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# MICROSTRUCTURE AND MECHANICAL BEHAVIOR OF CARBIDES

By

Graham E. Hollox

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Third Technical Report
To ARO(D)
Contract DA-31-124-ARO-D-467

Seventh Technical Report
To NASA
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MARTIN MARIETTA

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## Abstract

The need for improved materials in high temperature structural applications has stimulated research into the mechanical behavior of a number of materials including the refractory hard metals. The transition metal carbides are of particular interest for a number of reasons, for example: (a) these compounds include the materials having the highest melting points, (b) they are extremely strong, and (c) they deform plastically in a manner similar to fcc metals. The purpose of this paper is to review the present understanding - or lack of it - of the deformation process and the factors affecting the mechanical behavior of these technologically important materials. Consequently, the more interpretable information obtained in recent years from studies of single crystals, rather than that from sintered polycrystalline materials, is emphasized.

## 1. Introduction.

The refractory carbides include the compounds having the highest known melting temperatures and for this reason much interest has been shown in their high temperature mechanical properties. About ten or fifteen years ago considerable effort was directed towards evaluating their mechanical behavior for structural applications, but the results were disappointing. The materials were shown to be extremely brittle and very susceptible to thermal shock failure. In most of this work, however, sintered materials were used. This may have had a significant influence on the mechanical behavior since pores provide fracture sources and reduce strength. Consequently, current research is directed towards evaluating the properties of fully dense carbides using materials produced from the melt. Particular emphasis is being placed on understanding the factors which determine the mechanical behavior of these materials so that improvements in their properties may be made by controlled alloying. Such studies have been considerably enhanced in the last few years by the availability of single crystals. The purpose of this paper is to summarize some of the recent results obtained on single crystals, together with the more meaningful information obtained on polycrystalline carbides, and review the present understanding of the mechanical behavior of these potentially important materials.

## 2. Structure of Refractory Carbides.

Phase equilibria in transition metal-carbon systems have been the subject of several intensive investigations in the last few years. A detailed discussion of this is beyond the scope of this paper, and readers are referred to the reviews by Schwartzkopf and Kieffer[1] and by Storms[2]. Most of the discussion in this review will be limited to the Group IV and Group V monocarbides with the B-1, NaCl-type structure, isomorphs of which include the high temperature form of WC, UC[4], PuC, transition metal mononitrides and monoxides, and the corresponding rare earth compounds[5].

The titanium-carbon phase diagram[2], Fig. 1, is typical of the Group IV metal-carbon systems. The TiC phase exhibits a composition range from about $TiC_{0.6}$ to $TiC_{0.98}$. For Group V metal-carbon* systems, such as tantalum-carbon shown in Fig. 2, the phase diagram[2] shows similar features, but the homogeneity range of the MC carbide is reduced by the presence of the $M_2C$ carbide. At high temperatures, the $M_2C$ carbide has the $L^1 3$ hexagonal structure but ordering in the carbon sublattice modifies the structure to orthorhombic at low temperatures[6]. In both Group IV and V carbide systems, a eutectic between MC and carbon is formed at higher carbon contents, although there is a disagreement between various investigators concerning the composition and temperature in some systems[2,6,7].

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*Storms[2] indicates that the VC phase forms by a peritectic reaction, but more recent work[6,7] has indicated that the phase diagram is similar to that of the tantalum-carbon and niobium-carbon systems[2].

