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ABSTRACT. Properties associated with the application of tungsten prepared by the hydrogen reduction of WF_6 as a thermionic emitter are discussed. Two major areas have been investigated: (1) the quality of material available from a variety of sources, and (2) the resistance of this material to grain growth. Properties which have been determined during the evaluation program have been: (1) microstructure, both before and after extensive thermal treatments; (2) ductile-to-brittle transition temperature; (3) impurity content; and (4) hardness. Experimentation has shown that the resistance of vapor-deposited tungsten to grain growth is primarily structure sensitive, and in all cases where grain growth is observed, it starts at regions of marked grain misorientation, primarily a layer of small, equiaxed, randomly oriented grains which extends into deposited material up to 0.003 in. from the substrate surface. If this layer is removed prior to thermal treatment, resistance to grain growth is markedly improved.

INTRODUCTION. Early in the development of high-temperature nuclear fuels (i.e., for operation at 1800°C, or above), it became evident from considerations of the compatibility of prospective fuel materials with various candidate metallic cladding materials,(1,2,3) that no matter which fuel was considered (carbides or oxides) tungsten, or perhaps tungsten based alloys, qualified as the most promising material for long-time operation. However, when the fabrication of experimental assemblies was attempted with the use of conventional tungsten, it was not possible to maintain the structural integrity of thin sections when the parts were cooled after initial operation, because extensive grain growth caused severe embrittlement and a loss of resistance to thermal or mechanical shock.

On the other hand, preparation of thermionic emitters by the hydrogen reduction of WF_6 has resulted in reproducible high purity material which is relatively easy to machine and whose microstructure remains stable even after 1500 hours at 1800°C and in excess of 10 hours at 2500°C. An additional bonus obtained is a highly oriented structure resulting in a uniform work function surface.(4)

This paper deals with vapor-deposited tungsten from the standpoint of a user rather than a producer and deals with two major aspects: (1) an evaluation and comparison of vapor-deposited tungsten available from a number of sources, and (2) the resistance of vapor-deposited tungsten to grain growth. A third area, the influence of carbon, nitrogen, and oxygen additives upon the microstructure, resistance to grain growth, and mechanical properties of vapor-deposited tungsten is currently being investigated and the results obtained to date will be included in the presentation of this paper.

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EVALUATION PROGRAM. To evaluate the state-of-the-art of tungsten tubing, representative material was obtained from eight organizations and included in addition to tubing prepared by the hydrogen reduction of WF_6, extruded tubing, electro-deposited tubing, and tubing prepared by the hydrogen reduction of WCl_6 (see Table 1). All tubes fell within the following size ranges: Outer Diameter 0.271 in. to 0.500 in., Wall Thickness 0.007 in. to 0.045 in. Each specimen was evaluated with respect to: impurity content (see Tables 2 and 3); microstructure in the as-deposited condition and after four thermal treatments (1800°C for 100 hr., 2000°C for 15 hrs., 2200°C for 15 hrs., and 2500°C for 1 hr.); ductile-to-brittle transition temperature (by a ring compression test, see Table 4), and hardness. A detailed discussion of this program is included in Reference 5.

Conclusions which were drawn from this study are:

1. The chemical impurity content of vapor-deposited tubing from six sources is comparable. This is surprising considering that different starting materials, different experimental conditions, and different personnel were involved.

2. The metallic impurities are at a low level in all samples. The impurities present appear to be related to the mandrel material.

3. There is a positive correlation between the residual fluorine content and the ductile-to-brittle transition temperature of vapor-deposited tungsten tubing. This merits further investigation, such as the evaluation of tubing made by the same technique but with various fluorine contents (see Figure 1).

4. Extruded tungsten tubing has a very low fluorine content, but fluorine is probably the tungsten starting material.

5. The lowest fluorine content of the vapor-deposited tubing (Tube 8) is comparable to that found in the extruded tubing made by powder metallurgy techniques.

6. The grain growth of Tube 7, formed on the male mandrel, exhibited the least change after heat treatments. A great variety of responses to thermal treatment was observed; and many tubes showed evidence of extensive grain growth (see Section III, below).

