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BONDING, STRUCTURE AND MECHANICAL BEHAVIOR
OF VANADIUM CARBIDE SINGLE CRYSTALS

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By

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BONDING, STRUCTURE AND MECHANICAL BEHAVIOR

OF VANADIUM CARBIDE SINGLE CRYSTALS

Fourth Technical Report to N.A.S.A.

First Technical Report to ARO(D)

by

R. G. Lye, G. E. Hollox and J. D. Venables

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Abstract

An approximate band structure for VC has been derived. From this, it is concluded that the bonding in VC arises primarily from interactions between orbitals on the metal atoms, and that this component of the bonding is stronger in VC than in TiC. Measurements of the compressive yield strength of $VC_{0.85}$ single crystals over the range 900°-$1800^\circ C$ support this conclusion. However, a domain structure, associated with ordered carbon vacancies, has been observed in these crystals. The anisotropy introduced by such ordering may also contribute to the higher strength of this material.

I. Introduction

The refractory hardmetals constitute a group of compounds which appear to have great potential for future high temperature applications. Of these compounds, the cubic carbides TiC and VC are particularly interesting because of their high ratios of strength to density. Few of the carbides have been studied extensively, but the availability of TiC single crystals with various compositions in its wide phase field has permitted rather detailed investigations of its properties (1-3). These studies have confirmed the conclusions from earlier work on less well characterized materials that the properties of TiC and the other carbides are strongly dependent on carbon content. For example, the yield stress of TiC at $1000^{\circ}C$ has been shown to increase linearly from about 20,000 psi at a composition near $TiC_{0.7}$, to about 50,000 psi at $TiC_{0.97}$ (1).

It has been suggested that this increase in strength of TiC with carbon content is a consequence of an increase in the Peierls stress (1,4). This extremely temperature-sensitive lattice-friction stress arises from electronic interactions between the constituent atoms in the lattice. To deduce the nature of these electronic interactions, studies of the band structure of this material have been made (5), and it has been shown that the predominant contribution to the bonding is from covalent metal-metal bonds. However, the strength of these bonds increases with carbon content because (i) carbon atoms donate electrons to crystal states derived from metal atom wave functions, and thus increase the number of 3d-electrons available for metal-metal bonding, and (ii) the presence of carbon atoms in overlap regions of neighboring metal atom 3d-orbitals introduces a potential that increases the strength of the metal-metal interactions. Similar

behavior is expected in the other transition metal carbides, although modified in detail and strength by the individual characteristics of the metal atoms.

The present investigation is directed toward understanding the electronic interactions which govern the mechanical behavior of the carbides in general, so that alloying with other transition metal compounds can be used to modify their properties in a controlled manner. When the alloying elements have similar atomic radii and electronic levels, it is reasonable to assume that a semi-rigid band model will describe the resulting alloys (6). The properties of alloys formed from such elements are expected to depend on composition in a relatively simple way, and for this reason the TiC-VC system has been chosen to begin the study. The initial phase of the program, reported here, has been concerned with the properties of VC crystals.

II. Band Structure and Bonding in VC

In the simple two-center tight-binding approximation, the band structure of VC would be expected to differ from that of TiC because of differences in the one electron energies of the two metal atoms, and the two-center integrals between wave functions on neighboring atoms (7). Differences in the one electron energies (8) are expected to cause the 2s and 2p bands of carbon and the 4s band of vanadium to lie approximately 1 eV higher relative to the metal d-bands in the VC than they do in TiC. These displacements of the energy bands will modify the s-d and p-d hybridization, but in other respects should leave the d-bands relatively unchanged.

Because the lattice constants and metal atomic radii have approximately the same proportions in TiC and VC, many of the two-center integrals have similar values in the two compounds. However, the smaller lattice constant of VC will cause the carbon-carbon interactions to be somewhat stronger in this material than they are in TiC. Moreover, because the interactions between d-functions on neighboring metal atoms are influenced by the potential of carbon atoms in the overlap region, the effective values of the two-center integrals used to represent these interactions also will be greater in VC. Thus, the energy bands will be shifted and broadened in VC, but the principal characteristics of its band structure are expected to be closely similar to those of TiC, and these similarities will be reflected in the physical properties of the two compounds. In particular, because the initial and final states of important optical transitions are shifted by approximately equal energies, the optical properties of VC are expected to exhibit many of the prominent features found in the spectrum of TiC (2).

