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Single-Crystal Growth of Group IVB and VB Carbides by the Floating-Zone Method

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C. B. Finch, Y. K. Chang, and M. M. Abraham
Solid State Division

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SINGLE-CRYSTAL GROWTH OF GROUP IVB AND VB CARBIDES BY THE FLOATING-ZONE METHOD

C. B. Finch, Y. K. Chang, and M. M. Abraham

ABSTRACT

The floating-zone method for the growth of group IVB and VB carbides is described and reviewed. We have systematically investigated the technique and confirm the growth of large single crystals of $\text{TiC}_{0.95}$, $\text{ZrC}_{0.93}$, $\text{ZrC}_{0.98}$, $\text{VC}_{0.80}$, $\text{NbC}_{0.95}$, $\text{TaC}_{0.89}$. Optimal growth conditions were in the 0.5–2.0 cm/h range under 8–12 atm helium. Good crystal growth results were achieved with hot-pressed starting rods of 90–95% density, using a "double pancake" induction coil and a 200-kHz/100-kW rf power supply.

1. INTRODUCTION

The preparation of Group IVB and VB carbide single crystals has been an important recurring topic of research for over two decades. Large, high-quality, single-crystal samples are often required to investigate the physical properties of these high-temperature cubic materials of considerable fundamental interest. In addition, some carbide single crystals have practical applications as substrates, wear-resistant components, and high-temperature electronic devices. Their preparation extends crystal-growth procedures to extreme temperatures and growth conditions, entailing process temperatures of up to nearly 4000°C and gas pressures of up to 20 atm.

The floating-zone method (melt-growth) has been commonly employed to prepare large single-crystal samples of the transition metal carbides,¹⁻²⁵ although arc,^{26,27} flux,²⁸⁻³¹ and recrystallization³² procedures have also been occasionally used. In the floating-zone method, a molten zone, usually inductively heated, is passed slowly through a vertical polycrystalline carbide feed rod. With proper control, the solid crystallizing behind the zone is a single crystal. The molten zone is supported laterally by its surface tension and vertically by the solid rods. The technique employs no crucible and can produce high-purity homogeneous single crystals of dimensions often exceeding 1 cm.

This report discusses the floating-zone growth method as applied to Group IVB (Ti, Zr, Hf) and Group VB (V, Nb, Ta) carbides—all of which have a cubic structure and exist over a wide range of compositions. These materials have high melting points (up to 4000°C) and hardnesses (up to 3000 dph). The difficulty in obtaining good single crystals of these compounds prompted the presently described crystal growth program, the goal of which was to make a wide range of research specimens available for in-depth physical property studies. Concurrently, a systematic investigation was made on the floating-zone crystal growth process for these carbides. During the course of the experiments, several variations in the usual growth procedures were tested. The experimental results of this program and those of previous works are summarized here to assist others who may wish to grow crystals of these interesting materials.

2. EARLIER WORK

Carbide crystal growth by the floating-zone method was first discussed in 1968 by Precht and Hollox,¹ who grew VC single crystals as large as 1.0 cm diam \times 8 cm long with compositions ranging from VC_{0.75} to VC_{0.88}. Their use of 80–90% dense starting rods and ambient gas pressures up to 10 atm of helium reduced the arcing and induced a sharp thermal gradient at the growth interface. Growth was nominally at a rate of 0.5 cm/h with a stationary feed rod and boule rotation only. Crystals were characterized by metallography, X-ray diffraction, and carbon analysis. Precht and Hollox also did exploratory work on TiC.

Shortly thereafter, Haggerty, Lee, and Wenckus² and Lee and Haggerty³ described concurrent work on the floating-zone growth of ZrC, HfC, and TaC. Their experiments were performed under pressures up to 20 atm of argon, using 1-cm-diam starting rods of 60–70% theoretical density. Growth rates of up to 5 cm/h with stationary rods produced boules up to 1 cm diam \times 5 cm long. Rod fabrication, coil design, and growth procedures, including seeded growth of ZrC, were described in detail. Characterization was accomplished by metallography, X-ray diffraction, and chemical analysis.

In 1972, Billingham, Bell, and Lewis⁴ reported on the floating-zone growth of VC_{0.70} to VC_{0.90} crystals under argon pressures up to 20 atm and at growth rates up to 1.0 cm/h. The resultant boules, 1 cm diam \times 10 cm long, were characterized by electron diffraction as well as by chemical, metallographic, and X-ray techniques.

At about the same time, Packer and Murray⁵ studied the use of an eddy-current concentrator to produce single crystals of TiC, ZrC, VC, and NbC under 1–2 atm of argon or helium. They used hot-pressed stationary starting rods of 90% theoretical density with growth rates of 0.5 cm/h. Maximum single-crystal dimensions were unstated. Characterization was by metallography, X-ray diffraction, and chemical analysis.

In 1973 and 1976, Kumashiro, Itoh, and Misawa^{6,7} described the single-crystal growth of TiC under 3–17 atm of argon. Starting-rod densities were up to 82% theoretical and maximum growth rates were 1.5 cm/h, but no comment was made on possible rod rotation. Although some difficulty was

reported with arcing, crystals as large as 1.2 cm diam \times 4 cm long were grown. Crystals were characterized by X-ray diffraction, scanning electron microscopy, etch-pit analysis, electron microprobe analysis and electrical resistivity.

In 1975, Scheerer, Fink, and Riechart⁸ described the growth of TiC. They passed a stable zone through 95% dense starting rods of 1.2 cm diam, both rotating at 20 rpm, at a zone speed of 1.5 cm/h. Growth atmospheres of 12 atm argon and 12 atm argon 5% H₂ were used with three-turn uniplanar induction coils. Resultant boules up to 1 cm diam \times 10 cm long were characterized by electron microprobe, neutron diffraction, and chemical analysis.

Subsequently, A. N. Christensen⁹ reported the seeded growth of TiC crystals under pressures up to 20 atm helium. He used growth rates of 0.7 cm/h and rod rotations of up to 20 rpm. Crystals as large as 0.8 cm diam \times 10 cm were evaluated primarily by X-ray diffraction, and a preference for the [110] or [111] growth direction was indicated.

In 1979, F. Yajima et al.¹⁰ described the growth conditions for TiC after performing extensive compositional analyses on starting rods, solidified zones, and resulting crystals. They confirmed TiC growth under 10 atm helium at rates up to 2 cm/h and perfected the procedure for the growth of crystals of a near-constant composition up to 1 cm diam \times 10 cm long. Crystals were characterized by chemical analysis and X-ray diffraction.

In 1980, Kharkhardin et al.¹¹ reported the growth of ZrC and NbC single crystals. These authors passed a stable zone through 1-cm-diam-starting rods at growth rates up to 24 cm/h under 3 atm argon and evaluated their crystals by X-ray diffraction and spectrochemical analysis.

