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A FLOATING ZONE TECHNIQUE FOR THE GROWTH OF CARBIDE SINGLE CRYSTALS

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Second Technical Report to ARO-D

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Sixth Technical Report to NASA

MARTIN MARIETTA

A FLOATING ZONE TECHNIQUE FOR
THE GROWTH OF
CARBIDE SINGLE CRYSTALS

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by

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Abstract

Single crystals of pure and alloyed carbides of different carbon-to-metal ratio have been prepared using a floating zone technique. This paper discusses application of this technique specifically to the growth of VC single crystals. Longitudinal variations in composition from about $VC_{0.82}$ to $VC_{0.75}$ are observed when a rod of initial uniform composition $VC_{0.75}$ is zone refined. Variations in composition from about $VC_{0.85}$ to $VC_{0.88}$ are produced in rods initially of composition $VC_{0.88}$. However, since $VC_{0.83}$ is close to the melting-point maximum in the VC phase, little variation in composition is observed on zone refining. These variations in composition are as expected from considerations of the phase diagram and the principles of zone refining. The production of rods of constant composition utilizing the principles of zone levelling is discussed.

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I. Introduction

The cubic transition metal carbides exhibit very high melting points (2500-4000°C), extremely high strengths, and deformation characteristics similar to the f.c.c. metals (1,2). They represent, therefore, a potentially important class of materials for high temperature structural applications. Unfortunately, many studies of the properties of the carbides have utilized sintered material of dubious quality, whereas the provision of experimental data of sufficient reliability to allow fundamental interpretation usually entails working with well-characterized single crystals. Such crystals have now been prepared using a floating zone technique, and this paper is concerned with the application of this technique to the growth of VC single crystals.

The mechanical properties of the carbides are strongly influenced by stoichiometry (1,3,4), and for this reason it was necessary to prepare crystals of various carbon-to-metal ratios. Specifically, crystals of $VC_{0.75}$, $VC_{0.83}$ and $VC_{0.88}$ were required. Considerations of the phase diagram (5) and the general principles of zone refining (6) suggest that crystals of these compositions will differ in growth behavior, particularly with respect to the occurrence and severity of longitudinal composition gradients within the crystals. For example, a molten zone passed along a rod of nominal composition $VC_{0.75}$ would be expected initially to deposit solid of composition close to $VC_{0.82}$ (Fig. 1), and the composition of the solidifying material will change progressively until zone levelling occurs, that is, when the composition of the freezing solid is the same as that which