The expected behavior has been observed experimentally in comparative studies of the reflectivity from TiC and VC. In the present work, measurements were made of the near-normal-incidence reflectivity from a mechanically polished (100) face of a $C_{0.85}$ single crystal. A modified Beckman DK-2 spectrophotometer was used for the spectral region from 0.5 eV to 5 eV. For the region from 3.5 eV to 14 eV, measurements were made with a Jarrell-Ash Model 78-660 vacuum ultraviolet monochromator using a 1 meter focal length grating and a hydrogen-filled Tanaka capillary discharge tube as the light source. A composite of the results from several measurements is shown in Fig. 1, together with the near-normal-incidence
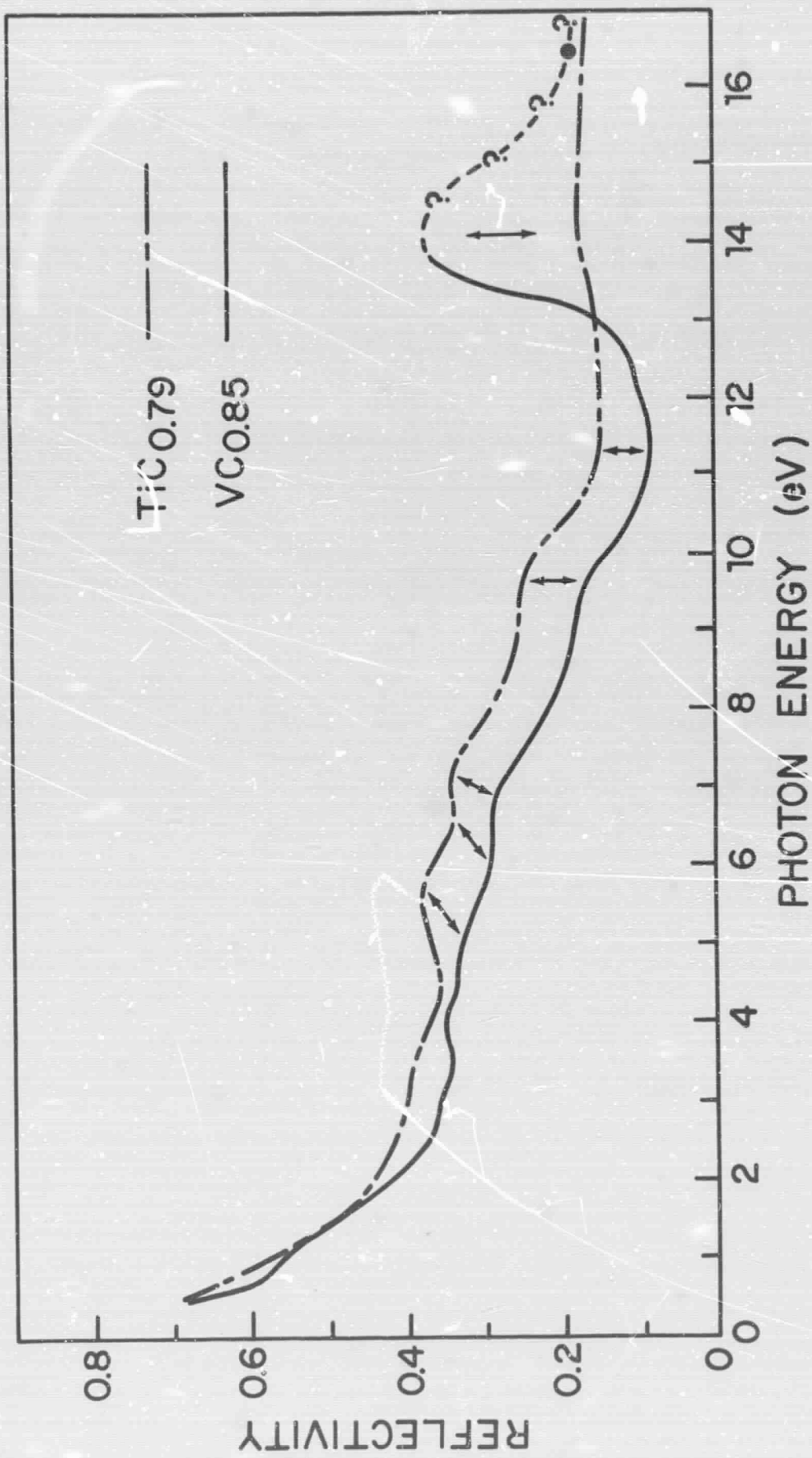
Fig. 1. Near-normal-incidence reflectivity of $VC_{0.85}$ (solid curve) and $TiC_{0.79}$
(broken curve). Arrows indicate what are believed to be corresponding
features of the two spectra.

reflectivity from a cleaved (100) surface of a $TiC_{0.79}$ single crystal (2). The spectra are indeed similar, which indicates that the principal high-energy band gaps are equal in the two carbides to within approximately $\pm$ 0.5 eV.

The band structure near the Fermi level is also expected to be similar in the two carbides. Many of the prominent features in the density-of-states curve near the Fermi level are determined primarily by the d-bands of the fcc array of metal atoms, and these features are relatively unaffected by small changes in the band parameters. Thus, the calculated density-of-states curve for TiC shown in Fig. 2 (2) can be used as a guide in estimating the properties of VC. In TiC, the Fermi level of the stoichiometric compound falls near the minimum (a) in Fig. 2. When carbon is removed from the lattice, the band structure changes slightly, but the prominent features in the density-of-states curve remain. As the electrons contributed by carbon atoms are removed, the Fermi level moves to lower energies and the density of states at the Fermi level increases toward the maximum at (A).

When allowance is made for the extra electron of vanadium and for the higher energy (lower occupancy) of the 2s, 2p, and 4s bands in VC, the Fermi level of $VC_{0.88}$ is estimated to fall near the minimum (b). As carbon is removed from the $VC_{0.88}$ lattice, the Fermi level moves to lower energies and, as in TiC, the density of states at the Fermi level increases. In VC, however, the Fermi level moves within the region (b)-(B), so that the increasing density of states appears to be associated with a maximum that is different from the one that determines the behavior of TiC[*].