Y. Kumashiro et al.^{12,13} described the growth of ZrC, NbC, and TaC. They grew boules in up to 10 atm argon at speeds of 0.6 to 1.0 cm/h and performed extensive crystal characterizations.

Otani et al.¹⁴⁻²² published numerous articles on the growth of all the Group IVB and VB carbides. They presented detailed data on starting-rod and zone compositions to achieve a constant crystal composition along the growth axis. Their experiments were performed under 10-15 atm helium, using 60-80% dense starting rods degassed in a graphite sleeve in vacuum. Growth rates varied from 0.5-2.0 cm/h for all carbides. In most cases, rod

counter-rotation of up to 10 rpm was employed to grow boules as large as 1 cm diam \times 8 cm long. Characterization was performed primarily by metallography and X-ray diffraction.

J. A. Wysocki et al.²³ recently reported the growth of TiC using >90% dense, hot-pressed starting rods. Growth rates were 0.4 cm/h, with both rods rotating at 3 rpm in the same direction. Boules up to 2 cm diam were grown.

Finally, Mackie and Hinrich²⁴ reported the floating-zone growth of 3-mm-diam ZrC crystals in an arc furnace in lieu of the usual induction heating.

Our experiments confirm most of the previous work. The results are described in the following sections.

3. STARTING ROD PREPARATION

Although previous papers on floating-zone growth of the carbides¹⁻²⁴ emphasize the importance of homogeneous starting rods of known composition, there is considerable variation in the rod density. (See Table 1.) We obtained reproducible results easily only when starting rods were densified above 90%. Although rods of over 80% density are difficult to prepare by conventional ceramic technology, 90-95% dense material can be readily fabricated by 80-MPa hot pressing of isostatically pressed "green" preforms for 4 h at temperatures up to 2200°C.

The chemical purity, particle size, and particle shape of the starting powders used in rod fabrication are important. Table 2 presents these data for the powders used by the present authors. The relatively coarse particle sizes cited suggest the need of additional powder pulverization to achieve optimal densification. This step, which is time consuming and risks powder contamination from the grinding media, can be circumvented by direct hot pressing. Hot pressing was performed under 1×10^{-3} Pa vacuum, using Poco graphite* die assemblies (80-MPa load up to 2200°C for 4 h). The density

*Obtained from Poco Graphite, Inc., 1601 S. State Street, Decatur, Texas 76224. This graphite has an extremely fine grain size (4 μ m) and a high compressive strength (~145 MPa).

Table 1. Polycrystalline carbide rods used in floating-zone crystal growth experiments

Compound	Ref.	Process temp. (°C)	Duration (min)	Load (MPa)	Maximum density (% T.D.)	Maximum dimensions OD × l(cm)	Impurities (wt %) (as-pressed rod)
VC	1	1700	120	0	90	1.5 × 15.0	----
TiC	1	1700	120	0	78	1.5 × 15.0	----
ZrC	2	2400	<5	14	71	1.0 × 12.0	O:0.08; N:0.02
HfC	2	2875	<5	14	72	1.0 × 12.0	O:0.07; N:0.02
TaC	2	2875	<5	14	74	1.0 × 12.0	O:0.08; N:0.02
TiC	5	---	---	---	---	1.0 × ?	99.8% pure
ZrC	5	---	---	---	90	"	" "
VC	5	---	---	---	---	"	" "
NbC	5	---	---	---	---	"	" "
TiC	6	2000	---	0	82	1 × 20	----
TiC	8	---	---	---	96	1.25 × 20	O:0.3; N:0.1; Fe:0.03
TiC	9	---	---	---	---	1.0 × 15	O 0:0.04; N:0.9; W:2.5
TiC	10	1900	120	0	>80	1 × 20	Co:0.07;Fe:0.07;Cr:0.02;Zn:0.02
ZrC	11	2500	60	---	---	1.0 × 7.0	Fe:0.12;Si:0.32;W:0.45
NbC	11	2500	60	---	---	1.0 × 7.0	Fe:0.12;Si:0.18;W:0.32
NbC	12	2300	---	0	70	1 × 20	Ta:0.1
HfC	17	2000	30	0	62	1 × 20	O:0.14;N:0.03;W:0.2;Zr:2.3
ZrC	15	2000	120	0	70	1 × 20	W:0.1;Hf:0.04;Ti:0.01
TaC	16	2300	30	0	65	1 × 20	Nb:0.8;O:0.02;N:0.02
NbC	17	2100	---	0	75	1 × 20	O:0.1;N:0.02
VC	20	1900	60	0	80	1 × 20	O:0.02;N:0.03
TiC	23	---	---	---	>90	3.8 × 30	----
NbC _{1.20}	24	2000	120	80	95	1.25 × 12	Fe:0.01;Ta:0.16;W:0.12
TaC _{1.40}	24	2000	120	80	94	1.00 × 8.0	----
TiC _{0.96}	24	1800	120	80	96	1.25 × 8.0	----
ZrC _{1.15}	24	2200	240	80	95	1.25 × 8.0	----
HfC _{1.30}	24	2200	240	80	97	1.00 × 9.0	----
ZrC _{0.98}	24	2200	240	80	95	1.25 × 8.0	----

Table 2. Commercial carbide powders used in carbide starting-rod fabrication

Compound	Supplier	Particle size ^a (μm)			Surface area (m^2/g)	Carbon ^c content (wt %)	Oxygen ^d content (wt %)	Other impurities ^e (wt. %)
		<10%	<50%	<90%				
TiC	Starck ^f	3	5	14	0.8	19.4	0.2	Co:0.01;Cr:0.01;Fe:0.01;Ni:0.01;W:0.02
TiC	Cerac ^g	1	5	10	2.1	19.7	0.4	Co:0.002;Cr:0.006;Fe:0.01;Si:0.003;W:0.015
ZrC	Starck ^f	8	20	42	0.5	11.4	0.12	Hf:0.005;Ti:0.005;W:0.02
ZrC	Teledyne ^h	5	13	27	0.2	12.0	0.08	Hf:0.005
HfC	Starck ^f	3	9	20	0.1	6.2	0.11	Zr:0.03; Ti:0.005; W:0.005; V:0.1
HfC	Cerac ^g	2	5	12	0.6	6.5	0.2	Zr:0.006;Ti:0.006; V:0.05
VC	Starck ^f	4	15	44	1.1	19.5	0.4	---
NbC	Cerac ^g	2	5	16	1.2	10.8	0.72	Fe:0.01;Ta:0.16;W:0.10
TaC	Starck ^f	1	5	26	0.5	6.2	0.11	---
C	Cabot ⁱ	2	5	10	8.0	---	---	---

^aMicromerograph or Microtrac (lowest value).

