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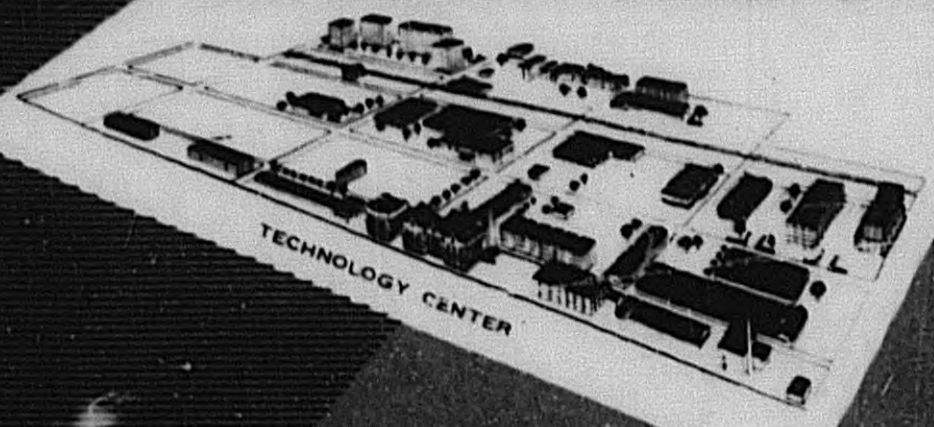

DEVELOPMENT AND EVALUATION OF HIGH-TEMPERATURE TUNGSTEN ALLOYS

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Quarterly Report No. 1
Contract AT(33-3)-4
Task I

AEC RESEARCH AND DEVELOPMENT REPORT

ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
Chicago 16, Illinois

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October 1, 1959 - December 31, 1959

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January 20, 1960

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ABSTRACT

High-tungsten alloys were prepared by powder metallurgy techniques. Room-temperature strength properties were determined for W-Ni-Fe compositions with quaternary additions of Cr, Pd, and Ru; tungsten levels ranged from 80 to 94 wt%. Small (1-3 wt%) ruthenium additions were the most effective in improving strength. The oxidation resistance of a number of tungsten-base alloys was measured at 2000F. Quaternary W-Ni-Fe base alloys containing Al, Ru, Ti, and Zr were the most oxidation resistant, having values similar to unalloyed tungsten. Oxidation protection of a 90W-6Ni-4Fe material was accomplished by a fused coating of AMS 4775; the composite was tested for 482 hours in air at 2000F without damage to the base alloy.

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DEVELOPMENT AND EVALUATION OF HIGH-TEMPERATURE TUNGSTEN ALLOYS

I. INTRODUCTION

This progress report covers the period October 1, 1959, to December 31, 1959, summarizing work performed on ARF Project 2158, "Development andEvaluation of High-Temperature Tungsten Alloys" (title unclassified).

Major efforts under this program have been concerned with the development of high-tungsten alloys for use at temperatures up to 2000F. Fabricability and elevated-temperature strength and stability are of primary importance; consideration has also been given to oxidation protection. Powder metallurgy techniques have been used in the preparation of materials under investigation.

A number of tungsten-base alloy systems have been studied during earlier phases of this program. The most promising compositions from the standpoint of workability and elevated-temperature stability are based on the W-Ni-Fe system. Small quaternary additions of ruthenium to the W-Ni-Fe base produced large increases in strength without undue loss of ductility. These materials were prepared by cold-pressing the blended metal powders, followed by liquid-phase sintering in a hydrogen atmosphere. Experimental work during this reporting interval included a study of various material processing techniques, in order to determine the feasibility of producing large sections of complex shape. Alloy development work was continued, with some compositions containing less than 90 wt% tungsten. The oxidation resistance of a number of alloys was investigated, and testing of protective coatings was conducted at 1600 and 2000F for times in excess of 500 hours.

II. DISCUSSION OF RESULTS

A. Alloy Development

Experimental efforts under the alloy development phase of this program were directed into two separate categories. The first consisted of determining the properties of a series of W-Ni-Fe-Ru alloys; the purpose of these studies was to optimize compositions in this promising system. New alloys were also prepared in an effort to develop improved oxidation resistance and to investigate the effects of various quaternary additions to the W-Ni-Fe base.

