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TUNGSTEN WHISKERS BY VAPOR-PHASE GROWTH

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By A. G. Starliper and H. Kenworthy

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TUNGSTEN WHISKERS BY VAPOR-PHASE GROWTH

by

A. G. Starliper[1] and H. Kenworthy[1]

ABSTRACT

Laboratory studies were made to produce whiskers of tungsten over a wide range of operating temperatures.

Hydrogen reduction of tungsten hexachloride in a vacuum furnace at temperatures from 2,700° to 3,300° C yielded a small quantity of tungsten whiskers, provided a low degree of supersaturation was maintained.

Direct measurements of 3,000,000 to 4,000,000 psi were obtained for the ultimate tensile strengths of individual whiskers averaging 3 to 4 microns in diameter with average aspect ratios of 1,000. This compares with strengths of 300,000 to 400,000 psi for 13-micron-diameter commercial filaments.

INTRODUCTION

The objective of this research was to develop techniques for growing tungsten whiskers and to study some of the physical characteristics of these whiskers. The theoretical strength of tungsten of perfect atomic structure and its well-known high-temperature strength suggest a variety of intriguing potential uses for these tiny crystals.

There is currently great interest in the formation of composites to provide materials of superior properties. This interest is evident in the efforts of numerous investigators to combine fine wires or filaments or whiskers with dissimilar materials. Only a few composites are now produced in whisker form in sufficient quantities to support whisker-composite research. Examples of these are sapphire, silicon carbide, aluminum nitride, and boron carbide. There is incentive for change in this situation since perfect metal crystals have theoretical strengths up to 1,000 times those of commercial metals. Whiskers most nearly approach theoretical strengths, because they contain minimal imperfections in atomic arrangement. Examples of measured tensile strengths of whiskers are iron, 1,900,000; silicon, 555,000; copper, 440,000; silver, 250,000; and zinc, 55,000 psi.

[1]Supervisory research extractive metallurgist, Rolla Metallurgy Research Center, Bureau of Mines, Rolla, Mo.

A common nonmetallic composite is exemplified by the resin-glass fiber of a fishing rod which has a strength of 250,000 psi.[2] Whiskers are structurally more nearly perfect than fibers; thus they yield potentially stronger composites.

GENERAL WHISKER INFORMATION

Any fibrous growth of a solid may be regarded as a form of whisker. It is convenient to distinguish between whiskers that grow spontaneously or as a result of an applied stress from the bulk solid and whiskers that grow from vapor, from solution, or from a melt. The latter types are more ordered in structure and, thus, have more tensile strength. The present study pertains to tungsten growths formed by vapor deposition.

The aspect ratio (length to diameter) of whiskers may vary considerably; however, for practical purposes a value of 100 or greater is very desirable. Potassium whiskers have been grown to 0.7 mm in length by 5 microns in thickness, zinc to 17 mm in length by 3 microns in thickness, while mercury whiskers have been grown to 2.5 mm in length by 0.01 micron in thickness.

A generally accepted explanation of the initiation of deposition from a vapor is that condensing atoms seek substrate sites of relatively low surface energy, which provide the best bonding. Unordered atomic arrangements such as found at step or screw dislocations are prime deposition sites. Screw dislocations are the most likely sites for the initiation of whisker growth since a screw dislocation should propagate and remain at the whisker tip as the whisker grows in length.[3]

The growth rate of whiskers is not a direct function of the probable impingement rate of atoms on the tip. Experience has shown that the correlation between predicted or calculated whisker growth rates and observed rates is very poor. For example, researchers[4] concerned with growing mercury whiskers found that the whiskers grew 5,000 times faster than could be accounted for by the rate of impingement of mercury atoms on the growing tip. The theory of atom adsorption on the sides and migration to the tip of the whisker is one explanation of the unexpectedly rapid growth rates of whiskers.

Evolution from metal plating, to chunky metal crystals, then to whisker growths was a function of atom-impingement rate. Control of the degree of supersaturation of tungsten over the substrate was accomplished by regulating temperature, gas-mixture ratios, and gas-feed rates. Tungsten has such a high boiling point that the capacities of conventional equipment are many hundreds of degrees deficient. Therefore, very dilute gas mixtures were necessary to achieve the low degrees of supersaturation that are prerequisite to

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[2]Hibbard, W. P., Jr. Composites. Chem. Eng., v. 70, No. 23, Nov. 11, 1963, p. 208.

[3]Wert, C. A., and R. M. Thomson. Physics of Solids. McGraw-Hill Book Co., New York, 1964, pp. 96-98.

[4]Sears, G. W. A Growth Mechanism for Mercury Whiskers. Acta Metallurgica, v. 3, July 1955, pp. 361-366.

unidirectional growth. Also, partial vacuum was employed to achieve the supersaturation effect of a few hundred degrees higher temperature. However, no attempt was made to develop more sophisticated equipment capable of directly attaining a low supersaturation by approaching the temperature of boiling tungsten.

