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Chemical Vapor Deposition of Hafnium Carbide

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Prepared by W. R. WILCOX, J. R. TEVIOTDALE, and R. A. CORLEY
Electronics Research Laboratory
for
Materials Sciences Laboratory
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Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
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21

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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04695-67-C-0158. It was prepared by the Electronics Research Laboratory at the request of the Materials Sciences Laboratory.

This report, which documents research conducted from January 1966 through July 1967, was forwarded for review and approval, on 25 October 1967, to Captain William D. Bryden, Jr., SMTRE.

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Approved

D. D. King, Director
Electronics Research Laboratory

W. C. Riley, Director
Materials Sciences Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

William D. Bryden, Jr., Capt.
Project Officer

ABSTRACT

Chemical vapor deposition of hafnium carbide yielded whiskers, needles, dendrites, faceted crystals, and adherent coatings. The gas stream compositions and the mass transfer conditions determined the habit of the deposit. The deposits were obtained at temperatures ranging from 1100 to 1800°C.

CONTENTS

TABLE

FIGURES

I. INTRODUCTION

Hafnium carbide has the highest melting point of any binary compound; therefore, its various potential applications are a subject of vital interest to the aerospace industry. The experiments described herein were performed as a means to investigate the chemical vapor deposition of hafnium carbide, with particular interest placed upon the possible production of high strength single crystal whiskers for composite materials.

In 1931 Moers[1] used a gaseous mixture of $HfCl_4$, H_2, and toluene to vapor-deposit crystalline hafnium carbide on a tungsten filament heated at 2400 to 2800°C. More recently Lepie[2] deposited hafnium carbide on graphite using $HfCl_4$ and methane in a He gas carrier.

The pyrolytic depositions described here were accomplished in graphite tubes and by the use of various gas mixtures and dopants. The resulting crystal habits included whiskers, needles, needle dendrites, bulbous dendrites, faceted crystals, and smooth, adherent polycrystalline layers.

II. EXPERIMENTAL PROCEDURE

The depositions were carried out on an induction-heated graphite tube, 1.2 cm i.d., which was contained in a vertical, 9 cm i.d. quartz tube. (The experimental details are summarized in Table I.) Refractory oxide fiber and tubes and graphite felt were utilized jointly and singly for thermal insulation. A typical temperature distribution is shown in Fig. 1. The reactant gases were introduced at the top and removed at the bottom of the tube.

