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STUDY OF GROWTH PARAMETERS FOR REFRACTORY CARBIDE SINGLE CRYSTALS

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I INTRODUCTION

Interest in the refractory carbides has increased recently in anticipation of many new applications requiring the use of superrefractories. However, during the research and development work on these materials, difficulties have been encountered in attaining and reproducing desired physical properties. Little is known about ultimate intrinsic physical properties or about the influences of stoichiometric changes, impurities, and grain boundaries on these properties. In obtaining this type of information, single crystals of various carbide compositions would be of great value. At present, the only crystals readily available are of titanium carbide, grown by the Verneuil process, and little is known of their structure and perfection.

Stanford Research Institute has been engaged by the National Aeronautics and Space Administration to investigate the application of new techniques and procedures to the growth of single crystals of tantalum carbide, hafnium carbide, and solid solutions of these carbides. The new techniques being investigated fall into two classes: (1) a-c arc melting and induction plasma melting for Verneuil crystal growth; and (2) recently developed methods of liquid metal solution growth of crystals. Arc-Verneuil techniques are presently being studied. Forty nine crystal growth runs were made during this quarter.

Participating in the investigation during this period were J. W. Fowler (crystal growing experiments) and J. B. Saunders (X-ray analyses).

II SUMMARY AND CONCLUSIONS

Mixed solid solution boules have been grown with 40% hafnium carbide/60% tantalum carbide and 20% hafnium carbide/80% tantalum carbide starting powders. These boules were polycrystalline. There was little change in metal ratio for the 20/80 composition, but the hafnium content of the 40/60 composition was reduced to 35% of the total metal content. For both compositions the carbon content was reduced to approximately 45 at. %. Hydrogen in the furnace atmosphere had little effect on the carbon content.

A few long hafnium carbide boules were grown with large single crystal sections, as determined by X-ray diffraction. These boules were grown at rapid rates, 5-10 cm/hr, and contain subgrain boundaries. We believe additional boules of this type will be suitable after cutting, for evaluation of single crystal properties.

Several modifications to equipment and operating procedures were made to improve the quality of tantalum carbide boules. Preliminary analyses indicate that the carbon content of tantalum carbide boules has not been increased over that obtained in 10% H_2/90% Ar gas mixture using previous operating practices.

III CRYSTAL GROWTH STUDIES

A. Operation of the Arc-Verneuil Furnace

During this report period, a few minor changes were made in the arc-fusion crystal growth apparatus and some operating procedures were modified. Crystal growth experiments were run after each alteration to determine its effect on boule growth characteristics and crystal quality.

An interval timer was installed in the particle feeder circuit to lower the average particle feed rate. The feeder now has a variable on and off period within a brief cycle, which is continuously repeated.

Several crystal growth runs have aborted because the boule dislodged from the seed holder during growth. Small tantalum pins inserted vertically into the graphite anchor the carbide boule that is subsequently formed by dropping carbide particles onto the liquid cap of the tantalum pin. Gas turbulence surrounding the boule, gas evolution from under the tantalum pin, and flow of liquid tantalum contribute to dislodging the boule. The effect of the diameter and length of tantalum pins on retention of the boule was investigated after smaller diameter pins, substituted for the 1/8-inch pins originally used, were found to be unsatisfactory. Tantalum pins of 1/16-inch diameter melted below the boule and failed to secure it; however, pins of 1/8-inch diameter were satisfactory when longer than 3/4 inch. Shorter pins of 1/8-inch diameter tend to be ejected with the boule. Tantalum pins 1/8 inch in diameter by 1 inch long are now being used in all crystal growth experiments.

In an attempt to retard the preferred vaporization of carbon from tantalum carbide during crystal growth, the surface area of hot carbon surrounding the boule was increased. This was done by using larger electrodes and using a pyrolytic graphite heat shield. The horizontal

electrode diameter was varied between 1/4 inch and 1/2 inch. Power fluctuations caused frequent overloads and circuit interruptions when 1/2-inch electrodes were used, even though the power supply circuit breaker limit had been increased to 250 amps per horizontal electrode. The boules made when 1/2-inch electrodes were used were slightly larger in diameter, but no improvement in their carbon stoichiometry was obtained. Consequently, we have returned to the use of 1/4-inch and 5/16-inch electrodes.