^bBrunauer-Emmet-Teller Gas Adsorption (BET).

^cOrsat volumetric.

^dNeutron activation.

^eSpark-source mass spectrograph.

^fH. C. Starck, 280 Park Avenue, NY 10017.

^gCerac, Inc., P.O. Box 1178, Milwaukee, WI 53201.

^hTeledyne Wah Chang Albany, P.O. Box 460, Albany, OR 97321.

ⁱCabot Corp., 125 High Street, Boston 021100.

increased to greater than 90% of the theoretical value, with a commensurate reduction in the porosity and enhancement of the thermal conductivity. The as-pressed rods were then ground to a uniform diameter with diamond or Borazon tools, the surface temperature being kept below 100°C during the grinding. Use of these rods resulted in molten zones which formed uniformly and displayed no coupling irregularities.

The increased thermal conductivity of the hot-pressed rods compensated for localized compositional and density variations which often created problems with lower-density material. Table 1 summarizes the rod dimensions, compositions, and densities used by various authors. Densities above 90% were fabricated by hot pressing while sintering procedures were usually used for the lower density rods.

4. APPARATUS FOR FLOATING-ZONE GROWTH OF CARBIDES

The features necessary for successful carbide crystal growth are embodied in the A. D. Little High-Pressure Crystal-Growth Furnace, (Fig. 1)[†] originally developed during the 1960s for crystal growth of refractory materials. This system was first used for the carbides by Haggerty, Lee, and Wenckus.² Subsequent authors^{6,7,9,10,12-23} used the same system to grow all of the Group IVB and Group VB carbides, and our results confirm its highly reliable operation.

The apparatus provides the capability of conducting experiments under inert-gas pressures up to 100 atm (pressures above 20 atm do not appear to be beneficial for most carbide compositions). It incorporates a diffusion pump for evacuating the system before admission of the inert gas. The system has coaligned, rotatable (0–20 rpm) top and bottom water-cooled drive shafts which secure the starting rods. The drive shafts are translatable vertically in independent and/or synchronized modes. Ample visibility is provided by two viewing ports which, when used with internal mirrors, afford views of the zone from different angles. Chamber access for cleaning,

[†]Now marketed by Technical Specialities and Services, Inc., 57 N. Putnam St., Danvers, Massachusetts 01923.

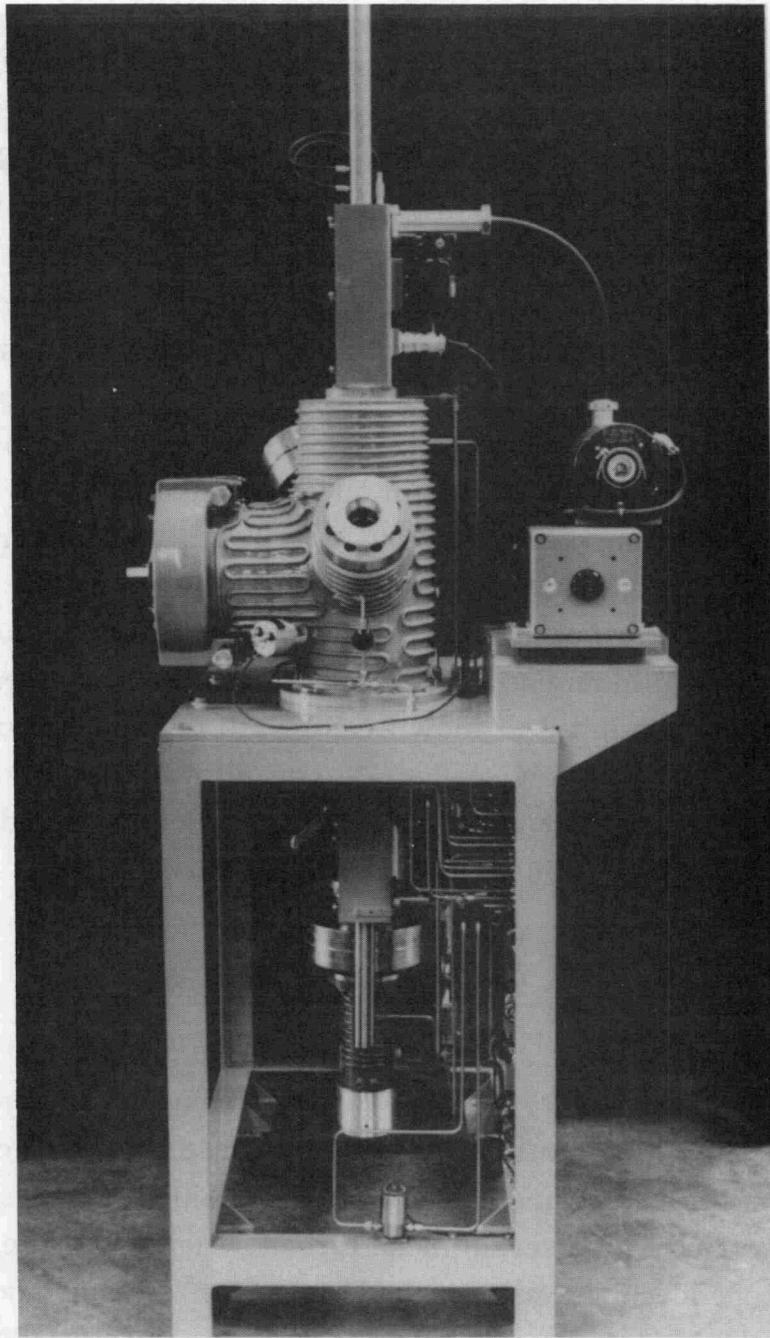


Fig. 1. A. D. Little high-pressure crystal-growth furnace.

coil placement, and starting rod mounting is convenient. The water-cooled chamber is large enough to accommodate rods 2 cm diam \times 10 cm long.

In our experiments, adequate cooling water pressure (700-kPa) was provided by a booster pump. The 700-kPa pressure was required to force sufficient cooling water (5-L/min) through a suitable coil (typically a "double pancake," i.e., two parallel planes of two concentric turns each, fabricated from 4- or 5-mm OD copper tubing). Our apparatus was powered by a 100-kW, 200-kHz induction power supply (generator). The generator output was passed through a 2:10 current transformer. During typical carbide crystal growth, 2–5 A of plate current passing through the transformer primary at up to 12.5 kV was converted to 10–25 A through the coil at up to 2.5 kV. No internal thermal shielding was used in our experiments.

