DMIC Report 193
October 23, 1963

TUNGSTEN RESEARCH AND DEVELOPMENT REVIEW
1960-1962

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Battelle Memorial Institute
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2. To supplement established Service activities in providing technical advisory services to producers, melters, and fabricators of the above materials, and to designers and fabricators of military equipment containing these materials.

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Contract No. AF 33(616)-7747
Project No. 2(8-8975)

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1960 - 1962

by

J. L. Ratliff, W. A. Gibeaut, and H. R. Ogden

to

OFFICE OF THE DIRECTOR OF DEFENSE
RESEARCH AND ENGINEERING

DEFENSE METALS INFORMATION CENTER
Battelle Memorial Institute
Columbus 1, Ohio

PREFACE

This review of Government-sponsored research and development programs on tungsten is based on a study by the Defense Metals Information Center for the benefit and use of Government agencies engaged in, or interested in, tungsten technology. The essential details of the study are presented here because of their wide interest to organizations producing, using, or investigating tungsten and its alloys. Contractual information on research and development programs on tungsten appears in the Appendix.

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SUMMARY

Government-sponsored tungsten research and development efforts encompass a broad range of technological activities. Typifying the extreme limits of efforts since January, 1960, studies have ranged from preparation of unalloyed metal to development of high-integrity fabricated shapes of tungsten-base materials. The distribution of research and development activities is illustrated in the tabulation below, which lists nine major areas of tungsten technology and shows the extent to which each has received Government support. These nine major areas outline the broad over-all effort, and each is summarized within this report by brief technical discussions of 104 separate studies on 79 research programs. A listing of the 79 programs is given in the Appendix.

Major Area	Individual Studies on Government-Sponsored Programs
Preparation of Metal	3
Consolidation	26
Primary and Secondary Working	21
Joining	9
Fabrication and Performance of Rocket Nozzles	7
Oxidation and Other High-Temperature Reactions	6
Protective Coatings	5
Properties	12
Physical Metallurgy	15
TOTAL	104

Based upon this review of tungsten research and development, it can be concluded that a well-balanced over-all program was developed and pursued during the period 1960 - 1962 and now continues. The majority of the work to date constitutes only initial efforts and, although considerable progress has been made, continued efforts in all areas are desirable.

INTRODUCTION

This report is a review of 79 tungsten research and development programs sponsored by the Government which were either in progress as of January 1, 1960, or were initiated since that date but prior to 1963. Work begun in 1963 had not progressed enough to warrant review at the time of the special DMIC study on which this report is based.

The body of this report presents a technical summary of the over-all research and development efforts on tungsten. This is divided into separate categories of more specific emphasis according to technology. Included for each area of technology is a brief statement of research objectives, a few significant details concerning the approach of the programs, and a short summary of any important developments or conclusions. The Appendix to the report identifies each program referenced in the report, with a brief description, under categories identical to those in the body of the review.

PREPARATION OF METAL

Tungsten Powder

The objective of work in this area is to prepare tungsten powders of submicron particle size. Two programs[1, 2]* with these intended objectives have demonstrated the feasibility of preparing powder with a mean diameter of less than 0.01 micron. Vitro Laboratories' approach[1] is to first prepare electrically conducting anodes from mixtures of carbon and tungstic oxide (WO_3). These anodes are then vaporized in a high-intensity-arc chamber using graphite as the cathode material. Condensation of the supercooled vapors resulted in the particulation of fine oxide which is ultimately reduced by hydrogen to form metallic tungsten powder.

During the reduction step it was found that very fine low-purity powder resulted from prolonged low-temperature reduction cycles, while short high-temperature cycles yielded powders with larger mean diameters and higher purities. For example, reducing at 716 to 842 F (380 to 450 C)** for 46 hours resulted in a powder with a purity of 95.25 per cent tungsten and a mean surface area of 46.7 sq m per gram. A 3-hour reduction cycle at temperatures between 572 and 1517 F (300 and 825 C) gave 99.78 per cent pure material with a surface area of 6.6 sq m per gram. Powders with surface areas exceeding 20 sq m per gram were found to be pyrophoric when exposed to air.

In work sponsored by the AEC, Union Carbide[12] has also produced powder material with a surface area between 5 and 10 sq m per gram, and has further demonstrated the ability of this material to be sintered at lower temperatures, i.e., 2552 to 2912 F (1400 to 1600 C), and/or shorter times to densities exceeding 90 per cent of theoretical.

High-Purity Tungsten

The preparation of ultrapure tungsten was achieved by the Alloyd Corporation[3] by first zone refining WCl_6, followed by hydrogen reduction of the chloride vapor [illegible]

*Referenced programs are listed and annotated in the Appendix.

**Throughout the report centigrade temperatures are shown in parentheses [illegible] a coherent metal deposit. Analytical data from this material showed total metallic impurities ranging between 30 and 400 parts per million and a total interstitial impurity content of 10 ppm.

Vapor deposition is being used to prepare tungsten nozzle liners at High Temperature Materials, Inc.[33], Bureau of Mines (Rolla, Mo.)[17], National Bureau of Standards[16], and Battelle Memorial Institute[34]. In this process, which is discussed in more detail later in this report, tungsten of relatively high purity is deposited by the hydrogen reduction of WF_6.

CONSOLIDATION

Powder Metallurgy

Powder Compaction

The Hughes Tool Company[4], in conducting a systematic study of the compaction behavior of tungsten powder, among others, has shown that important differences exist between the consolidation characteristics of ductile metallic powders and brittle ceramic materials. Results from this work indicated that voids in metallic compacts are eliminated by plastic deformation of the composite particles. Fragmentation which occurs while compacting ceramic materials provides a great number of smaller particles which settle out to occupy interstices thus densifying these structures. Most significant from this study were steps taken toward clarifying erroneous hypotheses as to what forces operate during powder compaction. The former concepts of particles sliding past one another during compaction and of resultant particle interlocking as an explanation for green strength do not appear to be valid.

Plasma Spraying

The objective of work in this area was to demonstrate the feasibility of directly preparing pieces of hardware of high density by plasma-arc spraying of tungsten powder or wire. This process was investigated by both the General Electric Company and the Massachusetts Institute of Technology under three Navy-sponsored programs.

Two of these were conducted at MIT[5,6] where both open-air and inert-atmosphere deposition techniques were studied; the latter offered somewhat more latitude in the resultant properties of the deposits. With the exception of spraying angle (90 degree impingement was optimum) while spraying in the open air, the operating arc variables offered little control over the density of the deposits. Deposit densities were variable between 65 and 85 per cent of theoretical for respective spray angles of 15 and 90 degrees. The entire process was improved by spraying under a protective nitrogen atmosphere which allowed the substrate temperature to be increased to 1200 to 1500 F as oxidation was no longer a limiting factor. Under these conditions, the operating arc variables were more effective in modifying the deposit densities as controlled values between 50 and 91 per cent of theoretical were obtained. For a given arc operating condition, powder particle size was also found to influence the resultant density. Densities of 6[illegible] and 82 per cent were accomplished while spraying 3- and 150-micron particles, respectively. From this work, it was concluded that the sprayed deposits were too porous for some purposes, therefore, efforts were made to effect a denser structure by

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sintering after deposition. All of the sprayed tungsten was found to be brittle in bending at room temperature.

The General Electric Company[7] investigated both a consumable-wire-fed arc-spray gun and a commercial powder-fed plasma jet as to their abilities to produce high density-high strength deposits of unalloyed tungsten. From this work, it was found that equivalent density levels between 84 and 88 per cent were obtainable by either process while spraying on a cold mandrel open to the atmosphere. However, the powder-spray process was preferred since in the as-sprayed condition at room temperature it was nearly two and-a-half times stronger than similar wire-sprayed deposits. Evaluation of 30-mil-thick powder-sprayed deposits revealed an as-sprayed interstitial content of 2300 ppm oxygen and 200 ppm nitrogen, which could be reduced to 28 ppm and 10 ppm, respectively, by prolonged heat treatments under hydrogen and vacuum. Such heat treatment resulted in improved bend ductility as the transition temperature was decreased from a level above 2000 F to 900 F.

In efforts to obtain higher densities, General Electric also investigated the possibility of activated sintering. Dilute blended powder alloys were initially sprayed, then sintered for 1 hour at 2800 F. From this work, the W-5Re-1Ni composition was selected for further study on the basis of its high density (98 per cent) after spraying and sintering, and its single-phase structure. However, an attempt to prepare a rocket-nozzle configuration from this alloy by spraying and sintering on a graphite mandrel resulted in severe distortion and cracking. Generally, this behavior was attributed to a poor distribution of the deposit thickness and residual stresses known to exist in plasma-sprayed coatings.

Spraying with the protection of a nitrogen atmosphere, and elevating substrate temperatures to 2000 F, were also investigated as means of obtaining high-density deposits. As a result, deposits with densities between 90 and 92 per cent of theoretical were produced. All of this work employed powder with an average particle size near 25 microns.

Slip Casting

The Union Carbide Metals Company[8] investigated the process of slip casting and sintering as a method of consolidating tungsten powder. No details were given with respect to the nature of this process as applied to tungsten powder. Therefore, it is assumed that the operations involved were similar to those commonly used by the ceramic industry for the consolidation of refractory oxides. It was shown that densities ranging from 60 to 93 per cent of theoretical could be obtained by this process mainly through variations in the sintering treatment after slip casting.

Sintering

A review of the research programs related to tungsten sintering indicates that this process is currently being applied to three areas of technology:

(1) The production of uniformly high-density (greater than 92 per cent of theoretical) billets for primary working

(2) The fabrication of porous tungsten ionizers for use in ion-propulsion systems

(3) The further densification of plasma-jet-sprayed components.

The Fansteel Metallugrical Corporation[26] in their Navy-sponsored Tungsten Sheet Rolling Program demonstrated an ability to prepare high-quality sintered billets 1 by 6 by 13 inches with uniform densities ranging between 93 to 95 per cent of theoretical. To achieve these results, Fansteel conducted a preliminary screening phase in which they evaluated numerous powder grades and pressing and sintering conditions. From this it was concluded that 3 to 4-micron-diameter powder pressed hydrostatically at 35,000 psi followed by induction sintering for 8 to 10 hours in hydrogen at 2300 C was a near optimum and practical combination of the processing parameters required to produce uniformly high-density billets for primary working. Although the resultant quality of these billets was high, workers at Fansteel concluded that sintering temperature was the most important variable and that for massive sintering more consideration should be given to the goal of attaining higher temperature capabilities (4712 to 4892 F, 2600 to 2700 C), thus shortening times at temperature.

Other sintering investigations[9,10] are attempting to prepare porous-tungsten components for potential use in ionic propulsion systems with cesium vapor. The selection of tungsten for this application is based on the high work function of its surface for electron emission. This property, in conjunction with the small ionization potential of cesium vapor, provides nearly ideal conditions for the subsequent contact ionization of cesium.

The two basic structural requirements for a porous ionizer were established to be interconnecting porosity and individual pore sizes not exceeding 1 micron in diameter. Also, the porosity should be stable at operating temperatures sustained at up to 2000 F for periods of 1 to 2 years.

NASA, at the Lewis Research Center,[9] explored the feasibility of preparing, by powder-metallurgical methods, ionizing components which met the above requirements. Specifically, the effects of powder particle size and compaction and sintering conditions were evaluated with respect to their end effects on the permeability of sintered tungsten bodies. From this work it was found that functional ionization components could be prepared by die pressing 1-micron powder in 0.018-inch-thick platelets at 25,000 psi and then sintering these for 20 hours at 2750 F. Generally, the difficulty encountered was an inability to achieve a satisfactory permeability in conjunction with the proper pore size. For example, hydrostatic pressing 1-, 10-, and 20-micron powder at 58,000 psi and sintering for 20 hours at temperatures between 2250 and 2900 F resulted in material which either lacked permeability or possessed pore diameters exceeding 1 micron.

Thompson Ramo Wooldridge Inc.[10] has also investigated the metallurgical problems associated with the development of porous-tungsten ionization components. The objective of this research is to produce ionizers with more uniform pore size and permeability and to develop improved joining techniques which will allow leaktight joints to be made between the ionizer and its supporting structure.

Two programs[5,6] have also dealt with the problem of achieving further densification of plasma-sprayed material by subsequent sintering. Generally, their approach was to initially study the "activation" effect that nickel is known to have on the sintering of tungsten powder. Amounts of nickel ranging from 0.025 to 5.0 weight per cent [illegible] added to tungsten by two methods, coreduction of the oxides and coating unalloyed powder with nickel nitrate. The results indicated that tungsten sintering could be activated with a minimum amount of nickel if it was present on the surface of the powder, that is, applied by the coating process. For example, coated tungsten containing 0.25 per cent nickel was sintered to 98 per cent of theoretical density in 16 hours at 2012 F (1100 C) while coreduced powder compacted in an identical manner and containing 1 per cent nickel required 27 hours at 2012 F (1100 C) to attain the same density.

This knowledge was then applied to the densification of plasma-sprayed deposits with as-sprayed densities of 85 per cent of theoretical. Nickel additions were accomplished by infiltrating the deposits with a Zn-8Ni solution which, after vaporization of the zinc, left 0.2 to 0.4 per cent residual nickel in the tungsten structure. Subsequent sintering of the deposits for 1 hour at 2372 F (1300 C) demonstrated that densities up to 95 per cent of theoretical could be obtained.

As a continuation of their nickel-activated sintering studies, MIT[6] has explored the effects of other Group VIII metals on the sintering characteristics of tungsten compacts. Generally, densification rates were significantly increased by small amounts of palladium, rhodium, platinum, and ruthenium (added as chlorides) listed in the order of decreasing acceleration effect. With palladium, the most effective element, densities of 93.5 and 99.5 per cent of theoretical were obtained after sintering a W-9.25 Pd alloy for 30 minutes and 16 hours, respectively, at 2012 (1100 C). The proposed mechanism for the improved rates of densification assumes that the activating element forms a "carrier phase" layer on the surface of the tungsten particles which in turn modifies the rate of interfacial diffusion of tungsten atoms between particles.

Melting and Casting

Electron-Beam Melting (EBM)

Electron-beam melting, as a method for consolidating tungsten and its alloys, was investigated by the Mallory-Sharon Metals Corporation.[11] The melting was performed at the Stauffer-Temescal Company where a 3-inch-diameter ingot of unalloyed tungsten was triple melted under a vacuum ranging from 0.05 to 0.10 micron with power consumptions between 200 and 260 kw. Analytical data for this material indicated that the total interstitial content (C, O, N, H) was reduced from 930 ppm to 120 ppm. Further information concerning resultant ingot grain size and melting rate was not available, however, for normal EBM tungsten the grain size is known to be large, for example, approaching 1 inch in diameter, and the melting rate slow, that is, 5 to 10 pounds per hour with a power input of 250 kw.

The Stauffer Metals Company also melted unalloyed tungsten and tungsten-base alloys for the General Electric Company[36] under an Air Force-sponsored welding program. The purpose of this work was to provide General Electric with the materials required for their program. In all, 12 ingots were drip melted a total of five times each into a 2 to 4 inch-diameter water-cooled retractable copper mold. Eleven of these ingots were dilute tungsten-base alloys containing Ta, Re, B, C, Zr, Hf, Y, and Th while the twelfth was "grain refined" unalloyed tungsten. For the latter, a minor alloy addition, proprietary to Stauffer, was added for grain refinement. As a result, the grain size was reduced approximately one order of magnitude. Sidewall appearance was quite good for all of the ingots, with only minor remnants of surface laps. A typical analysis of these materials indicated a total interstitial content of only 7 ppm.

Consumable Arc Melting (CAM)

Although more control is possible with electron-beam melting, consumable arc melting under vacuum is generally the preferred process for melting tungsten and tungsten-base alloys. When compared on the basis of equivalent power inputs, the arc process produces ingots of equivalent purity and sidewall quality with significantly increased melting rates.

