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REVIEW OF RECENT DEVELOPMENTS IN THE TECHNOLOGY OF TUNGSTEN

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This memorandum briefly reviews a number of current developments of general interest in the technology of tungsten. Most of this information was received by DMIC during the period August through October, 1961.

Consolidation and Fabrication

Tungsten and tungsten-base alloys continue to occupy an important place in space-materials engineering. As an example, the development program on large ion-propulsion engines will require experimental work[1]** to produce porous tungsten ionizers having adequate size, uniformity of porosity, channel diameter, and service life.

A program is under way to develop a new procedure for making tungsten sheet. Early experimental work has included blending tungsten powder with small amounts of nickel and iron powders (2.8 and 1.2 per cent, respectively), cold compacting the mixture into slabs, and then liquid-phase sintering in a hydrogen atmosphere at 1530 C.[2] The sintered slabs have been cross rolled at 750 F to about 40 per cent reduction, and electron-beam zone refined to remove the nickel and iron. At a temperature of 1900 C, a vacuum of 10^{-5} mm Hg, and a zone travel of about 2 inches/hr, the nickel content is reduced to about 0.1 per cent. Preliminary data indicate that the ultimate tensile strength is about the same as that of tungsten sheet consolidated by more conventional procedures.

A program at Wah Chang Corporation[3] is aimed at the pilot production of an extruded tungsten structural shape intended for operation above 3000 F. The target extrusion is a tee having a maximum section diameter of 2 inches, a flange and stem thickness of 0.250 inch ± 0.010 inch, and a minimum length of 10 feet. Arc-melted tungsten or tungsten - 2 per cent molybdenum alloy is the intended starting material.

The effect of annealing temperatures on both doped and undoped tungsten foils has been the subject of recent Dutch research.[4] The as-rolled texture is described as centered about the (001) [110] position with a spread of ± 30 degrees about the rolling direction as an axis. The doped foil showed a small increase in recrystallization temperature over the undoped counterpart. However, a marked difference in the recrystallized structure was observed. The secondary recrystallization texture was found to be (001) [320] and (001) [230] for both the doped and undoped foils with about 97 per cent deformation.

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**References are listed at the end of this memorandum.

A part of the current fiber metallurgy work at Armour Research Foundation is concerned with the development of tungsten felts made from matted tungsten wire.[2] Wire 0.006 inch in diameter is chopped into short lengths, kinked, and pressed into mats. The mats are then infiltrated with copper-nickel alloys of various compositions, in an effort to form a tungsten to tungsten bond at the fiber contacts. The ultimate objective of the work is to develop copper-cooled tungsten-fiber rocket-nozzle materials. Maximum strengths have been obtained through the use of copper-rich nickel alloys. The fiber strengthening mechanism in all cases is presumed to result from a Ni-W or a Ni-W-Cu bond between the tungsten fibers.

Continued melting and extrusion studies at the Climax Molybdenum Company have included a nearly pure tungsten alloy (W-0.02 per cent Zr-0.01 per cent C), and a 50 per cent tungsten alloy (balance largely molybdenum and about 2 per cent total of columbium, titanium, zirconium, and carbon as strengthening elements).[5] Cracking of the arc-cast ingots of the 50/50 alloy was a persistent problem. However, some ingots of this type, as well as of the high-tungsten alloy, were extrudable and were subsequently rolled. The W-0.02 per cent Zr-0.01 per cent C alloy was extruded at temperatures between 3200 and 3400 F at ratios of 4:1 and 5:1. On the basis of earlier work, the 0.02 per cent zirconium addition is reported to raise the recrystallization temperature of tungsten about 700 F.

In a project on the "Fabrication and Properties of Tungsten and Tungsten Alloy Single Crystals", it has been possible to swage, forge, and roll at temperatures of about 500 to 700 C lower than those customarily used for polycrystalline tungsten.[6] Both tungsten and tungsten-alloy crystals (with individual additions of Cb, Zr, Ti, Hf, Ir, Ta, TaC, ThO_2, and K_2SiO_3 plus Al_2O_3) were grown by an arc modification of the Verneuil process. The higher purity single crystals had ductile-brittle transition temperatures below room temperature when surfaces were properly prepared. Recrystallization temperature for a number of cold-worked single crystals were determined. These varied between about 1500 C and 2000 C according to composition and history of individual specimens.