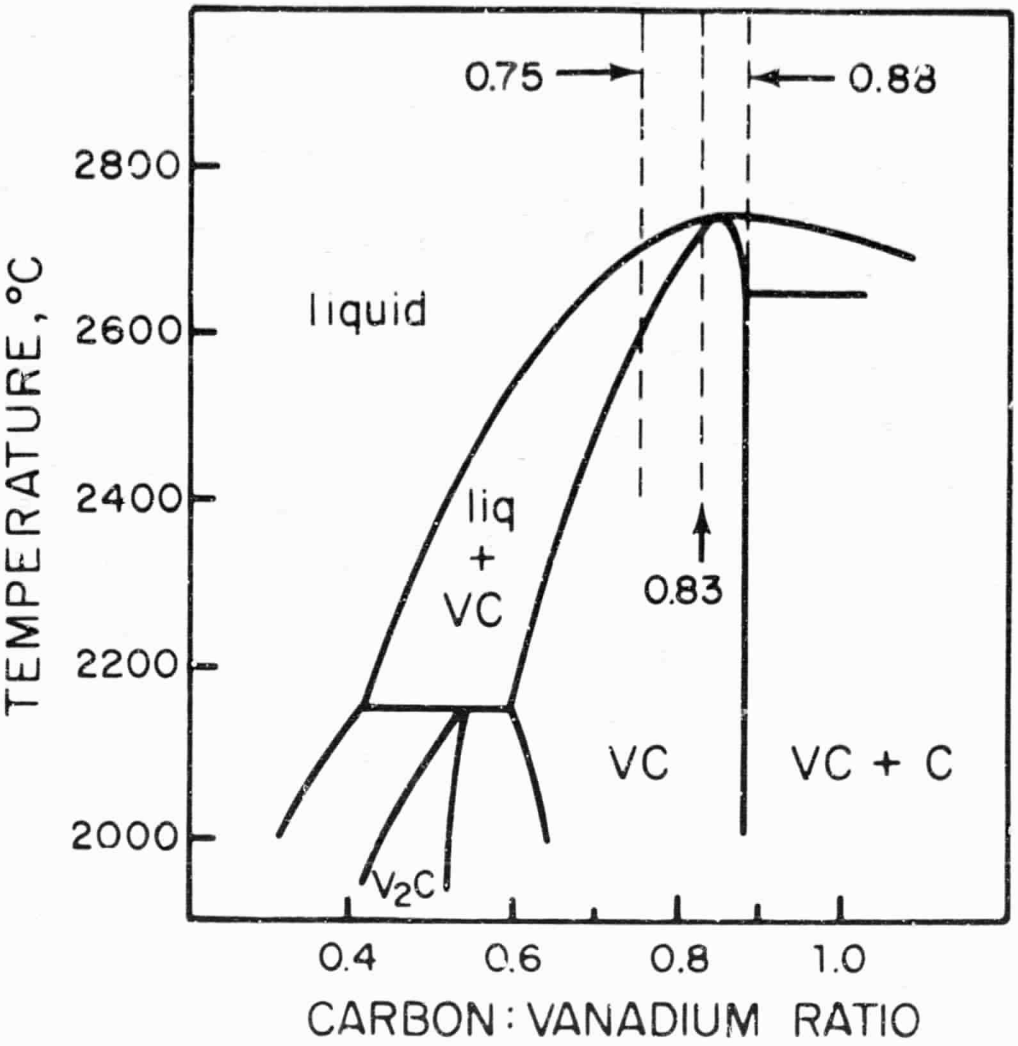

Fig. 1. Part of the vanadium-carbon phase diagram [after Adelsburg and Cadoff (5)].

is melting into the zone. Under these conditions, the composition of the final liquid zone would be expected to be about $VC_{0.63}$. Similarly, a variation in composition from about $VC_{0.85}$ to $VC_{0.88}$ would be expected on zone melting a rod of initial composition $VC_{0.88}$. However, a rod of starting composition $VC_{0.83}$ may be expected to yield solids having comparatively little variation in composition, since this composition is close to that of the melting point maximum. It will be shown that the results of this work are in accord with these expectations.

Apparatus and Growth Technique

The raw material used was powder of composition $VC_{0.92}$, supplied by Consolidated Astronautics, Inc. Starting materials of nominal compositions $VC_{0.88}$, $VC_{0.83}$ and $VC_{0.75}$ were produced by blending this powder with 5, 10 or 20 w/o vanadium, respectively. The resulting aggregates were isostatically pressed to 50,000 psi at room temperature to produce rods about 7 in. long and 0.75 in. diam. After sintering at $1700^{\circ}C$ for 2 hrs in a vacuum of 10^{-5} torr., the density of these rods averaged between 80% and 90% of theoretical. They were then diamond-ground to a constant diameter of 0.60 in. prior to zone melting.

The crystal growth apparatus is shown schematically in Fig. 2. The specimen was held in a graphite holder between two water-cooled copper chucks, the lower of which could be rotated. The upper chuck could be moved independently of the direction of zone travel to compensate for density changes and to maintain zone stability. A 50 KW r.f. generator was