Previous work has shown that 90 wt% W-Ni-Fe-Ru alloys possess considerably greater elevated-temperature strength than other ternary or quaternary tungsten-base compositions studied under this program. During the current reporting interval, several new W-Ni-Fe-Ru compositions were studied wherein the tungsten content ranged from 85 to 94 wt%; ruthenium levels were 1 to 3 wt%. The room-temperature properties of these materials were not markedly affected by the tungsten contents, as shown in Table I. Strength levels were similar for the 85W-7.5Ni-5Fe-2.5Ru* and the 94W-3Ni-2Fe-1Ru alloys. Both compositions had transverse-rupture strength values in excess of 300,000 psi; these results were similar to those reported for 90W-Ni-Fe-Ru alloys studied previously. Microstructures of the materials containing ruthenium were characterized by an exceptionally fine grain size. Some porosity was encountered in hydrogen-sintered compacts containing more than 2 wt% ruthenium. Vacuum sintering produced significant property improvements in these alloys by reducing the porosity. The effect of vacuum sintering on elevated-temperature properties of W-Ni-Fe-Ru alloys is under study. In addition, the thermal stability of these materials is being investigated by annealing treatments of at least 200 hours at temperatures in the range of 1400 to 1700F. Such annealing treatments have resulted in the appearance of an intermediate phase in the matrix of W-Ni-Fe alloys. The effects of ruthenium and other quaternary additions on this precipitated phase are being thoroughly investigated.

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* Compositions are reported in weight per cent.

Alloy development efforts have also included a study of the effects of additions of chromium and palladium to the W-Ni-Fe base. Previously reported data for W-Ni-Fe-Cr alloys were for compositions containing at least 90 wt% tungsten; these materials were characterized by high strength and low ductility at room temperature. More recent investigations included alloys at lower tungsten levels; the higher matrix volumes are expected to promote ductility and oxidation resistance. On the basis of room-temperature tests, no significant property improvements were noted in W-Ni-Fe-Cr alloys at reduced tungsten levels; data are presented in Table I. The oxidation resistance of these compositions is discussed under a subsequent section of this report.

Studies of tungsten-base alloys containing palladium have included the binary W-Pd; a ternary W-Ni-Pd, and a quaternary W-Ni-Fe-Pd material. Initial investigations of the binary W-Pd alloy showed that, although strength levels were not adequate, a desirable low solubility of palladium in tungsten was indicated. Preliminary test results of a 90W-7Ni-3Pd alloy showed strength and ductility values considerably below those of W-Ni-Fe materials. Microstructures consisted of rounded tungsten-rich grains in a single phase matrix; hardness values were similar to those of W-Ni-Fe alloys. Quaternary 90W-Ni-Fe-Pd alloys containing 2 wt% palladium had slightly lower room temperature strength and ductility than the W-Ni-Fe base; elevated-temperature properties have not been evaluated.

Alloy development efforts will be continued in an effort to improve currently available materials. Vacuum sintering and other techniques discussed in subsequent sections of this report will be utilized when necessary.

B. Oxidation Resistance

Previous data concerning the oxidation resistance of tungsten-base alloys developed under this program have been reported in weight gain/cm^2/hr. The testing procedure during the current reporting interval has been modified to the extent that results are expressed in displacement of the metal surface per unit time. Test specimens are first heated in air for 15- or 30- minute intervals; the oxide films are then carefully removed from each side of the sample by abrasive papers until a clean metal surface is exposed. Test

TABLE I

ROOM TEMPERATURE PROPERTIES OF TUNGSTEN-BASE ALLOYS

Composition(wt%)	Transverse Rupture Strength(psi)	Deflection (in.)[a]	Hardness VPN(10kg)
94W-3Ni-2Fe-1Ru	303,000	0.185	363
86W-7Ni-4Fe-3Ru	b	0.125	400
85W-7.5Ni-5Fe-2.5Ru	314,000	0.250	394
90W-7Ni-3Pd	78,000	0.02	309
90W-4.8Ni-3.2Fe-2Pd	270,000	0.275	290
80W-10Ni-10Cr	185,000	0.045	
86W-7Ni-7Cr	290,000	0.110	440
82W-8Ni-2Fe-8Cr	246,000	0.075	
84W-6Ni-4Fe-6Cr	214,000	0.090	

a. Span length 1.25 in.
b. Porous sample.

results using this method are readily duplicated, and are of more practical value than the weight-gain data.