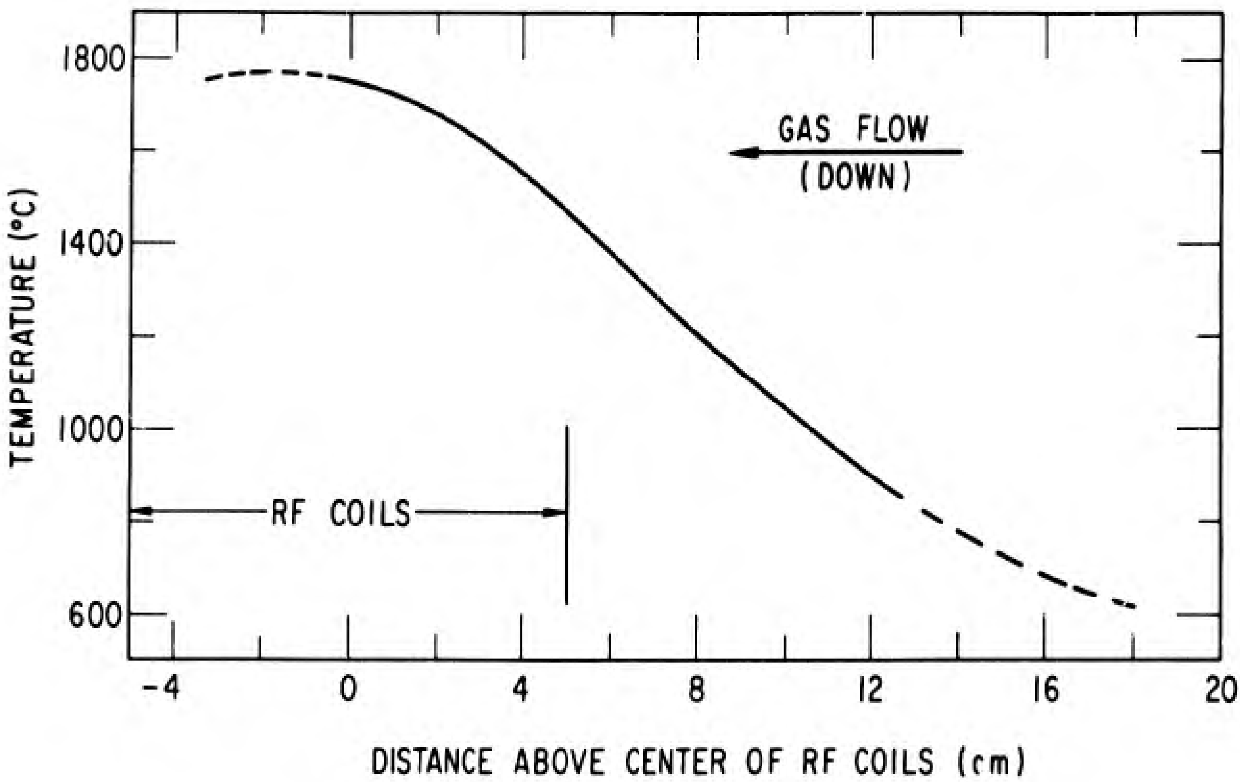

Fig. 1. Typical temperature profile in vertical induction-heated graphite tube. Taken with tungsten-rhenium thermocouple in center of tube.

Table I. Summary of hafnium carbide deposition experiments.

Run	Experimental arrangement	Reactants: SCFH[a] gas	Reactants: mm Hg[b] additive	Length of run (min)	Approx peak[c] temp. (°C)	Hafnium carbide products: Habits	Hafnium carbide products: Approx[d] position	Size (mm)	Hardness (Knoop no.)	Comments
A	C susc.[e]	0.5 He	12 $HfCl_4$	180	2000	Needles[i,j]				Melted Al_2O_3 tube
		0.1 H_2	37 toluene			Shiny globs[i]				
B	C susc.[e]	0.5 H_2	12 $HfCl_4$	75	1800	Needles[i,j]	C felt			
		0.1 He	6.3 toluene			Shiny globs[i]	C felt			
						Crystal octahedrons	C felt			
C	C tube h[f]	0.6 H_2	14 $HfCl_4$	165	1950	Needles[j]	4 cm on			
		0.2 H_2	6.3 toluene			Needle dendrites[k]	Al_2O_3 tube			
D	C tube c[g]	0.6 H_2	16 $HfCl_4$	165	1650	Thick, shiny coating[i,l]	5 cm			
		0.2 H_2	6.3 toluene			Needles[i,j]	5 cm			
						Needles[i,j]	5 cm on Al_2O_3 tube			
						Bulbous dendrites[i,m]	3 cm			
E	C tube c[g]	0.5 H_2	12 $HfCl_4$	270	1650	Thick, shiny coating[l]	5 cm	0.5	1750	Electron microprobe showed bulbous dendrites 15-32 at. % Hf
		0.05 H_2	6.3 toluene			Bulbous dendrites[m]	3 cm	0.5 x 0.7	600	
F	C tube c[g]	0.2 H_2	5.5 $HfCl_4$	240	1650	Very thin, metallic coating	1 cm	0.02		
G	C tube c[g]	0.4 He	11 $HfCl_4$	120	1650	Very thin, gold-colored, metallic coating	0 cm	0.08		> 20 wt % Hf by spectrochemical analysis
H	C tube c[g]	0.6 H_2	7.5 $HfCl_4$	[illegible]	1930	About the same as Runs D and E				
		0.2 H_2	6.3 toluene							
		0.8 H_2	---							
I	C tube e[h]	0.4 H_2	10 $HfCl_4$	120	1700	Thin, shiny coating[l]	6.1-6.9 cm	0.1		Black smoke in outlet
		0.1 H_2	6.3 toluene			Thin layer of bulbous dendrites[m]	5.3-6.1 cm			
		0.4 H_2	1 $AlCl_3$							
J	C tube e[h]	0.4 H_2	5.5 $HfCl_4$	60	1700	Very thin, shiny coating[l]	6.0-8.0 cm			
		0.1 H_2	6.3 toluene			Bulbous dendrites[m]	4.2-6 cm			
		0.4 H_2	0.55 $HgCl_2$							
K	C tube e[h]	0.6 H_2	10 $HfCl_4$	180	1700	Thick, shiny, bumpy coating[l]	6.7-9.5 cm			
		0.1 H_2	6.3 toluene			Thick deposit of bulbous dendrites[m]	3.5-6.7 cm			
		0.2 H_2	4.7 $VOCl_3$							
L	C tube e[h]	0.6 H_2	10 $HfCl_4$	150	1800	Faceted, rough crystals[n]	5 cm			Black smoke in outlet for P_{WCl_6} ≥ 16 mm Hg; spectrochemical analyses showed no W in these deposits
		0.2 H_2	6.3 toluene			Rough, grey needles, needle dendrites, and books[k]	3.5-4.5 cm	0.01 x 0.5	1590	
		0.1 H_2	60 WCl_6			Gold-colored, metallic globules	1.5 cm			
M	C tube e[h]	0.3 H_2	10 $HfCl_4$	60	1800	Thin, flaky coating[k]	9-11 cm			Dry Ar, black smoke in outlet, crystals bigger on edge
		0.1 H_2	6.3 toluene			Thin, smooth coating[l]	8-9 cm			
		0.4 Ar-10% HCl	---			Powdery deposit	7-8 cm			
						Faceted crystals of various habits[n]	4.5-7 cm			