A pyrolytic graphite heat shield has been designed and fabricated. It is a 2-inch diameter, thin-walled dome that surrounds the boule as shown in Fig. 1. Each of three windows cut in the side walls of the

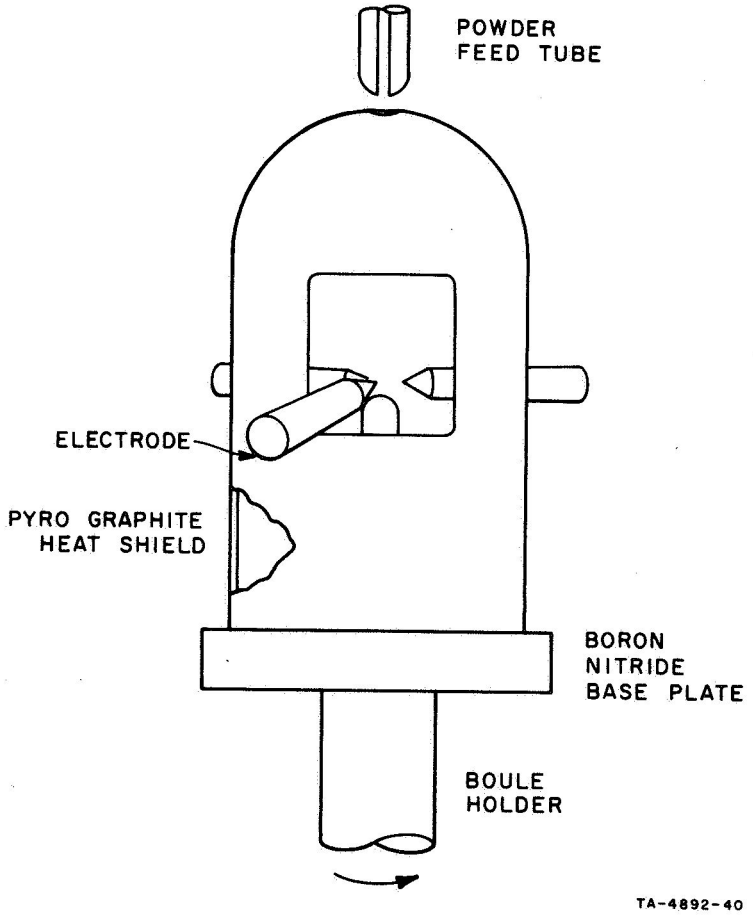

FIG. 1 PYROLYTIC GRAPHITE HEAT SHIELD

heat shield allows entrance of one electrode and provides a view of an alternate electrode. Observation of the electrodes is required to control the electrode stand-off distance. The heat shield rests on an insulating boron nitride platform that is attached to the seed holder. When the seed is rotated, the heat shield also rotates until the horizontal electrodes butt against the sides of the windows and prevent further rotation. This sequence properly aligns the heat shield window with respect to the outer observation ports in the furnace shell. A few short boules have been grown, but they have not yet been analyzed. During crystal growth the inside surface of the heat shield has a brightness temperature of 2300°C and the outside surface brightness temperature is 1650°C. Additional tests and analyses will be made in the next quarter.

The speed of rotation of boules was systematically studied. Some rotation is required to distribute heat evenly and compensate for any eccentricity in the deposition of particles on the boule. At excessive rotation speeds, a centrifugal oscillation or apparent whipping of the boule causes it to become eccentric with respect to the axis of rotation. The best rotation speed for the 1/4-inch-diameter boules is 10 to 16 rpm.