Table II presents oxidation test data for a wide range of tungsten-base alloys at 2000F; the results for unalloyed tungsten are included for comparison. The oxidation resistance of most compositions is inferior to that of tungsten. The reason for this is not clearly understood, as the matrix phase in W-Ni-Fe alloys represented by the 18W-49Ni-33Fe sample shown in Table II has comparatively high oxidation resistance. One of several possibilities is that tungsten oxides in combination with oxides of nickel and iron form low-melting eutectics, resulting in accelerated oxidation. Table II shows that small additions of Al, Ti, Ru and Zr to the W-Ni-Fe base result in improved oxidation resistance; the alloy containing zirconium was slightly superior to unalloyed tungsten. Microstructures of these alloys were generally finer grained than the ternary W-Ni-Fe materials. However, tungsten solubility in the matrix may be a major factor in determining the resistance to oxidation of the composite. In the case of W-Ni-Cr alloys, a nickel-chromium-rich matrix may be expected to offer improved oxidation resistance. Data from Table II show that the 86W-7Ni-7Cr composition is only slightly superior to the 90W-6Ni-4Fe material. The high hardness values found in the matrix phases of W-Ni-Cr alloys are associated with solution of an appreciable quantity of tungsten, thereby reducing the effectiveness of the nickel-chromium-base envelope. Further oxidation tests will be conducted to determine the factors which contribute to the oxidation resistance of these tungsten-base alloys.

C. Oxidation Protection

Results of oxidation tests on the tungsten-base alloys described in the preceding section dictate the need for protective coatings for elevated-temperature operation in air. Experimental work during the current reporting interval indicates that a fused nickel-chromium base alloy coating affords good protection to the 90W-6Ni-4Fe material for 500 hours in static air to at least 2000F. The coating, AMS 4775, was applied as a suspension of alloy powder in a collodion-acetone solution. Although spray-coating techniques were found to give a more uniform covering, the specimens currently under test were coated by brushing. After drying, the coatings were fused in a dry

TABLE II

OXIDATION TEST DATA FOR TUNGSTEN-BASE ALLOYS AT 2000F FOR 15 MINUTES

Composition (wt%)	Thickness Change (in.)[a]
90W-6Ni-4Fe	0.017
90W-6Ni-4Co	0.016
90W-7Ni-3Pd	0.012
86W-7Ni-7Cr	0.011
85W-7.5Ni-5Fe-2.5Ru	0.008
90W-5.85Ni-3.9Fe-0.25Al	0.0075
90W-4.5Ni-3Fe-2.5Ti	0.006
99W-0.5Ni-0.5Fe	0.006
Unalloyed W	0.005
90W-4.5Ni-3Fe-2.5Zr	0.004
18W-49Ni-33Fe[b]	0.001

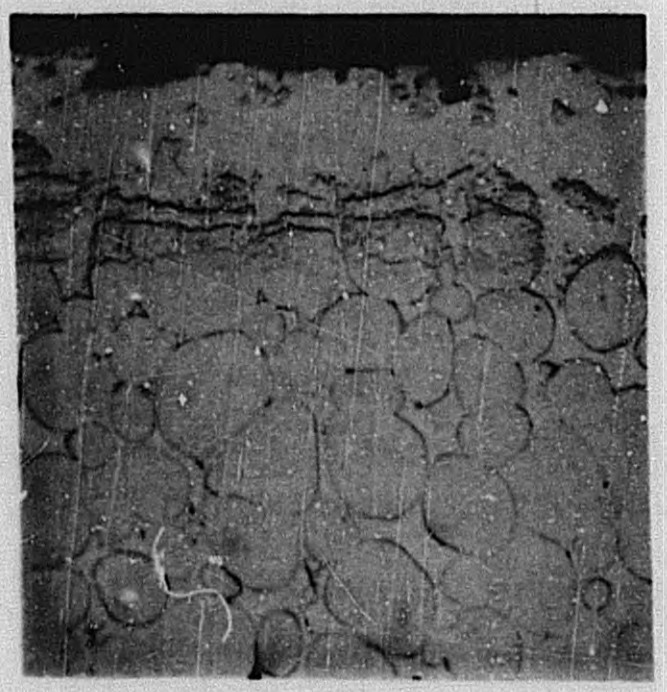
a. Both sides of sample oxidized.
b. Arc-melted ingot representing matrix phase composition in W-Ni-Fe alloys.