[a] Footnotes appear at end of table.

Table I. Continued.

Run	Experimental arrangement	Reactants: SCFH[a] gas	Reactants: mm Hg[b] additive	Length of run (min)	Approx peak[c] temp. (°C)	Hafnium carbide products: Habits	Hafnium carbide products: Approx[d] position	Size (mm)	Hardness (Knoop no.)	Comments
N	C tube e[h]	0.3 H_2	15 $HfCl_4$	150	1800	Rough, grey coating[l]	4.8-6.4 cm			Dry Ar
		0.1 H_2	6.3 toluene			Thick deposit of needles & whiskers[o]	4-4.8 cm			
		0.4 Ar	---			Crystal flakes	3-4 cm			
						Rough, intergrown, polyhedral crystals[n]	2.5-3 cm	0.1	2500	
						Very small, faceted, shiny crystals	0.5-2.5 cm			
O	C tube e[h]	0.4 Ar	13 $HfCl_4$	160	1800	Short whiskers[o]	8-7 cm			Dry Ar, C deposited in needle matrix
		0.2 Ar	6.3 toluene			Needles[j]	6-7 cm			
		0.2 Ar	---			Coating[l]	9-10 cm			
P	C tube e[h]	0.2 He	24 $HfCl_4$	165	1800	Thin, bumpy, grey coating	4.8-6.3 cm			
		0.2 He	6.3 toluene			Thin, smooth, grey coating[l]	3.0-4.8 cm			
		0.4 He	---			Rough, intergrown, polyhedral crystals[n]	2.5-3 cm			
						Very small, shiny, faceted crystals	1.5-2.5 cm			
Q	C tube e[h]	0.4 He	10 $HfCl_4$	135	1800	Silver globular coating, loosely adhering	1.5-6.5 cm	0.5		Black smoke in outlet. C black deposited at 1 cm below coil center
		0.1 CH_4	(760 + CH_4)							
		0.8 He	---							
R	C tube e[h]	0.4 Ar	10 $HfCl_4$	120	1550	No deposit				Ar flush
		0.2 Ar	6.3 toluene							
		0.2 Ar	---							
S	C tube e[h]	0.4 Ar	10 $HfCl_4$	120	1800	Needle dendrites and books[k]	1-2.5 cm			Ar flush
		0.2 Ar	6.3 toluene			Very thin globular coating[l]	0-0.5 cm			Dry, O_2-free Ar
		0.2 Ar	---							
T	C tube e[h]	0.4 Ar	10 $HfCl_4$	120	1800	Shiny, crystal octahedrons[m]	3.3-4.6 cm	0.06		Not flushed, fresh $HfCl_4$; carbon in jog in tube
		0.2 Ar	6.3 toluene			Poly branched spikes[p] adjacent to above	3.8-6 cm	0.1 (length)		
		0.2 Ar	---							
U	C tube e[h]	0.4 Ar	0.07 $HfCl_4$	570	1800	Polycrystalline branched spikes[l, p]	0-2.5 cm 3-3.5 cm	0.2		Dry Ar, position of spikes depended on jog
		0.4 Ar	0.01 toluene			Bulbous dendrites[n]	2.5-6 cm			
		0.2 Ar	---							