Single crystals of ultrapure tungsten are commercially available from Westinghouse Electric Corporation's Bloomfield, New Jersey, facility.[7] Single-crystal rods 10 inches long and 0.2 inch in diameter with purities as high as 99.9975 per cent have been made by electron-beam zone melting.

General Electric is advertising tungsten sheet 2 feet in width. Thicknesses down to 0.150 inch are expected to be available by the end of 1961, and thicknesses down to 0.010 inch early in 1962.

According to a note in The Iron Age[8], quartz lamps are being used to provide heat up to 1000 F as an aid in processing tungsten sheet at Republic Aviation.

Work is in progress on the development of an asymmetric roll-formed tungsten nozzle liner for the Polaris A-3 first stage.[9] The process involves forming truncated cones with included angles of 60 and 30 degrees by hot rolling tungsten plates. These cones will be hot spun to the asymmetrical shape.

Experimental fabrication of wide tungsten sheet by single-point deformation is under way.(3) The objective is the production of tungsten sheet 18 inches wide by 48 inches long by 0.063 inch thick. Flow turning will be used to produce a tungsten tube about 6 inches in diameter from an isostatically pressed and sintered ring blank. The tube will then be slit longitudinally and flattened to produce sheet. Early work indicates that powder-metallurgy blanks are preferable to cast blanks for this purpose.

Alloys

Maykuth and Ogden(10) have provided a list of tungsten alloys of the greatest current interest together with a brief summary of their properties.

A promising tungsten-base alloy that can be consolidated by a powder-metallurgy procedure at lower temperatures than those required for pure tungsten has been recently noted.(2) This is a W-20Th alloy made by blending and compacting the component powders in a protective atmosphere and then sintering. It has room-temperature compressive plasticity and can be severely rolled or hammer forged at 1000 C without cracking. With a melting point above 2000 C it is expected to be useful at temperatures where tungsten bonded with lower melting metal (e.g. with nickel) would fail.

Summary results of an extensive survey of alloys in the Ta-W-Re and the Ta-W-Hf systems have recently become available.(11) The most important tungsten-base alloys represented in this study contained less than 10 per cent tantalum and rhenium.

Final results of another extensive study of tungsten-base alloys also have become available.(12) This study has been oriented more toward production, mechanical working, and properties determination.

The constitutional diagram of the tungsten-osmium binary system has been described in detail.(13) On the tungsten-rich end of this system, the bcc α-W primary solid solution retains approximately 18.5 at. % osmium at the peritectic temperature of 2945 C. The solubility of osmium drops to about 6 at. % at 1200 C.

Mechanical Properties

Some preliminary mechanical-properties data on three alloys of current interest are presented in Tables 1 through 4.(14)

TABLE 1. LOW-TEMPERATURE TENSILE RESULTS FOR AN 85:15 W-Mo FORGING AT .020 IN./MIN CROSSHEAD SPEED

Temp, F	0.2% Offset Yield Strength, psi	Ultimate Tensile Strength, psi	Reduction in Area, %	Elongation, %
530	78,570	91,250	30.9	6.5
435	86,260	98,860	34.4	8.9
285	90,460	103,800	16.1	9.5

TABLE 2. HIGH-TEMPERATURE TENSILE PROPERTIES OF FORGING AT .020 IN./MIN CROSSHEAD SPEED

Specimen Location	Temp, F	0.2% Offset Yield Strength, psi	Ultimate Tensile Strength, psi	Reduction in Area, %	Elongation, %
Web	3000	36,813	38,021	55	22.8
Thick edge	3000	42,964	43,718	68	20.7
As extruded	3000	34,500	36,000	78	27.8
Web	3500	8,771	11,403	71	68.3
Thick edge	3500	7,920	10,496	92.5	98.6
As extruded	3500	8,060	11,190	95	85

TABLE 3. STRESS-RUPTURE PROPERTIES OF AS-EXTRUDED TUNGSTEN ALLOYS AT 3000 F

Composition, %	Stress, psi	Time to Rupture, hr	Reduction in Area, %	Elongation, %
W-0.52Cb	25,000	0.8	92	42.7
	20,000	3.8	89	53.3
	15,000	32.45	89.6	51.2
W-5Mo	20,000	0.63	86.6	37.9
	12,500	4.41	90	64.9
W-15Mo	25,000	0.65	73	35.3
	20,000	3.89	74	33.0
	15,000	5.02	83.4	45.9
	12,500	12.82	79.0	46.7