Five tantalum carbide crystal growth experiments were conducted in gaseous freon (F_2CCl_2) and freon-argon gas mixtures to investigate the feasibility of using freon to replenish carbon vaporized from the boule without introducing H_2 and H radicals into the plasma. These experiments showed that freon cannot be used to sustain an arc-plasma and that freon quenches argon plasmas as readily as hydrogen does. Arc stability could not be maintained unless the freon content of the gas was less than 5%. Carbon content of tantalum carbide boules was not significantly affected by this amount of freon when compared with 10% hydrogen in argon. Lattice parameter measurements indicate that the carbon content is about 43 at. %.

B. Solid Solution Hafnium Carbide/Tantalum Carbide Boules

Mixed carbide powders of 40% hafnium carbide/60% tantalum carbide and 20% hafnium carbide/80% tantalum carbide were received from Wah Chang Company. These powders were made by carburizing previously hydrided alloys of tantalum and hafnium. The chemical analyses of these mixed carbides and the current stocks of hafnium carbide powder and tantalum carbide powder are summarized in Table I.

Several boules of both mixed carbides were grown in argon and argon-hydrogen mixtures at a pressure of 1 atm. The boules were single phase but polycrystalline.

X-ray diffraction analyses and X-ray fluorescent analyses, with a LiF monochrometer, were used to determine changes in metal compositions and estimate carbon losses. Standard curves were made, plotting relative hafnium and tantalum X-ray fluorescent intensity (peak height/sum of peak heights for both hafnium and tantalum) versus the known metal composition of several carbides. The tantalum L_α and hafnium L_α fluorescent peaks were used. These curves, shown in Fig. 2, were made with the following starting powders: tantalum carbide, hafnium carbide, 40% hafnium carbide/60% tantalum carbide, and 20% hafnium carbide/80% tantalum carbide.

Lattice parameters were determined for these same materials using X-ray diffraction. These data, shown as closed circles in Fig. 3, conform reasonably well with a linear relationship between lattice parameter and composition for our starting powders of solid solution carbide mixtures. There was considerable line broadening of the 40% hafnium carbide/60% tantalum carbide, indicating incomplete homogenization of this starting material. Similar lattice parameter data by Deadmore[2] are shown as open circles in Fig. 3.

Fluorescent analyses of crushed boules are given in Table II. These analyses used the standard curves of Fig. 2. Although there was some loss of carbon in these boules, this is not expected to affect the metal analyses because of the low total carbon content and low X-ray absorption coefficient of carbon.

Table I

ANALYSIS OF CURRENT CARBIDE STARTING MATERIALS (ppm)
1 November 1966

Impurity	TaC	HfC	40% HfC 60% TaC	20% HfC 80% TaC
Al	<10	< 25	500	20
B	< 1	5	10	5
Cb(Nb)	<50	<100	490	--
Cd	< 1	< 1	< 1	< 5
Co	< 5	--	< 5	<10
Cr	15	175	<10	<20
Cu	<10	< 40	15	<40
Fe	70	520	380	150
Mg	<10	< 10	<10	<20
Mn	<10	< 10	<10	<20
Mo	<10	10	10	<20
Ni	<10	10	40	<20
O	179	2720	3400	790
Pb	< 5	< 5	< 5	<20
Si	30	< 40	30	<40
Sn	<10	< 10	<10	<20
Ta	--	<200	--	--
Ti	<10	175	<10	<50
V	<10	< 5	<10	<20
W	--	< 20	--	--
Zn	<10	--	<10	<50
N	132	--	55	35
C,wt.%	6.16	5.97	6.28	6.06
C,at.%*	49.5	47.5	50	48.6
Zr	<50	3.15 wt.%	--	--

* Apparent atom percent since free carbon is included.

