc current, the bottom of the mold (26)(27) comprises the electrical contact for the other side of the circuit. The heat

generated by the arc (22) between the electrode and the mold bottom, or between the electrode and the molten bath of molybdenum at the top (2) of the casting or ingot, continuously melts the metal at the end of the electrode.

When the entire charge has been delivered to the electrode-forming mechanism and the last compact has been formed, melting is discontinued. The arc may be allowed to die out, owing to the increasing length of the arc gap as the end of the stationary electrode melts away, or the arc power can be intentionally disconnected. The casting is usually cooled in the mold under vacuum to temperatures near 400 F before air is bled into the system and the vacuum seals are broken, after which a new charge is loaded into the hopper and the same or another mold is attached to the main chamber.

The casting is removed from the mold by unfastening the bottom from the cylindrical shell and raising this shell upward off the casting which remains upri[illegible] on the base. After removal of the casting, the mold is reassembled and [illegible]ain fastened to the main chamber of the melting machine for a subsequent he[illegible]

[illegible] photograph of PSM-4 is shown in Figure 3.

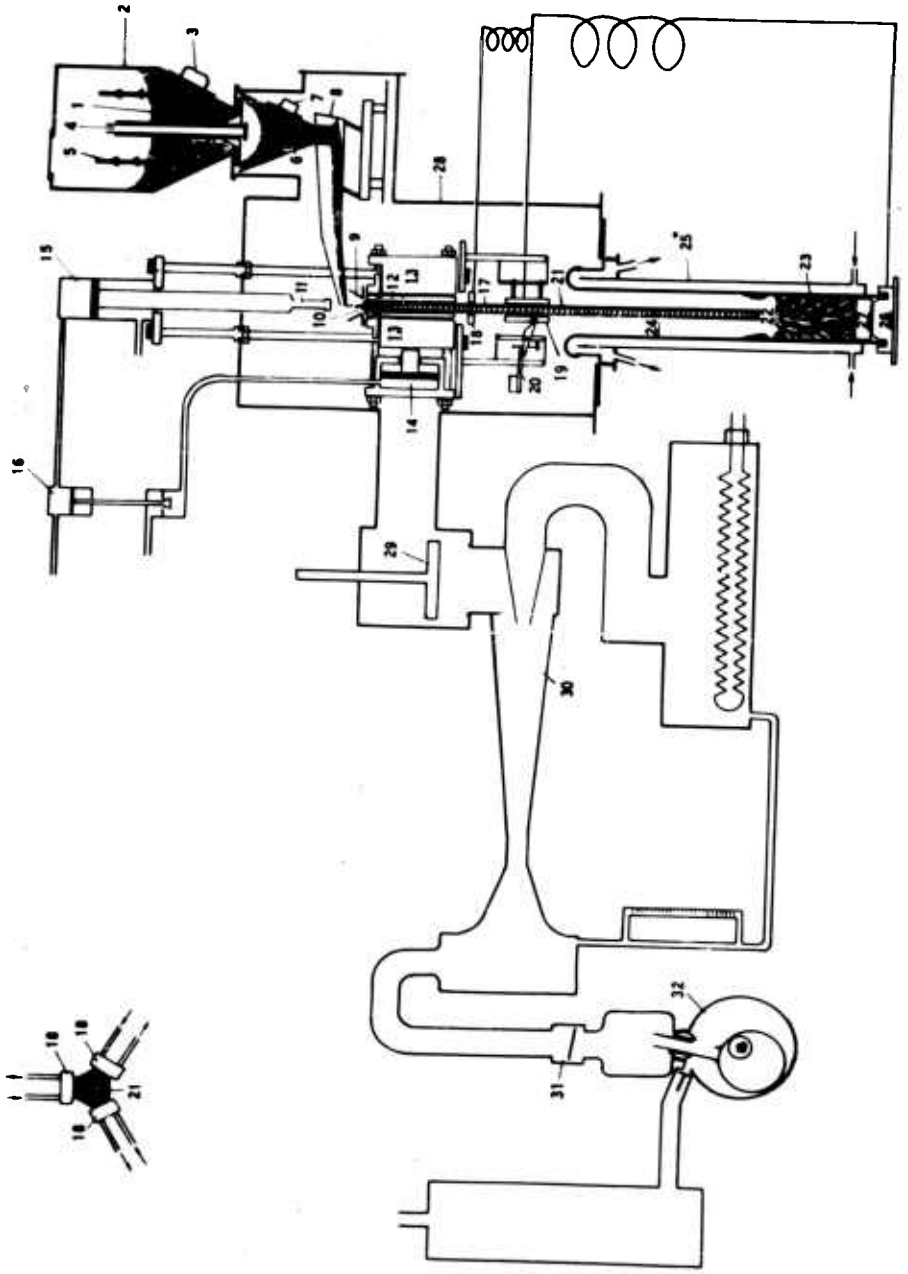


FIGURE 2 — CONSUMABLE ELECTRODE VACUUM ARC FURNACE FSM-4

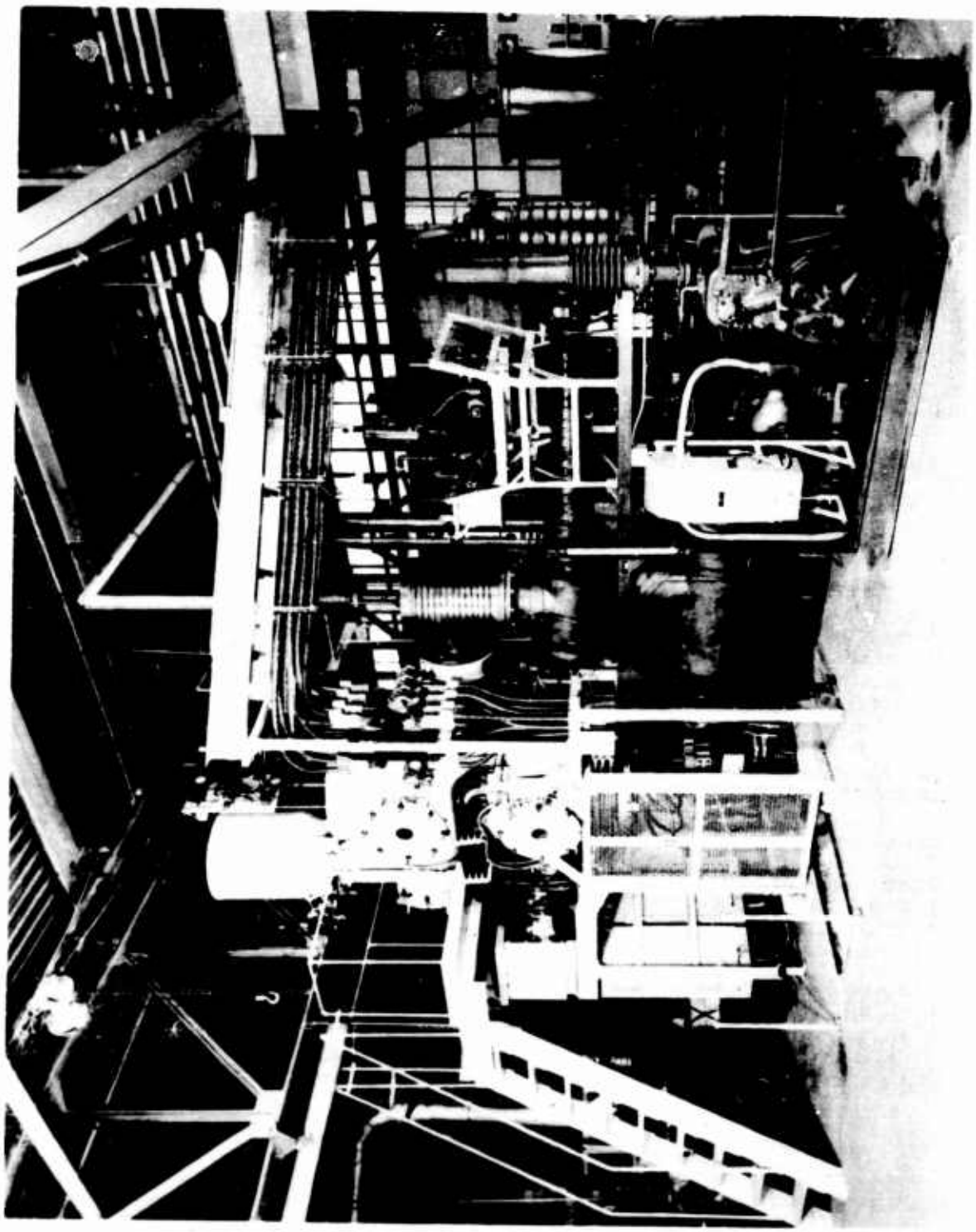


FIGURE 3 — GENERAL VIEW OF PSM-4 FURNACE

DEOXIDATION AND HOT PLASTICITY

Before the Office of Naval Research sponsored research on molybdenum and molybdenum-base alloys, the art of casting molybdenum had progressed to a point where it was known that certain impurities must be eliminated, or at least substantially diminished, if fabrication into wrought shapes were to be possible. Studies of the cast metal, based on spectrographic and vacuum fusion analyses, metallographic examination, and forging tests, led to the conclusion that oxygen was the impurity having the most deleterious effect upon plasticity and was at the same time the most difficult to remove.

The hot shortness, attributed to the presence of oxygen, results from the fact that almost no oxygen is soluble in molybdenum in the solid state. Any oxygen present unites with the molybdenum to form an oxide which is insoluble in the matrix and which resides principally at the grain boundaries of the cast metal. The product of the arc-casting process has a coarse, columnar structure and a relatively small grain boundary area. Therefore, the influence of impurities resident at the grain boundaries (such as molybdenum oxide) is particularly deleterious to plasticity. It has been established that 0.005% oxygen, when present in arc-cast molybdenum in the form of molybdenum oxide, is sufficient to render the product unforgeable.

To attain low oxygen content and prevent further oxidation, melting was conducted in vacuum and carbon was used as a deoxidant. During the melting process, carbon unites with the oxygen of the charge to form carbon monoxide. The function of the vacuum is to carry off the carbon monoxide, driving the reaction toward the equilibrium end point, at which the carbon and oxygen contents of the ingot are sufficiently low to permit forging. In the early states of the arc-casting development, carbon was added in excess of the stoichiometric ratio to insure that the maximum benefit of the carbon would be attained, and vacuum fusion analysis indicated 0.001% to 0.004% oxygen in the molybdenum castings. Metallographic examination revealed that the deleterious oxide phase was almost entirely absent from the grain boundaries. Excess of carbon eliminated the oxide phase from the grain boundary but resulted in the formation of the molybdenum carbide phase, which precipitated in the grain boundary. Although a small excess of molybdenum carbide was not deleterious to forgeability, excessive amounts of the carbide at the grain boundaries appeared to be responsible for reduced ductility and accelerated corrosion of wrought arc-cast molybdenum.

As part of the research on molybdenum-base alloys under sponsorship of the Office of Naval Research, further refinement in deoxidation was necessary, in view of the increased strength and greater resistance to deformation of the alloys, if plasticity were to be improved. Furthermore, the more effective deoxidation would increase the amount of alloying that could be tolerated in forgeable molybdenum.

Some of the alloying elements under investigation had high vapor pressures at the temperatures used in the melting and casting of molybdenum. These elements were completely lost--or their recovery was unpredictable--upon melting in vacuum. Therefore, in the re-evaluation of deoxidation, melting under an inert atmosphere at a positive pressure (greater than one atmosphere) was considered.

Specifically, the goals of the deoxidation program were to reduce the carbon content of the ingots while keeping the oxygen content below 0.005%, the established maximum for forgeability; to provide additional knowledge concerning the melting and deoxidation of molybdenum under inert atmosphere at a positive pressure; and to establish the feasibility of using deoxidizers or neutralizers other than carbon, or in addition to carbon, for the general purpose of increasing the ductility of molybdenum at room and elevated temperatures and increasing the amount of alloying element that could be added to arc-cast molybdenum without destroying forgeability.

Generally speaking, the deoxidizing or neutralizing action can be thought of as proceeding by one of the following mechanisms:

(1) The deoxidant and oxygen would form a gaseous product that would be removed by the vacuum pumps when melting was conducted in vacuum or by dilution of the ambient atmosphere when melting was conducted under a positive pressure of inert gas. Dilution is not feasible when carbon or any other deoxidizer is used in an inert atmosphere; the gaseous product generated by the reaction must be removed at such a rate that its partial pressure is comparable to that obtained when melting in vacuum, and the rate at which the inert gas would flow to accomplish this simply by dilution is prohibitively great.

(2) The product of reaction would be either solid or liquid at the temperature of melting molybdenum; in either case it would be insoluble in liquid molybdenum, forming a slag at the surface of the melt. This would be removed by cropping the solidified ingot.

(3) The products of reaction could be soluble in the liquid but insoluble in the solid and would thus precipitate upon solidification. In form and distribution, the precipitate could be less deleterious than molybdenum oxide.

(4) An element might be added which would permit greater solubility of oxygen in solid molybdenum.

Mechanisms 3 and 4 would not result in a lower oxygen content but would merely change the form and distribution of the oxygen from that of molybdenum oxide to that of some other oxide or would increase the solid solubility of oxygen in molybdenum. Therefore, this type of process will be referred to as neutralization rather than deoxidation.

All the heats of the deoxidation program were designed on the basis of these four possible mechanisms.

Methods of Evaluating Deoxidation

A number of methods of evaluating the effectiveness of deoxidation were used during the course of the investigation: hardness tests, vacuum fusion analysis, metallographic examination, forging, bend tests, and hot tensile tests.

Hardness. As a general rule, the purer a metal the lower its hardness. Therefore, hardness was used as a measure of effectiveness of removal of impurities, hence effectiveness of deoxidation. The hardness measurements were made at room temperature on a Vickers machine.

Vacuum Fusion Analysis. In the early stages of this investigation, vacuum fusion analysis of molybdenum had not been developed to the point where sufficiently accurate oxygen determinations could be made for use as a guide to the effectiveness of deoxidation. For example, metallographic examination of castings produced by melting in vacuum sintered bars containing 0.001% to 0.005% carbon revealed an abundant amount of oxide at the grain boundaries; 0.0019% to 0.0035% oxygen was reported for these castings on the basis of vacuum fusion analysis. Ingots prepared in like manner but with a residual carbon content of 0.044% and having a microstructure devoid of oxide contained 0.0053% oxygen, according to vacuum fusion analysis.

As improved methods of deoxidizing molybdenum were being developed in this laboratory, Battelle Memorial Institute and other workers in the field were perfecting vacuum fusion analyses for molybdenum-base alloys. Toward the end of our studies on deoxidation, vacuum fusion analysis could be made for oxygen in molybdenum in the range of one part per million. Had such precision been available at the outset of the program, vacuum fusion analysis would have been a useful guide for these experiments. The precision now attainable still leaves something to be desired, however; for the analyses indicate total oxygen present, whereas only a portion of the total oxygen is of primary concern--that which appears in the form of oxide at the grain boundaries.

Careful metallographic examination of cast molybdenum reported to contain 3 to 5 parts oxygen per million revealed trace amounts of oxide at the grain boundaries. These observations indicate the exceedingly low solubility of oxygen in molybdenum at the temperatures now employed for working.

Metallographic Examination. In view of the handicaps associated with vacuum fusion analysis, the deoxidation program depended to a large extent on metallographic examination, especially examination of the surface produced by fracturing the cast metal, for revealing the effectiveness of deoxidation. Early work on deoxidation of arc-cast molybdenum with carbon in vacuum showed that the degree of deoxidation was reflected in the appearance of the grain surfaces upon fracture*. Parke and Ham** presented fractographs illustrating grain surfaces of well-deoxidized ingots and ingots containing a large amount of excess phase, tentatively identified as molybdenum oxide. The presence of a large amount of recognizable oxide at the grain boundaries was definitely established as deleterious to the forgeability and plasticity of molybdenum.

Forging. Although the ultimate criterion of the effectiveness of deoxidation was the forgeability of the ingots, there was much to be learned regarding techniques of forging molybdenum. Variations in forging practice were imposed upon variations in deoxidation. In the preliminary evaluation of forgeability, cylinders 1" in diameter by 1" long were machined with the cylindrical axis parallel to the longitudinal axis of the ingot. For some of the ingots, sound stock was sufficient only for samples 3/4" in diameter by 3/4" long. All the cylinders were upset 50% in 1/8" steps and were reheated between each step. On the basis of visual examination, the upset cylinders were rated according to the scale shown in Figure 4.

Alloys whose average rating in the upset-cylinder test was 1 to 4 on the scale were considered worthy of further study in the form of larger ingots. Forging was performed on a 1000-pound air hammer and later on a 600-ton forging press. Heating of the large specimens for forging was conducted in a gas-fired furnace under a reducing atmosphere or in a furnace with a hydrogen atmosphere. The technique of forging was modified during the investigation; sometimes the dies were flat, or one or both were provided with 60° or 90° V recesses to accommodate the ingot.

The forging tests were conducted at 2000, 2300, and 2600 F. Preliminary studies outside the scope of the contract indicated that better forging recovery was obtained when a hydrogen-atmosphere furnace was used than when a gas-fired furnace was used to heat for forging. When the ingots were heated in a gas-fired furnace, oxidation occurred at the grain boundaries and created a notch effect which promoted surface cracking on subsequent forging. The surface cracks penetrated the billet as forging was continued. Ingot 844 and all subsequent ingots were heated for forging in a hydrogen atmosphere unless otherwise stated. All ingots of lower number were heated in a gas-fired furnace.

Bend Tests. In evaluating deoxidation practice, it was believed that ductility would be indicative of the degree of deoxidation and grain boundary strength. A simple beam bending test was used for measuring ductility of the cast metal. In adopting this test, it was recognized that factors such as

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* C. A. Zappfe and M. Clogg, Jr., Transactions, American Society for Metals, vol 34 (1945)

** R. M. Parke and J. L. Ham, Transactions, American Institute of Mining and Metallurgical Engineers, vol 171 (1947)

1. NO DETECTABLE SURFACE RUPTURES
2. SHORT CRACKS
3. MEDIUM LENGTH INTERGRANULAR CRACKS
4. SMALL BURSTS
5. ONE LARGE BURST
6. GROSS RUPTURE



FIGURE 4 – SCALE FOR RATING FORGEABILITY OF UPSET CYLINDERS

rate of strain, temperature of test, grain size, and orientation were critical factors with respect to ductility and type of fracture. These factors were, therefore, maintained as constant as possible so that the only variable would be the deoxidation practice.

Because of lack of sufficient material for thorough investigation of transition from brittle to ductile failure as a function of temperature at a constant strain rate, bend tests were made at room temperature only, and the bend angle obtained was used as a measure of the degree of deoxidation attained. The specimens for the beam bending tests were 0.250" by 0.150" by approximately 1". The specimens were loaded at the center of a 5/8" span. A platen speed of 0.005" per minute (a tension strain rate of approximately 0.0002" per inch per second on the tension side of the specimen) was used unless otherwise specified. Bearing surfaces were 1/16" diameter hardened drill rod. The maximum load and bend angle (sustained before cracking) were measured. The permanent deformation prior to fracture was determined by measuring the distance traveled by the cross-head, which for all practical purposes was the same as the deflection at the center of the loaded beam. This distance was correlated with the bend angle measured after fracture when the halves of the fractured beam were assembled. The geometry of the bend test jig permitted a maximum bend angle of 115°.

Two types of specimens were cut: one with the columnar, as-cast grains of the castings longitudinal, and one transverse, to the major axis of the specimens. The surfaces of the specimens were prepared by polishing through 000 metallographic paper.

Experience gained in the course of this investigation has shown that when metallographic examination reveals oxide at the grain boundaries of molybdenum castings, the bend ductility, especially in the transverse direction, will be zero. However, if the specimen is well deoxidized--that is, no oxide is evident on the fracture and microstructure--a minimum bend angle of 2° may be expected at room temperature in transverse specimens when the deflection rate is 0.005" per minute. Transverse bend ductility is more critical than longitudinal ductility.

Although the metallographic examination seems to correlate well with the minimum bend ductility obtained, the maximum bend ductility could not be predicted from appearance of the microstructure. The maximum bend ductility is of especial interest, however, for two reasons: it is an indication of lower transition temperature, and it indicates that that material shows promise of resistance to high temperature embrittlement and might thus be more suitable for welding. The matter of embrittlement is discussed in a later section of this report.

Tensile Tests at Elevated Temperature. Early experience showed that the fractures occurring during forging were for the most part intergranular. The lower strength of the grain boundaries was attributed to the presence of nonmetallic impurities at the grain boundaries. Intergranular cohesive strengt:

was considered to be a function of the amount and distribution of the impurities, and thus would serve as a guide in deoxidation studies. A tensile test was used to measure the intergranular strength at temperatures which would be likely to be encountered in forging. To promote grain boundary fracture, the strength of the matrix was increased through addition of alloying elements.

Preliminary experiments conducted at temperatures in the range 1800 to 3000 F at the fastest rates of strain that could be obtained with a universal hydraulic tensile testing machine indicated that failures in all cases occurred with appreciable ductility and were a composite of intergranular and transgranular fracture, and that it would be impossible by this method to evaluate variations in deoxidation practice which were known to affect forgeability.

The original plans were modified when it was observed that cracks developed at the surface of a test specimen before extensive reduction of area occurred. An attempt was made to correlate deoxidation practice with stress and reduction of area at the time of appearance of the first crack, but the correlation was not definite and the procedures were not developed further. A detailed discussion of the elevated temperature tensile tests on cast materials and the conclusions derived from them appears in the second annual report under this contract.

Production of Heats

The experimental heats were made in the two small melting units, the Research Bar Machine and PSM-3. Analyses of representative heats* used in the deoxidation study are shown in Table 1. The prefix "B" indicates heats made in the bar machine. These were usually 2" to 2-1/2" in diameter and weighed about six pounds. The castings from PSM-3 were from 3" to 4" in diameter and weighed from 10 to 40 pounds. Both machines could be operated in vacuum of the order of 1μ pressure at the start of melting and at a pressure of less than 50μ during melting. Tank argon was the principal inert atmosphere used for heats made at above atmospheric pressure. The argon was purified by passage over titanium and zirconium chips and was recirculated during melting. All deoxidizing and neutralizing agents were added without difficulty in the form of powder or chips.

It should be pointed out that the production of molybdenum by arc melting a consumable electrode imposes certain restrictions upon the studies of deoxidation and neutralization. At no stage is the entire heat molten and it is not possible to vary beyond the narrow limits in the arc-melting method the time during which the heat is molten or the temperature of the melt. The variables which are feasible and at the same time of interest are the atmosphere surrounding the melt and the deoxidizing and neutralizing agents, which must be an integral part of the charge.

To make rare earth metals suitable for addition to the charge of the consumable electrode melting machines, it was necessary to machine chips from the commercially available lumps. In view of the rapid oxidation of the rare

* For details of heats not discussed here, see the four preceding annual reports

TABLE 1

REPRESENTATIVE HEATS MADE FOR DEOXIDATION STUDIES

HEAT NO.	ADDITIONS, %	ANALYSIS, %	MELTED IN	HARDNESS DPN	FORGEABILITY RATING** 2000 F	2300 F	2600 F	BEND ANGLE DEGREES LONG.	TRANS.
739		.045 C	VACUUM		1	1	2		
1007	.028 C	.011 C	VACUUM	176	1	1	1	35	11
1201	.03 AL	.002 C, .012 AL	ARGON	185	6	6	6	0.	0
1202	.05 AL	.002 C, .027 AL	ARGON	185	6			1,2	0
1203	.10 AL	.002 C, .076 AL	ARGON	152	1	1	2	39	4
1204	.15 AL	.003 C, .12 AL	ARGON	163	2	2		27	5
1079	.3 AL*	.001 C, .018 AL	VACUUM	168	0 RECOVERY				
1105	.2 LCA, .05 AL		ARGON	175	3	2	6	36	2,3
1106	.2 LCA		ARGON	166	6	4	6	20	1
1111	.1 LCA, .027 C	.007 C, .004 RE	VACUUM	181	0 RECOVERY			48	19
1045	.3 LCA	.003 C, .005 CE	VACUUM	187	26,56% RECOVERY AT 2300 F			68	51,5
1061	2,0 LCA		VACUUM	166	4	6	6		1,3
1064	5,0 LCA	.075 C, 1,69 CE, .004 RE	ARGON	168	6	6	6		4
1073	.1 CE	.003 C, .003 CE	VACUUM	188				2,7	1,6
1114	.5 CE		VACUUM	161	2	1	2	78	9
B124 TOP		.005 C, .016 TH	VACUUM	174	0 RECOVERY				
B124 BOT		.010 C, .000 TH	"	179		"			
B184	.033 C, .07 TH	.033 C, .091 TH	VACUUM	183	2	2			
B197	.033 C, .30 TH		VACUUM	179	5	6			0
1078	.031 C, .2 TI	.005 C, .18 TI	VACUUM	186	0 RECOVERY				
1100	.041 C, .21 TI	.015 C, .21 TI	VACUUM	188	85% REC 2600 F, 89% REC 3000 F				
792	.5 TI	.003 C, .42 TI	VACUUM	185	4	4	4	59	9
793	.5 TI (AS HYDRIDE)	.005 C, .36 TI	VACUUM	180	4	4	4	58	27
1112	.030 C, .52 TI	.015 C, .49 TI	VACUUM	191	0 RECOVERY			44	23
1205	.027 C, .05 ZR	.010 C, .056 ZR	VACUUM	179	1	1	2	68	33
794	.25 ZR	.000 C, .23 ZR	VACUUM	180	5	4	4		66
796	.25 ZR	.002 C, .21 ZR	ARGON	178	2	4	4	48	30
757	.041 C, .1 (90LI-10AL)	.021 C	VACUUM	170	1	2	3	55	6
758	.15 (90LI-10AL)	.008 C, .034 AL***	ARGON	176	4	6	6	18	1
828	.10 (50LI-50CA), .036 C	.016 C	VACUUM	177	1	2	2		
951	.1 AL, .1 CA PHOSPHIDE	.004 C, .085 AL	ARGON	169	4	3	3		
755	.041 C, .06 CA PHOSPHIDE	.027 C	VACUUM	166	3	5	3	9	5
873	.4 MG		ARGON	163	0 RECOVERY				
756	.75 V	.004 C, .69 V	VACUUM	175	4	4	6	1	
B150	1.5 MG	.002 C	ARGON		4	3	3		

* ADDED AS MOLYBDENUM-ALUMINUM ALLOY

** APPEARANCE OF UPSET CYLINDER RATED ACCORDING TO THE SCALE SHOWN IN FIGURE 4

*** PART OF THE ALUMINUM ORIGINATED FROM THE ALUMINUM-CONTAINING MOLYBDENUM CHIPS WHICH FORMED 20% OF THE CHARGE

earth metals in air, especially when they are in the form of fine particles, these metals were machined under kerosene and the chips were washed several times in carbon tetrachloride and sealed in vacuum until used. The lithium-aluminum and calcium-aluminum alloy chips used for deoxidation were likewise machined under kerosene, washed, dried, and sealed in vacuum until used.

When titanium and zirconium were added in the form of their hydrides, these were prepared by heating pure titanium or zirconium chips in dry, purified hydrogen.

Except for a few heats, all of those of Table 1 were melted without difficulty. Thorium, because of its high emissivity, reduces the voltage for a given arc gap with a given arc current, which in turn reduces the power input. As a result, superheating was inadequate in the first heats made with thorium and the ingots did not fill the mold. Melting of later heats was governed, not by the current-voltage relationship, as normally, but by setting the feed on the bar machine at a given rate. The current registered by the meters was allowed to rise to a higher level than usual. This resulted in much sounder ingots and better filling of the mold and was an expedient solution to the problem. Arc control with thorium is difficult at best and commercial production is not yet feasible.

When the heats were melted under argon and aluminum was added as deoxidizer, the power input during melting was substantially higher than for carbon-vacuum heats, and as a result some of the earlier heats were not sufficiently superheated for the casting to fill the mold. The result was gross macroporosity at the surface of the castings.

The ingots from the bar machine and from PSM-3 were quartered lengthwise, and a longitudinal face of one of the quarters was ground, polished, and macroetched. From examination of this surface, the ingot was judged on the basis of mold filling, general quality, and macro grain size. Later, bend-test specimens, both parallel and normal to the major axes of the grains, were machined from this segment, because of the ease with which the grains could be seen on the polished and etched surface. Sections 1/4" thick were cut from the mid cross-section of the second quarter for fractographic and micrographic examination and for hardness measurements. The two quarters remaining were machined to cylinders one inch in diameter to be used for forging tests.

The larger ingots, from PSM-3, were melted in three-inch and four-inch diameter molds and weighed 30 to 100 pounds. After casting, a transverse slice one inch thick was cut from the mid-section for metallographic examination and determination of hardness and bend ductility. The remaining pieces were forged.

Reappraisal of Carbon-Vacuum Deoxidation

As mentioned in the introduction, it was established that melting in vacuum combined with deoxidation with carbon would yield forgeable molybdenum. In the early development, the presence of a large amount of recognizable oxide at the grain boundaries was definitely established as deleterious to the

forgeability and plasticity of molybdenum. As the deoxidizing technique was improved, sufficient carbon was retained in the ingot that carbide rather than oxide remained at the grain boundaries, but this condition did not consistently insure good recovery on hammer forging. The degree of forgeability usually could not be correlated with variations in residual carbon content. Part of this spread in degree of forgeability was undoubtedly due to the fact that experience was being gained in how to forge molybdenum and that the procedures were being changed; therefore, variation of recovery could be attributed, to some extent, to variation in forging procedure. It was felt, however, that despite variations in forging techniques, general know-how of the deoxidation process was insufficient and that further improvement could be attained which would result in a product much more amenable to forging and working.

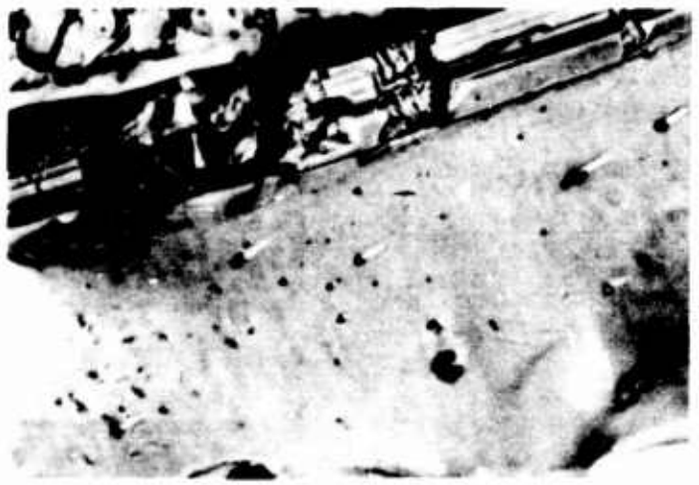
In the re-evaluation of the deoxidation practice, a reliable tool was needed to serve as a guide for the investigation. Vacuum fusion analysis, as mentioned earlier, did not correlate with forgeability or with observed microstructure. Although there was not complete correlation between observed microstructure and efficiency of deoxidation as manifested by forgeability, it was felt that small improvement in metallographic techniques for examining fractured surfaces would yield useful data regarding the effectiveness of deoxidation and the resultant forgeability. Extending metallographic examination of fractured surfaces to higher magnification and better resolution revealed not only the feathery carbide noted on the intergranular facets at the lower magnifications, but also in some ingots a phase consisting of scattered dots or specks--a condition called "speckling" throughout this report. The amount of speckling observed varied greatly from ingot to ingot. In the case of hammer forging, the amount of speckling could be correlated with forging recovery, good forging recovery being associated with absence, or only a small amount, of speckling.

When speckling appeared on the fractures there also appeared in the microstructures of conventional metallographic specimens minute, black or gray dots, predominantly at the grain boundaries, visible at magnifications of 1500X and greater. Nevertheless, speckling was more clearly revealed in the fractographs than in the polished specimens. Metallographic evidence indicated that the speckles were discrete particles, but it was considered desirable to obtain confirmation by other means. The question, whether the speckles were voids or solid particles, suggested examination by optical and electron microscopes of fractured surfaces or surfaces treated by shadow-casting techniques.

For optical examination, several fracture specimens were shadow-cast with copper*. The specimens were mounted in a vacuum chamber near a tiny quartz crucible from which metallic copper was vaporized and copper atoms were deposited on the surfaces of the specimens except in the areas shaded from the crucible by protruding ridges or peaks. The angle between the average surface and the line to the crucible was such as to give shadows about five times longer than the height of any peak. Copper was chosen for

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* Shadow-casting experiments were conducted by Dr. L. O. Brockway, Department of Chemistry, University of Michigan



M1875 X2000

FIGURE 5 - FRACTURED SPECIMEN OF INGOT 888
SHADOW-CAST WITH COPPER

the shadowing because of the contrast between its reddish color and the silver color of molybdenum. One such specimen from Ingot 888 showed some speckles with shadows and some without, Figure 5. Those with shadows were particles extending above the surface; those without shadows were either holes in the surface or were flush with the surface. Holes would occur if the speckles were solid particles which did not divide but which remained attached to either of the two surfaces formed in fracturing, leaving a recess on the other surface. Optical examination of the shadow-cast surfaces provides evidence for regarding most of the speckles as solid particles, not voids.

Attempts to prepare surface replicas of fractures for examination in the electron microscope were unsuccessful because the surfaces were so rough that the thin collodion films ruptured badly on being separated from the surface. No attempt was made to smooth the surfaces for fear of destroying the speckles.

Since the shadow-casting technique indicated the presence of a discrete phase, electron diffraction was used in an attempt to identify the phase by focusing an electron beam upon the fractured surface. Owing to the gross roughness of the fractured surfaces, no patterns were obtained to identiry the character of the second phase resident in the grain boundaries.

Even though the character of the excess phase was not identified by electron diffraction techniques, it is strongly suspected that speckling is the manifestation of small amounts of molybdenum oxide. In work conducted at this laboratory outside the contract, an experiment was performed to determine

the relation between the amount of speckling and the partial pressure of oxygen during melting of the ingot. The initial step in this experiment was to pump the melting chamber to the minimum pressure and to check the tightness of the system by determining the leak rate. The partial pressure of oxygen was gradually increased, and pressure of the system was measured repeatedly as melting progressed. The ingot was sectioned at the various positions corresponding to different levels in oxygen content of the melting atmosphere, and specimens were obtained for fractographic and micrographic examination as well as for chemical analysis for carbon content. The experimental data are summarized in Table 2 and Figures 6-9.

TABLE 2

OXYGEN PRESSURE AND CARBON CONTENT AT FOUR POSITIONS IN INGOT 990

0.04% carbon added in the form of AGR graphite
Melting rate, 8.56 pounds per minute

Oxygen Pressure μ	%C	Figure No.	Comments
15	0.031	6	Fracture shows carbide only. Grain boundaries are devoid of speckling.
100-140	0.015	7	Fracture shows carbides and severe speckling. Grain boundary shows excess phase and carbides.
275	0.008	8	Fracture contains massive oxide, speckling, and carbide feathers. Photomicrograph shows plate-like oxide at grain boundaries and a small amount of carbide.
>1000	0.010	9	Fracture contains massive oxide and speckling, as well as sheets of oxide. No carbides were visible. Photomicrograph shows plate-like oxide and speckling.

The data of Table 2 present good evidence that the degree of speckling can be influenced by the amount of oxygen available in the melting atmosphere. The speckles are apparently particles of oxide which form if the oxygen content exceeds its solubility in molybdenum. It is reasoned that as the partial pressure of nitrogen was not changed in the system during melting, neither nitrogen nor its compounds are associated with speckling. The elimination of speckling in carbon-reduced, vacuum-melted castings, therefore, appears to depend upon the removal or substantial reduction of oxygen of the charge and ambient atmosphere.

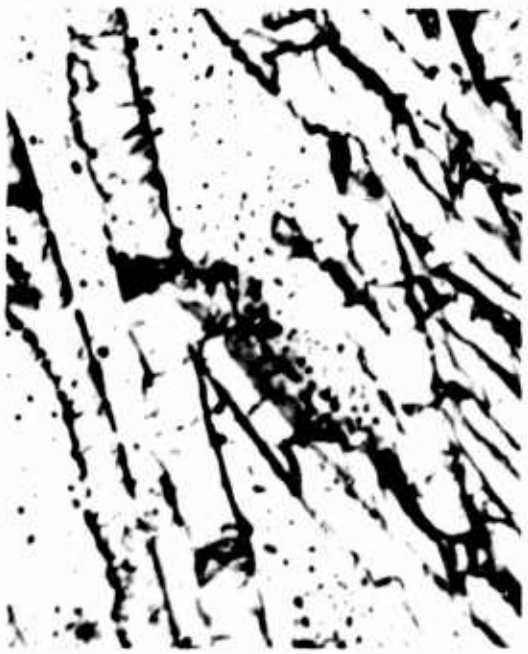


(A) FRACTOGRAPH, X2000 (M1964)

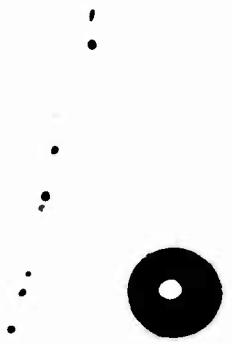


(B) ELECTROPOLISHED, X2000 (M1965)

FIGURE 6 — PORTION OF INGOT 990 MELTED AT 15 MICRONS
0.031% CARBON



(A) FRACTOGRAPH, X2000 (M1958)



(B) ELECTROPOLISHED, X2000 (M1960)

FIGURE 7 — PORTION OF INGOT 990 MELTED AT 100—140 MICRONS
0.01[illegible]% CARBON



A) FRACTOGRAPH, X2000 (M1953)



(B) FRACTOGRAPH, X2000 (M1955)

(C) ELECTROPOLISHED, X2000 (M1956)

FIGURE 8 — PORTION OF INGOT 990 MELTED AT 275 MICRONS
0.008% CARBON



(A) FRACTOGRAPH, X2000 (M1962)



(B) FRACTOGRAPH, X2000 (M1943)

(C) ELECTROPOLISHED, X2000 (M1944)

FIGURE 9 — PORTION OF INGOT 990 MELTED AT 1000 MICRONS
>0.010% CARBON

Several attempts were made to lower the oxygen content of the regular arc-cast molybdenum. Improvements made in the melting apparatus were aimed at attaining lower pressures, which would serve to reduce the oxygen content of the ambient atmosphere during melting and to improve the removal of products of deoxidation. Arc melting with the consumable electrode restricts the melting rate to a fairly narrow range. Furthermore, the use of water-cooled copper molds imposes a solidification time which is also fixed and is relatively short. Both of these factors limit the time during which the molten pool prevails and during which deoxidation reactions are most rapid; hence, the time for removal of oxygen by a deoxidizer is limited. To achieve as complete removal as possible in the limited time, the amount of oxygen to be removed must be relatively small. Experiments have shown that when excessive amounts of oxygen are present in the starting materials, there are more residual oxides in the castings than when the oxygen content of the charge is relatively low.

To establish a basis for specification, the maximum oxygen content in a charge to be effectively deoxidized with carbon in the time available during melting, vacuum fusion analyses were obtained on several starting powders from which castings had been produced that exhibited various amounts of speckles on the surfaces of fractures. These analyses indicated that a maximum total oxygen content of about 0.04% was allowable for the production of carbon-deoxidized, vacuum-melted castings essentially free from grain boundary oxides. In view of the time-consuming nature of the vacuum fusion tests and the fact that this laboratory was not equipped with a vacuum fusion apparatus, an alternate test was developed which comprised the determination of the loss of weight of a sample of powder held in dry hydrogen at 1900 F for 30 minutes. It was recognized that this loss of weight did not provide a measure of the total oxygen content of the powder, but it did indicate the amount of oxygen present on the surface of the powder in both the adsorbed and chemically combined states, and since the surface oxygen comprised by far the major portion of the total oxygen, this test provided a satisfactory basis for the evaluation of the powder charge.

The metallographic examination of molybdenum powder revealed the presence of nonmetallic inclusions near the centers of the grains; these nonmetallics have been identified as unreduced molybdenum oxide, and it was determined by experiment that these oxides could not be removed by treatment of the powder with dry hydrogen under any conditions of time and temperature which could be considered practical for the production of molybdenum powder. Although it was observed that the amount of internal oxide in the powder regularly purchased for the production of arc-cast molybdenum was of a low order and was relatively consistent, samples of some special powders exhibited such quantities of internal oxides that they were rejected as unsatisfactory. The procedure of determining the loss of weight in dry hydrogen at 1900 F was adopted as a control procedure and experience showed that the values obtained from this test correlated satisfactorily with the amount of speckling and presence of oxide films on the fractured surfaces of castings. From these correlations it was established that a loss of weight in dry

hydrogen of 0.04% was the maximum that could be tolerated if satisfactory castings were to be produced by carbon deoxidation and vacuum melting. Accordingly, this maximum loss of weight was written into the powder specification, along with a metallographic evaluation of the amount of internal unreduced oxides and a maximum carbon content of 0.02%.

These improvements brought about consistent production of forgeable ingots of unalloyed molybdenum, melted in vacuum and deoxidized with carbon, containing 0.04% to 0.05% residual carbon, having a microstructure devoid of speckling, and having a hardness of 180 ± 4 DPN. The bulk of the data on carbon-vacuum molybdenum shows bend angles from about 2° to 12° prior to fracture in the transverse bend test; the average is about 4°. Heat 739 is typical of ingots produced during this period. It contained 0.045% residual carbon and had the microstructure shown in Figure 11.

In view of the deleterious effect of excessive amounts of carbide discussed earlier, the amount of carbon added was gradually reduced, and it was found that the residual carbon could thus be lowered to about 0.010% before the amount of speckling appeared that is associated with poor recovery on forging. An ingot containing 0.011% carbon (1007), whose macrostructure is shown in Figure 10, is typical of what was accomplished in this direction. Very little speckling appears in the microstructure, Figure 12, and, as would be expected from the low carbon content, very little carbide as well. The hardness of the casting was a little lower than that of the average as-cast molybdenum produced by deoxidation with carbon in vacuum. Ingots exhibiting the small amount of speckling of Ingot 1007 were forged without difficulty. The results of the upset-cylinder tests are given in Table 2. The recovery upon forging larger sections was between 80% and 90% on the basis of weight of the machined casting.

Recent vacuum fusion analyses on arc-cast molybdenum having microstructure similar to that of Figures 11 and 12 have reported oxygen contents of 0.0001% to 0.0005%.

Aluminum as a Deoxidizer

The affinity of aluminum for oxygen and nitrogen suggested that aluminum might be useful as a deoxidizer and neutralizer for molybdenum.

When aluminum is added to a heat containing sufficient carbon to accomplish deoxidation and melting is conducted in vacuum, no beneficial effects are noted, and the microstructure corresponds to the residual carbon content, much the same as in heats deoxidized with carbon alone.

An attempt was made to deoxidize molybdenum with aluminum in vacuum despite the high vapor pressure of aluminum (about 530 mm Hg at the melting point of molybdenum). It was considered possible that aluminum would form an oxide such as Al_2O_3 and that the vapor pressure of the oxide would be sufficiently high at the temperature of the molten metal that the oxide would escape from the bath and condense on the cold surfaces of the furnace chamber.



(A) INGOT 1007
0.011% CARBON
CAST IN VACUUM
(P881)

(B) INGOT 1079
0.001% CARBON
0.018% ALUMINUM
CAST IN VACUUM
(P922)

(C) INGOT 1203
0.002% CARBON
0.076% ALUMINUM
CAST IN ARGON
(P971)

(D) INGOT 1105
0.2% LAN-CER-AMP
AND 0.05% ALUMINUM
ADDED
CAST IN ARGON
(P936)

(E) INGOT 794
0.000% CARBON
0.23% ZIRCONIUM
CAST IN VACUUM
(P824)

FIGURE 10 — MACROSTRUCTURE OF ARC-CAST MOLYBDENUM
LONGITUDINAL QUARTER SECTION, X1



(A) FRACTOGRAPH, X2000 (M1323)



(B) ELECTROPOLISHED, X2000 (M1639)

FIGURE 11 — MICROSTRUCTURE OF MOLYBDENUM CONTAINING 0.045% CARBON
INGOT 739, DEOXIDIZED WITH CARBON IN VACUUM, AS CAST



(A) FRACTOGRAPH, X2000 (M1991)



(B) ELECTROPOLISHED, X2000 (M1992)

FIGURE 12 — MICROSTRUCTURE OF MOLYBDENUM CONTAINING 0.011% CARBON
INGOT 1007, DEOXIDIZED WITH CARBON IN VACUUM, AS CAST.
LOW OXYGEN CONTENT, SMALL AMOUNT OF EXCESS CARBIDE.

Several heats were melted in vacuum with aluminum as the only deoxidant added to the charge. Initially, aluminum was added to the charge as the pure metal, but this proved to be unsatisfactory. To avoid complications arising from the low melting point and high vapor pressure of pure aluminum, the metal was added to other heats as a molybdenum-rich, molybdenum-aluminum alloy as well as in the form of $MoAl_2$.

Heat 1079 is typical of the series. All of the heats contained excessive speckling and sheet-like oxide at the grain boundaries, such as is shown in Figure 13, regardless of the mode of aluminum addition. As would be expected from the oxide content, these heats were brittle and hot short. Although 0.30% aluminum was added to Heat 1079, only 0.018% aluminum was retained in the casting. It is concluded from the appearance of the microstructure that, for all practical purposes, the aluminum had vaporized before it could react with the oxygen.

It was evident that effective use of aluminum as a deoxidizer or neutralizer for molybdenum would require melting at pressures above the vapor pressure of aluminum at the temperature involved. As an exploratory investigation of melting in inert atmosphere at pressures above atmospheric, several heats were made starting with (1) a sintered bar (produced by powder metallurgy), and (2) a bar of arc-cast molybdenum which had previously been melted and deoxidized with carbon in vacuum. The castings obtained in this way contained about the same amounts of carbon and oxygen as in the original bars. The arc was smoother and easier to control in argon atmosphere than in helium; therefore, argon was used in all subsequent experiments with positive pressure atmosphere.

After the feasibility of melting under inert atmosphere at positive pressure had been established, deoxidation with aluminum was again attempted. Preliminary heats indicated that about 85% of the aluminum addition was retained in the casting when melted under argon. To determine the potential of aluminum as a neutralizer of the commercial grades of molybdenum powder available, experiments were performed with gradually increasing amounts of aluminum (Ingots 1201-1204). In general, the macrostructure of these ingots was slightly coarser than that of carbon-vacuum molybdenum (Figure 10, Ingot 1203). The heat melted in argon, to which 0.03% aluminum was added, contained as excessive amount of molybdenum oxide and speckling, Figure 14. As the aluminum content was increased, the amounts of oxide and speckling decreased progressively. Less oxide and speckling appeared in heats to which 0.05% aluminum was added, Figure 15, and addition of 0.10% and 0.15% aluminum eliminated speckling and grain boundary impurities, Figures 16-17. Further additions within the solubility limits of aluminum in molybdenum did not produce a change in microstructure.

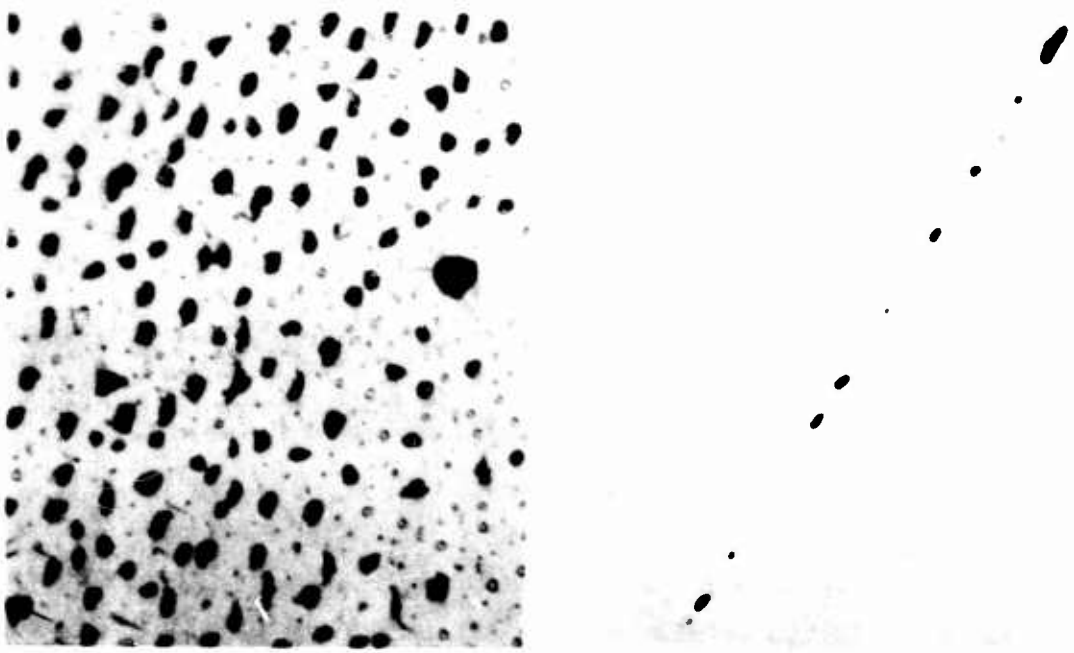
All of the heats melted with aluminum in argon atmosphere contained some microporosity, and their density was between 99.4% and 99.8% of the theoretical. The oxygen content of these heats (by vacuum fusion analysis) was of the same order of magnitude as that of the initial charge, 0.004-0.013%, indicating that very little oxygen is actually removed during melting. The presence of 0.03% to 0.05% Al_2O_3 in the casting was established by wet chemical analysis.



(A) Fractograph, X2000 (M2231) (B) Electropolished, X2000 (M2217)

FIGURE 13 - MICROSTRUCTURE OF MOLYBDENUM DEOXIDIZED WITH ALUMINUM IN VACUUM
Heat 1079, 0.001% Carbon, 0.018% Aluminum, as cast

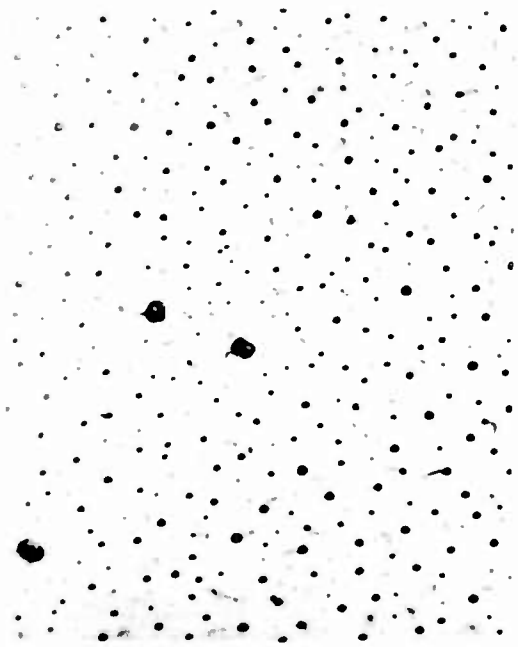
The Al_2O_3 phase was difficult to detect and eluded positive identification by metallographic examination, but a rather gross change in microstructure as the molybdenum oxide is eliminated from the grain boundaries is demonstrated in Figures 14-17. When oxides are present at the grain boundaries, as in Figure 14, fracture is intergranular. If sufficient aluminum is added that aluminum oxide is formed in preference to molybdenum oxide, particles appear at the grain boundaries (Figure 16) and fracture is intragranular. Inability to detect particles of Al_2O_3 in the microstructure may be associated with the fact that they are not concentrated at the grain boundaries but are distributed within the grains and must be very fine. Some inconclusive evidence exists that they are associated with the microporosity detected in the microstructures. The hardness of inadequately neutralized heats (1201) was 185 DPN; as the aluminum addition became sufficient to remove gross speckling from the grain boundaries (0.10-0.20% aluminum), the hardness dropped to the range 150-165 DPN, which is substantially below that of carbon deoxidized heats. This decrease in hardness is attributed to the greater purity of matrix, that is, lower oxygen, nitrogen, and carbon.



(A) FRACTOGRAPH, X2000 (M2619)

(B) ELECTROPOLISHED, X2000 (M2694)

FIGURE 14 – MOLYBDENUM DEOXIDIZED WITH 0.03% ALUMINUM IN ARGON
HEAT 1201, 0.002% CARBON, 0.012% ALUMINUM, AS CAST



(A) FRACTOGRAPH, X2000 (M2659) (B) ELECTROPOLISHED, X2000 (M2681)

FIGURE 15 — MOLYBDENUM DEOXIDIZED WITH 0.05% ALUMINUM IN ARGON
HEAT 1202, 0.002% CARBON, 0.027% ALUMINUM, AS CAST



(A) FRACTOGRAPH, X2000 (M2620) B) ELECTROPOLISHED, X2000 (M2695)

FIGURE 16 — MOLYBDENUM DEOXIDIZED WITH 0.10% ALUMINUM IN ARGON
HEAT 1203, 0.002% CARBON, 0.076% ALUMINUM, AS CAST



(A) FRACTOGRAPH, X2000 (M2621) (B) ELECTROPOLISHED, X2000 (M2696)

FIGURE 17 — MOLYBDENUM DEOXIDIZED WITH 0.15% ALUMINUM IN ARGON
HEAT 1204, 0.003% CARBON, 0.12% ALUMINUM, AS CAST

The forgeability in the range 2000-2600 F of molybdenum neutralized with aluminum could be correlated with microstructures of the castings. When neutralization was inadequate, recovery was poor; when oxide was eliminated from the grain boundaries, recovery was in the range 70-80%, based on the weight of the machined castings.

The effect of adding aluminum and carbon together when melting under argon is similar to that of adding aluminum alone, except for the presence of molybdenum carbide in amounts commensurate with the carbon content.

Deoxidation with Rare Earth Metals

Rare earth metals were used for deoxidation and/or neutralization of molybdenum. Some heats were melted in vacuum and some in argon atmosphere. The rare earth metals were added in the form of misch metal*, Lan-Cer-Amp**, and commercially pure cerium. The method in which these were prepared for addition to the melt has already been described.

From the point of view of results obtained, there is little choice among the three forms of rare earth metals. The macrostructure, microstructure, and forgeability of the castings were essentially the same when equivalent amounts of rare earth metals were added. Deoxidation with rare earth metals in amounts up to 0.5%, whether in vacuum or in argon, produced macrostructure and grain size similar to those shown for Ingot 1105, Figure 10. Addition of 2% (1061) and 5% (1064) rare earth metal produced marked grain refinement. The heats deoxidized with rare earth metals did not fill the mold as well as the heats deoxidized with carbon in vacuum, the ingot to which 5% rare earth metal was added being the poorest in this respect.

Addition of rare earth metals up to 0.2%, in vacuum or in argon, did not accomplish sufficient deoxidation to remove the oxide phase from the grain boundaries. Figure 18 shows the microstructure typical of heats to which 0.2% rare earth metal was added. The sheet-like molybdenum oxide is prominent on the fractured surface. As more rare earth metal was added, the amount of oxide in the microstructure decreased. Addition of 0.3% rare earth metal to vacuum melted heats produced the microstructure shown in Figure 19, in which there is no evidence of molybdenum oxide at the grain boundaries.

Further increase in the amount of rare earth metal added for deoxidation produces a new phase that appears predominantly at the grain boundaries. The amount of this phase increases as the amount of rare earth metal added increases. The microstructures of heats deoxidized with 0.5% and 5% rare earth metal are shown in Figures 20 and 21, respectively. The composition of the second phase has not been determined. It is a relatively soft structure and is retained only with difficulty during polishing.

If the heats were melted in argon, 0.5% rare earth metal was necessary to produce a microstructure free of grain boundary oxide. Increasing additions of rare earth metal lead to the appearance of the second phase.

* 50-70% cerium, 22-25% lanthanum, remainder is other rare earth metals

** 30% min. lanthanum, 45-50% cerium, 20-24% "didymium" and yttrium, 1% max. iron and unreduced salts

If sufficient rare earth metal was added to prevent molybdenum oxide from forming at the grain boundaries, the hardness of the casting was in the range 163 to 172 DPN, and the hardness remained in this range when substantial amounts of second phase were formed by addition of more rare earth metal (up to 5%). The hardness of comparable heats deoxidized with carbon in vacuum was about 180 DPN.

Microstructure was a general indication of forgeability of ingots deoxidized and/or neutralized with rare earth metals. Specimens containing the sheet-like oxide were hot short. As the rare earth metal addition became sufficient to prevent oxide from forming at the grain boundaries, forging could be performed at 2000-2600 F. In the optimum range (0.25% to 0.50% rare earth metal added), the recovery of sound metal on forging was about 35%; recovery of comparable material deoxidized with carbon in vacuum was about 85%. As the amount of rare earth metal added increased above 0.5% and the amount of second phase in the grain boundaries correspondingly increased, forgeability was impaired. When 2% or more rare earth metal was added, the molybdenum was totally unforgeable. In general, recovery on forging was erratic and did not correlate clearly with microstructure.

Two additional experiments were performed with rare earth metal additions: First, a heat (1111) was melted in vacuum with insufficient carbon for complete deoxidation and insufficient Lan-Cer-Amp, if used alone. The combination produced a clean ingot with low residual carbon, 0.007%, Figure 22. Second, since it had previously been observed that either rare earth metal additions of less than 0.25% or aluminum additions of less than 0.05% were not sufficient for complete deoxidation, two heats were melted in argon with the addition of 0.2% Lan-Cer-Amp, one with 0.05% aluminum (1105) and one without aluminum (1106). The heat to which no aluminum was added contained massive oxide, whereas the one to which a small amount of aluminum was added was free from oxide. The effects of aluminum and rare earth metals in deoxidizing Heat 1106 appear to be additive.

In summary, the results of this investigation indicate that rare earth metals can be used to supplant or supplement other deoxidizers and neutralizers of molybdenum, in conjunction with vacuum melting or melting in an inert atmosphere. Forgeable arc-cast molybdenum containing less than 0.005% carbon can be produced when rare earth metals are used for deoxidation and/or neutralization. Nevertheless, further investigation is necessary to bring deoxidation with rare earth metals to the quality attainable with carbon in vacuum. It is believed that part of the inconsistency of the results of deoxidation with rare earth metals is due to oxidation of the rare earth metals as they are converted to suitable size for melting. Improvement might be attained by blending the rare earth metals under argon and transferring them directly to the melting machine without exposure to air.



FRACTOGRAPH, X2000 (M2168)

FIGURE 18 — MOLYBDENUM DEOXIDIZED WITH 0.1% CERIUM, CAST IN VACUUM

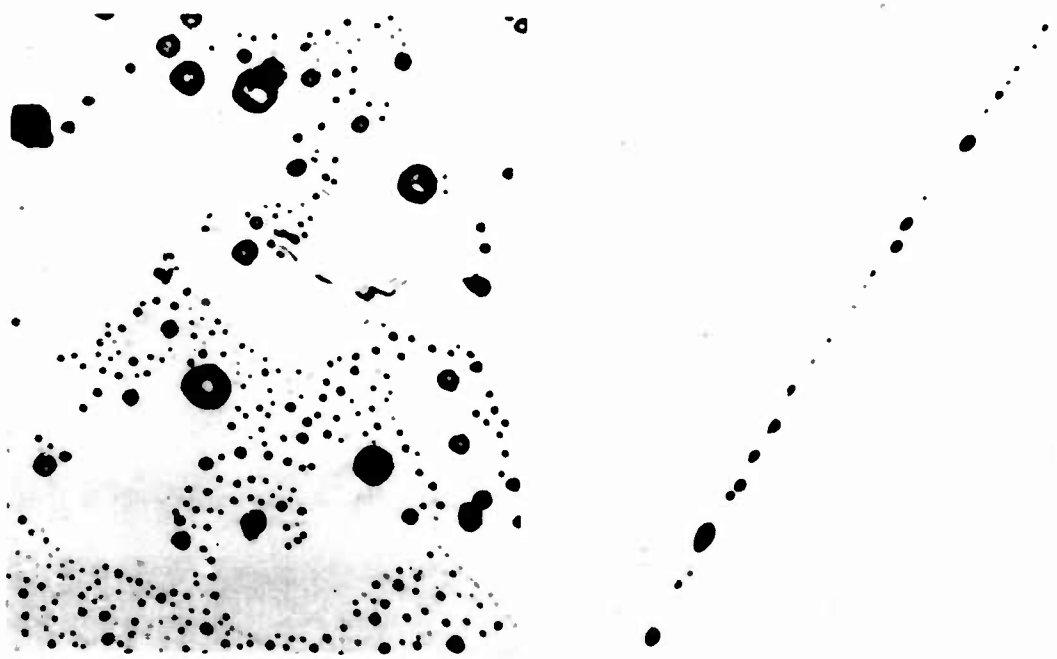
HEAT 1073, 0.003% CARBON, 0.003% CERIUM



(A) FRACTOGRAPH, X2000 (M2108) (B) ELECTROPOLISHED, X2000 (M2112)

FIGURE 19 — MOLYBDENUM DEOXIDIZED WITH 0.3% LAN—CER—AMP, CAST IN VACUUM

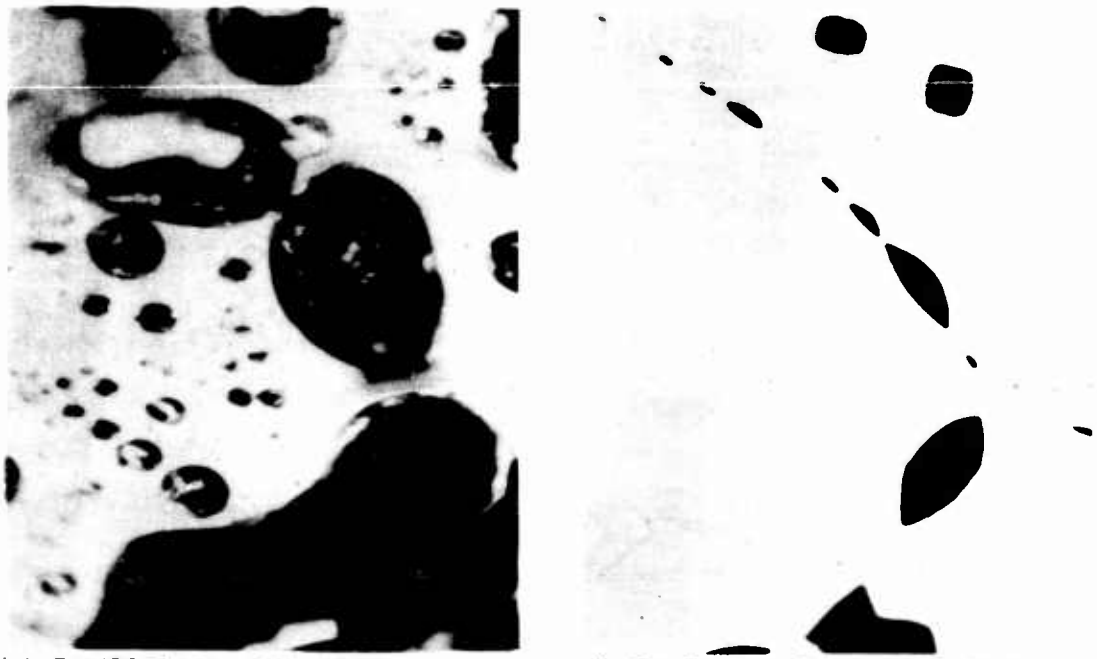
HEAT 1045, 0.003% CARBON, 0.005% CERIUM, 0.007% OTHER RARE EARTH METALS



(A) FRACTOGRAPH, X2000 (M2330) (B) ELECTROPOLISHED, X2000 (M2331)

FIGURE 20 — MOLYBDENUM DEOXIDIZED WITH 0.5% CERIUM, CAST IN VACUUM

HEAT 1114



(A) FRACTOGRAPH, X2000 (M2122) (B) POLISH-ETCH BUFF, X2000 (M2127)

FIGURE 21 — MOLYBDENUM DEOXIDIZED WITH 5% LAN—CER—AMP, CAST IN ARGON

HEAT 1064, 0.075% CARBON, 1.69% CERIUM, 1.99% OTHER RARE EARTH METALS



(A) FRACTOGRAPH, X2000 (M2354) (B) ELECTROPOLISHED, X2000 (M2355)

FIGURE 22 — MOLYBDENUM DEOXIDIZED WITH 0.1% LAN–CER–AMP AND 0.027% CARBON, CAST IN VACUUM

HEAT 1111, 0.007% CARBON, 0.004% RARE EARTH METALS

Deoxidation with Thorium

Thorium was added to the sintered molybdenum bar used as the electrode in several vacuum-melted bar machine heats. Metallographic examination of the resultant ingot (B124, Figure 23) showed that thorium would react with oxygen and molybdenum oxide and form thorium oxide in the casting. Replacing molybdenum oxide with thorium oxide was without beneficial effect, and the forgeability of the ingot was nil.

Thorium was added to arc-cast molybdenum bars and these were remelted in vacuum (B184, B197). The castings contained oxide at the grain boundaries, but the oxide was different from molybdenum oxide. Since sufficient carbon was present in these heats for complete deoxidation, the oxide was attributed to the thorium addition.

Deoxidation with thorium in argon yielded sporadic results. Those heats in which the residual thorium content was low (0.01% or less) were free of oxide at the grain boundaries. As the residual thorium content increased, the oxide phase, different from molybdenum oxide, appeared in the grain boundaries.

In general, our experience with thorium as a deoxidizer has not been encouraging. Thorium introduces difficulties in arc control. It reacts with oxygen in the melt to form thorium oxide which is insoluble in molybdenum and which precipitates at the grain boundaries, where it is a hindrance to forging if present in substantial amounts.



(A) Fractograph, X500 (M751)

(B) Electropolished, etched in NaOH + $K_3Fe(CN)_6$, X1000 (M753)

FIGURE 23 - MOLYBDENUM DEOXIDIZED WITH 0.016% THORIUM, CAST IN VACUUM
Heat B124, 0.005% Carbon

Titanium and Zirconium as Deoxidizers

In view of the high affinity and the rather high solid solubility of oxygen and nitrogen in titanium and zirconium, the use of these metals as deoxidizers and neutralizers for molybdenum was explored. The results obtained with the two metals were similar and will be discussed together.

In a series of vacuum melted heats (793-794), titanium and zirconium were added to the charge, either in the form of the pure metal or as the hydride. No carbon was added, since the effects of titanium and zirconium alone were under consideration. The macrostructures of these heats are represented in Figure 10 and were somewhat finer grained than those of molybdenum deoxidized with carbon in vacuum. The sheet-like oxide that would have appeared in the grain boundaries if no deoxidizer had been added was now in the form of spherical particles (Figure 24) somewhat larger than the speckles described earlier in this section. These spherical particles have not been definitely identified; they differ in appearance from molybdenum oxide and are thought to be the oxide of the added metal (titanium or zirconium).

In spite of the improvement in the amount and distribution of the oxide phase resulting from addition of zirconium or titanium in vacuum, the forgeability of the castings was hardly better than that of molybdenum containing sheet-like oxide at the grain boundaries. Nevertheless, these heats exhibited good ductility at room temperature, as measured by the bend test. The improved bend ductility is probably associated with the finer, more nearly equiaxed grains of these ingots.

Since deoxidation with titanium or zirconium alone in vacuum did not yield a forgeable product, it was postulated that titanium or zirconium might be used in conjunction with less than the normal amount of carbon. Heats 1078, 1100, 1112, and 1205 were produced in accordance with this postulate; they were carbon-vacuum heats to which less carbon was added than is normally required for full deoxidation, and titanium or zirconium were added to supplement the carbon. The prime purpose of these heats was to reduce the residual carbon content of the ingot.

The 0.05% zirconium added to Heat 1205 apparently aided deoxidation, Figure 25. A little speckling was evident on the fracture but not in the microstructure--much less than would be expected in a corresponding carbon-vacuum ingot made without the addition of zirconium.

Titanium was used as the auxiliary deoxidizer in Heats 1078, 1100, and 1112. The 0.005% residual carbon and speckling on the grain boundary surfaces and in the microstructure, Figure 26, indicate that 0.2% titanium was inadequate for complete deoxidation. When sufficient carbon was added to leave a residual of 0.015%, 0.2% titanium deoxidizer produced a cleaner ingot, although some speckling was visible (Figure 27). When the residual carbon was maintained at 0.015% and the titanium addition was raised to 0.5% (1112), the ingot was devoid of oxide (Figure 28). It was difficult to obtain an intergranular fracture of this ingot.

The addition of zirconium to molybdenum melted in argon produced an ingot containing what appeared to be zirconium oxide at the grain boundaries and within the grains, Figure 29. The microporosity normally encountered with heats melted in argon was also present. Because of poor forgeability--although it was somewhat better than for ingots containing sheet oxide--molybdenum neutralized in this way was not investigated further.

Heats melted in argon and deoxidized or neutralized with small amounts of aluminum combined with titanium or zirconium contained a small amount of titanium or zirconium oxide. The amount of oxide was so small, however, that the microstructure and forgeability were similar to those of molybdenum deoxidized with aluminum alone.

Other Deoxidizers and Neutralizers

In addition to aluminum and rare earth metals, a 90Li-10Al alloy (758), magnesium (873, B150), and aluminum with calcium phosphide (953) were used for deoxidation and neutralization of molybdenum under a positive pressure of argon. The microporosity and cast grain size of the ingots produced in this way were similar to those of other heats melted in argon, see the section on Aluminum as a Deoxidizer. Substantial amounts of nonmetallic inclusions were observed at the grain boundaries; and, in view of this substantial amount of nonmetallics, it is not surprising that the ingots deoxidized with these miscellaneous agents failed to forge.

Ca_3P (755), 90Li-10Al alloy (757), and 50Li-50Ca alloy (329) were added to various heats in conjunction with carbon and melted in vacuum. None of these additions improved the cleanliness of the castings beyond that obtained by the use of carbon alone.

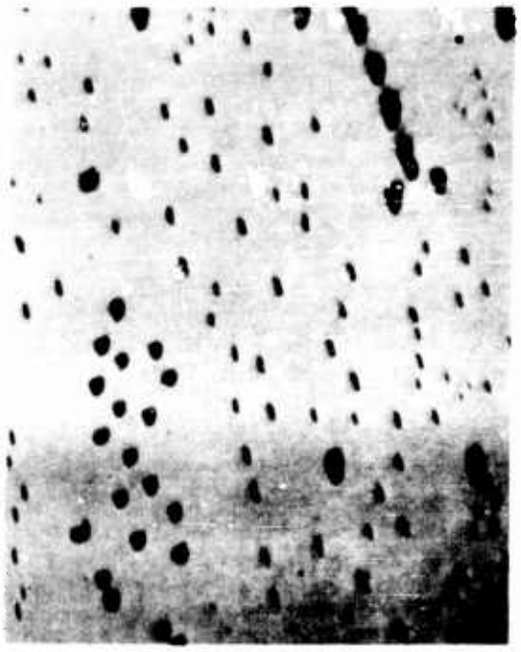
An attempt was made to deoxidize molybdenum in vacuum with vanadium alone (756). The casting contained a large amount of nonmetallic inclusions at the grain boundaries and within the grains.

Summary

The comparatively low ductility of cast molybdenum and molybdenum-base alloys is related to the coarse, columnar grain structure resulting from the mode of melting and casting and to the oxides residing in the relatively small amount of grain boundary area. The present study was directed towards elimination and/or neutralization of oxygen in arc-cast molybdenum and its alloys. The results of the investigation are summarized as follows:

1. Grain boundary oxides may appear at exceedingly low oxygen content. It is estimated that the solubility of oxygen in solid molybdenum is somewhat less than 0.001%.

2. Molybdenum melted in vacuum and deoxidized with carbon and containing between 0.0001% and 0.0005% oxygen has been obtained by improving the vacuum melting equipment and establishing more rigid specifications for the starting materials. The presence of oxide at the grain boundaries in the form of very fine dots (referred to as "speckling") can be detected by careful metallographic examination when the oxygen content is as low as 0.0005%.



(A) FRACTOGRAPH, X2000 (M1528)



(B) ELECTROPOLISHED, ETCHED 3 MIN. IN WEAK SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION, X2000 (M1595)

FIGURE 24 — MOLYBDENUM DEOXIDIZED WITH TITANIUM IN VACUUM

HEAT 792, 0.003% CARBON, 0.42% TITANIUM



(A) FRACTOGRAPH, X2000 (M2622)



(B) ELECTROPOLISHED, X2000 (M2680)

FIGURE 25 — MOLYBDENUM DEOXIDIZED WITH ZIRCONIUM AND CARBON IN VACUUM

HEAT 1205, 0.010% CARBON, 0.056% ZIRCONIUM



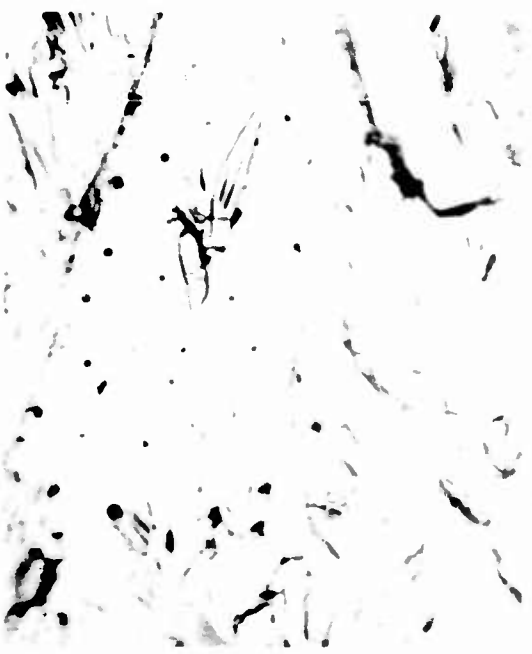
(A) FRACTOGRAPH, X2000 (M2215)



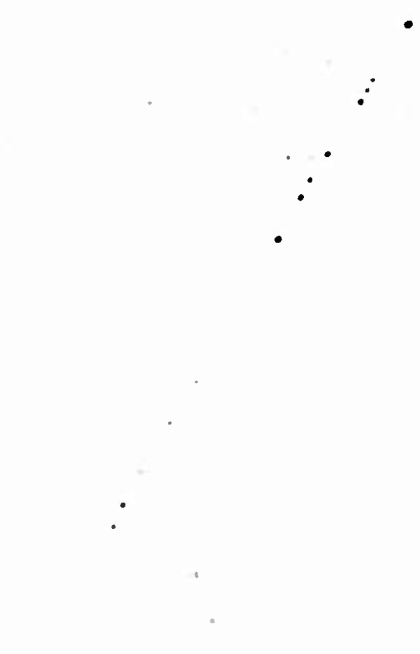
(B) ELECTROPOLISHED, X2000 (M2207)

FIGURE 26 – MOLYBDENUM DEOXIDIZED WITH CARBON AND 0.2% TITANIUM IN VACUUM

HEAT 1078, 0.005% CARBON, 0.18% TITANIUM



(A) FRACTOGRAPH, X2000 (M2279)



(B) ELECTROPOLISHED, X2000 (M2280)

FIGURE 27 – MOLYBDENUM DEOXIDIZED WITH CARBON AND 0.2% TITANIUM IN VACUUM

HEAT 1100, 0.015% CARBON, 0.21% TITANIUM



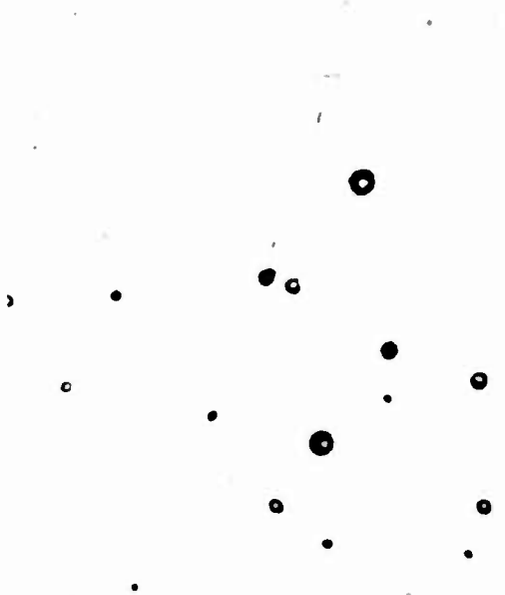
(A) FRACTOGRAPH, X2000 (M2365) (B) ELECTROPOLISHED, X2000 (M2366)

FIGURE 28 — MOLYBDENUM DEOXIDIZED WITH CARBON AND 0.5% TITANIUM IN VACUUM

HEAT 1112, 0.015% CARBON, 0.49% TITANIUM



(A) FRACTOGRAPH, X2000 (M1563)



(B) ELECTROPOLISHED, ETCHED 3 MIN. IN WEAK SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION, X2000 (M1593)

FIGURE 29 — MOLYBDENUM DEOXIDIZED WITH 0.25% ZIRCONIUM IN ARGON

HEAT 719, 0.002% CARBON, 0.21% ZIRCONIUM

3. The effect of carbon on the solubility of oxygen in molybdenum is not known exactly, but there are indications that the solubility of oxygen is greater when carbon is present.

4. If titanium or zirconium are used in addition to carbon for deoxidation in vacuum, workable molybdenum is obtained with a lower residual carbon content than when carbon is used alone. If the residual oxygen content is such that there is speckling when carbon is the sole deoxidizer, the addition of titanium or zirconium produces grain boundaries devoid of speckling, although neither actually reduces the residual oxygen content. When titanium or zirconium are used as auxiliary deoxidizers, less carbon is required for the deoxidation required to render the metal forgeable.

5. When molybdenum is melted under a positive pressure of argon, essentially none of the oxygen present in the charge is removed. If aluminum is added, an aluminum oxide is produced and appears in the grains as well as the grain boundaries in a form and distribution that alleviates the hot shortness associated with molybdic oxide at the grain boundaries and permits forging. Neutralization with aluminum in argon yields forgeable molybdenum essentially free of carbon (0.000% to 0.005%).

6. Rare earth metal additions--whether melting is conducted in vacuum or in argon--are partially effective in neutralizing the oxygen in molybdenum and its alloys. In general, the resultant cast product does not yield as high recovery on forging as molybdenum deoxidized with carbon in vacuum or neutralized with aluminum under a positive pressure of inert gas.

CAST MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS

Its high melting point, availability, and ease of production by the arc-cast process make molybdenum a logical choice for high-temperature structural applications. While pure molybdenum is satisfactory for a number of these, the increased strength attainable through alloying widens the field of use considerably.

The basis of the investigation of molybdenum-base alloys was the development of a metallic material having high strength at elevated temperatures, that is, at temperatures above those now served by iron-, cobalt-, and nickel-base alloys. At the outset of the investigation a few data were available on the strength of binary molybdenum-base alloys; essentially no data were at hand on more complex molybdenum-base alloys. It was known, however, that wrought (forged and rolled) shapes would be the most useful; essentially single-phase alloys were expected to be most readily worked, and, therefore, were investigated first.

The alloying elements were selected on the basis of a review of the literature and previous experience, both of which indicated that only the transition metals were sufficiently soluble in solid molybdenum to alter its properties significantly without introducing new phases. Since it seemed desirable to determine the effect of the various elements in solid solution before attempting to evaluate the effects of new phases, most of the elements selected were transition metals. The exceptions were Al, Be, B, Ca, C, Mn, N, and Si. The complete list of twenty elements studied follows: Al, Be, B, Ca, C, Cr, Co, Fe, Mg, Mn, Ni, Nb, N, Si, Ta, Ti, U, V, W, and Zr.

In general, examination of the cast metals preceded preparation and study of the wrought alloys. Study of the castings was concerned principally with determinations of the following:

1. Solid solubility and the nature of the first excess phase developed in molybdenum-rich alloys.

2. The effects of alloying elements on deoxidation of molybdenum and on the grain size and microstructure of the castings.

3. The alloy systems which are amenable to heat treatment (precipitation hardening) for control of mechanical properties.

4. The effects of alloying elements on hardness and hot working characteristics of the castings.

Graded Ingots

The investigation was started on a series of graded ingots in which the concentration of the alloying element was gradually increased from zero to a percentage which would be sufficient to produce a second phase or, in the absence of a second phase, to a percentage which would establish the characteristics of the solid solution. Since in most cases well-deoxidized, arc-cast bar stock was used, deoxidation was a secondary problem. The later,

more thorough study of deoxidation was treated in the preceding section. The mechanical characteristics of the bar melting machine were especially suited to the preparation of such ingots, and the graded ingot made available from a single heat a series of alloys which otherwise would have required the preparation of many heats at the expense of considerable time, material, and effort. The graded ingots were divided into small, homogeneous sections which were used for metallographic examination, x-ray diffraction studies, and hardness tests at room and elevated temperatures. The sections were also analyzed chemically, and the results of all the tests and examinations were correlated with chemical composition. These correlations indicated the concentrations of alloying elements which warranted more extensive investigation on ingots of uniform concentration.

Segregation and coring were not serious in the more dilute alloys, but at the higher alloy concentrations, coring was often pronounced. To minimize coring, most of the samples were held for 50 to 60 hours at 2450 F in argon and cooled at 100 F, or less, per hour.

When the study was extended to ternary molybdenum-base alloys, the bar machine was used to make graded ingots in which the concentration of one of the alloying elements was a constant, arbitrarily selected so that the hardness of the binary alloy at 1600 F would be about 90 DPN, and in which the concentration of the second alloying element was gradually increased from zero to a percentage which would yield an alloy of about 200 DPN at 1600 F.

Ingots of uniform composition were made in PSM-3 and PSM-4, for the most part. Some small castings of uniform composition for study of the first excess phase in materials of high alloy content were made by pressing a powder charge and melting it in a crucible in an induction furnace capable of operating either in vacuum or in argon and attaining temperatures up to 4100 F. This furnace is described in the second annual report under this contract. A schematic drawing of the furnace is shown in Figure 30.

Grain Size, As Cast

The longitudinal sections of the graded ingots illustrate the effect of alloying elements on the as-cast grain size. The sections, shown in Figures 31-35 for the binary alloys and Figures 36-41 for the ternary alloys, were cut from graded ingots produced in molds 2" or 2-1/2" in diameter. In making a direct comparison between grain size shown in these figures and that shown in the discussions of deoxidation and mechanical properties of wrought alloys, it should be remembered that there is considerable difference in mold diameter. The ingots for deoxidation and mechanical property studies were cast in 3" to 8" diameter molds and were coarser grained (at a given alloy content) than the 2" or 2-1/2" diameter ingots.

Cast grain size is of interest in connection with forgeability of arc-cast molybdenum ingots. The desired effect in improving forgeability is to produce castings of minimum grain size. From the macrostructures shown in the above figures, alloy content appears to be particularly effective; and,

for control of grain size only, the preferred elements are those which cause grain refinement with a minimum increase in hardness in the forging temperature range. However, we cannot utilize the alloy content necessary to accomplish sufficient refinement before the hot hardness and the resultant resistance to deformation of the ingot is too high for successful forging at the temperatures and in the equipment currently available for processing large sections.

To arrange the alloying elements in order of effectiveness in reducing grain size, the grain sizes shown in the various macrographs of this and preceding reports were rated according to an arbitrary classification. These ratings were compared with the hardnesses developed by the alloys at 3000 F, a temperature selected as representative of the probable range in which such alloys would be forged. Alloys with unusually high carbon content were not considered in the rating. The order of preference of elements for reducing cast grain size with minimum increase in hardness is, first, Ti, and then, in decreasing order, Be, Zr, V, Fe, Al, Cr, Si, Co. Titanium is at the top of the list because of its very mild effect on hot hardness, although a considerable quantity is required to refine the grain appreciably. Be and Zr are probably of most practical value in the respect that only small additions are required to produce significant grain refinement. There is little choice among Fe, Al, Cr, Co, Si and Ni.

The elements Mn, W, Nb, Ta and U do not reduce cast grain size significantly.

The effect on the cast grain size by addition of two alloying elements (ternary alloys, Figures 36-41) is approximately the sum of the individual effects of each alloying element.

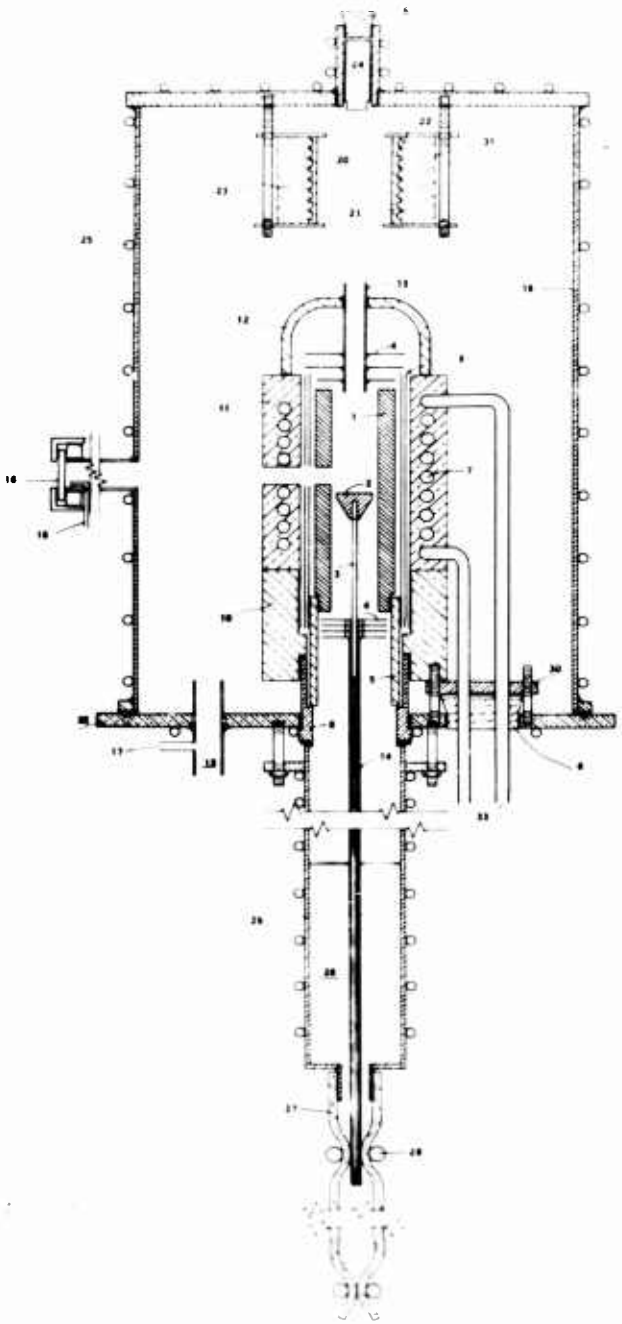
Hardness

As mentioned in the introduction, the property upon which the development of molybdenum-base alloys was based was their potential high temperature strength. The methods of measuring high temperature strength are many and varied, and hot hardness has proved to be a reliable indication of the results to be expected in the more time-consuming creep-rupture tests. It is more than likely that hot hardness is a necessary, if not sufficient, condition for good high-temperature, load-carrying ability or strength. For the purpose of preliminary evaluation of the strength of molybdenum-base alloys, hardness was determined from room temperature to 3000 F.

The process of arc casting provides alloys which are homogeneous and stress free. Chemical analyses have revealed no serious segregation, and annealing at high temperatures has little effect upon the hardness of the castings. Hardness in the as-cast condition therefore reflects only solid-solution hardening and may be used to evaluate the hardening effects of various elements so long as their solubility is not exceeded.

CLIMAX MOLYBDENUM CO. 33

APRIL 15 1951



1 MOLYBDENUM SUSCEPTOR
2 SPECIMEN SUPPORT
3 MOLYBDENUM ROD
4 MOLYBDENUM REFLECTORS
5 STABILIZED ZIRCONIA SLEEVE
6 RUBBER STOPPER
7 HEAVY WALL COPPER TUBE INDUCTION COIL
8 COPPER SLEEVE
9 SPIRAL SHEET MOLYBDENUM REFLECTOR
10 POROUS ALUNDUM BRICK
11 ZIRCONIA CEMENT
12 ZIRCONIA CAP
13 ZIRCONIA TUBE
14 STEEL ROD
15 VACUUM CONNECTION
16 ARGON INLET
17 ARGON OUTLET
18 OBSERVATION WINDOW
19 BRASS CASE
20 ARGON PURIFIER
21 ALUNDUM MUFFLE
22 MOLYBDENUM ELEMENT
23 TITANIUM GRANULES
24 MICALEX THERMOCOUPLE SUPPORT
25 COOLING COILS
26 QUENCHING OIL
27 RUBBER TUBING
28 PINCH CLAMP
29 COPPER QUENCH TANK
30 TRANSITE STOPPER RETAINER
31 NICKEL SCREEN
32 BRASS BASE PLATE
33 CONNECTIONS TO WATER AND TO 50 KW 10,000 CYCLE M.G. SET THROUGH $7\frac{1}{2}$ IN. DIA. $5\frac{1}{2}$ TURN BALANCING INDUCTOR

FIGURE 30 – INDUCTION FURNACE FOR HEAT TREATING OR MELTING IN PURIFIED ARGON

(P795)

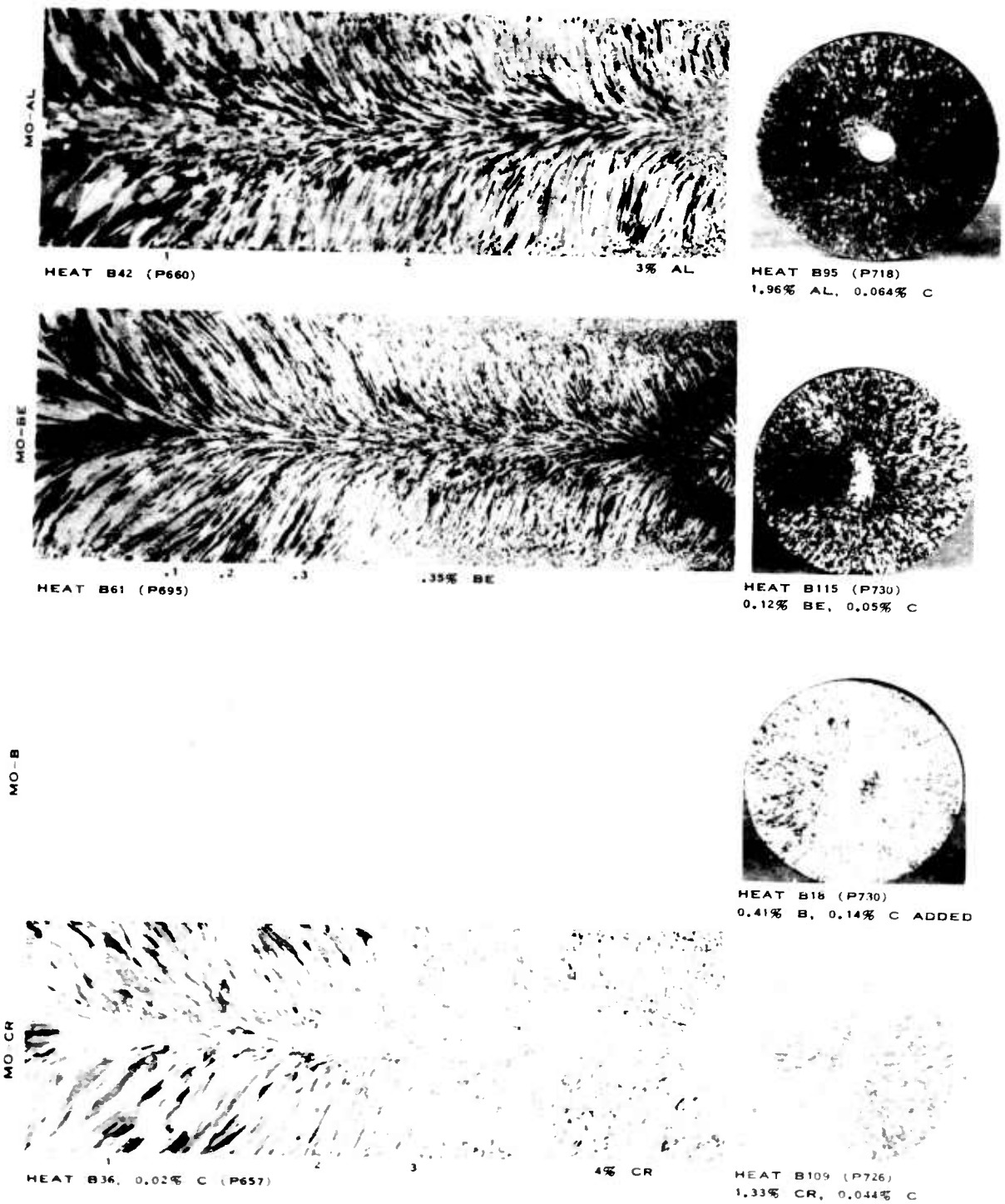


FIGURE 31 – ETCHED LONGITUDINAL AND CROSS SECTIONS OF GRADED INGOTS, x1

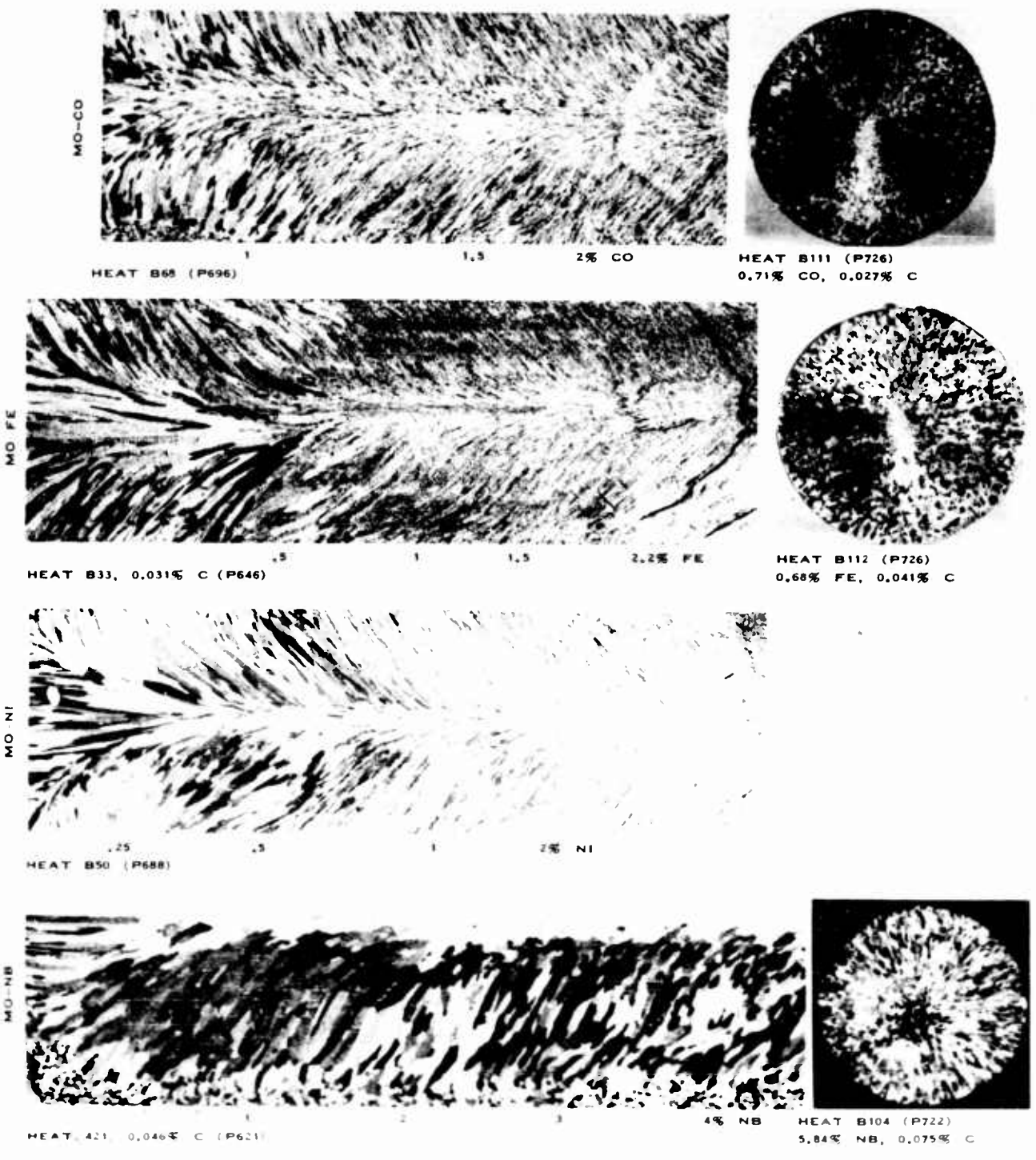


FIGURE 32 — ETCHED LONGITUDINAL AND CROSS SECTIONS OF GRADED INGOTS, x1

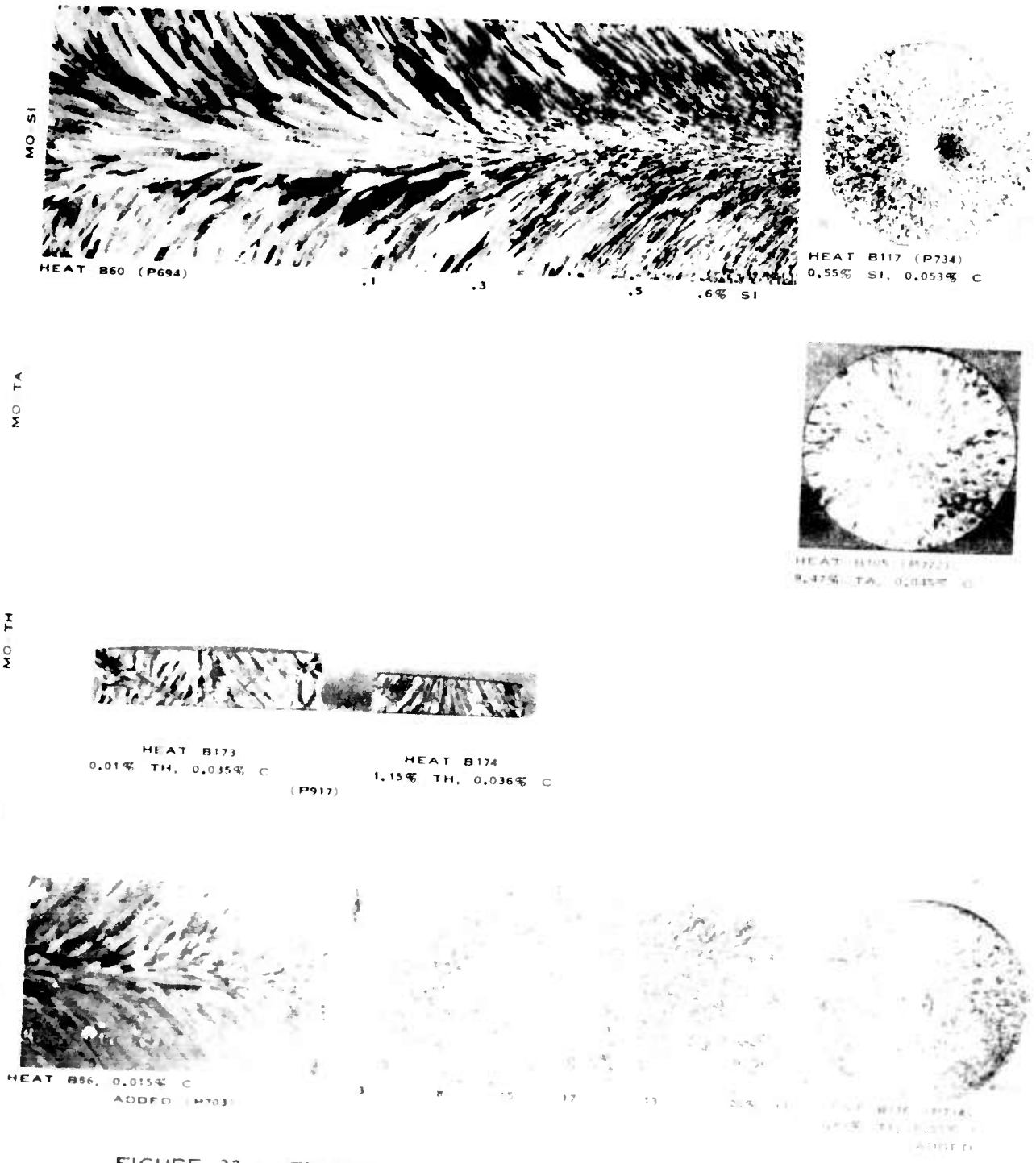
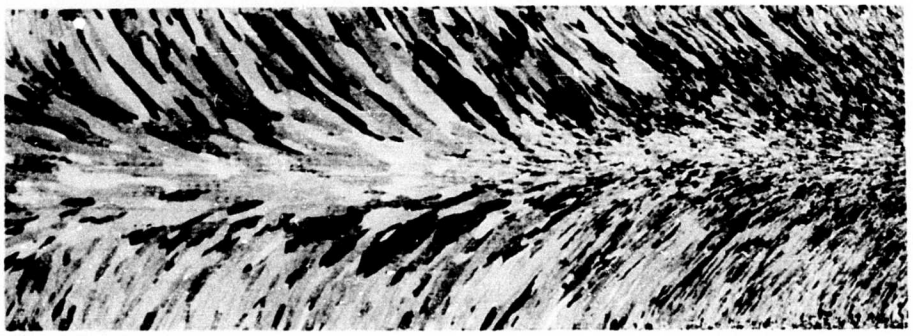
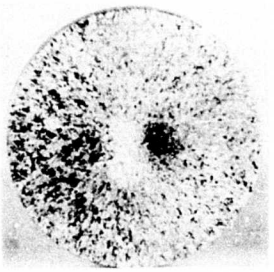


FIGURE 33 – ETCHED LONGITUDINAL AND CROSS SECTIONS OF GRADED INGOTS.

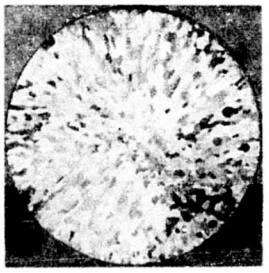


HEAT B60 (P694) .1 .3 .5 .6% SI



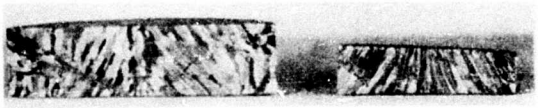
HEAT B117 (P734)
0.55% SI, 0.053% C

MO-SI



HEAT B105 (P722)
8.47% TA, 0.045% C

MO-TA

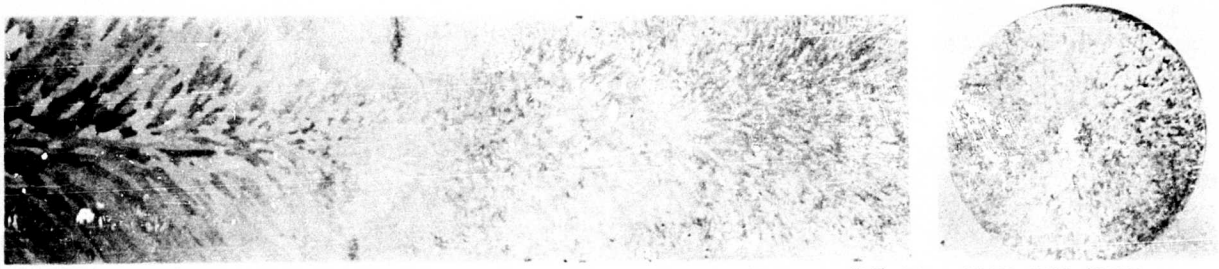


HEAT B173
0.01% TH, 0.035% C

HEAT B174
1.15% TH, 0.036% C

(P917)

MO-TH



HEAT B86, 0.015% C ADDED (P703) 3 8 15 17 13 20% TI

HEAT B116 (P734)
3.83% TI, 0.05% C ADDED

MO-TI

FIGURE 33 — ETCHED LONGITUDINAL AND CROSS SECTIONS OF GRADED INGOTS. x1



HEAT 1064 (P912)
5% LAN-CER-AMP ADDED
0.075% C
1.69% CE
1.99% OTHER RARE EARTH METALS



HEAT 1061, 2% LAN-CER-AMP ADDED (P912)

FIGURE 35 – ETCHED LONGITUDINAL SECTIONS OF INGOTS DEOXIDIZED WITH RARE EARTH METALS, x1

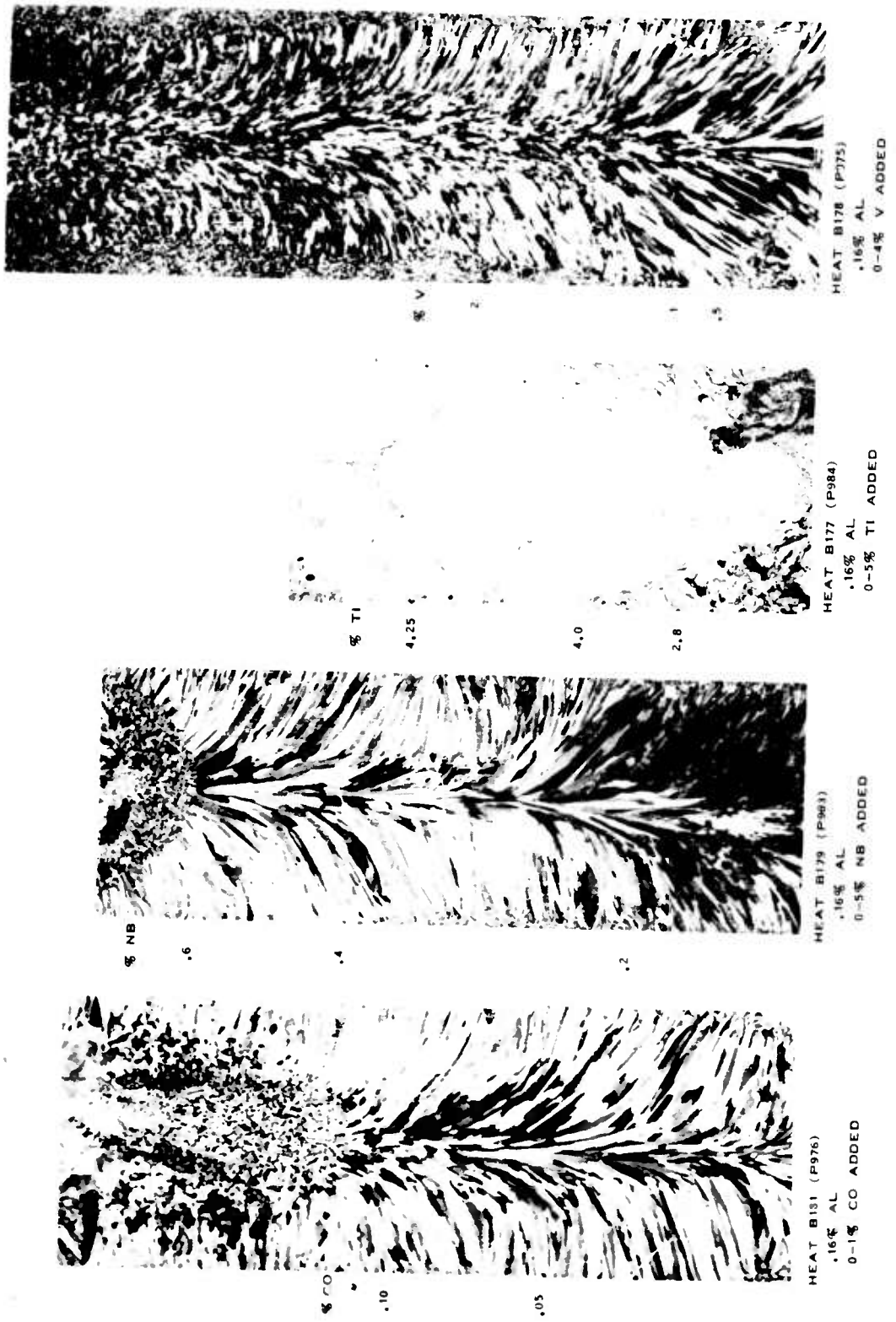


FIGURE 36 — ETCHED LONGITUDINAL SECTIONS OF TERNARY MOLYBDENUM-BASE ALLOY GRADED INGOTS, X1

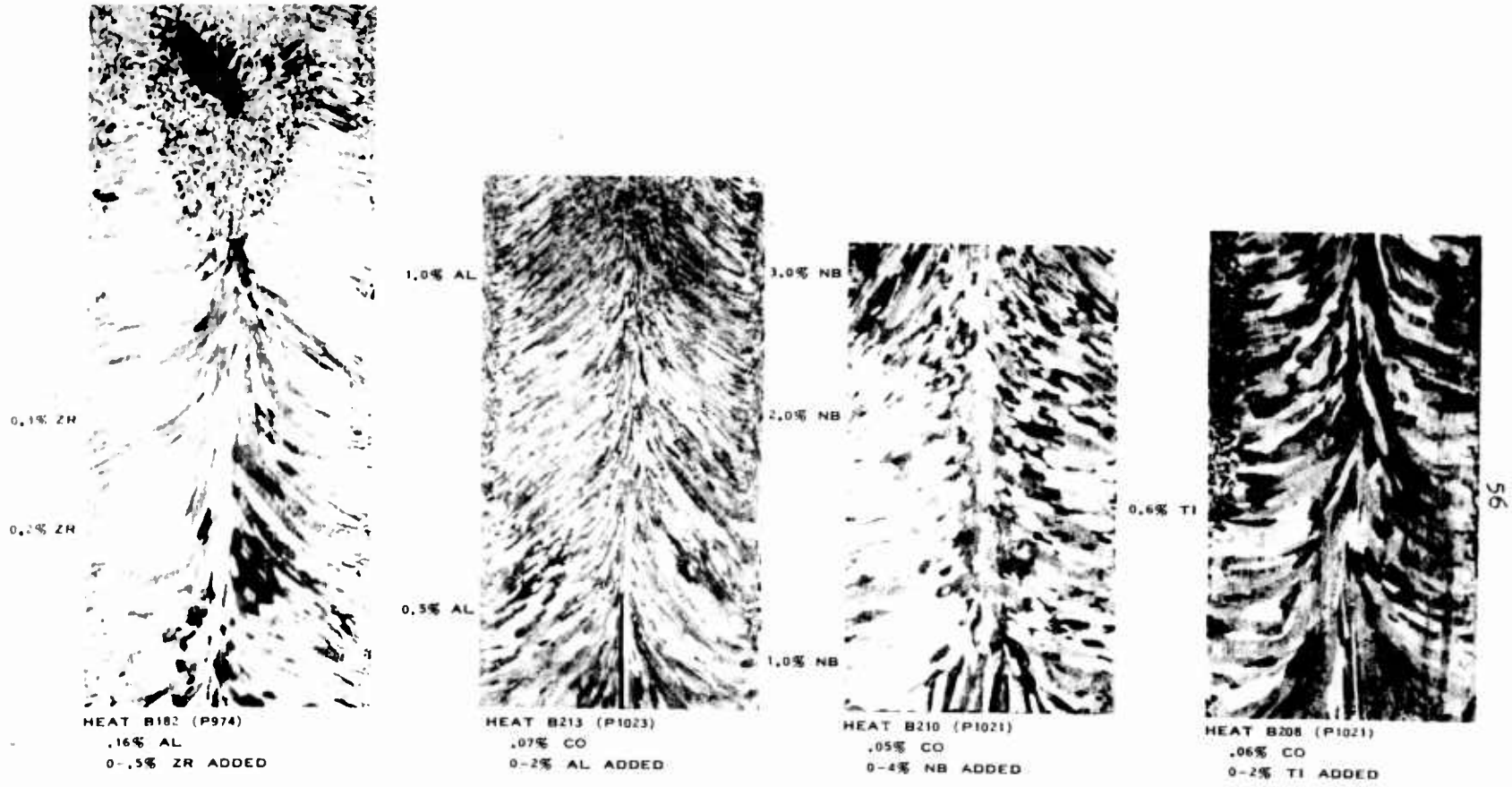


FIGURE 37 – ETCHED LONGITUDINAL SECTIONS OF TERNARY GRADED INGOTS OF MOLYBDENUM–BASE ALLOYS, x1

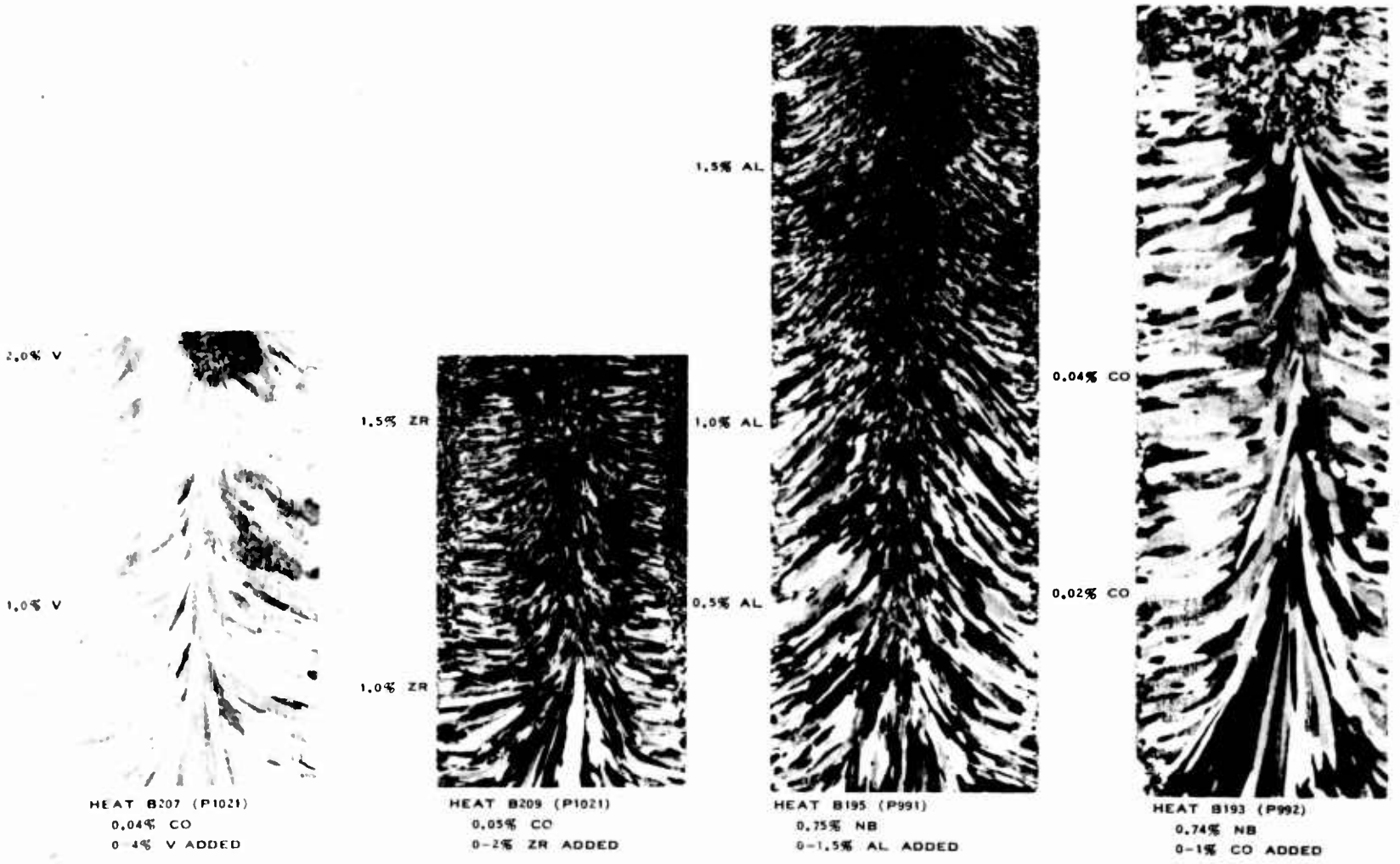


FIGURE 38 – ETCHED LONGITUDINAL SECTIONS OF TERNARY GRADED INGOTS OF MOLYBDENUM–BASE ALLOYS, x1

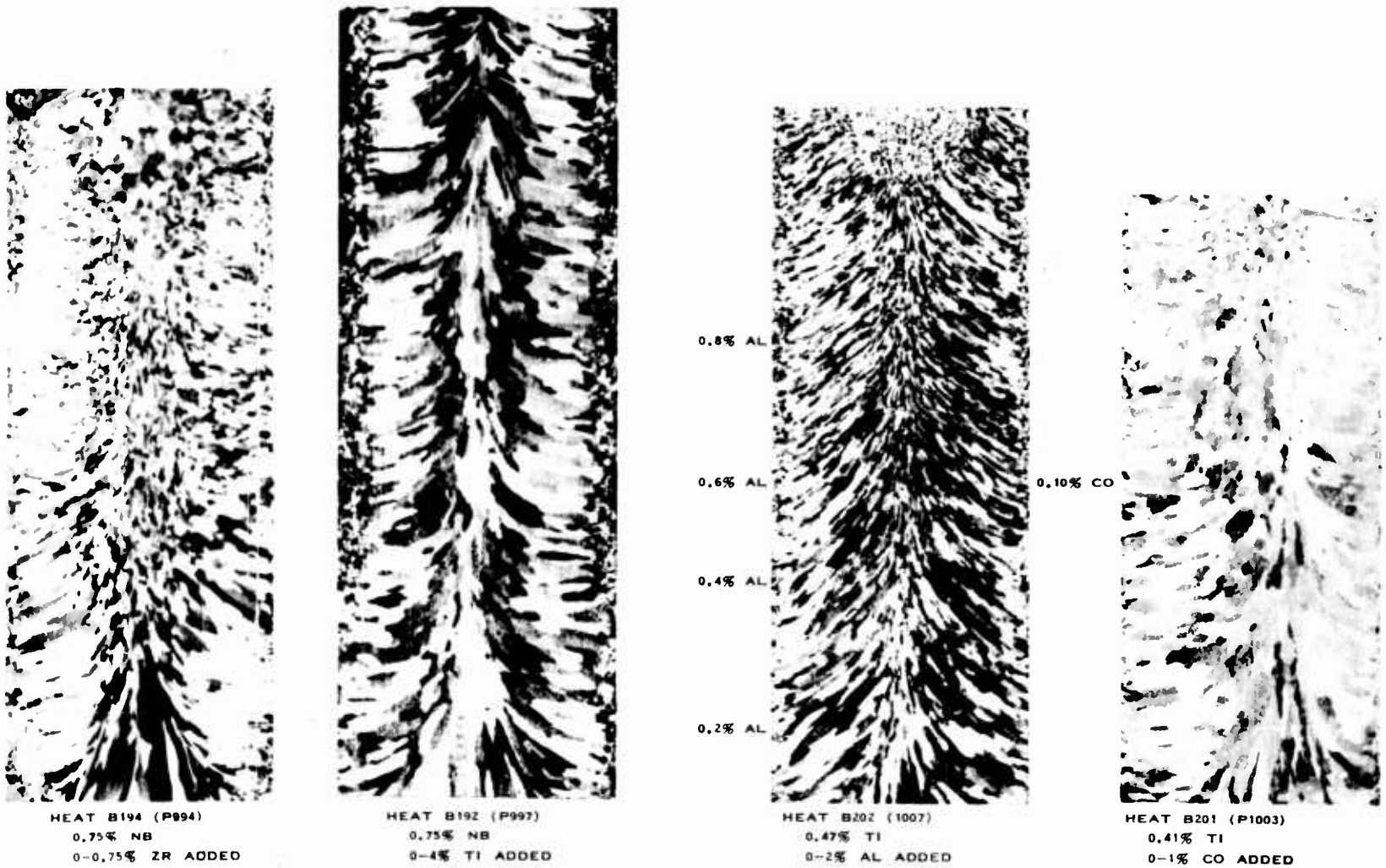


FIGURE 39 -- ETCHED LONGITUDINAL SECTIONS OF TERNARY GRADED INGOTS OF MOLYBDENUM-BASE ALLOYS, X1

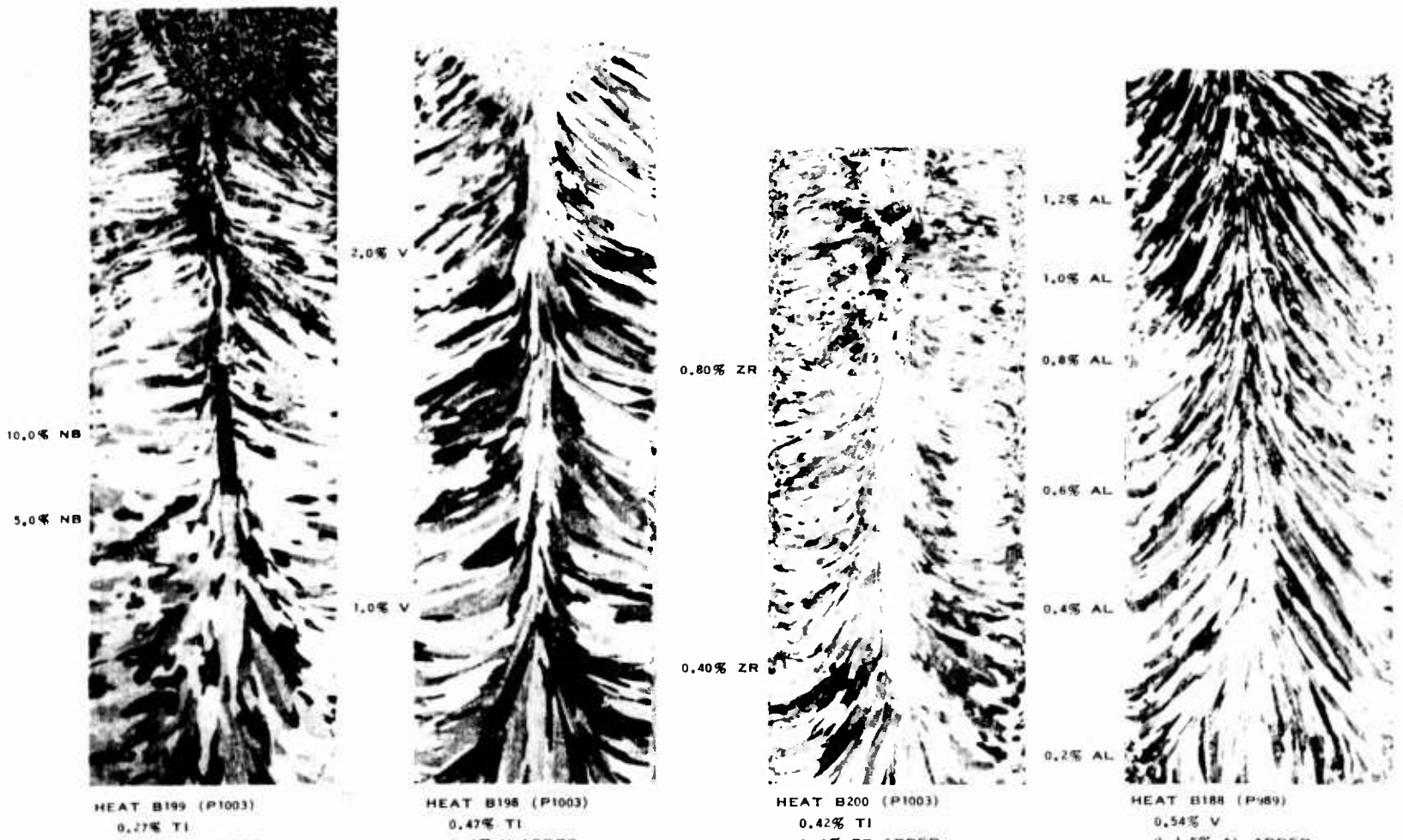


FIGURE 40 – ETCHED LONGITUDINAL SECTIONS OF TERNARY GRADED INGOTS OF MOLYBDENUM–BASE ALLOYS, x1

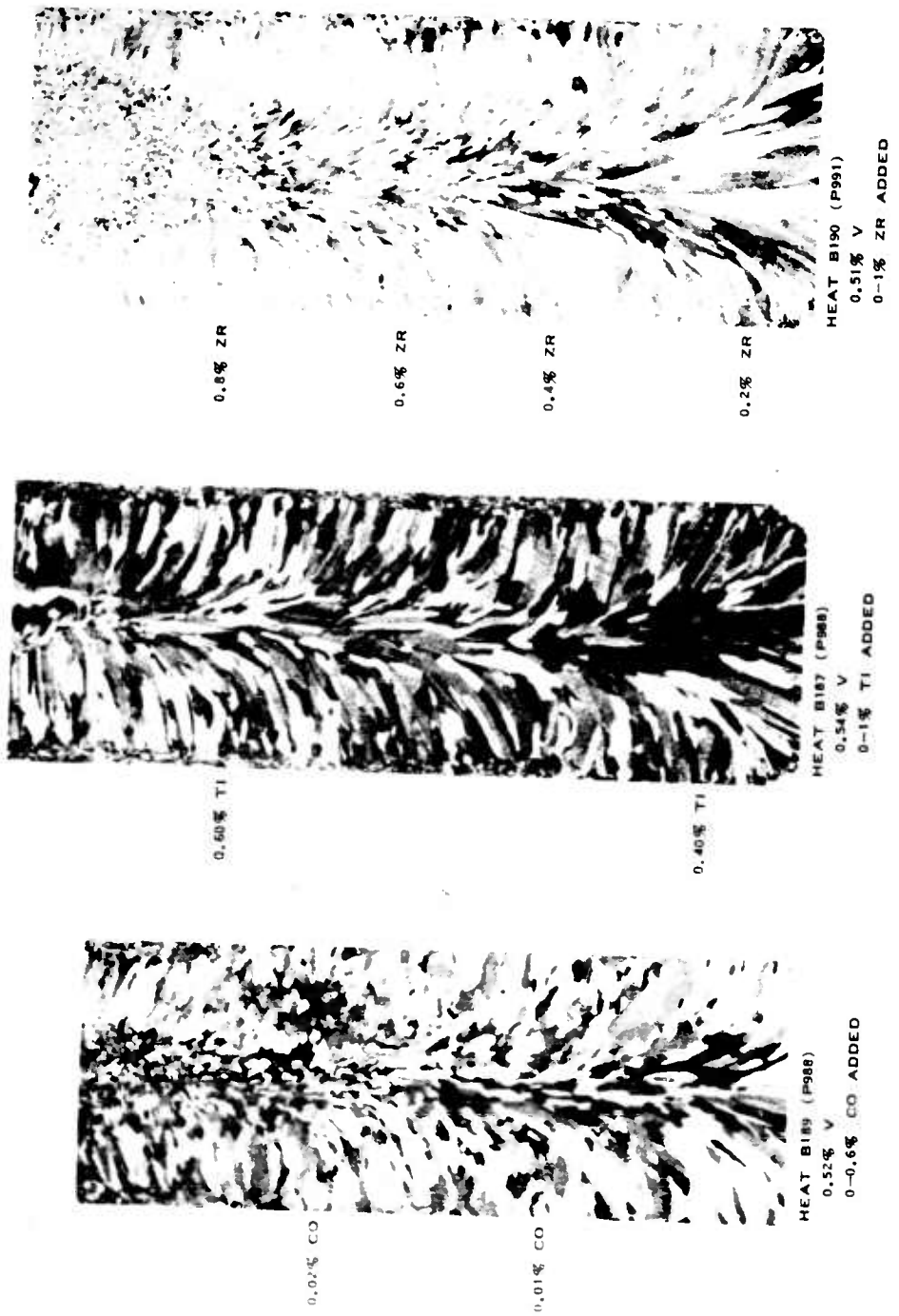


FIGURE 41 – ETCHED LONGITUDINAL SECTIONS OF TERNARY GRADED INGOTS OF MOLYBDENUM-BASE ALLOYS, X1

The hardness at room temperature was determined by means of a standard Vickers machine. The apparatus for determination of Vickers hardness up to 1600 F was described by Bens* and has been modified in only minor details. A 10 kg load was used in determining hardness from room temperature to 1600 F.

In the early development and evaluation of molybdenum alloys, a hardness tester devised for operation at temperatures up to 3000 F, and known as the dynamic hardness tester, was designed and built at this laboratory. The apparatus is described in the first annual report, and a critical appraisal of its shortcomings appears in Appendix B of the fourth annual report.

To determine hardness at elevated temperatures in terms of widely accepted units and to circumvent the shortcomings of the dynamic hardness tester, the apparatus was redesigned to embody the principles of the Vickers hardness test, as shown in Figure 42. The standard diamond penetrator was rejected because of susceptibility to oxidation and the possibility of forming carbides and/or welding to the specimen. The use of synthetic sapphire (Al_2O_3) as the penetrator alleviates these difficulties, and although sapphire (9 Mohs) is softer than diamond (10 Mohs), the hardness of the metallic specimens at any given temperature is so much less than that of sapphire at the same temperature that sapphire is an adequate penetrator. The sapphire rods used as penetrators were 1/8" in diameter and about 1" long, and were mounted at the end of a molybdenum rod. The working end of the sapphire was ground to the standard Vickers angle, that is, to a square-base pyramid having an angle of 136° between opposite faces. The molybdenum rod in which the sapphire was mounted extended out of the furnace through a gas-tight seal and the load on the rod was applied by dead weight. The penetrator was enclosed in a molybdenum-wound furnace evacuated to about 30μ and filled with purified argon to a pressure of 1" Hg above atmospheric pressure. The argon was further purified during the test by recirculation through titanium chips at 1600 F. Immediately before the impression was made, the pressure of the system was reduced to atmospheric pressure.

In actual operation of this modified Vickers hot hardness tester, the penetrator is about 1/8" above the specimen, and the specimen and penetrator are at the same temperature when the impression is made; there is no cooling of the specimen by the penetrator. To make the impression, the penetrator is gently lowered on the specimen without impact. In the tests reported here, the total load on the penetrator was 5 kg. The preferred specimen size is 3/16" to 3/8" thick by 1-1/4" to 2" diameter. The specimen is fastened to the stage by a molybdenum bolt.

The indentations on the specimen are at a point 1/2" from the center. The stage holding the specimen is rotated through a small angle after each impression is made, and thus about 40 impressions are accommodated on a single specimen. In the determination of hardness of molybdenum-base alloys up to 3000 F, impressions were made at intervals of 200 F on heating to and cooling from the maximum temperature.

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* F. P. Bens, Transactions, American Society for Metals, v 38 (1947), 505

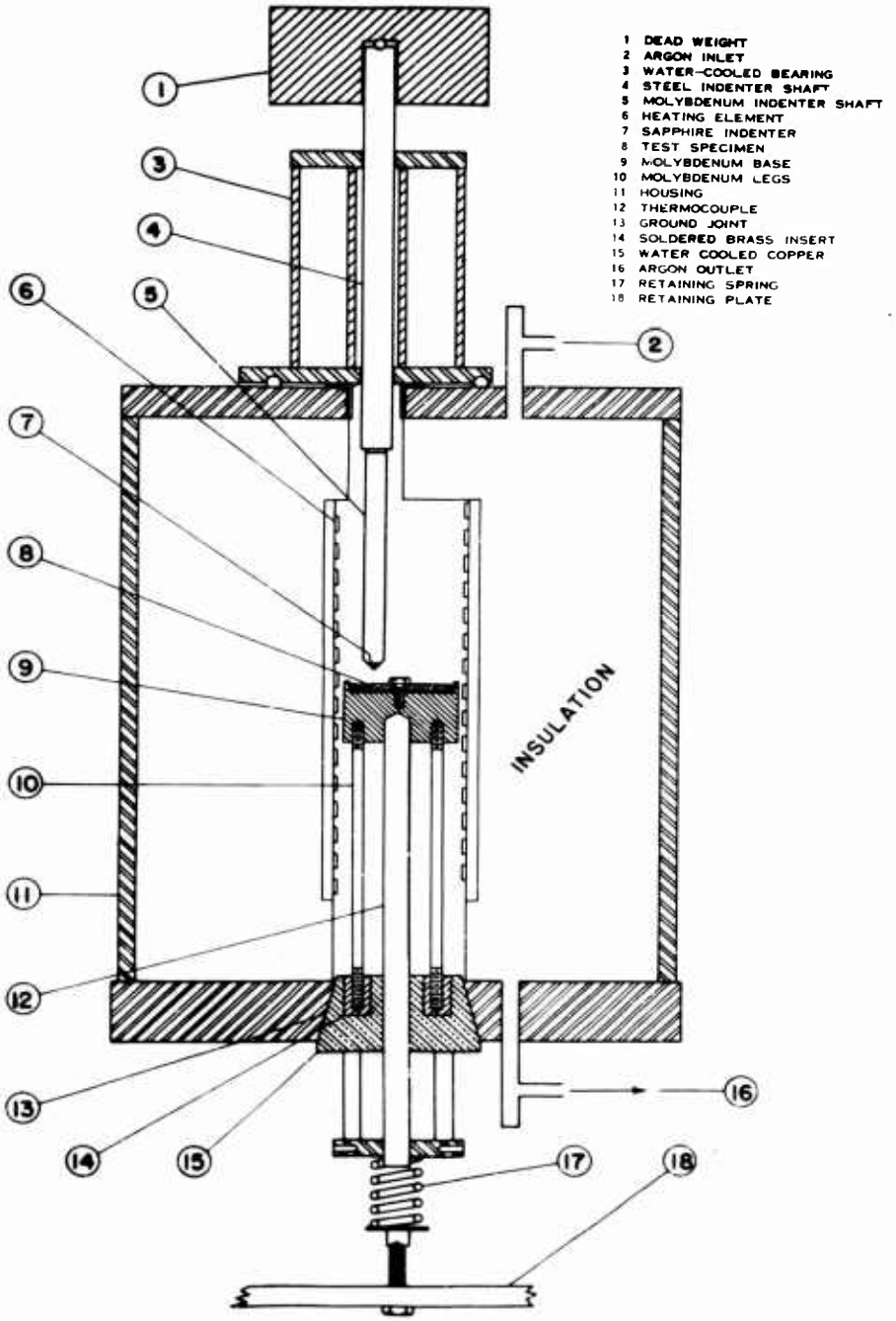


FIGURE 42 — HOT HARDNESS TESTER FOR TESTS TO 3000 F

(P1300)

The rate at which the hardness of molybdenum was increased by various alloy additions was given in the first annual report, but the curves were based on graded ingots in which the alloy gradient was steep and rose rapidly to rather high concentrations of added alloying elements. Since the time of the first annual report, many specimens have become available from various heats of uniform composition. Hardness values obtained from these miscellaneous samples provide the basis for the summary plots, Figures 43-45, of hardness as a function of alloy content at room temperature, 1600 F, and 3000 F for molybdenum-base binary alloys. Individual curves of hardness as a function of test temperature are included in the appendix as Figures C1-C8. Hardness as a function of alloy content for the ternary alloys is summarized in Figures 46-51. The data are based on graded ingots in which one of the alloying elements was held at a constant composition while the other was varied. Hardness vs temperature for ternary alloys of uniform composition are presented as Figures C9-C12 in the appendix.

The hardness of molybdenum deoxidized with carbon and cast in vacuum is 180 $\pm$ 4 DPN at room temperature. As small amounts of Al, Si, Cr, Fe, Co, or Ni are added, the hardness drops gradually until a minimum is reached. Further additions of these elements cause the hardness to increase (Figure 43). The value of the minimum hardness depends upon the alloying element added. The effect of these elements is apparent in the ternary alloys also even when only one of the added elements belongs to this group.

It is unexpected that any element in solid solution will reduce the hardness of molybdenum, and it may be significant that the alloying elements producing the initial drop in hardness are all transition elements of the first long period of the periodic table. Although the mechanism by which the hardness is lowered by these elements has not been explored, it is postulated that one or both of the following factors may be operative:

1. Small additions of the elements Al, Cr, Si, Fe, Co and Ni remove, or at least neutralize, certain minute impurities which otherwise are present in solid solution.

2. The above elements alter the solubilities of oxygen and/or carbon in the matrix, resulting from the solution of the alloying element.