The carbide starting rods were secured to the top and bottom drive shafts by graphite or molybdenum adaptors and were electrically isolated ($>10,000 \Omega$) from the rest of the apparatus by boron nitride or aluminum oxide insulators. To minimize adverse effects from thermal expansion, the top-rod holder was designed to allow free upward motion and rotation of the rod but no downward motion (see Fig. 2). Our mirrors were of titanium evaporated on quartz glass and remained relatively free of carbide sublimates during a typical run.

5. GROWTH PARAMETERS

For acceptable single-crystal growth, a homogeneous molten zone of appropriate composition must be vertically traversed through a carbide-feed rod of a prescribed composition. The zone composition is consistent with the phase diagram of the relevant metal-carbon system.^{33,34} The process, often called zone leveling, was described by Pfann.³⁵ The method is especially applicable to solid-solution growth, where the crystallizing phase has a different composition from the liquid. Growth of a specific crystal composition can be achieved from an appropriate liquid zone at any point above the eutectic. Because of the compositional difference between the liquid and solid phases, growth normally proceeds more slowly than for congruently meeting materials. For the particular case of the carbides the

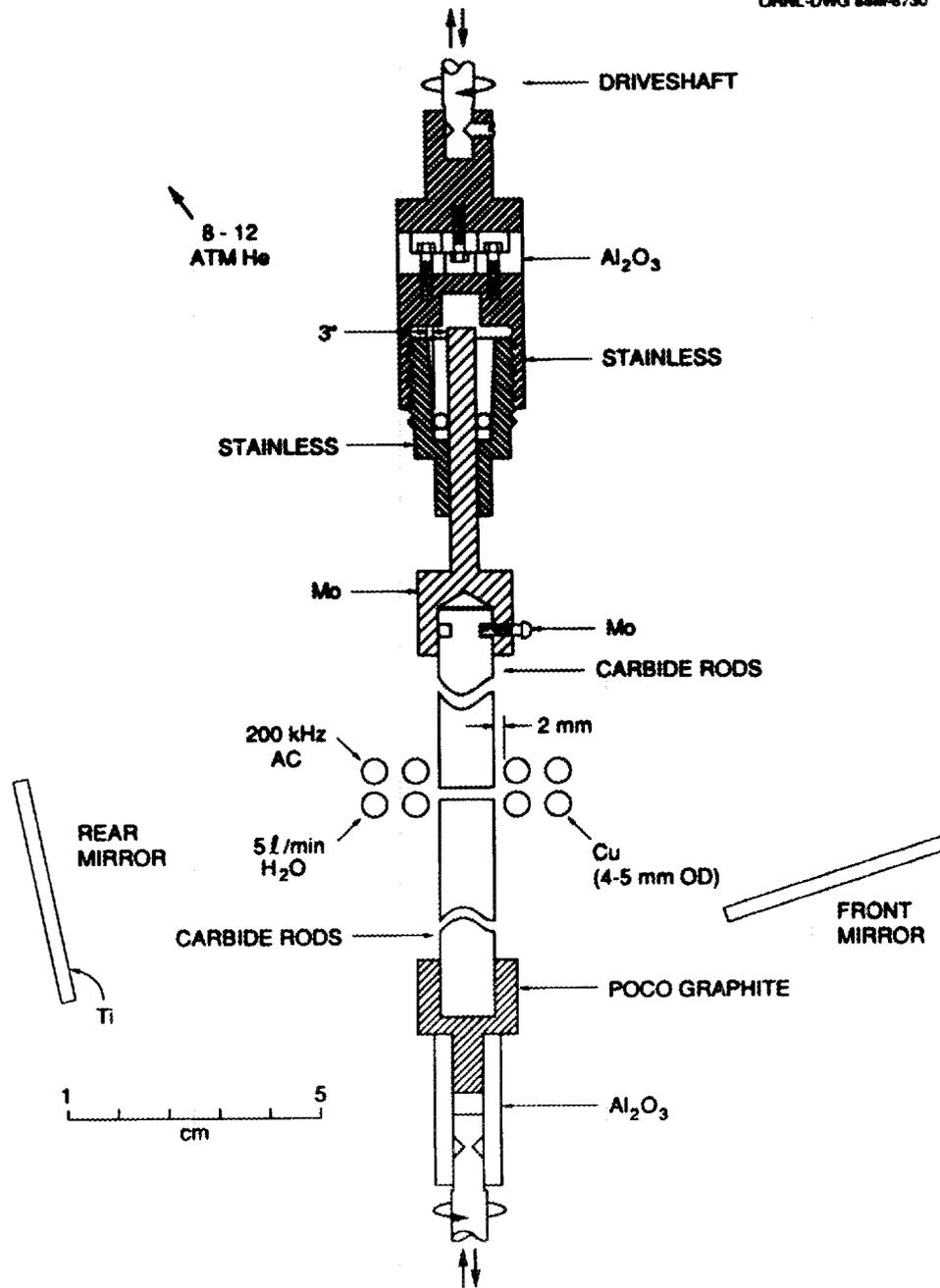


Fig. 2. Growth assembly at the start of a typical run, including a self-adjusting, top rod holder.

zone composition changes due to preferential volatilization of either carbon or the metal. To compensate for this, the zone and starting rods are prepared enriched with the more volatile constituent.

5.1 GAS AMBIENT

The species and pressure of the ambient gas used during growth are critical. Usually, an inert gas whose absolute pressure ranges between 1 and 20 atm is employed, depending on the carbide being grown. The gas most often used is He, although Ar, Ar-He, and Ar-H mixtures are also cited. The elevated gas pressure suppresses evaporation from the zone and reduces undesirable arcing. The gas, purified of O₂ and H₂O, is introduced into the evacuated growth chamber ($<10^{-3}$ Pa) to a pressure 70–80% of that desired during the growth.

Helium has a high ionization potential and a high thermal conductivity. These properties minimize arcing and produce a growth interface having a steep thermal gradient, conducive to single-crystal growth at relatively fast rates. The argon and argon mixtures are more prone to arcing compared with pure helium. They produce a less pronounced growth interface thermal gradient, and often result in distorted zone visibility. However, they can be used when pure helium is not available.