hydrogen atmosphere for about 10 minutes at 2200F. Oxidation tests were conducted in still air at 1600 and 2000F, and the specimens were weighed frequently. The AMS 4775 coating gave exceptionally good protection at 1600F; after 616 hours, the total weight gain was only 0.42 mg/cm^2. Figure 1 is a photomicrograph of the coating and base metal after the test. The coating in this area is about 0.003 in. thick, and a diffusion zone of about 0.002 in. exists between the coating and the 90W-6Ni-4Fe base. Most of the diffusion occurred during the 2200F fusing operation rather than during the 1600F oxidation test. The 90W-6Ni-4Fe material was considerably altered by the lengthy heat treatment at 1600F; at this temperature, a precipitate is formed in the matrix, as illustrated in Figure 2. The particles are finely dispersed, and hardness measurements in the matrix areas show no increase due to the precipitate. Previous work has shown this precipitate to be formed upon annealing W-Ni-Fe materials at temperatures in the range of 1400 to 1700F; the fine particles may be a nickel-tungsten intermediate phase, or tungsten which has precipitated due to changes in solubility. Room-temperature tests of this material show a slight increase in tensile strength without loss of ductility. Heating to temperatures in the range of 2000F will dissolve the precipitate.

Oxidation testing of the AMS 4775 coatings was also conducted at 2000F. Figure 3 shows the microstructure of a coated specimen after 482 hours at 2000F. The AMS 4775 layer is about 0.005 in. thick, and a thin diffusion zone may be observed; the 90W-6Ni-4Fe base metal is relatively unaffected. Weight gains were somewhat higher at this temperature than were measured at 1600F. Figure 4 illustrates the weight gain as a function of time. It may be noted that a major portion of the weight gain occurred during the first twenty-five hours of the test; the oxidation rate during the latter portion of the test was comparatively slow. The average weight gain was 0.02 mg/cm^2/hr, and the test was concluded prior to indications of failure. Coated specimens are nowbeing tested at 2100F, and initial results show weight gain values similar to those presented in Figure 4.

D. Processing Techniques

Property data presented in the preceding sections were obtained from specimens prepared by cold pressing followed by hydrogen sintering.



Neg. No. 19373 X 250

Fig. 1

AMS 4775 coating on 90W-6Ni-4Fe alloy after 616 hr in air at 1600F. The tungsten grains are disturbed for a depth of about 0.002 in. Etched and repolished.