EXPERIMENTAL PREPARATION AND EVALUATION OF TUNGSTEN GROWTHS

Materials

Of the known methods of whisker formation: spontaneous reaction, precipitation from solution, bulk stress, and vapor deposition, vapor deposition by reduction of a tungsten halide was chosen for forming tungsten whiskers in this investigation. Several tungsten halides volatilize at low temperatures, and their vapors may be thermally decomposed or chemically reduced. Tungsten hexachloride fits this category, and, in addition, the high temperatures concomitant with its reduction to metal and with low supersaturation is conducive to whisker growth.

A high-purity crystalline tungsten hexachloride was prepared in the Bureau laboratories at Rolla, Mo. Prepurified hydrogen was selected as the reductant. Grade A helium was the inert carrier gas and also served as a diluent to depress the degree of supersaturation of the gaseous tungsten.

Equipment

Four types of heat source were used in heating reaction substrates: Resistance-wound tube furnaces, induction furnaces, a wire heated by electrical resistance, and a high-temperature vacuum furnace heated by a tungsten mesh element. Auxiliary chambers were used to vaporize the tungsten hexachloride. Accessory equipment included gas flowmeters, needle valves, microvalves, and temperature measuring devices. A program controller was used to promote gradually increased heating of the tungsten hexachloride-volatilization chamber in order to maintain a constant rate of flow of vaporous tungsten chloride to the reaction chamber.

Low-Temperature Vapor-Phase Reduction of Tungsten (VI) Chloride

Previous work at this Research Center had shown that tungsten hexafluoride could be hydrogen reduced from the gas phase at temperatures above 450° C;[5] initial reductions of tungsten hexachloride were conducted at 350° C. It was immediately apparent that the chloride was not as readily reduced as the fluoride. Temperatures in succeeding experiments were increased to the furnace limit of 1,150° C, which did not completely reduce the hexachloride to metal. At this temperature a profusion of acicular growths up to 1 inch in length was obtained. They ranged in color from orange to green. The average aspect ratio was about 50. Analysis of these acicular whiskers showed them to

[5] Nieberlein, V. A., and H. Kenworthy. High-Purity Tungsten by Fluoride Reduction. BuMines Rept. of Inv. 5539, 1959, p. 8.

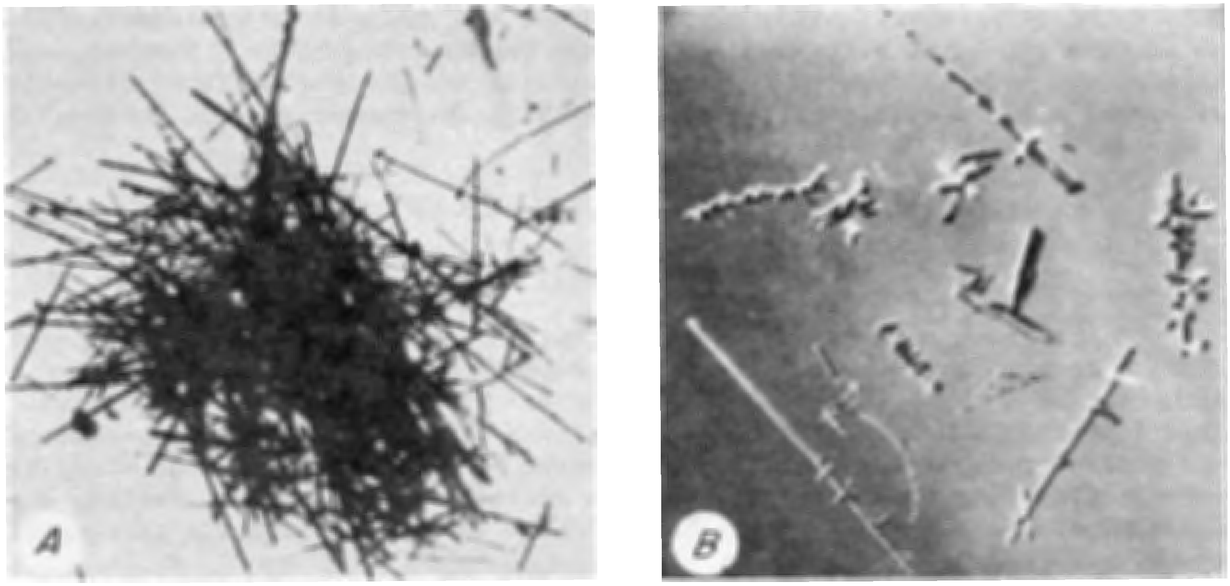

FIGURE 1. - Typical Subchloride Crystals From Low-Temperature Reaction. *A*, Massed deposit (X 9); *B*, detail of branched growth (X 100).

consist of approximately 73 percent tungsten (V) chloride, 23 percent tungsten (IV) chloride, and 4 percent tungsten (II) chloride. Figure 1A shows a mass of subchloride whiskers and figure 1B shows a few individual branched growths.