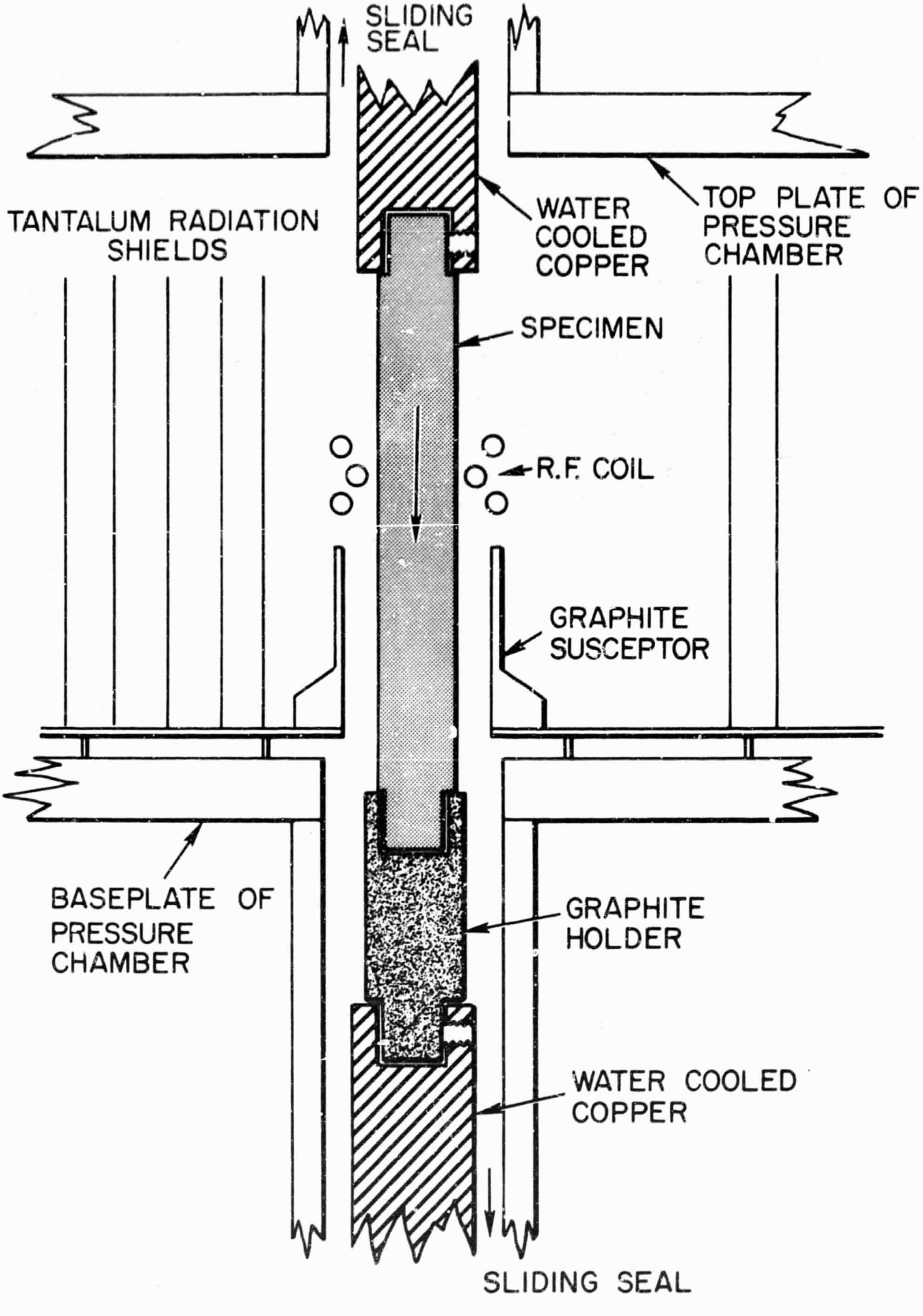

Fig. 2. Schematic representation of the zone refining apparatus.

used as a power source, and the molten zone was produced by a three-turn coil, the clearance between the center turn and the sample being about 0.20 in. This comparatively large separation was found necessary in order to inhibit disturbance of the melt by volatilization products which condense on the water-cooled work coil. The furnace chamber was pressurized with ten atmospheres of helium to reduce preferential volatilization of vanadium from the VC at temperatures above 2000°C. Argon was used initially for this purpose, but was found to be unsuitable because of its lower ionization potential.

The molten zone was passed from the bottom to the top of the rods at a rate of ~ 0.2 in./hr by lowering the specimen through the work coil. An afterheater, operating at a temperature between 1500-2000°C, was provided by a graphite susceptor placed below the work coil. This served to reduce thermal shock cracking by reducing temperature gradients in the crystal.

Results and Discussion

A typical VC crystal some 3 in. long and 0.4 in. in diameter produced by passing a single molten zone through a sintered rod of starting composition $VC_{0.75}$ is shown in Fig. 3. In that part of the specimen which was below the initial position of the work coil, surface melting has occurred, and consequently the sintered rod extends as a cone into the initially melted material. This is illustrated by the section in Fig. 4(b). A fully-dense columnar-grained polycrystalline material, Fig. 4(c), forms