Except for the initial reduction in hardness produced by the six alloying elements referred to above, all of the alloy additions over the concentration range investigated increased the room-temperature hardness approximately linearly with increasing alloy content, but with various degrees of effectiveness, over the range investigated, that is, with different slopes of the hardness vs alloy percent curves for the different alloying elements. The variation in hardening coefficient (increase in hardness divided by concentration in atomic percent of a given element in solid solution) is, of course, closely related to the fundamental atomic properties such as atomic diameter and basic crystal structure. The hardness at 1600 F for all of the alloys was greater

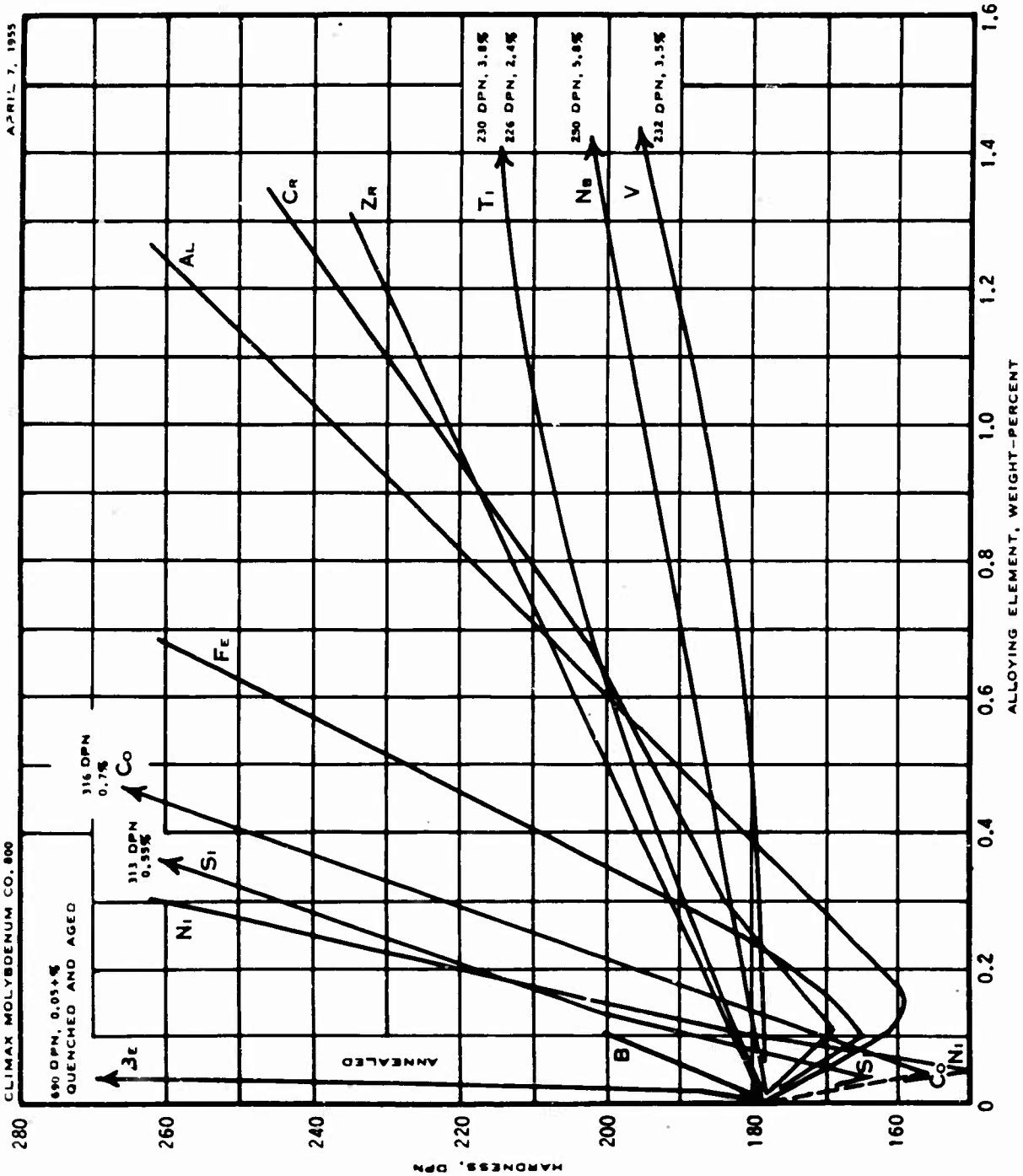


FIGURE 43 – EFFECT OF VARIOUS ELEMENTS ON THE HARDNESS AT ROOM TEMPERATURE OF MOLYBDENUM AS CAST

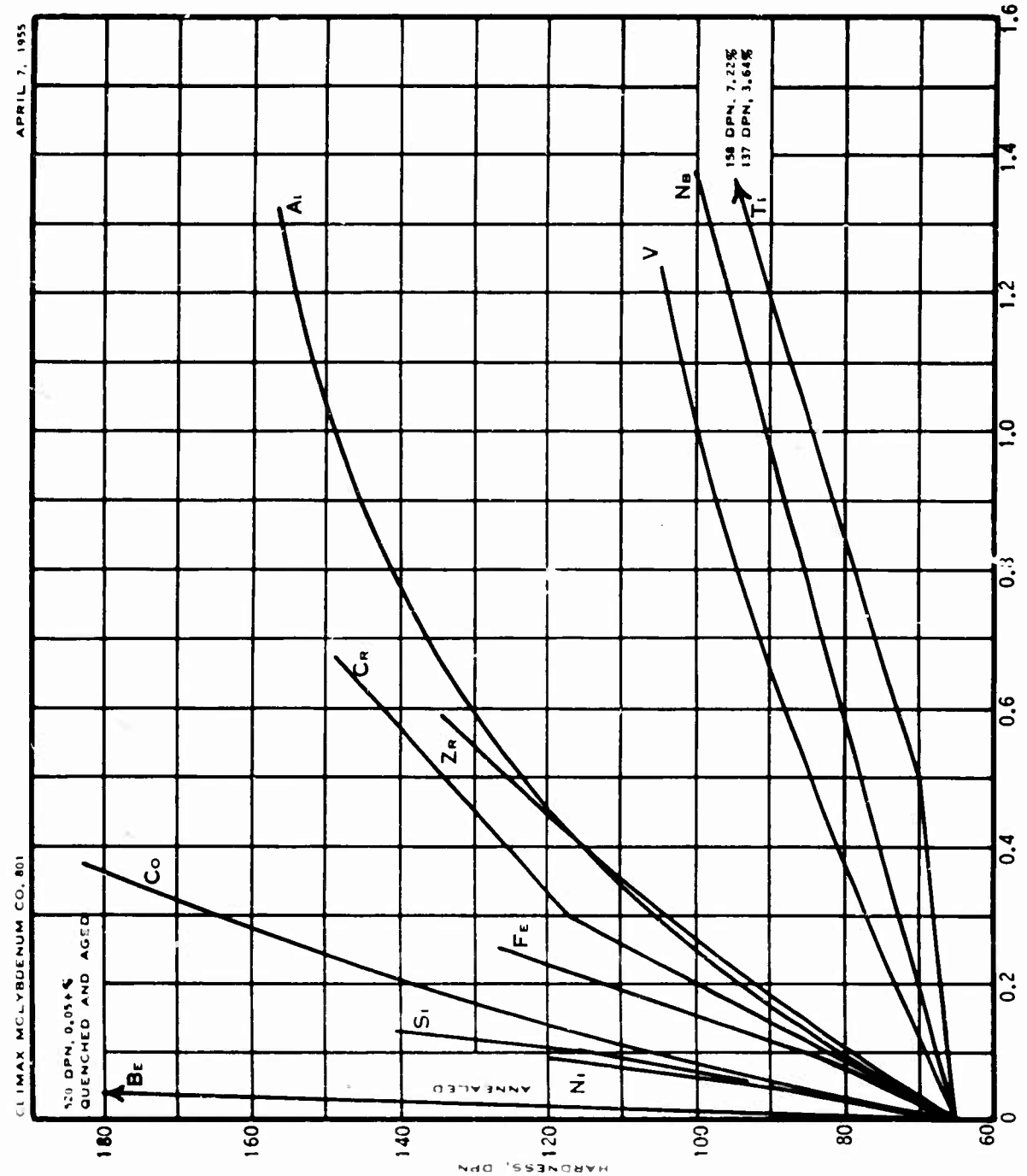


FIGURE 44 – EFFECT OF VARIOUS ELEMENTS ON THE HARDNESS AT 1600 F OF MOLYBDENUM AS CAST

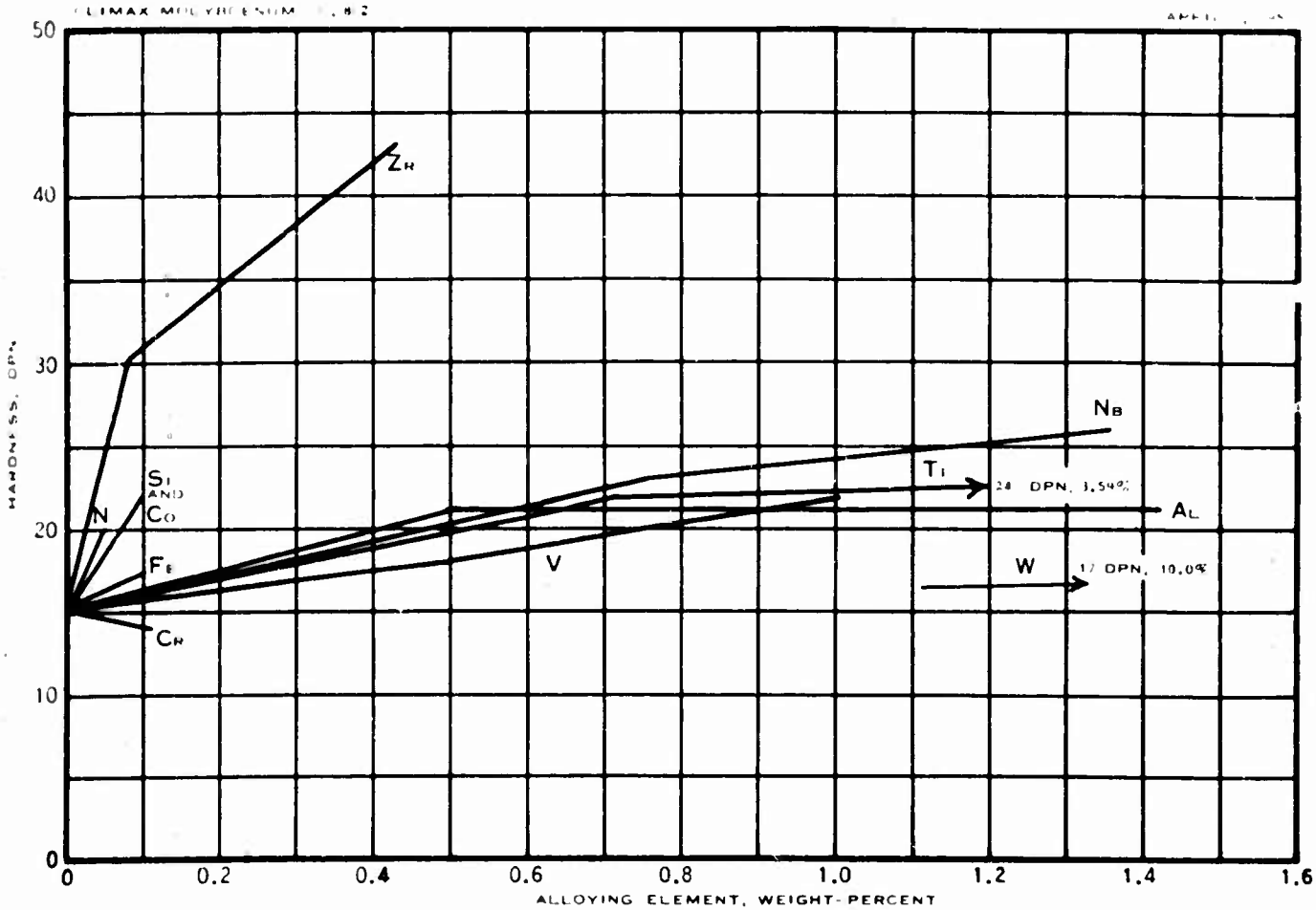


FIGURE 54 – EFFECT OF VARIOUS ELEMENTS ON THE HARDNESS AT 3000 F OF MOLYBDENUM AS CAST

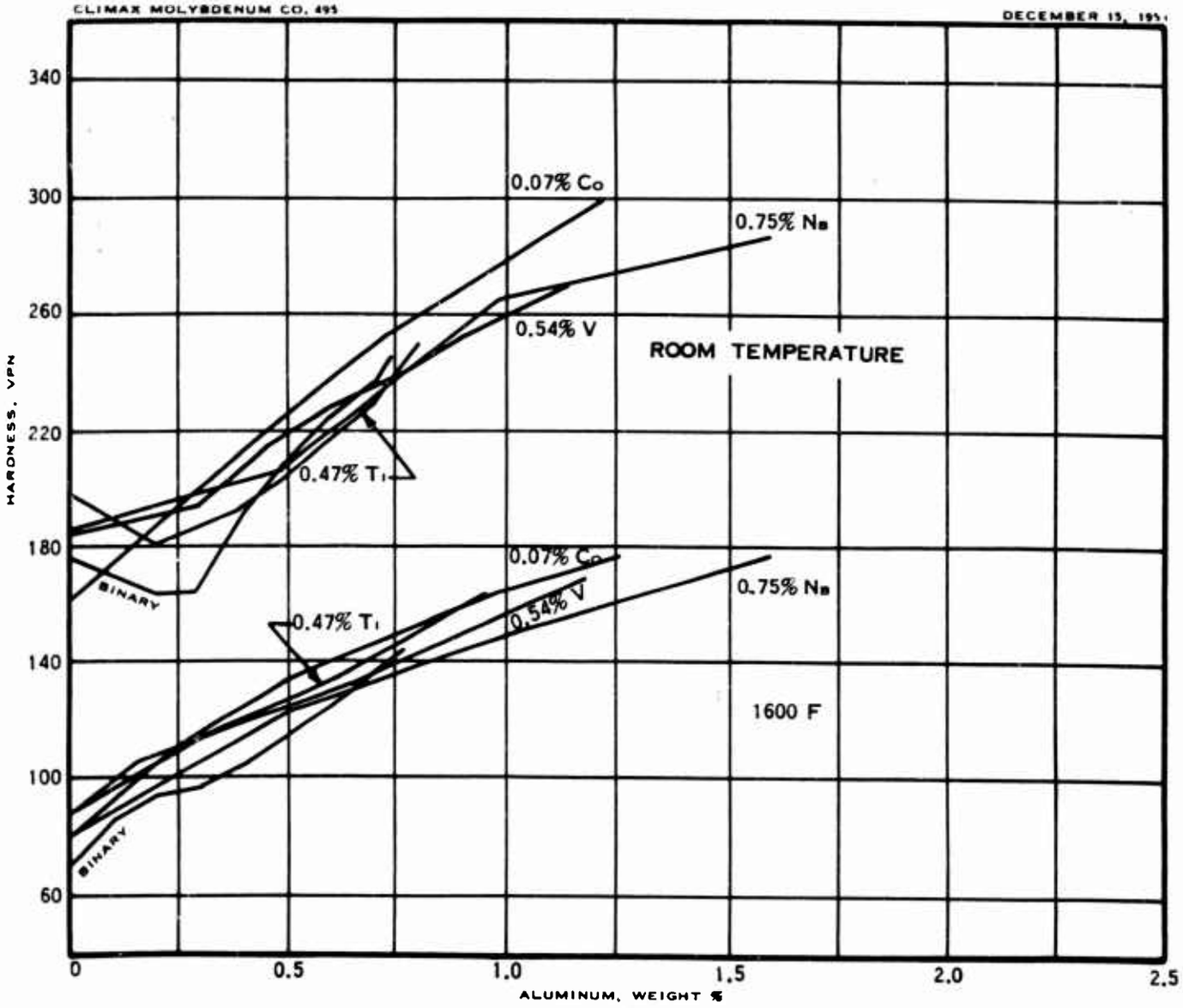


FIGURE 46 – EFFECT OF ALUMINUM CONTENT UPON THE HARDNESS OF TERNARY MOLYBDENUM–BASE ALLOYS

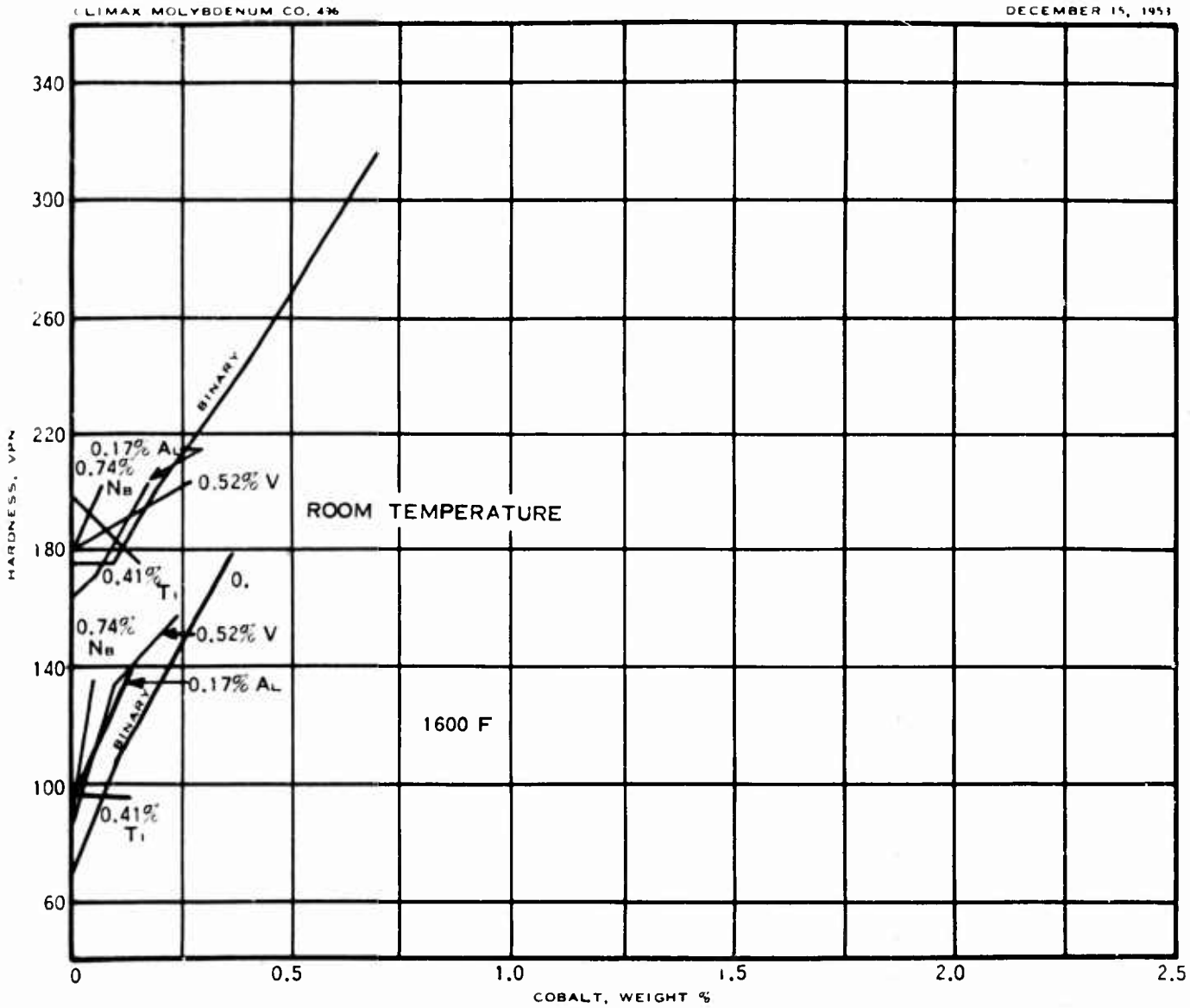


FIGURE 47 – EFFECT OF COBALT CONTENT UPON THE HARDNESS OF TERNARY MOLYBDENUM–BASE ALLOYS

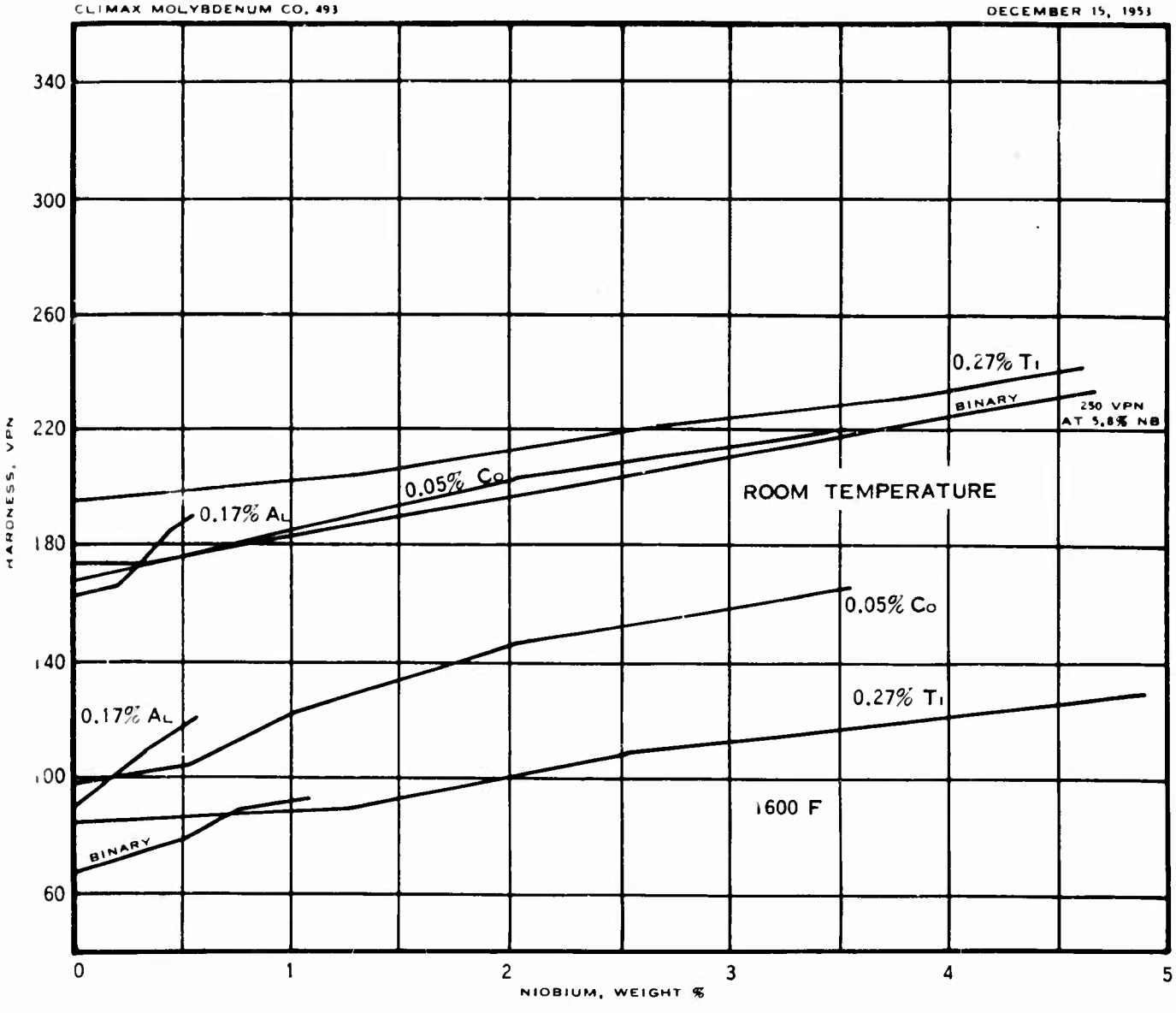


FIGURE 48 – EFFECT OF NIOBIUM CONTENT UPON THE HARDNESS OF TERNARY MOLYBDENUM-BASE ALLOYS

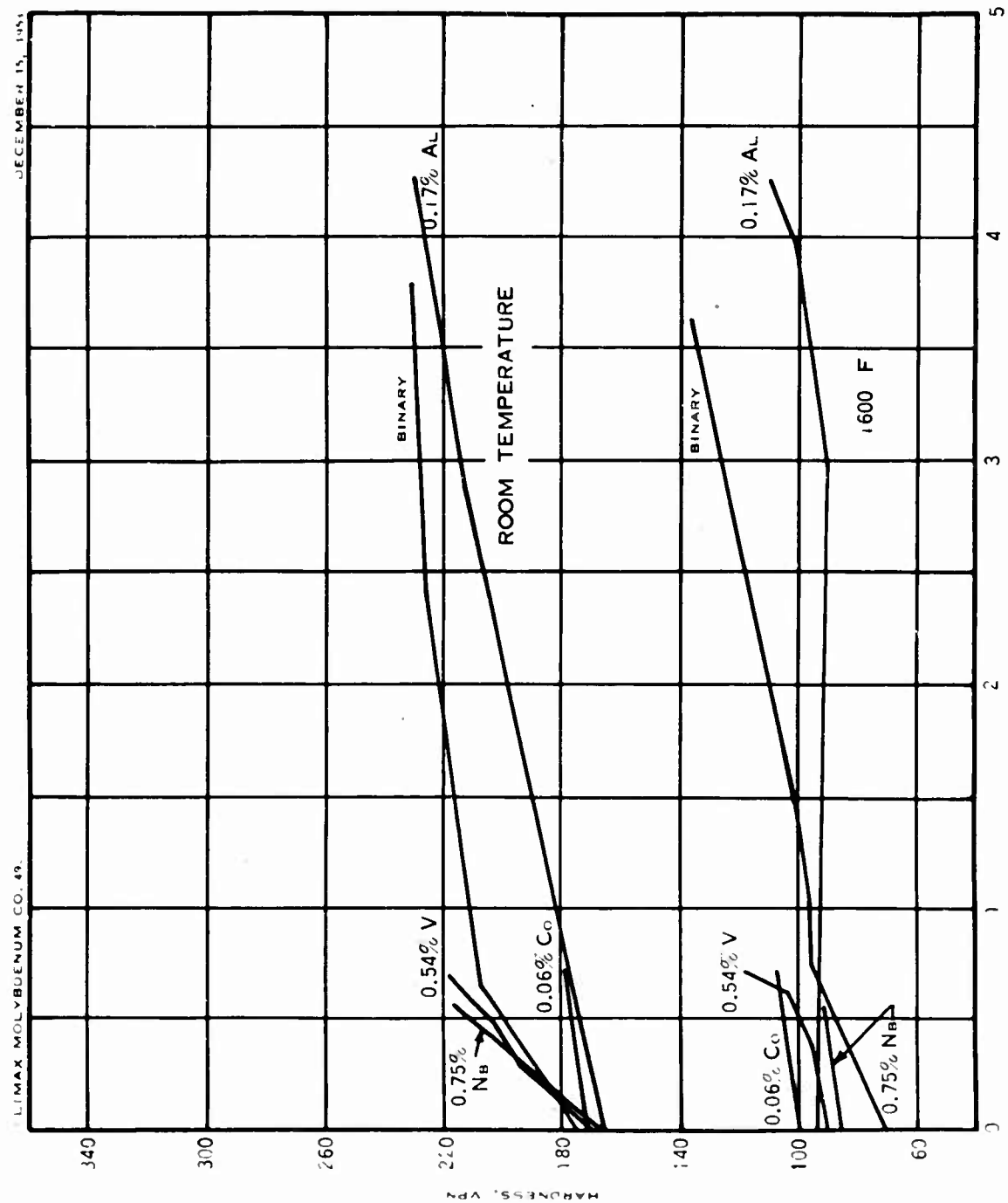


FIGURE 49 — EFFECT OF TITANIUM CONTENT UPON THE HARDNESS OF TERNARY MOLYBDENUM—BASE ALLOYS

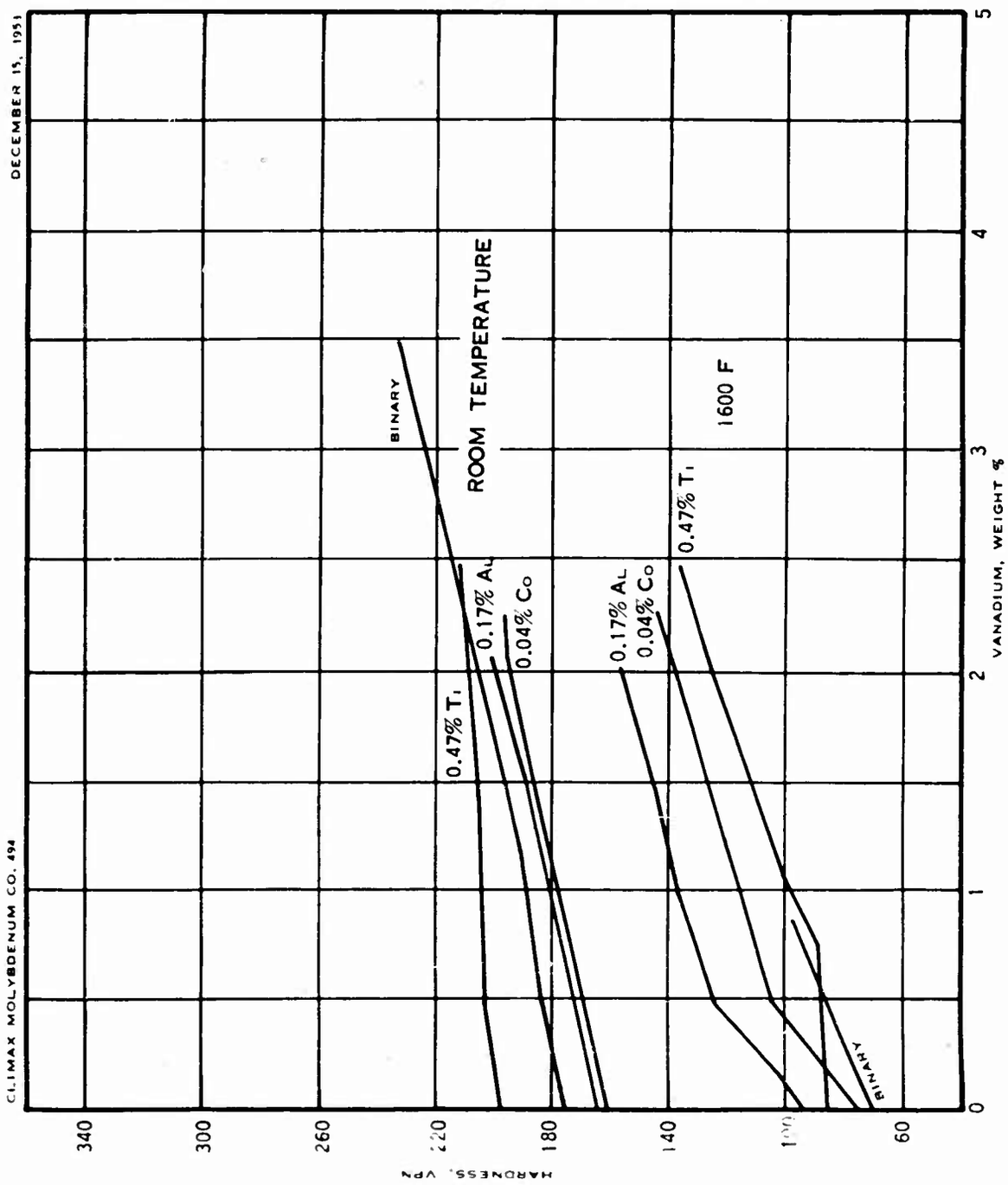


FIGURE 50 – EFFECT OF VANADIUM CONTENT UPON THE HARDNESS OF TERNARY MOLYBDENUM–BASE ALLOYS

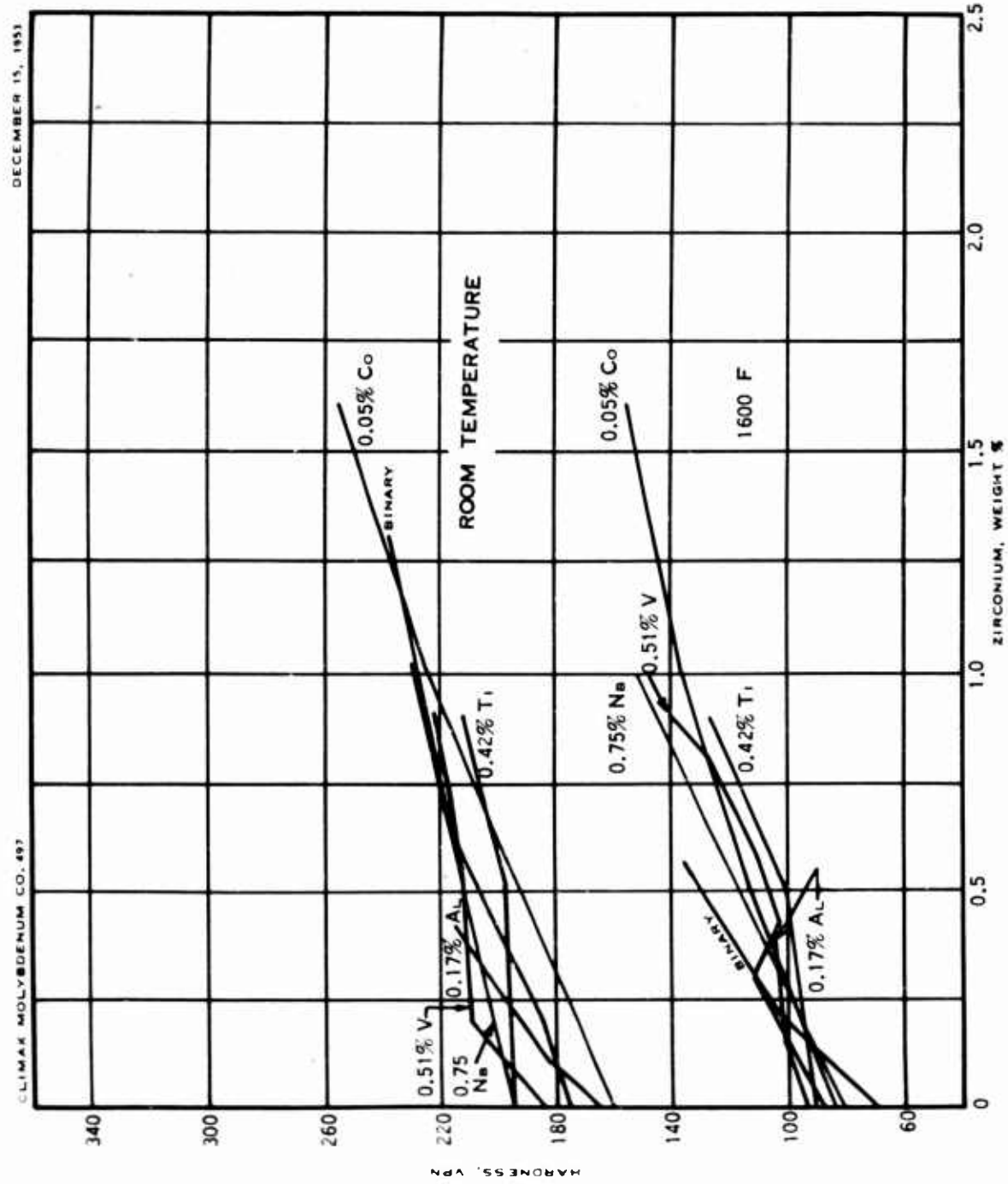


FIGURE 51 – EFFECT OF ZIRCONIUM CONTENT UPON THE HARDNESS OF TERNARY MOLYBDENUM–BASE ALLOYS

than that of unalloyed molybdenum. At 3000 F. all the alloys were harder than unalloyed molybdenum, except the 0.11% Cr alloy; however, this is based on data for a chromium alloy which showed a room temperature hardness below that of unalloyed molybdenum.

Considering the individual plots of hardness vs test temperature (Figures C1-C12), it will be noted that hardness generally decreases rapidly with increasing test temperature from room temperature to about 800 F. As the testing temperature is raised above about 800 F, the hardness does not change appreciably until a considerably higher temperature is reached. This phenomenon of practically constant hardness with increase in temperature terminates at temperatures between 1600 and 2400 F, depending on the alloy system under investigation. As the testing temperature is raised further, the hardness decreases with increasing temperature. When titanium or zirconium have been added, the break in the hardness curve occurs at higher temperatures; whereas, the break occurs at the lower temperatures for unalloyed molybdenum and the other molybdenum-base alloys of the group under consideration. Similar relationships were observed for the ternary molybdenum-base alloys. In general, the hardening effects of addition of two alloying elements to molybdenum are somewhat less than additive.

Solid Solubility of Alloying Elements

To determine the limit of solid solubility of each element in molybdenum, the change in lattice parameter with concentration was determined. Within the limit of solid solubility, the lattice parameter varies uniformly with concentration of the solute. Above the limit of solubility, the parameter of the matrix remains constant. The lowest concentration of alloying element at which a maximum deviation in lattice parameter from that of molybdenum occurs may be accepted as the limit of solid solubility of that element.

The determination of lattice parameter was carried out using filings from the cross sections of the graded ingots. The filings were annealed in purified argon atmosphere to remove the effects of cold work, and the composition of the filings was obtained either from the interpolation of chemical analysis data available from the graded ingot, or from analyses which were performed on the filings themselves after the x-ray studies had been completed. Determination of the lattice parameter was carried out using a back-reflection focusing camera 225.82 mm in diameter. Unfiltered copper radiation was used for the target material. Computations of lattice parameter were made by the method of M. V. Cohen*. The specimen temperature was carefully measured and the lattice parameter values were corrected to 25 C (A_{25}) using the coefficient of expansion of pure molybdenum.

To determine the change in solid solubility with temperature, samples containing excess phases were heated to various temperatures and quenched. Because of the slow approach to equilibrium, no attempt was made to evaluate solubility limits at temperatures below 2000 F.

* Review of Scientific Instruments, vol 6 (1935)

All heat treating was conducted in an argon atmosphere. Use of vacuum was avoided since many of the alloys, especially in the form of filings, would change composition in vacuum owing to evaporation. Preferential oxidation of the filings from alloys containing titanium or zirconium occurred even with the precautions outlined, and in these cases the lattice parameter for these alloys was determined on solid samples, the surface of which had been removed chemically after heat treatment. Therefore, lattice parameters reported for these alloys are based entirely on solid samples.

A summary of the change in lattice parameter for given concentrations determined during this project for binary alloys is given in Figure 52. Curves for the individual alloy systems are given in the first annual report.

The limit of solid solubility is presented in Figure 53 on the basis of weight percent.

Evidence in the literature indicates that chromium, tantalum, niobium, and tungsten are completely soluble at all temperatures. It is considered likely that vanadium is also completely soluble at all temperatures. Titanium is now known* to be completely soluble in molybdenum above 1625 F and soluble to the extent of approximately 70% at 1110 F. It is also known** that the solubility of zirconium and uranium in molybdenum is only partial.

The limit of solid solubility was not exceeded in any of the ternary systems investigated. The lattice parameter data are summarized in Figure 54.

The lattice parameter of a ternary molybdenum-base alloy is a function of the amounts of alloying elements present. The effects of two alloying elements simultaneously present are approximately algebraically additive.

Phase Diagram Studies

The solid solubilities of a number of elements in molybdenum reported in the preceding section served as the initial study for the construction of binary phase diagrams. The equilibrium diagrams for the Mo-C, Mo-Co, Mo-Fe, Mo-Ni, Mo-Nb, Mo-Ta, Mo-Ti, and Mo-W systems were already known, and the Mo-V system is believed to form a continuous series of solid solutions with molybdenum above certain temperatures. By additional experiments, the molybdenum-rich ends of the phase diagrams of the Mo-Al, Mo-Be, Mo-B, and Mo-Si systems were worked out because it was believed that they involved intermetallic compounds formed by eutectic or peritectic reactions and concerning which little knowledge was available.

The information to be presented was gained by metallographic and x-ray studies of powder pellet induction furnace heats and bar machine heats. The special induction furnace (Figure 30) was used both for melting powder pellets and solid samples in zirconia crucibles and for heat treating experiments.

* M. Hansen, E. L. Kamen, H. D. Kessler, and D. J. McPherson, Transactions, American Inst. Mining and Metallurgical Engineers, vol 191 (1951)

** R. F. Domagala, D. J. McPherson and M. Hansen, Ibid., vol 197 (1953)
P. C. L. Pfeil. The constitution of uranium-molybdenum alloys. J. Inst. Metals (London), vol LXXVII (1950)

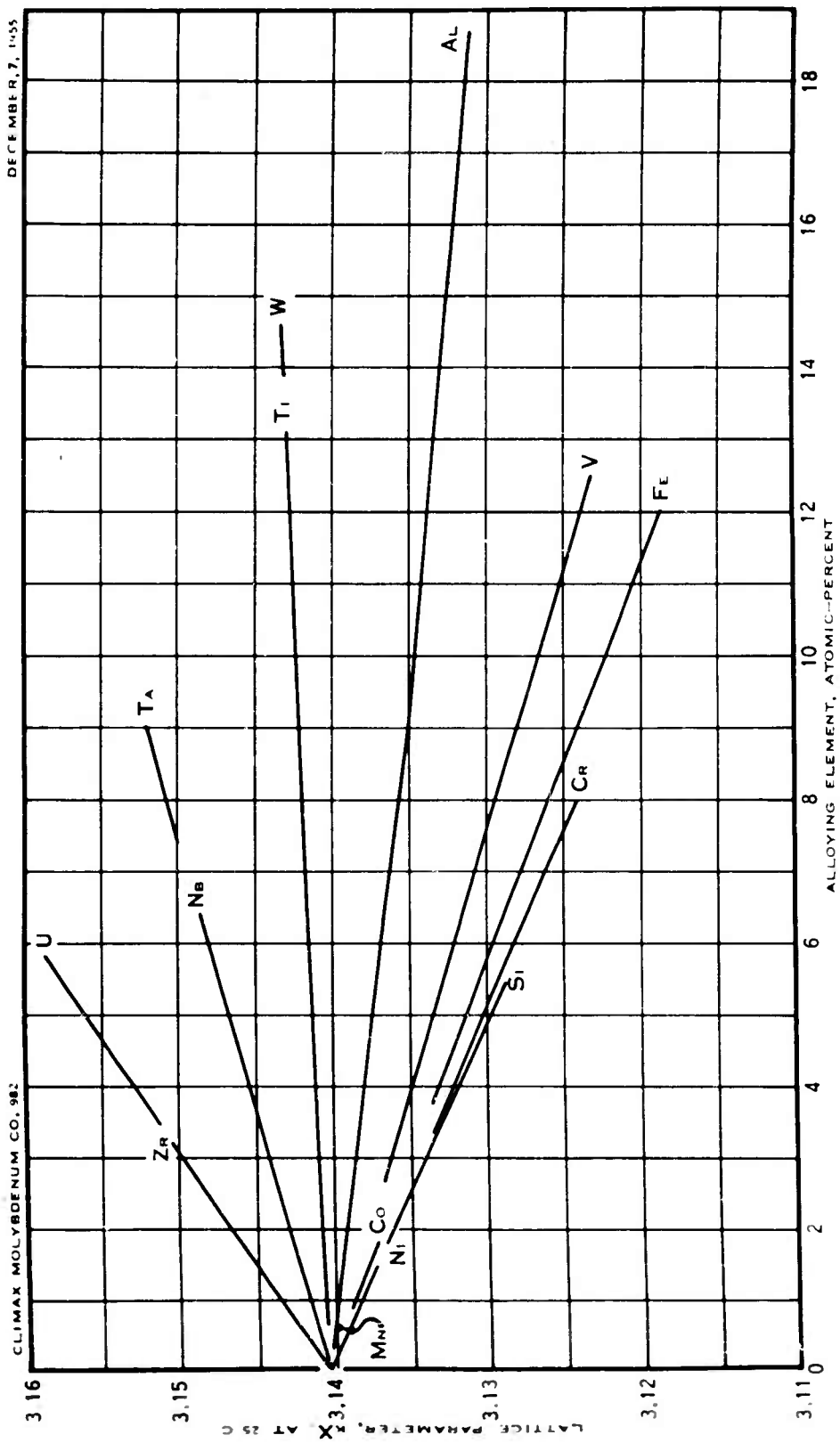


FIGURE 52 EFFECT OF VARIOUS ELEMENTS ON THE LATTICE PARAMETER OF MOLYBDENUM

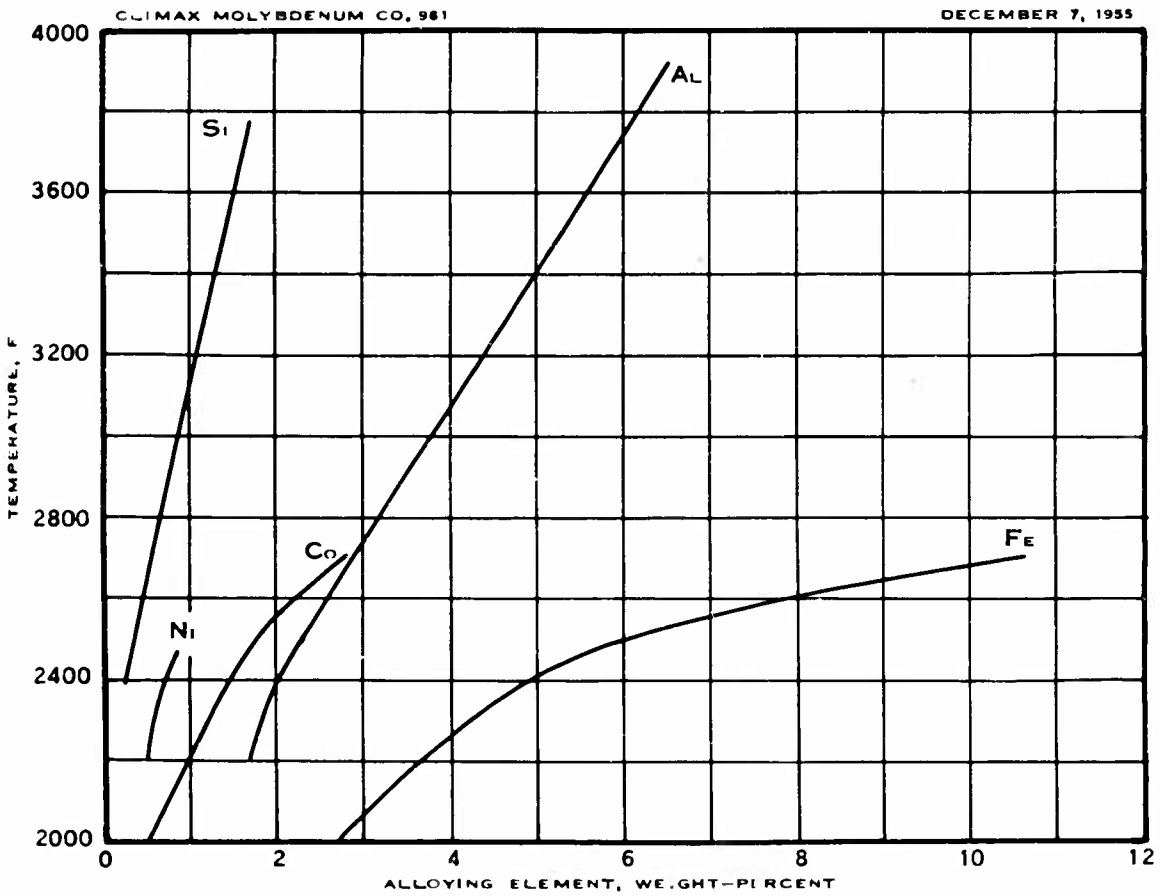


FIGURE 53 – SOLUBILITY LIMIT OF VARIOUS ELEMENTS IN MOLYBDENUM

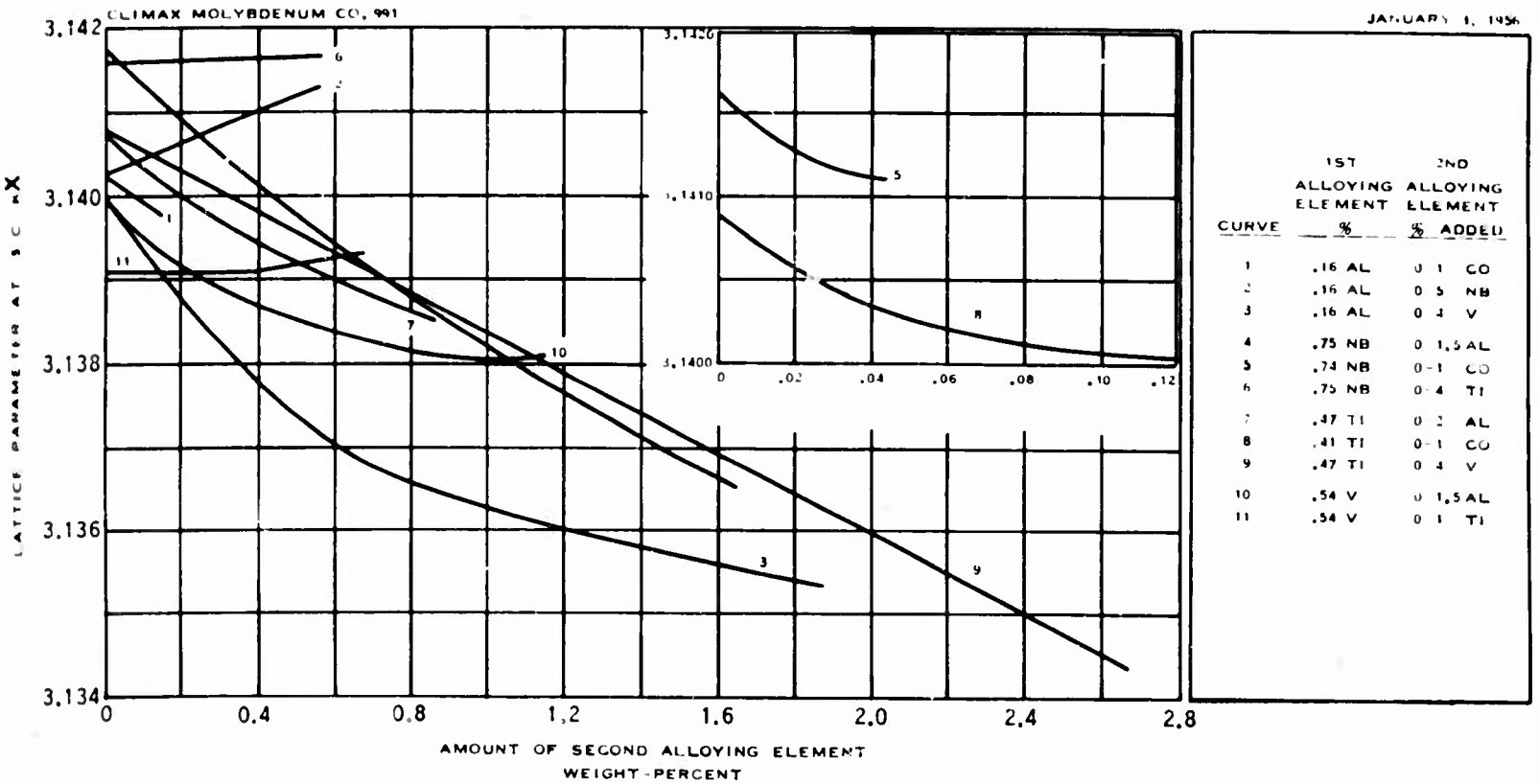


FIGURE 54 – LATTICE PARAMETER OF SOME TERNARY MOLYBDENUM–BASE ALLOYS

A purified argon atmosphere was used for all heat treating and melting experiments. The argon was purified for two to eight hours at 1300 to 1500 F after evacuation of the furnace and admitting argon. All temperatures were measured by means of an optical pyrometer calibrated up to 3100 F against a Pt-Pt/Rh thermocouple. The calibration curve was used to obtain the corrections to be applied for emissivity and window absorption. Eutectic or peritectic temperatures were located approximately by noting whether samples had melted in the zirconia crucibles after heating to various temperatures and were later established more exactly by reheating previously melted samples in zirconia crucibles notched in such a way that the samples could be observed by the optical pyrometer.

The phase diagrams presented are based on x-ray powder patterns, x-ray lattice parameter measurements, and on metallographic structures.

Molybdenum-Aluminum System. The heats and thermal treatments used for determining the molybdenum-rich end of the molybdenum-aluminum phase diagram are presented in Table 3. The aluminum powder used in the charge was 99+% pure atomized aluminum produced by the Aluminum Company of America.

Determination of the solid solubility of aluminum in molybdenum was based on Heat B66. The presence of lines other than those of α-molybdenum on the x-ray film used in the lattice parameter measurement of the sample quenched from 3900 F demonstrated the presence of undissolved compound.

The occurrence of the new phase in Heat B66 is illustrated in Figure 55. In the cast condition, three phases are believed to be present, as shown in Figure 55a. The black lines running through the central white band are cracks in the hard compound. The other white areas are α-molybdenum and the mottled areas appear to be a eutectic. This suggests a common type of system involving a peritectic and a complementary eutectic. This heat contained about 0.025% carbon, which is probably associated with the eutectic but, as will be shown later, is not necessary to the formation of the eutectic. Upon aging at 3000 F, after a solution treatment at 3950 F, equilibrium is approached, leaving only two distinct phases, as shown in Figure 55b.

The microstructure at the top of graded Ingot B121, containing only 0.016% carbon, also shows some of the eutectic as well as particles of the compound believed to form peritectically.

Several small induction furnace heats were also prepared. It was found possible to melt pressed pellets of a powder mixture containing 15% or more aluminum without exceeding 3950 F and with little change in composition. Heats of this type containing from 15.8% to 40% aluminum were studied metallographically and by x-ray diffraction to assist in determining the nature of the phase diagram. Quenching from the liquid state at 3900 F of Heat T-Al-8, containing 13.38 weight-% aluminum, produced the structures shown in Figure 56. No carbon was present in these heats, but three phases are represented in what appears to be a mixture of α-molybdenum, two compounds, and a eutectic between

TABLE 3

MOLYBDENUM-ALUMINUM HEATS FOR PHASE DIAGRAM STUDIES

Induction Furnace Heats*

Heat	Al in Charge Wt-%	Al in Charge At-%	Maximum Temp, F	Holding Time, Min.	Cooling Rate	Remarks
T-Al-1		25.0	3750		furnace cool	sintered
			3970		quenched	sintered
T-Al-2	12.6	33.3	3500		furnace cool	sintered
			3860		quenched	sintered
T-Al-3	15.8	40.0	3860		quenched	melted
T-Al-4	15.8	40.0	3785		quenched	partly melted
T-Al-5		33.3	3970		quenched	melted
T-Al-6	21.9	50.0	3470	4	quenched	melting started at 3200 F
T-Al-7	21.9	50.0	3070	5	quenched	sintered porous
T-Al-8	15.8	40.0	3900		quenched	melted, 13.88% Al by analysis
T-Al-9	10.0		3900		quenched	melted
T-Al-10	21.9	50.0	3225		quenched	just melted
T-Al-12	21.95	50.0	3490	10	furnace cool	melted
T-Al-13	36.0	67.0	3490	10	furnace cool	melted
T-Al-14	40.0		3200	1	furnace cool	melted, 39.58% Al by analysis,
			2600	60	furnace cool	d = 5.1 g/cc

Bar Machine Heats**

Heat	% Al	% C Added
B66	7.01	0.025
B121	2-10 added (graded)	0.016

* 10 to 20 g of pressed powder pellets melted in zirconia crucibles in argon.

** Bars were arc melted in 2" dia mold under argon.

the two compounds. X-ray powder patterns confirmed the presence of a small amount of α-molybdenum and two compounds in this structure. It is believed that the white areas represent either the first compound (part of which formed peritectically at 3900 F and part of which was rejected on cooling prior to the formation of a eutectic between this compound and another containing more aluminum) or a mixture of the first compound and α-molybdenum. The disposition of α-molybdenum is not certain. A very similar structure was obtained by quenching Heat T-Al-4 from 3785 F, but only very faint α-molybdenum lines were obtained on this sample. The composition and crystal structure of these compounds will be discussed later.

The approximate composition and temperature of the eutectic referred to was established by identifying and estimating the volume of the extra eutectic phase occurring in Heats T-Al-6, T-Al-10 and T-Al-12, containing 21.9 weight-% aluminum (50 atomic-%). Figure 57 shows the structures obtained on quenching T-Al-10 from a liquid at 3225 F. The speckled white area in the picture at higher magnification reacts to etching in a manner similar to that of the second phase found in the more dilute alloys at equilibrium. The sample was not analyzed chemically, but since an analysis of Heat T-Al-8 indicated that only a small amount of aluminum was lost on melting, it is assumed that the actual eutectic composition lies at approximately 22 weight-% aluminum.

The peritectic and eutectic temperatures were established by observing the melting of the induction furnace heats through an optical pyrometer. Samples containing 15.8% aluminum melted at from 3860 to 3900 F. The 10% aluminum sample melted at 3900 F. From these data we placed the peritectic temperature at approximately 3900 F.

Samples containing appreciable amounts of the eutectic constituent were found to be at least partially melted at temperatures above 3200 F. A sample containing 21.9% aluminum, the microstructure of which is nearly all eutectic phase, was observed to melt fairly rapidly at 3225 F. The eutectic temperature is therefore placed at 3200 F.

The structure of the compound, common to Heat T-Al-4 containing 15.8 weight-% aluminum and to Heat B66 containing 6.85 weight-% aluminum, was found by the powder x-ray method to be the same as that of Mo_3Si, the beta tungsten type, cubic, A15, O_h^3 Pm3n, $a_{29.5} = 4.9393$ kX. As compound Mo_3Al has not been previously reported in the literature, the x-ray data are given in Table 4. They were obtained from powder patterns of Heat T-Al-9 (10% aluminum) quenched from 3900 F. Copper radiation and nickel filter were used. Relative intensity was estimated by eye. The lattice parameter was computed from back-reflection patterns, using copper radiation, obtained from Specimen B66, held 63 hours at 2000 F.

From this evidence and also from estimates of the percentages of this compound observed metallographically in Heat B66 after quenching from 3950 F and annealing 5-1/2 hours at 3000 F, it is concluded that the compound in question is Mo_3Al.

On the basis of the theoretical density of Mo_3Al (8.623 g per cc) and of α-molybdenum saturated with aluminum at 3000 F, it was calculated that the observed density (8.92 g per cc) would correspond approximately to the relative volume percentages of α-molybdenum and of the compound metallographically observed in Heat B66 (Figure 55b). The calculated density of the α-molybdenum is based on the lattice parameter corresponding to a sample saturated with aluminum at 3000 F.

The d-values, but not the structure, of the compound $MoAl_2$ were furnished by Mr. R. Wachtell, of the American Electro Metal Corporation, in a private communication. Corresponding values were obtained from powder patterns of Heat T-Al-14, containing 39.58 weight-% aluminum, which, as shown in Figure 58, contained Mo_3Al as a eutectic, plus a large excess of the compound in question. Traces of an unidentified dark-etching phase were also found in Heat T-Al-14. The x-ray diffraction patterns also contained all of the lines corresponding to the d-values of Mo_3Al (Table 4) as well as some extra lines. For comparison, the d-values and relative intensities of Heat T-Al-14 are listed in Table 5 along with those found for Mo_3Al and those reported for $MoAl_2$ by Wachtell. The correspondence is considered sufficient to warrant the conclusion that the eutectic in question is composed of Mo_3Al and $MoAl_2$. However, the structure and origin of $MoAl_2$ have not been deduced. The sample of Heat T-Al-14 used for x-ray studies was melted at 3200 F, cooled in the furnace, then crushed and annealed 45 hours at 2600 F in argon. Copper radiation and a nickel filter were used. Intensities were estimated visually.

The observations of solid solubility, melting point, metallographic and x-ray studies are summarized in the tentative equilibrium diagram of Figure 59. A dashed line is included showing change in lattice parameter with aluminum concentration for α-molybdenum. The liquidus lines were not established experimentally.

TABLE 4

d-Values, Relative Intensities and Miller Indices of Mo_3Al

d (Å)	I	(hkl)	d (Å)	I	(hkl)
3.44	M	110	1.16	W	411,330
2.44	M	200	1.10	M	420
2.19	VS	210	1.07	S	421
2.00	M	211	1.05	W+	332
1.73	W	220	1.00	VW	422
1.55	M	310	.966	W	510
1.42	M	222	.915	W+	520,432
1.30	M+	320	.900	M	521
1.31	M+	321	.872	M	440
1.23	M	400			

TABLE 5

d-Values and Relative Intensities of Heat T-Al-14 Compared to Those Found for Mo_3Al and Those Reported* for $MoAl_2$

Heat T-Al-14		Mo_3Al		$MoAl_2$		Heat T-Al-14		Mo_3Al		$MoAl_2$	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
4.46	MW					1.59	W				
3.81	MW			3.86	.19	1.58	W				
3.67	MW			3.71	.21	1.55	W	1.55	MW		
3.44	MW	3.44	M			1.52	MW				
3.36	MS			3.40	.35	1.457	MW				
3.28	M			3.31	.27	1.435	W				
3.11	VW					1.42	M	1.42	M		
2.92	VW					1.40	MW			1.41	.16
2.87	VW					1.38	M			1.38	.22
2.46	M			2.46	.25	1.37	M	1.36	M+		
2.44	M	2.44	M			1.35	VW				
2.27	S			2.27	.76	1.33	MW			1.34	.16
2.22	S			2.23	1.0	1.32	MW	1.31	M+		
2.20	MS	2.19	VS			1.25	M			1.24	.19
2.12	MS			2.13	.43	1.23	MS	1.23	M		
2.01	MS	2.00	M	2.03	.19	1.22	W				
1.94	M			1.95	.32	1.18	W				
1.81	M			1.82	.30	1.16	W	1.16	W		
1.74	VW	1.73	W			1.14	M				
1.68	VW					1.12	MW				
1.64	M					1.11	M	1.10	M		
1.62	MW					1.08	M	1.07	S		

* private correspondence from Mr. R. Wachtell - American Electro Metal Corporation



(A) AS CAST, X1000 (M1187)



(B) OIL QUENCHED FROM 3950 F, AGED 8-1/2 HR AT 3000 F, X1000 (M1182)

FIGURE 55 – HEAT B66, 7.01% ALUMINUM, 0.025% CARBON
ELECTROPOLISHED AND ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION

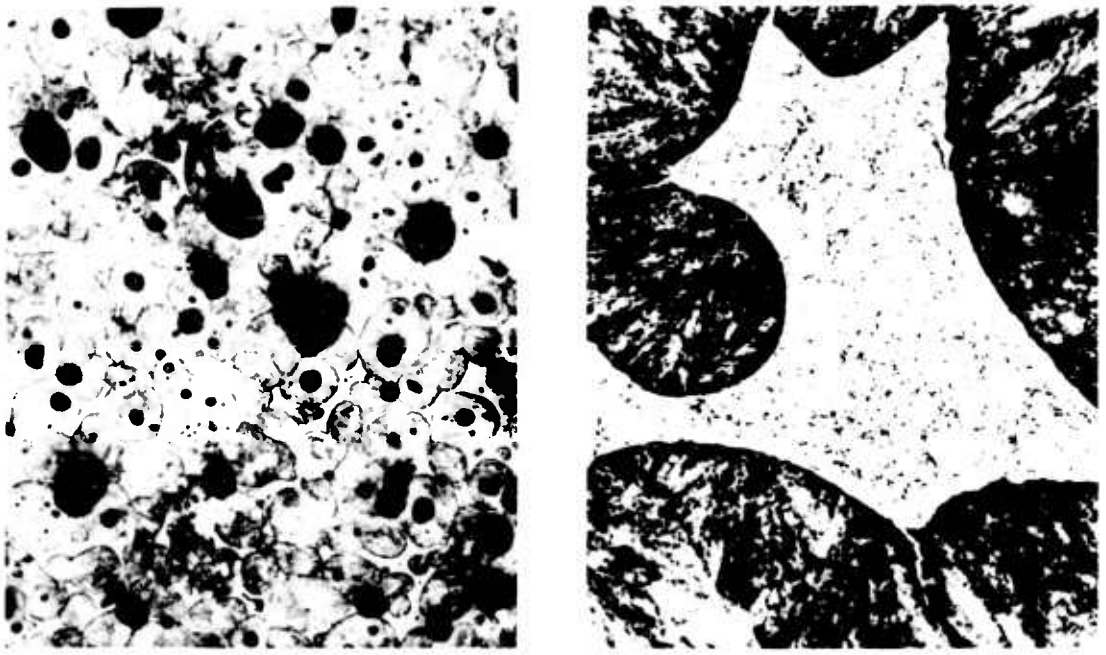


(A) ELECTROPOLISHED, X100 (M1180)



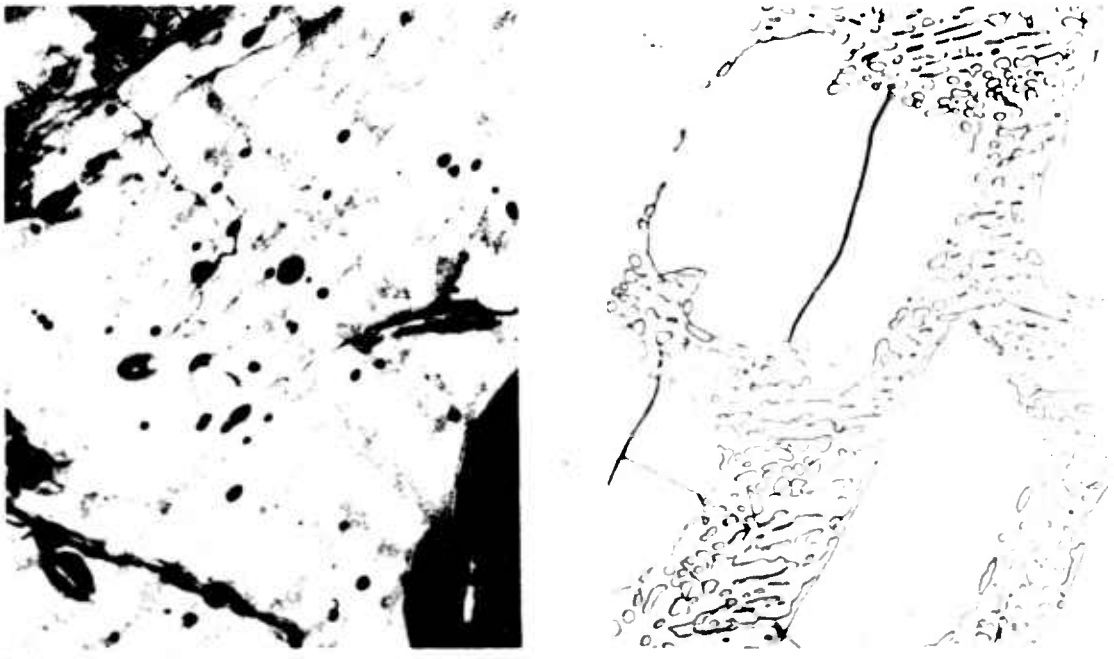
(B) POLISH ETCH BUFF, X100 (M1135)

FIGURE 56 – HEAT T-AL-8, 13.88% ALUMINUM, BALANCE MOLYBDENUM
PRESSED POWDER MIXTURE, OIL QUENCHED FROM LIQUID AT [illegible] F
ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION



(A) X100 (M1136) (B) X1000 (M1137)

FIGURE 57 – HEAT T–AL–10, 21.9% ALUMINUM, BALANCE MOLYBDENUM
PRESSED POWDER MIXTURE, OIL QUENCHED FROM LIQUID AT 3225 F, POLISH-ETCH BUFF, ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION



(A) X100 (M1218) (B) X1000 (M1219)

FIGURE 58 – HEAT T–AL–14, 39.58% ALUMINUM, BALANCE MOLYBDENUM
PRESSED POWDER MIXTURE, FURNACE COOLED FROM 2600 F, ELECTRO-POLISHED, ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION

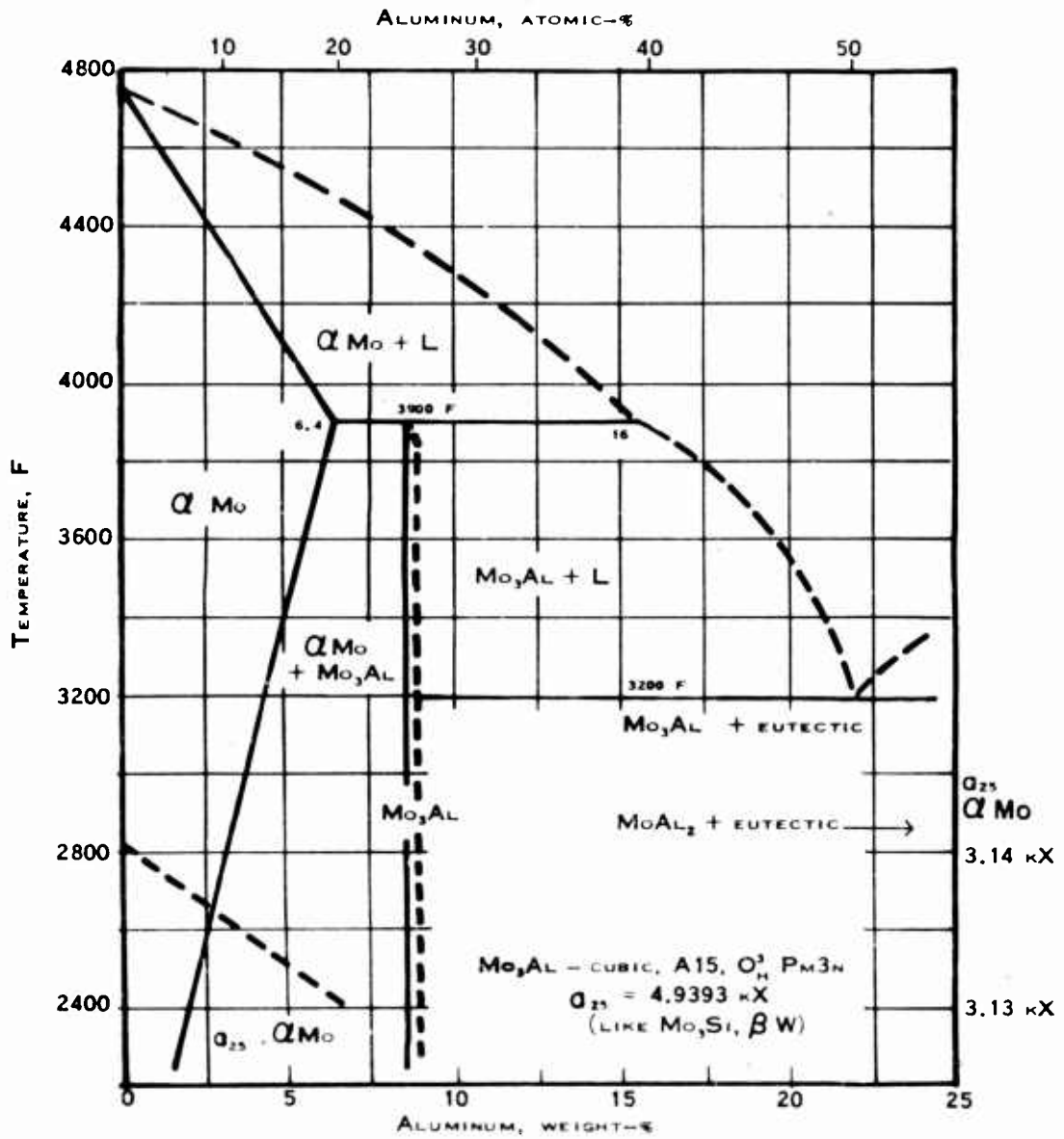


FIGURE 59 — TENTATIVE EQUILIBRIUM DIAGRAM FOR THE MOLYBDENUM–ALUMINUM SYSTEM (0 TO 0.02% C)

Molybdenum-Beryllium System. The heats used for preparation of the molybdenum-rich end of the molybdenum-beryllium system are listed in Table 6. Technical grade beryllium powder, 95 ± 2% pure, obtained from the Beryllium Corporation, was added to the charge. Hardness data were used to determine solubility in the same manner as the lattice parameter data were used to determine solid solubility for the molybdenum-aluminum system.

TABLE 6

MOLYBDENUM-BERYLLIUM HEATS FOR PHASE DIAGRAM STUDIES

Induction Furnace Heats*

Heat	Be in Charge wt-%	Maximum Temp, F	Holding Time, hr	Cooling Rate	Remarks
T-Be-1	6.5	2600	2	slow cool	sintered 495 DPN
	(0.1% C	3400		quenched	melted
	added)	3400		quenched	just melted
		2500	2	slow cool	
T-Be-2	6.5	2600	2	slow cool	sintered 539 DPN

Graded Bar Machine Heats**

Heat	% Be	% C Added	Melting Bar
B123	0.01-3.77	0.016	rolled arc cast
B165	0-0.25 added	0.009	pressed and sintered
B166	0-0.40 added	0.01	pressed and sintered

* 10 to 20 g of pressed powder pellets melted in zirconia crucibles in argon.
** Bars were melted in 2" dia mold under argon.

The rapid variation of the hardness of the solid solution with concentration of beryllium was used to establish a tentative solid solubility line. The hardnesses of saturated samples quenched from various temperatures were compared with the hardnesses of unsaturated samples of known concentration quenched from temperatures close to the solidus temperature. The hardness data obtained are those given in Table 7 and Figure 50. The accuracy of the hardness vs composition line is limited by the accuracy of the chemical analyses rather than that of the hardness test. Several of the points on the hardness vs composition curve are based on spectroscopic analyses. If the hardness of a saturated sample quenched from temperature T_1 is H_1 (from the curve to the right in Figure 50), then the solubility at temperature T_1 was assumed to be that corresponding to hardness H_1 on the curve to the left.

This assumes that the hardness depends only on the amount of beryllium retained in solid solution and neglects the possibility that a small amount of precipitation on cooling from the quenching temperature would affect the hardness. The amount of second phase in the saturated samples was small enough to warrant neglecting its effect on hardness.

TABLE 7

COMPOSITION, TREATMENT AND HARDNESS OF SAMPLES FROM BAR MACHINE HEATS USED FOR STUDIES OF THE HARDNESS OF HEAT TREATED MOLYBDENUM-BERYLLIUM ALLOYS

Sample No.	% C	% Be	Quenching Temp, F	Hardness DPN
B61	0.018 added	0.30	3750	427
B85	0.077	0.098	3000	334
			3750	428
B96M	0.048	0.050	3550	410
			2800	289
			3500	436
			3750	426
B115M	0.045	0.095	3000	340
			2800	287
			3500	422
B115B	0.045	0.44	3000	343
			2800	282
			3500	426
			3750	431
B129	0.050	0.029	3550	316
			3550	332
B146-A1	0.033	0.030*	3550	328
-A2		0.043*	3550	379
-A3		0.045*	3550	428
-B1		0.038*	3550	353
-B2		0.040*	3550	365
-B3		0.042*	3550	425
B146	0.033	approx 0.15	3600	430**

* spectroscopic analysis
** quenched samples used for aging experiments

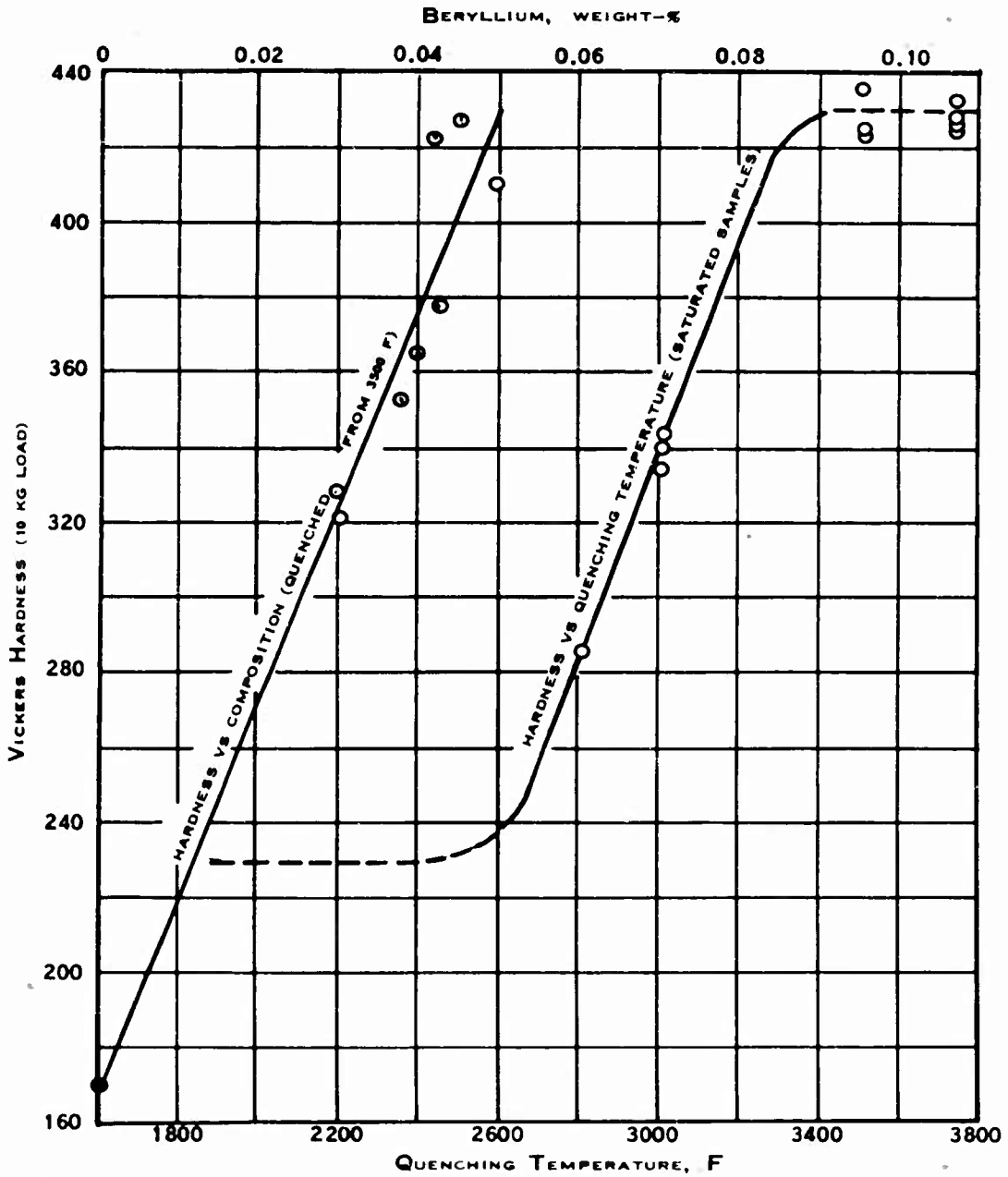


FIGURE 60 – EFFECT OF BERYLLIUM CONTENT AND QUENCHING TEMPERATURE UPON HARDNESS OF CAST MOLYBDENUM–BERYLLIUM ALLOYS (0.02 TO 0.05% C)

The solidus temperature was located by two methods. A small carbon-free ingot was prepared by melting a pressed powder mixture in a zirconia crucible in argon and was found metallographically to be composed mostly of eutectic. This was reheated in argon and observed to melt at 3400 F. Confirming evidence of a eutectic reaction at approximately this temperature was gained by observing that the grain boundary constituent of arc-cast samples had an entirely different appearance when reheated to 3210 F and quenched than when reheated to 3450 F and quenched. The 3450 F treatment left a eutectic type structure at the grain boundaries similar to that obtained as cast, indicating that the eutectic was liquid at 3450 F. This is shown in Figure 62. On the other hand, the 3210 F treatment agglomerated the eutectic, indicating that the eutectic was solid at 3210 F. The samples contained 0.045% carbon. These observations place the solidus slightly below 3400 F in the absence of carbon and between 3210 F and 3450 F in the presence of 0.045% carbon.

The eutectic composition, 6.5% beryllium, shown in the equilibrium diagram, Figure 64, is only approximate. It was deduced by estimating the volume of excess α-molybdenum in a hypoeutectic, graded, bar machine heat containing 3.77% beryllium and approximately 0.015% carbon (Heat B123). The structure of this alloy as cast is shown in Figure 61a. It was also found that a sample containing 6.5% beryllium and 0.1% carbon and melted in a zirconia crucible in argon by induction heating contained only a small amount of excess α-molybdenum beyond that contained in the eutectic portion of this structure. The structure of this alloy is illustrated in Figure 63.

The compound involved in the eutectic structure of Heat B123, containing 3.77% beryllium and only 0.015% carbon, was definitely identified as $MoBe_2$ by x-ray methods.

The positions of lines obtained on a powder pattern using copper radiation were found to correspond with those reported by L. Misch* for the compound $MoBe_2$. The structure of the compound is hexagonal, $C14$, D^4_{6h}, C_6/mmc; $a = 4.43$ kX, $c = 7.28$ kX, $\frac{c}{a} = 1.6$. This structure resembles that of $MgZn_2$, $CrBe_2$ and WBe_2. It is not absolutely certain that the compound involved in Heat B123 is the same as that observed in higher carbon heats containing less beryllium, since the compound in the high beryllium, low-carbon heat remains nearly white after etching in oxalic acid, as shown in Figure 61b; whereas, the compound appearing in the low beryllium heats containing more carbon turns quite black when subjected to the same etchant, as, for example, in the alloy containing 0.12% beryllium and 0.045% carbon, shown in Figure 62. It is considered likely that the dark etching phase is based on the $MoBe_2$ structure but contains a considerable amount of carbon in solution. This belief stems partly from the absence of Mo_2C in the microstructures of quenched samples containing considerable amounts of beryllium and up to 0.05% carbon.

An approximate equilibrium diagram for molybdenum-rich alloys of the Mo-Be-C system is presented in Figure 64.

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* L. Misch. Crystal structure of some beryllium alloys. Metallwirtschaft, vol 15 (1936)

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An approximate equilibrium diagram for molybdenum-rich alloys of the Mo-Be-C system is presented in Figure 64.

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* L. Misch. Crystal structure of some beryllium alloys. Metallwirtschaft, vol 15 (1936)



(A) X100 (M676)
ELECTROPOLISHED, ELECTROLYTIC ETCH IN MODIFIED ELECTROLYTE



(B) X1000 (M1237)
ELECTROPOLISHED, ELECTROLYTIC ETCH IN OXALIC ACID

FIGURE 61 – HEAT B123 (TOP) 3.77% BERYLLIUM, 0.016% CARBON, AS CAST

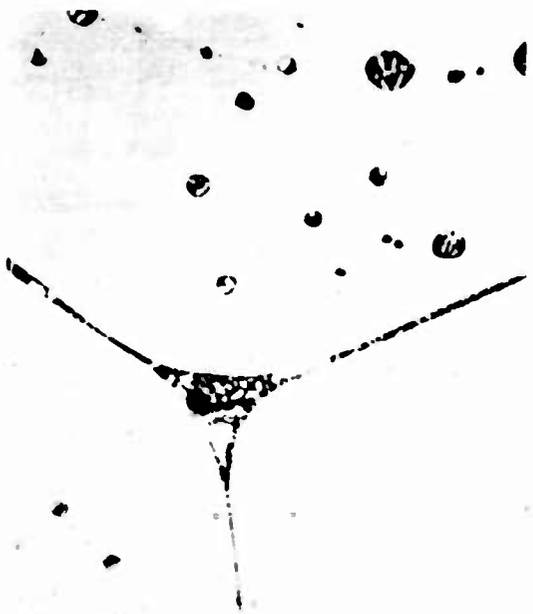


FIGURE 62 – HEAT B115M, X1000
0.12% BE, 0.045% C, OIL QUENCHED FROM 3450 F, ELECTROPOLISHED, ELECTROLYTIC ETCH IN OXALIC ACID (M948)



FIGURE 63 – HEAT T–BE–1, X100
6.5% BE, 0.1% C, PRESSED POWDER MIXTURE, ELECTROPOLISHED, ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE (M901)

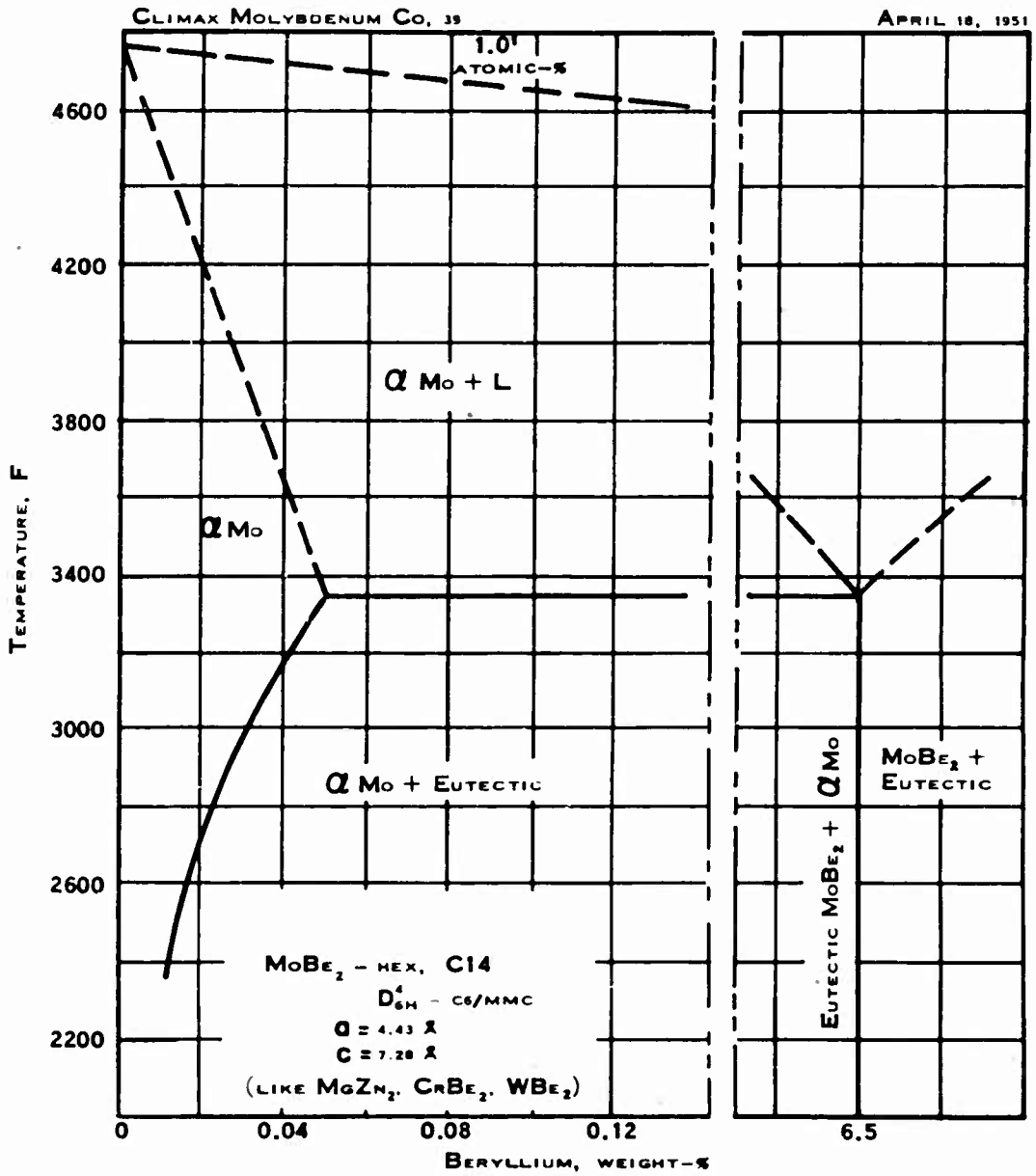


FIGURE 64 -- PARTIAL EQUILIBRIUM DIAGRAM FOR THE MOLYBDENUM–BERYLLIUM SYSTEM (0.02 TO 0.05% C)

Molybdenum-Boron System. The heats used are shown in Table 8. The first indication of a limited solubility of boron in molybdenum was obtained from metallographic examination of a heat (B18) containing 0.038% boron and 0.016% carbon (added as B_4C), in which a Widmanstätten precipitate was observed, as shown in Figure 65.

TABLE 8

MOLYBDENUM-BORON HEATS FOR PHASE DIAGRAM STUDIES

Induction Furnace Heats*

Heat	B in Charge Wt-%	B in Charge At-%	Maximum Temp, F	Holding Time, hr	Cooling Rate	Remarks
T-B-1	5.42	33.3+	3970	10	quenched	well sintered
T-B-2	2.50		3780		furnace cool	sintered
			4050	2	furnace cool	melted at 4000 F

Bar Machine Heats**

Heat	% B	% C	Melting Bar
B18	0.038	0.016, added as B_4C	rolled arc cast
B113	0.099	0.080, added as B_4C	rolled arc cast
B161	0-0.69, graded	0.009	pressed and sintered

* 10 to 20 g of pressed powder pellets melted in zirconia crucibles in argon.

** Bars were melted in 2" dia mold under argon.

In continuing investigations of the molybdenum-boron system, a heat (B113) containing 0.099% boron and 0.080% carbon, added as B_4C, was studied metallographically after annealing for two hours at 3200 F to agglomerate the phases and to facilitate identification. The structure obtained is shown in Figure 66. It is similar to those obtained in Mo-Be-C alloys after similar treatment, the white Mo_2C being associated with a new phase which etched very dark.

A graded, carbon-free ingot was prepared in argon (B161). The ingot was sound, and metallographic examination revealed increasing amounts of a eutectic from bottom to top of the ingot in the as-cast condition. Figure 67 shows the structure at the top, containing 0.69% boron and 0.009% carbon; the new phase in this case is not etched dark. The effects of carbon on the etching characteristics of this phase were not studied as extensively as in the Mo-Be-C system, but it is believed that the difference in etching characteristics of the compound in the low-carbon and the high-carbon heats is due to the presence of carbon in the compound rather than to a difference in the crystallographic structure of the compound in the presence of carbon.

An estimate of the volume percent of second phase present, together with knowledge of the composition and densities, permits the deduction that the compound involved in the top sample of Heat B161 is Mo_2B.

A small heat (T-B-1), made by sintering and partially melting a pressed pellet of molybdenum and 5.42% boron powders, consisted of particles of hard compound interspersed with a small amount of eutectic, as shown in Figure 68. The compound Mo_2B corresponds to 5.34% boron. It is believed that loss during sintering reduced the boron content to slightly less than this amount. The structure of the compound in this sample was found by the x-ray powder method to be the same as that reported for the compound Mo_2B*, namely, tetragonal, C16, D_{4h}^{18}, a = 5.543 Å, c = 4.735 Å, c/a = 0.854. This compound is isomorphous with $CuAl_2$, Fe_2B, Ni_2B, and Co_2B.

On the basis of the amount of eutectic observed in the 0.69% boron alloy (Heat B161), the eutectic composition was estimated to be 2.5 weight-% boron. Therefore, in order to prepare 100% eutectic, a 2.5% boron-molybdenum alloy was melted in an induction furnace under argon atmosphere. The resulting structure consisted of the eutectic with a considerable amount of excess α-molybdenum, as shown in Figure 69. The eutectic composition was then estimated by calculating the composition which would lead to equal volumes of Mo_2B and α-molybdenum, taking into account the slight difference in density between the two phases. The approximate eutectic composition found in this manner was 2.75 weight-% boron.

All of the metallographic work as well as the hardness studies indicated a very low solid solubility of boron in molybdenum. No data are available for a quantitative estimate of the maximum solid solubility. However, the α-molybdenum in Sample B161, containing 0.69 weight-% boron, after quenching from 3900-3950 F, was found to have a lattice parameter of 3.14014 kX, which is only slightly lower than that of the same sample slow cooled (3.1407 kX). This indicates a low solubility and, unexpectedly, a substitutional type of solid solution. It is not considered, however, that the nature of this solid solution has been established with certainty.

The eutectic temperature was located quite precisely by reheating a sample of the 2.5 weight-% boron heat and watching it melt through an optical pyrometer. Melting occurred rather rapidly at 4000 F. It is considered likely that during the melting the temperature may have been about 50 degrees above that for equilibrium between liquid and solid, and since the eutectic is also present in the sample of T-B-1 heated to only 3970 F (Figure 68), the eutectic temperature is placed at 3950 F.

These metallographic, x-ray and melting point observations are summarized in the tentative equilibrium diagram of Figure 70.

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* Roland Kiessling, Acta Chem. Scand., vol 1 (1947), 893-916

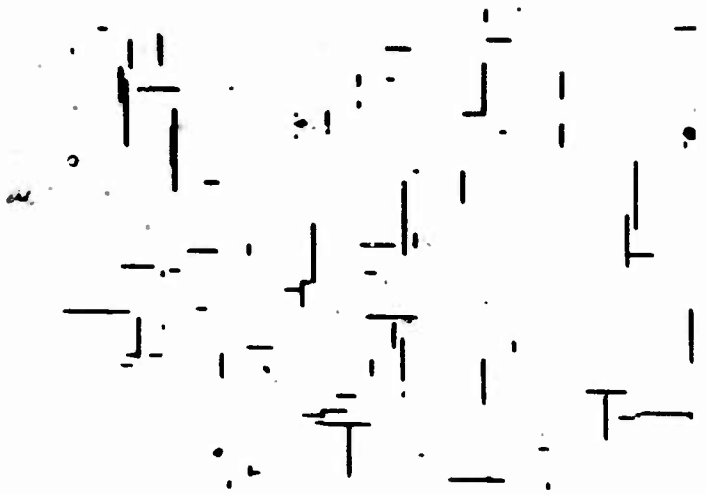


FIGURE 65 — HEAT B18, 0.038% B, 0.016% C
AS CAST, 171 DPN, X1000 (10220)

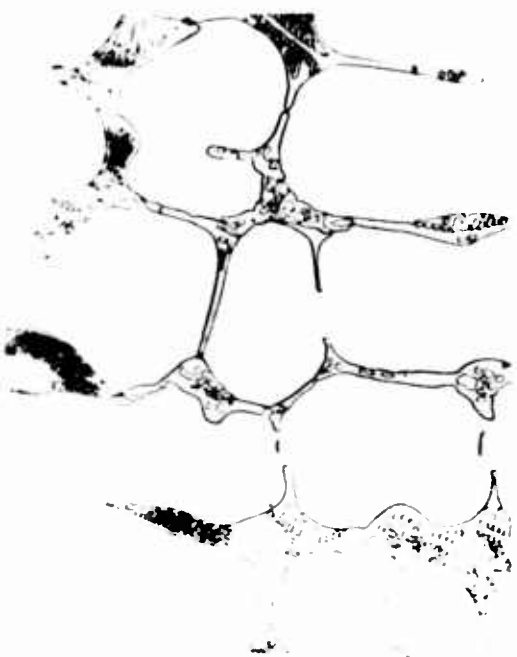


FIGURE 66 — HEAT B113, 0.099% B, 0.080% C
SLOW COOLED AFTER 2 HR AT 3200 F,
ELECTROPOLISHED, X1000 (M739)

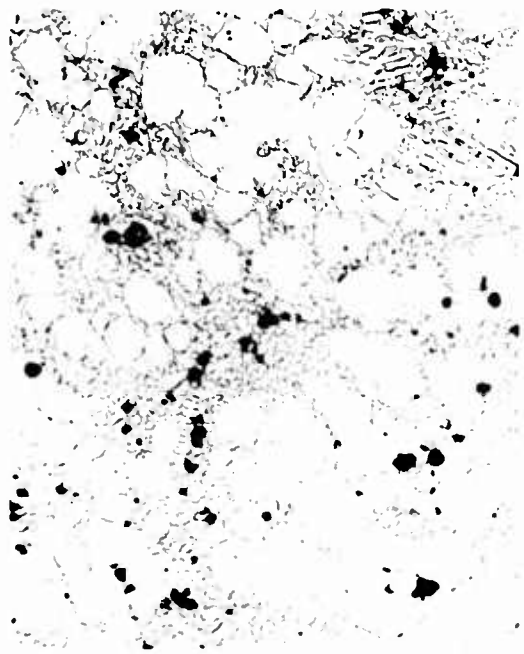


FIGURE 67 — HEAT B161 (TOP) 0.69% B,
0.009% C, AS CAST, ELECTROPOLISHED,
X1000 (M980)

ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION



FIGURE 68 — HEAT T-B-1, 5.42% B. QUENCHED AFTER PARTIALLY MELTING AT 3970 F, PRESSED POWDER MIXTURE. POLISH-ETCH-BUFF
X1000 (M1142)



(A) X100 (M1196)



(B) X1000 (M1197)

FIGURE 69 — HEAT T-B-2, 2.50% B, FURNACE COOLED AFTER REMELTING AT 4050 F, PRESSED POWDER MIXTURE, ELECTROPOLISHED

ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION

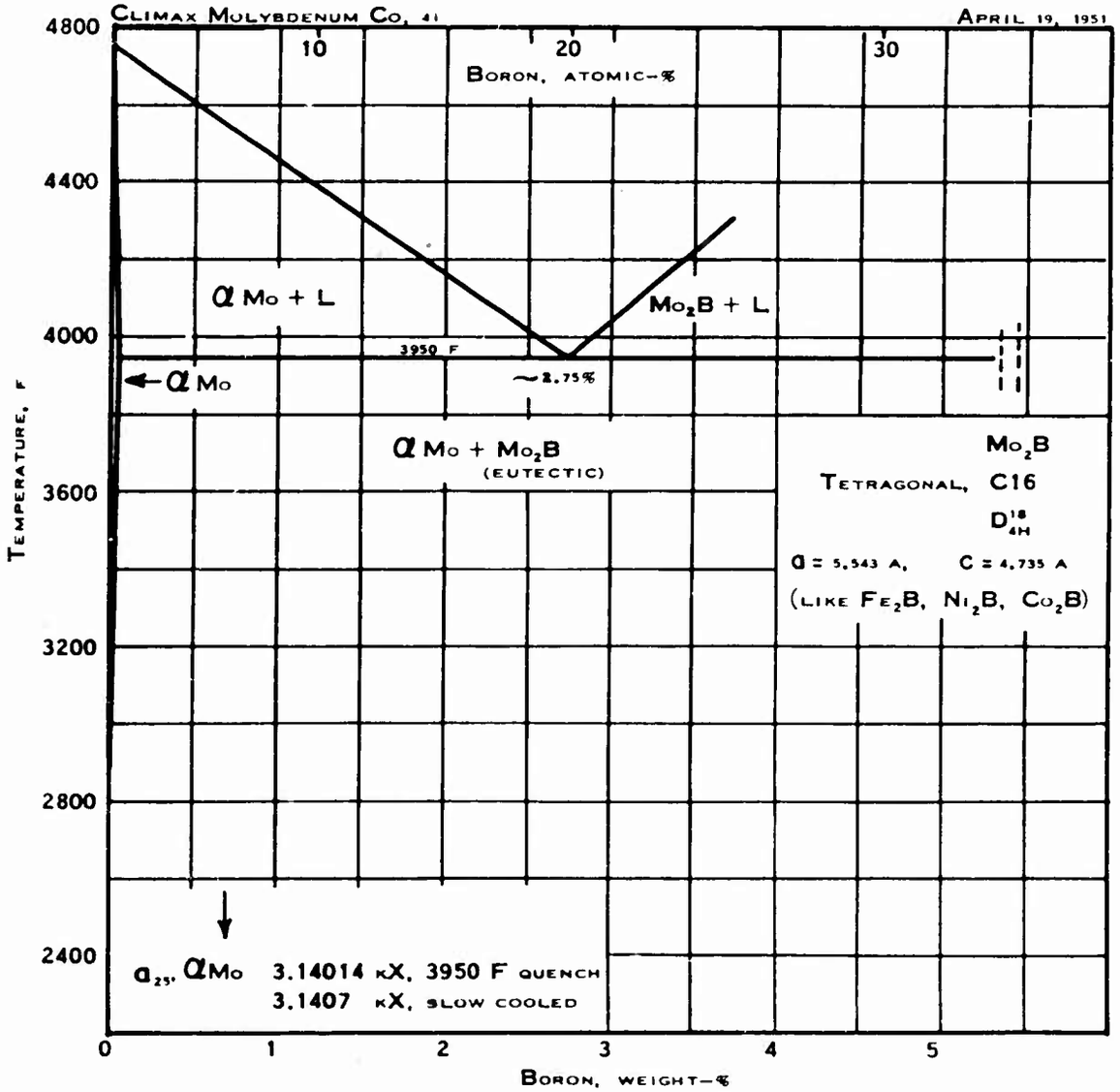


FIGURE 70 – PARTIAL EQUILIBRIUM DIAGRAM FOR THE MOLYBDENUM–BORON SYSTEM

Molybdenum-Cobalt System. The three heats shown in Table 9 were used for study of the new phases in molybdenum-rich molybdenum-cobalt alloys.

TABLE 9

MOLYBDENUM-COBALT HEATS

Heat	Melting Atmosphere	% Co	% C	Melting Procedure
B47	static tank argon	12.6	0.033	arc melted
T1	hydrogen	28.47	0.017 added	15-g induction furnace heat
T2	hydrogen	38.17	0.020 added	15-g induction furnace heat

As in the Mo-Fe alloys, two new phases are encountered, one stable above 2282 F and one below. In this case, however, the phase stable at the higher temperature (eta) is based on Co_2Mo_3 (60 atomic-% Mo) and at the low temperature (epsilon), is based on either CoMo (50 atomic-% Mo) as reported by Sykes, or Co_7Mo_6 (53.8 atomic-% Mo). The recent work of Henglein and Kohsok claims that Co_7Mo_6 is correct, that this is isomorphous with Co_7W_6, Fe_7Mo_6 and Fe_7W_6, and that the structure is rhombohedral, space group D^5_{3d}-R3m. The general behavior of these alloys as deduced by our metallographic studies is that to be expected from the equilibrium diagram of Sykes and Graff. Their symbols will be retained in the following discussion, except that the molybdenum-rich solid solution will be referred to as α-molybdenum instead of delta.

The structure of Ingot B47, containing 12.6% cobalt, after various heat treatments will be used to illustrate the structure of these alloys.

Holding two hours at 2700 F and quenching to retain the eta phase gave the structure shown in Figure 71a, consisting only of eta, darkened by the etch, and primary alpha.

Holding for two hours at a lower temperature (2450 F) did not provide sufficient time to remove all the epsilon. On quenching, the three-phase structure of Figure 71b was obtained. Again, the eta phase is dark and cracked. The residual epsilon is clear white and cracked, and the alpha is speckled. Holding 63 hours at 2000 F permitted complete transformation of the eta to epsilon plus secondary alpha as shown in Figure 71c.

These studies agree qualitatively with the diagram of Sykes and Graff, but provide no confirmation of the formulae claimed for these phases. In an attempt to confirm the formulae reported (Co_2Mo_3 and CoMo or Co_7Mo_6), small



(A) HELD 2 HR AT 2700 F, QUENCHED. ELECTROLYTIC AND MECHANICAL POLISH. ELECTROLYTIC ETCH IN 1% AQUEOUS OXALIC ACID, IMMERSED IN WEAK SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION X100 (M28)



(B) HELD 2 HR AT 2450 F, QUENCHED. MECHANICAL POLISH. ELECTROLYTIC ETCH IN 0.05% AQUEOUS OXALIC ACID, IMMERSED IN WEAK SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION X1000 (10369)



(C) HELD 63 HR AT 2000 F, QUENCHED. ELECTROLYTIC AND MECHANICAL POLISH. ETCHED ELECTROLYTICALLY IN 1% AQUEOUS OXALIC ACID. X1000 (M117)

FIGURE 71 – HEAT B47, 12.6% COBALT, 0.033% CARBON. 50 HR AT 2450 F, SLOW COOL, FOLLOWED BY INDICATED HEAT TREATMENT

ingots (T1 and T2) containing almost exactly 40 and 50 atomic-% cobalt, respectively, were made. These were held for two hours at 2450 F and quenched. According to the diagram, this should give pure epsilon and pure eta, respectively, if equilibrium were attained. Nevertheless, as shown in Figure 72, the 40-atomic-% cobalt alloy (28.47 weight-% cobalt) contained three phases and the 50-atomic-% alloy (38.17 weight-% cobalt), at least two. Probably two hours were insufficient to approach equilibrium very closely, but it is surprising that the other phases, if transient, should remain in such large quantities.

Work by D. Summers-Smith* reports that Co_2Mo_3 decomposes peritectoidally to form Co_7Mo_6. Since this type of transformation would be quite sluggish, it may be the cause of some of the results obtained in the present studies. Additional references are given below.**

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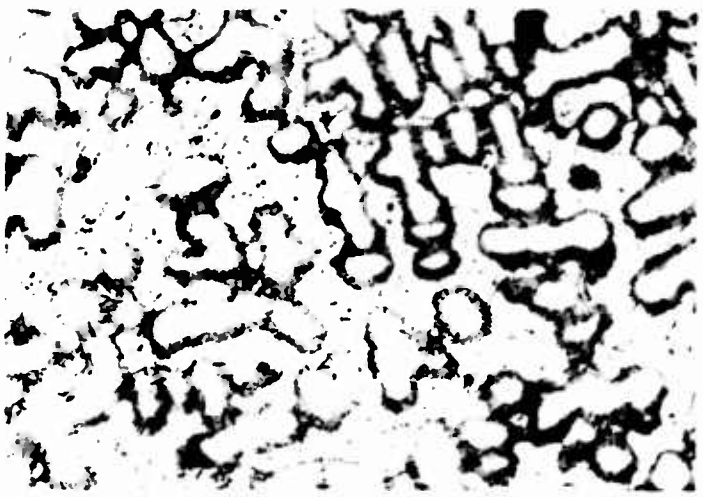
* D. Summers-Smith. Nature, vol 168 (1951), 786

** W. P. Sykes and H. F. Graff "The System Cobalt-Molybdenum" Transactions ASM, vol 23 (1935)

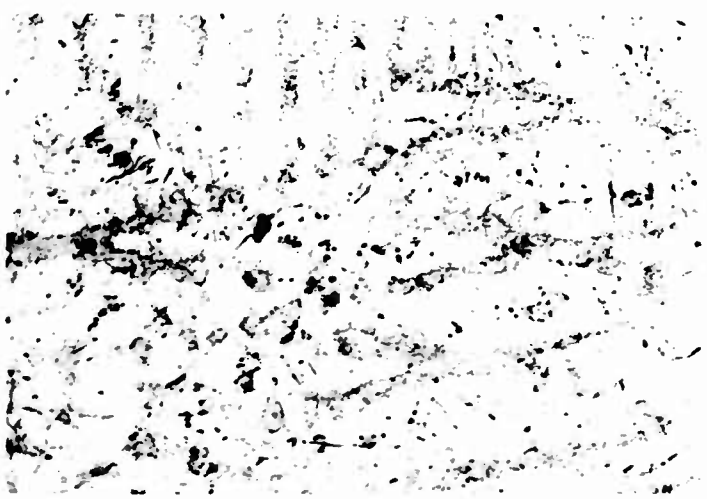
W. Köster and W. Tonn "The Binary Systems: Cobalt-Tungsten and Cobalt-Molybdenum" Z. Metallkunde, vol 24 (1932)

A. Westgren "Crystal Structure and the Composition of the Intermediate Iron-Tungsten and Iron-Molybdenum Phases" Science Reports Tohoku Imperial University, K. Honda Anniversary Vol (1936)

E. Henglein and H. Kohsok "Determination of the Phase Co_7Mo_6" Revue de Metallurgie, vol 46 (1949)



(A) HEAT T1, 28.47% CO, 0.017% C ADDED. ELECTROLYTIC ETCH, 5–10 SEC. IN 1% OXALIC ACID, IMMERSED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION (M155)



(B) HEAT T2, 38.17% CO, 0.020% C ADDED. ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION (M156)

FIGURE 72 — MOLYBDENUM–COBALT ALLOY
2 HR AT 2450 F, OIL QUENCHED. X100

Molybdenum-Iron System. In general, the metallographic and x-ray studies of melted and cast molybdenum-iron alloys have confirmed qualitatively the work of Sykes* and the equilibrium diagram in the ASM Handbook (1948).

Reference to the Fe-Mo diagram in the ASM Handbook will be of assistance in interpretation of the structures of this system. The first excess phase at temperatures below 2156 F is epsilon which corresponds to Fe_3Mo_2 or Fe_7Mo_6; the formula Fe_7Mo_6 was proposed by Arnfelt and Westgren*, but was not confirmed by Goldschmidt*. Above 2156 F the first excess phase is zeta, which corresponds to FeMo. Goldschmidt* has presented convincing evidence that this phase is isomorphous with the sigma phase of the Fe-Cr and Fe-Cr-Mo systems; therefore, it will be referred to as sigma in this report. The molybdenum-rich solid solution will be referred to as the alpha solid solution (α-Mo).

Figure 73a shows the three phases in question as they occurred in Ingot B45 as cast. The large, white, cracked areas are sigma, the lamellar structure is epsilon plus alpha, and the slightly darkened clear areas are primary alpha.

Quenching from 2450 F (or 2700 F) retained the sigma phase in situ in the α matrix as illustrated in Figure 73b. On holding either as-cast, slowly cooled or quenched samples at 2000 F, the sigma phase breaks up into epsilon and excess alpha, as snown in Figure 73c.

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* W. P. Sykes "The Iron-Molybdenum System" Transactions ASST, vol 10 (1926)

W. P. Sykes "Fe-Mo Iron-Molybdenum" Metals Handbook, 1948 Edition, published by the American Society for Metals

H. Arnfelt "On the Constitution of the Iron-Tungsten and the Iron-Molybdenum Alloys" Carnegie Scholarship Memoirs, vol XVII (1928)

H. Arnfelt and A. Westgren "Crystal Structure and Composition of Intermediate Phases Present in Iron-Tungsten and Iron-Molybdenum Alloys" Jernkontorets Annaler. vol 119 (1935)

H. J. Goldschmidt "An Outline of the Ternary Systems Fe-Cr-W and Fe-Cr-Mo" B.S.A. Group Research Office, Sheffield, England

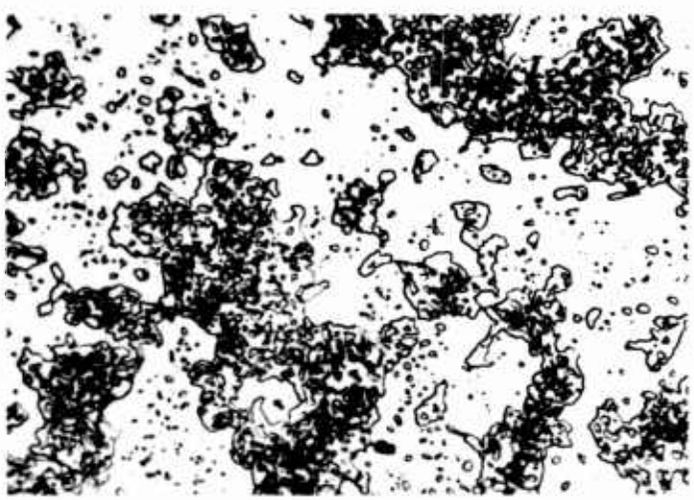
H. J. Goldschmidt "A Molybdenum Sigma Phase" Research. vol 2 (1949)



(A) AS CAST MECHANICAL POLISH, ELECTROLYTIC ETCH IN HYDROCHLORIC ACID, SULFURIC ACID AND METHYL ALCOHOL X1000 (10301)



(B) HELD 50 HR AT 2450 F, SLOW COOL, RE-HEATED TO 2450 F, HELD 2 HR, QUENCHED. MECHANICAL POLISH, ELECTROLYTIC ETCH IN HYDROCHLORIC ACID, SULFURIC ACID AND METHYL ALCOHOL. X1000 (10365)



(C) HELD 50 HR AT 2450 F, SLOW COOL, 63 HR AT 2000 F, QUENCHED. ELECTROLYTIC ETCH IN MODIFIED MOLYBDENUM ELECTROLYTE X1000 (M114)

FIGURE 73 – PHASES IN THE MOLYBDENUM-RICH END OF THE Mo-Fe SYSTEM

HEAT B45, 14.4% FE, 0.023% C

Molybdenum-Nickel System. An equilibrium diagram and a brief description of the phases of the molybdenum-nickel system are given in the ASM Handbook (1948). The diagram indicates a maximum solid solubility of 0.9% nickel. The three heats of Table 10 were prepared for study of the phases in the molybdenum-rich alloys.

TABLE 10

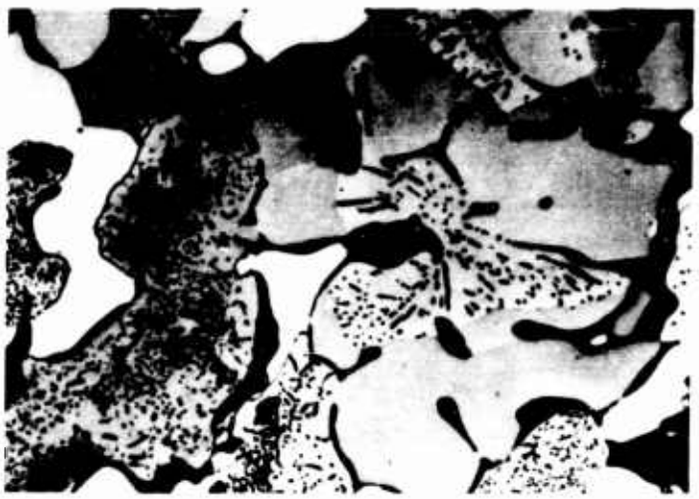
MOLYBDENUM-NICKEL ALLOYS

Heat	Melting Atmosphere	% Ni	% C	Melting Procedure
B34	static tank argon	0-2.6	0.025	arc melted
B53	static tank argon	0-3.65	0.001	arc melted
T3	hydrogen	37.16	0.018 added	15-g induction furnace heat

Metallographic work consistently revealed three phases in molybdenum-rich Mo-Ni alloys typified by Heat B53, Figure 74. A sample of lower nickel content from this same ingot still revealed three phases, even after holding 36 hours at 2400 F, followed by 90 hours at 2000 F (Figure 74b). Since only 0.001% carbon was present and since the sample was not quenched, it seems that either equilibrium was not attained or that some phase change occurred on cooling. The phase diagram in the ASM Handbook, however, gives no indication of a phase change of this sort.

A sample containing 0.027% carbon and slightly more nickel (B34) presents a similar structure after holding 50 hours at 2450 F and slow cooling (Figure 75). In this case the white phase could be a carbide, but close examination reveals particles of intermediate shading as well. The matrix is α-molybdenum in both cases.

A small (10-gram) induction heat corresponding to the composition MoNi was made in an effort to isolate this phase for identification. The structure as cast is shown in Figure 76a and is three phase, although one of the phases does not appear clearly in this picture. Holding four hours at 2100 F and cooling rapidly left the distinctly three-phase structure shown in Figure 76b. Although the general sluggishness of these alloys may account for some of these observations, the behavior of the Mo-Ni alloys so far studied is not that expected on the basis of the equilibrium diagram in the ASM Handbook. More work involving carefully-controlled and probably long-time heat treatments will be necessary to clarify the nature of these alloys.



(A) TOP, 0.001% C, 3.6% NI, AS CAST. ELECTROLYTIC ETCH IN MODIFIED MOLYBDENUM ELECTROLYTE AND 3 MIN. IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION X1000 (10516)



(B) 1.4% NI, LESS THAN 0.001% C, 86 HR AT 2400 F, SLOW COOL, 90 HR AT 2000 F, SLOW COOL. MECHANICAL POLISH, ETCHED IN SODIUM HYDROXIDE AND POTASSIUM FERRICYANIDE SOLUTION, THEN ELECTROLYTICALLY IN MODIFIED MOLYBDENUM ELECTROLYTE. X1000 (M56)

FIGURE 74 – MOLYBDENUM–NICKEL ALLOY
HEAT B53

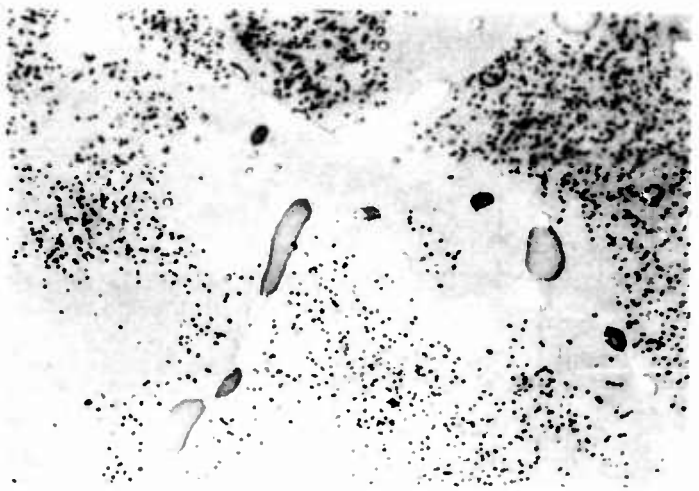
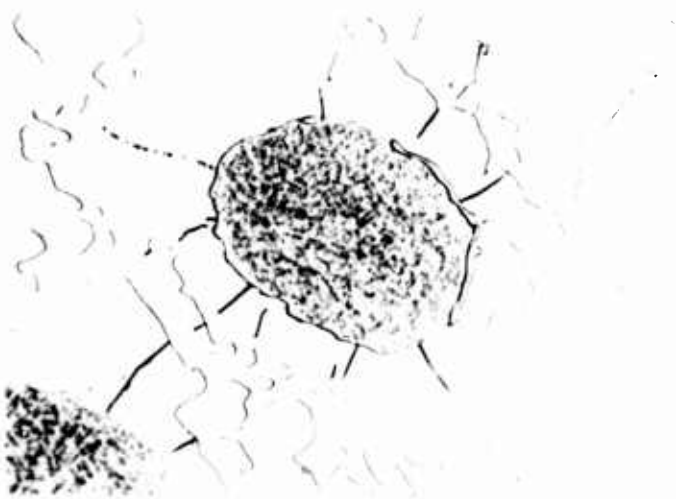


FIGURE 75 — MOLYBDENUM–NICKEL ALLOY
HEAT B34, 2.5% NI, 0.027% C. HELD 50 HR AT 2450 F, SLOW COOL. MECHANICAL POLISH. ETCHED IN SODIUM HYDROXIDE AND POTASSIUM FERRICYANIDE SOLUTION. X1000 (10316)



(A) AS CAST. MECHANICAL POLISH. ETCHED IN MODIFIED MOLYBDENUM AND SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION. X100 (M55)



(B) 4 HR AT 2100 F, AIR QUENCHED. MECHANICAL POLISH. ELECTROLYTIC ETCH IN 1% AQUEOUS SOLUTION OF OXALIC ACID. X1000 (M65)

FIGURE 76 — MOLYBDENUM–NICKEL ALLOY
HEAT T3. 17.16% NI, 0.02% C ADDED

Molybdenum-Silicon System. The heats used in establishing the molybdenum-rich end of the molybdenum-silicon phase diagram are listed in Table 11. The solid solubility has been shown in the previous section. Two types of silicon powder were used: "specially purified" from du Pont and 99.86% silicon containing 0.005-0.015% iron, from Electro Metallurgical Division, Union Carbide and Carbon Corporation.

TABLE 11

MOLYBDENUM-SILICON ALLOYS

Induction Furnace Heats*

Heat	Si in Charge, Wt-%	Maximum Temp, F	Holding Time, min.	Cooling Rate	Remarks
T-Si-0	5.5	3290		furnace cool	sintered, porous
T-Si-1	5.0	3600		furnace cool	sintered, porous
T-Si-2	5.5	3600		furnace cool	sintered, porous
T-Si-3	6.0	3600		furnace cool	sintered, porous
T-Si-4	6.0	3785		quenched	melted (5.82% Si by analysis)
T-Si-5	8.86	3760	7	quenched	just melted
		3920		furnace cool	melted
T-Si-6	15.0	3830	10	furnace cool	sintered
		4000	5	furnace cool	melted, molten at 3990 F
T-Si-7	12.5	3800	3	furnace cool	well sintered
T-Si-8	12.5	4010	10	furnace cool	melted
T-Si-9	8.86	3850	5	furnace cool	melted, molten at 3795 F

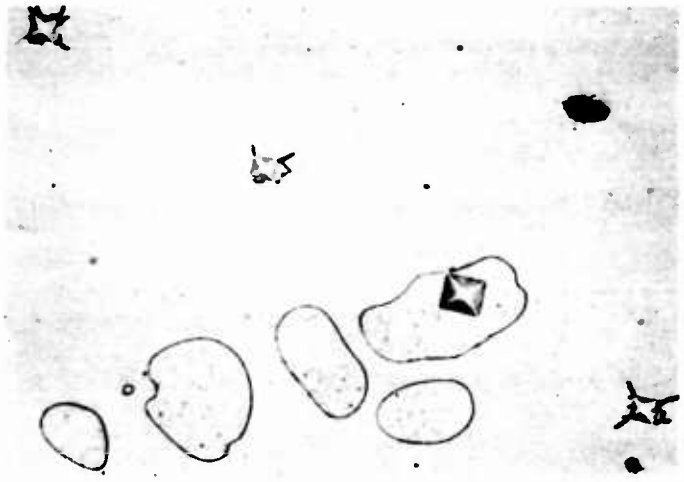
Bar Machine Heats**

Heat	% Si	% C Added
B74	7.48	<0.01
B122	0.54-2.39 graded	0.016

* 10 to 20 g of pressed powder pellets melted in zirconia crucibles in argon.

** Bars were melted in 2" dia mold under argon.

About 80 volume-% of a new phase (Figure 77) and about 20% α-molybdenum solid solution was present in a bar machine ingot containing 7.48 weight-% silicon. The new phase was chemically separated and found to correspond in composition to Mo_3Si. Assuming that this compound is formed by a simple eutectic reaction and that the eutectic composition is approximately that



M358 X1000

FIGURE 77 - Heat B74, Mo-Si, 7.48% silicon - as cast (the matrix is the new phase). Etched 30 seconds in $NaOH+K_3Fe(CN)_6$

corresponding to equal parts by volume of α-molybdenum and Mo_3Si, it was estimated that tne eutectic composition lay at 5.5 weight-% silicon. Metallographic examination of Heat T-Si-4 (Figure 78) containing 5.82% silicon revealed a slightly larger volume of Mo_3Si than of α-molybdenum. The dendrites are α-molybdenum. This is considered sufficient to warrant adoption of the previously estimated value, 5.5 weight-% silicon, as the eutectic composition. As shown in Table 11, Sample T-Si-4 was reheated and found to melt, for all practical purposes, isothermally at 3760 F. This is taken as the eutectic temperature.

Fi st Compound. X-ray powder patterns obtained both on the compound separated chemically from Heat B74 and on the Sample T-Si-4 (Figure 78, 5.82% silicon) revealed two phases: the α-molybdenum solid solution, and Mo_3Si with the crystal structure of beta tungsten, as reported by Templeton and Dauben*. The microstructure of T-Si-4 contains a small amount of dark constituent between the other phases, but this is believed to be an impurity.

To determine the melting point of Mo_3Si or the temperature at which it formed from the liquid and to obtain samples suitable for an accurate measurement of the lattice parameter of this compound, two heats (T-Si-5 and T-Si-9) of Table 11 were made by melting pressed powder mixtures of 8.86% silicon, balance molybdenum. One (T-Si-5) was heated to 3920 F and the other to 3850 F. Both were completely melted. Heat T-Si-9 was studied metallographically and

* D. H. Templeton and C. H. Dauben, Acta Cryst. 3, 261-2 (1950)

subjected to both the powder type and the back-reflection type x-ray tests. As cooled in the furnace, it proved to consist mostly of a single phase as shown in Figure 79. The x-ray powder patterns confirmed the cubic structure ($A15$ O_h^3 $Pm3n$, beta tungsten type) reported by Templeton and Dauben and previously found for the Mo_3Si separated from Heat B74. The powder patterns also registered lines characteristic of α-molybdenum and the etching characteristics of the minor phase were those to be expected for α-molybdenum. Probably a small amount of silicon was lost on melting, as in the case of Heat T-Si-4. This would account for the presence of the α-molybdenum. The lattice parameter of Mo_3Si was found to be 4.8866 kX (4.8965 Å) by using the back-reflection method and applying Cohen's corrections. The value reported by Templeton and Dauben is 4.890 ± 0.002 Å.

Second Compound. The work of Brewer et al* suggested the existence of a compound "$MoSi_{0.65 \pm 0.05}$" corresponding to Mo_3Si_2. Brewer et al reported the a values, but not the structure, of this compound. A pressed powder mixture (Heat T-Si-6 of Table 11) containing 15% silicon, balance molybdenum, represents the composition most nearly corresponding to Mo_3Si_2 (16.25% silicon) which we have studied. The pressed pellet was sintered but not melted on heating to 3830 F. On reheating, it began to melt at 3950 F and was completely molten at 3990 F. This alloy in the furnace-cooled condition was examined metallographically and by the x-ray powder method and found to consist primarily of a single phase (Figure 80) with d values corresponding almost exactly to those reported by Brewer. Since the silicon content (15% minus a probable small loss on melting) is slightly less than the 16.25% required to form Mo_3Si_2, a small amount of Mo_3Si was expected to be present and was found in the photomicrographs. The expected weak lines corresponding to Mo_3Si were also found on the x-ray films. Copper radiation was used in the x-ray work.

Intermediate Structures. Quenching of Mo-Si alloys from the liquid did not produce the complicated three-phase structures obtained in the peritectic Mo-Al system. In further contrast to the Mo-Al system, compositions richer in silicon than Mo_3Si were found to have melting ranges even higher than those containing less silicon. Powder mixtures corresponding to Mo_3Si did not seem to have a definite melting point as would be expected if melting were congruent. It is believed that these observations conform to a eutectic-peritectic type of diagram.

In order to determine whether a eutectic exists between the two compounds Mo_3Si and Mo_3Si_2, two pressed powder heats (T-Si-7 and T-Si-8 of Table 11) were prepared containing 12.5% silicon. Heating T-Si-7 to 3800 F produced only a sintered mass, whereas heating T-Si-8 to 4010 F resulted in complete melting. It was, therefore, concluded that no eutectic existed between these compounds.

The microstructure of T-Si-8 (12.5% silicon added) as furnace cooled after melting is shown in Figure 81. The x-ray powder patterns of this alloy consist of reflections from Mo_3Si and Mo_3Si_2. Since the temperature required to melt this composition completely (4000 F) was found to be higher than that required

* Leo Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, Journal Am. Ceramic Soc., vol 33, No. 10, October 1, 1950

to melt the Mo_3Si composition completely (3350 F) and was, in fact, about the same as that required to melt the Mo_3Si_2 completely, it is presumed that the Mo_3Si is formed peritectically by reaction of Mo_3Si_2 with the liquid, rather than by a eutectic reaction. No metallographic evidence was obtained that suggested the formation of Mo_3Si by a phase transformation involving α-molybdenum or Mo_3Si_2 in the solid state. The manner of formation of Mo_3Si_2 is not known. It may also form peritectically by reaction of some higher silicon compound with the liquid phase.

The tentative equilibrium diagram of Figure 82 has been constructed on the basis of the data and considerations discussed. It differs slightly from that of Kieffer and Cerwenka* in the region of formation of the Mo_3Si compound. Kieffer indicates some doubt in this area.



FIGURE 78 (M1061) X100

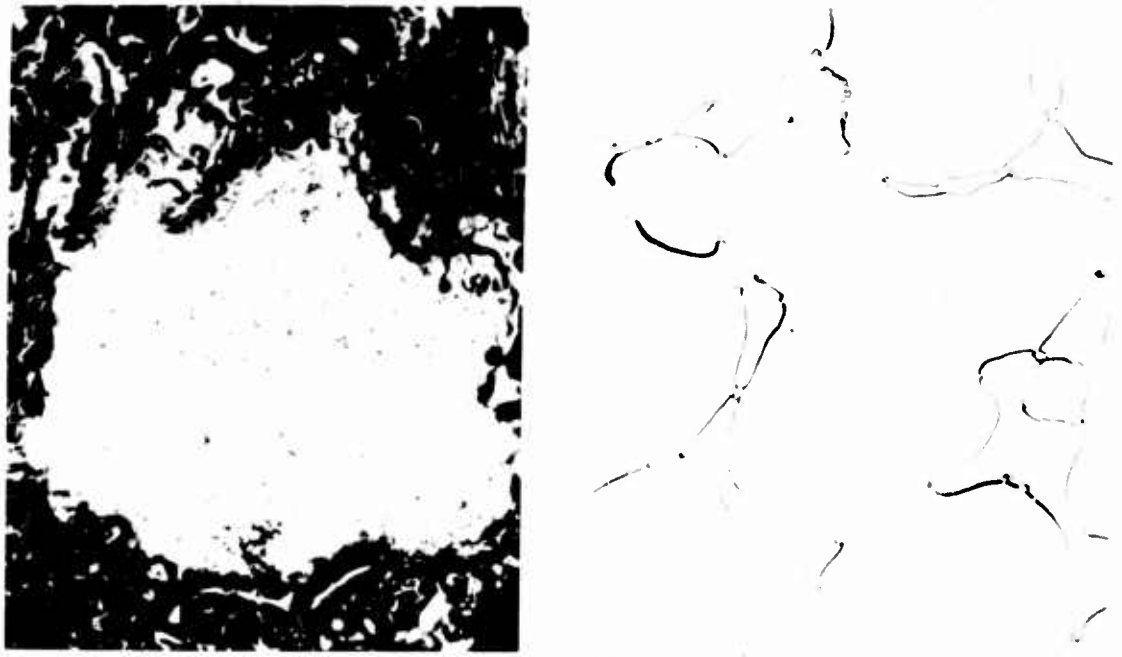
Heat T-Si-4 - Oil quenched after remelting at 3760 F - 5.82% silicon. Electropolish, etch - $NaOH+K_3Fe(CN)_6$



FIGURE 79 (M1279) X100

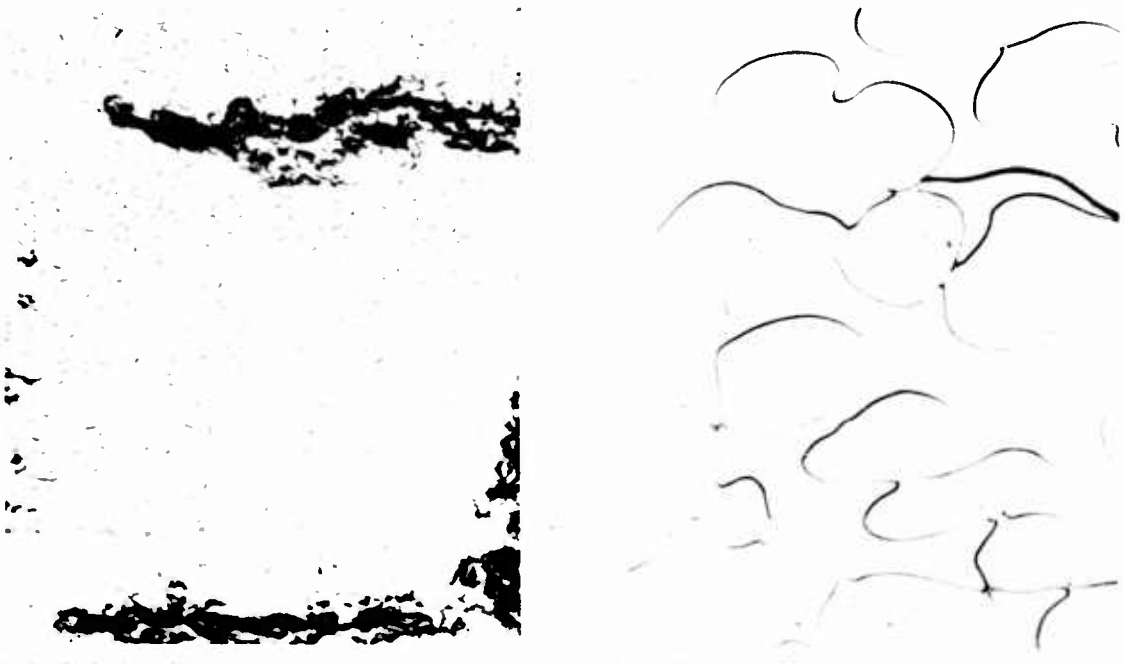
Heat T-Si-9 - Furnace cooled from liquid at 3850 F - 8.86% silicon added. Electropolish, etch - $NaOH+K_3Fe(CN)_6$

* R. Kieffer and E. Cerwenka. Z. Metallkunde, vol 43 (1952), 101



(A) X100 (M1274) (B) X1000 (M1275)

FIGURE 80 — HEAT T Si 6. FURNACE COOLED FROM LIQUID AT 4000 F.
15.0% SI ADDED. ELECTROPOLISH. ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION



X100 M1268 (B) X1000 (M1269)

FIGURE 81 — HEAT T Si 8. FURNACE COOLED FROM LIQUID AT 4010 F.
12.5% SI ADDED. ELECTROPOLISH. ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION

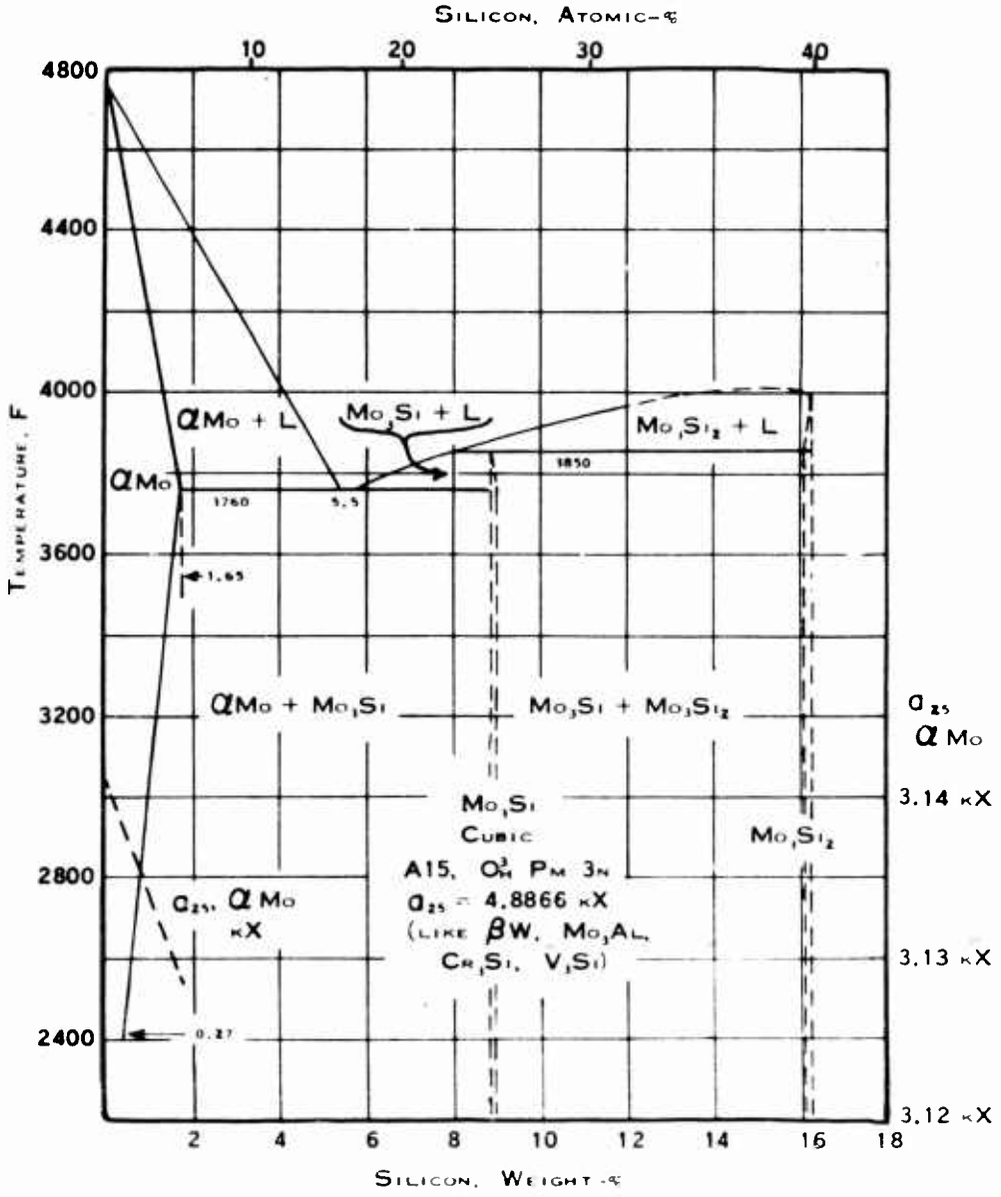


FIGURE 82 – PARTIAL EQUILIBRIUM DIAGRAM FOR THE MOLYBDENUM-SILICON SYSTEM

Molybdenum-Uranium System. Metallographic examination of a sample from the bottom of Ingot B90 containing less than 23% uranium revealed large quantities of a new phase, together with some oxide, as shown in Figure 83. The microhardness impressions indicate the relative hardness of the phases. By traverse along the graded specimen it was established that the dark phase is α-molybdenum. The white phase is presumably alpha or beta uranium solid solution since it is only slightly harder than the α-molybdenum.



FIGURE 83 (M476) X1000

Heat B90, Mo-U, 23% uranium, as cast. Appearance and relative hardness of new phase (light). Etched in $NaOH+K_3Fe(CN)_6$

This indicates that, at equilibrium, a phase other than the body-centered cubic solid solution exists in this alloy system near 23 weight-% (12 atomic-%) uranium at temperatures below 1427 F.

Molybdenum-Vanadium System. Metallographic examination of graded ingots containing up to 33.5% vanadium gave no evidence of phases other than the α-molybdenum solid solution and oxide inclusions. A photomicrograph of the 33.5% vanadium alloy held for two hours at 3510 F and slow cooled is presented in Figure 84.



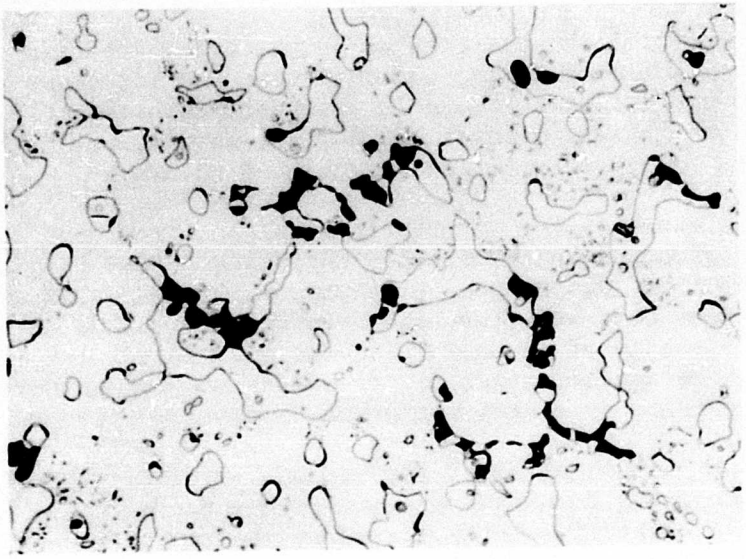
FIGURE 84 (M421) X1000

Heat B89, Mo-V, 33.5% vanadium, 0.015% carbon added. Shows only oxide and cracks.
Etched in $NaOH+K_3Fe(CN)_6$

Molybdenum-Zirconium System. Figure 85a shows the 3% zirconium alloy after annealing and slow cooling and presents metallographic evidence of the solubility of zirconium up to at least 3%. The black particles are oxides. Figure 85b shows the structure obtained in a segregated section of Heat B73 after annealing 90 hours at 2450 F. This figure suggests that a second phase occurs in the system at a zirconium content above 3%.



(A) HELD 2 HR AT 3500 F, SLOW COOL, X1000 (M398)



(B) SEGREGATED SECTION, HELD 90 HR AT 2450 F, X1000 (M397)

FIGURE 85 – MOLYBDENUM–ZIRCONIUM ALLOY

HEAT B73, 3.0% ZIRCONIUM, 0.037% CARBON
ETCHED IN HOT 2% HYDROFLUORIC ACID
AND THEN IN HOT 3% NITRIC ACID

Precipitation Hardening Alloys

In the initial studies of the molybdenum-beryllium alloys, it was observed that small additions of beryllium produced an extreme increase in as-cast hardness. Furthermore, annealing the cast alloys in the temperature range 2000 to 3000 F brought about an appreciable drop in hardness. These hardness changes, coupled with metallographic examinations, indicated the possibility of a precipitation hardening mechanism in the molybdenum-rich end of the molybdenum-beryllium system. The determination of the limit of solubility of beryllium in molybdenum already described was the base upon which studies of precipitation hardening were made. The molybdenum-rich end of the molybdenum-beryllium system is shown in Figure 64.

In the investigation of precipitation hardening, a sample of 0.15% beryllium alloy (Heat B146) was heated to place as much beryllium as possible in solid solution in molybdenum, quenched to retain the beryllium in supersaturated solid solution, and then aged at 1500, 1750 and 2000 F. The changes in hardness with aging time were determined. Figure 86 shows these changes. It will be noted that the maximum hardness due to precipitation hardening can be produced either by holding for 45 minutes at 2000 F or for six hours at 1750 F. The chart also shows that the overaging process at 1750 F is slow and suggests that the strength and hardness at elevated temperatures of precipitation hardened molybdenum-beryllium alloys can be maintained over a period of about 75 hours in service, at least for operating temperatures up to 1750 F. The hot hardness of a sample fully aged at 1750 F was 570 DPN at 1400 F and 520 DPN at 1600 F.

The microstructural changes induced by the aging treatments are shown in Figure 87. These photomicrographs indicate that the structure associated with the maximum age hardness is one in which no visible precipitation has occurred within the grains, even at 2000X (left-hand column); the overaged condition reveals such precipitation (right-hand column).

Figure 88 illustrates the structures resulting from quenching from a high temperature (3600 F) and from fully annealing a cast sample at 2500 F, respectively. Apparently, the quenching temperature was sufficiently high to result in the eutectic structure shown in Figure 88a, which is believed to be a ternary eutectic of Mo-Be-C. The fully annealed structure of Figure 88b shows the agglomeration of the excess molybdenum-beryllium phase. This structure corresponds closely with the completely overaged condition.

To expand the investigation of molybdenum-beryllium alloys, a series of heats was made employing powder as the starting material. These heats are listed in Table 12. The five heats listed at the top of the table were melted in vacuum and the poor recovery of beryllium is evident. The six remaining heats were melted in an atmosphere of argon. Aluminum was added to all heats except the last to aid in deoxidation. The recovery of beryllium was greatly increased.

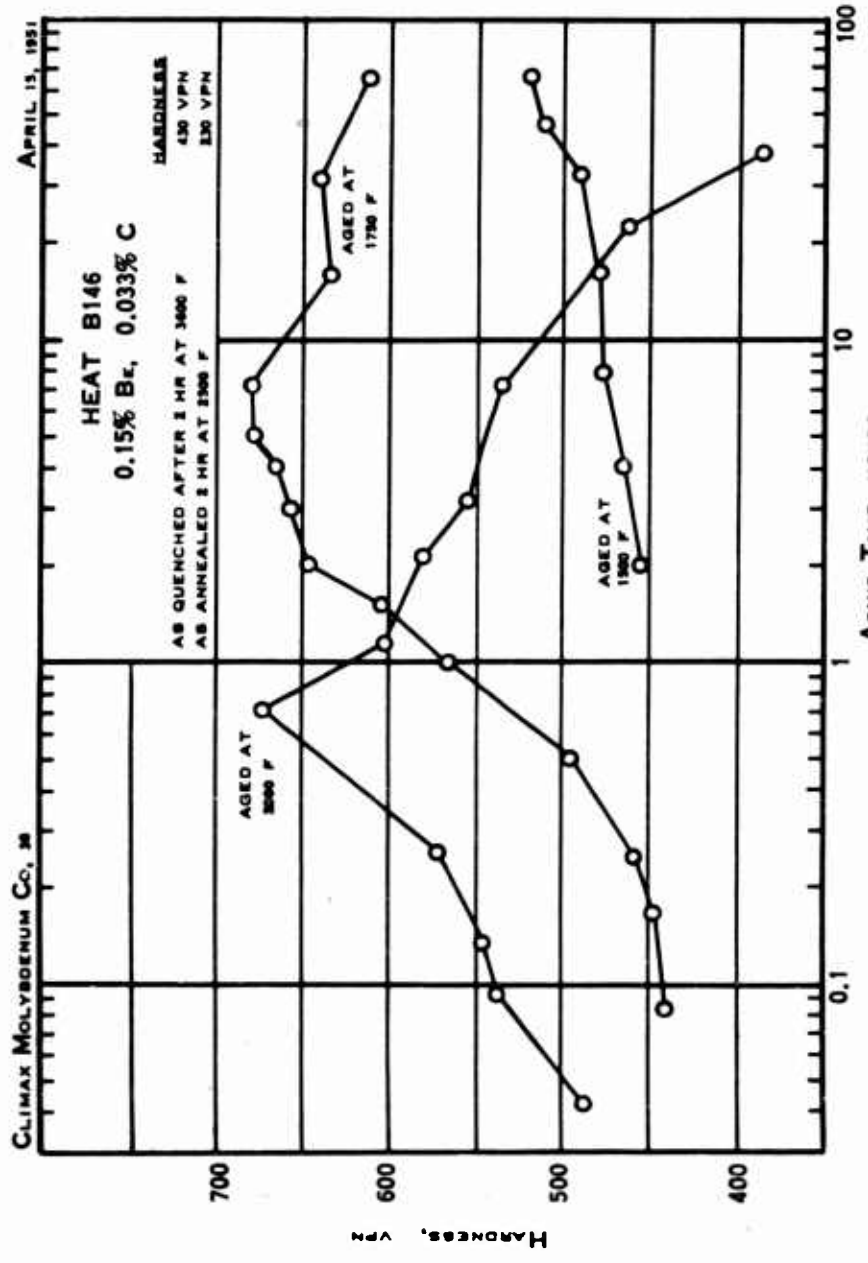
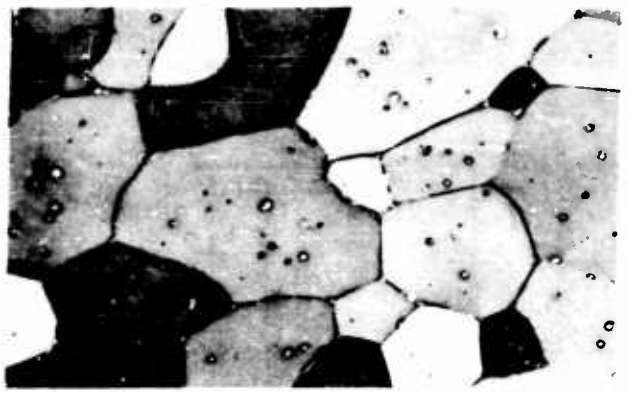


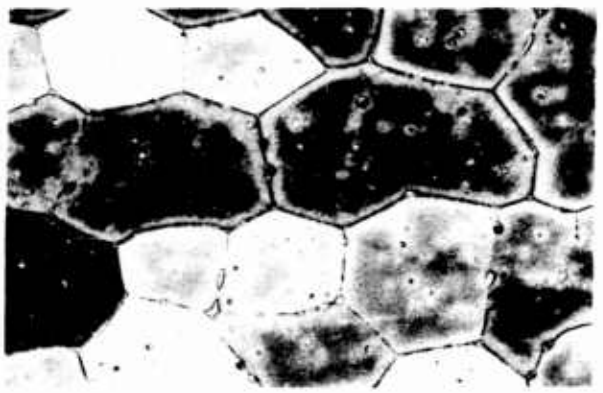
FIGURE 86 – EFFECT OF AGING ON HARDNESS OF MOLYBDENUM–BERYLLIUM ALLOYS

AGED 64-3/4 HOURS AT 1500 F



X100 NORMAL ETCH (M994)

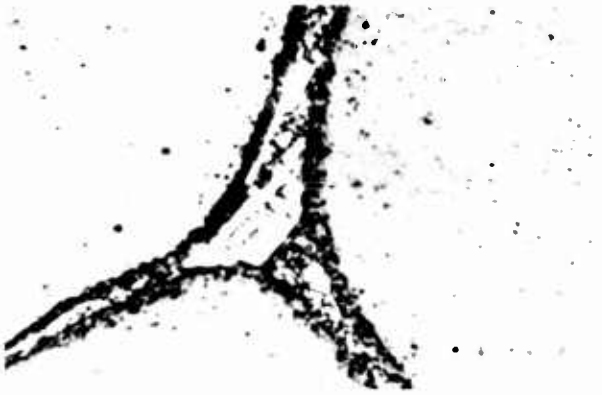
AGED 64-1/2 HOURS AT 2000 F



X100 NORMAL ETCH (M999)



X2000 NORMAL ETCH (M995)



X2000 NORMAL ETCH (M1000)



X2000 LIGHTLY ETCHED (M1044)



X2000 LIGHTLY ETCHED (M1035)

FIGURE 87 — MICROSTRUCTURAL CHANGES INDUCED BY AGING MOLYBDENUM-BERYLLIUM ALLOYS

HEAT B146, 0.031% C, 0.15% BE. HELD AT 3600 F FOR TWO HOURS AND OIL QUENCHED BEFORE AGING. ELECTROPOLISHED, ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION



(A) OIL QUENCHED FROM 3600 F. ELECTROPOLISHED, ETCHED DURING POLISHING. X2000 (M969)



(B) ANNEALED AT 2500 F. ELECTROPOLISHED, ELECTROLYTIC ETCH IN OXALIC ACID. X2000 (M957)

FIGURE 88 — MICROSTRUCTURES OF QUENCHED AND FULLY ANNEALED MOLYBDENUM–BERYLLIUM ALLOY

HEAT B146, 0.033% C, 0.15% BE

TABLE 12

POWDER MACHINE HEATS USED FOR STUDIES OF THE HARDNESS OF HEAT TREATED MOLYBDENUM–BERYLLIUM ALLOYS

Heat No.	Additions, %			Analyses, %			Hardness, dpn		Quenching Temp, F	Hardness, dpn, As Quenched	Aging		Hardness dpn As Aged
	C	Be	Al	C	Be	Al	Cast	Annealed[1]			Time, Hr	Temp, F	
							Cast in vacuum						
566[2]	0.05	0.5	0	0.042	0.015	0		264	3400	357	5	1750	305
593	0.04	0.05	0	0.061	0.004	0	170						
599[2]	0.04	0.05	0	0.052	0.005	0	196						
600	0.04	0.10	0	0.036	0.010	0	171		3400	201			
631	0.04	0.25	0	0.051	0.032	0	230	220	3400	270	2	1750	241
							Cast in argon						
663	0	0.05	0.10	0.004	0.035	0.085	202		3600	211	4	1800	218
684	0	0.10	0.15	0.003	0.068	0.144	290		3600	285	4	1800	307
									3800	296	3	1800	343
											3 1/2	1800	351
715	0.02	0.20	0.15	0.027	0.137	0.130	400	253	3350	423	4	1800	306
											5	1800	582
716	0	0.20	0.15	0.006	0.137	0.156	375	297	3350	348	4	1800	370
											5	1800	403
									3800	408	3	1800	602
											3 1/2	1800	614
											4	1800	638
											5	1800	637
717	0.02	0.15	0.15	0.026	0.098	0.132	398	259	3350	410	4	1800	561
											5	1800	566
718	0.05	0.20	0	0.055	0.147		419	250	3350	429	4	1800	550
											5	1800	558

[1] Annealing consisted of holding two hours at 2500 to 2600 F and cooling in Sil-O-Cel

[2] 10% tungsten also added

These heats were made by pressing, sintering and melting mixed powders in 3 to 3 1/2 in. molds. The vacuum heats were also used for deoxidation studies.

All of the heats cast in argon were too hard to be machined by conventional methods in the as-cast state. Annealing in the temperature range 2500 F to 2600 F, however, softened them sufficiently to permit machining without great difficulty. The lower carbon heats (e.g., 716) require higher quenching temperatures than the higher carbon heats (e.g., 718) to produce maximum quenched hardness. The maximum quenched or quenched and aged hardness, however, can be produced with as little as 0.006% carbon present.

Metallographic structures of the last five heats listed in Table 12 are illustrated in Figures 89-93. Figure 89 shows the as-cast structure of a nearly carbon-free heat (684). Comparison of the hardness obtained on quenching a sample of this heat (296 DPN) with the quenched hardness of comparable heats made in the bar melting machine (400 DPN) indicates that not all of the beryllium present in the alloy is available for the hardening process and suggests that the "inert" form is beryllium oxide.

As shown in Table 12, the heat containing 0.137% beryllium and 0.027% carbon (715) apparently had sufficient "active" beryllium to attain hardnesses, as quenched from 3350 F and after aging for four hours at 1800 F, near the maxima for these two conditions. The structure of this alloy in the quenched condition is shown in Figure 90a. The beryllium-rich phase is present in excess both at grain boundaries and within the grains. A small amount of the eutectic structure is present (single round area) and no white carbides are visible. The structure in the annealed condition (Figure 90b), however, does reveal the presence of carbides, both at grain boundaries and associated with the eutectic structure, furnishing evidence that some carbon is retained in solution on quenching and that some carbon is associated with the eutectic. For comparison, the as-quenched structure of a nearly carbon-free heat (716) is presented in Figure 91a, and the absence of the eutectic phase suggests that the eutectic temperature is above 3350 F for this composition. Figure 91b shows the annealed structure. The precipitation of fine particles in the matrix is the only observed structural change. These nearly carbon-free molybdenum-beryllium alloys quenched from temperatures of 3800 F exhibit the same hardening phenomena on quenching and on subsequent aging as the carbon-containing alloys quenched and aged at lower temperatures.

From the data of Table 12, a comparison of the hardnesses induced by heat treatment for Heats 715 and 717 indicates that 0.098% beryllium is insufficient to yield the maximum hardening for compositions of this type. When no aluminum is present (Heat 718), 0.14% beryllium is also insufficient. The structures of Heats 717 and 718 are shown in Figures 92-93.

In short, carbon-deoxidized heats made in the PSM-3 machine required higher beryllium concentrations for maximum hardening than bar machine heats of equal carbon content, and aluminum-deoxidized heats (nearly carbon free) required not only higher beryllium contents, but also a higher quenching temperature for maximum hardening. The necessity for more beryllium in powder machine heats than in bar machine heats can be accounted for, in part at least, by the fact that the raw material contains more oxygen and that some of the

beryllium added in the charge is oxidized to BeO, which remains in the heat in this form. Although its presence is detected as beryllium in chemical analysis, it is inactive in the hardening reaction. When present in the alloy, residual carbon occurs in the eutectic. It lowers the eutectic temperature which, in turn, limits the temperature of solid solubility. Metallographic examinations have revealed an intimate association between the carbide phase and the molybdenum-beryllium eutectic.



FIGURE 89 (M1200) X1000

MICROSTRUCTURE OF LOW-CARBON, MOLYBDENUM-BERYLLIUM ALLOY, AS CAST

Heat 084, 0.003% C, 0.068% Be, 0.144% Al - Electropolished, etched in $NaOH+K_3Fe(CN)_6$



(A) OIL QUENCHED FROM 3350 F, AGED 5 HOURS AT 1800 F (M1265)

(B) ANNEALED 2 HOURS AT 2600 F (M1261)

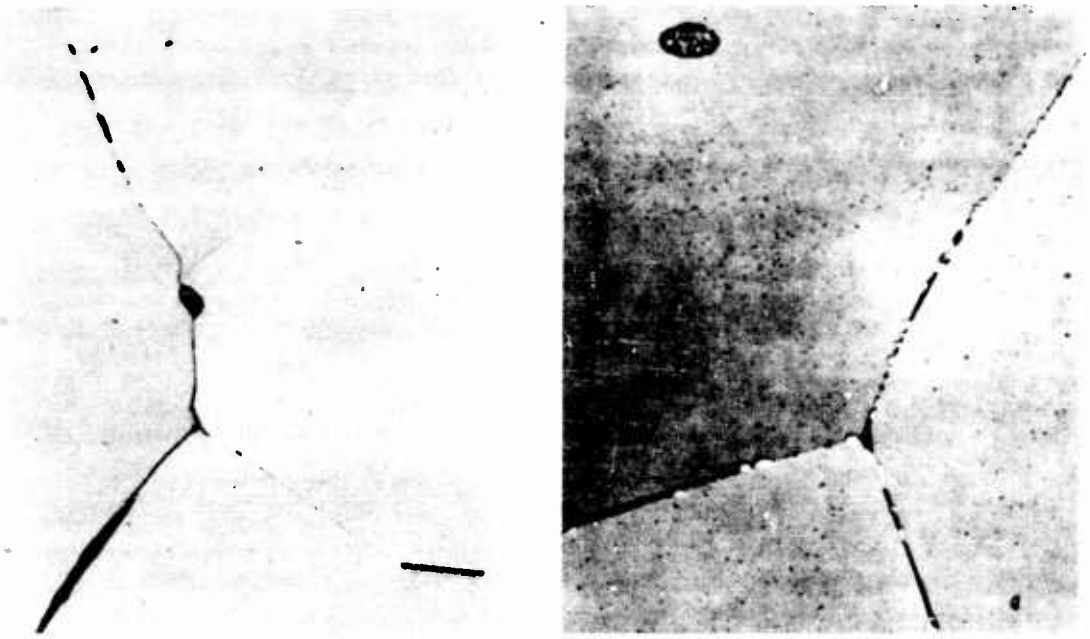
FIGURE 90 — MICROSTRUCTURE OF 0.137% BERYLLIUM ALLOY, HEAT 715
0.027% C, 0.137% BE, 0.130% AL
ELECTROPOLISHED, ELECTROLYTIC ETCH IN OXALIC ACID, X1000



(A) OIL QUENCHED FROM 3350 F (M1238)

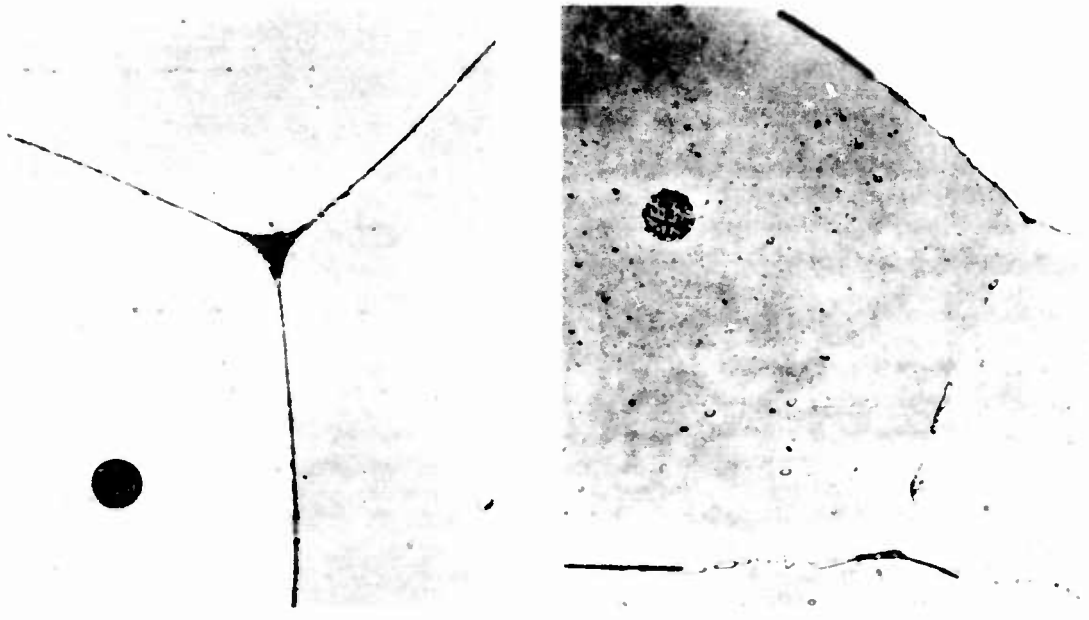
(B) ANNEALED 2 HOURS AT 2600 F (M1262)

FIGURE 91 — MICROSTRUCTURE OF 0.137% BERYLLIUM ALLOY, HEAT 716
0.006% C, 0.137% BE, 0.156% AL
ELECTROPOLISHED, ELECTROLYTIC ETCH IN OXALIC ACID, X1000



(A) OIL QUENCHED FROM 3350 F (M1239) (B) ANNEALED 2 HOURS AT 2600 F (M1263)

FIGURE 92 – MICROSTRUCTURE OF 0.098% BERYLLIUM ALLOY, HEAT 71.
0.026% C, 0.098% BE, 0.132% AL
ELECTROPOLISHED, ELECTROLYTIC ETCH IN OXALIC ACID, X1000



(A) OIL QUENCHED FROM 3350 F (M1240) (B) ANNEALED 2 HOURS AT 2600 F (M1264)

FIGURE 93 – MICROSTRUCTURE OF 0.147% BERYLLIUM ALLOY, HEAT 718
0.055% C, 0.147% BE
ELECTROPOLISHED, ELECTROLYTIC ETCH IN OXALIC ACID, X1000

Some additional experiments were conducted with Heats 715 and 716 to compare the heat-treating characteristics of carbon-free molybdenum-beryllium alloys deoxidized with aluminum with the heat-treating characteristics of the carbon-deoxidized alloys previously studied, and to determine whether drastic quenching from solution temperature was necessary to develop maximum hardening on aging. In Table 13 are presented the data pertinent to the experiments and the hardnesses determined at various stages of the heat treatments.