Experiments were conducted to reduce these growths to metal without loss of their whisker characteristics. Hydrogen reductions were made in a stainless steel bomb at temperatures of from 200° to 600° C, under a 2,000-psi hydrogen atmosphere. The best results were obtained at the maximum temperature at which a 33-percent weight loss was registered. In these experiments, the larger diameter whiskers were spotted with small areas of metallic tungsten while the smaller diameter whiskers appeared to be nearly completely metallized. Under magnification, all whiskers were seen to be scaly and showed longitudinal and transverse cracks, see figure 2. To obtain complete chloride reduction would have required removal of the hydrogen chloride formed by the reduction reaction, higher pressures, or temperatures beyond the safe working range of the equipment. The volume shrinkage upon removal of chlorine, without structural compensation to maintain competent whiskers, appeared to doom this low-temperature approach. It should be noted, however, that strong carbon and graphite fibers have been made by pyrolysis of hydrocarbons,[6] which involves a shrinkage.

Intermediate-Temperature Vapor-Phase Reduction of Tungsten (VI) Chloride

An induction-furnace work coil was placed around a graphite-tube reaction chamber to obtain reduction temperatures higher than 1,150° C. It was found

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[6]deKeyser, W. L., and R. Cypres (assigned to the Universite Libre de Bruxelles). Belgian Pat. 496,711. Oct. 16, 1950.

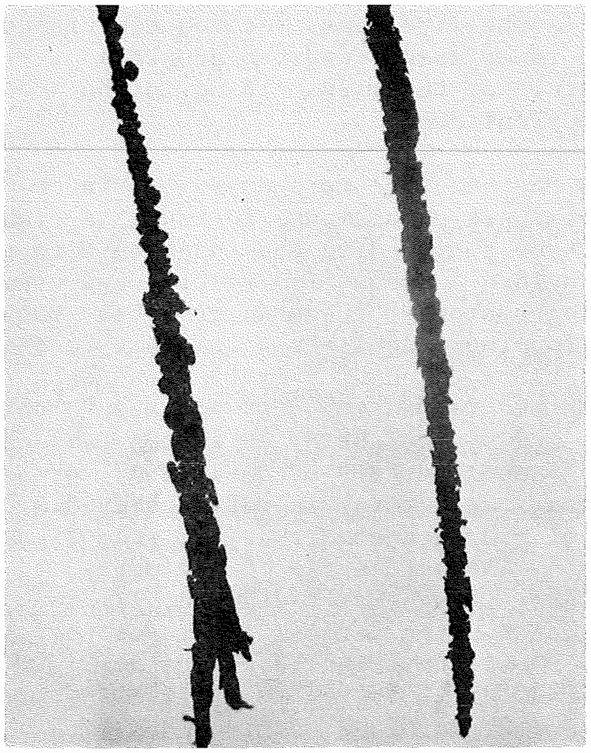

FIGURE 2. - Partially Reduced Subchloride Crystals (X 300).

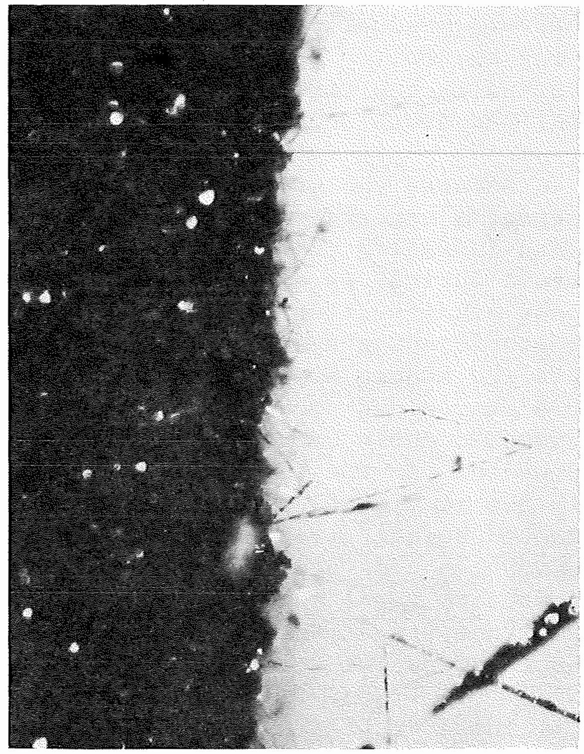

FIGURE 3. - Tungsten-Tungsten Subchloride Whiskers on Tungsten Substrate (X 100).

that tungsten growths did not nucleate on graphite or on tungsten strips placed within the induction work coil; however, when the tungsten substrate strips were moved outside the intense magnetic field, tungsten deposition took place.

In successive experiments, temperatures were raised from 1,300° to 2,400° C and the gas compositions were varied. A considerable number of growths were formed, but only a few were in the shape of whiskers. Aspect ratios were about 70 for the growths. Although reduction was far more complete than previously, about 40 percent of the tungsten still remained as tungsten (II) chloride. Note light-appearing metallic areas on whiskers in figure 3.

High-Temperature Wire Furnace Reduction of Tungsten (VI) Chloride

To obtain more complete reduction of tungsten chloride, tungsten wire heated by electrical resistance was used not only as a source of heat but also as a substrate for tungsten growths. Wires from 30 to 80 mils in diameter by 6 inches in length were utilized at temperatures from 2,600° to 3,200° C. Initial growths were noted at temperatures as low as about 2,700° C. Wire temperature during a typical run was initially held fairly constant at a selected temperature between 3,000° and 3,200° C. Localized temperature, however, gradually rose above this range as the wire cross section diminished owing to erosion (possibly atom migration to adjacent tungsten growths). Eventually the circuit was broken as a result of the wire melting in the smallest cross section due to increased current density.