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[*]These features of the density-of-states curve are characteristic of 3d bands in an fcc lattice, but they are modified somewhat by hybridization interactions in the carbide lattice.
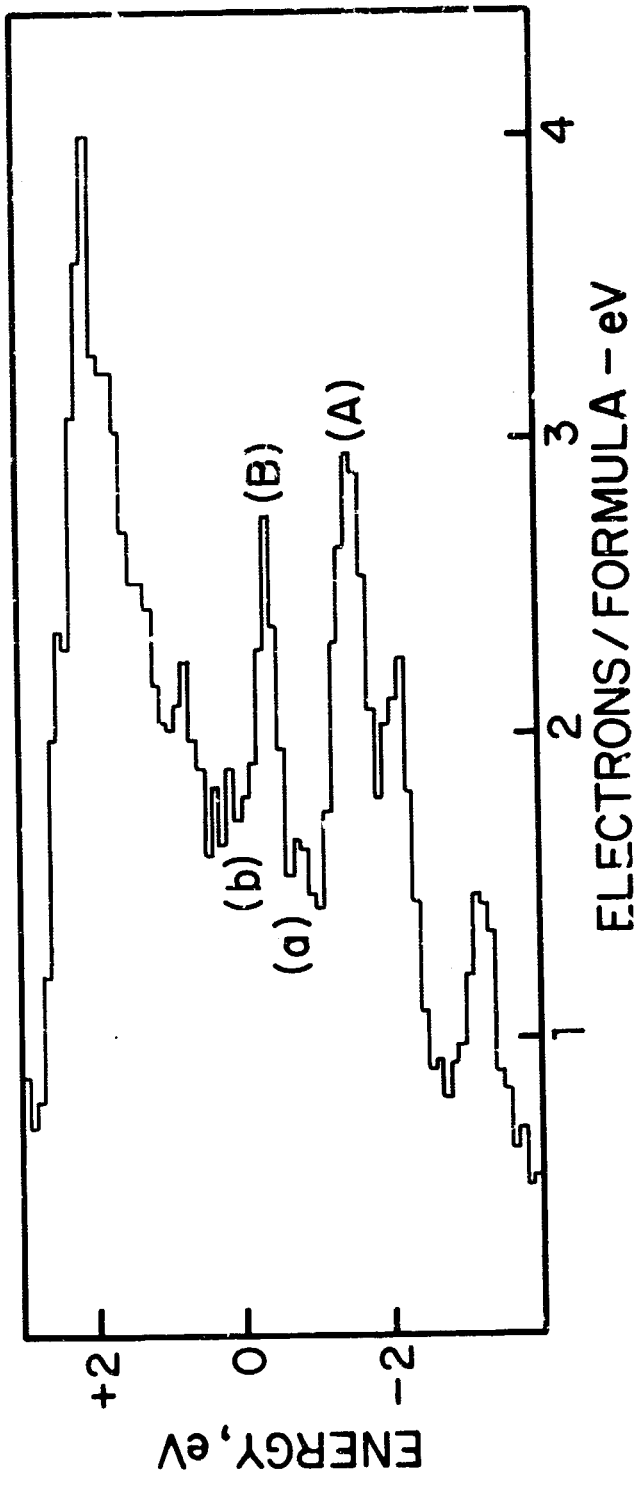
Fig. 2. A portion of the density-of-states curve computed for TiC. Fermi energies for TiC_x fall in the range (a)-(A), for VC_x in the range (b)-(B).

A variation in density of states with composition similar to the dependence suggested here has been observed by Bittner and Goretzki (9) in their measurements of magnetic susceptibility. It appears possible, therefore, to account for both the magnetic susceptibility and the optical reflectivity of VC with only small modifications to the band structure of TiC. The Hall coefficient of VC observed by Tsuchida et al. (10) also can be explained if the d-bands are broadened to the extent that an electron pocket containing one electron/metal atom is formed at the center of the Brillouin zone by energy bands with d_ϵ symmetry. Figure 5 shows a proposed band structure for VC which includes this electron pocket at $\Gamma_{2'5}$ and has the 2s, 2p, 4s, and 4p bands raised by approximately 1 eV from their positions in the band structure of TiC.