[a]Uncorrected flow rates in standard cubic feet per hour as measured on rotameters at room temperatue and ~ 1 atm pressure. [b]As calculated from container temperature, known vapor pressure data, and assumption of gas saturated coming out. [c]For those positions given in "cm," temperature is that at center of coils; otherwise it is maximum temperature in deposition chamber. [d]Position given in "cm" correspo is to that on Fig. 1 and represents distance above center of rf coil. If no material given, deposit was found inside graphite tube. [e]2.5-cm-o.d. x 6.3-cm-long graphite susceptor on graphite pedestal, surrounded by graphite wool and alumina tube. [f]3.8-cm-o.d. x 35-cm-long graphite tube hanging from wires and surrounded by 4.4-cm-i.d. alumina tube and refractory oxide wool insulation. [g]3.8-cm-o.d. x 46-cm-long graphite tube with 1.2-cm hole drilled to below center of heat zone where four small exit holes intersect. Reactants introduced into top. Surrounded by zirconia or alumina tube and refractory oxide wool insulation. [h]Same as g above, except with 1.2-cm axial hole clear through to bottom end. [i]Samples positively identified as hafnium carbide by x-ray analyses. [j]Figure 7. [k]Figures 8 and 9. [l]Adherent layer, usually somewhat bumpy, Fig. 2 [m]Dull grey, bulbous dendrites, Figs 3 and 4 [n]Faceted polyhedral crystals with rough, grey surfaces, Figs. 5 and 6. [o]Figure 10. [p]Figures 11 through 14

Carrier gases were passed through powdered and liquid reactants in constant-temperature chambers. Originally, copper and brass were employed for these chambers and the gas lines. This resulted in a slight deposition of Cu in the upper portions of the reactor. Substitution of nickel and stainless steel (Run S) eliminated the Cu deposition but did not noticeably alter the deposition characteristics of the hafnium carbide.

The apparatus was thoroughly flushed with He before and during heating and prior to each deposition. The He had been passed over heated Ti chips to remove O_2 and H_2O. Except where otherwise noted, all other gases were only dried by being passed through Drierite and Aquasorb.

III. RESULTS

The experimental results, too, are summarized in Table I. The first depositions (Runs A, B, C) were carried out with the reactants passed external to the graphite rod and tube susceptors. Hafnium carbide deposition did not take place on the graphite, but in cooler portions of the apparatus. These deposits were difficult to separate from the other products—C, SiC, and Al_2O_3. Consequently, all subsequent runs were performed with the reactants passed down the inside of the graphite tube susceptor.