NASA, at the Lewis Research Center,[12] melted 3/4-inch-diameter, 100 per cent dense swaged rod into 1-1/2-inch-diameter ingots. Using 3400 amperes at 23 volts in reverse polarity (electrode positive and ingot negative) they achieved a very rapid melting rate which had little or no effect on the initial 99.95 per cent purity of the swaged-rod electrode. After melting, it was necessary to remove 1/8 inch from the radius of the ingot sidewall to obtain a smooth defect-free surface.

The Westinghouse Corporation, under three Government contracts, has been active in the field of tungsten and tungsten-base-alloy consumable arc melting. Two programs were sponsored by the Navy while the third is being funded by the Air Force. A review of the melting developments and experiences in each follows.

> In one program for the Navy[13], unalloyed tungsten and W-5Re were melted into 2-inch-diameter ingots from 5/8 to 1-inch-diameter electrodes. Each electrode was composed of several sections joined end-to-end by TIG (argon) welding. Initially, attempts were made to melt these materials using d-c straight polarity, however, this approach was later abandoned in favor of an a-c power supply as numerous difficulties were encountered. Among these were radiation damage to the exposed inner areas of the furnace and frequent burn-outs of the water-cooled copper crucible. Both of these difficulties were attributed to the large power partition associated with d-c straight-polarity melting — theoretical estimates are that 90 to 95 per cent of the power is dissipated at the anode or molten pool. Switching to a-c power tended to split the power equally between the electrode tip and molten pool thereby reducing the temperature in contact with the copper crucible and increasing the temperature on the electrode tip. As a result, less power was required to cast ingots of equivalent diameter by employing a-c power.
>
> In the second Navy program[15], the objective of consumable arc melting was to establish the process parameters for preparing large ingots of tungsten and W-Mo alloys for subsequent conversion to rocket nozzles by forging and machining. Although this technique was abandoned in favor of the vacuum arc skull-melting technique, considerable data were generated which were significant to the early technology of consumable arc melting:

(1) A definite size effect was found to be associated with d-c straight-polarity melting. Below a critical value of mold-to-electrode diameter ratio, melting was not possible.

(2) As the electrode density increased from 70 to 100 per cent of theoretical, the melting rate decreased for a given mold-to-electrode diameter ratio and power level.

(3) A relationship was found to exist between the electrode density and the melting voltage which may be stated as follows: as the electrode density increases the voltage required to melt increases.

(4) Additions of molybdenum to tungsten resulted in ingots with significantly finer grain sizes than normally observed in molybdenum, molybdenum-base alloys, or unalloyed tungsten.

Furthermore, during this program, it was found that both unalloyed tungsten and W-30Mo could be melted into high-integrity ingots. However, 15 attempts to melt the W-50Mo alloy were unsuccessful in producing a sound crack-free ingot.

As Phase I under the Air Force program, Westinghouse[14] reviewed the literature and compiled a state-of-the-art report on consumable vacuum arc melting. Following this review, a facility was established at WADD with the intended capability of melting unalloyed tungsten. In particular, this report emphasized the design parameters related to the selection of vacuum systems and power supplies, the design of water-cooled molds and stirring coils, and the fabrication of consumable electrodes.

The objective of subsequent melting investigations conducted in this facility established melting practices for selected tungsten-base alloys. Initially, melting was attempted with the W-6Mo-6Cb alloy, however, due to severe ingot cracking, attention was shifted to the W-6Mo-2Cb composition. This composition was successfully melted into 3-1/2-inch-diameter ingots using electrodes 1-1/2 inches in diameter of 89 to 94 per cent density. Melting rates between 0.65 and 2.55 pounds per min were achieved for d-c straight-polarity power inputs ranging between 160 and 200 kw. Both increased melting rates and minor additions of zirconium (0.06 to 0.12 per cent) and carbon (50 to 270 ppm) were found to decrease the as-cast grain size of the W-6Mo-2Cb alloy. Ingot grain size was increased by low melting rates and minor additions of titanium (0.04) and oxygen (500 to 1000 ppm). The latter levels of oxygen were tolerable in the initial sintered electrodes as nearly all of it was eliminated during arc melting.

Other investigators melting unalloyed tungsten and tungsten-base alloys include the Oregon Metallurgical Company[22], Universal Cyclops Steel Corporation[27], Climax Molybdenum Company[19,22], Wah Chang Corporation[18], and the Crucible Steel Company[69,70]. Generally, these melting efforts are only directed toward the production of billets for primary working to fulfill other specified end objectives. For example, the first three contractors listed above are supplying 4-inch-diameter by

8-inch-tall ingots of the W-15Mo alloy to Thompson Ramo Wooldridge for consumption in their tungsten-forging program[22]. Material from all three sources was selected since it was recognized that differences in ingot processing by the different vendors might influence forgeability. In this connection, Oremet cold presses, surface welds, and double melts their electrodes using a-c power with an addition of 0.5 per cent titanium as a deoxidizer. Universal Cyclops does not employ a deoxidizer and single melts hydrogen-sintered electrodes using d-c straight polarity. Climax Molybdenum utilizes its press-sinter-melt (PSM) process in which powder is continuously pressed, resistance sintered, and melted with a-c power. Climax frequently uses carbon additions for deoxidation.

Universal Cyclops[27], Climax Molybdenum[19], and Crucible Steel[69,70] are also supplying ingots to their own manufacturing and alloy development programs.

Skull Melting and Centrifugal Casting

The Westinghouse Electric Corporation[15] concluded that of the three processes, powder metallurgy (size limited), vacuum arc melting (fabrication limited), and skull casting, the latter appeared most attractive for the production of tungsten and tungsten-alloy rocket nozzles. Proceeding with this concept, they produced the first thin-wall skull casting ever made from W-50Mo, W-30Mo, W-10Mo, W-1Mo, and pure tungsten, in that order. The target casting configurations were Polaris A2 nozzle throat inserts. For these castings the minimum wall thickness and ID were 0.175 inch and 3.58 inches, respectively, while the respective maximum values of wall thickness and OD were 0.91 inch and 6.20 inches. High-purity graphite was found to be the best mold material as it minimized both entrapped-gas porosity and contamination through carburization of the final casting. At the end of this development program Westinghouse demonstrated an ability to pour pure-tungsten castings weighing between 50 and 65 pounds with a grain size of approximately 0.0625 inch in diameter, 20 per cent smaller than the grains in arc-cast ingots.

The Wah Chang Corporation, working under a Navy contract,[30] investigated skull melting followed by centrifugal casting as a means of preparing large-diameter thin-wall blanks of tungsten for subsequent point deformation to yield wide sheet material. They were successful in preparing 6-inch-diameter rings with a wall thickness of 0.200 inch. This process seemed to have the advantage of improved purity in conjunction with a relatively small cast grain size, effected by rapid cooling in the thin section. However, one of the blanks displayed severe intergranular failure during subsequent flow turning at 1900 F.

Vapor Deposition

Vapor deposition of tungsten is most common in the direct preparation of tungsten-lined graphite rocket-nozzle inserts; it also qualifies as a consolidation process. Four organizations, National Bureau of Standards[16], Bureau of Mines (Rolla, Mo.)[17], Battelle Memorial Institute[34], and High Temperature Materials[33], have studied the vapor-deposition process under Navy contracts. The reactant gases used in all programs were WF_6 and H_2, which yielded a fine-grained columnar deposit of tungsten with its growth axis perpendicular to the graphite substrate. In general, high-purity deposits, 100 per cent dense, were obtained with total interstitial and metallic impurities below 50 ppm and 100 ppm, respectively. Of further interest were microhardness studies of the vapor-deposited tungsten which indicated an average value of 500 Knoop (corresponding to 395 Vickers) and an inverse relationship between grain size and hardness. Specifically, with respect to the deposition process, the Bureau of Standards found that the presence of HF gas accelerated the rate of deposition and that deposits with grain sizes of 10^{-5}cm could be obtained with low ratios (2 to 1 or less) of H_2 to WF_6.

PRIMARY AND SECONDARY WORKING

Extrusion

The research and development programs concerned with tungsten extrusion are directed primarily toward establishing the optimum parameters required to break down as-cast ingot structures. The merits for ingot breakdown of both high-energy-rate Dynapak machines and conventional high-speed presses are being investigated. One other program, currently in progress, has as its objective the extrusion of a structural shape with a tee cross section.

Conventional high-speed extrusion (5 to 25 inches per second) is being investigated by the Wah Chang Corporation[18], Climax Molybdenum Company[19], Thompson Ramo Wooldridge Inc.[22], Universal Cyclops Steel Corporation[27], and the Crucible Steel Company[69,70]. However, only Wah Chang is devoting its entire effort to optimizing the extrusion process for as-cast tungsten ingots.

Wah Chang[18] has selected the W-3Mo alloy for their Air Force-sponsored extrusion program because its as-cast grain size, which is smaller than that of unalloyed tungsten, favors fabricability. The measure of satisfactory accomplishment in this program will be the production of extrusions 10 feet in length with tee cross sections that can be circumscribed in a 2-inch-diameter circle. The flange width shall be two times the stem length. Also, the flange and stem shall have a thickness of 0.25 ± 0.1 inch and a surface finish of 150 rms or smoother.

The Allegheny Ludlum Steel Corporation is conducting the extrusion work for Wah Chang. The approach being followed is to first establish the parameters for extruding short rounds using reduction ratios between 11 to 1 and 17 to 1. Thus far, five billets, each 3.5 inches in diameter by 5 inches long, have been extruded using zirconia-faced dies. Extrusion temperatures ranged between 3200 to 4000 F, with corresponding maximum press pressures of 181,000 to 197,000 psi. Prior to extrusion, each billet was given either a 1-inch radius or a 110-degree conical nose. Ultimately, Wah Chang will examine the extrudability of wrought billets prepared by forging arc-cast ingots and the re-extrusion of 8-inch-diameter ingot material given a prior reduction of 3 to 1.

Areas of technology to be optimized in this program include

(1) Extrusion temperature, pressure, and speed

(2) Billet lubrication

(3) Die materials, configurations, and coatings.

In a combined extrusion and alloy development program, the Climax Molybdenum Company(19) studied the extrudability of five arc-cast W-Mo-C, W-C, and W-Zr-C alloys. All of the extrusion work was conducted on the high-speed press available in the High Temperature Metals Fabricating Facility at the Aeronautical Systems Division, Wright-Patterson Air Force Base. Billets 3 inches in diameter by 6 inches long were extruded to rounds using reduction ratios between 3 to 1 and 6 to 1 at temperatures between 2000 and 3600 F. Both Al_2O_3-faced dies and unfaced dies were used. There was less resistance to extrusion and a greater per cent recovery with the Al_2O_3-coated dies than with the uncoated dies. Among the results of this program was the calc[illegible]ion of extrusion constants for each alloy over a broad range of extrusion temperatures. From this work it was shown that the following list of the five alloys corresponded to the order of increasing resistance to extrusion at 3000 F: W-0.01C, W-10Mo-0.01C, W-50Mo-0.01C, W-30Mo-0.01C, and W-0.1Zr-0.01C. Generally, recoveries between 50 and 80 per cent were obtained for the W-C and W-Mo alloys while no sound material was obtained from the W-Zr composition.

The TAPCO Division of Thompson Ramo Wooldridge(22) has optimized the extrusion of 3-inch-diameter ingots of W-15Mo at a 5.5 to 1 reduction ratio. The objective of this work was to develop an extrusion process whereby round lengths could be prepared reproducibly to serve as primary working billets in their Air Force-sponsored forging program. Excessive and erratic die wash, while extruding at temperatures between 3600 and 4000 F, was the major difficulty encountered in this work. TAPCO feels that the success of a high-temperature extrusion operation depends on effectively insulating the steel die from the hot billet through the application of die coatings. Working from this premise, coatings of both Al_2O_3 and ZrO_2 were studied, with the results indicating ZrO_2 to be most effective. For example, the die wash was minimized to 0.015 inch while producing a 1.5-inch-diameter extrusion 30 inches long.

Furthermore, TAPCO found that extrusion constants for identical alloy ingot compositions were a function of melting practice. This conclusion was drawn as consistently different, and therefore, characteristic, extrusion constants were obtained while extruding material from three independent vendors.

Additional tungsten and tungsten-base alloy extrusion is also being conducted by the Universal Cyclops Steel Corporation(27) and the Crucible Steel Company(69,70), as the preliminary ingot-conversion step in their respective sheet-rolling and alloy-development programs. Both contractors have demonstrated the feasibility of extruding as-cast ingots to sheet-bar configurations, i.e., rectangular cross sections. Crucible Steel is converting 1.5-inch-diameter ingots to 0.5 by 0.7-inch cross sections, while Universal Cyclops has extruded 0.6 by 2-inch cross sections from 3-inch-diameter billets.

The Westinghouse Electric Corporation[20], NASA[12], and the California Institute of Technology[21] studied the feasibility of applying the high-energy-rate Dynapak extrusion process to unalloyed tungsten and tungsten-base alloys. In this work NASA[12] and CIT[21] partially extruded 1-inch-diameter powder-metallurgy billets and arc-cast ingots of unalloyed tungsten. Reduction ratios up to 45 to 1 and temperatures up to 3800 F were used with the results indicating less resistance to extrusion for the arc-cast ingots than for the powder-metallurgy billets. Both investigators used Model 1200 Dynapak machines.

The Westinghouse Electric Corporation[20], in research to compare the high-energy-rate and press-extrusion processes, partially extruded three arc-cast ingots of W-0.57Cb, each 3 inches in diameter by 4 inches long. Using a reduction ratio of 4 to 1 in conjunction with a constant "fire pressure", extrusion lengths were found to be a direct function of the billet temperature which ranged between 3200 and 3900 F. From this work, the following conclusions were drawn with respect to the Dynapak process in comparison with conventional high-speed press extrusion:

(1) The surface of Dynapak-extruded bars is significantly improved over press-extruded bars when limited but similar lubricating techniques are used.

(2) The billet temperature at extrusion required for true hot working is lower for the Dynapak process than for press extrusion. (Considerable adiabatic heating of the billet probably occurs during extrusion with the Dynapak.)

(3) The recrystallization temperature of Dynapak-extruded material is lower than that of material which is press extruded at the same temperature.

(4) There is a severe limitation on the amount of metal that can be extruded by the Dynapak process.

Forging

At least four forging-development programs for tungsten and tungsten-base alloys are currently in progress. Two of the four are being conducted by Thompson Ramo Wooldridge Inc. under separate contracts from the Air Force[22] and Navy[23] while the third and fourth, also funded by the Navy, are employing the independent efforts of Ladish[24] and Steel Improvement and Forge[25] Company. DMIC has no technical progress reports from any of the Navy programs, therefore, this review is limited to forging developments to date under Air Force Contract AF 33(600)-41629 by Thompson Ramo Wooldridge Inc. In this connection, it is further recognized that considerable tungsten forging is also being conducted under subcontracts or directly on purchase orders from prime contractors. Generally, such work has been directed toward the production of throat and nozzle inserts for solid-fuel rocket motors. However, most of the forging development coming from these efforts are also restricted from this review as they are reported in classified documents issued periodically by the prime contractors.

In their Air Force-sponsored work[22], the TAPCO Division of Thompson Ramo Wooldridge Inc. has demonstrated the feasibility of forging a complex thin-section leading-edge support configuration from a 1.25-inch-diameter arc-cast and extruded billet of the W-15Mo alloy. Each forging weighs approximately 3 pounds and was specially designed so as to present difficulties as severe as can presently be anticipated for structural tungsten-alloy forgings.

Prior to forging, each extruded billet was completely recrystallized by annealing for 1 hour at 3500 F. Forging was then accomplished at 2150 F in three steps, preblock, blockdown, and coin, to yield a sound product with minimum material loss and excellent surface finish. Immediately following the coining step, each forging was stress relieved for 30 minutes at 2150 F and then buried in silica sand for slow cooling. later, another stress-relief anneal of 1 hour at 2400 to 2500 F was also applied.