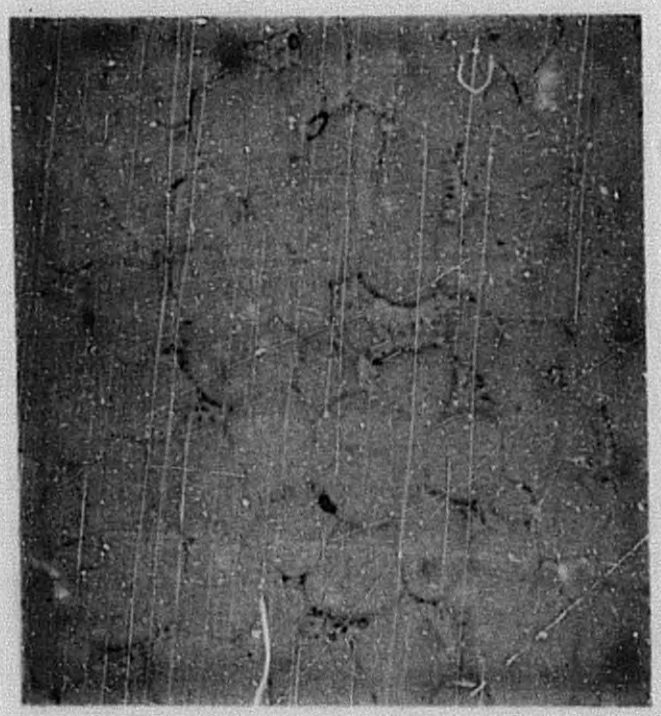


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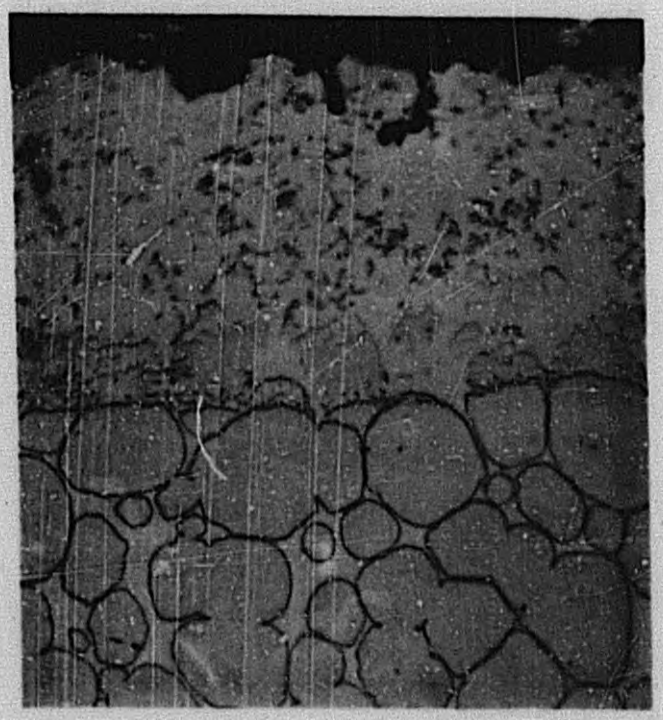
Fig. 2

Fine precipitate in matrix of a 90W-6Ni-4Fe alloy after 616 hr at 1600F. Etchant: HNO_3 + HF + glycerine.



Neg. No. 19374 X 250

Fig. 3

AMS 4775 coating on 90W-6Ni-4Fe alloy after 482 hr in air at 2000F. Very little diffusion has occurred between the tungsten grains and the adjacent coating. Unetched.