Material	Wah Chang Lot No.
Tantalum carbide	SP106526B
Hafnium carbide	SP8662A
40% hafnium carbide, 60% tantalum carbide	SP86617A
20% hafnium carbide, 80% tantalum carbide	SP86615B

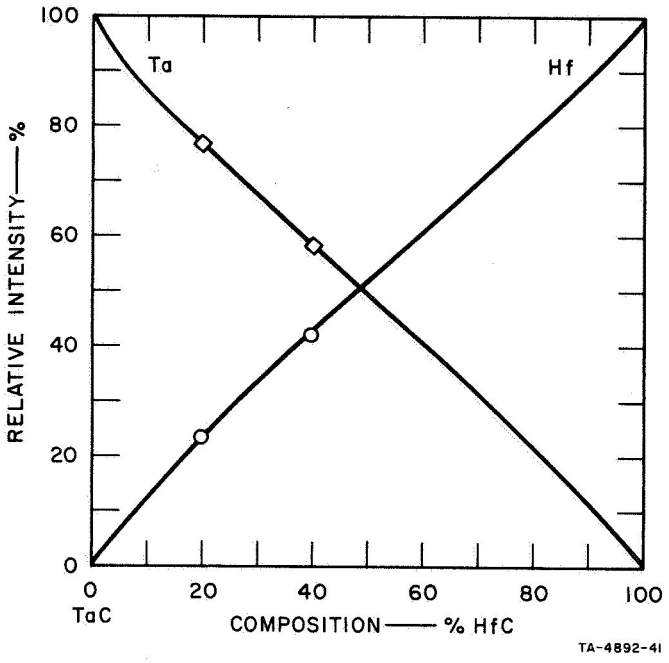

FIG. 2 RELATIVE X-RAY INTENSITY vs COMPOSITION FOR FLUORESCENT ANALYSIS OF MIXED CARBIDE SOLID SOLUTIONS

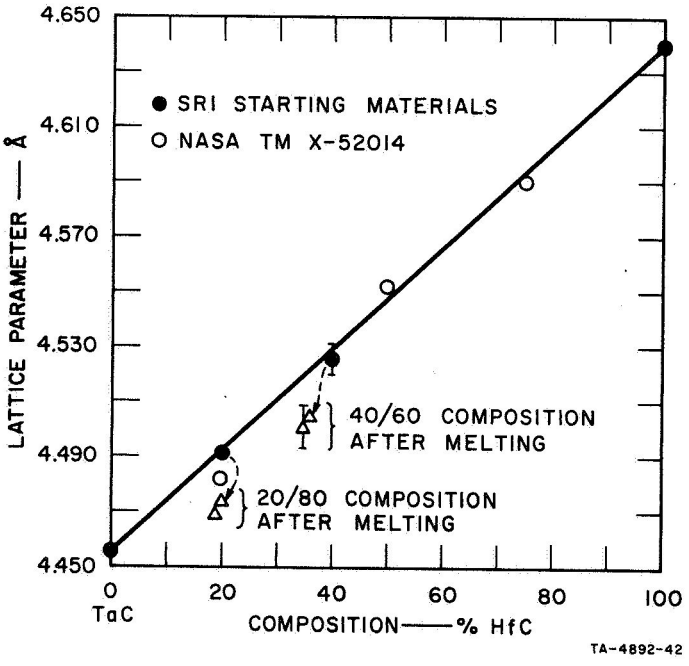

FIG. 3 LATTICE PARAMETER vs METAL RATIO FOR FULLY CARBURIZED MIXED CARBIDE SOLID SOLUTIONS

Table II

X-RAY ANALYSES OF MIXED CARBIDE BOULES

Carbide Powder Composition	Run No.	Atmosphere	Boule Metal Composition	
			%H_f	%Ta
40% HfC 60% TaC	9-30-2(66)	Argon, 1 atm	36	64
40% HfC 60% TaC	10-5-1(66)	10% H_2-Ar, 1 atm	35	65
20% HfC 80% TaC	10-6-1(66)	Argon, 1 atm	19	81
20% HfC 80% TaC	10-7-1(66)	5% H_2-Ar, 1 atm	20	80

It can be seen from Table II that the hafnium content in the 40/60 carbide decreased from 40% to about 35% of the total metal content of the boules, while the hafnium content of the 20/80 carbide did not change significantly. These data agree with the relative hafnium and carbon vaporization rates determined by Deadmore[2] for mixed hafnium carbide/tantalum carbide solid solutions. Deadmore's data are reproduced in Fig. 4. The hafnium and tantalum vaporization rates are almost equal at the 20% hafnium carbide/80% tantalum carbide composition, and therefore the metal ratio will not change while the compound is held at vaporizing temperatures. At the 40% hafnium carbide/60% tantalum carbide composition, the hafnium vaporization rate is significantly higher than that of tantalum, causing a reduction in the hafnium/tantalum ratio of the residual carbide upon heating to vaporizing temperatures.