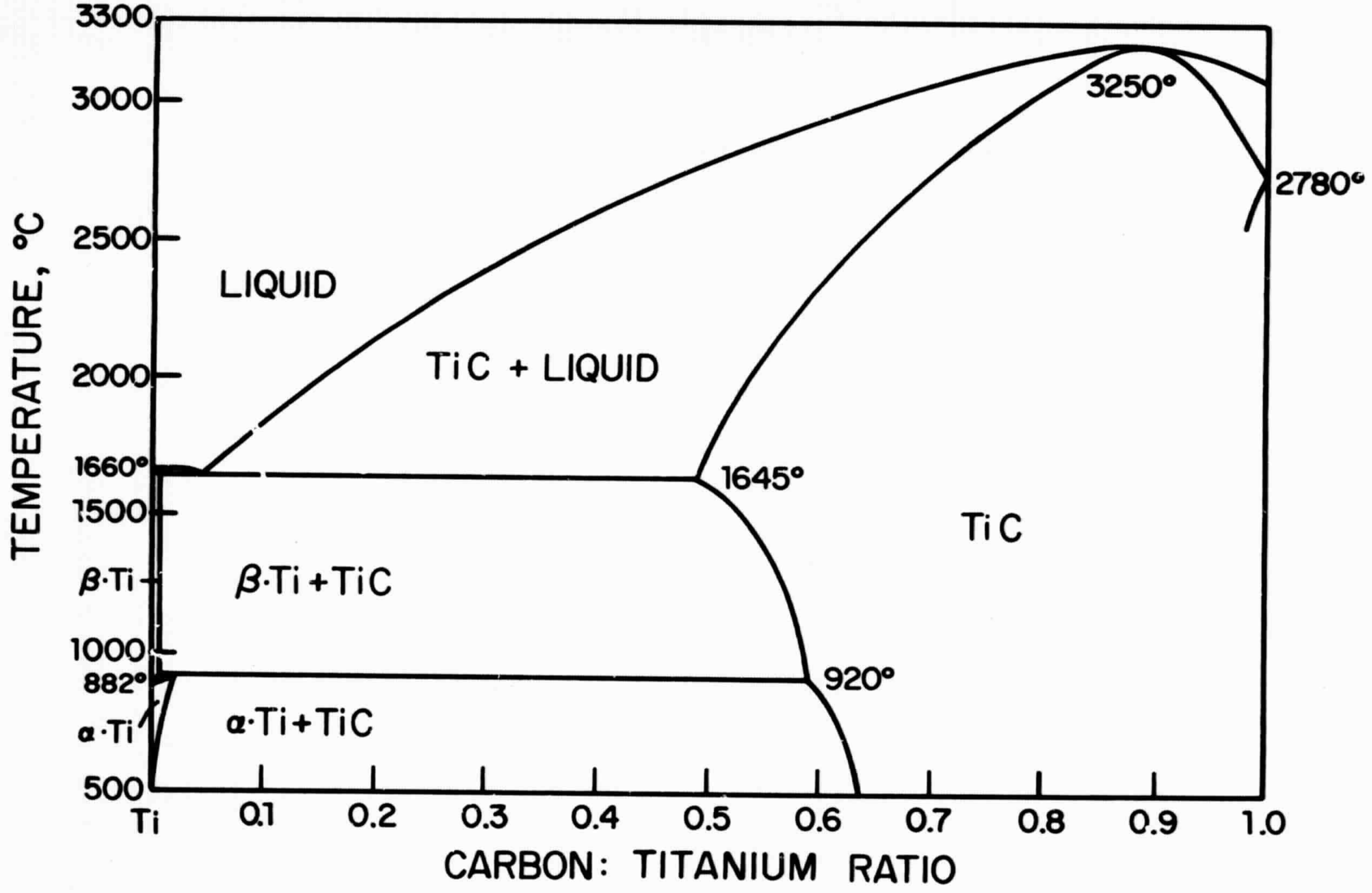

Figure 1. The titanium-carbon equilibrium diagram. The TiC phase exists over a range in composition by incorporating vacancies in the carbon sublattice (after Storms[2]).