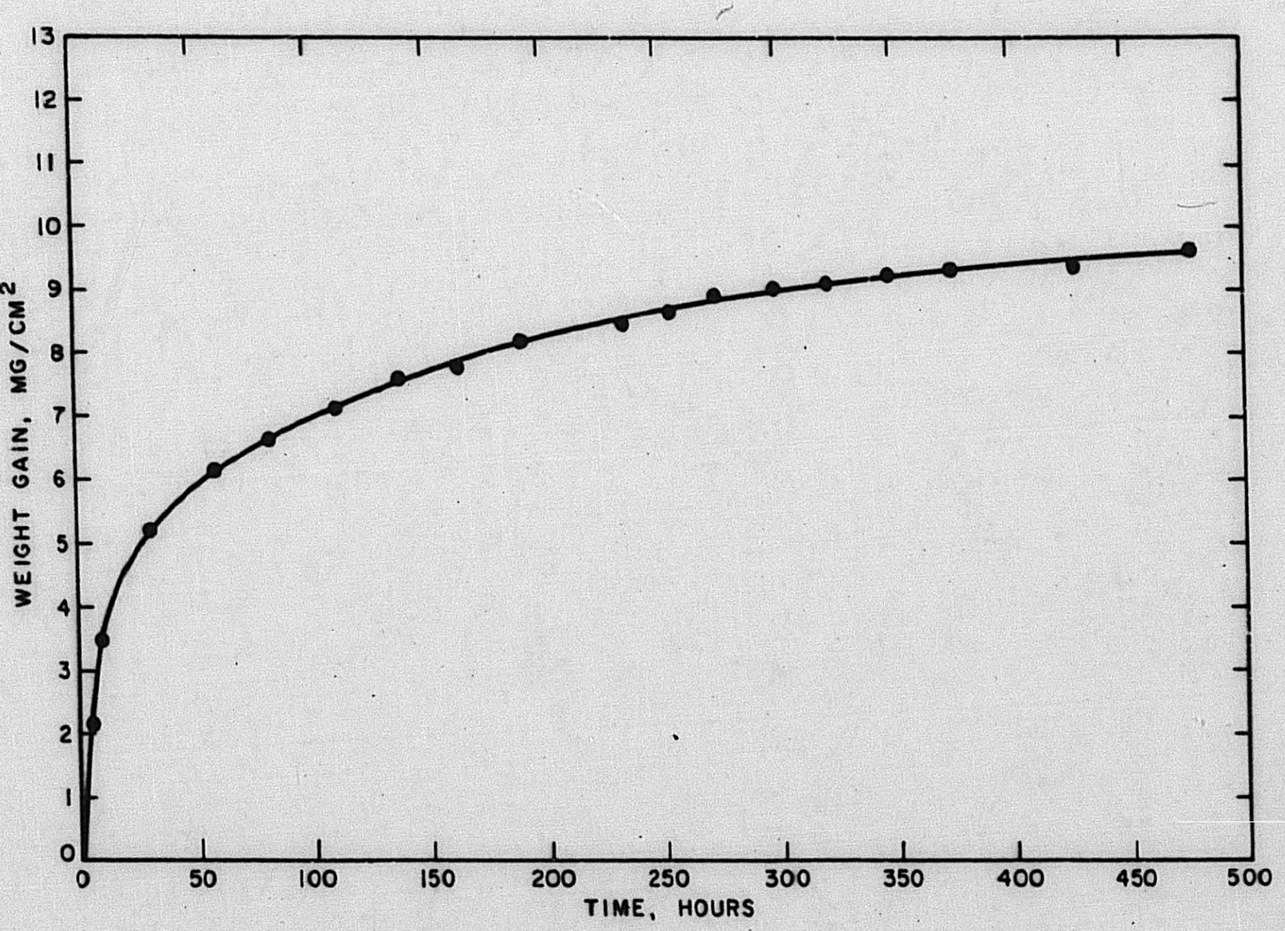


FIG. 4 - 2000F OXIDATION TEST RESULTS FOR A 90W-6Ni-4Fe ALLOY COATED WITH AMS 4775.

Other processing techniques were utilized in the fabrication of tungsten-base alloys under study.

Vacuum sintering was found to give improved room-temperature properties in W-Ni-Fe base alloys containing quaternary additions of Ru, Ti and Zr. In the case of ruthenium, the porosity usually associated with hydrogen sintering was eliminated, and clean microstructures were produced. Attempts to sinter W-Ni-Fe-(Ti, Zr) alloys in hydrogen were unsuccessful because of traces of oxygen in the furnace atmosphere. Vacuum-sintering improved the microstructures of these materials although some oxides were present. Initial results on W-Ni-Fe-Ru alloys sintered under an inert atmosphere were inferior to those for vacuum-sintered material. Vacuum sintering will be used to prepare W-Ni-Fe-(Nb, Ta) alloys which exhibited large quantities of unreduced oxides after hydrogen sintering.

Slip casting of W-Ni-Fe powders in plaster molds was initially devoted to a 95W-3Ni-2Fe composition. More recent efforts have included ternary materials at the 90, 97, and 98 wt% tungsten levels. Satisfactory room-temperature properties were obtained from slip-cast, sintered 90W-6Ni-4Fe specimens. Test results for a 98W-1.2Ni-0.8Fe alloy showed a slightly lower strength than for the cold pressed and hydrogen-sintered material. Efforts will be devoted to establishing the minimum matrix level required for complete densification of slip-cast materials. This process has yielded very satisfactory results at the 95 wt% tungsten level, and specimens having a 1-inch wall thickness have been sintered to full density.