If the arguments discussed above are applicable, the bonding in VC is very nearly the same as it is in TiC. That is, it arises in large part from essentially covalent interactions between wave functions on the metal atoms (metal-metal bonding), but because the carbon atoms are located in the overlap region, these interactions are stronger than they would be in (hypothetical) fcc vanadium metal. However, this metal-metal bonding probably is somewhat stronger in VC than in TiC because the smaller lattice constant permits the vanadium wave functions to overlap closer to the cores of the carbon atoms. Because the lower d-states are more strongly bonding and the bonding portion of the d-band is more nearly filled, the d-band of VC contributes relatively more to the cohesion of VC than it does in TiC, whereas the 2p, 4s, and 4p bands contribute less. The 2s band has only a secondary effect on the bonding of both compounds. A slightly
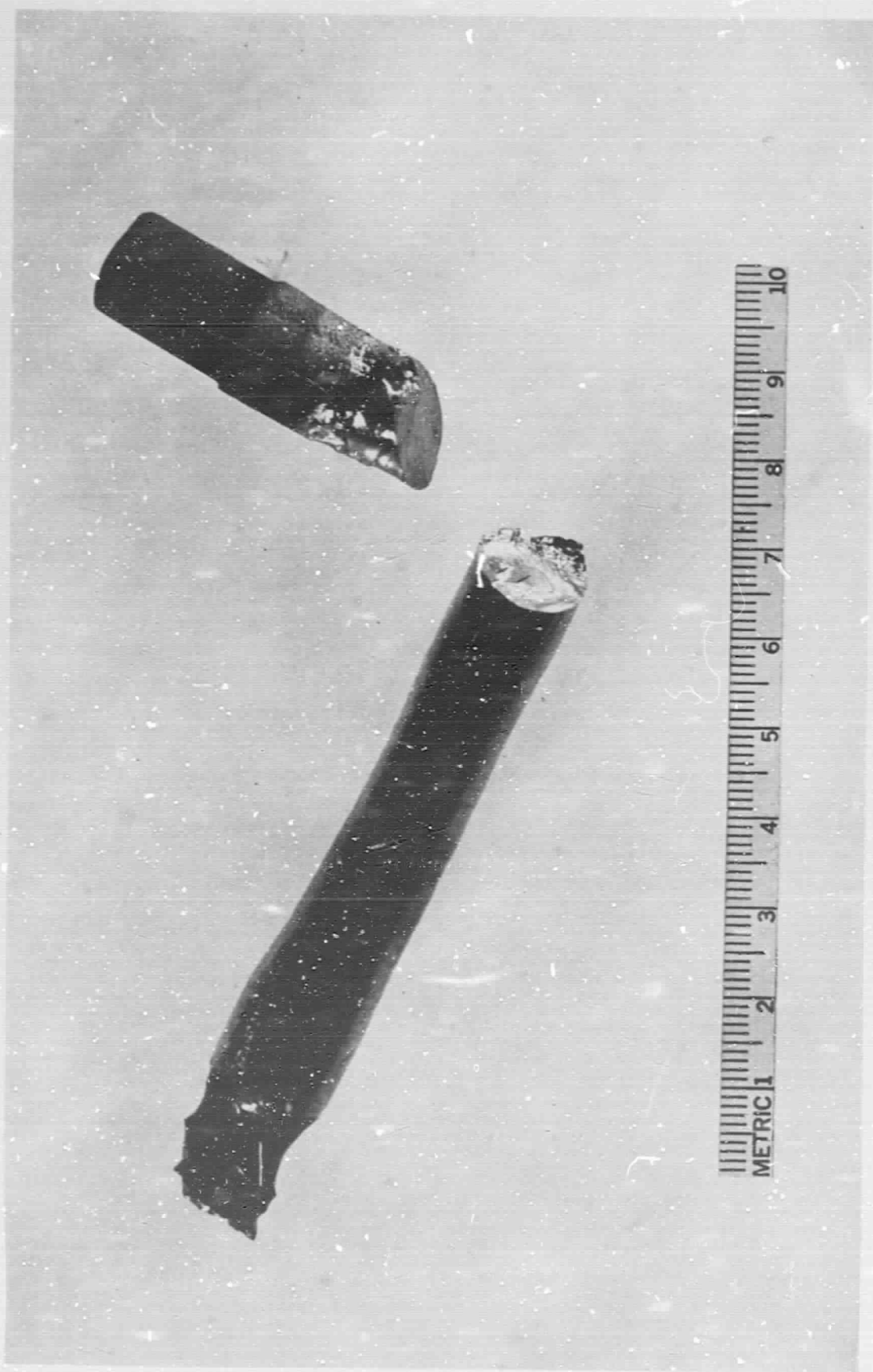
Fig. 4. A single crystal of VC about 1 cm. in diameter and 8 cm. long, grown by the floating-zone technique.

larger transfer of electrons occurs from carbon to vanadium states in VC, so that the ionic contribution to the bonding may be somewhat larger than it is in TiC, but in neither compound does it appear to contribute an important part of the cohesive energy.

In most respects, then, the mechanical behavior of VC should be similar to that of TiC, but the enhanced bonding due to interactions between metal atom d-orbitals may increase the effective Peierls stress in VC and thereby increase its hardness and strength. Qualitative support for this conclusion has been obtained from studies of the mechanical properties of VC, but the results are not yet conclusive because of interfering effects introduced by the presence of an unusual substructure in the crystals.

III. Growth and Structure of VC

Single crystals of $VC_{0.85}$ have been grown under 10 atmospheres pressure of pure helium using a conventional floating zone technique (11). Isostatically pressed and sintered carbide rods were heated with an r.f. induction coil, and a molten zone about 1 cm. in height passed along the rod at a rate of approximately 1 cm/hr. Preferential growth of one grain occurred, usually with a low index direction close to the axis of the rod. Under optimum conditions, crystals greater than 1 cm. in diameter and 8 cm. long were produced in this manner, Fig. 4. The crystals were annealed at $1800^{\circ}C$ for 5 hrs, followed by furnace cooling. Chemical analysis indicated that the material contained approximately 0.1 w/o each of oxygen and nitrogen, as well as traces of metallic impurities. However, since all such impurities form mutually soluble compounds at these low concentrations, they are not likely to influence the properties of the material significantly.