For all compositions of these mixed carbides other than 100% hafnium carbide, the carbon vaporization rate exceeds the total metal vaporization rate and there is a net loss of carbon in the residue as a result of heating or boule growth. The carbon loss is accompanied by a reduction in lattice parameter (see Fig. 3). The change in lattice parameter with carbon content is unknown for $hafnium_x$ $tantalum_{1-x}$ carbide compounds, but can be inferred from a weighted average of similar data for hafnium

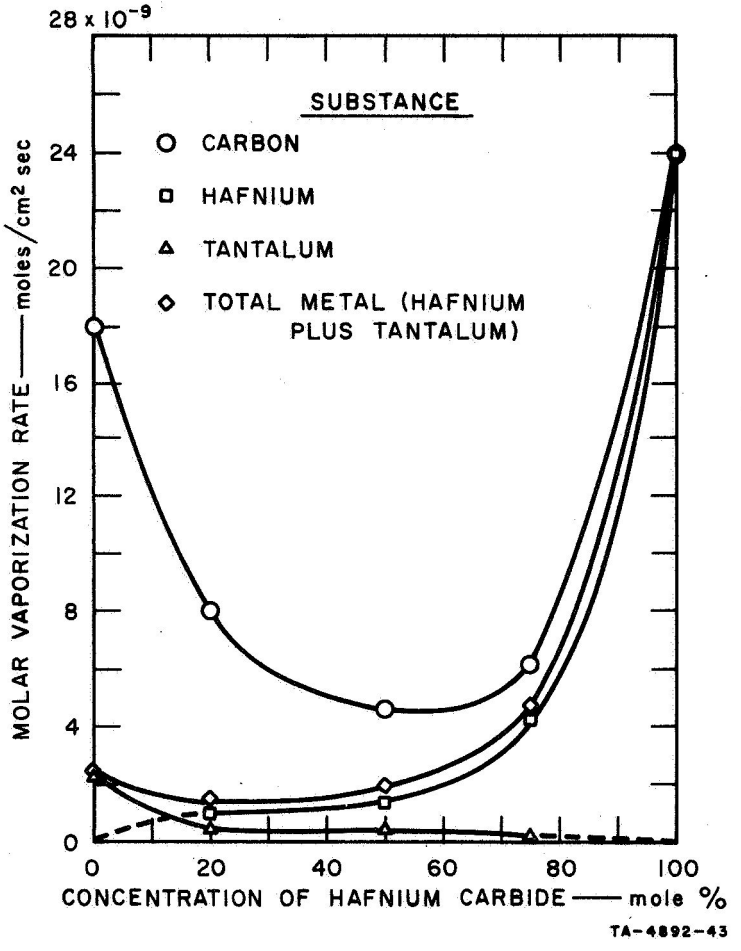

FIG. 4 MOLAR VAPORIZATION RATES OF CARBON, HAFNIUM, TANTALUM, AND TOTAL METAL (hafnium plus tantalum) FOR TANTALUM CARBIDE-HAFNIUM CARBIDE AT 2600°C IN VACUUM. Calculated from 20-hour sublimate compositions and instantaneous vaporization rate. (Deadmore)

carbide[3,4], and tantalum carbide.[5,6,7] This comparison indicates a carbon content of 45-47 at. % for the 20/80 carbide boules and 44-46 at. % for the 40/60 carbide boules. Hydrogen in the atmosphere during crystal growth has little effect on either the carbon content or metal ratio of the mixed carbide boules.