7. Columnar structures which are deposited in a highly oriented manner will exhibit less grain growth than those deposited in a less oriented manner. When grain growth does occur, it is initiated in the fine grains first deposited.

8. Grain growth of vapor-deposited tubing is not primarily related to the chemical impurity content. Tubes 7 and 8 were comparable in impurity content but had vastly different structures after heat treatment.

9. Extensive grain growth took place in the extruded tubing during heat treatment.

10. The ductile-to-brittle transition temperatures of extruded tungsten tubing and of the best vapor-deposited tubing are comparable.

11. No correlation was found between hardness and any other variable, i.e., impurity content, microstructure, or ductile-to-brittle transition temperature.

12. The hardness ranged (the spread of the averages obtained from different tubes) from 299-394 DPH using a 15 gm load and from 342-502 DPH using a 100 gm load. If one ranked the specimens by order of increasing hardness for the values obtained under one load, the ranking would not be the same using the second load. The difference appears to be in the structure sensitivity of the values obtained with the larger load since the impression extends beyond a single grain.

This program is currently comtinuing with the evaluation of tubing submitted by laboratories in addition to those previously included; and also the re-evaluation of tubing from laboratories which believe that they have improved their processing techniques.

RESISTANCE TO GRAIN GROWTH. Tungsten prepared by vapor-deposition techniques is generally quite resistant to grain growth. However, it has been observed that materials prepared by different laboratories (see section above) exhibited a variety of behavior with respect to this characteristic and even material from those laboratores which normally produce grain growth resistant materials would occasionally evidence extensive grain growth. The lack of predictability as to whether or not a given specimen of vapor-deposited tungsten would exhibit grain growth led to confusion and undertainty in the use of this material. This paper presents the conclusions of some experiments which were designed to gain a greater understanding of the behavior of this material, and thereby lead to greater confidence in its use. Although only conclusions are presented below, a more detailed treatment of this subject is presented in Ref. 6. The conclusions which were drawn are:

1. Vapor-deposited tungsten can exhibit remarkable resistance to grain growth for up to 11 hrs. at 2500°C (see Figure 4), and for longer periods at lower temperatures.

2. While one cannot say the contaminant level of the tungsten never plays a role in its resistance to grain growth, it has been demonstrated that tungsten of similar chemistry but of different structure can exhibit widely different responses to thermal treatment (see Figure 2).

3. Structures appear to play a very important role with respect to the resistance to grain growth, and it can be stated categorically that whatever grain growth has been observed in tungsten which has not been subjected to mechanical strain, it has started at a region of small, equiaxed, randomly oriented grains formed during the initial stages of deposition (see Figure 3), growth initiated in this region then proceeds in a wave-like fashion through the remainder of the material, consuming the columnar grains in its path. It is apparent that a lack of driving force due to highly oriented structures and resultant low angle grain boundaries is the reason for the high resistance to grain growth rather than a pinning of the grains' boundaries to prevent their migration. Preliminary observations indicate that if the original orientation is the $\{100\}$ parallel to the substrate surface, this orientation is not changed even by extensive grain growth.

4. If the layer of fine, randomly oriented, equiaxed grains is removed, grain growth is not observed to occur even after 11 hrs. at 2500°C (see Figure 4).

5. Tubes of small diameter (less than 1/8 in.) exhibit a greater tendency towards grain growth than do tubes of a larger diameter; and tubes formed in a female mandrel are more subject to grain growth than those formed on a male mandrel.

6. The artificial formation of a fine-grained structure by the periodic interruption of the deposition process or by the addition of particulate matter to the gas stream to cause heterogeneous nucleation may impair the resistance of the material to grain growth by introducing a larger degree of grain misorientation and thereby a larger driving force for grain growth.