Examination of these crystals by optical microscopy, transmission electron microscopy and selected area diffraction has revealed the existence of a superlattice and an associated domain structure, Fig. 5 (a,b, and c). The super- lattice appears to result from the ordering of carbon vacancies, as has been suggested by de Novion et al. (12) on the basis of X-ray diffraction data ob- tained from $VC_{0.89}$ powders. The domain structure results, in turn, from the fact that this superlattice can assume several possible orientations within the VC crystal lattice. The superlattice spots obtained by electron diffraction from crystals grown at RIAS ($VC_{0.85}$) can be indexed on the basis of an hexagonal unit cell, but not on the basis of the cubic unit cell derived by de Novion et al (5). This difference may indicate that the type of vacancy ordering occurring in VC is a function of carbon content.

The existence of an hexagonal superlattice within the fcc VC lattice introduces an anisotropy which has a profound effect on the response of such crystals to polarized light. The strong birefringence associated with this anisotropy allows the domain structure to be observed optically when the domains are sufficiently large; each domain exhibits a coloration different from that of its neighbors when the crystal is viewed in reflected polarized light between crossed Nicols, Fig. 5 (c).

The present observations demonstrate that VC cannot, in general, be re- garded as an isotropic material, and it is expected that the consequences of departures from isotropy will be evident in many of its physical properties, and perhaps also in its mechanical behavior. The latter possibility will be dis- cussed briefly in the next section.
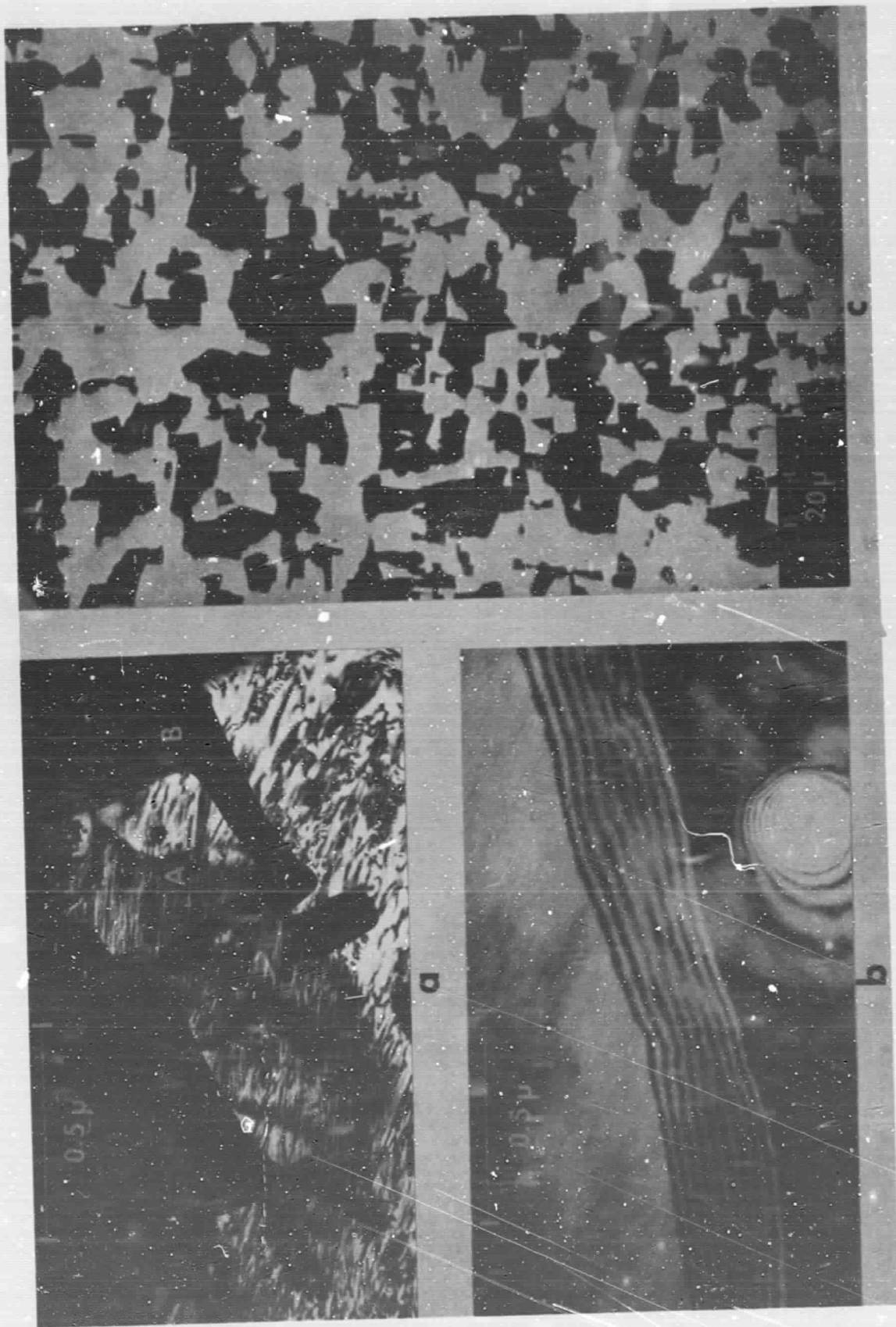
Fig. 5. Domain structure in single crystal VC$_{0.85}$. (a) Dark field transmission electron micrograph taken with a superlattice spot from domain at A. Domain at B remains dark. (b) Bright field electron micrograph showing domain wall. (c) Optical micrograph of domain structure taken with polarized light between crossed Nicols. Original contrast provided by differences in color between domains.