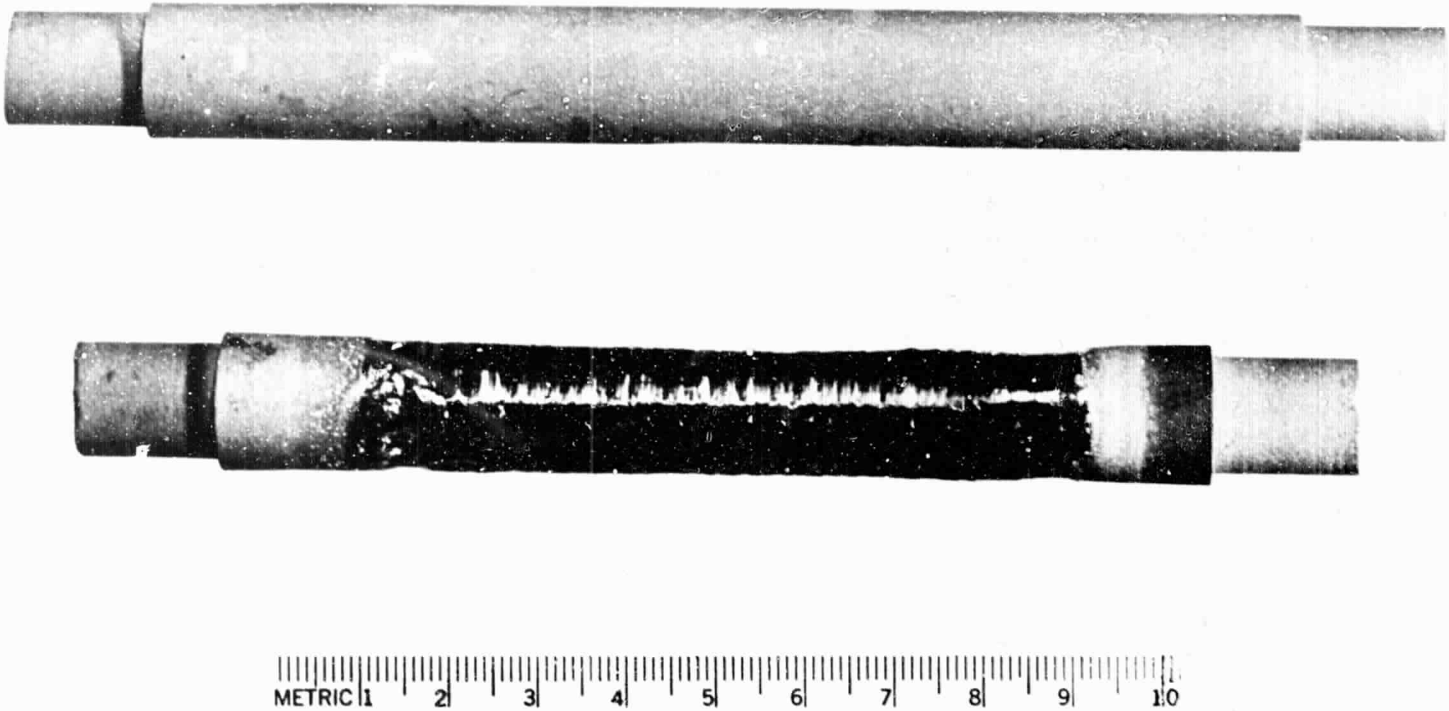

Fig. 3. A typical crystal of VC about 8 cms long and 1 cm in diameter.