ADDITIVES. As mentioned in the introduction, work is currently in progress to study the effects of oxygen, carbon, and nitrogen when added to vapor-deposited tungsten. The work is occasioned by the fact that when high purity tungsten is placed in contact with a nuclear fuel, the establishment of equilibrium conditions requires that carbon, oxygen, or nitrogen (dependent upon the uranium compound employed) must be present in the tungsten cladding. Additions are being made both during deposition by doping the hydrogen used to reduce the WF_6, and by the use of gas-metal reactions with previously deposited tungsten. The influence of these additives upon the microstructure, resistance to grain growth, the ductile-to-brittle transition temperature, and the high temperature strength are being measured. Although few results have been obtained to date, those available at that time will be presented at the conference.

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Table 1

DESCRIPTION OF TUBES INCLUDED IN EVALUATION

Tube No.	Mfgr. Code	Forming Method	Mandrel		Layers	
			Male	Female	Uninterrupted	Interrupted[d]
1	A	Vapor-deposited		x	x	
2	A	Vapor-deposited		x	x	
3	B	Electrodeposited	x		x	
4	C	Vapor-deposited		x		x
5	D	Vapor-deposited		x		x
6	D	Vapor-deposited		x	x	
7	E	Vapor-deposited	x		x	
8	E	Vapor-deposited		x	x	
9	F	Extruded at 1800°C				
10	F	Extruded at 1800°C				
11	F	Extruded at 1200°C				
12	F	Extruded at 1200°C				
13[a]	F	Extruded, 6 to 12 in., at 1200°C				
14[a]	F	Extruded, 12 to 18 in., at 1200°C				
15[a]	F	Extruded, 18 to 24 in., at 1200°C				
16[b]	G	Vapor-deposited	x			x
17[c]	H	Vapor-deposited	x		x	

[a] Tubes 13, 14, and 15 are three sections of one tube extruded at 1200°C; Tube 13 is the 6 to 12 in. section from the lead end, and 14 and 15 are subsequent 6 in. sections.

[b] Formed by the hydrogen reduction of WCl_6.

[c] Formed by the hydrogen reduction of WF_6 which had been converted from WCl_6 .

[d] The deposition was periodically stopped to form a layered structure.

Table 2

FLUORINE; CARBON, NITROGEN, OXYGEN, AND HYDROGEN CONTENT OF TUNGSTEN TUBING[a]

(In ppm)

Tube No.	Mfgr. Code	F_2	C	N_2	O_2	H_2
1	A	29.3	7.7-6.7	10, 7	10, 16	3, 7
2	A	46	12.5-10.0	9, 10	8, 7	3, 3
3	B	13	---	8, 7	105,116[b]	6, 6
4	C	26	6.7	2, 5	3, 6	2, 3
5	D	44.4	6.1-7.3	3, 6	32, 37	4, 4
6	D	35	6.6-6.5	1, 2	7, 10	4, 4
7	E	9	6.4-6.0	5, 5	6, 7	3, 3
8	E	4	6.2-6.5	5, 3	12, 11	4, 4
9	F	3	11.0-11.6	11, 10	22, 20	4, 4
10	F	4	7.9	20, 14	6, 7	2, 2
11	F	4	6.7-7.6	13, 14	6, 19	2, 2
12[b]	F					
13	F (6 to 12 in.)	3	5.7-6.5	20, 15	8, 9	3, 3
14[b]	F (12 to 18 in.)					
15[b]	F (18 to 24 in.)					
16	G	22 (Cl_2)	6.1	5, 8	12, 20	2, 3
17	H	18	23, 22	<1, 1	4, 8	10,5

[a] Due to participation in various programs of evaluation a high degree of confidence has been established for the accuracy of carbon, oxygen, and hydrogen analyses. However, the nitrogen analyses are quite uncertain.

[b] There was an oxide film on the inside of the tube which perturbed the analysis.

[c] Samples 12, 14, and 15 were not submitted for analysis.