A more detailed analysis of the domain structure is in preparation and will be presented elsewhere (13).

IV. Mechanical Behavior of $VC_{0.85}$ Crystals

The mechanical properties of single crystals of $VC_{0.85}$ have been investigated over the temperature range 900°-1800°C. Compression specimens, approximately 8mm × 3mm × 3mm in size, were cut from the annealed crystals using an annular diamond saw, and their surfaces were mechanically polished in the usual manner, finally using 1/4µ diamond paste. Compression tests were conducted in an Instron machine equipped with a Brew 1064 tungsten-mesh furnace maintained at a vacuum of 10^{-6} Torr.

To establish the deformation mechanisms in VC, crystals were compressed along [001] and [012] directions, for which the Schmidt factor is greatest on the {110} ⟨1̄10⟩ and {111} ⟨1̄10⟩ systems, respectively. The slip patterns observed on specimens compressed along [001] directions did not allow conclusive identification of the operative systems, probably because of interference between several systems. However, Fig. 6 shows the slip line structure exhibited by the (02̄1) face of a crystal deformed in the [012] direction at 1400°C. The pattern is consistent with slip occurring on {111} planes, and the 'wavy' appearance of the slip lines is characteristic of a material of high stacking fault energy. These observations are similar to those made earlier on TiC of similar stoichiometry (1,3), so that it is likely that the dislocation structures and slip mechanisms of VC are similar to those observed in TiC.
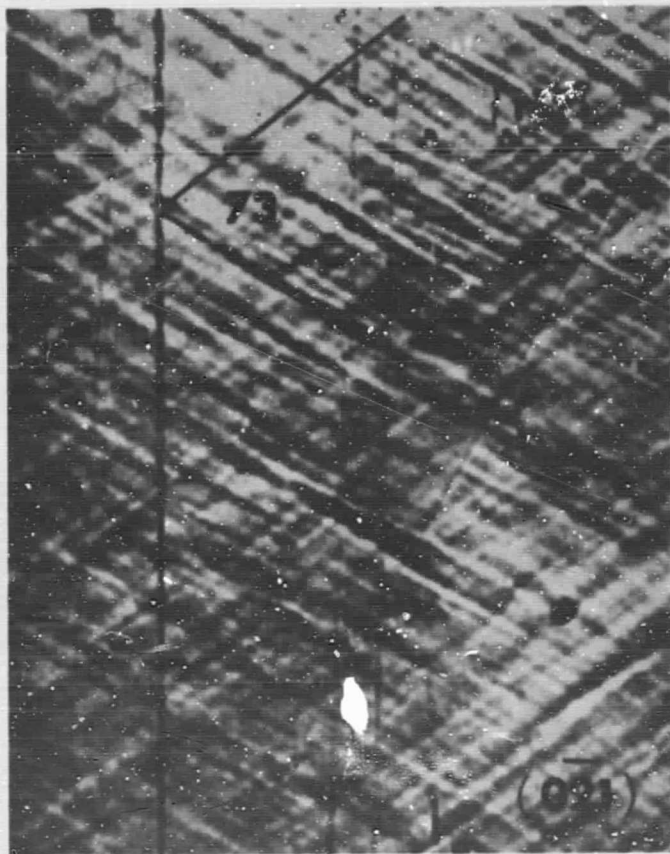
Fig. 6. Slip lines on the (0$\bar{2}$1) face of a VC$_{0.85}$ crystal compr[...]ed 2% along [012] at 1400°C. The 73° angle between intersecting slip lines is consistent with slip on {111} planes.

Preliminary measurements of the critical resolved shear stress (c.r.s.s.) for slip on the {111} $\langle 1\bar{1}0 \rangle$ system of $VC_{0.85}$ are presented in Fig. 7. These results may be compared with data from TiC and ZrC crystals of similar stoichiometry. The c.r.s.s. of $VC_{0.85}$ is greater than that of either of the other carbides, but decreases rapidly from a value of about 25 kg/mm^2 (36,000 psi) at 1250°C, to 2 Kg/mm^2 (2,800 psi) at 1550°C. The rate of decrease in strength above the brittle to ductile transition temperature ($\sim$ 1200°C) is even more rapid than that observed previously for TiC or ZrC. Nevertheless, the ratio of compressive yield strength to density at 1250°C is greater than 400,000 in., which considerably exceeds that for either pure TiC ($\sim$ 125,000 in.) or boron-doped TiC (190,000 in.) at this same temperature. However, the superior properties of VC in the unalloyed state are limited to the temperature range 1200-1300°C because of its rapid decrease in strength with increasing temperature.