TABLE 13

ADDITIONAL HEAT TREATING TESTS ON MOLYBDENUM-BERYLLIUM-CARBON AND MOLYBDENUM-BERYLLIUM-ALUMINUM ALLOYS

Heat No.	Solution Temp, F	Solution Time, hr	Quenching Medium	Hardness As Quenched DPN	Aging Temp, F	Aging Time, hr	Hardness As Aged DPN
716	3350	2	oil at room temp.	348	1800	5	403
	3500	6	"	360	1800	5	528
	3800	2	"	408	1800	5	637
					1800	9	637
					2000*	4	534
					2000*	8	506
					2000*	16	455
715	3500	2	Mo block, room temp.	340	1800	4	505
					1800	6	597
	3500	2	Al at 1800 F	-	1700**	4	378
					1800*	4	478
					1800*	6	491
	3500	2	Mo block, room temp.	377	not aged		

* same sample as aged at lower temperature
** approximately 1700 F; "isothermal" treatment, that is, aged without cooling to room temperature and reheating

In all of the heat treatments, argon was used for protection against oxidation; the specimens were never exposed to air while hot. After the furnace chamber had been evacuated and filled with argon, titanium metal in the chamber was heated to remove oxygen and nitrogen before the molybdenum-beryllium alloy was heated to the solution temperature.

Small cylindrical specimens, 1/2" diameter by 7/16" long, were used for the tests on Heat 715; the specimens were drilled so that they could be mounted on the lower end of a vertical molybdenum rod which could be lowered into a bath of molten aluminum or into a hole in a molybdenum block.

The heat-treated specimens were examined carefully for cracks and chemical surface effects; it was found that cracking occurred only on grinding. The outer layers of the specimens remained soft, owing to oxidation of beryllium, and the depth of this affected zone (0.003" to 0.015") depended upon the purity of the argon atmosphere.

The specimens quenched in molten aluminum were left in the bath for only a short time, then raised slightly above the bath for aging. The temperature of the specimen above the aluminum bath could not be determined precisely, since the thermocouple was some distance from the specimen; therefore, this temperature was estimated.

Small rectangular specimens, approximately 1/2" by 1/2" by 1/4", were used for Heat 716. These were quenched by dropping from the furnace directly into oil at room temperature. The as-quenched hardness of this low-carbon alloy was higher after holding at 3800 F for two hours than after holding for two hours at 3350 F or even for six hours at 3500 F. After aging for five hours at 1800 F, a higher hardness was developed in the sample quenched from 3800 F (two hours) than in the other two samples, which were quenched from 3350 F (two hours) and 3500 F (six hours), respectively. It is concluded, therefore, that the temperature for maximum solubility of beryllium or the eutectic temperature is about 3800 F for molybdenum-beryllium alloys containing very little carbon (less than 0.01%); whereas, the eutectic temperature of similar alloys containing 0.02 to 0.05% carbon is near 3350 F.

The hardness of 637 DPN, which was obtained in the low-carbon alloy after quenching from 3800 F and aging for five to nine hours at 1800 F, was only slightly less than the maximum hardness obtained in a complete survey of age hardening characteristics of several higher carbon heats, i.e., 675 DPN.

When the low-carbon alloy was further aged at 2000 F the hardness was reduced to 534 DPN in four hours and continued to decrease as time at 2000 F was increased. This relatively rapid loss of hardness indicates that the hardness and strength developed by aging this alloy would not be available for applications at temperatures near the 2000 F level.

The higher carbon alloy, Heat 715 (0.02% C), when cooled from 3500 F by radiation and conduction of heat to a molybdenum block at room temperature instead of by oil quenching, attained a hardness of 597 DPN after aging for six hours at 1800 F, a value not far below the maximum obtainable with this alloy. When the same alloy was quenched in molten aluminum at 1800 F and held at temperatures in the range 1800 F to 1700 F for four hours before being cooled to room temperature, the hardness developed was 378 DPN. Reheating to 1800 F for an additional time of four hours resulted in an increase of hardness to 478 DPN, and an additional two hours at 1800 F raised the hardness to 491 DPN.

Although appreciably below the maximum hardness of which the alloy is capable, the lower hardnesses developed in the samples cooled from the quenching temperature at the slower rates employed in these experiments may be useful for certain purposes. The fact that slower quenching rates can be used successfully to develop a useful increase in hardness of the alloy indicates that larger sections (or parts) than the samples used in the experiments described here may be hardened practically, and that the alloys have the possibility of being employed for useful parts where certain of the characteristics of metallic molybdenum are essential, but where higher hardness is a requisite. Slower rates of quenching from the high solution temperatures also decrease the tendency toward distortion or cracking.

Mo-Al and Mo-Si Alloys

A few experiments were performed to determine whether molybdenum-rich Mo-Al and Mo-Si alloys are susceptible to age hardening, in view of the increasing solubility of aluminum and silicon in molybdenum with increasing temperature. It was found that neither the Mo-Al nor the Mo-Si alloys responded to precipitation hardening treatments. These experiments were described in detail in the second annual report.

MECHANICAL PROPERTIES OF WROUGHT ALLOYS

The properties of molybdenum-base alloys depend to some extent upon the methods used in their production and fabrication. At the present time, large bodies of molybdenum are worked with equipment and at temperatures used in the steel industry. Although the temperatures employed are in the range 1800 F to 2600 F, molybdenum and molybdenum-base alloys so fabricated are not hot worked in the true sense of the word but are strain hardened in various degrees. The process is more accurately defined as "hot cold-working". True hot working of most commercial metals and alloys is performed at temperatures equivalent to approximately 85% of their melting points; for molybdenum, this would mean working at about 4000 F. Facilities for working molybdenum at so high a temperature are not now readily available and would be expensive to build, requiring changes in design and tool materials. Moreover, the rapid oxidation of molybdenum at 4000 F poses a problem that has yet to be solved. Even on a laboratory scale, little effort has been expended toward the solution of these admittedly difficult problems.

As discussed under the section on cast properties, alloying elements increase the hardness and strength of the molybdenum solid solution. The limit of alloying element that can be tolerated in workable molybdenum (under the conditions of working now in use) is reached before the limit of that element in solid solution. This investigation is therefore concerned with those molybdenum-rich, solid solution alloys which are neither too hard nor too strong, by virtue of their alloy content, to be worked at the temperatures, and with the equipment available. Inasmuch as these are solid solution alloys, their mechanical properties can be modified only by control of the degree of strain hardening.

Methods of Working

Specimens used for the study of mechanical properties of wrought molybdenum-base alloys were obtained from bars that had been worked by several methods from ingots produced in the PSM-3 and PSM-4 machines. Most of the heats weighed from 90 to 300 pounds and were cast in molds 3" to 8" in diameter. The macro- and microstructures of the castings were described in the preceding section. Although the investigation is concerned primarily with alloys, unalloyed molybdenum is included as a datum plane with which to compare them. In this section, the term "unalloyed molybdenum" includes molybdenum deoxidized with carbon or rare earth metals in vacuum or neutralized with aluminum in argon; all the heats containing aluminum were melted in argon atmosphere. The ingots, with their casting diameter, chemical composition, and hardness at room temperature and 1600 F, are listed in Table 14.

Methods of working alloys of molybdenum were developed gradually. In the later stages of development, it was possible to take advantage of recent progress in primary working in the steel industry. At first, methods of forging were studied; but, as the Sejournet-Ugine process of extrusion was perfected,

TABLE 14

INGOTS FOR MECHANICAL PROPERTY STUDIES

Heat No.	Mold Dia, in.	Additions, %		Analyses, %		Hardness as Cast, DPN	
		Carbon	Alloy	Carbon	Alloy	Rm Temp	1600 F
936	6	0.034		0.008			
937	6	0.042		0.015			
1159	7.5	0.047		0.040		187	59
1045	4	(0.3 LCA)		0.003	0.005 Ce,0.007 RE*	187	77
1252	8		0.20 Al	0.003	0.15 Al		
1063	8		0.20 Al	0.003	0.17 Al	169	88
1058	8		0.60 Al	0.006	0.49 Al	192	108
987	4		0.60 Al	0.003	0.53 Al	192	118
1059	8		1.00 Al	0.004	0.81 Al	240	142
983	4		1.00 Al	0.004	0.88 Al	229	139
1155	7.5		1.25 Al			231	147
1154	7.5		1.37 Al			255	157
1176	4		1.70 Al		1.43 Al	280	141
1463	5	0.048	0.65 Cr	0.033	0.11 Cr	173	75
677	4	0.069	0.15 Co	0.056	0.05 Co	159	94
1144	7.5	0.040	0.12 Co	0.020	0.074 Co	169	92
1145	7.5	0.040	0.25 Co	0.022	0.123 Co	170	110
652	4	0.066	0.32 Co	0.046	0.14 Co	212	117
1146	7.5	0.040	0.37 Co	0.018	0.165 Co	185	116
1173	4	0.046	0.50 Co	0.037	0.19 Co		
1464	5	0.039	0.25 Fe	0.026	0.09 Fe	164	76
1153	7.5	0.040	0.11 Ni	0.008	0.044 Ni	160	98
1465	5	0.039	0.15 Ni	0.021	0.05 Ni	148	93
988	4	0.035	0.25 Nb	0.019	0.24 Nb	180	61
1082	8	0.051	0.30 Nb	0.032	0.31 Nb		
660	4	0.065	0.30 Nb	0.041	0.34 Nb	199	82
978	4	0.036	0.50 Nb	0.019	0.52 Nb	189	77
1057	8	0.052	0.78 Nb	0.033	0.75 Nb	197	80
979	4	0.036	0.75 Nb	0.022	0.76 Nb	190	76
1279	7.5	0.038	1.00 Nb				
1147	7.5	0.033	1.04 Nb	0.012	1.10 Nb	190	95
1148	7.5	0.033	1.30 Nb	0.013	1.36 Nb	204	100
1152	7.5	0.040	0.10 Si	0.011	0.088 Si	178	121
1466	5	0.044	0.10 Si			170	105

* RE = other rare earth metals

TABLE 14 (continued)

INGOTS FOR MECHANICAL PROPERTY STUDIES

Heat No.	Mold Dia, in.	Additions, %		Analyses, %		Hardness as Cast, DPN	
		Carbon	Alloy	Carbon	Alloy	Rm Temp	1600 F
1100	3	0.041	0.21 Ti	0.015	0.21 Ti	188	
1268	7.5	0.034	0.25 Ti	0.014	0.22 Ti	174	
1137	3	-	0.5Ti-0.2Al	0.003	0.44Ti-0.23Al	168	
1132	7.5	0.035	0.51 Ti	0.024	0.45 Ti	185	73
1348	7.5	0.044	0.50 Ti	0.021	0.46 Ti	180	65
1393	8	-	0.5Ti-0.15Al	0.006	0.50Ti-0.12Al	164	
1008	4	0.040	0.64 Ti	0.034	0.65 Ti		
1048	4	(0.3 LCA)	1.00 Ti	0.028	0.69Ti,0.12RE*	190	89
1133	7.5	0.038	1.03 Ti	0.014	0.85 Ti	206	81
1134	7.5	0.038	1.29 Ti	0.010	1.05 Ti	204	83
1138	7.5	0.038	1.55 Ti	0.014	1.22 Ti	214	89
1009	4	0.040	1.28 Ti	0.036	1.26 Ti	212	96
1080	8	0.041	1.50 Ti	0.036	1.41 Ti		
1143	7.5	0.042	2.06 Ti	0.018	1.66 Ti	209	102
1010	4	0.040	1.92 Ti				
1281	7.5	0.043	2.50 Ti	0.023	2.09 Ti	208	
651	4	0.080	3.00 Ti	0.051	2.29 Ti	212	117
885	7	0.082	3.08 Ti	0.047	2.46 Ti	222	107
887	7	0.082	2.52 Ti	0.048	2.66 Ti	222	107
1174	4	0.043	4.20 Ti	0.027	3.59 Ti	219	86
1051	8	0.047	0.60 V	0.027	0.54 V	203	84
1012	4	0.043	0.60 V	0.030	0.56 V	192	84
667	4	0.075		0.049	0.66 V	186	93
1049	4	(0.3 LCA)	1.00 V	0.001	0.85 V**	184	89
669	4	0.081		0.047	0.87 V	188	100
672		0.076		0.057	0.88 V		
1052	8	0.047	1.20 V	0.029	1.00 V	200	98
1013	4	0.043	1.20 V	0.035	1.14 V		
653	4	0.084		0.056	1.22 V	186	105
1053	8	0.047	1.50 V	0.032	1.24 V	208	105
1151	7.5	0.040	1.25 V	0.006	1.25 V	190	99
1014	4	0.043	1.50 V	0.032	1.39 V		
1175	4	0.043	1.62 V	0.033	1.46 V		
1390	8	0.027	0.05 Zr	0.018	0.054 Zr	168	85
1207	7.5	0.036	0.09 Zr	0.019	0.09 Zr	187	81
1062	8	0.052	0.10 Zr	0.036	0.11 Zr	189	85
1041	4	0.040	0.20 Zr	0.021	0.21 Zr		
1149	7.5	0.033	0.20 Zr	0.013	0.22 Zr	186	95
1150	7.5	0.033	0.40 Zr	0.015	0.43 Zr	194	118

* RE = other rare earth metals

** 0.003 Ce, 0.003 RE

TABLE 14 (continued)

INGOTS FOR MECHANICAL PROPERTY STUDIES

Heat No.	Mold Dia, in.	Additions, %		Analyses, %		Hardness as Cast, DPN	
		Carbon	Alloy	Carbon	Alloy	Rm Temp	1600 F
1435	6	-	0.28Al-0.06Co			165	114
1436	6	-	0.53Al-0.50V	0.005	0.42Al-0.51V	188	89
1437	6	-	0.53Al-0.06Zr	0.003	0.42Al-0.06Zr	181	
1455	5	0.039	0.12Co-0.50V	0.025	0.06Co-0.47V	162	87
1454	5	0.039	0.12Co-0.06Zr	0.027	0.06Co-0.07Zr	151	97
1217	7.5	0.034	0.24?Co-0.20Ti	0.030	0.11Co-0.18Ti	158	99
1001	8	0.043	0.30Nb-0.19Ti	0.032	0.31Nb-0.16Ti		
1060	7.5	0.042	0.31Nb-0.19Ti	0.026	0.32Nb-0.18Ti	188	54
1457	5	0.038	0.50Nb-0.50V	0.024	0.46Nb-0.48V	187	75
1451	5	0.034	0.50Nb-0.50Ti	0.014	0.50Nb-0.43Ti	191	71
1456	5	0.038	0.50Nb-0.06Zr			186	67
1452	5	0.039	0.25Ti-0.75V	0.030	0.22Ti-0.75V	185	75
1453	5	0.034	0.25Ti-0.06Zr	0.024	0.22Ti-0.08Zr	181	77
1458	5	0.038	0.50V-0.06Zr			191	82

development of forging procedures was abandoned in favor of the extrusion method, which had an inherent advantage for working the coarse grained, columnar structure of cast molybdenum. Thus, two types of working were studied: (1) forging followed by rolling and (2) extrusion followed by rolling.

Forging and Rolling

In the early stages of the study of working molybdenum-base alloys, ingots 4" in diameter were forged and rolled. The ingots were turned to remove unsound metal from the surface and forged to billets of octagonal cross-section on a 1,000-pound air hammer. The lower die of the hammer contained a 90°-V recess. The turned cast sections were heated to 2600 F in a gas-fired furnace and were forged to octagons 2" to 2-1/4" across the flats (diameter of inscribed circle). The octagonal billets were rolled in commercial tool steel rolling mills to 1-1/8", 7/8", or 5/8" diameter. A 10" jobber mill (hand rounds) was used for rolling the 1-1/8" rounds, and a guide mill for rounds less than 1" in diameter.

Later in the program a 600-ton forging press was acquired by the Climax laboratory. The 4" diameter castings were cut into two 12" lengths and machined to 3-1/2" diameter. The machined castings were heated in hydrogen and press-forged between a flat, top die and a 60°-V, bottom die to about 2-1/4" diameter by somewhat over 20" long (20" was the minimum length acceptable for rolling on the commercial mill engaged). Prior to rolling, the billets were annealed for one hour at 3000 F, cropped, and machined to remove surface defects. The bulk of the metal lost in processing occurred at this stage. The billets were rolled to 1" and 5/8" diameter bars at Universal-Cyclops Steel Corporation on a commercial tool steel rolling mill at 2200-1900 F. A flow sheet showing the processing of the ingot containing 0.52% niobium, Figure 94, is typical of the processing of all the 4" diameter ingots subjected to forging and rolling. The recovery data on alloys hammer forged or press forged and subsequently rolled are presented in Table 15. In this table, recovery after forging and total recovery are based on the weight of the turned casting submitted for fabrication.

In forging molybdenum and molybdenum-base alloys, four factors are the source of most of the difficulties. The first is the increasing resistance of the alloys to plastic deformation at the forging temperatures available (up to 3000 F) as the concentration of the alloying elements increases. The second is the columnar, large-grained structure which develops in these alloys during the solidification of the progressively solidified casting. The coarse crystals, with the resulting limited grain surface area, accentuate the deleterious effect of impurities residing at the grain boundaries. The third factor is the type of stress imposed upon the cylindrical casting by conventional hammer and press forging equipment. The unfavorable distribution of stresses during the working operation and the relatively high strain rates imposed upon the coarse-grained castings do not favor working, and there is a tendency for the castings to crack as the resistance of the alloy to plastic deformation becomes higher.

CLIMAX MOLYBDENUM CO. 247
DECEMBER 1, 1952

FIGURE 94
FORGING SCHEDULE
INGOT 978

0.019% CARBON
0.52% NIOBIUM
CAST IN VACUUM

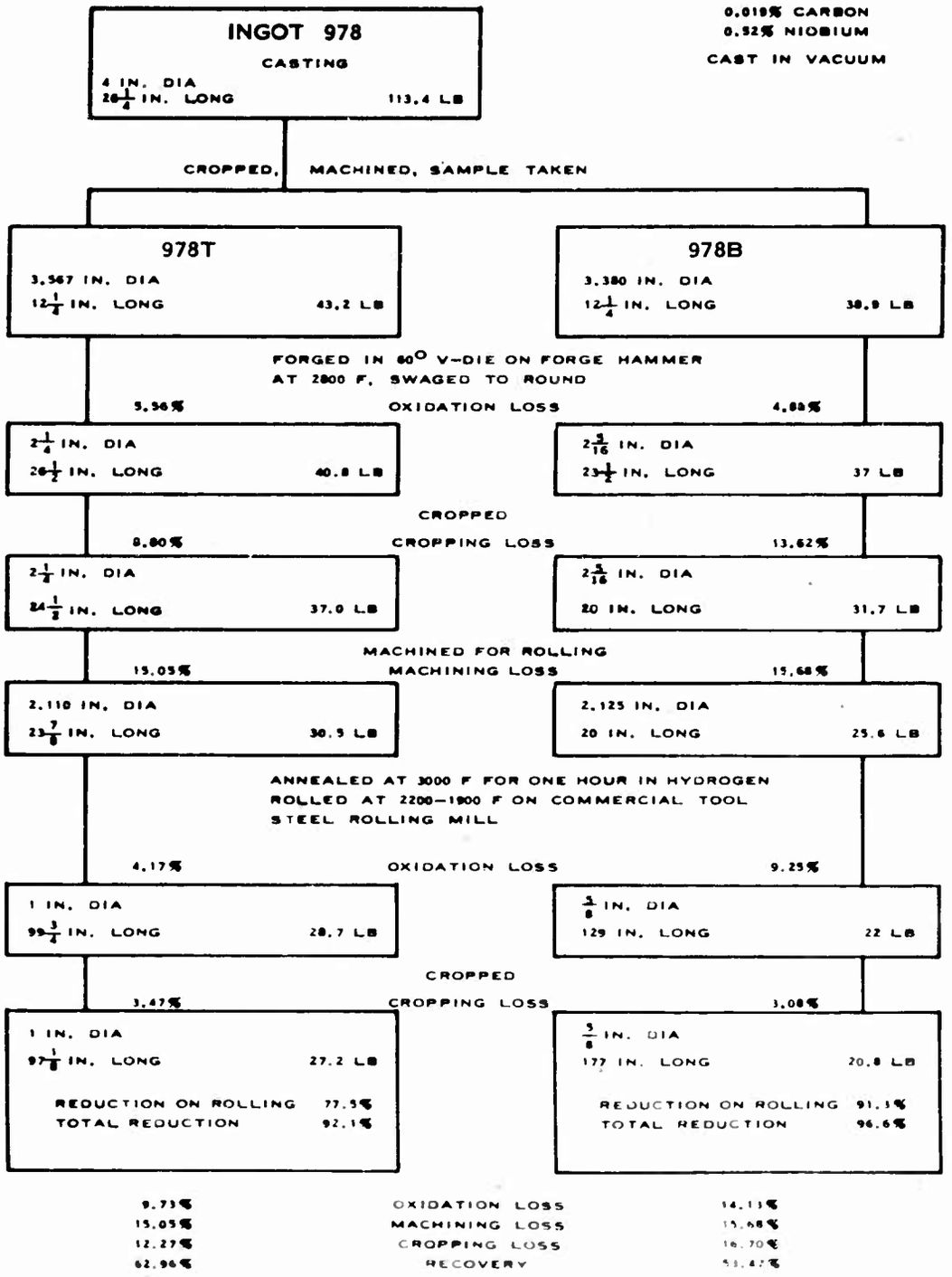


TABLE 15

FORGING AND ROLLING RECOVERY OF HEATS FOR MECHANICAL PROPERTY STUDIES

Heat No.	Alloy, %	Hardness at 1600 F DPN	Forging Temp, F	Recovery on Forging %	Diameter of Rolled Bars, in.	Total Recovery after Forging and Rolling, %
			Billets Forged on Air Hammer			
677	0.05 Co	94	2600	84.6	5/8, 7/8	78.0
652	0.14 Co	117	"	cracked		
660	0.34 Nb	82	"	87.2	5/8, 7/8	82.8
651	2.29 Ti	117	"	69.2	5/8	28.1
885	2.46 Ti	107	"	52.1	5/8, 7/8	39.3
667	0.66 V	93	"	86.5	5/8, 1-1/8	76.5
669	0.87 V	100	"	83.0	5/8, 1-1/8	68.2
653	1.22 V	105	"	67.1	1-1/8	47.0
			Press-Forged Billets			
1045*	unalloyed	77	2300	37.80	5/8	35.74
987T	0.53 Al	118	2300-2600	cracked		
987B	"	118	2600	76.95	5/8	64.61
983T	0.88 Al	139	3000	cracked		
983B	"	139	3100	cracked		
986T	0.24 Nb	61	2800	73.21	5/8	65.40
986B	"	61	2800	73.74	1	66.67
978T	0.52 Nb	77	2800	70.60	1	62.96
978B	"	77	2800	65.81	5/8	63.47
979T	0.76 Nb	76	3000	cracked		
979B	"	76	3000	cracked		
1008T	0.65 Ti		3000	cracked		
1008B	"		2600-3000	cracked		
1043B*	0.69 Ti	89	2600	54.1	5/8	47.38
1009T	1.26 Ti	96	2600	55.36	5/8	51.21
1009B	"	96	3000	cracked		
1010B	1.92 Ti**		2600	cracked		
1012T	0.56 V	84	2600	59.76	5/8	53.57
1012B	"	84	2600	58.60	1	56.64
1013T	1.14 V		2400	cracked		
1013B	"		2400	cracked		
1014B	1.39 V		2400	cracked		
1049T*	0.85 V	89	2600	67.5	5/8	64.65

* deoxidized with rare earth metals

** added

The fourth difficulty in forging resulted from the high rate of oxidation of molybdenum at the forging temperature. Even though the billets were protected by hydrogen atmosphere during heating, forging was conducted in air. There is some evidence that internal oxidation of molybdenum alloys proceeds by means of preferential grain boundary penetration. The process is accelerated by the formation of fine surface cracks during forging, and the penetration of oxide into the grain boundaries causes hot shortness.

Under these circumstances, it was found that recovery of sound forged stock in the order of 40% to 80% could be obtained from alloy ingots 3-1/2" in diameter, containing up to 0.53% aluminum, 0.52% niobium, 1.26% titanium, or 0.85% vanadium; but when higher concentrations of these alloys were subjected to hammer and press forging, recovery dropped to 30% or less.

The first forging experiments with molybdenum and its alloys were made at a time when their hardness could be measured conveniently only at temperatures up to 1600 F. An empirical relation between hardness and strength (hence resistance to deformation) of the alloys was established. This relation indicated that fair recovery on hammer forging could be attained for alloys having a hardness of 100 DPN at 1600 F if the ingots were properly deoxidized. As the hardness rose to 112 DPN at 1600 F, recovery was appreciably less, and alloys harder than 125 DPN at 1600 F cracked during attempts to forge.

Extrusion and Rolling

Extrusion of 6-1/2" Diameter Blanks. The Sejournet-Ugine extrusion process* has proved feasible for initial breakdown of large sections of vacuum-cast, unalloyed molybdenum and mild molybdenum-base alloys and has yielded substantially greater recovery of sound metal than methods previously used. Extrusion followed by rolling was used in the working of most of the ingots under this contract. The ingots, 7-1/2" to 8" in diameter, were machined to 6-1/2" diameter in preparation for extrusion at Babcock and Wilcox Company, Tubular Products Division, by the Sejournet-Ugine method.

A unique feature of this method is the use of glass as lubricant for billet and die. In the method as it was conducted at Babcock and Wilcox, the hot billets were wrapped in a fiberglass mat and extruded through a die lubricated with wads of fiberglass in a horizontal hydraulic press limited to a force of 2,400 tons. The 3-3/4" to 4-1/4" diameter dies were cleaned, sand blasted, and ground after each extrusion and re-used. The diameter of the container was 6-3/4". The force necessary for extrusion was measured with a Brush recorder connected to SR-4 strain gages mounted on the tie rods of the press.

Two pieces of equipment were available at Babcock and Wilcox for heating the molybdenum extrusion blanks, a salt bath whose maximum temperature was 2300 F and a gas-fired Selas furnace whose maximum temperature was 2600 F. The salt bath had the advantage of affording some protection against oxidation and the disadvantage of lower extrusion temperature. The higher temperature was chosen for the first extrusions. Accordingly, extrusion blanks

* U.S. Patents 2,538,917 and 2,630,220. Steel, v 130, No. 22 (1952), 92

through No. 1250 were heated to 2600 F in the gas-fired furnace. As more extrusion data were accumulated, it was found that for all practical purposes the extrusion force did not increase when the extrusion temperature was dropped to 2300 F. The total recovery on extrusion was about the same for both methods of heating but slightly in favor of the salt bath at 2300 F. Therefore, for heats of higher number than 1250, the extrusion blanks were heated to 2300 F in the salt bath, which reduced the amount of external oxidation and internal oxidation along the grain boundaries.

Extrusion data obtained in the earlier experiments on molybdenum-base alloys are presented in Table 16, and a typical flow sheet is presented in Figure 95.

The billets of the first group in Table 16 were preheated in a Salem furnace at 1600 F and then in a Selas gas-fired furnace at 2600 F. The time at 2600 F was 15 to 20 minutes. Two sheets of fiberglass were used as billet lubricant and three wads of fiberglass, three pieces of 1/8" thick plate glass, and molybdenum disulfide were used between the die and the billet.

Because of the high extrusion pressures encountered in the first group, the billets of the second group were held for 30 to 45 minutes; lower pressures were required for extrusion. As indicated in Table 16, the lubricants were different for the second group of billets. The die lubricant for the second group consisted of two wads of fiberglass and two plates 1/8" thick. One sheet of fiberglass equivalent in thickness to two of the sheets used for the first group was tried as the lubricant. This glass sheet was too heavy to be picked up easily by the billets heated to 2600 F in the gas-fired furnace. Barium chloride sprinkled on the fiberglass improved the adherence of the cold glass mat to the hot billet. The advantage of using barium chloride was apparent from the fact that the only reason for failure to extrude Billet 1147 was that inadvertently barium chloride had not been sprinkled on the fiberglass sheet. The fiberglass did not adhere to the billet, hence there was no lubrication for the billet in the attempted extrusion. A second attempt to extrude this billet failed when the billet cracked severely. Ordinarily, if a billet fails to go through the press on the first attempt--whatever the reason--microcracks arise, which are rapidly propagated upon the second attempt at extrusion. The difference in lubricating techniques between the two groups made little difference in extrusion pressure (compare the pressures for the 1.25% vanadium alloys, 1053 and 1151).

Table 17 indicates the losses sustained during processing of the 6-1/2" diameter castings by extrusion and rolling. The greatest loss occurred on initial breakdown. The loss from the first stage of working was due to the necessity of machining the surface to remove cracks prior to further working. The second large loss was due to cropping to remove end bursts--a loss that would be less, percentagewise, if longer castings were extruded.

In general, as the concentration of a given alloying element was increased, the recovery of sound, extruded stock decreased. The recovery of sound stock of molybdenum containing 0.61% aluminum, 0.11% cobalt, 0.75% niobium, 2.09% titanium, 1.25% vanadium, or 0.11% zirconium was in the order

TABLE 16

EXTRUSION DATA FOR MOLYBDENUM-BASE ALLOYS
6-1/2" Diameter Blanks

Group 1 - Billet lubricant: two sheets of fiberglass
Die lubricant: 3 wads, 3 plates, and MoS_2

Heat	Alloy Content %	Length in.	Wt. lb.	Time at 2600 F, min.	Die Dia. in.	Pressure, tons Brush Recorder Start	Brush Recorder Run	Dial Start	Dial Run
1051	0.54 V	14-1/4	172	18	4	1780	1400		
1052	1.00 V	14-3/4	175	17	4	1830	1410	1800	1400
1053	1.24 V	9	106	15	4.25	1820	1520	1800	1400
1057	0.75 Nb	15-3/8	186	15	4	1600	1580		
1058	0.49 Al	13-1/8	157	25	4.25	1120	1120	1200	1200
1062	0.11 Zr	14	169	15	4	1600	1600		
1063	0.17 Al	18-3/8	222	15	4	1220	1160		

Group 2 - Billet lubricant: one sheet of fiberglass + $BaCl_2$.
Die lubricant: 2 wads, 2 plates
Die diameter: 4"

Heat	Alloy Content %	Length in.	Wt. lb.	Time at 2600F, min. Ingot in Furnace	Time at 2600F, min. Furnace at Temp.	Pressure, tons Brush Recorder Start	Pressure, tons Brush Recorder Run	Resistance to Deformation, psi Peak	Resistance to Deformation, psi Aver.
*1059	0.81 Al	15-3/16	172	54	44	1610	1430	69,000	61,200
1132B	0.47 Ti	12-1/4	149	90	55				
1133	0.90 Ti	15	159	73	59	1670	1670	71,500	71,500
1134	1.05 Ti	15	180	30	15	2280	1750	97,500	76,500
1138	1.27 Ti	15	179	38	25	1880	1880	80,800	80,800
1143	1.66 Ti	15	182	54	42	1800	1600	77,000	68,500
1144	0.07 Co	14-7/8	182	43	27	1670	1670	71,400	71,400
1145	0.12 Co	12-1/4	150	40	27	1930	1820	85,000	80,000
1146	0.17 Co	14-3/4	182	43	29	1930	1670	82,500	71,400
1147	1.10 Nb	14-1/2	172	49	32		sticker**		
1148	1.36 Nb	14-1/4	177	49	40	1790	1680	77,200	72,500
1149	0.22 Zr	13-1/4	162	45	35	2030	2030	88,600	88,600
1150	0.43 Zr	13-1/2	167	42	32	2400+	sticker***		
1151	1.25 V	13-5/8	165	54	43	1680	1570	73,400	68,500
1152	0.10 Si	14	171	50	40	1920	1710	83,000	74,000
1154	1.25 Al	12-3/4	152	46	36	1850	1570	79,000	69,000
1155	1.10 Al	13	155	54	43	1420	1580	69,500	62,300

* billet diameter was 6-3/8" instead of 6-1/2"
** insufficient billet lubrication
*** alloy too hard at 2600 F for extrusion on this press

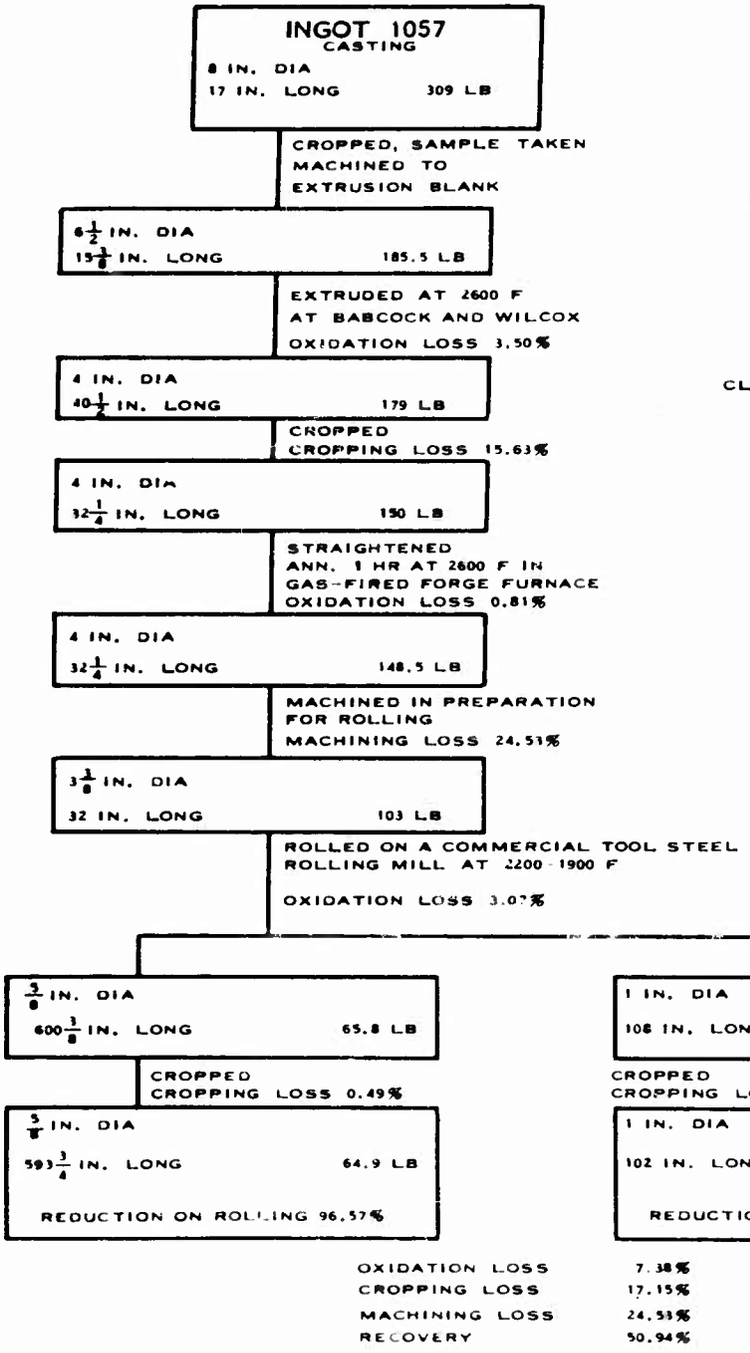


FIGURE 95

WORKING SCHEDULE
INGOT 1057

0.033% CARBON
0.75% NIOBIUM

CAST IN VACUUM

CLIMAX MOLYBDENUM CO. 265
FEBRUARY 2, 1951

TABLE 17

RECOVERY OF 6-1/2" DIAMETER EXTRUSION BLANKS ON EXTRUSION AND ROLLING

Heat No.	Alloy, %	Hardness, DPN, at 2300 F	Hardness, DPN, at 2600 F	Extrusion Temp, F	Recovery on Extrusion, %	Total Recovery on Extrusion and Rolling, %
937				2600	64.13	56.71
1159		35	25	2600	71.15	63.90
1063	0.17 Al			2600	73.36	66.39
1058	0.49 Al	47	34	2600	66.45	43.45
1059	0.81 Al			2600	56.91	cracked
1155	1.25 Al[a]			2600	cracked	
1154	1.37 Al[a]			2600	cracked	
1144	0.074 Co	48	34	2600	52.08	39.09
1145	0.123 Co			2600	cracked	
1146	0.165 Co			2600	cracked	
1153	0.044 Ni			2600	not extruded	
1057	0.75 Nb	51	40	2600	55.53	50.94
1279	1.00 Nb[a]			2300	cracked	
1147	1.10 Nb			2600	cracked[b]	
1148	1.36 Nb	59	45	2600	cracked	
1152	0.088 Si			2600	cracked	
1268	0.22 Ti			2300	33.74	26.49
1132	0.45 Ti	58	43	2600	65.23	53.15
1348	0.46 Ti	52	35	2300	63.11	47.64
1393	0.50 Ti[c]			2300	55.77	47.04
1133	0.85 Ti			2600	60.13	45.28
1134	1.05 Ti			2600	cracked	
1138	1.22 Ti			2600	64.99	50.87
1143	1.66 Ti			2500	cracked	
1281	2.09 Ti			2300	55.77	47.04
1051	0.54 V			2600	67.73	53.84
1052	1.00 V	47	35	2600	67.43	52.63
1053	1.24 V			2600	cracked	
1151	1.25 V			2600	63.45	54.12
1390	0.05 Zr	52	41	2300	62.00	49.36
1207	0.09 Zr	52	41	2600	47.11	36.17
1062	0.11 Zr			2600	51.60	cracked
1149	0.22 Zr			2600	cracked	
1150	0.43 Zr			2600	stopped press	
1217	0.11 Co 0.18 Ti	44	30	2600	45.26	29.31
1060	0.32 Nb 0.18 Ti	42	31	2600	60.21	52.53

[a] added [b] owing to lack of lubrication [c] plus 0.12% Al

TABLE 17

RECOVERY OF 6-1/2" DIAMETER EXTRUSION BLANKS ON EXTRUSION AND ROLLING

Heat No.	Alloy, %	Hardness, DPN, at 2300 F	Hardness, DPN, at 2600 F	Extrusion Temp, F	Recovery on Extrusion, %	Total Recovery on Extrusion and Rolling, %
937				2600	64.13	56.71
1159		35	25	2600	71.15	63.90
1063	0.17 Al			2600	73.36	66.39
1058	0.49 Al	47	34	2600	66.45	43.45
1059	0.81 Al			2600	56.91	cracked
1155	1.25 Al[a]			2600	cracked	
1154	1.37 Al[a]			2600	cracked	
1144	0.074 Co	48	34	2600	52.08	39.09
1145	0.123 Co			2600	cracked	
1146	0.165 Co			2600	cracked	
1153	0.044 Ni			2600	not extruded	
1057	0.75 Nb	51	40	2600	55.53	50.94
1279	1.00 Nb[a]			2300	cracked	
1147	1.10 Nb			2600	cracked[b]	
1148	1.36 Nb	59	45	2600	cracked	
1152	0.088 Si			2600	cracked	
1268	0.22 Ti			2300	33.74	26.49
1132	0.45 Ti	58	43	2600	65.23	53.15
1348	0.46 Ti	52	35	2300	63.11	47.64
1393	0.50 Ti[c]			2300	55.77	47.04
1133	0.85 Ti			2600	60.13	45.28
1134	1.05 Ti			2600	cracked	
1138	1.22 Ti			2600	64.99	50.87
1143	1.66 Ti			2600	cracked	
1281	2.09 Ti			2300	55.77	47.04
1051	0.54 V			2600	67.73	53.84
1052	1.00 V	47	35	2600	67.43	52.63
1053	1.24 V			2600	cracked	
1151	1.25 V			2600	63.45	54.12
1390	0.05 Zr	52	41	2300	62.00	49.36
1207	0.09 Zr	52	41	2600	47.11	36.17
1062	0.11 Zr			2600	51.60	cracked
1149	0.22 Zr			2600	cracked	
1150	0.43 Zr			2600	stopped press	
1217	0.11 Co 0.18 Ti	44	30	2600	45.26	29.31
1060	0.32 Nb 0.18 Ti	42	31	2600	60.21	52.53

[a]added [b]owing to lack of lubrication [c]plus 0.12% Al

of 55% after extrusion. The molybdenum-nickel alloy was not submitted for extrusion, because it was incompletely deoxidized. The molybdenum-silicon alloy cracked on extrusion. The recovery of molybdenum-titanium alloys was erratic: The 1.22% and 2.09% titanium alloys extruded well, the 1.05% and 1.66% titanium alloys cracked. The 0.43% zirconium alloy stopped the press, and failure to extrude was attributed to the high resistance of this alloy to deform at 2600 F. Apparently, the upper limit of zirconium content for satisfactory extrusion at 2600 F on the 2400-ton press is somewhat below 0.2%. For all practical purposes, the recoveries on extrusion of the 0.5% titanium alloys were the same, whether extruded at 2300 F or 2600 F.

Subsequent to the first extrusion experiments, a super hot hardness tester was designed and constructed to measure the hardness of metals at temperatures up to 3000 F. Successful operation of this unit made it possible to correlate the hardness of arc-cast alloys at temperatures used for the extrusion process, and from these empirical data a relationship between hot hardness at the extrusion temperature and the recovery of sound stock from extrusion was made. It was apparent from this correlation that the hardness of 45 DPN at 2600 F could be considered the limit for successful extrusion with the equipment employed.

The extrusions were machined to remove surface defects and annealed for one hour at 2600-2800 F before further reduction. The extrusions were rolled to 2" diameter on a hand-round, tool steel mill at Universal-Cyclops Steel Corporation. The 2" diameter billets were rolled to 1" and 5/8" diameter bars in a guide mill. For all rolling, the bars were heated in a gas-fired furnace at a temperature estimated to be 2200 F. The number of passes between reheatings depended upon the resistance of the bar to rolling and on-the-spot decisions of the operators. The average reduction by rolling for the 1" diameter bars was 92.14% and for the 5/8" diameter bars 97.78%. The loss due to rolling alone (oxidation and cracking) was about 12%. Only two bars which appeared to have extruded well failed on rolling, the 0.81% aluminum (1059) and the 0.11% zirconium (1062).

As the alloy content approaches the maximum for successful extrusion, the strain hardening developed upon subsequent rolling makes it desirable to introduce recrystallization anneals during the rolling process. It has been found that a 4" diameter extruded and recrystallized billet of unalloyed molybdenum can be rolled to 5/8" diameter without additional recrystallization annealing; undoubtedly, partial recrystallization occurs on reheating during rolling. The partial recrystallization serves to reduce the amount of strain hardening and permits additional deformation. For alloyed molybdenum, however, the amount of recrystallization that occurs during reheating is insufficient and a full recrystallization anneal is desirable at about 2" diameter before continuing rolling to 5/8" diameter. In the early fabrication of the alloys the intermediate recrystallization anneal was not used, but in later portions of the program it aided in rolling and led to greater recovery of sound stock on rolling.

Extrusion of 4" Diameter Blanks. During the course of the investigation, it became possible to reduce the cost of the experiments by starting with a smaller extrusion blank. Babcock and Wilcox Company equipped their extrusion press with a 4-1/4" diameter container. A mold for producing 4" diameter extrusion blanks was not immediately available; therefore, the first three castings were made in a 6" diameter mold. Subsequent castings were made in a 5" diameter mold, and all were machined to extrusion blanks 4.030" in diameter by 9-5/8" long. Since this series was to be the first attempt at extruding molybdenum-base alloys in the new container, four pilot castings of unalloyed molybdenum were extruded to provide experience in the use of the new container and in handling the smaller billets. The extrusion blanks were heated to 2300°F in a salt bath and extruded through 2-1/4" diameter dies. A schedule typical of this group of extrusions is shown in Figure 96; the extrusion data are presented in Table 18.

The high resistance to deformation of two of the billets of unalloyed molybdenum (1387, 1460) was attributed to a time-delay mechanism governing the motion of the ram. (This mechanism is used in the extrusion of certain materials to allow time for melting of the lubricant.) For the remainder of the extrusions, the time-delay circuit was eliminated and in each subsequent push the motion of the ram was uninterrupted. The deformation pressure dropped accordingly (see Heats 1467 and 1468). The 0.1% silicon alloy (1466) stopped the press, probably because of too short a soaking time before extrusion. It was removed from the press, machined, and re-extruded. During extrusion of the Mo-Co-Zr billet (1454), the pressure rose continually and finally stopped the press when the billet had gone through half way. The Mo-Al-Co billet (1435) stopped the press. The remainder of the billets were extruded to 2-1/4" diameter by 31" long. They were cropped to remove end bursts.

All of the alloys extruded from 4" diameter to 2-1/4" diameter were worked further by rolling to 1/2" diameter. The minimum length of billet acceptable for rolling at Universal-Cyclops Steel Corporation, where the rolling was conducted, was about 18". The cropping necessary to remove cracked metal from a few of the extrusions reduced the length of sound stock well below 18". The short bars were lengthened by forging on a press with a 90°-V, bottom die and a flat, top die. None of the bars were forged to less than 1-1/4" diameter. The Mo-Fe (1464) and Mo-Al-Zr (1437) alloys appeared to be sound when cropped after extrusion, but they cracked during subsequent rolling. It is believed that failure during rolling was not attributable to the rolling process per se, but rather to incomplete removal of cracks after the primary working by extrusion.

The recoveries on extrusion and rolling listed in Table 18 should be qualified, for two reasons: first, the 4" diameter extrusion blanks required a change in tools and equipment for extrusion, and some of these modifications were used for the first time in the Babcock and Wilcox press when the alloys of Table 18 were extruded; second, the alloys of this group were prepared and processed for the first time. In general, however, the alloys exhibiting no oxide phase on the fracture surfaces and having elevated-temperature strength near that of unalloyed molybdenum yielded the best recovery in the form of bar stock.

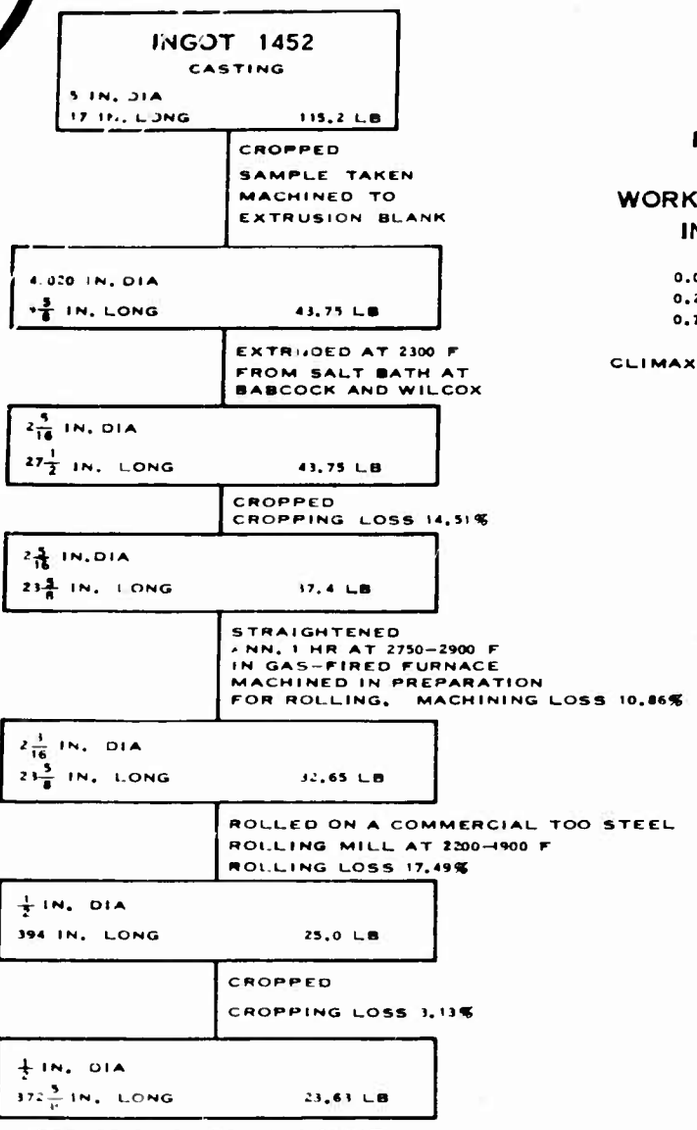


FIGURE 96

WORKING SCHEDULE
INGOT 1452

0.030% CARBON
0.22% TITANIUM
0.75% VANADIUM

CLIMAX MOLYBDENUM CO. 885
JUNE 29, 1955

LOSS ON EXTRUSION	25.17%
LOSS ON ROLLING	20.62%
RECOVERY	54.01%

TABLE 18

RECOVERY OF 4" DIAMETER EXTRUSION BLANKS ON EXTRUSION AND ROLLING

Heat No.	Mold Dia, in.	Additions, % Carbon	Additions, % Other	Chemical Analysis, % Carbon	Chemical Analysis, % Other	Length of Billet, in.	Time at Temp, min.	Force, tons	Resistance to Deformation, psi maximum	Resistance to Deformation, psi average	Recovery, % Extrusion* to 2-1/4" dia	Recovery, % Rolling to 1/2" dia
1387		unalloyed molybdenum				5-7/8	50	810-800	82000	81000		
1460		"		"		8-3/4	60	940-850	90000	81000		
1467		"		"		8-3/4	90	560-605	53900	58000		
1468		"		"		8-3/4	75	665-665	63500	63500		
1463	5	0.048	0.65 Cr	0.033	0.11 Cr	9-5/8	140	810-760	76000	71500	76.8	62.02
1464	5	0.039	0.25 Fe	0.026	0.09 Fe	"	60	680-640	64000	60000	78.89	0
1465	5	0.039	0.15 Ni	0.021	0.05 Ni	"	150	830-810	78000	76000	60.89	43.76
1466	5	0.044	0.10 Si	-	-	"	35	1000	---sticker----		0	0
				re-extrusion		"	75	760	72000	72000	0	
1435	6	-	0.28 Al 0.06 Co	-	-	"	110	--------sticker---------			0	-
1436	6	-	0.53 Al 0.50 V	0.005	0.42 Al 0.51 V	"	105	715-690	67000	64500	21.89	8.62
1437	6	-	0.53 Al 0.06 Zr	0.003	0.42 Al 0.06 Zr	"	120	750	70000	70000	10.33	0
1451	5	0.034	0.50 Nb 0.50 Ti	0.014	0.43 Ti 0.50 Nb	"	100	665-620	62500	58000	35.73	27.93
1452	5	0.039	0.25 Ti 0.75 V	0.030	0.22 Ti 0.75 V	"	115	760-720	71500	67500	72.55	52.51
1453	5	0.034	0.25 Ti 0.06 Zr	0.024	0.22 Ti 0.07 Zr	"	130	-------unrecorded-------			10.44	8.04
1454	5	0.039	0.12 Co 0.06 Zr	0.025	0.06 Co 0.07 Zr	"	60	780-1000	part sticker		22.44	18.04
1455	5	0.039	0.12 Co 0.50 V	0.025	0.06 Co 0.47 V	"	90	710-620	66500	58000	72.44	54.24
1456	5	0.038	0.50 Nb 0.06 Zr			"	75	500	51500	51500	18.00	14.29
1457	5	0.038	0.50 Nb 0.50 V	0.024	0.46 Nb 0.48 V	"	65	640-610	60000	67000	67.11	44.02
1458	5	0.038	0.50 V 0.06 Zr	-	-	"	65	700-665	66000	62500	0	-

* Prior to rolling, all specimens on which recovery is less than 50% were lengthened by forging.

To investigate the extrusion of smaller castings, several 1-1/4" diameter blanks were machined from 4" diameter castings and extruded on a full eccentric, 750-ton, crank-type press designed for valve extrusion, at Thompson Products Company, Tapco Division. Glass lubrication was used on both billet and die--for the billet, a fiberglass blanket 1/4" x 3-1/4" x 10", and for the die, a disk of plate glass 1/8" thick x 1-1/4" diameter with two wads of fiberglass cemented to each side with sodium silicate. The blanks were heated in a Globar furnace in argon to a maximum of 2650 F.

Four heats of higher alloy content than could be extruded from the 6-1/2" diameter extrusion blank on the 2,500-ton press at Babcock and Wilcox were included in this group: 0.19% cobalt (1173), 3.59% titanium (1174), 1.46% vanadium (1175), and 1.43% aluminum (1176). In addition, two alloys were included for comparison of deoxidation practice and variation in rolling schedule: 0.31% niobium (1082) and 0.31% niobium, 0.16% titanium (1001). These last had been extruded previously at Babcock and Wilcox. Blanks 1-1/4" in diameter were machined directly from the Babcock and Wilcox extrusion of Ingot 1001, whereas the extrusion from Ingot 1082 was rolled to 1-1/4" diameter.

The ingot containing 1.43% aluminum was extruded, but the extrusion had a poor surface and some surface cracks. The other alloys extruded at Thompson Products Company were sound. To obtain more suitable stock for testing and to work the metal further, the bars extruded at Thompson Products were rolled at 2450 F to 1/2" diameter at the University of Michigan on a slow-speed, two-high rolling mill with square, oval, and round passes. The distance between the rolls could be varied, and rolling was more like hand-round than guide-mill rolling. A gas-fired furnace was used for heating the work to the rolling temperature. In these operations each bar was given two passes per heat; the reduction per heat was considerably less in these experimental operations than in the commercial rolling at Universal-Cyclops.

The critical step in the production of wrought molybdenum is the primary breakdown of the cast structure. Once this difficulty is surmounted, subsequent deformation by rolling or forging is accomplished without appreciable loss of material. Arc-cast molybdenum alloy ingots are initially worked with maximum recovery by the Sejournet-Ugine extrusion process. Press forging may be successful for the lean alloys, but extrusion is regarded as preferable for the initial working of all arc castings.

The maximum amounts of alloying elements in binary molybdenum-base alloys that have been extruded successfully from 6-1/2" diameter blanks, using extrusion temperatures of 2300-2600 F with Babcock and Wilcox equipment, are as follows: 0.81% aluminum, 0.11% cobalt, 0.75% niobium, 2.09% titanium, 1.25% vanadium, and 0.11% zirconium. Molybdenum-base alloys of higher alloy content have been worked, but only on a laboratory scale. The maximum alloy content for ternary molybdenum-base alloys has not been fully established. Qualitatively, as-cast hardness serves as an indication of the possibility of extruding castings 4" to 6-1/2" in diameter. On the whole, alloys not exceeding a hardness of 45 DPN at 2600 F have been extruded successfully at 2600 F. At 2300 F the critical hardness is about 55 DPN. As the alloy content increases, to facilitate further deformation, it becomes desirable to eliminate the strain hardening incurred by extrusion by recrystallization annealing after extrusion and at intermediate stages of the rolling process.

True Hot Working of Molybdenum

The objective of this program was true hot working of arc-cast molybdenum in an inert atmosphere, in such a way that no residual strain-hardening could be developed from the working process. It has been experienced with other metallic materials that true hot working is accomplished at temperatures in the vicinity of 80% to 90% of the melting point. On this basis it was estimated that the required working temperature for molybdenum and its alloys would be about 4000 F. Two experiments were conducted, in which attempts were made to forge 2-1/2" diameter arc-cast molybdenum ingots on a 600-ton hydraulic press enclosed in a cover made from translucent vinyl plastic sheet. The ingots were heated in an induction furnace also in the enclosure.

In the first experiment, an enclosure was constructed around the hydraulic press, of sufficient size and shape to accommodate the operator. Figure 97 illustrates the general layout of the equipment used for this test. The operator, wearing a self-contained breathing apparatus, was admitted by means of a double-sealed access port. The port was constructed of the same material as the enclosure proper, and the atmosphere seals were provided by a lining of sponge rubber 4" wide x 1/2" thick, as illustrated. In the second experiment, the enclosure was constructed along the lines sketched in Figure 98. The plastic sheet was sealed to the upper and lower platens of the press, with sleeves and gloves set into the front to permit manipulation from the outside. Aluminum foil was placed within the enclosure to protect the plastic sheet from direct radiation from the ingot.

Neither of the experiments was successful, owing, it was believed, to several causes. First, the size and shape of the enclosures, especially in the initial attempt, were not conducive to thorough outgassing and permitted various degrees of atmosphere contamination. Second, although a very low contamination level was obtained in the second experiment, degassing of the internal components of the system occurred upon introduction of the heated ingot. Finally, the 4-mil plastic sheet used in the canopies had insufficient toughness for such an application.

Failures of the ingots subjected to forging in these two experiments were intergranular and usually took place during the initial application of force. The mechanism governing the failures appears to be one of grain boundary oxidation. This premise requires the supposition that the atmosphere within the enclosure (even under optimum conditions whereby MoO_3 was not formed on a heated molybdenum wire probe) contained sufficient oxygen to form some lower oxide, such as MoO_2, on the surface of the ingot. It is then reasonable to assume that after the surface layer is converted to MoO_2, molecular oxygen is available to diffuse into the ingot, reacting as it diffuses inward to form MoO_2. Diffusion rates are known to be many times greater along grain boundaries than through grains, owing to the high concentration of lattice imperfections at the boundaries. Oxygen therefore diffuses rapidly along the grain boundaries, effectively enveloping each grain with MoO_2. When the polycrystalline system is then subjected to stress in the pressing operation, intergranular failure results from the low strength of the oxide envelope.

Figure 99 is a photomicrograph of an unetched area near the surface of an ingot forged in the initial experiment. The dark specks in this field represent an oxide of molybdenum. The oxide particles are highly concentrated at the grain boundaries and to a lesser degree within the grains. This condition was encountered in various degrees in all of the ingots forged by this scheme.

Two related factors are believed to have contributed to forging failures encountered here as compared to the normal practice of forging in air. First, the temperature of the ingot was higher in these tests; accordingly, the solubility and diffusion rate of oxygen were greater than those encountered in normal practice. Secondly, in air, loss of metal due to volatilization of surface layers probably took place more rapidly than the inward diffusion of oxygen, resulting in an effectively lower concentration of oxygen in subsurface layers than obtained upon heating in a less active atmosphere.

A more detailed account of this program may be found in the 4th Quarterly Report - 5th Year, June 1 to September 30, 1954, prepared under this contract.

Recrystallization

Since the wrought molybdenum-base alloys of this investigation are of the substitutional, solid solution type, the principal methods of altering their mechanical properties are through the mechanisms of strain hardening and recrystallization. Recrystallization temperature is, of course, dependent upon degree of strain hardening.

Much of the current interest in molybdenum and its alloys concerns applications at elevated temperature, in the range at which strain hardened unalloyed molybdenum will recrystallize. One of the principal objectives of the solid solution alloying of molybdenum is to raise the recrystallization temperature of the strain hardened metal, so that the mechanical properties developed by strain hardening may be used at elevated temperatures. To establish the effectiveness of the various alloying elements, the alloys were hot cold-worked a given amount and then the recrystallization temperature was determined. To apply a molybdenum-base alloy to a part designed to operate at a given elevated temperature, it is necessary to balance the amounts of strain hardening required to develop high temperature tensile properties with the minimum temperature at which the strain hardened material will recrystallize. It is therefore of primary concern to the investigator of molybdenum-base alloys to determine the relationships between the recrystallization tendencies and the amount of strain hardening and mechanical properties developed. Secondly, during the course of this program, considerable effort has been expended in determining the effects of annealing treatments upon the microstructure and hardness of wrought molybdenum and its alloys.

CLIMAX MOLYBDENUM CO. 648
SEPTEMBER 3, 1954

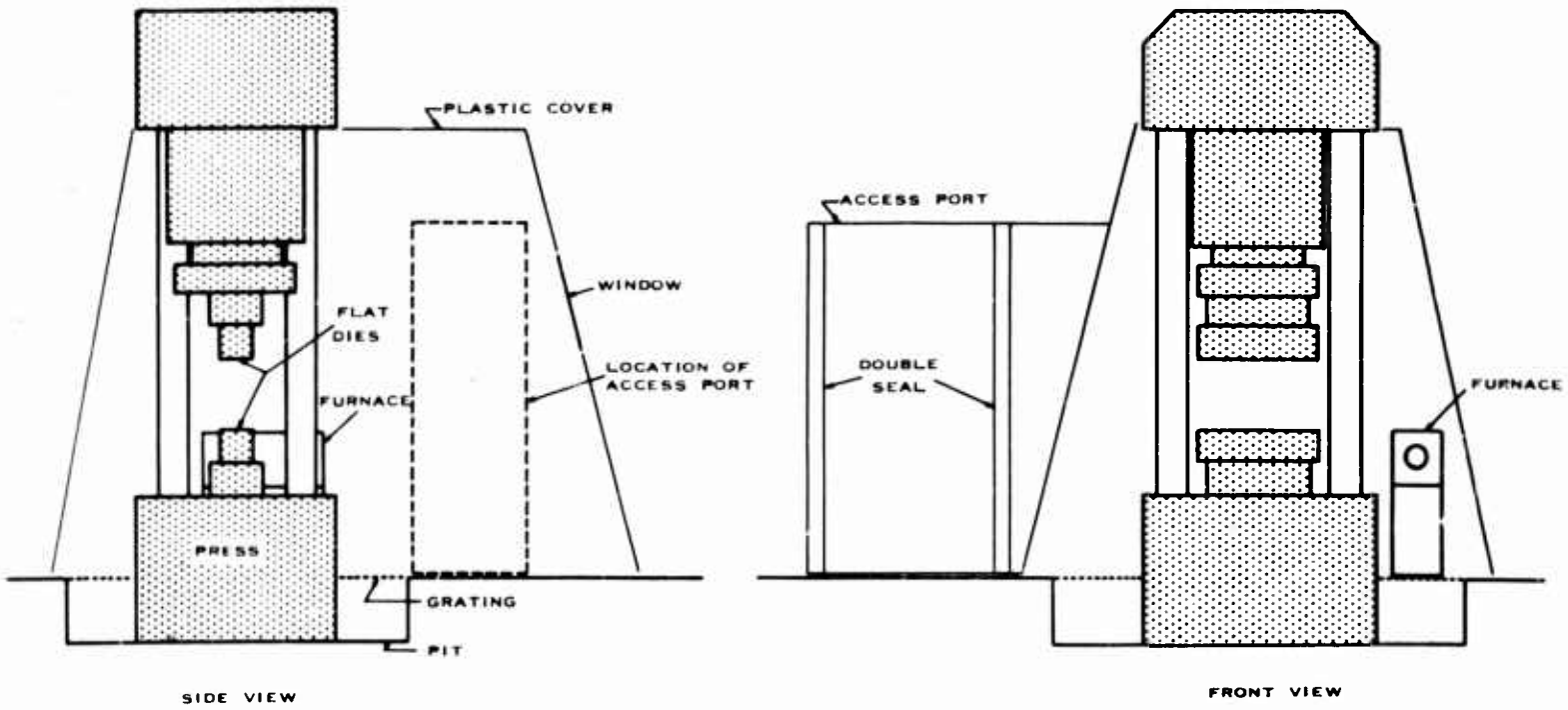


FIGURE 97 – ENCLOSURE COVERING PRESS AND FURNACE IN INITIAL FULL-SCALE ATTEMPT AT WORKING MOLYBDENUM UNDER AN INERT ATMOSPHERE

CLIMAX MOLYBDENUM CO. 661
SEPTEMBER 11, 1954

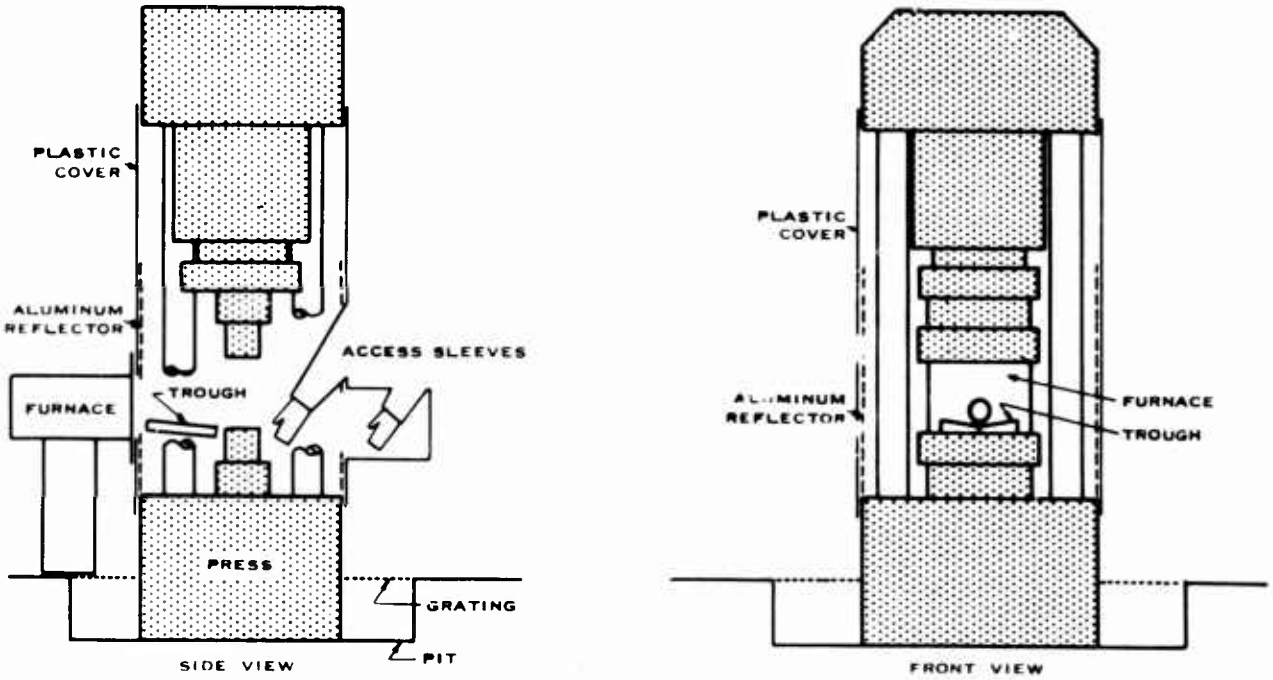


FIGURE 98 — ENCLOSURE COVERING PRESS AND FURNACE IN SECOND FULL-SCALE ATTEMPT AT WORKING MOLYBDENUM UNDER AN INERT ATMOSPHERE

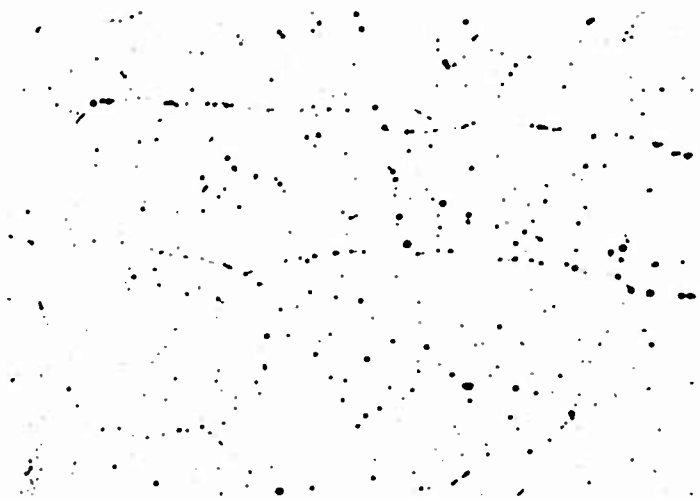


FIGURE 99 — AREA NEAR THE SURFACE OF INGOT 977
0.025% CARBON, 0.25% NIOBIUM, AS FORGED,
UNETCHED. ELECTROLYTIC POLISH, X1000
(M4142)

Molybdenum and molybdenum-base alloys recrystallize in the classical manner*, that is, by means of recovery, primary recrystallization, grain growth, and, under proper conditions, secondary recrystallization. The following experiments were performed to determine the changes in structure of strain hardened molybdenum upon heating. A selected area on a sample of hot cold-worked molybdenum was examined after various heat treatments in a protective atmosphere. Inasmuch as the annealing treatments were carried out in a reducing atmosphere of purified hydrogen, the oxide produced by etching was removed, and it was necessary to re-etch (but not to repolish) the surface under study after each heat treatment. By this method, the changes that occurred in specific types of structures could be closely scrutinized, and some insight into the recrystallization process could be obtained.

Figure 100 is a photomicrograph at 1000 diameters of a 5/8" diameter rolled bar of molybdenum containing 0.015% carbon (937) and is typical of hot rolled bars of molybdenum and molybdenum-base alloys. The elongation of the original grains and intragranular fragmentation are typical of molybdenum that has not sustained extreme cold work, that is, where cold work was conducted at sufficiently elevated temperature or where the amount of plastic deformation was low.

Figure 101 shows the structure of the same bar (but not the same area) after an anneal of one hour at 2000 F. Several nearly equiaxed, recrystallized grains formed and the subgrain boundaries became more distinct. The sharpening of subgrain boundaries was the result of heat treatment in the temperature range where recovery takes place. The subgrains evident in Figure 101 and in subsequent photomicrographs are thought to be representative of the reorientation-domain type of structure.

Figures 102-111 reveal the same area after the indicated periods of exposure at 2100 F in an atmosphere of purified hydrogen. The formation of a stress-free grain at a reorientation-domain boundary may be observed in the area marked "1" on the photomicrographs. After one hour at 2000 F, Figure 101, area "1" appears only as a reorientation-domain boundary somewhat more distinct than most of its neighbors. The area was not materially altered by heating 10 or 20 minutes at 2100 F (Figures 102-103) but after a total exposure of 60 minutes the boundary was noticeably broadened. Repolishing the specimen, removing a minimum of surface, revealed that a clear-etching grain had formed in this area. Subsequent heating of the specimen caused the newly formed grain to grow to the size shown in Figure 107.

Figures 101-107 illustrate the continual shifting and change in shape of the grain marked "2" with increasing time at temperature, although recrystallization was not complete. Figures 108-111 illustrate additional changes in Grain 2 after recrystallization in the immediate area was complete. The behavior of Grain 2 in these photomicrographs is illustrative of several principles concerning grain growth**:

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* "ASM Handbook", American Society for Metals, 1948, p 259

** "Progress in Metal Physics", Bruce Chalmers, editor, Interscience Publishers, Inc., New York, vol 3 (1952) 266, 274

1. Grain growth occurs by grain boundary migration, not by coalescence of adjacent grains.

2. A curved boundary migrates toward its center of curvature.

3. Grain boundary migration may be retarded by inclusions or voids.

4. Where grain boundaries meet at angles different from 120°, the grain included by the more acute angle will be consumed, so that all angles approach 120°.

The validity of the grain boundary migration theory is confirmed in Figure 110, where the shadows (lines remaining from previous etchings of the sample) clearly indicate the migration of the boundary. The shadows in this case also illustrate the movement of curved grain boundaries toward their centers of curvature. The retardation of grain boundary migration is evident in Figures 102-106. In Figure 102, a small spherical void is observed just below Grain 2. The boundary of this grain migrated until, after 40 minutes at 2100 F, it touched the void (Figure 104). In subsequent heatings, the boundary curved around the void, suggesting that the void retarded migration.

In Figure 108 the angle formed by the boundaries at the upper left of Grain 2 is less than 120°. Migration upon subsequent heatings seems to confirm the theory that grains of this geometry tend to be consumed during grain growth.

To show the process of recrystallization in a less severely worked sample, a second series of photomicrographs was made (Figures 112-114). The sample used for this series was a completed stress-rupture specimen from the same heat of unalloyed molybdenum (937). The stress-rupture specimen was fully recrystallized before testing and sustained a load of 22,300 psi for two hours when tested at 1600 F. The amount of work hardening in this specimen was maximum at the location of the fracture and gradually decreased as the distance from the fracture increased, until it was essentially nil in the threaded portion. Figure 112 is a photomicrograph of the specimen after stress-rupture testing and shows the strain hardened structure. There is no evidence of recrystallization. The shapes of the grains and appearance of the network within the grains changed as the specimen was heated for one hour at 2200 F (Figure 113) and 2300 F (Figure 114). High energy areas, and hence the first evidences of recrystallization, would be expected at intersections of the original grain boundaries. Several such areas, marked "X" in the large grain of Figure 112, are sites of new grains after an anneal of one hour at 2000 F. Annealing for one hour at 2300 F (Figure 114) resulted in growth of the new grains and a sharper delineation of the subgrain structure. Annealing for one hour at 2400 F produced virtually complete recrystallization and a large, yet heterogeneous, grain size in the structure under observation. The coarse grains of the recrystallized structure are undoubtedly associated with the low level of cold work at this position on the stress-rupture specimen.



FIG 100 — AS ROLLED, ELECTROPOLISHED (M2825)



FIG 101 — ANNEALED 1 HR AT 2000 F, ELECTROPOLISHED (M2859)

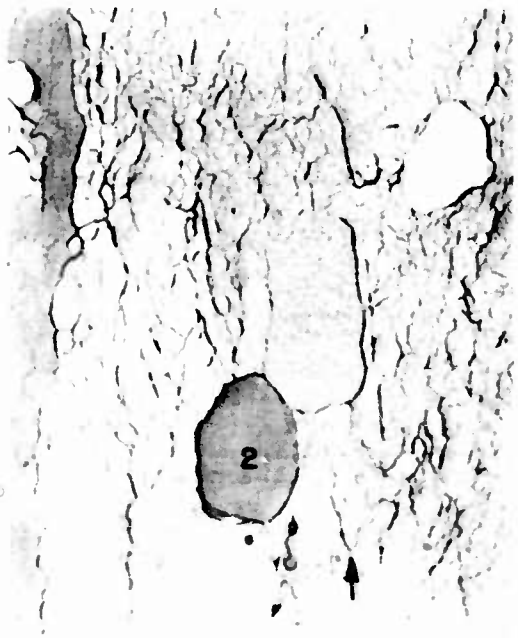


FIG 102 — ANNEALED 1 HR AT 2000 F + 10 MIN. AT 2100 F (M2860)

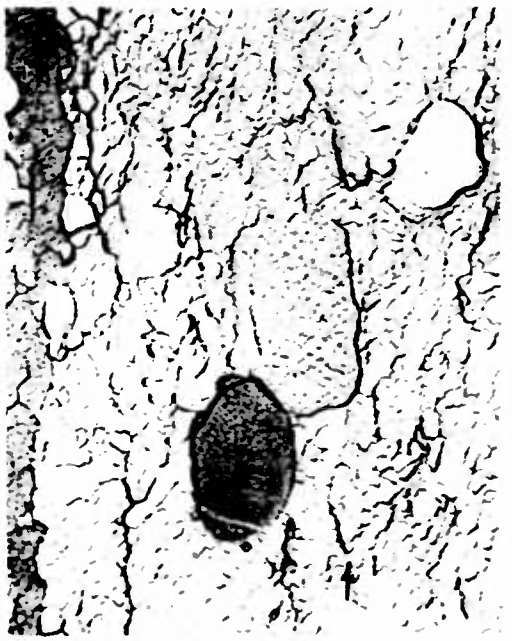


FIG 103 — ANNEALED 1 HR AT 2000 F + 20 MIN. AT 2100 F (M2864)

PROGRESS OF RECRYSTALLIZATION IN UNALLOYED MOLYBDENUM

HEAT 937, 0.013% CARBON, 5/8 IN. DIA ROLLED BAR, ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION, X1000



FIG 104 — ANNEALED 1 HR AT 2000 F + 40 MIN. AT 2100 F (M2873)



FIG 105 — ANNEALED 1 HR AT 2000 F + 60 MIN. AT 2100 F (M2875)



FIG 106 — ANNEALED 1 HR AT 2000 F + 100 MIN. AT 2100 F (M2877)



FIG 107 — ANNEALED 1 HR AT 2000 F + 100 MIN. AT 2100 F, REPOLISHED 15 SEC. AND ETCHED (M2878)

PROGRESS OF RECRYSTALLIZATION IN UNALLOYED MOLYBDENUM

(CONTINUED)

ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION, X1000



FIG 108 — ANNEALED 1 HR AT 2000 F + 160 MIN. AT 2100 F (M2879)

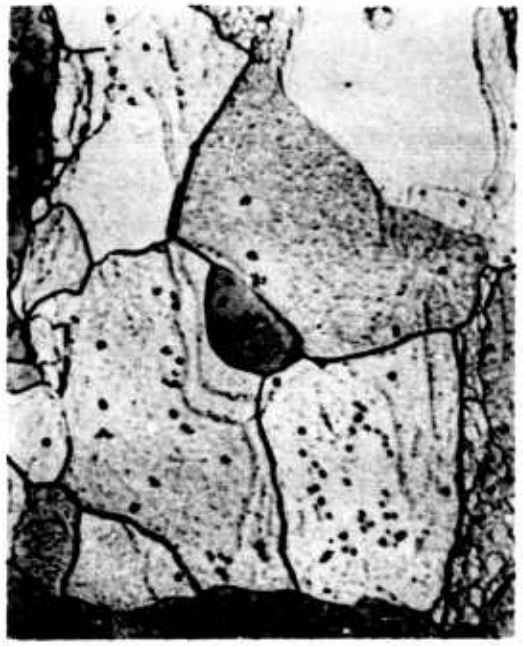


FIG 109 — ANNEALED 1 HR AT 2000 F + 250 MIN. AT 2100 F (M2890)



FIG 110 — ANNEALED 1 HR AT 2000 F + 370 MIN. AT 2100 F (M2968)



FIG 111 — ANNEALED 1 HR AT 2000 F + 370 MIN. AT 2100 F, REPOLISHED 15 SEC. AND ETCHED (M2969)

PROGRESS OF RECRYSTALLIZATION IN UNALLOYED MOLYBDENUM

(CONTINUED)

ETCHED IN SODIUM HYDROXIDE - POTASSIUM FERRICYANIDE SOLUTION, X1000



FIG 112 — AS TESTED IN STRESS RUPTURE, ELECTROPOLISHED (M3199)



FIG 113 — ANNEALED 1 HR AT 2200 F AFTER STRESS-RUPTURE TEST (M3201)



FIG 114 — ANNEALED 1 HR AT 2300 F AFTER STRESS-RUPTURE TEST (M3202)

RECRYSTALLIZATION OF STRESS-RUPTURE SPECIMEN 937

RUPTURE IN 2 HR AT 1600 F AND 22,300 PSI, ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE SOLUTION, X1000

The transition from a strain-hardened structure to a stress-free, fully recrystallized structure is qualitatively similar for unalloyed molybdenum and for molybdenum-base alloys containing aluminum, chromium, cobalt, nickel, niobium, or vanadium, in the concentrations studied. Wrought molybdenum-base alloys containing titanium or zirconium undergo similar changes, but a difference is observed in the appearance of recrystallized grains.

The structural changes with increasing temperature of samples representative of the two groups are illustrated in Figures 115-116, showing the effect of annealing treatment on hardness and microstructure of 5/8" rounds of unalloyed molybdenum (937) and the 0.45% titanium binary alloy (1132).

The structure of unalloyed molybdenum as rolled (Figure 115) changed only a minor degree upon heating to 1800 F. Several minute, stress-free, recrystallized grains appeared after one hour at 1900 F, and several large recrystallized grains appeared after treatment at 2000 F; but the major portion of the microstructure still consisted of worked grains, and the hardness was still relatively high. After one hour at 2100 F, the hardness had dropped significantly and the structure consisted predominantly of recrystallized grains with only a trace of worked structure remaining. Complete recrystallization, as evidenced by work-free, equiaxed grains, was accomplished by annealing for one hour at 2150 F.

The 0.45% titanium alloy (Figure 116) was more highly fragmented and higher in hardness in the worked condition than the unalloyed molybdenum described above. The structure of this alloy was unchanged by heating for one hour at temperatures below 2200 F. A small number of stress-free grains were in evidence after heating to 2200 F; but after heating to 2300 F for one hour, only remnants of the worked structure were observed and the specimen had reached nearly minimum hardness at room temperature. Heating for one hour at 2400 F produced virtually complete recrystallization, although close scrutiny of the microstructure revealed very minute amounts of strain hardened structure. Complete freedom from strain hardening was obtained by treatment at 2450 F. The difference in appearance of fully recrystallized specimens of the two materials is apparent in the illustrations. Recrystallized grains of unalloyed molybdenum are equiaxed; those of the molybdenum-titanium alloy tend to be rectangular, with the longer axes aligned parallel to the direction of working.

In considering the effects of various alloying elements on the recrystallization temperature of wrought molybdenum, one limitation must be recognized. As noted in the previous section, processing from casting to wrought product was by necessity conducted almost entirely by outside agencies. Consequently, precise control could not be exercised over factors such as finishing temperature, number of heatings, and number of passes per heating--factors of extreme importance from the standpoint of the amount of strain hardening, and thus the recrystallization temperature, of the product.

Unless otherwise specified, the bars under study were rolled at 2200 F from recrystallized extrusions approximately 3-1/2" in diameter to the finished size, the reduction of area after recrystallization treatment varying from 95% to 89.6%. The diameters of the finished bars were 1/2", 5/8", 7/8", 1", and 1-1/8".

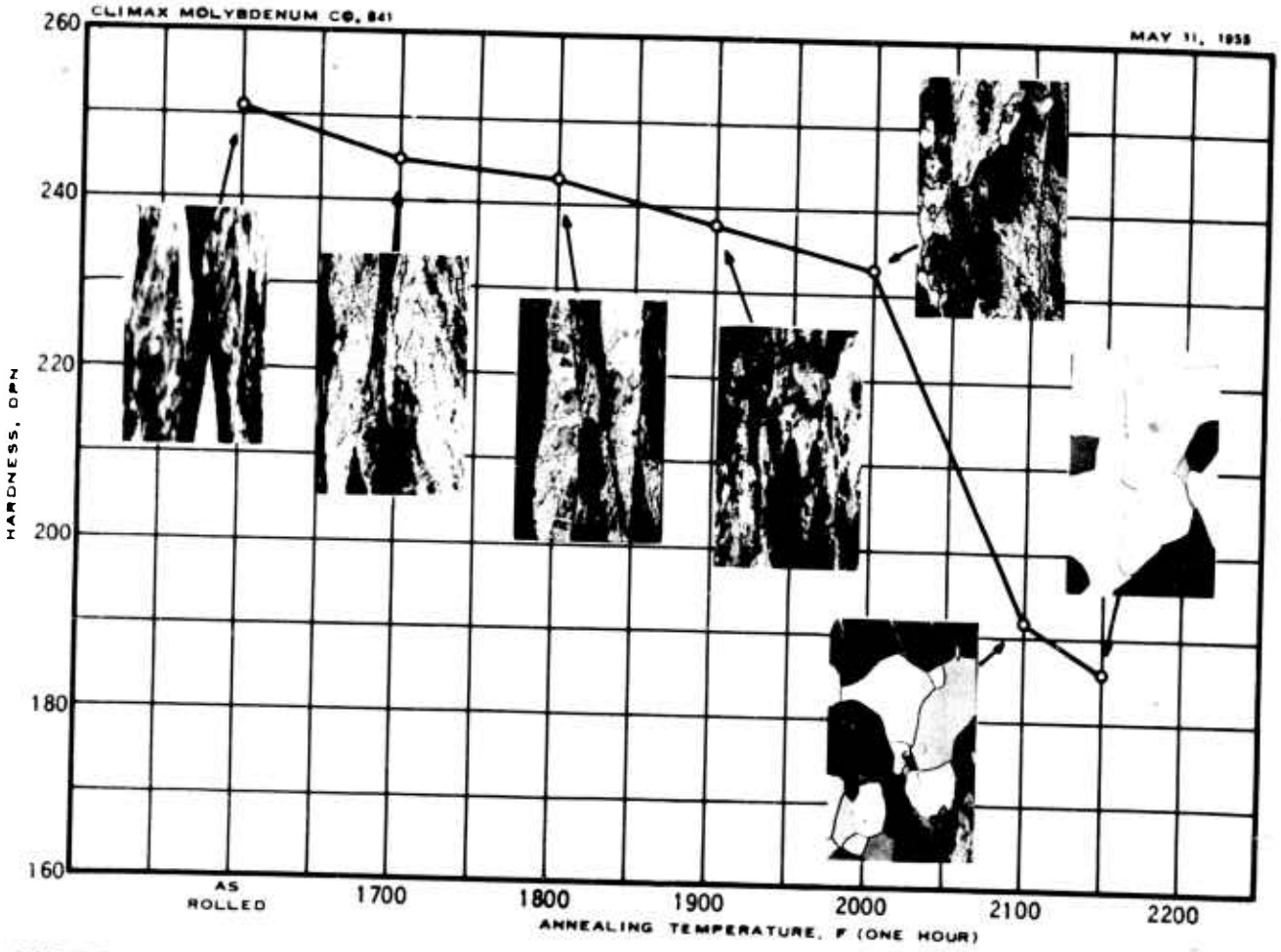


FIGURE 115 – EFFECT OF ANNEALING TEMPERATURE ON THE HARDNESS AND MICROSTRUCTURE OF UNALLOYED MOLYBDENUM, HEAT 937 (0.015% C)

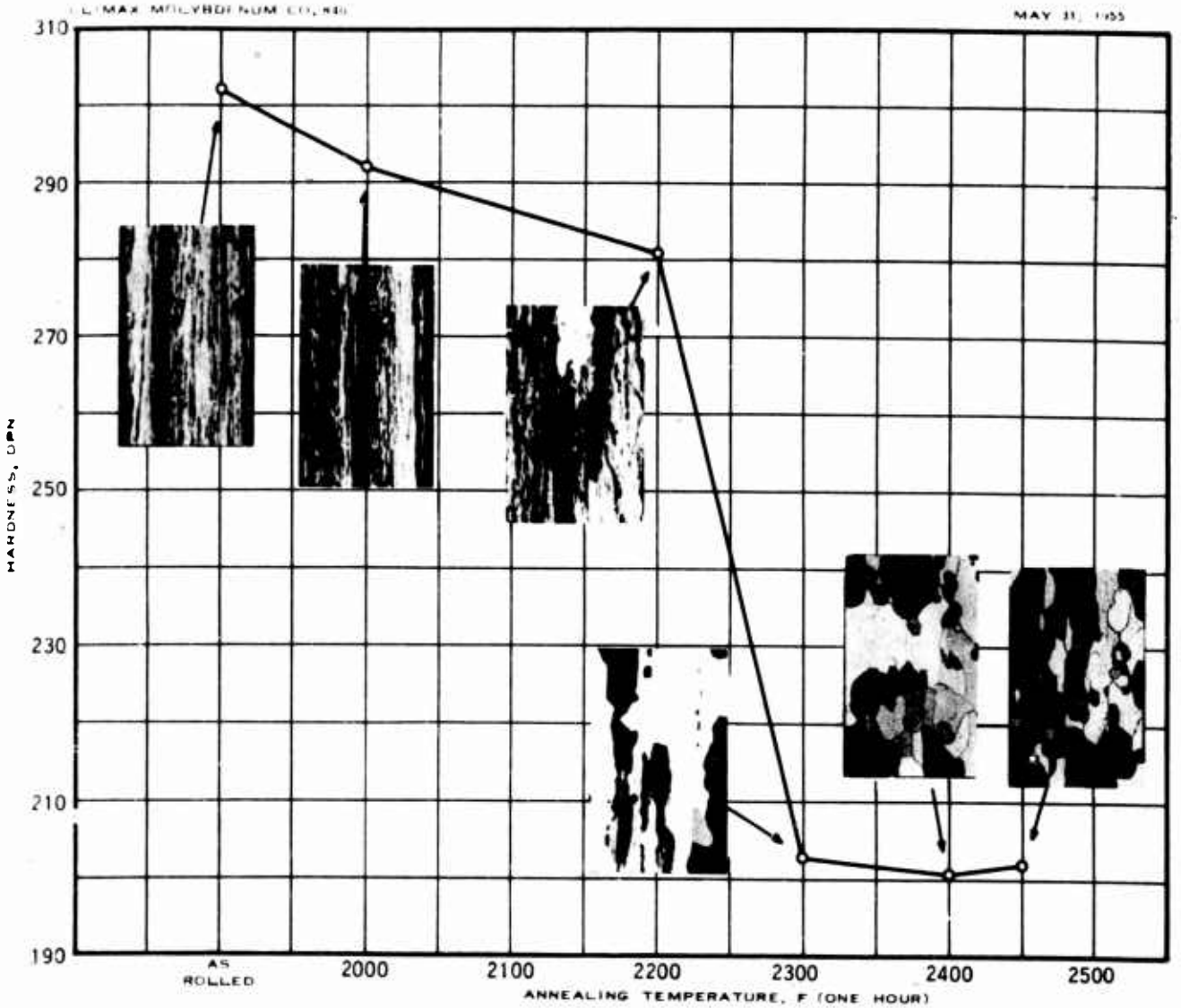


FIGURE 116 – EFFECT OF ANNEALING TEMPERATURE ON THE HARDNESS AND MICROSTRUCTURE OF 0.45% TITANIUM – MOLYBDENUM, HEAT 1132 (0.024% C)

Inasmuch as variations in the degree of strain hardening existed from heat to heat, it was necessary to observe the changes in microstructure and hardness of each material as a function of annealing temperature. Small samples of the material under study were heat treated for one hour at various temperatures in an atmosphere of tank hydrogen. The minimum temperature (to the nearest 50 F) required to produce a completely strain-free, recrystallized structure was determined by metallographic examination of the heat-treated samples. To correlate the change in microstructure with mechanical properties, Vickers hardnesses at room temperature (10-kilogram load) of all the treated samples were determined.

The effect of alloying elements upon recrystallization temperature is summarized for the binary alloys in Figures 117-118, in which the temperature for complete recrystallization in one hour is plotted as a function of percent of alloying element. The recrystallization temperatures of the individual alloys are listed in Table 19. The changes in room-temperature hardness as a function of temperature are plotted in Figures 119-124. The terminal points of these curves indicate complete recrystallization as determined metallographically. The percent recrystallization as a function of annealing temperature is plotted in Figures 125-129. In these curves, for the few cases where partial recrystallization was observed in the as-rolled condition, the plot origin indicates the amount of recrystallization present.

The 1/2" diameter bars of nine heats (672, 1001, 1080, 1082, 1100, 1137, 1173, 1174, and 1175) listed in Table 19 were rolled at 2450 F at the University of Michigan from 3/4" diameter extrusions and sustained 33% reduction on rolling. The remainder of the bars were rolled at approximately 2200-1900 F at Universal-Cyclops from extrusions 3" to 4" in diameter. The lower amount of reduction on rolling and the higher rolling temperature employed for the 1/2" diameter bars resulted in recrystallization temperatures higher than those of other bars of comparable alloy contents. The 7/8", 1", and 1-1/8" diameter bars sustained less reduction on rolling than the 5/8" bars and consequently had higher recrystallization temperatures. The increase in recrystallization temperature was erratic, being only 50 F for some of the bars and as much as 400 F for others. This undoubtedly reflects the variation in processing which was difficult to control.

Study of Figures 119-124 shows that some of the bars attained minimum hardness at temperatures significantly below that required for complete recrystallization (compare the 0.50% Ti, 0.12% Al alloy, 5/8" dia, Bar 1393, with the 0.54% V alloy, 1" dia, Bar 1051; Figures 121 and 123). Structurally, the materials behaving in this way attained a high degree of recrystallization after treatment at relatively low temperature, but higher temperatures were required to remove the last remnants of worked structure. This condition appears in the tabulated data as a wide spread between the temperatures corresponding to 95% and 100% recrystallization, and appears in the plots of percent recrystallization vs annealing temperature as a relatively gradual approach to 100% recrystallization with increasing annealing temperature. This condition is thought to be significant in that materials behaving in this way should exhibit nearly minimum mechanical properties after exposure to temperatures much

TABLE 19

RECRYSTALLIZATION TEMPERATURES FOR MOLYBDENUM AND MOLYBDENUM-BASE ALLOY BARS OF INDICATED SIZES

Heat	Analysis, %	Temperature, F, for Indicated Amount of Recrystallization in One Hour					
		1/2" Dia		5/8" Dia		1" Dia	
		Recrystallized		Recrystallized		Recrystallized	
		95%	100%	95%	100%	95%	100%
936	0.008 C			2000	2100		
937	0.015 C			2110	2150		
1159	0.040 C					2160	2200
1045	0.005 Ce, 0.007 rare earth			2350	2400		
1252	0.15 Al			2100	2150		
1063	0.17 Al			2100	2200	2140	2250
1058	0.49 Al			2120	2150	2220	2300
987	0.53 Al			2140	2200		
1463	0.11 Cr	1970	2000				
677	0.05 Co			2100	2150	2120	2150 (7/8" D)
1144	0.074 Co			1970	2000	2050	2150
1173	0.19 Co	2020	2100				
1465	0.05 Ni	1850	1950				
988	0.24 Nb			2100	2200	2400	2500
1082	0.31 Nb	2270	2300				
660	0.34 Nb			2100	2150	2130	2150 (7/8" D)
978	0.52 Nb			2120	2200	2400	2450
1057	0.75 Nb			2170	2250	2220	2300
1100	0.21 Ti	2570	2700				
1268	0.22 Ti			2250	2350		
1137	0.44 Ti, 0.23 Al	2520	2700				
1132	0.45 Ti			2400	2450	2400	2600
1348	0.46 Ti			2360	2450		
1393	0.50 Ti, 0.12 Al			2200	2450		
1048	0.69 Ti, 0.12 rare earth			2400	2500		
1133	0.85 Ti			2360	2500	2450	2650
1138	1.22 Ti			2280	2500	2400	2600
1009	1.26 Ti			2600	2900		
1080	1.41 Ti	2700	2800				
1281	2.09 Ti			2510	2750		
651	2.29 Ti			2700	2800		
885	2.46 Ti			2510	2700	2660	2800 (7/8" D)
887	2.66 Ti					2860	3000 (1 1/8" D)
1174	3.59 Ti	2800	3000				

TABLE 19 (CONTINUED)

Heat	Analysis, %	Temperature, F, for Indicated Amount of Recrystallization in One Hour					
		1/2" Dia		5/8" Dia		1" Dia	
		Recrystallized		Recrystallized		Recrystallized	
		95%	100%	95%	100%	95%	100%
1051	0.54 V			2050	2100	2200	2500
1012	0.56 V			2100	2150	2120	2200
667	0.66 V			2130	2150	2230	2250 ($1\frac{1}{8}$" D)
1049	0.85 V, 0.003 Ce, 0.003 rare earth			2410	2500		
669	0.87 V			2250	2300	2350	2400 ($1\frac{1}{8}$" D)
672	0.88 V	2400	2500				
1052	1.00 V			2110	2150	2250	2350
1151	1.25 V			2160	2200	2500	2600
1175	1.46 V	2500	2600				
1390	0.054 Zr			2400	2450		
1207	0.09 Zr			2580	2750	2750	2900
1436	0.42 Al, 0.51 V	2130	2200				
1217	0.11 Co, 0.18 Ti			2030	2100		
1455	0.06 Co, 0.47 V	1970	2000				
1454	0.06 Co, 0.07 Zr	2360	2500				
1001	0.31 Nb, 0.16 Ti	2650	2700				
1060	0.32 Nb, 0.18 Ti			2370	2450		
1451	0.50 Nb, 0.43 Ti	2360	2550				
1457	0.46 Nb, 0.48 V	2180	2300				
1456	0.50 Nb*, 0.06 Zr*	2430	2500				
1452	0.22 Ti, 0.75 V	2260	2350				
1453	0.22 Ti, 0.08 Zr	2460	2500				

* NOMINAL

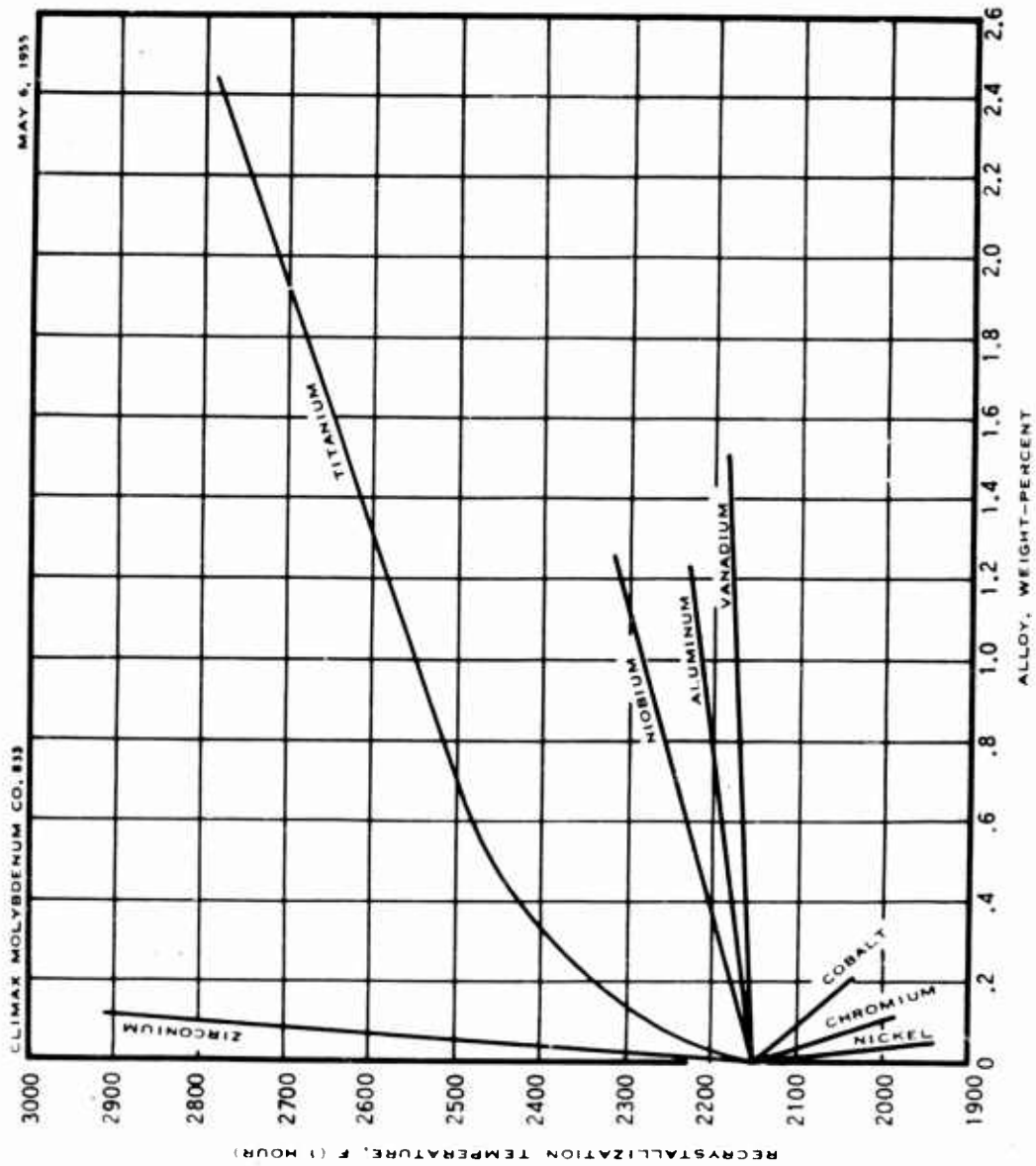


FIGURE 117— EFFECT OF ALLOY CONTENT UPON THE RECRYSTALLIZATION TEMPERATURE OF WROUGHT MOLYBDENUM ($\frac{1}{2}$" AND $\frac{5}{8}$" ROLLED ROUNDS)

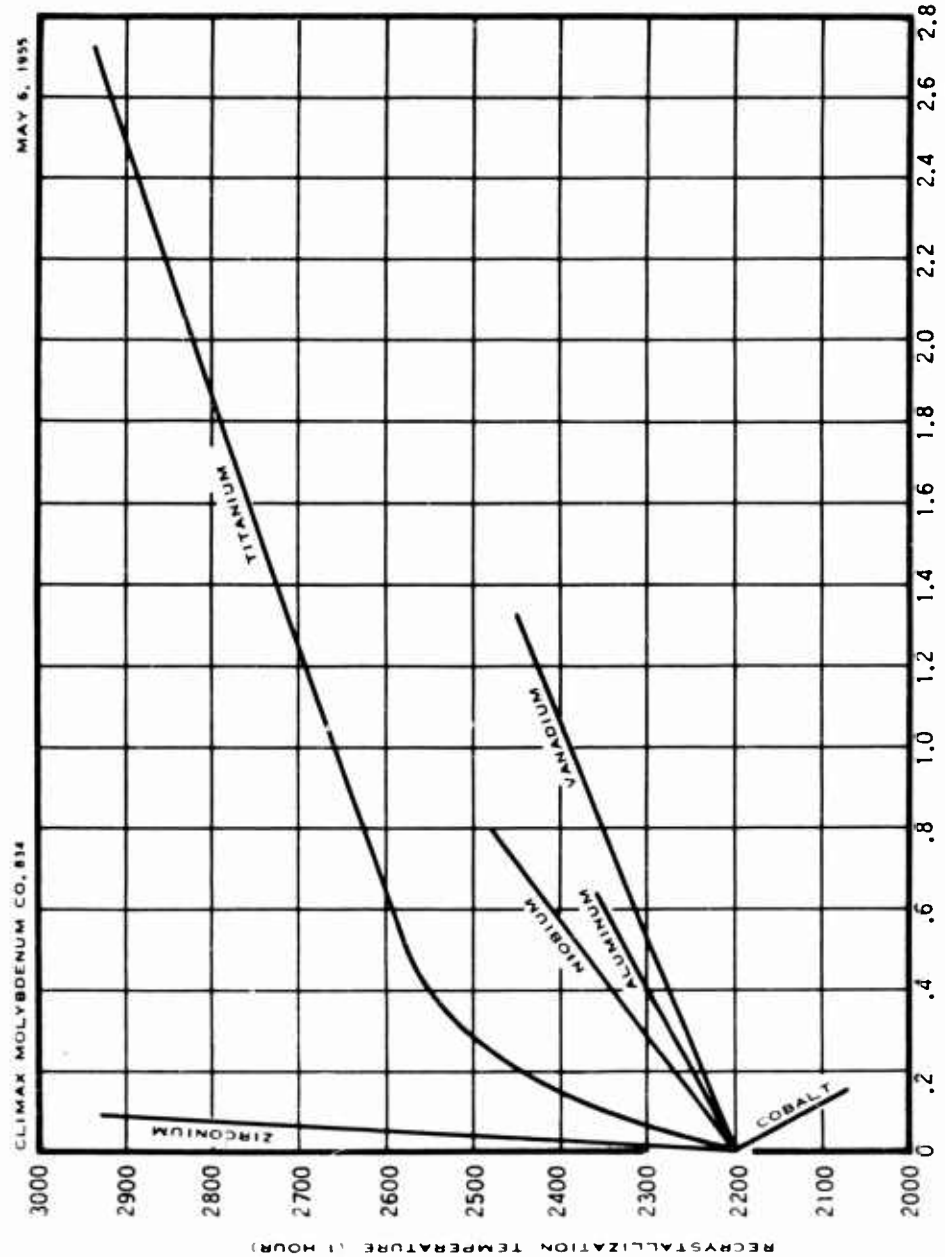


FIGURE 118 – EFFECT OF ALLOY CONTENT UPON THE RECRYSTALLIZATION TEMPERATURE OF WROUGHT MOLYBDENUM ($\frac{7}{8}$", 1", AND $1\frac{1}{8}$" ROLLED ROUNDS)

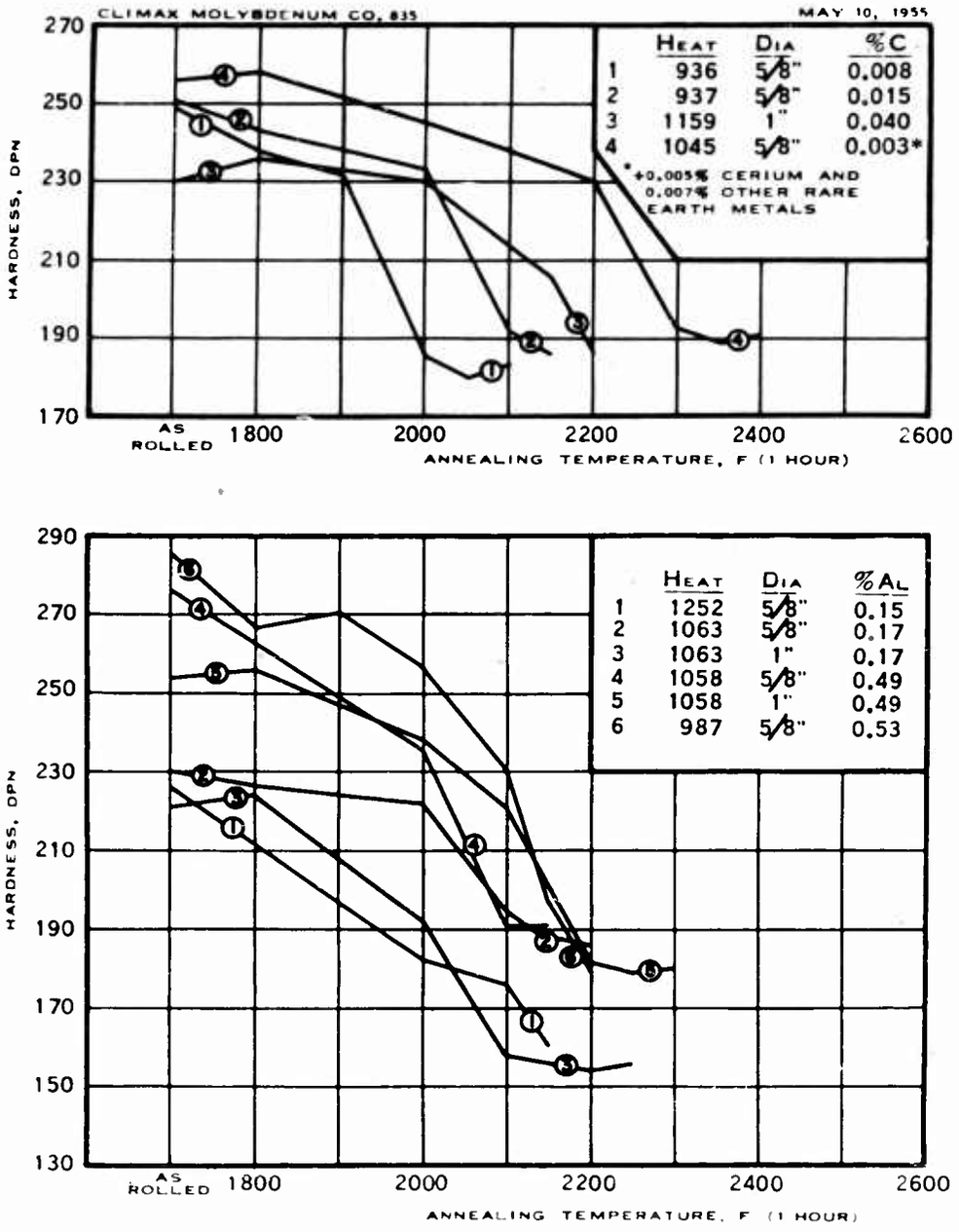
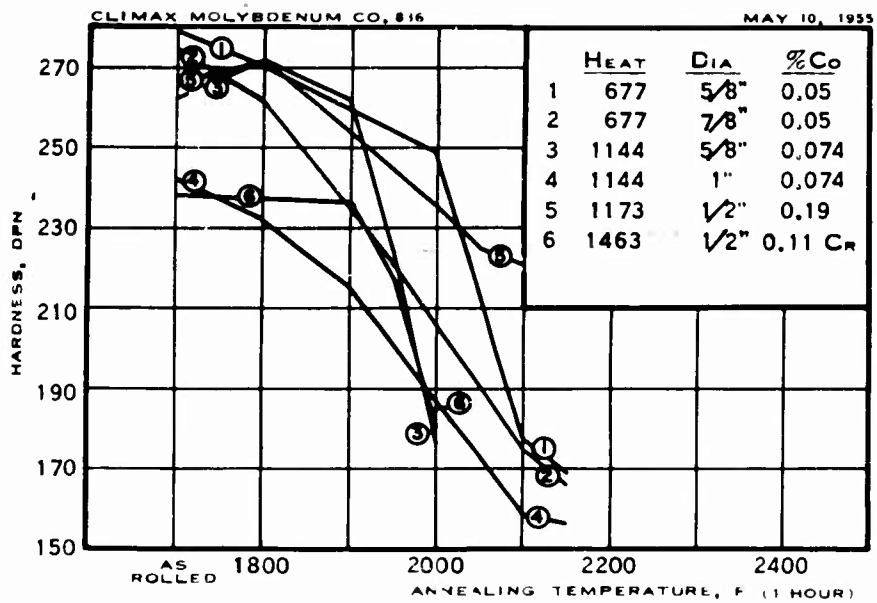


FIGURE 119 — HARDNESS AT ROOM TEMPERATURE VS. ANNEALING TEMPERATURE FOR INDICATED MOLYBDENUM AND MOLYBDENUM—BASE ALLOY BARS



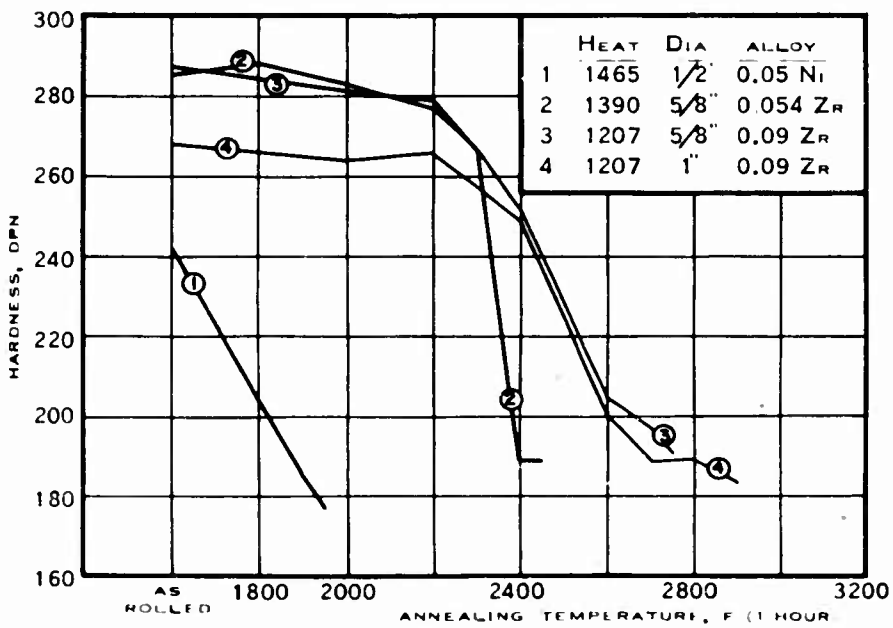
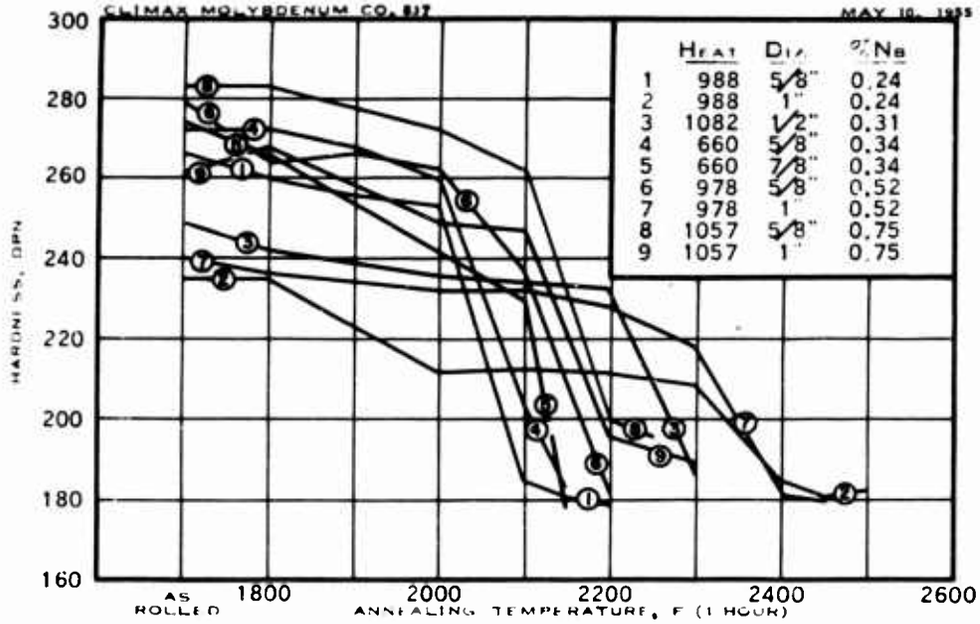


FIGURE 120 - HARDNESS AT ROOM TEMPERATURE VS. ANNEALING TEMPERATURE FOR INDICATED BINARY MOLYBDENUM BASE ALLOYS



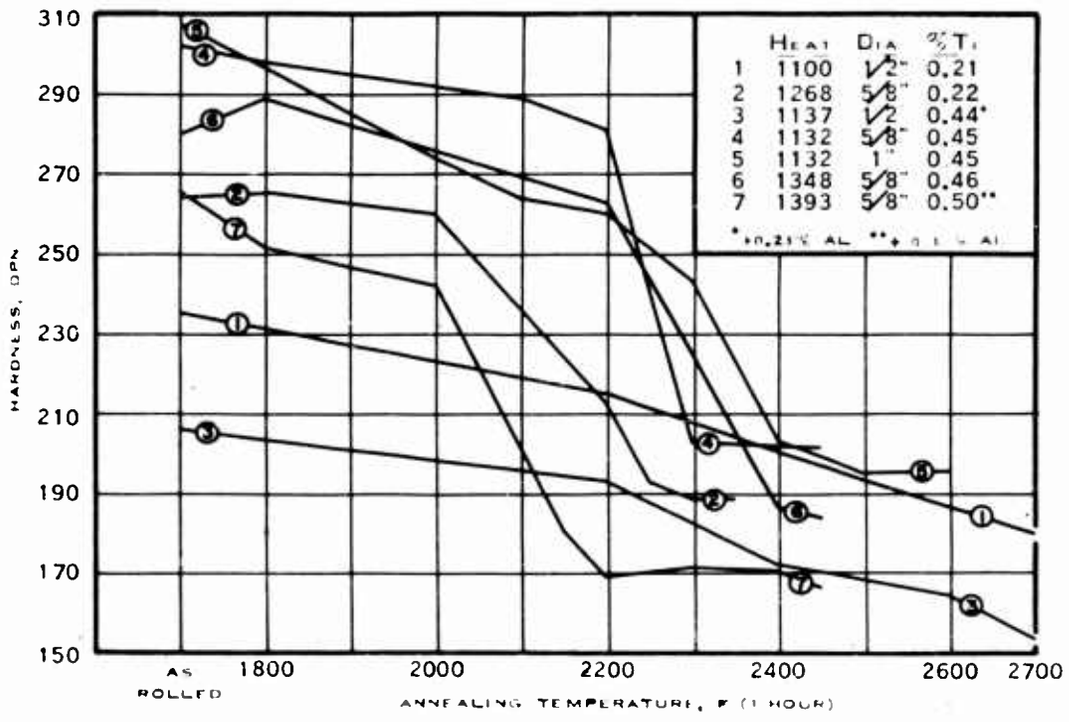


FIGURE 121 — HARDNESS AT ROOM TEMPERATURE VS. ANNEALING TEMPERATURE FOR INDICATED MOLYBDENUM - NIOBIUM AND MOLYBDENUM — TITANIUM ALLOY BARS

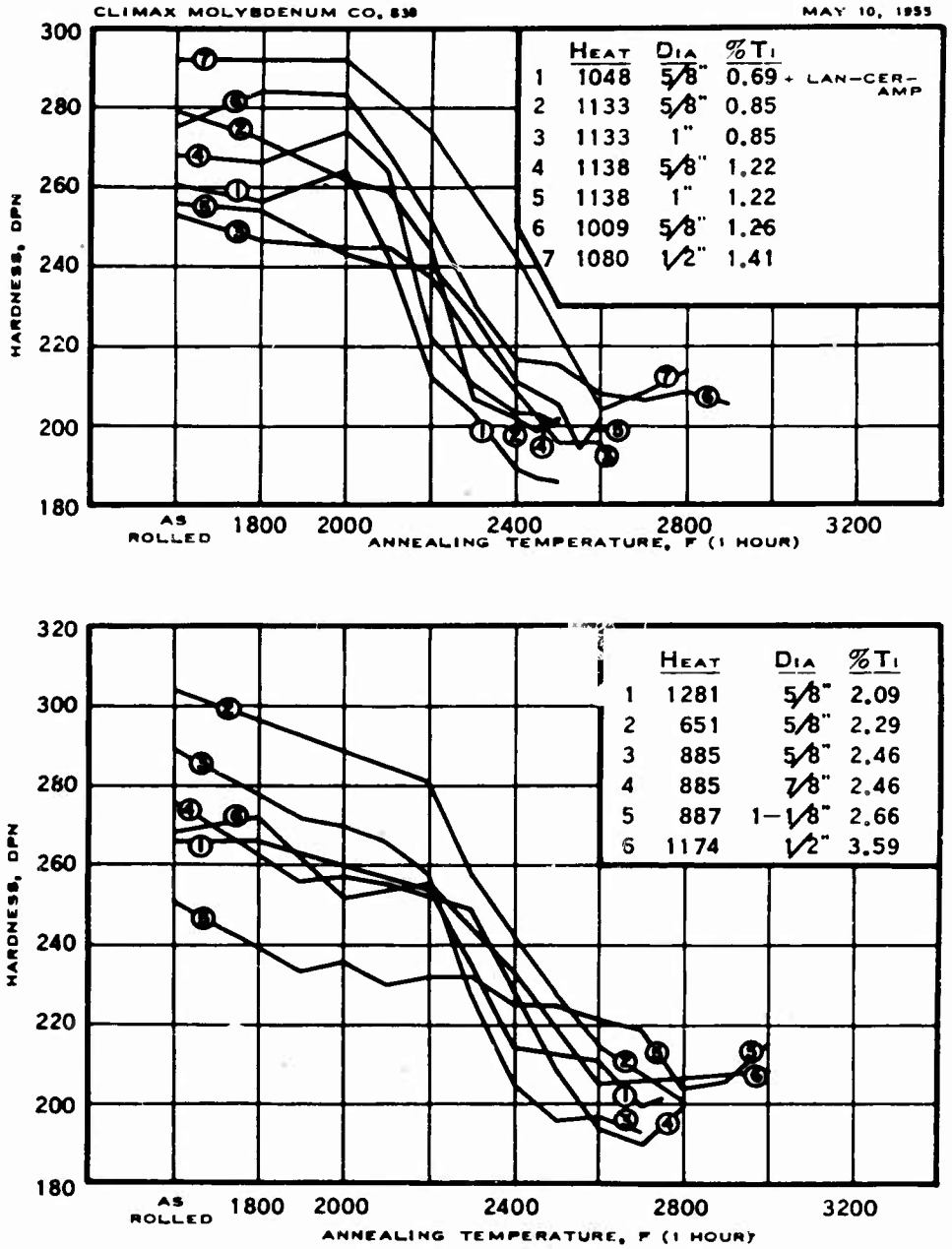


FIGURE 122 — HARDNESS AT ROOM TEMPERATURE VS. ANNEALING TEMPERATURE FOR INDICATED MOLYBDENUM—TITANIUM ALLOY BARS

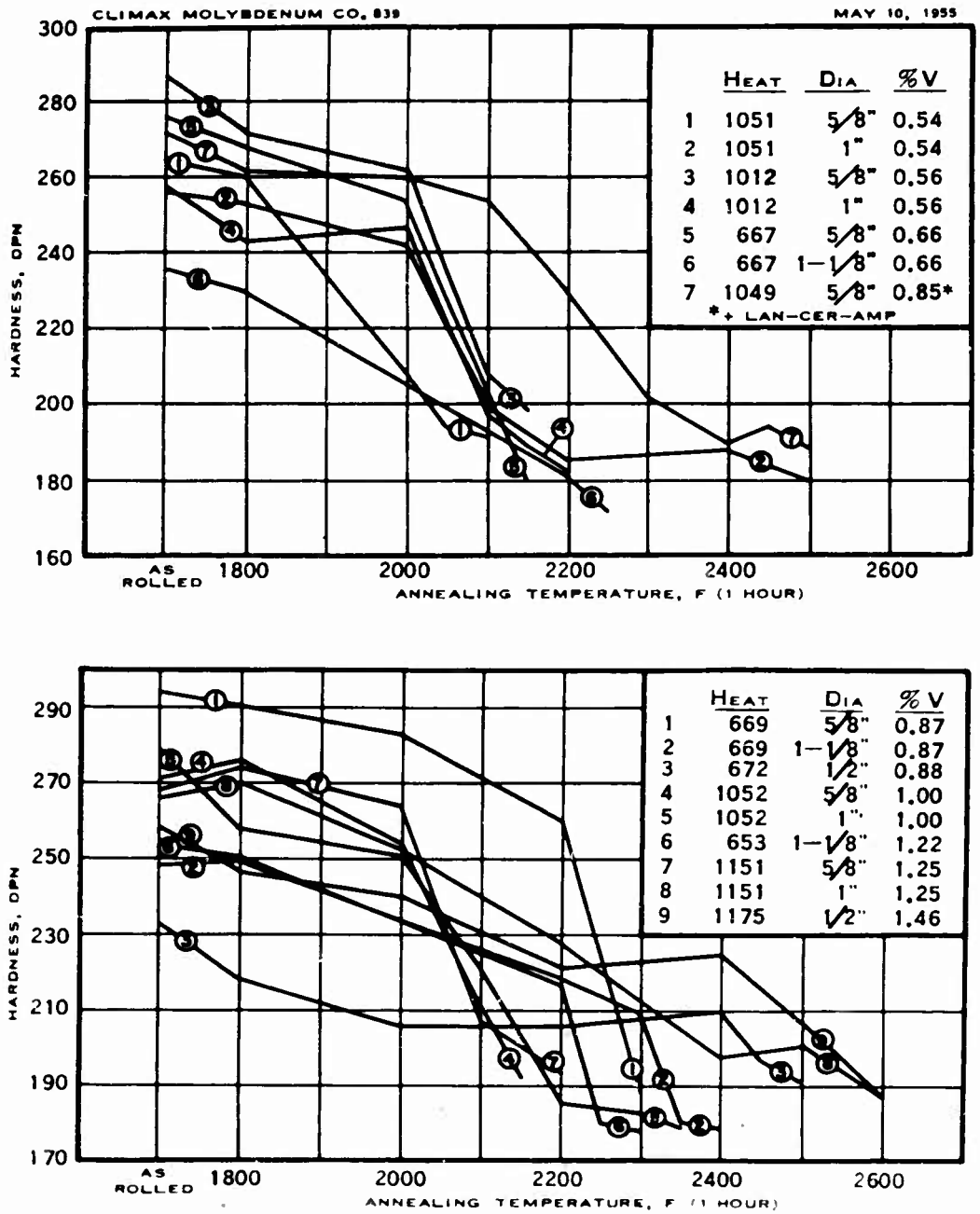
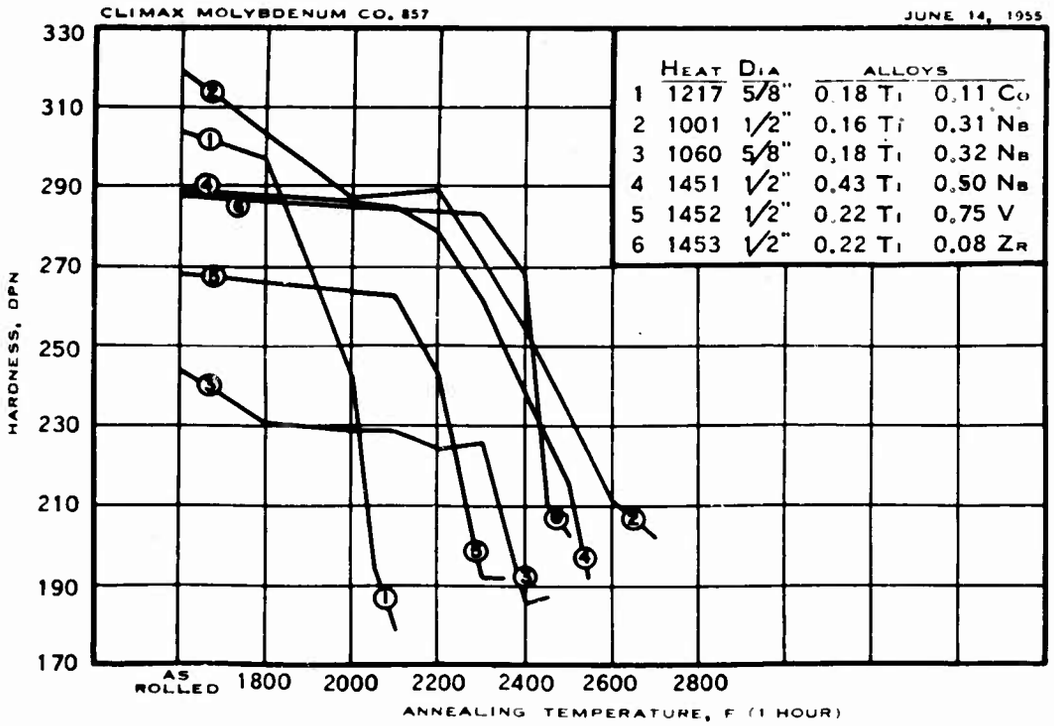


FIGURE 123 — HARDNESS AT ROOM TEMPERATURE VS. ANNEALING TEMPERATURE FOR INDICATED MOLYBDENUM-VANADIUM ALLOY BARS



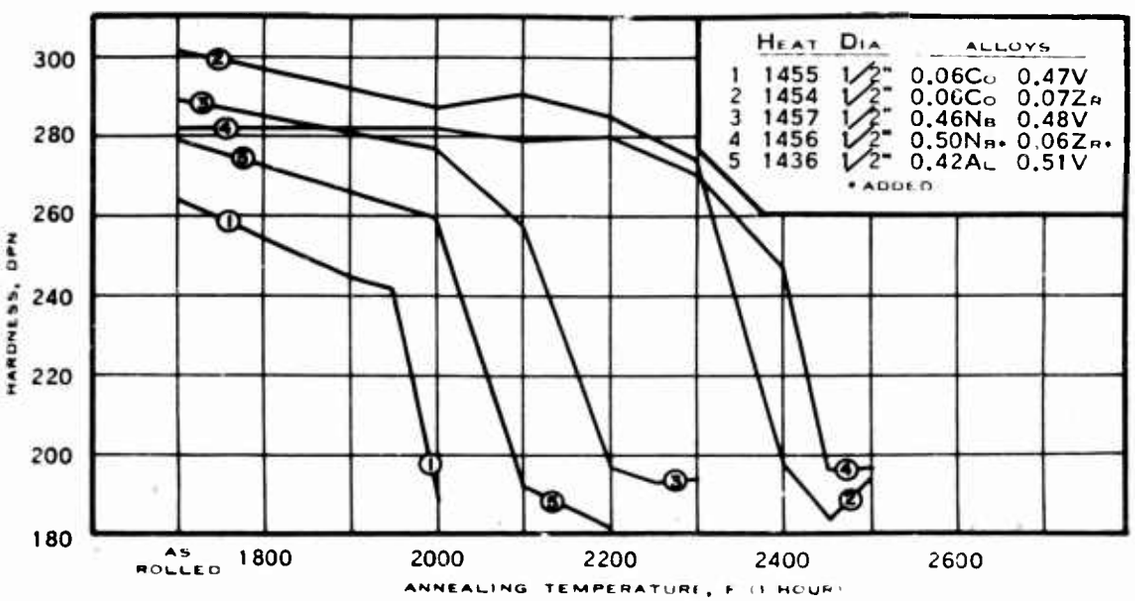


FIGURE 124 – HARDNESS AT ROOM TEMPERATURE VS ANNEALING TEMPERATURE FOR INDICATED TERNARY MOLYBDENUM BASE ALLOY BARS

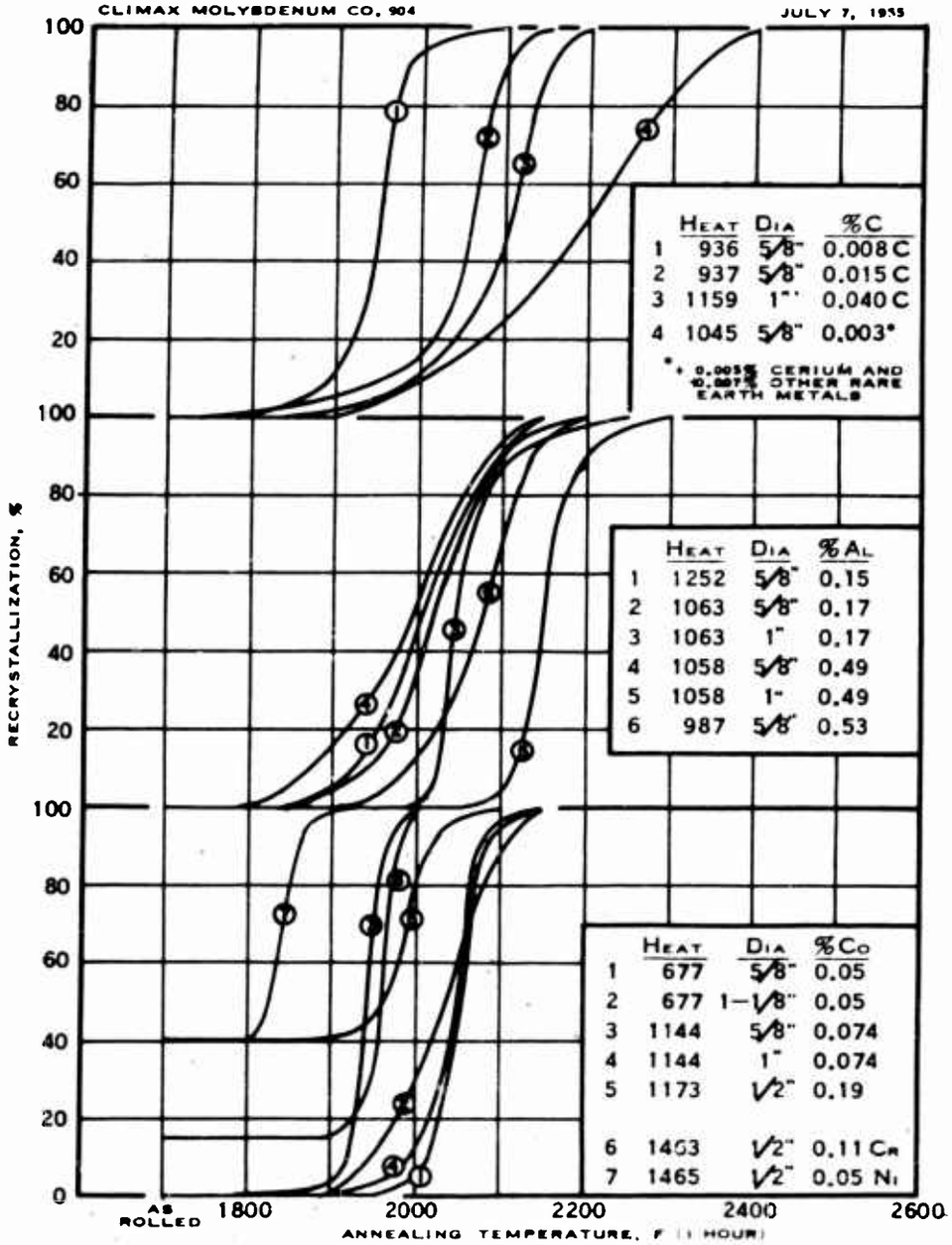


FIGURE 125 – RECRYSTALLIZATION VERSUS ANNEALING TEMPERATURE FOR UNALLOYED MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS

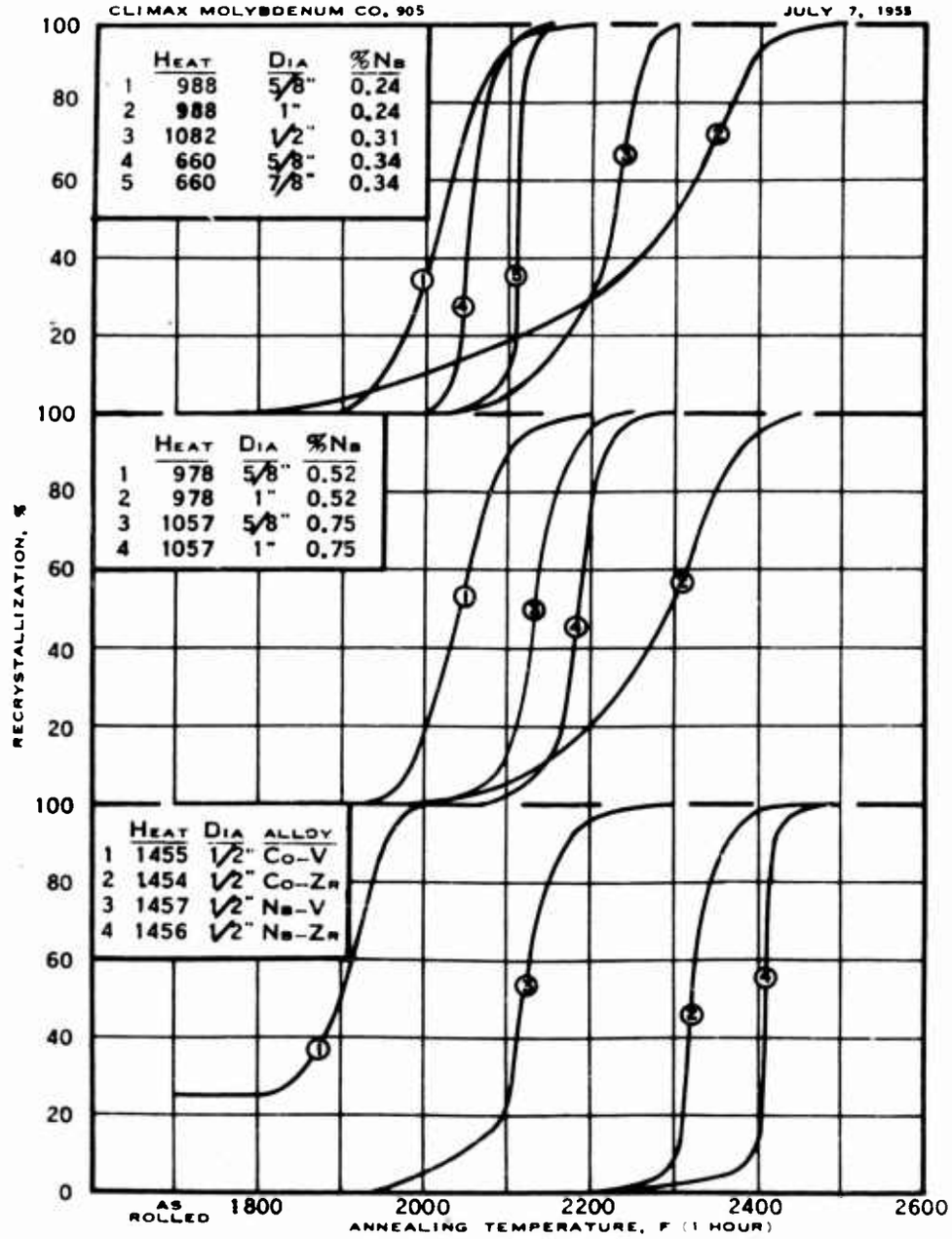


FIGURE 126 – RECRYSTALLIZATION VERSUS ANNEALING TEMPERATURE FOR MOLYBDENUM – BASE ALLOYS

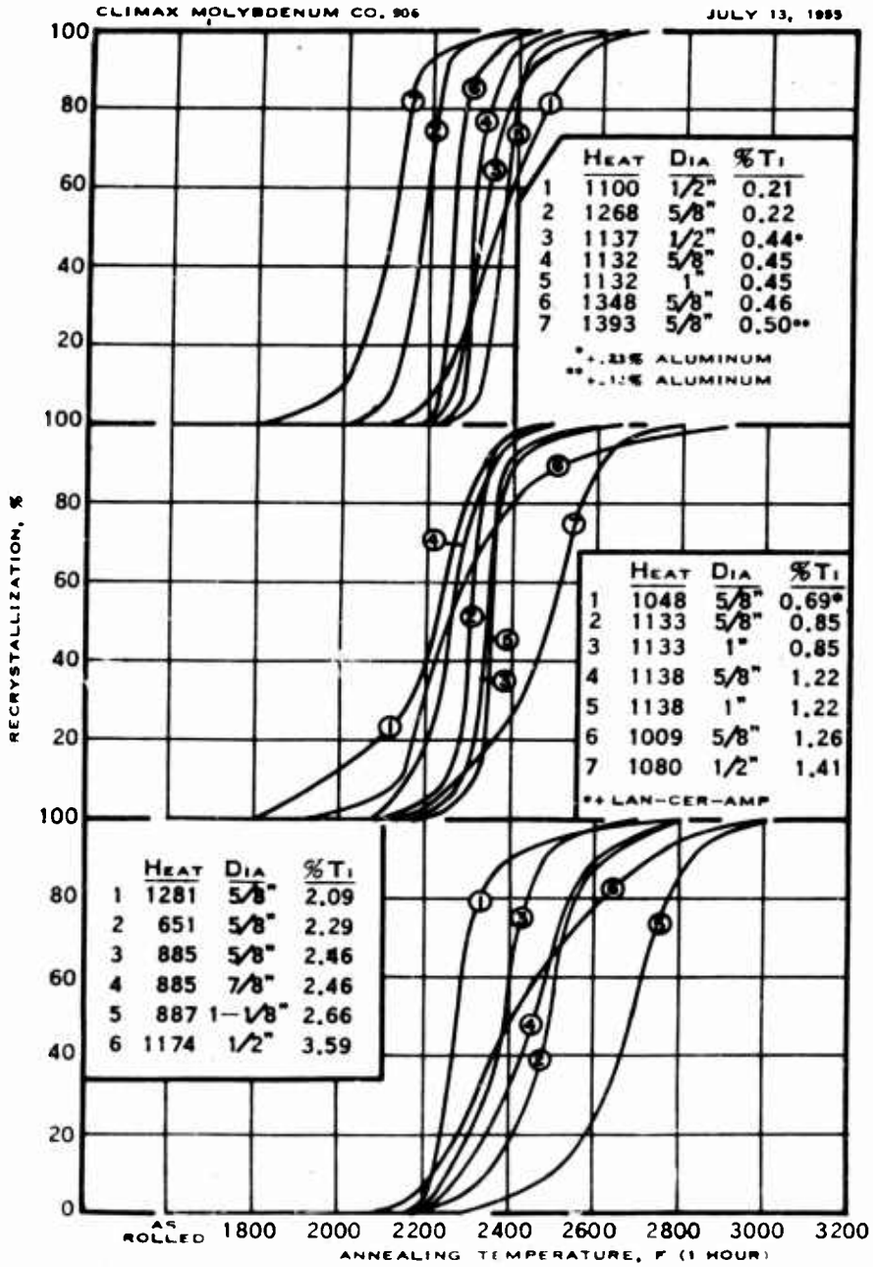


FIGURE 127 – RECRYSTALLIZATION VERSUS ANNEALING TEMPERATURE FOR MOLYBDENUM-BASE ALLOYS

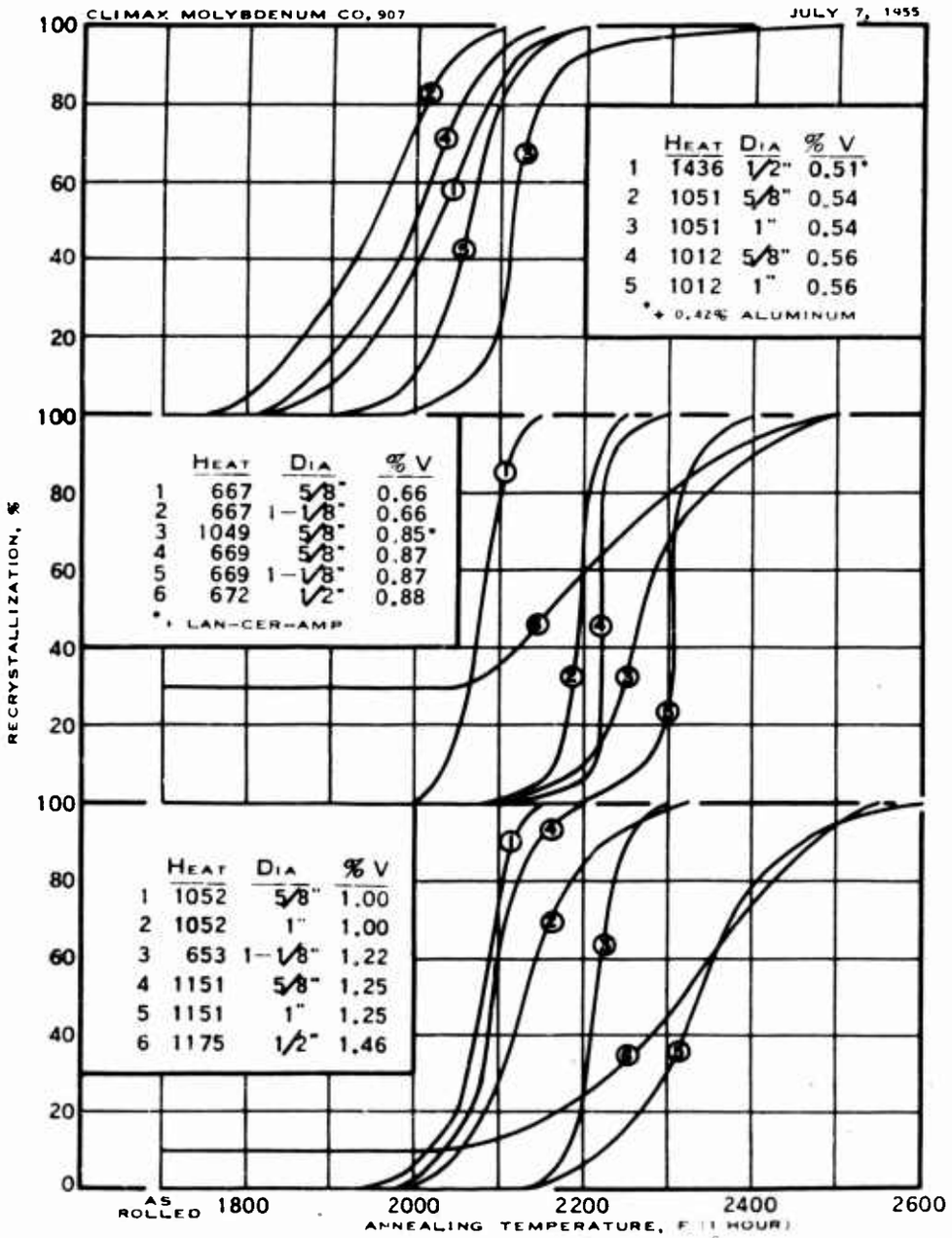


FIGURE 128 – RECRYSTALLIZATION VERSUS ANNEALING TEMPERATURE FOR MOLYBDENUM-BASE ALLOYS

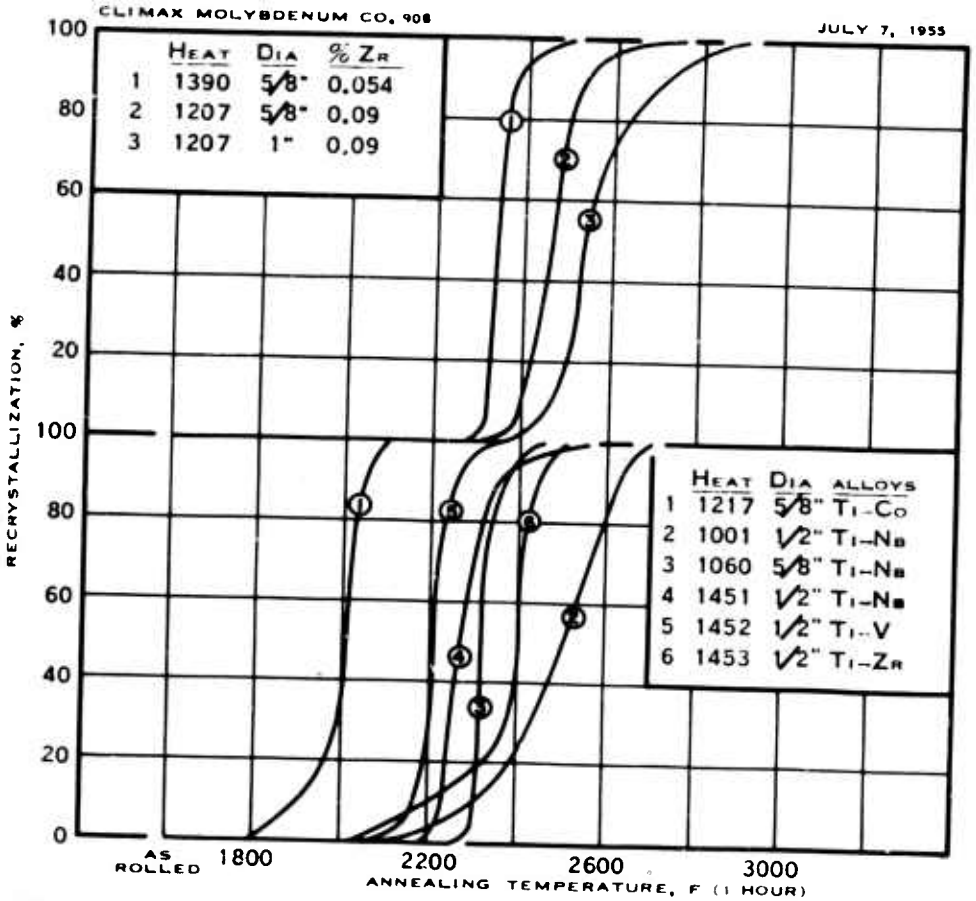


FIGURE 129 – RECRYSTALLIZATION VERSUS ANNEALING TEMPERATURE FOR MOLYBDENUM–BASE ALLOYS

lower than the reported temperature of complete recrystallization. In selecting a molybdenum-base alloy for service requiring optimum properties and exposure to elevated temperatures, it would be more realistic to design toward some allowable degree of recrystallization (or allowable loss of hardness or strength) than toward a reported temperature of complete recrystallization.