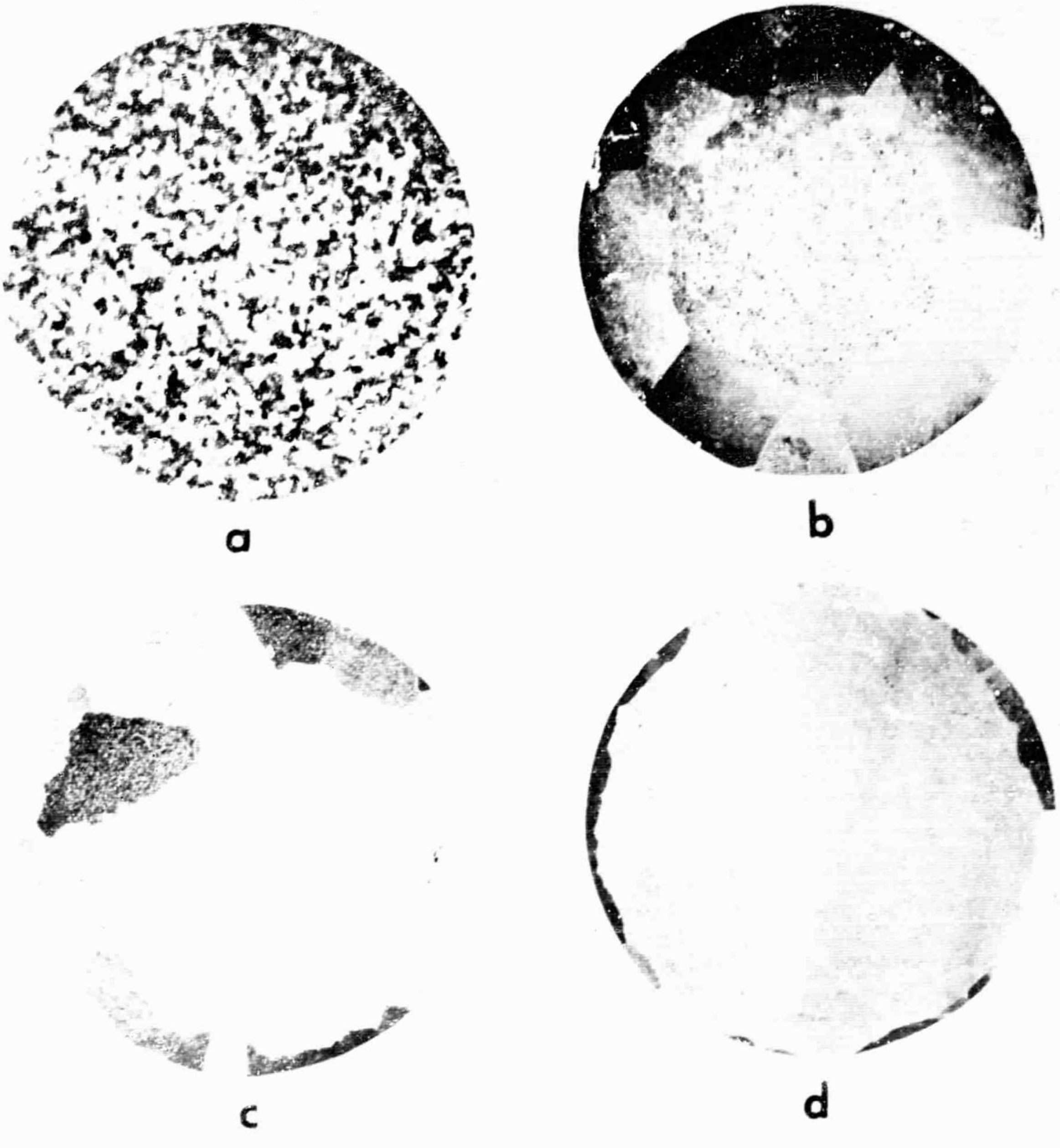

Fig. 4. Stages in the nucleation of a carbide single crystal using the floating zone technique. (a) The initial sintered rod, (b) the initially melted area, (c) typical grain growth and (d) single crystal, which occasionally exhibits an outer polycrystalline rim. (Magnification × 6.)

from this region. In subsequent movement of the zone, preferential growth of one grain occurs, the growth direction being random, although showing a preference for the low index directions.

A macroscopic defect often observed when fast growth rates ($> \sim 0.6$ in./hr) are utilized, is a narrow polycrystalline outer rim, Fig. 4(d). The crystals produced by this technique also contain sub-grain boundaries, but the overall dislocation density, as determined by means of transmission electron metallography and etch pitting techniques, is low, and most dislocations are confined to sub-grain boundaries.

Debye-Scherrer powder photography, chemical analysis and optical metallography have been used to characterize the crystals produced. Chemical analyses and measurements of the lattice parameter, summarized in Fig. 5, indicate that when a rod of nominal composition $VC_{0.75}$ is zone melted, the first solid deposited has a composition close to $VC_{0.82}$. As the crystal forms, the carbon-to-metal ratio decreases, and the zone to solidify last contains a precipitate identified by X-ray diffraction as V_2C, Fig. 6(a). Chemical analysis indicates that the composition of this zone is about $VC_{0.62}$, which is within the V_2C + VC phase region. In accord with the expectations mentioned earlier, it is apparent that a zone levelling condition has been attained in this crystal, since the composition of the final molten zone is close to that anticipated from the phase diagram for the solidification of material of nominal composition $VC_{0.75}$.