5.2 COIL DESIGN

A number of coil designs have been reported for carbide single-crystal growth (see Table 3). We have verified, as a general rule, that a single-turn coil is not always suitable because insufficient power is transferred to the load. The most simply fabricated and reliable coil is the four-turn biplanar ("double pancake"), fabricated from 4–5 mm OD, 0.8-mm-wall copper tubing.⁹ In our case, this coil gave satisfactory results with our 100-kW, 200-kHz generator and 2:10 current transformer in all of the carbide growths reported. The cooling water flow through the coil was approximately 5 L/min, resulting in an exit water temperature increase of $<10^{\circ}\text{C}$ during all of our carbide growth experiments. The distance between the coil inside

Table 3. Growth parameters of group IVB and VB metal carbide single crystals

Ref.	Crystal boules		Coil (ID, cm)	Ambient gas (pressure, atm)	Maximum traverse rate (cm/h)	Feed rod rotation (rpm)	Interface rotation (rpm)	Initial zone composition	Feed rod	
	Comp.	Diam. (cm)							Comp.	Density (% T.D.)
1	VC _{0.75-0.88}	1.5	3/1(2.5) ^a	He(10)	0.5	no	10	VC _{0.62->0.88}	VC _{0.75-0.88}	80-90
2	ZrC _{0.88}	1.0	2/2(?) ^b	Ar(20)	5.0	no	no	---	ZrC _{0.97}	68-71
2	HfC _{0.94}	1.0	2/2(?) ^b	Ar(20)	5.0	no	no	---	HfC _{1.24}	65-72
2	TaC _{0.90}	1.0	2/2(?) ^b	Ar(20)	5.0	no	no	---	TaC _{1.24}	72-74
3	ZrC _{0.95}	0.6	2/2(?)	Ar(1)	3.0	no	no	---	---	60-70
4	VC _{0.70-0.90}	1.0	1/3(?) ^c	Ar(20)	1.0	---	---	---	VC ^d	90
5	TiC _{0.89}	1.0	C ^e	Ar,He(1)	0.5	no	no	---	TiC _{0.8}	HP ^f
5	VC _{0.77-0.84}	1.0	C ^e	Ar,He(1)	4.0	no	no	---	VC _{0.84}	HP ^f
5	NbC _{0.83}	1.0	C ^e	Ar,He(1)	---	no	no	---	NbC	HP ^f
6	TiC _x	1.2	1/3(2.0) ^c	Ar(10-17) Ar-3%He(10-17)	1.5	---	---	---	TiC ^d	68-82
7	TiC _{1.00}	1.5	---	---	---	---	---	---	---	---
8	TiC _{0.89-0.97}	1.2	1/3(1.7) ^c	Ar(10-12) Ar-5%H ₂ (10-12)	1.5	20 cw	20 ccw	---	TiC _{0.91-0.96}	96
9	TiC _x	1.2	2/2(2.0) ^b	He(10-20)	0.7	---	---	---	TiC _{0.94}	HP ^f
10	TiC _{0.55-0.94}	1.0	2/3(1.6) ^g	He(10)	2.0	20 cw	20 ccw	TiC _{0.40-1.27}	TiC _{0.40-0.95}	>80
11	ZrC _{0.88}	0.8	---	Ar(3)	24.0	---	---	---	ZrC _{0.97}	---
11	NbC _{0.92}	0.8	---	Ar(3)	24.0	---	---	---	NbC _{0.97}	---
12	NbC _{0.85-0.90}	0.8	2/2(?) ^b	Ar(3-10)	1.0	---	---	---	NbC _{1.0}	60-70
13	ZrC _{0.90}	0.8	2/3(?) ^g	Ar(10)	---	---	---	---	---	---
13	TaC _{0.83}	0.8	2/4(?) ^h	Ar(10)	---	---	---	---	---	---
14	ZrC _{0.93}	1.0	2/3(1.4)	He(10)	2.5	---	0.3	ZrC _{1.15}	ZrC _{0.98}	60-70
14	ZrC _{0.98}	1.0	2/3(1.4)	He(10)	2.4	---	0.3	ZrC _{1.7}	ZrC _{1.08}	60-70
16	TaC _{0.95}	1.0	2/3(1.6) ^g	He(10)	1.5	10	no	TaC _{2.2}	TaC _{1.4}	60-65
17	HfC _{0.96}	0.9	2/3(1.5) ^g	He(15)	1.25	10(cw)	10(ccw)	Hf=1.7	HfC _{1.30}	60
18	TiC _{0.96}	1.0	2/3(1.8) ^g	He(8)	0.5	8(cw)	8(cw)	TiC _{1.3}	TiC _{0.99}	75
19	NbC _{0.95}	1.0	2/3(1.6) ^g	He(10)	1.25	8(cw)	8(ccw)	NbC _{1.24}	NbC _{1.20}	60-70
20	VC _{0.73-0.88}	0.9	2/3(1.6) ^g	He(8)	1.5	no	6	VC _{0.53-0.96}	VC _{0.70-0.87}	80
23	TiC	2.0	2/2(2.6) ^b	He(40)	0.4	3(cw)	3(cw)	---	---	96

Table 3. (Continued)

Ref.	Crystal boule		Coil (ID, cm)	Ambient gas (pressure, atm)	Maximum traverse rate (cm/h)	Feed rod rotation (rpm)	Interface rotation (rpm)	Initial zone composition	Feed rod	
	Comp.	Diam. (cm)							Comp.	Density (% T.D.)
24	ZrC _{0.93}	0.3	arc	Ar-25%He(1.0)	30.0	no	5	---	ZrC _{0.99}	90
25	TiC _{0.95}	1.2	2/2(1.8) ^b	He(12)	0.8	no	5	TiC _{1.3}	TiC _{0.98}	95
25	ZrC _{0.93}	1.2	2/2(1.7) ^b	He(12)	0.8	no	5	ZrC _{1.15}	ZrC _{0.98}	95
25	ZrC _{0.98}	1.2	2/2(1.7) ^b	He(12)	0.8	no	5	ZrC _{1.7}	ZrC _{1.08}	96
25	VC _{0.80}	1.2	2/2(1.7) ^b	He(8)	1.2	no	10	VC _{0.83}	VC _{0.83}	80
25	NbC _{0.95}	1.1	2/2(1.7) ^b	He(12)	1.2	no	5	NbC _{1.2}	NbC _{1.2}	94
25	TaC _{0.89}	1.0	2/2(1.6) ^b	He(12)	1.2	no	no	---	TaC _{1.4}	95
25	TaC _{0.80}	1.1	2/2(1.7) ^b	He(12)	2.5	no	5	TaC _{0.71}	TaC _{0.95}	94

^aThree parallel planes of one turn each.

^bTwo parallel planes of two concentric turns each wound in same direction from 4–5mm OD copper tubing.

^cOne plane of three concentric turns.

^dCommercial powder of unstated composition.

^eConcentrator

^fHot pressed

^gTwo planes of three concentric turns.

^hTwo planes of four concentric turns.

diameter and the starting-rod peripheral surface was 2–3 mm, requiring accurate rod coalignment in preparation for a run. The actual distance between the coil inside diameter and the zone peripheral surface during growth was slightly greater than 2–3 mm since the average zone diameter during growth is typically 0.70–0.80 of the starting rod diameter.