Because the growth developments with the hot wire were unusually interesting, a somewhat detailed description of these experiments follows. A sight glass installed in the side of the steel tube surrounding the tungsten wire to permit optical pyrometer readings also provided a means of directly observing under magnification the nucleation and progression of tungsten growths. Each growth followed a definite pattern while forming. At first a low flat-topped wartlike nodule appeared, followed by a nucleus foundation similar in shape to a many-sided tree stump. On this stumplike foundation next appeared a thin truncated cubic or polygonal crystal that grew in height by extension but not in width. At the same time the stumplike base gradually became thinner probably due to migration of atoms to the crystal. A crystal rapidly achieved a limited height after which visible vertical growth ceased, but the stumplike foundation continued to disappear causing a fair percentage of the early growths to topple and stick to the substrate. A schematic drawing, figure 4, shows the stages through which a growth passed while forming. Some of the described nuclei and growths are shown on substrate wires in figure 5.

These growths were fully metallized and either four or six sided with sharp angles and brilliant reflective surfaces. Elliptical craters were present on the faces of several mature crystal growths. Aspect ratio for an average crystal was 20, and a length was 1 mm.

Results showed that the ultimate length of mature crystals was fairly uniform and that they achieved that length in a comparatively short time. The probable limiting factor for length of growth was temperature, because the tip temperature decreased very rapidly as the growth tip moved outward from the

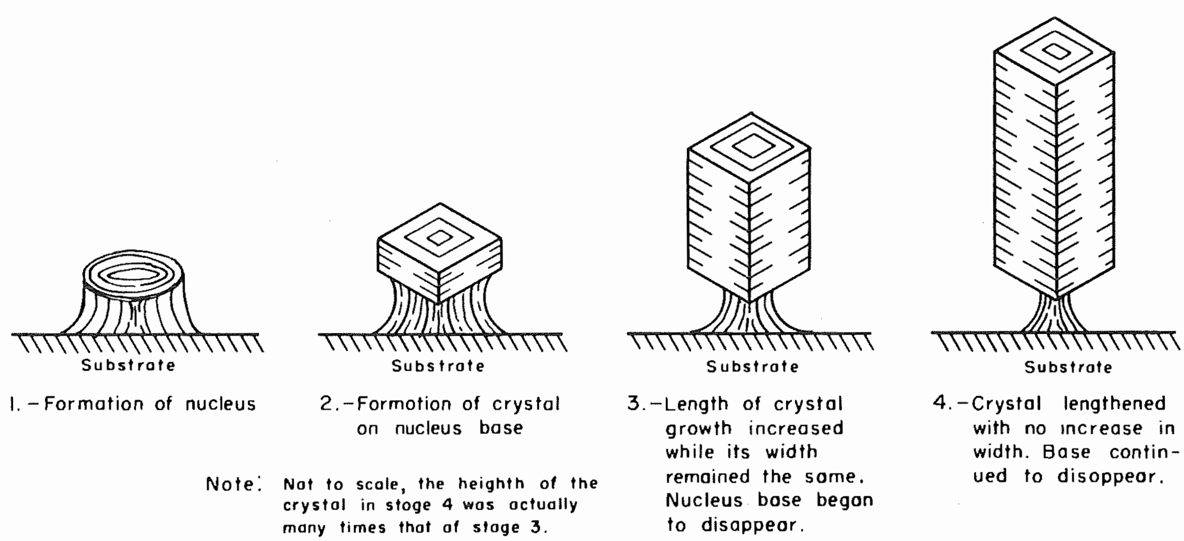

FIGURE 4. - Growth Stages of a Tungsten Crystal.