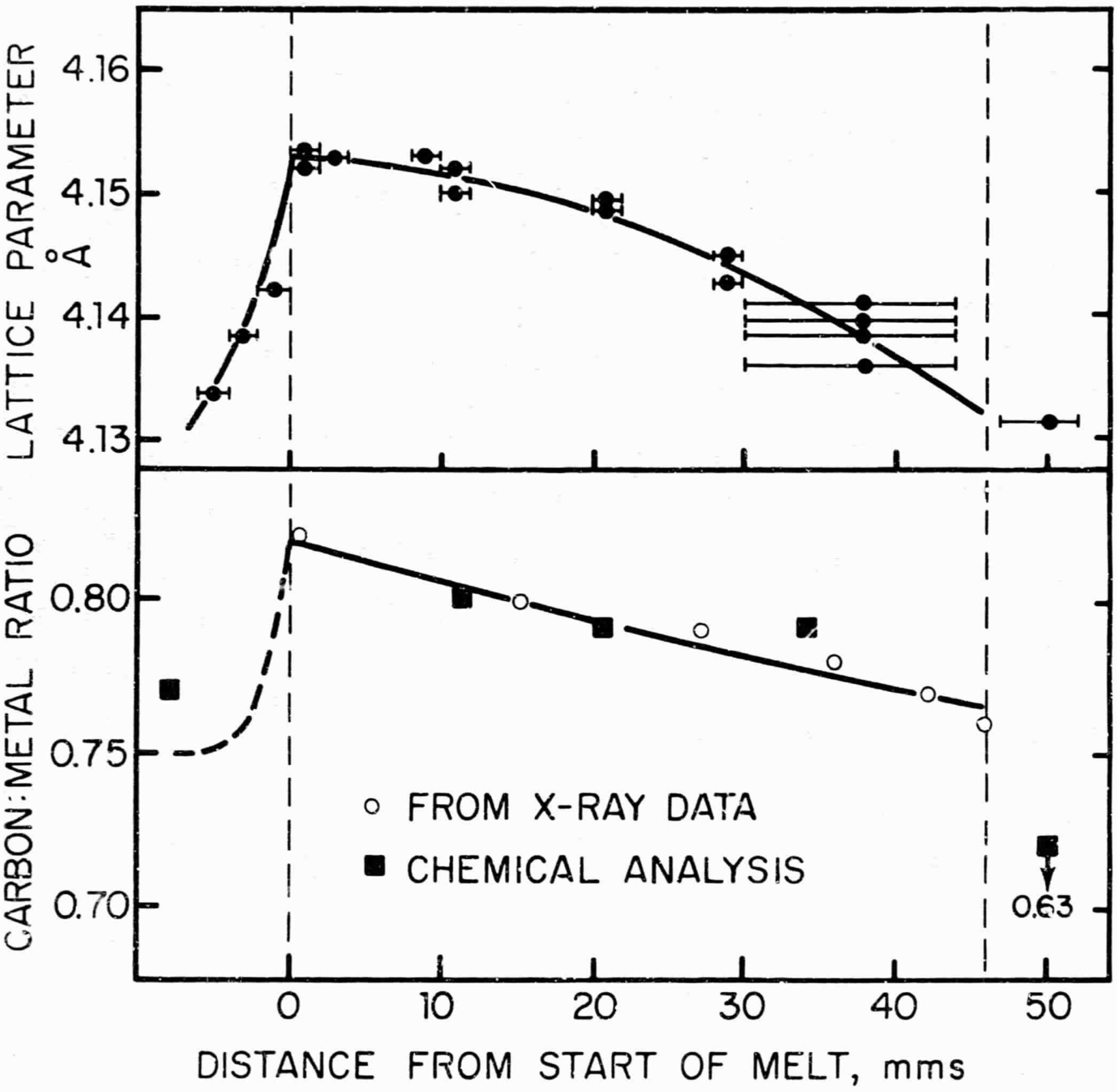

Fig. 5. The variation in carbon-to-metal ratio along a crystal produced by zone-melting a sintered rod initially of uniform composition $VC_{0.75}$. [Lattice parameter was related to composition using the results of Storms (7).]