Table 3

METALLIC IMPURITY CONTENT OF TUNGSTEN TUBING

(In ppm)

Tube No.	Mfgr. Code	Al	Cu	Fe	Mg	Mn	Mo	Ni	Si	Ti
1	A	<1	N<0.5[a]	<1	0.5	N<0.5	N<100	1	<2	N<6
2	A	N<1	<0.5	<1	0.5	N<0.5	N<100	<1	<2	N<6
3	B	4	600	2	<0.5	N<0.5	800	200	2	N<6
4	C	<1	1	20	1	1	N<100	4	6	N<6
5	D	<1	<0.5	1	<0.5	N<0.5	N<100	<1	<2	N<6
6	D	6	<0.5	100	0.5	N<0.5	N<100	4	2	N<6
7	E	2	N<0.5	<1	0.5	N<0.5	N<100	N<1	<2	N<6
8	E	1	N<0.5	<1	0.5	N<0.5	N<100	<1	2	N<6
9	F	4	1	20	0.5	0.5	N<100	2	8	N<6
10	F	3	N<0.5	80	<0.5	N<0.5	N<100	200	<2	N<6
11	F	2	<0.5	60	<0.5	1	100	10	<2	N<6
12[b]	F									
13	F(6 to 12 in.)	1	<0.5	10	0.5	N<0.5	200	8	2	N<6
14[b]	F(12 to 18 in.)									
15[b]	F(18 to 24 in.)									
16	G	2	<0.5	10	1	N<0.5	N<100	<1	10	N<6
17	H	2	<0.5	5	<0.5	1	N<100	200	8	<6

NOTE: Elements not listed above were not detected in any of the samples.

[a] N = Not detected.

[b] Samples 12, 14, and 15 were not submitted for analysis.

Table 4

DUCTILE-TO-BRITTLE TRANSITION TEMPERATURE[a]

Tube No.	Mfgr. Code	Lowest Temperature at which any Deformation Occurred (°C)
1	A	260-325
2	A	365-375
3	B	<180
4	C	285[b]
5	D	240-270[b]
6	D	170
7	E	175-200
8	E	140[b]
9[c]	F	
10	F	130[b]
11	F	130[b]
12[c]	F	
13	F (6 to 12 in.)	>160[b]
14[c]	F (12 to 18 in.)	
15[c]	F (18 to 24 in.)	
16	G	260-270

[a] Determined by ring compression test.

[b] These values were determined on split rings that fractured in a brittle fashion at the 12 and 6 o'clock positions. Higher temperatures were required to obtain deformation without fracture of the full ring.

[c] Samples 9, 12, 14, and 15 were not submitted for this evaluation.