The next series of experiments were performed with roughly stoichiometric ratios of $HfCl_4$ to toluene (1:7) in hydrogen. The deposit was relatively insensitive to variations in flow rate, temperature, and reactant concentration (Runs D, E, H). Invariably a hard, bumpy, adherent coating (Fig. 2) of hafnium carbide formed about 6 cm above the center of the hot zone. This coating was attacked slightly by HF, thus indicating that it was carbon deficient. Immediately below there was a thick deposit of bulbous dendrites (Figs. 3 and 4). Electron microprobe analyses showed that these varied randomly in composition from 15 to 32 at. % Hf, thus indicating the presence of considerable excess carbon.

Various additives were employed in the hope of producing other growth habits: $AlCl_3$ (Run I), $HgCl_2$ (Run J), and $VOCl_3$ (Run K) had only slight effects. However, large quantities of WCl_6 caused a dramatic change (Run L). Near the top of the graphite tube, an excellent coating was

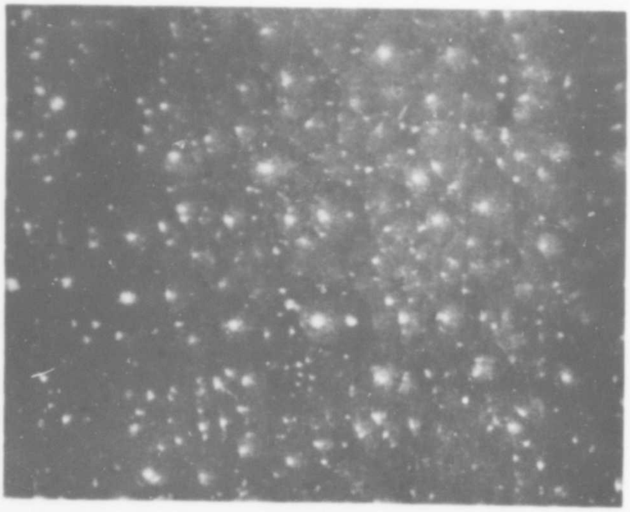

Fig. 2
Top view of coating from
Run E. 29X

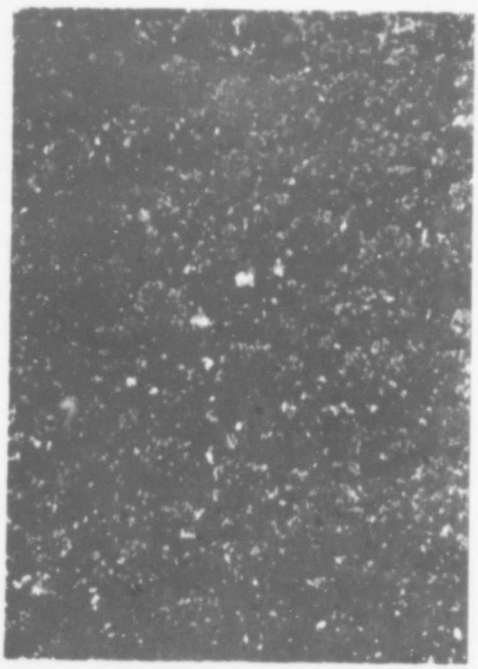

Fig. 3. Top view of bulbous dendrites from Run E. 11X

Fig. 4. **Bulbous dendrites from Run E (encapsulated in plastic; those on top partly polished off).** 29X

obtained. Spectrochemical analyses showed it to be tungsten carbide with only about 5 wt % hafnium present. Small, faceted hafnium carbide crystals (similar to the one in Figs. 5 and 6) were found 5 cm above the center of the rf coils. A large deposit of needles was below this. The needles were arranged separately (Fig. 7) and in dendritic clusters resembling books (Figs. 8 and 9). Spectrochemical analyses revealed no tungsten in the hafnium carbide deposits, thus making it doubtful that WCl_6 had any direct habit-modifying effect. Rather it appears that the deposition of tungsten carbide altered the gas composition, which caused the habit change.