Induction heating, using atmospheres of $90N_2 - 10H_2$ or $90A - 10H_2$, has been under investigation for the sintering of large W-Ni-Fe compacts. Some difficulties have been experienced in determining optimum heating rates so that shrinkage can proceed uniformly. Specimens are brought to the sintering temperature (2680 - 2800F) in less than one hour; this rate is much more rapid than that used in hydrogen sintering in a molybdenum-wound tube furnace. Further efforts will be conducted using induction heating, as this flexible technique is adaptable to the fabrication of large parts.

III. SUMMARY

Tungsten-base alloys have been prepared using powder metallurgy techniques. Quaternary W-Ni-Fe-Ru compositions were studied at tungsten levels ranging from 85 to 94 wt%. Room-temperature transverse-rupture strength values were above 300,000 psi, and ductility was reduced by increasing ruthenium contents. Ternary W-Ni-Cr and quaternary W-Ni-Fe-Cr alloys were prepared at tungsten levels as low as 80 wt%; these materials contained 6 to 10 wt% chromium and exhibited low ductility. Low strength and ductility were found in a 90W-7Ni-3Pd composition, although a 90W-4.8Ni-3.2Fe-2Pd material had good strength and moderate ductility.

The oxidation resistance of a number of tungsten-base alloys was reported. Specimens were heated in air at 2000F, and the oxide films were removed to determine the displacement of the metal surface. Highest oxidation resistance was found in quaternary W-Ni-Fe alloys containing Al, Ti, Ru, and Zr; these materials, and a 99W-0.5Ni-0.5Fe alloy, had metal losses similar to that of unalloyed tungsten. The 90W-6Ni-4Fe material oxidized over three times more rapidly than pure tungsten; the reason for this rapid rate is not understood in view of the relatively good oxidation resistance of the matrix phase.

Fused coatings of a nickel-chromium-base alloy, AMS 4775, were effective in protecting the 90W-6Ni-4Fe material from oxidation for about 500 hours at 2000F. The weight gain averaged 0.02 mg/cm^2/hr, and a major portion of the gain occurred during the first 25 hours of testing. Microstructural evidence shows that only a very thin layer of the base metal was affected. Tests of the AMS 4775 coating at 1600F showed a weight gain of about 0.4 mg/cm^2 in 616 hours. Preliminary tests at 2100F show weight gains similar to those reported for the 2000F test temperature.

Processing techniques under study included vacuum sintering, slip casting, and induction heating of tungsten-base alloys. Vacuum sintering was found to improve microstructures of W-Ni-Fe-(Ru, Ti, Zr) quaternary alloys. Slip casting of W-Ni-Fe alloys in plaster molds included

materials at 98 wt% tungsten level; good sintered density and moderate room-temperature strength was obtained. Induction heating of compacted W-Ni-Fe alloys, using atmospheres of $90N_2$-$10H_2$ or 90A-$10H_2$, was continued. Complete densification was not obtained in all cases; irregular shrinkage may be due to the extremely rapid heating rate.

IV. FUTURE WORK

Alloy development efforts will be continued with additional emphasis on vacuum - or inert-atmosphere sintering. Further consideration will be given to the effects of a precipitated intermediate phase resulting from annealing in the range of 1400 to 1700F in W-Ni-Fe base alloys. Oxidation tests of these tungsten-base alloys will be continued in order to determine the factors which contribute to oxidation resistance. Although initial work on protective coatings shows promise, some improvement may be made in the base alloy to prevent catastrophic oxidation in case of a coating failure. The AMS 4775 coating will be tested at 2100F and possibly at a higher temperature to determine the upper limit of use in air. Various material processing techniques will be investigated with the objective of producing larger and more complex shapes.

V. LOGBOOKS AND CONTRIBUTING PERSONNEL

Date for this report are recorded in ARF Logbooks C-8488, -8489, -8490, -8491, -8492, -8553, -8554, -8885, -8886, and -9113.

The following personnel have been the principal contributors to the planning and execution of this work:

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J. R. Dvorak	-	Metallography
A. L. Hess	-	Project Technician
F. C. Holtz	-	Project Leader
J. J. Connelly, Jr. LCDR	-	AEC Project Leader
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Respectfully submitted,

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