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STUDY OF GROWTH PARAMETERS FOR REFRACTORY CARBIDE SINGLE CRYSTALS

By: R. W. Bartlett

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F. A. Halden

F. A. Halden, Director
Ceramics and Metallurgy Division

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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.

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

During this reporting period the arc-Verneuil crystal growing furnace was operated using tantalum carbide, hafnium carbide, and mixtures of these carbide powders. None of the boules grown were single crystals throughout.

Dense stoichiometric boules of hafnium carbide were grown in one atmosphere of argon. Some of these boules contained only a few grain boundaries, and single crystal sections were cut from one of these boules. The tantalum carbide boules were carbon-deficient but substantially free of Ta_2C. Boules grown with physical mixtures of hafnium carbide and tantalum carbide particles were nonhomogeneous.

Carbon enrichment experiments employing solid state diffusion of carbon into tantalum carbide boule wafers were conducted. The orientation of grains in tantalum carbide boules was also studied using the Laue X-ray diffraction method. The primary difficulty preventing growth of acceptable single crystals of both refractory carbides is the elimination of grain boundaries during growth.

Author

III CRYSTAL GROWTH STUDIES

A. Arc-Verneuil Apparatus

Operating difficulties have been encountered with the crystal growing furnace because of arc extinguishment in atmospheres containing hydrogen. In principle, a high frequency arc-stabilizing circuit can be superimposed on the low frequency power supply circuit of the crystal growing furnace to ensure that the arc will not extinguish under marginal operating conditions. A comparatively large high frequency and high voltage generator is required to overcome the parasitic capacitance of the electrode holder (160 picofarads). A BC-610 E radio transmitter capable of operating at 350 watts was adapted for use at a frequency of 2 Mc to stabilize one of the three horizontal electrodes of the crystal growing furnace. With this power supply, the high frequency voltage drop across the arc was approximately 200 volts. This was an improvement over the immeasurable voltage obtained with the 10-watt oscillator power supply previously used as an arc-stabilizing circuit. However, a 200-volt potential across the electrode gap is not a significant improvement over the 30-volt potential imposed by the low frequency main arc power supply and is only of marginal value in stabilizing the arc plasma. After installation, the BC-610 generator was used for the growth of several tantalum carbide boules. Eventually its use was discontinued because of its marginal effect on crystal growth.

An improved system for viewing the boule during growth was installed to aid the operator in more precisely controlling the location of the boule with respect to the horizontal plane of the electrodes. A convex objective lens is used to project an enlarged image of the boule on a screen on which an orthogonal coordinate grid is superimposed. The top of the boule can now be held within 0.2 mm of a predetermined position.

B. Tantalum Carbide Experiments

During the early part of the quarter, several tantalum carbide boules were grown having various lengths up to 1-3/4 inches, but none of them was a single crystal. Gas mixtures of 5 to 10% hydrogen in argon at a total pressure of 0.5 atm were used. Very little second phase Ta_2C appeared in these boules, but occasionally some Ta_2C formed near the surface-decarburized zone and occasionally a small amount of Ta_2C could be seen decorating grain boundaries. Grain boundaries tended to be columnar in the direction of crystal growth.

Boules were also grown using a particle feed mixture of tantalum carbide and graphite powders in an attempt to improve the carbon ratio of the resulting crystals. Crushed graphite, -270 +325 mesh, was mixed with tantalum carbide powder. No improvement in the carbon content of the boules resulted from these tests. Because of the low density and slow settling rate of the graphite particles, very few of them may have come in contact with the boule. Flow meters were changed to permit more rapid flow of gas through the injection tube carrying feed particles to the boule but this did not affect the carbon content. Since no improvement in the carbon stoichiometry was obtained in these experiments, further crystal growth studies employing mixtures of graphite and tantalum carbide have been deferred.

Several crystal growth experiments were run in which the top of the boule cap was held at different locations in relationship to the plane of the electrodes. If the cap rises above the electrode plane, a necking or pinching effect occurs on the hemispherical cap which tends to draw up a thin quasi-extruded region in the center of the cap. We are uncertain as to the cause of this effect but believe it is a result of the hot gas streaming upward from the electrodes over the surface of the boule. This jet is the result of a pressure generated by the arc discharge heating the gas environment, and it tends to draw the liquid cap along with the jet. If the neck of the boule becomes too long it will topple over, often touching one of the electrodes. If the boule is lowered, the neck melts back into a hemispherical cap. The

most stable melting conditions occur when the cap is slightly below the plane of the electrodes.