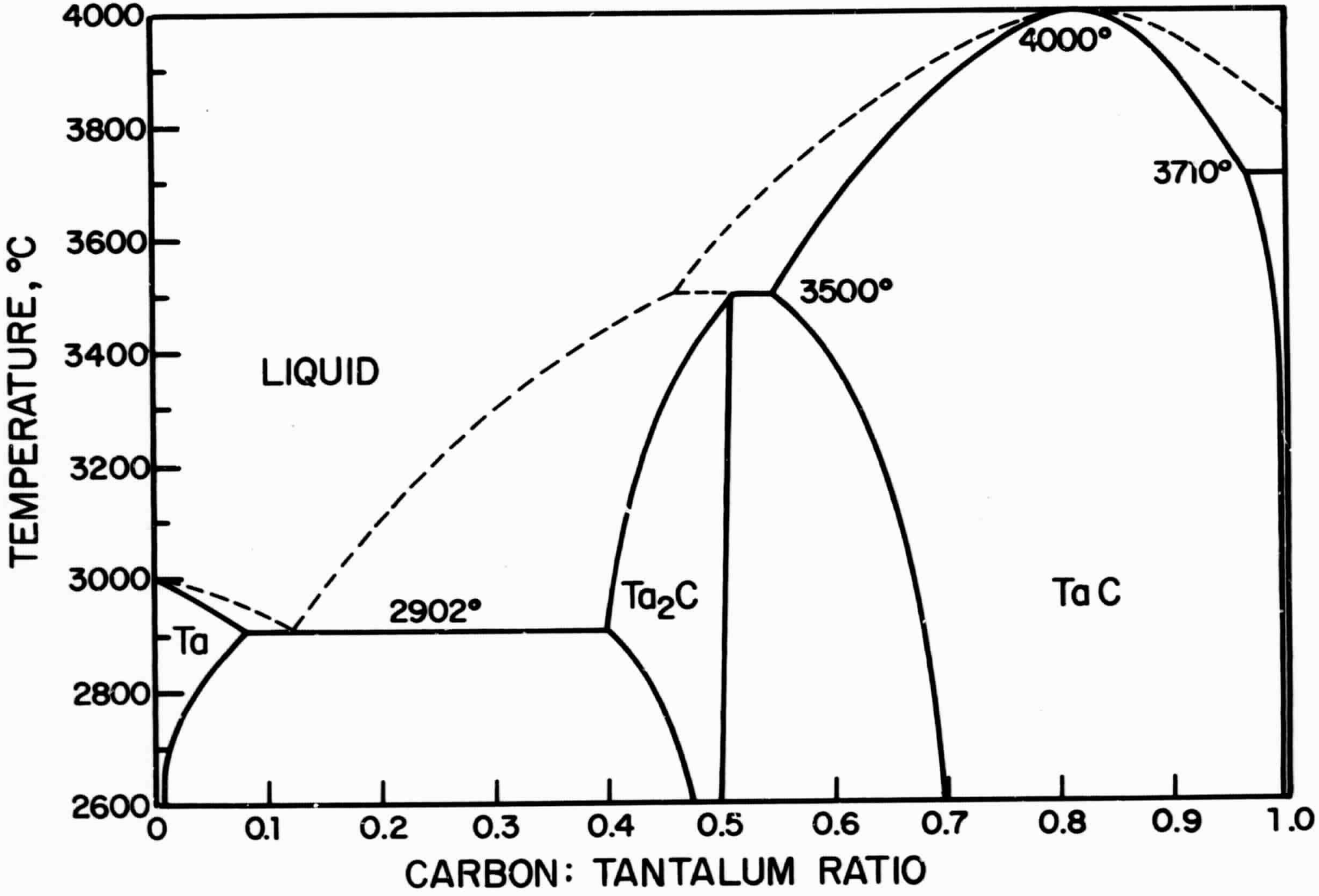

Figure 2. The tantalum-carbon equilibrium diagram (after Storms[2]).

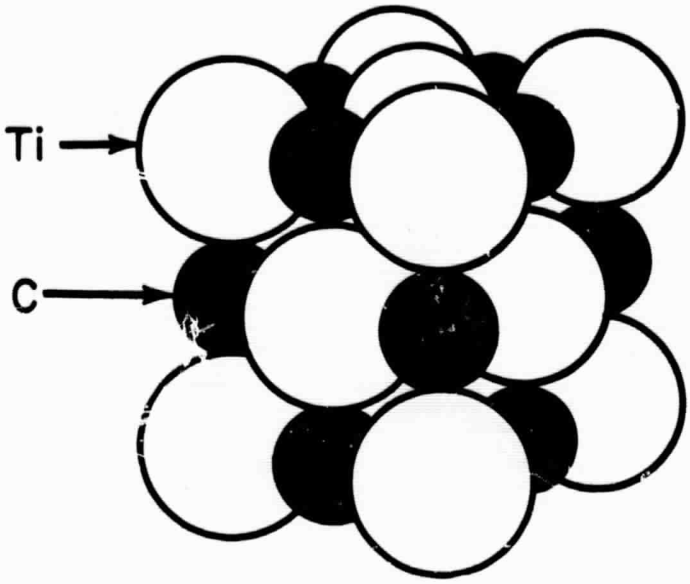

Figure 3. The structure of the cubic carbides.