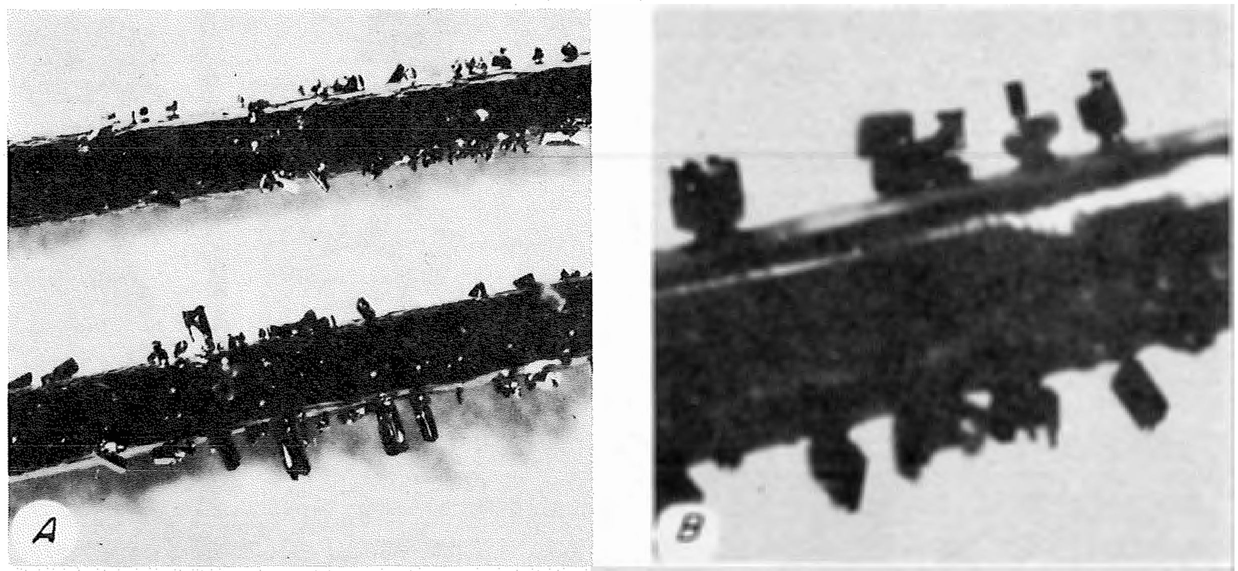

FIGURE 5. - Typical Tungsten Growths on Tungsten Wire From High-Temperature Reaction. *A*, Wire thinned and crystal population decreased adjacent to melt-through point (X 20); *B*, detail of complex crystals on stumplike supports (X 70).

hot-wire substrate. In addition, as the distance of the tip from the wire increased, the degree of supersaturation increased since tungsten atom depletion was less prevalent away from the substrate. To partially overcome this growth-limiting temperature condition two and three parallel wires spaced about 2 mm were used. Although more growths appeared on the wire areas which faced each other, the increase in growth length was slight.

Efforts were made to add heat to the space around the substrate wire by the use of an induction furnace with a graphite susceptor. Results confirmed previous findings that whiskers would not grow in a magnetic field.

Brewer[7] shows that the temperatures of hot-wire operation should have thermally decomposed most of the tungsten hexachloride to metal at 1-atmosphere pressure. A hot-wire experiment was made in which hydrogen was omitted from the gas mixtures. No deposits were formed, and no thinning of the wire took place. This evidence indicated that under experimental conditions a reducing agent was essential to metallization of tungsten hexachloride and growth of whiskers at temperatures in the order of 3,000° C.

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[7]Brewer, L., and others. The Thermodynamic Properties of Molybdenum and Tungsten Halides and the Use of These Metals as Refractories. Paper No. 8 in The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, ed. by L. L. Quill. McGraw-Hill Book Co., Inc., New York, 1950, pp. 271-311.

FIGURE 6. - Vacuum-Furnace Feeder Arrangement.

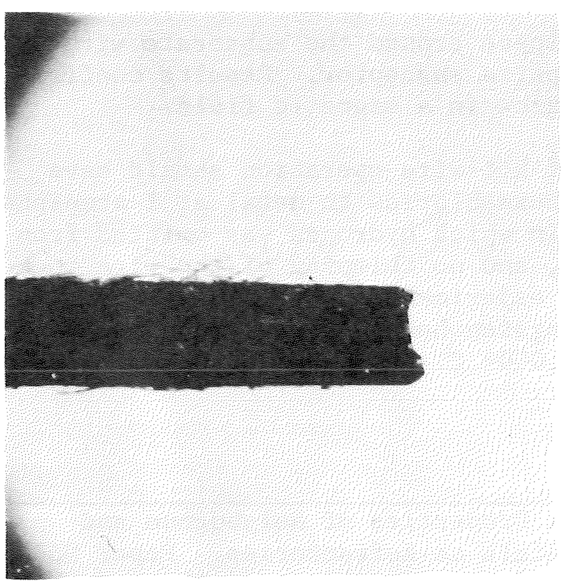

FIGURE 7. - Tungsten Whiskers on 30-Mil Wire (X 150).

High-Temperature Vacuum Furnace Reduction of Tungsten (VI) Chloride

The previous studies showed that results should be improved if the space around the substrate were uniformly heated for a distance at least equal to whisker length. Subsequent experiments were performed in a vacuum furnace heated by a cylindrical tungsten-mesh element. The furnace was modified to accept a vapor-deposited 5/16-inch (ID) tungsten tube (substrate) through the heating element and was fitted with a freeze trap ahead of the vacuum pump. A tungsten chloride vaporizer-feeder was made by wrapping a Vycor[8] tube with electrical resistance heating wire. The furnace and feeder are shown in figure 6.

[8]Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

Pressure in the furnace was varied from 1 to 200 mm mercury, temperature was varied from 2,700° to 3,300° C, time was varied from 30 to 60 minutes, and tungsten in the gas mixture was varied from 100 to 1,800 ppm. Gas velocity at 1-mm pressure was about 9,000 cm/min compared with 25 cm/min for previous runs at atmospheric pressure. No adverse effects on whisker nucleation or growth could be attributed to this increase in gas velocity; however, when operating at 200-mm pressure scarcely any whisker growth occurred.