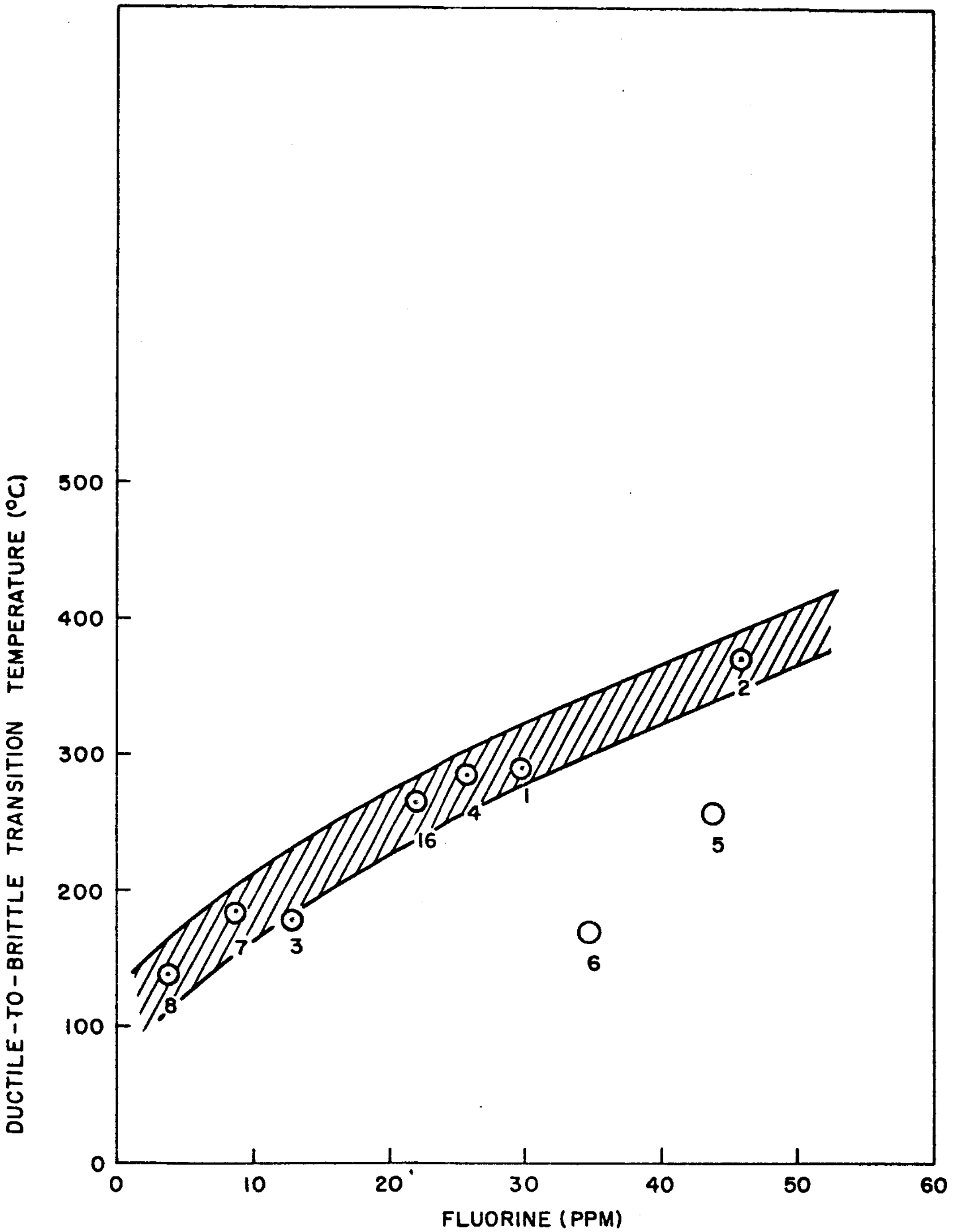
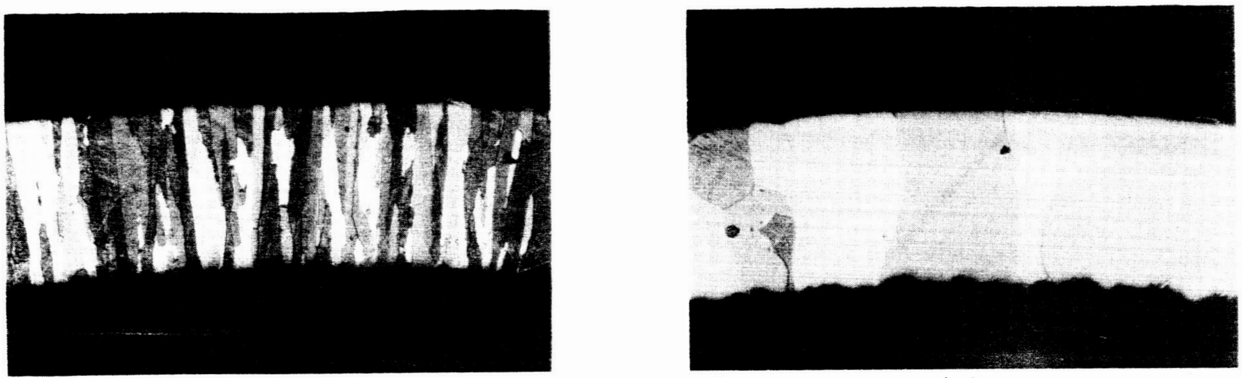


Figure 1

Ductile-to-brittle transition temperature as a function of fluorine content (vapor-deposited tubing). Data point identification refers to tube numbers as shown in Table 2; data point 16 is plotted with respect to chlorine rather than fluorine content.