One of the boules cross sectioned normal to the direction of growth was examined by Laue back reflection X-ray techniques. This boule had a large central single crystal core surrounded by several smaller grains. By using a goniometer, the central crystal was found to be oriented with its (100) plane close to perpendicular with the growth direction. The boule was oriented slightly off of the growth axis to bring the (100) plane of the central crystal perpendicular with the incident X-ray beam. The resulting diffraction pattern is shown in Fig. 1a. Using this fixed orientation of the boule, with respect to the incident X-ray beam, the boule was translated in a direction normal to the incident beam so that a series of back reflection Laue photographs could be taken at various stations across the boule. The diffraction pattern of the grain adjacent to the central core on the right side is shown in Fig. 1b. This diffraction pattern was indexed with an (833) orientation, which is very close to a (311) orientation. The angle between the (100) and (833) planes is 27.7°, which is far too large to permit classifying the boundary as a subgrain boundary. However, in this case the (833) grain has a special relationship to the (100) grain. The (833) orientation can be obtained by a 27.7° rotation of the (100) grain about the $[0\bar{1}1]$ axis which is perpendicular to the growth direction. Note the identical symmetry of both photographs in Fig. 1 with the $[0\bar{1}1]$ axis slightly tilted from a horizontal alignment. Similar preferred orientation effects based on rotation about $[0\bar{1}1]$ were observed with the other crystals adjacent to the central core.

Some experimental studies were undertaken to increase the carbon content of carbon deficient tantalum carbide boules by a post-growth treatment. Boules grown earlier in this investigation that had been cross sectioned longitudinally and showed evidence of Ta_2C precipitation throughout the boule were cross sectioned in the transverse direction to provide wafers approximately 1/16 inch thick. The wafers were surrounded with graphite powder and subjected to diffusion anneals at $2000^{\circ}C$ in argon or vacuum. Although the rate of diffusion of carbon