As a result of the dramatic effect of WCl_6, a series of experiments (Runs M-U) were performed with a wide range of reactant gas compositions, but without added metallic halides (with the exception of $HfCl_4$). A wide variety of habits were obtained (Figs. 10 through 14). Clearly, inert gas encourages the formation of needles, whiskers, and faceted crystals. The reproducibility was poor however, and generalizations are difficult to make.

Mass transfer appears to be influential, as shown by Runs M, T, and U. In these runs the carbon rod was drilled off-center from both ends. The intersection of these nonconcentric holes resulted in ledges where both holes traversed the same position and in jogs where the holes ended. Much larger crystals grew on the edge formed by the intersection of the holes in Run M (see Fig. 5). The position of deposits differed appreciably in the adjacent holes in Runs T and U. In Run T large quantities of carbon were deposited in the dead space formed by a jog.

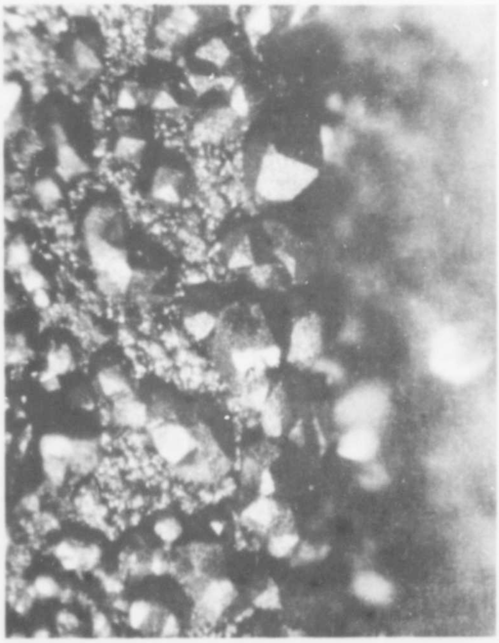

Fig. 5. **Crystals from Run M, on edge formed by intersection of nonconcentric holes.** 45×