Departing from this coil design, a three-turn triplanar coil was successfully employed for VC.¹ Japanese researchers used 3-mm copper tubing with six-turn biplanar designs.²² These coils are efficient and produce a sharp growth interface thermal gradient, although they are more prone to overheating and failure than are coils made from 4–5 mm tubing. Two groups of researchers^{4,8} employed a three-turn uniplanar coil, which gave satisfactory results for VC and TiC.

5.3 FORMATION AND MAINTENANCE OF A STABLE ZONE

The initial positioning of the top and bottom starting rods is critical in establishing a zone. The rods are advantageously situated with a vertical 1-mm gap between them, which can be observed through the middle spacing of a biplanar coil (see Fig. 2). The degree of incandescence of the top and bottom starting rods should be approximately equivalent during heat up. The advent of zone formation is indicated by the appearance of visible sinter lines several millimeters above and below the zone to be, and the appearance of a glassy-appearing surface (semiliquid) on the feed rod. Fuming occurs from the liquid carbide, with incandescent vapors drifting upwards. This is followed by formation of a droplet between the two rods and the gradual spreading of the droplet until a zone, (identifiable by its homogenous appearance and the visible eddy-current mixing at its surface), is visible. Difficulties may be encountered at this point if rod homogeneity and purity are not adequate.

After homogeneous zone formation, power is reduced slightly until a stable or barely turbulent zone is achieved. The zone diameter is controlled to ~0.75 of the feed-rod diameter by independent motion of the drive shafts, since larger zone diameters are likely to spill. When complete zone liquidity is ascertained, rod rotation may be initiated at rates up to 10 rpm. Although

the two rods may be counter-rotated, the rod with the crystal/liquid interface is preferentially rotated for best results. The synchronized traverse of the two rods through the coil is then initiated in the upward or downward direction at an appropriate rate. For a constant zone composition, the power input, which is controlled manually on the basis of a constancy in zone height and diameter, should not change throughout the growth run.

Unwanted solidification is indicated by the cessation of turbulence at the zone surface and the disappearance of vapors. Solid particles become visible on the zone surface, and mechanical disturbances (binding) occur during rotation. To correct this, power is gradually increased until the binding stops and the solid particles disappear. Turbulence again becomes visible, and the fuming reappears.

5.4 TRAVERSE RATE

Table 3 compares our growth parameters and results with those of previous authors for Group IVB and VB carbides. Satisfactory single-crystal growth depends on the establishment of a stable zone and its continued maintenance throughout a run. The typical growth rate, proportional to the interface traverse rate, is between 0.5 and 2.5 cm/h, depending on the carbide being grown. When the rate exceeds 2.5 cm/h, polycrystalline growth is likely to develop. At less than 0.5 cm/h, maintaining a constant zone composition is difficult because of volatilization. Furthermore, the amount of material produced during a run of convenient duration is limited.

5.5 ARCING, INHOMOGENEOUS MELTING, CRUST FORMATION, AND ZONE SPILLAGE

Previously mentioned were problems involving arcing to inhomogeneities in low-density starting rods. This undesirable occurrence results in the formation of a liquid core above and/or below the intended zone. Concurrently, a peripheral crust of the original rod remains. The crust is invariably cracked and interferes with uniform inductive coupling, making power control difficult and often resulting in spillage.

It is uncertain whether the arcing and the crust are the result of intrinsic rod inhomogeneities or whether they are the result of extrinsic oxide impurities on the rod surface. In any event, the problem is surmounted by the use of high-density (i.e., >90%) starting rods that had been hot-pressed in a graphite die. This procedure results in a minimum of arcing and gives uniform zone formation. When high-density rods were not available, low-density rods were given a preliminary sintering pass at a temperature slightly below the zone melting temperature.

5.6 CONDENSATION OF ZONE EVAPORATION PRODUCTS ON COIL

The water-cooled copper coil is a natural site for condensation of solid sublimates evaporating from the molten-zone or near-zone regions of the feed rod. These sublimates form as particulates, globules, and dendrites, and their presence induces arcing, disrupts thermal equilibrium, and impedes visibility. The condensates often grow into the zone itself, causing mechanical disturbances and inducing spurious crystallite nucleations. Partial visibility of the zone can be maintained by equipping the system with additional mirrors to provide views from angles not obstructed by the condensates. In the absence of complete visibility, it is often feasible to continue a zone pass when arcing does not occur and power input is constant. Rod rotation assists in removal of the coil sublimates, but never completely eliminated the problem. A larger-diameter coil is often indicated because it provides a larger interval between the zone and the sublimates. Unfortunately, the rf coupling efficiency is reduced with the larger coil.

5.7 SPECIFIC GROWTHS

The specific carbide growths during which we confirmed many of the results of the earlier workers are outlined in the following sections. All of our experiments were performed in the high-pressure crystal-growth system described above. The resulting crystals were characterized by X-ray diffraction, chemical analysis, and metallography.

5.7.1 TiC

The interest in TiC results from its high hardness and acceptability as a substrate material for epitaxial growth of SiC.²³ At the same time, it is a difficult carbide to grow because of its tendency to crack during growth. In addition, a peripheral polycrystalline rim is always present in boules, regardless of crystal size, growth direction, or interface thermal gradient. This effect is apparently associated with the W-shaped growth interface characteristic of the Group IVB carbides. (The center and periphery of the growing boule are significantly cooler than the intermediate radial points.)

We used >95% dense hot-pressed rods with the zone and rod compositions suggested by Otani.¹⁵ Our growth atmosphere was 10–12 atm helium. Growth rates were 1–1.5 cm/h, with rod rotations at 0–10 rpm. Boules usually had a predominant central grain with a peripheral multigrained rim and were as large as 1.2 cm diam × by 6 cm long. The polycrystalline rim persisted despite various alterations of coil design. Thermal shielding was also attempted but had no appreciable effect in diminishing the polycrystalline rim. It appeared from crystallographic orientation of the central grain that the various TiC grains had diverse growth directions, with a preference for the [110] and [111].

5.7.2 ZrC

ZrC also forms boules with a polycrystalline rim and a predominant central grain. However, the low volatilization from the molten zone and the decreased cracking made ZrC growth more reproducible than that of TiC. We used hot-pressed, >95% dense rods to grow 1.2-cm-diam, 4-cm-long ZrC boules (Fig. 3). Starting rod and zone compositions corresponded to those of Otani et al.¹⁴ with growth under 10–12 atm helium at ~1 cm/h.

5.7.3 HfC

Attempts to grow HfC_{0.95} using 1.0-cm-diam >95% dense starting rods of HfC_{1.3} composition and HfC_{1.7} zone composition under 12 atm helium

were unsuccessful. In most cases, a homogeneous stable zone could not be maintained long enough to allow even a short-zone pass.