In the form of 5/8" and 1" diameter rolled bars, carbon-deoxidized, unalloyed molybdenum, Figures 119 and 125, attained complete recrystallization after one hour at 2150 F and 2200 F, respectively. When rare earth metals were used as a neutralizing agent (1045), the annealing range between 0% and 100% recrystallization was markedly broadened. Heat treatment of one hour at 2400 F was required to complete the recrystallization of Bar 1045.

Aluminum, either as a neutralizing agent or as an alloy addition, had a very minor effect on recrystallization. Variation of aluminum content from 0.15% to 0.53% resulted in a range of recrystallization temperatures from 2150 to 2200 F for 5/8" diameter bars and 2250 to 2300 F for 1" diameter bars.

The small amounts of cobalt, chromium, and nickel contained in the alloys under study depressed the recrystallization temperature of wrought molybdenum, while niobium and vanadium exerted only a slight positive effect upon recrystallization temperature. Additions of titanium raised the recrystallization temperature of molybdenum to a marked degree, but the effect was not linear throughout the composition range under consideration. The increase in recrystallization temperature per unit increase in titanium content was more rapid between zero and 0.5% than at higher concentrations. The most promising of the alloying elements studied, from the standpoint of retarding structural transformation of strain hardened molybdenum, was zirconium. From the charts it is evident that only small percentages of zirconium were needed to raise the temperature of recrystallization considerably. The ability of strain hardened molybdenum-zirconium alloys to resist recrystallization makes them particularly useful for applications requiring high strength in conjunction with exposure to elevated temperatures, in that the properties developed through strain hardening are retained under much more severe service conditions than for all of the other molybdenum-base alloys studied, excepting those containing high percentages of titanium.

Cursory examination of the recrystallization data for ternary alloys reported in Table 19 indicates a trend toward additive effects of the individual elements; that is, ternary alloys containing two elements that normally raise the recrystallization temperature usually had recrystallization temperatures higher than those of binary molybdenum-base alloys containing comparable amounts of either of the component elements alone. The departure from quantitatively additive behavior is shown in Table 20.

TABLE 20

RECRYSTALLIZATION TEMPERATURES OF TERNARY MOLYBDENUM-BASE ALLOYS

Bar	Alloy Content, %		Additive Recryst. Temp, F	Actual Recryst. Temp, F	Departure from Additive F
1436	0.42 Al	0.51 V	2190	2200	+ 10
1217	0.11 Co	0.18 Ti	2270	2100	- 170
1455	0.06 Co	0.47 V	2120	2000	- 120
1454	0.06 Co	0.07 Zr	2560	2500	- 60
1060	0.32 Nb	0.18 Ti	2370	2500	+ 130
1451	0.50 Nb	0.43 Ti	2515	2550	+ 35
1457	0.46 Nb	0.48 V	2220	2300	+ 80
1456	0.50 Nb*	0.06 Zr*	2580	2500	- 80
1452	0.22 Ti	0.75 V	2365	2350	- 15
1453	0.22 Ti	0.08 Zr	2870	2500	- 370

* added

The "additive recrystallization temperatures" listed in Table 20 were obtained in the following manner: The datum temperature of 2150 F was taken for the recrystallization temperature of unalloyed molybdenum. The departure from this datum temperature caused by each of the alloying elements in the ternary systems under consideration was determined from the plot of composition of binary molybdenum-base alloys vs recrystallization temperature, Figure 118. The additive recrystallization temperatures for the ternary alloys were then obtained by adding the effects of the individual components to the datum temperature of 2150 F.

It is apparent from the tabulated data that the majority of the recrystallization temperatures determined experimentally were lower than the predicted additive values; that is, the cumulative result of adding two elements to molybdenum was usually less than the sum of the individual effects in binary alloys. Three exceptions were ternary compositions containing niobium with titanium or vanadium--all of which required temperatures for complete recrystallization above those predicted on the basis of additive effects. The Mo-Al-V alloy (1436) behaved about as predicted from the empirical data. The ternary alloy containing 0.31% Nb and 0.16% Ti (1001) was omitted from this analysis inasmuch as it was processed according to a schedule quite different from that used for the other ternary alloy bars.

The greatest departure from truly additive effects of individual alloying elements was exhibited by the Mo-Ti-Zr alloy (1453). The experimental recrystallization temperature for this alloy was some 300 F below the predicted additive value. The temperature of recrystallization was, in fact, lower than would be expected for a binary alloy containing 0.08% zirconium alone.

The grain size of specimens of all the wrought materials studied was determined after heat treatment at the lowest temperature required to produce complete recrystallization. The grain boundary intercept method was used to obtain a numerical expression of grain size. This method consisted of magnifying an etched sample of the material under consideration 500 times and counting the number of grain boundaries intersecting a line five inches long. For the sake of clarity, the data are reported as number of grains per 0.1 linear inch. Each grain size value reported herein is the average of at least ten such counts obtained at random locations. To eliminate errors due to the anisometric structures encountered in certain specimens, half of the readings were obtained with the sample oriented in one direction, and the remainder with the sample rotated 90°.

Table 21 lists grain sizes of fully recrystallized molybdenum and molybdenum-base alloys. From examination of the data, no generalizations are immediately obvious relating recrystallized grain size to the composition or processing of the alloys. A general relationship exists between amount of strain hardening (as measured by hardness as rolled) and fully recrystallized grain size, but the scatter observed in the data suggests that other factors are involved. It appears that grain size is a complex function of alloy addition and mode of deoxidation, as well as amount of prior strain hardening. The spread in these data is also attributable to the method of determining recrystallization temperature, the criterion being complete freedom from worked grains as determined metallographically. As noted earlier, certain of the materials studied attained minimum hardness and virtually complete recrystallization (above about 95%) at temperatures well below those required to remove the last vestiges of strain hardening. Thus, the grains formed during the early stages of recrystallization were subject to growth at various rates during subsequent treatments at higher temperatures.

It appears from these data that bars fabricated from heats deoxidized with rare earth metals are coarser grained after recrystallization than bars similar in other respects but prepared from heats deoxidized with carbon.

The smallest grain size exhibited by a recrystallized, binary molybdenum-base alloy was 212 grains per 0.1" for the 0.05% nickel alloy (1465). A ternary molybdenum-base alloy containing 0.06% cobalt and 0.47% vanadium had 297 grains per 0.1". Both of these alloys were fully recrystallized at very low temperatures.

A study was made of the tendency toward grain coarsening with exposure to temperatures above that of recrystallization. Small samples from wrought sections of several of the alloys were heated for one hour at temperatures up to 3900 F, and the grain size was again determined by the grain boundary intercept method. The results are presented in Figures 130-135 as plots of grain size against exposure temperature.

It appears that grain growth is generally independent of composition of molybdenum-base alloys in the range studied. Those alloys exhibiting fine recrystallized grains tend to have the finest grains after exposure to intermediate temperatures (in the neighborhood of 3000 F), but after exposure to

3900 F all of the alloys were relatively large grained. The grain size of the bulk of the alloys was in the range from 2 to 20 grains per 0.1" after exposure to 3900 F. Only two alloys--those containing 0.19% and 0.20% aluminum (948 and 814)--had in excess of 20 grains per 0.1" after exposure to 3900 F.

In summary:

1. Wrought molybdenum and molybdenum-base alloys have been found to recrystallize in the classical manner.

2. The temperature required to complete the recrystallization process depends on the processing history and composition.

3. Of the alloying elements studied, zirconium and titanium were most effective in raising the recrystallization temperature of molybdenum.

4. Recrystallization temperatures for ternary alloys were generally lower than would be predicted on the basis of quantitatively additive effects of the individual alloying elements.

5. A wide range of recrystallized grain sizes was observed for the materials under investigation; however, none of the additions studied were particularly effective in inhibiting grain growth after exposure to 3900 F.

TABLE 21

GRAIN SIZE OF RECRYSTALLIZED MOLYBDENUM AND MOLYBDENUM-BASE ALLOY BARS OF INDICATED SIZES

Heat	Analysis %	Grain Size grains per 0.1" Bar Size 1/2"	5/8"	1"
936	0.008 C		86	
937	0.015 C		93	
1159	0.040 C			56
1045	0.005 Ce 0.007 RE*		44	
1252	0.15 Al		113	
1063	0.17 Al		116	38
1058	0.49 Al		94	59
987	0.53 Al		99	
1463	0.11 Cr	188		
677	0.05 Co		165	152[a]
1144	0.074 Co		198	94
1173	0.19 Co	93		
1465	0.05 Ni	212		
988	0.24 Nb		98	16
1082	0.31 Nb	76		
660	0.34 Nb		139	128[a]
978	0.52 Nb		111	28
1057	0.75 Nb		124	75
1100	0.21 Ti	20		
1268	0.22 Ti		126	
1137	0.44 Ti 0.23 Al	25		
1132	0.45 Ti		144	115
1348	0.46 Ti		150	
1393	0.50 Ti 0.12 Al		132	
1048	0.69 Ti 0.12 RE*		70	
1133	0.85 Ti		109	77
1138	1.22 Ti		109	57
1009	1.26 Ti		96	
1080	1.41 Ti	90		
1281	2.09 Ti		90	
651	2.29 Ti		106	
885	2.46 Ti		104	35[a]
887	2.66 Ti			43[b]
1174	3.59 Ti	58		

Heat	Analysis %	Grain Size grains per 0.1" Bar Size 1/2"	5/8"	1"
1051	0.54 V		134	85
1012	0.56 V		159	72
667	0.66 V		155	80[b]
1049	0.85 V 0.003 Ce 0.003 RE*		56	
669	0.87 V		169	63[b]
672	0.88 V	49		
1052	1.00 V		121	104
1151	1.25 V		174	44
1175	1.46 V	53		
1390	0.054 Zr		169	
1207	0.09 Zr		126	83
1436	0.42 Al 0.51 V	123		
1217	0.11 Co 0.18 Ti		176	
1455	0.06 Co 0.47 V	297		
1454	0.06 Co 0.07 Zr	211		
1001	0.31 Nb 0.16 Ti	130		
1060	0.32 Nb 0.18 Ti		72	
1451	0.50 Nb 0.43 Ti	193		
1457	0.46 Nb 0.48 V	163		
1456	0.50 Nb** 0.06 Zr**	166		
1452	0.22 Ti 0.75 V	166		
1453	0.22 Ti 0.08 Zr	149		

* other rare earth metals
** added

[a] 7/8" dia [b] 1-1/8" dia

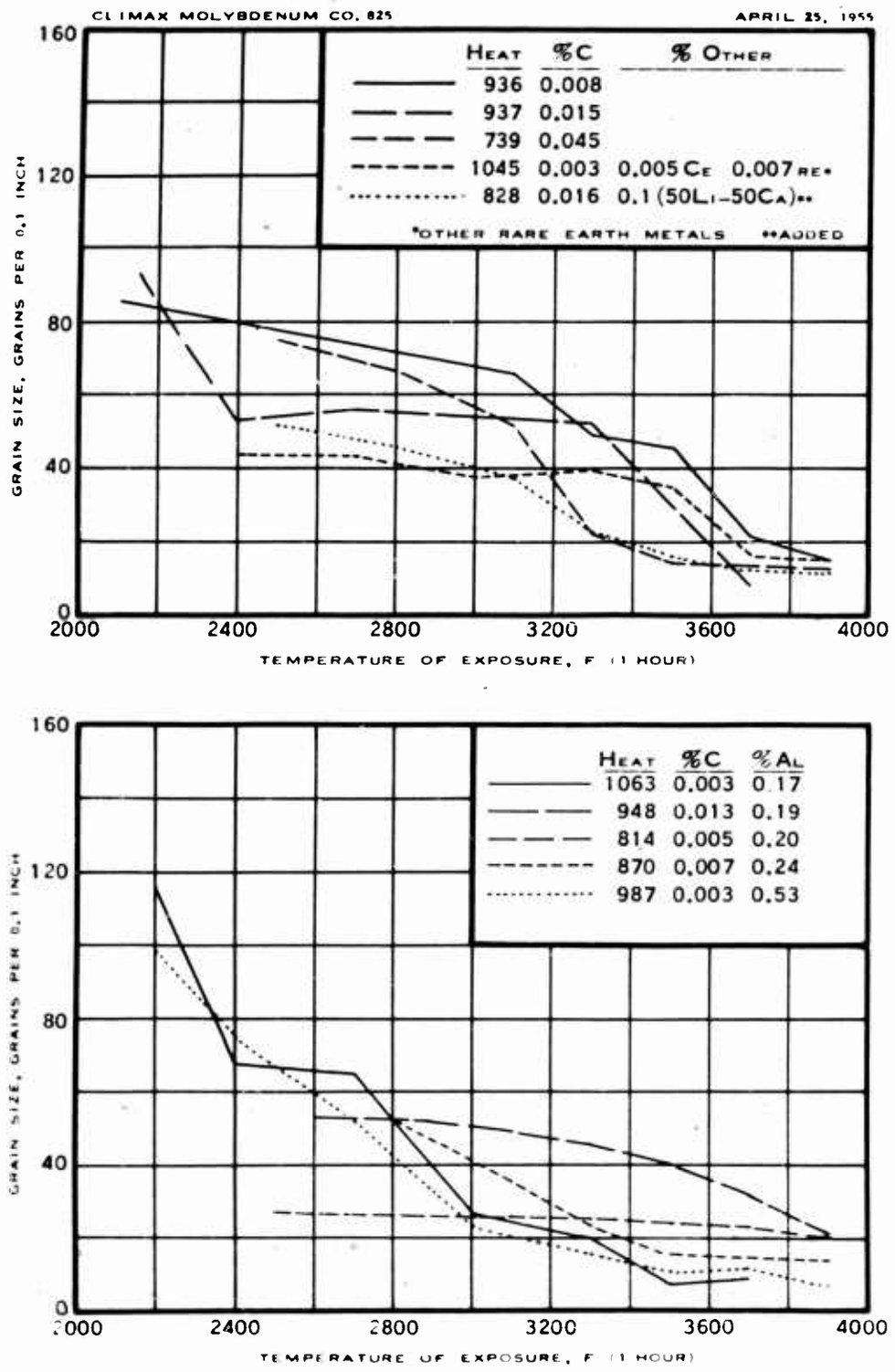


FIGURE 130 - GRAIN SIZE OF INDICATED UNALLOYED MOLYBDENUM AND MOLYBDENUM-ALUMINUM ALLOYS AFTER EXPOSURE OF ONE HOUR AT INDICATED TEMPERATURES

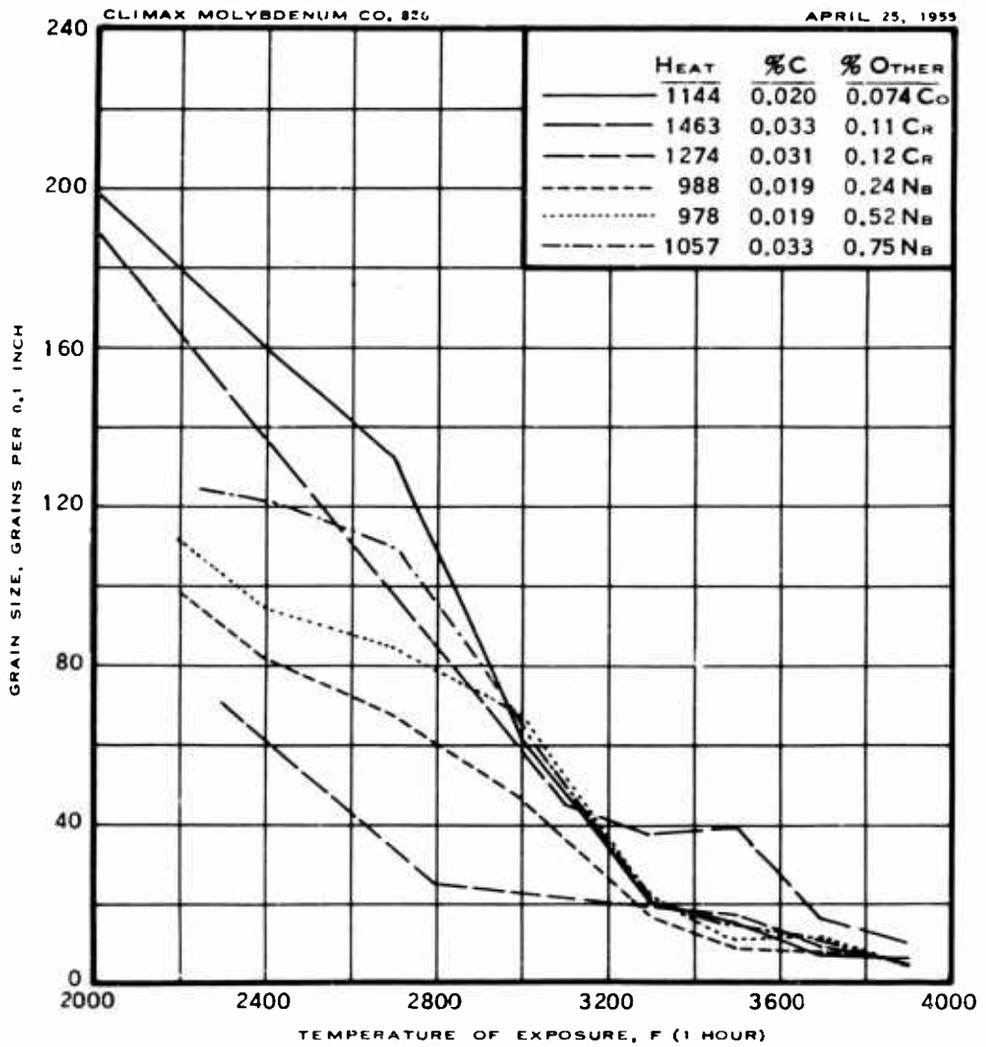


FIGURE 131 – GRAIN SIZE OF INDICATED MOLYBDENUM–COBALT, MOLYBDENUM CHROMIUM, AND MOLYBDENUM–NIOBIUM ALLOYS AFTER EXPOSURE OF ONE HOUR AT INDICATED TEMPERATURES

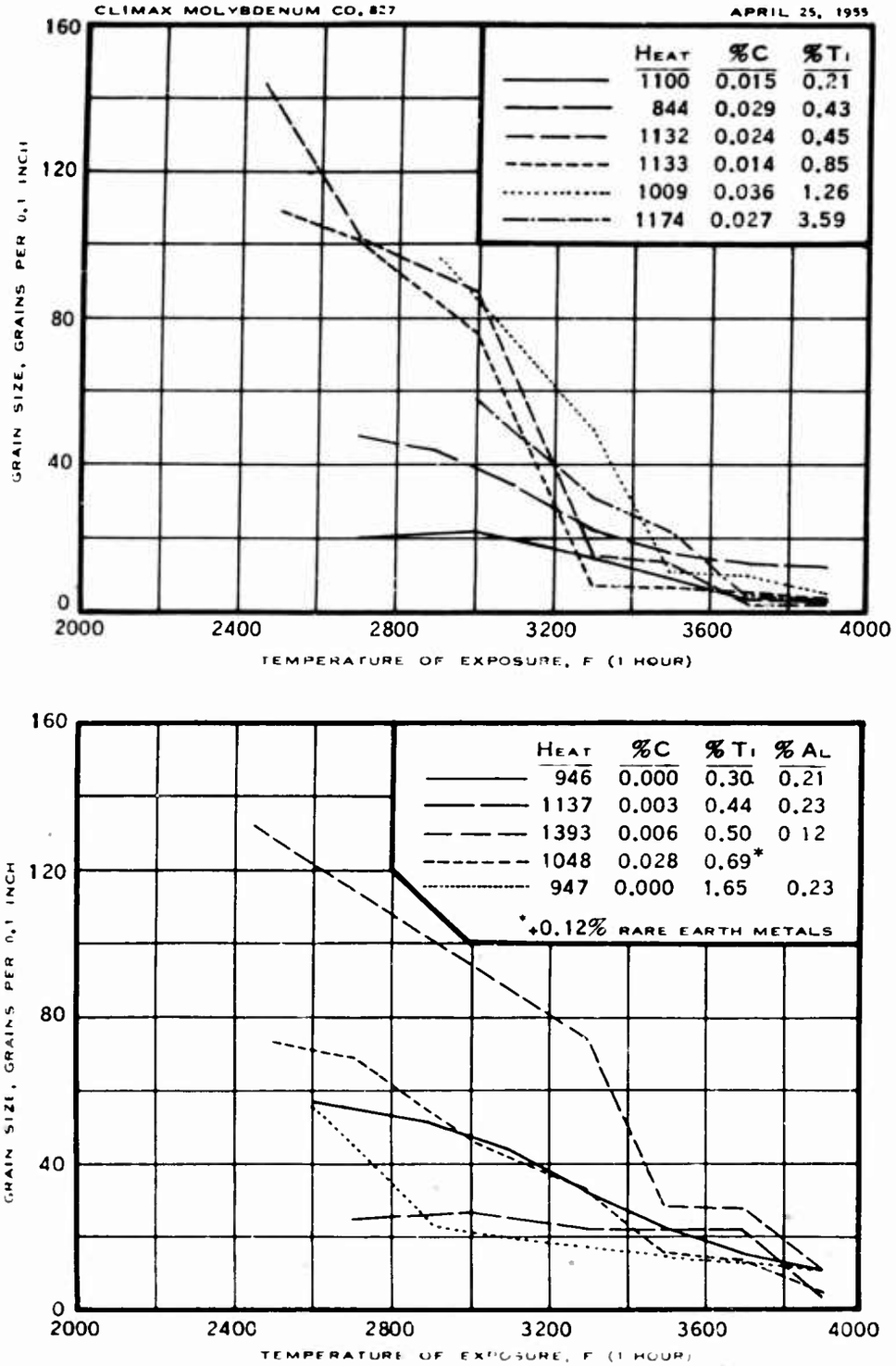


FIGURE 132 - GRAIN SIZE OF INDICATED MOLYBDENUM--TITANIUM ALLOYS AFTER EXPOSURE OF ONE HOUR AT INDICATED TEMPERATURES

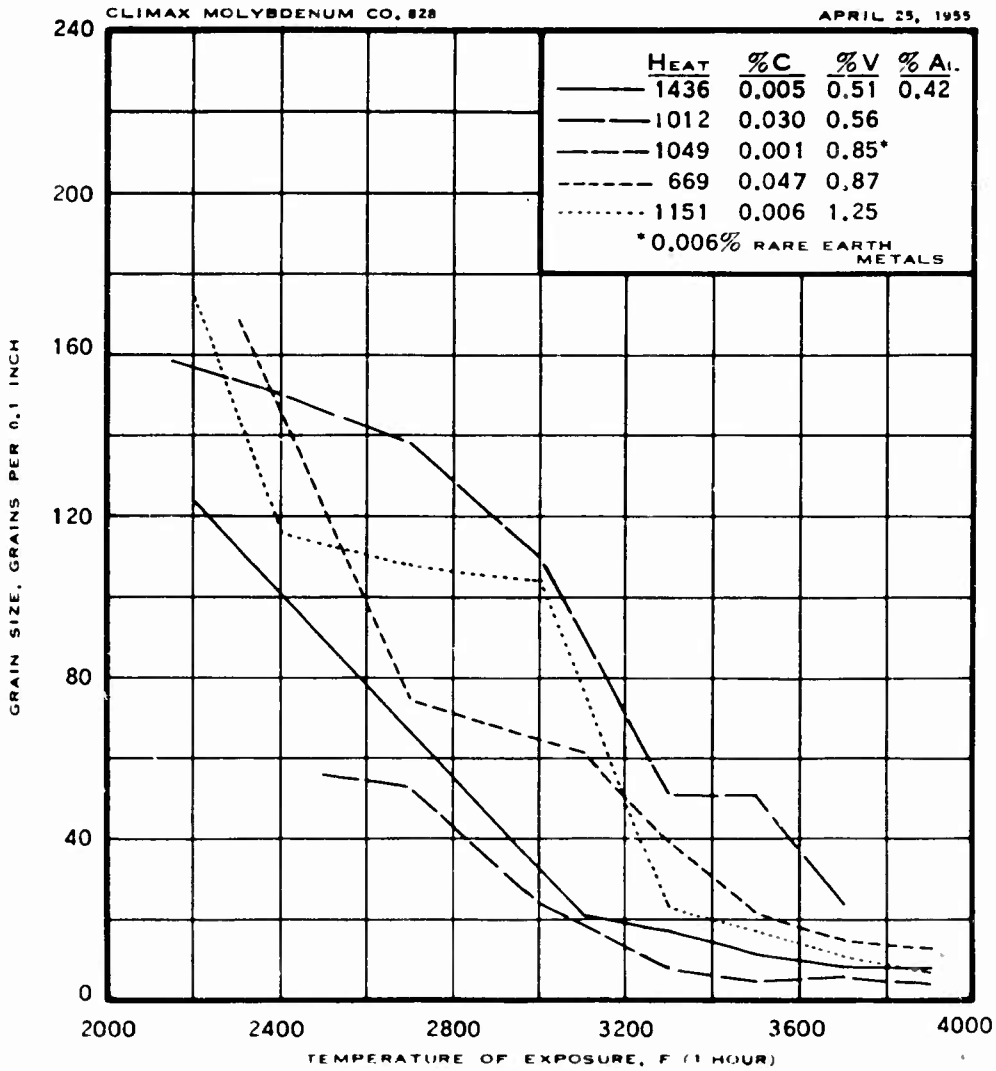


FIGURE 133 – GRAIN SIZE OF INDICATED MOLYBDENUM–VANADIUM ALLOYS AFTER EXPOSURE OF ONE HOUR AT INDICATED TEMPERATURES

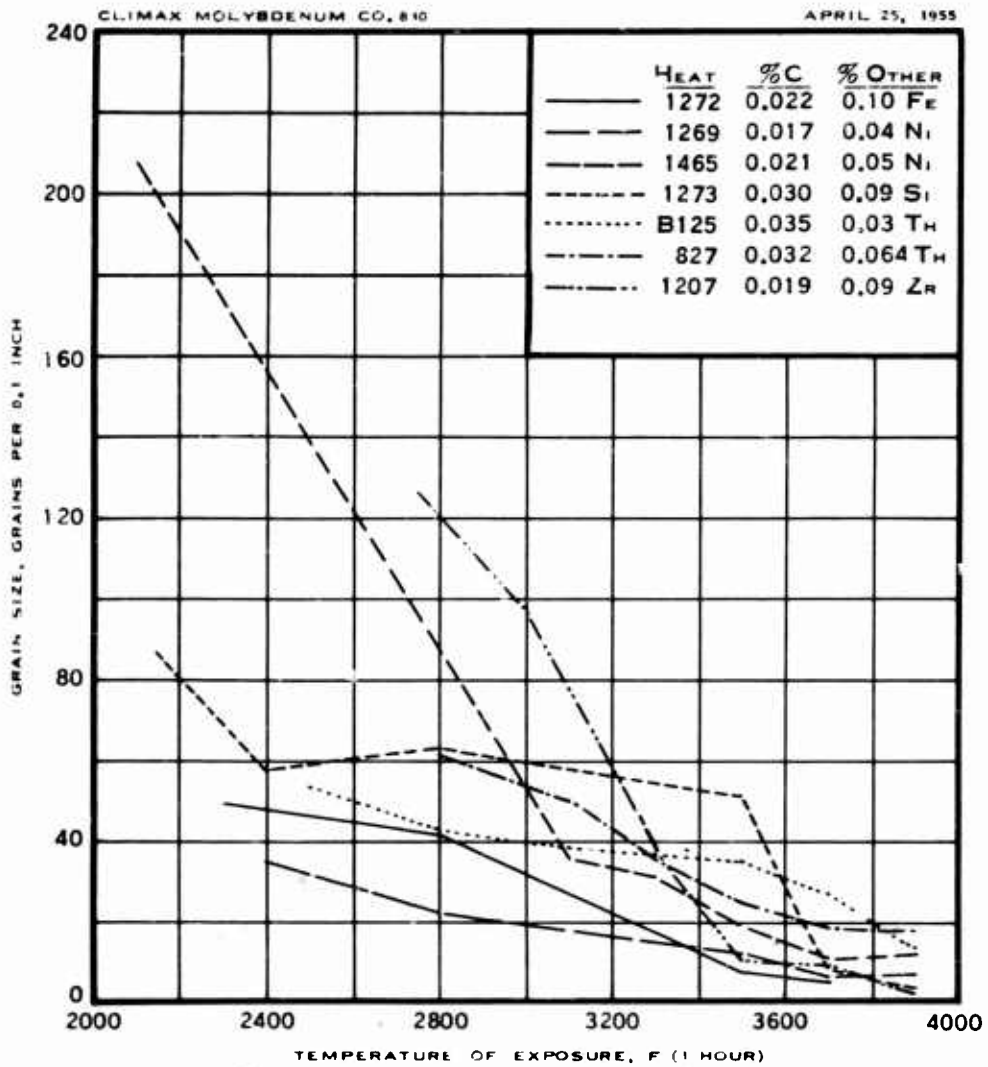


FIGURE 134 – GRAIN SIZE OF INDICATED MOLYBDENUM-BASE ALLOYS AFTER EXPOSURE OF ONE HOUR AT INDICATED TEMPERATURES

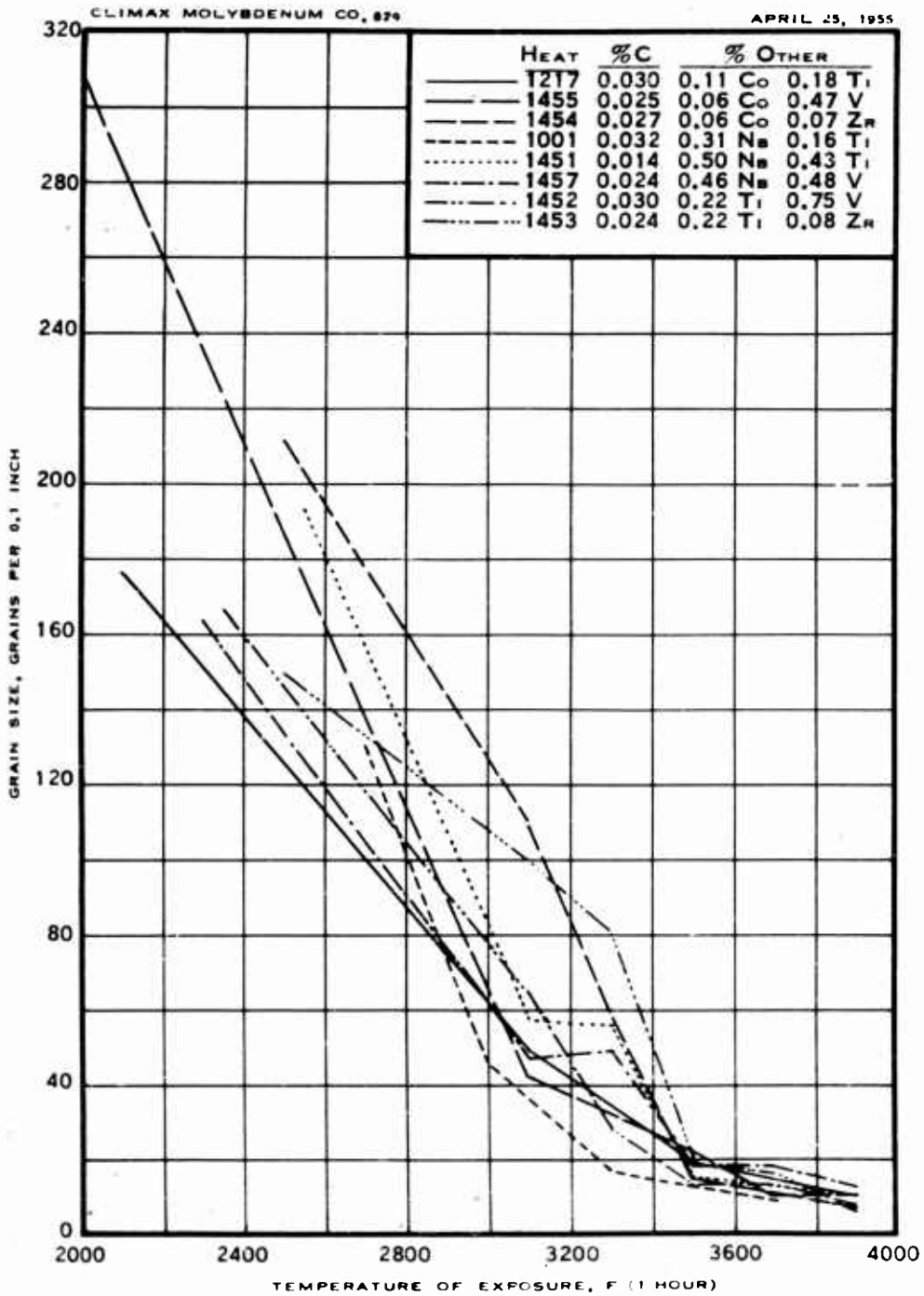


FIGURE 135 – GRAIN SIZE OF INDICATED TERNARY MOLYBDENUM - BASE ALLOYS AFTER EXPOSURE OF ONE HOUR AT INDICATED TEMPERATURES

Hardness

Vickers hardness determinations have been made at room temperature on all the wrought materials included in this program. These materials were tested as worked and after heating to increasingly high temperatures until full recrystallization had been accomplished. The results were presented as curves of hardness vs annealing temperature in the preceding section of this report (Figures 119-124). The hardnesses of hot cold-worked bars of 1/2" and 5/8" diameter ranged from 226 to 319 DPN, while those of 7/8", 1", and 1-1/8" bars were from 221 to 306 DPN. Recrystallization reduced the hardness values to the range 155 to 210 DPN. Hardnesses obtained on fully recrystallized samples agreed closely with the values for the same materials as cast.

The difference in hardness between the rolled bars and the recrystallized samples, which is considered a measure of rate of strain hardening, is greater for all but a few of the alloy heats than for unalloyed molybdenum. Of all the alloys studied, those containing cobalt or zirconium had the highest ratio of rate of strain hardening to alloy content. Data for molybdenum-titanium alloys indicated a peak in the relationship in the vicinity of 0.50% titanium.

Vickers hardness determinations have been made from room temperature to 1600 F, at intervals of 200 F, on a majority of the alloys. Three structural conditions were represented in the tests at elevated temperature, namely, as rolled, stress relieved, and fully recrystallized. Plots of hardness as a function of testing temperature are contained in Figures D1-D28, Appendix D. Figures 136-137 summarize these data by comparing the hardnesses at 1600 F of all the bars tested in the stress relieved and fully recrystallized conditions.

In general, the observations noted for hot hardness of cast alloys hold for wrought alloys of similar composition. On the basis of weight-percent of alloying element, cobalt appears to exert the most profound influence on elevated temperature hardness. Zirconium and aluminum follow in decreasing order with respect to relative hardening effect. Although the hardness of unalloyed molybdenum at 1600 F is enhanced by additions of niobium, titanium, and vanadium, these elements must be present in greater amount than cobalt to bring the hardness near that of the molybdenum-cobalt alloys. The greatest hardness at 1600 F for a stress-relieved specimen was exhibited by the 0.11% cobalt-0.18% titanium ternary alloy (1217). The highest hardness for a fully recrystallized specimen at 1600 F was exhibited by the 0.19% cobalt alloy (1173), followed closely by the 0.11% cobalt-0.18% titanium alloy.

Deoxidation with rare earth metals did not noticeably alter the hot hardness of unalloyed molybdenum. The hardness of titanium and vanadium alloys deoxidized with rare earth metals was somewhat lower, however, than would be predicted on the basis of data on heats deoxidized with carbon.

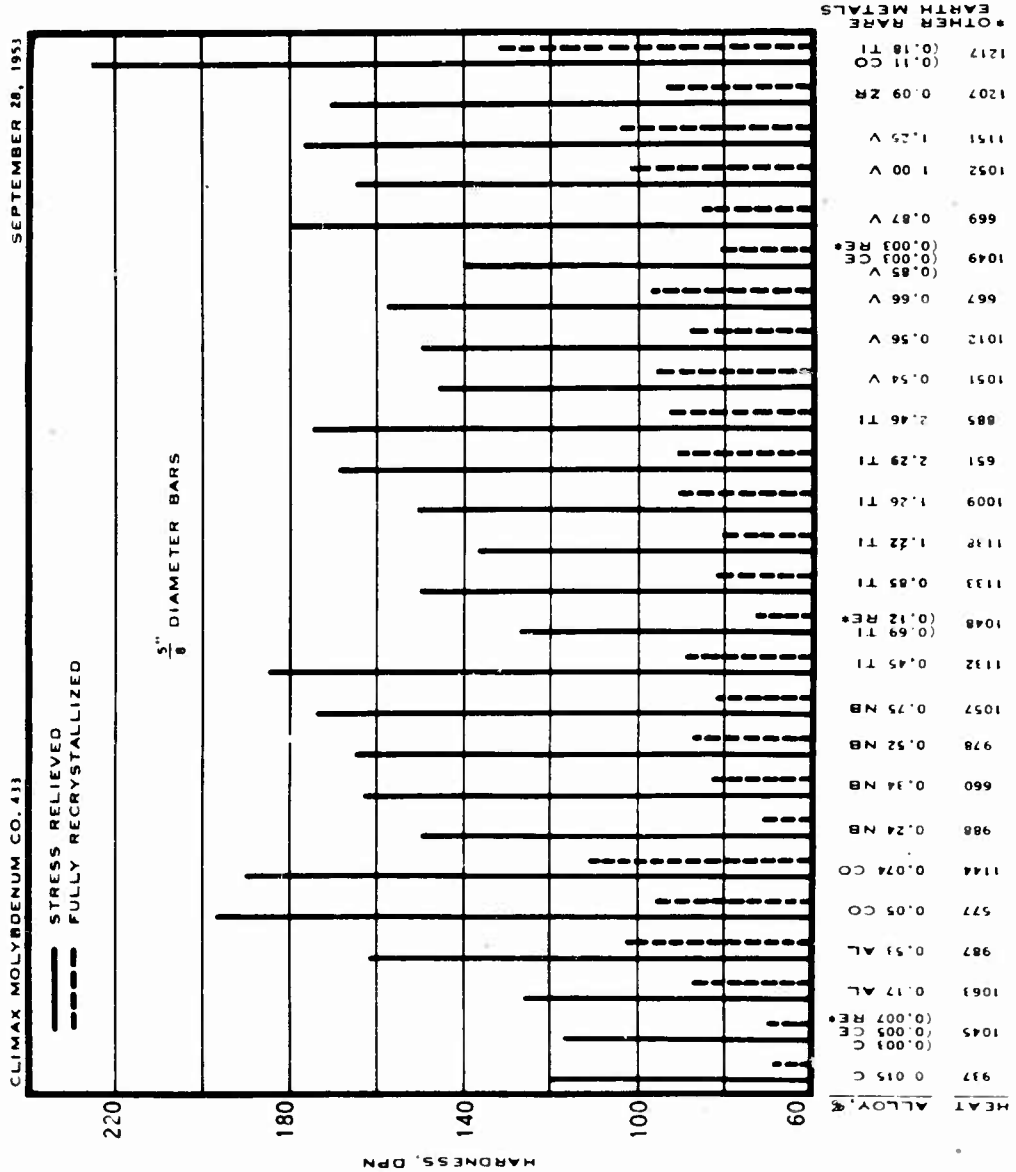


FIGURE 136 – HARDNESS AT 1600 F OF $\frac{5}{8}$" DIAMETER MOLYBDENUM AND MOLYBDENUM–BASE ALLOYS

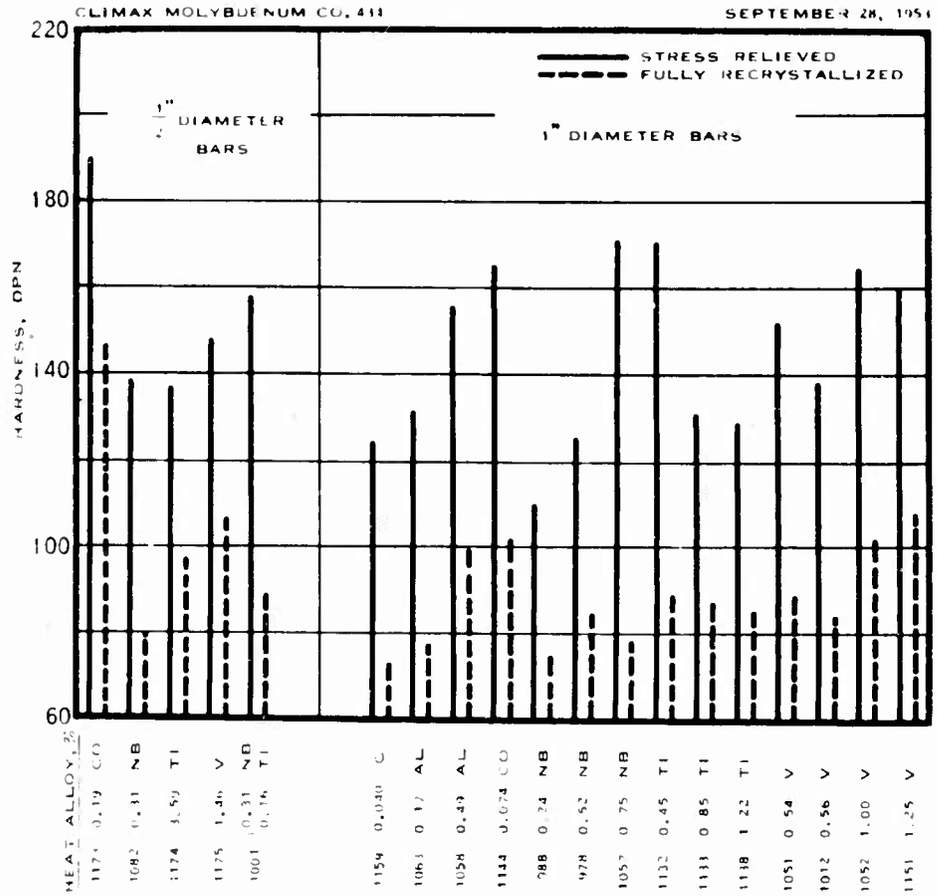


FIGURE 137 – HARDNESS AT 1600 F OF INDICATED $\frac{1}{2}$" AND 1" DIAMETER MOLYBDENUM AND MOLYBDENUM–BASE ALLOYS

The amount of hot cold-work on the metal before recrystallization has practically no effect on the hot hardness of fully recrystallized specimens. In the as-rolled or stress-relieved conditions, the 5/8" bars were slightly harder as a rule than the 1" bars from room temperature to 1600 F. The hardness differential between 5/8" and 1" diameter bars of like composition was not so great as the difference in tensile strength, as noted later in this report. Probably, in the case of the tensile tests, a specimen-size factor was present in addition to the factor of amount of hot cold-work.

The drop in hardness from room temperature to 1600 F for a representative group of bars is presented in Table 22. Curves of hardness as a function of testing temperature for unalloyed molybdenum, Figures D1-D3, Appendix D, reveal a rapid drop in hardness from room temperature to about 400 F. Bars showing a high differential in hardness between room temperature and 1600 F behave in about the same manner as unalloyed molybdenum, with a rapid change in hardness from room temperature to 600 F. As the drop in hardness shown in Table 22 becomes smaller, however, the relationship between hardness and testing temperature approaches linearity.

TABLE 22

DROP IN HARDNESS BETWEEN ROOM TEMPERATURE AND 1600 F FOR RECRYSTALLIZED MOLYBDENUM AND MOLYBDENUM-BASE ALLOY BARS

Ingot	Alloy, %	Drop in Hardness, Room Temp. to 1600 F, DPN 5/8" Dia Bars	1" Dia Bars
937	0.015 C	120	
1159	0.040 C		124
1045	0.005 Ce, 0.007 RE	124	
1063	0.17 Al	76	88
1058	0.49 Al		81
1144	0.074 Co	69	62
1217	0.11 Co, 0.18 Ti	56	
1173	0.19 Co	(1/2") 47	
988	0.24 Nb	121	115
1132	0.45 Ti	109	107
1138	1.22 Ti	124	116
1012	0.56 V	121	104
1151	1.25 V	89	70
1207	0.09 Zr	108	

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Tensile Strength

Of all the tests employed to evaluate metallic materials, the tensile test has attained almost universal acceptance as a criterion of performance. This is due to several factors, among the more important of which are the high degree of reproducibility of the test, the somewhat greater sensitivity of the test to metallurgical variables than, for example, the hardness test, and, of by no means minor importance, the extensive backlog of data obtained under standard test conditions on virtually every engineering material in use, or even contemplated for use.

In the course of this investigation, tensile tests have been performed on approximately fifty wrought, binary and ternary molybdenum-base alloys. Variables in the test program included amount of reduction by rolling, test temperature, and structural condition. Rolled bars of 1/2", 5/8", 7/8", 1", and 1-1/8" diameter were available for test. Test temperatures for the majority of the alloys were room temperature, 750, 1200, and 1600 F. The amount of stock available for some of the alloys limited the testing temperatures to room temperature and 1600 F. Tensile tests were conducted only at room temperature on 1/2" diameter bars rolled at the University of Michigan from small extrusions made at Thompson Products Company.

Structural conditions represented in the tensile test program were as-rolled, stress-relieved, and fully recrystallized. In the later stages of the program, stress-relief treatments were carried out at temperatures 100 F below those required to initiate recrystallization; in the earlier stages, one hour at 1800 F was used exclusively for the stress-relief treatment.

Gage sections for specimens machined from 1/2" or 5/8" diameter bars were 0.250" diameter by 1-1/4" long; those machined from 7/8", 1", and 1-1/8" diameter bars were 0.475" diameter by 2-3/8" long. All tests were run at strain rates of 3% per hour during elastic deformation and 60% per hour during plastic deformation. Stress-strain records were obtained for each test, and 0.1% offset yield strengths were calculated for specimens not exhibiting a drop in load at the yield.

A partial pressure of argon was maintained within the furnace to minimize oxidation of specimens tested at 750 F and above. To monitor the effectiveness of the protective atmosphere, periodic dimensional checks were made on the specimens tested at elevated temperatures at locations not subjected to plastic deformation, and the reduction in diameter due to oxidation was in no instance in excess of one percent.

The behavior of molybdenum and its alloys in the tensile test closely paralleled that of other metallic materials. An elastic range was observed in which the average modulus of elasticity was between 49×10^6 and 50×10^6 psi. Two distinct types of behavior were noted after the elastic limit was reached. Specimens representative of fully recrystallized or lightly strain hardened materials generally exhibited an upper and lower yield point, while

highly strain hardened materials exhibited a gradual transition from elastic to plastic deformation. Increasing the test temperature inhibited the tendency toward a drop in load after the (upper) yield point, regardless of structural condition. Tensile specimens exhibited various amounts of localized deformation after attaining the ultimate load. The tendency toward localized deformation was usually greater the higher the test temperature.

The tensile test data are tabulated in Table D1, Appendix D. Figures 138-141 show tensile strength as a function of alloy content for binary molybdenum-base alloys. Figures 142-143 itemize tensile strengths of all the 1/2" and 5/8" diameter bars except those 1/2" diameter bars rolled at the University of Michigan from small extrusions made at Thompson Products Company. As noted earlier in this report, the bars produced in this manner received much less working than bars processed by rolling to final size from 3" or 4" diameter extrusions.

The effect of processing variables on properties of wrought sections was briefly discussed earlier, in the section dealing with recrystallization of bar stock; also, in evaluating tensile properties, consideration must be given to processing variables. Factors such as finishing temperature and amount of reduction per pass could not be controlled accurately; thus, two bars with similar amounts of total reduction may not necessarily have retained the same amount of cold work.

For example, two 5/8" round bars containing 0.54% and 0.56% vanadium respectively (1051 and 1012) exhibited rather widely divergent properties in the "as-rolled" condition, having room-temperature tensile strengths of 104,400 and 121,500 psi, respectively. The hardnesses of these two alloys as rolled were 265 and 287 DPN, respectively, indicating that the 0.56% vanadium alloy was strain hardened to a greater degree at 5/8" diameter and would be expected to develop higher strength than the companion material. Upon full recrystallization, the tensile strengths of the two alloys were essentially the same; the slightly higher strength of the 0.56% vanadium alloy indicated that variables other than vanadium concentration had a minor effect.

Variables other than those attributable to processing were, of course, encountered in the large number of materials studied under this program. For example, test-to-test variations due to slight differences in specimen preparation or minor eccentricities of specimen alignment in the test apparatus undoubtedly affected the results. The net effect of variables of this type, however, was considered of much less significance than the effects of processing variables.

The effects of increasing concentration of specific alloying elements on the tensile strength of 5/8" diameter bars is shown in Figures 138-141. Comparisons between the various alloy systems studied have been made on the basis of structure rather than annealing temperature. Thus, although recrystallized samples of molybdenum-cobalt alloys exhibited a higher ratio of strength to alloy content than molybdenum-zirconium alloys, the latter required much higher temperatures for recrystallization and therefore would be expected to retain properties developed through strain hardening after exposure to higher temperatures than would be the case for molybdenum-cobalt alloys.

Relatively small amounts of cobalt or zirconium exerted profound effects on tensile strength in all conditions studied. The single molybdenum-nickel alloy of this investigation exhibited good strength properties when tested at 1600 F. At room temperature, however, it displayed low tensile strength and virtually no ductility.

In the single chromium alloy studied, chromium was found to be more effective in raising the tensile strength of the base metal in the recrystallized condition than in the strain-hardened condition.

The relationship between tensile strength and titanium content indicated optimum properties in the vicinity of 0.5% titanium. The relationship was more evident from tests on stress-relieved samples than from tests on fully recrystallized samples. The trends in these data indicate that, for this alloy system, factors other than purely solid solution effects are operative. Molybdenum-base alloys containing niobium or vanadium generally increased in strength with increasing alloy content, although the relationships were inconclusive at the higher vanadium contents, owing to inconsistencies in the data. Additions of aluminum were significantly more effective in increasing tensile strength at 1600 F than at room temperature.

Results obtained for specific compositions are shown in Figures 142-143; it will be noted that several of the ternary alloys were consistently among the strongest alloys. Particularly impressive were those ternary alloys containing 0.11% cobalt and 0.18% titanium (1217) and 0.06% cobalt and 0.07% zirconium (1454). The ternary alloy containing 0.50% niobium and 0.43% titanium (1451) had the highest tensile strength at room temperature of all the materials studied, exhibiting an ultimate strength of 132,600 psi in the as-rolled condition. The highest strength obtained in tests at 1600 F was 100,000 psi by the 0.11% cobalt, 0.18% titanium alloy.

Examination of the results with a molybdenum-titanium alloy (1048) and a molybdenum-vanadium alloy (1049), both deoxidized with rare earth metals, indicates that lower strengths were obtained than would be anticipated for materials of similar alloy content deoxidized with carbon.

The observations noted for 1/2" and 5/8" diameter stock apply qualitatively to the larger bar sizes. Quantitatively, the 7/8", 1", and 1-1/8" bars were lower in strength in the strain-hardened condition than smaller bars of the same composition. After recrystallization, the factor of amount of cold work assumed a position of secondary importance, and the tensile strengths of bars of similar composition were much less dependent upon bar size.

Yield strengths for as-rolled and stress-relieved samples representing all bar sizes averaged approximately 80% of tensile strengths, regardless of test temperature. For fully recrystallized materials, yield strengths averaged 80% of tensile strength at room temperature; as the test temperature was increased, however, the ratio decreased and the yield strengths averaged about 35% of the tensile strengths at 1600 F.

A statistical analysis of data for all tests run at room temperature on 1/2" or 5/8" bars would reveal a mean elongation value of about 30%. A relatively minor occurrence of points in the vicinity of 0 to 2% elongation would be noted on a plot of frequency of occurrence vs elongation, owing to the fact that certain of the compositions studied exhibited transition temperatures above room temperature under the conditions of the tensile test. If a similar plot were constructed to cover tests at 1600 F, two peaks would be noted, one at 18-20% elongation for all as-rolled and stress-relieved samples and one at 50% elongation for all recrystallized samples. Thus elongation generally decreased between room temperature and 1600 F for strain-hardened specimens but increased for fully recrystallized specimens. Reduction of area was observed to increase with increasing test temperature regardless of structural condition.

Ductility measurements for 7/8", 1", or 1-1/8" bars were usually lower than for 5/8" bars of similar composition. At least a part of the decline in ductility was attributed to the effect of specimen gage diameter, it being recognized that the smaller the gage diameter, the greater the indicated ductility.

The relationship between hardness and tensile strength is shown in Figures 144 and 145 for a large number of molybdenum-base alloys. Tensile strength generally varied linearly with hardness, although the data obtained at room temperature were best expressed by a line of somewhat different slope and position from those obtained at elevated temperatures. For a rough approximation of tensile strength at either room or elevated temperature, when only the Vickers hardness is known, a satisfactory formula is

$$\text{Tensile Strength in psi} = 400 \times \text{DPN}$$

That factors other than hardness enter into determination of ultimate tensile strength is evidenced by the spread in data in Figures 144 and 145. The relationships presented in these figures, then, are of value only as general guides in predicting tensile strength at a given hardness level.

The results of tensile tests on the 1/2" diameter bars rolled at the University of Michigan from extrusions prepared at Thompson Products Company are given at the conclusion of Table D1, Appendix D. These values are significantly lower than would be anticipated on the basis of results on 5/8" diameter bars. The chief difference is, of course, in the total amount of work and degree of strain hardening. The majority of the 5/8" diameter bars were rolled from 4" diameter extrusions, while the 1/2" bars were rolled from extrusions about 3/4" in diameter, which in turn had been prepared from 1-1/4" diameter cast cylinders.

At room temperature the ultimate strengths of the better molybdenum-base alloys are somewhat lower than those of certain of the heat resisting alloys currently under consideration. For example, the tensile strength at room temperature of Inconel X in the aged condition is reported* as 162,000 psi, and that of S-816, also in the aged condition, as 140,000 psi. In tests at

* Alan Levy, Metals for short time service at high temperatures. Materials and Methods. April 1955

1600 F, however, molybdenum-base alloys display marked superiority to the other alloys. The stronger heat resisting alloys had tensile strengths at 1600 F less than 55,000 psi, that of S-816 being reported as 51,000 psi. It will be noted that at 1600 F, even the tensile strength of unalloyed molybdenum, when tested in the strain-hardened condition, exceeded that of the S-816 alloy; in the fully recrystallized condition, some of the molybdenum-base alloys could compete with S-816.

Concerning creep-rupture properties, to be described in a later section, it has been indicated that the superiority of molybdenum-base alloys to the "superalloys" becomes more pronounced as the test temperature is raised above 1600 F. For example, at 1800 F, the better superalloys fail in the short-time tensile test at about 25,000 psi*, whereas the 100-hour rupture lives of the better molybdenum-base alloys are in the vicinity of 60,000 psi.

Ductility, Toughness, and Transition from Ductile to Brittle Behavior

It was demonstrated in the foregoing section that at room temperature under the conditions of the tensile test almost all of the molybdenum-base alloys studied exhibited appreciable ductility. To state that a given sample of molybdenum is either "ductile" or "brittle" is a non sequitur, however, inasmuch as molybdenum, like other body-centered cubic metals, undergoes a transition from brittle to ductile behavior and this transition is profoundly influenced by certain physical aspects of the test, such as temperature, strain rate, and stress system. Thus, the statement that a sample when tested in tension at room temperature is either brittle or ductile merely indicates the position of the transition zone with respect to room temperature under the stress and strain conditions of the test. For example, the tension test may not differentiate between two specimens representing different materials or different structural conditions of the same material. Determination of transition zones--specifically transition temperatures under conditions of uniform strain rate and stress geometry--permits an additional degree of sensitivity in grading compositions (or structural conditions) not available from a study of ductility at one temperature alone.

The specific temperatures obtained in transition tests are unimportant in an absolute sense. It would be indeed fortuitous if the conditions arbitrarily used in the transition tests were ever encountered in service. Specific values are important relatively, however, inasmuch as they indicate which materials would more successfully sustain adverse service conditions.

Transition temperature ranges for molybdenum-base alloys under the conditions of the Charpy V-notch impact test were above room temperature, with the lowest ranges starting at about 450 F. Impact strengths at temperatures lower than the transition temperature range were generally five foot-pounds or less. Above the transition temperature range, impact specimens did not fail under the maximum available energy, 120 foot-pounds.

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* Mean lives, Ref. 6.

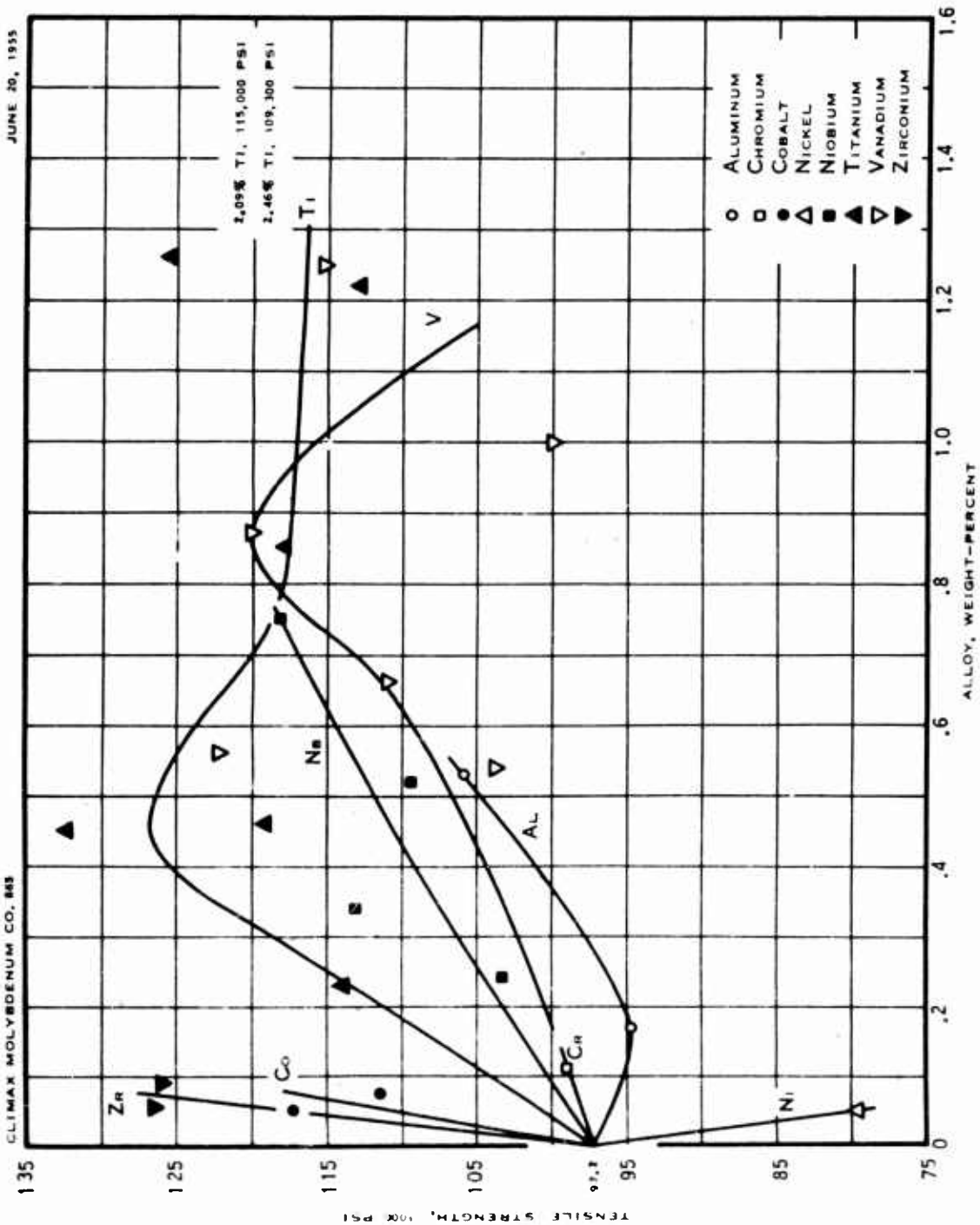


FIGURE 138 – TENSILE STRENGTH AT ROOM TEMPERATURE VS. ALLOY CONTENT OF 5/8" ROUND BARS IN THE STRESS RELIEVED CONDITION

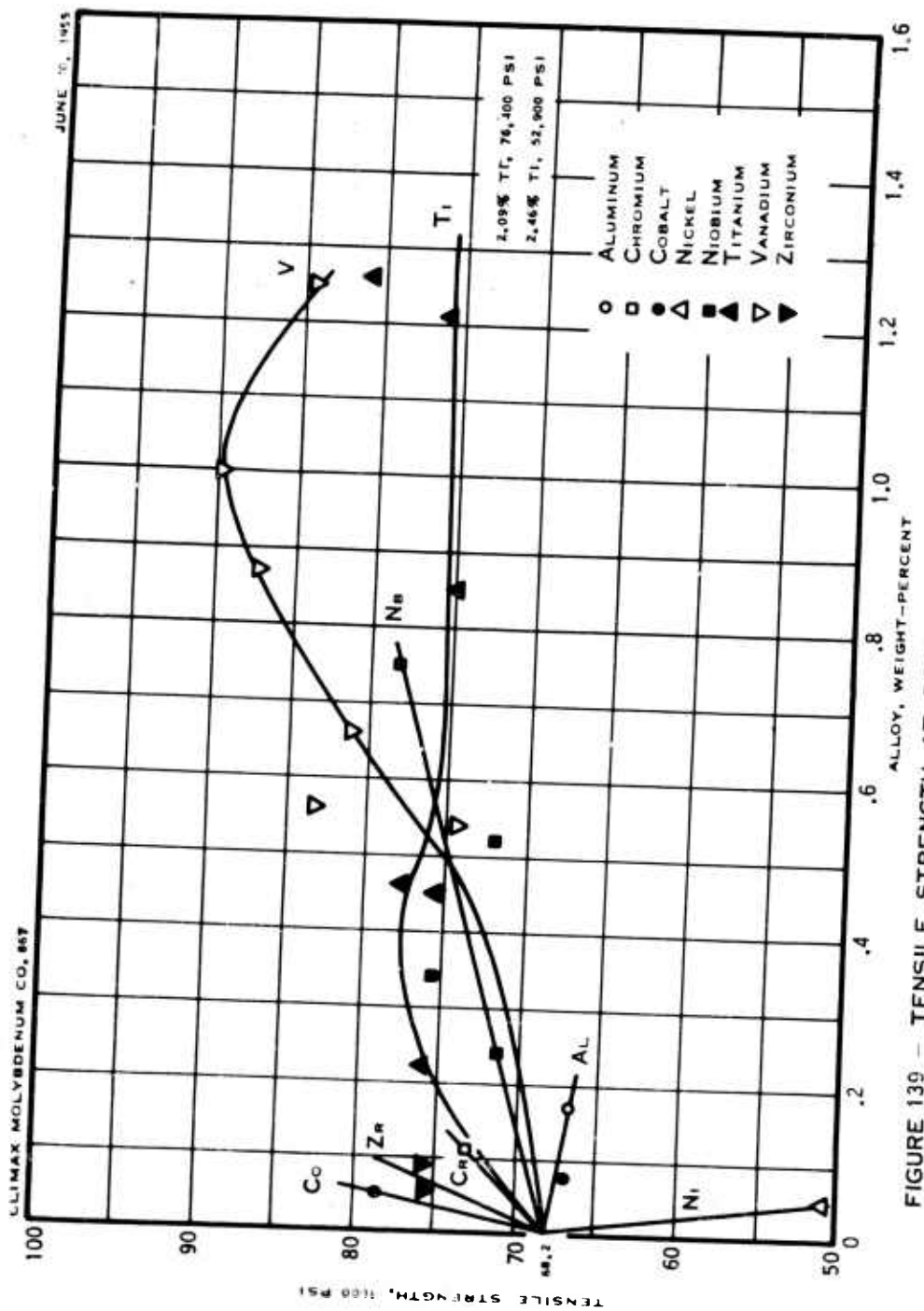


FIGURE 139 – TENSILE STRENGTH AT ROOM TEMPERATURE VS. ALLOY CONTENT OF 5/8" ROUND BARS IN THE FULLY RECRYSTALLIZED CONDITION

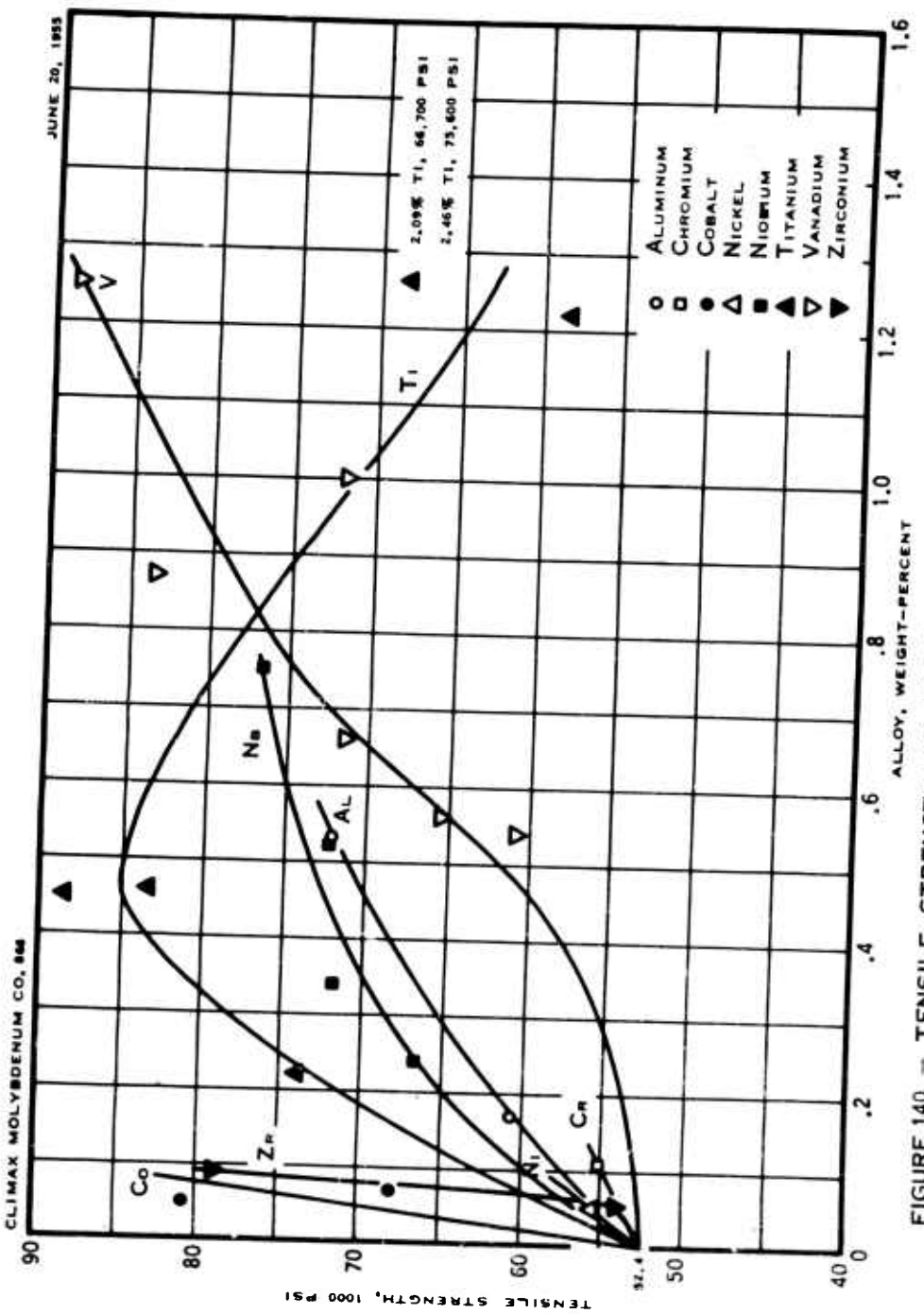


FIGURE 140 — TENSILE STRENGTH AT 1600 F VS. ALLOY CONTENT OF 5/8" ROUND BARS IN THE STRESS RELIEVED CONDITION

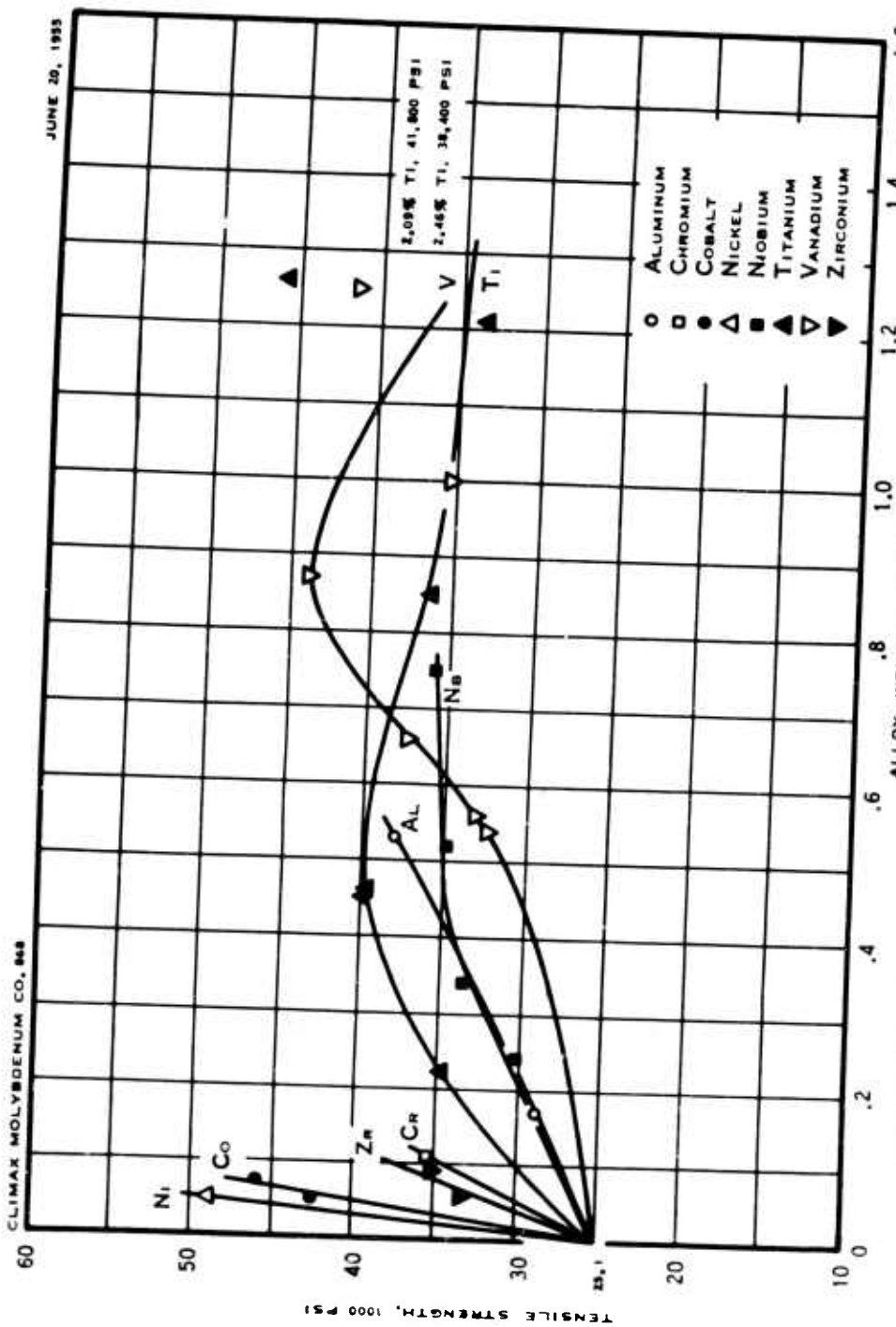


FIGURE 141 – TENSILE STRENGTH AT 1600 F VS. ALLOY CONTENT OF 5/8" ROUND BARS IN THE FULLY RECRYSTALLIZED CONDITION

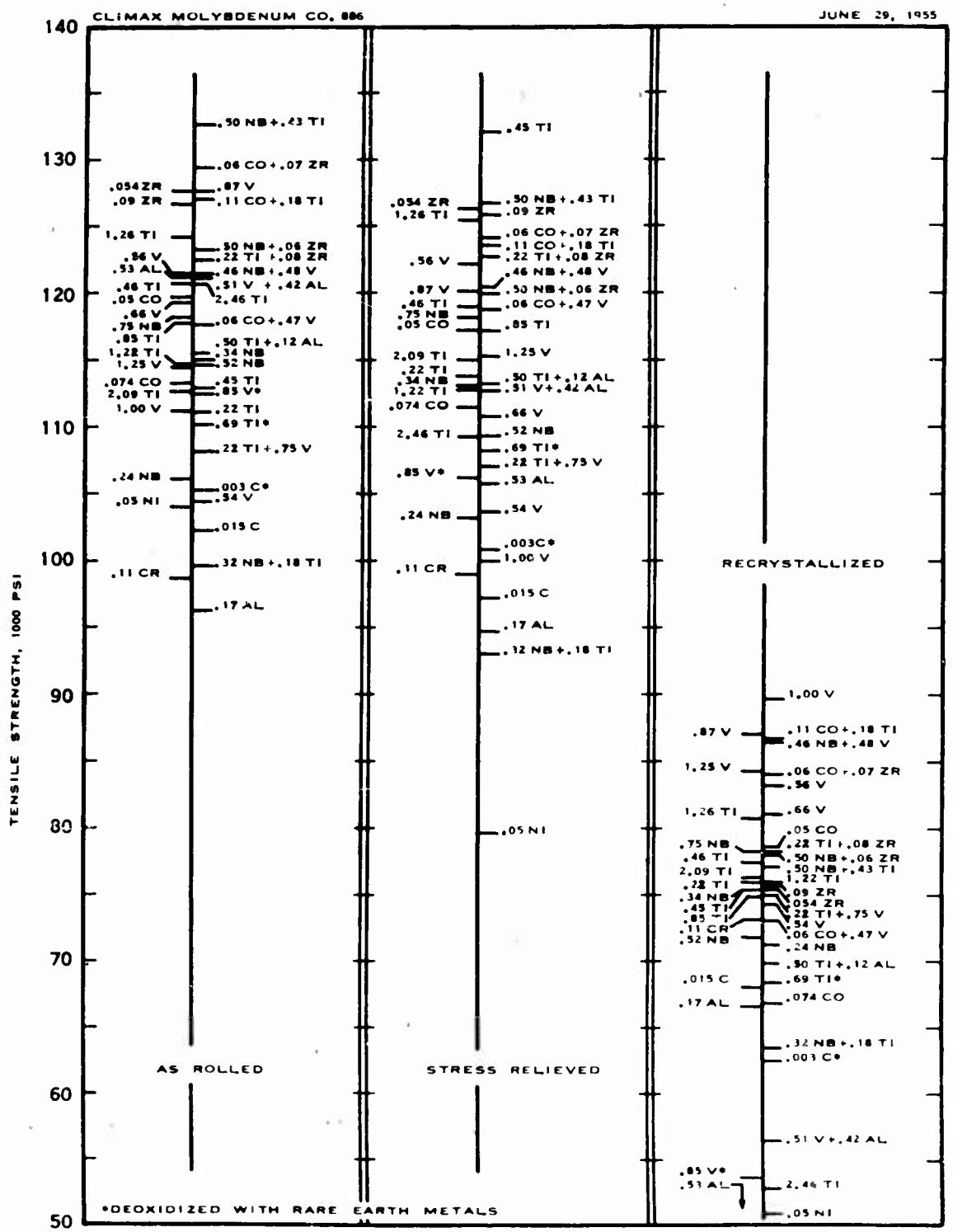


FIGURE 142 – COMPARISON OF TENSILE STRENGTHS OF 1/2" AND 5/8" DIAMETER ROLLED BARS TESTED AT ROOM TEMPERATURE

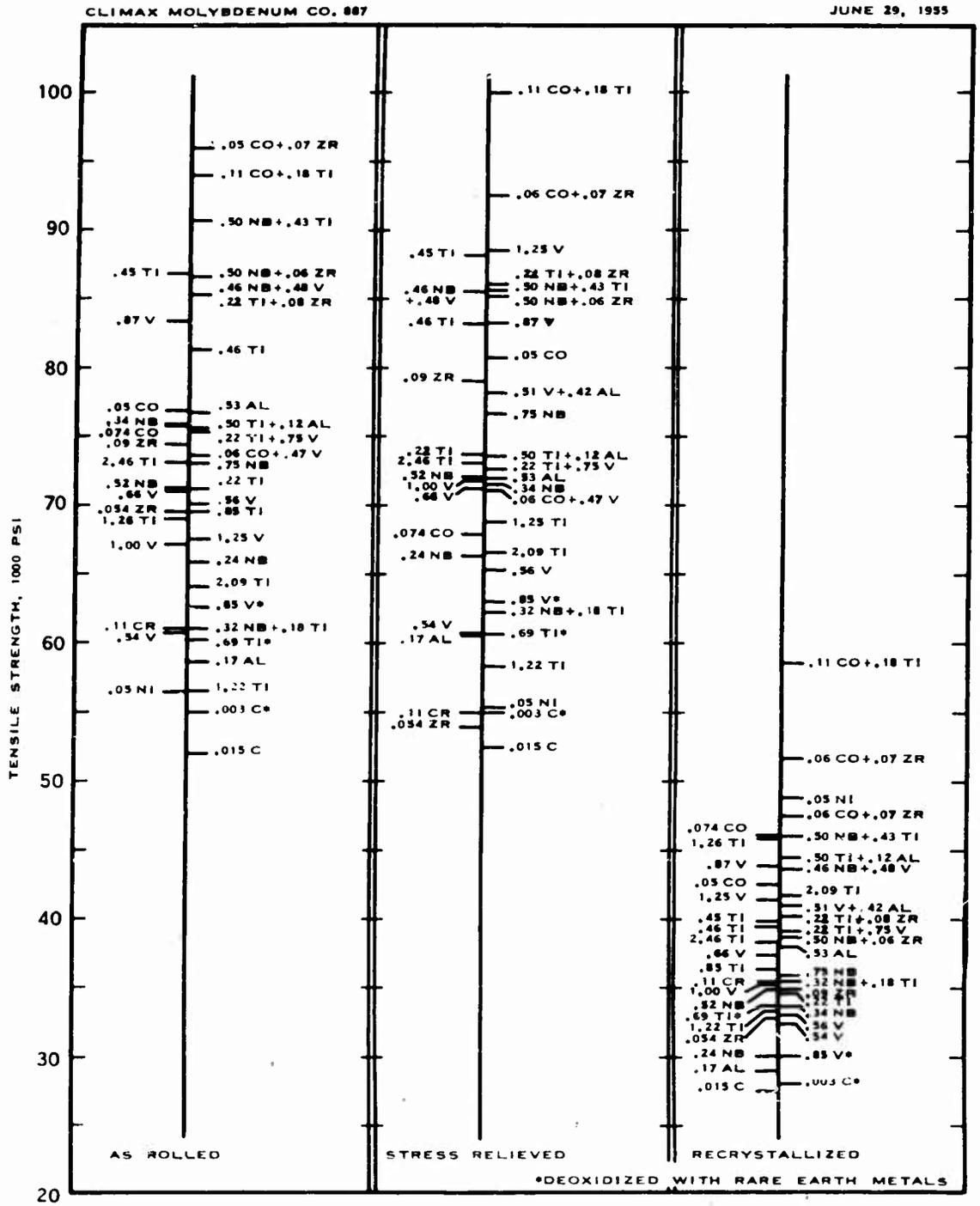


FIGURE 143 — COMPARISON OF TENSILE STRENGTHS OF 1/2" AND 5/8" DIAMETER ROLLED BARS TESTED AT 1600 F

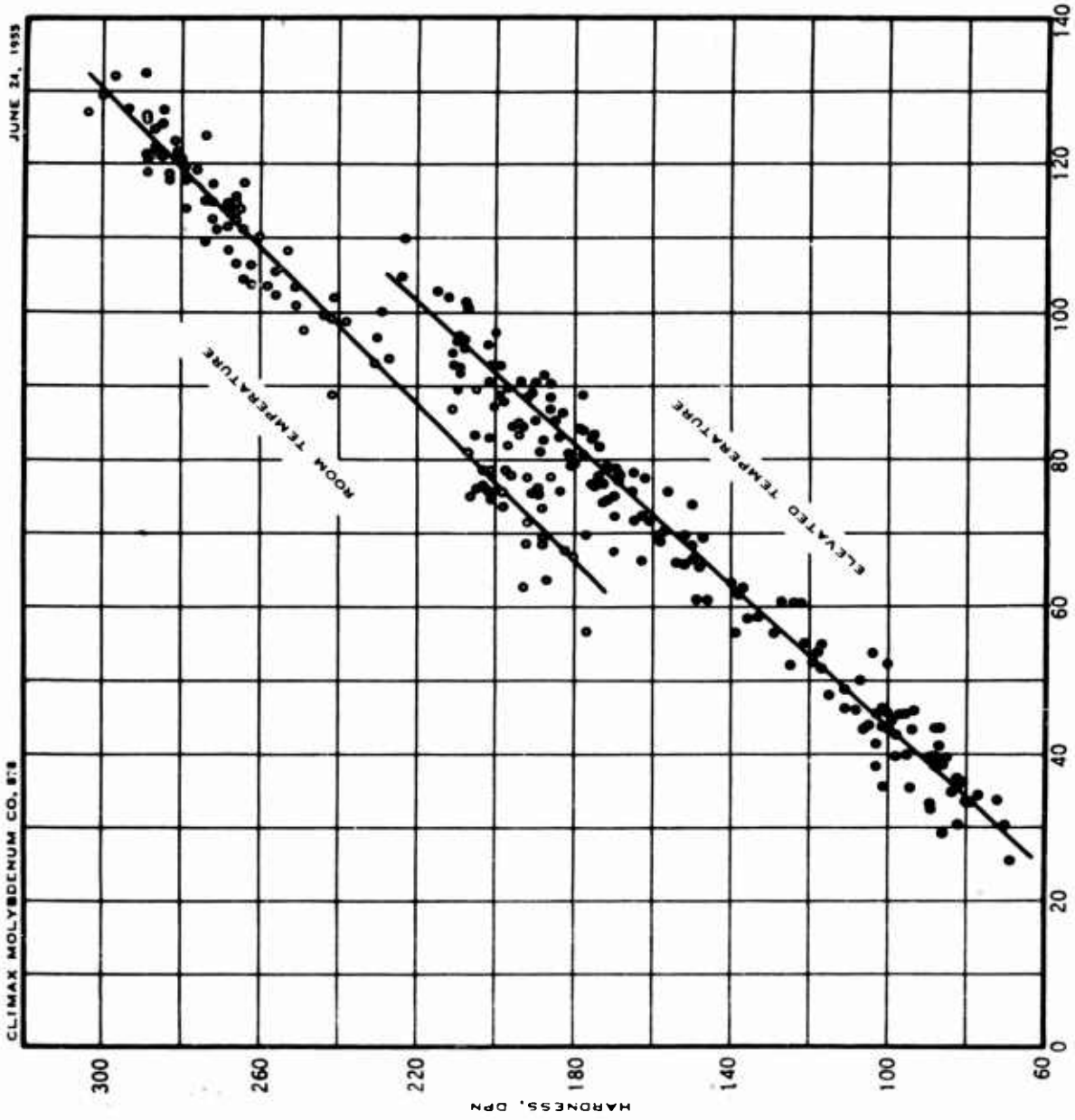


FIGURE 144 – TENSILE STRENGTH VS HARDNESS FOR 1/2" AND 5/8" MOLYBDENUM–BASE ALLOY BARS

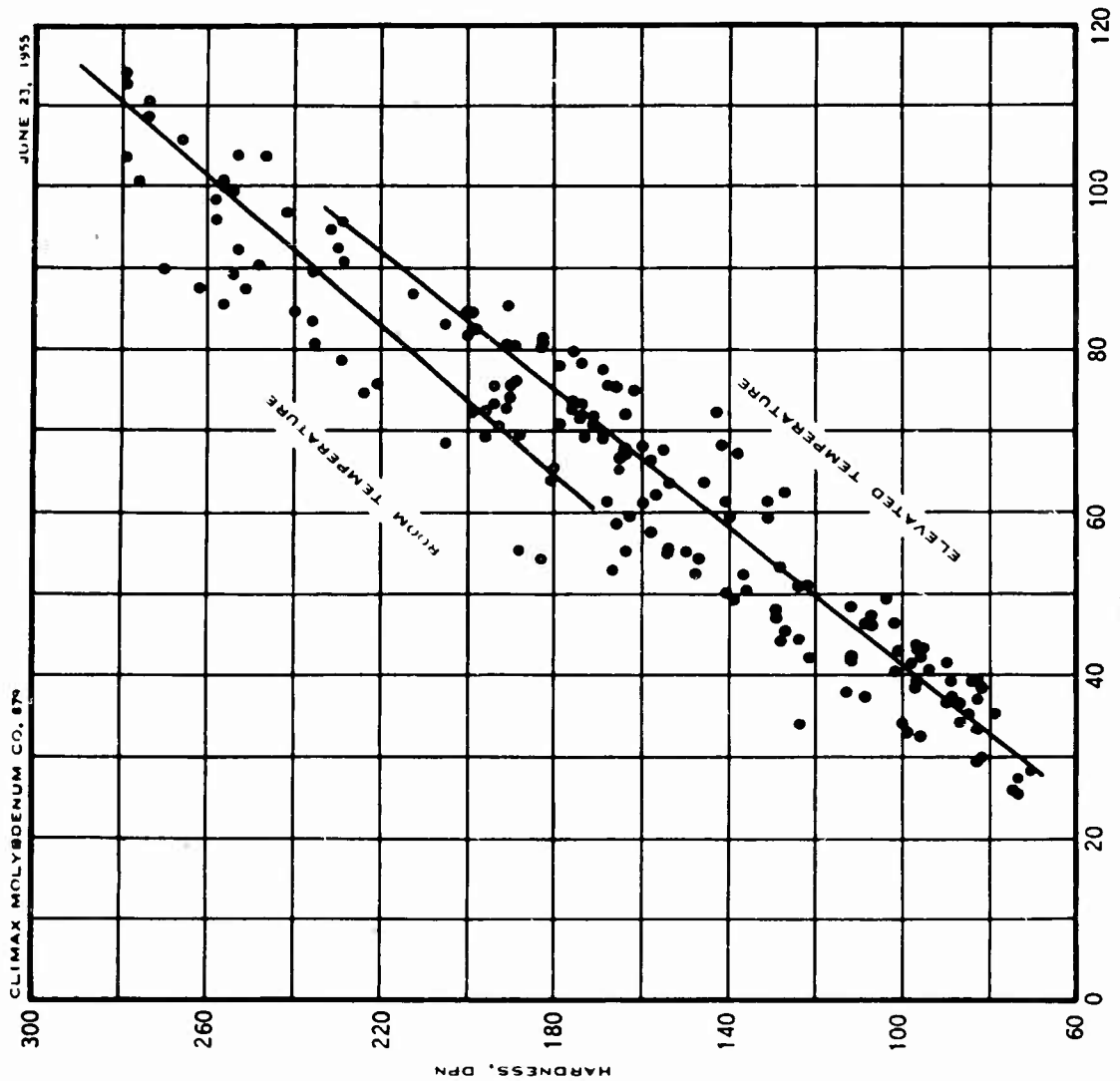


FIGURE 145 — TENSILE STRENGTH VS HARDNESS FOR 7/8", 1", AND 1-1/8" MOLYBDENUM-BASE ALLOY BARS

Transition temperature ranges under the conditions of the tensile test were generally below room temperature, although some exceptions were noted. The lowest transition temperature range recorded was in the neighborhood of -90 F.

Impact Transition Temperature

Impact transition temperatures were determined for unalloyed molybdenum and 23 molybdenum-base alloys on specimens machined from 5/8" and 1" diameter bars in the as-rolled, stress-relieved, and fully recrystallized conditions. Standard V-notch Charpy test specimens were used. They were heated in air to the test temperature and transferred rapidly to the Charpy machine for test.

Curves showing absorbed energy as a function of testing temperature for the alloys tested are given in the Appendix, Figures D29-D49. Summary curves showing transition temperature ranges are given in Figures 146-147. For these plots, the transition temperature range is arbitrarily defined as the range between the lowest temperature at which the energy absorption is 20 foot-pounds and the lowest temperature at which a specimen will absorb 120 foot-pounds without fracture.

The extent and general level of the transition temperature range was lower for specimens from 5/8" diameter bars than for specimens from 1" diameter bars from the same heat or of similar composition, in the as-rolled and stress-relieved conditions. Transition temperature ranges for fully recrystallized specimens from the two bar sizes were usually about the same. In general, the transition from brittle to ductile behavior occurred over a narrower temperature range for the fully recrystallized structures than for the strain hardened structures.

Transition temperature ranges (as defined for Figures 146-147) for as-rolled and stress-relieved bars 5/8" in diameter were significantly lower for carbon-free heats (1063, 1048, and 1049) than for unalloyed molybdenum deoxidized with carbon. As-rolled, unalloyed molybdenum containing an excess phase, such as molybdenum carbide, has a higher transition temperature range than solid-solution alloys of molybdenum containing no excess phase. After recrystallization, however, all of the carbon-free alloys exhibited a marked increase in notched-bar transition temperature.

It is evident from Figure 146 that the addition of niobium did not significantly alter the transition temperature range of unalloyed molybdenum deoxidized with carbon. Titanium lowered the range slightly for most of the alloys in the structural conditions studied. Molybdenum-vanadium alloys deoxidized with carbon generally had higher Charpy transition temperature ranges than unalloyed molybdenum. Molybdenum-cobalt alloys in the as-rolled or stress-relieved conditions were comparable to unalloyed molybdenum; after recrystallization, their transition temperature range was higher. The transition temperature range for the 0.07% cobalt alloy in the recrystallized condition, for example, was from 1300 F to above 1900 F. The transition temperature ranges of the molybdenum-zirconium alloy were somewhat lower, and of the Mo-Co-Ti alloy significantly higher, than those of unalloyed molybdenum.

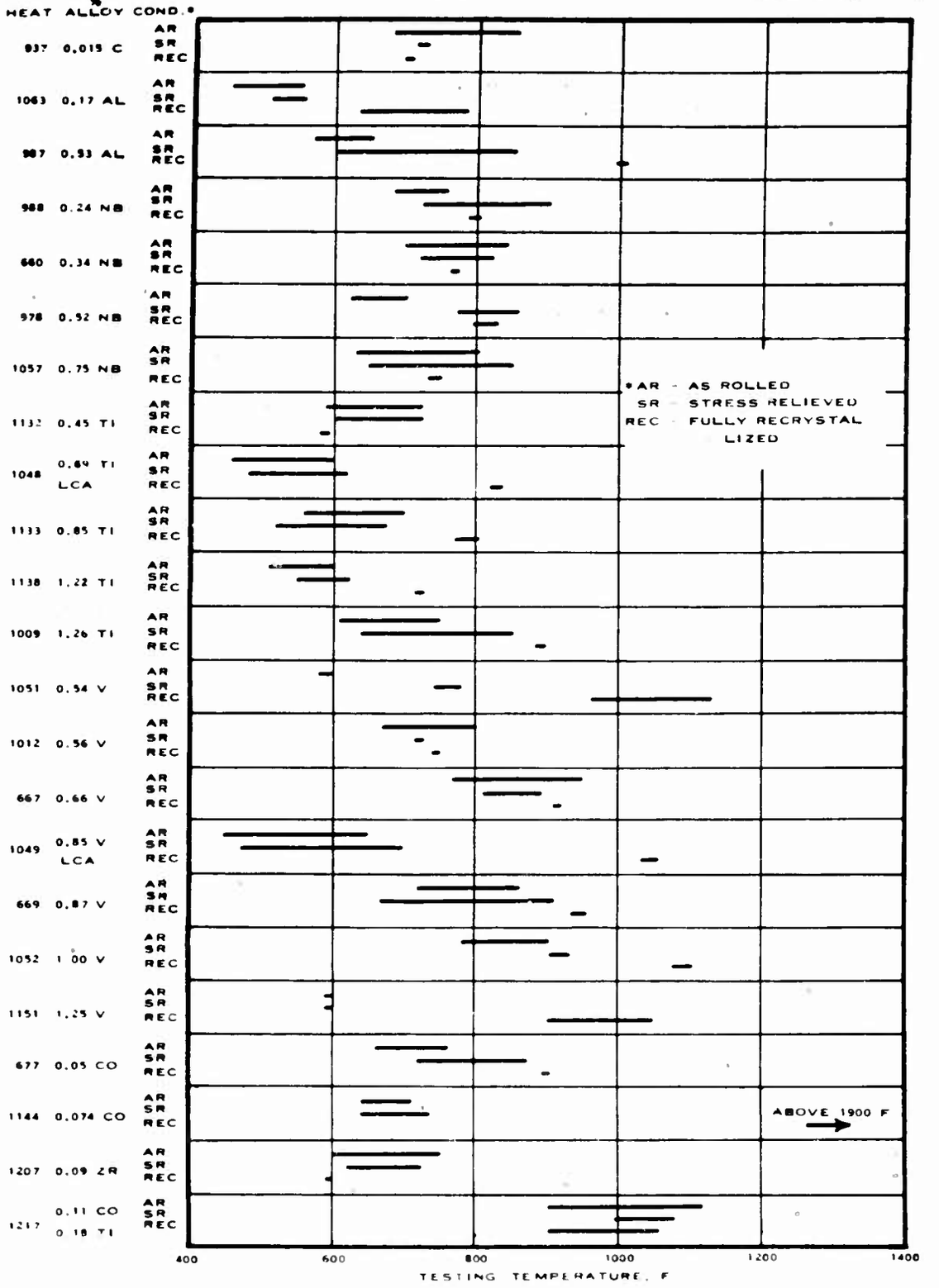
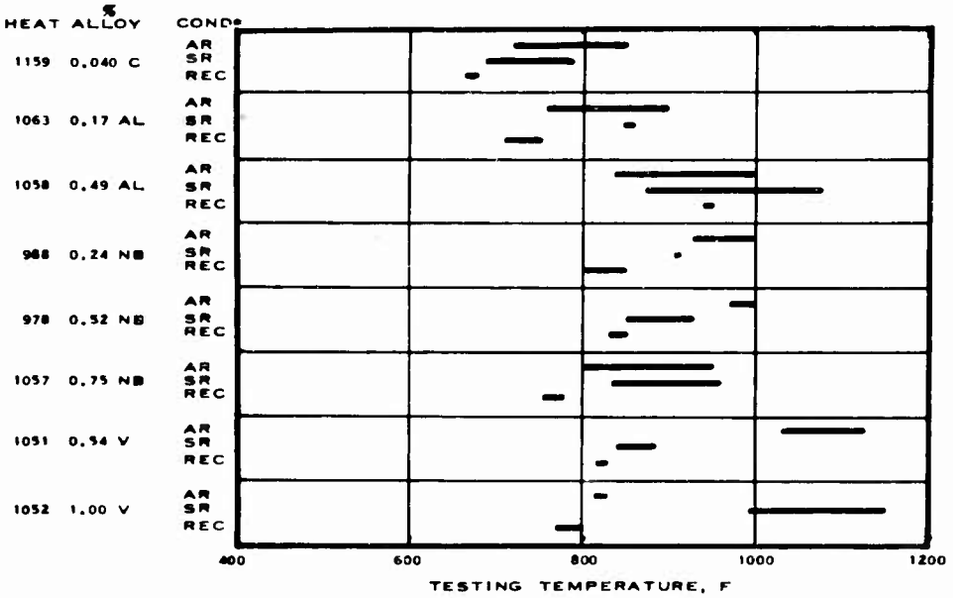


FIGURE 146 – V-NOTCH IMPACT TRANSITION TEMPERATURE RANGES FOR $\frac{5}{8}$" DIAMETER MOLYBDENUM AND MOLYBDENUM BASE ALLOY BARS



* AR - AS ROLLED
SR - STRESS RELIEVED
REC - FULLY RECRYSTALLIZED

FIGURE 147 - V-NOTCH IMPACT TRANSITION TEMPERATURE RANGES FOR 1" DIAMETER MOLYBDENUM AND MOLYBDENUM-BASE ALLOY BARS

The behavior of 1" diameter bars of unalloyed molybdenum deoxidized with aluminum was different from that of 5/8" diameter bars of the same composition. Whereas the latter exhibited transition temperature ranges below that of unalloyed, carbon-deoxidized molybdenum in the strain hardened condition, the transition temperature ranges for the 1" diameter bars were above those of unalloyed molybdenum. In fact, the transition temperature ranges of all the 1" diameter bars prepared from alloy heats were above those of unalloyed molybdenum deoxidized with carbon in vacuum, regardless of structural condition.

Tensile Transition Temperature

Tensile transition tests were conducted on unalloyed molybdenum and 15 molybdenum-base alloys available either as 1/2" or 5/8" rolled rounds. Factors such as gage dimensions and strain rates were identical with those described for tensile strength determinations in the preceding section of this report. Test temperatures were controlled between -100 and +700 F by the methods shown in Table 23.

TABLE 23

METHODS OF MAINTAINING TEST TEMPERATURES

Temperature Range, F	Medium	Control
-100 to +31	methanol	dry ice
+32 room	water	ice
room +179	water	immersion heater
+180 +349	glycerine	immersion heater
+350 +700	air	resistance furnace

Results of tensile transition tests are summarized in Figure 148. For this summary plot, the tensile transition temperature range was defined as the range between the lowest temperature at which the elongation of the tensile specimen after fracture was 20% of the maximum and the lowest temperature at which the elongation was 80% of the maximum. Detailed plots of tensile properties vs testing temperature are presented in the Appendix, Figures D50-D73.

Qualitative correlations were found between transition temperature ranges determined by V-notch impact tests and tensile tests. The following observations were made in both tests: Aluminum-deoxidized molybdenum (1063) exhibited a lower transition range in the strain hardened condition than unalloyed molybdenum deoxidized with carbon; after recrystallization, the ranges were about the same for the two types of deoxidation. Recrystallized samples of nominally 0.5% aluminum-molybdenum alloys had higher transition temperatures than unalloyed molybdenum.

Quantitatively, the higher strain rate encountered in the impact test resulted in transition ranges at higher temperatures than those determined by tension tests. There was a trend in the tensile transition tests for recrystallized samples, particularly those containing aluminum, titanium, or zirconium, to exhibit broader transition ranges (more gradual increase in elongation with increasing test temperature) than in the impact tests.

The role played by an excess phase in locating the transition temperature range discussed under the impact test applies to the tensile transition test data as well. Unalloyed molybdenum containing 0.015% carbon (937) and thus a greater amount of free carbide than unalloyed molybdenum containing 0.008% carbon (936) has the higher transition temperature range. The 0.015% carbon material had more free carbide than the 0.5% titanium alloy deoxidized with aluminum (1393) and likewise had a higher transition temperature range.

Recrystallized samples of the 0.074% cobalt alloy (1144) indicated a transition range between 170 and 190 F. This compared with a transition range above 1500 F for this alloy in the Charpy test. The 0.11% chromium alloy (1463) had transition ranges somewhat below those of unalloyed molybdenum. The 0.05% nickel alloy exhibited transition temperatures higher than those obtained for any other material in the program. The high transition range for this alloy is probably associated with the appreciable amounts of oxide which were noted in the cast structure but which were not eliminated in the normal carbon-deoxidation, vacuum-arc melting process.

Additions of titanium generally lowered the transition range of molybdenum. Relatively minor differences were detected between carbon-deoxidized alloys containing 0.22% and 0.46% titanium. The aluminum-deoxidized titanium alloy (1393) exhibited the lowest transition temperature range in the as-rolled condition of all of the materials studied. This alloy, however, was comparable to carbon-deoxidized titanium-molybdenum in the recrystallized condition.

A pronounced broadening of the transition zone was displayed by all of the alloys containing zirconium when tested in the recrystallized condition; thus, measurable amounts of ductility were observed in these materials at quite low temperatures. For example, recrystallized samples of the 0.50% niobium, 0.06% zirconium ternary alloy (1456) attained 20% of maximum ductility at -100 F. On the other hand, the zirconium-bearing alloys were inferior to unalloyed molybdenum when tested in the strain hardened condition. The remainder of the ternary alloys were for the most part appreciably higher in transition temperature range than binary alloys containing either one of the alloying elements.

In the preceding discussion, the criterion establishing the tensile transition temperature was ductility, or more specifically, elongation. During the course of the testing program, tensile and yield strength, as well as elastic limit data, were obtained for each specimen. On the whole, the changes in strength and elastic limit were not as dramatic as the changes in ductility

that were encountered and could be interpreted as due solely to changes in test temperature--that is, strength and elastic limit showed no major changes within the temperature ranges where major changes in elongation and reduction of area were observed.

To test the validity of these observations under conditions of uniform strain rate, several tests were conducted on as-rolled and fully recrystallized specimens of the aluminum-deoxidized, 0.50% titanium alloy (1393), in which the strain rate was maintained at 60% per hour in both the elastic and plastic ranges.

Figures 149-150 compare the results obtained when a strain rate of 60% per hour was used throughout the test with those obtained earlier at an elastic strain rate of 3% per hour. It will be noted that no values are plotted in Figure 150 for yield strength and elastic limit for the tests run at the higher strain rate at testing temperatures of -40 F and 0 F. The fracture stress under the conditions of these tests was lower than the flow stress; therefore, no elastic limit or yield stress values were recorded.

The increase in elastic strain rate resulted in a rise of 40 F in the transition temperature range, based upon elongation for samples as rolled, and a rise of approximately 20 F for fully recrystallized samples. The use of the higher elastic strain rate, of course, produced significantly higher values for yield strength and elastic limit. In none of the experiments to determine the transition temperature of molybdenum and molybdenum-base alloys has any indication been observed of a relationship between yield strength or elastic limit and transition temperature range as defined by elongation or reduction of area in the tensile test. Strain rate, of course, has an effect upon yield strength and elongation, but the effect is to shift the position of the curves for yield strength and elongation vs temperature rather than to change their general form.

An over-all evaluation of transition temperature studies carried out on molybdenum and molybdenum-base alloys indicates a greater dependence upon type, size, and distribution of excess phase constituents than upon alloying additions *per se*.

Effect of Molybdenum Carbide

Excess phases resulting from the deoxidation of molybdenum with carbon can be classified as those distributed in relatively large amounts, sometimes at the grain boundaries, and those appearing as much smaller precipitates at random locations. Unalloyed molybdenum and many of the alloys studied fall into the first classification, while the molybdenum-base alloys containing titanium or zirconium are in the second. As a class, alloys containing titanium or zirconium are characterized by transition temperature ranges lower than that of unalloyed molybdenum of comparable carbon content. It will also be observed that a relationship exists whereby the lower the carbon content (of alloys containing massive carbides) the lower the transition temperature range. It appears, then, that the greater the amount of (or the more agglomerated) the carbide phase in molybdenum, the higher the transition temperature range.

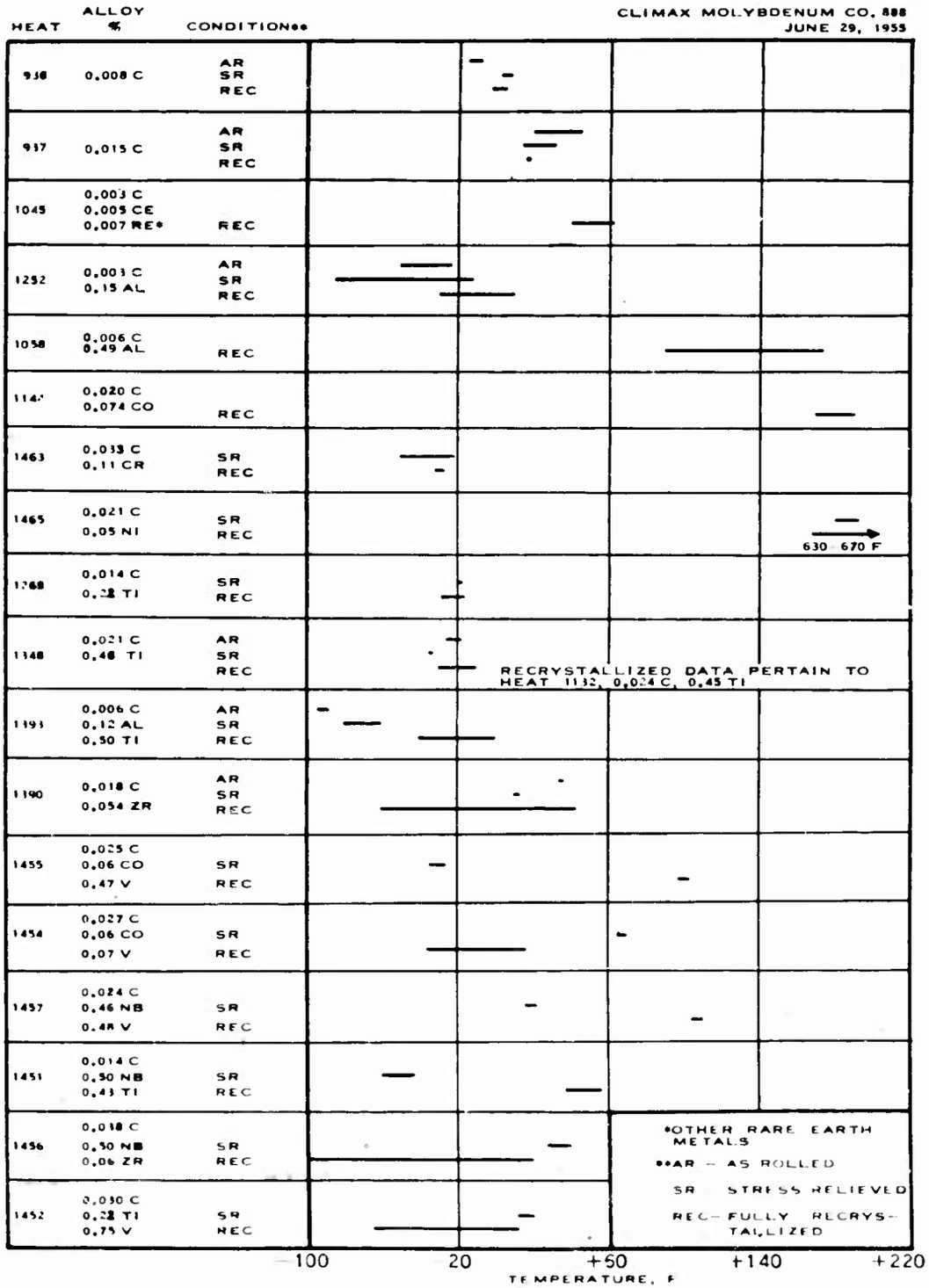


FIGURE 148 - TENSILE TRANSITION TEMPERATURE RANGE FOR INDICATED UNALLOYED MOLYBDENUM AND MOLYBDENUM BASE ALLOYS

TEMPERATURES CORRESPONDING TO 20% TO 80% OF MAXIMUM ELONGATION

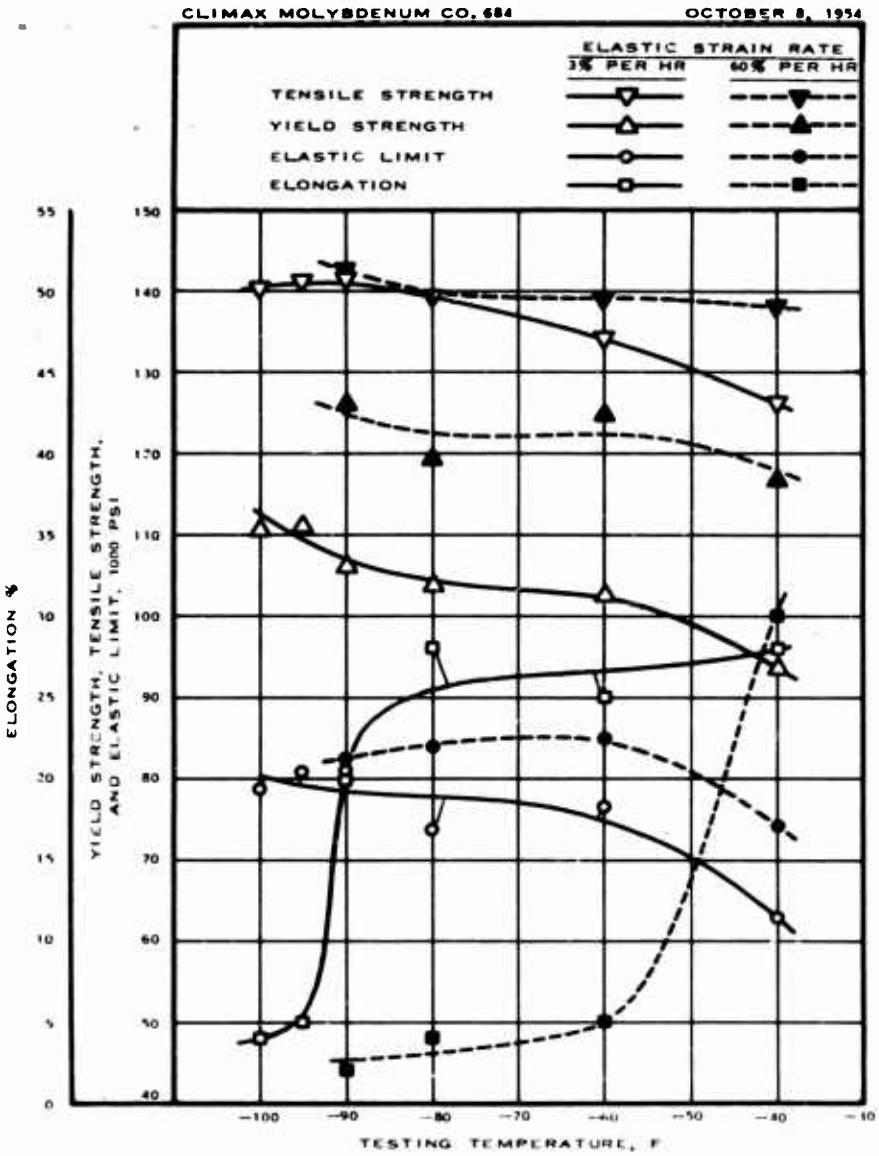


FIGURE 149 – TENSILE PROPERTIES OF Mo-Al-Ti ALLOY $\frac{5}{8}$" DIAMETER, AS ROLLED, HEAT 1393

0.006% CARBON, 0.12% ALUMINUM, 0.50% TITANIUM

TESTED AT INDICATED ELASTIC STRAIN RATES
PLASTIC STRAIN RATE – 60% PER HOUR

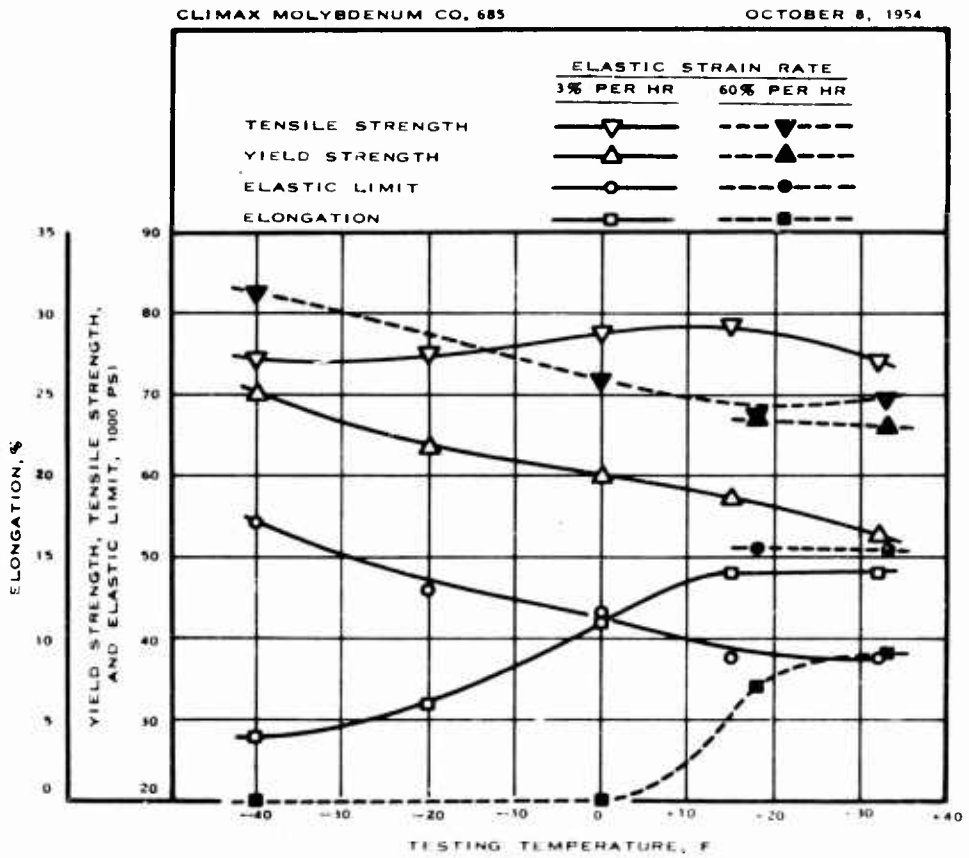


FIGURE 150 -- TENSILE PROPERTIES OF Mo-Al-Ti ALLOY $\frac{5}{8}$" DIAMETER, RECRYSTALLIZED, HEAT 1393

0.006% CARBON, 0.12% ALUMINUM, 0.50 TITANIUM

TESTED AT INDICATED ELASTIC STRAIN RATES
PLASTIC STRAIN RATE, - 60% PER HOUR

Carbon-Free or Low-Carbon Molybdenum

Molybdenum deoxidized with either aluminum or rare earth metals contains minute inclusions, the size and distribution of which are not materially altered within the temperature range required to recrystallize these materials. As a class, these materials exhibited low transition temperature ranges when tested in the as-rolled or stress-relieved conditions. The recrystallization treatment generally brought about a pronounced increase in transition temperature. The behavior of the carbon-free materials apparently cannot be attributed directly to the microscopic inclusions, owing to their stability within the temperature range required to produce complete recrystallization.

Effect of Nonmetallics

Molybdenum-base alloys containing appreciable amounts of oxide or other nonmetallic inclusions in the cast structure--notably the 0.05% nickel alloy (1465)--displayed high transition temperature ranges. Furthermore, transition temperature ranges obtained for recrystallized samples were substantially higher than for strain hardened samples. This was thought to result from a precipitation or diffusion of nonmetallics at the grain boundaries during the recrystallization heat treatment.

The factors affecting transition temperature range are believed to be closely related to those causing embrittlement of molybdenum after exposure to elevated temperatures. The difference is one of degree, since the elevated-temperature exposure provides more energy for diffusion of impurities and results in grain growth and less grain boundary area per unit volume and therefore concentrates the nonmetallics.

Creep-Rupture Properties

One of the principal objectives of this project has been the development of molybdenum-base alloys for elevated temperature service. Load-carrying ability at elevated temperatures is one of the most important considerations in rating the alloys developed to date.

Creep-rupture tests have been conducted at Battelle Memorial Institute on unalloyed molybdenum and many of the binary and ternary alloys produced under this contract. The tests were conducted in vacuum at 1600, 1800, and 2000 F. Later in the program the tests at 1600 F were omitted. Rupture specimens were machined from 1/2" or 5/8" diameter bar stock. In general, three tests designed to produce rupture in approximately 1, 10, and 100 hours were conducted at each testing temperature for each heat in each structural condition. As the program progressed, two specimens were used to determine the slope of the stress-rupture curve, aiming at rupture in 10 and 100 hours. Tests extending longer than the arbitrarily assigned limit of 300 hours were discontinued. Creep rates were calculated for all tests that sustained the applied loads sufficiently long to produce time-deformation data.

The results of the creep-rupture tests are presented as log-log plots of stress vs time to rupture in Figures 151-167 for all of the materials tested. Individual test data may be found in the Appendix, Table D2.

To compare the various molybdenum-base alloys for which creep-rupture data have been obtained, the stress to produce rupture in 100 hours has been tabulated. Table 24 presents these data for the alloys tested in the stress relieved (strain hardened) condition; Table 25, for the alloys tested in the fully recrystallized condition.

On comparison of the stresses required to produce rupture in 100 hours at 1600 F for any given alloy in the stress relieved and the recrystallized conditions, it is found that the load-carrying capacity in the stress relieved (strain hardened) condition is approximately twice that of the same alloy in the recrystallized condition. As the testing temperature is raised to 1800 F and 2000 F, the load-carrying capacity in the strain-hardened condition approaches that of the recrystallized condition for alloys recrystallizing in the range 1900-2250 F. However, those alloys recrystallizing above 2250 F continued to be twice as strong in the strain hardened condition as in the recrystallized condition, when tested at 1800 F and 2000 F. This is evidence of the great value of alloying elements that raise the recrystallization temperature of molybdenum. The alloys having lower recrystallization temperatures, when tested in the strain hardened condition, exhibited various degrees of recrystallization as a result of testing at 1800 F and 2000 F in the longer tests.

An attempt has been made to evaluate the factors contributing to increased creep-rupture strength in molybdenum-base alloy systems for which creep data are available on more than one alloy. In general, alloying increases the creep-rupture strength of molybdenum. This effect is evident with alloys in the recrystallized condition, but in the strain hardened condition the effect of differences in fabrication (and the resultant variation in degree of strain hardening) overshadows the effect of alloying. Furthermore, those alloys which markedly raise the recrystallization temperature of molybdenum are the most effective in raising creep-rupture strength.

Only in the series of molybdenum-aluminum and molybdenum-niobium alloys is there a direct relation between amount of alloying element and creep-rupture strength. As the aluminum content is increased from 0.17% to 0.53% or the niobium content is increased from 0.24% to 0.75%, the creep-rupture strength is increased for all three test temperatures and for both structural conditions.

In the molybdenum-cobalt and molybdenum-vanadium series, the relationship between creep-rupture strength and alloy content is erratic; but, since the heats in these groups were fabricated by different methods, the absence of a direct relationship between strength and alloy content may be partly attributed to the fabrication variables.

TABLE 24

CREEP-RUPTURE STRENGTH OF WROUGHT, ARC-CAST MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS IN THE STRESS-RELIEVED CONDITION

Stress to Produce Rupture in 100 Hours, psi

1600 F		1800 F		2000 F	
31000	Unalloyed Mo	14500	0.05 Ni	8000	0.06 Co, 0.47 V
36000	0.17 Al	15500	0.11 Cr	9000	0.11 Cr
37000	0.074 Co	17000	0.06 Co, 0.47 V	9000	0.05 Ni
41000	0.54 V	18000	0.17 Al	10000	0.17 Al
41000	0.56 V	19000	0.074 Co	10500	0.074 Co
41000	Mo + RE	22000	Unalloyed Mo	10500	0.54 V
42000	2.09 Ti	22000	0.56 V	11500	0.53 Al
43000	1.22 Ti	24000	0.54 V	11500	0.24 Nb
44000	0.69 Ti, RE	24000	0.11 Co, 0.18 Ti	11500	1.00 V
45000	0.53 Al	27500	0.53 Al	12500	0.42 Al, 0.51 V
46000	0.85 V, RE	28000	Mo + RE	13000	Unalloyed Mo
47000	0.66 V	28000	0.66 V	13000	Mo + RE
>48000	0.32 Nb, 0.18 Ti	29000	1.26 Ti	13000	0.56 V
49000	0.85 Ti	30000	0.24 Nb	13500	0.34 Nb
49000	1.00 V	31000	1.22 Ti	14000	0.05 Co
49000	1.25 V	31000	0.42 Al, 0.51 V	15500	0.87 V
50000	1.26 Ti	32000	1.00 V	16000	0.52 Nb
53000	0.24 Nb	32000	0.50 Nb, 0.43 Ti	16500	0.11 Co, 0.18 Ti
53000	0.50 Ti, 0.12 Al	33000	0.05 Co	17000	0.69 Ti, RE
53000	0.87 V	33000	2.09 Ti	18500	1.22 Ti
55000	0.05 Co	33000	0.85 V, RE	19500	1.26 Ti
58000	0.34 Nb	34000	0.69 Ti, RE	20500	0.85 V, RE
60000	0.22 Ti	34000	0.50 Ti, 0.12 Al	21000	2.09 Ti
64000	0.52 Nb	34000	1.25 V	22000	0.75 Nb
67000	0.11 Co, 0.18 Ti	36000	0.85 Ti	22000	0.50 Ti, 0.12 Al
68000	0.45 Ti	37000	0.34 Nb	22000	0.85 Ti
69000	0.75 Nb	38500	2.46 Ti	22000	2.46 Ti
69000	0.09 Zr	40000	0.87 V	22000[e]	0.50 Nb, 0.43 Ti
73000	0.05 Zr	43000	0.52 Nb	24500	0.46 Nb, 0.48 V
		>45000	0.32 Nb, 0.18 Ti	26000	0.22 Ti, 0.75 V
		48000	0.22 Ti	31000	0.22 Ti
		51000	0.75 Nb	>33000	0.32 Nb, 0.18 Ti
		52000	0.22 Ti, 0.75 V	34000	0.45 Ti
		53000	0.45 Ti	34000	0.06 Co, 0.07 Zr
		54000	0.46 Nb, 0.48 V	39000	0.09 Zr
		56000	0.09 Zr	40000	0.05 Zr
		60000	0.06 Co, 0.07 Zr	40000[e]	0.50 Nb, 0.06 Zr
		62000	0.05 Zr	50000[e]	0.22 Ti, 0.08 Zr
		>63000	0.50 Nb, 0.06 Zr		
		66000	0.22 Ti, 0.08 Zr		

[e] estimated from incomplete data

> Values are lower than the true stress for 100-hour life.

TABLE 25

CREEP-RUPTURE STRENGTH OF WROUGHT, ARC-CAST MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS IN THE FULLY RECRYSTALLIZED CONDITION

Stress to Produce Rupture in 100 Hours, psi

1600 F		1800 F		2000 F	
16000	Unalloyed Mo	11500	Unalloyed Mo	9000	Unalloyed Mo
18500	0.17 Al	13000	0.17 Al	9000	0.11 Cr
20000	Mo + RE	13000	0.42 Al, 0.51 V	9000	0.05 Ni
20000	0.85 V + RE	13000	0.11 Cr	9200	0.17 Al
21000	0.53 Al	13000	0.05 Ni	9500	0.06 Co, 0.47 V
21000	0.54 V	14000	Mo + RE	10000	0.53 Al
22000	0.24 Nb	15000	0.074 Co	10000	0.69 Ti + RE
23000	0.56 V	15000	0.54 V	10500	0.54 V
23000	0.69 Ti + RE	15500	0.66 V	11000	0.24 Nb
23500	1.22 Ti	16000	0.53 Al	>11000	0.42 Al, 0.51 V
25000	0.34 Nb	16000	0.85 V + RE	11500	Mo + RE
25000	0.074 Co	16000	0.06 Co, 0.47 V	11500	0.074 Co
26000	0.66 V	17500	0.24 Nb	11500	2.09 Ti
26000	0.05 Co	17500	0.56 V	11500	0.66 V
27000	1.00 V	17500	1.22 Ti	11500	0.85 V + RE
27500	0.85 Ti	18000	1.00 V	11500	1.25 V
>28000	0.22 Ti	18500	0.69 Ti + RE	12000	0.56 V
29000	2.09 Ti	19000	0.11 Co, 0.18 Ti	13000	1.00 V
29000	0.87 V	19500	0.85 Ti	13500	0.34 Nb
30500	0.32 Nb, 0.18 Ti	20000	0.34 Nb	14000	1.22 Ti
31000	0.52 Nb	21000	0.05 Co	14000	0.87 V
31000	0.05 Zr	21000	2.09 Ti	>14000	0.32 Nb, 0.18 Ti
>32000.	0.09 Zr	21500	0.87 V	15000	0.11 Co, 0.18 Ti
33000	0.50 Ti, 0.12 Al	>22000	0.22 Ti, 0.08 Zr	15000	0.52 Nb
34500	0.45 Ti	23000	0.50 Ti, 0.12 Al	15000	0.85 Ti
35000	0.11 Co, 0.18 Ti	24000	0.22 Ti	15500	0.50 Ti, 0.12 Al
37000	0.75 Nb	24000	0.32 Nb, 0.18 Ti	15500	0.05 Co
40500	1.26 Ti	25000	0.05 Zr	>17000	0.46 Nb, 0.48 V
		>25000	0.50 Nb, 0.06 Zr	17500	0.22 Ti
		25500	0.52 Nb	18000	0.75 Nb
		27000	0.22 Ti, 0.75 V	18500	0.22 Ti, 0.75 V
		27000[e]	0.46 Nb, 0.48 V	20000	0.06 Co, 0.07 Zr
		27500	0.09 Zr	20000	0.50 Nb, 0.43 Ti
		28000	0.45 Ti	21000	0.45 Ti
		28500	0.75 Nb	21000	0.05 Zr
		29000	0.06 Co, 0.07 Zr	21000	0.50 Nb, 0.06 Zr
		30000	0.50 Nb, 0.43 Ti	22000	1.26 Ti
		38000	1.26 Ti	22000	0.09 Zr
				>22000	0.22 Ti, 0.08 Zr

[e]estimated from incomplete data

> Values are lower than the true stress for 100-hour life.