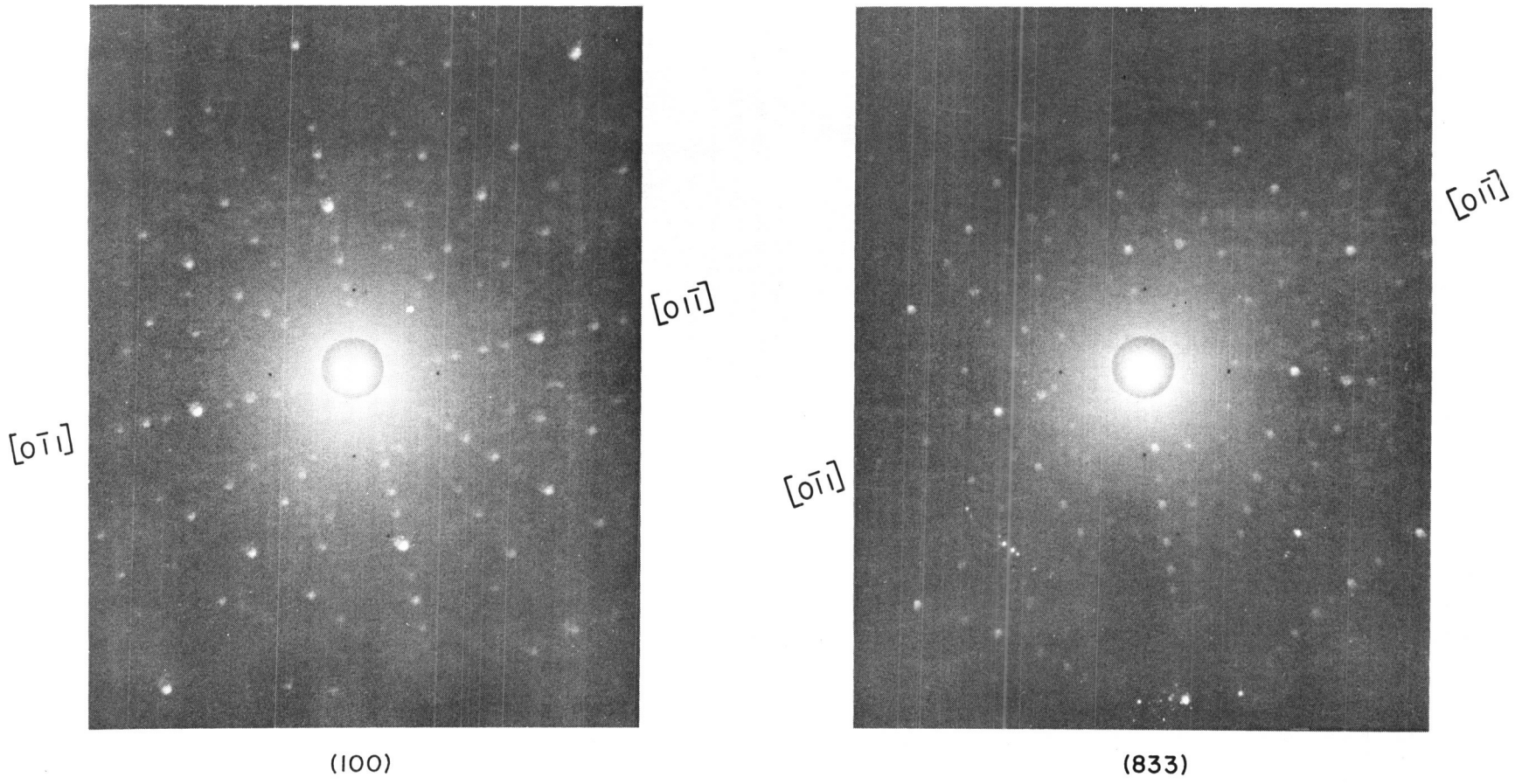


FIG. 1 LAUE (BACK REFLECTION) X-RAY DIFFRACTION PATTERNS FROM ADJACENT GRAINS IN A TaC BOULE — GRAINS ARE ORIENTED BY ROTATION 27.7° ABOUT [0$\bar{1}$1]

in TaC at this temperature was expected to be very slow, the amount of carbon needed to compensate for the Ta_2C was very small. The results of a 24-hour test at 2000°C are shown in Fig. 2. Evidence that Ta_2C has been removed from most of the polycrystalline TaC wafer is shown by the micrographs obtained after cross sectioning the diffused wafers. The subcarbide, Ta_2C, was restricted to a few crystals in the central core region, which appears as the light colored region in the dark field micrograph (Fig. 2-15X). A light field enlargement of this region is shown in the bottom of Fig. 2.

Precipitation of the Ta_2C phase can usually be controlled during crystal growth with the hydrogen/argon ambient atmosphere. The diffusion experiments indicate that if single crystal boules can be grown in atmospheres that contain little, if any, hydrogen it may be possible to back-diffuse carbon to remove all the Ta_2C by reaction to form additional TaC. However, this step would probably generate many imperfections in the crystal and might even cause recrystallization to occur. The primary problem with tantalum carbide crystal growth remains one of getting grain boundaries to grow laterally to the growth direction so a preferred-orientation crystal can predominate and lead to the elimination of grain boundaries with further growth of the boule.

C. Hafnium Carbide Experiments

Hafnium carbide powders and mixed hafnium carbide/tantalum carbide powders suitable for use in crystal growing experiments were not delivered on July 1 as expected. Wah Chang Corporation was unable to produce carbide particles large enough to meet the desired size specifications, -200 +325 mesh, with their conventional synthesis techniques. An alternate technique employing hydrogen annealing to form hydrides of hafnium and hafnium/tantalum solid solutions was employed. The hydride powders were sieved to select a size fraction which was subsequently carburized at high temperatures to produce carbide powders in the desired size range. The hafnium carbide powders were received in late August and the mixed solid-solution carbide powders had not been received at the end of the report period. An analysis of the hafnium carbide