5.7.4 VC

The high surface tension and relatively low density of molten VC result in a relatively long molten zone (length = $1.5 \times$ rod diameter), allowing good visibility. Sintered rods of ~80% density gave reproducible results under 8 atm helium at growth rates up to 1.2 cm/h. A VC_{0.80} boule is shown in Fig. 3.

5.7.5 NbC

The floating-zone technique gave excellent results for NbC. The starting rod densities were ~95% of theoretical. The starting rod and zone compositions determined by Otani et al.¹⁹ were used to grow both NbC_{0.89} and NbC_{0.95} boules under 12 atm helium. Growth rates were between 0.5 and 1.0 cm/h, with optional rotation. Volatilization from the zone was not excessive, and boules frequently developed into single crystals across their entire diameter (Fig. 4).

5.7.6 TaC

This carbide was more difficult to grow than NbC because of the considerable volatilization from its molten zone. Stationary, hot-pressed, rods of greater than 90% density gave good results in 12 atm helium at traverse rates up to 2.5 cm/h. Crystal compositions successfully grown were TaC_{0.80} and TaC_{0.89}.

6. CRYSTAL EVALUATION

As-grown carbide boules are resistant to room-temperature oxidation and do not oxidize appreciably at temperatures below 500°C.³⁴ The boules

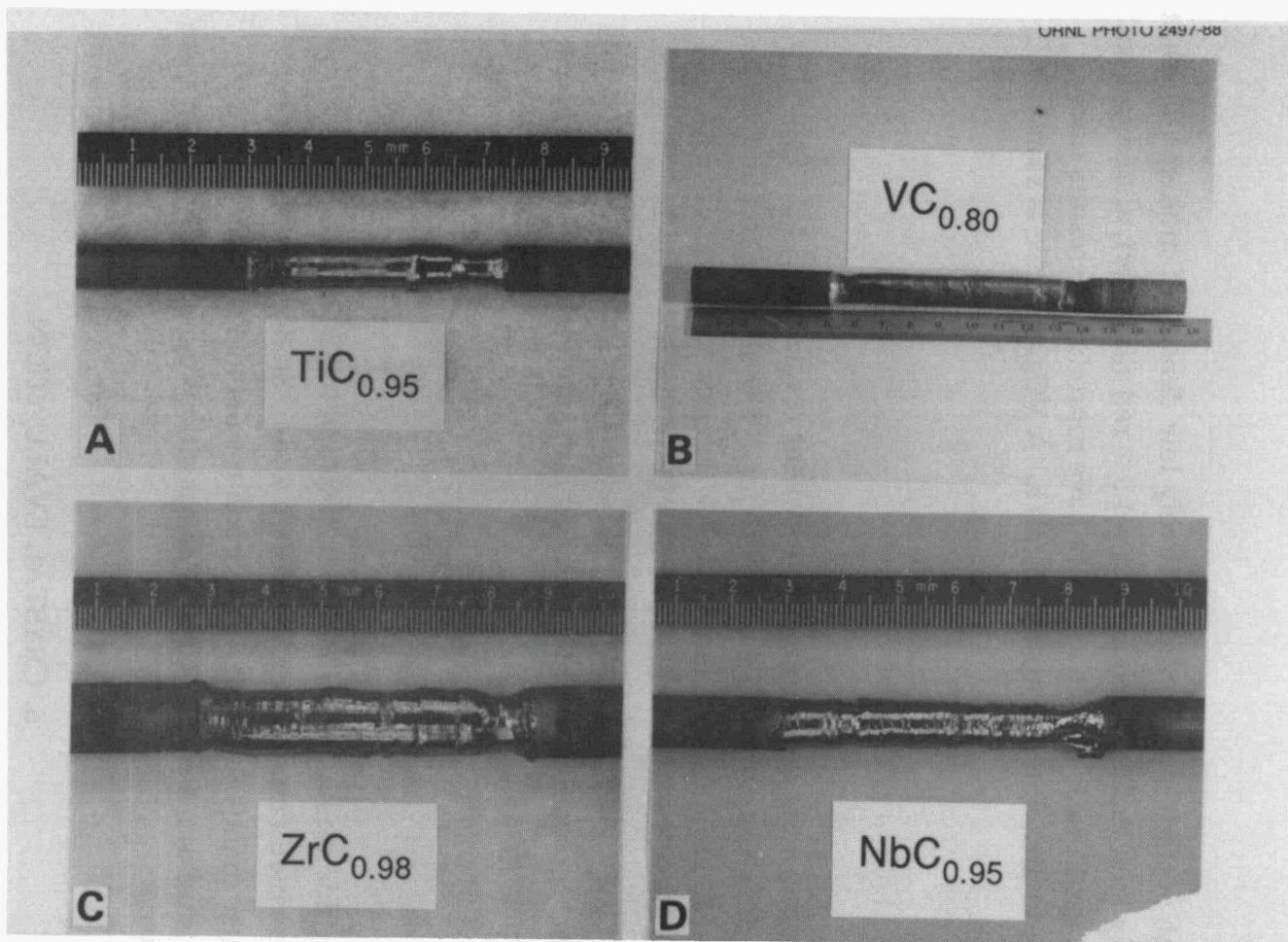


Fig. 3. Optimal Group IVB and VB carbide boules grown in this work: (a) $\text{TiC}_{0.95}$, (b) $\text{VC}_{0.80}$, (c) $\text{ZrC}_{0.98}$, and (d) $\text{NbC}_{0.95}$.

were sectioned with a 0.5-mm-thick diamond wafering saw, rotating at 100–150 rpm under ethylene glycol coolant. Single-crystal grains were identifiable from the relief on the sawed surfaces (Fig. 4). Surface defects resulting from the sawing were removed by electropolishing in concentrated acid (e.g., HNO₃:HF). Samples were also cut by electron discharge machining, but this procedure usually resulted in surface oxidation. Polishing was done by standard metallographic procedures, using epoxy mounting with diamond grits on silk laps. Several boules grown in this work are shown in Fig. 3, and a photograph of a NbC_{0.95} boule section shown in Fig. 4, reveals a predominantly single-crystal grain.

Crystal perfection was ascertained by Laue back-reflection photographs. The lattice parameter (equatable to composition)^{27,28} was also determined by X-ray powder diffraction. The metal/carbon (M/C) variation across a boule surface could be ascertained by secondary ion mass spectrometry (SIMS) techniques. This was done for the case of ZrC_{0.98} (see Fig. 5), and the determination indicated a relatively constant M/C ratio. Carbon content was most reliably determined using the Orsat volumetric method,³⁶ which gave an accuracy of ±0.2 wt % in the range of 5–20 wt % C. In the Orsat method, the amount of CO₂ gas produced by sample combustion in oxygen is measured by a volumetric technique.