C. Grain Boundaries in Arc-Verneuil Boules

Complete elimination of grain boundaries is the major obstacle to growth of satisfactory single crystals. The largest boundary-free sections have been obtained with hafnium carbide. On the average, the mixed carbides have been slightly less coarse-grained than tantalum carbide. However, there are considerable differences between several boules of the same material. Grain boundaries are eliminated during formation of the boule by a gradual expansion in cross section of the dominant grains, in the classical manner for flame fusion crystal growth. However, new grains are occasionally nucleated both at or near the surface and internally. In cross section, the surface grains appear as isolated semicircles and the internally nucleated grains appear as a broad root spreading out from the nucleation point as the grain grows upward. The initial tip of an internal grain nucleated in a hafnium boule is shown in Fig. 5. This new grain grew to be about 1/8 inch across.

There is no evident relationship between impurity content and grain size of boules. The largest grains were obtained with hafnium carbide, one of the least pure starting powders. Good boules have been obtained from collected excess hafnium carbide powder put through the crystal growing furnace a second time without being cleaned after the first run.

Studies of boule cross sections were made to secure information on the configuration of the liquid cap. When the arc discharge is terminated during crystal growth, the molten cap quickly solidifies. A fine-grained structure results that contrasts sharply with the coarse-grained or single crystal boule below the molten cap. The change in grain size indicates the location of the liquid/solid interface when the arc is

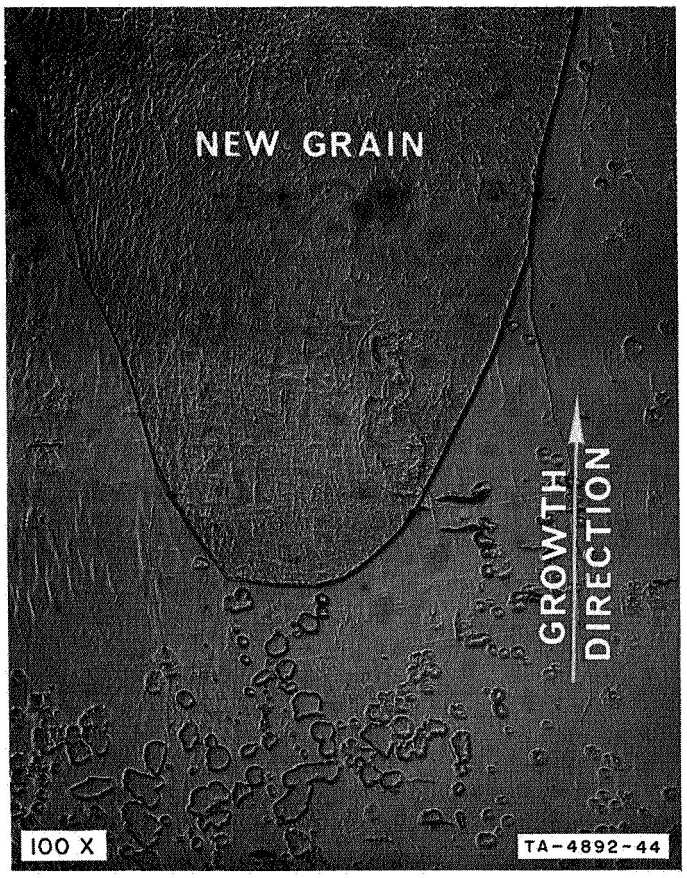

FIG. 5 NUCLEATION REGION FOR GROWTH OF NEW GRAIN IN HAFNIUM CARBIDE, (100X)

quenched. On this basis, molten caps on 1/4-inch-diameter boules are judged to be 1 to 2 mm deep. A photograph of a typical quenched cap is shown in Fig. 6.