The observation that VC is the strongest of these carbides at equivalent stoichiometry would ordinarily be somewhat surprising, because the melting point - which is often taken as a measure of the stability of a solid - of VC (2650°C max.) is considerably less than that of TiC, (3250°C max.) (15). However, the increased strength of the metal-metal bonding in VC over that in TiC predicted in Section II correlates directly with these observations.

On the other hand, there may be other factors influencing the strength of VC which also must be taken into account, for example, the effects of vacancy ordering and domain structure. Domain walls, such as that shown in Fig. 5 (b), probably act as barriers to dislocation motion. Thus the rapid fall-off in strength of VC in the temperature range 1200-1300°C, Fig. 7, might result from the disappearance of these barriers after some order-disorder transition, or from
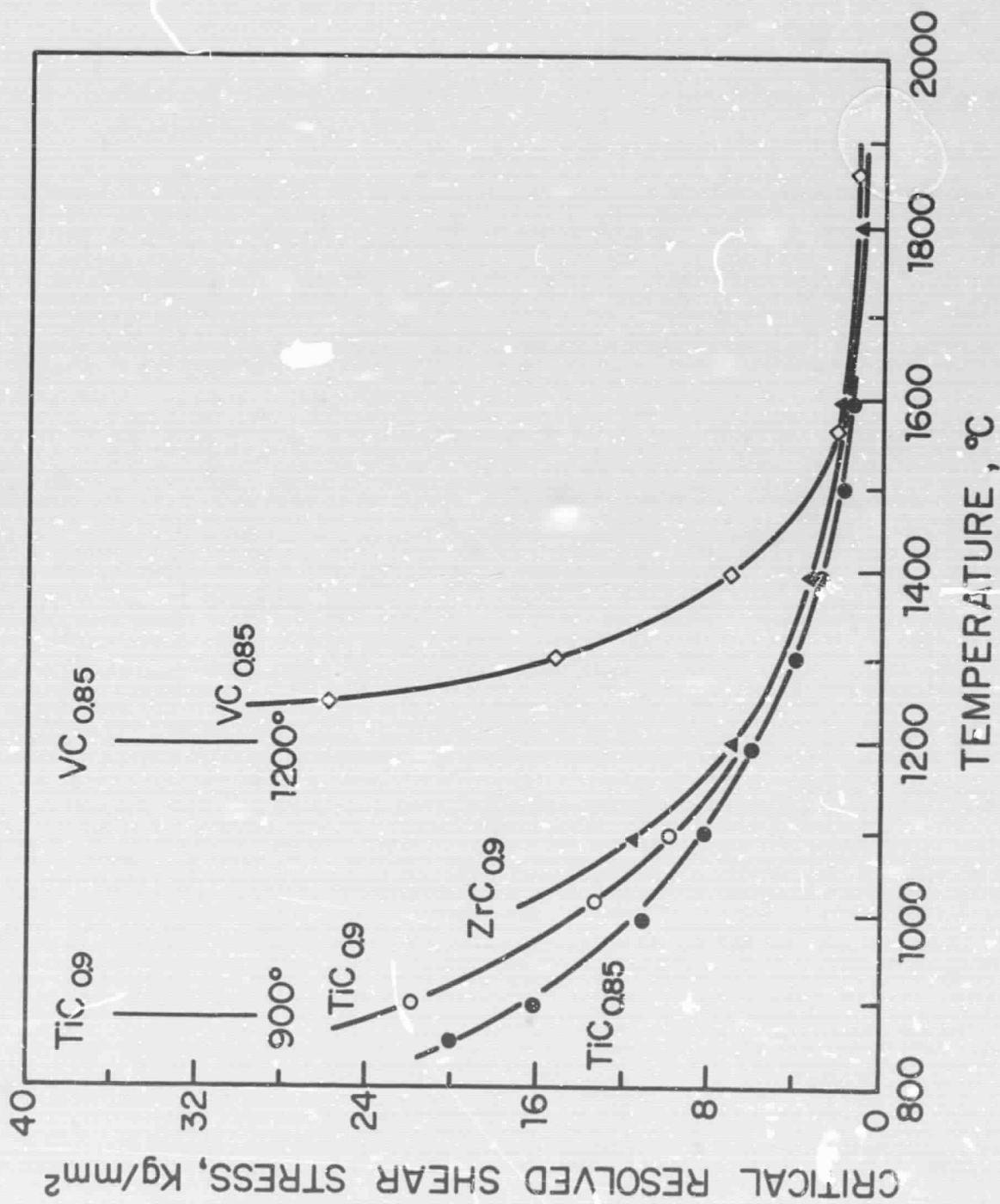
Fig. 7. The critical resolved shear stress for slip on the {1l1} ⟨1l̄0⟩ slip system of VC$_{0.85}$ as a function of temperature, for comparison with similar measurements on TiC [after Williams (1)] and ZrC [after Haggerty and Lee (14)].

domain-wall movement at these temperatures. Preliminary results are in accord with this possibility, inasmuch that metallographic studies have demonstrated that domain configuration is changed by annealing at $1300^\circ C$, but not by annealing at $1250^\circ C$.