Rolling

Separate Air Force- and Navy-sponsored sheet-rolling programs are being conducted to develop the manufacturing methods and technology required for the production of defect-free, highly formable unalloyed tungsten sheet material. The Fansteel Metallurgical Corporation was selected to conduct the Navy's program[26] while the Universal Cyclops Steel Corporation is fulfilling the Air Force contract.[27]

Fansteel's[26] work, in which they applied the powder-metallurgical approach, is currently complete. The final objectives of this program were to roll 0.250, 0.100, 0.060, 0.020, and 0.01-inch-thick plate and sheet in flat sizes up to 18 by 48 inches with 89 to 98 per cent cold work.

To obtain the required dimensions, Fansteel sintered 1 by 6 by 13-inch hydrostatically compacted billets at temperatures up to 4262 F (2350 C) to obtain densities ranging between 93 and 95 per cent of theoretical. Using reductions of 20 to 25 per cent per pass, rolling temperatures began at 2642 F (1450 C) and finished as low as 2012 F (1100 C). Sheet evaluation included dimensional and ultrasonic inspection, chemical analysis, recovery and recrystallization behavior, and the determination of selected mechanical properties, including bend ductility and notched and unnotched tensile properties.

From prior experimental rolling studies and property evaluations, Fansteel found that the lowest transition temperature was obtained from sheet which received a minimum of 92 to 95 per cent reduction during rolling with no in-process recrystallization anneals. Furthermore, both the proper combination of time and temperature to accomplish stress-relief annealing and the proper balance of deformation between rolling directions (cross rolling) were also found to have a significant influence on the transition temperature. Specifically, a 1 to 1 ratio for cross rolling, in conjunction with a 10-minute stress-relief anneal at 2282 F (1250 C) gave a 3T bend transition temperature of 100 F. This was the lowest transition temperature obtained by Fansteel, and corresponding values for straight-rolled sheet annealed according to a similar procedure were about 200 F higher. In their production lots of large-size sheets, Fansteel used the 1 to 1 cross-rolling ratio and a 5-minute stress-relief anneal at 2057 F (1125 C) to obtain transition temperatures ranging between 280 and 180 F for the longitudinal direction and 400 and 280 F in the transverse direction.

The Universal Cyclops Steel Corporation[27] is vacuum arc melting pressed-and-sintered electrodes to obtain arc-cast ingots of unalloyed tungsten. The end objective of this program is to roll twenty 36 by 96-inch sheets in thicknesses of 20, 40, and 63 mils.

Sheet bars for initial rolling experiments were produced by either extruding and forging 3-inch-diameter arc-cast billets to 2 by 0.75-inch cross sections or by directly extruding to a 2 by 0.6-inch cross section. This material, both recrystallized and as forged or as extruded, was then rolled to sheet at temperatures ranging between 2700 F (initial) and 1900 F (final). Evaluation parameters included surface finish, rolling and recrystallization behavior, lamination tendency, bend ductility, and tensile properties. Following this evaluation, it was found that the lowest longitudinal transition temperature for a 4T bend, 200 F, was obtained from material stress relieved 1 hour at 1700 F and gives a minimum reduction of 92 per cent during rolling without recrystallization. Furthermore, for sheet in this condition, stress-relief annealing was limited to temperatures below 1900 F for a 1-hour holding time.

Working under an AEC contract, the Los Alamos Scientific Laboratory[28] has investigated the feasibility of directly rolling tungsten sheet from unalloyed powder. From this study, it was found that 80 to 85 per cent dense sheet, 65 mils thick by 2.5 inch wide, could be rolled from powders coarser than 3 microns. Subsequent sintering at 3092 F (1700 C) gave strip 90 to 95 per cent dense. Attempts to roll material thicker than 70 mils were unsuccessful as the resultant sheet was severely laminated.

Point Deformation

The Wah Chang Corporation has been most active in the field of point deformation with end objectives to produce 20-, 40-, and 63-mil-thick tungsten sheet ranging in width up to 36 inches and in length to 96 inches. Wah Chang is working under two separate programs sponsored by the Air Force and the Navy to develop technology in this area, as follows.

> There is no information in DMIC on the Air Force program[29] other than the initial state-of-the-art survey which issued in January, 1962. Significantly, the results of the survey at that time showed that extensive work had been reported on the fabrication of tungsten cones and nozzles by point deformation. However, only the Solar Aircraft Company and Pratt & Whitney Aircraft indicated experience with the manufacture of tungsten cylinders. No organization reported producing tungsten sheet by flow turning. Generally, it was concluded that flow turning offered numerous advantages over more conventional methods for the forming of less ductile metals. The two techniques for preparation of starting blanks, which appeared most promising, and were chosen, were (1) sintering and ring rolling and (2) sintering, rolling, forming, and joining.
>
> Working under a subcontract for Wah Chang[30] on the Navy program the Pratt & Whitney Aircraft Company has demonstrated an ability to flow turn four tungsten starting materials. (1) pressed and sintered, (2) sintered and forged, (3) sintered and rolled, and (4) arc cast, extruded, and rolled.

These materials were all successfully reduced into 90-degree cones by flow turning 20 to 25 per cent. Conical forming was done before attempting cylindrical flow turning, mainly to evaluate the performance of the various candidate materials. The lowest working temperature, 600 F, was for the arc-melted material while the as-sintered blanks required temperatures up to 1400 F.

Cylindrical flow turning to produce long cylinders of tungsten sheet was successful while using working temperatures ranging between 1400 and 1725 F. Starting blanks for this work were prepared by forming and welding 1/8-inch-thick sintered and rolled sheet into cylinders. Both molybdenum and tungsten filler metals were used in joining. Of the two, tungsten was preferred as stronger joints with deeper weld penetration resulted, thereby minimizing weld failure during the early stages of flow turning.

Machining

An extensive Air Force-sponsored program concerning the machinability of unalloyed tungsten, along with other refractory metals, is in progress at Metcut Research Associates, Inc.[31] This work and a limited study previously conducted at Westinghouse[15] as part of a skull-melting program, are the only contracts on record at DMIC dealing with the machinability of tungsten and tungsten-base alloys.

In the earlier work conducted at Westinghouse[15], it was found that the machinability of arc-cast W-Mo alloys was generally poor when attempted with conventional tooling, and decreased with increasing tungsten content. Rigidity of equipment seemed to be one of the most important prerequisites to successful machining of unalloyed tungsten. All of the machining operations, which included turning, drilling, and sawing, were performed dry. Experience indicated that tungsten could be successfully turned using the following conditions. cutting speed, 150 ft per min, feed, 0.010 in. per rev, and depth of cut, 0.1875 in. Under these conditions, a tool life of 3 to 4 cubic inches of metal per edge was obtained for Kenametal Grade K-[illegible] carbide inserts. Standard high-speed-steel drills used at very slow speeds and high feed rates enabled drilling. Sawing was used extensively in this program and was found to be more reliable than abrasive cutting techniques. High-speed-steel blades with four teeth per inch gave the best performance. Specific conditions were 34 strokes per min and 0.003 to 0.005-inch depth of cut per stroke with an 800-pound load.

Metcut[31] is conducting a systematic and extensive study of the many variables which influence the performance of several machining processes. Specifically, a number of the variables being studied are (1) tool grade, (2) tool geometry, (3) condition of material to be machined, (4) cutting rate, (5) feed rate, (6) depth of cut, (7) table speed, (8) down feed, (9) cross feed, (10) wheel speed, (11) cutting fluid, and (12) cutting temperature. Optimization among these many variables on the basis of tool life at room temperature yielded the following results for unalloyed pressed-and-sintered tungsten with densities ranging between 70 to 96 per cent of theoretical.

Machining Operation	Tungsten Density	Maximum Tool Life Achieved: Minutes	Inches of Work Travel	Holes	G-Ratio
Turning	70	25	X	X	X
	90	11	X	X	X
	93	20	X	X	X
Face milling	85	X	72	X	X
	93	X	27	X	X
End milling	85	X	31	X	X
	93	X	45	X	X
Drilling	93	X	X	7	X
Grinding	93	X	X	X	5.2

The effect of workpiece temperature was also investigated in conjunction with the drilling experiments. These results were significant and indicated that drill life could be extended from 7 holes (0.213-inch diameter by 0.500 inch deep) at room temperature to 10 and 27 holes with workpiece temperature of 400 and 800 F, respectively.

FABRICATION AND PERFORMANCE OF ROCKET NOZZLES

Power Roll Forming

Under two programs[7,32] funded by the Navy, the General Electric Company has developed the technology required for successfully roll forming tungsten into thin-wall rocket-nozzle liners. A brief technical summary of each program follows.

The objective of the first program[7] was to develop a roll-forming process capable of producing thin-wall tungsten rocket-nozzle liners for the Polaris A2A rocket motor. The successful approach to this manufacturing problem included four basic steps:

(1) Power roll forming a truncated cone with a 30-degree included angle from a 0.240-inch-thick by 11-inch-diameter tungsten plate

(2) Formation of the nozzle contour shape by spinning the cone onto a converging-diverging mandrel

(3) Stress-relief annealing for 1 hour at 1900 F

(4) Trimming the contoured cone and flanging the forward end to complete the nozzle fabrication.

All of the forming operations were carried out at a temperature of 1800 F. This was established as the lowest permissible forming temperature, provided that blanks of starting material with suitable prior histories were available for forming. In this connection, it was found that the prior metallurgical history of the starting material must be carefully controlled. The best results were obtained from material which had been warm worked 40 to 70 per cent, had a smooth surface finish, and was subsequently recrystallized to a fine-grain structure.

The Aerojet General Corporation fired one of the nozzle liners produced by the above procedure. After 10 to 11 seconds at 6200 F and 625 psi the liner failed and ejected. From an evaluation of the debris it was concluded that failure occurred because (1) the liner thickness (46 mils) was insufficient and (2) a severe reaction occurred between the tungsten and its graphite backup to form low-melting carbides.

Further conclusions from this program were that there is apparently no minimum size of part which can be manufactured from unalloyed tungsten by roll forming, although a wall thickness of 20 mils seems to be the thinnest section practical.

The second program[32] has as its objective the manufacture of three tungsten exit liners conforming to Aerojet-General specifications and six nozzle inserts conforming to specifications supplied by the Allegheny Ballistics Laboratory. The technology developed under the program described above[17] is being successfully applied to this manufacturing effort. To date, the three exit liners for Aerojet-General have been fabricated and delivered.

Plasma Spraying and Vapor Deposition

Five programs, each funded by the Navy, come under the major heading of "Plasma Spraying and Vapor Deposition". Although novel in concept, an appraisal of both the plasma-spraying and vapor-deposition processes for the manufacture of rocket-nozzle configurations is strongly justified on the basis of economic considerations. The main potential advantage of these processes over roll-forming techniques is that they offer a direct means for the formation of rocket-nozzle components.

The General Electric Company[7] has conducted the only program on record at DMIC which dealt specifically with the plasma-spray deposition of tungsten to form rocket nozzles. In this work, tungsten nozzle inserts, specified by the Atlantic Research Corporation (ARC), were built up by arc spraying either 40-mil wire or minus 200-mesh powder on removable mandrels. However, during the time allotted to this program, the effort to develop a reliable method for spray fabricating tungsten nozzles and exit liners was not successful.

Nozzle inserts (84 to 88 per cent dense) prepared by both powder and wire spraying were tested at ARC using an aluminized solid propellant and chamber pressures up to

900 psi. Neither type of nozzle performed satisfactorily under these conditions. Severe errosion resulted in both cases, although the powder-sprayed tungsten performed somewhat better than the wire-sprayed tungsten.

Markedly improved tungsten deposits resulted when deposition was accomplished in an inert-atmosphere chamber. Nozzles prepared in this manner were tested at GE using the liquid-propellant combination of LOX and JP-4 and at ABC using aluminized solid propellants. The test results from these firings were inconclusive.

Four contractors, High Temperature Materials, Inc.[33], Bureau of Mines (Rolla, Mo.)[17], National Bureau of Standards[16], and Battelle Memorial Institute[34], have studied the vapor deposition of tungsten on graphite rocket nozzles and on exit-liner inserts. Deposition in each case was accomplished by the reduction of WF_6 by hydrogen.

Hardware commitments by High Temperature Materials[33] included two first-stage exit liners and six second-stage throat inserts for Polaris A-3 rocket motors. Also, four second-stage inserts were prepared for subsequent testing at the Allegheny Ballistics Laboratory. As a result of this work, technology and facilities were developed which were sufficient for the production, in quantity, of nozzles with uniform coatings of vapor-deposited tungsten in thicknesses up to 0.250 inch. One of the major obstacles in the preparation of crack-free nozzles was obtaining a graphite mandrel that matched the coefficient of expansion of tungsten. Missmatch between the two coefficients led to residual stresses within the tungsten and subsequent cracking during cooling to room temperature.

Additional mechanical-property studies of vapor-deposited tungsten indicated that it compares favorably in strength with powder-metallurgy tungsten. Also, the recrystallization temperature of vapor-deposited tungsten was found to be greater than 3632 F (2000 C).

Each of the three remaining programs concerning vapor deposition were administered by the Special Projects Office of the Navy. Contracting firms were Battelle Memorial Institute[34], the National Bureau of Standards[16], and the Bureau of Mines (Rolla, Mo.)[17]. All of the contractors studied the deposition of tungsten on graphite inserts; only the Bureau of Mines succeeded in obtaining an adequate mechanical bond between the two materials. In this work, as-coated tungsten layers, with and without rhenium barrier layers between them and the graphite, ranged between 50 to 100 mils in thickness. Several of the nozzles prepared by the Bureau of Mines performed satisfactorily when tested at the Aerojet General Corporation using aluminized solid propellant with flame temperatures and chamber pressures up to 6180 F and 1000 psi, respectively.

JOINING

Welding

The Hamilton Standard Division of the United Aircraft Corporation(35), working with unalloyed tungsten, demonstrated the feasibility of producing sound crack-free electron-beam welds in thicknesses up to 0.10 inch. Evaluation of welded coupons to determine optimum welding conditions included tensile testing at room temperature, 2200, 2500, and 2800 F and bend testing. Maximum weld strength and ductility were associated with minimum fusion and heat-affected zones in combination with a small grain size and a smooth continuous weld bead. At temperatures approaching that for recrystallization, weld strengths were equivalent to those of the base metal. However, at room temperature weld strength was only 50 per cent of the base-metal strength. The transition temperature of the best welds was 1100 F, as compared to 650 F for recrystallized base metal. Undercut weld beads were initially a problem; this difficulty was eliminated by combining X-beam oscillations (in direction of bead) with extremely high welding speeds. For 50-mil sheet, the final weld conditions were 145 kv, 16 ma, 100 ipm, with a 0.065 X-beam oscillation. These conditions gave a very narrow fusion zone and nearly eliminated the heat-affected zone.

The General Electric Company, under separate programs sponsored by the Navy and Air Force, has been very active in the field of electron-beam welding. A review of the welding technology accumulated under each program follows.

> The end objective of the welding phase of the program for the Navy(7) was to demonstrate the feasibility of manufacturing rocket nozzles by girth welding roll-formed cones to form the required converging-diverging shape. Trial welding studies and evaluations were initially conducted on sheet coupons before attempting to join roll-formed cones. The results obtained from the evaluations were nearly identical to those subsequently achieved by Hamilton Standard, that is, poor low-temperature ductility and tensile strength. It was concluded that although the production of nozzles was feasible, the extreme brittleness and low fracture strength at room temperature placed a serious limitation on the fabrication of nozzles by welding.
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> As a part of the program for the Air Force,(35) the properties of fusion welds produced in powder-metallurgy tungsten sheet and in electron-beam-melted tungsten sheet were evaluated. Welding was accomplished by both TIG and electron-beam techniques. In this connection, considerable porosity was noted in the welds of powder metallurgy tungsten while none were observed in the welds of the electron-beam material. Depending on the preparation technique applied to the as-welded coupons (anneal and/or polish), the zero-ductility transition temperature varied between 356 and 482 F (190 and 250 C).
>
> In an effort to improve the low-temperature ductility of tungsten through alloying, a series of 10 binary and ternary alloys containing dilute additions of rhenium, tantalum, zirconium, hafnium, yttrium, thorium, and

carbon were electron-beam melted and rolled to sheet. The transition temperature of each alloy, both recrystallized and as welded, was then determined by bend testing. From this work, it was found that the weldments in the alloys exhibited bend ductilities equivalent to those observed in recrystallized nonwelded samples of the same material. The lowest transition temperature, 302 F (150 C), was obtained with the composition W-0.97Hf-0.033C.