TABLE 4. TENSILE PROPERTIES OF ARC-CAST AND EXTRUDED TUNGSTEN ALLOYS AT .020 IN./MIN CROSSHEAD SPEED

Composition, %	Temp, F	Ultimate Tensile Strength, psi	0.2% Offset Yield Strength, psi	Reduction in Area, %	Elongation, %
W-15Mo	3000	36,000	34,500	78	27.8
	3250	24,450	23,500	80	34.9
	3500	11,190	8,060	95	85
	4000	5,570	4,080	97	125
W-0.52Cb	3000	38,210	35,075	80	32.6
	3250	22,640	18,660	63.2	46.9
	3500	13,040	7,710	64.7	55.6
	4000	7,250	4,500	90	81.7
W-5Mo	3000	30,840	29,850	83	28.7
	3250	14,770	10,200	95	66.3
	3500	10,450	5,630	97.9	89.8
	4000	5,400	3,670	95	116

Some experimental elevated-temperature-strength measurements have been made elsewhere on W-TaC, W-HfO_2, and W-ThO_2 alloys(15), with the results as shown in Tables 5 through 8.

TABLE 5. 3000 F TENSILE PROPERTIES OF W-TaC ALLOYS

(Worked 60 per cent at 1700 C and annealed 1/2 Hr at 1600 C)

Alloy, %	0.2% Offset Yield Strength, psi	Ultimate Tensile Strength, psi	Elongation, %	Reduction in Area, %
0.1	6,800	9,200	23	43
0.1	6,900	8,900	27	41
0.65	14,000	19,000	21	37
0.65	12,000	16,000	17	36
1.0	13,500	22,000	21	37
1.0	7,600	9,600	16	37
0.38[a]	16-26,000	22-32,000	7-33	16-42

(a) Optimum alloy appears to be at about 0.35 per cent TaC.

TABLE 6. HIGH-TEMPERATURE TENSILE DATA OF THE W-0.5 PER CENT HfO_2 ALLOYS

Working Temp, C	0.2% Offset Yield Stress, psi	Ultimate Tensile Strength, psi	Elongation, %	Reduction in Area, %	Test Temp, F
1700	9,700	13,800	21	44	2700
1700	14,800	20,000	21	38	3000
1600	8,800	14,800	29	44	2700
1600	7,900	13,100	17	20	3000

TABLE 7. HIGH-TEMPERATURE CREEP OF PURE TUNGSTEN

Test Temperature, F	Stress, psi	Life, hr	M.R.C., %/hr	Rupture Strain, %
2700	12,500	3.3	3.7	18
Ditto	12,500	3.0	1.75	11
"	10,000	16.0	0.320	11
"	10,000	25.0	0.085	5
"	7,500	30.0	0.075	5
"	7,500	97.0	0.029	6
3000	7,500	2.5	0.632	8
Ditto	5,000	21.0	0.037	2
"	6,000	16.0	0.069	3.2
"	5,000(a)	34.0	0.34	2.0

(a) Test interrupted by furnace failure. The stress vs. rupture time appears to be normal at 3000 F.

TABLE 8. 3000 F CREEP DATA OF W-2 PER CENT ThO_2 ALLOYS

Material	Stress, psi	Life, hr	M.R.C., %/hr	Rupture Strain, %
Commercial	15,000	4.4	0.383	3.5
	12,500(a)	5.7	0.22	3.3
	7,500	10.5	0.076	1.3
Coprecipitated	15,000	2.0	0.79	3.3
	12,500	3.3	0.34	2.6
	10,000	4.9	0.33	2.7

(a) This test was interrupted several times.

These data should be accepted as tentative rather than as final.

Oxidation

An extensive summary of tungsten oxidation has recently appeared as a Defense Metals Information Center publication.[16] An effort to correlate some of the available data on tungsten oxidation has been made by Ong.[17] An approximation for the rate of attack of metallic tungsten above 700 C is presented as follows:

$$\text{Rate} = \frac{d\left(\frac{m}{A}\right)}{dt} = 5.89 \times 10^6 \; e^{-12,170/T} \; P^{1/2} \; \text{mgW/cm}^2 \text{ hr} ,$$

where m/A is the weight change per unit area, per unit time t, T is temperature in degrees absolute, and P is the oxygen pressure in atmosphere.

A paper presented at the Eighteenth IUPAC symposium is of interest in tungsten oxidation.[18] The authors discuss the thermodynamics of the WO_3-water vapor reaction to form a gaseous hydroxide.

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