V. Acknowledgements

References

1. W. S. Williams, J. Appl. Phys. **35**, 1329 (1964).

2. R. G. Lye and E. M. Logothetis, Phys. Rev. **147**, 622 (1966).

3. G. E. Hollox and R. E. Smallman, J. Appl. Phys. **37**, 4818 (1966).

4. G. E. Hollox and R. E. Smallman, Proc. Brit. Ceram. Soc. **6**, 317 (1966).

5. R. G. Lye, <u>Atomic and Electronic Structure of Metals</u> (A.S.M., Cleveland, 1967), (in press).

6. J. L. Beeby, Phys. Rev. **135**, A130 (1964).

7. J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

8. F. Herman and S. Skillman, <u>Atomic Structure Calculations</u> (Prentice-Hall, Inc., New Jersey, 1963).

9. H. Bittner and H. Goretzki, Monatsh. Chem. **93**, 1000 (1962).

10. T. Tsuchida, Y. Nakamura, M. Mekata, J. Sakurai and H. Takaki, J. Phys. Soc. Japan **16**, 2453 (1961).

11. W. Precht and G. E. Hollox, 1967 (to be published).

12. C. H. deNovion, R. Lorenzelli, and P. Costa, Compt. Rend. **263**, 775 (1966).

13. J. D. Venables, 1967 (to be published).

14. J. Haggerty and W. Lee, (presented at A.C.S. Annual Meeting, Washington, 1966).

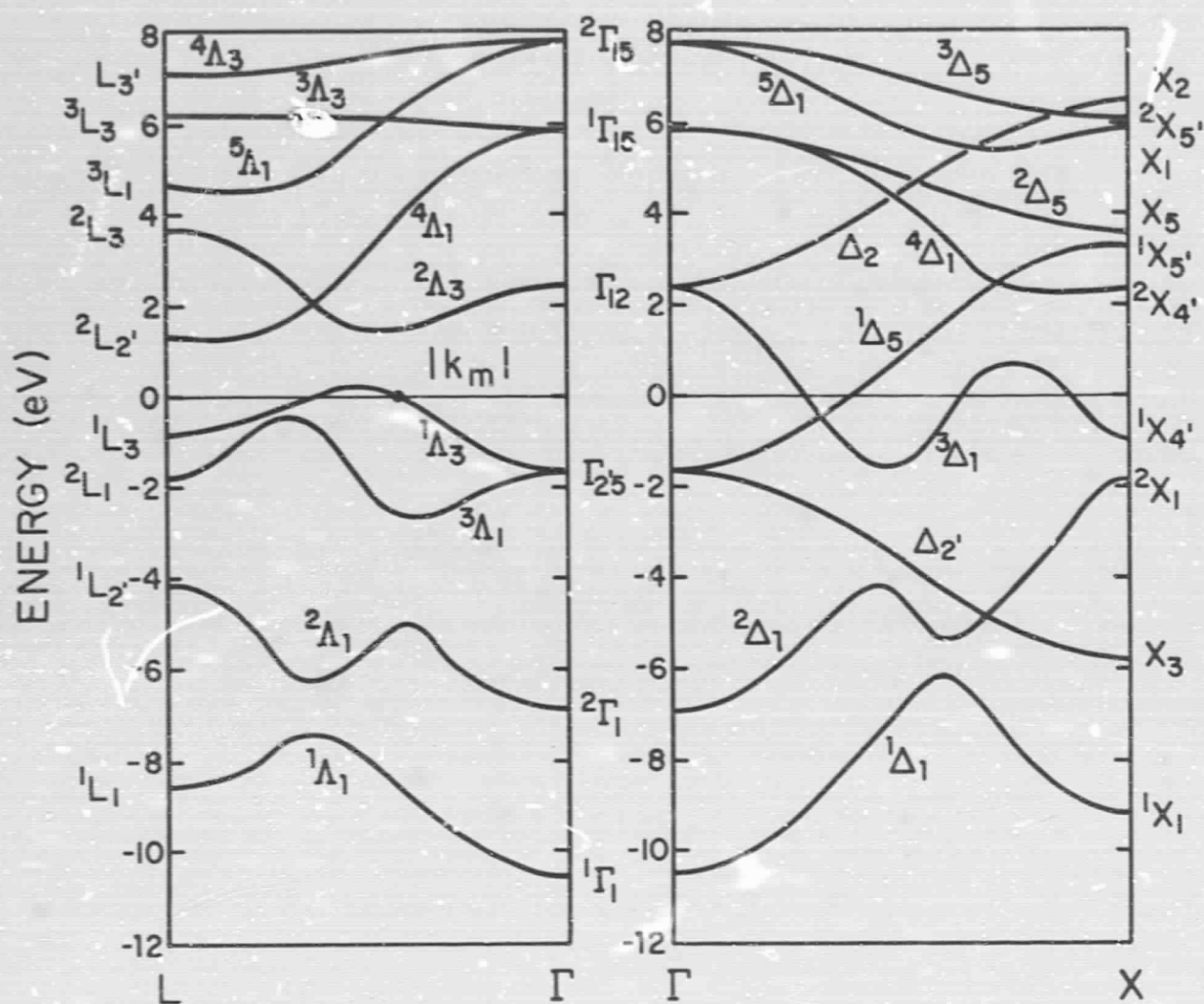15. E. K. Storms, Los Alamos Scientific Laboratory Report LA-2943, (1964).

Fig. 3. Preliminary estimate of the band structure of VC obtained by means of a two-center, tight-binding approximation.

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