There has been no metallographic evidence of carbide particles being trapped in the boule without melting. Nevertheless, nucleation of new grains may be caused by carbide particles settling to the liquid/solid interface before melting or dissolving in the liquid carbide cap. These particles could act as nuclei for growth of new grains and would not appear in their original size when the boule is cross-sectioned. This problem may be increased when a carbon-deficient molten carbide cap is present with a lower liquidus temperature than the melting point of the stoichiometric carbide particle. This consideration may explain

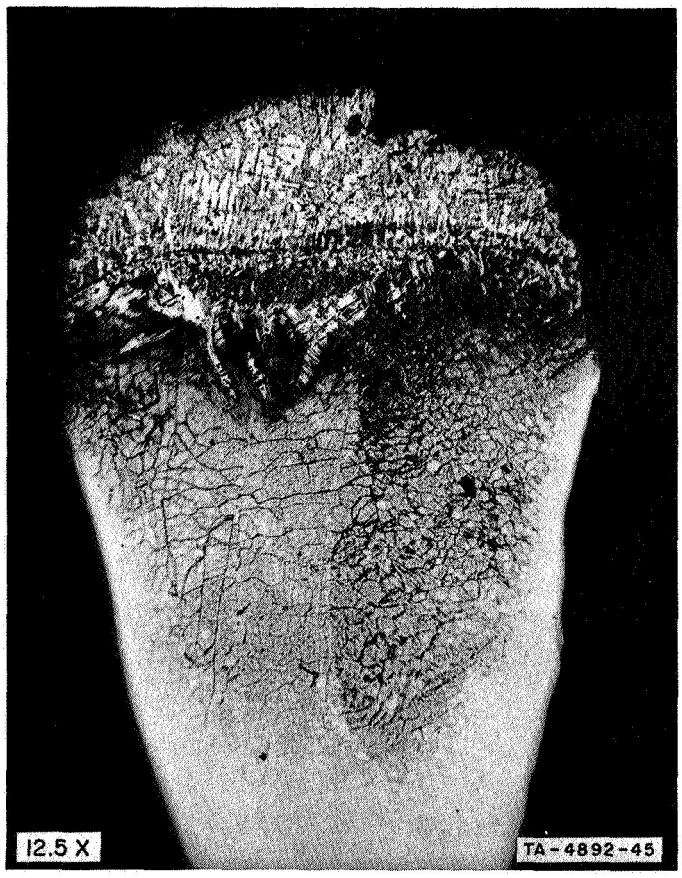

FIG. 6 CROSS-SECTION OF TANTALUM CARBIDE BOULE INDICATING REGION OF MOLTEN CAP (12.5X)

the larger grain sizes obtained with 100% hafnium carbide, since there is not a disproportionate carbon loss from the liquid and associated reduction in liquidus temperature when this carbide composition is melted. A series of growth experiments, using different particle sizes but in all other respects identical, is being conducted to determine if there is a relationship between particle size and subsequent grain size that could be related to nucleation of new grains by unmelted particles. Particle sizes of -200 +325 mesh, -270 +325 mesh, and -325 mesh are being used. The tests with hafnium carbide have been completed and showed no effect. Tests on tantalum carbide remain to be done.

Some settling calculations have been made for tantalum carbide particles entering the liquid cap. Table III lists estimated particle entering velocities that will yield a particle penetration of 1 mm before viscous drag arrests the particle motion. Further gravity settling may occur if the solid carbide has a higher density than the liquid. Estimates of actual particle velocities at impact with the liquid cap are now being calculated.

Table III

TANTALUM CARBIDE PARTICLE ENTERING VELOCITY REQUIRED TO PENETRATE 1 mm IN LIQUID TANTALUM CARBIDE, ASSUMING μ = 0.01 poise

Particle Size	200 mesh	270 mesh	325 mesh
Particle Velocity	23 cm/sec	44 cm/sec	65 cm/sec

The growth rate of boules has been varied over a range of 1 to 10 cm/hour. The fewest grain boundaries have been obtained with long boules grown at fast rates, 5-10 cm/hr. Some of these boules have lengths exceeding 3 inches. We will attempt to produce several of these boules in the next quarter. Subgrain boundaries usually appear after polishing hafnium carbide sections that, by X-ray diffraction, are single crystals. The X-ray diffraction test consists of a series of back reflection Laue photographs taken at various steps across the cut boule. The subgrain boundaries are not apparent in diamond sawcut material, while primary grain boundaries can be detected after diamond cutting. The subgrain boundaries often end within the boule and their depth of etching often changes abruptly. Examples of subgrain boundaries in hafnium carbide single crystal sections are shown in Fig. 7.