Placing relatively coarse (30- and 80-mil) tungsten wires in the hot zone of the tungsten tube caused the majority of the whiskers to collect on the wires rather than on the tungsten tube. When 1/2-mil (25.4 microns equal 1 mil) tungsten wire was wrapped around the larger wires, whisker production on the wires increased further. Due to the high purity of the vapor-deposited

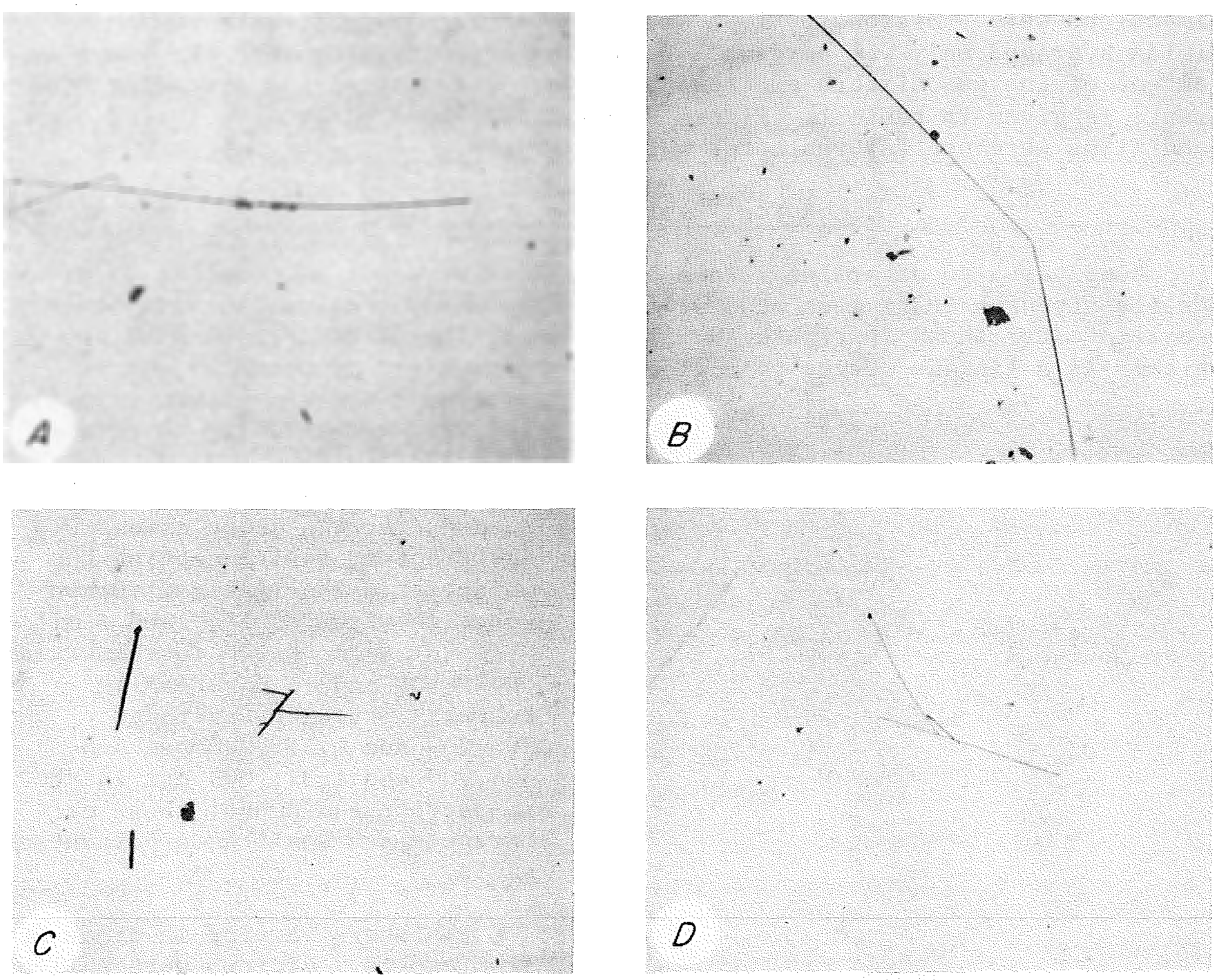

FIGURE 8. - Typical Tungsten Whisker Configurations (X 150). *A*, Cross growth, 4-micron diameter by 2.5 = mm length; *B*, knee growth, 5.8 = micron by 3.6 = mm; *C*, branched growth, 12-micron average diameter; *D*, side growth, 6-micron by 2.8 mm.

tungsten tube, there may not have been as many nucleation sites on the tube as on the drawn tungsten wires. Whiskers grown on the 1/2-mil wire were the greatest in length and smallest in diameter. Figures 7 and 8 show the several variations in whisker growths, such as cross growth, knee or angle growth, branched growth, side growth. The dendritic or branched growths were made at relatively high degrees of tungsten supersaturation.

Furnace temperatures were undoubtedly considerably above those of the gas stream in the deposition zone of the tungsten tube, because the high velocity of the gases gave little time for heat transfer. Some tungsten subchloride was identified near the inlet end of the tungsten tube.