M-8584-1 (a) 100X

Specimen Formed on Male Mandrel
After 1 Hr at 2500°C

M-8585-1 (b) 100X

Specimen Formed in Female Mandrel
After 1 Hr at 2500°C

COMPARATIVE CHEMISTRY OF ABOVE SPECIMENS

Element	Concentration (ppm)[a]	Concentration (ppm)[b]
C	6.2	6.4
O	6.5	11.5
N	5	4
H	3	4
F	9	4
Fe	<1	<1
Mg	0.5	0.5
Ni	N<1	<1
Si	<2	2

NOTE: No other metallic impurities were detected in either specimen by spectrographic analysis.

[a] Specimen shown on left above.

[b] Specimen shown on right above.

Figure 2

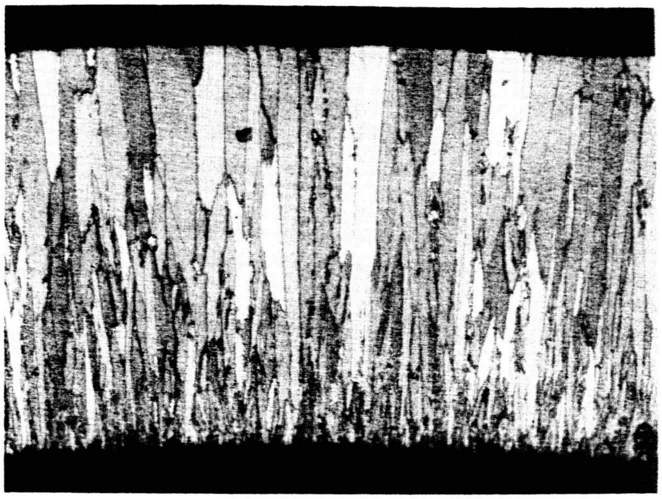
Illustration of Lack of Correlation Between Impurity Content and Grain Growth
Note that even though the impurity content is very similar the resistance to grain growth is quite different.

M-8600-1 100X

Figure 3

Grain Growth in 1/8 in. Diameter Tube After 1 Hr at 2500°C.

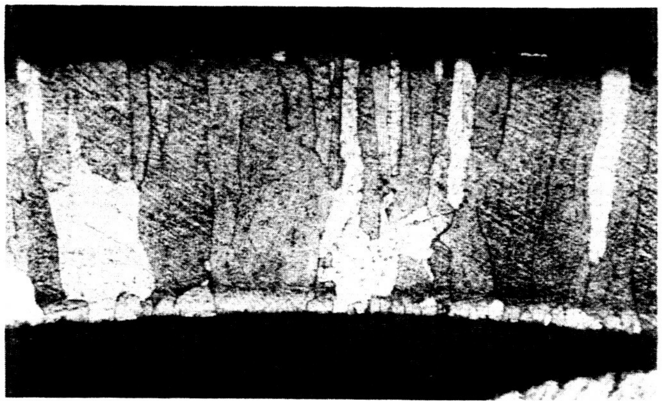
Note that the small equiaxed grains formed during initial stages of deposition have grown and are moving through the remainder of the specimen much like a wavefront.



(a)

M-9905-1 135X

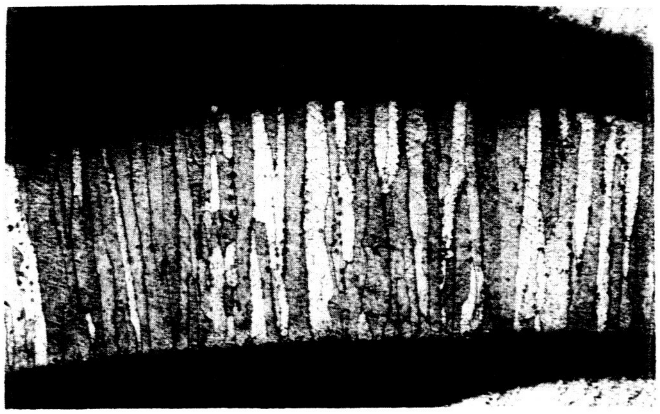
As Deposited



(b)

M-10035-1 135X

Not Electropolished
After 11 hr at 2500°C



(c)

M-10034-1 135X

Electropolished
After 11 hr at 2500°C

Figure 4

Influence of Electrolytically Removing the Layer of Fine, Randomly Oriented Grains on the Resistance to Grain Growth.