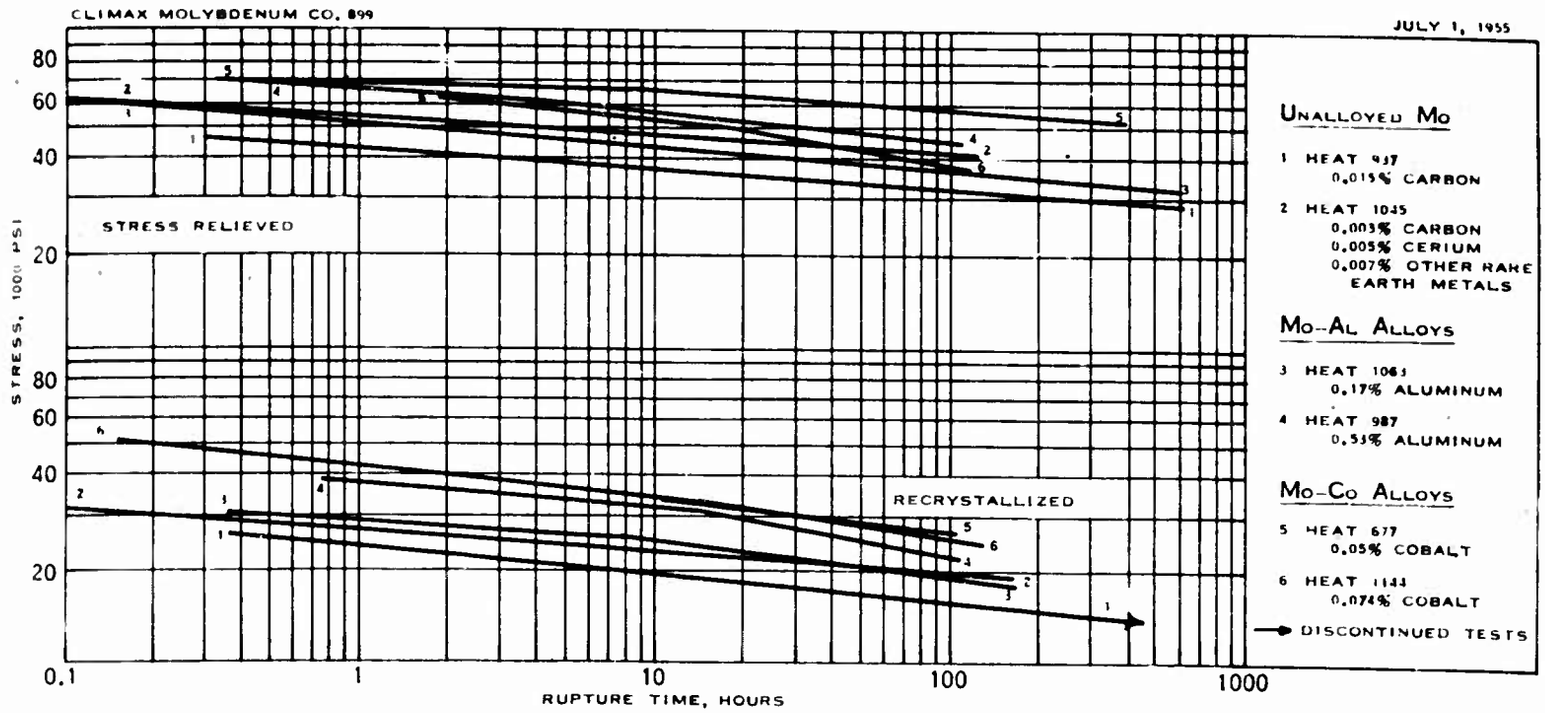


FIGURE 151– CREEP RUPTURE STRENGTH OF UNALLOYED MOLYBDENUM AND Mo-Al AND Mo-Co ALLOY BARS TESTED AT 1600 F

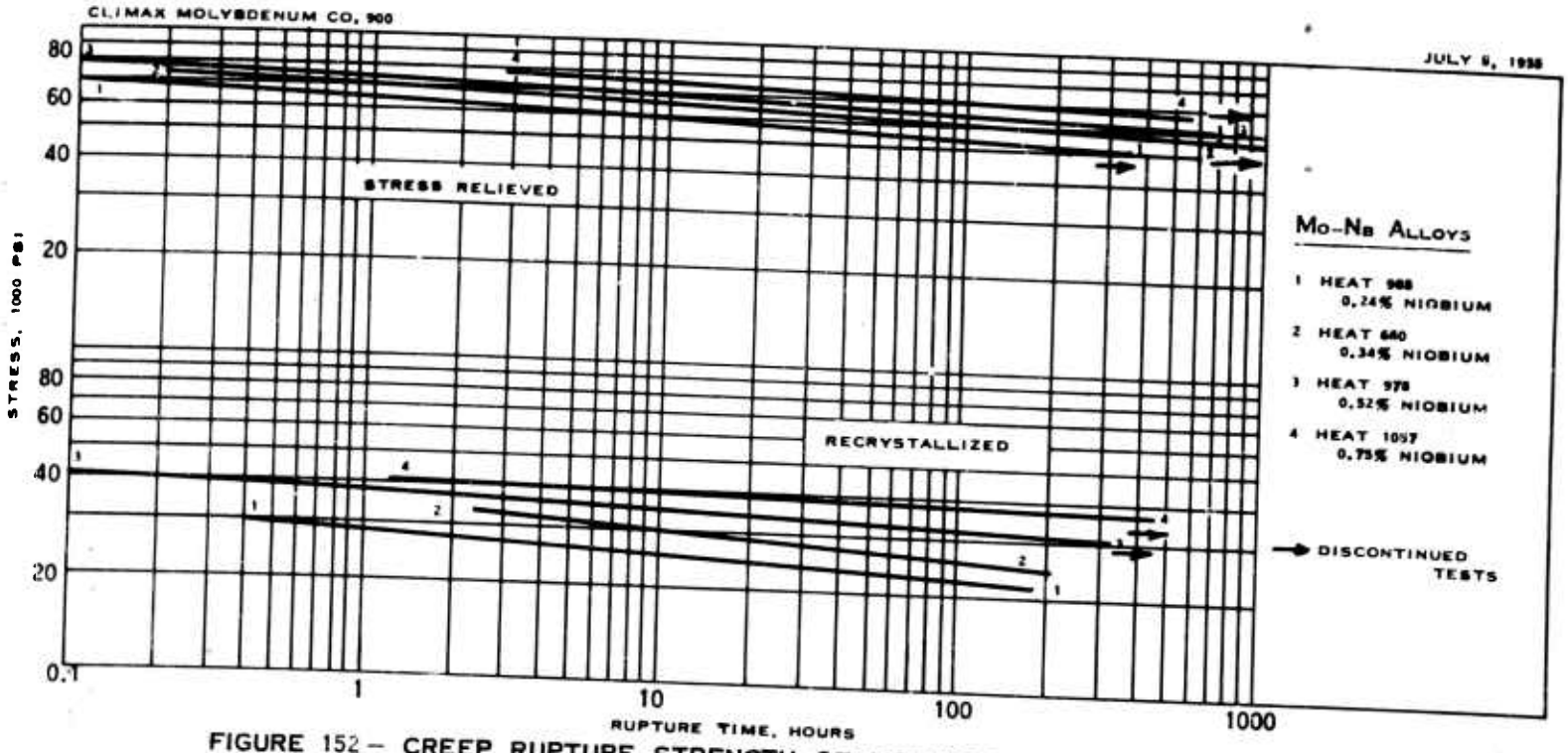


FIGURE 152 – CREEP RUPTURE STRENGTH OF MOLYBDENUM–NIOBIUM ALLOY BARS TESTED AT 1600 F

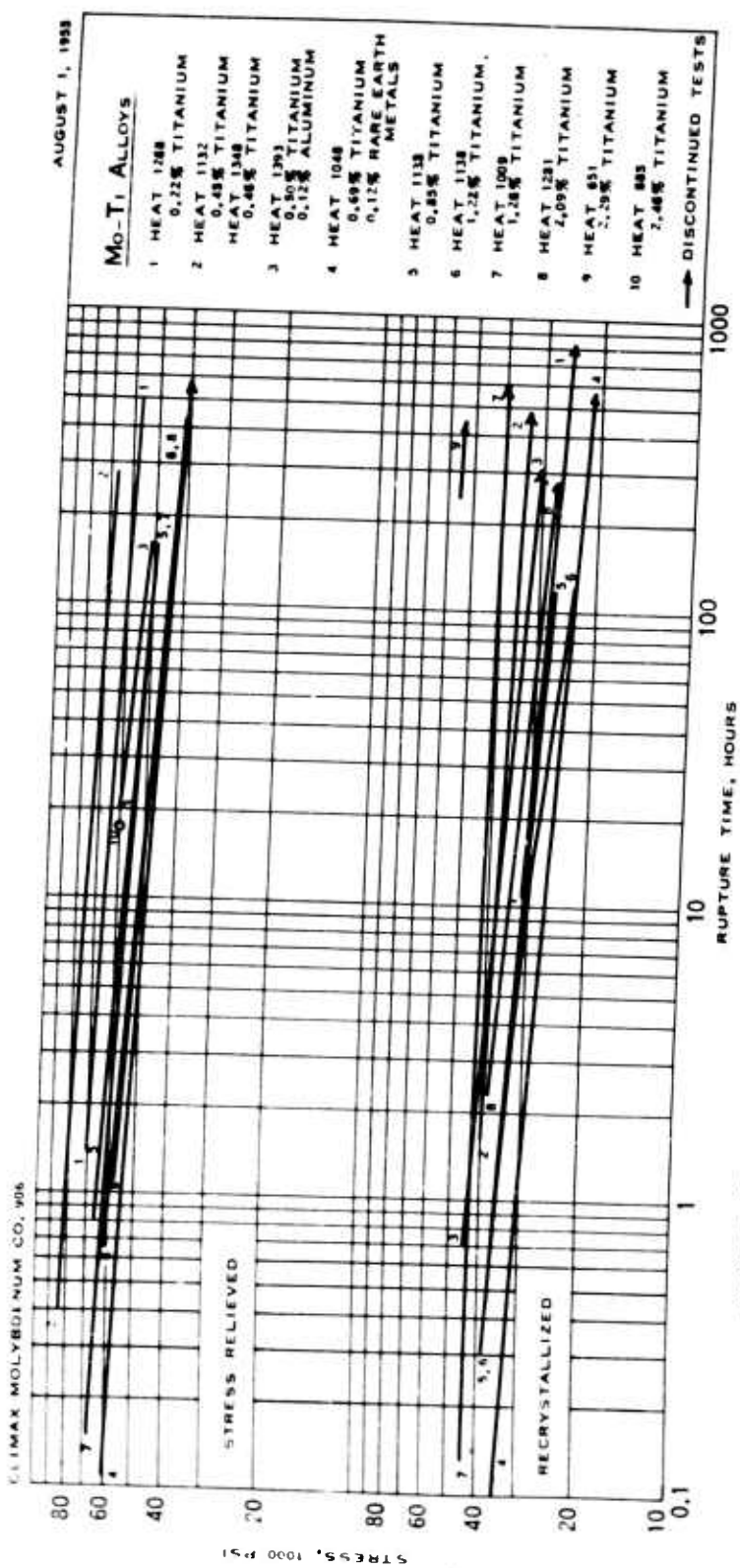


FIGURE 153 – CREEP RUPTURE STRENGTH OF MOLYBDENUM–TITANIUM ALLOY
BARS TESTED AT 1600 F

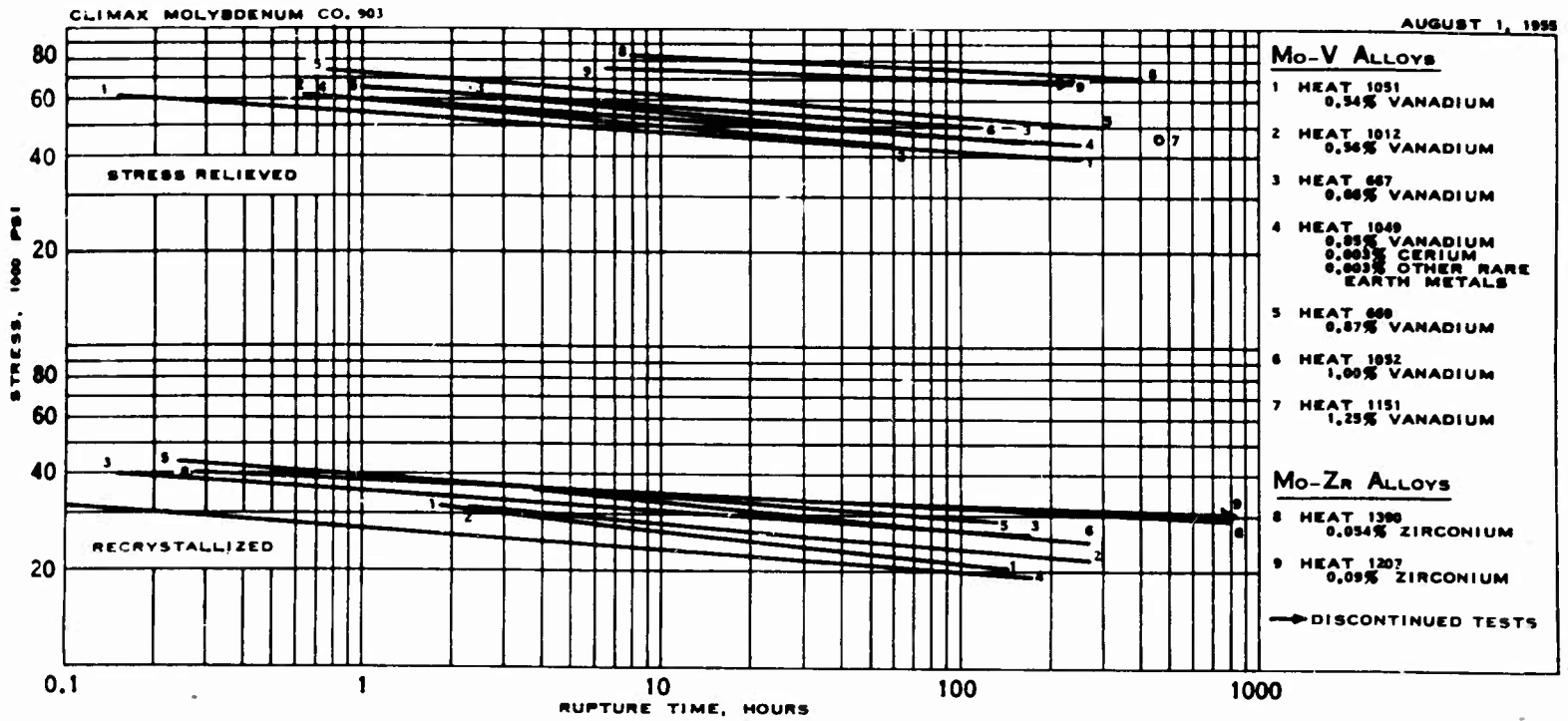


FIGURE 154 – CREEP RUPTURE STRENGTH OF Mo-V AND Mo-Zr ALLOY BARS TESTED AT 1600 F

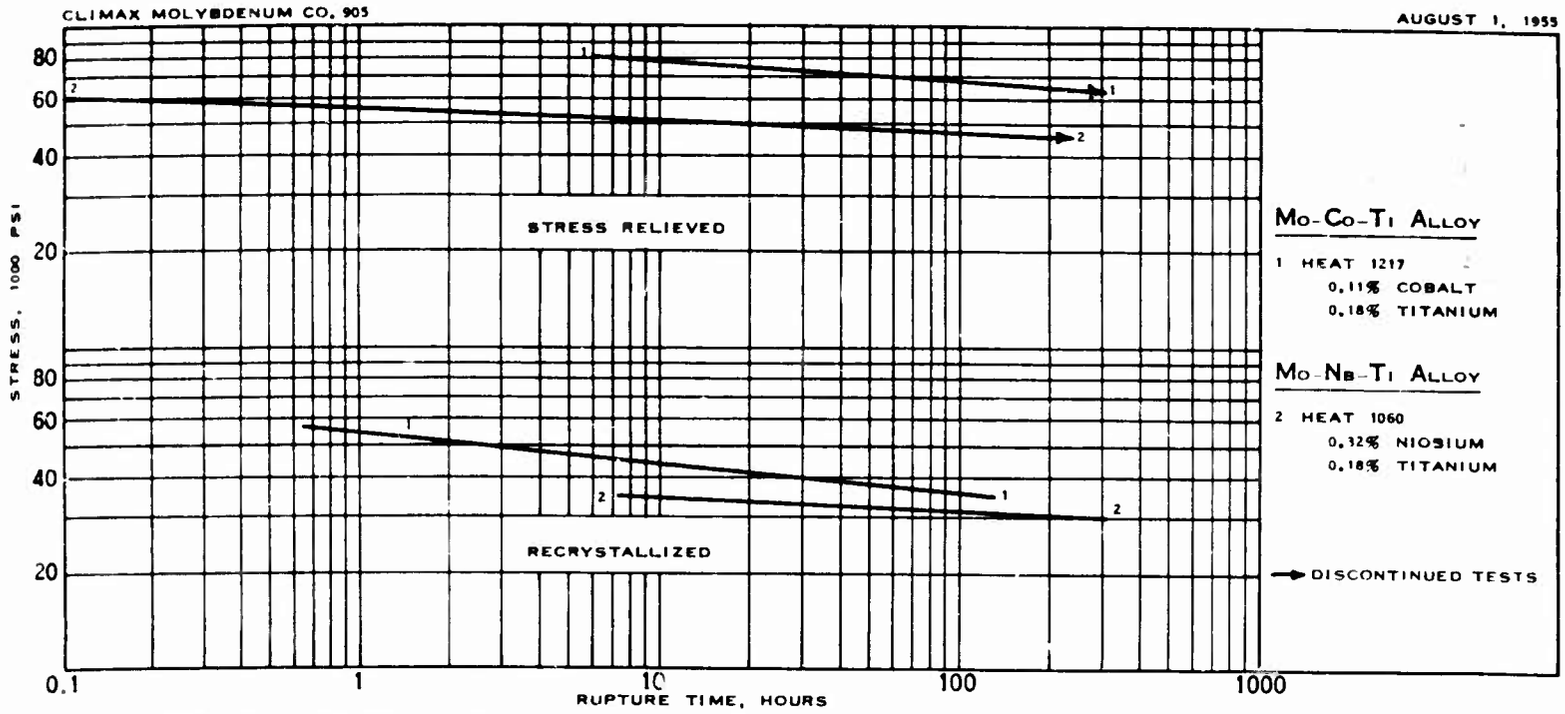


FIGURE 155 – CREEP RUPTURE STRENGTH OF Mo-Co-Ti AND Mo-Nb-Ti ALLOY BARS TESTED AT 1600 F

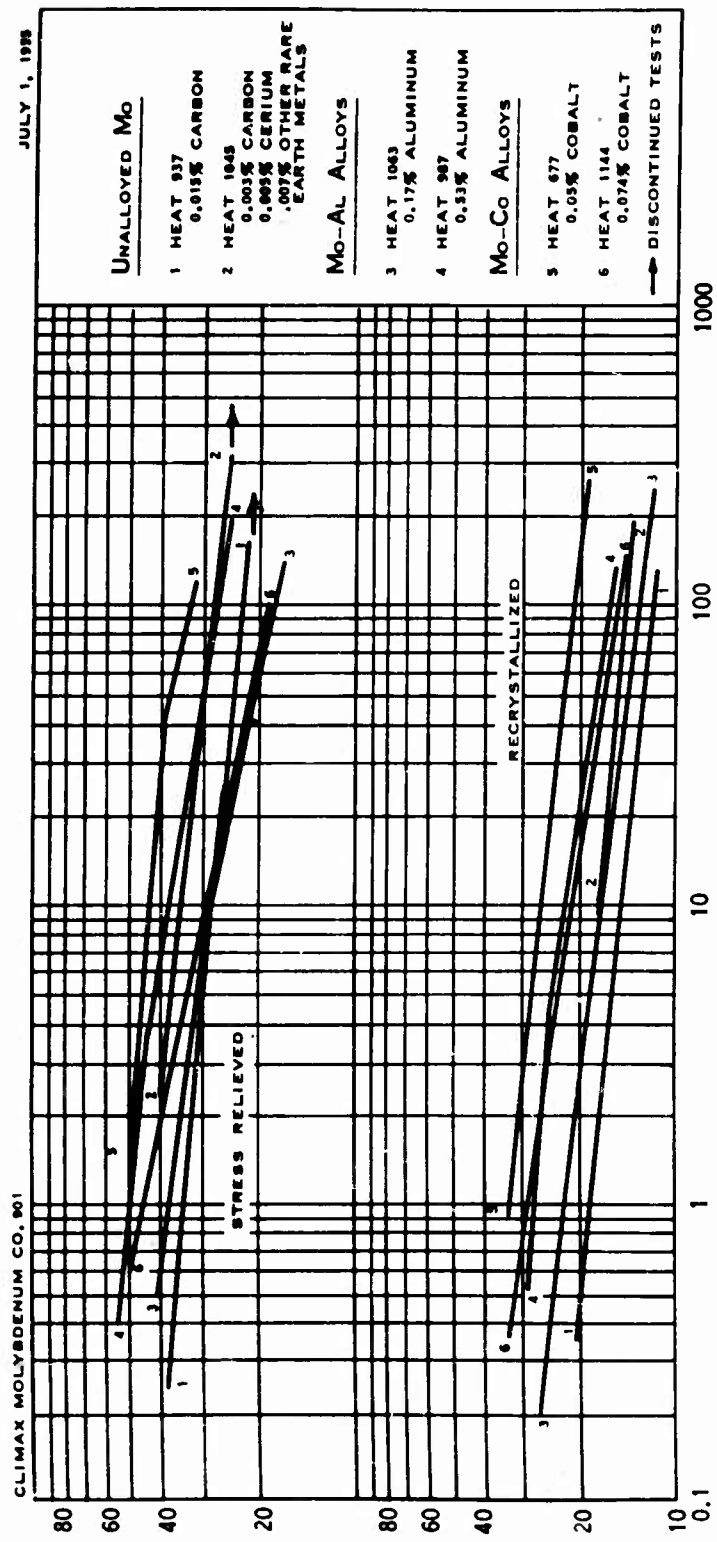


FIGURE 156 – CREEP RUPTURE STRENGTH OF UNALLOYED MOLYBDENUM AND Mo-Al AND Mo-Co ALLOY BARS TESTED AT 1800 F

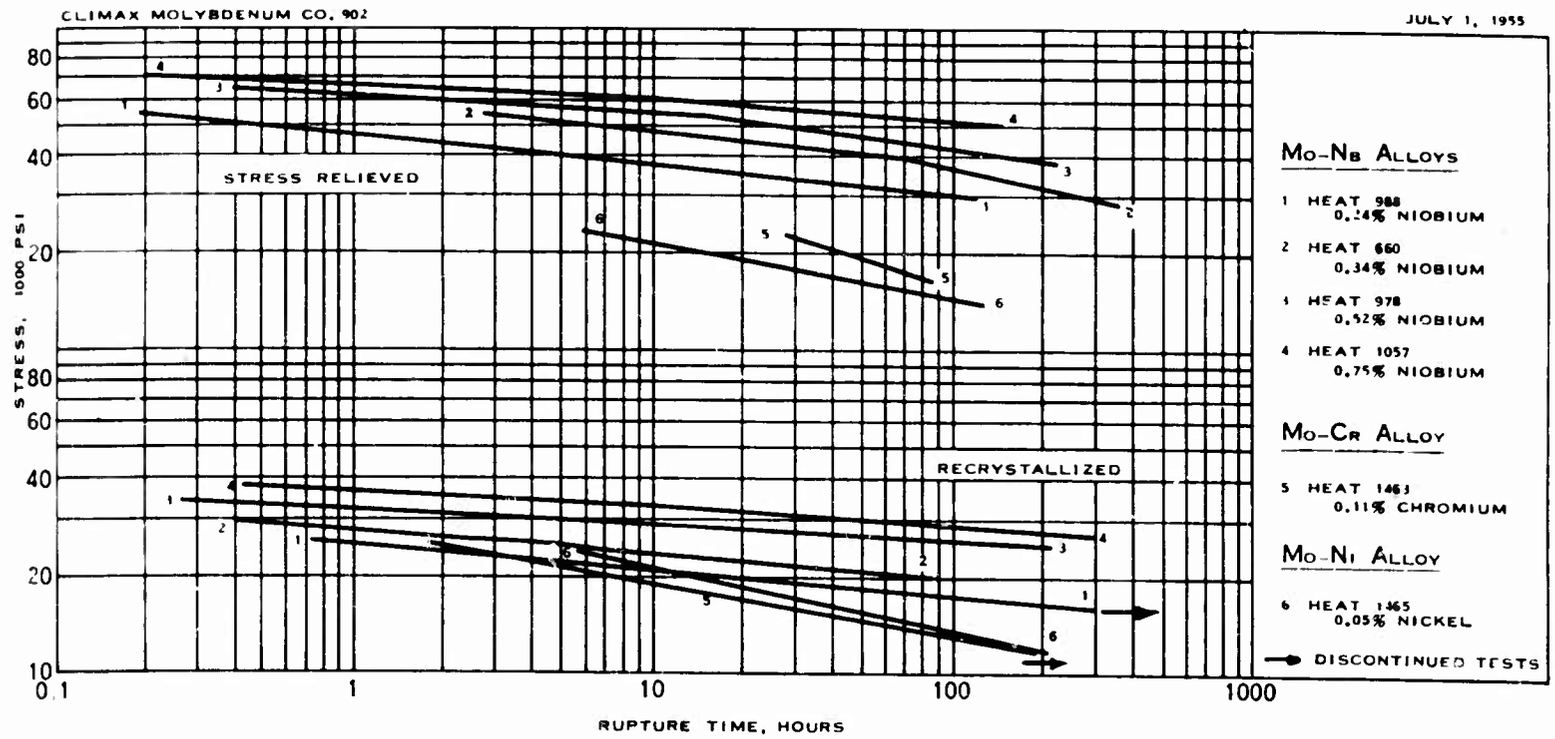


FIGURE 157– CREEP RUPTURE STRENGTH OF MOLYBDENUM–NIOBIUM ALLOY BARS TESTED AT 1800 F

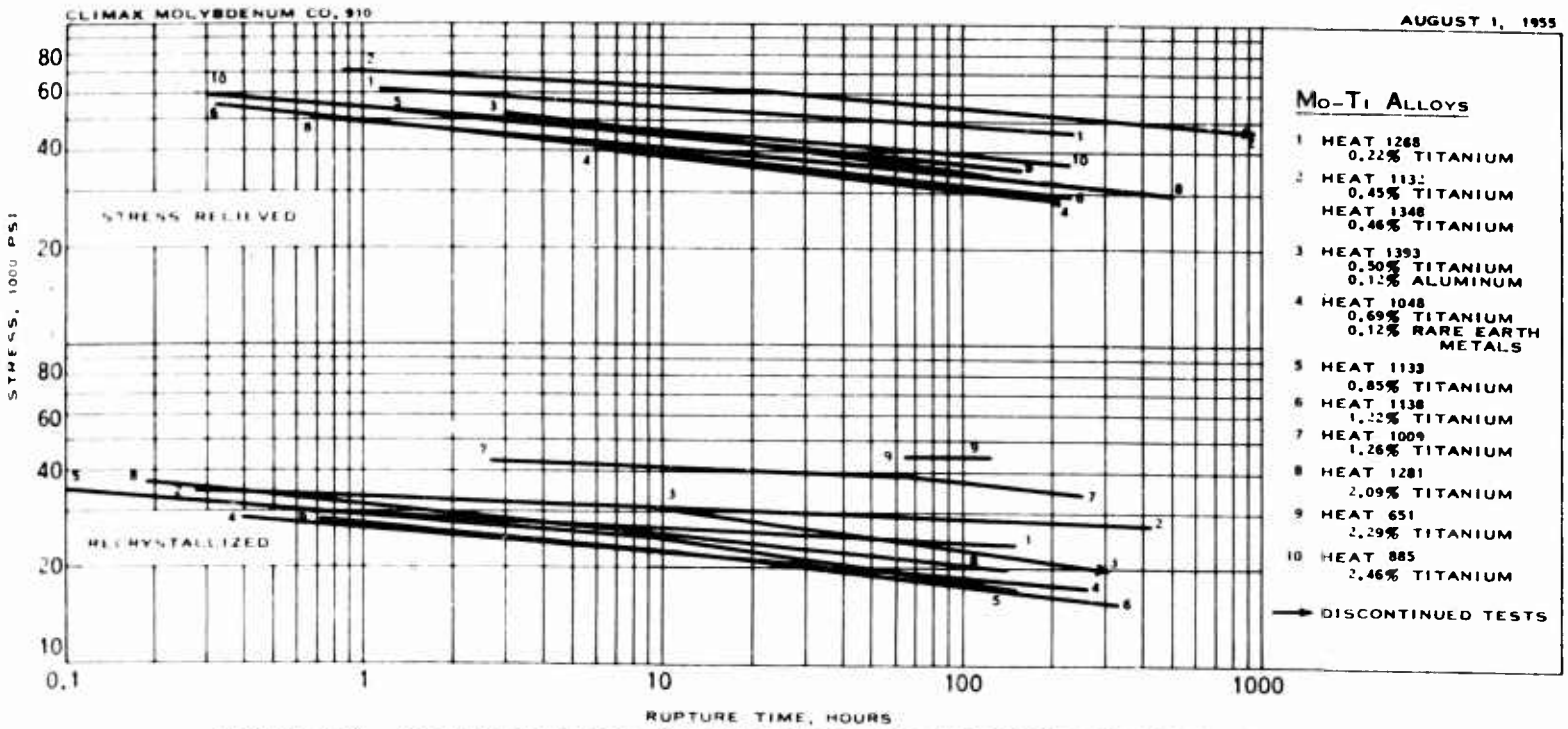


FIGURE 158 - CREEP RUPTURE STRENGTH OF MOLYBDENUM - TITANIUM ALLOY BARS TESTED AT 1800 F

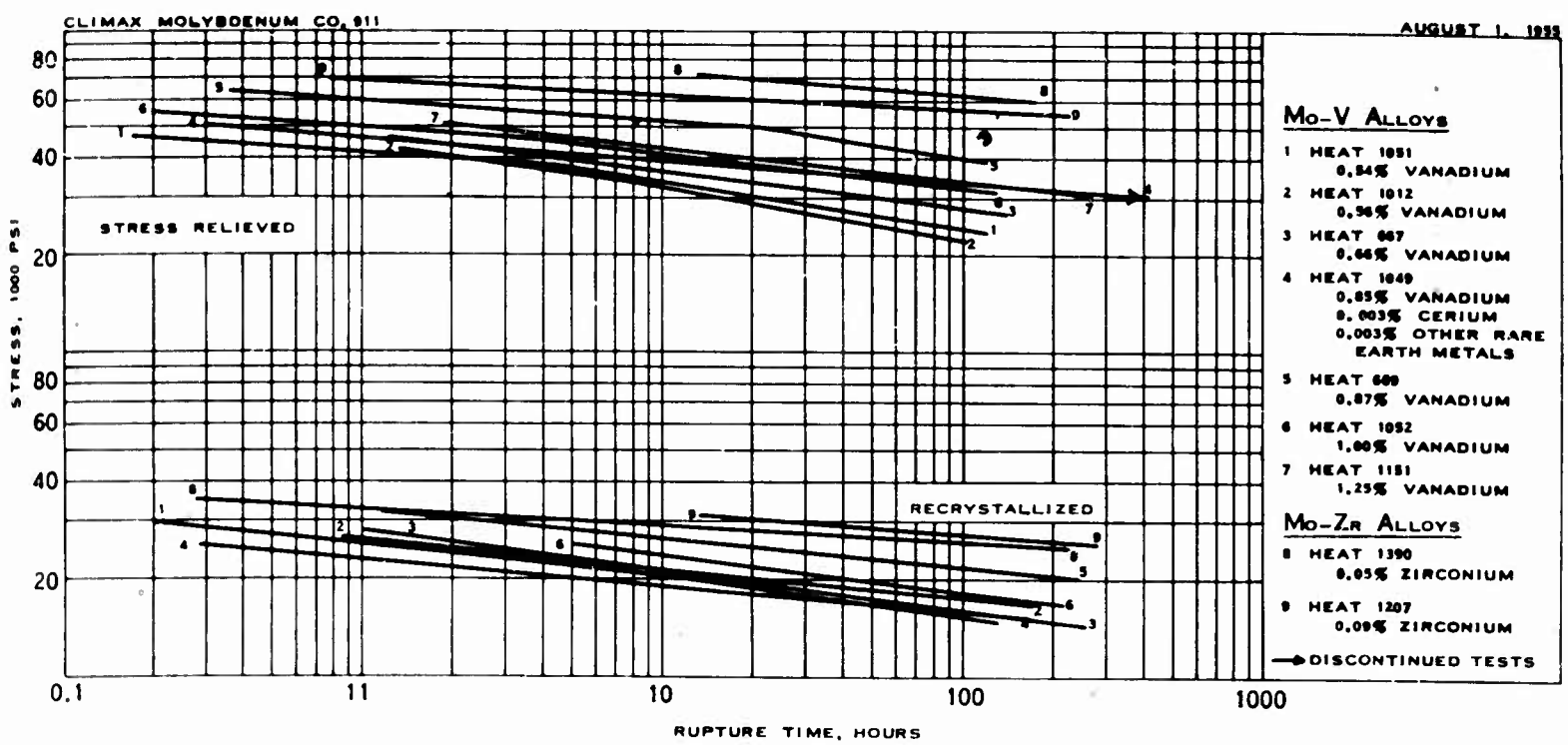


FIGURE 159 – CREEP RUPTURE STRENGTH OF Mo-V AND Mo-Zr ALLOY BARS TESTED AT 1800 F

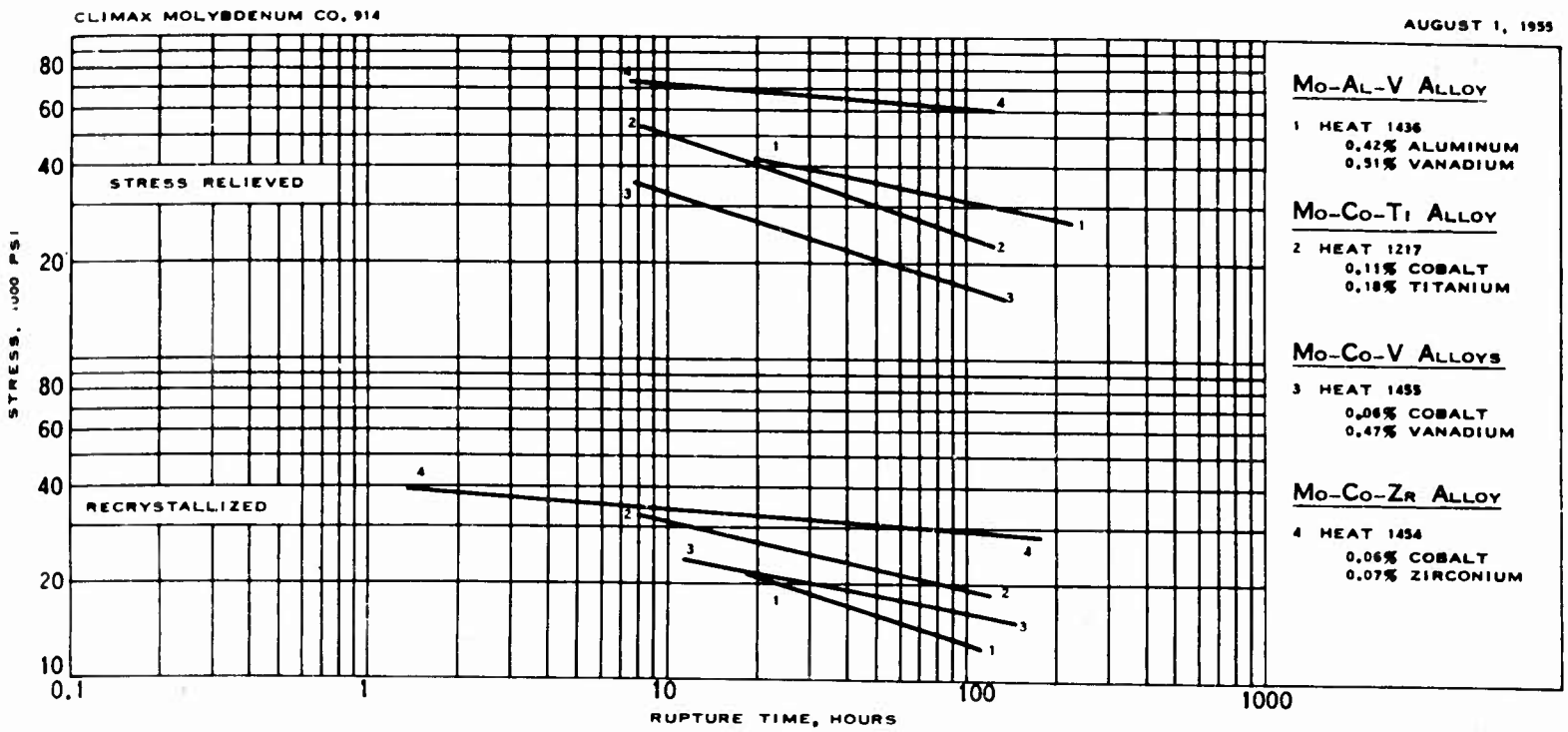


FIGURE 160 – CREEP RUPTURE STRENGTH OF TERNARY MOLYBDENUM–BASE ALLOY BARS TESTED AT 1800 F

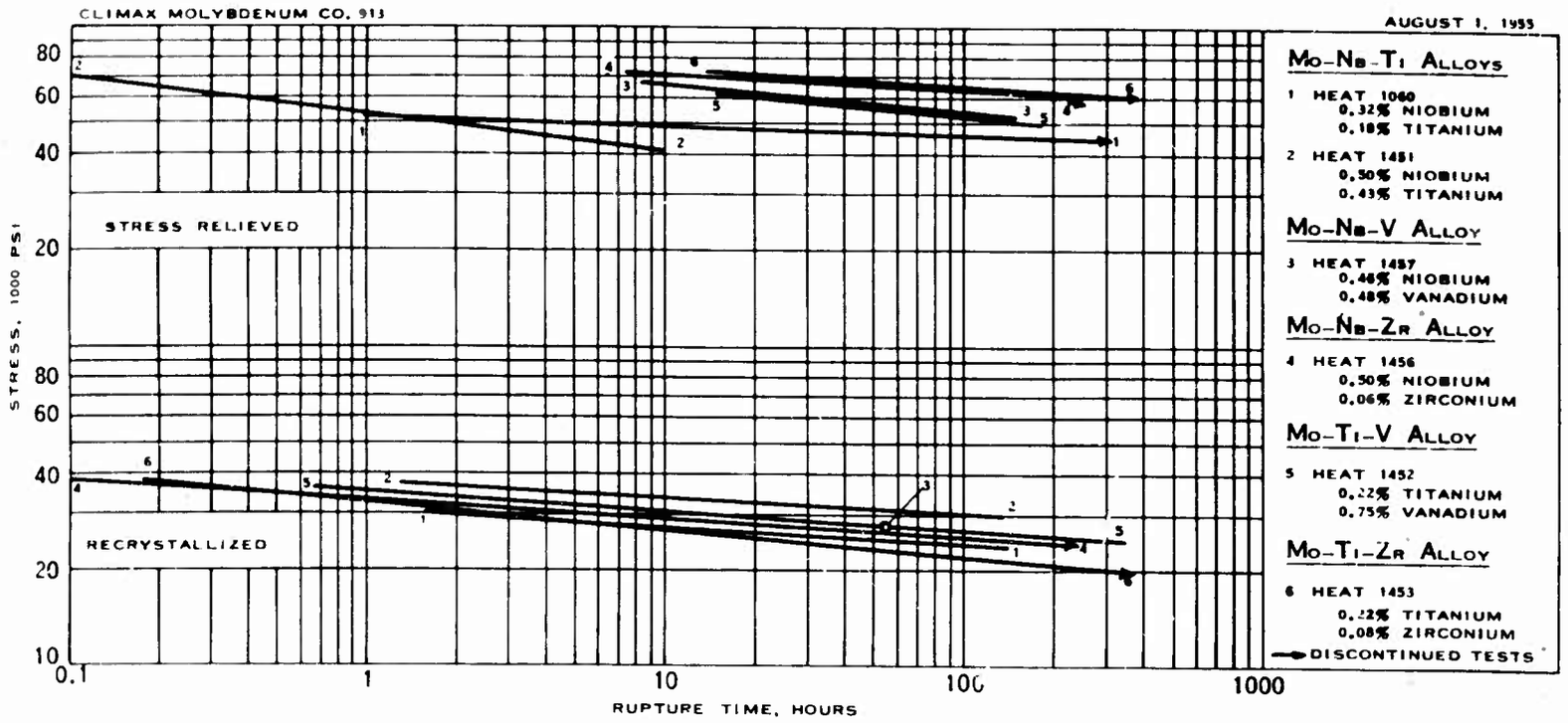


FIGURE 161 – CREEP RUPTURE STRENGTH OF TERNARY MOLYBDENUM–BASE ALLOY BARS TESTED AT 1800 F

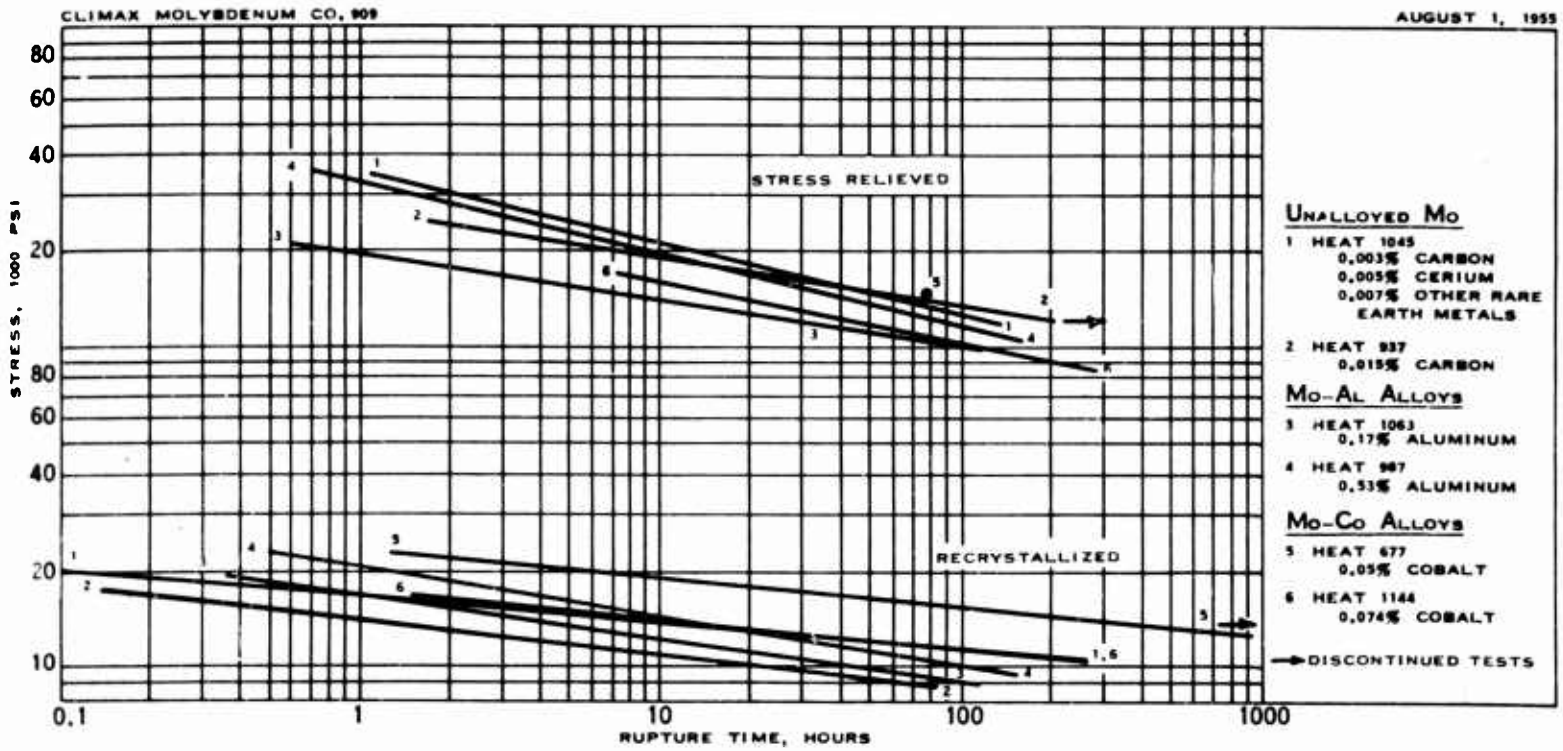


FIGURE 162– CREEP RUPTURE STRENGTH OF UNALLOYED MOLYBDENUM AND Mo-AL AND Mo-Co ALLOY BARS TESTED AT 2000 F

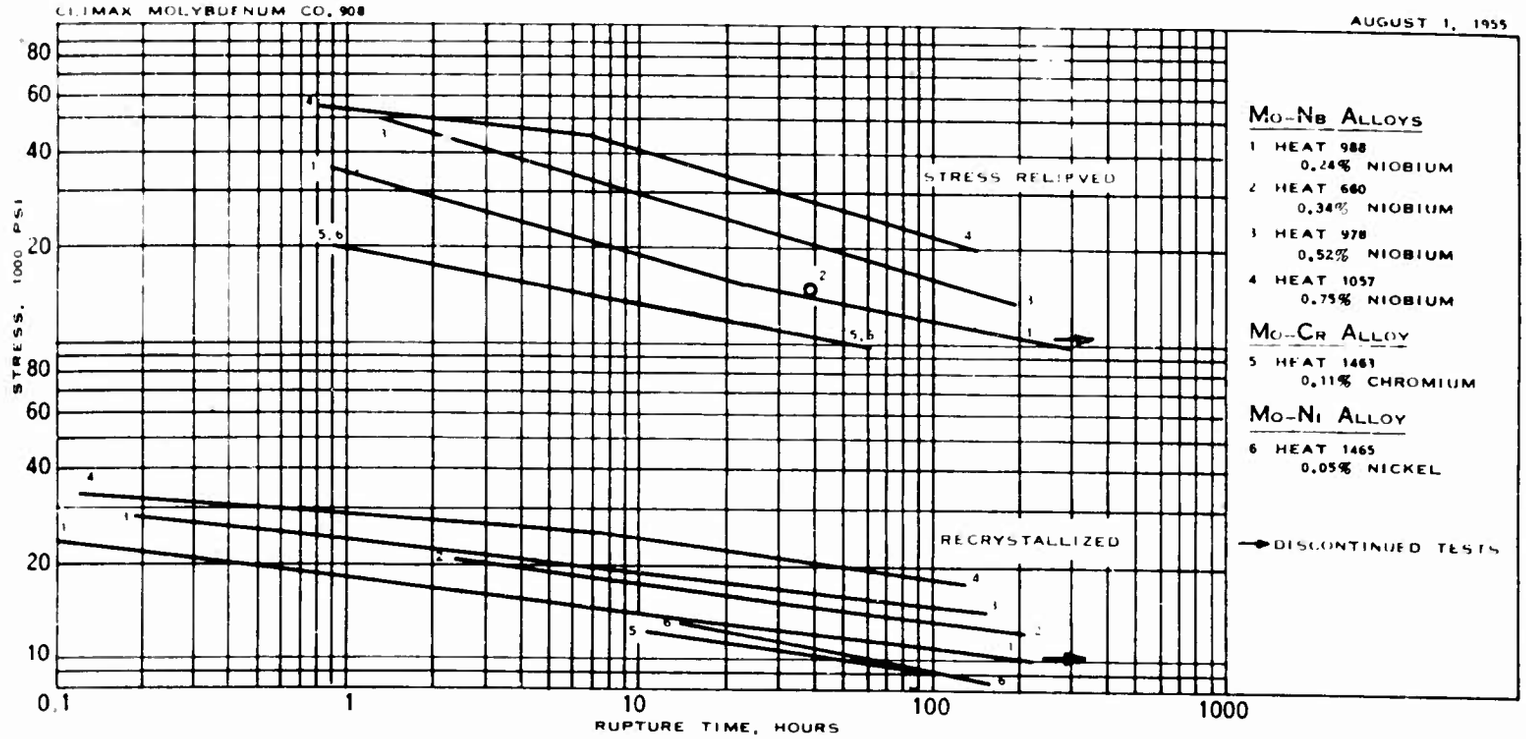


FIGURE 163 – CREEP RUPTURE STRENGTH OF Mo-Nb, Mo-Cr, AND Mo-Ni ALLOY BARS TESTED AT 2000 F

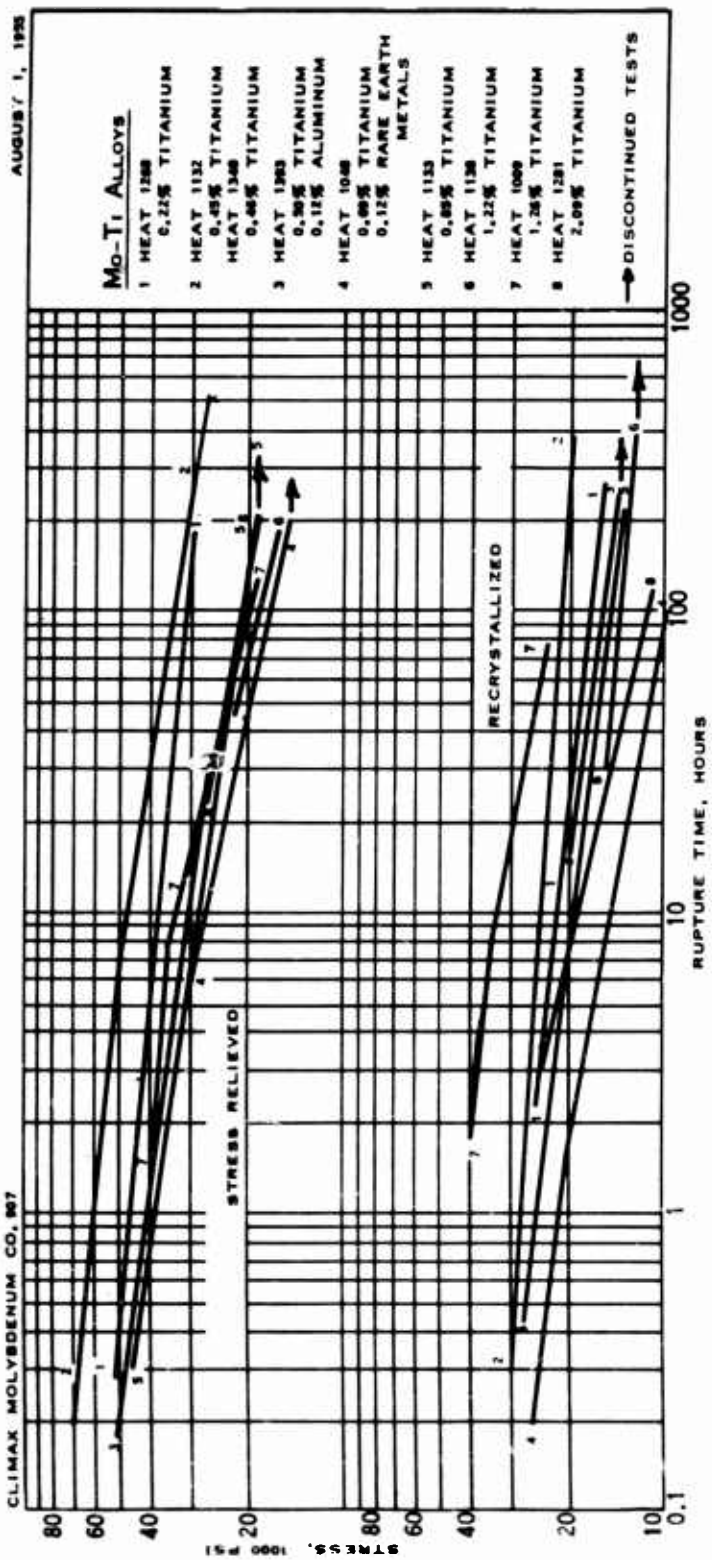


FIGURE 164 – CREEP RUPTURE STRENGTH OF MOLYBDENUM–TITANIUM ALLOY
BARS TESTED AT 2000 F

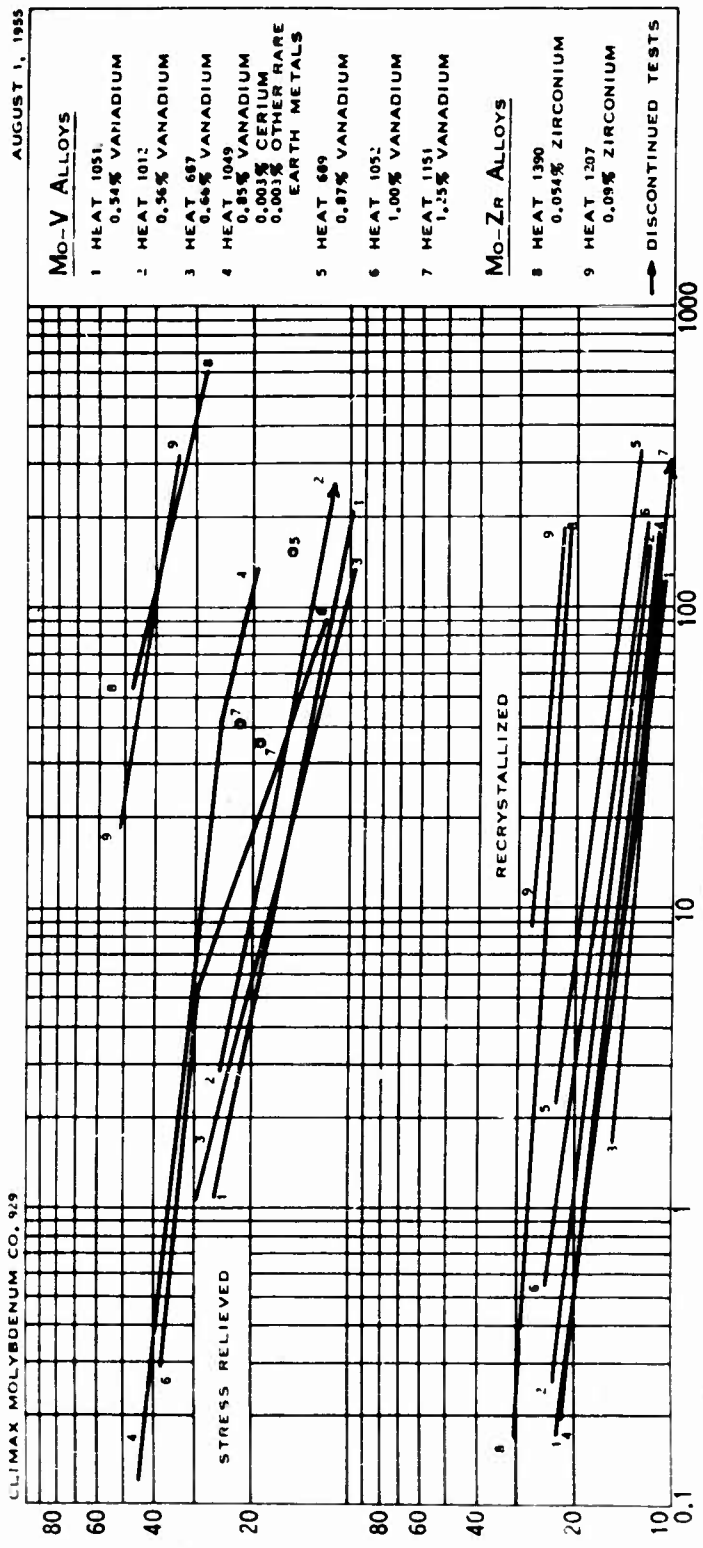


FIGURE 165 — CREEP RUPTURE STRENGTH OF Mo-V AND Mo-Zr ALLOY BARS TESTED AT 2000 F

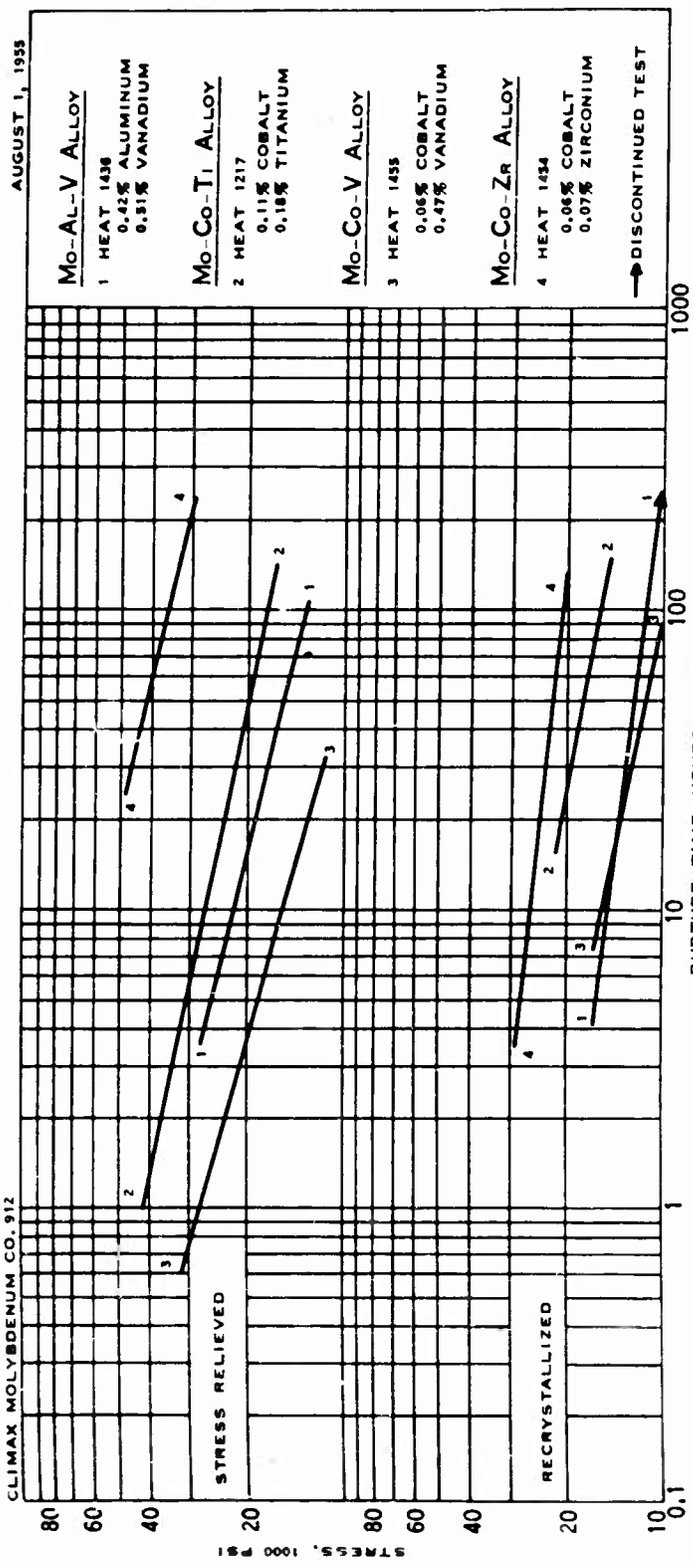


FIGURE 166 – CREEP RUPTURE STRENGTH OF TERNARY MOLYBDENUM–BASE ALLOY BARS
TESTED AT 2000 F

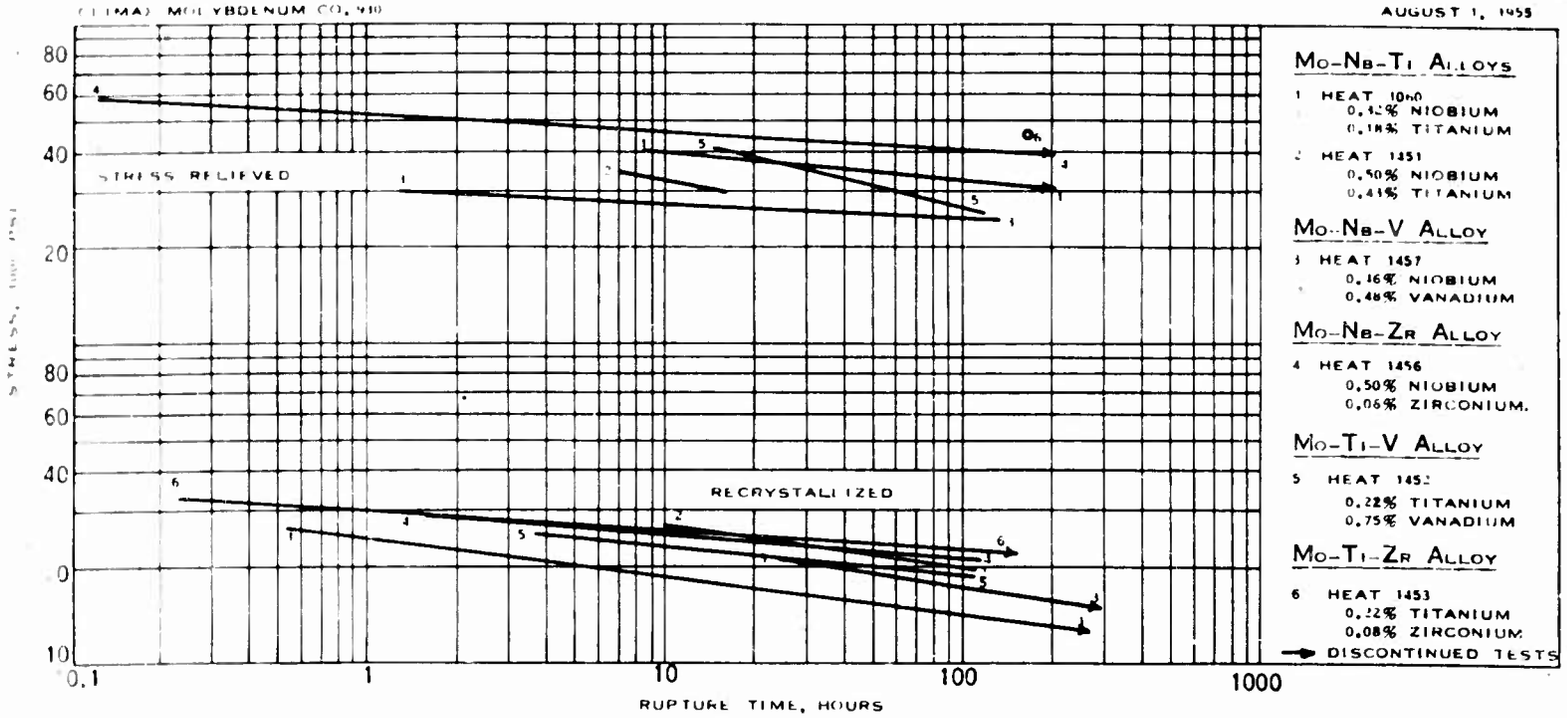


FIGURE 167 CREEP RUPTURE STRENGTH OF TERNARY MOLYBDENUM-BASE ALLOY BARS TESTED AT 2000 F

Sufficient data were obtained for alloys of the molybdenum-titanium system to indicate that the relationship between rupture strength and alloy content was not linear. Considering the alloys of Tables 24 and 25, but excluding for the moment the 1.26% titanium alloy made with crystal bar titanium and the 0.69% titanium alloy deoxidized with rare earth metals, there remain five alloys in the range 0.22% to 2.09% titanium which were prepared from sponge titanium and were fabricated as nearly alike as possible. A plot of stress to produce rupture in 100 hours as a function of titanium content is shown in Figure 163. It is evident that for all three testing temperatures and both structural conditions the molybdenum-titanium alloy of maximum strength contains about 0.5% titanium. The peak is more pronounced in the stress-relieved condition than in the fully recrystallized condition.

The 1.26% titanium alloy was prepared from crystal bar titanium. In the recrystallized condition, this alloy was markedly superior in creep-rupture strength to the 1.22% titanium alloy produced from sponge titanium, and even superior to the 0.5% titanium alloy. In the stress-relieved condition, however, the 1.26% titanium alloy was not superior to the 0.5% titanium alloy. This is attributed to the fact that the 1.26% titanium ingot was much smaller than the 0.5% titanium ingot and therefore did not sustain as much work as the other ingots; its final reduction in rolling was less than for the other molybdenum-titanium binary alloys; therefore, it would not be expected to be as strong in the strain-hardened condition.

The two facts brought out above, that is, the existence of an optimum composition at about 0.5% titanium and the advantage of using crystal bar titanium as a starting material, strongly suggest that the mechanism by which titanium increases the strength of molybdenum cannot be attributed solely to solid solution effects.

Binary molybdenum-zirconium alloys also exhibit high creep-rupture strength. An insufficient number of alloys in the molybdenum-zirconium system were studied under the present investigation to determine an optimum zirconium content. Raising the zirconium content of the binary alloys from 0.05% to 0.09% increased their creep-rupture strength in the recrystallized condition at all three testing temperatures. In the stress-relieved condition, the 0.05% zirconium alloy was slightly stronger at all three testing temperatures.

Direct comparison of the creep-rupture strengths of ternary molybdenum-base alloys and the corresponding binary molybdenum-base alloys cannot be made, for the ternary alloys were fabricated from smaller castings. Fabrication schedule and total amount of deformation seem to exert as much influence on rupture strength as variation in composition in the range under investigation. A few qualitative observations may be made, however.

The alloy containing 0.42% Al and 0.51% V (1436) was stronger than the corresponding binary alloys in the stress-relieved condition but was weaker in the recrystallized condition.

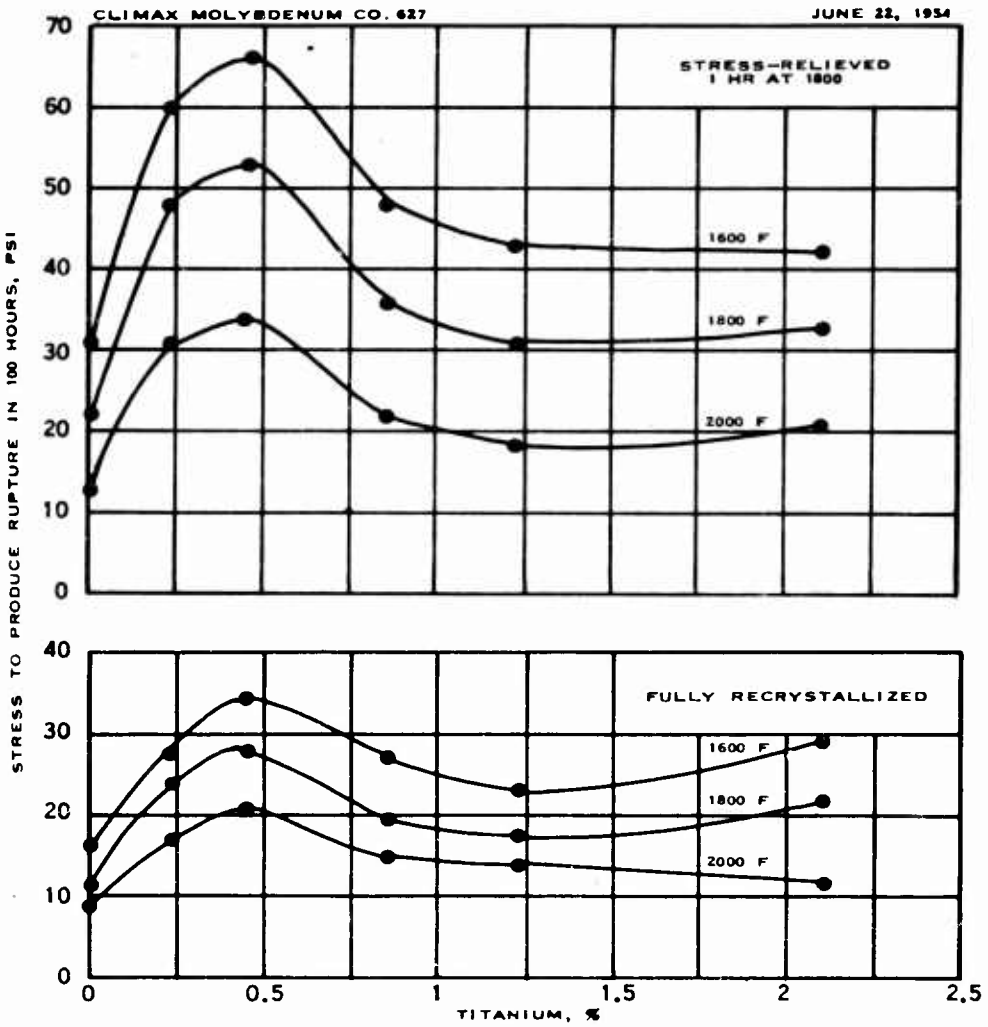


FIGURE 168 – STRESS TO PRODUCE RUPTURE OF MOLYBDENUM–TITANIUM ALLOYS IN 100 HOURS AT 1600, 1800, AND 2000 F

Ternary alloys containing cobalt as one of the alloying elements, on the whole, were not as strong as the corresponding binary alloys at 1800 F and 2000 F. At 1600 F there was one exception; the 0.11% Co, 0.18% Ti alloy was stronger in both the stress-relieved and the recrystallized conditions than the corresponding binary alloys containing similar amounts of cobalt or titanium alone.

The ternary alloys containing niobium and titanium, although stronger than the binary alloys with like amounts of niobium, had no advantage over the binary alloys with like amounts of titanium. Ternary alloys containing niobium and vanadium or zirconium or containing titanium with vanadium or zirconium were stronger than the corresponding binary alloys. Indeed, the ternary molybdenum-base alloy containing 0.22% Ti and 0.08% Zr, in the stress-relieved condition, has greater creep-rupture strength at 1800 F and 2000 F than any other metallic material now known.

Inasmuch as unalloyed molybdenum and the 0.5% titanium binary alloy are readily produced by the arc-casting process and fabricated without difficulty and at the same time represent in a general way the extremes of the range of mechanical properties attainable at present, they have been used for the bulk of the applications for molybdenum-base materials studied to date. For this reason, design curves for these materials are presented (Figures 169-174) through the courtesy of Battelle Memorial Institute. In addition to the rupture-time data, these figures show the data available for the relation between stress and time for certain amounts of total deformation. It should be noted that these figures are semi-log plots, the stress being plotted on Cartesian co-ordinates to separate the total deformation curves. On these plots, the stress-rupture time curve for the stress-relieved molybdenum appears to have a slightly steeper slope at all three test temperatures.

In addition to excellent load-carrying ability at elevated temperatures, molybdenum-base alloys have also exhibited good ductility. Mean elongation values for tests involving stress-relieved specimens varied between 15% and 20%, being somewhat higher the higher the test temperature. The lowest values obtained were in the neighborhood of 10%. Mean values for fully recrystallized specimens were in the range from 40% to 55%, although a greater dependence upon variables such as composition and rupture life was noted than for stress-relieved specimens. That is, the total range of elongation values obtained for tests on recrystallized specimens was greater than that obtained for stress-relieved samples. In general, elongation values increased slightly with increasing test temperature, regardless of specimen condition. Measurements of reduction of area did not show the dependence upon test variables noted for the elongation data, averaging somewhat above 80% for each test temperature and specimen condition.

In concluding the discussion of creep-rupture properties of molybdenum-base alloys, a comparison is made with other materials now in use or proposed for service at elevated temperatures. For this purpose, a chart prepared by Cross and Simmons* is reproduced in Figure 175. We have taken the liberty of

* Howard C. Cross and Ward F. Simmons, Alloys and their properties for elevated temperature service. "Utilization of Heat Resistant Alloys", American Society for Metals, 1954, p 92

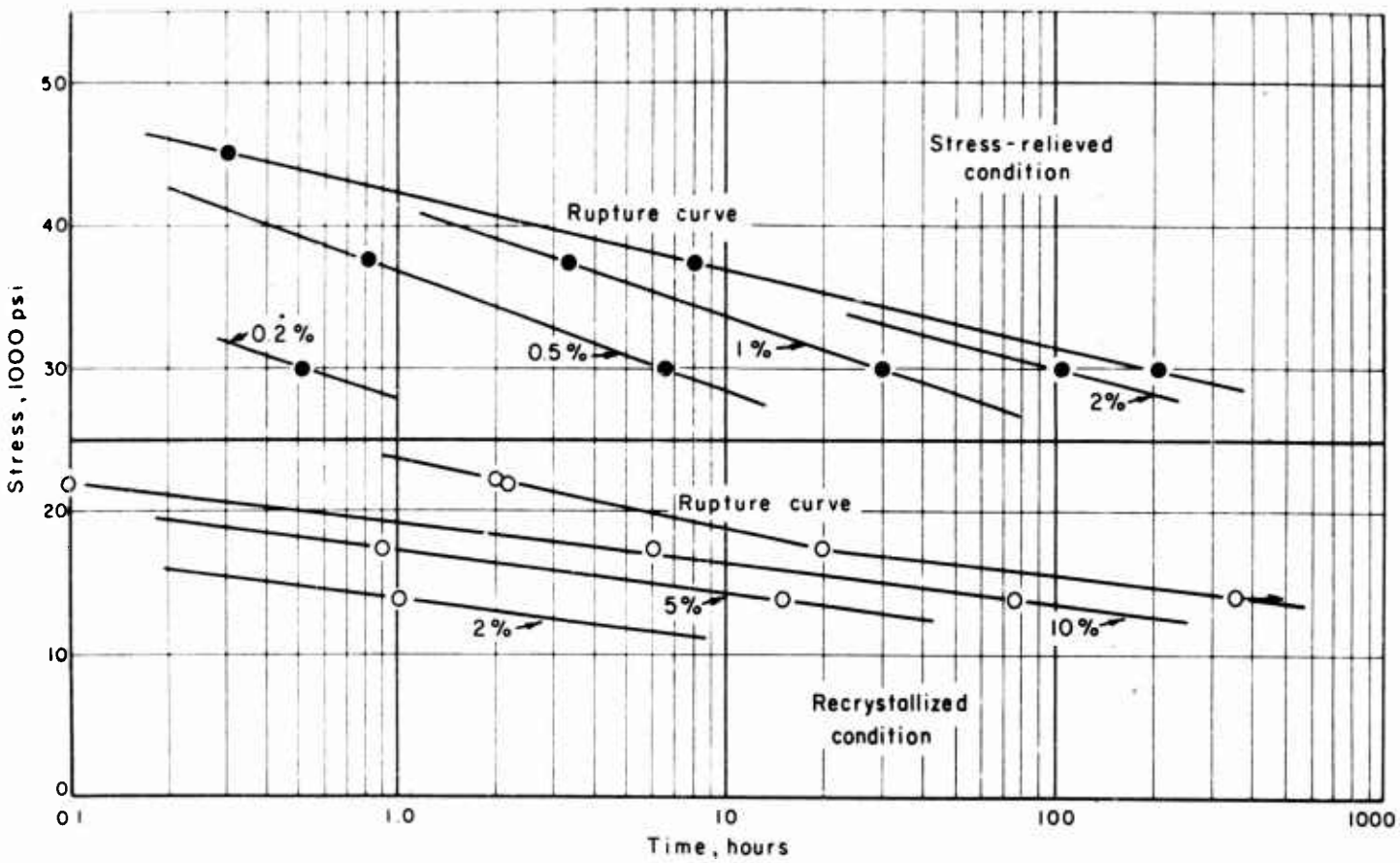


FIGURE 169 — RELATIONSHIP BETWEEN STRESS AND TIME FOR INDICATED AMOUNTS OF TOTAL DEFORMATION FOR UNALLOYED MOLYBDENUM (0.015% C) TESTED IN VACUUM IN THE STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1600 F

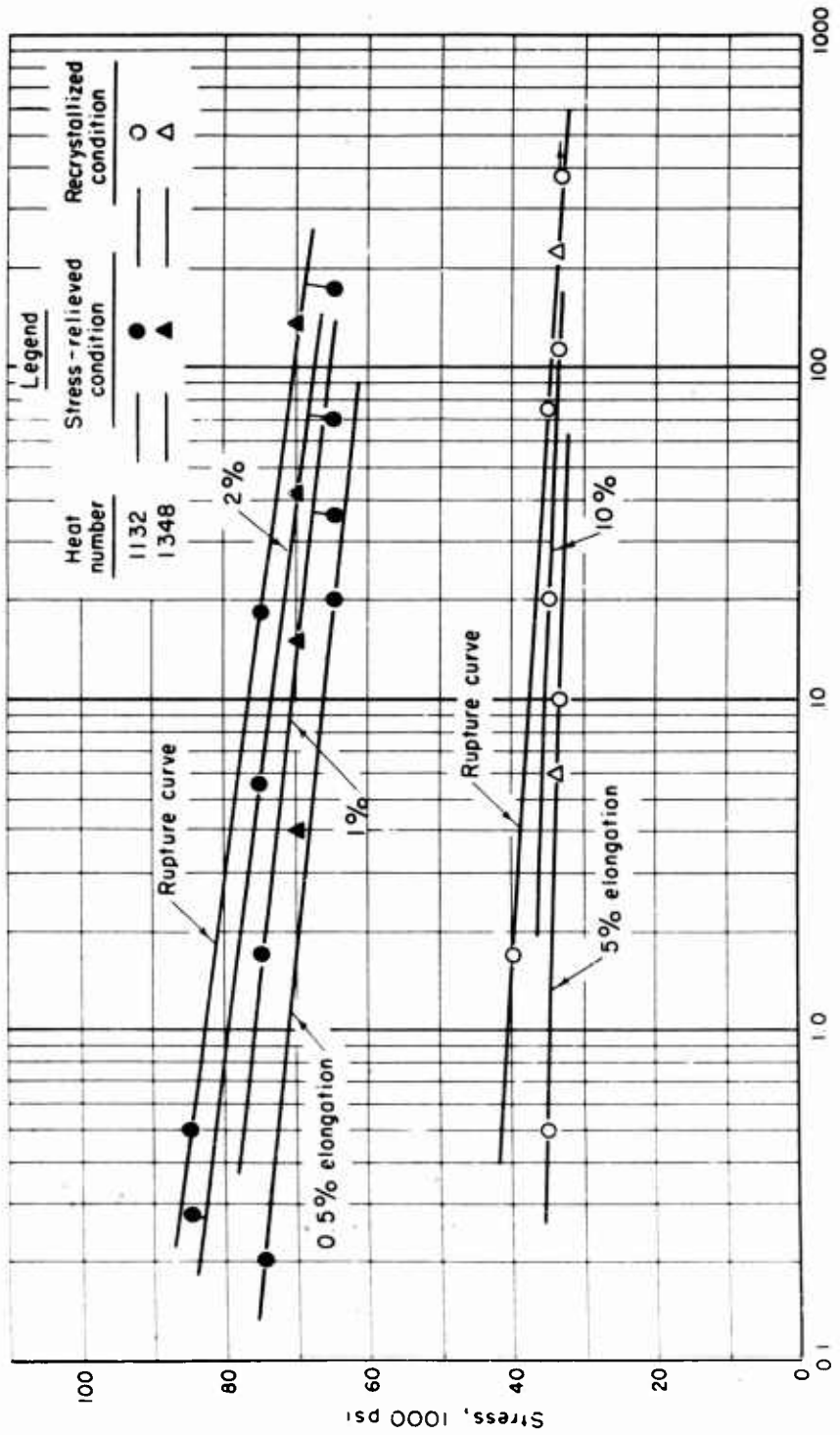


FIGURE 170 – RELATIONSHIP BETWEEN STRESS AND TIME FOR INDICATED AMOUNTS OF TOTAL DEFORMATION FOR THE MOLYBDENUM–BASE 0.45% TITANIUM ALLOY TESTED IN VACUUM IN THE STRESS–RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1600 F

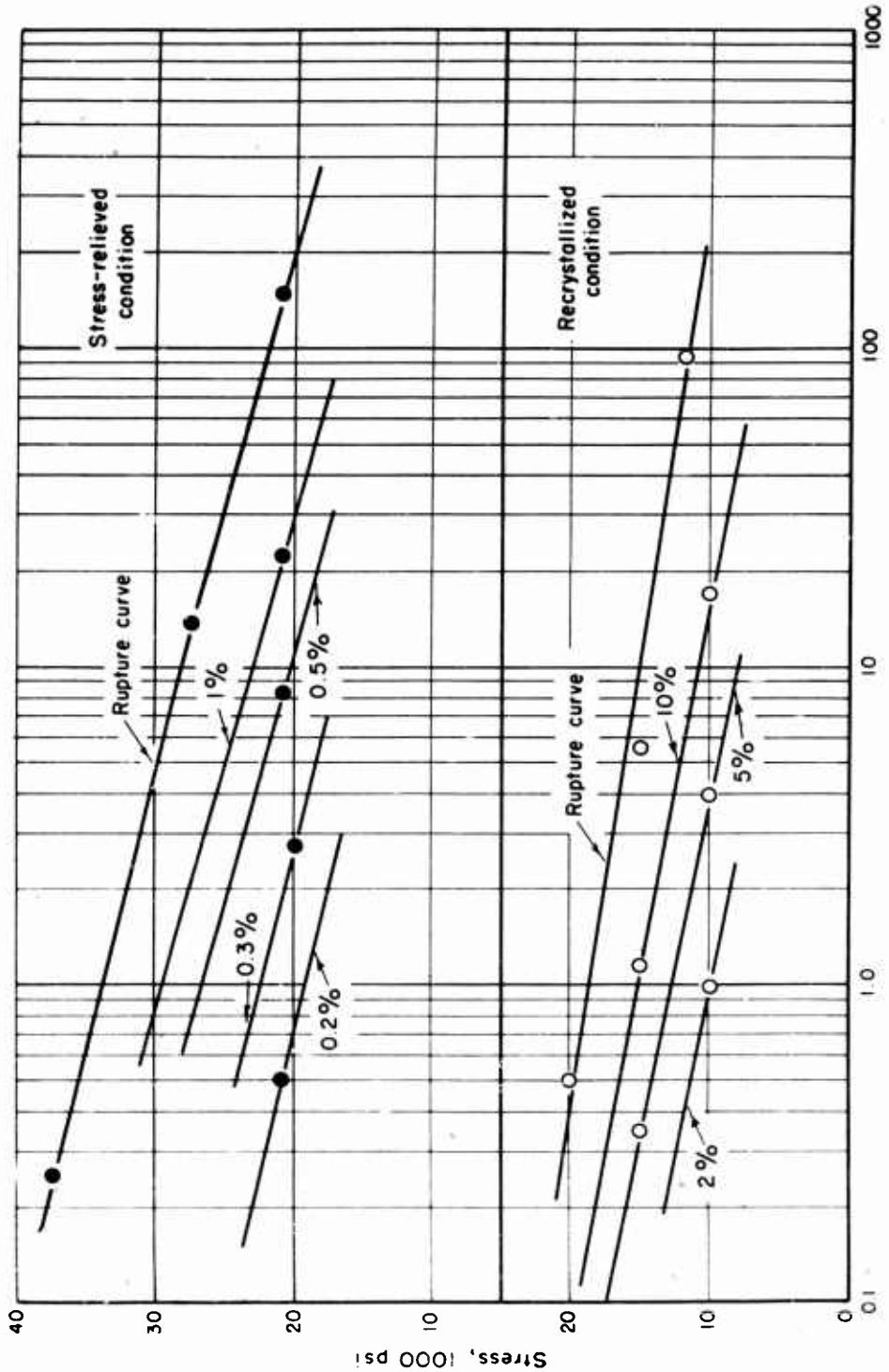


FIGURE 171 — RELATIONSHIP BETWEEN STRESS AND TIME FOR INDICATED AMOUNTS OF TOTAL DEFORMATION FOR UNALLOYED MOLYBDENUM (0.015% C) TESTED IN VACUUM IN THE STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1800 F

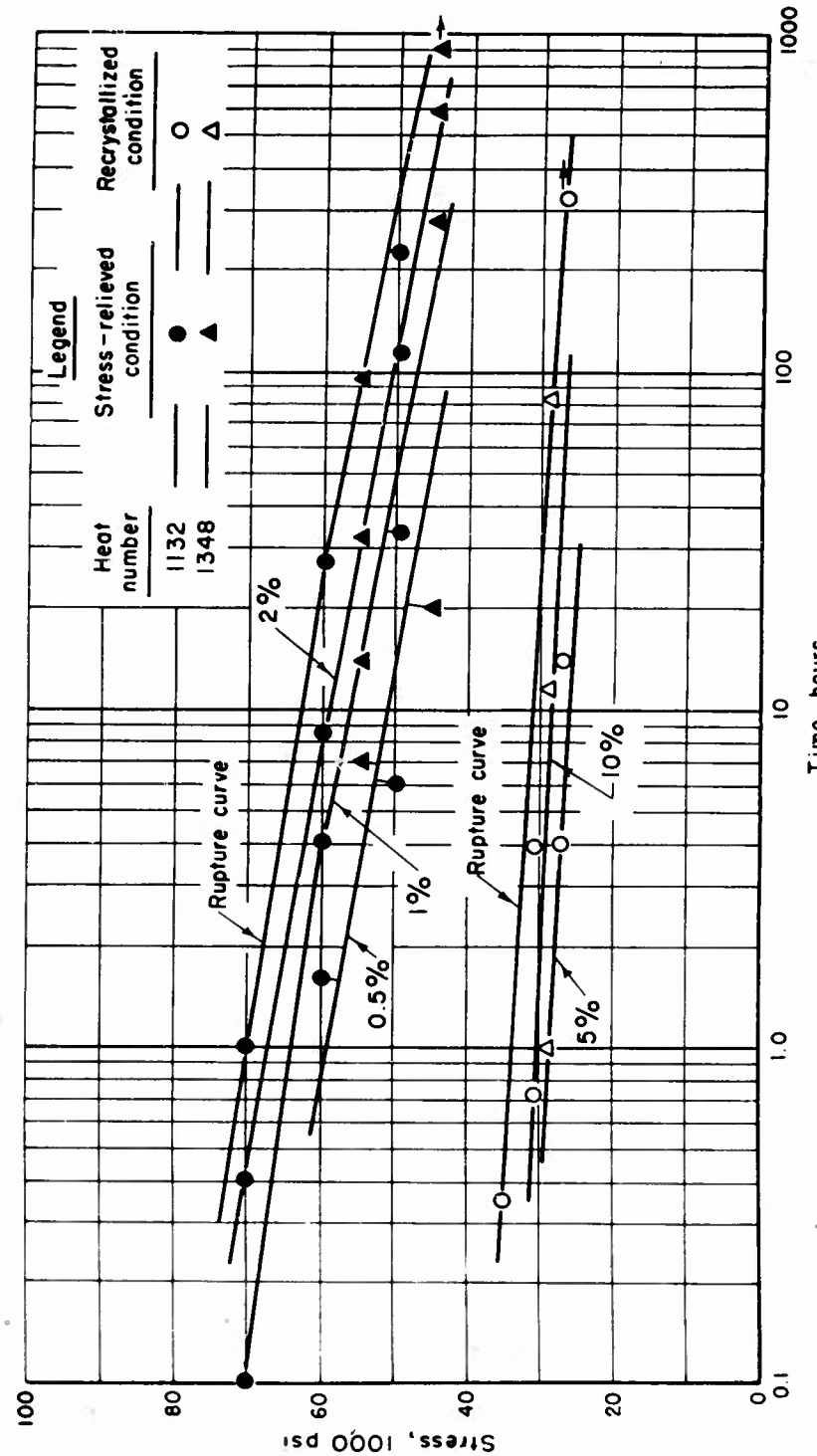


FIGURE 172 – RELATIONSHIP BETWEEN STRESS AND TIME FOR INDICATED AMOUNTS OF TOTAL DEFORMATION FOR THE MOLYBDENUM–BASE 0.45% TITANIUM ALLOY TESTED IN VACUUM IN THE STRESS–RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1800 F

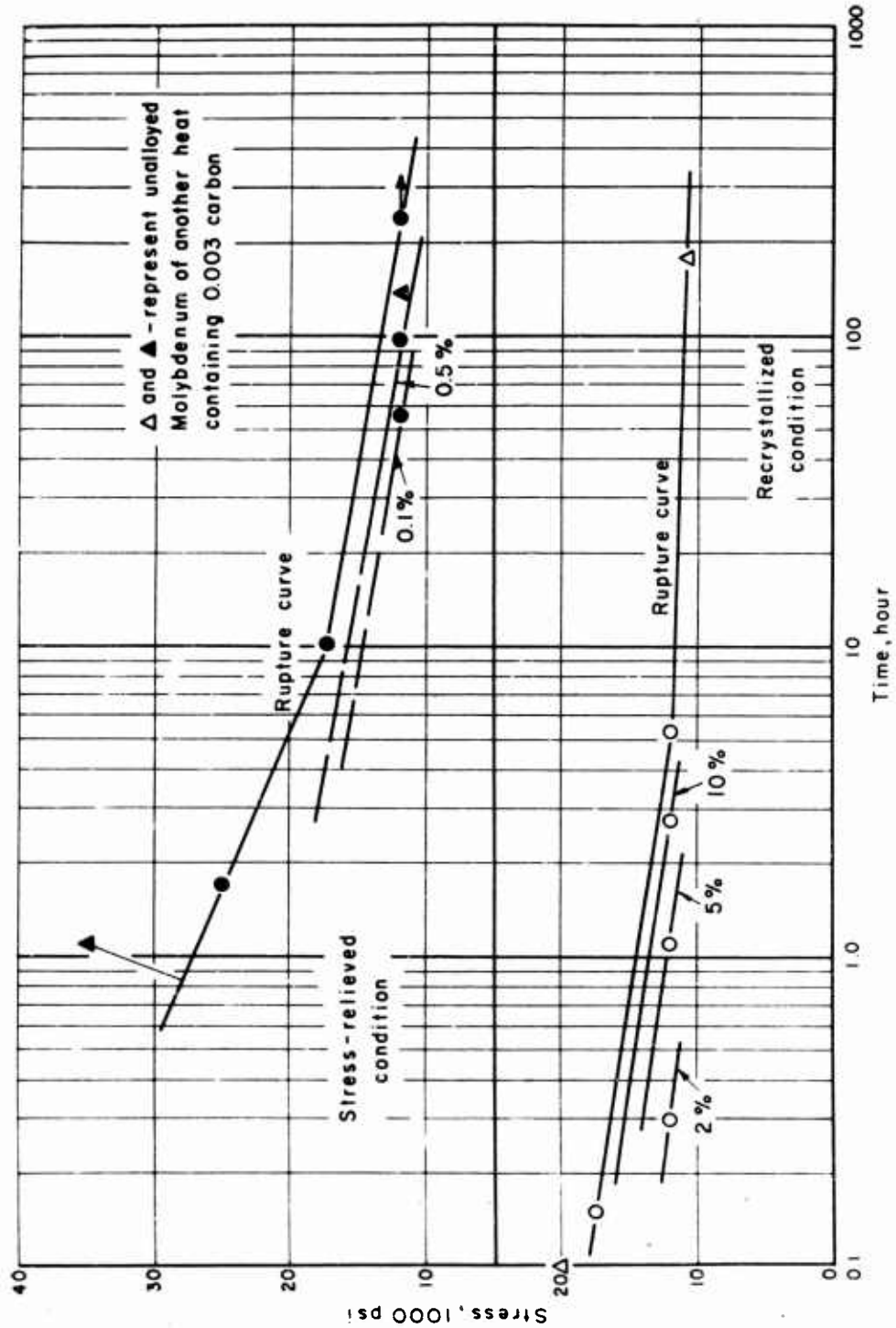


FIGURE 173 — RELATIONSHIP BETWEEN STRESS AND TIME FOR INDICATED AMOUNTS OF TOTAL DEFORMATION FOR UNALLOYED MOLYBDENUM (0.015% C) TESTED IN VACUUM IN THE STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 2000 F

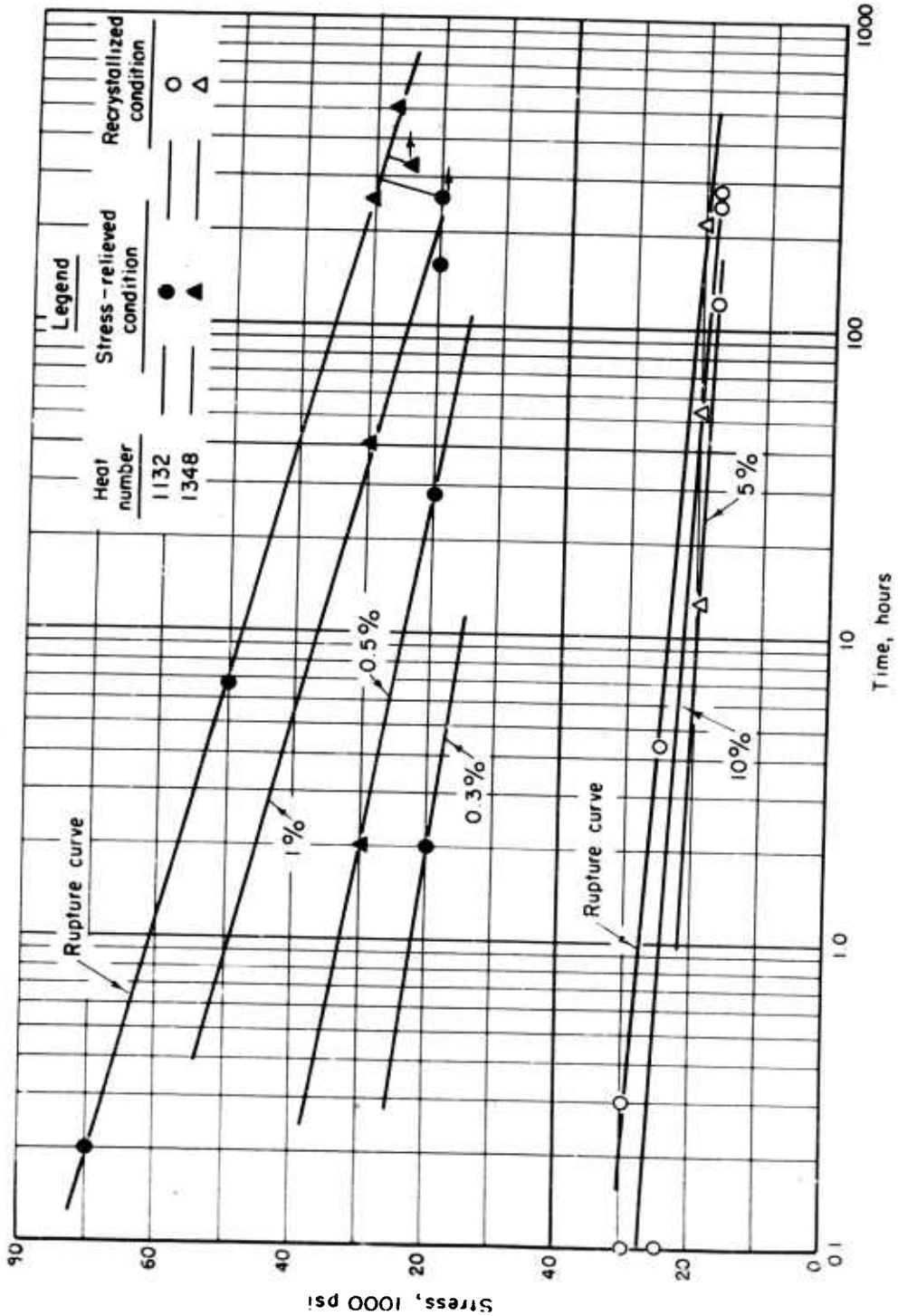


FIGURE 174 – RELATIONSHIP BETWEEN STRESS AND TIME FOR INDICATED AMOUNTS OF TOTAL DEFORMATION FOR THE MOLYBDENUM-BASE 0.45% TITANIUM ALLOY TESTED IN VACUUM IN THE STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 2000 F

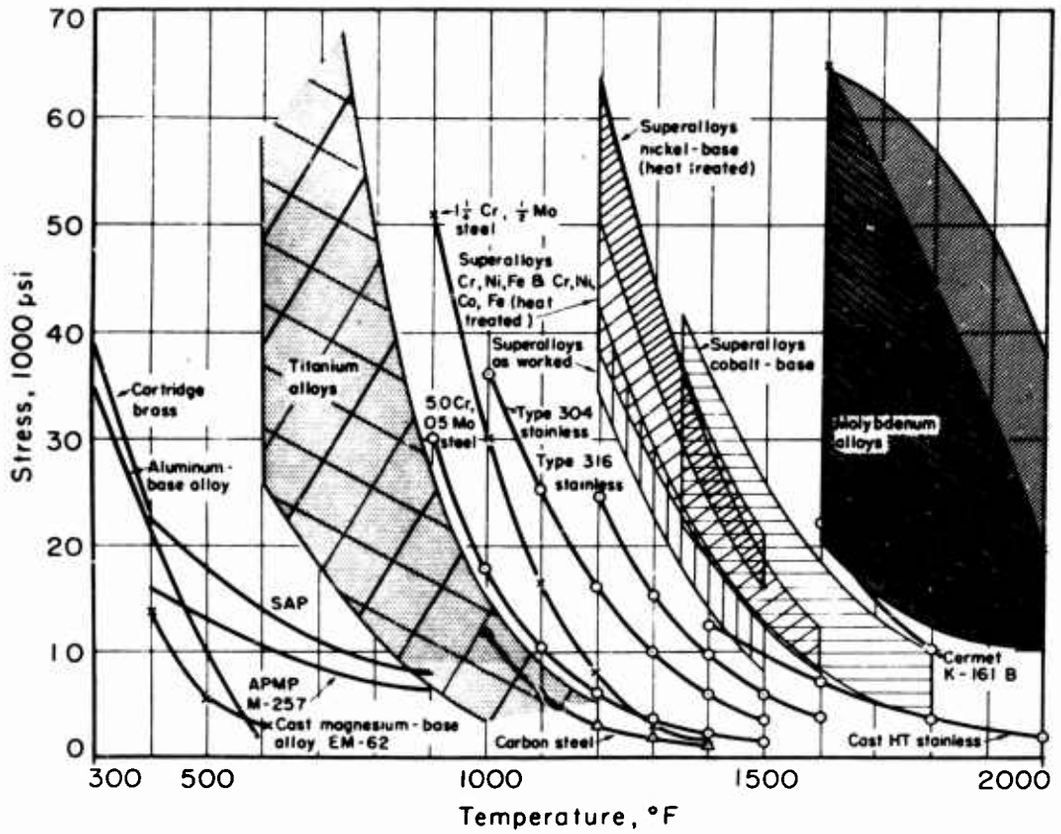


FIGURE 175 – STRESS VS. TEMPERATURE CURVES FOR RUPTURE IN 1000 HOURS (P1301)

modifying the area for molybdenum-base alloys and have extended it to include our most recent creep-rupture data. The lower boundary of the area represents unalloyed molybdenum, which--although having the lowest strength of the group of molybdenum-base materials--surpasses all of the other metallic materials in creep-rupture strength. The investigations sponsored by the Office of Naval Research and described in this Summary Report have indicated the potentiality of molybdenum-base alloys and demonstrated the remarkable strength of molybdenum-base alloys as a class.

Thermal Expansion and Thermal Conductivity

Inasmuch as molybdenum-base alloys have shown outstanding properties at elevated temperatures, thermal data of aid to design engineers have been determined.

The coefficient of linear thermal expansion of unalloyed molybdenum deoxidized with carbon and of five molybdenum-base alloys was determined by Battelle Memorial Institute. Unalloyed molybdenum was chosen for the datum plane with which to compare the alloys. The various alloys were selected on the basis of maximum amount of alloying element compatible with ability to be fabricated, and the 0.5% titanium alloy was included as representative of an alloy having outstanding strength at elevated temperature and now in commercial production. For all practical purposes, the coefficients of thermal expansion of intermediate alloys in the Mo-Co, Mo-Nb, Mo-Ti, and Mo-V systems can be interpolated from the data presented here. The alloys were prepared by Climax Molybdenum Company and are listed in Table 26. The essence of the report submitted by Battelle Memorial Institute is as follows:

"The first dilation measurements were made in a vertical quartz-tube recording dilatometer in which the specimens were protected by a vacuum of approximately 2×10^{-5} mm Hg. In some thermal cycles, the cooling curves did not end at the point from which the heating part of the cycle started. This suggested the possibility of a specimen-length change from thermal cycling. Since the precise measurements of specimen length had not been made before the thermal cycles, length changes could not be determined. A check of a lever system in the dilatometer showed the presence of some hysteresis in its action.

"In order to check fully for a change of length with thermal cycling, two thermal cycles from 20 to 1000 C were given each of the duplicate specimens. Specimen lengths were measured by an electro-limit gage before and after the two thermal cycles. Specimen dilation during the thermal cycles was measured with a dial indicator with divisions of 0.0001 inch. As before, the maximum heating and cooling rate was 5 degrees C per minute and the specimen was protected by a vacuum of approximately 2×10^{-5} mm Hg.

TABLE 26

MEAN LINEAR THERMAL EXPANSION COEFFICIENTS OF MOLYBDENUM AND SOME MOLYBDENUM-BASE ALLOYS
(average of two cooling curves)

Heat	Chemical Analysis %	Recryst. Temp, F *	Temp. Range C	Mean Coef. of Thermal Exp. 10^{-6} per °C	Temp. Range C	Mean Coef. of Thermal Exp. 10^{-6} per °C
937	0.015 C	2150	20-100	5.69	20-600	5.86
			20-200	5.72	20-700	5.90
			20-300	5.75	20-800	5.96
			20-400	5.78	20-900	6.01
			20-500	5.81	20-1000	6.07
1057	0.033 C	2250	20-200	5.80	20-600	5.73
	0.75 Nb		20-300	5.79	20-700	5.74
			20-400	5.76	20-800	5.77
			20-500	5.75	20-900	5.82
					20-1000	5.86
1144	0.020 C	2000	20-200	5.58	20-600	5.53
	0.074 Co		20-300	5.60	20-700	5.51
			20-400	5.58	20-800	5.55
			20-500	5.54	20-900	5.61
					20-1000	5.67
1348	0.021 C	2450	20-100	5.50	20-600	5.83
	0.46 Ti		20-20(	5.50	20-700	5.90
			20-30(	5.57	20-800	5.98
			20-40(	5.66	20-900	6.05
			20-500	5.75	20-1000	6.13
1138	0.014 C	2500	20-200	5.58	20-600	5.47
	1.22 Ti		20-300	5.56	20-700	5.52
			20-400	5.53	20-800	5.58
			20-500	5.49	20-900	5.65
					20-1000	5.75
1151	0.006 C	2200	20-200	5.61	20-600	5.60
	1.25 V		20-300	5.61	20-700	5.64
			20-400	5.60	20-800	5.67
			20-500	5.60	20-900	5.73
					20-1000	5.77

* fully recrystallized by heating one hour at temperature

"Table 26 shows linear thermal expansion coefficients as mean values over the temperature ranges shown. The coefficients were calculated for cooling curves only as previous experience has shown cooling curves to be affected less than heating curves by unequal quartz expansion in the dilatometer. All values have been fully corrected for quartz expansion as determined specifically in the dilatometer used. The accuracy of the values in Table 26 is estimated to be ± 2%. Length measurements made of the specimens before and after two thermal cycles indicated that any changes of length did not exceed ± 25 microinches per inch.

"The expansion coefficients of the six specimens are all very much alike. Differences are mostly within the limits of experimental error. Specimen 1057 appears, however, to have a significantly higher coefficient than the other three."

Thermal-conductivity measurements on unalloyed molybdenum and the 0.5% titanium alloy were also made at Battelle Memorial Institute. Their report is quoted below:

"The apparatus and method used in making the thermal-conductivity measurements are essentially the same as the steady-heat-flow method described by M. S. Van Dusen and S. M. Shelton, 'Apparatus for Measuring Thermal Conductivity of Metals up to 600 C', National Bureau of Standards Journal of Research, Volume 12, 1934, pages 429-440. The method, in brief, consists in heating one end of a specimen, measuring the temperature gradients along the specimen, and determining the rate of heat flow through the specimen by means of a metal standard of known thermal conductivity attached to the cold end of the specimen. Radial heat flow into, or away from, the specimen is minimized by radiation shielding and an encircling guard tube in which temperatures are adjusted, as nearly as possible, to match those in the specimen and standard at corresponding levels. The specimens were protected by a vacuum of approximately 2 x 10^{-5} mm Hg during the measurements.

"Five 36-gage Chromel-Alumel thermocouples were wedged in holes equally spaced along the specimen, and two similar thermocouples were placed in the Armco-iron standard. This permitted the calculation of four thermal-conductivity values, each at a different mean temperature, for each thermal equilibrium. Data were recorded for four thermal equilibria on the alloy specimen and, for five equilibria on the molybdenum specimen.

"Table 27 shows interpolated thermal-conductivity values for unalloyed molybdenum (Heat 990) and the 0.5% titanium alloy (Heat 1132), taken from a best curve drawn through the experimental points. The maximum deviation of any one experimental point for unalloyed molybdenum from the best curve was 7%, while the average deviation was 3%. The maximum deviation of any one experimental point for the alloy from the best curve was 2%, while the average deviation was 1%. The maximum error of the thermal-conductivity values shown in Table 27 is estimated to not exceed 5%, the chief uncertainty being the thermal conductivity of the Armco-iron standard. The error in comparing the thermal conductivities of the molybdenum and the alloy is estimated to not exceed 2%, as the same Armco-iron standard was used in measuring both materials."

TABLE 27

INTERPOLATED THERMAL-CONDUCTIVITY VALUES OF UNALLOYED MOLYBDENUM AND MOLYBDENUM-0.5% TITANIUM ALLOY

	Thermal Conductivity, watts $cm^{-2}cm\ C^{-1}$*	
	Unalloyed Mo Heat 990	Mo-0.5% Ti Alloy Heat 1132
Temp., C	Recrys. at 2250 F	Recrys. at 2700 F
20**	1.25	1.18
100**	1.23	1.17
200	1.21	1.15
300	1.18	1.14
400	1.16	1.12
500	1.14	1.10
600	1.11	1.10
700	1.10	1.10
800	1.09	1.09
900	1.08	1.08.

* 1 watt $cm^{-2}cm\ C^{-1}$ = 0.2389 cal $sec^{-1}cm^{-2}cm\ C^{-1}$ = 57.79 btu $hr^{-1}ft^{-2}ft\ F^{-1}$

** extrapolated

EFFECT OF VARIATION IN STRAIN HARDENING ON MECHANICAL PROPERTIES AND RECRYSTALLIZATION TEMPERATURE

It has been demonstrated that arc-cast molybdenum and its alloys can be wrought and that they exhibit outstanding strength at elevated temperatures. It has also been shown that considerable differences exist in the mechanical properties of these wrought materials, depending upon the amount of strain hardening to which they have been subjected. Measurement of the effect of strain hardening on mechanical properties and resistance to recrystallization was the goal at which the studies reported in this section were aimed.

In the experiments described here, two materials were selected for study of the effect of degree of strain hardening on recrystallization temperature and mechanical properties: unalloyed molybdenum deoxidized with carbon in vacuum, and one of the strongest alloys yet tested, the binary alloy of molybdenum containing 0.50% titanium. The rolling temperatures selected were the extremes of the range within which molybdenum-base materials are currently rolled, that is, 1800 F, the minimum temperature at which rolling is stopped for reheating (and the finishing temperature for bar stock), and 2200 F, the temperature to which the work is normally reheated. The studies were primarily concerned with the later stages of working, which have the most effect upon the properties of the product. Cast sections 6-1/2" in diameter were extruded at 2300 F. The extruded billet was recrystallized before rolling and then rolled to 1-1/4" diameter bars in the fashion described in the section on fabrication. The specimens were fully recrystallized by treatment for one hour at 2200 F for the unalloyed molybdenum and 2700 F for the 0.50% titanium alloy.

The fully recrystallized bars were rolled to 1/2" square at 1800 and 2200 F at the University of Michigan, to maintain constant total deformation. A recrystallization anneal was inserted at various stages of rolling to produce the various degrees of strain hardening desired in the 1/2" square bars. An example of the procedure is illustrated in the diagram of Figure 176. Table 28 summarizes the working schedules and intermediate recrystallization annealing of the two alloys. The 0.5% titanium alloy cracked excessively when the rolling was conducted at 1800 F, and only two bars were obtained.

The appearance of the worked structures obtained in this study is shown in Figures 177 and 178. The generally increasing amounts of strain with increasing reduction are evident in this series of photomicrographs. Reductions in excess of 15% seem to be necessary before significant grain fragmentation is produced; that is, at lower reductions, the grain contours are similar to those of recrystallized structures, and the only effect of the working has been a lattice distortion within the grains.

There are no major differences in the structure of unalloyed molybdenum and 0.5% titanium-molybdenum worked equivalent amounts. Samples rolled at 1800 F appear to be more severely worked than those rolled similarly at 2200 F. This is, of course, as would be expected. It will be noted below, however, that samples worked at 1800 F were generally lower in hardness and strength than samples worked an equivalent amount at 2200 F.

CLIMAX MOLYBDENUM CO. 916 JULY 13, 1955

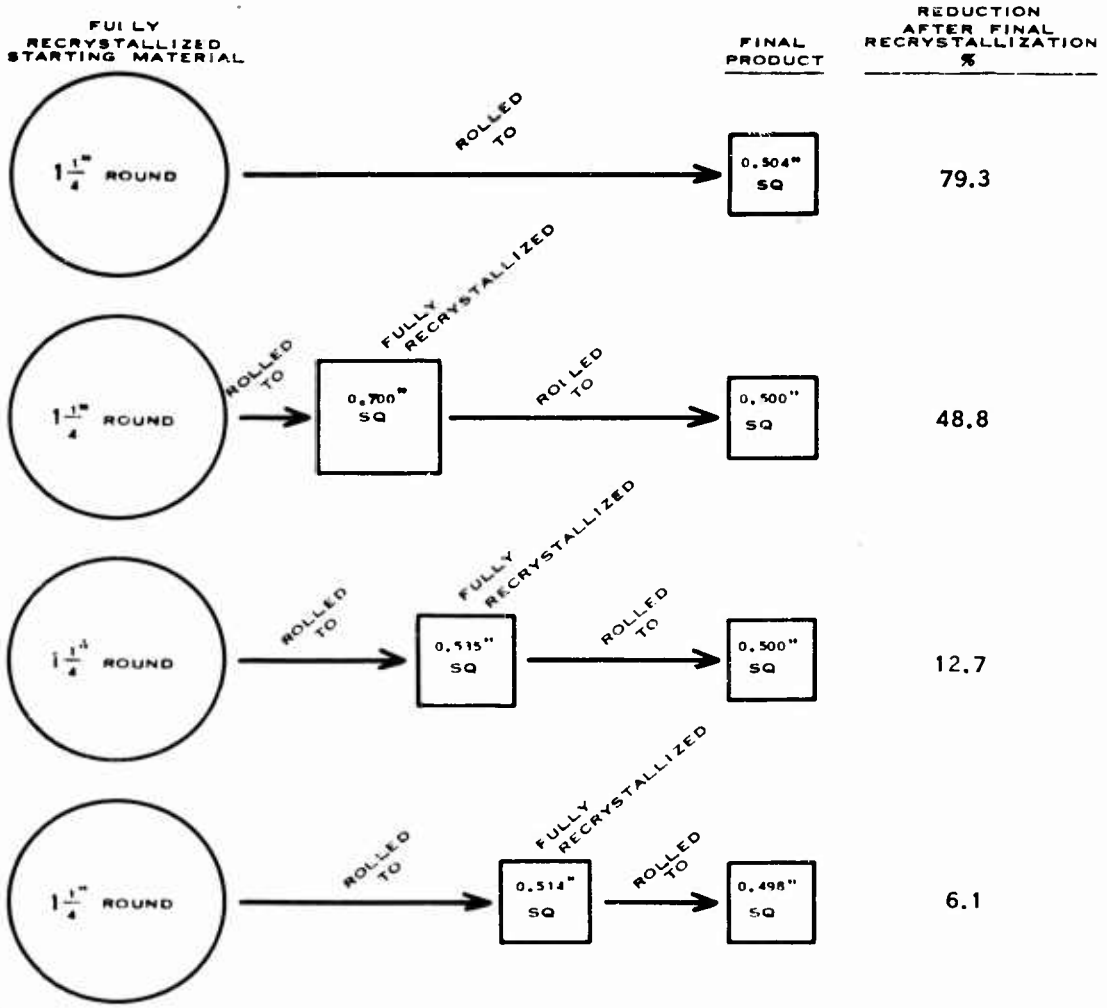


FIGURE 176 – PROCEDURE USED FOR OBTAINING VARIOUS DEGREES OF STRAIN HARDENING IN 1/2" SQUARE BARS

TABLE 28

REDUCTION ON ROLLING FROM 1-1/4" DIAMETER TO 1/2" DIAMETER

Heat	Initial Rolling				Recrys. Temp, F	Second Rolling		Reduction on Final Rolling, %
	Rolling Temp, F	Average Side, in.	Length, in. As Rolled	Length, in. Cropped		Rolling Temp, F	Dimensions	
1289	1800	.504	27-1/2	27-1/16				79.3*
Unalloyed	1800	.700	14-1/4	14-3/8	2300	1800	.500 x .502 x 27-5/8	48.8
Molybdenum	1800	.584	20-3/8	19-11/16	2200	1800	.502 x .502 x 25-5/8	26.1
	1800	.535	25-3/4	25-7/16	2200	1800	.500 x .500 x 28-1/8	12.7
	1800	.521	27-1/4	26-5/16	2200	1800	.497 x .499 x 27-3/4	8.6
	1800	.514	25-7/8	25-1/2	2200	1800	.498 x .498 x 26-1/4	6.1
	2200	.504	29-1/4	28-7/8				79.3*
	2200	.698	14-1/2	14-3/8	2300	2200	.502 x .502 x 27-9/16	48.3
	2200	.587	20	19-5/8	2300	2200	.503 x .503 x 26-3/16	26.6
	2200	.547	23-3/4	23-7/16	2200	2200	.496 x .503 x 27-5/8	16.6
	2200	.526	26-1/2	26-1/8	2200	2200	.498 x .498 x 28-7/16	10.4
	2200	.511	26-1/4	25-7/8	2200	2200	.498 x .498 x 26-11/16	5.0
1348	1800	.694	15-1/4	14-15/16	2600	1800	.501 x .504 x 27-7/8	47.6
0.46% Ti	1800	.546	25	24-3/16	2500	1800	.500 x .500 x 27-11/16	16.1
	2200	.502	21-5/8	21				79.5*
	2200	.703	14-1/2	14-3/16	2600	2200	.502 x .502 x 27-1/2	49.0
	2200	.586	16-3/8	15-5/8	2500	2200	.500 x .500 x 20-3/4	27.2
	2200	.550	23-7/8	23-5/8	2500	2200	.498 x .502 x 17-7/16 .496 x .503 x 10-5/16	17.4 17.5
	2200	.536	19	18-3/4	2500	2200	.496 x .502 x 21-1/8	13.3
	2200	.526 x .516	10-3/4	9-7/8	2500	2200	.495 x .503 x 10-3/8	8.3
	2200	.510	26-1/2	26-1/4	2500	2200	.498 x .498 x 27-1/16	4.7

* reduction after first and only rolling



FIGURE 177 — MICROSTRUCTURES OBTAINED ON ROLLING UNALLOYED MOLYBDENUM

HEAT 1289, 0.025% CARBON, X250
(M4969-M4980)

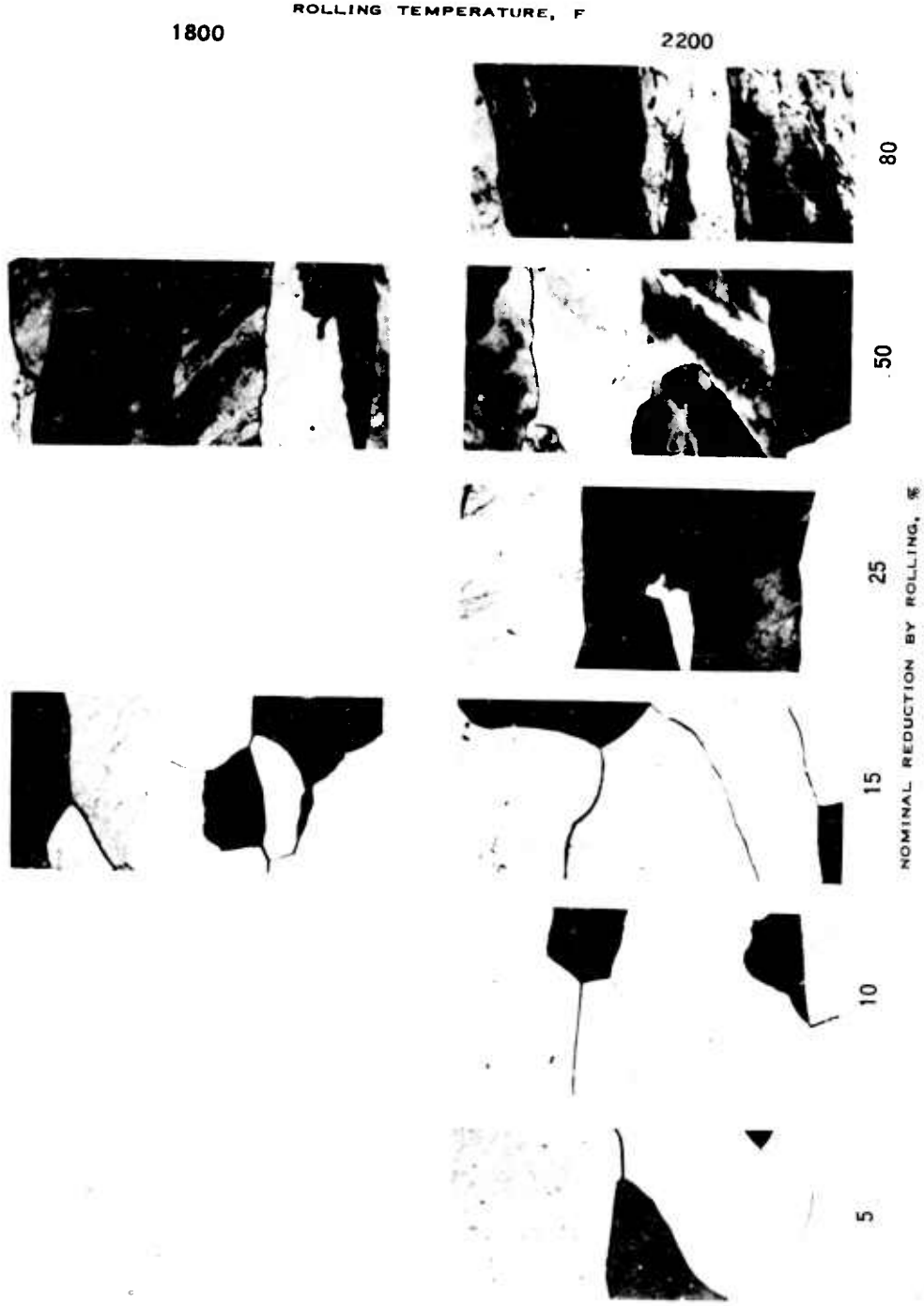


FIGURE 178 – MICROSTRUCTURES OBTAINED ON ROLLING 0.5% TITANIUM ALLOY

HEAT 1348, 0.46% TITANIUM, X250
(M5044-M5051)

Hardness and Tensile Strength

Vickers hardness determinations were made on each bar in the as-rolled condition. Tensile specimens having gage diameters of 1/4" and gage lengths of 1" were taken from each rolled bar. Tensile tests were performed at room temperature at strain rates of 3% and 60% per hour in the elastic and plastic portions of the test, respectively.

Figure 179 presents room-temperature hardness for as-rolled bars as a function of amount of plastic deformation. Room-temperature tensile test data for as-rolled bars are presented in Table 29 and Figure 180.

The generally lower level of hardness of unalloyed molybdenum compared with that of a molybdenum-titanium alloy having a comparable amount of rolling is evident from Figure 178. This relationship is particularly noticeable at the higher reductions, inasmuch as the molybdenum-titanium alloy continued to increase in hardness as the reduction of area increased up to 80%, whereas unalloyed molybdenum increased only slightly in hardness at reductions beyond about 40%.

Similarly, the difference in tensile strengths of the 0.46% titanium alloy and unalloyed molybdenum (Figure 180) is greater at high rather than at low amounts of reduction. The principal difference between the hardness and tensile strength data is that at low reductions tensile strength does not increase as rapidly as hardness per unit increase in amount of reduction.

The hardness and tensile strength of the molybdenum-titanium alloy rolled at 2200 F were higher than those of the same alloy rolled the same amount at 1800 F. A similar relationship existed for unalloyed molybdenum at the lower reductions. The accepted theory of strain hardening bears an inverse relationship to working temperature, other factors being equal.

A cursory investigation was made into possible factors contributing to the apparently contradictory behavior. First, the grain size prior to final working was determined. In general, the bars rolled at 2200 F exhibited coarser grain prior to final rolling than those rolled at 1800 F. Second, hardness surveys of the cross-sections of the bars rolled at 1800 F and 2200 F indicated that the strain hardening was uniform in both cases. Third, there was no evidence that the bars rolled at 2200 F were more contaminated with oxygen than those rolled at 1800 F. The data obtained do not explain the discrepancy in behavior of the bars rolled at 1800 F and 2200 F.

The properties of hardness and tensile strength were shown in an earlier section to be approximately proportional. The data at hand, however, afforded the possibility of determining whether the method used to arrive at a given hardness level affected tensile properties. In other words, would comparable tensile properties be obtained from a strain-free material worked to a given intermediate hardness level and a strain-hardened sample of the same material annealed to the same hardness level?

TABLE 29

TENSILE PROPERTIES AT ROOM TEMPERATURE OF UNALLOYED MOLYBDENUM (1289) AND 0.5% TITANIUM ALLOY (1348) ROLLED TO 1/2" SQUARE

Heat	Rolling Temp, F	Reduction by Rolling, %	Yield Str, psi	Tensile Str, psi	El, %	R.A. %
1289	1800	6.1	55,600	73,600	56	57.9
0.025% C		8.6	57,100	73,300	53	33.7
		17.1	61,400	76,800	50	53.1
		26.1	68,200	80,900	40	59.4
		48.8	83,500	91,500	41	65.4
		79.3	82,600	98,900	24	23.2
1289	2200	5.0	62,800	74,600	45	47.1
0.025% C		10.4	66,200	78,200	42	37.1
		16.6	69,900	80,600	36	43.3
		26.6	71,400	84,000	23	20.4
		48.3	81,400	92,700	11	11.6
		79.3	89,100	98,600	24	27.3
1348	1800	16.1	65,700	81,200	38	31.7
0.46% Ti		47.6	87,000	99,700	37	66.4
1348	2200	4.7	56,500	77,100	45	43.1
0.46% Ti		8.3	66,100	78,900	42	33.9
		13.3	67,800	78,900	34	31.2
		17.5	70,700	84,500	40	35.9
		27.2	73,200	87,900	39	39.3
		49.0	92,500	102,200	25	37.8
		79.5	103,900	114,400	34	66.6

TABLE 29

TENSILE PROPERTIES AT ROOM TEMPERATURE OF UNALLOYED MOLYBDENUM (1289) AND 0.5% TITANIUM ALLOY (1348) ROLLED TO 1/2" SQUARE

Heat	Rolling Temp, F	Reduction by Rolling, %	Yield Str, psi	Tensile Str, psi	El, %	R.A. %
1289	1800	6.1	55,600	73,600	56	57.9
0.025% C		8.6	57,100	73,300	53	33.7
		17.1	61,400	76,800	50	53.1
		26.1	68,200	80,900	40	59.4
		48.8	83,500	91,500	41	65.4
		79.3	82,600	98,900	24	23.2
1289	2200	5.0	62,800	74,600	45	47.1
0.025% C		10.4	66,200	78,200	42	37.1
		16.6	69,900	80,600	36	43.3
		26.6	71,400	84,000	23	20.4
		48.3	81,400	92,700	11	11.6
		79.3	89,100	98,600	24	27.3
1348	1800	16.1	65,700	81,200	38	31.7
0.46% Ti		47.6	87,000	99,700	37	66.4
1348	2200	4.7	56,500	77,100	45	43.1
0.46% Ti		8.3	66,100	78,900	42	33.9
		13.3	67,800	78,900	34	31.2
		17.5	70,700	84,500	40	35.9
		27.2	73,200	87,900	39	39.3
		49.0	92,500	102,200	25	37.8
		79.5	103,900	114,400	34	66.6

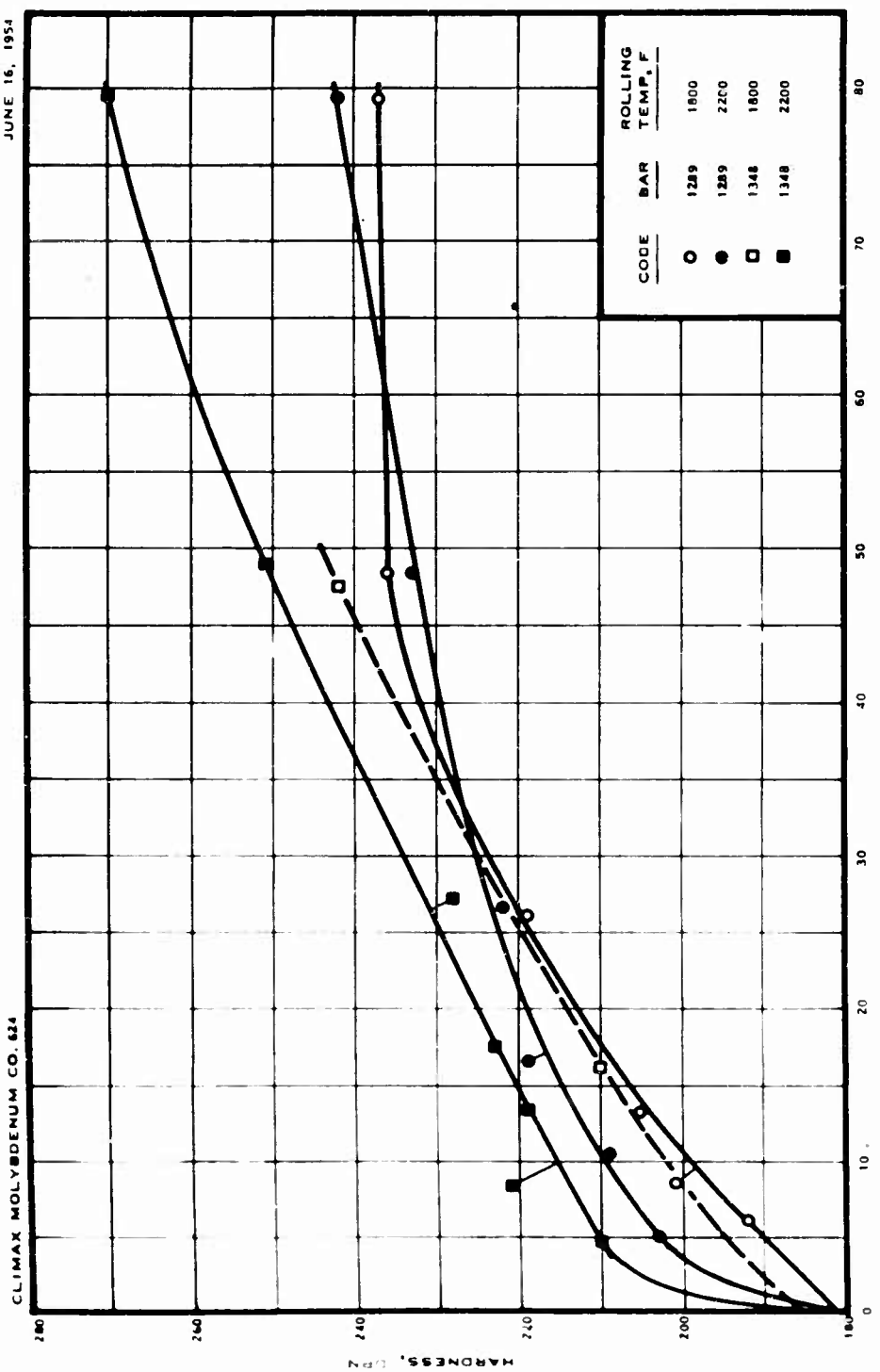


FIGURE 179– HARDNESS VS. PERCENT REDUCTION OF 1/2" SQUARE BARS 1289 (0,025% C) AND 1348 (0,021% C, 0.46% T_i)

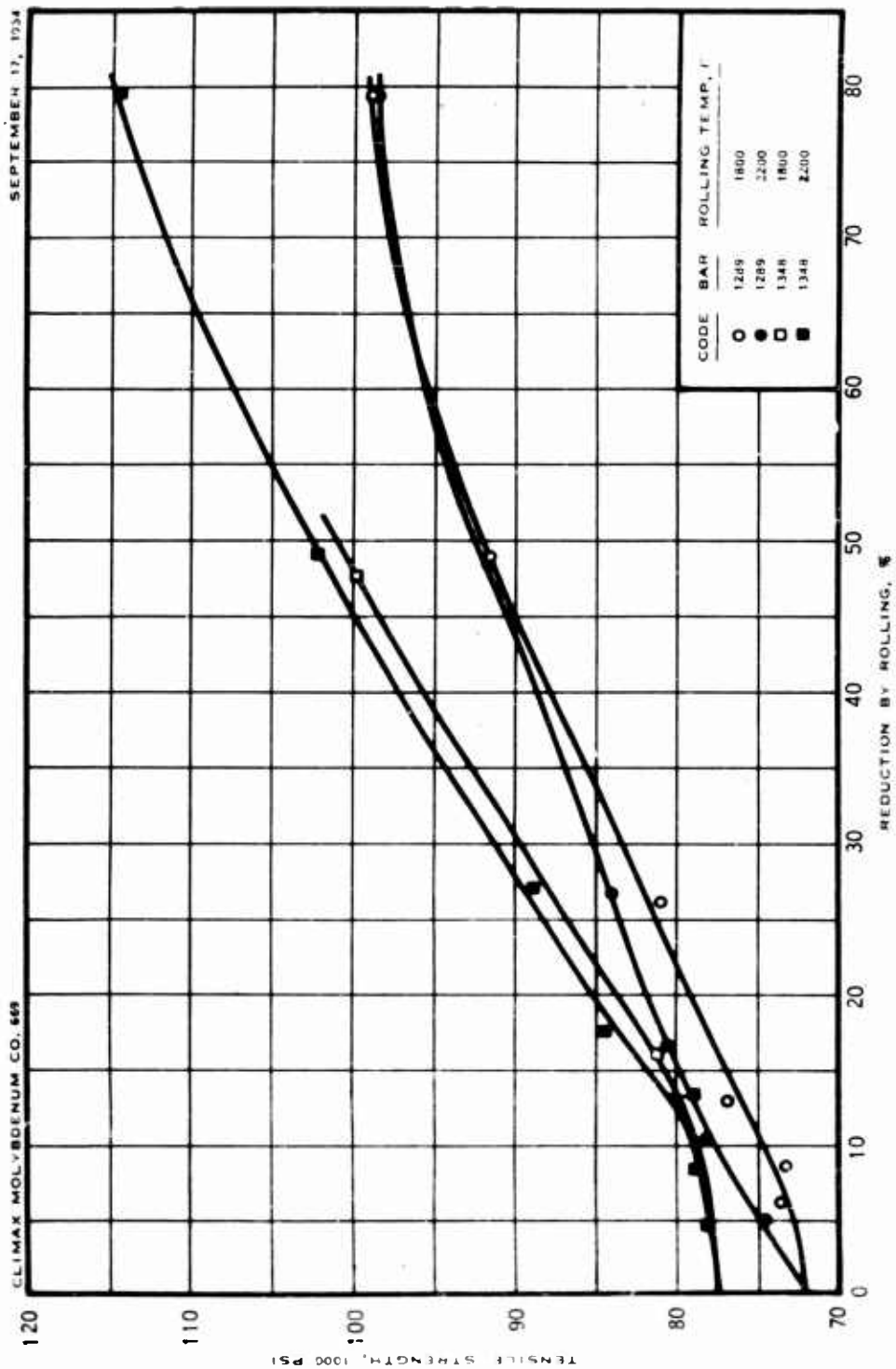


FIGURE 180 – TENSILE STRENGTH VS. PERCENT REDUCTION OF $\frac{1}{2}$" SQUARE BARS
1289 (0.025% C) AND 1348 (0.021% C, 0.46% Ti)

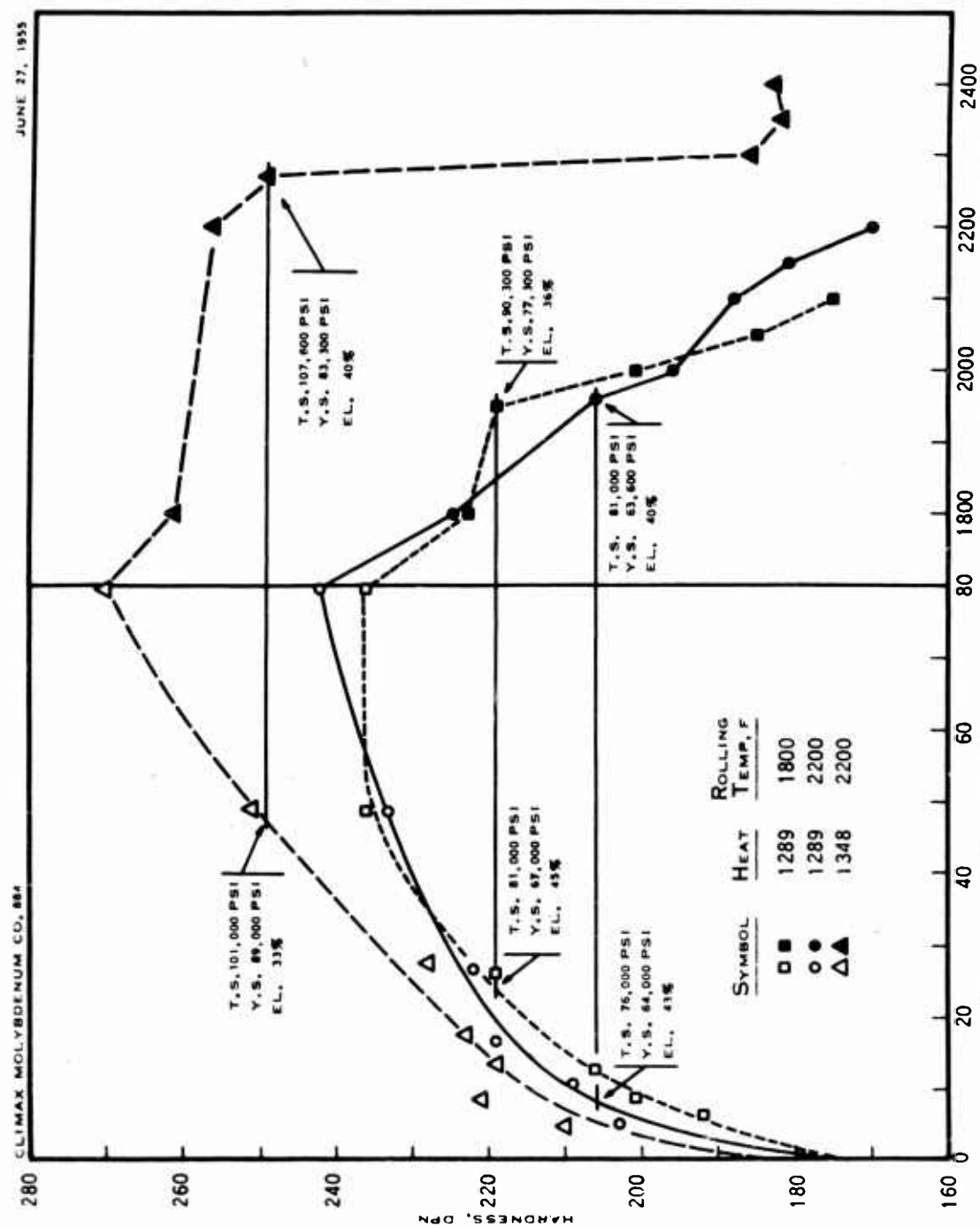


FIGURE 181 – COMPARISON OF TENSILE PROPERTIES OBTAINED BY COLD WORKING TO A GIVEN HARDNESS WITH THOSE OBTAINED BY ANNEALING TO THE SAME HARDNESS

The data pertaining to this problem are shown in Figure 181. Hardness is plotted as a function of amount of reduction on the left side of the chart and as a function of annealing temperature for the most severely worked samples on the right side. The data presented in this chart were obtained in the following manner: Samples of the most severely worked bars were annealed at temperatures designed to produce hardness values intermediate between the fully strain-hardened and fully recrystallized conditions. Tensile test specimens were then machined from the annealed bars. The hardness values obtained for the annealed bars were projected to intersect the curves of hardness vs reduction by rolling. The tensile properties on the left side of the chart were obtained by interpolation from plots of tensile and yield strengths and elongation as a function of reduction by rolling, using the reduction values obtained from the intersections of the isohardness lines with the strain hardening curves.

The tensile strength values obtained for the annealed samples were consistently higher than those of the samples work hardened to the same hardness. Yield strength and elongation figures did not show a conclusive trend in these tests.

Recrystallization Temperature

Small samples from each bar were annealed for one hour at various temperatures in an atmosphere of tank hydrogen. The annealed samples were sectioned and examined metallographically for evidence of recrystallization. Vickers hardness tests were performed on each annealed sample.

Figures 182-185 show the effect of annealing temperature on hardness at room temperature for the bars rolled at 1800 and 2200 F. The terminal points of the curves indicate complete recrystallization on the basis of metallographic observation. Within the limits of experimental error, these families of curves follow idealized behavior in that the higher the amount of reduction, the lower the recrystallization temperature. Hardness after complete recrystallization tends to be higher for the less severely worked samples, owing possibly to the effect of differing grain size.

Figure 186 relates recrystallization temperature to amount of reduction. It will be noted that the curves corresponding to unalloyed molybdenum and the molybdenum-titanium alloy intersect in the vicinity of 20% reduction, indicating that for reductions under this amount unalloyed molybdenum exhibits a greater resistance to recrystallization than the 0.46% titanium alloy.

Curves of hardness as a function of temperature for unalloyed molybdenum reduced 79.3, 16.6, 10.4, and 5.0% at 2200 F are included in Figures 187 and 188. Of interest here is the fact that the more severely worked bar (79.3% reduction) drops in hardness rapidly in the range between about 1800 and 2300 F and is actually lower in hardness at 2300-3000 F than any of the less severely

worked bars. The rapid change in hardness between 1800 and 2300 F is due to recrystallization during testing, and therefore the hardness on cooling is representative of a fully recrystallized structure. As the amount of strain hardening is decreased, recrystallization temperature increases, and, for reductions of 16% or less, only partial recrystallization occurs under the conditions of the hot hardness test. When the reductions are in the order of 5 to 10%, very little loss of hardness at room temperature occurs as a result of exposure at 3000 F.

Similar results for the 0.46% titanium alloy, Figure 177, indicate that reductions of 4.7 to 79.5% produce sufficient strain hardening in the material that it becomes fully recrystallized in the hot hardness test. On cooling, the hardness is identical with that of as-cast material. These results seem to be consistent with the recrystallization data presented in Figure 183, wherein the recrystallization temperature (and thus the effect of temperature during hardness testing) was less for the titanium alloy than for unalloyed molybdenum at the low reductions.

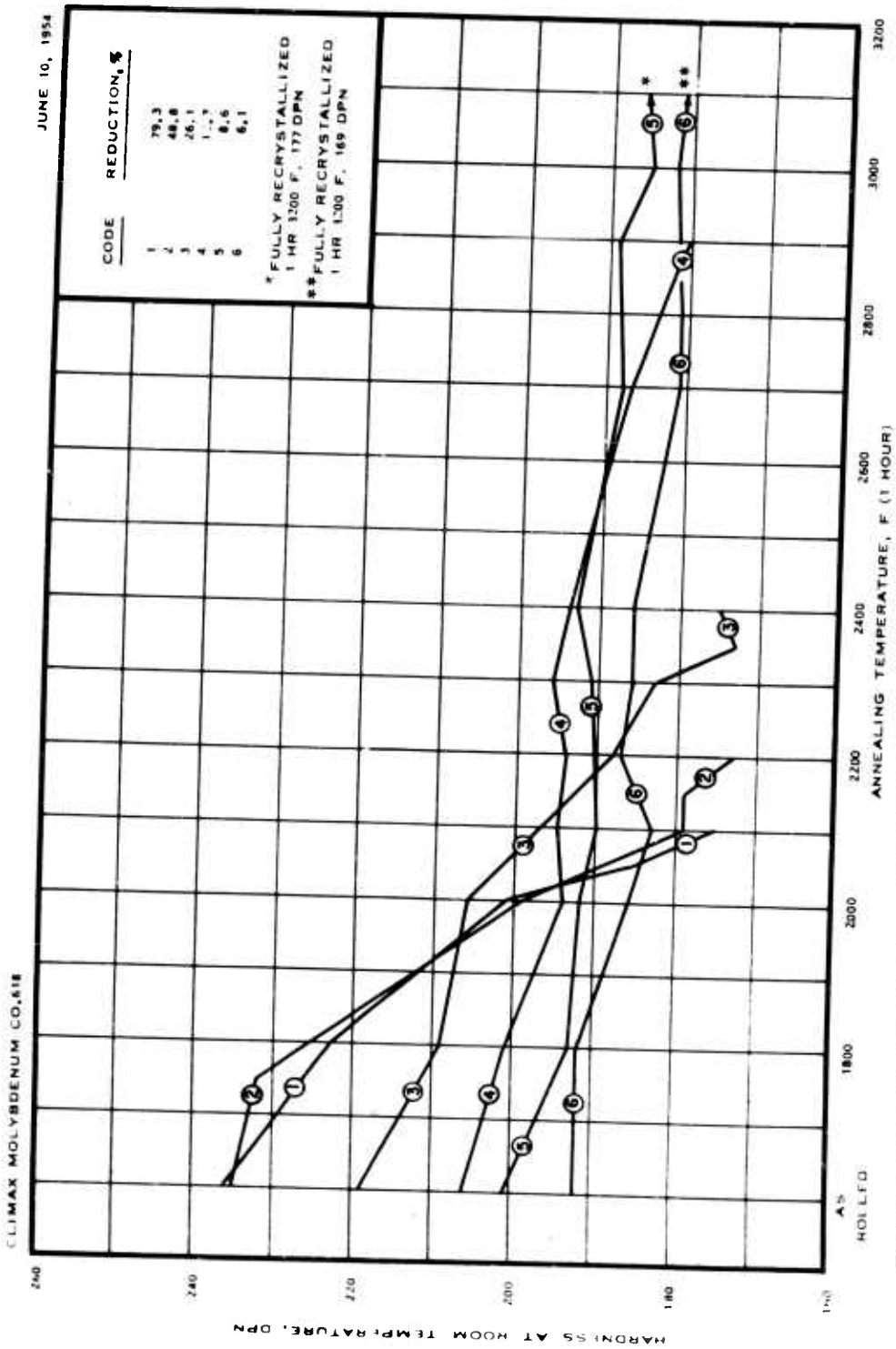


FIGURE 182 – HARDNESS VS. ANNEALING TEMPERATURE FOR HEAT 1289 (0.025% C) ROLLED TO 1/2" SQUARE AT 1800 F WITH INDICATED AMOUNTS OF REDUCTION

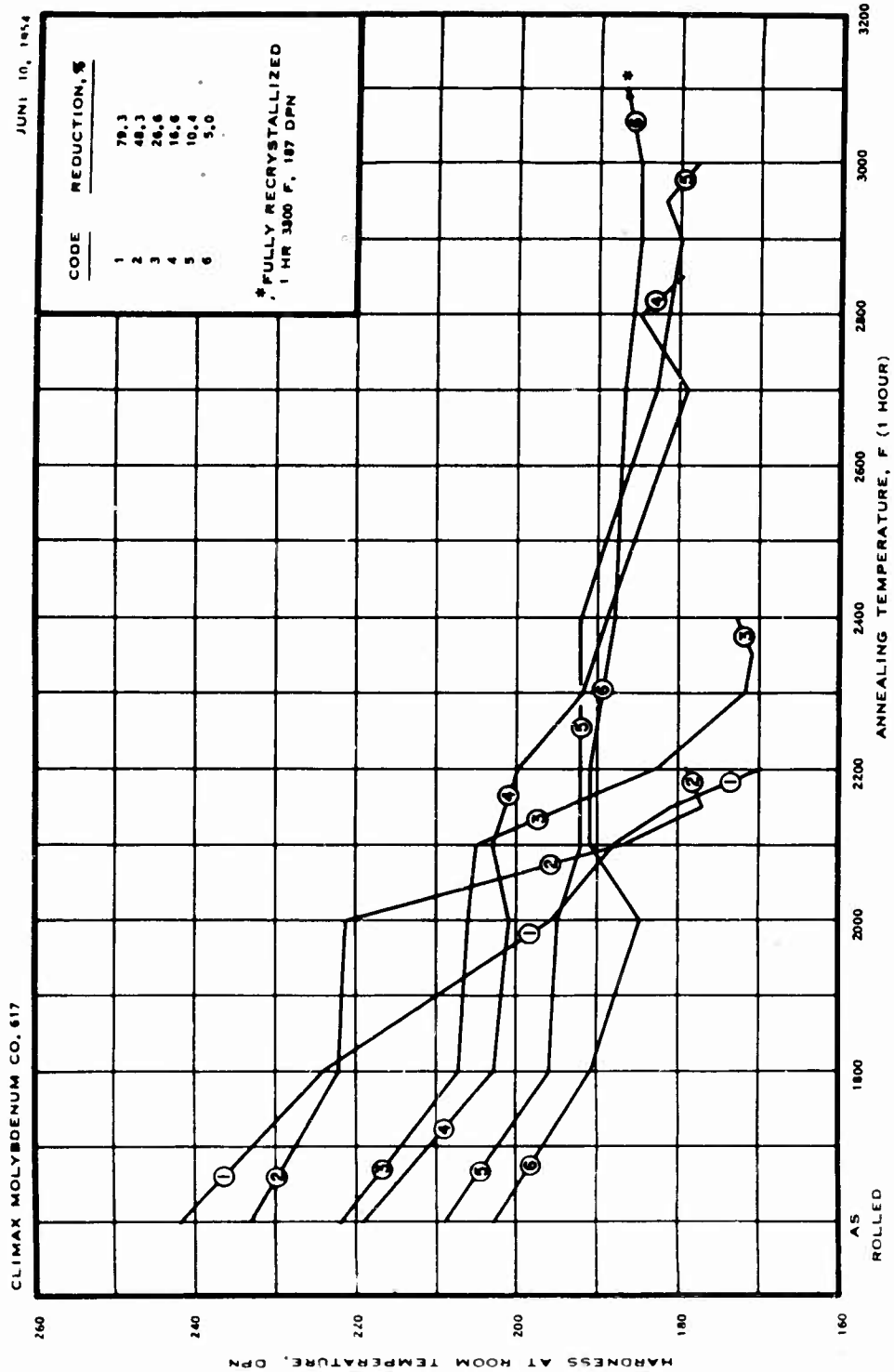


FIGURE 183 — HARDNESS VS. ANNEALING TEMPERATURE FOR HEAT 1289 (0.025% C) ROLLED TO ½" SQUARE AT 2200 F WITH INDICATED AMOUNTS OF REDUCTION

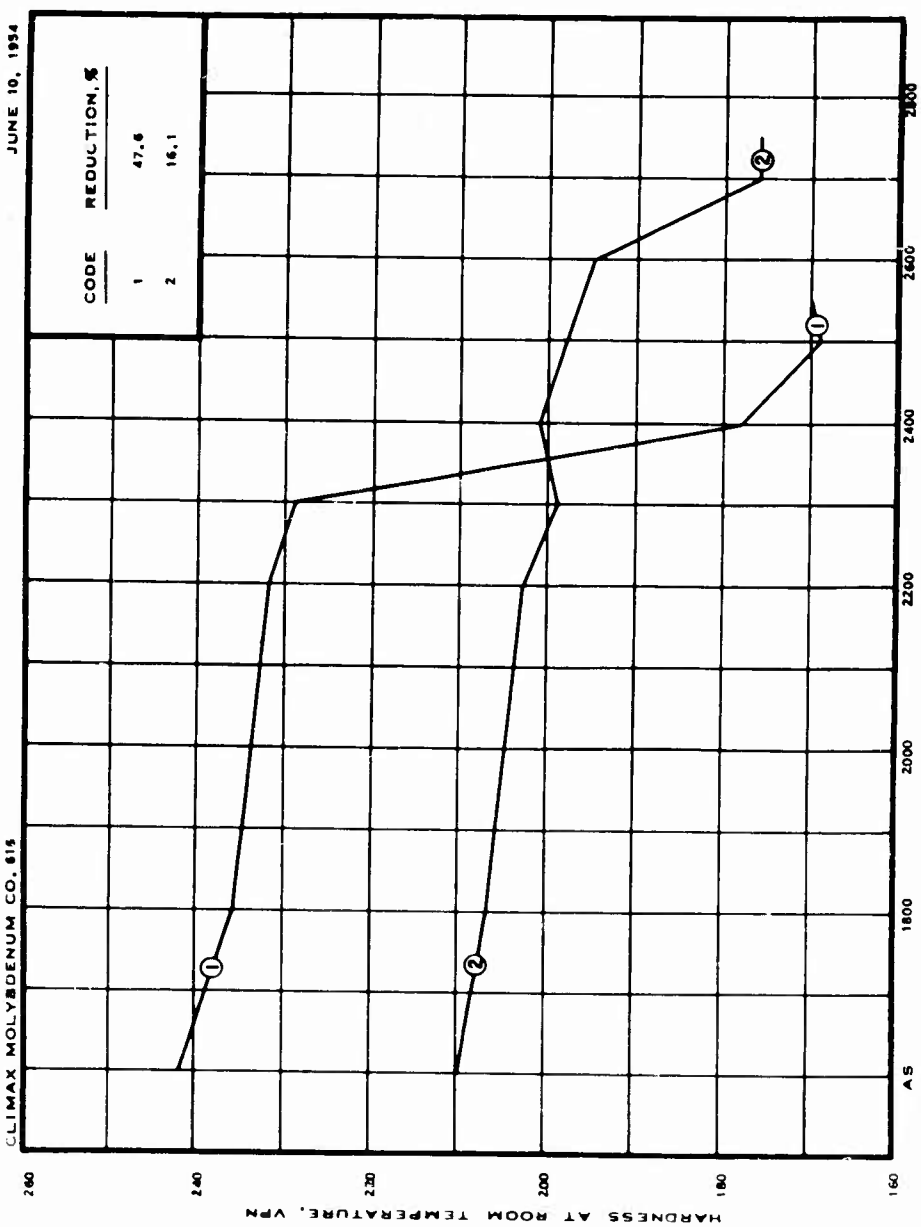


FIGURE 134 – HARDNESS VS. ANNEALING TEMPERATURE FOR HEAT 1348 (0.021% C, 0.46% Ti) ROLLED TO 1/2" SQUARE AT 1800 F WITH INDICATED AMOUNTS OF REDUCTION

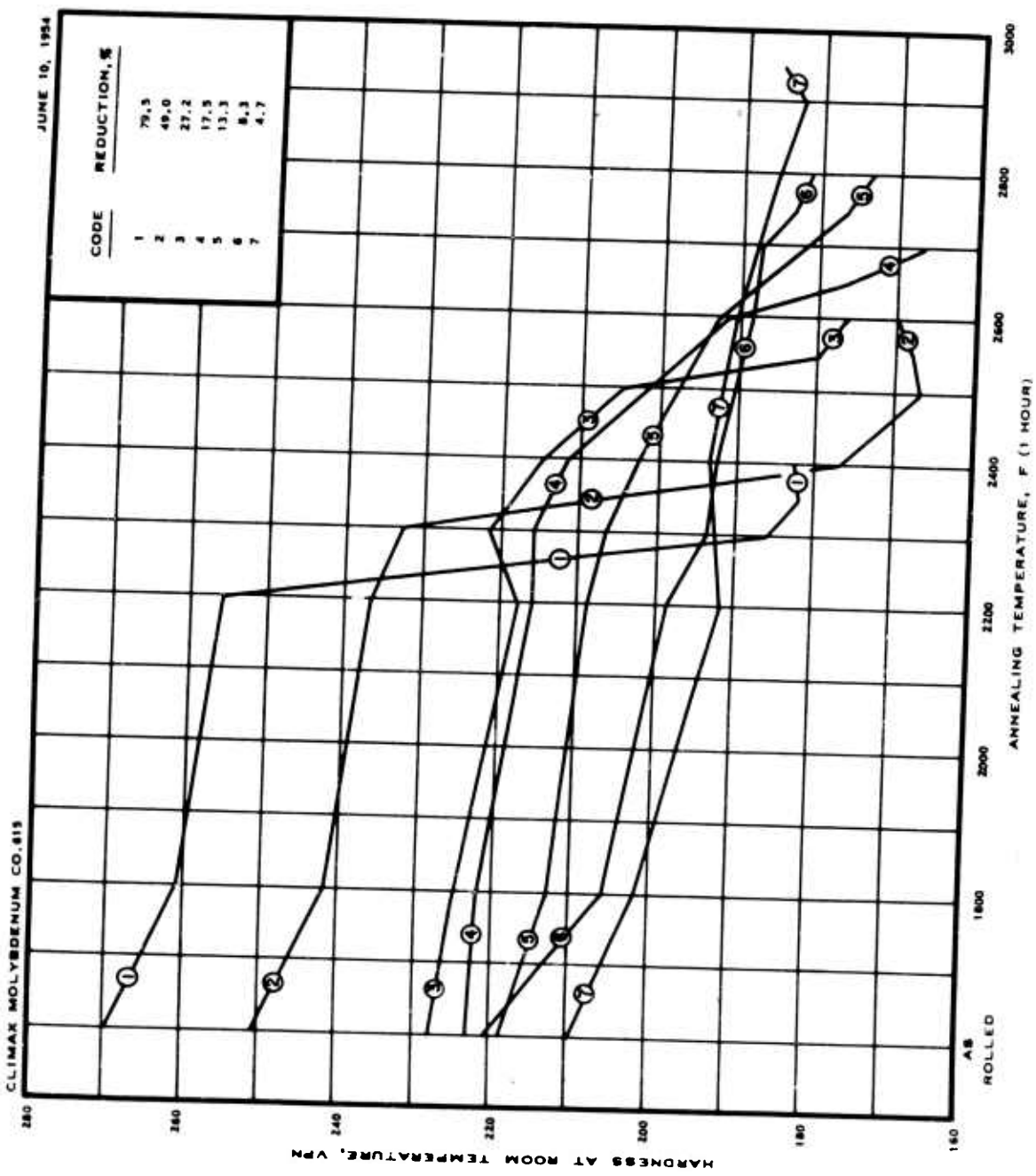


FIGURE 185 — HARDNESS VS. ANNEALING TEMPERATURE FOR HEAT 1348 (0.021% C, 0.46% T_i) ROLLED TO 1/2" SQUARE AT 2200 F WITH INDICATED AMOUNTS OF REDUCTION

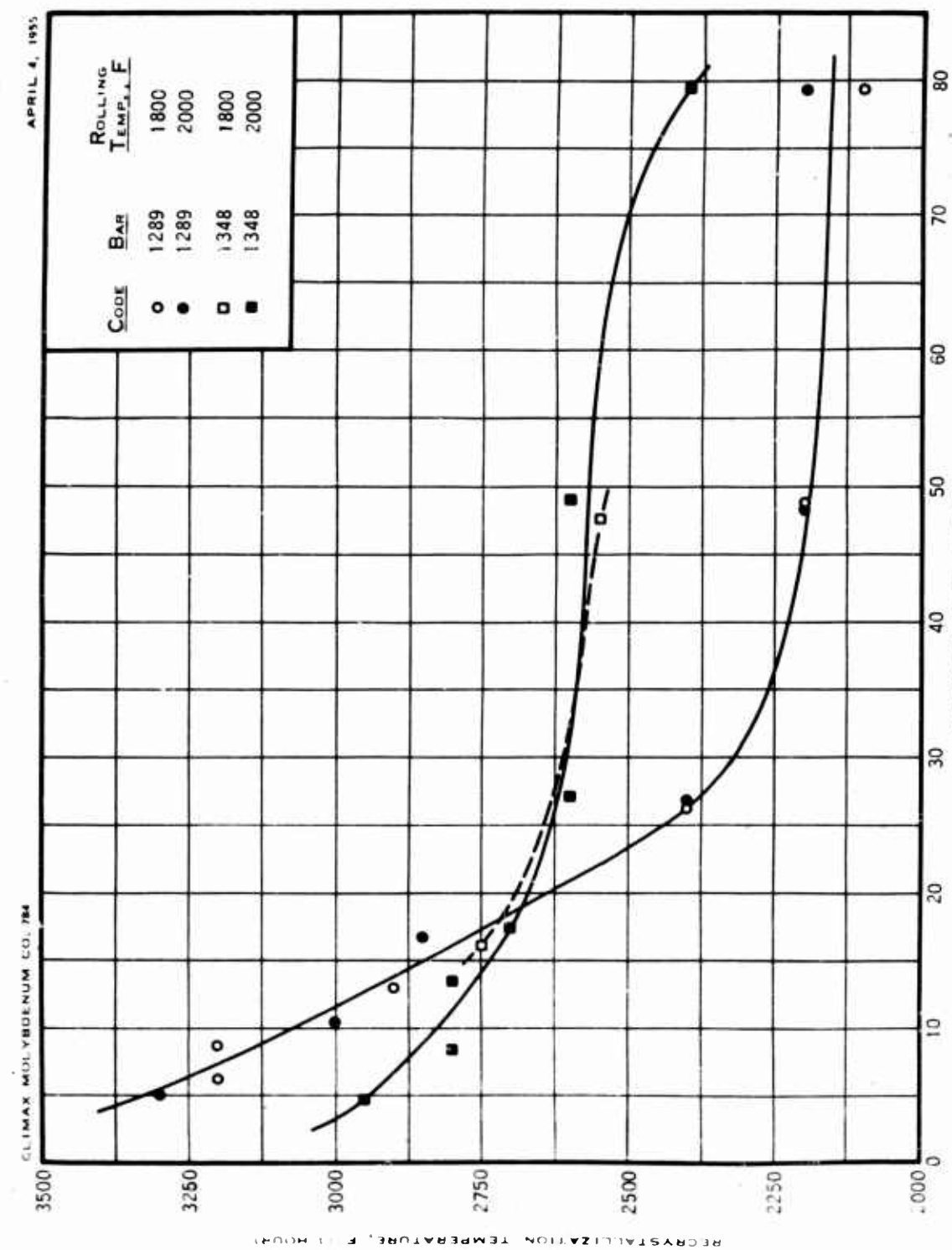


FIGURE 186 — TEMPERATURE OF COMPLETE RECRYSTALLIZATION VS PERCENT REDUCTION FOR $\frac{1}{2}$" SQUARE BARS 1289 (0.025% C) AND 1348 (0.021% C, 0.46% T_i)

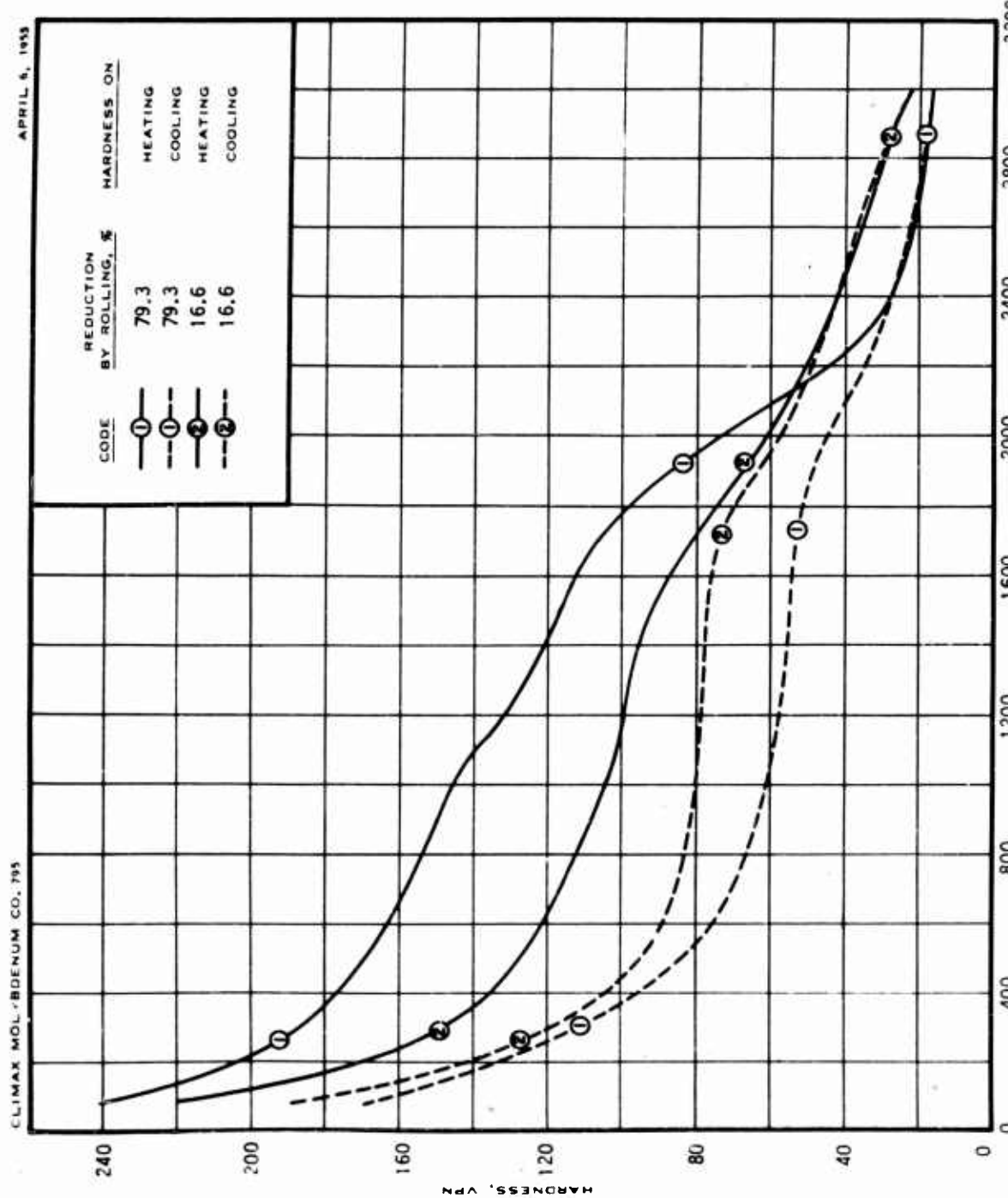


FIGURE 187 – HARDNESS VS TEMPERATURE FOR BAR 1289 (0.025% C) ROLLED TO $\frac{1}{2}$ INCH SQUARE AT 2200 F WITH INDICATED AMOUNTS OF REDUCTION

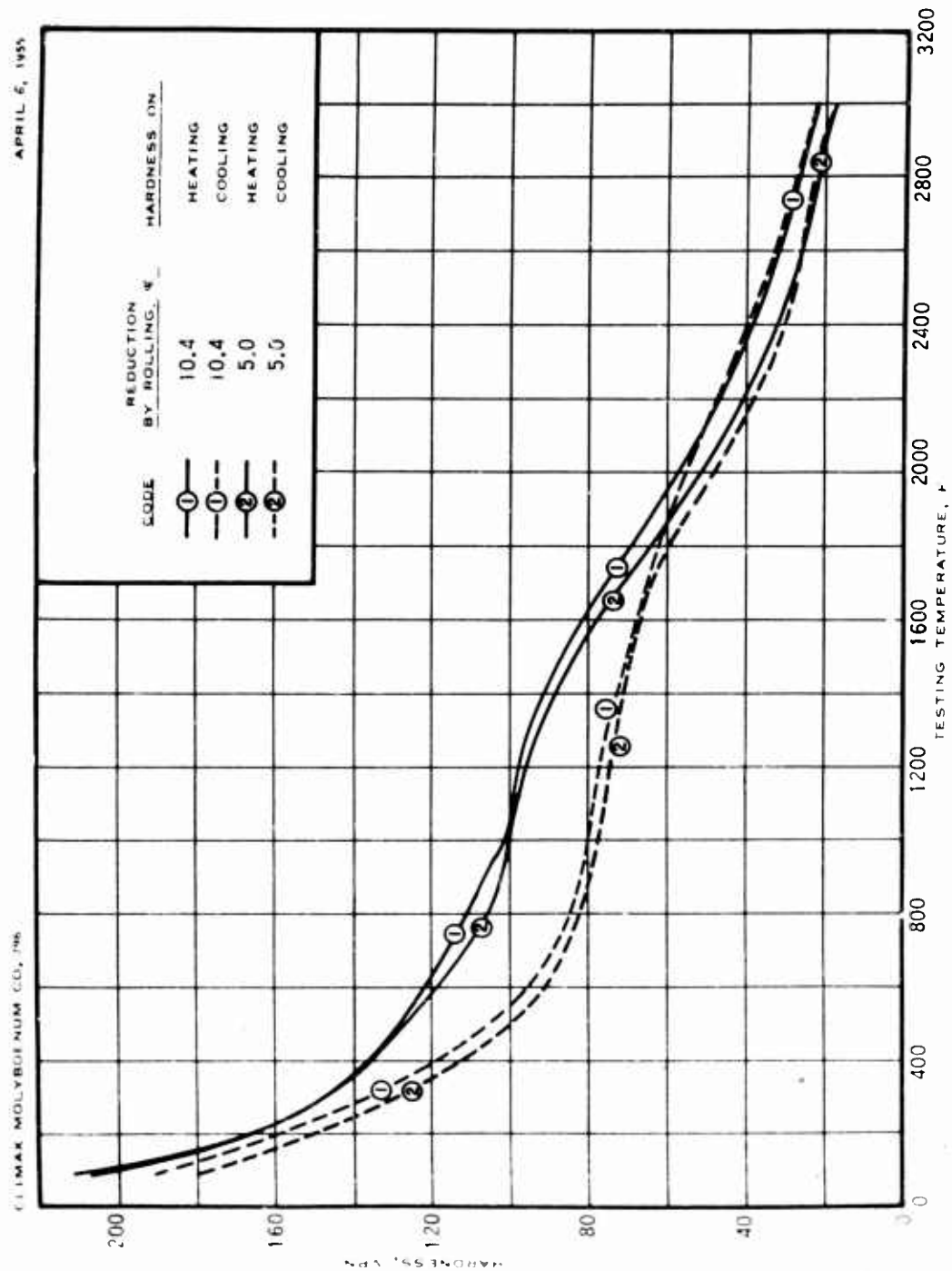


FIGURE 165 HARDNESS VS TEMPERATURE FOR BAR 1289 (0.025% C) ROLLED TO $\frac{1}{2}$ INCH SQUARE AT 2200 F WITH INDICATED AMOUNTS OF REDUCTION

EMBRITTLEMENT RESULTING FROM EXPOSURE TO ELEVATED TEMPERATURES

Wrought molybdenum and molybdenum-base alloys decrease in room-temperature ductility when exposed to exceedingly high temperatures (3200 F and above). This decrease in room temperature ductility occurs gradually as the temperature of exposure is increased. The temperature or temperature range of transition from brittle to ductile behavior of molybdenum is increased because of such elevated temperature treatments of the wrought material. Variation in transition temperature of wrought materials based on tensile tests and impact tests are reported in the section on mechanical properties. In this section we discuss the transition temperature as affected by exposure to elevated temperature, studied by means of the bend test.

In considering experiments of the type recorded here, it must be remembered that the ductility of any test specimen is a function not only of the material being tested, but also of the testing temperature, rate of application of strain, and mode of stressing. Stated somewhat differently, a critical temperature--or temperature range--exists for a given material, specimen geometry, and strain rate above which ductile behavior and below which brittle behavior is experienced. In a similar manner, critical strain rates are observed for isothermal tests conducted on specimens of like design. It follows that the term embrittlement implies a deleterious shift in the critical ranges of factors such as temperature and strain rate so that under the specific conditions of test, low ductility is obtained. It also follows that the term embrittlement is ambiguous unless all of the conditions are noted under which an embrittlement test is made. The results reported in this section represent embrittlement as indicated by beam bending tests run at uniform strain rate at room temperature.

Approximately 70 compositions of wrought molybdenum and its alloys, representing variations in deoxidation practice and alloy content, have been exposed to elevated temperatures up to and including 3900 F, and the effect on bend ductility was evaluated by means of the bend test.