Aeroprojects is currently investigating the development of technology and equipment for the ultrasonic welding of tungsten sheet under respective Navy[37] and Air Force[38] contracts. To date, under the Navy program[37], the conditions for accomplishing tungsten-tungsten joints have been established using 5-mil-thick sheet. However, subsequent testing and examination of coupons welded at an acoustical power input of 1600 watts revealed severe cracking in the weld-zone areas, in conjunction with poor tensile-shear-strength properties. The technical plan for the Air Force-sponsored program[38] has three phases. Under Phase I, the feasibility of producing ultrasonic welds in combinations of tungsten with other refractory materials and superalloys was demonstrated. Phase II, currently in progress, has as its objective the development of equipment and techniques to join thicknesses of tungsten up to 0.10 inches. Theoretical estimates indicate that electrical power inputs of approximately 25 kw to the transducer assembly may be required to fulfill this objective. The performance characteristics of the welding equipment developed under Phase II will be evaluated in Phase III.

Brazing and Bonding

Considerable effort, under four Government contracts, has been devoted to the development of low-temperature brazing alloys for high-temperature service. Although the alloy systems being studied in each program differ, nearly identical approaches in each are being followed with respect to the evaluation and testing techniques employed. Separate discussions of the four programs are presented as follows.

In work conducted for the Army at the Massachusetts Institute of Technology[39] the concepts of activated sintering developed under previous projects[5,6] were applied to the joining of 5-mil-thick tungsten strip. High-quality lap (single and double) joints were accomplished by initially electroplating 10^{-5} to 10^{-6}-inch layers of nickel or palladium on the surfaces to be joined and then diffusion bonding the clamped assembly for short periods of time in the temperature range 832 to 2012 F (1000 to 1100 C). All of the resultant joints were brittle in bending and tension at room temperature, but remained sound with a load-carrying capacity at temperatures up to 4000 F (2200 C). Extensive recrystallization occurred in the tungsten adjacent to the bonding interface in each sample and it was concluded from theoretical considerations that grain growth would inevitably accompany any transport process which permits tungsten to bond to itself.

The Solar Aircraft Company[40] recently completed work on a program for the Navy with the intended objective of developing low-temperature (below that for tungsten recrystallization) brazing alloys for high-temperature service from the reactive Pt-B system. The maximum remelt-temperature capability of this system is 4460 F, corresponding to a peritectic reaction in the W-Pt system. Braze-alloy compositions from Pt-1B to Pt-4.5B were evaluated for remelt temperatures after resistance brazing for 5 seconds at 2000 F and then diffusion heat treating for various time-temperature combinations. The highest remelt temperatures obtained were between 3800 and 3900 F. Subsequent metallographic examination of the brazed joints revealed that the remelt temperature was limited by the presence of W_2B (melting point = 3450 F). No recrystallization was noted in the base metal. Further work attempted to eliminate or minimize the formation of W_2B through the addition of halide salts to the initial braze-alloy mixture. Boron halides are volatile; therefore, it was thought but not proven that the boron concentration could be reduced through volatilization with a corresponding increase in the remelt temperature from 3800 to 4200 F.

Under an Army contract currently in progress at Aerojet General Corporation[41], three groups of braze alloys have been selected for study, as follows:

(1) Pure metals or combinations of them

(2) Binary chromium alloys

(3) Commercially available brazing alloys.

Initially, 11 alloys were chosen which included aluminum, 72Ti-28Ni, LM Nicrobraze, Coast Metals 62, GE J8100, Premabraze 101, 50Ti-50Ni, 40Ti-40Ni-20Cr, 25Ti-50Ni-25Cr, 50Cr-50Ni, 38Cr-62Pd. Lap-joint assemblies of unalloyed tungsten and each alloy were brazed for 5 minutes at temperatures ranging from 1320 to 2700 F. All of the alloys except aluminum and the Ti-Ni-Cr combinations gave good joints. After brazing, the lap joints were diffused for 2 to 19 hours at temperatures between 1950 and 2250 F. In each instance, the diffusion heat treatments were insufficient to produce recrystallization in the base metal, however, subsequent metallographic examination revealed extensive recrystallization in the tungsten adjacent to the braze alloy. Evaluation of the brazed joints included remelt testing on single-lap joints and shear-strength testing on double-lap specimens. The highest remelt temperatures, approximately 4500 F, were consistently obtained for Coast Metals 62, GE J8100 and LM Nicrobraze using an induction-heating technique. Final evaluation included the fabrication of a segmented standard (MERM) rocket nozzle by brazing stacks of 60-mil-thick tungsten washers into the required nozzle configuration. Only the three braze alloys showing the highest remelt temperatures were employed for this final test. Only the nozzle brazed with Coast Metals 62 performed satisfactorily during a 60-second test fire at 4900 F and 750 psi.

Further work was conducted with Coast Metals 62 and a re-evaluation of the remelt temperature indicated a value of only 4000 F. For this work an oxyacetylene-flame heat source was used for a close simulation of nozzle firing conditions. At present, 4000 F is considered to be an unsatisfactory remelt temperature for tungsten-to-tungsten joints, therefore, other braze alloys with potential for increased remelt temperatures are being studied. These include 50Cr-50Ni, 62Pd-38Cr, and nickel.

Work at the General Electric Corporation[38] for the Air Force includes the development of brazing materials for columbium-base alloys as well as unalloyed tungsten. With respect to unalloyed tungsten, the objective is to develop braze alloys with brazing temperatures near 3000 F with remelt temperatures greater than 3500 F. Eight columbium- and tantalum-base ternary compositions potentially capable of fulfilling the objectives of this program have been selected for study. Each of these alloys consists of two or more metals, compatible with tungsten to some extent, plus a melting-temperature depressant such as silicon or boron. The initial brazing studies conducted to date have been confined to the binary compositions 80Cb-20Ti and Cb-2.2B. Both of these alloys increased the bend transition temperature in the vicinity of the joint to a point 50 to 100 F above that of the recrystallized base metal, which was 600 F.

OXIDATION AND OTHER HIGH-TEMPERATURE REACTIONS

The current and projected uses for tungsten in rocket and spacecraft applications at ultrahigh temperatures has presented numerous problems. The most difficult problem is oxidation resistance, but others include erosion and corrosion in rocket-nozzle exhaust atmospheres and melting reactions when tungsten is in contact with other refractory materials.

Oxidation

Westinghouse[42] has conducted a fundamental study of the oxidation of tungsten and its alloys involving oxidation kinetics, thermodynamic measurements of the tungsten-oxygen system, and crystal-structure studies. Oxidation kinetics were studied by exposing tungsten at 932 to 3092 F (500 to 1700 C) in an atmosphere of oxygen at 1×10^{-1} to 1×10^{-3} mm of mercury. It was found that oxidation was diffusion controlled below 1112 F (600 C). Cracked surface oxide resulted in an inconsistent fit of oxidation data to the parabolic rate law between 1202 and 1742 F (650 and 950 C). Above 2192 F (1200 C) and at a pressure of less than 1×10^{-4} in an atmosphere of oxygen, the oxide vaporized as fast as it formed. Oxidation between 1472 and 3092 F (800 and 1700 C) was found to be independent of the oxide evaporation rate and to be linear, resulting in either no protection or the formation of a very thin barrier layer. A strongly adherent purple scale formed on the substrate, but kinetic data revealed it to be nonprotective. Alloying tungsten with tantalum improved the oxidation resistance. W-10Ta and W-25Ta oxidized at a rate 40 per cent that of unalloyed tungsten, while the oxidation rate of W-50Ta appeared to be about 10 per cent of that for tungsten.

The heat of formation and free energy of formation were determined for WO_2, $W_{18}O_{49}$, $W_{20}O_{58}$, and WO_3, and values were compared with those from other investigators.

The Ohio State University[43] recently completed a 3-year investigation of the oxidation behavior of tungsten. Thermodynamics, kinetics, and oxide volatility were studied. Experimental chemical-equilibria data were used to calculate heat and free-energy values and to establish the stability of the various oxide species. A proposed W-O phase diagram shows the phases W_3O (from another investigator), WO_2, $W_{18}O_{49}$, $W_{20}O_{58}$, and WO_3. The upper temperature at which W_3O is stable was taken from other work as 1337 F (725 C). $W_{20}O_{58}$ and $W_{18}O_{49}$ were calculated to be unstable below 903 and 1085 F (484 and 585 C), respectively. Hence, the coexistence of WO_2 and WO_3 is possible below 904 F (485 C).

Oxidation of tungsten at 1256 to 2012 F (680 to 1100 C) under 0.05 to 0.21 atmosphere of oxygen demonstrated that the mechanism is diffusion of oxygen ions through the scale to the metal-oxide interface. Kinetics initially followed the parabolic rate law, but then changed to linear behavior with increased time. WO_2 was observed only at low temperatures and for very short times. An intermediate blue oxide, thought to be $W_{18}O_{49}$ or $W_{20}O_{58}$ grew to a limiting thickness of 10 microns and then decreased in thickness. The outer oxide region was porous WO_3 at all temperatures. Activation energies calculated from rate constant data were 35 kcal in the parabolic range and 36.5 kcal in the linear range; indicating that diffusion through the blue oxide layer was the controlling step in both processes. Only WO_2 formed when tungsten was oxidized under 1×10^{-10} atmosphere of oxygen. The parabolic rate constant for WO_2 growth under these conditions appeared to be a linear function of the one-fifth power of the oxygen pressure, which agrees with the oxidation mechanism proposed for a metal-deficient lattice. The protection afforded by the WO_2 layer broke down when $W_{18}O_{49}$ formed.

The study of oxide volatility revealed that the volatilization rates increase with temperature according to an Arrhenius plot. Volatilization rates of WO_2, $W_{18}O_{49}$, and $W_{20}O_{58}$ increased linearly with the partial pressure of water vapor. Volatilization rates increased in the following order (temperature and water-vapor-pressure constant): (1) WO_2, (2) $W_{18}O_{49}$, and (3) WO_3.

Lockheed[44] has studied the oxidation behavior of tungsten at 2372 to 5432 F (1300 to 3000 C) at air pressures from 1 to 40 mm of mercury. Oxidation rates were linear with time (at constant pressure), and tungsten oxide was found to volatilize as rapidly as it formed, leaving the tungsten surface bright and clean. An Arrhenius rate equation established the heat of activation to be 31,500 calories per mole. The linear rate constant K was found to be pressure (p) dependent according to the relationship

$$K = 14\, p^{0.62},$$

indicating that the linear rate constant decreases with decreasing pressure. Surface-recession measurements showed that a tungsten sheet exposed at 3200 F (1760 C) under 1 mm air pressure for 1 hour would suffer a reduction in thickness of 12 mils.

A sharp break occurred in plots of oxidation rate versus temperature at 3182 to 3452 F (1750 to 1900 C) due to dissociation of WO_3. The rate changed again at 4892 F (2700 C), presumably due to volatilization of tungsten.

The University of California[45] has studied the reaction kinetics of O_2, N_2, and NO with tungsten at 3050 to 4220 F (1950 to 2600 K) under 1×10^{-8} to 1×10^{-6} atmosphere of gas pressure. It was found that the rate of reaction of tungsten with oxygen decreases with increasing temperatures. This is because at a fixed pressure of O_2 the surface concentration of oxygen decreases with increased temperature, due to decreased probability of surface reaction. Hence, the oxidation activation energy was dependent on both pressure and temperature. This presumably was because surface oxygen concentration was the rate-det rmining step, which depended in turn upon the O_2 pressure and the temperature.

A tungsten filament was heated to 4580 F (2800 K) in 1×10^{-6} atmosphere of nitrogen, with no evidence of reaction.

Nitric oxide is known to dissociate to O_2 and N_2 at a hot filament. Other investigators have established that the activation energies for tunsten-oxygen and tungsten-nitric oxide reactions were nearly the same, so it was expected that NO dissociation was not the rate-controlling step in the oxidation process. The rate of tungsten oxidation by NO was found to be three times that for the corresponding pressure of oxygen.

Erosion and Corrosion in Nozzle Environments

Tungsten degradation under simulated solid-propellant nozzle conditions has been studied by Stanford Research Institute[46]. Tungsten rod was positioned perpendicular to a high-velocity-arc plasma to obtain surface temperatures of 5072 to 6062 F (2800 to 3350 C) while CO_2 and Al_2O_3 were injected separately (different test runs) into the plasma. Tungsten erosion by CO_2 was primarily dependent on the CO_2 flux incident upon the tungsten surface and relatively independent of specimen temperature and type of tungsten (pure tungsten or W-2Th). The principal erosion product was a yellow powder identified as WO_3 by X-ray diffraction. Therefore, the erosion mechanism was believed to be formation and vaporization of the tungsten oxide. The investigation of tungsten erosion by Al_2O_3 is not yet completed.

The chemical reactions between tungsten and some constituents found in the exhaust stream of solid-propellant motors were also studied under static conditions in the temperature range from 3632 to 5792 F (2000 to 3200 C). The following reactions were observed, listed in decreasing order of importance:

(1) $3H_2O + W \rightarrow WO_3 + 3H_2$

(2) $3CO_2 + W \rightarrow WO_3 + 3CO$

(3) $9HCl + Al_2O_3 + \frac{3}{2} W \rightarrow 2AlCl_3 + \frac{3}{2} WO_2Cl_2 + \frac{9}{2} H_2$

(4) Transfer of tungsten through liquid Al_2O_3.

Experiments suggested that increasing the HCl in exhaust gas would decrease the amount of alumina deposited on nozzle and jetevator surfaces by Equation (3). The combinations of W + HCl, W + CO, W + H_2, W + N_2, W + Al_2O_3 + CO, W + Al_2O_3 + H_2, and W + Al_2O_3 + N_2 were virtually nonreactive. There was no significant reaction between tungsten and liquid Al_2O_3.

Atlantic Research Corporation[47] also has investigated the reactions between tungsten and the hot combustion products of solid propellants. One series of experiments consisted of passing pure gas over a tungsten filament heated to 4600 to 5500 F. The principal conclusions were

(1) H_2O and CO_2 rapidly oxidize tungsten. Increased partial pressures of H_2 and CO, respectively, decrease the oxidation rate due to decreased driving force.

(2) HCl and HF were essentially nonreactive.

Another experimental technique consisted of embedding a tungsten wire in a propellant strand and burning the propellant in a combustion bomb under nitrogen pressures of 300 to 1000 psi. Flame temperatures ranged from 4700 to 6500 F, combustion products ranged from neutral to slightly oxidizing. The test results agreed with observations of subscale rocket motor tests, namely,

(1) A fluorocarbon (binder) propellant did not affect tungsten.

(2) Slightly oxidizing propellants resulted in tungsten oxidation.

(3) W_2C formed with one particular propellant (Arcite 373).

(4) Tungsten melting occurred at the 6500 F flame temperature.

PROTECTIVE COATINGS

For those applications wherein oxidation or erosion resistance of tungsten is inadequate it becomes necessary to apply a refractory coating to the surface to obtain the desired surface stability. The technology of tungsten coatings is not nearly so advanced as for columbium and molybdenum, because of the difference in emphasis placed on these materials for structural applications where coatings are necessary.

General Telephone[48] is analyzing the basic factors involved in oxidation protection of tungsten to establish criteria for coatings for service above 3300 F. Silicide coatings were found to be limited to temperatures below 3600 F by the following factors.

(1) Melting of the W_5Si_3-WSi_2 eutectic seems to cause failure at about 3450 F.

(2) The calculated evaporation rate of the protective SiO_2 oxide is quite high at 3600 F (about 1 g per sq cm per hr).

(3) The Si + SiO_2 → 2SiO (gas) reaction could account for significant coating loss at 3600 F.