Fig. 6. Crystals from Run N. 18×

Fig. 7
Hafnium carbide needles from Run L in situ (WCl_6 run). 45×

Fig. 8
"Books" from Run L *in situ*; made up of needle dendrites. 29×

Fig. 9
Hafnium carbide needle dendrites and crystal from Run L. 450×

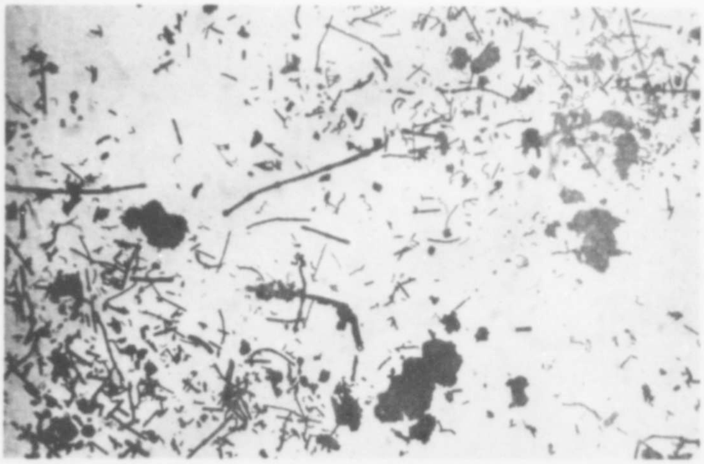

Fig. 10
Whiskers from Run O.
450×

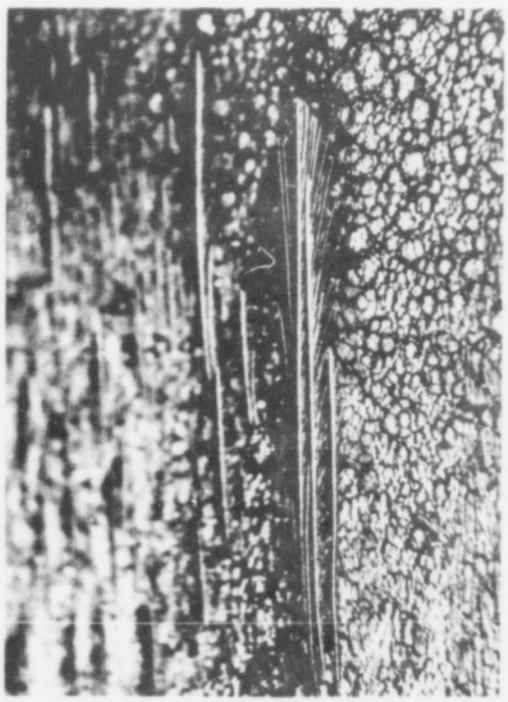

Fig. 11. Branched spikes from Run U, pointing upstream. 11×

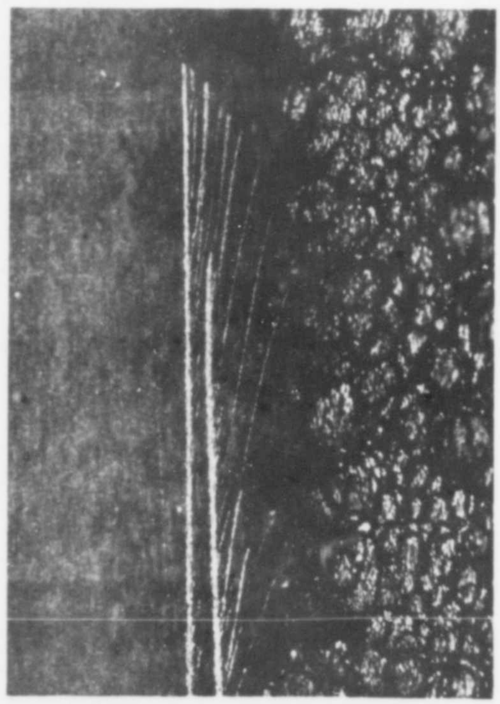

Fig. 12. Branched spikes from Run U. 29×

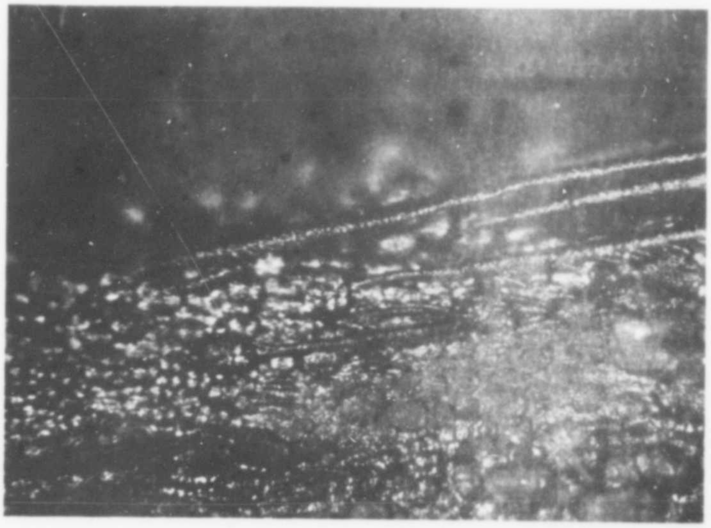

Fig. 13
View of origin of
branched spikes.
36X

Fig. 14
Branched spikes after etching in
Hf-HNO_3. 29X

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IV. CONCLUSIONS

It was shown that a wide variety of habits of hafnium carbide could be produced by variations in the gas composition. Depositions occurred at temperatures as low as about 1100°C. However, higher temperatures appear to be necessary somewhere in the deposition chamber (see Run R). Mass transfer conditions had a large influence on habit. Changes in gas composition during flow down the graphite cylinder probably are very significant.

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