Blanks were so obtained from each material that when a minimum of 0.030" was removed from each surface after exposure the final specimen size was 0.250" wide by 0.150" thick by 1" in length. In all cases, the long dimension of the bend specimen was parallel to the working direction of the material. Exposure time was one hour in an atmosphere of purified argon. Specimens were supported on a 5/8" span and centrally loaded at a constant deflection rate of 0.005" per minute. The maximum possible angle of bend for the equipment used was 115°.

The compositions of the materials studied, as well as the bend test results, are presented in Figures 189-193. Inasmuch as all of the test specimens were wrought materials and were heated at temperatures well above that required for complete recrystallization, the minor variation in fabrication histories from heat to heat was not considered to be significant. Specimens of heats reported in the chapter on mechanical properties were machined directly from rolled bar stock. All other specimens were taken from 1/4" thick plates flattened at approximately 1800 F.

Data obtained for carbon deoxidized, unalloyed molybdenum (Figure 189) definitely indicate that carbon plays an important role in the mechanism of embrittlement. The 0.008% carbon material (936) retained near maximum ductility after exposure to 3500 F, while the 0.045% carbon material (739) exhibited low ductility after exposure at 3400 F.

Heats deoxidized with lithium-calcium or lithium-aluminum additions were generally less resistant to embrittlement than low-carbon, unalloyed molybdenum. One heat deoxidized with 0.5% Lan-Cer-Amp* (1101) retained significant ductility after exposure at 3700 F, whereas a heat deoxidized with 0.3% Lan-Cer-Amp (1045) was brittle under the conditions of the bend test after exposure at 3500 F. Heats deoxidized with cerium alone were generally low in ductility under all conditions of exposure. It will be noted that a heat containing 0.11% cerium and 0.008% carbon (1142) was less resistant to embrittlement than the heat containing 0.008% carbon alone (936). It is believed that the poor results obtained for the cerium-bearing materials were due to the presence of an unidentified second phase as noted in the section of this report dealing with deoxidation.

Two low-carbon, aluminum deoxidized heats (814 and 870) exhibited good resistance to embrittlement under the conditions of these experiments. On the other hand, a heat of similar aluminum content but higher in carbon (948) failed with little or no plastic deformation over the complete range of exposure temperatures. Similarly, low-carbon heats containing, respectively, 0.53 and 0.55% aluminum (987 and 942) yielded generally low results. The material containing 0.011% magnesium (874) was somewhat less resistant to embrittlement than one of approximately similar carbon and aluminum contents (814).

In the early stages of the program on embrittlement, high hope was held for the performance of alloys in the molybdenum-thorium system on the basis of tests on a heat containing 0.03% thorium (B125). Repeated efforts to duplicate these results were unsuccessful, as indicated in the graph, Figure 190. It must be concluded now that the original heat was abnormal in some respect and that molybdenum-thorium alloys (in the composition range studied) are no better than unalloyed molybdenum with respect to resistance to embrittlement.

Additions of cobalt or zirconium (lower portion of Figure 190) were evidently ineffectual in inhibiting embrittlement.

Considering the molybdenum-titanium binary system, Figure 191, those heats deoxidized with carbon alone were not noticeably superior to unalloyed molybdenum deoxidized with carbon. Three nominally 0.5% titanium, molybdenum alloys deoxidized with Lan-Cer-Amp (1048) or aluminum (946 and 1137) did, however, exhibit good resistance to embrittlement. Molybdenum-titanium alloys containing in excess of 1% titanium gave low bend ductilities regardless of the mode of deoxidation.

On the basis of data reported in Figure 192, additions of vanadium or niobium offer no promise for solution of the problem of embrittlement of molybdenum by exposure to elevated temperatures. A similar statement may be made for additions of chromium, iron, nickel and silicon, Figure 193.

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* 30% min. lanthanum, 45-50% cerium, 20-24% "didymium" and yttrium, 1% max. iron and unreduced salts

Of the seven ternary molybdenum-base alloys studied (lower portion of Figure 193), none resisted embrittlement as well as unalloyed molybdenum.

Although it was not considered within the scope of the present study to determine the mechanism whereby the ductility of molybdenum is lowered by exposure to elevated temperature, some observations are in order, owing to the obvious correlation between embrittlement and deoxidation practice. It appears that the embrittlement of wrought molybdenum is closely related to the brittle behavior of cast molybdenum and that both are more dependent upon deoxidation and neutralization practices than upon the type or amount of alloying element.

The lack of room temperature ductility of cast molybdenum and wrought molybdenum after exposure to high temperatures appears to be dependent upon minute amounts of oxygen present as MoO_2 and located predominantly at the grain boundaries. The low strength and low ductility of the oxide phase is thought to be an important contributing factor in the low ductility of the metal.

On the whole, failures encountered in the embrittlement studies were transgranular, although the relative frequency of intergranular facets on fracture surfaces increased as the exposure temperature was raised. It is believed that the actual mechanism of failure depends upon stress-concentrating effects of the contaminated grain boundaries and subsequent propagation of cracks through the grains.

The sources of the oxygen are thought to be threefold, that is, the casting process, fabrication steps, and exposure to the embrittling temperatures. Quantitative measurements of the amount of oxygen picked up in each step have not been made. The good ductility observed in most wrought molybdenum and molybdenum-base alloys heated in the temperature range required for recrystallization is attributed to the fact that the fineness of grain of these products dilutes the harmful phase below a critical concentration. As the metal is exposed to increasingly higher temperatures, however, two things happen. First, minute quantities of oxygen are absorbed from the heating atmosphere in addition to that already present in the metal. Second, grain size is increased, resulting in less boundary area per unit volume and a concentrating effect of the oxide phase.

Figures 194a and 194b illustrate representative areas from an 0.008% carbon heat (936) heated at 3500 and 3700 F. The relatively higher concentration of oxide as evidenced by grain boundary speckling is noted in the sample heated at 3700 F.

Further credence to the idea that MoO_2 at the grain boundaries causes loss of ductility is gained from the work of others[1,2] who show that both rate of heating and rate of cooling from the high temperature affect room-temperature ductility. Thus rapid cooling enhances ductility, inasmuch as some of the MoO_2 which may have been in solution at the high temperature either precipitates within the grains or remains in supersaturated solution.

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[1] Timothy Perry, H. S. Spacil and John Wulff, Effect of oxygen on welding and brazing molybdenum. The Welding Journal, Sept. 1954, Supplement, pp 442-448

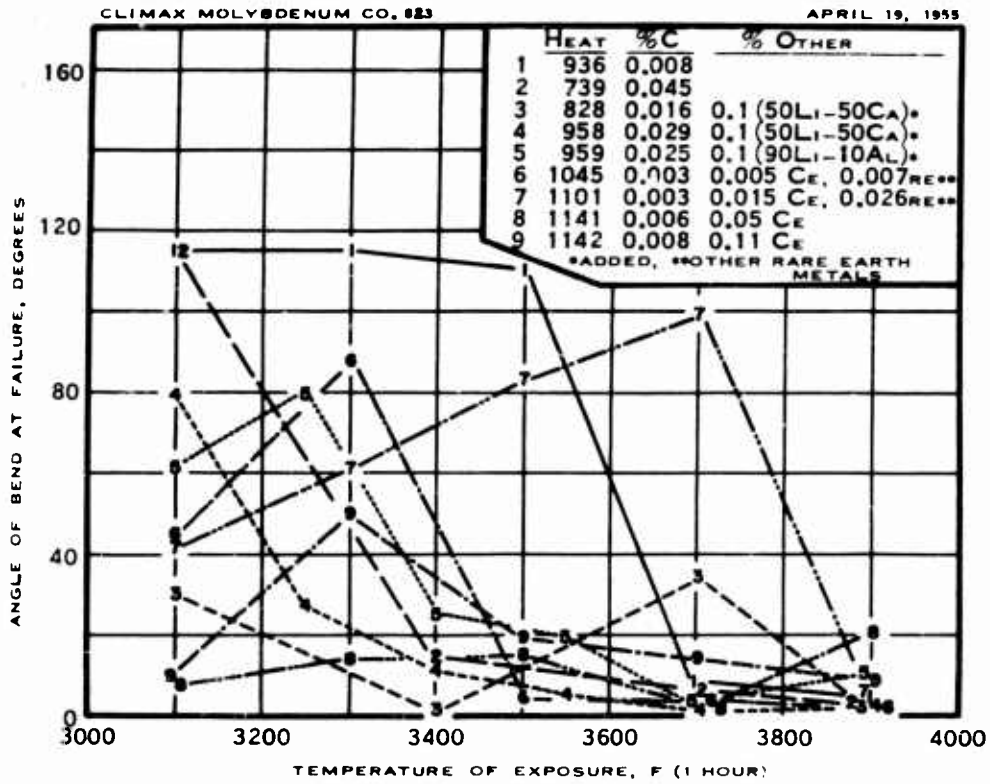
[2] S. L. Case, Summary Report on A Metallurgical Study of Molybdenum, to Office of Naval Research, Navy Department, Contract N9onr-82100, Project NR 039-003, Battelle Memorial Institute. October 15, 1954

The data accumulated in the present studies show that deoxidation and neutralization variables affect resistance to embrittlement to a greater extent than changes in alloy content. Such alloying elements as vanadium, niobium, nickel, silicon, and cobalt do not change the embrittlement temperature of molybdenum. These elements accomplish little in the way of deoxidation or neutralization. Elements such as titanium and zirconium, on the other hand, decrease the amount of MoO_2 evident on the fracture surface of the cast metal, either by neutralization or deoxidation. These elements, when present in the wrought product, cause it to be more resistant to embrittlement. It is necessary to expose molybdenum-base alloys containing titanium or zirconium to appreciably higher temperatures to cause them to lose ductility at room temperature.

Aluminum, which is effective in neutralizing molybdenum--even though not particularly effective in removing oxygen--also serves to increase the resistance to embrittlement. The mechanism here, of course, can be attributed to the fact that Al_2O_3 forms at the expense of MoO_2; therefore, the amounts of MoO_2 in molybdenum neutralized with aluminum are substantially less.

It is thought that the case of molybdenum carbide, Mo_2C, is in some respects analogous to that of MoO_2 in its effect on embrittlement. As the carbon content is increased, the resistance of unalloyed molybdenum to embrittlement is decreased, and as the grains are coarsened, the carbides form continuous envelopes around the grains causing brittle fracture without much plastic deformation.

In summary, the loss of ductility of molybdenum after exposure to elevated temperatures was found to be more closely associated with deoxidation practice than with purely alloying additions. The basic cause of embrittlement is thought to be the presence of small amounts of oxygen (probably 1 to 5 ppm), presumably as MoO_2 situated at the grain boundaries. Potential methods for eliminating embrittlement seem to lie in the direction of eliminating the oxygen or neutralizing it to form a less deleterious oxide, or inhibiting grain growth so that the concentration of the harmful phase would be maintained below a critical level.



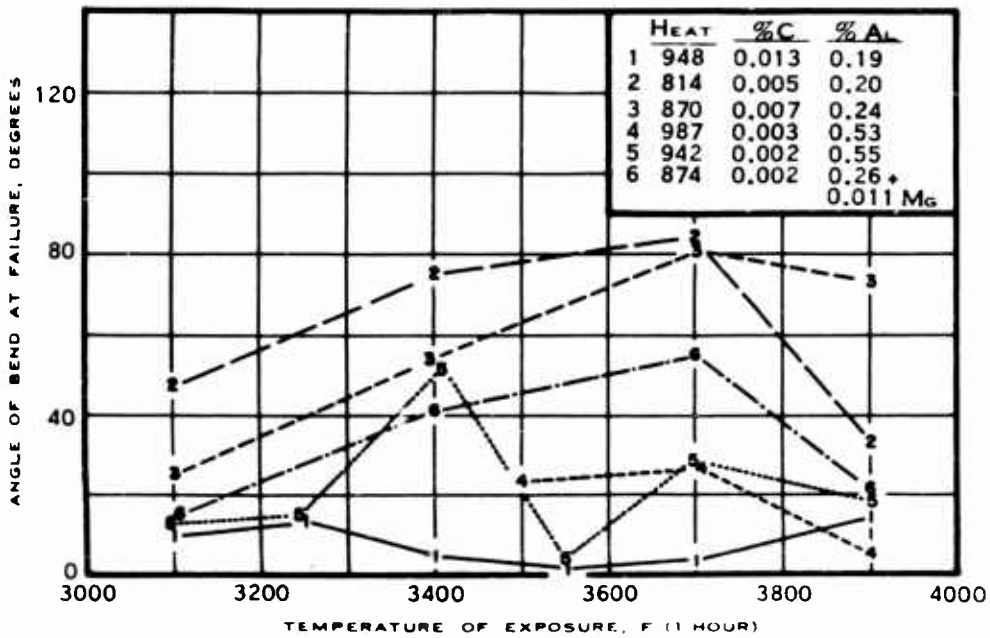
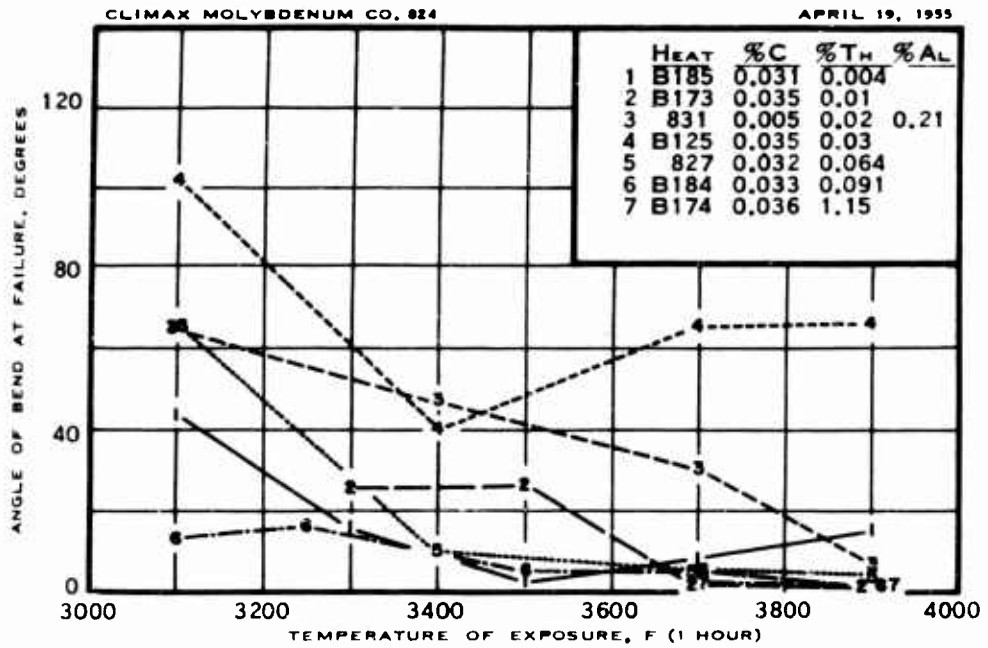


FIGURE 189 – BEND DUCTILITY OF INDICATED MOLYBDENUM AND MOLYBDENUM – ALUMINUM ALLOYS AFTER EXPOSURE FOR ONE HOUR AT INDICATED TEMPERATURES



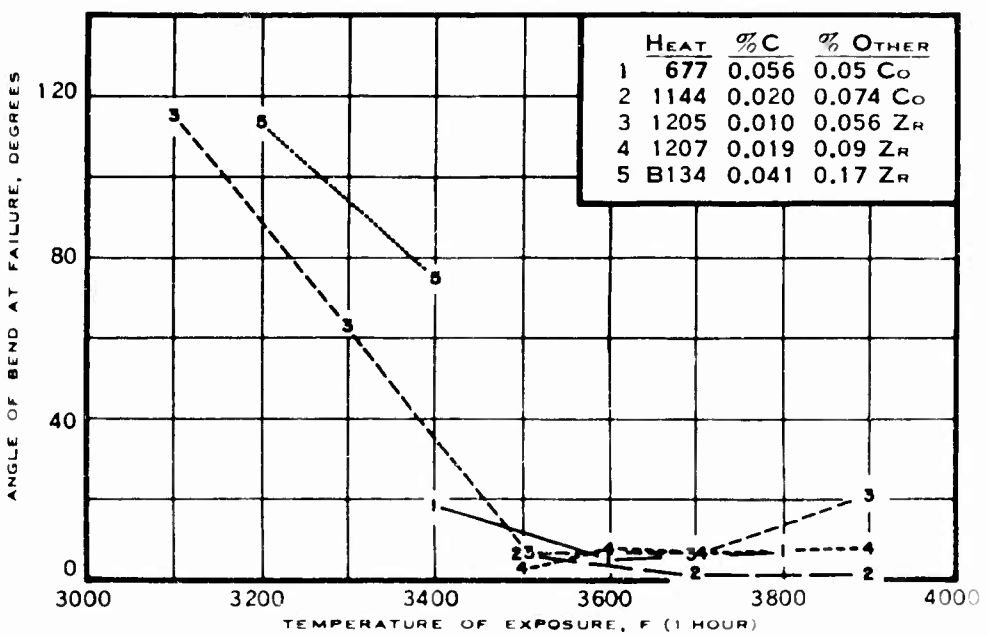
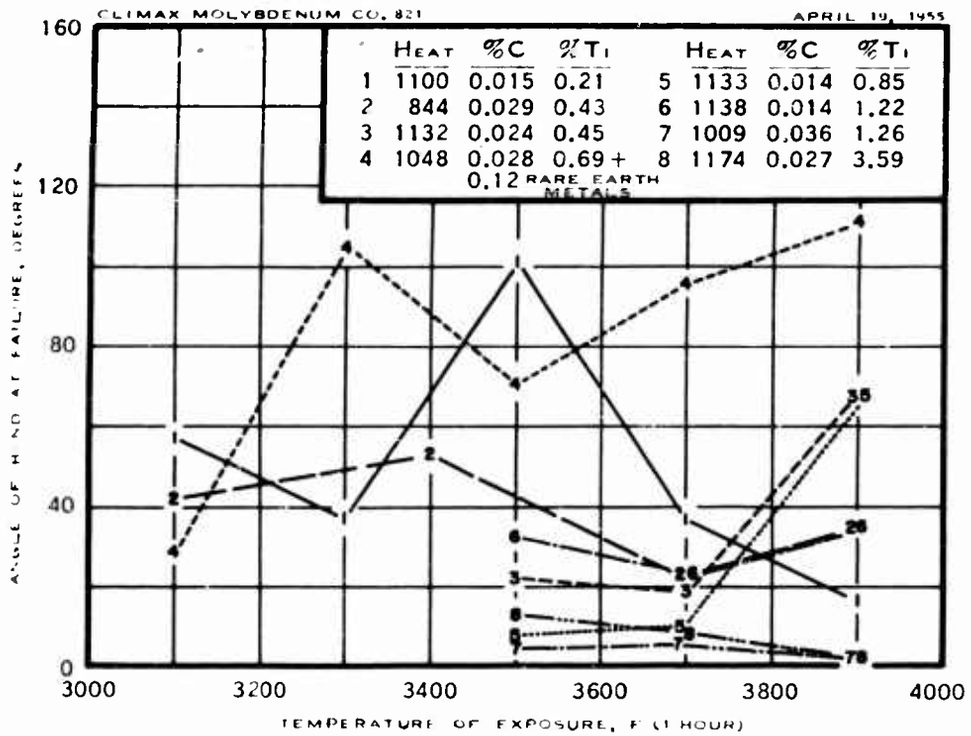


FIGURE 190 — BEND DUCTILITY OF INDICATED MOLYBDENUM - THORIUM, MOLYBDENUM - COBALT, AND MOLYBDENUM - ZIRCONIUM ALLOYS AFTER EXPOSURE OF ONE HOUR AT INDICATED TEMPERATURES



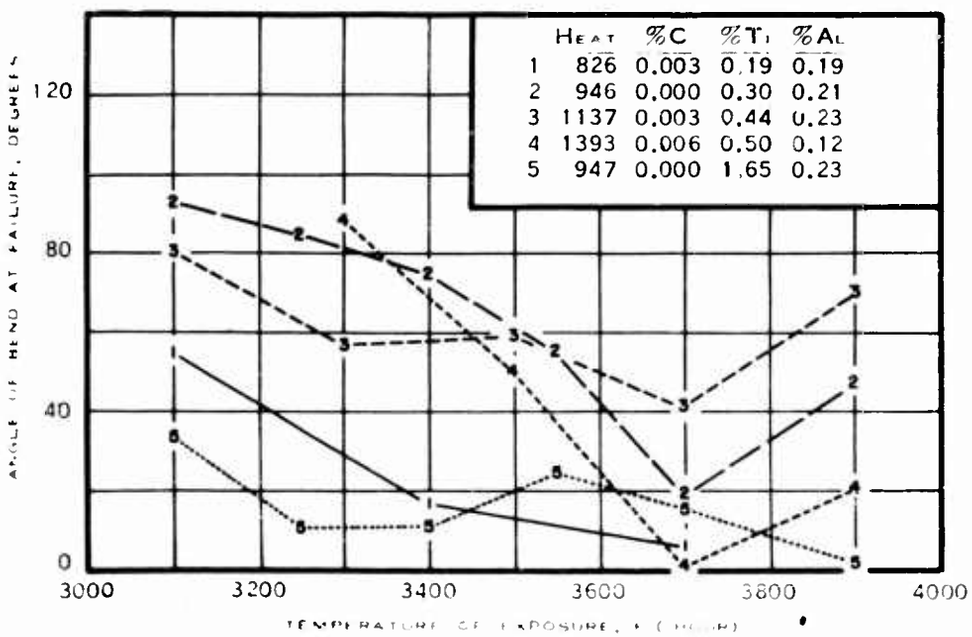
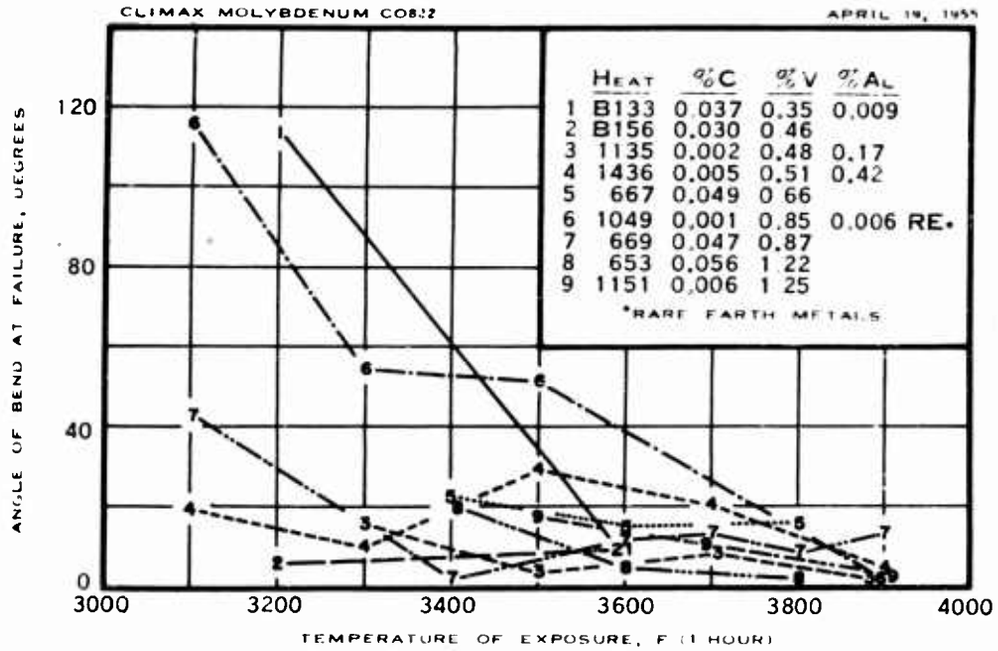


FIGURE 191 — BEND DUCTILITY OF INDICATED MOLYBDENUM TITANIUM ALLOYS



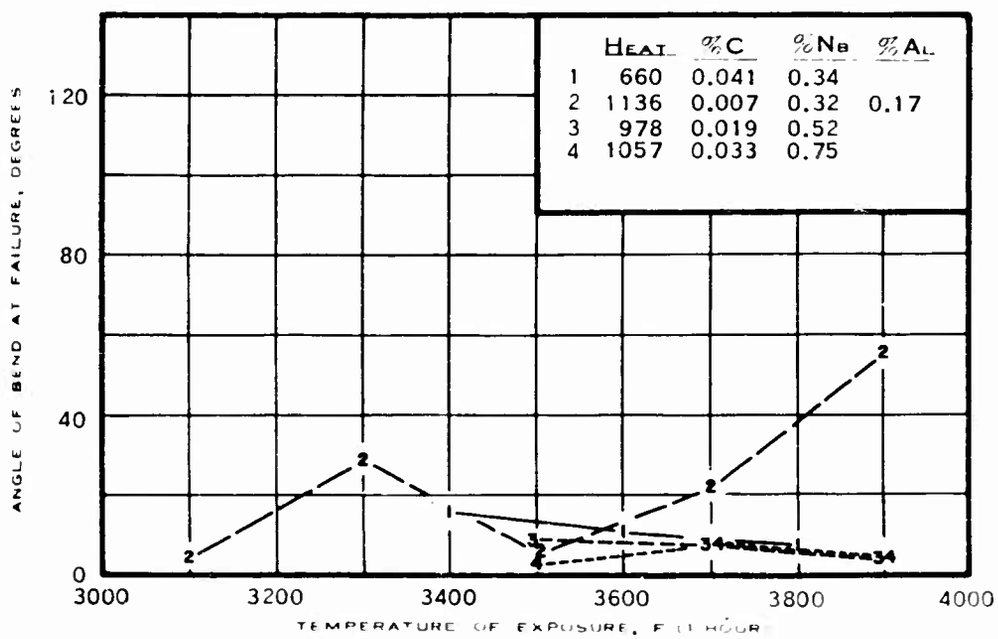
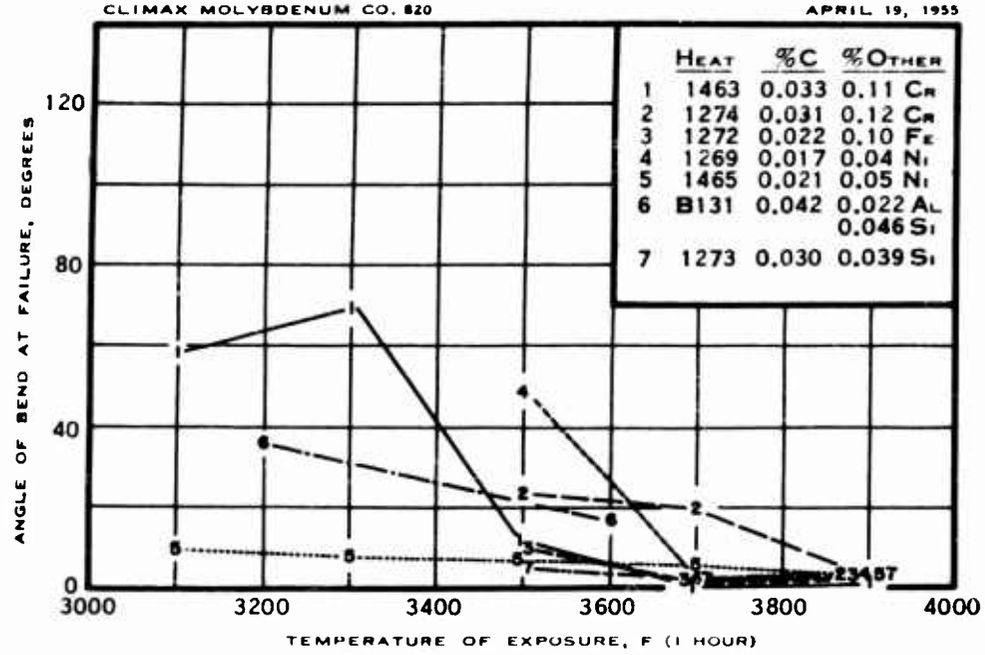


FIGURE 192 - BEND DUCTILITY OF INDICATED MOLYBDENUM VANADIUM AND MOLYBDENUM NIOBIUM ALLOYS AFTER EXPOSURE FOR ONE HOUR AT INDICATED TEMPERATURES



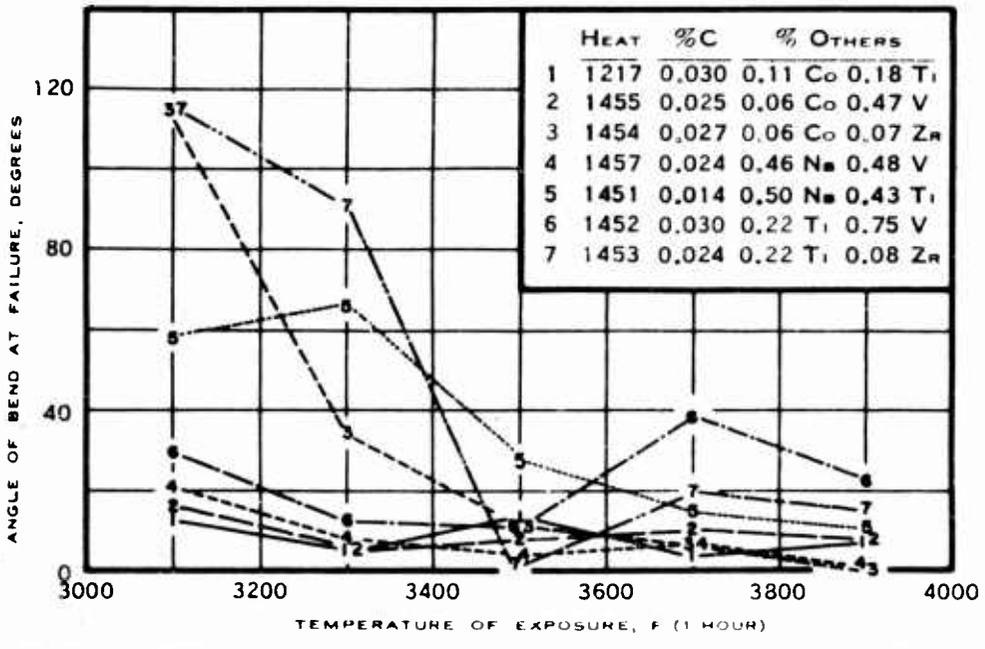


FIGURE 193 – BEND DUCTILITY OF INDICATED BINARY AND TERNARY MOLYBDENUM-BASE ALLOYS AFTER EXPOSURE FOR ONE HOUR AT INDICATED TEMPERATURES

(A) 3500 F, 1 HR IN PURIFIED ARGON (M4851)

(B) 3700 F, 1 HR IN PURIFIED ARGON (M4852)

FIGURE 194 — AREA NEAR SURFACE OF BEND TEST SPECIMEN
HEAT 936, 5 8" ROUND, X2000

COATINGS FOR PROTECTION OF MOLYBDENUM AGAINST OXIDATION

Oxidation Rates

Perhaps the most serious deterrent to the widespread use of molybdenum for service requiring load-carrying ability at elevated temperatures is its rapid oxidation. Like most metals, molybdenum develops an oxide coating under the proper conditions of temperature and oxygen concentration. Unlike most oxidation-resistant metals, however, the higher oxide of molybdenum, MoO_3, melts and vaporizes at temperatures above 1463 F. Thus, the oxidation reaction continues as long as a supply of oxygen (and molybdenum) is maintained.

Some measurements of the oxidation rates of molybdenum and its alloys have been made by subjecting cylindrical samples, 7/8" in diameter by 1/2" long, to flowing air (approximately one centimeter per second) at 1750 F. The samples were first degreased and weighed on an analytical balance and then exposed to the oxidizing atmosphere for periods totaling 1/2, 1, and 2 hours. The specimens were removed after each exposure period, cleaned mechanically, and reweighed. Oxidation rates calculated on the basis of loss in weight per unit area of surface are summarized in Figure 195.

Oxidation rates between 0.58 and 0.92 grams per square centimeter per hour were observed for the materials studied. Oxidation rates for Armco iron and SAE 1045 steel determined under essentially similar conditions have been reported as 0.070 and 0.049 grams per square centimeter per hour, respectively.* The contrast is even more striking in light of recent unreported data obtained at this laboratory, in which the oxidation rate of unalloyed molybdenum at 1750 F was found to be in the neighborhood of 1.50 grams per square centimeter per hour at air velocities of 15 centimeters per second and above. These data indicate that at an air velocity of one centimeter per second, such as was used in the work reported here, insufficient oxygen was provided to react with all of the available molybdenum.

Considering the data presented in Figure 195, niobium, vanadium, and zirconium exercised only slight influence on the rate of oxidation of molybdenum within the range of compositions studied. Titanium produced a measurable increase in oxidation. Aluminum lowered the rate of oxidation, but the effect was most pronounced between 0% and 0.17% aluminum. It will be noted that the pronounced effect of titanium on oxidation rate was also at the low end of the composition range. Inasmuch as aluminum and titanium contents of this low magnitude are considered primarily as deoxidizing agents, and inasmuch as the unalloyed molybdenum deoxidized with rare earth metals was markedly superior to carbon-deoxidized molybdenum in oxidation resistance, Figure 195, it is postulated that some relationship exists between deoxidation during melting and oxidation rate.

Cobalt additions enhanced the resistance of molybdenum to oxidation. Were it not for the limiting effects of cobalt additions on workability, it is possible that significant reductions in oxidation rate could be realized within the molybdenum-cobalt system.

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* C. A. Siebert. The effect of carbon content on the rate of oxidation of steel in air at high temperatures. Transactions, American Society for Metals, vol 27 (1939), 752-757

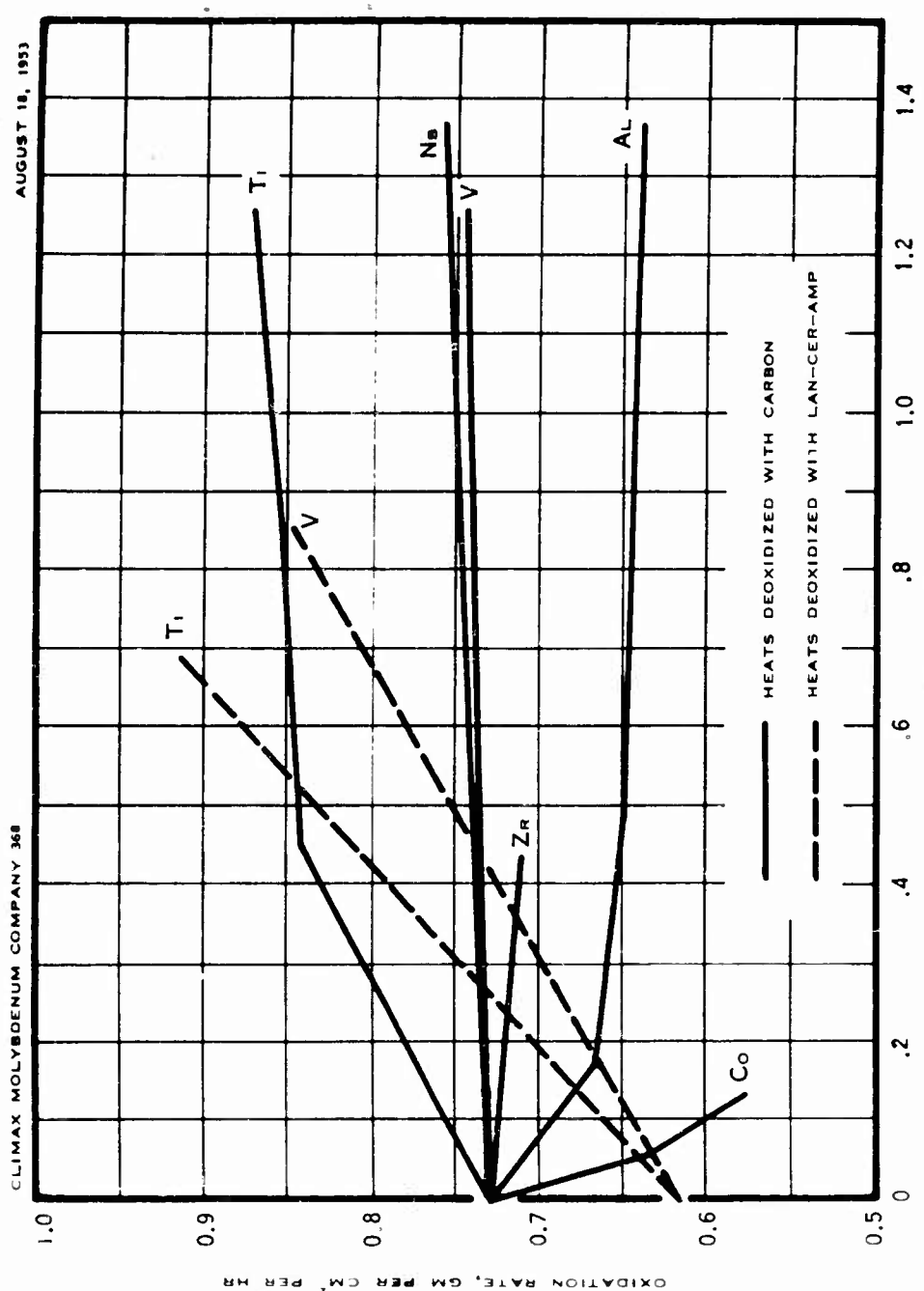


FIGURE 195 — RATES OF OXIDATION OF SOME MOLYBDENUM-BASE ALLOYS AS A FUNCTION OF ALLOY CONTENT

OXIDATION TESTS IN FLOWING AIR AT 1750 F

Unalloyed molybdenum deoxidized with rare earth metals oxidized at a somewhat slower rate than molybdenum deoxidized with carbon; titanium- and vanadium-containing alloys deoxidized with rare earth metals, however, oxidized at slightly faster rates than the same alloys deoxidized with carbon only.

Protective Coatings

The problem of protecting molybdenum from oxidation at high temperatures has received, deservedly so, considerable attention, both at this and at other laboratories. It was not considered in the best interest of all concerned to duplicate the work of other investigators in this field; rather, it was desired to investigate certain facets of the problem for which exiguous results were available. Thus, the major portion of the effort here was directed toward coatings of molybdenum from liquid cementation baths.

The process involved immersion of molybdenum panels in a molten bath consisting of the coating metal mixed with a second metal of low solubility for molybdenum. The second desirable characteristic of the cementation bath (in addition to low mutual solubility of the carrier metal and molybdenum) was that its liquidus temperature be sufficiently low that molybdenum would not lose its ductility during immersion. To meet the solubility requirement, copper and tin were used as the carrier metals. Chromium, nickel, and silicon were investigated as the coating materials.

The procedure involved preparation of a mechanical mixture of the coating and carrier metals of the desired proportions and heating the mixture in a molybdenum crucible under an atmosphere of either tank hydrogen or purified argon. The samples for coating were cut from 0.060" unalloyed molybdenum sheet. The edges of the test panels were rounded by filing prior to immersion in the cementation bath. Coatings were evaluated either by oxidation test or by metallographic examination. The oxidation test was conducted as follows: The test panel was placed on two small refractory supports in a furnace at 1800 F. The refractory supports were in contact with the coating over an area about 1/16" wide by 1/2" long. Air moving at a velocity of about 25 feet per minute was passed over the surface of the sample to maintain an oxidizing atmosphere. For the initial eight hours of test, the panel was observed closely for evidence of failure of the coating (emission of molybdic oxide vapor). If no evidence of oxidation was noted during this period, the sample was removed from the furnace once every 24 hours thereafter, cooled to room temperature, and inspected visually for failure areas.

As can be seen from the data reported, the results of the oxidation test on duplicate panels prepared under the same conditions of immersion were somewhat inconsistent. In some cases, premature failure was traced to sharp edges or corners of the panel, where, owing to the surface tension of the bath, there presumably had been less build-up of the coating than on flat surfaces or on curved surfaces of larger radius.

The results of oxidation tests are presented in Table 30. Panels immersed in a copper, 1% chromium bath failed immediately in the oxidation test. Similarly, immersion in a copper bath containing 5% nickel for 22 hours at 2600 F under hydrogen afforded no protection for molybdenum under the conditions of the oxidation test.

None of the panels prepared by immersion in the copper-silicon bath under hydrogen atmosphere exhibited noteworthy resistance to oxidation. The two panels prepared under an argon atmosphere, on the other hand, showed creditable resistance in these experiments, the better specimen surviving for 325 hours in the oxidation test.

An investigation of the effect of preparation of the surface of panels coated from a 90% copper, 10% chromium bath were inconclusive in that all of the samples offered only token resistance to oxidation.

Metallographic examination of coated panels not subjected to the oxidation test revealed that a coating 0.0025" thick had been built up by immersion for 20 hours in the copper-silicon bath at 2600 F. The thickness of the coating was not a linear function of immersion time, however; the rate of build-up of the coating decreased with increasing time. There was a significant difference in the metallographic appearance of the panels coated in hydrogen and in argon. Those prepared in hydrogen contained a narrow zone of small dots, possibly molybdenum oxide, between the coating and the base metal; while those prepared in argon contained a semi-continuous layer tentatively identified as copper, about 0.003" to 0.005" thick, between the coating and the base metal. The role played by this intermediate layer in the superior oxidation resistance of the panels prepared under argon is problematical.

A layer of chromium approximately 0.0005" thick was developed by immersion for 24 hours in the 10% chromium bath. A representative area of the sample coated under these conditions after electrolytic surface polishing is shown in Figure 196. Figure 197 is a high-magnification photomicrograph illustrating the chromium-molybdenum interface of a sample coated under the same conditions after a copper pre-coat. The copper underlayer presumably dissolved in the bath before a significant build-up of chromium occurred.

It will be noted that the molybdenum grains adjacent to the molybdenum-chromium interface in Figures 196 and 197 show a varied resistance to attack by the etchant. This situation has been interpreted as indicative of various degrees of solution of chromium in the molybdenum, with the lighter etching areas representing the higher concentrations of chromium. In general, the light etching areas follow the contours of grain boundaries, indicating a higher rate of diffusion through grain boundaries than through the grains.

The desirability of obtaining higher concentrations of chromium in the cementation bath led to the choice of tin as the carrier. A study was made of coatings produced from a tin-chromium bath in which chromium concentration, temperature, time, and atmosphere were varied. Surface preparation of all samples coated in the tin-chromium bath was accomplished by cleaning in the molten caustic bath.

Table 30 itemizes experiments with the tin-chromium bath in which coated samples were subjected to oxidation testing. Numerous additional samples were evaluated metallographically.

Experiments were carried out either under tank hydrogen or purified argon. Generally, the coatings prepared under hydrogen, Figure 198, contained specks as well as an unidentified phase near the outer surface. Coatings prepared under purified argon were relatively free of oxide, as illustrated in Figure 199. From the standpoint of oxidation resistance, none of the coatings prepared in hydrogen withstood oxidation testing for more than half an hour, whereas the best sample prepared in purified argon did not fail after 510 hours in test.

A phenomenon occurred during operations in hydrogen which hampered successful evaluation of the process. After a short period of time at temperature, dendrites were observed growing from the top of the molybdenum crucible that contained the bath. The length of the dendrites increased with time and seemed to be accompanied by an increasing viscosity of the bath, indicating, possibly, a concurrent depletion of the tin content of the bath. To verify this supposition, a sample of the dendritic growth was submitted for x-ray diffraction analysis. Results of the analysis showed the material to be predominantly tin, with a small amount of Cr_2O_3.

Experiments in which the chromium content of the cementation bath was varied indicated coating thickness to be a direct function of chromium concentration. The factor of bath fluidity, however, limited the practicable chromium content to something less than 40% to 50%. Fluidity of the bath was also limited, of course, by the bath temperature as well as by chemical changes occurring in the bath while at temperature.

A small percentage of calcium metal turnings was added to the tin-chromium bath in several experiments in an effort to insure freedom from oxidation of the bath and of the molybdenum test panels. The calcium addition appeared to enhance wetting of the panel by the molten bath. It had no measurable effect, however, on the coating itself as evaluated by oxidation resistance; although, admittedly, experiments directed solely toward this end were not performed. An x-ray diffraction pattern of a coating prepared from a bath to which calcium had been added indicated the presence of calcium oxide on the extreme surface. Analysis of the same specimen after removal of the extreme surface by means of a wire brush did not reveal calcium or any of its compounds to be present. It is thought that calcium oxide present in the slag above the cementation bath mechanically adhered to the sample when it was withdrawn from the bath.

Bath temperature was varied from 2500 to 2800 F in one series of experiments designed to investigate this variable. Results of these experiments indicated that temperature was not critical within the limits investigated as long as sufficient fluidity of the bath was provided. A bath containing 20% chromium was found to have insufficient fluidity at 2500 F for good sample coverage, while the same situation existed for a 40% chromium bath at 2600 F.

Coating thickness was a function of time, but the relationship was by no means linear. The rate of increase of the coating thickness decreased with increasing time. This is as would be expected, inasmuch as the coating thickness would be governed by the applicable diffusion rate.

It is indeed encouraging that two specimens withstood the conditions of the oxidation test for periods of 325 and 510 hours. These results would appear to lend credence to the feasibility of applying oxidation-resistant coatings to molybdenum by a liquid cementation process. Difficulty in obtaining satisfactory protection for panels treated in somewhat similar cycles is interpreted only as a measure of the extremely critical nature of the variables of the process.

TABLE 30

RESISTANCE TO OXIDATION AT 1800 F OF MOLYBDENUM COATED BY LIQUID CEMENTATION

Bath Composition, %	Bath Temp, F	Atmosphere	Immersion Time	Time to Failure, hr
99Cu-1Cr	2600	hydrogen	17 hr	0
"	"	"	20 hr	0
95Cu-5Cr	2600	argon	24 hr	1/2
90Cu-10Cr	2600	argon	24 hr	1[a]
"	"	"	24 hr	1[a]
"	"	"	24 hr	1[b]
"	"	"	24 hr	3[b]
90Cu-10Si	2600	hydrogen	4 hr	1/2
"	"	"	5 hr	3
"	"	"	7 hr	2
"	"	"	20 hr	3
"	"	argon	20 hr	30
"	"	"	20 hr	325
95Cu-5Ni	2600	hydrogen	22 hr	0
78Sn-18Cr-4Ca	2800	argon	10 min	10
"	"	"	1 hr	5[c]
80Sn-20Cr	2800	hydrogen	10 sec	1/2
"	"	"	10 min	1/2
68Sn-28Cr-4Ca	2700	argon	4 hr	510[d]
"	"	"	4 hr	250[e]
"	2800	"	5 hr	5[f]
67Sn-28Cr-5Ca	2800	hydrogen	1 min	1/2
70Sn-30Cr	2800	hydrogen	1 min	1/2
"	"	"	20 min	1/2
"	"	"	40 min	1/2
48Sn-48Cr-5Ca	2800	argon	15 min	20

[a] test panels electrolytically polished prior to immersion, all other panels prepared by hot caustic dip unless otherwise noted

[b] sample sand blasted, then given copper coating prior to immersion

[c] failure traced to wire used to hold sample in cementation bath

[d] sample removed after 3 hours in the oxidation test chamber and hammered lightly between flat dies to remove slag, returned to test, removed after 510 hours without failure

[e] sample removed, surface brushed with wire brush; failed immediately on return to test

[f] sample not failed, removed from test for metallographic examination, vid. Figure 199



FIGURE 196 — MOLYBDENUM PANEL IMMERSED IN 90% COPPER, 10% CHROMIUM CEMENTATION BATH AT 2600 F FOR 24 HOURS UNDER ARGON ATMOSPHERE. POLISH-ETCH-BUFF. ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE. X500 (M3968)



FIGURE 197 — MOLYBDENUM PANEL SPRAYED WITH COPPER, IMMERSED IN 90% COPPER, 10% CHROMIUM CEMENTATION BATH UNDER ARGON ATMOSPHERE FOR 24 HOURS AT 2600 F. POLISH-ETCH-BUFF. X2000 (M4246)



FIGURE 196 — MOLYBDENUM PANEL IMMERSED IN 90% COPPER, 10% CHROMIUM CEMENTATION BATH AT 2600 F FOR 24 HOURS UNDER ARGON ATMOSPHERE. POLISH-ETCH-BUFF. ETCHED IN SODIUM HYDROXIDE + POTASSIUM FERRICYANIDE. X500 (M3968)



FIGURE 197 — MOLYBDENUM PANEL SPRAYED WITH COPPER, IMMERSED IN 90% COPPER, 10% CHROMIUM CEMENTATION BATH UNDER ARGON ATMOSPHERE FOR 24 HOURS AT 2600 F. POLISH-ETCH-BUFF. X2000 (M4246)



FIGURE 198 — MOLYBDENUM PANEL IMMERSED IN 80% TIN, 20% CHROMIUM CEMENTATION BATH AT 2800 F FOR 1/2 MINUTE IN HYDROGEN ATMOSPHERE. POLISH-ETCH-BUFF. X2000 (M4252)



FIGURE 199 — MOLYBDENUM PANEL IMMERSED IN 68% TIN, 28% CHROMIUM, 4% CALCIUM CEMENTATION BATH IN PURIFIED ARGON ATMOSPHERE AT 2800 F FOR 5 HOURS. POLISH-ETCH BUFF. X2000 (M4248)

ACKNOWLEDGMENT

To the authors has fallen the task of compiling the results of experimental work in which they have been engaged almost continuously for the last six years, and in which at one time or another the personnel of the entire laboratory has taken part. The authors particularly wish to thank Alvin J. Herzig, president, and George A. Timmons, vice president, for their guidance and advice. Many of the data were determined when the project was under the supervision of F. P. Bens, J. L. Ham, and H. E. Hostetter, each of whom was responsible in turn for the progress made in the earlier years of the contract. We are indebted to R. H. Maurer and H. E. Trapp for devising methods of chemical analysis of specific alloys and for making the numerous analyses, and to W. C. Coons and G. C. Woodside for the extensive metallographic examinations. The experimental ingots were produced under the direction of E. K. Leavenworth and R. G. Yingling. The mechanical and physical tests were ably performed by many of the laboratory engineers, among whom we thank especially J. P. Binkelman, H. H. Blackett, R. E. Herfert, and C. S. Torgerson. Lastly, we thank our patient secretarial staff for preparation of the manuscript.

* * * * * * *

This report covers work conducted at the Detroit Research Laboratory of Climax Molybdenum Company. The developments disclosed have been or will be embodied in patent applications assigned to the Climax Molybdenum Company.

APPENDIX A

PROCEDURES FOR CHEMICAL ANALYSIS OF MOLYBDENUM-BASE ALLOYS

by Robert H. Maurer

DETERMINATION OF ALUMINUM IN MOLYBDENUM-BASE ALLOYS

The procedure recommended is suitable for the determination of aluminum in binary alloys of molybdenum and aluminum. If other metals are present which are insoluble in ammonium hydroxide under the given conditions, the final residue obtained will be a mixture of these oxides. The method is valuable even for mixtures of metals in that it serves to separate small quantities of these alloying metals from large amounts of molybdenum. When the removal of molybdenum is complete, further separations can then be more readily accomplished with the smaller amounts. Methods for separation of mixtures of these oxides will depend upon the particular combination present.

A standard solution of aluminum was prepared from the pure metal. Synthetic samples were prepared by adding known amounts of standard aluminum solution to a solution of pure molybdenum metal in hydrochloric and nitric acids. Complete recovery of the added aluminum was obtained by the following procedure:

Weigh a sample of such size as to contain not more than 0.05 g aluminum. Dissolve the chips with a mixture of concentrated HCl and HNO_3 containing 10 ml HCl and 3 ml HNO_3 for each gram of sample. Heat gently until the sample is decomposed. Add 100 ml H_2O, a little ashless filter paper pulp and 5 or 6 drops of phenol red indicator (0.1 g dissolved in 100 ml of 25% ethyl alcohol). Add concentrated NH_4OH from a burette until the first permanent red color of the indicator appears, then add 0.7 ml excess NH_4OH. Sufficient NH_4OH must be added to keep the molybdenum in solution, but a large excess increases the solubility of $Al(OH)_3$. The recommended excess has been found satisfactory. Heat the solution to boiling and boil one minute. Remove from the hot plate, let settle until the solution is cool, or better, overnight. Filter through No. 42 Whatman paper or its equivalent, rinsing the beaker several times with cold 2% NH_4Cl, pouring the rinsings through the filter paper. Wash the precipitate in the filter paper four times with cold 2% NH_4Cl solution, then carefully examine the filtrate. Occasionally the precipitate becomes peptized and runs through the filter. If any cloudiness is observed in the filtrate, it must be allowed to settle overnight and refiltered through a tight paper. The clear filtrate is then discarded. The tendency of the precipitate to form colloidal dispersions has not been observed in subsequent precipitations. Apparently the presence of the large amount of molybdenum favors the peptization of the hydroxide precipitate.

Place the original beaker under the funnel and, using a wash bottle, wash the precipitate thoroughly with hot HCl (1-1). At least three washings are usually required to dissolve all of the precipitate on the paper. Wash the paper twice with hot water and then once with cold 3% NH_4OH. Reserve the filter paper. Dilute the filtrate and washings to 100 ml, add ashless filter paper pulp and phenol red indicator and add NH_4OH until neutral, then add 0.7 ml excess. Heat to boiling and boil for one minute. Remove from the hot plate and let settle, then filter through the reserved paper. Wash four times with hot 2% NH_4Cl. Again dissolve the precipitate with hot HCl (1-1), catching the filtrate in the original beaker. Wash the paper twice with hot water.

By this time, the repeated filtrations and washings have usually rendered the filter paper unsuitable for the third filtration. Place the paper in a weighed platinum crucible and set it aside. Dilute the filtrate to 100 ml and make a third precipitation with NH_4OH as before. Filter through a fresh paper, scrub the beaker with a policeman and pour the rinsings through the filter paper. Wash four or five times with hot 2% NH_4Cl. Transfer the paper and precipitate to the crucible containing the first paper. Dry and ignite the paper at a low temperature until the paper is burned, then ignite for 30 minutes at 1800 F. Cool, add 7-8 drops H_2SO_4 (1-1) and 5 ml HF. Carefully evaporate the solution in the crucible on the hot plate until dry. Very carefully increase the temperature of the crucible on an asbestos pad over a burner until no further fumes are given off. Heat in the free flame for a few minutes, then ignite in the muffle furnace for 30 minutes at 1800 F. Cool and weigh as Al_2O_3.

A blank must be carried through the entire procedure, using a weight of pure Mo equal to the weight of sample used. The weight of the blank obtained is deducted from the weight of oxide obtained in the sample.

Factor: $Al_2O_3 \longrightarrow Al = 0.5292$

DETERMINATION OF BERYLLIUM IN MOLYBDENUM-BASE ALLOYS

Experimental: Preparation of a standard beryllium solution

The only beryllium compound available was a sample of anhydrous BeO obtained from the Eimer and Amend Division of the Fisher Scientific Company. After several unsuccessful attempts with various reagents, it was found that this material dissolves readily in HF. H_2SO_4 is added to this solution and the solution evaporated to SO_3 fumes. The beryllium is now in solution in the concentrated sulphuric acid.

Weigh 1.1095 g of BeO in a tared platinum dish. Add 25 ml HF and warm till solution is complete. Cool to room temperature and carefully add 20 ml H_2SO_4. A precipitate forms at this point which redissolves after the solution is evaporated to SO_3 fumes. Cool to room temperature and transfer the sulphuric acid solution to a 500 ml volumetric flask containing 200 ml H_2O. Thoroughly rinse the platinum dish and add the rinsings to the flask. Cool the flask to room temperature and dilute to 500 ml with water. Twenty-five milliliters of this solution should contain 0.0200 g Be.

Transfer three 25 ml portions of this solution to 400 ml beakers and add 100 ml H_2O. Add some filter paper pulp and ten drops of phenol red indicator. Now add concentrated NH_4OH till the first permanent red of the indicator appears, then add 0.7 ml excess. Heat the solution to boiling, remove from the hot plate and let settle. Filter through No. 42 Whatman filter paper and wash four or five times with hot 2% NH_4NO_3. Dry and ignite the paper and precipitate in a weighed platinum crucible till all carbon is gone. Finally,

ignite at 980 C for 30 minutes. Cool and weigh. The average of the three closely agreeing determinations was 0.02015 g Be. This is well within the limits of experimental error, and it is assumed that 25 ml of the standard solution contain 0.0200 g of beryllium.

The accuracy of the procedure given below was checked by adding 25 ml portions of the standard beryllium solution to two-gram samples of pure molybdenum chips. A blank containing two grams of molybdenum but no beryllium was carried through the entire procedure and the blank deducted from the final values obtained. The average of three closely agreeing determinations was 0.0196 g Be, or a negative error of 0.4 mg. This was considered acceptable.

Procedure: The size of sample used depends somewhat on the concentration present, but for most purposes, a two-gram sample is adequate and convenient to handle. Dissolve the sample in a 400 ml beaker with 30 ml concentrated HCl and 10 ml concentrated HNO_3. Heat gently until decomposition is complete and the brown color of nitrogen oxides has been expelled from the solution. Add 50 ml H_2O and a little ashless filter paper pulp. Add eight to ten drops of phenol red indicator solution (0.1 g dissolved in 100 ml of 25% ethyl alcohol). Now add concentrated NH_4OH until the first permanent red color of the indicator appears, then add 0.7 ml excess. Heat until the solution just begins to boil vigorously. Remove from the hot plate, let settle a few minutes, then filter through No. 42 Whatman filter paper or its equivalent. Rinse the beaker several times with hot 2% NH_4NO_3 solution, pouring the rinsings through the filter paper. Wash the paper four times with hot 2% NH_4NO_3 and discard the filtrate and washings. Place the original beaker under the funnel and, using a wash bottle, wash the paper and precipitate thoroughly with hot HCl (1-1). At least three washings are necessary to dissolve all of the precipitate on the paper. Wash the paper twice with hot water and finally, once with cold 3% NH_4OH. Reserve the filter paper. Adjust the volume of the filtrate and washings to approximately 100 ml, add a little ashless filter paper pulp, and repeat the precipitation with NH_4OH exactly as before. Filter through the same paper and wash with hot 2% NH_4NO_3 solution.

Transfer the paper and precipitate to a platinum crucible, dry and ignite until carbon is burned, and finally, ignite at 980 C. Cool the crucible to room temperature, add 2 ml H_2SO_4 (concentrated) and 5 ml HF. Evaporate until fumes of SO_3 are liberated. This treatment removes any SiO_2 which may be present at this stage of the analysis. Any SiO_2 which may be introduced from reagents in the last steps of the analysis will be compensated for by the blank. Transfer the H_2SO_4 solution in the crucible to a 250 ml beaker, dilute to 100 ml with 10% H_2SO_4 and add a little ashless filter paper pulp. Add phenol red indicator and again precipitate with NH_4OH exactly as previously described. This precipitation removes the last traces of molybdenum. Filter and wash the precipitate as before, then dry and ignite the residue in a weighed platinum crucible until carbon is decomposed. Finally, ignite at 980 C. Cool and weigh as BeO. Carry a blank through the entire procedure and deduct this blank from the weight of BeO obtained.

Note: The removal of SiO_2 before the removal of the last traces of molybdenum is recommended because of the difficulty encountered in treating the BeO precipitate with HF and H_2SO_4, when a minimum of H_2SO_4 is used. In some of our

earlier work, 0.0555 g BeO were treated with HF and two drops of H_2SO_4 (1-1). This is insufficient H_2SO_4 to convert all the Be to sulfate. Beryllium fluoride sublimes at elevated temperatures. In this experiment, white vapors were liberated on ignition at 980 C, some of which condensed on the sides of the crucible. Low results were obtained and the crucibles were cleaned only with difficulty. Boiling several hours in concentrated H_2SO_4 proved to be the most satisfactory method for cleansing the crucibles.

DETERMINATION OF BORON IN MOLYBDENUM-BASE ALLOYS

Tests with synthetic samples showed that the distillation-titration method used for the determination of boron in steel gave complete recovery of boron in molybdenum-base alloys when slight modifications were made in the method. Synthetic samples were prepared by adding a known amount of boron as boric acid to the flask containing the molybdenum metal.

The method consists of obtaining the boron in a solution containing very little HCl and not more than 25 ml H_2O. The boron is then converted to the ester, $B(OCH_3)_3$ with CH_3OH, which is then distilled. The ester is saponified, the alcohol expelled, and then titrated so that H_3BO_3 is the only acid present. The H_3BO_3 is titrated under conditions which give the compound NaH_2BO_3.

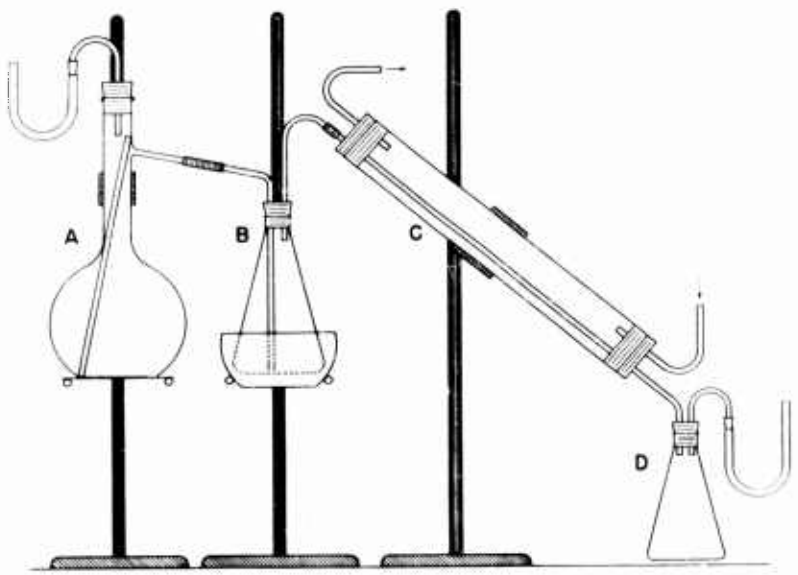
Solutions required:

Hydrochloric Acid - Approximately 0.1 N.

Sodium Hydroxide - 0.1 N, free from CO_2 and standardized as follows: C.P. boric acid is fused in platinum and when cool, 1.741 g is dissolved in water and diluted to 500 ml. This solution is exactly 0.1 N (1 ml represents 0.00108 g B). The 0.1 N NaOH solution is standardized against this by titrating as described in the method.

Phenolphthalein - 1% solution in 50% neutral C_2H_5OH.
Paranitrophenol - 1% solution in 75% neutral C_2H_5OH.
Methyl Alcohol - Anhydrous, C.P. and free from organic acids.
Calcium Chloride - Granular, anhydrous, C.P.
Mannite - Ordinary reagent.

Procedure: Transfer 3 g of drillings to a 300 ml Erlenmeyer flask, add 25 ml concentrated HCl and fit the flask with a reflux condenser. Through the reflux condenser, add 1 ml concentrated HNO_3 and warm gently until action stops. Continue the addition of HNO_3 in 1 ml portions until the sample is completely decomposed. Finally, boil the solution for two to three minutes. Cool to room temperature, rinse the condenser into the flask with a little water and remove the condenser. Use this flask as "B" (see accompanying figure). Add 1 g anhydrous $CaCl_2$ for each milliliter of solution. Connect the flask with the rest of the apparatus and begin distillation of alcohol from "A". When about 25 ml CH_3OH have condensed in "B", heat the water bath so that no further condensation of alcohol occurs.



DISTILLING APPARATUS FOR BORON (P738)

A, 500 ml flask for methyl alcohol, having a U-tube containing a little mercury as a safety trap, and a capillary "boiling tube" 3 mm in bore, the bore closed at 1 cm from lower end. B, flask of 250 ml capacity, supported in a casserole of water but not touching bottom. The outlet tube should be at least 15 cm high and of wide bore. The end inside of flask should be jagged to allow condensed liquid to drop back instead of jumping up the tube. C, glass condenser, 40 cm long. D, receiving flask of 300 ml capacity. The U-tube attached contains a little water to prevent the escape of any uncondensed methyl borate. E (not shown), a second condenser exactly like C, connected on one side to a flask like B, which has a one-hole stopper and rests in a water bath. A "boiling tube" is in this flask. On the other side is a receiver like D, but without the U-trap. This apparatus is used for distilling off the alcohol after the preliminary neutralization. F (not shown), filter pump. At the end of the side tube is an elbow connected to a two-hole stopper of a size to fit a 300 ml Erlenmeyer flask.

Collect 200 ml of distillate in receiver "D", shut off heat and disconnect apparatus. Add the contents of the trap to the receiver. Add 1 ml phenolphthalein solution and add NaOH solution (approximately normal) until the alcoholic solution is red. Transfer this solution to flask in the second distillation apparatus. Put in a "boiling tube" and distill until the liquid in the flask no longer boils. Transfer to a casserole and heat until all remaining alcohol has evaporated. Return the solution to the flask, add one drop of paranitrophenol and add HCl (1-1) drop by drop until acid (colorless) to paranitrophenol. A white precipitate is frequently found in the solution at this point. We have made no effort to identify this precipitate but from the recovery of boron obtained from known samples, the precipitate is not a compound of boron. Since this insoluble matter interferes with observing the end point in the neutralization of the excess acid, it should be removed by filtration through a small No. 40 Whatman filter paper. Wash the paper and residue several times with hot water. Catch the filtrate and washings in a 300 ml Erlenmeyer flask. Put in the boiling tube, heat on the steam bath, connect with a filter pump and distill under reduced pressure until the liquid is nearly cold. Break the vacuum, cool and then neutralize the excess acid with 10 N NaOH until a faint yellow color appears. This end point must be reached exactly. One drop of 10 N HCl should discharge the color and one drop of 10 N NaOH bring it back. At this end point all the HCl is neutralized and all the H_3BO_3 is still present.

Now add 1 g mannite and carefully titrate with standard 10 N NaOH to the phenolphthalein end point. Add another gram of mannite and, if the red color disappears, continue titrating until further addition of mannite does not cause the red color to disappear. Methyl orange may be used in place of paranitrophenol and glycerine instead of mannite, although paranitrophenol and mannite are preferred.

A blank run should be carried through the entire procedure, using a molybdenum metal or molybdenum-base alloy known to contain no boron. Correct the volume of 10 N NaOH required by the sample by the blank and multiply by the boron titer of the solution. One ml 10 N NaOH equals 0.00108 g boron.

DETERMINATION OF CHROMIUM IN MOLYBDENUM-BASE ALLOYS

The recovery of small additions of chromium to molybdenum metal when melted and cast in vacuum was shown by chemical analysis to be very low. Low recoveries may be expected in these alloys because of the high vapor pressure of chromium at the high temperatures involved and the low pressures in which the melting takes place. Some apparently inconsistent results obtained by chemical analysis raised a doubt as to the accuracy of the methods employed in the analysis of these alloys for chromium. After some experimental work, the following deviations from the standard procedure used for the determination of chromium in steel were found to yield accurate results.

It has been customary to add a drop or two of the manganous sulphate solution regularly kept in stock to any samples which contain no manganese. This is oxidized to permanganic acid and serves as an indicator for the complete oxidation of chromium. The stock manganous sulphate used is the regular Reinhardt's solution used for iron titrations and contains phosphoric acid. It was found that any phosphoric acid added to an acid solution of high molybdenum content produces a yellow precipitate of ammonium phosphomolybdate, after ammonium persulphate has been added to oxidize the chromium and manganese. Upon reduction of the chromium with excess ferrous sulphate, a blue color slowly develops in the solution. To prevent the formation of ammonium phosphomolybdate, which is readily reduced to molybdenum blue, no phosphate or phosphoric acid should be added to molybdenum-base alloys. For the addition of manganese to the solution, a 5% solution of manganous sulphate in 5% H_2SO_4 was prepared.

In routine steel analysis, several drops of 0.025 M o-phenanthroline ferrous complex are added to serve as an internal indicator for the titration of the excess ferrous sulphate with permanganate. With molybdenum-base alloys, the indicator end point was not clear and overtitration occurred. However, by omitting the indicator entirely and letting the permanganate serve as its own indicator, the end point was sharp and reproducible.

If the sample contains no tungsten, two-gram samples are dissolved in 25 ml H_2SO_4 (1-1) and 10 ml HNO_3. When solution is complete, evaporate the solution until SO_3 fumes are evolved. Cool, add 100 ml H_2O and warm till salts are in solution. Add one to two drops of the manganous sulphate solution, dilute to 200-250 ml and continue by the regular procedure, including any deviations previously noted.

When the sample contains tungsten, it must be removed. Dissolve two-gram samples in 30 ml HCl and 15 ml HNO_3. Digest till the WO_3 settles out as a bright yellow precipitate. Filter through No. 42 Whatman filter paper, or its equivalent, containing a little ashless paper pulp. Wash with hot 5% HCl and discard the precipitate. Add 25 ml H_2SO_4 (1-1) to the filtrate and evaporate as with the tungsten-free molybdenum-base material.

To check the accuracy of the procedure, a standard chromium solution was prepared from pure $K_2Cr_2O_7$. Dissolve 0.2828 g $K_2Cr_2O_7$ in 100 ml H_2O and add 20 ml HCl. Reduce the chromium with hydrogen peroxide and boil to decompose the excess peroxide. Dilute the solution to 1000 ml in a volumetric flask. One milliliter of this solution equals 0.0001 g Cr.

Two samples of chips were obtained, one being pure molybdenum and the other approximately 95% Mo and 5% W. Three different concentrations of chromium were checked, i.e., 0.05%, 0.15% and 0.30%. The chromium additions were made by adding the required amount of the standard solution to two-gram portions of the two molybdenum-base samples. Each determination was made in duplicate. The samples were then analyzed by the standard method for chromium with the changes listed above. The results are tabulated below:

Sample	% Cr Added	% Cr Recovered
Pure Molybdenum	0.05	0.04
Pure Molybdenum	0.15	0.14
Pure Molybdenum	0.30	0.29
95% Mo - 5% W	0.05	0.042
95% Mo - 5% W	0.15	0.14
95% Mo - 5% W	0.30	0.295

DETERMINATION OF COBALT IN MOLYBDENUM-BASE ALLOYS

The standard methods used for the determination of cobalt in steel are not directly applicable to molybdenum-cobalt alloys. A tentative method was outlined and modified as required by later developments. A discussion of the experimental work follows the detailed procedure. The following procedure was checked by additions of a standard solution of a pure cobalt salt and gave very accurate results.

Procedure: Transfer a two-gram sample to a 400 ml beaker and add 30 ml HCl and 15 ml HNO_3. Heat until solution is complete, then add 100 ml H_2O. Neutralize with a 25% solution of NaOH, then add an additional 5 ml. Digest at 80-90 C for 20 minutes, then filter through a fritted glass filtering funnel of fine (five micron) porosity. Wash the precipitate thoroughly with hot water. Discard the filtrate and washings. Dissolve the precipitate by adding 25 ml of a hot mixture of 20 ml HCl (1-1) and 5 ml HNO_3. After one minute apply suction until dry. Repeat the treatment with 25 ml of acid mixture and finally, wash thoroughly with hot water. Transfer the solution to the original beaker and make two additional precipitations with 25% NaOH, filtering and washing after each precipitation exactly as just described.

Dissolve the precipitate finally obtained in the HCl-HNO_3 mixture as before. Transfer this solution to a 250 ml beaker and add 10 ml H_2SO_4 (1-1). Carefully evaporate until dense fumes of SO_3 are evolved. Cool and add 50 ml H_2O. Add NH_4OH until the solution is ammoniacal, then add an excess of 35 ml. Add two grams $NaHSO_3$ and adjust the volume to 150 ml. Cool the solution to room temperature, then electrolyze at a current of one ampere for about one hour, using platinum gauze electrodes. When deposition is complete, lower the beaker slowly, washing the electrodes with cold water without interrupting the current. While still washing, break the contact, rinse the cathode in ethyl alcohol, dry at 100 C and weigh. The increase in weight represents pure metallic cobalt, provided no nickel is present. If nickel is present, it must be determined by precipitation with dimethylglyoxime and the weight of nickel deducted from the weight of the electrodeposit.

Experimental: A standard cobalt solution was prepared from reagent grade cobaltous nitrate and standardized by precipitation with alpha-nitroso-beta-naphthol, the precipitate being ignited and weighed as Co_3O_4.

Chips were obtained from two heats of vacuum-cast molybdenum alloys. Heat 185 is a Mo-Co alloy and Heat 357 is pure molybdenum with no alloy added. A measured amount of the standard cobalt solution was added to duplicate two-gram samples of Heats 185 and 357. Duplicate two-gram samples of Heat 185 were carried through the procedure with no addition of standard cobalt solution.

It was at first thought that if the three NaOH separations removed practically all of the molybdenum, the precipitate so obtained could be ignited and weighed directly as Co_3O_4. The results obtained by this treatment were all excessively high. These high values could be due to any one of, or a combination of several of the following:

(a) Silica contamination from attack of the beakers while digesting in the NaOH solution.
(b) Incomplete removal of molybdenum.
(c) Impurities in the molybdenum, such as iron, which are also precipitated by NaOH.
(d) The cobalt oxide obtained upon ignition of the precipitate may be some other oxide than Co_3O_4.

Examination of the ignited precipitates showed only traces of SiO_2 and molybdenum to be present. These were insufficient to account for the total error. When the residue was dissolved in H_2SO_4 and then made ammoniacal for the electrolysis, a slight precipitate was observed in the solution. This precipitate had the appearance of iron hydroxide, although no identification was made. Since the electrodeposition gave excellent results, no further work was done. It is probable that all of the factors listed contribute somewhat to the high values initially obtained.

The following table indicates the accuracy obtained by the recommended procedure:

Heat No.	Co Added, g	Co Obtained, g	Co Originally Present, g
357	0.0206	0.0207	none
185	0.0206	0.0308	0.0102
185	none	0.0098	0.0098

DETERMINATION OF IRON IN MOLYBDENUM-BASE ALLOYS

Two methods are employed for the determination of iron in molybdenum-base alloys, depending on the concentration of iron. When iron has been intentionally added as an alloying constituent and is present in appreciable amounts, a volumetric method is used. When no iron has been added and only traces are present, as impurities, the colorimetric method is applied. Both methods are given below:

Volumetric Method

Dissolve five grams of sample in 50 ml HCl and 25 ml HNO_3. When solution is complete, cool and dilute to 500 ml in a volumetric flask. Take 100 ml aliquot portions (1.0 g) for each sample and transfer it to a 400 ml beaker. Add concentrated NH_4OH till the solution is ammoniacal, then add 10 ml excess. Heat just to boiling, allow the precipitate to settle and filter through No. 40 Whatman filter paper or its equivalent. Add a little filter paper pulp to the filter paper before starting the filtration. Wash the precipitate thoroughly with hot water. Discard the filtrate. Dissolve the precipitate with hot HCl (1-1), catching the solution in the original beaker. Finally, wash the paper

with hot water. Make two additional precipitations and filtrations as described above. After the final precipitation, dissolve the precipitate again in hot HCl (1-1) and wash the paper with hot water. Evaporate this solution to a volume of 5 ml. Add 25 ml H_2O and 1 ml of 5% $KMnO_4$ and heat to boiling. Reduce the iron with normal $SnCl_2$ solution, being careful not to use more than two or three drops excess. Cool and complete the determination by the Zimmerman-Reinhardt procedure, titrating the ferrous iron with 0.01 N $KMnO_4$, which has been standardized against sodium oxalate.

The accuracy of this procedure was checked by adding a known amount of iron to a sample of pure molybdenum and also to two samples of molybdenum-iron alloys. The results obtained are listed in the following table:

Heat No.	% Fe Added	% Fe Recovered	% Fe Originally Present
354	1.00	1.027	0.027
163	1.00	1.85	0.85
163	none	0.87	0.87
184	1.00	1.50	0.50
184	none	0.50	0.50

Colorimetric Method

When only traces of iron are involved, the volumetric method given above is not suitable. After a brief survey of the literature, the o-phenanthroline method appeared to have sufficient sensitivity and seemed adaptable to molybdenum-base alloys. The original method was published by Fortune and Mellon, Industrial and Engineering Chemistry, Analytical Edition, Vol 10 (1938). The procedure we adopted is an adaptation of the method as given by Sandell in "Colorimetric Determination of Traces of Metals", Vol 3, p 273, Interscience Publishers, Inc.

If a spectrophotometer is available, it is more convenient to determine the percent of light transmitted at 500 millimicrons than to prepare a series of standards for comparison with the unknown. The iron concentration is then obtained from a calibration curve prepared from a number of samples of known iron content. Distilled water is used as the blank for which the instrument is adjusted to 100% transmittance.

The colored complex is prepared in a solution containing not more than 0.2 mg iron. The ortho-phenanthroline ferrous complex is very stable and follows Beer's law closely in this range.

Solutions required:

Standard Iron Solution - Dissolve 1 g of electrolytic iron in 100 ml 20% HCl and dilute to 1 liter. Take 10 ml of this solution and dilute to 1000 ml. One milliliter of this solution corresponds to 0.01 mg iron.

Hydroxylamine Hydrochloride - 10% solution.

Sodium Acetate - 2 M and 0.2 M solutions are convenient concentrations.

o-Phenanthroline - 0.5% solution of the monohydrate in water. Warm to effect solution.

Aluminum Solution - Dissolve 0.25 g of C.P. aluminum metal in 50 ml of 10% NaOH. Acidify with HCl and dilute to 250 ml at room temperature. 25 ml of this solution = 0.025 g aluminum. This aluminum solution is added to the solution of the sample to serve as a gathering agent for the small traces of iron precipitated by NH_4OH.

Procedure: Transfer 10 g of sample to a 600 ml beaker and add 75 ml HCl. Carefully add 40 ml HNO_3 in small portions so that the reaction does not become too violent. When solution is complete, add 100 ml H_2O and 25 ml of aluminum solution. Neutralize the acid with NH_4OH and add 15 ml excess. Heat to boiling and boil two to three minutes. Allow the precipitate to settle and filter through an 11 cm, No. 4 Whatman filter paper or its equivalent. Wash thoroughly with hot 1% NH_4NO_3 solution. Dissolve the precipitate from the paper with a stream of hot HCl (1-1) catching the solution in the original beaker. Wash the paper with hot water. Heat the solution, reprecipitate with NH_4OH, filter and wash as before. Ignite the paper and precipitate at 500 C in a platinum crucible. Cool, add 2-3 ml HCl and digest until solution is effected. Transfer the solution to a 100 ml volumetric flask and dilute to the mark.

Take an aliquot portion of the solution containing a maximum of 0.3 mg of iron and transfer to a 100 ml volumetric flask. To a similar aliquot portion add 1 ml of 10% hydroxylamine hydrochloride and a few drops of brom-phenol blue, then add a measured volume of sodium acetate until the solution turns purple (pH 3-6). Now adjust the pH of the working sample with an equal volume of sodium acetate after the addition of 1 ml of 10% hydroxylamine hydrochloride. Add 1 ml of o-phenanthroline (0.5%), mix, dilute to the mark and let stand five to ten minutes. Compare the color of the unknown solution with that of a standard solution of known iron content. The standard solution should have approximately the same concentration of iron as the unknown. The color is developed in the standard solution in the same manner and should have the same final pH as the sample solution.

Alternate Method of Titrating Ferrous Iron Solution

Reference: "Quantitative Inorganic Analysis" Kolthoff and Sandell, p 608, The Macmillan Company, publishers

The end point obtained by the Zimmerman-Reinhardt procedure is rather indefinite, especially when small amounts of iron are being titrated with 0.01 normal $KMnO_4$. A more permanent end point is obtained when the iron is titrated

with standard $K_2Cr_2O_7$ solution using a diphenylamine derivative as a redox indicator. The end point is sharp and the method has the additional advantage of using a standard dichromate solution. Potassium dichromate is a primary standard and the solutions require no standardization.

Solutions required:

Diphenylamine Sulfonic Acid - Dissolve 0.32 g of barium diphenylamine sulfonate in 100 ml H_2O. Add 3 ml concentrated H_2SO_4, heat to boiling and digest for ten minutes. Allow the $BaSO_4$ to settle and filter through a No. 42 Whatman paper. Cool to room temperature.

0.01 N $K_2Cr_2O_7$ - Dissolve 0.4903 g pure, dry $K_2Cr_2O_7$ in water and dilute to one liter.

Procedure: Obtain the iron in the ferrous condition by exactly the same procedure as in the preceding volumetric method. To the cool ferrous chloride solution, contained in a 400 ml beaker, add 10 ml of a saturated solution of mercuric chloride and let stand about two minutes. Add 200 ml H_2O, 10 ml H_2SO_4 (1-5), 5 ml H_3PO_4 (85%) and 12 drops of diphenylamine sulfonic acid indicator. Titrate with 0.01 N $K_2Cr_2O_7$ solution until a definite pink coloration is obtained which holds for at least one minute.

Deduct a blank from the titration which is determined by carrying a blank through the entire procedure. Add exactly the same amounts of reagents to the blank as are used in the sample.

DETERMINATION OF MANGANESE IN MOLYBDENUM-BASE ALLOYS

The bismuthate method commonly used for the determination of manganese in steels is very satisfactory for the estimation of manganese in molybdenum-base alloys.

Procedure: Dissolve 1 g of sample in a 300 ml Erlenmeyer flask with 15 ml H_2SO_4 (1-1) and 10 ml concentrated HNO_3. Heat until fumes of SO_3 are evolved, then cool nearly to room temperature. Add 75 ml H_2O and again cool to room temperature. Add 0.5 to 1 g of bismuthate (enough to leave a small excess undissolved), and agitate for one minute. Filter through an asbestos pad or through glass frit. Wash with cold 3% H_2SO_4 until the washings run through colorless.

To the filtrate add enough of an approximately 0.03 N ferrous sulphate solution to reduce the permanganic acid completely. Titrate with standard 0.03 N potassium permanganate solution to the appearance of a faint pink color.

Run a blank through all steps of the process, add exactly the same volume of ferrous sulfate solution and titrate with the standard permanganate solution.

The difference between the volumes of permanganate required represents the volume of standard permanganate that contains the same amount of manganese as the sample.

DETERMINATION OF NICKEL IN MOLYBDENUM-BASE ALLOYS

The standard dimethylglyoxime method for the determination of nickel is readily applicable to molybdenum-base alloys.

Solutions required:

Citric Acid - Dissolve 800 g citric acid in a solution containing 3500 ml H_2O and 400 ml H_2SO_4 (1-4).
Dimethylglyoxime - Dissolve 1 g of dimethylglyoxime in 100 ml of either methyl or ethyl alcohol.
Phenol Red Indicator - 0.1 g dissolved in 100 ml of 25% ethyl alcohol.

Procedure: Dissolve a sample containing not more than 0.03 g of nickel in 30 ml concentrated HCl and 10 ml concentrated HNO_3. When decomposition is complete, add 150 ml H_2O, 25 ml of citric acid solution and 5 drops of phenol red indicator. Add concentrated NH_4OH until the solution is definitely red, then add 25 ml of dimethylglyoxime solution. Digest at 60 to 70 C for 30 minutes, then filter through a No. 40 Whatman filter paper. Wash the paper and precipitate three or four times with hot water. Discard the filtrate and washings. Place the original beaker under the funnel and wash the paper with hot HCl (1-1) until the precipitate is completely dissolved, then wash several times with hot water.

Dilute the filtrate and washings to 200 ml, add 10 ml citric acid and 5 drops of phenol red indicator solution. Neutralize the solution with NH_4OH until the solution is definitely red, then add 25 ml of dimethylglyoxime solution. Digest for 30 minutes at 60 to 70 C, filter through a weighed fritted glass filtering crucible of medium porosity. Wash with hot water, then dry the precipitate at 110-120 C for two hours. Cool and weigh as nickel dimethylglyoxime which contains 20.32% Ni.

DETERMINATION OF NIOBIUM OR TANTALUM IN MOLYBDENUM-NIOBIUM OR MOLYBDENUM-TANTALUM ALLOYS

The procedure described in the following paragraphs is applicable only to alloys containing nothing but molybdenum and niobium or molybdenum and tantalum. If other elements are present in quantities greater than traces, the procedure must either be modified, or a new procedure developed.

For alloys containing up to 5% niobium or tantalum, a one-gram sample is adequate. For higher percentages, proportionally smaller samples should be taken. Transfer the weighed sample to a 250 ml beaker, add 15 ml concentrated HCl and 10 ml concentrated HNO_3. Cover with a watch glass and heat until the sample is decomposed. Remove the cover glass, rinsing it with water, add 10 ml H_2SO_4 (1-1) and heat the uncovered beaker until SO_3 fumes are evolved. Remove from the hot plate and cool to room temperature. Add 100 ml of a 10% solution of tartaric acid and add three drops methyl purple indicator to the solution. From a burette, add concentrated NH_4OH drop by drop until the solution turns a distinct green color.

Add 10 ml ammonium acetate* and 30 ml of a saturated solution of ammonium chloride. Then add 20 ml of a freshly prepared and filtered solution of 5 g tannic acid in 100 ml H_2O. Add 1 ml glacial acetic acid and stir. Heat on the hot plate until the solution just begins to boil, remove from the plate and allow the precipitate to settle for about five minutes. Filter the voluminous precipitate through a No. 40 Whatman paper containing a little paper pulp. Wash about five times with a cold 2% solution of NH_4Cl containing 0.5 g tannic acid per liter. Transfer the paper and precipitate to a platinum crucible and carefully heat until the paper is thoroughly charred. Ignite over a Meker or Fisher burner until the paper is completely destroyed and no further fumes of subliming MoO_3 are visible. Finally, ignite for 30 minutes in a muffle furnace at 980 C.

Remove the crucible from the furnace and cool to room temperature. Add 2 ml concentrated H_2SO_4 and about 10 ml HF (48%) to the platinum crucible, then heat on an asbestos pad on the hot plate until the HF is driven off and SO_3 fumes are given off. Cool, place the crucible in a 250 ml beaker containing 100 ml of 10% tartaric acid. Mix contents of crucible with the tartaric acid and remove the crucible, rinsing it with water.

Add three drops methyl purple indicator, neutralize with NH_4OH, add ammonium acetate and ammonium chloride, and reprecipitate the niobium or tantalum with tannic acid exactly as previously described. Add 1 ml glacial acetic acid, heat just to boiling, let settle and filter through No. 40 Whatman paper containing a little ashless filter paper pulp. Wash five times with cold 2% NH_4Cl containing 0.5 g tannic acid per liter. Char the paper and precipitate in a weighed platinum crucible and finally ignite to constant weight at 980 C. Cool and weigh as Nb_2O_5 or Ta_2O_5.

It is very important that blanks are carried throughout the entire procedure. The weight obtained on the blank is deducted from the weight of Nb_2O_5 or Ta_2O_5 obtained on each sample.

It is essential that all manipulations throughout the procedure be executed very carefully. Because of the relatively small weights taken and the high factor for converting Nb_2O_5 to niobium or Ta_2O_5 to tantalum, any slight loss of material or weighing errors can introduce considerable error in the final result.

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* Ammonium acetate solution: Dissolve 50 g $NH_4C_2H_3O_2$ in 50 ml H_2O and dilute to 100 ml.

DETERMINATION OF SILICON IN MOLYBDENUM-BASE ALLOYS

The determination of silicon in molybdenum-base alloys is essentially the same as the method commonly used for silicon in steels.

Procedure: Transfer two grams of sample to a porcelain casserole. Add 25 ml H_2SO_4 (1-1) and 10 ml concentrated HNO_3. Cover with a Speedyvap watch glass and when violent action stops, heat on the hot plate until strong fumes of SO_3 are evolved. Remove from the hot plate and cool to room temperature. Rinse down the watch glass and sides of the casserole with water, then add 50 ml H_2O and stir to mix the solution. Filter through a medium fast paper and wash alternately with hot 5% HCl and water until the residue has been washed three times with HCl. Finally, wash three times with hot water. Transfer the paper and residue to a platinum crucible, dry at a moderate temperature and finally ignite at 980 C. Cool to room temperature in a desiccator and weigh the crucible and contents. Add two drops H_2SO_4 (1-1) and 5 ml HF and evaporate to dryness on the hot plate. Ignite at 980 C, cool and again weigh the crucible and residue. The loss in weight is SiO_2.

DETERMINATION OF TITANIUM IN MOLYBDENUM-BASE ALLOYS

The procedure for the determination of titanium in a binary alloy of molybdenum and titanium is similar to the method for aluminum in molybdenum-aluminum alloys. The recovery of titanium by the recommended procedure was checked by the recovery of known amounts of titanium added to solutions of pure molybdenum metal, using this procedure.

Weigh a sample of such size as to contain not more than 0.05 g Ti. Dissolve the sample with a mixture of concentrated HCl and HNO_3, containing 10 ml HCl and 3 ml HNO_3 for each gram of sample. Heat gently until the sample is decomposed. Add 100 ml H_2O, a little ashless filter paper pulp, and 5 or 6 drops of phenol red indicator (0.1 g dissolved in 100 ml of 25% ethyl alcohol). Add concentrated NH_4OH from a burette until the first permanent red color of the indicator appears, then add 0.7 ml excess NH_4OH. Heat the solution to boiling and boil one minute. Remove from the hot plate, let settle until the solution is cool, then filter through No. 42 Whatman paper or its equivalent. Rinse the beaker several times with cold 2% NH_4Cl and pour the rinsings through the filter. Wash the paper and precipitate four times with cold 2% NH_4Cl. Discard the filtrate and washings.

Place the original beaker under the funnel and dissolve the precipitate by washing at least three times with hot HCl (1-1). Wash the paper twice with hot water, then once with cold 3% NH_4OH. Reserve the filter paper. Dilute the filtrate and washings to 100 ml, add ashless filter paper pulp, phenol red indicator, then add NH_4OH until the solution is neutral to the indicator, followed by an excess of 0.7 ml NH_4OH. Heat to boiling and boil for one minute. Remove from the hot plate, let settle, then filter through the reserved filter paper. Wash four times with hot 2% NH_4Cl.

From this point, either of two procedures may be followed, both of which are given. If appreciable amounts of Ti are present, i.e., 0.01 g or more, there is danger of spattering and consequent loss of the sample during the final treatment with H_2SO_4 and HF for the removal of silica unless great care is exercised in the evaporation and ignition. The alternate procedure avoids this danger but is slightly longer. Equally satisfactory results are obtained by both methods.

Procedure I: Dissolve the precipitate on the filter paper by washing at least three times with hot HCl (1-1), catching the solution in the original beaker. Wash the paper twice with hot water. By this time the filtrations and washings have torn the filter paper so that it is unfit for the third filtration. Place this paper in a weighed platinum crucible and set aside. Dilute the filtrate to 100 ml and make a third precipitation with NH_4OH exactly as the preceding one. Filter through a fresh filter paper and thoroughly police the beaker. Wash four times with hot 2% NH_4Cl. Transfer the paper containing the precipitate to the crucible containing the first paper. Dry, then ignite at a low temperature until the paper is destroyed, then ignite at 1800 F for 10 minutes. Cool, add 7-8 drops H_2SO_4 (1-1) and 5 ml HF. Place the crucible on an asbestos pad on the hot plate and carefully evaporate to dryness. Gradually increase the temperature of the hot plate to its maximum temperature. When no further fumes are evolved, place the crucible on an asbestos pad over a burner and very carefully increase the temperature until fumes are again evolved. Hold at this temperature till fuming stops, then increase the temperature to the full heat of the burner. Finally, heat in the muffle furnace at 1800 F for 30 minutes. The entire evaporation and fuming operation must be performed very carefully to keep the glassy looking residue in the crucible from spattering. If proper care is taken, the operation can be performed very successfully. Cool the ignited residue in a desiccator and weigh as TiO_2.

Procedure II: Transfer the paper and the precipitate to a platinum crucible. Dry, then ignite at a low temperature until the paper is destroyed. Then ignite for 10 minutes at 1800 F. Cool, add 2 ml concentrated H_2SO_4 and 5 ml HF. Evaporate on an asbestos pad on the hot plate until fumes of SO_3 are freely evolved. Cool, transfer the H_2SO_4 solution to a 250 ml beaker, rinsing the crucible thoroughly with water. Dilute the solution in the beaker to 100 ml with 10% H_2SO_4, add filter paper pulp and 5-6 drops phenol red indicator. Neutralize with NH_4OH and add an excess of 0.7 ml. Heat to boiling, boil one minute, then remove from the heat. Allow the precipitate to settle, then filter through No. 40 Whatman filter paper. Carefully police the beaker, then wash the precipitate on the paper four times with hot 2% NH_4Cl. Transfer the paper and residue to a weighed platinum crucible, dry, then ignite at a low temperature until carbon is destroyed. Finally, ignite for 30 minutes at 1800 F. Cool and weigh as TiO_2.

A blank must be carried through the entire procedure, using a weight of pure Mo equal to the weight of the sample used. The weight obtained on the blank is deducted from the weight of oxide obtained in the sample.

Factor: $TiO_2 \longrightarrow Ti = 0.5995$

DETERMINATION OF TUNGSTEN IN MOLYBDENUM-BASE ALLOYS

The determination of relatively small percentages of tungsten in the presence of large amounts of molybdenum is an analytical problem which is extremely difficult. The most frequently recommended procedure, using cinchonine to effect complete precipitation of tungstic acid, has never been entirely satisfactory in our hands. A new reagent, anti-1, 5-di-(p-methoxy-phenyl)-1-hydroxylamino-3-oximino-4-pentene, was recently proposed by Yoe and Jones, Industrial and Engineering Chemistry, Analytical Edition, Vol 16 (1944). Use of this reagent also proved unsatisfactory for the molybdenum-tungsten alloys because of excessive coprecipitation of molybdenum with the tungstic acid. So far as we have been able to find, there is no really satisfactory, practical method available in the literature for the analysis of this type of alloy.

The following procedure is relatively simple and practical for routine determinations. On the basis of synthetic samples, slightly low results are obtained. However, the results are not so low as to be unacceptable for most routine analysis. The results of synthetic samples are given after the procedure.

Procedure: For samples containing 5% or less of tungsten, use two-gram samples. For 5 to 20%, use one-gram samples, for over 20% use 1/2 gram or less. Transfer the weighed sample to a 400 ml beaker, add 30 ml* HCl (concentrated) and 10 ml HNO_3 (concentrated). Heat gently until the sample is decomposed. Digest below boiling for 20 to 30 minutes, remove the cover glass and evaporate to a volume of approximately 15 ml. Add 15 ml concentrated HCl, cover and digest for one hour at 95-100 C. Add 50 ml H_2O and continue digestion for two hours. Let stand overnight. Filter cold through red ribbon filter paper. Wash five times with cold 5% HCl. Ignite the paper and precipitate in a tared platinum crucible, first at low temperature to destroy carbon and finally at 730 C for one hour. Cool, add 2 drops H_2SO_4 (1-1) and 5 ml HF. Evaporate to dryness and again ignite at 730 C for 20 minutes. Cool and weigh as "impure WO_3".

Fuse the residue with 1 g Na_2CO_3 and dissolve the melt with water. Transfer the solution to a 500 ml volumetric flask and adjust the volume to exactly 500 ml at room temperature. The molybdenum in this solution is determined colorimetrically on a suitable aliquot portion of this solution. The size of the aliquot portion and the standard steel used for comparison varies with each sample and must be determined experimentally. Generally, a 20 to 25 ml aliquot portion is convenient.

To the measured aliquot portion add 5 ml H_3PO_4 (85%), 20 ml $HClO_4$ (70 to 72%), and 10 ml of a solution of molybdenum-free electrolytic iron in HCl. Ten milliliters of the iron solution contains 0.1 g Fe. Heat this solution to boiling to remove CO_2, cool to room temperature, and develop the color with $SnCl_2$ and NaCNS. Extract with butyl acetate and compare the colored extract with a similar solution prepared from a suitable standard steel. The weight of molybdenum found in the residue is calculated to MoO_3 and this weight deducted from the weight of "impure WO_3" found previously. The weight obtained, after deducting the MoO_3, is assumed to be pure WO_3.

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* Use 20 ml HCl for 1 g or less sample.

Experimental: A pure tungsten solution was prepared from Baker's C.P. tungstic acid as follows:

Ignite the tungstic acid in a platinum crucible at 745 C to constant weight. The resulting material is assumed to be pure WO_3 without further treatment. Transfer 0.5044 g WO_3 to a platinum crucible and add one gram Na_2CO_3. Fuse the Na_2CO_3 and when the solution of WO_3 is complete, cool and dissolve the melt in H_2O. Dilute the solution to 500 ml in a volumetric flask. 25 ml of this solution is equivalent to 0.0200 g tungsten.

Chips from the two heats melted and cast in vacuum were obtained. Heat 357 is pure molybdenum metal with no alloying constituent and Heat 307 is a molybdenum-tungsten alloy containing approximately 5% tungsten. Two-gram samples were used in all three of the following experiments, which were made in duplicate:

1. Heat 357 plus 0.0200 g tungsten
2. Heat 307 plus 0.0200 g tungsten
3. Heat 307 - no tungsten added

These three samples were treated exactly as described in the procedure with the results given in the table below:

Experiment No.	Heat No.	%W Added	%W Found	% Added W Recovered
1	357	1.00	0.93	0.93
2	307	1.00	6.35	0.93
3	307	none	5.42	-

DETERMINATION OF URANIUM IN MOLYBDENUM-BASE ALLOYS

Experimental: A standard solution of uranium was prepared from uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$. Dissolve 0.861 g of uranyl nitrate in water and dilute to one liter. According to Hillebrand and Lundell, Applied Inorganic Analysis, p 368, precipitation of uranium by ammonium hydroxide, followed by ignition and weighing as U_3O_8, is an accurate procedure for the determination of uranium if interfering elements are absent. Since reagent grade uranyl nitrate was used, no interfering elements should have been present, and the solution was standardized by this method. Using 50 ml portions of the standard solution, three closely agreeing determinations gave an average of 0.02035 g uranium. The standard solution was therefore assumed to contain this weight of uranium in 50 ml.

Synthetic samples containing 0.02035 g uranium were prepared by dissolving 2 g of pure molybdenum in 30 ml HCl and 10 ml HNO_3, and adding 50 ml of standard uranium solution to this solution of molybdenum. Attempts to separate uranium from molybdenum by repeated precipitation with NH_4OH were unsuccessful. Low results were obtained in every case.

Schoep and Steinkuhler, Bulletin de la Sociétés chimiques Belges, Vol 31 (1922), state that the separation of uranium from molybdenum can be performed quantitatively by precipitation with ammonium sulfide from a slightly ammoniacal solution. Using a slight modification of this procedure, closely agreeing checks recovered 0.02048 g uranium from synthetic solutions containing 50 ml of the standard uranium solution.

Procedure: The size of sample used depends somewhat on the concentration of uranium present, but for most purposes, a two-gram sample is adequate and convenient to handle. Dissolve the sample in a 400 ml beaker with 30 ml HCl and 10 ml HNO_3. Digest below boiling until oxides of nitrogen are expelled. Cool somewhat, add five to six drops of phenol red indicator and then add NH_4OH until the first permanent red of the indicator appears, then add 10 to 12 drops excess. A light colored precipitate of uranyl hydroxide appears at this point. Add 25 ml of ammonium sulfide and digest below boiling for 20 minutes. During the digestion, the hydroxide precipitate is converted to the less soluble sulfide which is black in color. Filter through No. 40 Whatman paper containing a little ashless paper pulp and wash eight to ten times with a solution containing 15 ml of ammonium sulfide and ten drops of ammonium hydroxide per liter.

Transfer the paper and residue to a platinum crucible, dry and ignite at a low temperature until the paper is destroyed. Finally, ignite at 980 C for 30 minutes. Cool the crucible to room temperature, add 2 g $KHSO_4$ and fuse till the melt is clear. Cool to room temperature and transfer the solid mass to a 250 ml beaker containing 50 ml H_2O and 10 ml H_2SO_4 (1-1). Dissolve the small remaining salt in the crucible by rinsing with hot water and add this to the main solution. Warm the beaker until solution is complete, add a little ashless filter paper pulp and five to six drops of phenol red indicator. Add carbonate-free NH_4OH until the first permanent red of the indicator appears, then add 10 drops excess. Heat the solution to boiling, let settle, filter through No. 40 Whatman paper and wash with hot 3% NH_4NO_3 solution. Dry and ignite in a weighed platinum crucible until carbon is destroyed. Finally, ignite for 30 minutes at 980 C. Cool and weigh as U_3O_8.

Factor: $U_3O_8 \longrightarrow U = 0.84802$

DETERMINATION OF VANADIUM IN MOLYBDENUM-BASE ALLOYS

The ferrous sulfate-persulfate method for the determination of vanadium in steels is readily adapted to this determination in molybdenum-vanadium alloys. The method is rapid and reproducible results have been obtained in the range 0 to 10% vanadium in molybdenum-vanadium alloys.

Solutions required:

Ferrous Sulfate - approximately 0.03 N.
16.68 g $FeSO_4 \cdot 7H_2O$
200 ml H_2SO_4 (1-3)
Dilute to 2 liters

Ferrous Sulfate - approximately 0.1 N.
55.6 g $FeSO_4 \cdot 7H_2O$
200 ml H_2SO_4 (1-3)
Dilute to 2 liters

Potassium Permanganate - 0.03 N and 0.1 N.
Standardize against sodium oxalate and use the theoretical titer.

Ammonium Persulfate Solution - 100 g $(NH_4)_2S_2O_8$ per liter of solution, freshly prepared each day.

Potassium Ferricyanide Indicator.

Rinse a few crystals of $K_3Fe(CN)_6$ with distilled water to remove any ferrocyanide.

Let dry in air, then dissolve 0.03-0.04 g of the salt in 50 ml water.

This solution must be prepared fresh daily.

Procedure: The weight of sample required depends upon the vanadium content of the alloy. One ml of 0.03 N $KMnO_4$ is equivalent to 0.0015285 g vanadium and one ml of 0.1 N $KMnO_4$ is equivalent to 0.005095 g vanadium. The sample taken should be of such size as to be handled conveniently and titrated with either the 0.03 or 0.1 N permanganate solution. Dissolve the sample in 25 ml H_2SO_4 (1-1) and 10 ml HNO_3. When solution is complete, add 30 ml of H_2SO_4 (1-1), remove the cover and evaporate to strong fumes of SO_3. Cool and dilute to 200 ml with water. Add a few drops of 1.5% $KMnO_4$ and boil to oxidize any organic matter. Cool to room temperature and reduce the excess permanganate and the vanadium with either 0.03 or 0.1 N ferrous sulfate solution, depending on the vanadium content. Test for complete reduction of vanadium by means of the $K_3Fe(CN)_6$ used as an external indicator on a spot plate. When an excess of ferrous sulfate is present, a drop of solution will turn the indicator blue.

Add 15 ml of the freshly prepared ammonium persulfate solution and shake for at least one minute. Titrate the vanadium with the standard permanganate solution most suitable for the particular vanadium content. The oxidation of V^{IV} to V^{V} by permanganate occurs slowly at room temperatures. Sufficient permanganate must be added so that the pink end point remains for at least 30 seconds.

DETERMINATION OF ZIRCONIUM IN MOLYBDENUM-BASE ALLOYS

Procedure: Decompose one to two grams of sample in 25 ml H_2SO_4 (1-1) and 10 ml concentrated HNO_3 in a covered beaker. When decomposition is complete, remove the cover and evaporate until strong fumes of SO_3 are evolved. Cool the solution to room temperature and add 100 ml H_2O. Add a little filter paper pulp and 20 ml of a freshly prepared 25% solution of $(NH_4)_2HPO_4$ and digest at 40 to 50 C for two hours. An appreciable amount of ammonium phosphomolybdate precipitates with the $ZrH_2(PO_4)_2$, coloring the precipitate yellow. Filter the solution through a No. 40 Whatman paper and wash twice with cold 3% NH_4NO_3 solution. Now wash the precipitate with cold 5% NH_4OH until all yellow color in the precipitate has disappeared. If the ammonium phosphomolybdate precipitate is large, it may be necessary to transfer the precipitate to a beaker and digest it in 5% NH_4OH until the yellow precipitate dissolves. Finally, wash the precipitate three times with cold 3% NH_4NO_3 solution.

Transfer the paper and precipitate to a platinum crucible and heat gently until the paper is charred. Ignite very carefully under good oxidizing conditions until the carbon is gone and finally, heat at 980 C for 20 minutes. Cool the crucible to room temperature, add four to five grams anhydrous sodium carbonate powder and mix the residue with the sodium carbonate using a platinum wire. Heat over a blast Meker burner until the sodium carbonate is completely molten. Cool and dissolve the melt in 100 ml H_2O. Remove the crucible and rinse carefully. Let the insoluble matter settle, then filter through a No. 42 Whatman paper containing a little ashless filter paper pulp in the apex of the cone. Wash three times with hot 1% Na_2CO_3 solution, then three times with hot water. Return the paper and residue to the same crucible, dry and heat gently till paper is charred. Ignite carefully until carbon is gone, then heat at 980 C for 20 minutes. Repeat the sodium carbonate fusion, solution, filtration and ignition exactly as before.

Add four to five grams $KHSO_4$ to the platinum crucible and mix thoroughly with a platinum wire. Fuse the $KHSO_4$ over a burner and heat until the melt is clear. Cool, and dissolve the melt in 100 ml of 10% H_2SO_4. Remove the crucible, rinsing it carefully. Add a little ashless paper pulp, five drops of phenol red indicator solution and add concentrated NH_4OH until the first permanent red color appears, then add ten drops excess. Heat just to boiling, let the precipitate settle and filter through No. 40 Whatman paper. Wash thoroughly with hot 3% NH_4NO_3. Transfer the paper and residue to a weighed platinum crucible, dry and ignite carefully at 980 C. Cool and weigh as ZrO_2. Deduct a blank obtained by carrying a weight of pure molybdenum (zirconium-free) equal to the sample weight through the entire procedure.

$$\text{Factor: } ZrO_2 \longrightarrow Zr = 0.7403$$

Discussion: The separation of zirconium from large amounts of molybdenum by means of NH_4OH is not satisfactory. Consistently high results were obtained on a standard solution containing two grams molybdenum and 0.0249 grams zirconium.

The recovery of zirconium by precipitation as phosphate is complete in a 10% H_2SO_4 solution. Some ammonium phosphomolybdate is always coprecipitated under these conditions. The ammonium phosphomolybdate is readily soluble in dilute NH_4OH solution while the zirconium remains insoluble. However, the large amount of washing required to remove the ammonium phosphomolybdate makes the weighing of the ignited residue as ZrP_2O_7 unreliable. The washings are never free of phosphate so that the composition of the final precipitate is always uncertain. For example, a sample containing 0.0249 grams zirconium yielded 0.0239 grams zirconium when weighed as ZrP_2O_7 and calculated to zirconium. The same residue, fused twice with Na_2CO_3 to remove phosphate, and finally precipitated with NH_4OH and weighed as ZrO_2 showed a recovery of 0.0249 grams zirconium.

DETERMINATION OF RARE EARTH METALS

Outline of Method

The combined rare earths are separated from molybdenum by repeated precipitation with excess ammonium hydroxide. The combined hydroxides of the rare earths are converted to oxides by ignition at 650 C. The oxides are dissolved in concentrated hydrochloric acid and the solution evaporated just to dryness. The rare earth chlorides are redissolved in a little water and then precipitated as oxalates with oxalic acid. The oxalates are ignited to oxides and weighed as combined rare earth oxides. The oxides are redissolved by fusion with $KHSO_4$ and the cerium oxidized to the tetravalent state by ammonium persulphate in the presence of silver nitrate. Cerium is then determined by titration with standard ferrous ammonium sulphate solution. The cerium is calculated to the oxide and this weight deducted from the total weight of combined rare earth oxides. No chemical methods are known for the quantitative separation of the other rare earths. Spectroscopic or flame photometer methods are usually used for quantitative determinations of the rare earths.

Solutions required:

0.0125N $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution - Dissolve 4.902 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 200 ml H_2O containing 20 ml H_2SO_4. Cool and dilute to 1 liter. Standardize against 0.0125N $K_2Cr_2O_7$ solution.

0.0125N $K_2Cr_2O_7$ solution - Dissolve 0.6129 g of the Bureau of Standards standard sample of $K_2Cr_2O_7$ in water and dilute to exactly 1000 ml. This is a primary standard.

Diphenylamine sulfonic acid - Dissolve 0.32 g of barium diphenylamine sulfonate in 100 ml H_2O. Add 3 ml H_2SO_4, heat to boiling and digest for 10 minutes. Allow the $BaSO_4$ to settle and filter through Whatman No. 42 paper. Cool to room temperature.

Silver nitrate - 1% solution.

Standardize the ferrous ammonium sulphate solution as follows: To 25 ml of the ferrous solution add 200 ml water, 10 ml H_2SO_4 (1-5), 5 ml H_3PO_4 and 12 drops diphenylamine sulphonic acid indicator. Titrate with the standard dichromate solution.

Procedure: Dissolve 5 g of sample in a 600 ml beaker with 75 ml HCl and 15 ml HNO_3. A blank containing 5 g of pure molybdenum is carried through the entire procedure. When solution is complete, add 100 ml H_2O and 4 or 5 drops of phenol red indicator solution (1% in 25% ethanol). Neutralize with NH_4OH, then add an excess of NH_4OH equal to about 10% of the total volume of solution, i.e., about 25 ml excess NH_4OH. Heat to boiling and boil for one minute. Allow to cool to room temperature, preferably overnight. Filter through Whatman No. 42 filter paper containing a little ashless filter paper pulp. Wash with cold 5% NH_4Cl solution containing 100 ml NH_4OH per liter. Place the original beaker under the funnel and dissolve the precipitate by washing the paper at least three times with hot HCl (1-1). Wash the paper three times with hot water, then once with cold 3% NH_4OH. Reserve the filter paper. Repeat the NH_4OH precipitation exactly as before, cool and filter through the reserved filter paper. Wash with ammoniacal NH_4Cl solution as before. Dry the paper and residue in a platinum crucible, then ignite at 980 C. Cool, add 2 ml H_2SO_4, 5 ml HF and evaporate to fumes of SO_3.

Transfer the H_2SO_4 solution to a 250 ml beaker and dilute to 100 ml. Add phenol red indicator and neutralize with NH_4OH, then add an excess of 10% by volume. Boil for one minute, cool to room temperature and filter through No. 40 Whatman paper containing a little ashless filter paper pulp. Wash with 5% NH_4Cl solution containing 100 ml NH_4OH per liter. Dry and ignite the paper at 500 C. Cool, add 5 ml HCl, cover and warm the crucible until the residue is completely dissolved. Transfer the solution to a 50 ml beaker, rinsing the crucible with a little water. Evaporate just to dryness, cool, add 20 ml saturated oxalic acid solution and digest below boiling for 30 minutes. Let stand overnight, filter through a 9 cm Whatman No. 42 paper and wash with 0.5% oxalic acid. Ignite in a weighed platinum crucible at 980 C, cool and weigh. Deduct the weight of the blank and the remainder is the weight of the rare earth oxides. Also included in this residue is any thorium, scandium, yttrium and lanthanum which may have been present originally.

Fuse the residue in 2-3 g $KHSO_4$ and dissolve the melt in 200 ml H_2O containing 10 ml H_2SO_4. Add 15 ml of the silver nitrate solution and 2 g of ammonium persulphate crystals. Boil gently for 10-15 minutes, then cool to room temperature. Add 2 drops of 0.025M ortho-phenanthroline ferrous complex and titrate with standard 0.0125 N ferrous ammonium sulphate solution. One ml 0.0125 N Fe $(NH_4)_2 (SO_4)_2 \cdot 6H_2O$ solution is equivalent to 0.0017517 g Ce or 0.0020518 g Ce_2O_3. Calculate the cerium to Ce_2O_3 and deduct this weight from the total weight of rare earth oxides. No satisfactory wet chemical methods are available for the quantitative separation of the other rare earths. The spectroscope and the flame photometer are used for the quantitative determination of the various rare earths, but neither of these instruments is available in this laboratory. As a reasonable approximation of the total rare earth

metals present, other than cerium, a factor for the conversion of the oxide to the metal which is the mean of all the factors for the rare earths should be satisfactory. Using the mean value of 0.866, the result obtained for rare earths as metals would be close to the true value, regardless of the actual distribution of the rare earths in the mixture under consideration.

Spectrographic Analysis

Prior to the development of wet chemical methods of determining rare earth metals in molybdenum and molybdenum-base alloys, a number of spectrographic determinations were made. Specimens of alloys containing rare earth metals were sent to New England Spectrochemical Laboratories, Ipswich, Massachusetts, for analysis. A list of the alloys, melting atmospheres, additions, and spectrographic analyses is given in Table A1. Analyses made by the method of wet chemistry described above are also given. The correlation between the results of the two types of analysis is poor, particularly when the rare earth metal additions were high. It was judged advisable to rely upon the wet chemical analyses; therefore, only these are given for the heats of the deoxidation series containing rare earth metals, Table A1.

DETERMINATION OF ALUMINUM AND COBALT IN MOLYBDENUM-ALUMINUM-COBALT ALLOYS

Synthetic mixtures of these metals were prepared from solutions of pure molybdenum and from standard solutions of cobalt and aluminum. This synthetic solution was equivalent to a solution of a ternary alloy containing 99.65% molybdenum, 0.25% aluminum and 0.20% cobalt. Tests with this synthetic mixture gave the following results:

(a) Complete recovery of aluminum was obtained by using the method for the determination of aluminum in the binary alloy of molybdenum and aluminum.

(b) Complete recovery of cobalt was also obtained by the method for its determination in the binary alloy of molybdenum and cobalt.

DETERMINATION OF ALUMINUM AND NICKEL IN MOLYBDENUM-ALUMINUM-NICKEL ALLOYS

A solution of a synthetic alloy of molybdenum, aluminum and nickel was prepared from solutions of pure molybdenum metal, pure aluminum metal and a standard solution of nickel prepared from reagent grade nickel nitrate. This solution was prepared to contain 5 g molybdenum, 0.0102 g nickel and 0.0125 g aluminum. Tests with this mixture gave the following results:

TABLE A1

SPECTROGRAPHIC DETERMINATION OF RARE EARTH METALS

Heat	Melting Atm.	Additions, % Rare Earth*	Additions, % Other	Spectrographic Analyses, % Ce	La	Nd	Pr	Other	Wet Chemical Analyses, % C	Other*
960	vacuum	0.1 M	0.04 C		0.045				0.033	
962	argon	0.2 M			0.045				0.003	
996	vacuum	0.2 M		0.02	0.040				0.002	
997	vacuum	0.5 M			0.055				0.002	
998	vacuum	0.5 M	0.026 C		0.042				0.014	
1002	vacuum	0.1 M	0.02 C		0.032				0.012	
1003	argon	0.1 M	0.05 Al		0.036			0.0033 Al	0.003	
1005	argon	0.5 M		0.030	0.045				0.005	
1006	argon	0.1 M	0.026 C	0.050	0.028				0.014	
1020	vacuum	0.2 LCA		0.090	0.032				0.004	
1024	vacuum	0.5 LCA		0.035	0.030				0.004	
1030	argon	0.5 LCA		0.028	0.035				0.003	
1045	vacuum	0.3 LCA		0.060	0.090				0.003	0.005 Ce, 0.007 RE
1048	vacuum	0.3 LCA	1.0 Ti		0.15	0.02	0.04	0.12 Ti	0.003	0.000 Ce, 0.12 RE
1049	vacuum	0.3 LCA	1.0 V	0.020	0.025				0.001	0.003 Ce, 0.003 RE
1061	vacuum	2.0 LCA		0.048	0.040					
				0.40	0.30					
1064	argon	5.0 LCA		0.14	0.055	0.03	0.075		0.075	1.69 Ce, 1.99 RE
				1.05	0.80	0.10	0.13			

* M - misch metal, LCA - Lan-Cer-Amp, RE - other rare earth metals

(a) Complete recovery of aluminum was obtained by using the method for the determination of aluminum in the binary alloy of molybdenum and aluminum.

(b) Complete recovery of the added nickel was also obtained by the dimethylglyoxime method used for its determination in the binary molybdenum-nickel alloy.

DETERMINATION OF ALUMINUM AND NIOBIUM IN MOLYBDENUM-ALUMINUM-NIOBIUM ALLOYS

Outline of Method

Aluminum and niobium are determined on separate samples. Both elements are separated from molybdenum by precipitation with ammonium hydroxide. Aluminum requires careful control of the pH for its complete precipitation while a large excess of ammonium hydroxide is necessary for all of the niobium to be precipitated.

Some niobium always accompanies the aluminum hydroxide precipitate obtained by the ammonium hydroxide precipitation. The niobium is precipitated by hydrolysis in a dilute hydrochloric acid solution containing sulphurous acid. The hydrolyzed niobium is removed by filtration and aluminum determined gravimetrically on the filtrate.

The precipitation of niobium with excess ammonium hydroxide is contaminated with aluminum hydroxide. Aluminum is dissolved by boiling with 5% HCl. Boiling the dilute HCl solution with sulphurous acid completely precipitates the niobium by hydrolysis. The precipitate is filtered, ignited and silica removed with hydrofluoric acid.

Aluminum

Weigh a sample of such size as to contain not more than 0.05 g aluminum. Dissolve the chips with a mixture of concentrated HCl and HNO_3 containing 10 ml HCl and 3 ml HNO_3 for each gram of sample. Heat gently until the sample is decomposed. Add 100 ml H_2O and 5 or 6 drops of phenol red indicator (0.1 g dissolved in 100 ml of 25% ethanol). Add concentrated NH_4OH from a burette until the first permanent red color of the indicator appears, then add 0.7 ml excess. Add a little ashless filter paper pulp and heat the solution to boiling. Boil for one minute, remove from the hot plate and let stand until the solution is cool, or better, overnight. Filter through No. 42 Whatman paper or its equivalent, rinsing the beaker several times with cold 2% NH_4Cl, pouring the rinsings through the filter paper. Wash the precipitate on the filter paper four times with cold 2% NH_4Cl solution.

Place the original beaker under the funnel and, using a wash bottle, wash the paper and precipitate thoroughly with hot HCl (1-1). At least three washings are required to dissolve all of the soluble matter on the filter. Wash the paper twice with hot water and then once with cold 3% NH_4OH solution. Reserve the filter paper. Dilute the filtrate to 100 ml, add phenol red indicator and add NH_4OH until neutral, then add 0.7 ml excess. Add a little ashless filter paper pulp, heat to boiling and boil for one minute. Remove from the hot plate, let settle and then filter through the reserved filter paper. Wash with hot 2% NH_4Cl. Place the paper and precipitate in a platinum crucible and ignite until the paper is destroyed. Fuse the residue with 4 or 5 g $KHSO_4$.* Dissolve the melt in 100 ml HCl (1-1) in a 250 ml beaker. Remove the crucible and rinse with water. Transfer the solution to a 600 ml beaker, dilute to 250 ml with water, and add 5 drops phenol red indicator. Neutralize with NH_4OH and add 0.7 ml excess. Add a little ashless filter paper pulp and heat to boiling for one minute. Let settle, filter through a No. 40 Whatman paper and wash with hot 2% NH_4Cl. Transfer the washed paper and residue to the original beaker and add 100 ml 5% HCl and 25 ml 6% H_2SO_3. Macerate the paper to a pulp and boil for three minutes. Digest just below boiling for fifteen minutes. Filter through a 12.5 cm Whatman No. 42 paper and wash with hot 2% HCl. Discard the paper and any insoluble residue. To the filtrate add phenol red indicator and neutralize with NH_4OH, then add 0.7 ml excess. Add a little ashless paper pulp and boil one minute. Let settle, then filter through No. 40 Whatman paper and wash with hot 2% NH_4Cl. Dry and ignite the paper and residue in a weighed platinum crucible until all organic matter is decomposed. Add 3 or 4 drops of H_2SO_4 (1-1) and 5 ml HF. Evaporate to dryness, then ignite at 1800 F for 20 minutes. Cool and weigh.

A blank must be carried through the entire procedure, using a weight of pure molybdenum equal to the weight of sample used. The weight of the blank obtained is deducted from the weight of the oxide obtained in the sample.

Niobium

Dissolve a sample containing not more than 0.02 g Nb in a mixture of concentrated HCl and HNO_3 containing 10 ml HCl and 3 ml HNO_3 for each gram of sample. Heat gently until the sample is decomposed, add 200 ml H_2O and 4 or 5 drops of phenol red indicator. Neutralize with NH_4OH and add 10 ml in excess. Boil for 15 minutes, add a little ashless filter paper pulp and cool to room temperature. Digest at least one hour at room temperature. Filter through No. 42 Whatman paper or its equivalent, containing a little ashless filter paper pulp. Wash with hot 2% NH_4Cl containing 1 ml NH_4OH per liter of solution. Place the paper and precipitate in a platinum crucible and ignite until all the paper is destroyed.** Fuse the ignited residue with 4 or 5 g $KHSO_4$ and dissolve the melt in a 250 ml beaker with 100 ml HCl (1-1). Remove the crucible and rinse it with water. Transfer the solution to a 600 ml beaker, dilute to about 250 ml and add 5 drops phenol red indicator. Neutralize with NH_4OH, then add 10 ml excess. Boil for 15 minutes, add a little ashless filter paper pulp and digest at room temperature for one hour. Filter through a No. 42 Whatman paper containing a little ashless filter paper pulp. Wash with hot 2% NH_4Cl containing 1 ml NH_4OH per liter of solution.

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* See Note 1
** See Note 2

Place the original beaker under the funnel and, using a wash bottle, wash the paper and precipitate thoroughly with hot HCl (1-1). At least three washings are required to dissolve all of the soluble matter on the filter. Wash the paper twice with hot water and then once with cold 3% NH_4OH solution. Reserve the filter paper. Dilute the filtrate to 100 ml, add phenol red indicator and add NH_4OH until neutral, then add 0.7 ml excess. Add a little ashless filter paper pulp, heat to boiling and boil for one minute. Remove from the hot plate, let settle and then filter through the reserved filter paper. Wash with hot 2% NH_4Cl. Place the paper and precipitate in a platinum crucible and ignite until the paper is destroyed. Fuse the residue with 4 or 5 g $KHSO_4$.* Dissolve the melt in 100 ml HCl (1-1) in a 250 ml beaker. Remove the crucible and rinse with water. Transfer the solution to a 600 ml beaker, dilute to 250 ml with water, and add 5 drops phenol red indicator. Neutralize with NH_4OH and add 0.7 ml excess. Add a little ashless filter paper pulp and heat to boiling for one minute. Let settle, filter through a No. 40 Whatman paper and wash with hot 2% NH_4Cl. Transfer the washed paper and residue to the original beaker and add 100 ml 5% HCl and 25 ml 6% H_2SO_3. Macerate the paper to a pulp and boil for three minutes. Digest just below boiling for fifteen minutes. Filter through a 12.5 cm Whatman No. 42 paper and wash with hot 2% HCl. Discard the paper and any insoluble residue. To the filtrate add phenol red indicator and neutralize with NH_4OH, then add 0.7 ml excess. Add a little ashless paper pulp and boil one minute. Let settle, then filter through No. 40 Whatman paper and wash with hot 2% NH_4Cl. Dry and ignite the paper and residue in a weighed platinum crucible until all organic matter is decomposed. Add 3 or 4 drops of H_2SO_4 (1-1) and 5 ml HF. Evaporate to dryness, then ignite at 1800 F for 20 minutes. Cool and weigh.

A blank must be carried through the entire procedure, using a weight of pure molybdenum equal to the weight of sample used. The weight of the blank obtained is deducted from the weight of the oxide obtained in the sample.

Niobium

Dissolve a sample containing not more than 0.02 g Nb in a mixture of concentrated HCl and HNO_3 containing 10 ml HCl and 3 ml HNO_3 for each gram of sample. Heat gently until the sample is decomposed, add 200 ml H_2O and 4 or 5 drops of phenol red indicator. Neutralize with NH_4OH and add 10 ml in excess. Boil for 15 minutes, add a little ashless filter paper pulp and cool to room temperature. Digest at least one hour at room temperature. Filter through No. 42 Whatman paper or its equivalent, containing a little ashless filter paper pulp. Wash with hot 2% NH_4Cl containing 1 ml NH_4OH per liter of solution. Place the paper and precipitate in a platinum crucible and ignite until all the paper is destroyed.** Fuse the ignited residue with 4 or 5 g $KHSO_4$ and dissolve the melt in a 250 ml beaker with 100 ml HCl (1-1). Remove the crucible and rinse it with water. Transfer the solution to a 600 ml beaker, dilute to about 250 ml and add 5 drops phenol red indicator. Neutralize with NH_4OH, then add 10 ml excess. Boil for 15 minutes, add a little ashless filter paper pulp and digest at room temperature for one hour. Filter through a No. 42 Whatman paper containing a little ashless filter paper pulp. Wash with hot 2% NH_4Cl containing 1 ml NH_4OH per liter of solution.

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* See Note 1
** See Note 2

Transfer the paper and precipitate to the original beaker and add 100 ml of 5% HCl and 25 ml of 6% H_2SO_3. Macerate the paper to pulp and boil for 3 minutes. Digest just below the boiling point for 15 minutes. Filter through a 12.5 cm Whatman No. 42 paper containing a little ashless filter paper pulp and wash with hot 2% HCl. Ignite in a weighed platinum crucible, first at a low temperature to burn off the paper and finally for 15 minutes at 1800 F. Cool, add 2 ml H_2SO_4 (1-1) and 2 ml HF. Evaporate to dryness on the hot plate, then ignite at 1800 F for 30 minutes. Cool and weigh the Nb_2O_5.

Note 1. Some samples contain Al_2O_3 as nonmetallic inclusions. This Al_2O_3 remains insoluble during the attack with HCl-HNO_3. If precautions were not taken to insure the solution of all the aluminum in the sample, the undissolved Al_2O_3 would remain with the Nb_2O_5 precipitate and yield apparently high values for niobium. Similarly, correspondingly low values would result in the aluminum determination. If the initial decomposition of the sample yields a perfectly clear solution, the ignition and fusion of the precipitate with $KHSO_4$ may be eliminated from both the determination of Al and Nb.

Note 2. It is not necessary to carry along a blank in the niobium determination. In a number of tests, the blank was found to be so small as to be of no consequence.

DETERMINATION OF ALUMINUM AND TITANIUM IN MOLYBDENUM-ALUMINUM-TITANIUM ALLOYS

The combined, impure Al_2O_3 and TiO_2 are obtained exactly as described in the method for the determination of aluminum or titanium in binary molybdenum-base alloys. A blank sample of pure molybdenum metal of the same weight as the sample to be analyzed is carried through the entire procedure.

After the weight of the combined oxides has been ascertained, fuse the residue with 1 to 2 grams of $KHSO_4$. Dissolve the melt in 200 ml of 10% (by volume) sulphuric acid. Add a little ashless filter paper pulp to the solution and cool to 5 to 10 C. Precipitate the titanium by the addition of 15 ml of a cold, freshly prepared solution of 6 g Cupferron in 100 ml water. Add the reagent by allowing it to run slowly down the side of the beaker and stirring continuously during the addition. Let settle 2 or 3 minutes, then check for completeness of precipitation by adding a little more reagent. The formation of a white, crystalline precipitate indicates complete precipitation. The titanium precipitate of Cupferron is yellow.

Filter through No. 40 Whatman paper containing a little ashless filter paper pulp. Wash the paper and precipitate five times with cold 10% H_2SO_4 solution containing 25 ml of the 6% Cupferron reagent per liter of solution. Transfer the paper and precipitate to a weighed platinum crucible and dry for two hours at 110 C. Char the paper on an asbestos pad over a Fisher or Meker burner. Ignite carefully until organic matter is destroyed, then finally ignite at 1800 F for 30 minutes. Cool and weigh the ignited residues. Deduct the weight of the blank residue and the remainder is pure TiO_2, of which 59.95% is titanium.

Aluminum is determined by difference. Deduct the weight of blank originally obtained from the weight of combined, impure Al_2O_3 and TiO_2. The weight obtained is pure Al_2O_3 + TiO_2. Now deduct the weight of TiO_2 obtained by the Cupferron method and the remainder is pure Al_2O_3, of which 52.92% is aluminum.

DETERMINATION OF ALUMINUM AND VANADIUM IN MOLYBDENUM-ALUMINUM-VANADIUM ALLOYS

A synthetic mixture of molybdenum, aluminum and vanadium was prepared from a solution of pure molybdenum metal and from standard solutions of aluminum and vanadium. This synthetic solution was equivalent to a solution of a ternary alloy containing 99% molybdenum, 0.75% vanadium and 0.25% aluminum. Tests with this synthetic mixture gave the following results:

(a) The method for the determination of vanadium in a binary molybdenum-vanadium alloy was equally satisfactory for the ternary alloy containing aluminum.

(b) Complete recovery of aluminum was obtained by using the method for the determination of aluminum in the binary alloy of molybdenum and aluminum. When vanadium was present, a very dark colored solution was obtained as the neutral point approaches with the addition of ammonium hydroxide. The appearance of a purplish color was assumed to be the neutral point to the phenol red indicator. This was the point taken for the addition of the excess ammonium hydroxide. Boiling, followed by digestion below boiling, caused the dark color to disappear and the normal red color of the indicator appeared. No dark color was observed in the subsequent precipitations with ammonium hydroxide.

DETERMINATION OF ALUMINUM AND ZIRCONIUM IN MOLYBDENUM-ALUMINUM-ZIRCONIUM ALLOYS

Outline of Method

The combined hydroxides of aluminum and zirconium are separated from the bulk of the molybdenum by repeated precipitation with NH_4OH. The hydroxides are ignited to the oxides in a platinum crucible. These oxides are redissolved by fusion with $KHSO_4$ and the melt dissolved in dilute H_2SO_4. Zirconium is then separated from aluminum by precipitation as phosphate. Zirconium is separated from phosphate by fusion with Na_2CO_3 and is then precipitated by NH_4OH and finally weighed as the oxide. Aluminum is determined in the filtrate

from the zirconium phosphate precipitate. The solution is partially neutralized, an acetic acid solution of 8-hydroxyquinoline added, and aluminum oxyquinolate precipitated by making the solution ammoniacal. After filtration, the organic matter is destroyed by evaporation with H_2SO_4 and HNO_3. Aluminum is then precipitated with NH_4OH and finally ignited and weighed as Al_2O_3.

Procedure: Dissolve a suitable weight of sample with HCl and HNO_3, using 10 ml HCl and 3 ml HNO_3 for each gram of sample. A blank containing an equal weight of pure molybdenum is carried through the entire procedure. When solution is complete, heat gently until most of the oxides of nitrogen are driven off. Add 100 ml H_2O, a little ashless filter paper pulp and five or six drops of phenol red indicator. Add NH_4OH until the first permanent red color of the indicator appears, then add a 0.7 ml excess. Heat to boiling and boil for one minute, remove from the hot plate and let stand until the solution is at room temperature. Filter through No. 42 Whatman paper and wash the precipitate with cold 2% NH_4NO_3. Discard the filtrate and washings.

Place the original beaker under the funnel and dissolve the precipitate by washing with hot HCl (1-1). Wash the paper twice with hot water and finally, once with cold 3% NH_4OH. Reserve the filter paper. Dilute the filtrate and washings to 100 ml and repeat the precipitation with NH_4OH. Boil one minute, let settle a few minutes, then filter through the reserved paper. Wash the precipitate with hot, dilute NH_4NO_3. Discard the filtrate and washings. Place the original beaker under the funnel, redissolve the precipitate with HCl and make a third separation with NH_4OH. Dry and ignite the final precipitate at 1800 F in a platinum crucible.

Fuse the residue with 4 or 5 g $KHSO_4$ and dissolve the cooled melt in 100 ml of 10% H_2SO_4. Cool to room temperature, add a little ashless filter paper pulp and 20 ml of a freshly prepared 25% solution of $(NH_4)_2HPO_4$. Digest for two hours at 40-50 C, then filter through No. 40 Whatman paper and wash four or five times with hot 2% NH_4NO_3. Reserve the filtrate and washings for the determination of aluminum.

Ignite the zirconium phosphate precipitate very carefully until the paper is destroyed. Finally, ignite at 1800 F. Now separate the zirconium from the phosphate by fusion with Na_2CO_3, and complete the zirconium determination as described in "The Determination of Zirconium in Molybdenum-Base Alloys".

Evaporate the reserved filtrate to approximately 150 ml. Add two drops of methyl orange indicator solution and add concentrated NH_4OH until the solution is just slightly acid to the indicator. If too much NH_4OH is inadvertently added at this point (indicated by formation of a precipitate in the solution), add two or three drops of concentrated H_2SO_4. Add 10 ml* 8-hydroxyquinoline solution (5 g dissolved in 100 ml 2N acetic acid), then add NH_4OH until alkaline, and finally an excess of 5 ml NH_4OH. Warm to 50-60 C and digest at this temperature until the precipitate becomes dense and crystalline. Cool and filter through No. 40 Whatman paper containing a little ashless filter paper pulp. Wash with a cold 3% NH_4OH containing 25 ml of the reagent previously neutralized with NH_4OH in one liter. Discard the filtrate.

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* This amount of reagent is adequate to precipitate 50 mg of aluminum. An excess of reagent does no harm. In any event, sufficient reagent should be added to color the solution yellow.

Return the paper containing the precipitate to the original beaker, add 10 ml concentrated H_2SO_4 and macerate the paper. Add 15 ml HNO_3, cover the beaker and heat until SO_3 fumes are evolved. Remove the beaker from the hot plate and cautiously add an additional 15 ml HNO_3. Again evaporate to SO_3 fumes. All organic matter should now be destroyed. Cool, add 75 ml H_2O and five drops of phenol red indicator. Add concentrated NH_4OH until the first permanent red color appears, then add an excess of 0.7 ml. Add a little ashless filter paper pulp, boil for one minute and let settle. Filter through a No. 40 Whatman paper and wash with hot 2% NH_4NO_3 solution. Dry and ignite at a low temperature until the paper is destroyed, then heat for 30 minutes at 1800 F. Remove silica by treatment with HF and a few drops of H_2SO_4 (1-1). Again ignite and weigh as Al_2O_3.

DETERMINATION OF COBALT AND NIOBIUM IN MOLYBDENUM-COBALT-NIOBIUM ALLOYS

Outline of Method

Cobalt and niobium are determined on separate samples. Cobalt, together with at least part of the niobium is separated from molybdenum as the sulfide in an ammoniacal solution. After filtration, the cobalt and niobium sulfides are decomposed with acid and the niobium precipitated by hydrolysis with sulfurous acid. The niobium is removed by filtration and cobalt determined in the filtrate by electroplating.

Cobalt

Transfer a 2 gram sample to a 400 ml beaker and add 25 ml HCl and 10 ml HNO_3. Heat gently until decomposition is complete. Dilute the solution to 100 ml, neutralize with NH_4OH and add 15 ml excess. Now add 25 ml of dark ammonium sulfide solution and digest below boiling for one hour. Filter through a No. 40 Whatman paper containing a little ashless filter paper pulp. Wash with a 2% NH_4Cl solution containing 10 ml of the ammonium sulfide solution per liter. Discard the filtrate and washings. Transfer the paper and the insoluble residue to the original beaker, add 20 ml HCl (1-1) and 5 ml HNO_3 (Sp.Gr.-1.20). Digest below boiling until the sulfides are decomposed. Dilute to 200 ml with water, add 25 ml H_2SO_3 (6%) and boil 3 minutes. Digest below boiling for 15 minutes. Filter through No. 42 Whatman paper and wash with 2% HCl. Discard the paper and any insoluble matter. Add 10 ml H_2SO_4 (1-1) to the filtrate and evaporate to strong fumes of SO_3. Cool slightly, add 5 ml HNO_3 and again evaporate to strong fumes. Cool, transfer the solution to a 250 ml beaker, rinsing the larger beaker thoroughly with water. Adjust the volume to about 75 ml, neutralize with NH_4OH, then add an excess of 35 ml. Add 2 g $NaHSO_3$ and cool the solution in running water.

Electrolyze for 1-1/2 hours using a current of 1 ampere. The electrodes should be made from platinum gauze and the solution stirred continuously during the electrolysis. Without interrupting the current, lower the beaker slowly while rinsing the cathode with distilled water. Remove the beaker,

shut off the current and disconnect the electrode. Dissolve the deposit from the electrode with approximately 25 ml HNO_3. Add 10 ml H_2SO_4 (1-1) to the solution and evaporate to strong fumes of SO_3. Cool, add 50 ml H_2O, neutralize with NH_4OH and add an excess of 35 ml. Add 2 g $NaHSO_3$ and cool to room temperature. Electrolyze for 1 hour, using a current of 1 ampere. Without interrupting the current, lower the beaker slowly while rinsing the cathode with distilled water. Remove the beaker, shut off the current and rinse the cathode with absolute ethyl alcohol. Dry at 105 C for 5 minutes, cool and weigh. The increase in weight of the cathode is cobalt.

$$\frac{\text{Weight of cobalt}}{\text{Weight of sample}} \times 100 = \% \text{ Cobalt}$$

Niobium

Tests with synthetic solutions show that niobium is quantitatively recovered without interference from cobalt by the standard tannic acid method, which is used for binary molybdenum-niobium alloys.

DETERMINATION OF COBALT AND TITANIUM IN MOLYBDENUM-COBALT-TITANIUM ALLOYS

Outline of Method

Both titanium and cobalt are separated from molybdenum by repeated precipitation with sodium hydroxide. The combined cobalt and titanium are obtained in a sulfuric acid solution, and the titanium is precipitated by Cupferron. The Cupferron precipitate is ignited and weighed as titanium dioxide. Organic matter is destroyed in the filtrate from the Cupferron precipitate and the cobalt in this solution is determined electrolytically.

This method, applied to synthetic samples, yielded results slightly high for the titanium and correspondingly low for cobalt, indicating that a little cobalt is included with the Cupferron precipitate. The error is approximately 5% of the total cobalt and titanium present. Since other factors in the program are even less accurate, this discrepancy was considered acceptable.

Procedure: Transfer a suitable weight of sample to a 400 ml beaker and add 10 ml HCl and 4 ml HNO_3 for each gram of sample. Heat gently until solution is complete, then add 100 ml H_2O. Neutralize with a 25% solution of NaOH, using litmus indicator, then add an excess of 5 ml. Digest at 80-90 C for 20 minutes, then filter through a fritted glass filtering funnel of fine porosity (5 micron). Wash the precipitate thoroughly with hot water. Discard the filtrate and washings. Dissolve the precipitate by adding 25 ml of a hot mixture of 20 ml HCl (1-1) and 5 ml HNO_3. After one minute apply suction until dry. Repeat the treatment with another 25 ml of the acid mixture and finally, wash thoroughly with hot water. Transfer the solution to the original beaker and make two additional precipitations with 25% NaOH, filtering and washing after each precipitation exactly as just described.

Dissolve the precipitate finally obtained in the HCl-HNO_3 mixture as before. Transfer the solution to the original beaker and add 20 ml H_2SO_4 (1-1). Evaporate on the hot plate until dense fumes are evolved. Cool, add 200 ml H_2O and cool to 10 C. Add 15 ml of a freshly prepared, cold 6% aqueous solution of Cupferron, slowly with stirring. Add a little ashless filter paper pulp, let settle, then check for completeness of precipitation by adding a little more reagent. A white precipitate indicates complete precipitation. Filter through No. 40 Whatman paper and wash five times with cold 10% H_2SO_4 containing 25 ml Cupferron solution per liter. Reserve the filtrate and washings for the cobalt determination. Drain the precipitate as completely as possible and transfer the paper and precipitate to a platinum crucible. Cautiously dry and then heat gently until the paper begins to char. The precipitate tends to liquefy and heating must therefore be done carefully. Gradually increase the heat until carbon is destroyed and finally, ignite at 1000 C for 20 minutes. Cool and weigh as TiO_2.

Evaporate the reserved filtrate to a volume of about 100 ml. Add 25 ml HNO_3 and continue the evaporation to SO_3 fumes. Cover with a Speedyvap cover glass and, without cooling, cautiously add 10 ml HNO_3 from a pipette. Again evaporate to SO_3 fumes. If the presence of organic matter is still indicated, repeat the HNO_3 additions until all organic matter is destroyed. Cool, transfer the solution to a 400 ml beaker and dilute to 100 ml. Neutralize with concentrated NH_4OH, then add 35 ml excess. Cool to room temperature, add 2 g $NaHSO_3$, then electrolyze for one hour at one ampere, using a weighed platinum gauze cathode. Cobalt is deposited as the metal on the cathode.

DETERMINATION OF COBALT AND VANADIUM IN MOLYBDENUM-COBALT-VANADIUM ALLOYS

Synthetic mixtures were prepared containing 4 grams molybdenum, 0.0222 grams vanadium and 0.0060 grams cobalt. Tests with these solutions indicated that:

(a) The method for the determination of vanadium in binary molybdenum-vanadium alloys is also applicable to this ternary system.

(b) Complete recovery of cobalt is obtained from this ternary alloy by the procedure used for the determination of cobalt in binary molybdenum-cobalt alloys. During the first precipitation of cobalt with sodium hydroxide solution, a dark blue color caused by vanadium compounds interferes somewhat with the observation of the neutralization point. However, this point is not critical and if a strip of wet litmus paper is placed on the side of the beaker, partially submerged in the solution, the change in color of the paper can readily be observed. The blue color of the solution disappears during the hot digestion of the solution. No blue color develops during the subsequent precipitations.

DETERMINATION OF COBALT AND ZIRCONIUM IN MOLYBDENUM-COBALT-ZIRCONIUM ALLOYS

Synthetic mixtures were prepared containing 5 grams molybdenum, 0.0125 grams zirconium and 0.0059 grams cobalt. Tests with solutions of this mixture indicated that complete recovery of both cobalt and zirconium was obtained by the procedures for the determination of these metals in binary molybdenum-base alloys.

DETERMINATION OF NIOBIUM AND TITANIUM IN MOLYBDENUM-NIOBIUM-TITANIUM ALLOYS*

Outline of Method

Titanium and niobium are separated from molybdenum by repeated precipitation with excess NH_4OH and weighed, after ignition, as the combined oxides, Nb_2O_5 + TiO_2. The oxides are redissolved by fusion in $KHSO_4$ and the titanium is determined spectrophotometrically. The transmittance of the yellow colored solution given by titanium in a sulfuric acid solution containing hydrogen peroxide is measured at 420 millimicrons. The niobium content is obtained by difference.

Procedure: Dissolve a 5 gram sample in a 600 ml beaker with 75 ml HCl and 15 ml HNO_3. When action is complete, cool somewhat and add 100 ml H_2O. Add 5 drops of phenol red indicator (0.1 g in 100 ml 25% ethanol), neutralize with NH_4OH and add 10 ml excess. Add a little ashless filter paper pulp, heat to boiling and boil for one minute. Remove from the hot plate and allow to cool to room temperature. Filter through an 11 cm Whatman No. 40 filter paper and wash three or four times with hot 2% NH_4Cl solution. Discard the filtrate and washings. Place the original beaker under the funnel and dissolve the precipitate from the paper by repeated washing with hot HCl (1-1). At least three washings are necessary. Now wash the paper three times with hot water and once with cold 3% NH_4OH. Reserve the filter paper and any insoluble residue it may contain.

Again add phenol red indicator and precipitate Nb and Ti with NH_4OH exactly as before. Add ashless filter paper pulp, boil one minute, cool to room temperature and filter through the reserved No. 40 Whatman paper. Wash with hot 2% NH_4Cl and discard the filtrate and washings. Dry and ignite the paper and residue at 1800 F in a platinum crucible until all organic matter is destroyed. Cool, add 2 ml H_2SO_4 and 5 ml HF. Evaporate to strong fumes of SO_3. Cool and transfer the H_2SO_4 solution to a 250 ml beaker. Dilute to 100 ml, add phenol red indicator and again precipitate Nb and Ti with NH_4OH, using 10 ml excess. Add a little ashless filter paper pulp, boil for one minute, then cool to room temperature. Filter through No. 40 Whatman paper and wash the precipitate

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* This method is not applicable if the titanium content is over 0.5%.

with hot 2% NH_4Cl. Dry and ignite the paper and residue in a weighed platinum crucible at a low temperature until carbon is destroyed, then ignite for 20 minutes at 1800 F. Cool and weigh. A blank containing five grams of pure molybdenum is carried through the entire procedure thus far. Deduct the weight of the blank from the weight of residue obtained in the sample. The remainder then is the weight of combined oxides, Nb_2O_5 + TiO_2.

Fuse the residue containing the combined oxides with three or four grams of $KHSO_4$. Dissolve the cooled melt in 100 ml of 10% H_2SO_4. Transfer this solution to a 250 ml volumetric flask and dilute the solution to exactly 250 ml with 10% H_2SO_4. Transfer an aliquot portion of this solution containing a maximum of approximately 1.0 mg of titanium to a 100 ml volumetric flask and dilute to the mark with 10% H_2SO_4. Transfer a portion of this solution to the spectrophotometer cuvette and adjust the instrument to 100% transmission with the solution in the beam of light at a wave length of 420 millimicrons. Now take 10-15 ml of the solution in a 50 ml beaker and develop the yellow titanium color by the addition of three drops of 3% H_2O_2. Measure the transmission of this solution in the spectrophotometer at 420 millimicrons* and obtain the weight of titanium present in the aliquot from the calibration curve.

Preparation of Calibration Curve

A standard solution of titanium containing 0.012 mg Ti/ml was prepared from reagent grade TiO_2. Dilute 10, 20, 30, 40, 50, 75 and 100 ml of this solution with 10% H_2SO_4 to 100 ml in volumetric flasks. Now measure the transmission of portions of these solutions exactly as described in the procedure. The aliquots taken above contain, respectively, 0.12, 0.24, 0.36, 0.48, 0.60, 0.90 and 1.2 mg Ti. Plot the percent transmission against the weight of titanium on coordinate paper. The relationship is linear.

Niobium is determined by difference. Find the total weight of titanium present in the five gram sample and multiply this weight by 1.6681 to convert it to TiO_2. Now deduct the weight of TiO_2 from the weight of combined oxides, Nb_2O_5 + TiO_2, previously obtained. The difference is Nb_2O_5, of which 69.90% is niobium.

DETERMINATION OF TITANIUM AND VANADIUM IN MOLYBDENUM-TITANIUM-VANADIUM ALLOYS

Outline of Method

Vanadium and titanium are determined on separate samples. Vanadium is determined by the procedure developed for the determination of vanadium in the binary molybdenum-vanadium alloy. The presence of titanium causes no interference.

* According to Milner, Proctor and Weinberg (Ind. and Eng. Chem., Anal. Ed., Vol 17, No. 3, p 142), maximum absorption for the titanium complex occurs at this wave length and therefore the greatest sensitivity.

Titanium, together with some vanadium, is separated from molybdenum by repeated precipitation with ammonium hydroxide, and the combined oxides weighed. The vanadium in the combined oxides is then determined volumetrically and calculated to V_2O_5 which is deducted.

Procedure: Weigh a sample of such size that the titanium hydroxide precipitate can be conveniently handled. In general, 0.05 g titanium is the maximum weight for convenient manipulation. Carry along a blank of pure molybdenum metal of the same weight as the sample being analyzed. Dissolve the alloy in a mixture of HCl and HNO_3 containing 10 ml HCl and 3 ml HNO_3 for each gram of sample. Heat gently until the sample is decomposed. Add 100 ml H_2O and 5 drops of phenol red indicator (0.1 g dissolved in 100 ml of 25% ethyl alcohol). Now add concentrated NH_4OH from a burette until the first permanent red color of the indicator appears, then add 0.7 ml excess NH_4OH. Add a little ashless filter paper pulp and heat to boiling. Boil for one minute, then remove the solution from the hot plate and cool to room temperature. Filter through a No. 42 Whatman paper or its equivalent. Rinse the beaker several times with cold 2% NH_4Cl and pour the rinsings through the filter. Wash the paper and precipitate four times with cold 2% NH_4Cl. Discard the filtrate and washings.