It was concluded that new types of coatings based on higher melting refractory oxides are necessary. ThO_2, HfO_2, UO_2, and ZrO_2 are the most suitable in terms of refractoriness and stability. The problem of producing such an oxide in situ on tungsten substrate is being studied as the next step in the research program.

New York University[49] established the feasibility of protecting tungsten from oxidation with silicide coatings applied by pack cementation. The major coating phase was identified as WSi_2. The coating provided oxidation protection at 3300 F for times up to 10 hours. The "disilicide pest", which is an anomalous mechanism causing reduced coating life at lower temperatures, resulted in coating lives of only 5 to 15 hours at 1200 to 2300 F.

Silicide-base coatings are also being studied under Air Force sponsorship at Thompson Ramo Wooldridge[50]. The coatings are applied by one or more pack-cementation cycles to incorporate desired modifiers, and they usually are given a final controlled preoxidation treatment in wet hydrogen. Titanium, zirconium, and boron appear to improve coating performance. Codeposition of tungsten plus silicon has been found superior to simple silicon deposition. Coating lives of the most promising coatings in furnace-oxidation tests are summarized in Table 1 below. The problem of anomalous failure at lower temperatures (1800 F) still remains to be solved for these coatings. The estimated maximum service temperature of 3650 F for TRW coatings is consistent with the 3600 F maximum predicted by General Telephone for all silicide-base coatings.

TABLE 1. CYCLIC-FURNACE-OXIDATION LIVES OF TRW TUNGSTEN-COATING SYSTEMS

	Protective Life[a], hours					
Coating System	1800 F	2500 F	3000 F	3300 F	3500 F	3600 F
Silicon[b]	-	22	16	0.2	-	-
(Si-W)-O	15 - 25	40 - 50	27 - 47	5 - 10	[illegible] - 8	1
Ti-Zr-(Si-W)-O	2 - 20	36	35 - 72	14 - 26	2 - 5	1
Ti-(Zr-B)-(Si-W)-O	-	-	34	16	-	-

(a) Specimens cycled between indicated temperature and room temperature at 1-hour intervals.
(b) Included for comparison.

Value Engineering[51] has investigated electrodeposited chromium-base cermet coatings for tungsten, and identified ZrB_2 and ZrO_2 as two of the most promising additives. Thirty minutes of protection was achieved in oxyacetylene-torch tests at 3900 F.

Manufacturing Laboratories, Inc.[52], has investigated diffusion barriers for tungsten under an Air Force contract. The purpose has been to develop a diffusion barrier for the interface between tungsten and an oxidation-resistant coating to eliminate the potential problem of deterioration of substrate or coating properties by diffusion.

Tungsten-barrier and barrier-chromium diffusion couples (exemplary of oxidation-resistant coating) were annealed at 3092 and 3272 F (1700 and 1800 C) and then evaluated by conventional diffusion-analysis techniques. Interdiffusion was found to decrease as the minimum solidus temperature of the tungsten-barrier binary system increased. Rhenium, ruthenium, and iridium were selected as the optimum barrier metals for tungsten. These selections do not take into account coating-barrier diffusion reactions, because practical tungsten-barrier-coating diffusion couples have not been evaluated.

PROPERTIES

The majority of the property data for tungsten and tungsten-base alloys have been contributed from research with objectives other than property studies. This is not unusual since the determination of mechanical and physical properties is generally the most common and sometimes the only means of evaluating the quality of a material. Therefore, being cognizant of the naturally large distribution of property data, this particular section is limited to only those contracts with specific objectives to determine selected properties. Following this plan, a review of contracts at DMIC indicate that a total of 12 programs qualify under the limitation imposed. Only 5 of these 12 are summarized in this section since detailed or significant information was not available from the remaining 7.

The National Aeronautics and Space Administration seems to be most active in the area of property studies on tungsten and tungsten-base alloys. In three separate studies(53,54,55) they have released data on: (1) effect of surface condition on the ductile to brittle transition temperature, (2) effect of strain rate on tensile properties at high temperature, (3) tensile and stress-rupture properties of some W-Mo alloys at high temperature. A brief summary follows.

> The effects of surface conditions on the ductile-to-brittle transition temperature of recrystallized tungsten were evaluated by testing in tension(53). Several surface treatments were applied with the results indicating an electropolished (10 mils removed from the diameter) or oxidized surface exhibited the lowest transition temperature, 415 F. Results from notched specimens ($K_t = 6$) indicated that the transition temperature is increased by 360 F, and that above the transition temperature tungsten is notch strengthened.
>
> The effect of strain rate on the tensile properties of recrystallized tungsten was evaluated from strain rates of 0.002 to 20 inches per inch per minute(54). Results from this work showed that at a constant temperature, increasing the strain rate increased the ultimate tensile strength significantly. Also, increasing the strain rate at temperatures above 3000 F increased the ductility.
>
> Tensile tests were conducted over the temperature range 2500 to 4400 F to determine the tensile properties of W-10Mo, W-25Mo, and W-50Mo alloys(55). Results showed the 10 and 25 per cent alloys to have higher tensile strengths than unalloyed tungsten at 2500 and 3000 F and equivalent strength to about 3500 F. Above 3500 F the strength of unalloyed tungsten was superior to that of either of the alloys. Stress-rupture tests were also conducted on the W-50Mo alloy over the temperature range 2500 to 3500 F in both the as-worked and recrystallized conditions.

The Hughes Tool Company[56], working under an Air Force contract, is studying the mechanical properties of commercially available tungsten sheet. In the initial quality-control phase, hardness, microstructure, chemical impurities, flexural properties, and tensile strength were determined on material from three vendors. From the test results generated during the first phase, a materials specification was established requiring a large hot-cold reduction during rolling for material for study during the second phase.

During the second phase, tensile tests were conducted on material from five different sources at room temperature, 1000, 2000, 3600, and 4400 F. In this connection it is significant to note that material from one producer consistently displayed a limited amount of plastic deformation at room temperature.

As a portion of the work conducted under a Navy contract, the Aerojet-General Corporation[57] determined the melting points and spectral and total emissivities for tungsten with densities from 70 to 90 per cent of theoretical. Spectral emissivities ranged from 0.37 to 0.415 and total emissivities ranged from 0.315 to 0.375 over the temperature range 2642 to 4982 F (1450 to 2750 C). Furthermore, a higher value of spectral emissivity (0.65μ) was indicated for porous tungsten than for dense tungsten.

PHYSICAL METALLURGY

Much effort has been and is currently being expended to improve the low-temperature ductility of tungsten and to develop workable high strength alloys for application in the 3000 to 4000 F temperature range. To complement these broad topics which fall within the scope of alloy development, a considerable amount of effort is also being devoted to more fundamental studies of the mechanical properties and alloying behavior of unalloyed tungsten. Therefore, this section dealing with the physical metallurgy of tungsten-base material is most easily discussed in two parts — alloy development and fundamental studies.

Alloy Development

In separate phases established under an Army contract, the Armour Research Foundation[65] is investigating liquid-phase sintering with respect to improved fabricability and low-temperature ductility.

The general objective under one phase is to lay the foundation for a new and improved technique of fabricating tungsten sheet. The new approach, which was recently demonstrated as being successful, takes advantage of the cold ductility of a two-phase W-Ni-Fe composition during breakdown rolling. Prior to finish rolling, the low-melting W-Ni matrix is removed by zone refining leaving essentially pure tungsten to be finished to sheet. The primary advantage to this unique process is that it improves material recovery and therefore the economy of the sheet-rolling process.

The second phase has as its objective the development of ductile tungsten alloys for use at temperatures above 36[illegible] F (2000 C). The approach employed liquid-phase sintering whe[illegible] particles were rounded and completely surrounded by a strong, ductile envelope phase. Ternary additions to W-Pt and W-Pd bases showed little or no promise for achieving the desired effects as envelope phases. However, subsequent work with W-15Th and W-20Th indicated that these alloys were capable of room-temperature deformation, possessed good high-temperature strength, and have melting points exceeding 3632 F (2000 C).

The General Electric Company[36] in work for the Air Force has completed a study of the flow and fracture behavior of ten W-Re, W-Ru, W-Hf, W-Hf-C, and W-B alloys. Each of the alloys was initially prepared by vacuum melting and was then extruded and rolled to sheet material for subsequent mechanical-property evaluations. The most significant finding from the property studies was the exceptional combinations of strength and ductility shown by a W-27Re alloy with some sigma phase present in the as-rolled structure. The ductile-to-brittle transition temperature for this alloy in either the wrought or fine-grained recrystallized conditions was about -100 F and the corresponding yield strength was approximately 400,000 psi. Transition temperatures in the range 75 to 150 F resulted from annealing treatments which produced larger grained single-phase structures in this same alloy.

Other important results from this work included information concerning the effect of interstitial solutes on ductility. It was found that fracture in tungsten-base materials was more dependent on changes in the distribution of interstitial atoms than on the grain size per se. By varying the cooling rate it was found that the transition temperature of certain alloys could be varied by nearly 300 F. Low cooling rates gave the lowest transition temperatures and presumably provide sufficient time for the interstitials to precipitate from solution and segregate to the grain boundaries, thus reducing dislocation locking and improving ductility.

In work for the Bureau of Naval Weapons, Battelle Memorial Institute[66] has demonstrated the additive effect of both inert oxide dispersions and critical amounts of Groups VII and VIII metals in lowering the ductile-to-brittle transition temperature of tungsten in both the wrought or recrystallized form. The lowest transition temperatures were in the range 167 to 185 F (75 to 85 C) as compared to 410 F (210 C) for unalloyed material. The most ductile alloys were W-5Re-2.2ThO_2, W-1Os-4.4ThO_2, and W-0.3Ir-4.4ThO_2. Furthermore, these ternary additions were found to increase the recrystallization temperature and decrease the recrystallized grain size.

The Climax Molybdenum Company has conducted extensive investigations to develop workable tungsten-base alloys with high-temperature properties superior to those of unalloyed tungsten. As discussed below, the majority of this work is included under three programs, two for the Navy[67,68], and a third for the Air Force[19].

> The effect of cobalt, columbium, hafnium, tantalum, vanadium, and zirconium were investigated for the Navy with respect to their effects on the lattice parameter, hardness, and oxidation resistance of tungsten[67]. Vanadium was the only element found to contract the tungsten lattice. Based on hardness measurements at room temperature and 1600 F, cobalt was the most potent hardener. Columbium, hafnium, tantalum, and zirconium all reduced the oxidation rate of tungsten but not to the extent that the effects were of any practical significance.

Successful extrusion procedures were developed for arc-cast unalloyed tungsten and the 10, 30, and 50 per cent molybdenum compositions each containing a 0.01 per cent addition of carbon on the study for the Air Force[19]. With the exception of unalloyed tungsten, each of these materials were successfully converted to bar stock by rolling. Testing indicated the best strength properties for the W-30Mo alloy and the best stress-rupture properties for the W-10Mo alloy. At 2400 F in the stress-relieved condition, W-30Mo had a tensile strength of 64,000 psi and W-10Mo withstood 2.6 hours at 40,000 psi before rupture.

The Navy project to develop vacuum arc-cast tungsten-base alloys which can be worked in the cast state and which will possess high strengths coupled with acceptable ductility in the wrought conditions is currently in progress[68]. Seven tungsten-base alloys containing dilute additions of molybdenum, columbium, hafnium, and zirconium are being studied. To date, all seven alloys have been successfully melted and converted to 1/2-inch bar stock by extrusion and swaging.

Under two Air Force contracts, the Crucible Steel Company[69,70] is investigating the tungsten-rich alloys within the W-Ta-Mo-Cb quaternary system. A brief summary of the objectives and achievements in each program is presented below.

In one program[69], 20 alloys were investigated for their structural potential at temperatures above 2500 F. The most outstanding tungsten-base alloy screened from these studies and tested in the as-extruded condition was W-5.7Mo-5.7Cb. The results of tensile and stress-rupture testing indicated an ultimate tensile strength of 62,000 psi at 3000 F and creep elongation of 0.09 per cent after stress-rupture testing 5 hours under 7,000 psi at 3000 F.

In the second program[70] the objectives were to evaluate sheet samples of six high-strength alloys from the W-Ta-Mo-Cb system and to increase the high-temperature strength of these alloys with dispersed carbide phases. Of the six alloys selected, only two were tungsten base, W-6Mo-6Cb and W-20Ta-12Mo. Subsequent tensile tests on these at 3000 F in the as-extruded condition (3 to 1 reduction) indicated ultimate strengths of 62,000 and 68,000 psi for the W-6Mo-6Cb and W-20Ta-12Mo compositions, respectively. Further attempts to fabricate these alloys to sheet were unsuccessful.

Additional work to achieve even greater high-temperature strengths resulted in two carbide-dispersion alloys, W-12Cb-0.14Zr-0.19C and W-12Cb-0.12Zr-0.29V-0.07C. Tensile tests at 3500 F in the as-extruded condition indicated ultimate strengths of 49,000 and 57,000 psi for the Zr-C and V-Zr-C alloys, respectively.

Fundamental Studies

Fundamental studies of the effects of standard metallurgical variables on the physical and mechanical properties of unalloyed tungsten and dilute tungsten-base alloys have been conducted by the Union Carbide Metals Company, Haynes Stellite Company, and the Westinghouse Electric Corporation. A brief discussion of this work, which was included under two Air Force-sponsored and one Navy-sponsored program, is presented as follows.

In work for the Air Force, the Union Carbide Metals Company(73) investigated the influence of fabrication, strain rate, temperature, and microstructure on the tensile properties of both polycrystalline-powder-metallurgy and arc-cast tungsten. Perhaps the most significant result from this work was the improved high-temperature ductility displayed by arc-cast material as compared to that of powder-metallurgy tungsten. For example, at 3002 F (1650 C) a reduction in area of more than 98 per cent was obtained for the arc-cast material, while only 40 per cent was obtained from the powder-metallurgy product. Several dilute tungsten-base alloys with titanium, zirconium, and columbium were also investigated. Results from this work indicated an unusually high tensile strength of 61,000 psi for the W-0.57Cb alloy. However, recent attempts by other investigators to reproduce this value have been unsuccessful.

The objective of the program for the Navy at Haynes Stellite(74) was to evaluate the fabricability and properties of tungsten and tungsten-base alloy single crystals. Sixty-five crystals, which included several dilute tungsten-base alloys, were included in the program. Fabrication of these materials was accomplished by swaging and a combination of forging and rolling at 2192 F (1200 C). As a result of these studies the single crystals were shown to have a significant fabrication advantage and their mechanical properties after working were shown to be equivalent to those of polycrystalline material.

Westinghouse(75) conducted an extensive research program for the Air Force to determine base-line data on the metallurgical properties of pure tungsten. In work with high-purity polycrystalline material, tensile and stress-rupture properties were determined to temperatures of 4000 and 3000 F, respectively. An analysis of these data showed a continuous decrease in ductility with increasing temperature, similar to that described above for prior Union Carbide work. This phenomenon will be a topic of further investigation in future work. Also for polycrystalline material, the effect of grain size on the ductile-to-brittle transition temperature revealed that the transition temperature depended more on the annealing temperature than on the grain size. This fact was attributed to differences between the states of the impurities in the lattice as effected by annealing temperature.

Single crystals were also studied. Their mechanism of purification during zone melting, their flow and fracture behavior, and their characteristic internal friction peaks were studied in efforts to establish base-line data for pure tungsten. Other work included mechanical-property determinations at temperatures up to 3000 F of alloys with dispersed second-phases of W-ThO_2, W-TaC, and W-HfO_2 and dilute solid-solution alloys of W-Ta and W-Cb. When compared with unalloyed tungsten at

3000 F, the dispersed-phase alloys displayed a significant ultimate strength advantage – 27 to 31,000 versus 15,000 psi. Of importance with respect to the solid-solution alloys, additions of 0, 35 and 5 per cent tantalum were found to increase the recrystallization temperature by 720 and 1080 F (400 and 600 C), respectively, above that noted for unalloyed material – 2192 F (1200 C).