Measurements of a number of whiskers showed a variation in diameter from 2.4 to 8 microns and a variation in length from 0.34 to 18 mm. The average dimensions were 5 microns by 1.95 mm, or an average aspect ratio of 390. Yields averaged only 0.1 percent. Dendrites began forming when the tungsten content of the gas mixture exceeded 550 ppm. A résumé of the preceding experiments is given in table 1. Figure 9 shows two types of growths formed when conditions were not favorable for whisker growth.

Mechanical Evaluation of Whiskers

Bend tests to determine strain on whiskers were not successful, so direct tensile-strength tests were made with the laboratory-constructed microscale tensile tester shown in figure 10. In essence, the method chosen used the whisker as a linkage member to pull a suspended weight or pendulum out of vertical, and the amount of pull was trigonometrically calculated from the weight, the distance pulled, and the length of the suspension. An epoxy cement was satisfactory for connecting the whiskers in the linkage. Drawn tungsten wires of 1/2- and 1-mil diameter were tested in commercial equipment and in our tensile tester. Strengths averaged 390,000 and 1,379,000 psi and 406,000 and 1,371,000 psi in the respective equipment; these differences are small on a percentage basis.

FIGURE 9. - Dendritic Growths Resulting From Unfavorable Conditions (X 150).

Whiskers varying in diameter from 4.5 to 7 microns were pulled in the microscale tensile tester to determine their tensile strength. The results varied from 2,472,000 to 3,798,000 psi with an average of 3,232,500 psi.

TABLE 1. - Experimental data from the three temperature-range investigations

	Temperature, ° C	Approximate gas mixture			Gas velocity,[1] cm/min	Time, minutes	Growths				
		H_2, pct	He, pct	W, ppm			Type	Yield, pct	Length, mm	Diameter, microns	Average aspect ratio
Low temperature:											
Test range.......	350-1,150	2-30	70- 98	65-2,000	0.1- 200	15-300	Crystals, subchloride acicular.	50-100	0-25	40 -200	50
Best conditions..	1,150	2	98	200	.1	300		100	25	50	-
Intermediate temperature:											
Test range.......	1,300-2,400	0-15	85-100	50- 510	14 - 50	360	Crystals, 60 pct W and; 40 pct WCl_2.	([2])	0- 2	1.5- 12	70
Best conditions..	2,400	4	96	150	22	360		([2])	2	4	-
High temperature:											
Wire furnace:											
Test range.....	2,700-3,200	0-35	65-100	50-3,000	5 - 61	10- 30	Crystals, metallic, squat.	([2])	0- 1	8 -150	20
Best conditions	3,200	20	80	100	20	30		([2])	1	50	-
Vacuum furnace:											
Test range.......	2,700-3,300	0-40	60-100	100-1,800	475 -1,500	30- 60	Whiskers, metallic; crystals, squat; dendrites.	<0.1	0-18	2.4- 8	390
Best conditions[3]	3,300	25	75	100- 300	950	60	Whiskers.........	.1	3- 5	2 - 4	1,000

[1]Based on atmospheric pressure and furnace temperature.
[2]Very low.
[3]Pressure of 1 mm Hg.