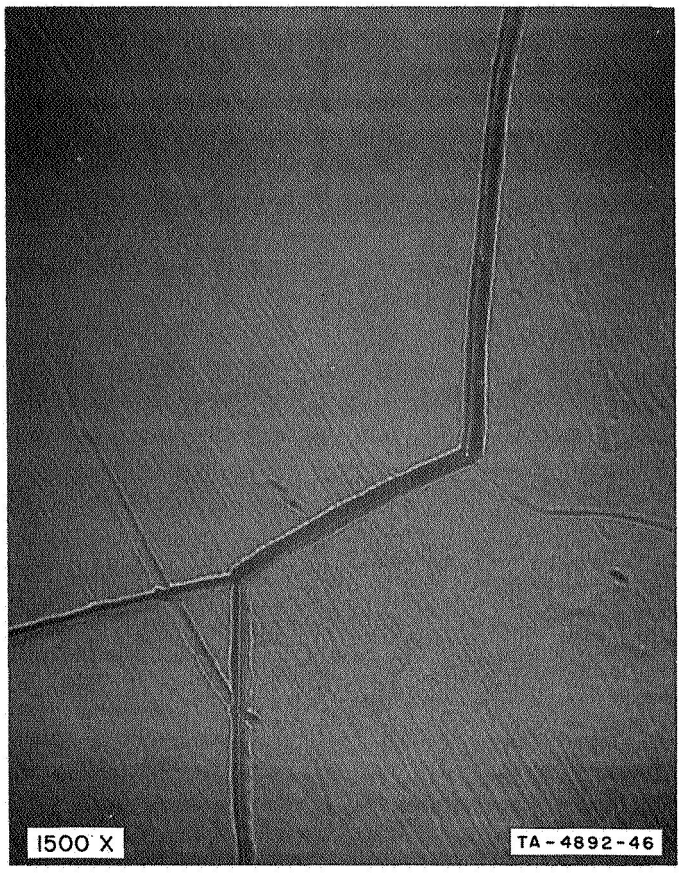

FIG. 7 SUBGRAIN BOUNDARIES IN SINGLE CRYSTAL OF HAFNIUM CARBIDE (1500X)

IV FUTURE WORK

Future work will include the following: (1) growth of long hafnium carbide boules at relatively high speed for sectioning and delivery to NASA; (2) continuation of experiments to evaluate the effect of the pyrolytic graphite shield (dome) on crystal growth; and (3) determination of particle size effects, if any, on average grain size for tantalum carbide boules.

REFERENCES

1. Deadmore, D. L., Vaporization of Tantalum Carbide-Hafnium Carbide Solid Solutions at 2500° to 3000°C, NASA TM X-52014 (1964).

2. Deadmore, Daniel, Influence of Time on Vacuum Vaporization Rate and Surface Compositional Stability of Tantalum Carbide-Hafnium Carbide Solid Solutions above 2000°C, NASA TN D-3503 (1966).

3. Cotter, P. G., and J. A. Kohn, Industrial Diamond Substitutes: I, Physical and X-ray Study of Hafnium Carbide, J. Am. Ceram. Soc., 37, 415 (1954).

4. Sara, R. V., and C. E. Lowell, Research Study to Determine the Phase Equilibrium Relations of Selected Metal Carbides at High Temperatures, Tech. Doc. Rept. No. WADD TDR-60-143, Part V, Contr. No. AF33(657)-8025, S1, Oct. 1964.

5. Sara, R. V., C. E. Lowell, and R. T. Dolloff, Research Study to Determine the Phase Equilibrium Relations of Selected Metal Carbides at High Temperatures, Tech. Doc. Rept. No. WADD TR 60-143, Part IV, Contr. No. AF 33(657)-8025, Feb. 1963.

6. Bowman, A. L., The Variation of Lattice Parameter with Carbon Content of Tantalum Carbide, J. Phys. Chem., 65, 1596 (1961).

7. Lesser, R. V., and G. Brauer, Karbidphasen des Tantals, Zeitschrift für Metallkunde, 49, 622 (1958).