Under a program sponsored by the Air Force, Battelle Memorial Institute(76) studied the notch and unnotched tensile properties of several refractory metals and their alloys, including unalloyed tungsten. Both stress-relieved and recrystallized rod material were tested in tension with the notch sensitivity of each material being evaluated by analyzing the notch-unnotched tensile-strength ratio, the ductility transition, and the fracture transition. The results of this study indicated that on the basis of notch-unnotched strength ratios, stress-relieved and recrystallized tungsten tend to become notch sensitive at temperatures below 482 and 752 F (250 and 400 C), respectively.

Nuclear Metals, Inc., as the prime contractor, has conducted one Air Force-sponsored program(77), and is currently engaged in another(78), in which they are determining the constitution diagrams and studying the diffusion characteristics of selected tungsten binary systems. Work under one contract(77) has to date included determinations of the W-Ir and W-Rh binary systems and several isotherms of the W-Mo-Os and W-Hf-Re ternary systems. Care was taken in obtaining reliable phase diagrams. In particular, the purity of the constituents was protected at all times, and the temperatures were determined to within ± 36 F(± 20 C). The objective of the diffusion studies at Nuclear Metals(78) includes a determination of the diffusion coefficients in the binary tungsten systems, W-Ru, W-Ir, W-Rh, and W-Pt. This work is being conducted with the aid of an electron-probe analyzer.

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APPENDIX

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APPENDIX

GOVERNMENT-SPONSORED RESEARCH RELATED TO TUNGSTEN — 1960-1962

This listing of Government-sponsored research and development programs related to tungsten technology includes all those known by DMIC to have been in force at least at some time during the period 1960-1962. The list is arranged according to technology, following the outline that appears in the Table of Contents. The item numbers for the various contracts are used as reference numbers in the report.

The Defense Metals Information Center maintains a file of information on research programs for all materials within its scope. This file is used as an indispensable aid in collecting technical information. It is extremely important to DMIC to know of the existence of research and development projects within its scope.

Preparation of Metal

A. Tungsten Powder

(1) Conducted by: Vitro Laboratories, Division of Vitro Corp. of America, West Orange, New Jersey (J. Holmgrin)
For: Air Force; WADD, Materials Central
Title: Submicron Powder Manufacturing Methods Development

Vitro Laboratories has completed a state-of-the-art survey on this subject and is currently engaged in the production of fine powders largely in the 1000 to 100-A range. Metals, oxides, and carbide materials are being studied.

(2) Conducted by: Union Carbide Nuclear Co.
For: Atomic Energy Commission
Title: Production of Ultra-Fine Tungsten Metal Powder

Improved tungsten powder has been produced experimentally that has a surface area of 5 to 10 square meters per gram. It can be isostatically pressed and then sintered at 1400 to 1600 C to reach over 90 per cent of theoretical density. The ultimate objective of the tungsten powder research is to make a high-density, ductile tungsten metal.

B. High-Purity Tungsten

(3) Conducted by: Alloyd Corporation, Cambridge, Massachusetts
For: Navy; BuAer
Title: Research on the Production of Ultra Pure Refractory Metals

The objective was to produce ultrapure refractory metals, i.e., tungsten, tantalum, molybdenum, and columbium, through the hydrogen reduction of purified chloride vapors.

Consolidation

A. Powder Metallurgy

1. Powder Compaction

(4) Conducted by: Hughes Tool Company (I. Shapiro)
For: Air Force; ASD
Title: Fundamental Study of the Compressibility of Powders

A systematic study of the compressibility of powders is being conducted to determine the basic underlying principles that relate the compressibility of powders to functions of their physical properties.

2. Plasma Spraying

(5,6) Conducted by: Massachusetts Institute of Technology, Cambrdo, Massachusetts (J. H. Brophy, H. W. Hayden, K. G. Kreider, and J. Wulff)
For: Navy; BuWeps
Title: Activated Sintering of Pressed Tungsten Powders and Plasma Jet Sprayed Tungsten Deposits

The strength and structure of plasma arc-sprayed tungsten deposits have been examined for air and protective-atmosphere chamber spraying. As deposited density was varied from 50 to 90 per cent. The application of nickel to activate densification of tungsten deposits by subsequent heat treatments was studied.

(7) Conducted by: General Electric Company, Cincinnati 15, Ohio (W. H. Kearns)
For: Navy; BuWeps
Title: Development of High Strength Materials for Solid Rocket Motors

The purpose of this program is to perform research and conduct feasibility studies leading to the development of ultrahigh-strength solid-fuel rocket cases by means of warm working. An additional phase is related to the development of special alloys which may have improved ductility and improved strength-to-weight ratios. The following are tasks: (1) continued arc-spraying studies with tungsten; (2) fabrication studies with tungsten; and (3) electron-beam-welding studies with tungsten.

Task 4 describes an investigation of electron-beam-welding parameters for tungsten sheet, mechanical properties of electron-beam welds in tungsten sheet, and welding of simulated rocket nozzles.

3. Slip Casting

(8) Conducted by: Union Carbide Metals Company, Niagara Falls, New York (R. W. Fountain)
For: Air Force; WADC, Materials Lab.
Title: Investigation of the Properties of Tungsten and Its Alloys

Objectives: An evaluation of selected physical and mechanical properties of slip-cast-and-sintered tungsten was conducted. The tests were conducted on a number of samples having densities ranging from 60 to 93 per cent of theoretical density. No details are given with respect to the nature of the slip-casting process.

4. Sintering

(9) Conducted by: Lewis Research Center, Cleveland, Ohio (N. T. Saunders)
For: NASA
Title: Experimental Method of Producing Porous Tungsten for Ion Rocket Engines

A preliminary study was conducted to develop a method of fabricating porous tungsten for ion-propulsion applications.

(10) Conducted by: Thompson Ramo Wooldridge Inc.
For: Air Force; WADD
Title: Porous Tungsten Emitters

This research is intended for investigation of the metallurgical problems associated with the development of a porous-tungsten surface-contact ion-source for potential use in ionic-propulsion systems with cesium. The major objective of this program will be to develop the metallurgical techniques required to produce tungsten emitters.

B. Melting and Casting

1. Electron-Beam Melting

(11) Conducted by: Mallory-Sharon Metals Corporation (J. Perryman)
For: Air Force; WADD, Materials Lab.
Title: Services and Facilities to Evaluate the Use of Electron Beam Melting

The purpose of this program was to evaluate the effectiveness of the electron-beam-melting process in reducing brittleness and/or improving impact properties of materials that are considered to be inherently brittle. Boron, boron carbide, tantalum carbide, and zirconium diboride were melted. The effect of melting variables on the properties of electron-beam-melted beryllium, tungsten, hafnium, vanadium, cobalt, and molybdenum were also determined.

2. Consumable Arc Melting

(12) Conducted by: Lewis Research Center, Cleveland, Ohio (F. A. Foyle, G. E. McDonald and N. T. Saunders)
For: NASA
Title: Initial Investigation of Arc Melting and Extrusion of Tungsten

The purposes of this study were to investigate arc melting as a method for producing dense tungsten ingots, to study extrusion as a method for breaking up the coarse grain structure of the arc-cast ingots, and to evaluate certain mechanical properties of arc-cast and extruded tungsten.

(13) Conducted by: Westinghouse Electric Corporation, Research Laboratory (L. L. Franz)
For: Navy; BuAer
Title: Research and Development in High-Strength, Heat-Resistant Alloys

This contract has as its object the development of high-strength, heat-resistant alloys based upon the metals tantalum and tungsten and containing appreciable percentages of rhenium, hafnium, zirconium, titanium, osmium, molybdenum, niobium or other high-melting metals.

(14) Conducted by: Westinghouse Electric Corporation (Carnahan)
For: Air Force; WADD, Materials Central
Title: Melting Variables for Refractory Metals

This program provides for the investigation of arc-melting variables to produce sound, fine-grained, homogeneous ingots of refractory alloys and to study the effects of grain structure and purity levels on the resistance to deformation and mechanical properties. This program will consist of two work areas: (1) basic vacuum arc melting program and (2) the internal support program.

3. Skull Melting and Centrifugal Casting

(15) Conducted by: Westinghouse Electric Corporation, Blairsville, Pennsylvania (A. E. LaMarche)
For: Navy, BuWeps
Title: Manufacturing Development of Tungsten Alloys for Rocket Nozzles

The program was divided into three phases: Phase I - a study of the effects of the controlled variables of the skull-melting process. Phase II - the extension of the skull-melting and casting technology developed under Phase I to W-10Mo, W-1Mo, and pure tungsten in that order; and Phase III - an attempt to establish a process specification for producing high-integrity castings of pure tungsten.

C. Vapor Deposition

(16) Conducted by: National Bureau of Standards, Dept. of Commerce
For: Navy; BuOrd, SPO
Title: Electrodeposition of Tungsten and Other Refractory Metals

The variables involved in the deposition of tungsten coatings by the vapor-phase reduction of tungsten hexafluoride with hydrogen were studied. No conditions were found that resulted in a large improvement in the rate of efficiency of deposition.

(17) Conducted by: The Bureau of Mines, U. S. Department of Interior, Washington, D. C. (F. W. Hoertel)
For: Navy; BuOrd, SPO
Title: Vapor Deposition of Tungsten on Graphite Nozzle Inserts

The objective of this program was to investigate the vapor-phase reduction of tungsten hexafluoride on graphite rocket-nozzle inserts. The Aerojet-General Corporation, Sacramento, California, is to supply the machined nozzle inserts. All components produced under the contract were ultimately delivered to this Corporation.

Primary and Secondary Working

A. Extrusion

(18) Conducted by: Wah Chang Corporation, New York, New York (J. Wong)
For: Air Force; WADD, Materials Central
Title: Tungsten Extrusion Development Program

This program involves five phases: Phase I - state-of-the-art survey; Phase II - billet process development; Phase III - development of the extrusion operation; Phase IV - verification of process uniformity and development of postextrustion operations; and Phase V - pilot production of the target section.

(19) Conducted by: Climax Molybdenum Company of Michigan, Detroit, Michigan (R. Q. Barr, G. G. Chesmar and M. Semchyshen)
For: USAF; WADD
Title: Development of Workable Molybdenum and Tungsten-Base Alloys

It is the objective of this program to conduct additional development work on several molybdenum- and tungsten-base alloys containing various additions of those alloying elements which have shown the ability to increase the high-temperature strength of molybdenum in previous investigations. Effort will be directed most specifically to arrive at compositions with an optimum balance of workability, low ductile-to-brittle transition temperature, high recrystallization temperature, and high hot strength.

(20) Conducted by: Westinghouse Electric Corporation
For: Air Force; WADD
Title: Research to Compare High Energy Rate and Extrusion Press Processes as Applied to Refractory Metal Alloy Deformation

The objective of this program is to compare the high energy rate (Dynapak) and extrusion press processes as applied to refractory-metal-alloy deformation. A comparison will be made in the properties and behavior of selected refractory-metal alloys extruded by conventional means and by the high-energy-rate (Dynapak) technique.

The objective of this program is to compare the high energy rate (Dynapak) and extrusion press processes as applied to refractory-metal-alloy deformation. A comparison will be made in the properties and behavior of selected refractory-metal alloys extruded by conventional means and by the high-energy-rate (Dynapak) technique.

(21) Conducted by: California Institute of Technology, Jet Propulsion Lab, Pasadena, California (D. P. Kohorst)
For: NASA
Title: Evaluation of Tungsten Extrusions Produced by the High-Energy-Rate Extrusion Process

A study was made to evaluate the high-energy-rate extrusion process as a means of producing test specimens for this program. Because of the difficulties encountered in hot-working tungsten, it was of prime interest to determine whether this fairly new and little-used process could yield specimens of the desired quality.

B. Forging

(22) Conducted by: Thompson Ramo Wooldridge Inc. (A. S. Nemy)
For: Air Force; AMC
Title: Tungsten Forging Development Program

The primary objective is the development of methods for producing tungsten forgings for use in air and spacecraft construction.

(23) Conducted by: Thompson Ramo Wooldridge Inc.
For: Navy; SPO
Title: Tungsten Forging

(24) Conducted by: Ladish
For: Navy; SPO
Title: Tungsten Forgings

(25) Conducted by: Steel Improvement and Forge Company
For: Navy; SPO
Title: Tungsten Forging

C. Rolling

(26) Conducted by: Fansteel Metallurgical Co., North Chicago, Illinois (G. Bodine)
For: Navy; BuWeps
Title: Production of High-Quality Tungsten or Tungsten-Alloy Sheet

Production of sheet 18 inches wide and approximately 48 inches long in connection with refractory-metal sheet-rolling program. The powder-metallurgy method of consolidation is being employed.

(27) Conducted by: Universal Cyclops Steel Corporation, Bridgeville, Pa. (C. Mueller)
For: Air Force; WADD, Materials Central
Title: Development of Tungsten Sheet Rolling Techniques

Objective: To develop processes and techniques for the production of defect-free, high-formability flat-rolled tungsten sheet products. The arc-melting method of consolidation is being employed in this program.

(28) Conducted by: University of California, Berkeley, California
For: Atomic Energy Commission
Title: The Powder Rolling of Molybdenum

The objective of this work was to demonstrate the feasibility of power rolling as a means of consolidation to directly produce molybdenum and tungsten sheet.

D. Point Deformation

(29) Conducted by: Wah Chang Corporation (J. Wong)
For: Air Force; WADD, Materials Central
Title: Development of Tungsten Sheet by Floturning Techniques

The objective of this program is to develop new or improved techniques for shear forming tungsten-alloy sheets. The measure of satisfactory accomplishment will be the production of acceptable sheets 36 by 96 inches in thicknesses of 20, 40, and 63 mils.

(30) Conducted by: Wah Chang Corporation, Albany, Oregon
For: Navy; BuWeps
Title: Investigation of the Feasibility of Manufacturing Tungsten Sheet by the Application of Point Deformation Techniques to a Suitable Preform

E. Machining

(31) Conducted by: Metcut Research Associates, Inc., Cincinnati, Ohio (J. Kahles)
For: USAF; WADD, Materials Central
Title: Machining of Refractory Materials

Purpose: Investigate and evaluate the machining characteristics of the refractory materials of importance to the aerospace industry. Phase I of this program consisted of a survey intended to isolate significant machining problems, followed by the formulation of a suitable machining research program. The machining program is being carried out as Phase II of the subject contract. Phase III will be devoted to studying machine tool requirements for refractory materials.

Fabrication and Performance of Rocket Nozzles

A. Power Roll Forming

(32) Conducted by: General Electric Company, Cincinnati, Ohio (D. J. Shipp)
For: Navy; BuWeps
Title: Development of Roll-Formed Tungsten Nozzle Components

The objectives of this program are to manufacture by the roll-forming process, at least three exit liners according to an Aerojet General specification and six nozzle inserts according to specifications from the Allegany Ballistics Laboratory.

B. Plasma Spraying and Vapor Deposition

(33) Conducted by: High Temperature Materials, Inc., Boston, Massachusetts
For: Navy, BuWeps
Title: Design, Development, and Fabrication of Vapor-Deposited Tungsten Components

Purpose: Produce tungsten coatings by vapor deposition on graphite-nozzle and exit liner substrates for use in the A-3 Polaris missile. Two configurations for throat inserts for the A-3 first-stage exit liner are required.

(34) Conducted by: Battelle Memorial Institute, Columbus, Ohio (J. M. Blocher, Jr.)
For: Navy; BuOrd, SPO
Title: Experimental Coatings of Tungsten-Molybdenum Alloys and Graphite

Equipment capable of producing tungsten coatings on graphite rocket-nozzle inserts through the vapor-phase reduction of tungsten hexafluoride was designed and constructed

Joining

A. Welding

(35) Conducted by: Hamilton Standard Division United Aircraft Corporation (H. S. Hokanson)
For: USAF; WADD, Materials Central
Title: Electron Beam Welding of the Refractory Metals

This program covers an investigation of electron-beam-welding procedures as related to the welding of molybdenum and tungsten. Primary emphasis will be placed on the evaluation of welding procedures which minimize the width of the fusion and heat-affected zones in order to obtain the maximum in ductility.