Although the M/C ratio has been related to other physical properties, the Orsat method gives the most reliable direct determination for carbon.

7. SUMMARY

The critical steps in the floating-zone growth of high-purity, Group IVB and VB carbide single crystals of a specific M/C ratio were reviewed and experimentally confirmed. Good crystal growth results were obtained with carbide feed rods of over 90% theoretical density. Growth rates were 0.5–2.5 cm/h under 8–12 atm helium.

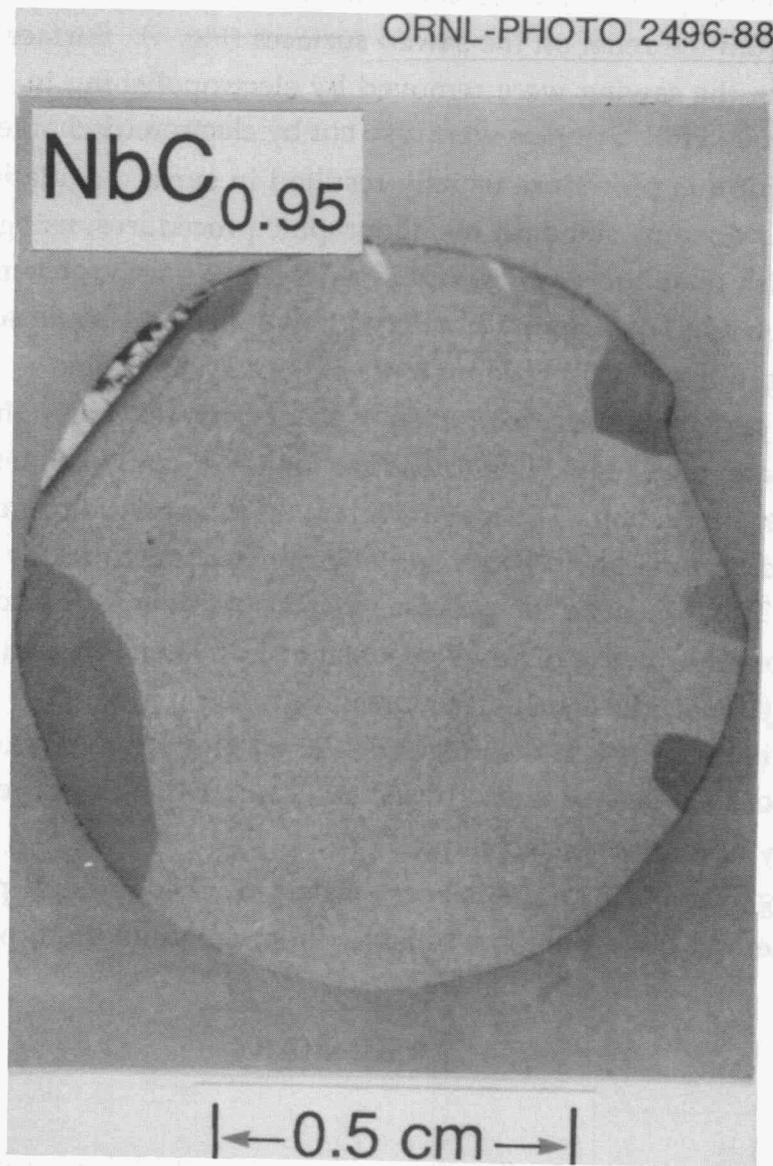


Fig. 4. Transverse section of $\text{NbC}_{0.95}$.

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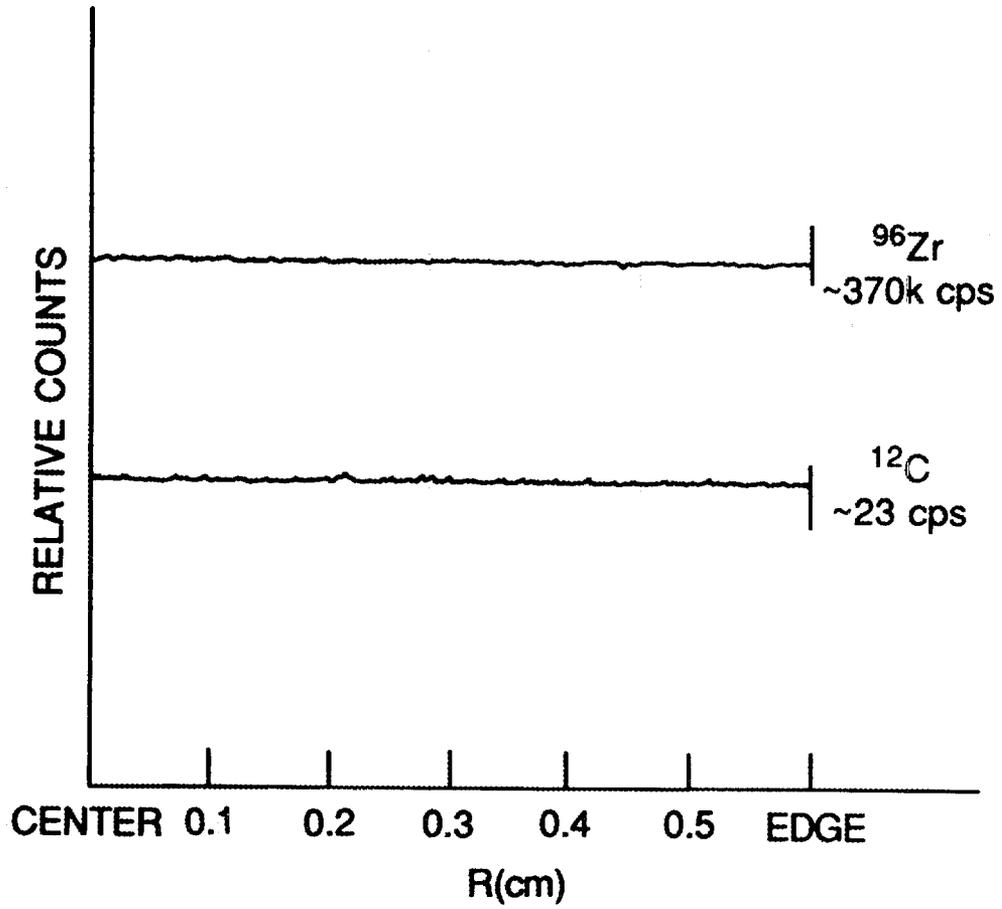


Fig. 5. Secondary ion mass spectrometer (SIMS) scan across the radius of a $\text{ZrC}_{0.98}$ boule, showing relative constancy of Zr/C ratio.

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