Place the original beaker under the funnel and dissolve the precipitate by washing at least three times with hot HCl (1-1). Wash the paper twice with hot water, then once with cold 3% NH_4OH. Reserve the filter paper. Dilute the filtrate and washings to 100 ml, add phenol red indicator, then add NH_4OH until the solution is neutral to the indicator. Add 0.7 ml excess NH_4OH, a little ashless filter paper pulp and heat to boiling. Boil for one minute, remove from the hot plate and allow the precipitate to settle. Filter through the reserved filter paper and wash four times with hot 2% NH_4Cl.

Transfer the paper and precipitate to a platinum crucible. Dry, then ignite at a low temperature until the paper is destroyed. Then ignite for ten minutes at 1800 F. Cool, add 2 ml H_2SO_4 and 5 ml HF. Evaporate on an asbestos pad on the hot plate until fumes of SO_3 are freely evolved. Cool, transfer the H_2SO_4 solution to a 250 ml beaker, rinsing the crucible thoroughly with water. Dilute the solution in the beaker to 100 ml with 10% H_2SO_4, add 5-6 drops phenol red indicator and neutralize with concentrated NH_4OH. Add an excess of 0.7 ml NH_4OH, a little ashless filter paper pulp and heat to boiling. Boil for one minute, allow the precipitate to settle, then filter through No. 40 Whatman filter paper. Carefully police the beaker, then wash the precipitate on the paper four times with hot 2% NH_4Cl. Transfer the paper and precipitate to a weighed platinum crucible, dry, then ignite at a low temperature until the carbon is destroyed. Finally, ignite for 30 minutes at 1800 F. Cool and weigh. The residue obtained at this point contains all of the titanium as TiO_2 plus part of the vanadium which is present as V_2O_5. Deduct the weight of the blank and the resulting weight is the combined weight of TiO_2 plus V_2O_5.

Fuse the combined oxides with 5 g $K_2S_2O_7$ and dissolve the melt in 100 ml of solution containing 25 ml H_2SO_4 (1-1). Rinse and remove the crucible and transfer the solution to a 500 ml Soxhlet flask. Dilute to about 200 ml and cool the solution to room temperature. Add 10 ml of approximately 0.03 N

ferrous sulfate solution to reduce the vanadium. Now add 15 ml of a freshly prepared solution of 10% $(NH_4)_2S_2O_8$ solution and shake for at least one minute. Titrate the vanadium with standard 0.01 normal $KMnO_4$. Calculate the vanadium to V_2O_5 and deduct this weight from the weight of combined V_2O_5 and TiO_2. The remainder is TiO_2.

Factors: 1 ml 0.01 normal $KMnO_4$ = 0.0009095 g V_2O_5
$TiO_2 \longrightarrow Ti = 0.5995$

DETERMINATION OF TITANIUM AND ZIRCONIUM IN MOLYBDENUM-TITANIUM-ZIRCONIUM ALLOYS

Outline of Method

Titanium and zirconium are determined on separate samples. In the titanium determination the titanium, together with the zirconium, is separated from molybdenum by repeated precipitation with ammonium hydroxide. Titanium is then determined colorimetrically.

Zirconium is separated from molybdenum and most of the titanium by precipitation as phosphate from sulfuric acid solution. The phosphate is converted to carbonate by sodium carbonate fusion and the zirconium finally precipitated with ammonium hydroxide. A small amount of titanium which always accompanies the zirconium is determined colorimetrically and the weight of impure zirconium dioxide is corrected for the titanium.

Titanium

Dissolve a sample containing not more than 0.02 g titanium in a mixture of HCl and HNO_3, using 10 ml HCl and 4 ml HNO_3 for each gram of sample. When action is complete, cool somewhat and add 100 ml H_2O. Add 5 drops of phenol red indicator (0.1 g in 100 ml 25% ethanol), neutralize with NH_4OH and add 0.7 ml excess. Add a little ashless filter paper pulp, heat to boiling and boil for one minute. Remove from the hot plate and allow to cool to room temperature. Filter through an 11 cm Whatman No. 42 filter paper and wash three times with cold 2% NH_4NO_3 solution. Discard the filtrate and washings. Place the original beaker under the funnel and dissolve the precipitate from the paper by repeated washing with hot HCl (1-1). At least three washings are necessary. Now wash the paper three times with hot water, then once with cold 3% NH_4OH. Reserve the filter paper and any insoluble residue it may contain.

Again add phenol red indicator and precipitate the titanium, together with the zirconium, by addition of an excess of NH_4OH. Add a little ashless filter paper pulp, heat to boiling, let settle and filter while hot through the reserved filter paper. Wash as before, then redissolve with HCl, catching the filtrate in the original beaker. Wash with hot water, place the paper and any insoluble residue in a platinum crucible and reserve. Add

phenol red indicator to the filtrate and make a third precipitation with NH_4OH exactly as before. Filter through No. 40 Whatman paper and wash with hot 2% NH_4NO_3 solution. Place the paper and precipitate in the platinum crucible containing the reserved filter paper, dry, then ignite at 1800 F until all carbon is destroyed.

Fuse the residue containing the combined oxides with three of four grams of $KHSO_4$. Dissolve the cooled melt in 100 ml of 10% H_2SO_4. Transfer this solution to a 250 ml volumetric flask and dilute the solution to exactly 250 ml with 10% H_2SO_4. Transfer an aliquot portion of this solution containing a maximum of approximately 1.2 mg of titanium to a 100 ml volumetric flask and dilute to the mark with 10% H_2SO_4. Transfer a portion of this solution to the spectrophotometer cuvette and adjust the instrument to 100% transmission with the solution in the beam of light at a wave length of 420 millimicrons. Now take 10-15 ml of the solution in a 50 ml beaker and develop the yellow titanium color by the addition of three drops of 3% H_2O_2. Measure the transmission of this solution in the spectrophotometer at 420 millimicrons* and obtain the weight of titanium present in the aliquot from the calibration curve.

A standard solution of titanium containing 0.012 mg Ti/ml was prepared from reagent grade TiO_2. Dilute 10, 20, 30, 40, 50, 75 and 100 ml of this solution with 10% H_2SO_4 to 100 ml in volumetric flasks. Now measure the transmission of portions of these solutions exactly as described in the procedure. The aliquots taken above contain, respectively, 0.12, 0.24, 0.36, 0.48, 0.60, 0.90 and 1.2 mg Ti. Plot the percent transmission against the weight of titanium on coordinate paper. The relationship is linear.

Zirconium

Zirconium is separated from molybdenum by the same procedure which is used for the determination of zirconium in the binary zirconium-molybdenum alloy. However, some titanium always accompanies the zirconium in this procedure, and the final weighed precipitate must be corrected for any TiO_2 present.

Fuse the ignited residue containing all of the zirconium, together with a little titanium, with 4 to 5 grams of $K_2S_2O_7$. Dissolve the melt in 100 ml of 10% H_2SO_4. Transfer the solution to a 200 ml volumetric flask and dilute to the mark with 10% H_2SO_4. Mix thoroughly, take an aliquot portion containing a maximum of one milligram of titanium and transfer it to a 100 ml volumetric flask. Dilute this solution to 100 ml with 10% H_2SO_4. Determine the titanium colorimetrically as described above under the method for titanium.

Calculate the total weight of titanium found in the zirconium precipitate to TiO_2. The factor for converting Ti to TiO_2 is 1.6681. Deduct the blank plus the weight of TiO_2 found from the weight of impure ZrO_2 and the remainder is pure ZrO_2.

Factor: $ZrO_2 \longrightarrow Zr = 0.7403$

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* According to Milner, Proctor and Weinberg (Ind. and Eng. Chem., Anal. Ed., vol 17. No. 3. p 142), maximum absorption for the titanium complex occurs at this wave length and therefore the greatest sensitivity.

DETERMINATION OF VANADIUM AND ZIRCONIUM IN MOLYBDENUM-VANADIUM-ZIRCONIUM ALLOYS

Synthetic mixtures were prepared containing 3 grams molybdenum, 0.0133 grams vanadium and 0.0125 grams zirconium. Tests with these solutions indicated that:

(a) The method for the determination of vanadium in binary molybdenum-vanadium alloys is also applicable to this ternary alloy.

(b) Complete recovery of zirconium is obtained from this ternary alloy by the same method used for the determination of zirconium in the binary molybdenum-zirconium alloys. The presence of vanadium causes no interference.

APPENDIX B

METALLOGRAPHIC TECHNIQUES FOR MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS

by William C. Coons

INTRODUCTION

The information presented in this appendix constitutes a general summary of the metallographic techniques employed in the preparation of molybdenum and molybdenum-base alloy specimens.

POLISHING TECHNIQUES

The majority of samples of molybdenum and molybdenum-base alloys prepared for metallographic study were polished electrolytically. The mounted samples were ground through 3/0 and, in some instances, 4/0 metallographic paper, then polished in an electrolyte consisting of 25 cc of concentrated H_2SO_4 and 175 cc of methyl alcohol. A direct current potential was maintained, producing a current flow of about one ampere per square centimeter of specimen area. The electrical circuit was such that the specimen was the anode, and a small piece of stainless steel sheet was the cathode. Polishing time varied with specimen size, the average time being in the vicinity of 1-1/2 minutes.

In the case of a few materials in which electrolytic polishing resulted in preferential attack of constituents, a relatively short period of electrolytic polishing was followed by conventional polishing and/or polish-etch-buffing. Diamond paste and "C-RO" polishing compound were used on metallographic wheels in conventional polishing. The term "polish-etch-buff" has been applied to a technique whereby "C-RO" polishing compound and a few drops of a concentrated solution of $K_3Fe(CN)_6$ are added to the polishing wheel.

ETCHING

The etchants usually used in connection with molybdenum and molybdenum-base alloys are tabulated below:

	Composition	Use
1.	10 g NaOH 30 g $K_3Fe(CN)_6$ 100 ml H_2O	immersion 20 sec
2.	1 g NaOH 35 g $K_3Fe(CN)_6$ 150 ml H_2O	immersion 4-6 min

3.	20-30 ml Solution 2 100 ml H_2O	immersion 12-16 min
4.	0.5 g $C_2O_4H_2$ 100 ml H_2O	electrolytic 4-6v, 10-20 sec
5.	10 ml HCl 4 ml H_2SO_4 120 ml CH_3OH	electrolytic 4-6v, 10-20 sec
6.	3 ml HNO_3 100 ml H_2O	immersion in hot solution 3-5 min
7.	2 ml HF 100 ml H_2O	immersion in hot solution 3-5 min

Generally speaking, the dilute NaOH-$K_3Fe(CN)_6$ etchant (No. 3) has proved to be satisfactory for unalloyed molybdenum, most solid solution molybdenum-base alloys, and some alloys containing additions in excess of the limit of solid solubility. The more concentrated NaOH-$K_3Fe(CN)_6$ etchants have been used in certain special instances or when only a cursory examination has been required, since there is less uniformity of attack with the concentrated reagent than with the dilute reagent.

A list of etching techniques satisfactory for molybdenum-base alloys containing excess phase constituents other than Mo_2C is presented below:

Alloy System	Etchant	Remarks
Mo-Al	2	
Mo-B	3	Second phase observed in as-polished specimen
Mo-Be	1	Second phase observed in as-polished specimen
Mo-Co	4 1	General structure Differentiation between eta (brown) and epsilon (unattacked) phases
Mo-Fe	5 1	General structure Darkened eta phase (solid solution of iron in molybdenum)
Mo-N	3	
Mo-Ni	5	

Alloy System	Etchant	Remarks
Mo-Si	2	Low silicon content (no second phase)
	1	High silicon content
Mo-Ti	2	Revealed fine network precipitate, probably a complex carbide form
Mo-Zr	2	Revealed fine network precipitate, probably a complex carbide form
	6	Attacked second phase without attacking light tan particles (zirconium oxide)
	7	Attacked zirconium oxide particles without attacking second phase
Mo-U	3	

APPENDIX C

HOT HARDNESS OF MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS AS CAST

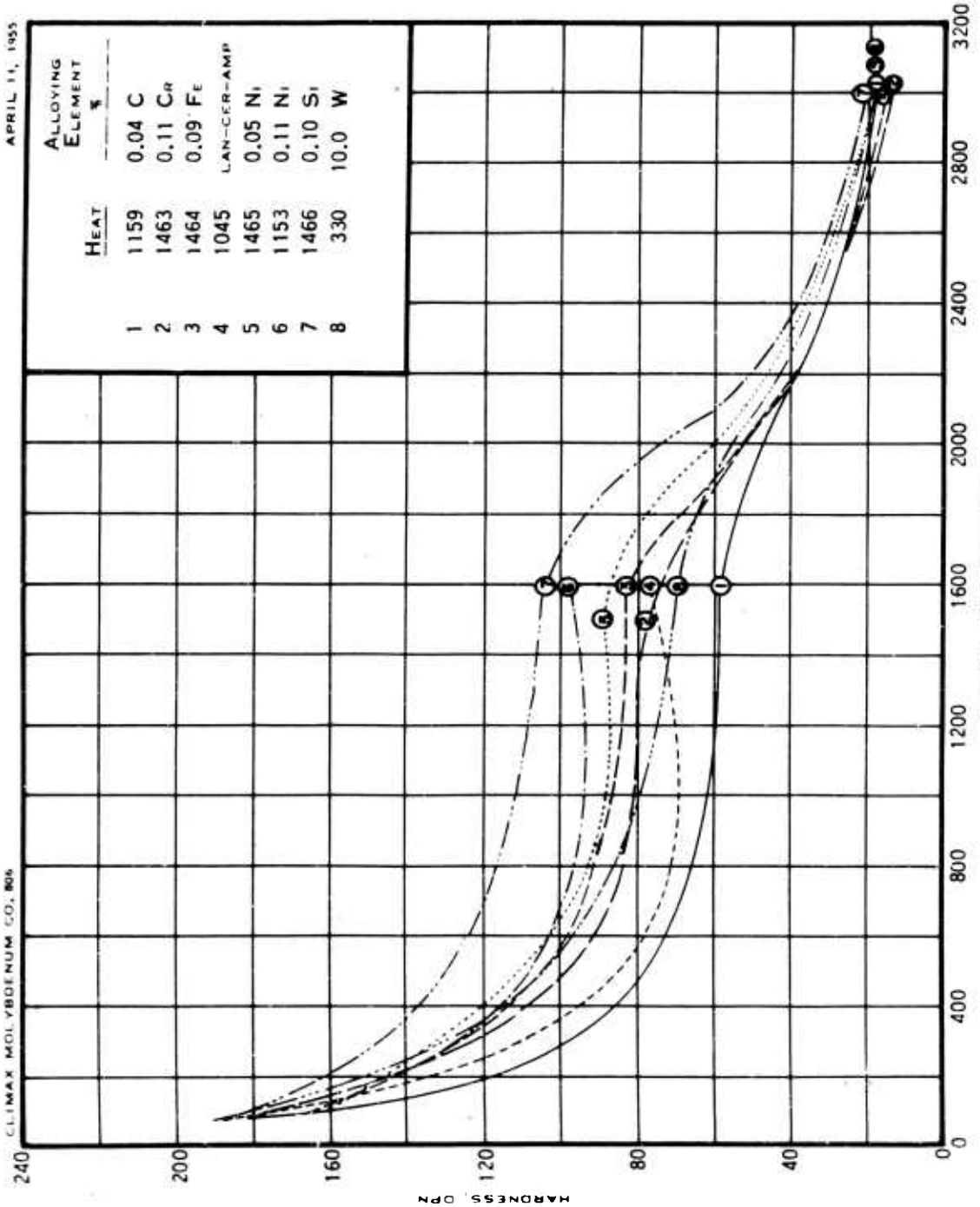


FIGURE C1 - HOT HARDNESS OF SOME MOLYBDENUM-BASE ALLOYS AS CAST

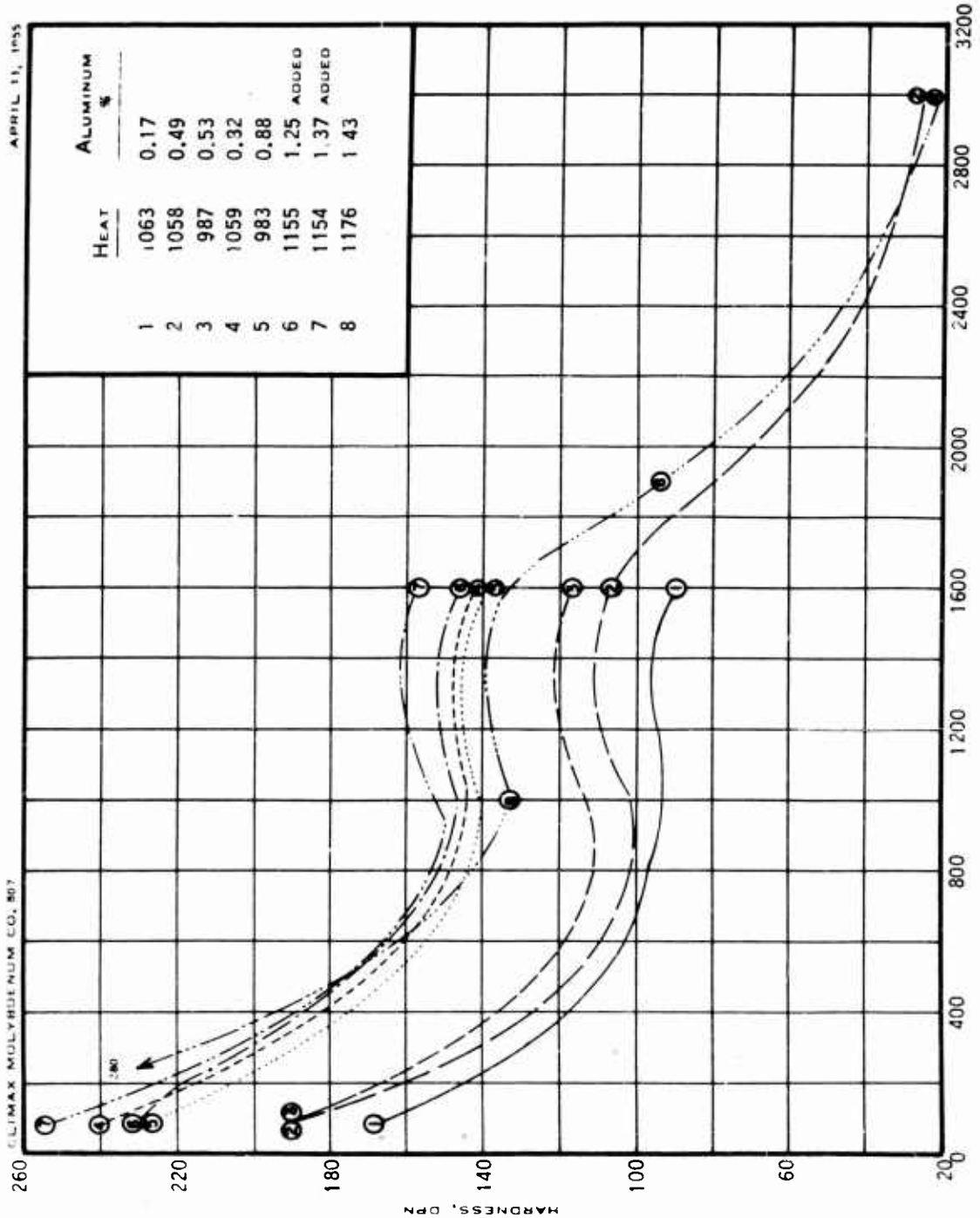


FIGURE C2 - HOT HARDNESS OF SOME MOLYBDENUM-ALUMINUM ALLOYS AS CAST

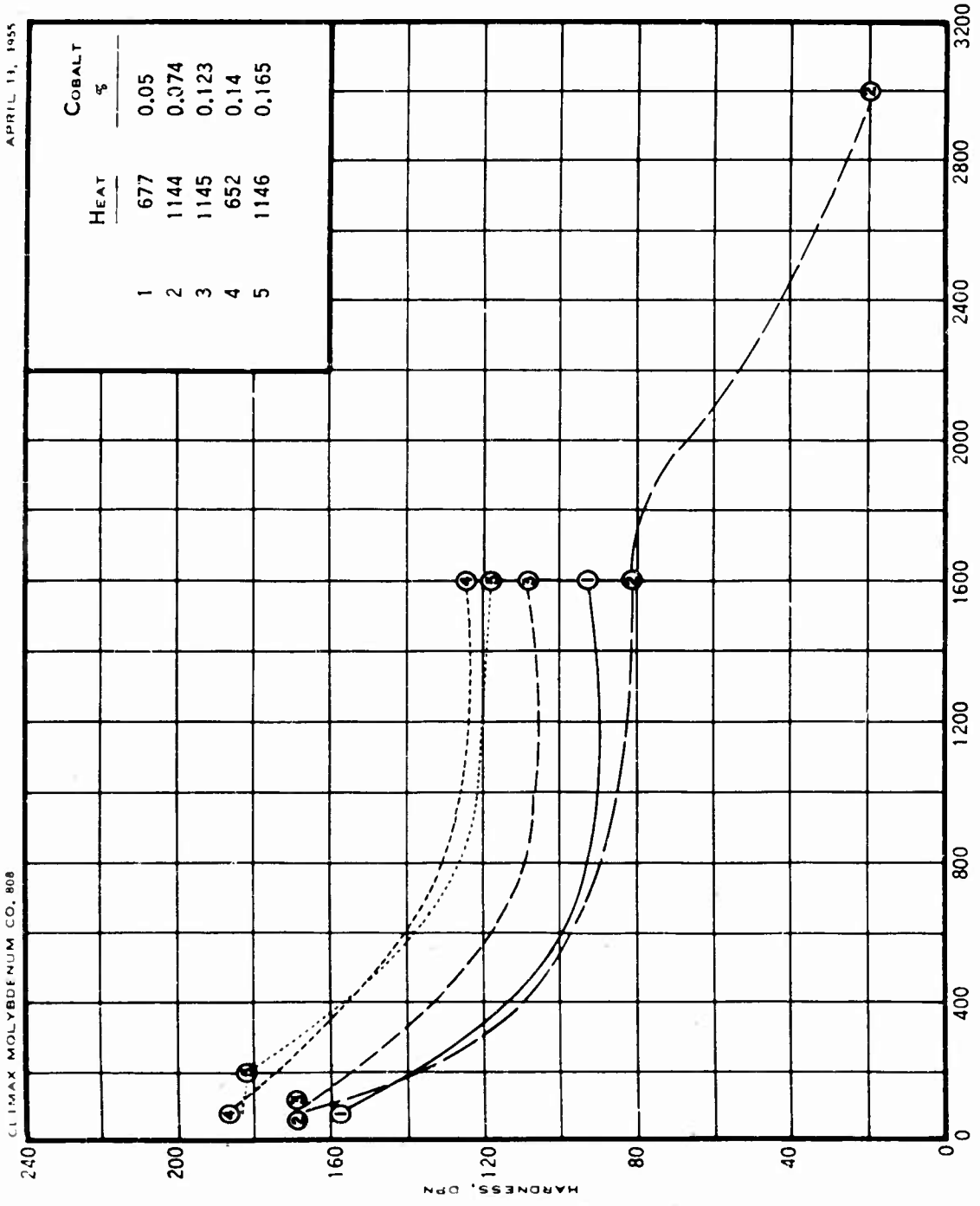


FIGURE C3 – HOT HARDNESS OF SOME MOLYBDENUM–COBALT ALLOYS AS CAST

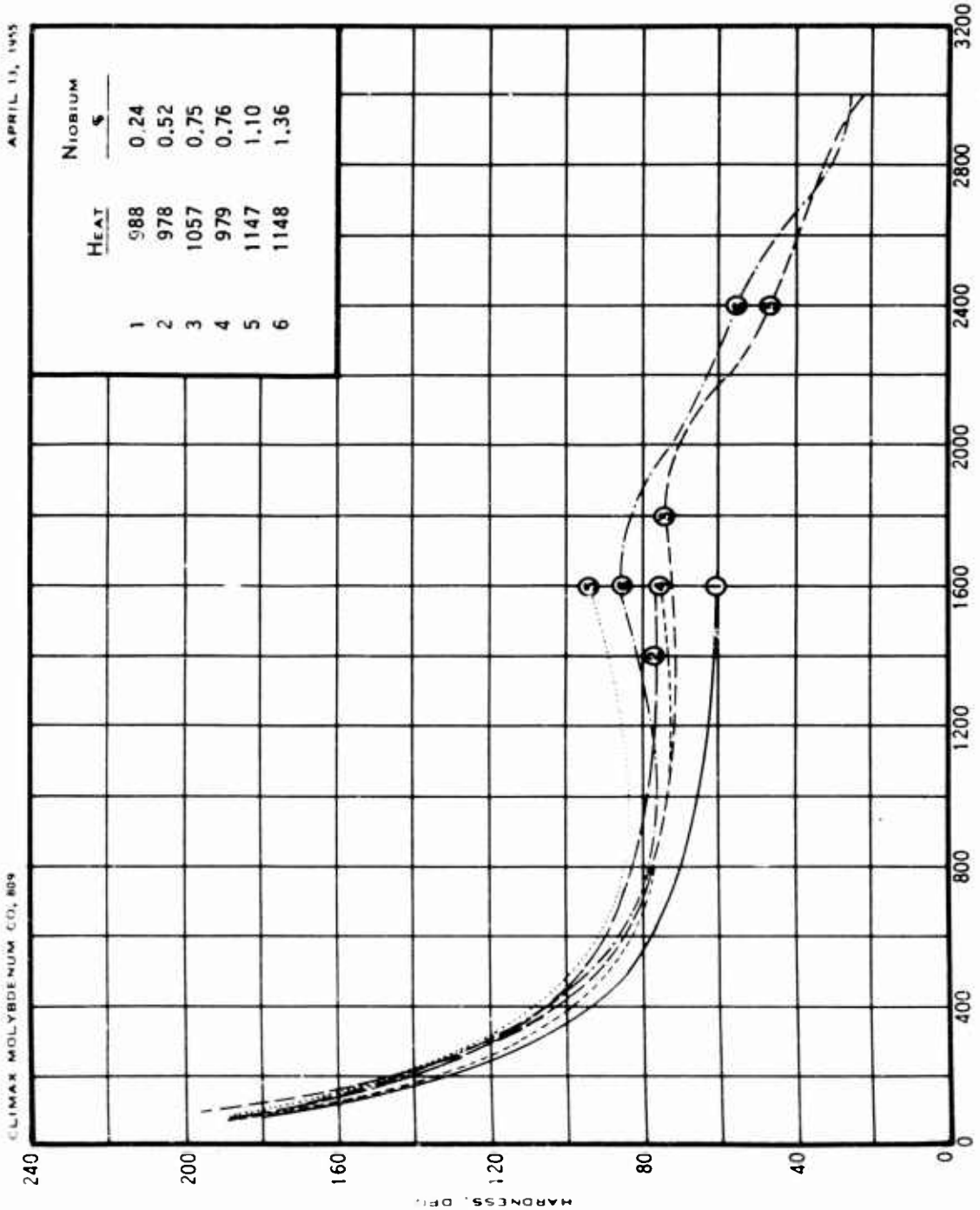


FIGURE C4 – HOT HARDNESS OF SOME MOLYBDENUM–NIOBIUM ALLOYS AS CAST

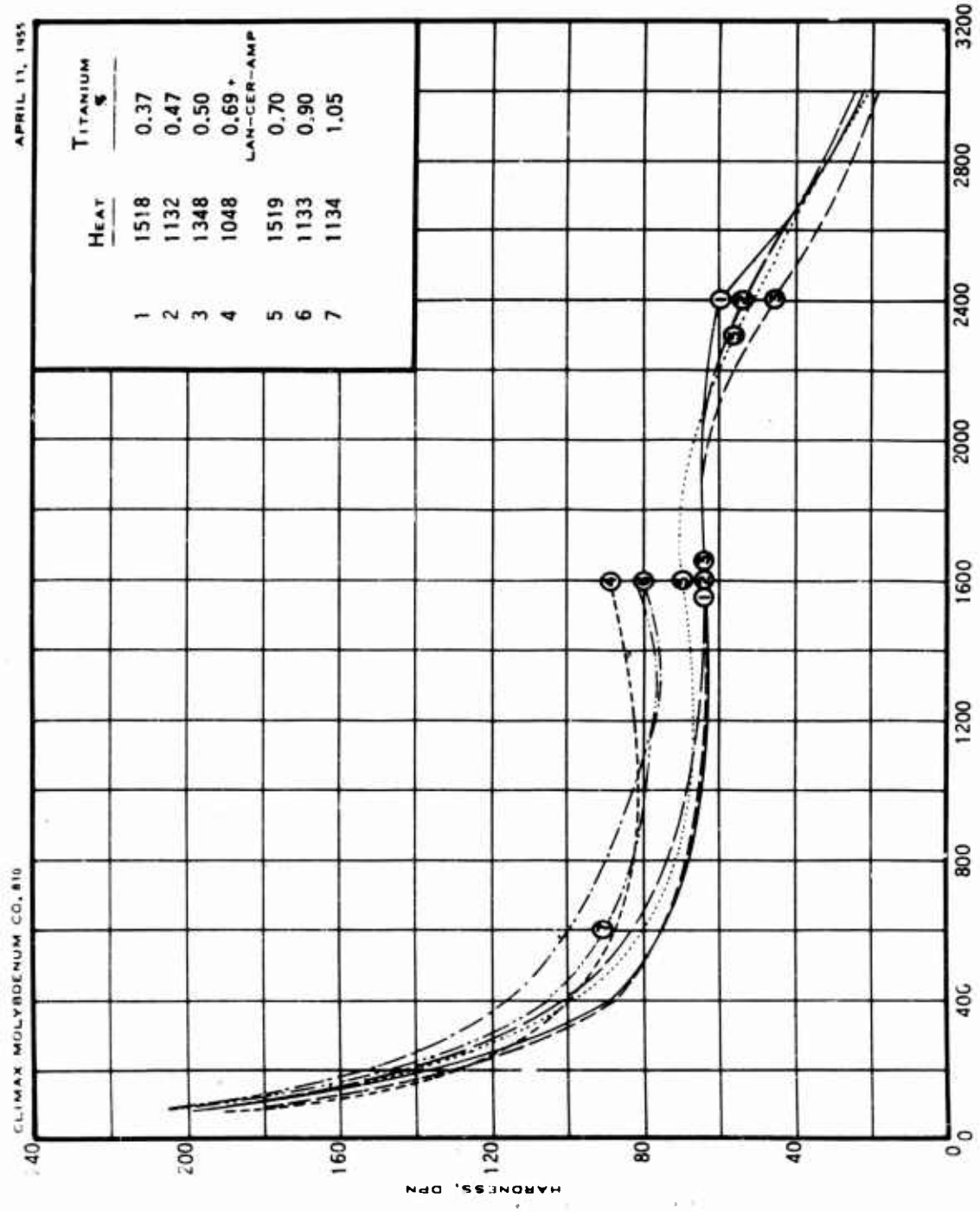


FIGURE C5 – HOT HARDNESS OF SOME MOLYBDENUM–TITANIUM ALLOYS AS CAST

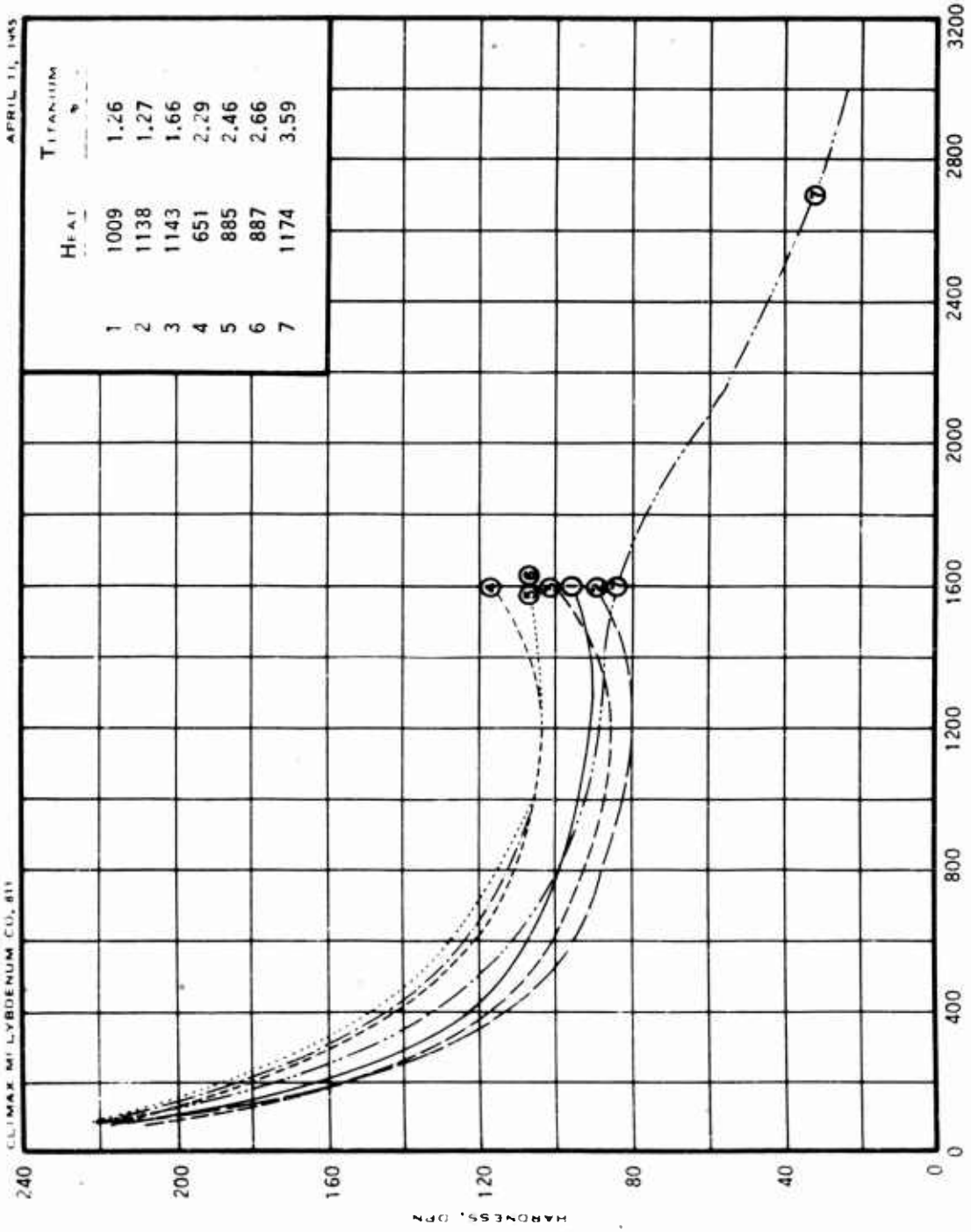


FIGURE C6 – HOT HARDNESS OF SOME MOLYBDENUM – TITANIUM ALLOYS AS CAST (CONTINUED)

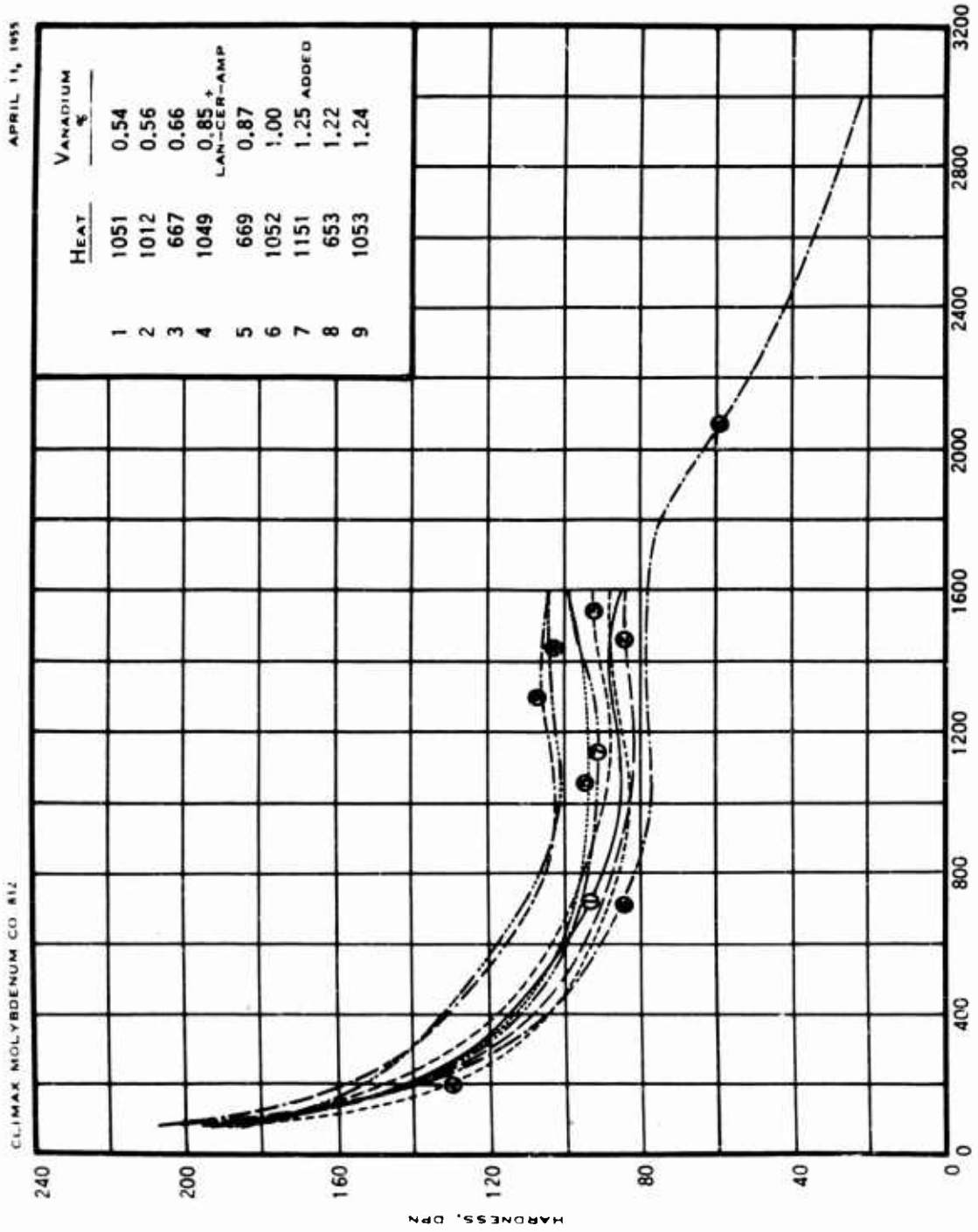


FIGURE C7 – HOT HARDNESS OF SOME MOLYBDENUM–VANADIUM ALLOYS AS CAST

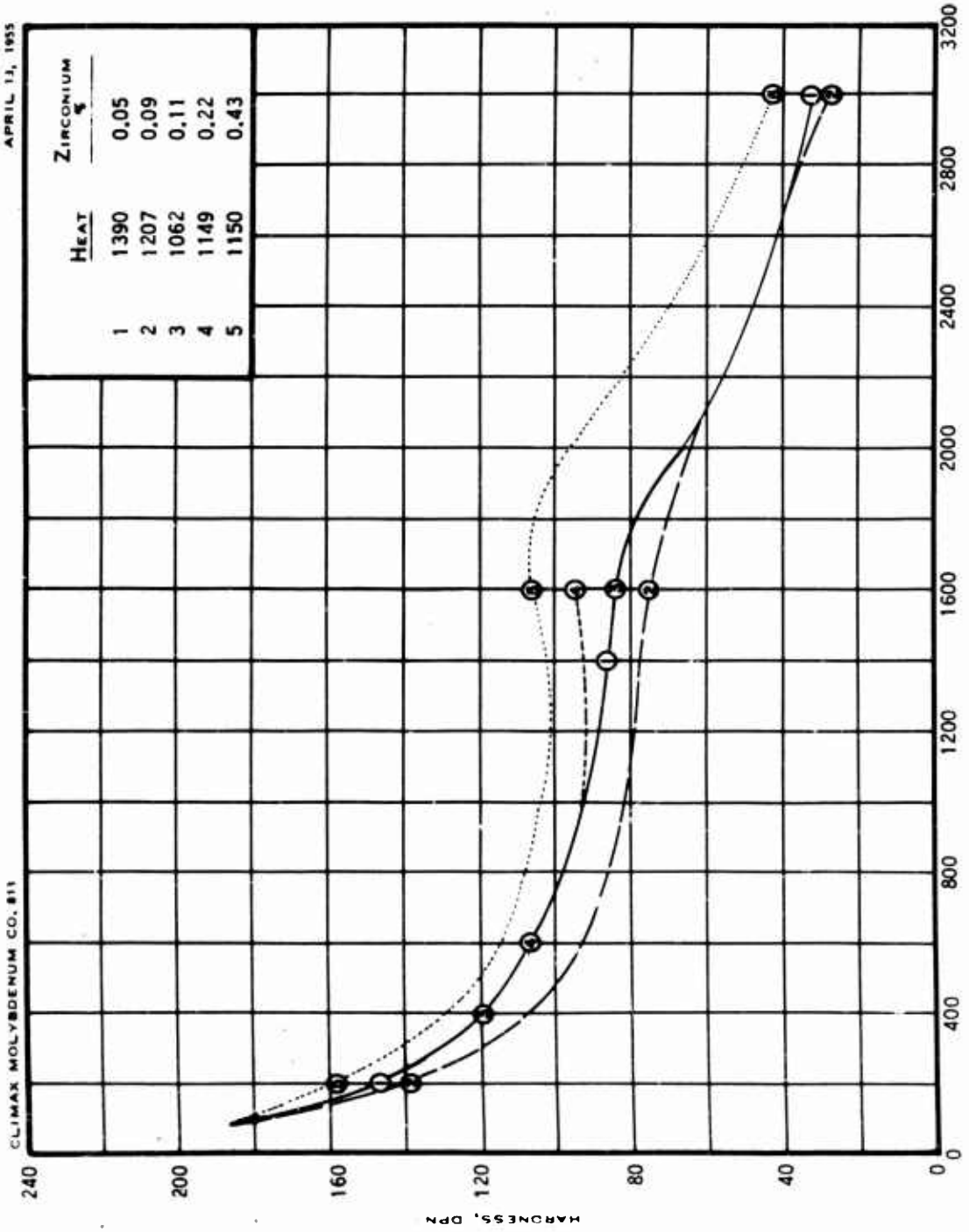


FIGURE C8 – HOT HARDNESS OF SOME MOLYBDENUM–ZIRCONIUM ALLOYS AS CAST

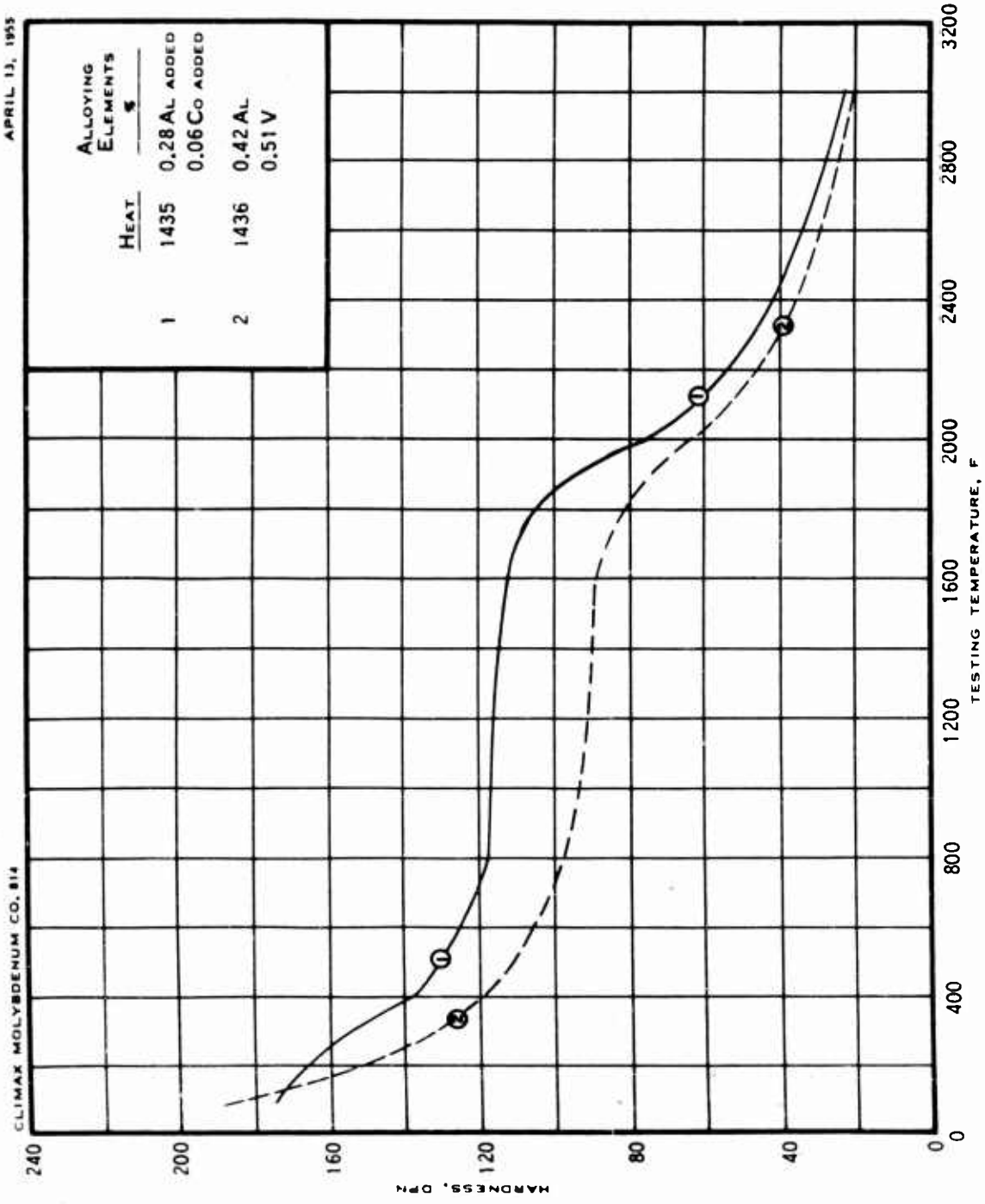


FIGURE C9 — HOT HARDNESS OF Mo-Al-V AND Mo-Al-Co ALLOYS AS CAST

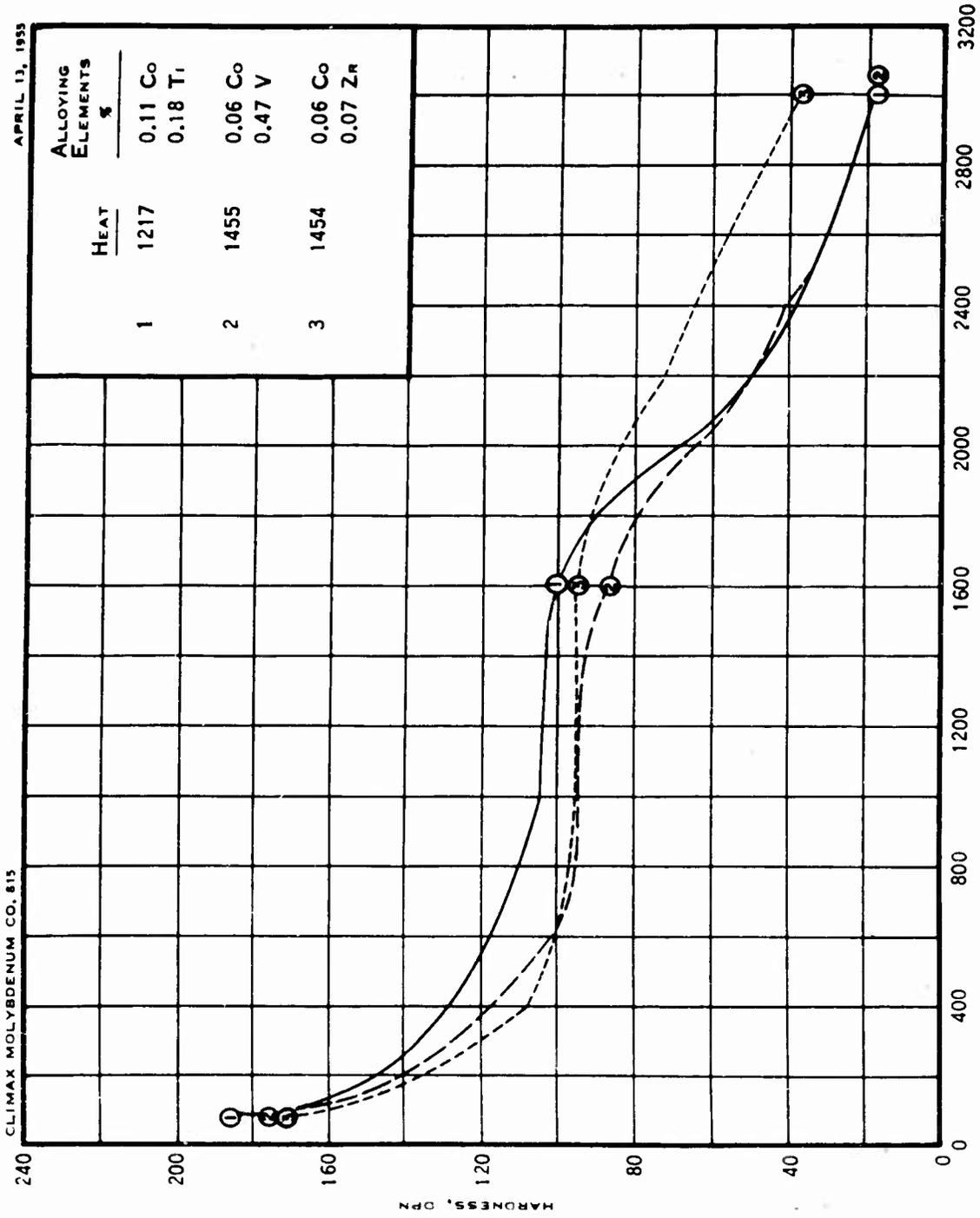


FIGURE C10– HOT HARDNESS OF Mo–Co–Ti, Mo–Co–V, AND Mo–Co–ZR ALLOYS AS CAST

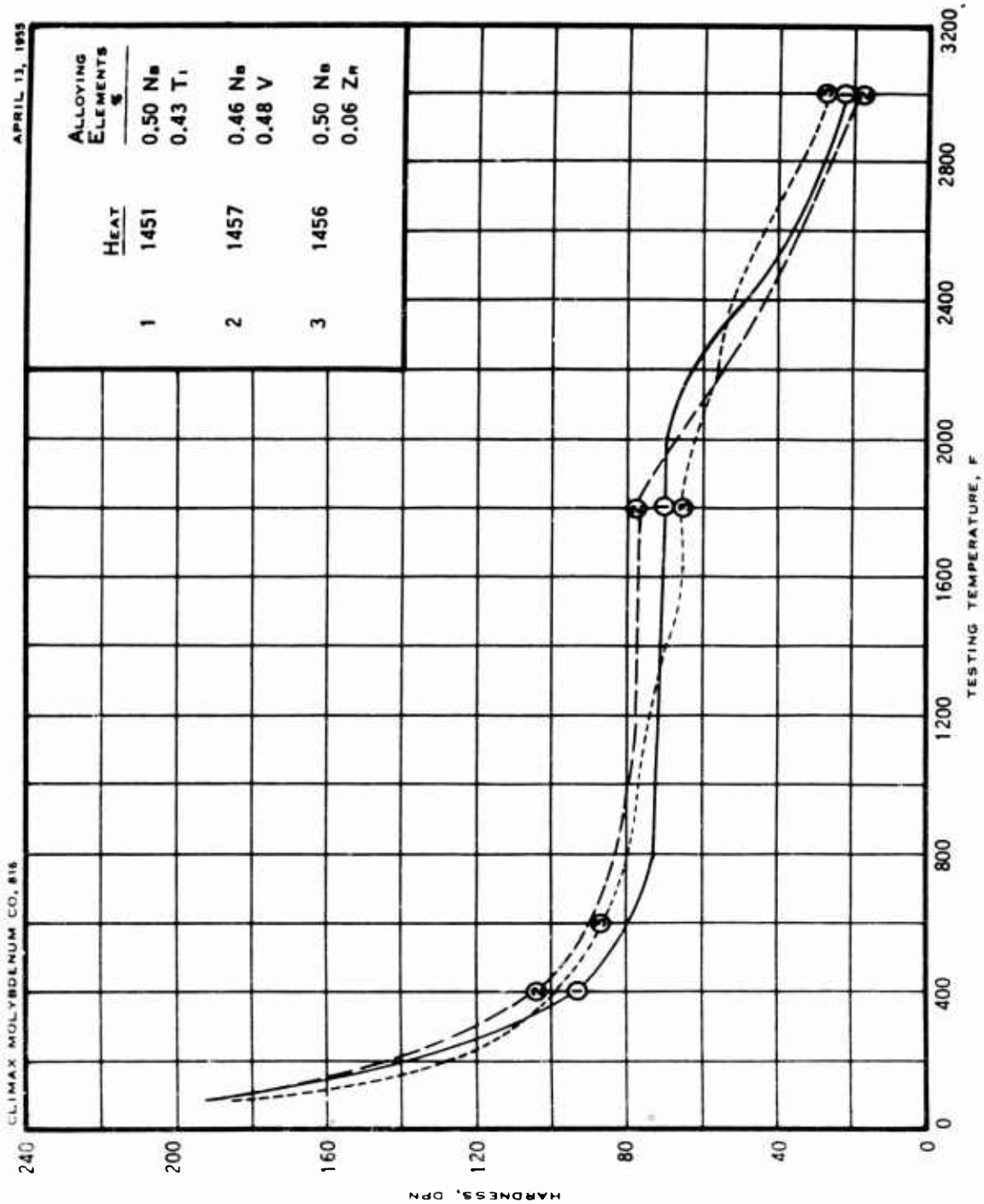


FIGURE C11 – HOT HARDNESS OF Mo-Nb-Ti, Mo-Nb-V, AND Mo-Nb-Zr ALLOYS AS CAST

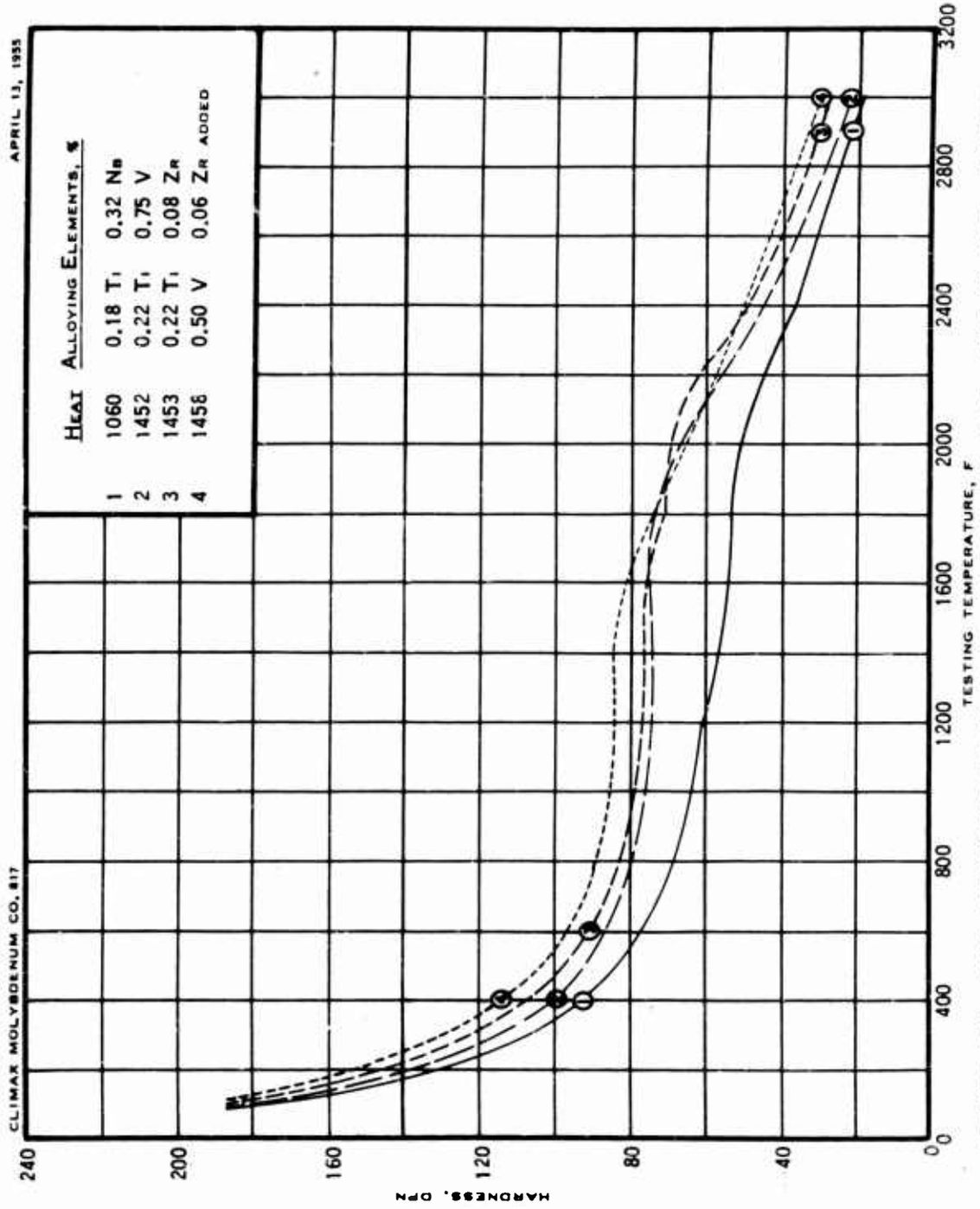


FIGURE C12– HOT HARDNESS OF Mo-Nb-Ti, Mo-Ti-V, Mo-Ti-Zr, AND Mo-V-Zr ALLOYS AS CAST

APPENDIX D

MECHANICAL PROPERTIES OF WROUGHT MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS

TABLE D1

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	(1) Elongation %	Reduction of Area %
		Bar 937 - Unalloyed Mo, 0.015% C				
5/8	as rolled	81	78,800*	102,200	40	61.1
		750	53,400*	79,300	20	82.4
		1200	49,800*	69,600	18	84.2
		1600	37,000*	52,000	24	88.6
	str. relieved (1800 F)	81	82,900*	97,200	42	69.0
		750	57,200*	62,400	20	81.2
		1200	48,100*	65,200	22	86.1
		1600	33,400*	52,400	24	88.6
	recrystallized (2150 F)	81	55,900	68,200	42	37.8
		750	21,000	39,200	60	84.7
		1200	11,000	33,600	57	84.8
		1600	7,600*	25,100	60	85.9
		Bar 1159 - Unalloyed Mo, 0.040% C				
1	as rolled	72	72,200*	92,400	30.5	35.5
		750	-	65,700	20	79.0
		1200	57,900*	72,500	16	79.0
		1600	41,900*	51,100	21	85.4
	str. relieved (1800 F)	81	75,400	89,600	29	37.9
		750	29,200	63,800	19.5	77.9
		1200	-	59,800	17.5	80.2
		1600	43,200*	51,000	20	83.6
	recrystallized (2250 F)	74	48,100	69,200	45	32.8
		750	16,600	38,600	51	83.2
		1200	10,300	34,300	48	87.5
		1600	-	27,400	49	89.9

(1) percent elongation in 1 in. for specimens from 1/2 in. and 5/8 in. dia bars; percent elongation in 2 in. for specimens from 1 in. dia bars

* 0.1% offset yield strength taken from stress-strain plot; all other yield strength values from drop in load

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
	Bar 1045 - Unalloyed Mo Deoxidized with Rare Earth Metals					
5/8	as rolled	78	83,300*	105,300	25	34.5
		1600	45,800*	55,000	11	51.3
	str. relieved (1800 F)	78	81,500*	100,900	9	13.8
		1600	43,400*	55,000	19	82.8
	recrystallized (2400 F)	78	46,600	62,500	2	12.3
		1600	11,300*	25,600	55	86.4
	Bar 1063 - 0.17% Al					
5/8	as rolled	78	75,200*	96,300	36	57.1
		750	59,400*	76,400	19	70.6
		1200	56,100*	68,900	16	77.1
		1600	40,700	58,700	20	76.1
	str. relieved (1800 F)	78	72,400*	94,700	40	63.1
		750	54,600*	74,100	24	74.7
		1200	54,900*	66,400	18	71.3
		1600	45,200*	60,600	18	74.1
	recrystallized (2200 F)	78	41,300	66,700	18	14.4
		750	21,900	43,500	58	81.1
		1200	15,800	39,800	50	79.8
		1600	10,800	29,100	49	80.9
1	as rolled	78	-	75,600	2	1.7
		750	53,600*	61,400	20	75.1
		1200	-	55,600	17.5	76.1
		1600	39,400*	47,200	21.5	81.0
	str. relieved (1800 F)	78	64,500	74,600	1.5	1.1
		750	-	58,900	20.5	76.8
		1200	-	55,200	19	75.0
		1600	-	48,200	18.5	79.3
	recrystallized (2250 F)	79	34,200	65,200	21.5	18.8
		780	10,700	39,300	56	80.3
		1200	10,300	36,900	46.5	79.4
		1600	12,500	25,900	56.5	88.7

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1058 - 0.49% Al			
1	as rolled	78	82,200*	89,200	1.5	0.6
		750	-	75,700	18.5	71.8
		1200	66,300*	71,700	17	71.9
		1600	55,300	61,500	17.5	76.0
	str. relieved (1800 F)	78	81,300	85,500	1	0.5
		750	67,700	74,100	19	72.3
		1200	65,500	70,800	16.5	69.5
		1600	-	62,300	18.5	78.8
	recrystallized (2300 F)	79	45,900	64,000	6	5.6
		750	26,200	42,200	40	73.1
		1200	25,500	46,600	41	81.4
		1600	13,700	34,100	50.5	83.2
			Bar 987 - 0.53% Al			
5/8	as rolled	78	102,000*	121,200	2	0.2
		750	79,600*	101,900	14.5	57.5
		1200	74,700*	91,400	16	66.9
		1600	55,400*	76,800	18	63.7
	str. relieved (1800 F)	78	98,200	105,800	3	2.0
		750	79,000*	88,400	19	60.4
		1200	66,600*	82,900	18	82.1
		1600	55,300*	72,100	19	68.6
	recrystallized (2200 F)	78	none	46,100	0	0
		750	43,800	56,200	42	72.3
		1200	37,900	51,400	41	80.0
		1600	17,700*	38,100	42	54.7
			Bar 677 - 0.05% Co			
5/8	as rolled	77	105,500	119,700	7	6.7
		750	-	101,000	15	61.7
		1200	-	93,800	14.5	61.8
		1600	-	76,900	25	72.5

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 677 - 0.05% Co (continued)			
5/8	str. relieved (1800 F)	76	106,500	117,200	28	58.2
		750	-	94,700	16	65.0
		1200	-	89,900	14	64.8
		1600	-	80,800	20	69.9
	recrystallized (2150 F)	76	74,900	78,600	49	64.6
		750	44,400	52,000	45	75.9
		1200	41,000	49,700	40	77.9
		1600	-	42,600	55	57.4
7/8	as rolled	75	88,700*	110,400	1	0.8
		1000	79,600*	94,700	12	58.3
		1600	71,800*	80,200	19	67.5
	str. relieved (1800 F)	75	99,800	104,700	1.5	1.2
		750	87,900*	92,600	15	59.5
		1200	81,700*	88,500	11.5	59.9
		1600	-	80,600	18	67.5
	recrystallized (2150 F)	75	74,300	76,900	43	32.6
		1000	38,000	48,200	43	78.3
		1600	13,700	41,400	45	81.2
			Bar 1144 - 0.074% Co			
5/8	as rolled	78	110,900	113,300	35	70.0
		750	94,300	94,300	22	78.2
		1200	84,900	87,000	19	80.0
		1600	-	75,700	26	80.0
	str. relieved (1700 F)	80	111,500	111,500	36	68.3
		750	95,000	95,000	23	77.8
		1200	-	87,800	19	77.4
		1600	44,600*	68,000	25	93.6
	recrystallized (2000 F)	80	66,900	66,900	5	4.4
		1200	49,100	53,800	43	82.4
		1600	-	46,100	62	57.5

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1144 - 0.074% Co (continued)			
1	as rolled	79	78,700*	97,000	19.5	23.2
		750	38,000*	75,800	20	73.7
		1200	62,300*	73,200	16	80.0
		1600	53,500*	66,900	23	85.3
	str. relieved (1800 F)	80	82,500	94,900	20.5	19.9
		750	68,500	73,900	18.5	74.4
		1200	44,800*	70,900	16	78.9
		1600	57,000*	67,400	24	79.3
	recrystallized (2150 F)	83	60,800	67,100	10.5	9.8
		750	42,200	48,500	45	76.7
		1200	36,400	46,700	37.5	84.5
		1600	14,200	41,700	46	91.5
			Bar 1463 - 0.11% Cr			
1/2	as rolled	75	80,800*	98,600	41	69.8
		1600	39,700*	61,100	25	89.5
	str. relieved (1800 F)	75	88,900*	99,000	44	71.1
		1600	44,800*	55,000	32	86.2
	recrystallized (2000 F)	75	72,600	73,100	56	67.8
		1600	13,900*	35,600	64	86.4
			Bar 1465 - 0.05% Ni			
1/2	as rolled	75	97,000*	99,000	40	69.3
		1600	28,300*	56,500	58	82.8
	str. relieved (1800 F)	75	-	79,600	0	0
		1600	30,300*	55,400	48	80.4
	recrystallized (1950 F)	75	-	50,900	0	0
		1600	19,900	48,900	32	30.2

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 988 - 0.24% Nb			
5/8	as rolled	78	91,000*	106,100	28	41.9
		750	62,800*	84,800	19	78.9
		1200	60,000*	78,000	19	82.0
		1600	45,600*	65,900	16	77.7
	str. relieved (1800 F)	78	90,000	103,300	34	63.6
		750	64,000*	83,600	17	71.1
		1200	54,100*	77,300	18	74.5
		1600	58,200*	66,500	20	82.1
	recrystallized (2200 F)	78	68,700	71,300	40	28.7
		750	25,800	39,700	54	86.6
		1200	15,500	36,300	43	76.6
		1600	16,700*	30,100	61	82.7
1	as rolled	78	70,100*	80,600	1	0.6
		750	51,100*	52,600	20	80.0
		1200	48,100*	50,700	19	83.1
		1600	39,700	44,200	19	84.9
	str. relieved (1800 F)	78	62,200	69,300	1	0.5
		750	43,800*	45,600	23	81.4
		1200	40,000*	41,900	21	85.9
		1600	35,300*	37,300	21.5	87.7
	recrystallized (2500 F)	76	40,000	55,200	3	2.5
		750	13,100	33,400	57.5	76.7
		1200	9,300	28,100	49	84.4
		1600	8,500	25,600	73.5	93.2
			Bar 660 - 0.34% Nb			
5/8	as rolled	78	105,800	115,000	26	43.3
		750	-	92,900	17	72.3
		1200	-	85,300	17.5	72.9
		1600	-	75,900	20	71.7
	str. relieved (1800 F)	76	98,500	113,100	32	57.5
		750	-	89,900	19	71.2
		1200	-	83,100	18	73.5
		1600	-	71,700	18	75.5

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 660 - 0.34% Nb (continued)			
5/8	recrystallized (2150 F)	76	68,700	75,600	58	58.4
		750	31,100	45,500	54	82.1
		1200	-	41,500	48	83.9
		1600	-	33,700	46	86.1
7/8	as rolled	73	92,000	108,900	5	5.1
		1000	64,500*	84,000	14	70.3
		1600	59,900*	71,600	14	75.3
	str. relieved (1800 F)	73	98,900	106,200	1.5	1.4
		750	77,700*	88,600	13.5	68.2
		1200	71,200*	81,800	14	66.2
		1600	-	72,500	14	72.1
	recrystallized (2150 F)	73	60,100	73,500	51	54.5
		1000	18,000	40,000	49.5	83.9
		1600	11,000*	32,700	40	85.5
			Bar 978 - 0.52% Nb			
5/8	as rolled	78	92,600*	114,600	28	54.8
		750	71,500*	92,500	18	68.8
		1200	50,900*	80,800	16	78.9
		1600	51,100*	71,300	18	73.9
	str. relieved (1800 F)	78	94,300	109,400	29	59.4
		750	68,300*	89,400	17	70.7
		1200	67,200*	82,700	16	72.9
		1600	58,600*	72,200	16	72.3
	recrystallized (2200 F)	78	62,800	71,900	27	21.8
		750	32,100	42,600	60	85.3
		1200	17,500	39,500	48	85.5
		1600	-	34,900	52	88.8
1	as rolled	78	73,000*	84,600	1	0.6
		750	58,400*	59,600	21	83.2
		1200	48,000*	54,400	17.5	79.8
		1600	-	49,400	18.5	80.4

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 978 - 0.52% Nb (continued)			
1	str. relieved (1800 F)	78	68,000	78,600	1.5	0.5
		750	50,000*	55,100	20.5	81.8
		1200	47,400*	52,400	18	83.1
		1600	40,700	44,200	22	79.8
	recrystallized (2450 F)	80	42,800	65,500	10	8.5
		750	11,100	36,600	47	78.6
		1200	8,900	33,000	50.5	82.7
		1600	9,600*	30,000	40.5	86.9
			Bar 1057 - 0.75% Nb			
5/8	as rolled	78	94,400*	118,300	32	62.5
		750	74,200*	96,600	17	73.8
		1200	-	89,000	17	77.3
		1600	41,400*	73,100	12	71.1
	str. relieved (1800 F)	78	96,000*	118,100	33	66.7
		750	73,700*	96,000	17	71.2
		1200	67,400*	88,400	16	73.7
		1600	48,700*	76,700	17	67.6
	recrystallized (2250 F)	78	66,400	78,400	53	70.1
		750	27,300	46,300	52	81.2
		1200	18,900	43,600	48	76.5
		1600	13,600	36,000	61	83.6
1	as rolled	78	none	87,400	0.5	0.2
		750	-	83,100	19	78.5
		1200	78,000	80,700	17	76.1
		1600	53,400*	72,100	16	72.9
	str. relieved (1800 F)	78	none	84,000	0.5	0.2
		750	74,500*	82,400	19	75.7
		1200	70,800*	78,100	16	76.8
		1600	59,300	69,100	18.5	71.0
	recrystallized (2300 F)	80	55,800	73,400	15.5	13.5
		750	15,200	43,400	53	83.8
		1200	13,800	38,700	47.5	85.1
		1600	-	35,100	49	83.7

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1268 - 0.22% Ti			
5/8	as rolled	76	83,200*	111,100	33	68.7
		1600	50,900*	71,200	19	82.7
	str. relieved (1800 F)	77	89,000*	113,800	34	66.0
		1600	51,100*	73,800	18	80.5
	recrystallized (2350 F)	75	59,800	76,000	53	42.3
		1600	12,900*	34,800	53	89.2
			Bar 1132 - 0.45% Ti			
5/8	as rolled	82	96,700*	112,900	29	59.7
		750	78,900*	100,400	18	76.1
		1200	80,600*	101,300	18	82.6
		1600	81,000*	86,900	17	84.0
	str. relieved (1800 F)	80	99,100*	132,100	31	70.0
		750	89,000*	110,000	18	72.8
		1200	84,000*	100,500	17	74.1
		1600	76,500*	88,300	15	71.1
	recrystallized (2450 F)	81	60,000	75,500	55	38.0
		750	30,200	45,600	47	86.4
		1200	-	43,700	45	86.2
		1600	15,400	39,900	47	88.4
1	as rolled	77	89,000*	115,100	30	46.8
		750	-	90,800	16	75.5
		1200	68,300*	84,900	15.5	74.5
		1600	64,800*	78,400	15.5	75.0
	str. relieved (1800 F)	83	87,900*	113,000	20	25.4
		750	71,300*	90,700	17	73.5
		1200	62,600*	84,700	16	71.9
		1600	62,800*	77,700	16	75.7
	recrystallized (2500 F)	74	53,900	72,500	22	18.7
		750	11,800	42,400	45	83.9
		1200	10,300	39,200	42.5	87.7
		1600	14,500	37,500	48.5	87.6

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1348 - 0.46% Ti			
5/8	as rolled	75	87,900*	120,800	33	66.4
		1600	55,500*	81,300	18	79.6
	str. relieved (1800 F)	75	87,600*	119,000	36	66.5
		1600	54,500*	83,200	18	76.0
	recrystallized (2450 F)	75	63,700	77,500	36	34.8
		1600	13,900	39,600	50	89.9
			Bar 1393 - 0.12% Al, 0.50% Ti			
5/8	as rolled	77	88,000*	115,500	31	54.4
		1600	55,500*	75,600	18	69.4
	str. relieved (1800 F)	77	91,000*	113,300	30	54.6
		1600	52,100*	73,700	16	73.2
	recrystallized (2450 F)	78	47,500	69,900	12	11.3
		1600	17,500	44,600	38	61.7
			Bar 1048 - 0.69% Ti, 0.12% R.E.			
5/8	as rolled	80	91,000*	110,100	22	38.5
		750	66,200*	84,200	20	52.3
		1200	59,800*	73,800	18	82.3
		1600	47,500*	60,300	17	77.3
	str. relieved (1800 F)	80	82,400*	108,300	34	46.1
		750	61,500*	78,100	19	73.8
		1200	62,000*	69,400	18	81.5
		1600	-	60,700	17	76.6
	recrystallized (2500 F)	80	53,700	68,400	8	6.3
		750	16,900	38,300	67	81.6
		1200	11,400	34,700	65	84.9
		1600	13,400*	33,800	41	84.8

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1133 - 0.85% Ti			
5/8	as rolled	78	88,300*	117,800	36	60.5
		750	68,900*	92,700	20	81.7
		1200	62,900*	81,800	20	87.0
		1600	47,000*	69,600	24	90.1
	str. relieved (1800 F)	78	88,100*	117,200	32	63.4
		750	73,300*	89,600	19	84.1
		1200	60,100*	79,300	22	79.2
	recrystallized (2500 F)	82	66,800	74,900	44	35.9
		750	14,900	43,300	47	90.0
		1200	-	41,100	48	94.8
		1600	11,200	36,400	50	79.7
1	as rolled	76	75,800*	103,800	19	19.2
		750	75,000*	75,300	21	80.3
		1200	58,100*	63,900	18.5	89.9
		1600	49,200*	61,300	21.5	83.7
	str. relieved (1800 F)	79	75,100*	103,600	26.5	28.4
		750	-	75,000	19.5	79.6
		1200	51,600*	68,100	17.5	85.0
		1600	45,100*	59,600	17.5	90.8
	recrystallized (2650 F)	80	67,400	72,300	12.5	12.1
		750	19,400	43,000	44.5	84.9
		1200	14,400	39,200	40.5	92.9
		1600	11,400	39,500	45.5	87.0
			Bar 1138 - 1.22% Ti			
5/8	as rolled	80	87,700*	114,100	37	66.1
		750	86,200*	91,500	18	85.6
		1200	63,100*	77,500	21	86.0
		1600	41,100*	56,500	17	83.3
	str. relieved (1800 F)	79	85,500*	112,900	37	65.9
		750	56,900*	84,400	21	82.4
		1200	56,100*	75,600	21	87.0
		1600	39,900*	58,400	25	83.8

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1138 - 1.22% Ti (continued)			
5/8	recrystallized (2500 F)	80	51,700	76,000	30	23.5
		750	-	43,300	45	86.2
		1200	-	38,300	45	87.0
		1600	23,100*	33,400	52	85.0
1	as rolled	76	75,000*	100,200	35.5	46.2
		1200	50,500*	62,600	17.5	88.3
		1600	47,900*	55,400	19	84.1
	str. relieved (1800 F)	78	73,800	99,000	31	33.5
		750	61,100*	67,900	14	53.4
		1200	58,100*	61,300	18	89.0
		1600	49,000*	53,500	22	88.1
	recrystallized (2600 F)	82	53,200	68,600	6.5	6.2
		750	23,900	40,900	46	79.3
		1200	13,400*	37,100	43	91.9
		1600	12,100	35,200	46	86.1
			Bar 1009 - 1.26% Ti			
5/8	as rolled	78	109,000*	124,200	4	1.6
		750	87,200*	92,600	19	79.8
		1200	64,900*	80,900	18	80.2
		1600	56,600*	69,100	20	82.2
	str. relieved (1800 F)	78	106,300*	125,500	20	24.6
		750	85,500*	95,500	18	77.8
		1200	71,000*	81,000	18	76.8
		1600	65,900	68,400	14	40.2
	recrystallized (2900 F)	78	61,400	80,800	19	18.2
		750	33,100	44,000	55	76.3
		1200	22,800	43,300	42	91.7
		1600	14,900*	45,900	29	40.7

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1281 - 2.09% Ti			
5/8	as rolled	77	79,700*	112,700	37	58.0
		1600	48,000*	64,200	21	80.3
	str. relieved	78	84,700*	115,000	37	54.3
	(1800 F)	1600	46,100*	66,700	21	75.2
	recrystallized	77	none	76,400	0	0
	(2750 F)	1600	21,000*	41,800	42	70.0
			Bar 885 - 2.46% Ti			
5/8	as rolled	73	96,300*	120,800	7	9.8
		1600	50,100*	73,200	16.5	62.7
	str. relieved	74	90,000*	109,300	2	4.7
	(1800 F)	1600	57,500*	73,200	16	67.2
	recrystallized	74	37,900	52,900	2	1.6
	(2700 F)	1600	10,100	38,400	36	56.7
7/8	as rolled	72	75,300*	100,400	1	0.7
		1600	48,400*	61,900	12.5	78.4
	str. relieved	73	76,500*	94,600	1	0.9
	(1800 F)	1600	54,700*	62,200	14	67.7
	recrystallized	73	38,100	52,100	1	0.7
	(2800 F)	1600	11,700*	35,600	39	86.9
			Bar 887 - 2.66% Ti			
1-1/8	as rolled	74	66,400*	87,500	2	1.6
		1600	42,700*	49,600	21.5	85.7
	str. relieved	74	69,800*	95,100	9.5	2.5
	(1800 F)	1600	44,300*	50,200	21.5	83.5
	recrystallized	74	46,100	52,200	0.5	0.8
	(3000 F)	1600	12,100	41,300	34	76.3

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1051 - 0.54% V			
5/8	as rolled	78	90,300*	104,400	40	71.0
		750	37,900*	81,000	18	79.0
		1200	-	76,900	20	68.7
		1600	-	60,900	15	72.5
	str. relieved (1800 F)	78	93,400	103,600	38	72.2
		750	41,400*	79,100	19	78.6
		1200	35,800	75,000	18	76.9
		1600	45,700*	60,800	21	75.4
	recrystallized (2100 F)	78	70,400	74,400	40	37.1
		750	41,400	45,500	55	81.6
		1200	26,300	45,500	40	83.6
		1600	13,300	32,400	52	79.8
1	as rolled	78	95,300	100,000	4	2.3
		750	75,200	76,100	15.5	78.3
		1200	-	73,900	16.5	75.1
		1600	48,600*	57,600	20	78.5
	str. relieved (1800 F)	78	85,100	92,200	3.5	4.0
		750	65,900	72,700	19	76.8
		1200	64,300*	68,200	17	75.3
		1600	-	50,300	17	88.9
	recrystallized (2500 F)	80	56,300	69,700	20.5	18.1
		750	16,700	42,200	50	80.0
		1200	14,100	41,800	32	86.8
		1600	13,300	32,500	50	86.9
			Bar 1012 - 0.56% V			
5/8	as rolled	78	98,000*	121,500	4	7.4
		720	81,200*	102,000	16	65.5
		1200	56,800*	90,100	18	73.1
		1600	44,800*	70,100	21	79.9
	str. relieved (1800 F)	78	76,600	122,200	26	39.2
		750	65,600*	90,600	9	69.6
		1200	-	83,000	16	74.5
		1600	60,200	65,400	23	75.9

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1012 - 0.56% V (continued)			
5/8	recrystallized (2150 F)	78	83,200	83,200	25	20.4
		750	34,700	45,900	53	79.9
		1200	24,200	45,400	39	80.2
		1600	14,400	33,100	41	79.3
1	as rolled	78	87,900	96,000	1	1.7
		750	72,300*	81,000	13	56.5
		1200	70,300*	75,600	16	75.7
		1600	-	59,600	19	80.2
	str. relieved (1800 F)	78	88,300	92,400	1.5	1.1
		750	67,800*	75,900	15	72.9
		1200	60,000*	71,900	16.5	78.7
		1600	55,500*	67,700	18.5	83.0
	recrystallized (2200 F)	79	61,900	70,600	19	15.9
		750	22,000	41,300	56.5	82.7
		1200	15,300	43,500	34	85.0
		1600	15,900	29,700	51	85.9
			Bar 667 - 0.66% V			
5/8	as rolled	77	110,300	119,400	22	25.3
		750	-	97,400	16	65.7
		1200	-	90,300	16	70.7
		1600	-	71,200	22	77.4
	str. relieved (1800 F)	77	91,700	110,900	34	63.1
		750	-	88,300	17	70.3
		1200	-	83,500	16	71.8
		1600	-	71,400	20	78.6
	recrystallized (2150 F)	78	81,000	81,000	47	55.9
		750	46,900	48,000	51	73.9
		1200	34,800	48,800	36	80.8
		1600	-	37,500	56	82.3
1-1/8	as rolled	74	79,700	83,500	1.5	1.4
		1000	55,900*	61,000	16	71.1
		1600	-	51,700	20	73.3

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 667 - 0.66% V (continued)			
1-1/8	str. relieved (1800 F)	74	73,100	83,700	4	3.7
		750	54,200*	60,500	21.5	70.2
		1200	47,200*	54,900	19.5	76.4
		1600	40,400*	51,200	21	74.7
	recrystallized (2250 F)	74	47,400	72,700	25	20.7
		1000	15,900	42,800	38	78.8
		1600	16,600*	35,100	43	91.0
			Bar 1049 - 0.85% V, 0.003% Ce, 0.003% R.E.			
5/8	as rolled	80	87,900*	112,500	16	24.6
		750	67,000*	90,500	15	71.9
		1200	67,400*	78,300	19	81.5
		1600	34,200*	62,600	19	76.7
	str. relieved (1800 F)	80	79,400*	106,200	2	2.4
		750	66,600*	85,200	17	71.8
		1200	62,100*	75,900	19	77.7
		1600	48,800*	63,100	21	81.7
	recrystallized (2500 F)	80	53,700	53,700	1	0
		750	23,300	39,900	57	83.1
		1200	16,300	38,700	44	82.8
		1600	11,600*	30,100	13	16.4
			Bar 669 - 0.87% V			
5/8	as rolled	74	114,500	127,800	1	0.8
		750	-	108,800	14	62.8
		1200	-	100,300	14	65.7
		1600	-	83,400	22	72.3
	str. relieved (1800 F)	74	112,800	120,100	1	1.2
		750	-	101,500	16	62.8
		1200	-	96,500	15	66.6
		1600	-	83,400	19	72.5

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 669 - 0.87% V (continued)			
5/8	recrystallized (2300 F)	77	87,100	87,100	32	24.3
		750	51,800	51,800	50	79.3
		1200	36,400	54,000	36	78.4
		1600	-	43,900	50	84.8
1-1/8	as rolled	74	85,100	90,300	1.5	1.4
		1000	56,300*	68,700	15.5	66.6
		1600	52,300*	59,600	15	71.6
	str. relieved (1800 F)	74	83,100	86,900	1.5	1.6
		750	63,000*	69,900	16.5	65.5
		1200	60,700*	68,900	15	68.1
		1600	55,100*	60,100	16.5	71.6
	recrystallized (2400 F)	74	51,000	74,700	23	19.4
		1000	23,600	47,000	41	78.1
		1600	14,200*	36,800	37	82.6
			Bar 1052 - 1.00% V			
5/8	as rolled	78	98,600	111,200	32	57.8
		750	72,200*	89,300	34	78.2
		1200	71,600*	86,400	15	69.5
		1600	-	67,200	18	74.0
	str. relieved (1800 F)	78	95,200	100,000	29	54.5
		750	68,500*	88,900	13	66.4
		1200	55,200	85,400	15	67.5
		1600	47,700	71,900	20	74.8
	recrystallized (2150 F)	80	89,700	89,700	28	21.6
		750	39,500	50,000	55	81.6
		1200	37,000	52,200	35.5	79.3
		1600	14,600	35,500	58	83.6
1	as rolled	78	96,500	103,600	2	1.1
		750	84,500	87,000	16	73.4
		1200	79,700*	85,500	13.5	69.1
		1600	-	59,200	20	77.5

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1052 - 1.00% V (continued)			
1	str. relieved (1800 F)	78	94,000	98,400	1.5	1.3
		750	76,600*	81,800	16.5	71.8
		1200	-	80,700	14.5	69.1
		1600	51,900	52,900	17	12.9
	recrystallized (2350 F)	80	70,200	72,900	24	20.8
		750	35,000	46,100	45	78.0
		1200	22,500	49,600	30	73.6
		1600	10,600	33,900	43	88.0
			Bar 1151 - 1.25% V			
5/8	as rolled	80	105,000	114,500	34	59.7
		750	85,600*	92,700	20	81.0
		1200	63,800*	90,600	19	81.2
		1600	45,600*	67,600	16	92.3
	str. relieved (1800 F)	80	103,900	115,200	27	47.0
		750	59,700*	86,800	19	80.0
		1200	69,400*	84,300	15	82.6
		1600	64,400*	88,600	20	79.4
	recrystallized (2200 F)	80	84,300	84,300	2	6.2
		750	46,900	47,900	46	88.2
		1200	33,500	53,600	35	84.1
		1600	-	41,500	48	86.9
1	as rolled	73	88,200	105,700	9	9.0
		750	76,400*	82,500	15	73.8
		1200	63,900*	81,200	15	72.0
		1600	61,800*	69,900	16.5	81.7
	str. relieved (1800 F)	83	97,100	98,900	2	1.7
		750	75,500*	80,900	15.5	63.6
		1200	59,100*	79,900	14	74.2
		1600	60,800	68,000	17	80.0
	recrystallized (2600 F)	76	54,200	54,200	1	2.1
		1200	19,000	47,500	33.5	85.9
		1600	14,900	37,900	41	89.7

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1390 - 0.054% Zr			
5/8	as rolled	77	108,400*	127,700	28	60.5
		1600	53,600*	69,600	17	75.0
	str. relieved (1800 F)	80	111,000*	126,400	26	58.9
		1600	42,800*	54,000	14	72.0
	recrystallized (2450 F)	80	59,300	75,600	23	18.9
		1600	17,600	32,900	46	79.0
			Bar 1207 - 0.09% Zr			
5/8	as rolled	82	108,200*	126,700	30	55.5
		750	-	104,900	18	78.7
		1200	68,800*	96,400	19	72.5
		1600	59,000*	74,400	15	78.1
	str. relieved (1800 F)	82	104,200*	125,900	29	40.0
		750	80,200*	102,900	19	71.1
		1200	72,300*	97,300	20	85.7
		1600	53,600*	79,000	18	86.1
	recrystallized (2750 F)	79	65,900	75,800	44	43.7
		750	21,100	48,700	44	91.1
		1200	19,400*	44,700	43	89.3
		1600	18,900	35,100	55	93.6
1	as rolled	87	92,600*	110,000	4.5	4.6
	str. relieved (1800 F)	87	91,600	105,700	4.5	3.7
	recrystallized (2900 F)	87	46,400	72,300	18	15.0
			Bar 1455 - 0.06% Co, 0.47% V			
1/2	as rolled	75	117,600	117,600	36	66.6
		1600	39,900	73,600	35	83.0

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
		Bar 1455 - 0.06% Co, 0.47% V (continued)				
1/2	str. relieved (1800 F)	75	118,800	118,800	44	70.2
		1600	38,700*	71,300	30	85.3
	recrystallized (2000 F)	75	71,800	73,200	7	6.2
		1600	36,400*	47,600	46	54.4
		Bar 1454 - 0.06% Co, 0.07% Zr				
1/2	as rolled	75	109,300*	129,500	25	52.3
		1600	52,100*	96,000	26	74.4
	str. relieved (2100 F)	75	121,300	124,100	33	55.7
		1600	72,800*	92,600	23	78.6
	recrystallized (2500 F)	75	67,900	84,100	46	54.7
		1600	19,100	51,800	52	88.2
		Bar 1217 - 0.11% Co, 0.18% Ti				
5/8	as rolled	78	117,200	127,100	15	19.6
		1600	76,600*	94,100	22	60.1
	str. relieved (1800 F)	78	113,600	123,600	5	4.8
		1600	-	100,000	22	64.5
	recrystallized (2100 F)	78	61,000	86,800	36	32.7
		1600	22,600	58,700	27	29.9
		Bar 1060 - 0.32% Nb, 0.18% Ti				
5/8	as rolled	76	88,200	99,600	30	67.6
		1600	50,300*	61,100	20	74.5
	str. relieved (1800 F)	76	75,600*	93,000	36	69.7
		1600	46,100*	62,400	20	77.5
	recrystallized (2450 F)	77	54,200	63,600	21	20.4
		1600	14,500*	35,600	44	82.5

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
		Bar 1457 - 0.46% Nb, 0.48% V				
1/2	as rolled	75	98,200	121,500	25	46.7
		1600	53,200*	85,300	14	60.0
	str. relieved (1800 F)	75	98,000	120,500	30	60.4
		1600	66,800*	85,700	18	79.2
	recrystallized (2300 F)	75	86,500	86,500	2	7.0
		1600	15,700*	43,700	44	77.3
		Bar 1451 - 0.50% Nb, 0.43% Ti				
1/2	as rolled	75	117,200*	132,600	25	50.8
		1600	76,800*	90,700	15	75.2
	str. relieved (2100 F)	75	104,300*	126,700	29	63.1
		1600	72,800*	85,800	17	77.9
	recrystallized (2550 F)	75	70,300	77,200	46	35.2
		1600	11,900	46,000	42	80.7
		Bar 1456 - Nominal Composition 0.50% Nb, 0.06% Zr				
1/2	as rolled	75	97,600*	123,200	25	54.9
		1600	62,700*	86,600	18	79.4
	str. relieved (2000 F)	75	101,000*	120,000	28	56.8
		1600	59,300*	85,300	20	80.2
	recrystallized (2500 F)	75	71,500	78,300	25	23.9
		1600	17,500	38,800	48	88.4
		Bar 1452 - 0.22% Ti, 0.75% V				
1/2	as rolled	75	89,200*	108,300	31	46.1
		1600	58,200*	75,400	16	66.2

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
			Bar 1452 - 0.22% Ti, 0.75% V (continued)			
1/2	str. relieved (2000 F)	75	90,500*	107,100	22	20.4
		1600	38,700*	72,700	17	70.0
	recrystallized (2350 F)	75	62,200	75,200	19	16.7
		1600	23,300*	39,200	46	74.3
			Bar 1453 - 0.22% Ti, 0.08% Zr			
1/2	as rolled	75	94,000*	122,500	31	55.2
		1600	67,600*	85,300	18	80.4
	str. relieved (2000 F)	75	97,400*	122,700	30	58.7
		1600	64,700*	86,100	17	77.5
	recrystallized (2500 F)	75	60,800	78,400	51	59.4
		1600	16,200	40,200	48	48.2
			Bar 1436 - 0.42% Al, 0.51% V			
1/2	as rolled	75	104,300*	121,100	8	7.0
	str. relieved (1800 F)	75	102,900*	112,700	4	5.4
		1600	60,100*	78,300	17	72.1
	recrystallized (2200 F)	75	53,200	56,500	4	4.0
		1600	15,300	41,100	38	53.2

TABLE D1 (continued)

TENSILE PROPERTIES AT ROOM AND ELEVATED TEMPERATURES
OF ROLLED MOLYBDENUM-BASE ALLOYS

Bar Dia In.	Condition	Testing Temp, F	Yield Str. psi	Tensile Strength psi	Elongation %	Reduction of Area %
	Bars Rolled at the University of Michigan					
	Bar 1082 - 0.31% Nb					
1/2	str. relieved (1800 F)	79	74,600	88,700	16	38.3
	recrystallized (2300 F)	80	54,800	69,400	48	37.1
	Bar 1001 - 0.31% Nb, 0.16% Ti					
1/2	str. relieved (1800 F)	81	100,600*	111,500	2	0.1
	recrystallized (2700 F)	81	59,100	73,500	44	37.1
	Bar 672 - 0.88% V					
1/2	as rolled	79	74,100*	82,100	1	1.0
	recrystallized (2500 F)	81	46,700	70,600	7	4.1
	Bar 1173 - 0.19% Co					
1/2	recrystallized (2100 F)	82	69,500	77,900	5	5.6
	Bar 1174 - 3.59% Ti					
1/2	str. relieved (1800 F)	82	70,400*	92,300	4	3.2
	recrystallized (3000 F)	79	56,900	56,900	0	0
	Bar 1175 - 1.46% V					
1/2	as rolled	79	86,100	88,900	1	1.0
	recrystallized (2600 F)	80	46,900	52,600	3	1.6

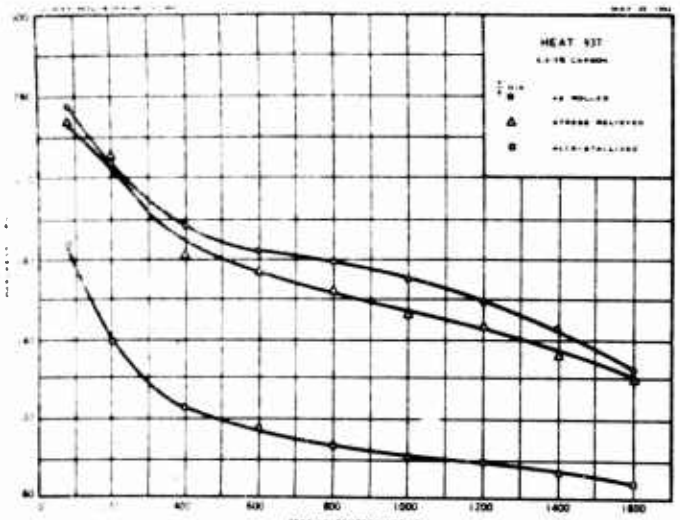


FIGURE D1 HOT HARDNESS OF ROLLED BARS OF UNALLOYED MOLYBDENUM

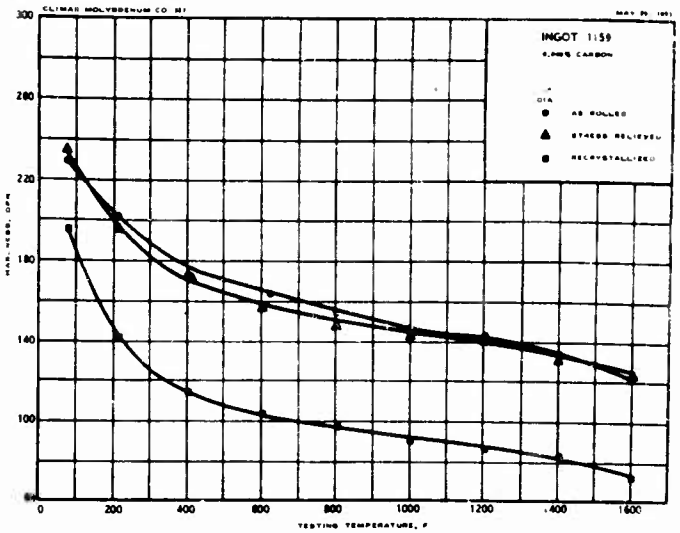


FIGURE D2 – HOT HARDNESS OF ROLLED BARS OF UNALLOYED MOLYBDENUM

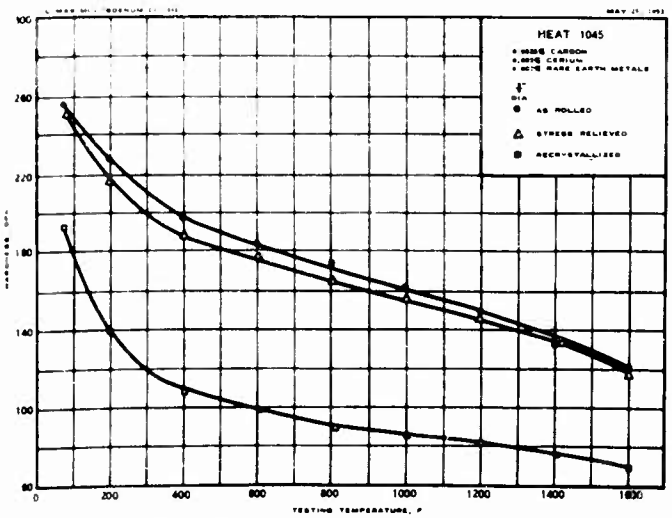


FIGURE D3 HOT HARDNESS OF ROLLED BARS OF MOLYBDENUM DEOXIDIZED WITH RARE EARTH METALS

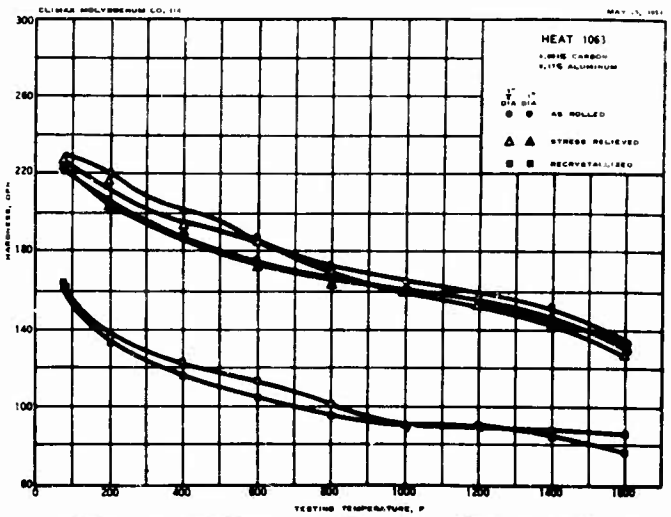


FIGURE D4 – HOT HARDNESS OF ROLLED BARS OF 0.17% ALUMINUM – MOLYBDENUM ALLOY

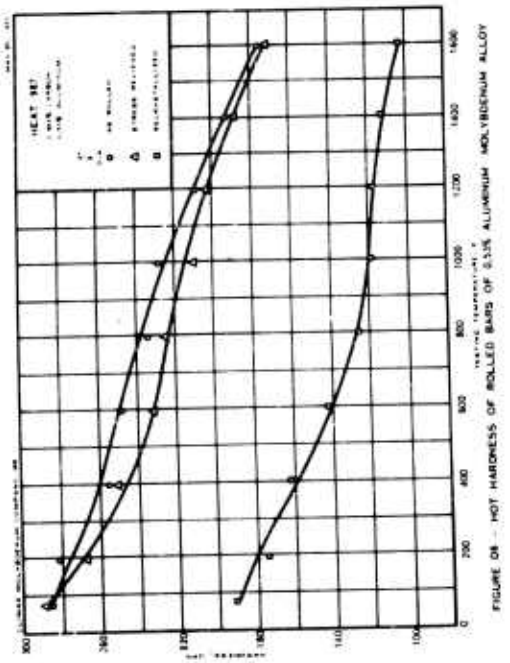


FIGURE D6 — HOT HARDNESS OF ROLLED BARS OF 0.5% ALUMINUM MOLYBDENUM ALLOY

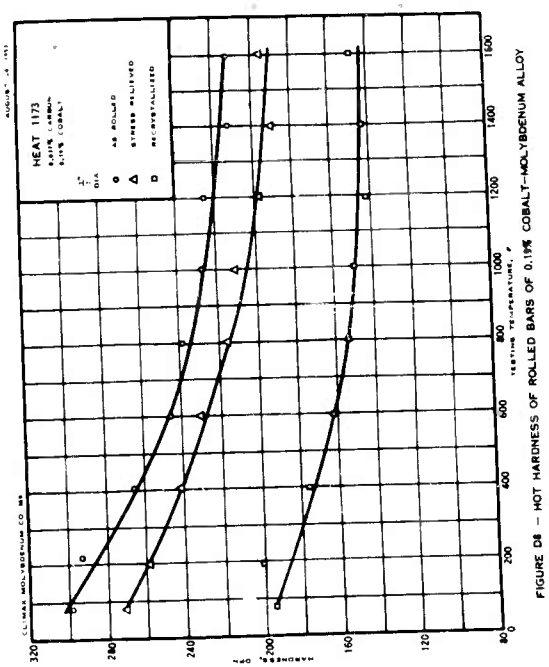
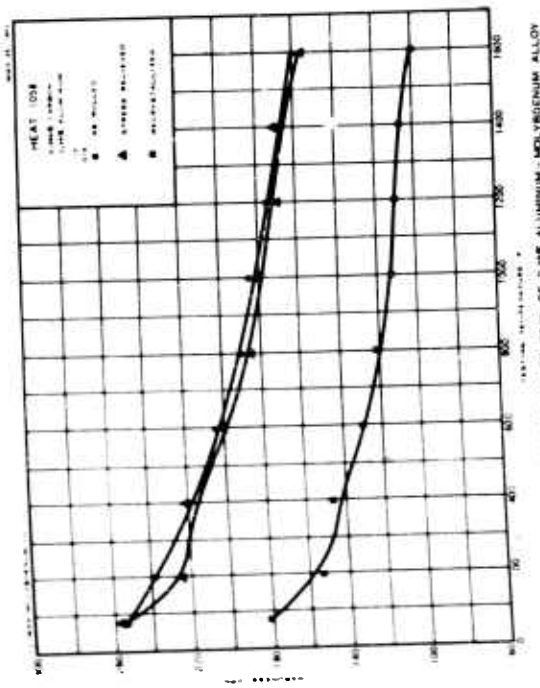


FIGURE D8 — HOT HARDNESS OF ROLLED BARS OF 0.19% COBALT–MOLYBDENUM ALLOY



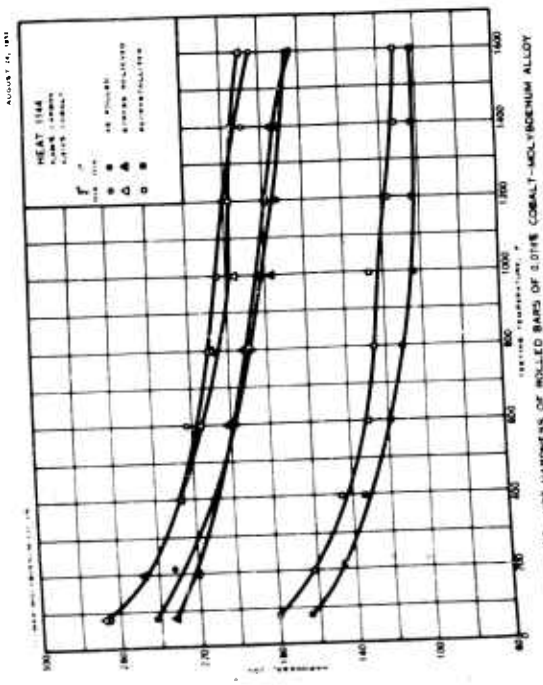


FIGURE D7 — HOT HARDNESS OF ROLLED BARS OF 0.01% COBALT–MOLYBDENUM ALLOY

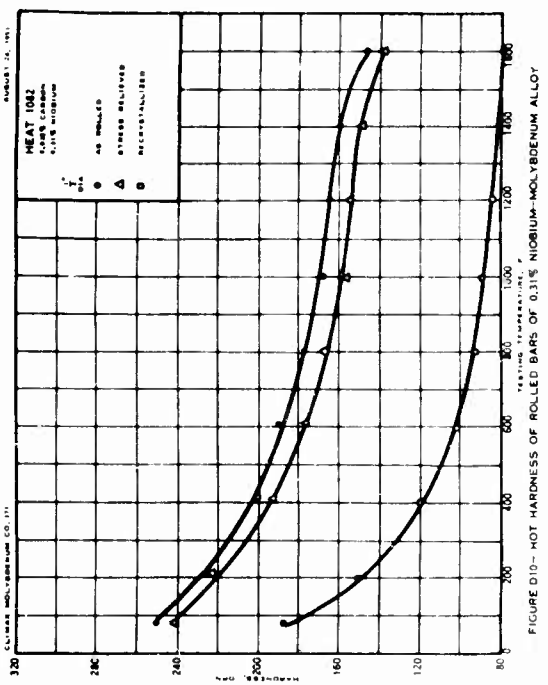


FIGURE D10 – HOT HARDNESS OF ROLLED BARS OF 0.31% NIOBIUM-MOLYBDENUM ALLOY

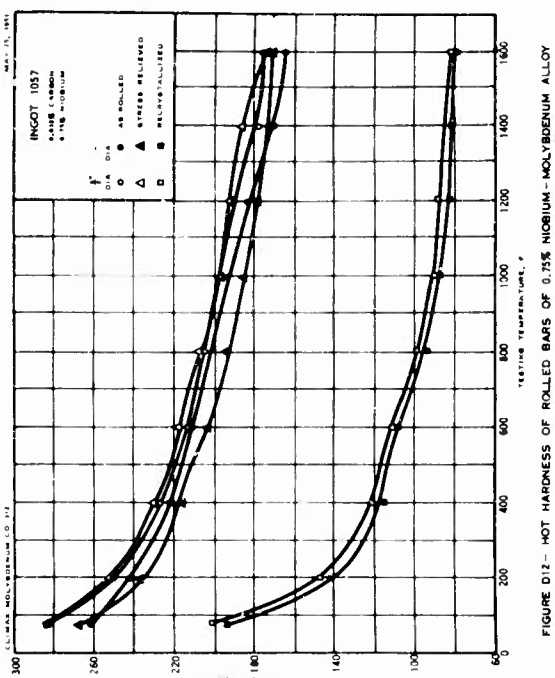
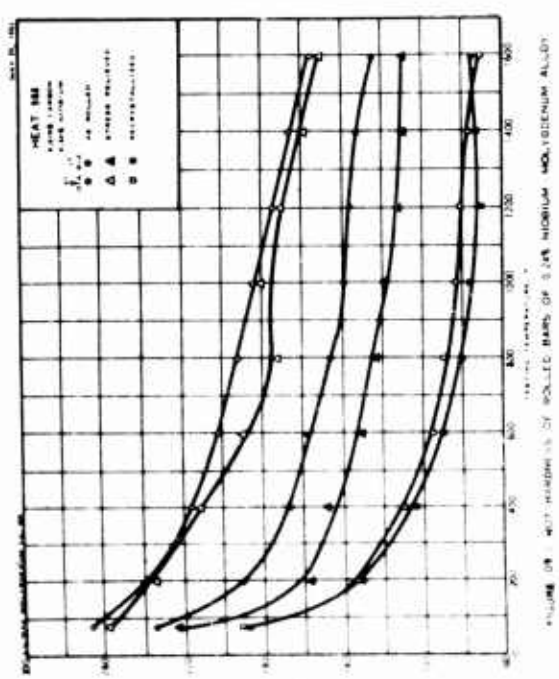
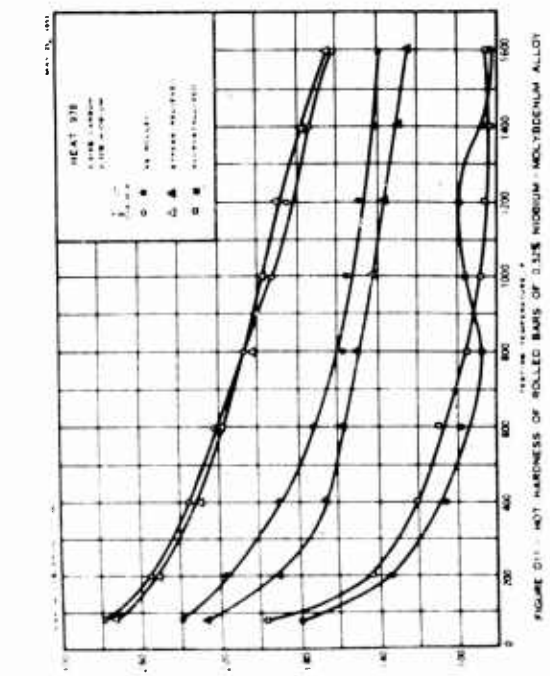