(36) Conducted by: General Electric Company, Cincinnati, Ohio (G. Hoppin)
For: USAF; WADD, Materials Central
Title: Investigation of Joining the Refractory Metals Tungsten and Columbium

Objective: Obtain a better understanding of the physical metallurgy related to joining the refractory metals tungsten and columbium. Investigations will be directed to fusion welding of tungsten alloys and the brazing of columbium and tungsten. Also a feasibility investigation is to be made of joining by diffusion bonding between certain refractory metals and iron, nickel, or cobalt-base alloys.

(37) Conducted by: Aeroprojects Inc., West Chester, Pennsylvania (C. R. Frownfelter)
For: Navy; B· Weps
Title: Ultrasonic Welding of Refractory Metals

The objective of this program is the investigation of the ultrasonic welding machine settings required and evaluation of properties of the welds obtainable for the following refractory metals or alloys: (1) Cb-10Mo-10Ti, (2) Mo-0.5Ti, and (3) tungsten.

(38) Conducted by: Aeroprojects Incorporated, West Chester, Pennsylvania (N. Maropis)
For: Air Force; ASD, ASRCTF
Title: Development of Ultrasonic Welding Equipment for Refractory Metals

Objective: Design, assemble, and evaluate heavy-duty ultrasonic spot- and seam-welding equipment for joining refractory materials and superalloys in thicknesses up to 0.10 inch and to develop necessary techniques for producing reliable welds in these materials.

B. Brazing and Bonding

(39) Conducted by: Massachusetts Institute of Technology, Cambridge, Massachusetts (J. H. Brophy, H. Heideklang, P. Kovach, and J. Wulff)
For: Army
Title: Joining of Refractory Metals - Tungsten

Concepts of activated tungsten diffusion have been applied to the joining of tungsten strip at temperatures ranging from 900 to 1100 C. Solid-state diffusion has been enhanced by electroplating a thin layer of either nickel or palladium on one of the mating surfaces.

(40) Conducted by: Solar Aircraft Company, San Diego, California (C. W. Haynes, Sr., and A. G. Metcalfe)
For: Navy; BuWeps
Title: Development of Low Temperature Brazing of Tungsten for High Temperature Service

This program is based on prior work at Solar Aircraft Company with the platinum-alloy reactive braze systems, namely platinum-boron plus tungsten and platinum-silicon plus tungsten. The program was proposed in five phases to develop these reactive braze systems to their full potential.

(41) Conducted by: Aerojet-General Corporation (C. Fournier)
For: Army; WAL
Title: The Study of the Diffusion Bonding of Tungsten and Tungsten Alloys

The purpose of this work is to fabricate complex rocket-nozzle-insert shapes from thin tungsten washers bonded by diffusion-brazing techniques.

Oxidation and Other High-Temperature Reactions

A. Oxidation

(42) Conducted by: Westinghouse Electric Corporation, Pittsburgh, Pa.
For: Air Force; WADD, Materials Central
Title. Investigation of the Kinetics and Thermodynamics of the Tungsten-Oxygen System

Objectives of this program are the determination of the mechanism of oxidation of tungsten and an investigation of the changes resulting from selected alloy additions. A major part of the program will be a fundamental study of the kinetics and thermodynamics of the tungsten - oxygen system above 1000 C.

(43) Conducted by: The Ohio State University (R. Speiser)
For: Air Force; WADC, Aeronautical Research Lab.
Title: The Oxidation Characteristics of Tungsten Over Suitable Temperature and Oxygen Pressure Ranges

A fundamental investigation will be conducted on the oxidation behavior of tungsten in the temperature range of 500 to 1400 C and at oxygen pressures of atmospheric and below. Emphasis will be placed on determining the rate-controlling process within these environmental ranges in order to better define the operative mechanism.

(44) Conducted by: Lockheed Missiles and Space Division
Title: Low Pressure, High Temperature Oxidation of Tungsten

The oxidation behavior of tungsten was studied at 1300 to 3000 C under 1 to 40 mm air pressure. (Perkins, R. A., Crooks, D. D., Journal of Metals, 13 (7), July 1961, pp 490-493.)

(45) Conducted by: University of California, Berkeley, California
For: Atomic Energy Commission
Title: Kinetic Studies of the Reactions Occurring Between Tungsten and Gases at Low Pressures and High Temperatures

The reaction kinetics were established for the reactions of tungsten with oxygen, nitrogen and nitric oxide at temperatures ranging from 1950 to 2600 K and at gas pressures from 10^{-8} to 10^{-6} atmosphere.

B. Errosion and Corrosion in Nozzle Environments

(46) Conducted by: Stanford Research Institute, Menlo Park, California (A. S. Neiman, O. Preston, and D. A. Brown)
For: Navy; BuWeps, SPO
Title: Tungsten and Rocket Motors

This study was concerned with the interactions between tungsten and the exhaust constituents from solid-propellant rocket motors. These interactions may be conveniently considered under three main categories: chemical, mechanical, and thermal. In this investigation, emphasis has been placed on the chemical interactions.

(47) Conducted by: Atlantic Research Corporation
For: USAF; WADD
Title: Refractory Metal Rocket Nozzle Deterioration

Reaction mechanisms between metals (tantalum, tungsten, Ta-10W, and various tungsten-base alloys) and propellant combustion environments are being studied to aid development of improved nozzle materials. Propellant variables include fluorine, chlorine, and nitrogen contents and oxidation ratios.

Protective Coatings

(48) Conducted by: General Telephone and Electronics Labs., Inc. (C. D. Dickenson)
For: Air Force; WADD
Title: Research on the Protection of Tungsten

Conduct an investigation into the definition, relative importance, and present knowledge of those factors which will determine the efficacy of any potential materials system in protecting tungsten from high-temperature oxidation.

(49) Conducted by: New York University (C. G. Goetzel)
For: Air Force; WADD, Materials Central
Title: Development of Protective Coatings for Tungsten

This program is undertaken for the development of protective-coating systems for tungsten, in order to utilize it as a structural material at high temperatures under oxidizing conditions. The contractor will explore the feasibility of applying intermediate diffusion barrier layers developed under AF 33(616)-5735 implementing improved bonding techniques, as well as possibilities of developing additional barrier systems based upon introduction of refractory constituents into the complex intermediate layer such as molybdenum or other refractory metals.

(50) Conducted by: Thompson Ramo Wooldridge Inc.
For: Air Force; WADD
Title: Development of Oxidation Resistant High Temperature Protective Coatings for Tungsten

Investigations are continuing into the formative and protective nature of metal bonded-metal modified oxides as coatings for protection of tungsten in the 2500 to 3500 F range. Protection for 10 hours including five thermal cycles to room temperature without failure, at 3300 C has been achieved.

(51) Conducted by: Value Engineering Company, Arlington, Virginia (J. Huminik)
For: Army; WAL
Title: Investigation of Oxidation and Erosion Resistant Coatings on Molybdenum, Tantalum, and Tungsten

The objective of this contract is to develop a rocket nozzle coating for tungsten, tantalum or molybdenum capable of reducing catastrophic oxidation and erosion under high-gas-velocity conditions.

(52) Conducted by: Manufacturing Laboratories, Inc. (B. S. Lement)
For: Air Force; WADD, Materials Central
Title: Investigation of Interdiffusion Barriers for Structural Refractory Metals

The contractor will conduct research to further evaluate the efficacy of various metals, alloys, or intermetallics as barriers to interdiffusion of structural refractory metals- tungsten, tantalum, molybdenum, columbium - with the eventual objective of developing duplex coatings to provide protection from high-temperature oxidation for said refractory metals.

Properties

(53) Conducted by: Lewis Research Center, Cleveland, Ohio (J. R. Stephens)
For: NASA
Title: Effect of Surface Condition on Ductile-to-Brittle Transition Temperature of Tungsten

The effects of surface conditions on the ductile-to-brittle transition temperature of specimens of commercially pure sintered tungsten were evaluated by tensile tests carried out in vacuum. Prior to testing, the specimens were vacuum-annealed at 3500 F for 1 hour, electropolished, and then given the desired surface treatment.

(54) Conducted by: Lewis Research Center, Cleveland, Ohio (R. W. Hall)
For: NASA
Title: Effect of Strain Rate on Mechanical Properties of Wrought Sintered Tungsten at Temperatures above 2500 F

The effect of strain rate from 0.002 to 20 in. per in. per min on the tensile properties of recrystallized tungsten was investigated over the temperature range 2500 to 4000 F.

(55) Conducted by: Lewis Research Center, Cleveland, Ohio (P. F. Sikora)
For: NASA
Title: High-Temperature Tensile and Stress-Rupture Properties of Some Alloys in the Tungsten-Molybdenum System

This investigation was undertaken to determine the high-temperature tensile properties of powder-metallurgy tungsten-molybdenum alloys at temperatures up to 4400 F. For this purpose, sintered and swaged bars of alloys containing 10, 25, and 50 weight per cent molybdenum were procured from a commercial vendor and were tensile tested at temperatures from 2500 to 4400 F. The 50 weight per cent molybdenum in tungsten alloy was stress-rupture tested at 2500, 3000, and 3500 F.

(56) Conducted by: Hughes Tool Company (H. S. Porechanian)
For: Air Force; WADD, Materials Central
Title: Design Data Manual on Tungsten

Physical- and mechanical-design data were obtained on several heats of commercially pure tungsten at temperatures up to 5000 F. The data showed the effect of various fabrication methods on the design properties of tungsten. The complete processing and fabrication history of each of the lots of material were recorded so that lots with similar property values may be reproduced at a later date for weapon-system manufacturers.

(57) Conducted by: Aerojet-General Corporation, Azusa, California (L. L. Gilbert)
For: Navy; BuWeps
Title: Porous Tungsten: Melting Point, Spectral Emissivity, and Total Emissivity for Densities From 70% to 90%

The three thermophysical properties: melting point, total emissivity, and spectral emissivity at 0.65-μ wavelength were determined for tungsten densities between 70 to 90 per cent of theoretical.

(58) Conducted by: Stanford University, Stanford, California (O. D. Sherby)
For: Air Force; ARL
Title: Research on the Metallurgical Variables Effecting the High Temperature Modulus of Elasticity

Research will be conducted to determine the effects of preferred orientation, magnetic state, and temperatures on the high-temperature modulus of elasticity of metals and alloys. The relationship between the crystal structure and the modulus of elasticity is also being investigated.

(59) Conducted by: University of Cincinnati (M. Hoch)
For: Air Force; ASD, Materials Center
Title: Measurement of the Thermophysical Properties Using an Induction Heating Technique

Investigate the feasibility of utilizing an induction-heating technique for the measurement of the thermophysical properties of solid materials and determine the specific heat, thermal conductivity, and thermal expansion of selected materials in the temperature range 1000 to 3000 C.

(60) Conducted by: University of Notre Dame, Notre Dame, Indiana (D. R. Morgan and E. A. Coomes)
For: Navy; ONR
Title: A Comparison of Oxygen on Tungsten and Molybdenum by Field Electron Microscopy

(61) Conducted by: Pratt & Whitney Aircraft, Div. of United Aircraft Corp., East Hartford, Conn.
For: NASA
Title: Measurement of Spectral and Total Emittance of Materials and Surfaces Under Simulated Space Conditions

Objective: To provide basic information on the radiant characteristics of materials suitable for space power and propulsion systems under high-vacuum conditions. The radiant characteristics of materials that are being measured are total hemispherical emittance and spectral normal emittance.

(62) Conducted by: Lessells and Associates, Inc. (F. C. Bailey)
For: Air Force; WADD, Materials Central
Title: Ultra High Temperature Material Evaluation

The objective of this program is to obtain structural design data on ultrahigh-temperature materials at temperature to 6000 F. Data will include the tensile, creep, and low cycle fatigue properties of tungsten. The equipment and instrumentation to obtain these data are being developed as part of this program.

(63) Conducted by: Fansteel Metallurgical Corporation
For: Air Force; WADD, Materials Central
Title: Alloy Specimens for Internal Effort

Mechanical-property design data will be obtained on commercially pure tungsten and a columbium-base alloy at various high temperatures. The columbium-base alloy is designated as Fansteel 82 and it will be tested in tension and stress rupture in either vacuum or an argon environment to assess its potential usefulness in space vehichles or missiles. Tensile and creep properties of tungsten will be determined in argon and vacuum atmospheres.

(64) Conducted by: Watertown Arsenal Laboratories, Watertown, Massachusetts
For: Army
Title: Effect of Alloy Additions on Ductile-Brittle Transition Temperature of Tungsten

Objective: To determine the effect of alloy additions on the ductile-brittle transition temperature of tungsten. Certain materials in varying percentages may reduce the transition temperature significantly and relieve problems in fabrication while retaining of increasing material capability of withstanding extreme conditions of temperature and stress.

Physical Metallurgy

A. Alloy Development

(65) Conducted by: Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill.
For: Army; WAL
Title: Research on Development and Application of a Theory for the Plastic Deformation of Cemented Alloys

Conduct research aimed at establishment and application of a theory for plastic deformation of cemented alloys. Design, fashion and evaluate cemented tungsten-alloy systems for the development of a refractory metal possessing ductility consistent with ambient temperature formability.

(66) Conducted by: Battelle Memorial Institute, Columbus, Ohio (H. R. Ogden)
For: Navy; BuWeps
Title: Development of a Ductile Tungsten Sheet Alloy

The primary objective of this research was to develop tungsten-base sheet alloys having excellent fabricability and ductile-to-brittle transition temperatures below room temperature. Secondary objectives were the development of high recrystallization temperatures and high elevated-temperature strengths in those alloys.

(67) Conducted by: Climax Molybdenum Company of Michigan, Detroit, Michigan (M. M. Semchyshen)
For: Navy; BuAer
Title: Binary Alloys of Tungsten

Conduct a survey of arc-cast binary alloys of tungsten with aluminum, silicon, vanadium, chromium, iron, cobalt, nickel, zirconium, hafnium, and tantalum in the cast form. The alloy systems will be classified by solid solubility, the nature of the first excess phase developed in tungsten-rich composition, amenability to heat treatment and rate of oxidation.

(68) Conducted by: Climax Molybdenum Company of Michigan, Detroit Michigan
For: Navy; BuWeps
Title: Investigation for the Purpose of Developing Improved Tungsten-Base Alloys on a Laboratory Scale and for Determining their Metallurgical Characteristics and Properties

(69, 70) Conducted by: Crucible Steel Company of America, Pittsburgh, Pennsylvania (E. J. Dulis)
For: Air Force; WADD, Materials Central
Title: Research on Refractory Alloys of Tungsten, Tantalum, Molybdenum and Columbium

An objective of the current investigation is to ascertain whether those most promising alloys can be processed to sheet form, and to evaluate their properties in sheet form. In addition, modifications are to be made of the optimum base compositions to provide a further significant increase in strength at 3000 F and higher by addition of alloying elements to form dispersed stable carbides, nitrides, borides, etc.

(71) Conducted by: NASA Lewis Research Center
For: NASA
Title: Investigation of Arc-Melted Tungsten Alloys

The primary purpose of this research is to develop tungsten-base alloys with better strength than pure tungsten at temperatures above 3000 F. In addition, alloys with better fabricability, lower ductile-to-brittle transition temperature, and better oxidation resistance are desired. Binary alloys with tantalum, molybdenum, columbium, and titanium in amounts ranging from 0.1 to 15 atomic per cent are under investigation.

(72) Conducted by: NASA Lewis Research Center
For: NASA
Title: Investigation of Dispersion-Strengthened Alloys Prepared by Powder Metallurgy Techniques

A fundamental study of dispersion strengthening of nickel-base materials prepared by mechanical mixing of fine metal and oxide powders has been in progress for some time. This work is being extended to include an investigation of dispersion strengthening in tungsten as well as nickel, using the submicron-size metal powders (0.03 micron) which have recently become available.