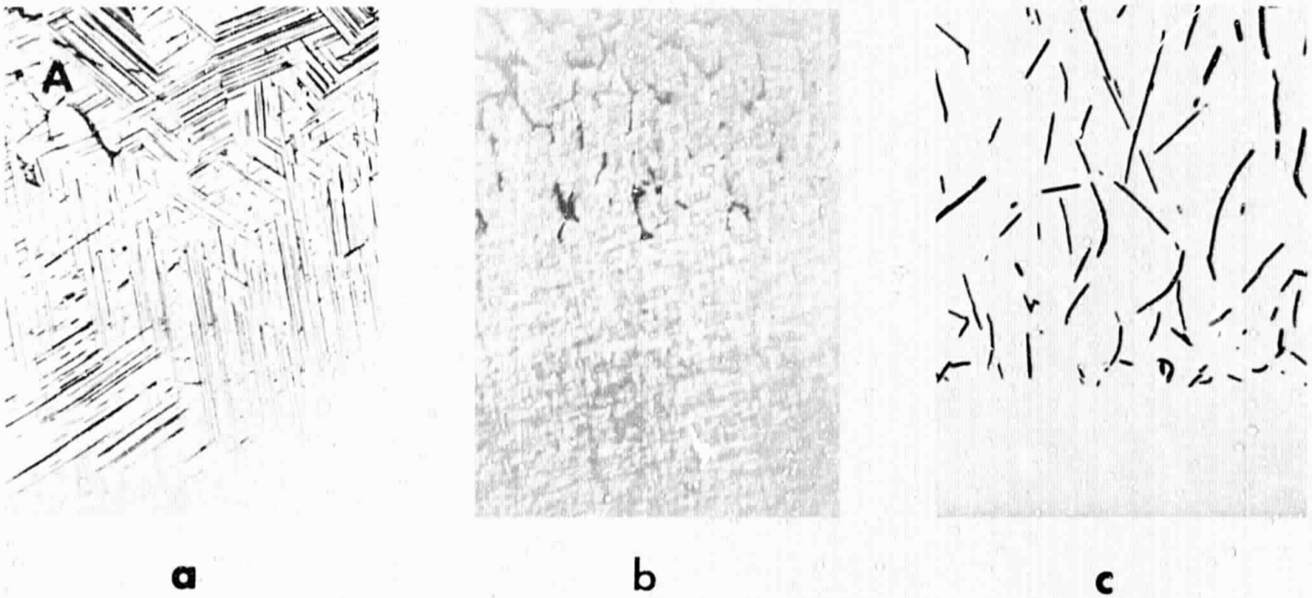

Fig. 6. Optical micrographs of the final solidified zone after one pass along rods of a) $VC_{0.75}$, b) $VC_{0.83}$ and c) $VC_{0.88}$ starting compositions. (Magnification × 60.)

Similar studies have established that crystals grown from material of composition $VC_{0.83}$ and $VC_{0.88}$ also behave in the predicted manner. For example, lattice parameter measurements and chemical analyses indicate that crystals produced from a sintered rod of composition $VC_{0.83}$ do not exhibit any marked longitudinal variation in composition. Thus the domain structure associated with this composition (8) is observed in the sintered rod, the crystal produced from it, and the final molten zone, Fig. 6(b). On the other hand, optical metallography studies indicate that the final molten zone in a rod of initial composition $VC_{0.88}$ contains graphite, Fig. 6(c). In accord with the expected composition gradients in a crystal of this composition, lattice parameter measurements suggest that its carbon content increases as zone refining progresses.

In zone refining, the variation in composition is normally expressed in terms of the distribution or partition coefficient k, where:

$$k = \frac{\text{the concentration of solute in the solid}}{\text{the concentration of solute in the liquid}}.$$

For $VC_{0.75}$, vanadium is the solute under consideration, and the distribution coefficient refers to its concentration with respect to that at the melting point maximum composition which appears to be close to $VC_{0.85}$. For $VC_{0.88}$ on the other hand, carbon is the solute species, and its concentration is compared to that at the maximum melting composition. At present the positions of phase boundaries in the carbides are not known precisely enough for exact equilibrium values of k to be calculated*. However, in this work, rods of some 10 zone lengths long were grown, and it appears that zone levelling was attained in a rod of initial composition $VC_{0.75}$. On the basis of Pfann's (6) computations of the variation in solute concentration with zone travel for various values of k, the present results indicate that the effective value of k is ~ 0.4-0.5. This value may be compared with that computed from the equilibrium diagram shown in Fig. 1, namely ~ 0.3-0.4. It appears therefore, that a qualitative evaluation of the likely variation in composition in zone refined VC and perhaps other carbides also, may be obtained using the value of k deduced from the phase diagram. In accord with this, the effective value of k for rods of starting composition $VC_{0.88}$ is ~ 0.1-0.2, and rods of constant longitudinal composition have not yet been produced, although the composition varies more slowly with distance than in the $VC_{0.75}$ starting rod. This result is consistent with the greater distance of zone travel required to attain zone levelling and thereby to produce a crystal of constant composition.

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*There are major discrepancies in recent determinations of phase equilibria in the vanadium-carbon phase system. Storms (7), for example, indicates that the VC phase forms peritectically. However, this type of phase diagram is not observed in any other metal-carbon system. Rudy et al. (9) and Adelsburg and Cadoff (5), on the other hand, indicate a phase diagram of the form shown in Fig. 1. There are minor discrepancies in the position of the melting-point maximum and, consequently, in the position of the phase boundaries associated with the liquidus and solidus lines. The present results appear to be more consistent with the diagram suggested by Adelsburg and Cadoff (5).

Although the composition variations observed in the crystals are relatively small, they may have a significant influence on mechanical behavior. For example, the two ordered compounds V_6C_5 ($VC_{0.84}$) (8) and V_8C_7 ($VC_{0.88}$) (10), occur at compositions close to the extreme limits expected after zone melting a rod of initial composition $VC_{0.88}$. Since the mechanical properties of these two compounds are different, it is important to produce crystals as nearly as possible of constant composition. This could be achieved by increasing the distance of zone travel or by controlling the molten zone composition to produce zone levelling conditions on initial melting. For example, rods of constant composition $VC_{0.75}$ could be produced by forming a molten zone initially in a sintered rod of composition $VC_{0.62}$ and passing this along a second sintered rod of composition $VC_{0.75}$.