FIGURE D12 – HOT HARDNESS OF ROLLED BARS OF 0.75% NIOBIUM-MOLYBDENUM ALLOY





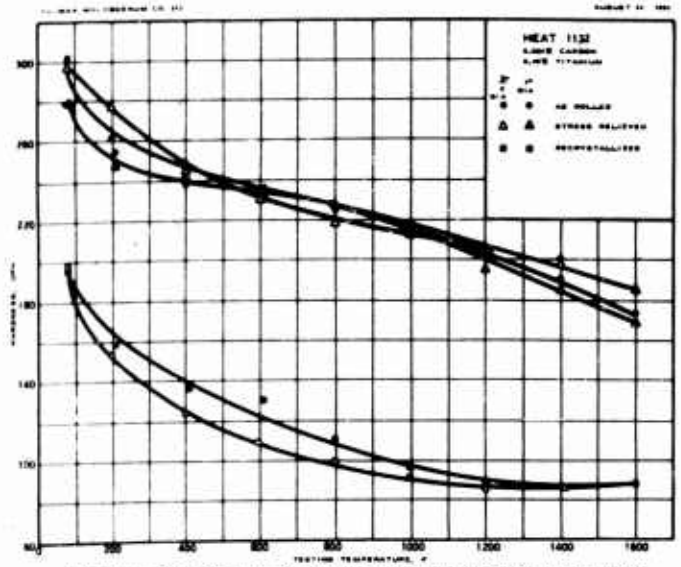


FIGURE D13 – HOT HARDNESS OF ROLLED BARS OF 0.69% TITANIUM–MOLYBDENUM ALLOY

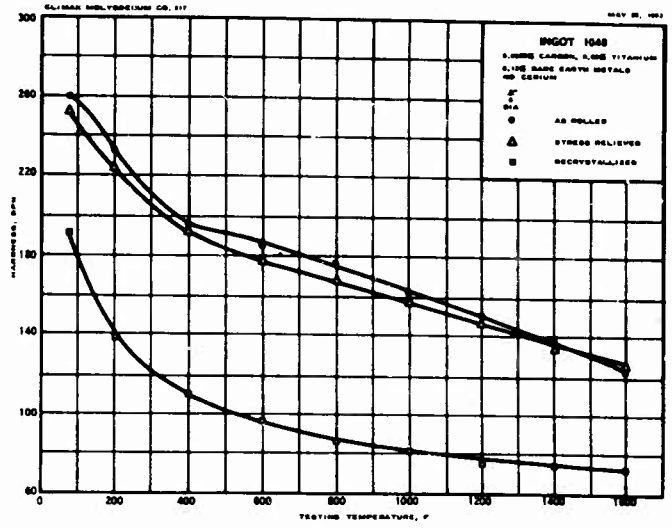


FIGURE D14 – HOT HARDNESS OF ROLLED BARS OF 0.69% TITANIUM – MOLYBDENUM ALLOY DEOXIDIZED WITH RARE EARTH METALS

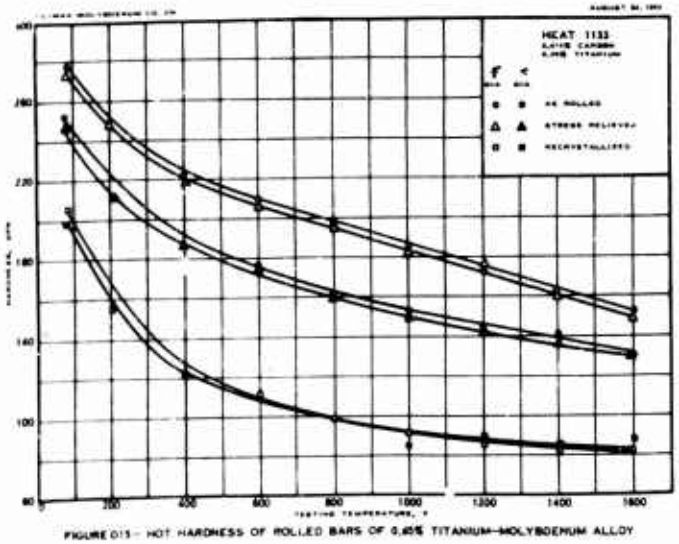


FIGURE D15 – HOT HARDNESS OF ROLLED BARS OF 0.69% TITANIUM–MOLYBDENUM ALLOY

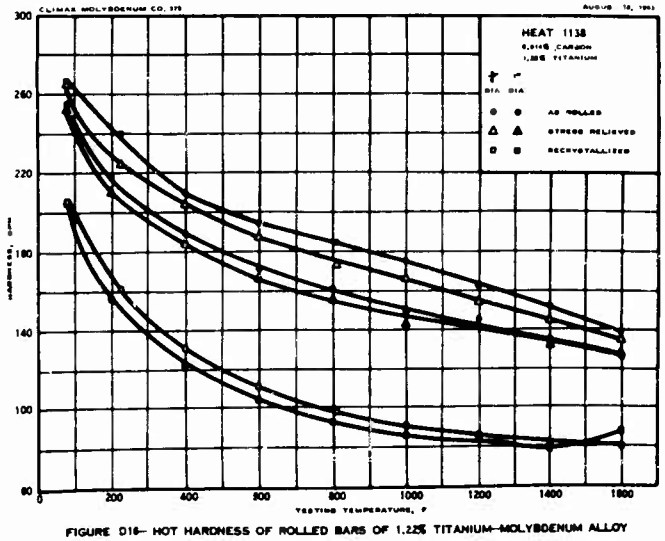


FIGURE D16 – HOT HARDNESS OF ROLLED BARS OF 1.22% TITANIUM–MOLYBDENUM ALLOY

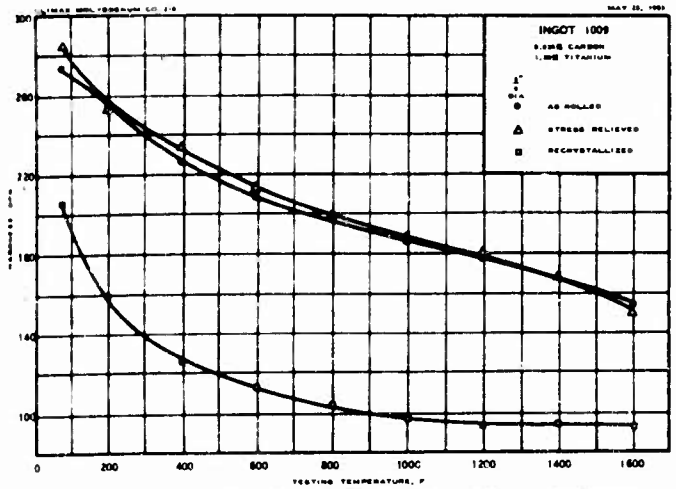


FIGURE D17 - HOT HARDNESS OF ROLLED BARS OF 1.26% TITANIUM - MOLYBDENUM ALLOY

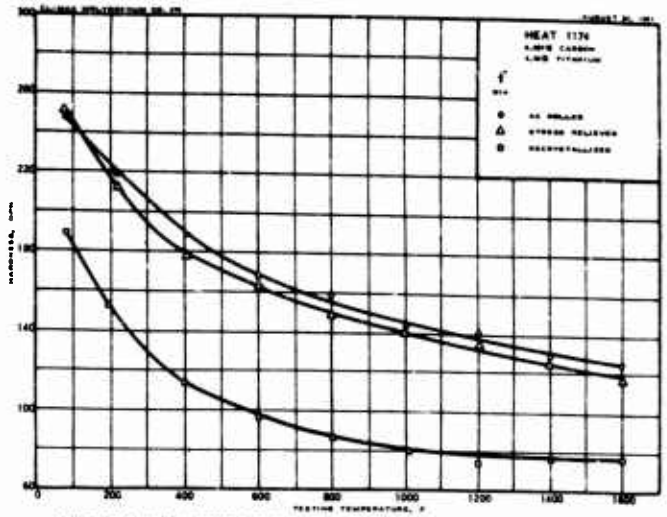


FIGURE D18 - HOT HARDNESS OF ROLLED BARS OF 3.59% TITANIUM-MOLYBDENUM ALLOY

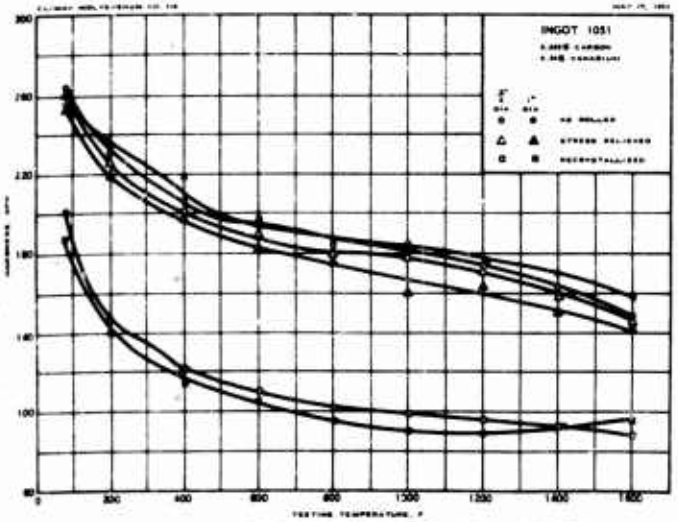


FIGURE D19 - HOT HARDNESS OF ROLLED BARS OF 0.54% VANADIUM-MOLYBDENUM ALLOY

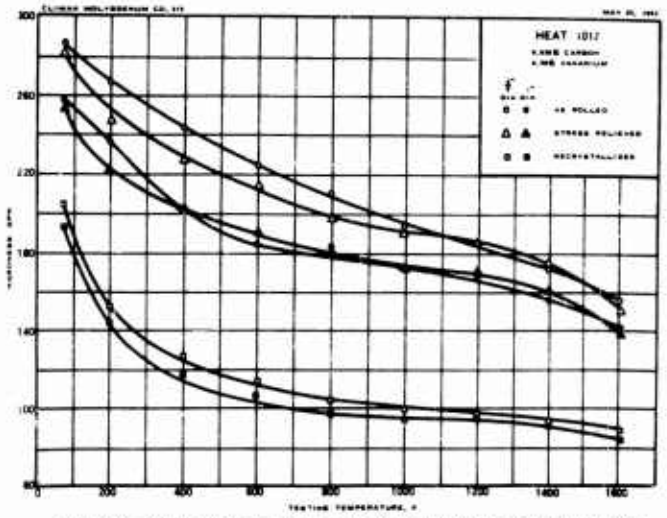


FIGURE D20 - HOT HARDNESS OF ROLLED BARS OF 0.96% VANADIUM - MOLYBDENUM ALLOY

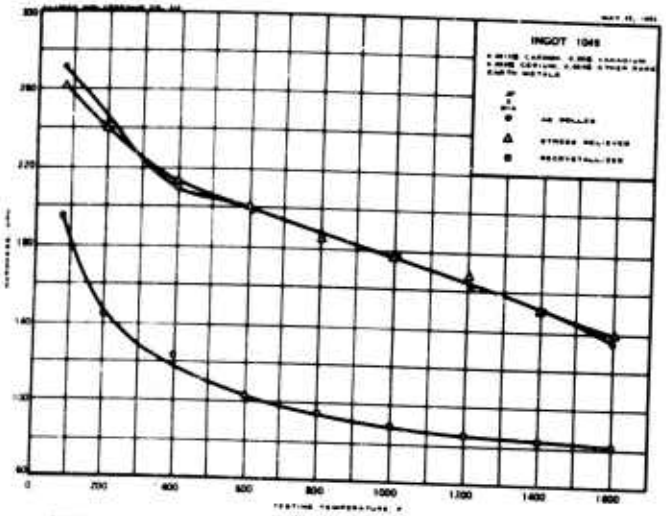


FIGURE D21 - HOT HARDNESS OF ROLLED BARS OF 0.85% VANADIUM - MOLYBDENUM ALLOY DEOXIDIZED WITH RARE EARTH METALS

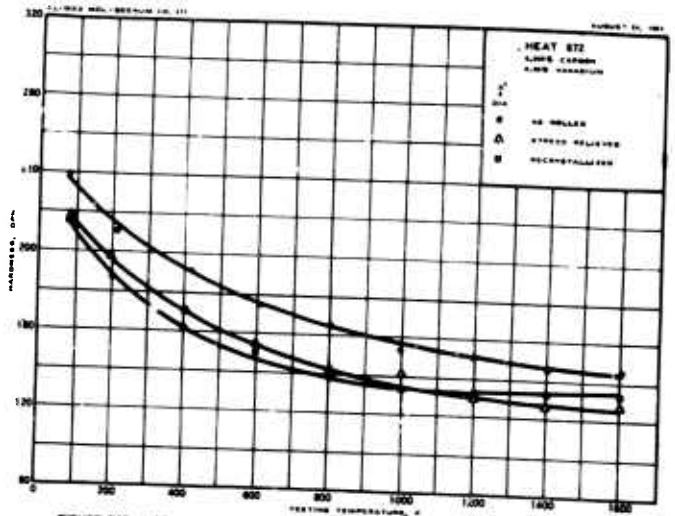


FIGURE D22 - HOT HARDNESS OF ROLLED BARS OF 0.52% VANADIUM - MOLYBDENUM ALLOY

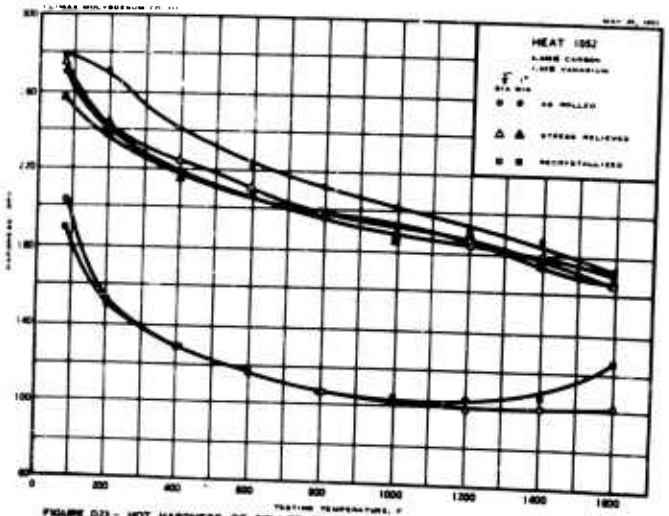


FIGURE D23 - HOT HARDNESS OF ROLLED BARS OF 1.02% VANADIUM - MOLYBDENUM ALLOY

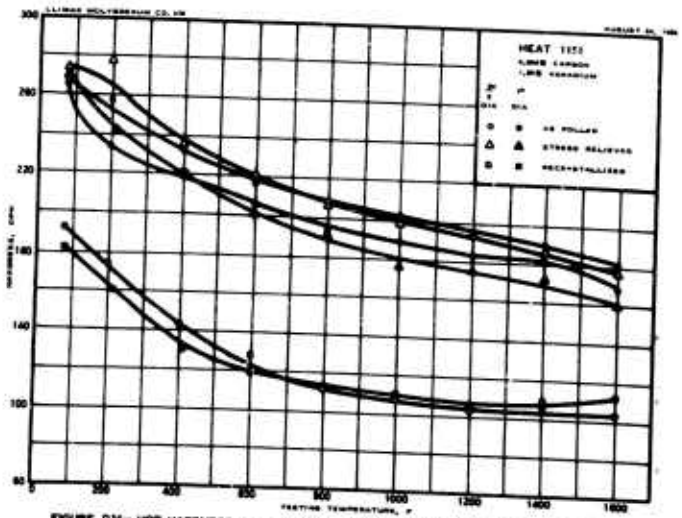


FIGURE D24 - HOT HARDNESS OF ROLLED BARS OF 1.25% VANADIUM - MOLYBDENUM ALL

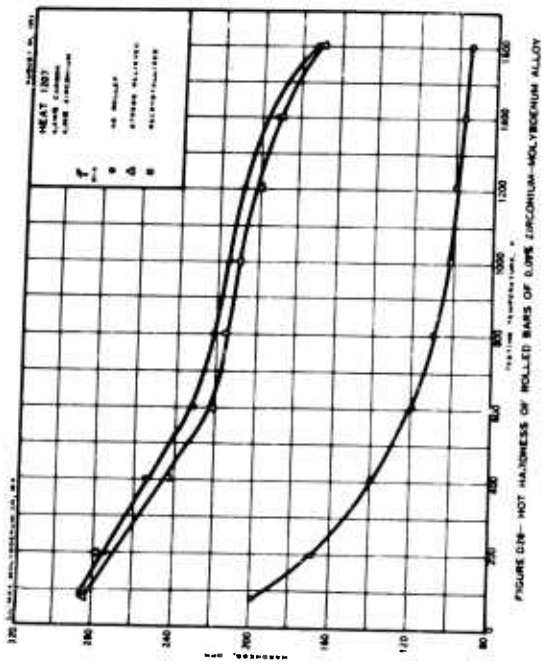


FIGURE D26— HOT HARDNESS OF ROLLED BARS OF 0.09% ZIRCONIUM-MOLYBDENUM ALLOY

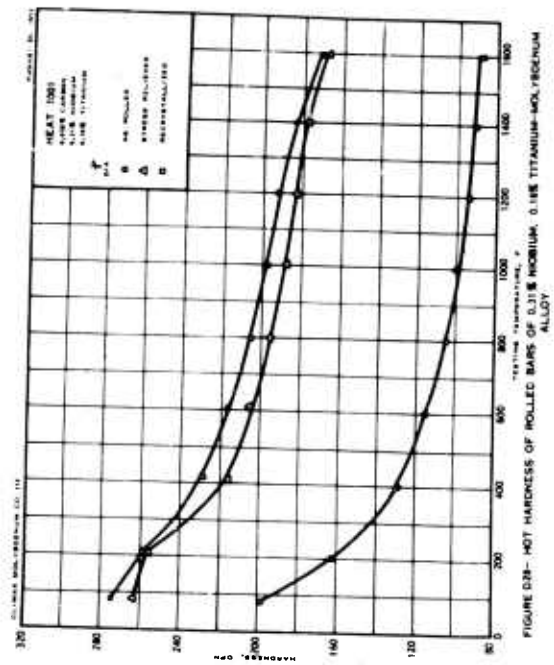


FIGURE D28— HOT HARDNESS OF ROLLED BARS OF 0.11% NIOBIUM, 0.11% TITANIUM-MOLYBDENUM ALLOY

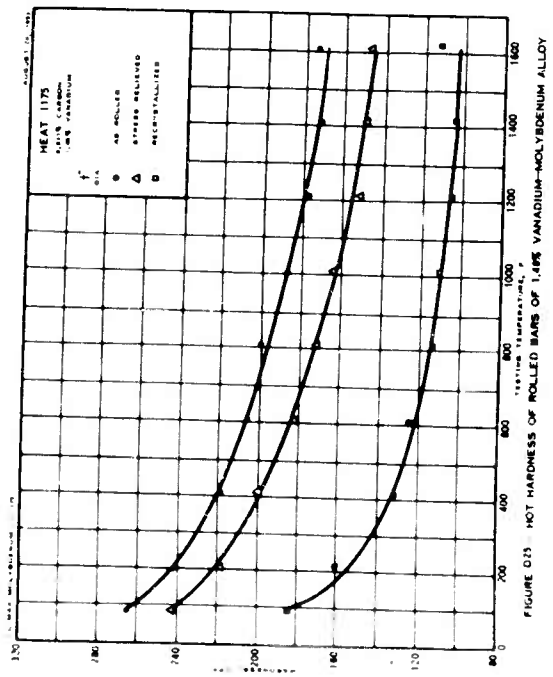


FIGURE D25— HOT HARDNESS OF ROLLED BARS OF 1.44% VANADIUM-MOLYBDENUM ALLOY

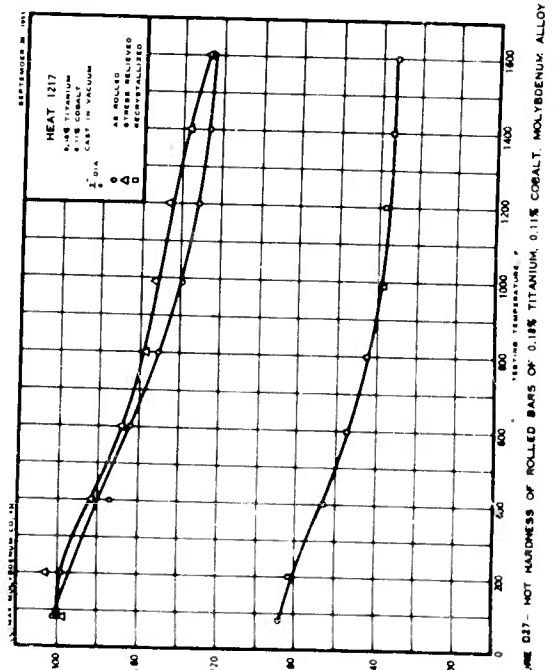


FIGURE D27— HOT HARDNESS OF ROLLED BARS OF 0.18% TITANIUM, 0.11% COBALT, MOLYBDENUM ALLOY

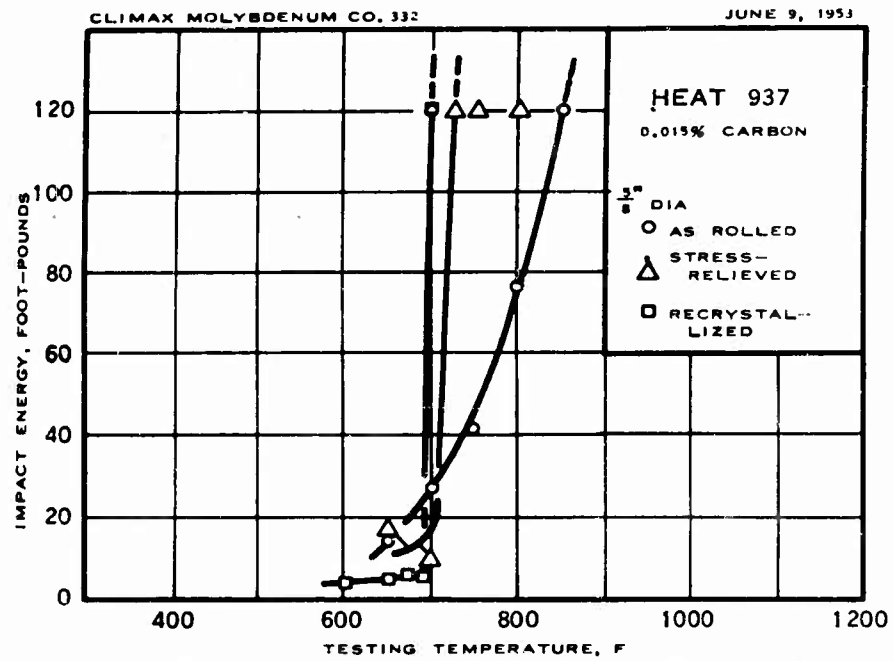


FIGURE D29– IMPACT (V-NOTCH) TRANSITION FOR UNALLOYED MOLYBDENUM

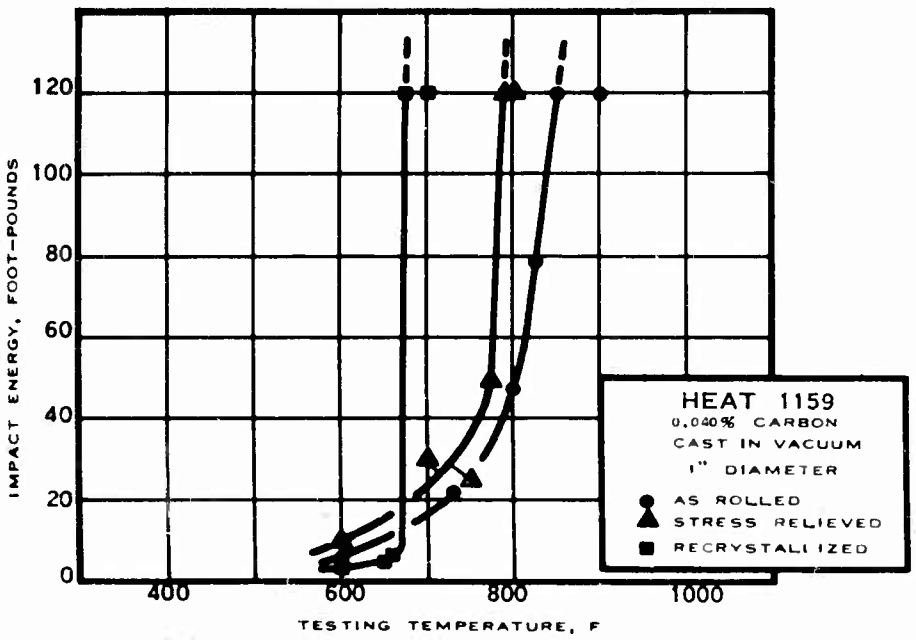


FIGURE D30– IMPACT (V-NOTCH) TRANSITION FOR UNALLOYED MOLYBDENUM

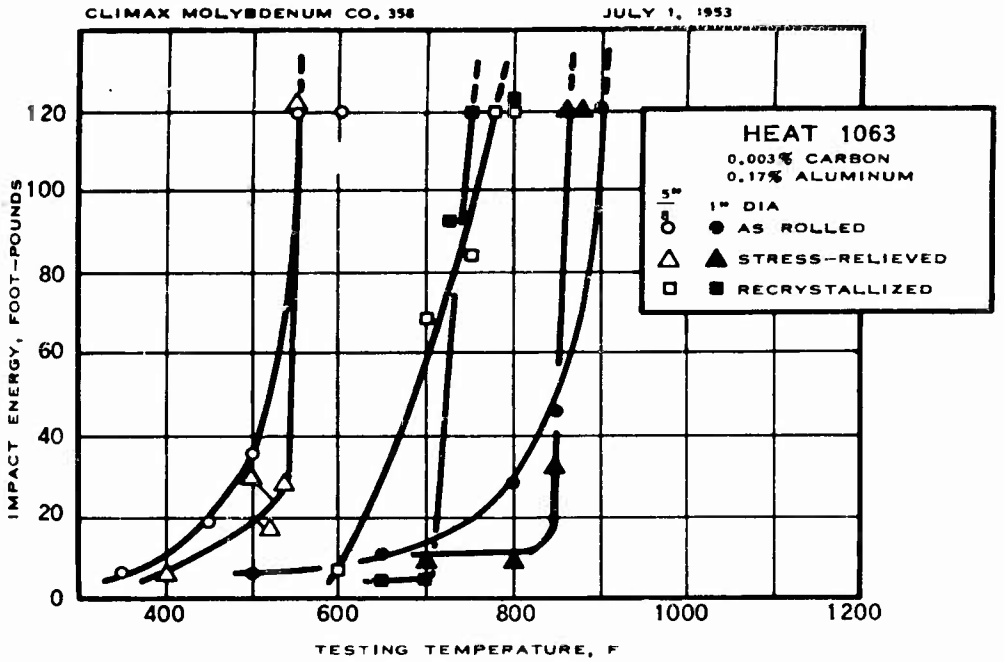


FIGURE D31– IMPACT (V–NOTCH) TRANSITION FOR 0.17% ALUMINUM – MOLYBDENUM ALLOY

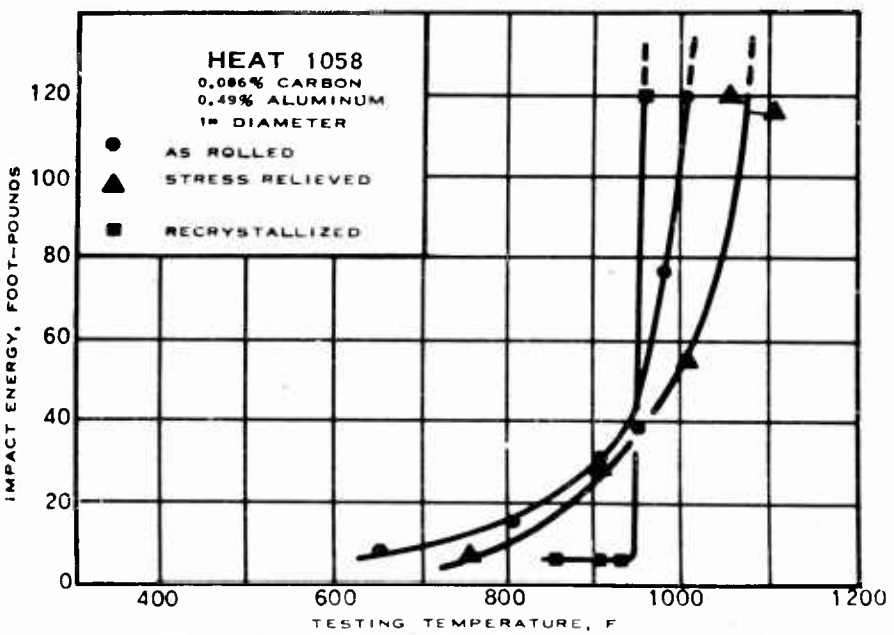


FIGURE D32– IMPACT (V-NOTCH) TRANSITION FOR 0.49% ALUMINUM – MOLYBDENUM ALLOY

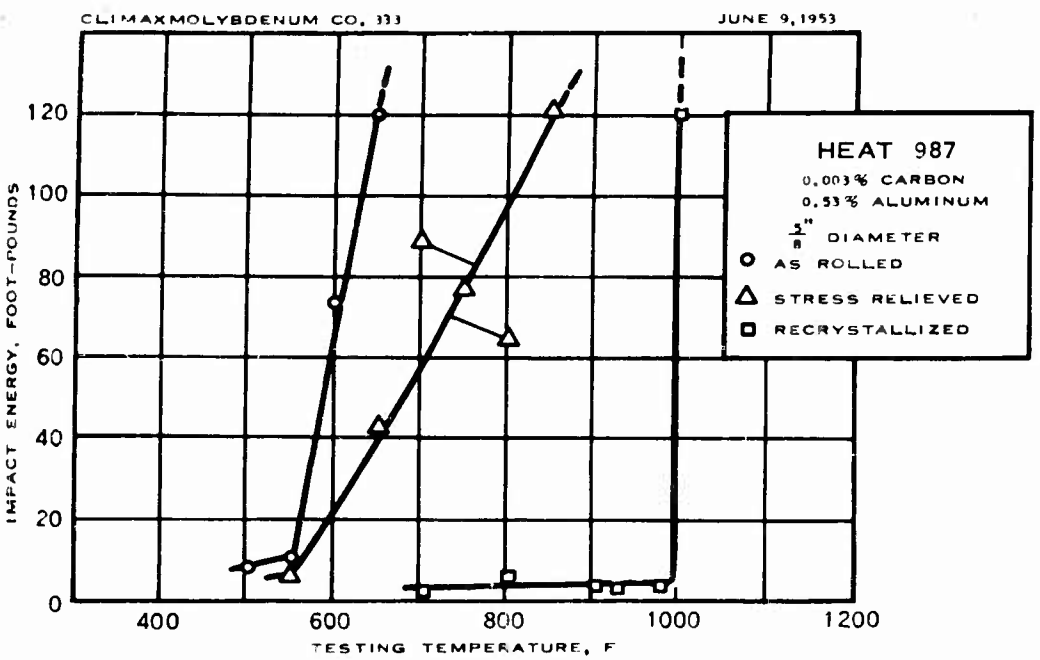


FIGURE D33– IMPACT (V–NOTCH) TRANSITION FOR 0.53% ALUMINUM – MOLYBDENUM ALLOY

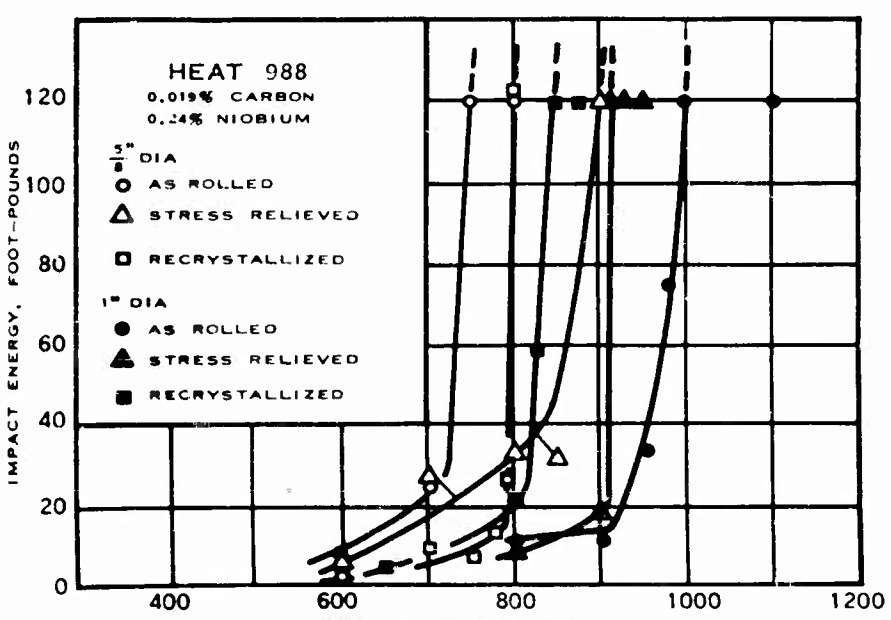


FIGURE D34 – IMPACT (V–NOTCH) TRANSITION FOR 0.24% NIOBIUM – MOLYBDENUM ALLOY

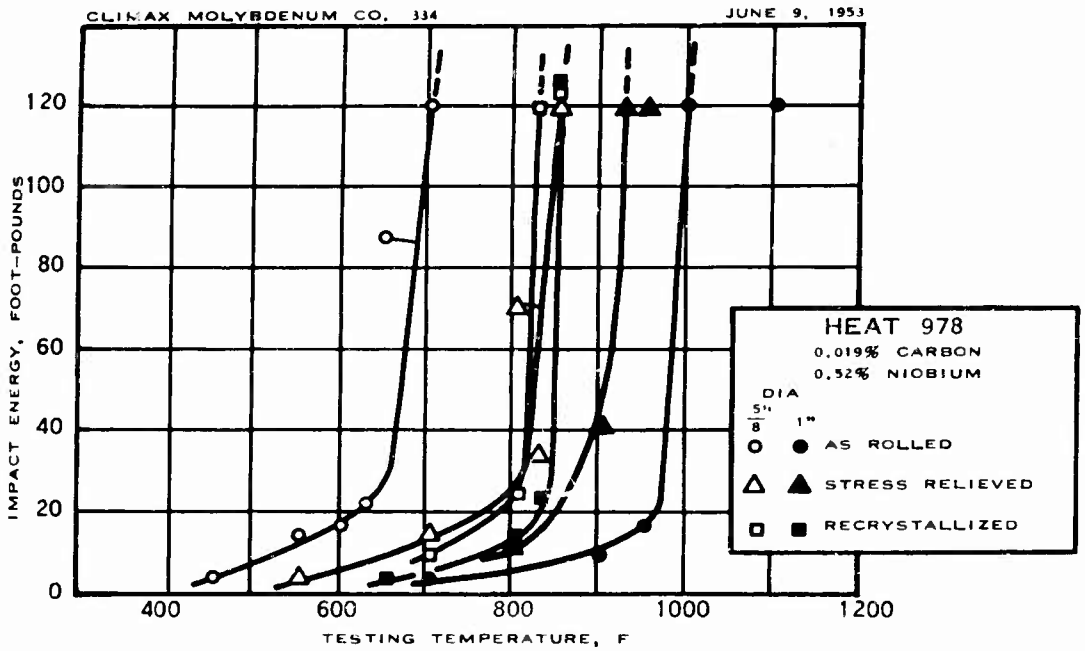


FIGURE D35– IMPACT (V–NOTCH) TRANSITION FOR 0.52% NIOBIUM – MOLYBDENUM ALLOY

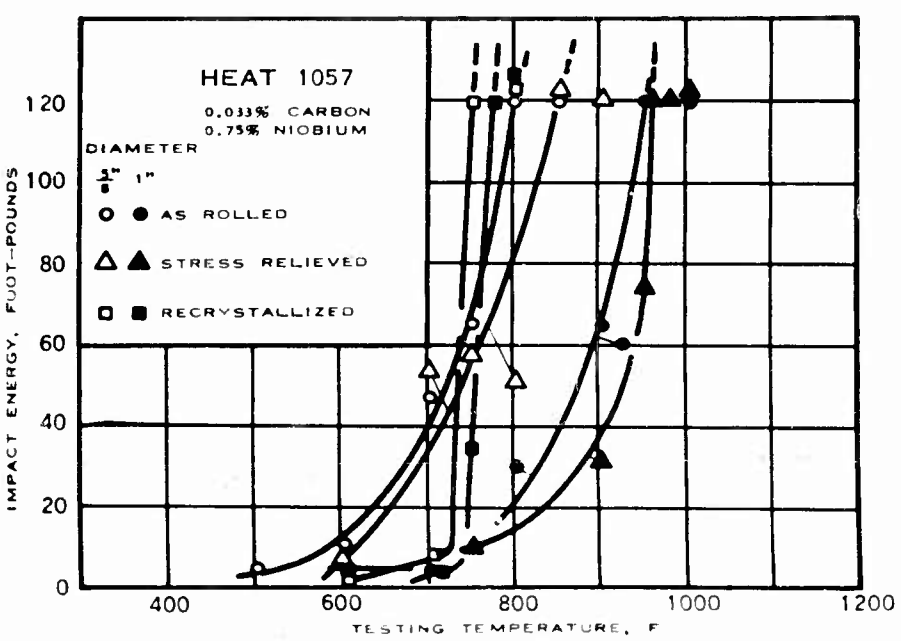


FIGURE D36– IMPACT (V–NOTCH) TRANSITION FOR 0.75% NIOBIUM – MOLYBDENUM ALLOY

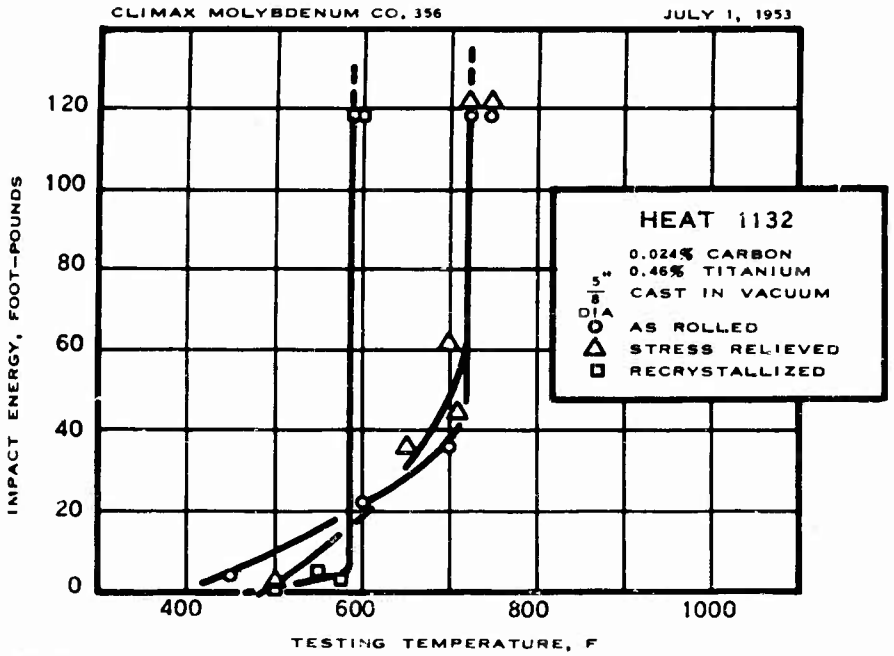


FIGURE D37— IMPACT (V-NOTCH) TRANSITION FOR 0.46% TITANIUM—MOLYBDENUM ALLOY

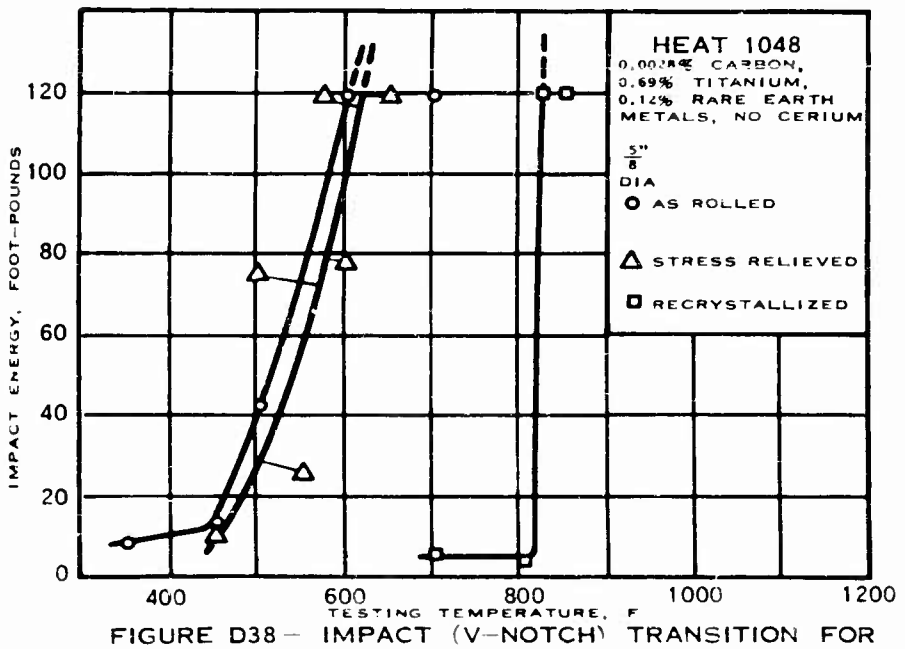


FIGURE D38— IMPACT (V-NOTCH) TRANSITION FOR 0.69% TITANIUM—MOLYBDENUM ALLOY

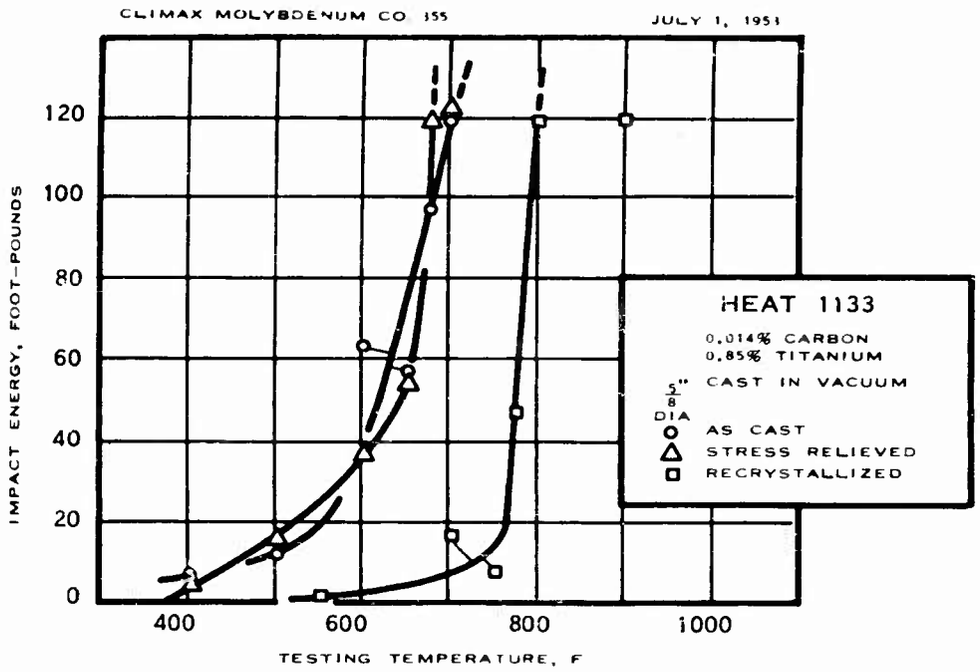


FIGURE D39— IMPACT (V-NOTCH) TRANSITION FOR 0.85% TITANIUM—MOLYBDENUM ALLOY

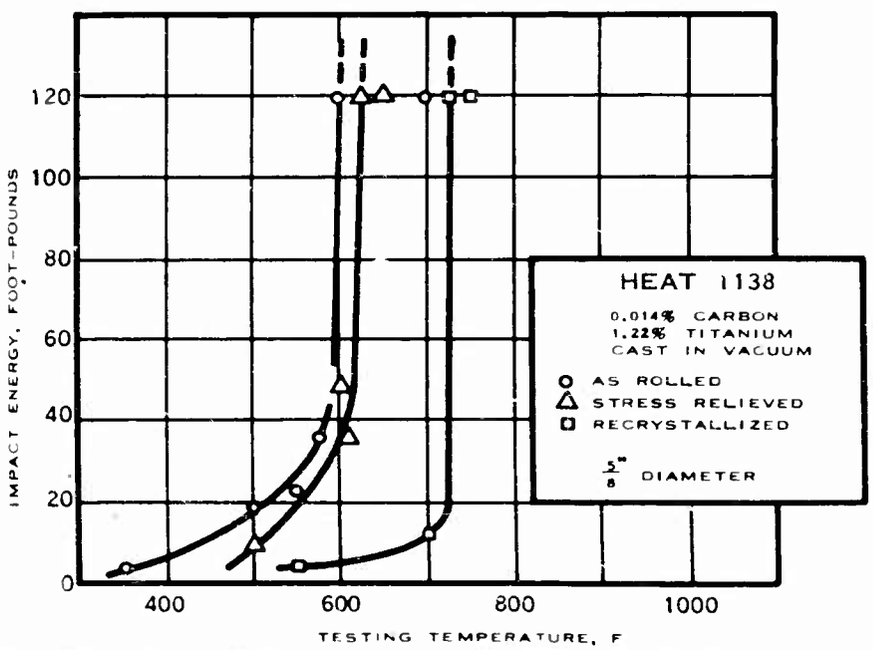


FIGURE D40— IMPACT (V-NOTCH) TRANSITION FOR 1.22% TITANIUM—MOLYBDENUM ALLOY

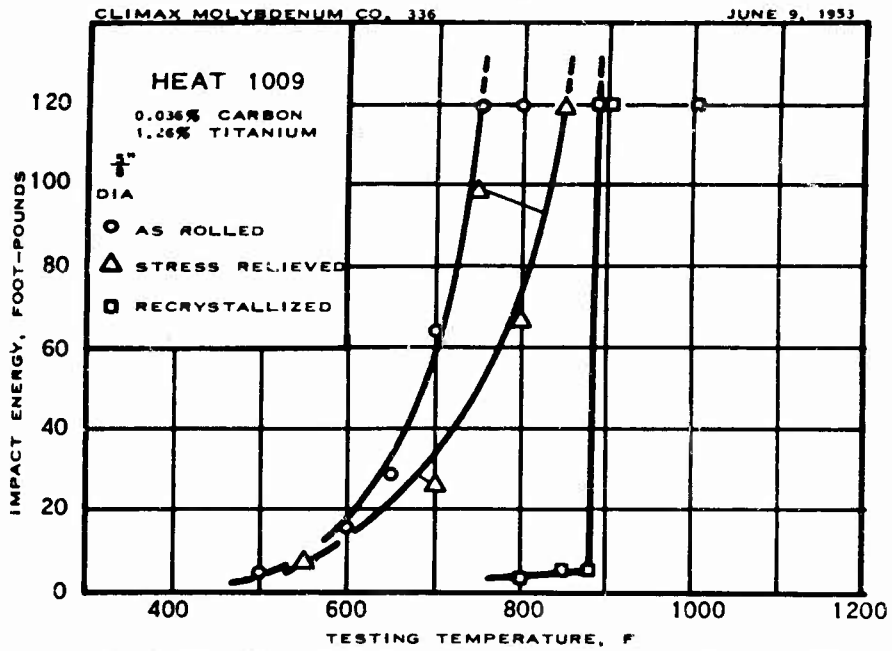


FIGURE D41– IMPACT (V–NOTCH) TRANSITION FOR 1.26% TITANIUM–MOLYBDENUM ALLOY

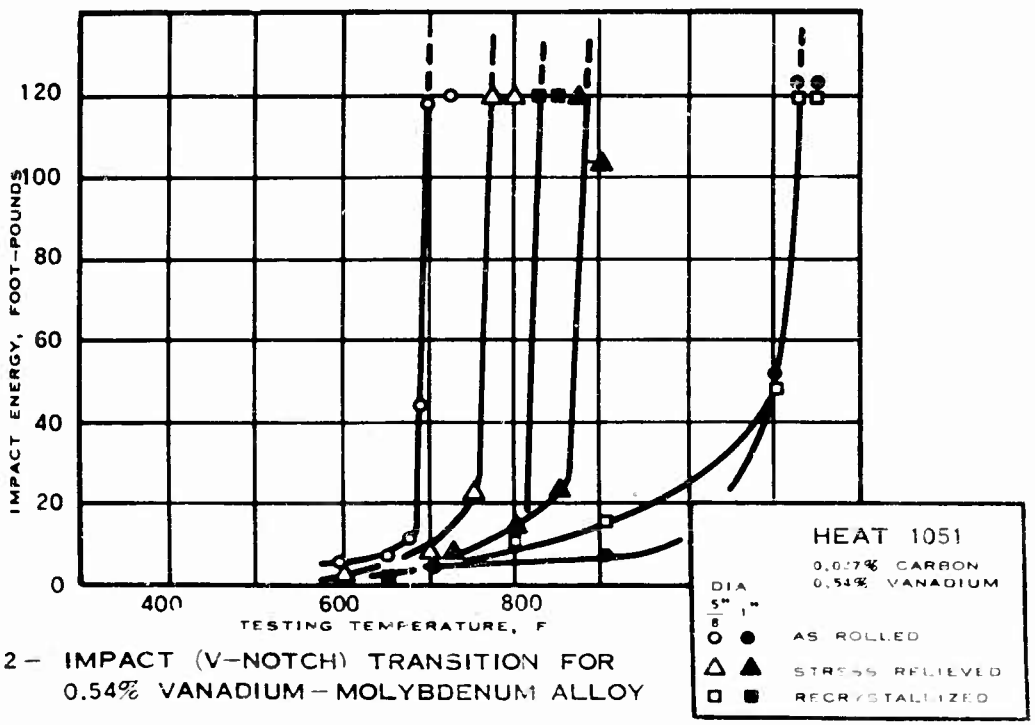


FIGURE D42– IMPACT (V–NOTCH) TRANSITION FOR 0.54% VANADIUM–MOLYBDENUM ALLOY

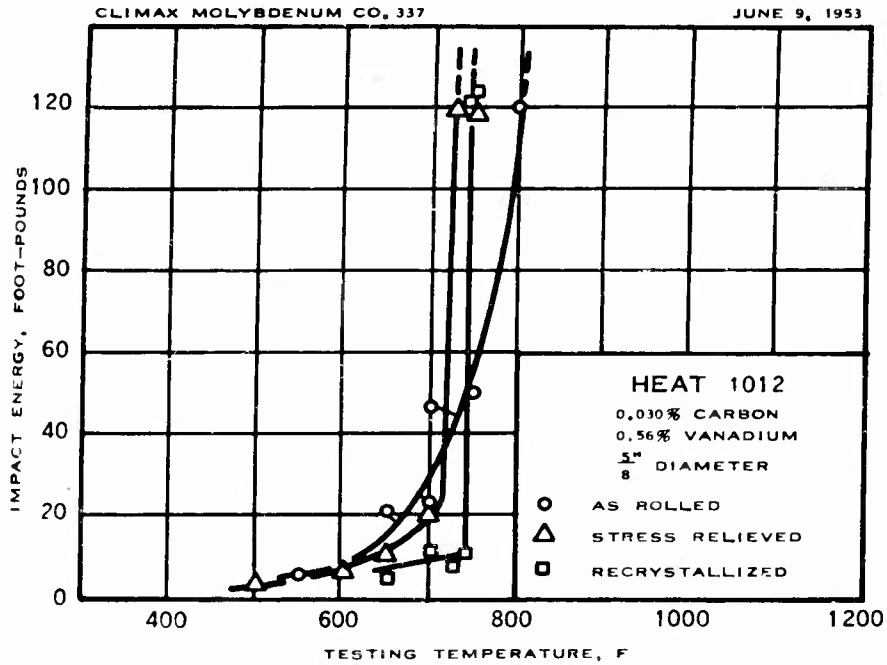


FIGURE D43– IMPACT (V–NOTCH) TRANSITION FOR 0.56% VANADIUM–MOLYBDENUM ALLOY

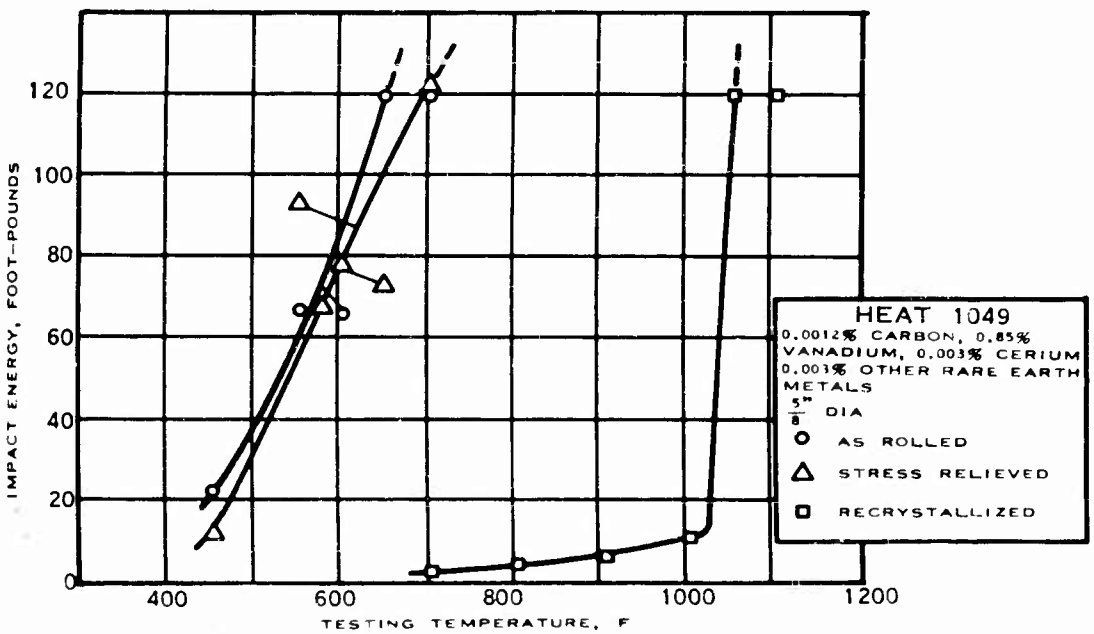


FIGURE D44– IMPACT (V–NOTCH) TRANSITION FOR 0.85% VANADIUM–MOLYBDENUM ALLOY

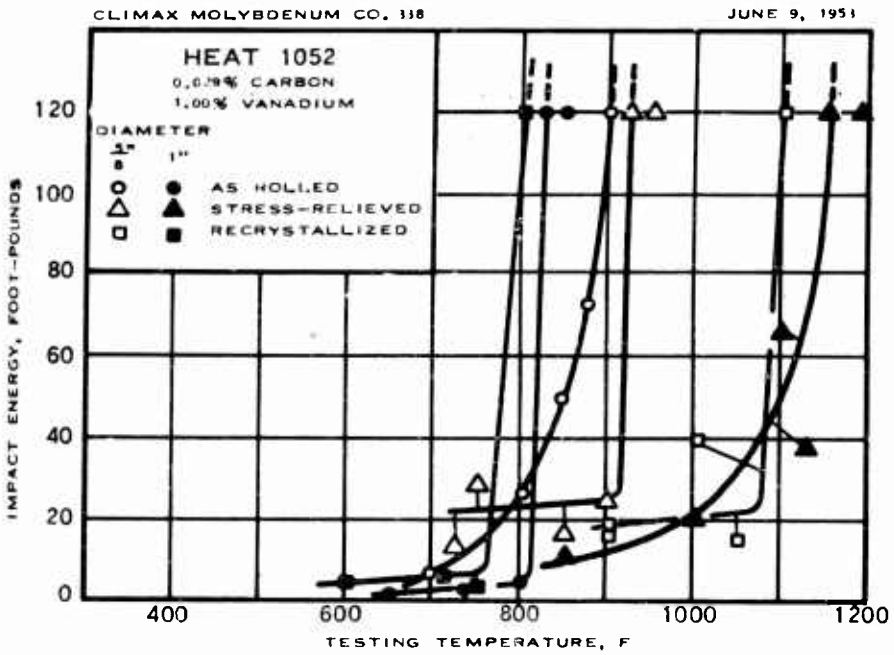


FIGURE D45 — IMPACT (V-NOTCH) TRANSITION FOR 1.00% VANADIUM — MOLYBDENUM ALLOY

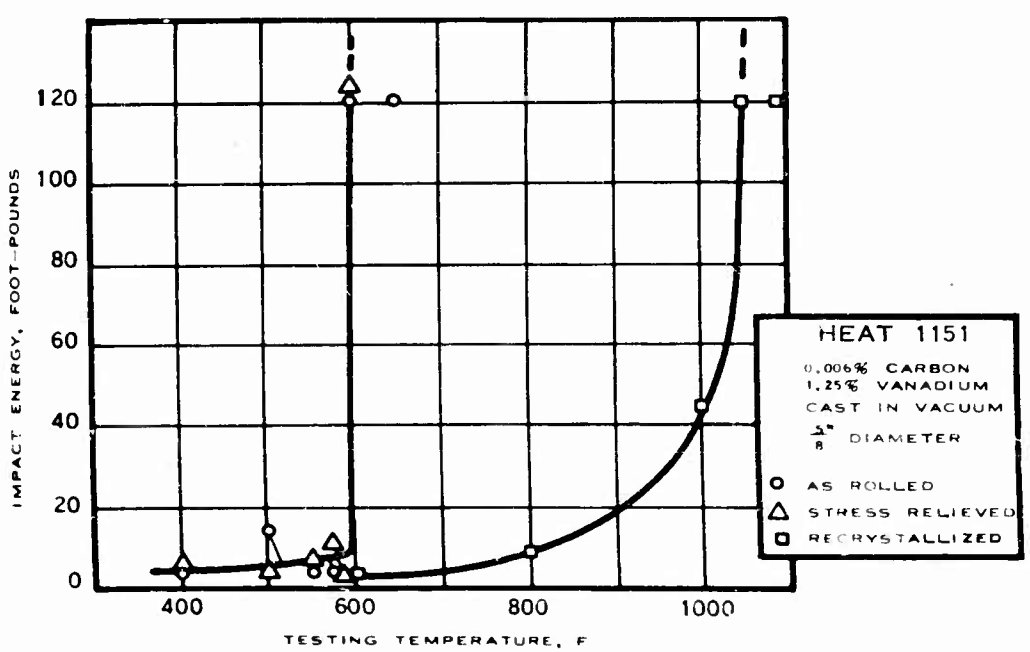


FIGURE D46 — IMPACT (V-NOTCH) TRANSITION FOR 1.25% VANADIUM — MOLYBDENUM ALLOY

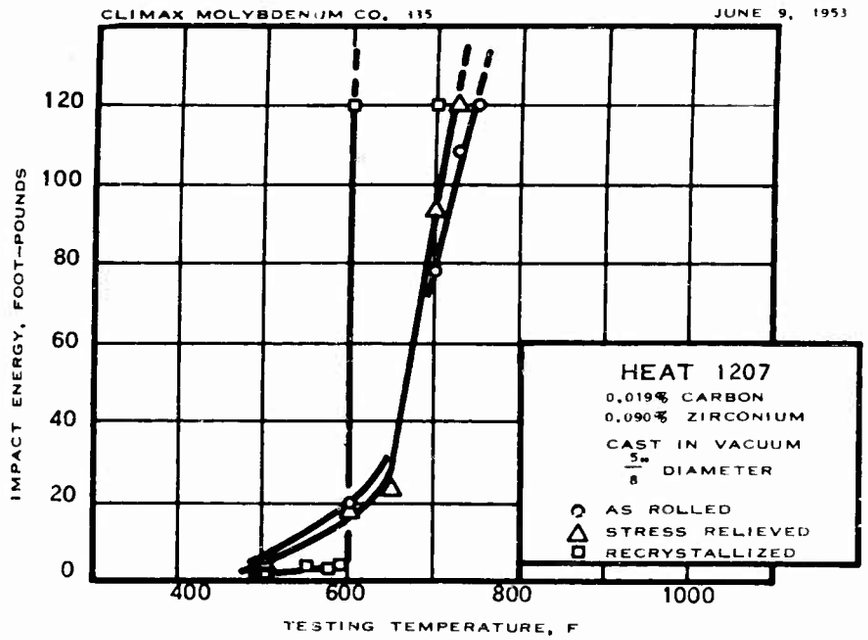


FIGURE D47— IMPACT (V—NOTCH) TRANSITION FOR 0.090% ZIRCONIUM—MOLYBDENUM ALLOY

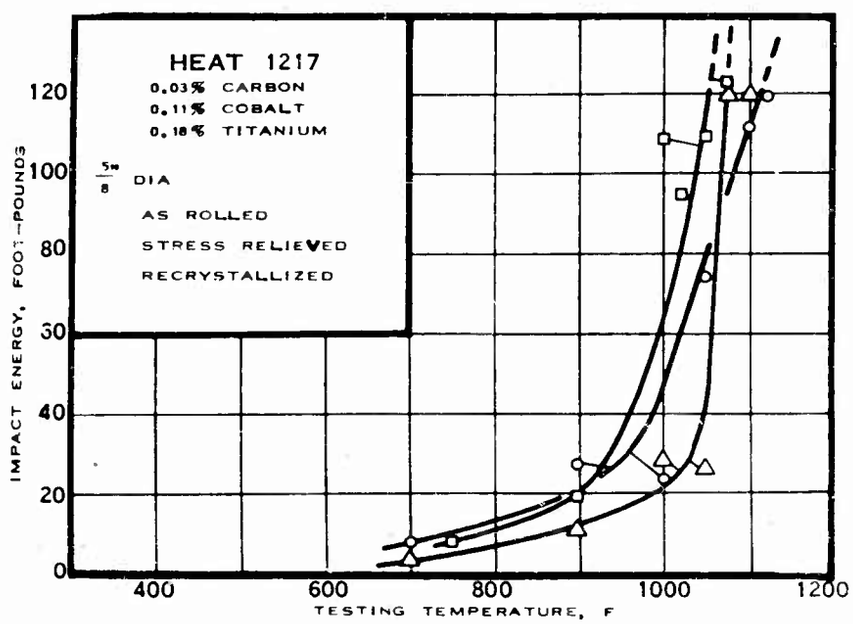


FIGURE D48— IMPACT (V—NOTCH) TRANSITION FOR 0.11% COBALT—0.18% TITANIUM—MOLYBDENUM ALLOY

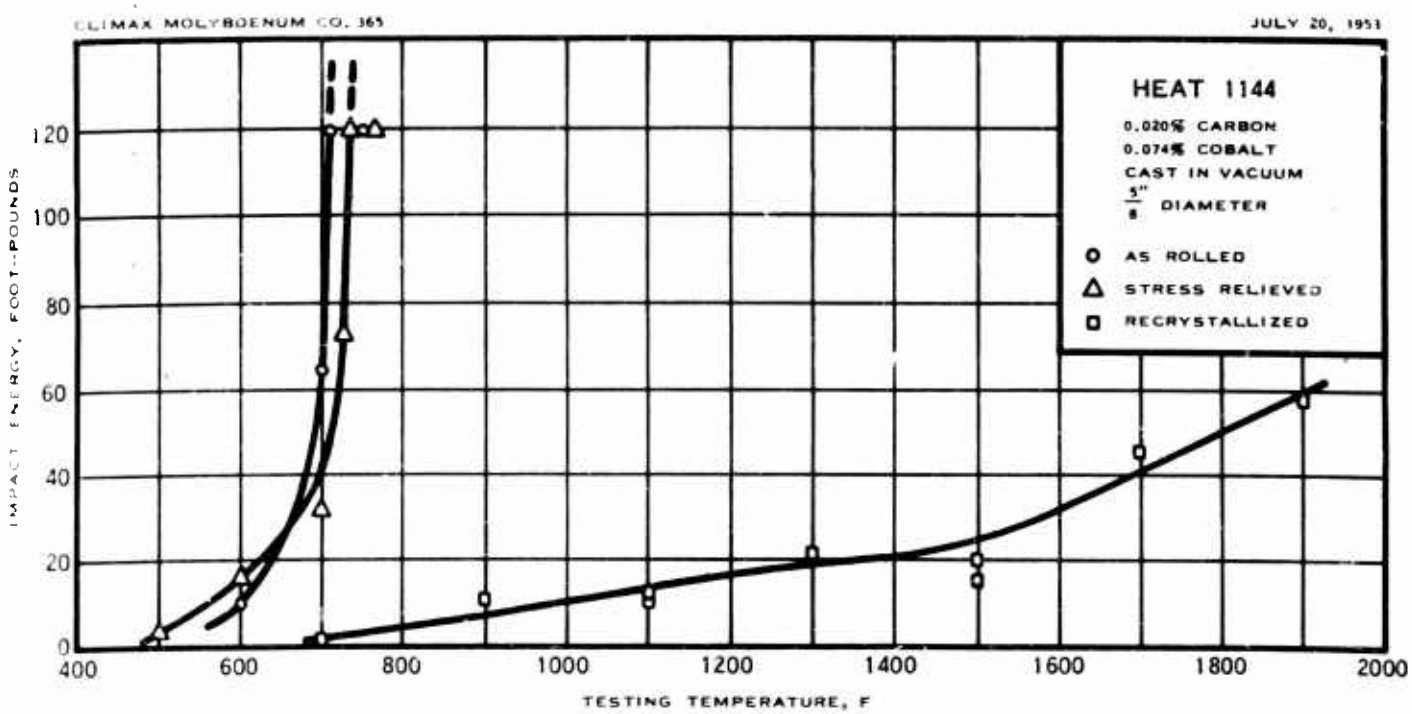


FIGURE D49– IMPACT (V–NOTCH) TRANSITION FOR 0.074% COBALT – MOLYBDENUM ALLOY

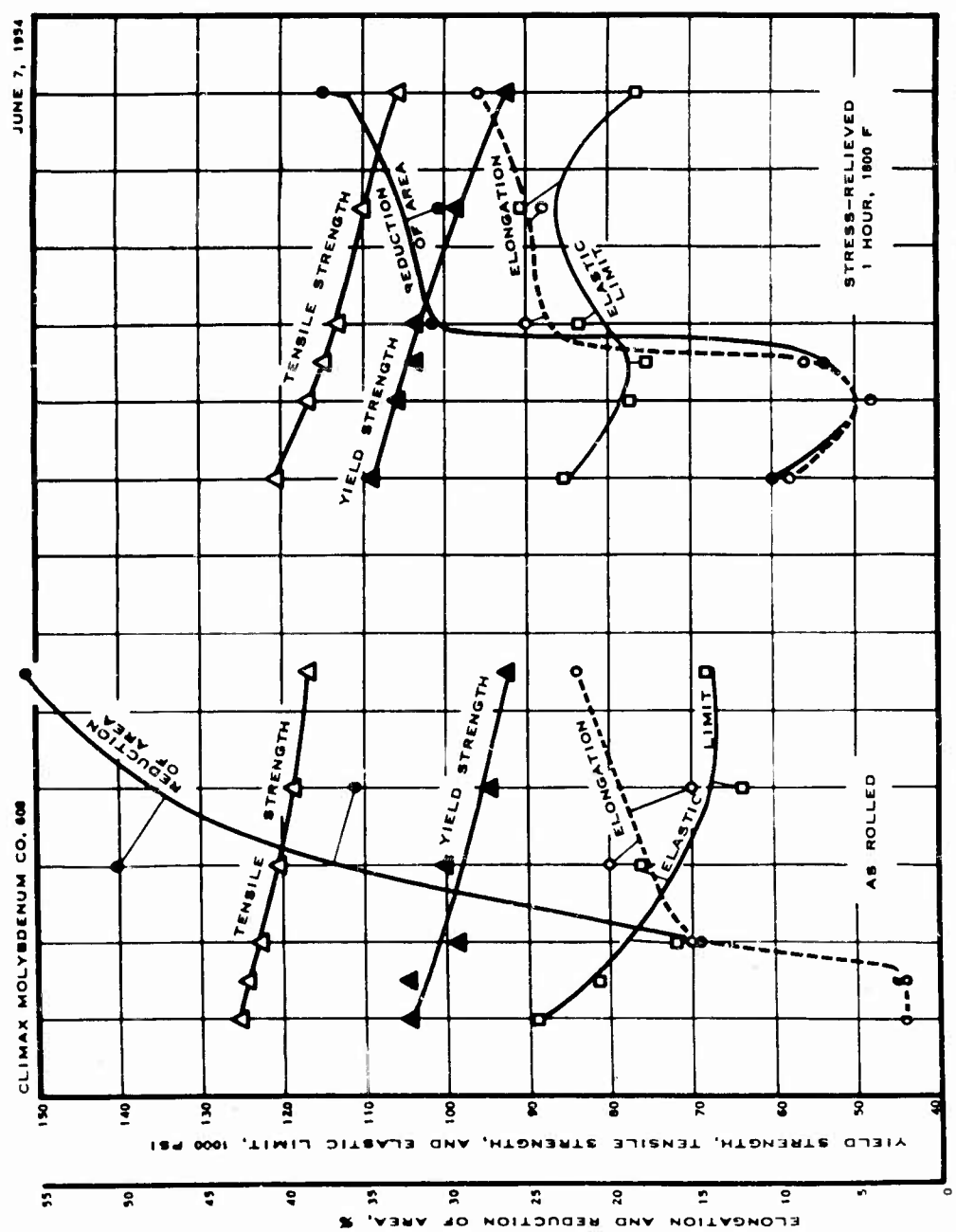


FIGURE D50— EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 936 (0.008% CARBON)

AS-ROLLED AND STRESS-RELIEVED CONDITIONS

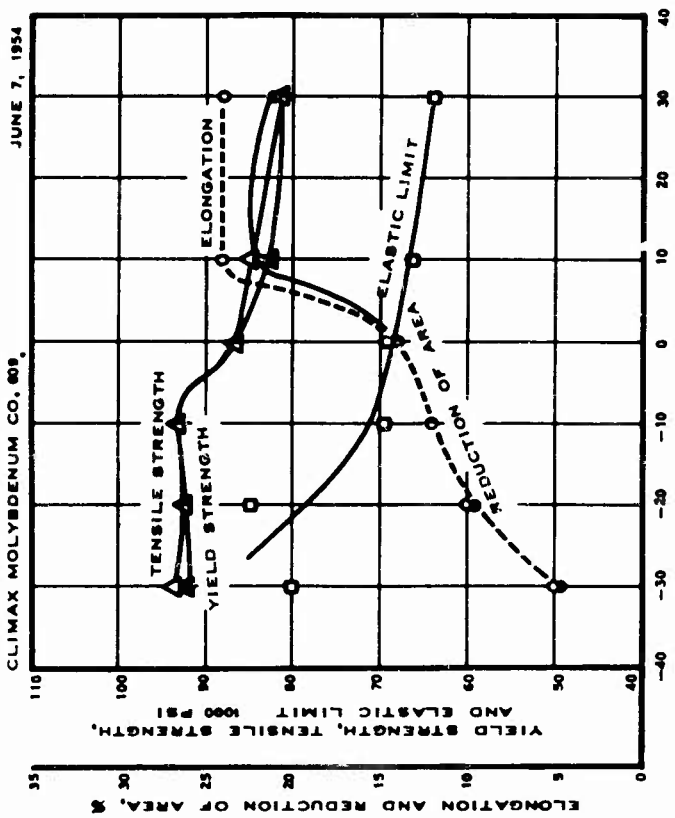


FIGURE D51 — EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 936 (0.008% CARBON)

RECRYSTALLIZED, 1 HOUR, 2150 F

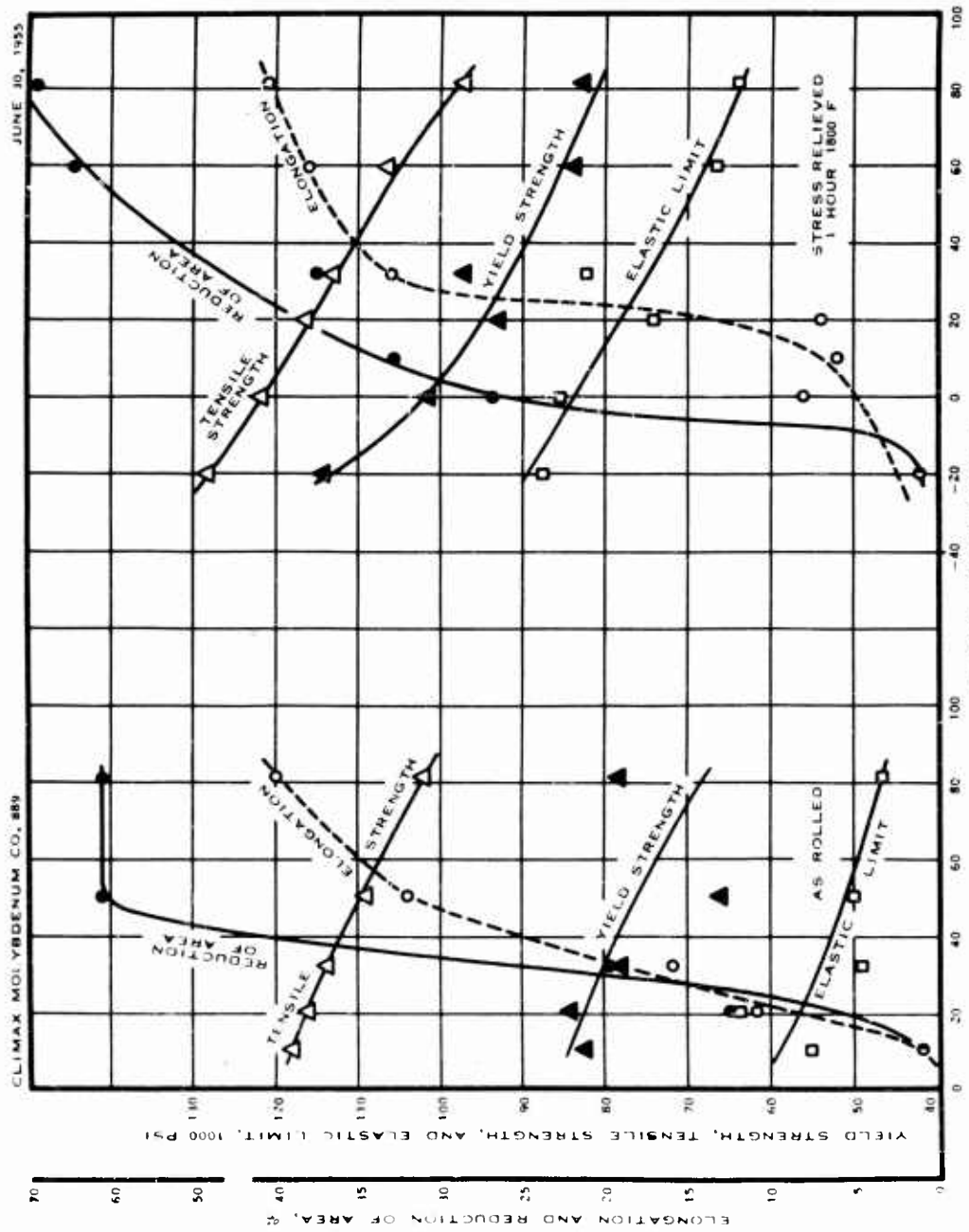


FIGURE D52— EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 937 (0.015% CARBON)
AS-ROLLED AND STRESS-RELIEVED CONDITIONS

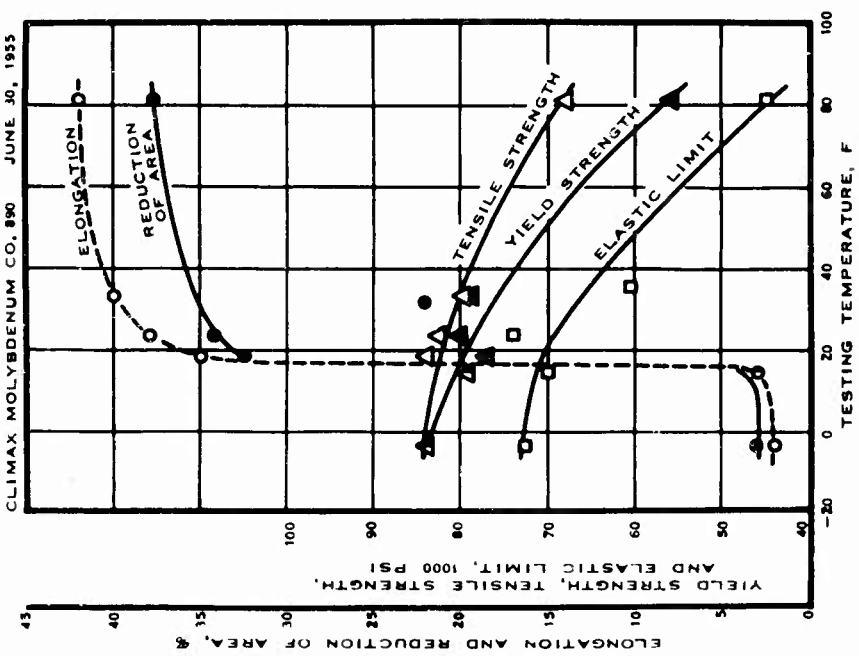


FIGURE D53— EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 937 (0.015% C)

RECRYSTALLIZED 1 HOUR 2150 F

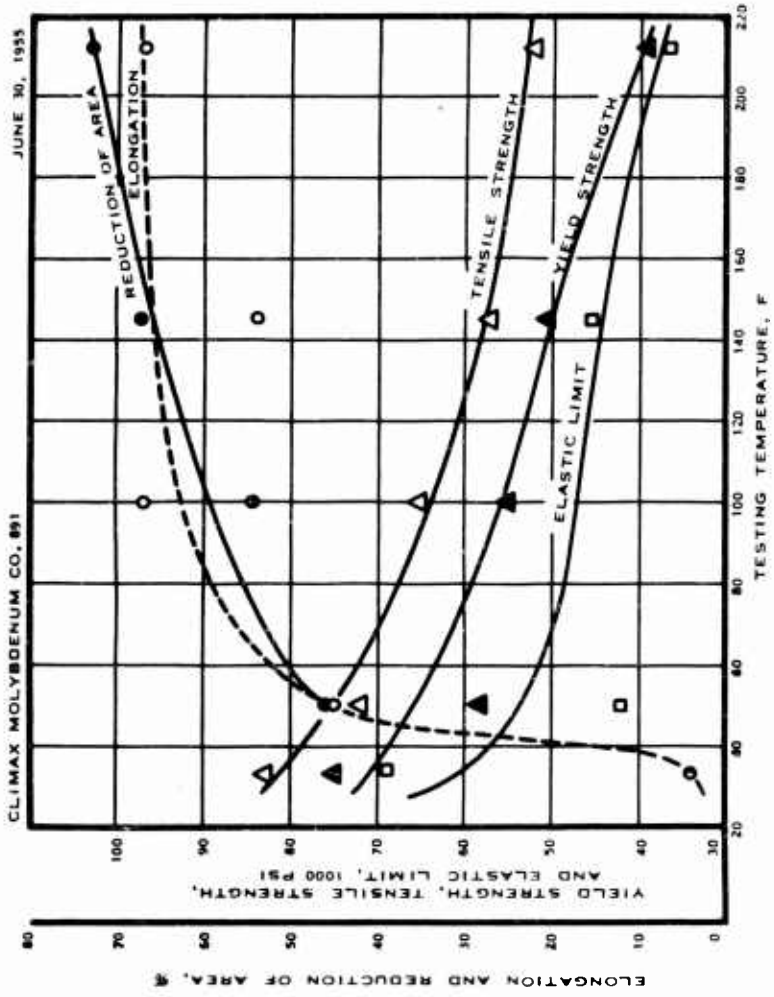


FIGURE D54— EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1045 (0.003% C, 0.005% C_E, 0.007% RE)
RECRYSTALLIZED 1 HOUR 2400 F

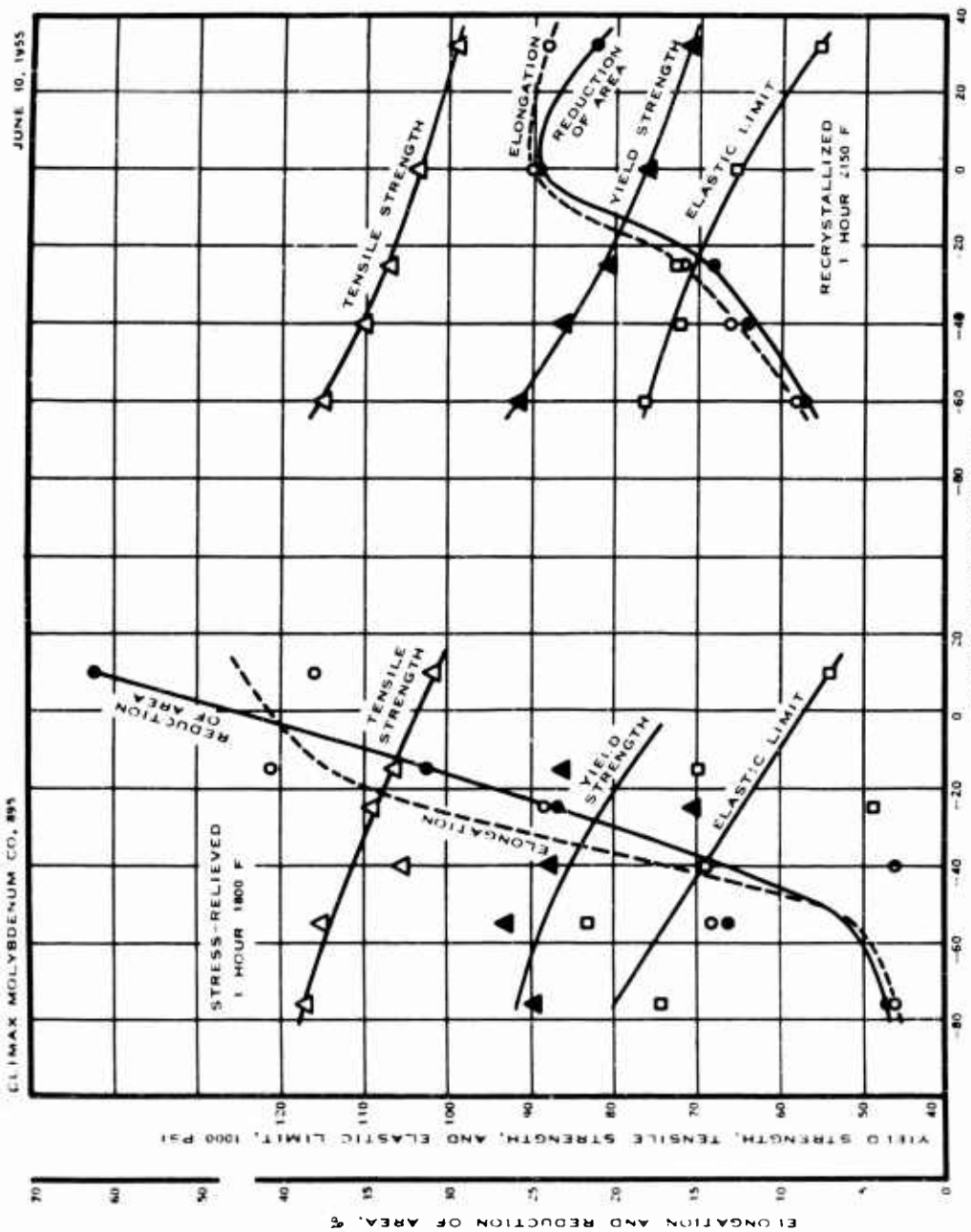


FIGURE D55 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1252 (0.003% C, 0.15% A_L)

AS-ROLLED AND STRESS-RELIEVED CONDITIONS

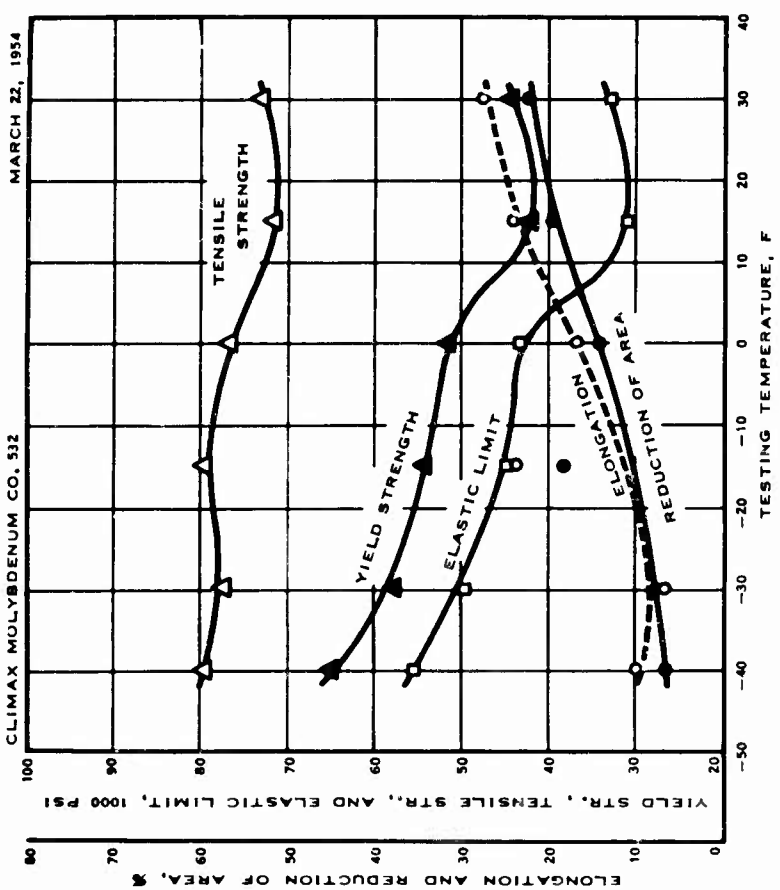


FIGURE D56 — EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1252 (0.15% ALUMINUM) RECRYSTALLIZED ONE HOUR AT 2150 F

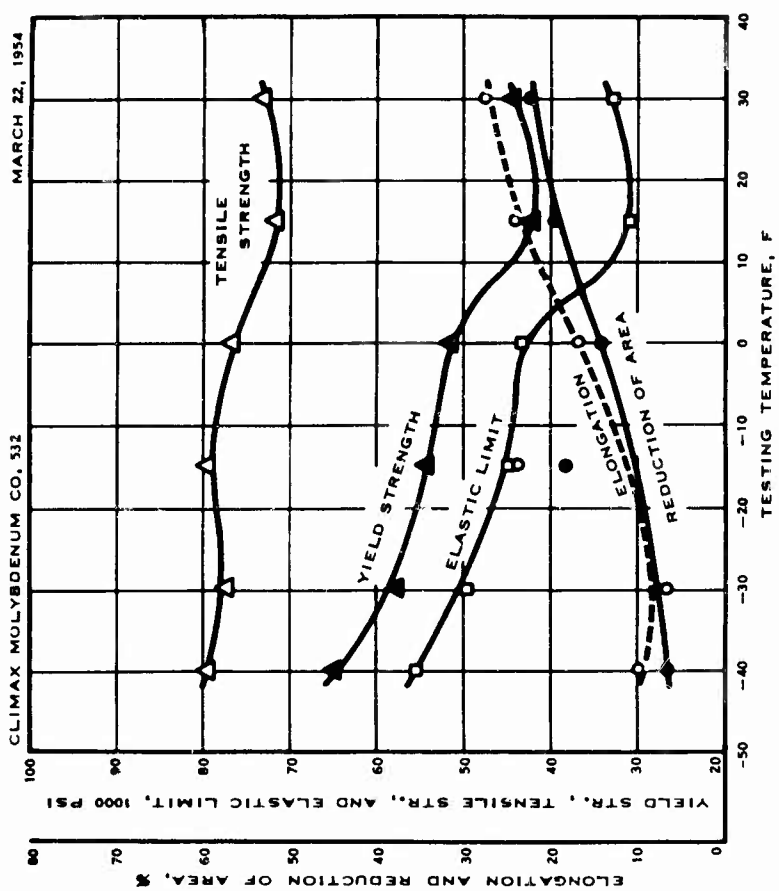


FIGURE D56 — EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1252 (0.15% ALUMINUM) RECRYSTALLIZED ONE HOUR AT 2150 F

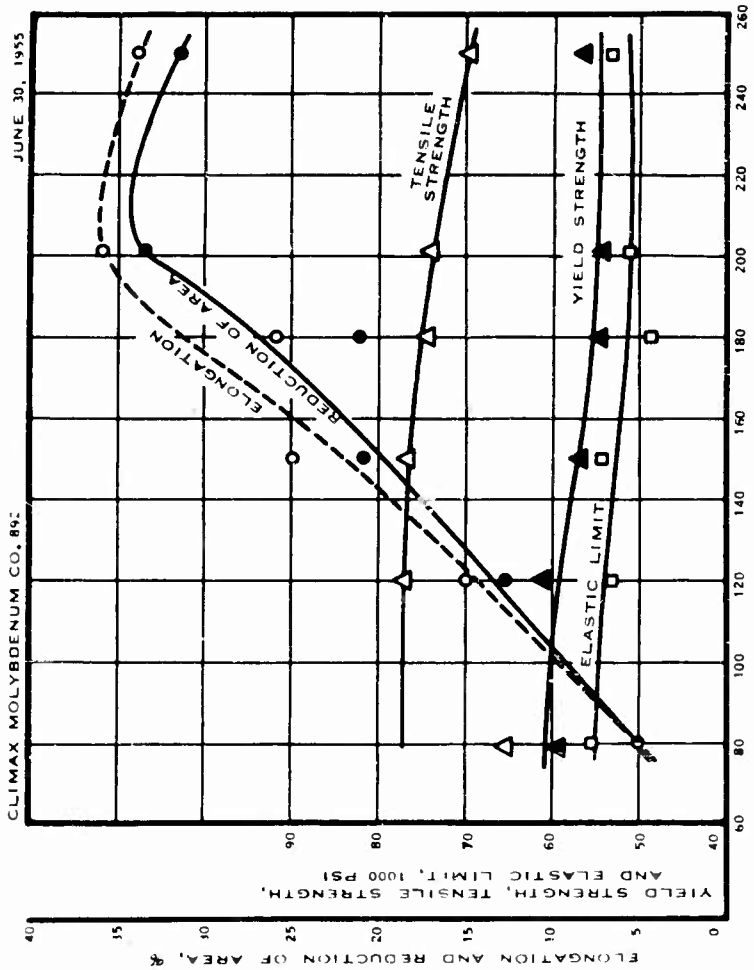


FIGURE D57 — EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1058 (0.006% C, 0.49% Al)

RECRYSTALLIZED 1 HOUR 2150 F

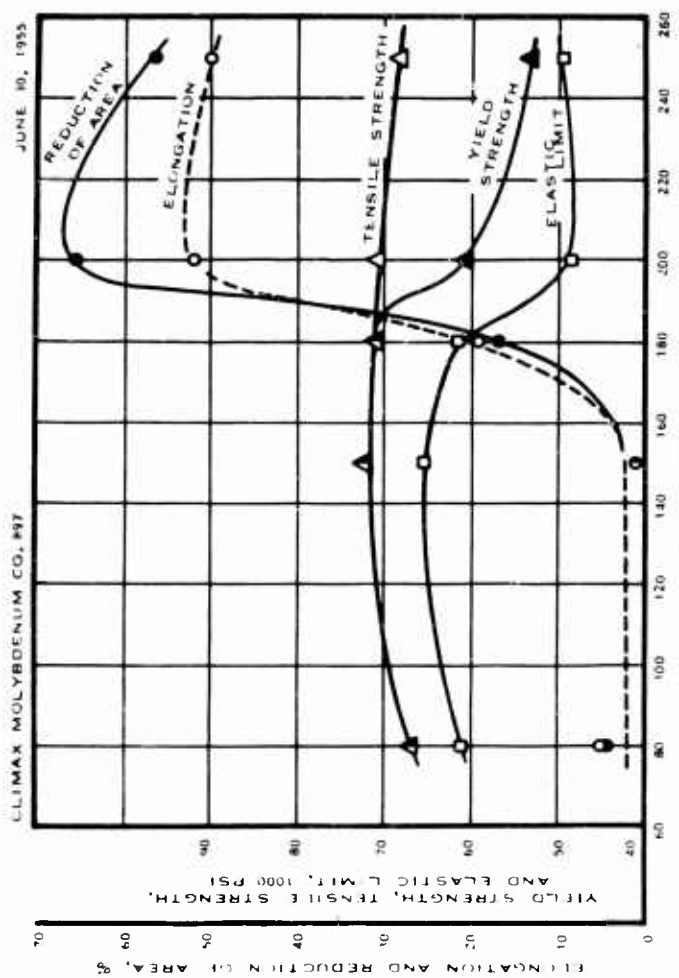


FIGURE D58 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1144 (0.020% C, 0.074% Co)

RECRYSTALLIZED 1 HOUR 2000 F

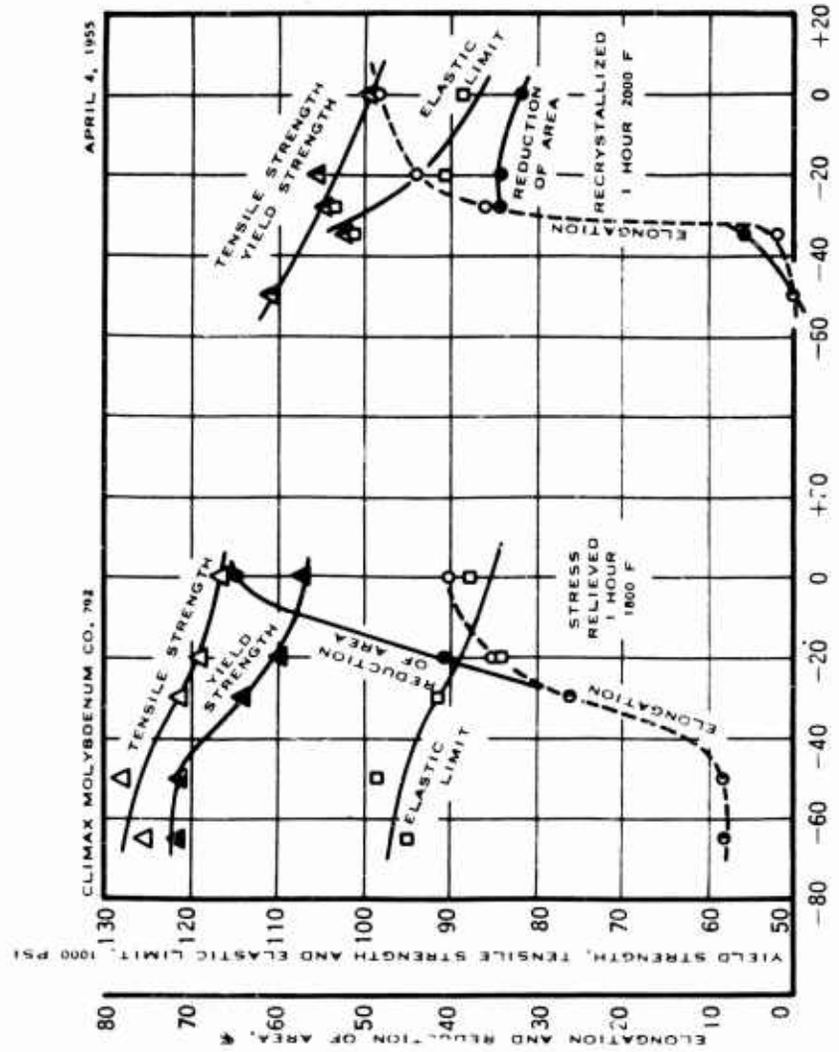


FIGURE D59 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF $\frac{1}{2}$" DIAMETER BAR 1463 (0.033 C, 0.11 C_R)

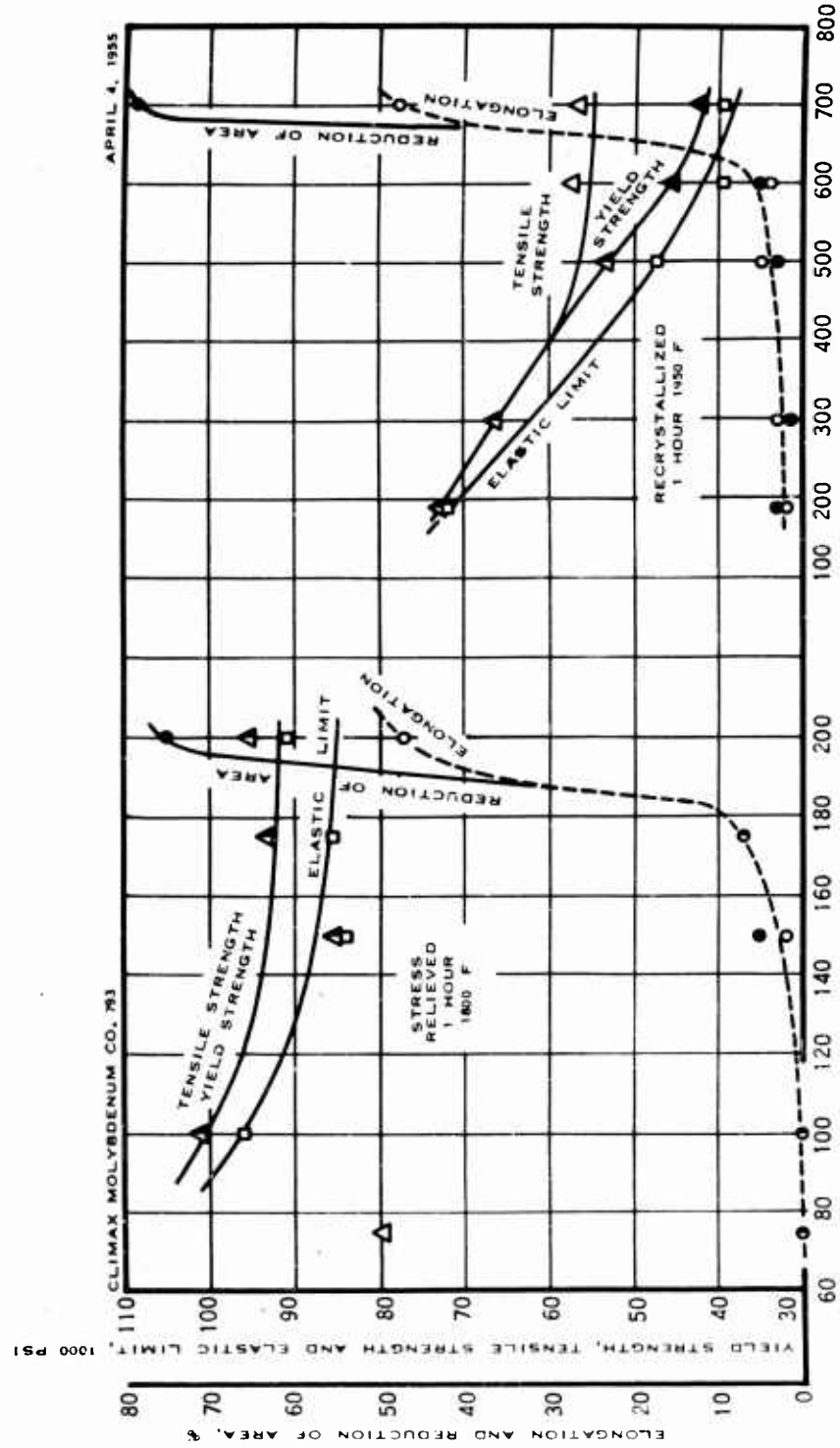


FIGURE D60 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF $\frac{1}{2}$" DIAMETER BAR 1465 (0.021 C, 0.05 Ni)

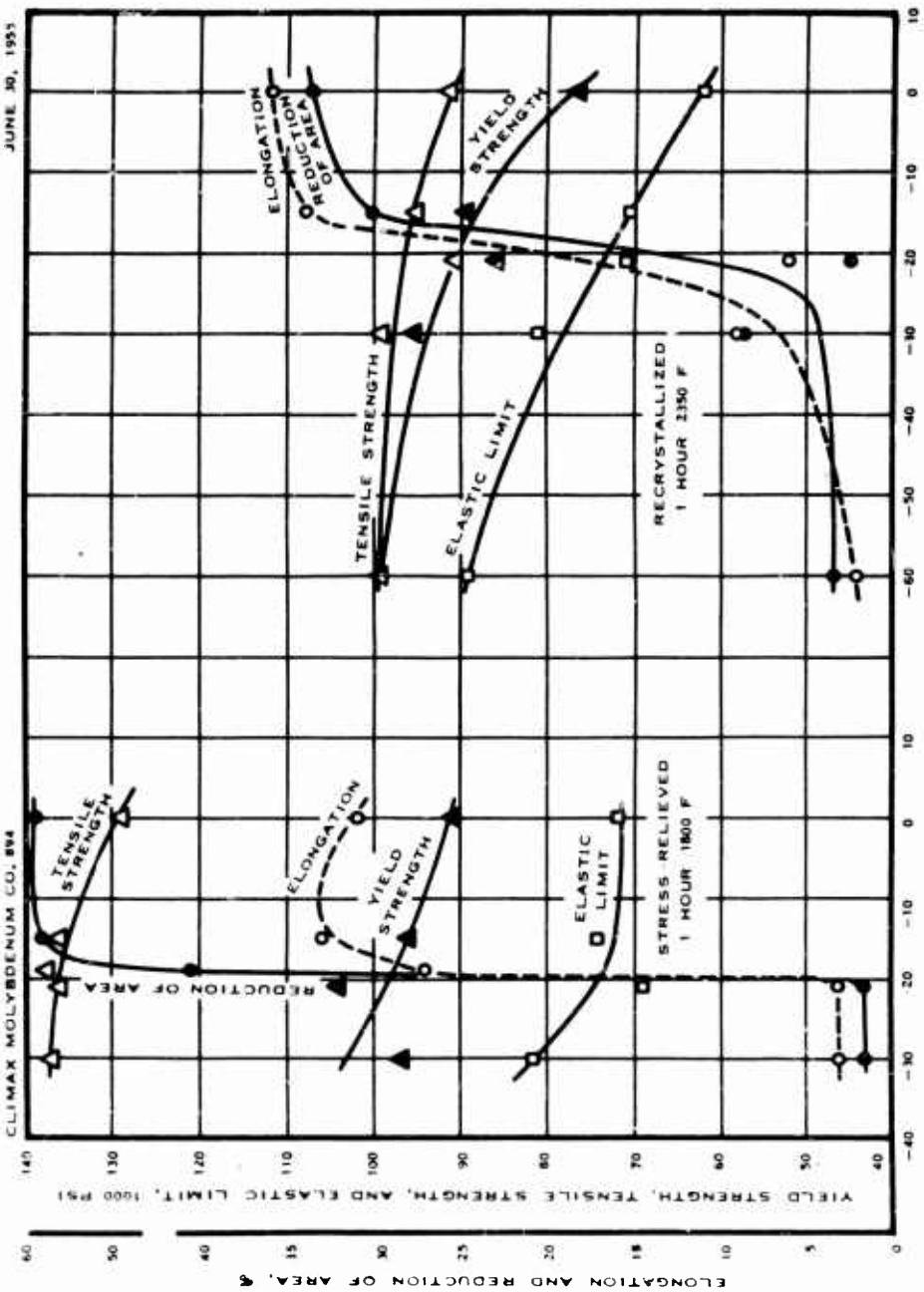


FIGURE D61 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1268 (0.014% C, 0.23% T_i)

AS-ROLLED AND STRESS-RELIEVED CONDITIONS

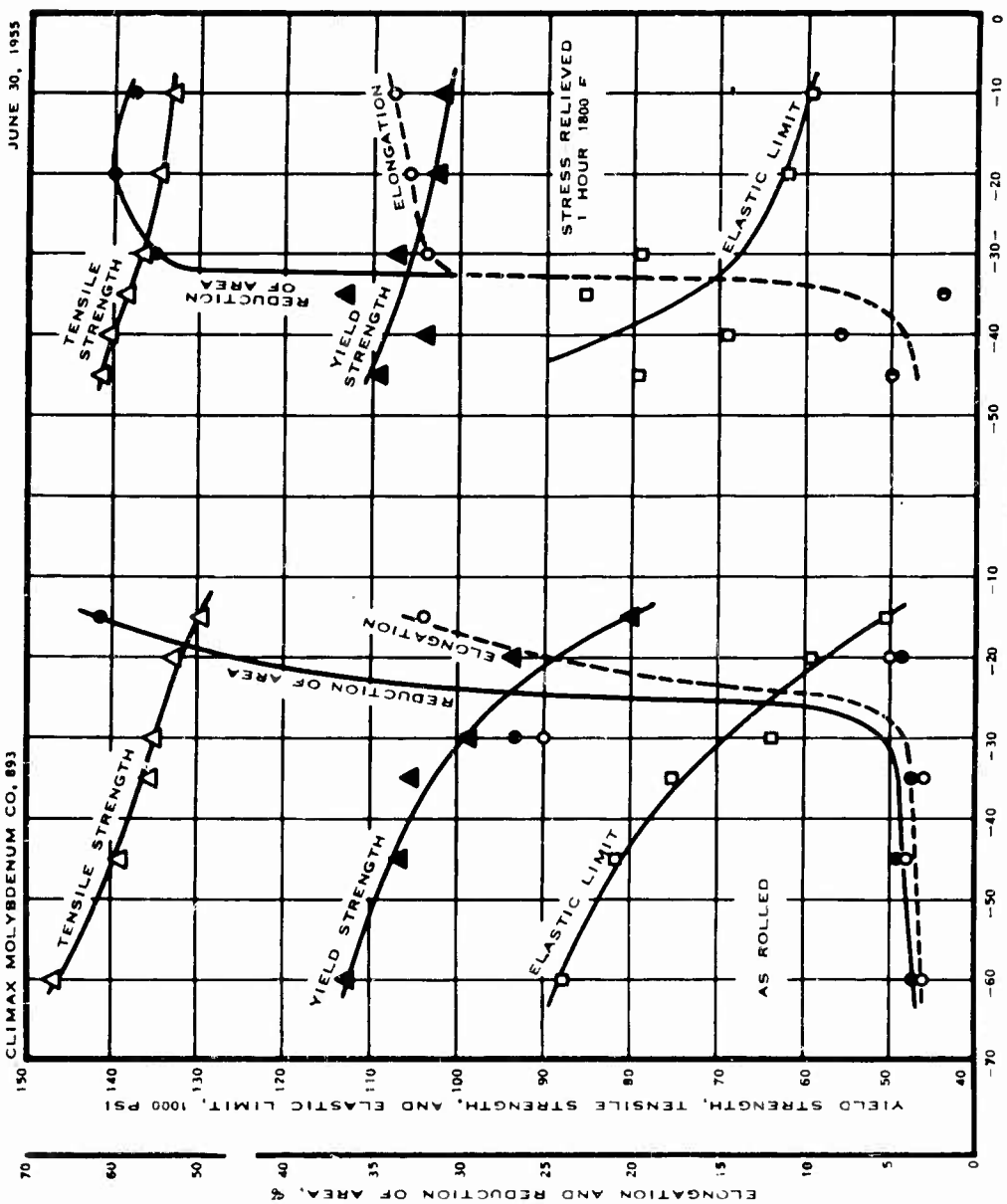


FIGURE D62 — EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1348 (0.021% C, 0.46% T_i)

AS-ROLLED AND STRESS-RELIEVED CONDITIONS

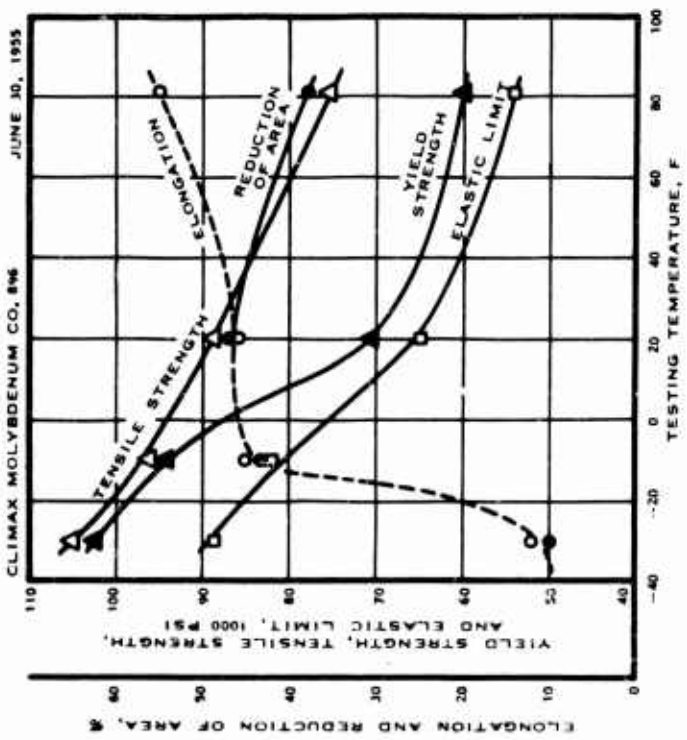


FIGURE D63 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1132 (0.024% C, 0.45% T_1)

RECRYSTALLIZED 1 HOUR 2450 F

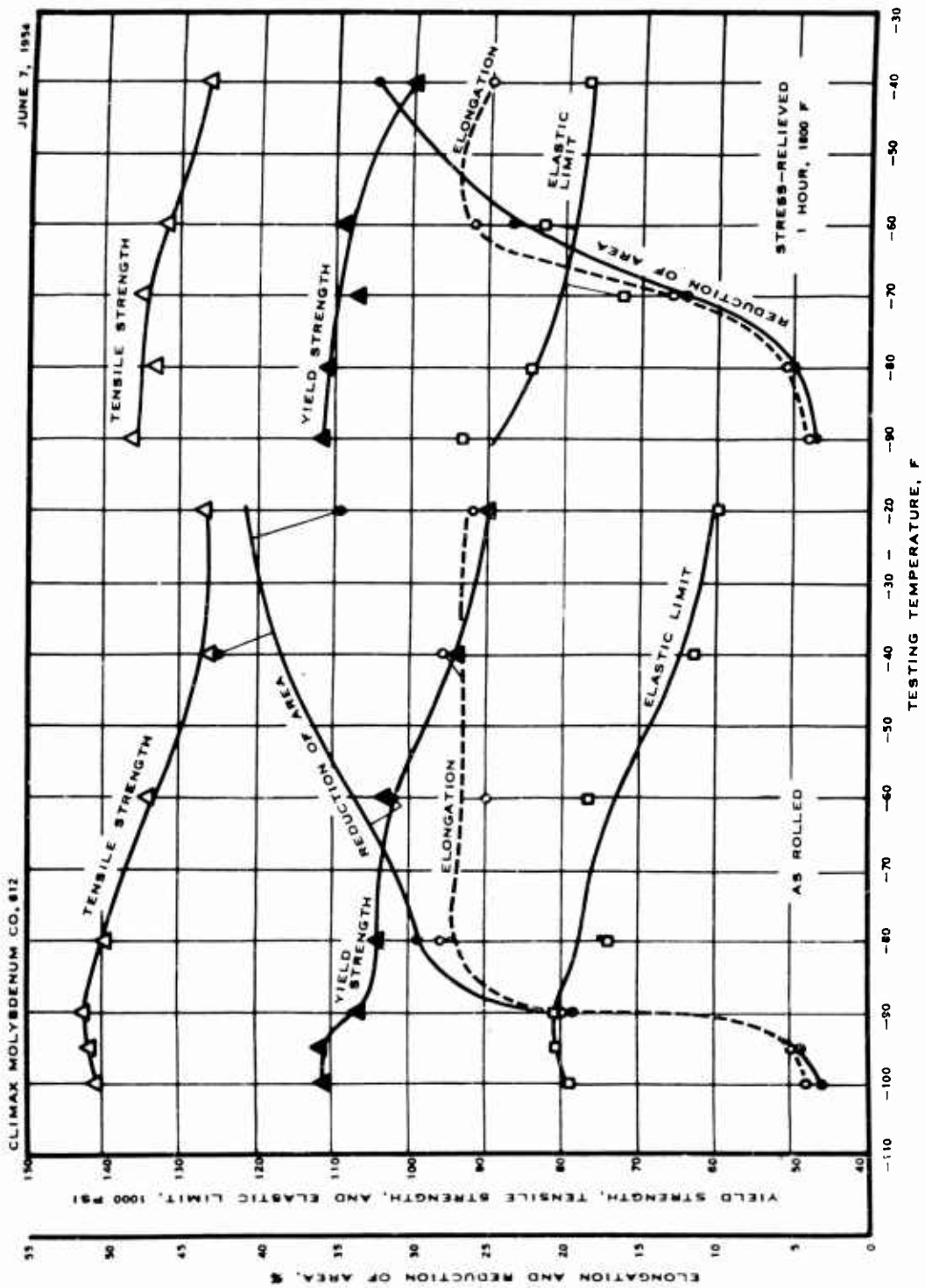


FIGURE D64 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1393 (0.006% CARBON, 0.12% ALUMINUM, 0.50% TITANIUM)
AS-ROLLED AND STRESS-RELIEVED CONDITIONS

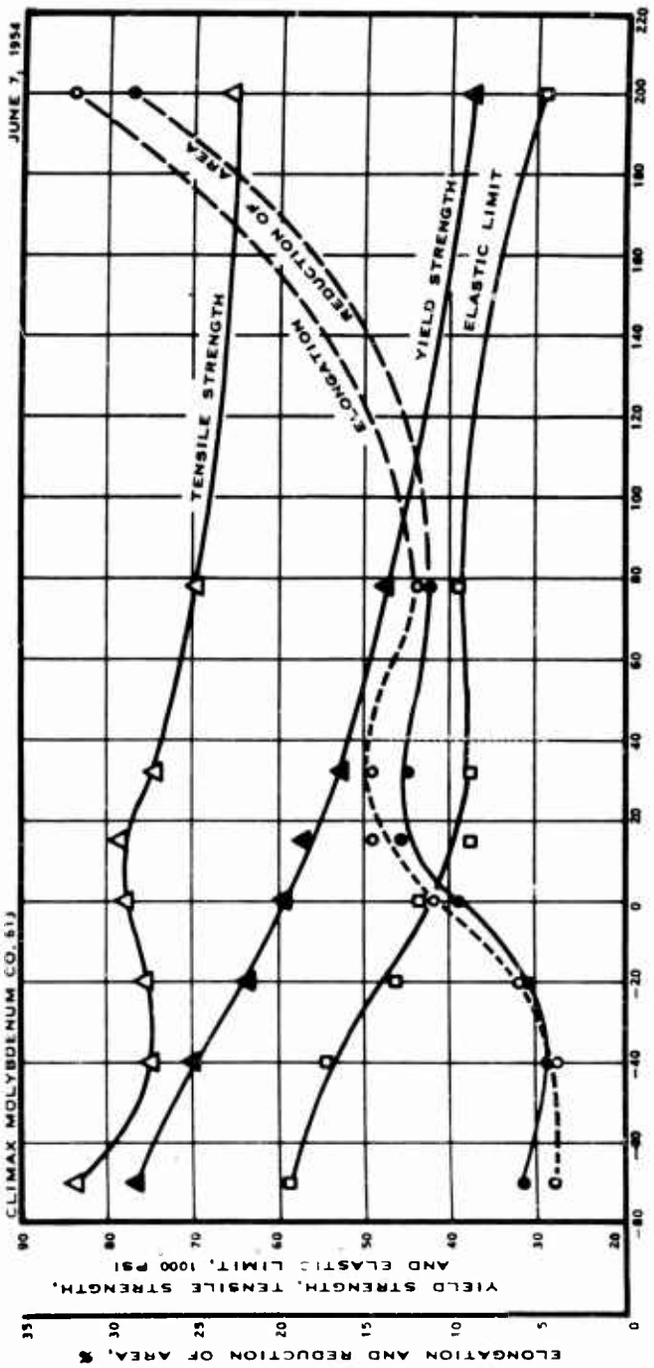


FIGURE D65— EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1393 (0.006% CARBON, 0.12% ALUMINUM, 0.50% TITANIUM

RECRYSTALLIZED, 1 HOUR, 2450 F

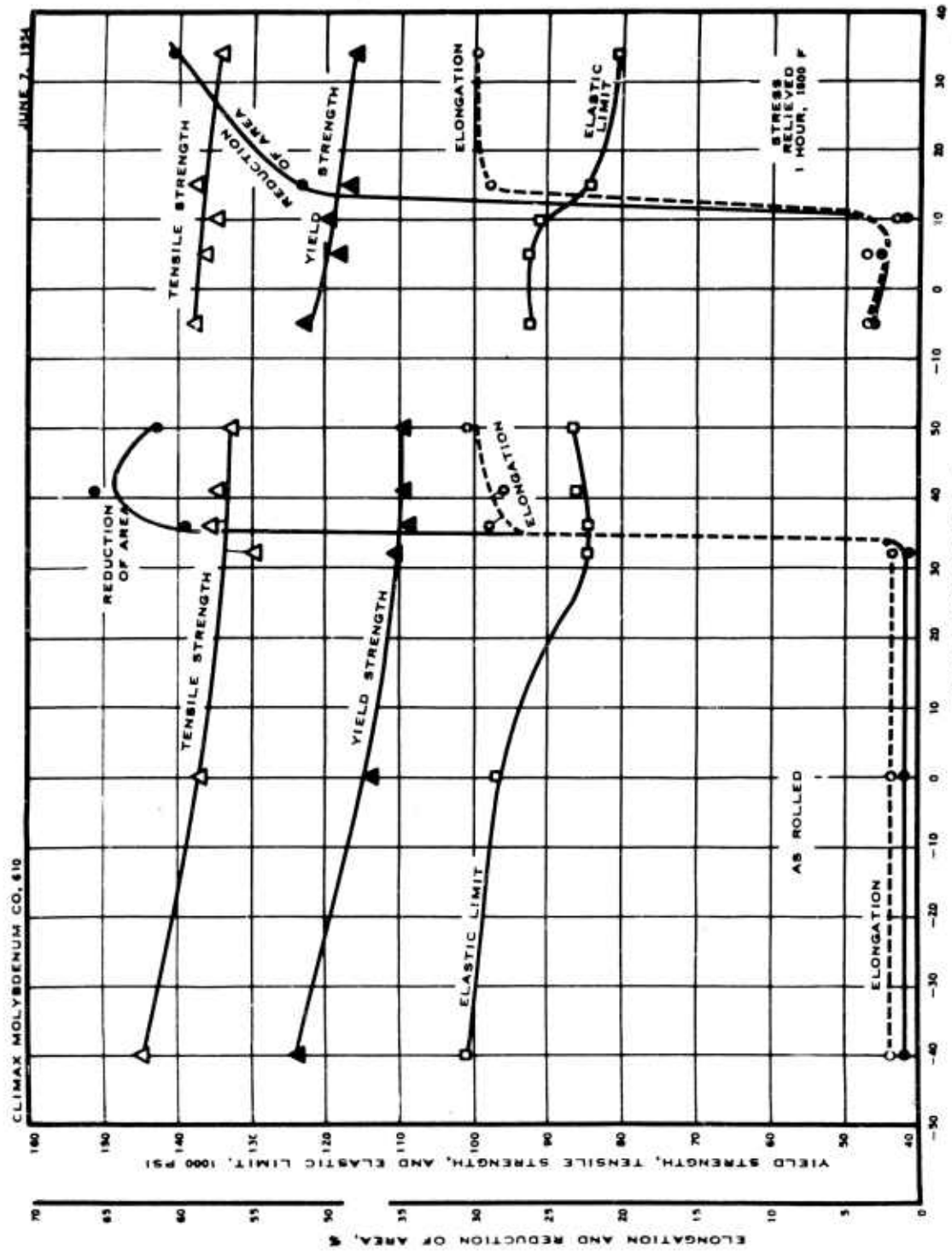


FIGURE D66— EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1390 (0.018% CARBON, 0.054% ZIRCONIUM)

AS-ROLLED AND STRESS-RELIEVED CONDITIONS

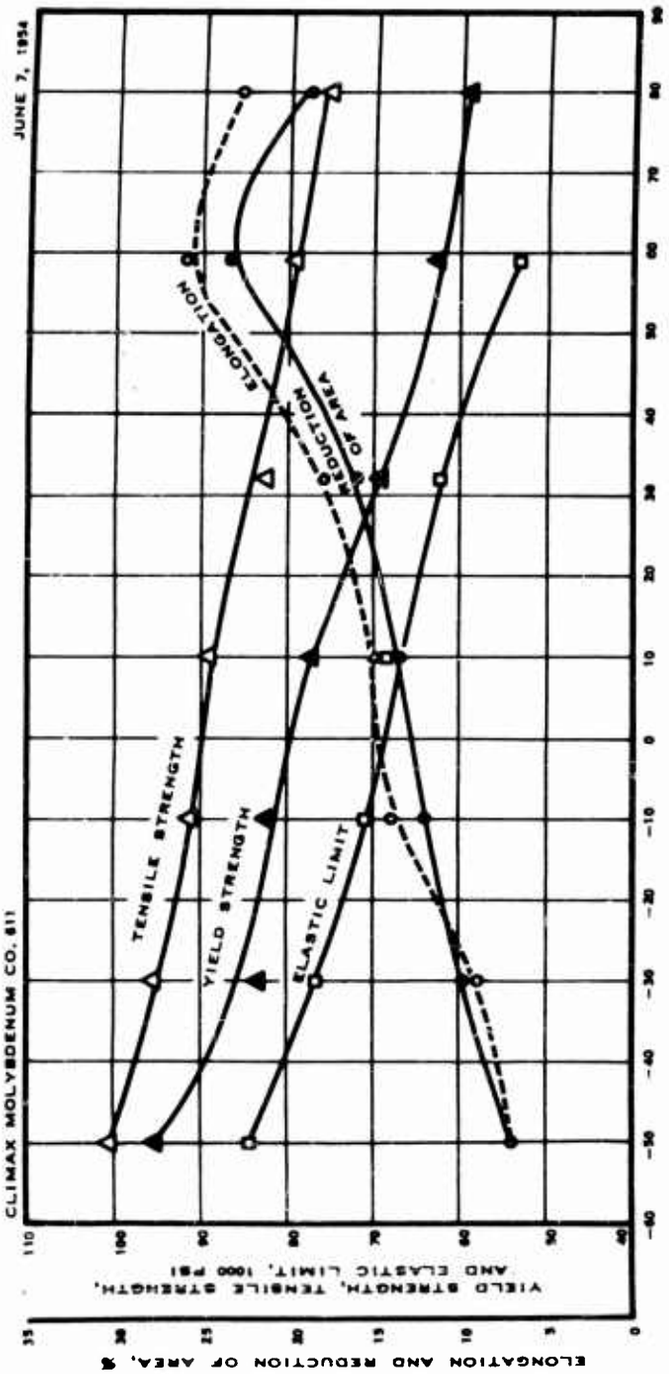


FIGURE D67 — EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF 5/8" DIAMETER BAR 1390 (0.018% CARBON, 0.054% ZIRCONIUM)

RECRYSTALLIZED, 1 HOUR, 2450 F

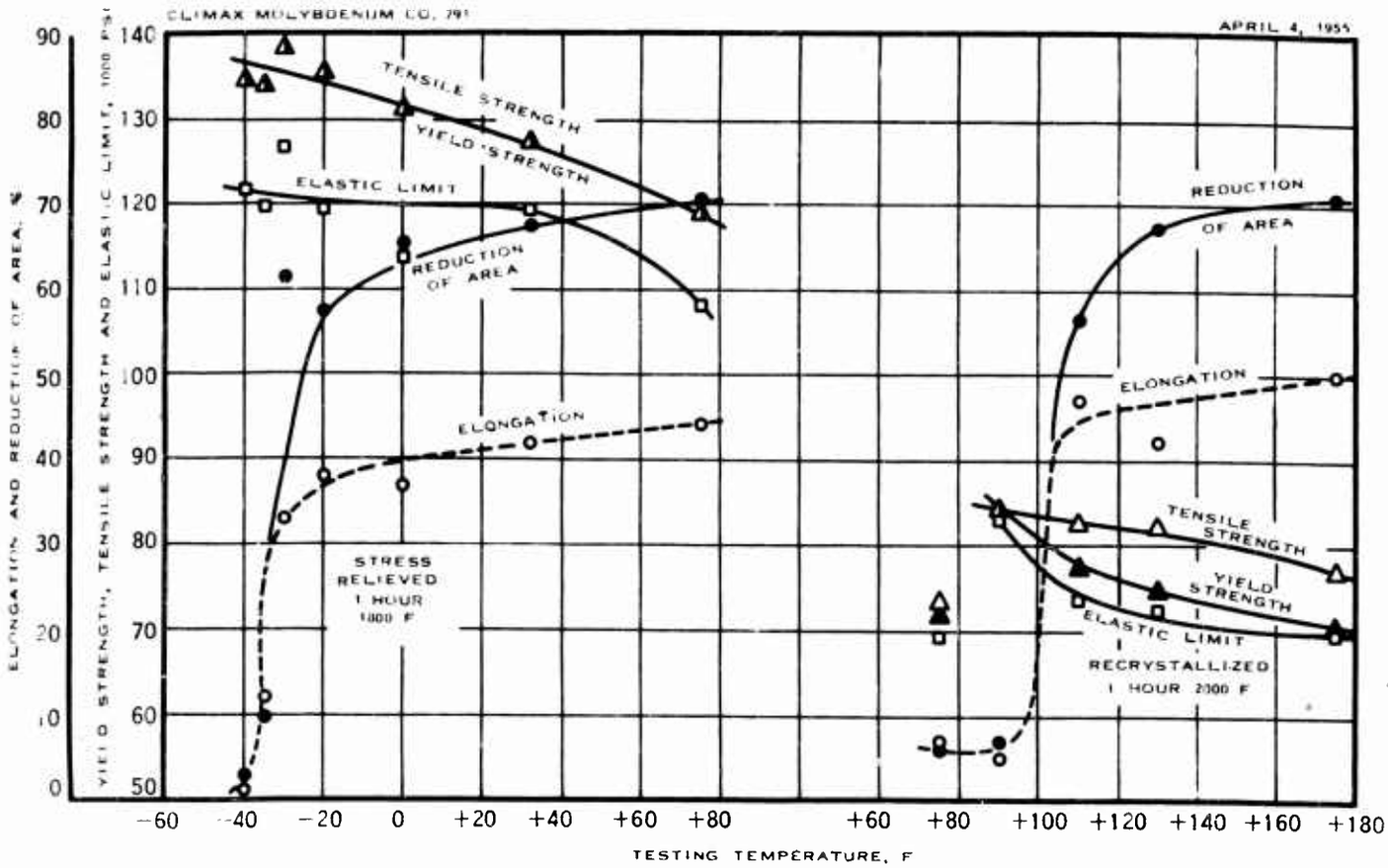


FIGURE D68– EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF $\frac{1}{2}$" DIAMETER BAR 1455 (0.025 C, 0.06 C_o, 0.47 V)

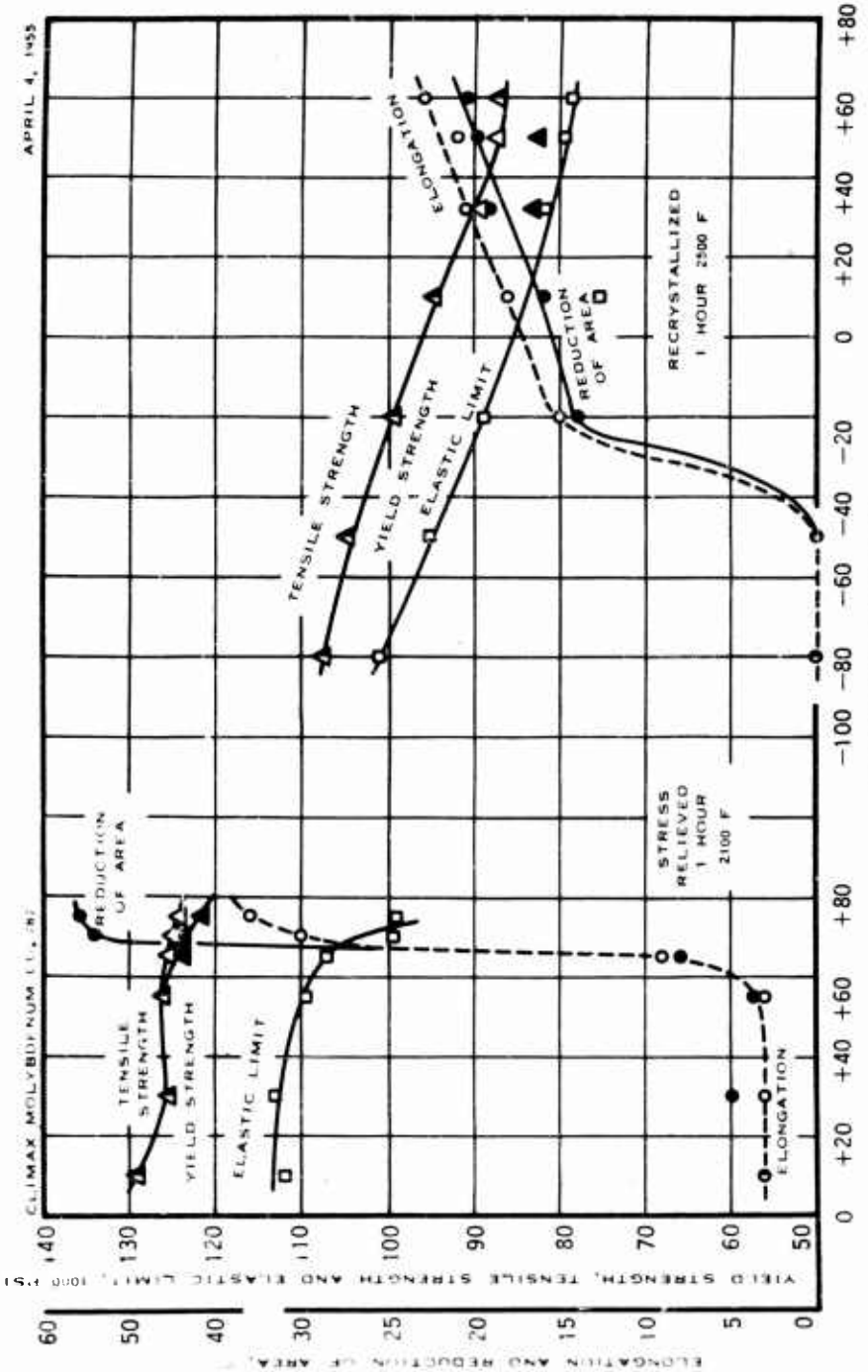


FIGURE D69– EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF $\frac{1}{2}$" DIAMETER BAR 1454 (0.027 C, 0.06 Co, 0.07 Z_R)

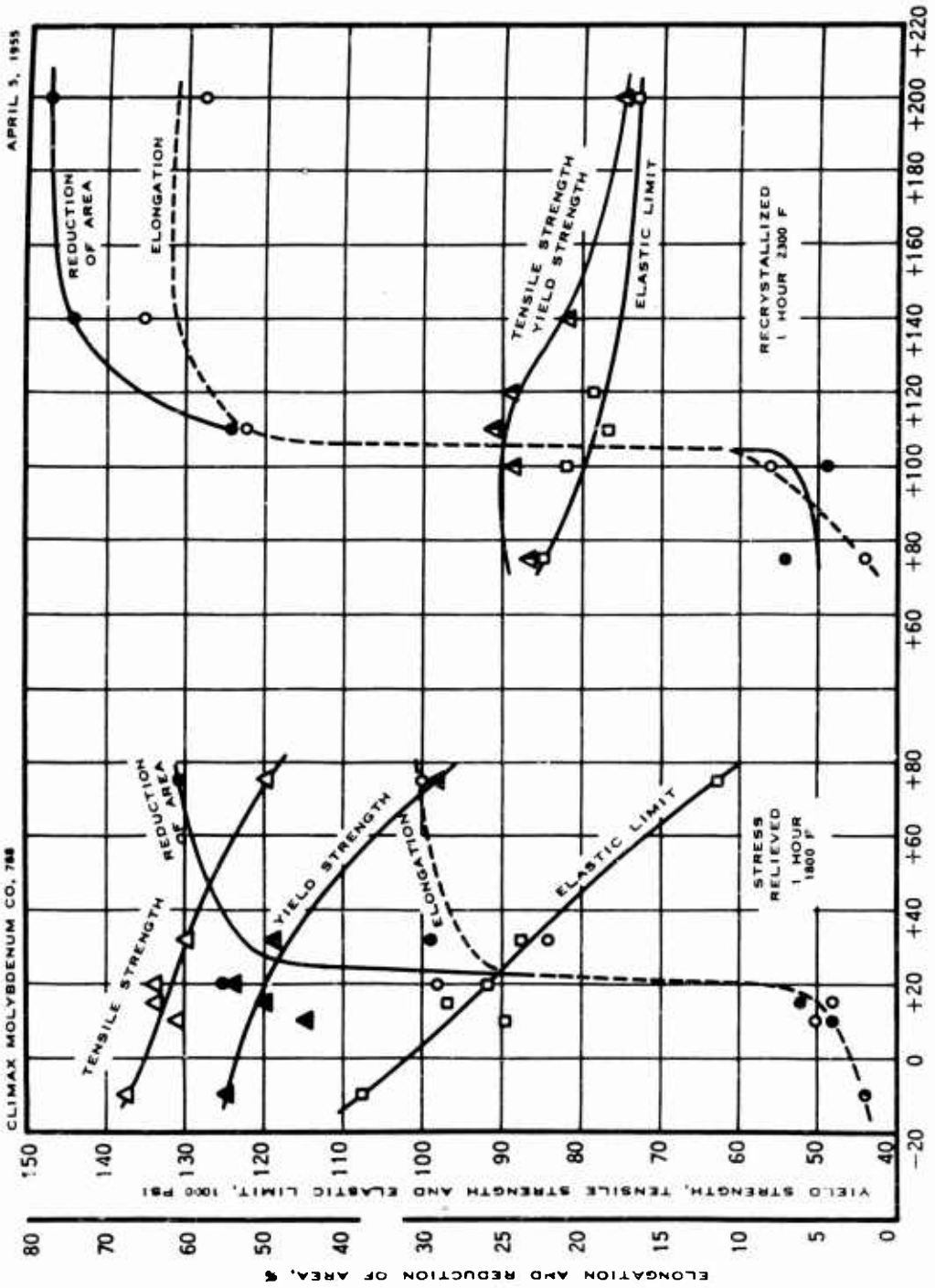


FIGURE D70– EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF $\frac{1}{2}$" DIAMETER BAR 1457 (0.024 C, 0.46 Ns, 0.48 V)

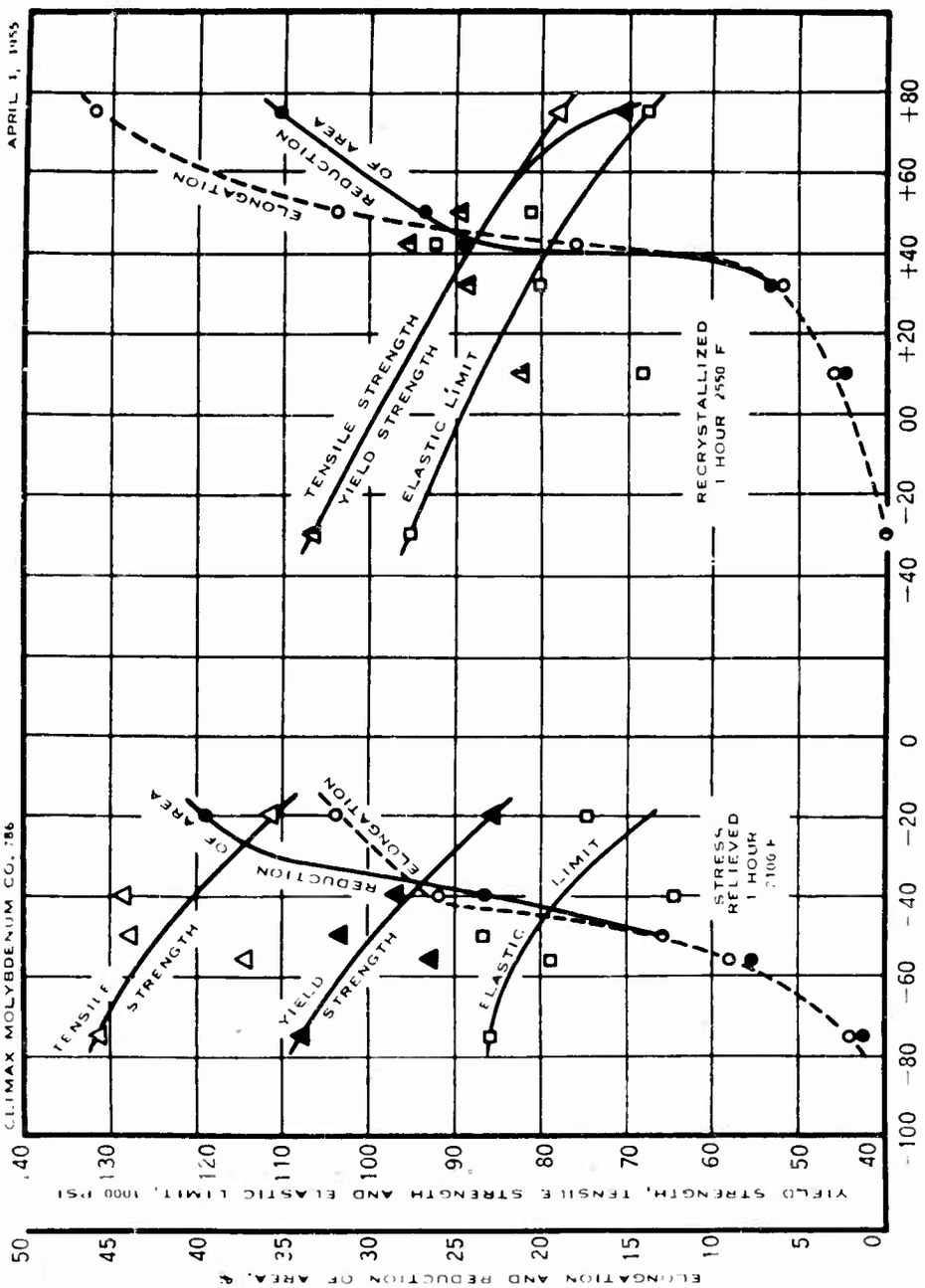


FIGURE D71 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF $\frac{1}{2}$" DIAMETER BAR 1451 (0.014 C, 0.43 T_i, 0.50 N_B)

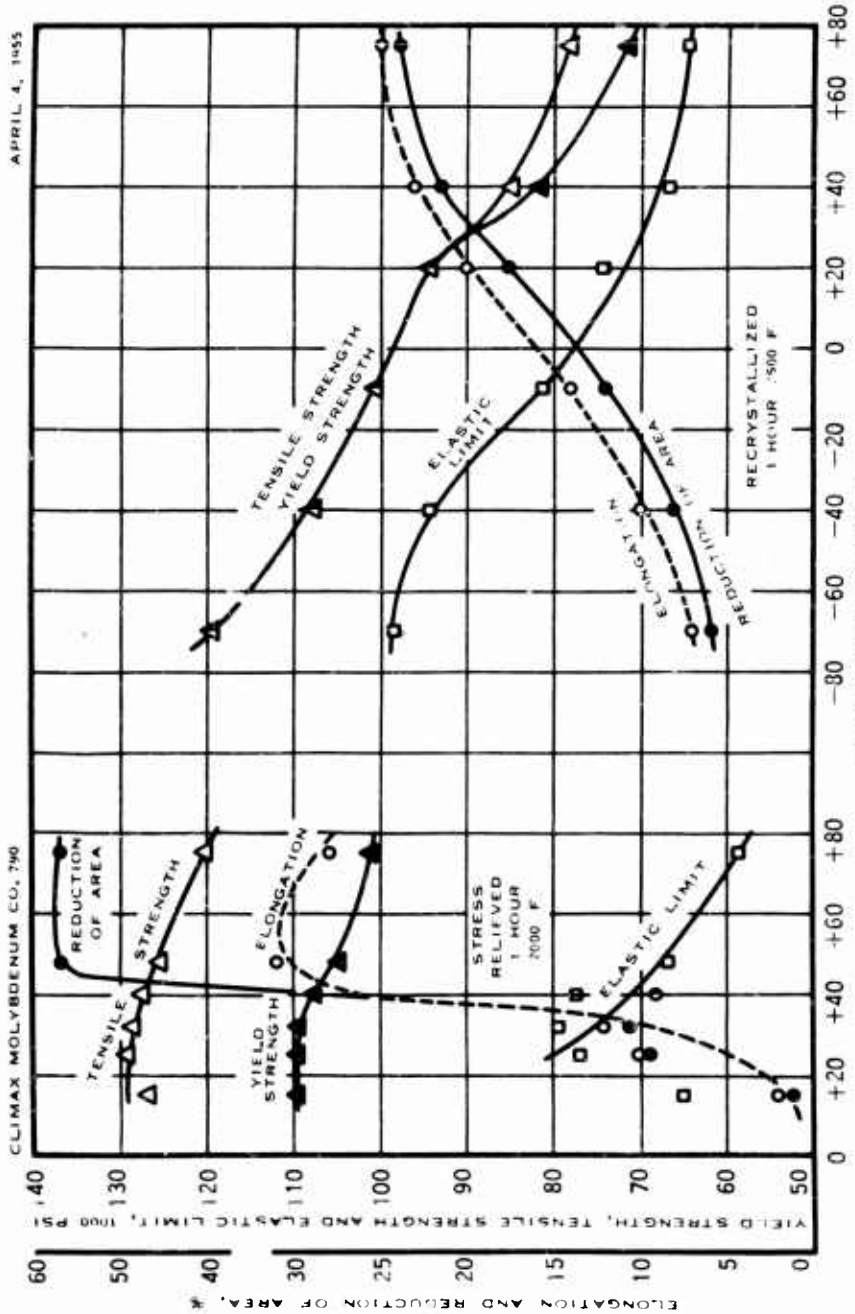


FIGURE D72 – EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF — DIAMETER BAR 1456 (0.038 C, 0.50 Nb, 0.06 Zr, ADDED)

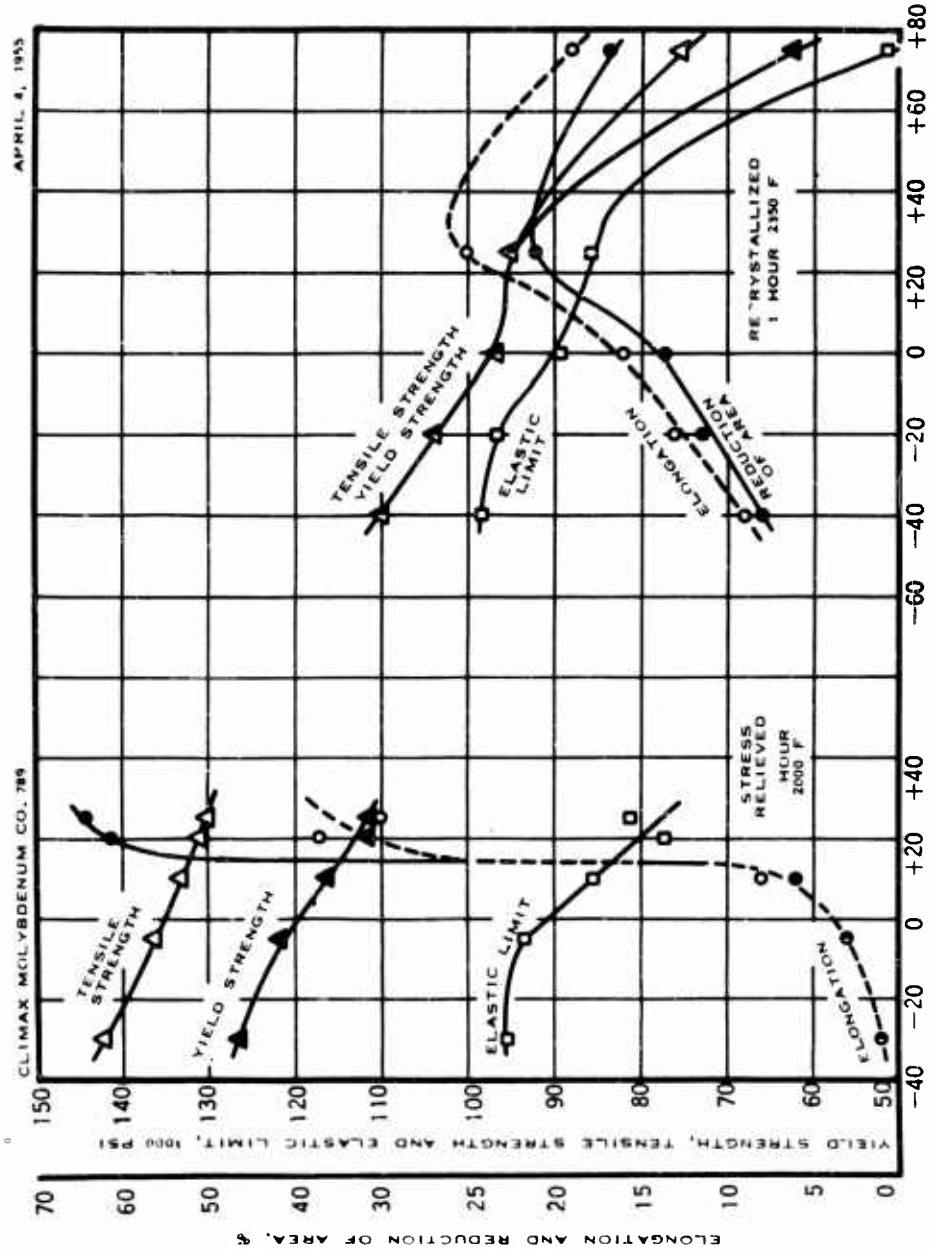


FIGURE D73– EFFECT OF TESTING TEMPERATURE ON TENSILE PROPERTIES OF $\frac{1}{2}$" DIAMETER BAR 1452 (0.030 C, 0.22 T$_i$, 0.75 V)

TABLE D2

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1600 F

Tests conducted by Battelle Memorial Institute

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
937	0.015 C	SR	45,000	0.3	17.4	92.0	-
		SR	37,500	8.0	17.8	92.9	1.7
		SR	30,000	206.3	18.0	93.4	0.012
		R_{2150}	22,300	2.0	54.9	94.0	12.2
		R_{2150}	22,000	2.2	64.2	93.1	10.5
		R_{2150}	17,500	19.7	40.7	86.5	0.95
		R_{2150}	14,000	353.5[a]	34.2	-	0.067
1045	0.003 C	SR	60,000	0.1	12.9	95.7	-
	0.005 Ce	SR	45,000	18.7	18.0	91.1	0.07
	0.007 RE	R_{2400}	30,000	on loading	51.6	96.0	-
		R_{2400}	20,000	97.9	52.0	97.3	0.19
1063	0.17 Al	SR	60,000	on loading	13.8	79.0	-
		SR	48,000	2.4	15.6	76.9	0.70
		SR	35,000	163.5	16.1	86.3	0.011
		R_{2200}	30,000	0.4	59.3	93.2	-
		R_{2200}	25,000	7.9	78.6	86.1	2.50
		R_{2200}	18,000	145.3	43.2	88.8	0.012
987	0.53 Al	SR	70,000	0.2	12.5	74.4	-
		SR	60,000	4.1	13.8	75.0	0.6
		SR	45,000	97.7	15.4	60.0	0.034
		R_{2200}	34,000	2.5	49.6	64.6	-
		R_{2200}	30,000	14.1	56.9	67.0	-
		R_{2200}	22,500	82.5	26.5	51.4	0.12
677	0.05 Co	SR	70,000	1.3	18.4	68.6	-
		SR	65,000	8.4	13.7	73.3	0.12
		SR	53,000	319.6	16.6	75.5	0.032
		R_{2200}	41,500	0.9	46.0	77.0	-
		R_{2200}	32,500	13.7	32.8	81.7	-
1144	0.074 Co	SR_{1700}	60,000	2.7	22.4	93.8	1.3
		SR_{1700}	50,000	15.9	47.5	89.1	0.20
		SR_{1700}	39,000	72.6	27.6	91.1	0.044
		R_{2000}	50,000	0.15	41.8	87.9	-
		R_{2000}	35,000	10.9	78.6	92.8	3.0
		R_{2000}	25,000	106.5	91.9	92.9	0.23

[a] discontinued

SR - stress relieved one hour at 1800 F unless otherwise indicated

R - recrystallized, held one hour at indicated temperature

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS
IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS
AT 1600 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
988	0.24 Nb	SR	70,000	on loading	12.3	88.7	-
		SR	60,000	4.1	12.8	85.6	0.45
		SR	50,000	300.0[a]	3.8	-	0.0046
		R_{2200}	30,000	0.5	51.9	95.2	-
		R_{2200}	25,000	34.0	44.8	91.4	0.70
		R_{2200}	22,500	39.6	23.9	52.1	0.25
660	0.34 Nb	SR	75,000	0.2	12.3	74.4	-
		SR	65,000	13.3	13.2	74.4	0.04
		SR	50,000	958.5[a]	1.6	-	0.002
		R_{2200}	32,500	2.9	43.5	84.6	-
		R_{2200}	25,000	59.6	27.7	75.0	-
		R_{2200}	24,375	136.8	35.4	53.8	0.087
978	0.52 Nb	SR	80,000	on loading	13.1	77.1	-
		SR	70,000	5.9	13.5	86.5	0.47
		SR	60,000	500.0[a]	3.0	-	0.0065
		R_{2200}	40,000	on loading	42.2	86.6	-
		R_{2200}	34,000	13.8	36.9	87.3	1.05
		R_{2200}	30,000	315.0[a]	22.1	-	0.042
1057	0.75 Nb	SR	75,000	9.5	14.8	75.5	0.31
		SR	65,000	377.2[a]	3.2	-	0.0058
		SR	50,000	424.9[a]	0.8	-	0.0006
		R_{2250}	40,000	1.4	43.2	89.4	-
		R_{2250}	37,500	76.4	47.3	46.3	0.12
		R_{2250}	32,800	341.6[a]	13.9	-	0.004
1268	0.22 Ti	SR	70,000	1.4	14.6	81.4	-
		SR	58,000	281.0	-	-	0.0045
		R_{2350}	30,800	16.5	36.8	90.7	1.0
		R_{2350}	25,000	600.0[a]	-	-	0.005
1132	0.45 Ti	SR	85,000	0.5	14.9	86.8	4.0
		SR	75,000	18.2	17.4	88.3	0.22
		SR	65,000	171.0	17.5	77.5	0.03
		R_{2450}	40,000	1.7	44.8	90.4	-
		R_{2450}	35,000	74.9	32.8	86.4	0.19
		R_{2450}	33,500	379.4[a]	15.3	-	0.027

[a]discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1600 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1348	0.46 Ti	SR	70,000	138.0	17.1	72.7	0.031
		R_{2450}	34,000	223.0	25.0	61.1	0.037
1393	0.12 Al	SR	60,000	21.2	16.0	81.8	0.14
	0.50 Ti	SR	52,000	128.2	15.7	78.5	0.025
		R2450	45,000	0.8	38.2	95.5	-
		R2450	34,500	34.9	30.0	62.2	0.13
		R2450	30,000	285.7[a]	-	-	0.002
1048	0.69 Ti	SR	60,000	0.15	12.1	90.5	-
	0.12 RE	SR	50,000	7.6	13.6	78.4	0.21
		SR	40,000	547.6[a]	2.4	-	0.0017
		R2500	35,000	on loading	34.7	82.2	-
		R2500	25,000	35.1	25.2	28.3	0.09
		R2500	20,000	411.9[a]	4.1	-	0.023
1133	0.85 Ti	SR	65,000	1.0	16.8	88.0	2.2
		SR	55,000	29.9	18.3	72.8	0.094
		SR	50,000	82.2	10.6	86.1	0.044
		R2500	37,500	0.5	41.6	91.4	-
		R2500	30,000	23.2	43.2	92.7	0.56
		R2500	27,500	92.7	43.3	92.3	0.05
1138	1.22 Ti	SR	60,000	0.8	10.1	71.0	-
		SR	45,000	74.9	15.4	68.4	0.044
		SR	40,000	330.3[a]	4.6	-	0.011
		R2500	38,000	0.3	42.7	96.0	-
		R2500	30,000	11.8	47.1	89.8	1.3
		R2500	25,000	69.5	60.8	95.3	0.3
1009	1.26 Ti	SR	67,000	0.15	15.0	95.0	-
		SR	60,000	2.5	15.8	95.7	0.53
		SR	50,000	91.0	22.2	91.4	0.048
		R2900	44,500	0.2	29.6	95.9	-
		R2900	40,000	472.6[a]	4.8	-	nil
		R2900	30,000	258.6[a,b]	-	-	nil
		R2900	50,000	on loading	28.6	95.8	-

[a] discontinued
[b] reloaded at a stress of 50,000 psi and failed when load was applied

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1600 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1281	2.09 Ti	SR	57,000	1.4	18.7	88.0	0.85
		SR	42,000	on loading	38.6	93.5	-
		SR	42,000	232.0	21.8	97.0	0.014
		R_{2750}	38,000	2.8	37.0	92.0	2.4
		R_{2750}	30,000	46.2	34.9	94.1	0.14
		R_{2750}	27,000	214.9[a]	-	-	0.0008
651	2.29 Ti	R_{3200}	32,500 45,000 55,000	450.0) 148.0) 242.0)	Time in test at various stresses; test discontinued after total of 840 hours		
885	2.46 Ti	SR	60,000	17.6	16.8	-	-
1051	0.54 V	SR	60,000	0.15	16.8	86.9	-
		SR	50,000	7.1	15.9	79.9	0.24
		SR	42,000	76.2	21.9	88.0	-
		R_{2100}	30,000	2.1	48.7	88.0	10.5
		R_{2100}	25,000	25.3	57.1	93.7	1.20
		R_{2100}	21,000	118.5	52.8	94.8	0.18
1012	0.56 V	SR	60,000	0.7	18.5	79.8	-
		SR	45,000	47.4	18.4	89.0	0.08
		SR	40,000	146.6	29.4	94.7	0.035
		R_{2150}	30,000	4.0	50.4	89.4	-
		R_{2150}	25,000	30.0	36.0	84.8	0.50
		R_{2150}	22,000	243.0	72.2	96.5	0.10
667	0.66 V	SR	60,000	2.8	13.6	74.6	-
		SR	50,000	68.4	14.8	78.1	-
		SR	46,000	131.4	22.1	79.5	0.024
		R_{2200}	40,000	0.15	-	-	-
		R_{2200}	32,500	5.0	41.8	84.6	-
1049	0.85 V 0.003 Ce 0.003 RE	SR	60,000	0.8	13.7	74.4	1.3
		SR	50,000	36.1	18.5	86.0	0.11
		SR	45,000	158.0	20.8	89.7	0.027
		R_{2500}	32,500	0.05	20.0	31.8	-
		R_{2500}	25,000	6.6	17.6	34.1	1.15
		R_{2500}	20,000	18.9	4.8	6.6	0.18

[a] discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1600 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
669	0.87 V	SR	75,000	1.3	10.9	74.4	-
		SR	60,000	6.1	9.5	59.2	0.25
		SR	50,000	268.9	11.2	45.4	-
		R_{2400}	42,000	0.4	-	-	-
		R_{2400}	32,500	19.5	40.0	77.2	-
1052	1.00 V	SR	65,000	1.0	13.6	84.0	2.2
		SR	55,000	25.5	14.5	84.8	0.12
		SR	50,000	81.6	16.9	86.9	0.048
		R_{2150}	35,000	4.0	45.2	88.9	4.6
		R_{2150}	28,000	61.7	45.2	85.3	0.33
		R_{2150}	25,000	220.4	53.7	85.3	0.091
1151	1.25 V	SR	45,000	431.3	18.7	88.7	0.010
1390	0.054 Zr	SR	80,000	16.8	12.8	79.0	0.21
		SR	72,000	176.1	15.8	79.5	0.028
		SR	65,000	194.1[a]	-	-	0.0016
		R_{2450}	40,000	0.4	46.2	93.6	-
		R_{2450}	33,000	31.0	28.8	95.0	0.55
1207	0.09 Zr	SR	85,000	0.05	13.6	88.4	-
		SR	75,000	7.4	13.7	87.3	0.32
		SR	70,000	49.2	18.3	88.6	0.09
		SR	60,000	305.0[a]	2.0	-	0.0027
		R2750	40,000	0.05	50.0	92.0	-
		R2750	35,000	3.0	46.2	92.6	4.8
		R2750	30,000	1266.2[a]	13.8	-	0.0046
1217	0.11 Co 0.18 Ti	SR	80,000	6.9	22.0	85.7	0.48
		SR	70,000	53.7	17.6	77.6	0.05
		SR	60,000	258.7[a]	-	-	0.014
		R_{2100}	56,000	0.7	46.8	84.2	-
		R_{2100}	35,000	99.4	57.1	80.4	0.34
1060	0.32 Nb 0.18 Ti	SR	65,000	on loading	15.0	82.7	-
		SR	60,000	on loading	12.4	80.0	-
		SR	46,000	186.1[a]	-	-	0.0003
		R_{2450}	40,000	on loading	37.6	89.7	-
		R_{2450}	33,000	11.2	38.4	90.7	1.3
		R_{2450}	30,000	209.9	29.1	83.1	0.06

[a]discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS
IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS
AT 1800 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
937	0.015 C	SR	37,500	0.25	14.9	94.0	-
		SR	27,500	13.6	17.1	91.0	-
		SR	21,000	144.8[b]	4.9	-	0.036
		R_{2150}	20,000	0.5	48.8	95.7	-
		R_{2150}	15,000	5.5	54.4	94.5	7.0
		R_{2150}	12,000	93.3	75.2	93.2	0.28
1045	0.003 C 0.005 Ce 0.007 RE	SR	40,000	2.7	19.0	95.2	-
		SR	25,000	318.0[a]	4.1	-	-
		R_{2400}	17,500	9.5	47.1	94.9	2.2
		R_{2400}	14,000	125.3	18.7	30.4	0.075
1063	0.17 Al	SR	40,000	0.6	18.6	83.6	2.4
		SR	30,000	8.0	16.0	87.6	0.31
		SR	20,000	67.9	32.8	91.4	0.026
		R_{2200}	25,000	0.2	52.6	88.7	-
		R_{2200}	20,000	2.9	67.9	92.3	8.0
		R_{2200}	12,500	148.8	62.8	97.6	0.14
987	0.53 Al	SR	55,000	0.4	19.7	80.4	-
		SR	45,000	3.9	18.4	83.0	1.0
		SR	25,000	185.0	21.0	85.7	0.028
		R_{2200}	30,000	0.4	57.3	91.7	-
		R_{2200}	25,000	4.0	50.3	90.1	8.5
		R_{2200}	17,500	54.9	39.6	92.1	0.34
1463	0.11 Cr	SR	23,000	28.3	27.8	92.2	0.10
		SR	20,000	42.5	40.3	95.0	0.06
		R_{2000}	25,000	1.9	77.2	94.0	-
		R_{2000}	11,500	209.0[a]	-	-	0.046
677	0.05 Co	SR	50,000	1.7	6.6	73.2	-
		SR	40,000	39.8	15.0	72.2	-
		SR	32,500	110.6	13.5	79.5	-
		SR	22,500	139.5	44.9	80.6	-
		R_{2200}	32,500	1.1	56.9	90.3	-
		R_{2200}	25,000	10.5	86.9	92.2	-
		R_{2200}	20,000	159.6	72.2	83.1	0.16

[a]discontinued
[b]test discontinued due to furnace failure

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS
IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS
AT 1800 F

Heat	Alloy, %	Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1144	0.074 Co	SR_{1700}	50,000	0.6	25.3	82.7	4.3
		SR_{1700}	30,000	10.8	37.3	83.5	0.21
		SR_{1700}	19,000	102.3	29.6	80.9	0.05
		R_{2000}	32,500	0.5	66.9	87.7	-
		R_{2000}	25,000	3.2	77.6	92.2	10.8
		R_{2000}	15,000	110.9	30.2	79.0	0.07
1465	0.05 Ni	SR	23,000	6.5	84.6	89.6	4.0
		SR	20,000	14.3	72.4	86.1	2.3
		R_{1950}	25,000	4.1	57.6	74.2	6.5
		R_{1950}	12,000	158.5	33.8	38.0	0.021
988	0.24 Nb	SR	55,000	0.2	13.1	90.7	-
		SR	35,000	32.8	13.1	90.7	0.030
		SR	27,500	51.2	14.2	92.9	0.0001
		R_{2200}	25,000	0.8	53.3	93.9	-
		R_{2200}	17,500	71.6	50.0	94.0	0.32
		R_{2200}	16,000	287.6[a]	28.9	-	0.086
660	0.34 Nb	SR	55,000	2.8	16.1	77.2	0.08
		SR	40,000	60.0	failed in adapter		-
		SR	30,000	298.6	22.5	73.1	0.005
		R_{2200}	30,000	0.4	58.5	91.0	-
		R_{2200}	25,000	4.0	46.7	87.6	-
		R_{2200}	20,000	97.4	60.3	87.9	0.26
978	0.52 Nb	SR	65,000	0.5	12.4	80.2	-
		SR	55,000	14.2	14.4	86.1	0.23
		SR	40,000	176.3	7.7[c]	7.8[c]	-
		R_{2200}	32,500	0.3	48.9	92.0	-
		R_{2200}	28,000	23.0	49.2	86.5	0.90
		R_{2200}	25,000	145.5	51.9	91.4	0.20
1057	0.75 Nb	SR	70,000	0.2	12.5	86.2	-
		SR	60,000	11.9	15.8	84.5	0.33
		SR	50,000	140.5	15.6	82.7	0.03
		R_{2250}	40,000	2 min	47.6	90.4	-
		R_{2250}	32,500	17.7	48.8	80.5	1.35
		R_{2250}	27,500	200.2	37.0	86.1	0.048

[a] discontinued
[c] low values probably caused by loss of vacuum for short time

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1800 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1268	0.22 Ti	SR	60,000	1.3	16.8	84.8	1.9
		SR	50,000	46.0	18.9	83.7	0.051
		R_{2350}	27,500	4.1	51.2	95.6	5.0
		R_{2350}	24,325	63.6	49.6	91.5	0.32
1132	0.45 Ti	SR	70,000	1.0	16.5	83.2	3.2
		SR	60,000	27.5	18.5	88.0	0.21
		SR	50,000	227.9	16.3	61.8	0.012
		R_{2450}	35,000	0.35	50.5	92.3	-
		R_{2450}	31,000	3.9	45.6	89.7	5.8
		R_{2450}	27,500	328.7[a]	22.4	-	0.014
1348	0.46 Ti	SR	55,000	94.6	18.0	83.6	0.037
		SR	48,000	550.0	12.8	51.7	0.003
		SR	45,000	910.0[a]	3.2	-	0.0014
		R_{2450}	29,000	82.3	63.2	89.4	0.32
1393	0.12 Al	SR	50,000	4.4	15.6	83.1	0.55
	0.50 Ti	SR	38,000	41.2	17.7	85.4	0.08
		R_{2450}	30,000	9.7	23.8	87.2	0.02
		R_{2450}	25,000	27.7	44.0	85.4	0.17
		R_{2450}	20,000	281.7[a]	-	-	0.0004
1048	0.69 Ti	SR	55,000	1/2 min	13.0	89.8	-
	0.12 RE	SR	40,000	7.8	14.5	88.3	0.32
		SR	30,000	142.1	17.9	95.0	0.027
		R_{2500}	30,000	0.2	36.0	95.2	-
		R_{2500}	22,500	12.4	38.9	93.7	0.62
		R_{2500}	17,500	209.5	41.9	80.8	0.016
1133	0.85 Ti	SR	52,000	2.1	18.6	91.4	1.5
		SR	40,000	42.9	11.7	90.1	0.10
		SR	35,000	148.5	15.5	85.7	0.022
		R_{2500}	35,000	0.1	40.7	87.5	-
		R_{2500}	25,000	8.6	45.2	90.8	1.7
		R_{2500}	21,000	52.8	52.8	92.9	0.42
1138	1.22 Ti	SR	50,000	0.7	17.4	71.1	3.1
		SR	40,000	12.0	19.1	92.3	0.27
		SR	30,000	155.9	15.2	62.9	nil
		R_{2500}	27,500	0.9	45.1	94.5	-
		R_{2500}	22,000	10.1	46.6	94.8	2.2
		R_{2500}	17,000	142.7	79.2	95.7	0.25

[a]discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1800 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1009	1.26 Ti	SR	50,000	2.7	18.3	94.0	11.0
		SR	40,000	35.9	26.2	92.9	0.15
		SR	35,000	56.7	21.1	92.3	0.089
		R_{2900}	47,000	on loading	38.9	95.4	-
		R_{2900}	40,000	57.9	24.2	94.7	0.02
		R_{2900}	35,000	231.0	17.3	91.4	0.002
1281	2.09 Ti	SR	62,000	on loading	13.3	90.5	-
		SR	50,000	0.8	16.4	91.7	0.25
		SR	30,000	359.3	10.3	42.1	0.007
		R_{2750}	35,000	0.4	52.3	90.7	-
		R_{2750}	26,000	14.5	51.1	95.4	0.05
		R_{2750}	21,500	76.6	36.8	95.4	0.006
651	2.29 Ti	R_{3200}	25,000 35,000 45,000	455.0) 97.0) 64.5)	Time in test at various stresses; test failed in threads after total of 616.5 hours		
885	2.46 Ti	SR	60,000	0.3	15.7	90.5	-
		SR	45,000	17.3	16.1	88.0	0.18
		SR	35,000	169.8	18.1	-	-
		R_{2700}	25,000	9.1	41.4	-	-
1051	0.54 V	SR	50,000	0.1	16.0	90.1	-
		SR	38,000	4.4	18.7	88.3	-
		SR	28,000	38.0	20.7	90.0	0.11
		R_{2100}	30,000	0.2	62.8	91.0	-
		R_{2100}	20,000	11.6	66.5	90.8	2.4
		R_{2100}	15,000	108.9	58.3	90.7	0.26
1012	0.56 V	SR	42,000	1.4	14.5	92.9	-
		SR	35,000	6.9	17.5	90.8	0.54
		SR	25,000	50.8	19.7	92.6	0.12
		R_{2150}	32,000	0.1	58.1	89.4	-
		R_{2150}	25,000	2.1	57.4	93.7	12.5
		R_{2150}	17,500	120.6	77.3	94.1	0.24

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS
IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS
AT 1800 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
667	0.66 V	SR	45,000	1.4	20.3	75.0	1.5
		SR	35,000	19.0	19.1	81.6	0.19
		SR	27,500	111.8	21.6	81.8	0.028
		SR	21,000	169.5	24.8	83.5	-
		R_{2200}	25,000	2.2	47.7	91.2	-
		R_{2200}	20,000	15.5	39.2	75.4	-
		R_{2200}	15,000	161.6	41.5	83.2	-
1049	0.85 V	SR	50,000	0.3	14.4	81.8	-
	0.003 Ce	SR	40,000	9.5	16.8	83.1	0.41
	0.003 RE	SR	30,000	381.1[a]	5.5	-	0.010
		R_{2500}	25,000	0.4	23.0	36.2	-
		R_{2500}	20,000	7.1	29.1	28.2	0.23
		R_{2500}	16,000	85.6	15.1	39.6	0.11
669	0.87 V	SR	70,000	0.1	12.2	67.6	-
		SR	50,000	20.5	16.2	66.4	0.14
		SR	40,000	104.3	16.4	73.8	0.004
		SR	31,000	338.6	7.9	-	-
		R_{2400}	32,500	0.8	45.3	91.0	-
		R_{2400}	25,000	19.7	48.4	91.5	-
		R_{2400}	20,000	203.5	43.2	69.7	0.087
1052	1.00 V	SR	55,000	0.2	14.5	89.1	-
		SR	45,000	4.1	15.5	88.0	0.82
		SR	35,000	42.3	19.5	86.4	-
		R_{2150}	25,000	5.9	60.2	87.7	5.0
		R_{2150}	20,000	43.9	43.7	85.7	0.54
		R_{2150}	17,000	197.4	48.3	91.8	0.14
1151	1.25 V	SR	50,000	2.3	18.9	91.8	1.3
		SR	38,000	36.7	18.9	89.4	0.14
		SR	30,000	216.9	20.5	89.1	0.019
1390	0.054 Zr	SR	70,000	20.5	14.9	78.4	0.24
		SR	62,000	111.7	18.5	76.6	0.05
		SR	55,000	209.1[a]	-	-	0.016
		R2450	35,000	0.3	41.8	94.8	-
		R2450	25,000	150.7	28.1	87.9	0.063

[a]discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 1800 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1207	0.09 Zr	SR	70,000	0.9	15.3	79.0	-
		SR	60,000	43.8	16.8	74.9	0.13
		SR	56,000	109.8	17.2	79.5	0.05
		R_{2750}	40,000	on loading	46.6	91.8	-
		R_{2750}	30,000	26.7	40.9	90.6	0.70
		R_{2750}	27,500	102.9	35.0	82.3	0.052
1436	0.42 Al	SR	40,000	23.6	19.2	79.6	0.34
	0.51 V	SR	27,000	210.5	14.4	72.0	0.0014
		R_{2200}	19,000	25.9	30.8	19.0	0.36
		R_{2200}	16,000	47.0	12.8	18.0	0.85
1217	0.11 Co	SR	50,000	9.9	27.2	87.2	0.2
	0.18 Ti	SR	32,000	40.3	21.7	41.8	0.04
		R_{2100}	30,000	10.5	49.6	35.9	1.0
		R_{2100}	25,000	26.3	24.4	32.1	0.54
1455	0.06 Co	SR	30,000	13.0	69.7	91.2	0.14
	0.47 V	SR	20,000	53.5	106.6	95.9	0.20
		R_{2000}	22,000	17.1	82.6	94.5	1.6
		R_{2000}	15,500	122.3	40.7	83.9	0.075
1454	0.06 Co	SR_{2100}	72,000	8.9	17.1	82.3	0.40
	0.07 Zr	SR_{2100}	60,000	105.9	21.6	84.5	0.056
		R_{2500}	46,200	0.1	52.4	89.5	-
		R_{2500}	30,000	47.0	56.9	93.7	0.52
1060	0.32 Nb	SR	55,000	on loading	11.9	83.1	-
	0.18 Ti	SR	50,000	5.5	11.0	87.0	0.27
		SR	43,000	289.4[a]	-	-	0.0035
		SR	35,000	173.5[a]	-	-	0.00045
		R_{2450}	30,000	1.9	35.8	87.5	1.6
		R_{2450}	24,000	100.1	30.2	77.5	0.01
		R_{2450}	16,000	224.6[a]	-	-	0.0036
1451	0.50 Nb	SR_{2100}	70,000	0.1	14.7	85.9	-
	0.43 Ti	SR_{2100}	52,000	1.4	18.4	90.4	2.7
		R_{2550}	43,500	on loading	40.9	99.4	-
		R_{2550}	30,000	97.2	32.0	96.7	0.018

[a] discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS
IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS
AT 1800 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1457	0.46 Nb 0.48 V	SR	65,000	10.7	15.5	80.4	0.40
		SR	55,000	87.1	18.2	86.0	0.023
		R_{2300}	28,000	54.6	38.4	70.1	0.20
		R_{2300}	15,000	168.7[a]	0.9	-	nil
1456	0.50 Nb 0.06 Zr	SR_{2000}	72,000	8.2	16.3	85.8	0.15
		SR_{2000}	60,000	199.4[a]	6.9	-	0.024
		R_{2500}	38,500	0.1	44.7	94.7	-
		R_{2500}	23,000	198.1[a]	3.8	-	0.002
1452	0.22 Ti 0.75 V	SR_{2000}	60,000	19.9	18.4	86.1	0.29
		SR_{2000}	50,000	150.3	24.3	89.8	0.025
		R_{2350}	38,200	0.15	48.8	92.0	-
		R_{2350}	25,000	288.4	46.4	80.9	0.066
1453	0.22 Ti 0.08 Zr	SR_{2000}	72,000	13.9	17.6	85.0	0.35
		SR_{2000}	60,000	282.5[a]	16.2	-	0.018
		R_{2500}	38,500	0.1	44.0	96.1	-
		R_{2500}	20,000	282.7[a]	0.86	-	-

[a]discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 2000 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
937	0.015 C	SR	25,000	1.7	19.5	92.3	-
		SR	17,500	10.0[c]	16.0	33.5	-
		SR	12,000	232.1[a]	6.4	-	0.023
		R_{2150}	17,500	0.15	60.1	83.1	-
		R_{2150}	12,000	5.3	41.3	63.0	3.0
1045	0.003 C	SR	35,000	1.1	13.8	84.6	2.5
	0.005 Ce	SR	12,000	137.0	34.4	90.0	0.080
	0.007 RE	R_{2400}	20,000	0.1	38.7	95.0	-
		R_{2400}	11,000	176.0	24.0	5.3	0.044
1063	0.17 Al	SR	30,000	0.4	21.6	88.2	6.0
		SR	20,000	1.0	41.6	84.0	2.0
		SR	11,000	69.7	25.6	15.2	0.084
		R_{2200}	18,000	0.5	64.7	83.6	-
		R_{2200}	14,000	2.8	50.9	40.1	4.5
		R_{2200}	9,500	85.2	46.6	82.0	0.20
987	0.53 Al	SR	35,000	0.7	25.0	83.0	2.8
		SR	14,000	37.0	38.7	84.2	0.15
		SR	11,000	136.9	23.6	80.5	0.04
		R_{2200}	23,000	0.5	67.8	97.1	-
		R_{2200}	15,000	11.2	70.2	91.9	2.0
		R_{2200}	10,000	112.8	51.5	83.8	0.095
1463	0.11 Cr	SR	20,000	1.1	32.0	90.8	-
		SR	12,000	18.2	50.0	85.2	0.90
		R_{2000}	12,000	12.6	53.6	86.3	1.1
		R_{2000}	10,000	49.6	41.6	87.6	0.4
677	0.05 Co	AR	15,000	76.3	20.6	39.6	-
		R_{2200}	22,500	1.6	52.9	84.3	-
		R_{2200}	16,000	55.5	56.9	86.4	0.34
		R_{2200}	13,000	880.0[a]	6.1	-	0.007
1144	0.074 Co	SR_{1700}	16,000	10.1	40.0	94.2	1.6
		SR_{1700}	11,000	72.6	50.7	95.0	0.30
		R_{2000}	16,000	1.9	66.9	40.9	11.0
		R_{2000}	11,000	164.3	19.2	54.4	0.028

[a] discontinued

[c] specimen overheated; rupture time estimated

AR - as rolled

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 2000 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1465	0.05 Ni	SR	20,000	1.0	96.6	89.0	-
		SR	12,000	18.5	98.3	90.0	2.4
		R_{1950}	12,000	22.1	98.3	89.8	1.65
		R_{1950}	10,000	61.5	54.1	67.9	0.39
988	0.24 Nb	SR	35,000	0.9	11.5	87.5	-
		SR	15,000	23.4	43.9	82.9	0.13
		SR	10,000	258.8[a]	12.7	-	0.045
		R_{2200}	23,000	0.1	54.6	94.3	-
		R_{2200}	15,000	4.8	37.0	48.6	5.6
		R_{2200}	10,000	225.8[a]	37.0	-	0.091
660	0.34 Nb	AR	15,000	37.7	38.6	70.6	-
		R_{2200}	20,000	2.4	70.8	91.0	-
		R_{2200}	15,000	36.7	73.7	92.2	-
		R_{2200}	12,500	174.8	46.6	80.7	0.10
978	0.52 Nb	SR	50,000	1.4	15.1	82.6	-
		SR	35,000	3.8	14.1	87.4	-
		SR	15,000	139.8	39.4	72.2	0.04
		R_{2200}	27,500	0.2	44.4	88.1	-
		R_{2200}	17,500	32.8[a]	-	-	0.84
		R_{2200}	15,000	109.3	44.1	86.8	0.18
1057	0.75 Nb	SR	55,000	0.8	19.7	84.9	-
		SR	45,000	6.5	16.8	84.2	0.33
		SR	20,000	139.2	48.0	46.4	0.13
		R_{2250}	32,500	0.12	56.0	88.2	-
		R_{2250}	25,000	7.4	48.4	79.3	0.40
		R_{2250}	20,000	49.9	48.0	72.2	0.46
1268	0.22 Ti	SR	50,000	0.3	15.2	90.1	-
		SR	30,000	125.1	16.4	86.2	0.0008
		R_{2350}	25,000	2.5	35.3	91.7	8.0
		R_{2350}	19,000	40.2	41.6	91.4	0.42
		R_{2350}	16,000	221.3	15.2	30.5	0.027

[a] discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 2000 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1132	0.45 Ti	SR	70,000	0.2	12.1	79.8	-
		SR	50,000	6.7	19.2	87.6	0.52
		SR	20,000	261.6[a]	2.4	-	0.004
		R_{2450}	30,000	0.3	48.3	79.7	-
		R_{2450}	25,000	4.4	51.7	86.7	6.0
		R_{2450}	18,000	280.0[a]	12.6	-	0.023
1348	0.46 Ti	SR	30,000	257.2	10.3	39.6	0.0042
		SR	27,000	501.2	11.5	6.8	0.009
		SR	25,000	335.8[a]	-	-	0.0062
		R_{2450}	20,000	221.1	32.8	88.2	0.11
1393	0.12 Al	SR	50,000	0.2	19.7	81.2	-
	0.50 Ti	SR	30,000	8.3	27.2	78.7	0.013
		R_{2450}	18,000	34.7	20.0	79.1	0.028
		R_{2450}	15,000	153.4	20.7	67.1	0.0005
1048	0.69 Ti	SR	55,000	on loading	14.4	87.0	-
	0.12 RE	SR	30,000	5.8	16.8	61.8	0.25
		SR	15,000	212.7[a]	3.2	-	-
		R_{2500}	25,000	0.2	34.8	72.3	-
		R_{2500}	17,500	4.3	12.0	45.6	1.05
		R_{2500}	12,000	36.7	3.9	4.6	0.037
1133	0.85 Ti	SR	45,000	0.4	16.6	92.1	-
		SR	35,000	4.5	17.6	88.2	0.50
		SR	18,600	214.0[a]	5.7	-	0.0012
		R_{2500}	26,000	0.6	40.6	84.3	-
		R_{2500}	22,000	2.0	31.7	26.7	5.5
		R_{2500}	14,000	228.8[a]	10.9	-	-
1138	1.22 Ti	SR	21,000	60.3	18.2	56.5	0.05
		SR	17,500	131.3	21.4	88.2	0.0023
		R_{2500}	15,000	42.1	48.4	86.5	0.60
		R_{2500}	12,500	377.7[a]	-	-	0.034
1009	1.26 Ti	SR	40,000	1.4	19.5	96.0	1.3
		SR	35,000	7.5	22.6	89.2	0.60
		SR	20,000	93.3	21.6	84.0	0.044
		R_{2900}	40,000	2.0	21.2	87.7	0.75
		R_{2900}	35,000	7.2	22.8	86.1	0.18
		R_{2900}	26,000	41.1	20.0	90.0	0.018

[a] discontinued

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 2000 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1281	2.09 Ti	SR	27,000	26.2	7.6	82.6	0.06
		SR	23,000	64.3	22.6	90.0	0.015
		R_{2750}	23,000	3.1	29.6	78.2	0.50
		R_{2750}	15,000	24.9	18.2	72.8	0.20
885	2.46 Ti	SR	50,000	0.15	15.1	87.9	-
		SR	35,000	13.3	21.3	83.6	-
		SR	25,000	69.5	21.4	-	-
		SR	12,500	500.0[a]	-	-	-
1051	0.54 V	SR	42,000	on loading	23.0	89.8	-
		SR	25,000	1.3	16.0	90.0	1.70
		SR	10,000	198.6	48.0	74.0	0.072
		R_{2100}	22,000	0.2	62.6	91.6	-
		*R_{2100}	11,000	75.0	50.0	87.2	0.21
		*R_{2100}	11,000	72.3	49.5	87.9	0.21
1012	0.56 V	SR	25,000	2.9	36.0	88.2	1.10
		SR	17,500	11.6	84.8	84.3	0.70
		SR	11,000	265.0[a]	10.3	-	0.018
		R_{2150}	23,000	0.3	58.4	90.0	-
		R_{2150}	17,500	3.7	52.8	89.0	4.8
		R_{2150}	12,000	125.0	44.8	85.5	0.002
1049	0.85 V	SR	45,000	0.12	15.9	85.1	-
	0.003 Ce	SR	25,000	39.8	18.4	75.0	0.018
	0.003 RE	SR	20,000	111.4	13.6	36.6	0.036
		R_{2500}	20,000	0.5	32.3	28.1	-
		R_{2500}	15,000	5.1	18.5	15.1	1.60
		R_{2500}	12,000	76.2	12.0	15.6	0.030
669	0.87 V	AR	15,000	150.8	12.3	54.9	-
		R_{2400}	22,500	2.4	62.7	83.0	-
		R_{2400}	15,000	75.1	51.9	77.7	0.16
		R_{2400}	12,500	263.7	49.2	75.0	0.024
1052	1.00 V	SR	42,000	0.1	22.0	81.7	-
		SR	30,000	5.0	40.0	91.0	1.10
		SR	17,500	26.8	59.3	92.0	0.14
		R_{2150}	24,000	0.6	31.4	91.0	-
		R_{2150}	17,000	8.8	32.0	82.2	1.9
		R_{2150}	12,500	130.8	45.6	79.8	0.14

[a]discontinued
*These two specimens were tested at the same stress by mistake

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 2000 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1151	1.25 V	SR	22,000	40.8	20.7	95.9	0.05
		SR	19,000	35.9	34.1	94.2	0.11
		R_{2200}	15,000	5.6	26.1	81.7	4.8
		R_{2200}	10,000	305.3[a]	-	-	0.009
1390	0.054 Zr	SR	45,000	62.8	12.3	31.9	0.1
		SR	30,000	405.2	13.6	2.9	0.0037
		R_{2450}	30,000	0.2	56.8	95.0	-
		R_{2450}	21,500	84.3	28.8	81.6	0.062
1207	0.09 Zr	SR	50,000	20.5	17.6	56.4	0.32
		SR	35,000	228.6	12.0	1[illegible]	0.015
		SR	25,000	160.8[b]	1.0	-	0.0028
		R_{2750}	26,000	9.9	44.0	80.9	0.10
		R_{2750}	22,000	119.6	32.7	82.0	0.082
		R_{2750}	18,500	175.6[a]	4.1	-	0.006
1436	0.42 Al	SR	22,000	8.8	57.6	85.8	0.50
	0.51 V	SR	16,000	35.1	40.0	24.9	0.18
		R_{2200}	16,000	4.3	18.4	10.5	2.0
		R_{2200}	10,000	195.5[a]	6.0	-	0.015
1217	0.11 Co	SR	40,000	1.1	32.0	89.0	1.3
	0.18 Ti	SR	20,000	35.6	67.6	92.7	4.0
		R_{2100}	20,000	19.5	68.0	81.8	1.3
		R_{2100}	17,000	53.7	71.4	91.2	0.42
1455	0.06 Co	SR	30,000	0.7	58.1	87.9	3.2
	0.47 V	SR	20,000	3.1	70.4	84.5	0.10
		R_{2000}	15,000	9.8	90.1	83.2	1.8
		R_{2000}	11,000	47.4	88.0	84.0	0.51
1454	0.06 Co	SR_{2100}	45,000	28.1	23.5	76.8	0.12
	0.07 Zr	SR_{2100}	30,000	157.7	15.4	36.4	0.026
		R_{2500}	28,000	3.7	33.0	89.8	5.3
		R_{2500}	21,000	65.8	45.6	76.5	0.29
1060	0.32 Nb	SR	40,000	9.8	15.2	84.1	0.3
	0.18 Ti	SR	31,000	198.2[a]	5.4	-	0.009
		SR	25,000	202.5[a]	-	-	0.002
		R_{2450}	25,000	0.8	34.6	90.0	-
		R_{2450}	12 000	258.4[a]	-	-	0.004

[a] discontinued

[b] failed in specimen holder

TABLE D2 (continued)

CREEP-RUPTURE DATA ON ARC-CAST MOLYBDENUM-BASE ALLOYS IN STRESS-RELIEVED AND RECRYSTALLIZED CONDITIONS AT 2000 F

Heat	Alloy, %	Heat Treatment	Stress psi	Rupture Time, hr	Elong. %	Reduction of Area, %	Creep Rate % per hour
1451	0.50 Nb 0.43 Ti	SR_{2100} SR_{2100} R_{2550} R_{2550}	33,000 30,000 26,000 22,000	12.6 7.9 11.9 43.7	17.2 26.4 28.0 37.7	70.2 85.0 92.0 96.8	0.18 3.8 0.30 0.09
1457	0.46 Nb 0.48 V	SR SR R_{2300} R_{2300}	30,000 26,000 20,000 15,000	15.3 27.9 31.0 227.1[a]	25.0 31.1 56.6 20.3	68.5 88.8 84.0 -	2.0 0.11 1.8 0.065
1456	0.50 Nb 0.06 Zr	SR_{2000} SR_{2000} R_{2500} R_{2500}	35,000 60,000 26,000 28,000 21,000	163.6[b] - 190.6[a] 1.7 93.1	6.15 12.5 0.25 58.3 41.6	- 67.2 - 92.8 84.4	0.015 - 0.0008 8.0 0.11
1452	0.22 Ti 0.75 V	SR_{2000} SR_{2000} R_{2350} R_{2350}	40,000 30,000 25,000 20,000	16.9 56.0 3.7 47.0	19.6 21.4 52.0 52.0	87.0 94.1 82.2 91.6	0.15 0.10 6.5 0.37
1453	0.22 Ti 0.08 Zr	SR_{2000} SR_{2000} R_{2500} R_{2500}	45,000 30,000 32,000 21,000	164.9 1[illegible]2[a] 0.3 160.0[a]	14.4 0.85 46.4 8.43	23.6 - 92.7 -	0.019 0.0019 - 0.031

[a] discontinued

[b] The stress on this test was increased in increments of 5,000 psi until failure at 60,000 psi, after the original test at 35,000 psi had been in progress for 163.6 hours

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