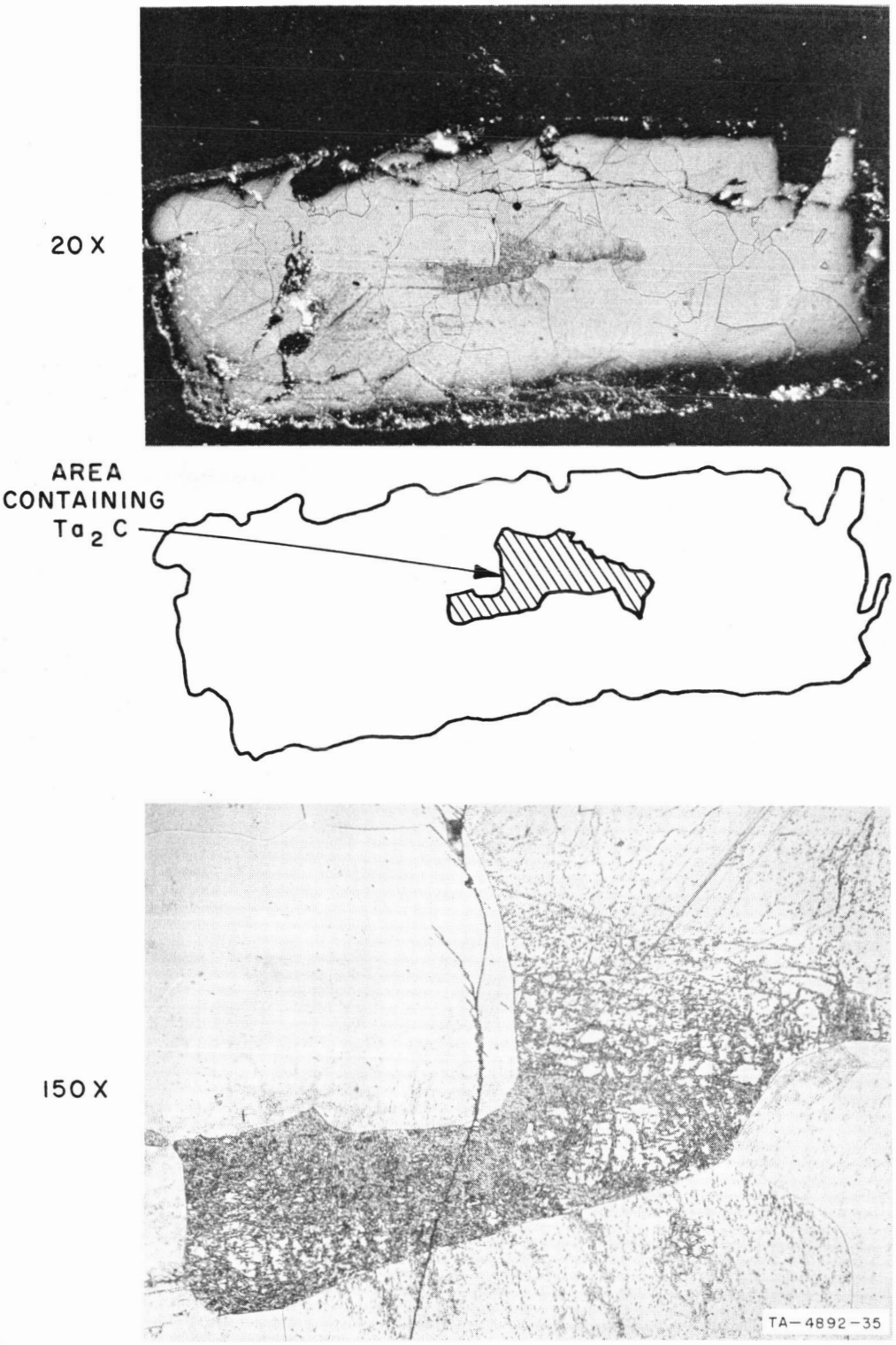


FIG. 2 CARBON DIFFUSION INTO CARBON DEFICIENT TANTALUM CARBIDE BOULE ORIGINALLY CONTAINING Ta_2C PRECIPITATES, 24 HOURS AT 2000°C

powder is given in Table I. The oxygen and iron contents are unusually high and the zirconium content is higher than is usually obtained for reactor grade hafnium carbide. The carbon content is 5.97 wt %, or 47 at. %, which is quite good if all the carbon is present as a monocarbide phase rather than as free carbon.