In this zone refining technique, the composition of VC is altered not only in carbon content, but also in impurity content. The boron content of samples is of particular importance in mechanical behavior studies (11-13). It is apparent that the distribution coefficient for boron is very low. Chemical analysis has shown that the boron content of an initial sintered rod was about 0.07%, while that in the melted material was < 30 ppm. However, the boron content in the final zone was 0.4%. Consistent with these composition changes, boride phases are not observed in the crystals produced, but have been detected in the sintered rods and in the final molten zone, e.g. at A in Fig. 6(a). An enlarged micrograph of such an area from the last zone to solidify when a $VC_{0.75}$ rod is zone refined is shown in Fig. 7(a) and compared with an alphagraph (14,15,16) of the same area Fig. 7(b).

Summary

This paper has demonstrated that single crystals of the refractory cubic carbides of controlled carbon-to-metal ratio can be produced using a floating zone technique. The technique described, utilizing rods of specific starting composition, high pressure inert gas environments to prevent volatilization of specific elements, and with adequate precautions to prevent thermal shock failure, can also be applied to produce single crystals of carbides other than VC, and also alloyed carbides. To date, in this program, good quality crystals of TiC and TiC-VC alloys have been produced by this method.

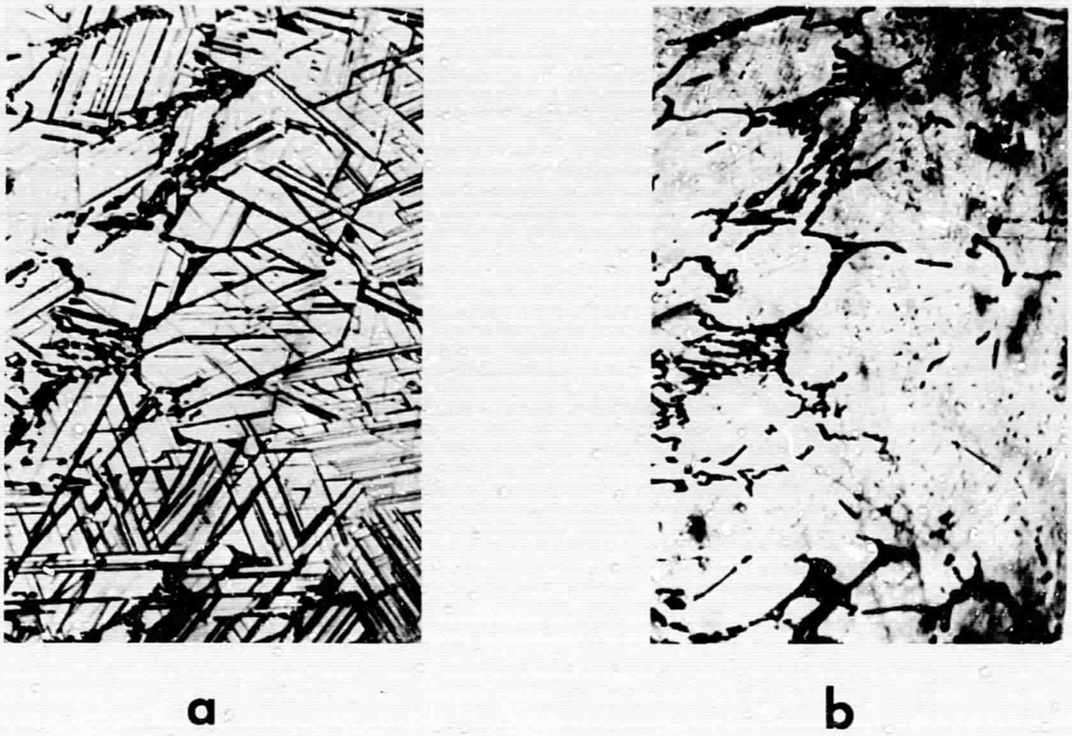

Fig. 7. Optical micrograph of (a) part of the final solidified zone in a $VC_{0.75}$ rod, compared with an alphagraph (b) of the same area. Magnification × 75.

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13. ABSTRACT

Single crystals of pure and alloyed carbides of different carbon-to-metal ratio have been prepared using a floating zone technique. This paper discusses application of this technique specifically to the growth of VC single crystals. Longitudinal variations in composition from about $VC_{0.82}$ to $VC_{0.75}$ are observed when a rod of initial uniform composition $VC_{0.75}$ is zone refined. Variations in composition from about $VC_{0.85}$ to $VC_{0.88}$ are produced in rods initially of composition $VC_{0.83}$. However, since $VC_{0.83}$ is close to the melting-point maximum in the VC phase, little variation in composition is observed on zone refining. These variations in composition are as expected from considerations of the phase diagram and the principles of zone refining. The production of rods of constant composition utilizing the principles of zone levelling is discussed.

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Distribution coefficient						