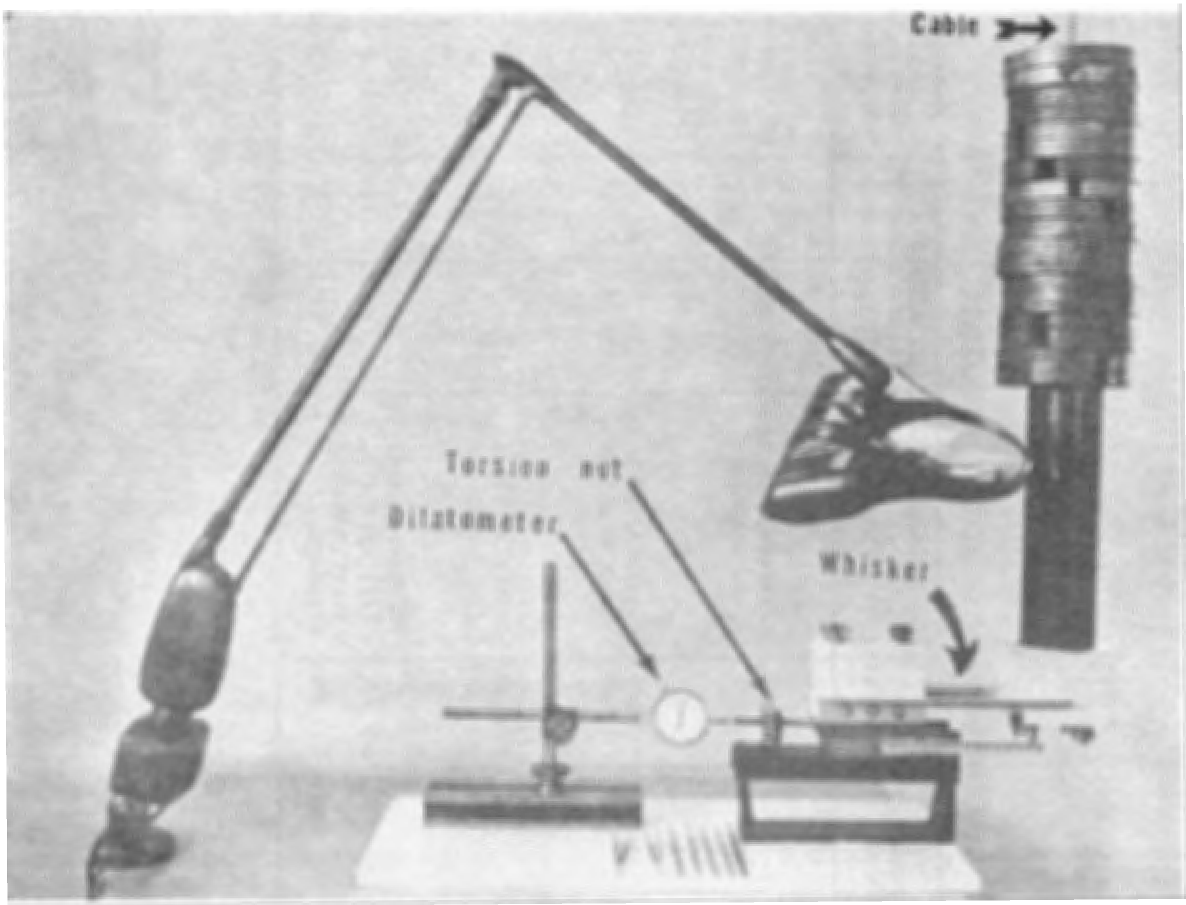

FIGURE 10. - Microscale Tensile Tester for Whiskers.

Examination of fracture surfaces found that prior to failure there was no evidence that the filaments underwent any plastic deformation near the fracture, which indicates that the filaments had very little, if any, ductility. Figure 11 shows one length of a whisker after pulling in the machine. The right end is at the break, and the left end is glued to a linkage head consisting of a 5-mil tungsten support wire.

CONCLUSIONS AND DISCUSSION

Acicular tungsten crystals with whisker dimensions and characteristics can be grown by vapor-phase reduction of tungsten hexachloride. Several conditions are requisite to obtaining even a very low yield of metallic whiskers. A temperature of at least 2,700° C is necessary to insure complete metallization of the growths. Reduction of tungsten hexachloride to metal apparently is by a combination of thermal dissociation and hydrogen reduction. A low degree of tungsten supersaturation is needed to obtain predominantly unidirectional growth rather than plating, and the presence of a pulsing magnetic field around the substrate may prevent whisker growth. The most desirable growths were obtained by deposition from gas mixtures containing 100 to 300 ppm of tungsten.

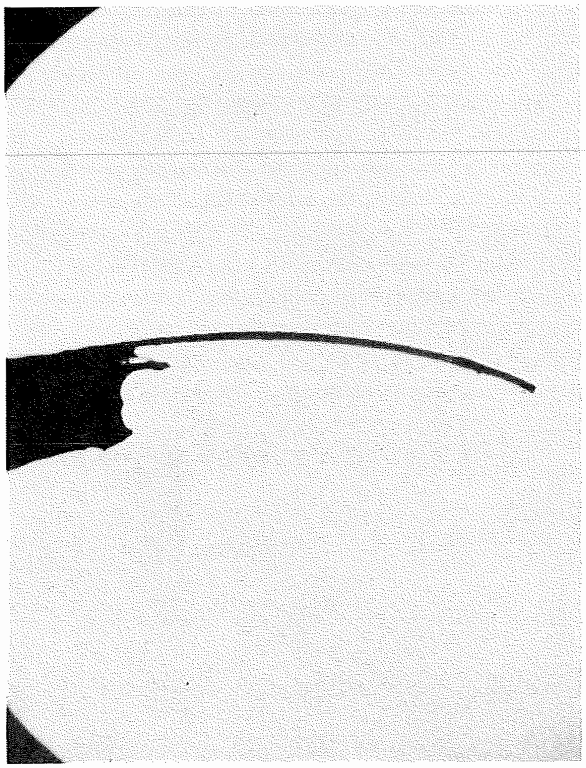

FIGURE 11. - Brittle Tensile Fracture of 7-Micron Whisker Mounted on 5-Mil Support Wire (X 300).

The velocity of the mixed tungsten hexachloride and carrier gas was much higher in a partial vacuum than at atmospheric pressure while the growths obtained were equal in quantity and quality.

The quality of whiskers produced by hot-wire methods is inferior to that of whiskers produced by reduction and growth on an externally heated tungsten surface. Tungsten can be strongly recommended as a substrate on which growth is readily initiated.

High yields and excellent dimensional quality tungsten subchloride whiskers were produced at moderate temperatures; however, the limitations of our equipment, 600° C temperature and 2,000 psi hydrogen pressure, made it impossible to reduce these whiskers to coherent tungsten filaments.

Conditions conducive to quantity deposition of tungsten whiskers in these studies were so far from ideal that whisker yields were very low and many oddly-shaped growths were formed. Operational temperatures much nearer the boiling point of tungsten and a lower degree of supersaturation would have improved the whisker growing results. The melting-point limitations of the container materials used permitted only operating temperatures near the melting point of tungsten.