Table I

EMISSION SPECTOGRAPHIC ANALYSIS OF HAFNIUM CARBIDE POWDER

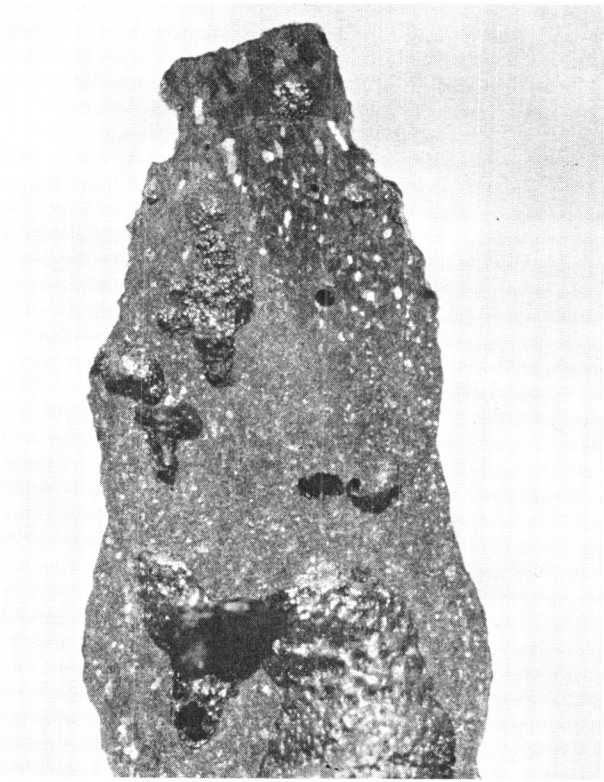
Wah Chang Lot SP 8662 A

Material	ppm
Al	<25
B	5
Cb	<100
Cd	<1
Cr	175
Cu	<40
Fe	520
Mg	<10
Mn	<10
Mo	10
Ni	10
O	2720
Pb	<5
Si	<40
Sn	<10
Ta	<200
Ti	175
V	<5
W	<20
C	5.97%
Zr	3.15%

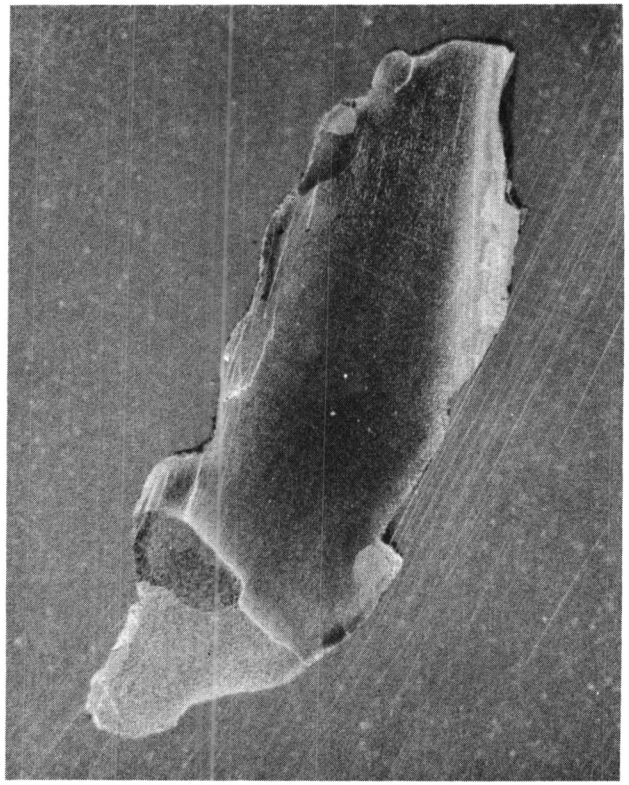
Before the -200 +325 mesh Wah Chang hafnium carbide was received, experiments using hafnium carbide of finer mesh sizes were conducted in the crystal growing furnace. The initial experiments were conducted with -325 mesh hafnium carbide which proved to be too fine. Most of the particles were scattered by the convective currents in the vicinity of the arc. Later, hot-pressed hafnium carbide was crushed and sieved to yield a -270 +325 mesh fraction which worked quite well in the crystal growing furnace.

Several experiments were conducted with this material to determine the optimum gas composition and total pressure for growing crystals. The results have shown that gas composition is not a critical factor in controlling the stoichiometry of hafnium carbide. Both constituents of hafnium carbide vaporize readily (see Quarterly Status Report III), but at approximately the same rate, leaving a residue with the desired metal-carbon ratio. Liquid hafnium carbide readily boils in vacuum, and the first boules produced in mixtures of hydrogen and argon having total gas pressures below 1 atm were very porous. The liquid cap became more quiescent as the total pressure was increased, and thus far the best results have been obtained at 1 atm of argon. X-ray lattice parameter measurements indicate that the hafnium carbide boules grown under these conditions have the maximum allowable carbon content of the monocarbide phase. Furthermore, metallographic examination did not reveal any free carbon in the boules examined. In Fig. 3 one of the early hafnium porous carbide boules is compared with a boule grown in 1 atm of argon which is free of voids. No difficulties are presently being encountered in growing void-free hafnium carbide boules.