B. Fundamental Studies

(73) Conducted by: Union Carbide Metals Company, Niagara Falls, New York (R. W. Fountain)
For: Air Force; WADC, Materials Lab.
Title: Investigation of the Properties of Tungsten and Its Alloys

Objectives: (1) determination of the mechanical properties of unalloyed tungsten at temperatures above 2500 F and (2) evaluation of the effects of fabrication, alloying, and other variables on the ductile-to-brittle transition temperature and on the elevated-temperature mechanical properties of tungsten. It has been found that a straight-line relationship exists between the reciprocal of the transition temperature and the log strain rate.

(74) Conducted by: Linde Company and Haynes Stellite Company, Divisions of Union Carbide Corporation
For: Navy; BuWeps
Title: Fabrication and Properties of Tungsten and Tungsten Alloy Single Crystals

The objective was to evaluate the fabricability and properties of tungsten and tungsten-alloy single crystals. This was accomplished with 65 crystals prepared with diameters ranging from 1/2 to 1 inch and lengths from 6 to 18 inches. Included in the program are several dilute alloys. The majority of crystals have been successfully swaged, forged or rolled at temperatures far below those required to fabricate polycrystalline tungsten.

(75) Conducted by: Westinghouse Electric Corporation, Lamp Division (R. H. Atkinson)
For: Air Force; WADD, Materials Central
Title: Physical Metallurgy of Tungsten and Tungsten-Base Alloys

To accomplish the development of high-strength tungsten-base alloys for use above 3000 F, the physical metallurgy of tungsten and tungsten alloys was studied. Alloy strengthening by dispersed second phases (carbides, oxides, borides) was also investigated.

Accomplishment of the program objective encompassed research in three areas: (1) physical metallurgy of high-purity tungsten; (2) tungsten-alloy single-crystal studies; and (3) fabrication studies of potential high-strength alloys.

(76) Conducted by: Battelle Memorial Institute, Columbus, Ohio (R. I. Jaffee)
For: Air Force; WADC, Materials Lab.
Title: Notch Sensitivity of Refractory Metals

A study was conducted to determine the effect of a notch on the tensile properties of four refractory metals and one alloy. One stress concentration factor was used and its effect was studied through a range of temperatures.

(77) Conducted by: Nuclear Metals, Inc., Concord, Massachusetts (E. J. Rapperport)
For: Air Force; WADD
Title: Determination of Refractory Metal Phase Diagrams

Nuclear Metals served as the prime contractor, with subcontracts at MIT and Westinghouse to establish constitution diagrams of the following systems:

W-Pd	Cb-Ir	Mo-Zr-Ti-C (min of two carbon levels up to 0.3 weight per cent C max)
Cb-Rh	Cb-Ru	
Mo-Ir	Mo-Zr-Ti	
W-Mo-Os	W-Re-Hf	Cb-Hf

(78) Conducted by: Nuclear Metals, Inc., Concord, Massachusetts, Subcontractor: Advanced Metals Res. (N. L. Peterson)
For: Air Force; WADD, Materials Central
Title: Determination of Diffusivities of Selected Elements in Refractory Metals Plus a Literature Survey of Diffusion

The contractor is conducting a survey of current and previous investigations of diffusion in refractory metals. Concurrently, an investigation of diffusion in refractory metals is being conducted. This is to consist of determining the diffusion coefficients and other related data for the tungsten-iridium, tungsten-ruthenium, tungsten-rhodium, tungsten-platinum, molybdenum-silicon, and columbium-chromium systems.

(79) Conducted by: Manufacturing Laboratories, Inc., Cambridge, Massachusetts (B. S. Lement and M. Cohen)
For: Air Force; ASD
Title: Substructures in Refractory Metals

The primary objectives of the program are as follows: (1) determination of the effect of substructures on ductile to brittle transition behavior, (2) determination of the role of substructures in fracture; (3) assessment of the contribution of substructures to the fibered condition and any subsequent alteration of properties due to fibering; (4) investigation of possible quantitative relationships between substructure parameters and yield behavior; and (5) appraisal of the effectiveness of substructures as an elevated-temperature-strengthening agent.

The contractor shall continue to conduct a comprehensive study of the nature of substructures, their relation to recovery and recrystallization and their effect on mechanical properties of the refractory metals tungsten, molybdenum, tantalum, and columbium.

LIST OF DMIC TECHNICAL REPORTS ISSUED
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DMIC Report Number	Title
46D	Department of Defense Titanium Sheet-Rolling Program – Uniform Testing Procedure for Sheet Materials, September 12, 1958 (PB 121649 $1.25)
46E	Department of Defense Titanium Sheet-Rolling Program – Thermal Stability of the Titanium Sheet-Rolling-Program Alloys, November 25, 1958 (PB 151061 $1.25)
46F	Department of Defense Titanium Sheet-Rolling Program Status Report No. 4, March 20, 1959 (PB 151065 $2.25)
46G	Department of Defense Titanium Sheet-Rolling Program – Time-Temperature-Transformation Diagrams of the Titanium Sheet-Rolling Program Alloys, October 19, 1959 (PB 151075 $2.25)
46H	Department of Defense Titanium Sheet-Rolling Program, Status Report No. 5, June 1, 1960 (PB 151087 $2.00)
46I	Statistical Analysis of Tensile Properties of Heat-Treated Ti-4Al-3Mo-1V Sheet, September 16, 1960 (PB 151095 $1.25)
46J	Statistical Analysis of Tensile Properties of Heat-Treated Ti-4Al-3Mo-1V and Ti-2.5Al-16V Sheet.
106	Beryllium for Structural Applications, August 15, 1958 (PB 121648 $3.00)
107	Tensile Properties of Titanium Alloys at Low Temperature, January 15, 1959 (PB 151062 $1.25)
108	Welding and Brazing of Molybdenum, March 1, 1959 (PB 151063 $1.25)
109	Coatings for Protecting Molybdenum From Oxidation at Elevated Temperature, March 6, 1959 (PB 151064 $1.25)
110	The All-Beta Titanium Alloy (Ti-13V-11Cr-3Al), April 17, 1959 (PB 151066 $3.00)
111	The Physical Metallurgy of Precipitation-Hardenable Stainless Steels, April 20, 1959 (PB 151067 $2.00)
112	Physical and Mechanical Properties of Nine Commercial Precipitation-Hardenable Stainless Steels, May 1, 1959 (PB 151068 $3.25)
113	Properties of Certain Cold-Rolled Austenitic Stainless Sheet Steels, May 15, 1959 (PB 151069 $1.75)
114	Ductile-Brittle Transition in the Refractory Metals, June 25, 1959 (PB 151070 $2.00)
115	The Fabrication of Tungsten, August 14, 1959 (PB 151071 $1.75)
116R	Design Information on 5Cr-Mo-V Alloy Steels (H-11 and 5Cr-Mo-V Aircraft Steel) for Aircraft and Missiles (Revised), September 30, 1960 (PB 151072-R $1.50)
117	Titanium Alloys for High-Temperature Use Strengthened by Fibers or Dispersed Particles, August 31, 1959 (PB 151073 $2.00)
118	Welding of High-Strength Steels for Aircraft and Missile Applications, October 12, 1959 (PB 151074 $2.25)
119	Heat Treatment of High-Strength Steels for Aircraft Applications, November 27, 1959 (PB 151076 $2.50)
120	A Review of Certain Ferrous Castings Applications in Aircraft and Missiles, December 18, 1959 (PB 151077 $1.50)
121	Methods for Conducting Short-Time Tensile, Creep, and Creep-Rupture Tests Under Conditions of Rapid Heating, December 20, 1959 (PB 151078 $1. [illegible])
122	The Welding of Titanium and Titanium Alloys, December 31, 1959 (PB 151079 $1.75)
123	Oxidation Behavior and Protective Coatings for Columbium and Columbium-Base Alloys, January 15, 1960 (PB 151080 $2.25)
124	Current Tests for Evaluating Fracture Toughness of Sheet Metals at High Strength Levels, January 28, 1960 (PB 151081 $2.00)
125	Physical and Mechanical Properties of Columbium and Columbium-Base Alloys, February 22, 1960 (PB 151082 $1.75)
126	Structural Damage in Thermally Cycled René 41 and Astroloy Sheet Materials, February 29, 1960 (PB 151083 $0.75)
127	Physical and Mechanical Properties of Tungsten and Tungsten-Base Alloys, March 15, 1960 (PB 151084 $1.75)
128	A Summary of Comparative Properties of Air-Melted and Vacuum-Melted Steels and Superalloys, March 28, 1960 (PB 151085 $2.75)
129	Physical Properties of Some Nickel-Base Alloys, May 20, 1960 (PB 151086 $2.75)
130	Selected Short-Time Tensile and Creep Data Obtained Under Conditions of Rapid Heating, June 17, 1960 (PB 151088 $2.25)
131	New Developments in the Welding of Metals, June 24, 1960 (PB 151089 $1.25)
132	Design Information on Nickel-Base Alloys for Aircraft and Missiles, July 20, 1960 (PB [illegible])
133	Tantalum and Tantalum Alloys, July 25, 1960 (PB [illegible])
134	Strain Aging of Refractory Metals, August 12, 1960 (PB [illegible] $1.75)
135	Design Information on PH 15-7 Mo Stainless Steel for Aircraft and Missiles, August [illegible], 1960 (PB [illegible])

DMIC REPORTS

DMIC Report Number	Title
136A	The Effects of Alloying Elements in Titanium, Volume A. Constitution, September 15, 1960 (PB 151094 $3.50)
136B	The Effects of Alloying Elements in Titanium, Volume B. Physical and Chemical Properties, Deformation and Transformation Characteristics, May 29, 1961 (AD 260226 $3.00)
137	Design Information on 17-7 PH Stainless Steels for Aircraft and Missiles, September 23, 1960 (PB 151096 $2.00)
138	Availability and Mechanical Properties of High-Strength Steel Extrusions, October 26, 1960 (PB 151097 $1.75)
139	Melting and Casting of the Refractory Metals Molybdenum, Columbium, Tantalum, and Tungsten, November 18, 1960 (PB 151098 $1.00)
140	Physical and Mechanical Properties of Commercial Molybdenum-Base Alloys, November 30, 1960 (PB 151099 $3.00)
141	Titanium-Alloy Forgings, December 19, 1960 (PB 151100 $2.25)
142	Environmental Factors Influencing Metals Applications in Space Vehicles, December 27, 1960 (PB 151101 $1.25)
143	High-Strength-Steel Forgings, January 5, 1961 (PB 151102 $1.75)
144	Stress-Corrosion Cracking – A Nontechnical Introduction to the Problem, January 6, 1961 (PB 151103 $0.75)
145	Design Information on Titanium Alloys for Aircraft and Missiles, January 10, 1961 (PB 151104 $2.25)
146	Manual for Beryllium Prospectors, January 18, 1961 (PB 151105 $1.00)
147	The Factors Influencing the Fracture Characteristics of High-Strength Steel, February 6, 1961 (PB 151106 $1.25)
148	Review of Current Data on the Tensile Properties of Metals at Very Low Temperatures, February 14, 1961 (PB 151107 $2.00)
149	Brazing for High Temperature Service, February 21, 1961 (PB 151108 $1.00)
150	A Review of Bending Methods for Stainless Steel Tubing, March 2, 1961 (PB 151109 $1.50)
151	Environmental and Metallurgical Factors of Stress-Corrosion Cracking in High-Strength Steels, April 14, 1961 (PB 151110 $0.75)
152	Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum, and Tungsten, April 28, 1961 (AD 257739 $3.50)
153	Physical Metallurgy of Nickel-Base Superalloys, May 5, 1961 (AD 258041 $1 [illegible]
154	Evolution of Ultrahigh-Strength, Hardenable Steels for Solid-Propellant Rocke[illegible] Cases, May 25, 1961 (AD 257976 $1.25)
155	Oxidation of Tungsten, July 17, 1961 (AD 263598 $3.00)
156	Design Information on AM-350 Stainless Steel for Aircraft and Missiles, July 28, 1961 (AD 262407 $[illegible])
157	A Summary of the Theory of Fracture in Metals, August 7, 1961 (PB 181081 $1.75)
158	Stress-Corrosion Cracking of High-Strength Stainless Steels in Atmospheric Environments, September 15, 1961 (AD 266005 $1.25)
159	Gas-Pressure Bonding, September 25, 1961 (AD 265133 $1.25)
160	Introduction to Metals for Elevated-Temperature Use, October 27, 1961 (AD [illegible] $2.50)
161	Status Report No. 1 on Department of Defense Refractory Metals Sheet-Rolling Program, November 2, 1961 (AD 267077 $1.00)
162	Coatings for the Protection of Refractory Metals From Oxidation, November 24, 1961 (AD 271384 $3.50)
163	Control of Dimensions in High-Strength Heat-Treated Steel Parts, November 29, 1961 (AD 270045 $1.00)
164	Semiaustenitic Precipitation-Hardenable Stainless Steels, December 6, 1961 (AD 274805 $2.75)
165	Methods of Evaluating Welded Joints, December 28, 1961 (AD 272088 $2.25)
166	The Effect of Nuclear Radiation on Structural Metals, September 15, 1961 (AD 265839 $2.50)
167	Summary of the Fifth Meeting of the Refractory Composites Working Group, March 12, 1962 (AD 274804 $2.00)
168	Beryllium for Structural Applications, 1958-1960, May 18, 1962 (AD 278723 $3.50)
169	The Effect of Molten Alkali Metals on Containment Metals and Alloys at High Temperatures, May 18, 1962 (AD 282932 $1.50)
170	Chemical Vapor Deposition, June 4, 1962 (AD 281887 $2.25)
171	The Physical Metallurgy of Cobalt-Base Superalloys, July 6, 1962 (AD 283356 $2.25)
172	Background for the Development of Materials To Be Used in High-Strength-Steel Structural Weldments, July 31, 1962 (AD 284265 $3.00)
173	New Developments in Welded Fabrication of Large Solid-Fuel Rocket-Motor Cases, August 6, 1962 (AD 284829 $1.00)
174	Electron-Beam Processes, September 15, 1962 (AD 287431 $1.75)
175	Summary of the Sixth Meeting of the Refractory Composites Working Group, September 24, 1962 (AD 287629 $1.75)
176	Status Report No. 2 on Department of Defense Refractory Metals Sheet-Rolling Program, October 15, 1962 (AD 288127 $1.25)
177	Thermal Radiative Properties of Selected Materials, November 15, 1962, Vol. I (AD 294345 $3 [illegible])
177	Thermal Radiative Properties of Selected Materials, November 15, 1962, Vol. II (AD 294346 $4 [illegible])
178	Steels for Large Solid-Propellant Rocket-Motor Cases, November [illegible], 1962
179	A Guide to the Literature on High-Velocity Metalworking, December 3, 1962
180	Design Considerations in Selecting Materials for Large Solid-Propellant Rocket-Motor Cases, [illegible] 1962
181	Joining of Nickel-Base Alloys, December [illegible], 1962
182	Structural Considerations in Developing Refractory Metal Alloys, January 31, 1963
183	Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum, and Tungsten [illegible] DMIC Report 152, February 7, 1963
184	Summary of the Seventh Meeting of the Refractory [illegible], May [illegible], 1963
185	The Status and Properties of Titanium Alloys [illegible], June 14, 1963
186	The Effect of Fabrication [illegible] [illegible], July 12, 1963
187	The Application of [illegible] Metals, August [illegible]

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DMIC Report Number	Title
188	The Engineering Properties of Columbium and Columbium Alloys, September 6, 1963
189	The Engineering Properties of Tantalum and Tantalum Alloys, September 13, 1963
190	The Engineering Properties of Molybdenum and Molybdenum Alloys, September 20, 1963
191	The Engineering Properties of Tungsten and Tungsten Alloys, September 27, 1963
192	Hot-Cold Working of Steel to Improve Strength, October 11, 1963

Battelle Memorial Institute, Defense Metals Information Center, Columbus, Ohio, TUNGSTEN RESEARCH AND DEVELOPMENT REVIEW, 1960-1962, by J. L. Ratliff, W. A. Gibeaut, and H. R. Ogden. October 23, 1963 [48] pp incl. illus., tables, refs.
(DMIC Report 193)
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2. Tungsten-Physical Metallurgy
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