Improvements in the external shape of hafnium carbide boules were made during this period using both the older lot of crushed and sieved hafnium carbide and a new lot of hafnium carbide powder, the composition of which is summarized in Table I. A hafnium carbide boule is shown in Fig. 4. The only major problem associated with growing hafnium carbide single crystals is the presence of grain boundaries within the boules. The boules are usually composed of a few large longitudinal grains aligned in the growth direction. In this respect the growth of hafnium carbide boules is very similar to the growth of tantalum carbide boules. All the boules grown thus far have been sectioned and examined for grain boundary content. Grain boundaries can be seen in the as-cut condition without polishing. Two small hafnium carbide sections have been cut out of a large grain of one boule. From polishing and inspection of the two major sides, these pieces appear to be single crystals of hafnium carbide.



POROUS, 10X



DENSE, 5X

TA-4892-36

FIG. 3 POROUS AND NONPOROUS HfC BOULES

FIG. 4 ARC-VERNEUIL HAFNIUM CARBIDE BOULE

Two crystal growth experiments were conducted in which a mixture of 50 wt % hafnium carbide and 50 wt % sodium chloride powders were fed onto a growing boule. The purpose of these experiments was to determine what effect chlorine had on the vapor transfer of hafnium away from the boule and to determine if seeding the arc plasma with a source of sodium vapor, which is easily ionized, had any effect on the stability of the arc. Sodium chloride did not affect the stoichiometry of the hafnium carbide boules resulting from these experiments. Because of the small volume of the arc region and the discrete injection of NaCl particles, it was not possible to maintain a continuous presence of sodium vapor in the arc. Consequently the use of sodium chloride had no lasting effect on stabilizing the arc.

D. Mixed HfC and TaC Experiments

A few attempts to grow mixed solid-solution HfC and TaC boules were made by heating a mixture of tantalum carbide particles physically mixed with hafnium carbide particles. Multiple diffraction peaks and spreading of the diffraction peaks for each diffracting (hkl) plane were observed when these boules were examined in the Norelco diffractometer. These results indicate that the boules were nonhomogeneous and that homogeneous solid-solution carbide crystals can only be grown by starting with feed particles that are also homogeneous. The atmosphere in which the boules were grown had a marked effect on their composition and homogeneity.

A powder feed mixture of 54% tantalum carbide and 46% hafnium carbide was used for the following experiments. The boule grown in 100% argon at 0.5 atm was examined by X-ray fluorescence and found to contain 80% tantalum carbide and 20% hafnium carbide. X-ray diffraction yielded four widely separated peaks for each (hkl). When the experiment was run in a hydrogen and argon mixture (95% argon and 5% hydrogen) at 0.5 atm, the tantalum hafnium ratio was much closer to the original composition. X-ray fluorescence indicated a metal ratio of 64% tantalum and 36% hafnium. Only two diffraction peaks occurred for each (hkl) plane, and these could only be resolved in the back reflection region (333).

The indicated compositions represented by these two peaks and based on an assumed regular monocarbide stoichiometry, i.e., not deficient in carbon, were 68% tantalum carbide and 73% tantalum carbide, respectively. Thus the boule grown in a partial hydrogen atmosphere is much more homogeneous than the boule grown in argon. The agreement between the carbide ratios estimated from X-ray diffraction and the metal ratios estimated from X-ray fluorescence is reasonably close. The two X-ray techniques are only quasi-quantitative at best and not sufficiently sensitive to be used to estimate the actual carbon content in the mixed solid-solution carbide.

IV FUTURE WORK

Mixed solid-solution carbide powders are expected to be received from Wah Chang Corporation in the very near future. Compositions ordered are 80% tantalum carbide/20% hafnium carbide and 60% tantalum carbide/40% hafnium carbide, in the sieve fraction -200 +325 mesh. Experimental crystal growth will commence using these powders when they are received. Gaseous freon (F_2CCl_2) has been received and will be tested as an atmosphere for the growth of tantalum carbide boules.