In the MC structures, metal atoms occupy a cubic lattice which is virtually close-packed, Fig. 3, the metal-metal distance being slightly greater than that in the pure metal structure - about 3% for Group IV carbides, and about 9% for Group V carbides. Carbon atoms occupy the octahedral interstices, complete packing of which would result in the composition $MC_{1.0}$, but the phases do not appear to attain this stoichiometric composition. This discrepancy has been attributed to the presence of oxygen and nitrogen impurities which occupy similar atomic positions to carbon in these structures[2]. However, such observations as (i) the existence of the isomorphous compound TiO over the composition range $TiO_{0.65}$ to $TiO_{1.25}$[8] and (ii) the upper limit of the VC phase being $VC_{0.89}$, suggest that the geometrical arrangements of atoms in the sodium chloride structure[9] is an incomplete explanation for the occurrence of these compounds. From studies of the band structure of VC, Lye[10] has deduced that the bonding states of the d-band are completely occupied at a composition close to $VC_{0.88}$, and has suggested that since additional carbon would contribute electrons to anti-bonding d-states, graphite may precipitate at higher concentrations. Similar considerations of the electronic structure of other carbides may explain the phase limits of these materials also.

A feature common to most of the cubic phases is the occurrence of a maximum melting-point within the single phase field, e.g. at $TiC_{0.87}$ (Fig. 1) and $TaC_{0.82}$ (Fig. 2). This suggests that ordering or compound formation may be occurring in the solid state.

Until recently, it was thought that vacancies were randomly distributed in the carbon lattice[11], but ordering has been observed in TiC at low carbon contents[‡12], and also in VC[13-15] throughout its composition range. Using X-ray diffraction techniques coupled with the nuclear magnetic resonance studies of Froidevaux and Rossier[13], de Novion et al.[14] concluded that a cubic superlattice was a consequence of carbon vacancy ordering in $VC_{0.88}$ and suggested that $VC_{0.88}$ should be described as an ordered cubic material, $V_8C_7$, with a lattice parameter twice that of the rocksalt structure. Venables et al.[15] have shown that $VC_{0.84}$ can be considered as hexagonal $V_6C_5$, and suggest that the previously designated cubic phase field is more correctly described by a series of ordered compounds $V_8C_7$, $V_6C_5$, etc. In all these structures, vanadium atoms are arranged on a slightly distorted face centered cubic lattice. Since the intensity of superlattice reflections is much lower than those arising from the cubic vanadium lattice, recognition by X-ray diffraction has been difficult. Although extra lines in the VC phase have been reported[2], these have generally been associated with impurities, and the cubic structure has been assigned to the complete range of composition[#].

As mentioned earlier, mononitrides and monoxides of the transition metals are isomorphous with monocarbides. Complete solid solution has been reported between these compounds except in cases where the lattice parameters differ by more than about 15% (e.g. VC-ZrC)[1] reminiscent of the

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[‡] Within the $\alpha$-Ti + TiC phase field according to the equilibrium diagram of Storms[2].

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[#] Except in specific discussion of compositions, this designation will be continued in this review to describe the VC phase.

empirical relationships deduced by Hume-Rothery[16] for metallic solid solutions. In addition, solid solubility of other carbides in the cubic carbides has been reported, for example, up to about 20 a/o of WC is soluble in TiC[1]. In many of the pseudo-binary systems a maximum melting-point composition has been reported[1]. These include TaC-20 a/o HfC which has the highest reported melting temperature for any material, 4000°C[17]. As in the single phase carbides exhibiting similar features, ordering or compound formation is suggested, but again no evidence for this has been reported. Recent work, however, indicates that much remains to be understood about the structure of these pseudo-binary solid solutions. For example, Venables[18] has observed superlattice reflections and two-phase structures in alloys from the previously designated solid solution between TiC and VC.

## 3. Mechanical Behavior of Group IV Carbides.

### 3.1. Titanium carbide.

#### 3.1.1. Plastic flow in TiC.

Single crystals of TiC stressed below about 800°C appear to be completely brittle[19], although some evidence for dislocation motion at room temperature has been obtained. Surface markings consistent with slip on {111} planes have been observed close to Knoop microhardness indentations[20] and close to friction tracks[21]. Moreover, Williams[20] has also shown that microhardness is dependent on the orientation of the indenter with respect to the active slip planes in TiC. The fracture strength is very dependent

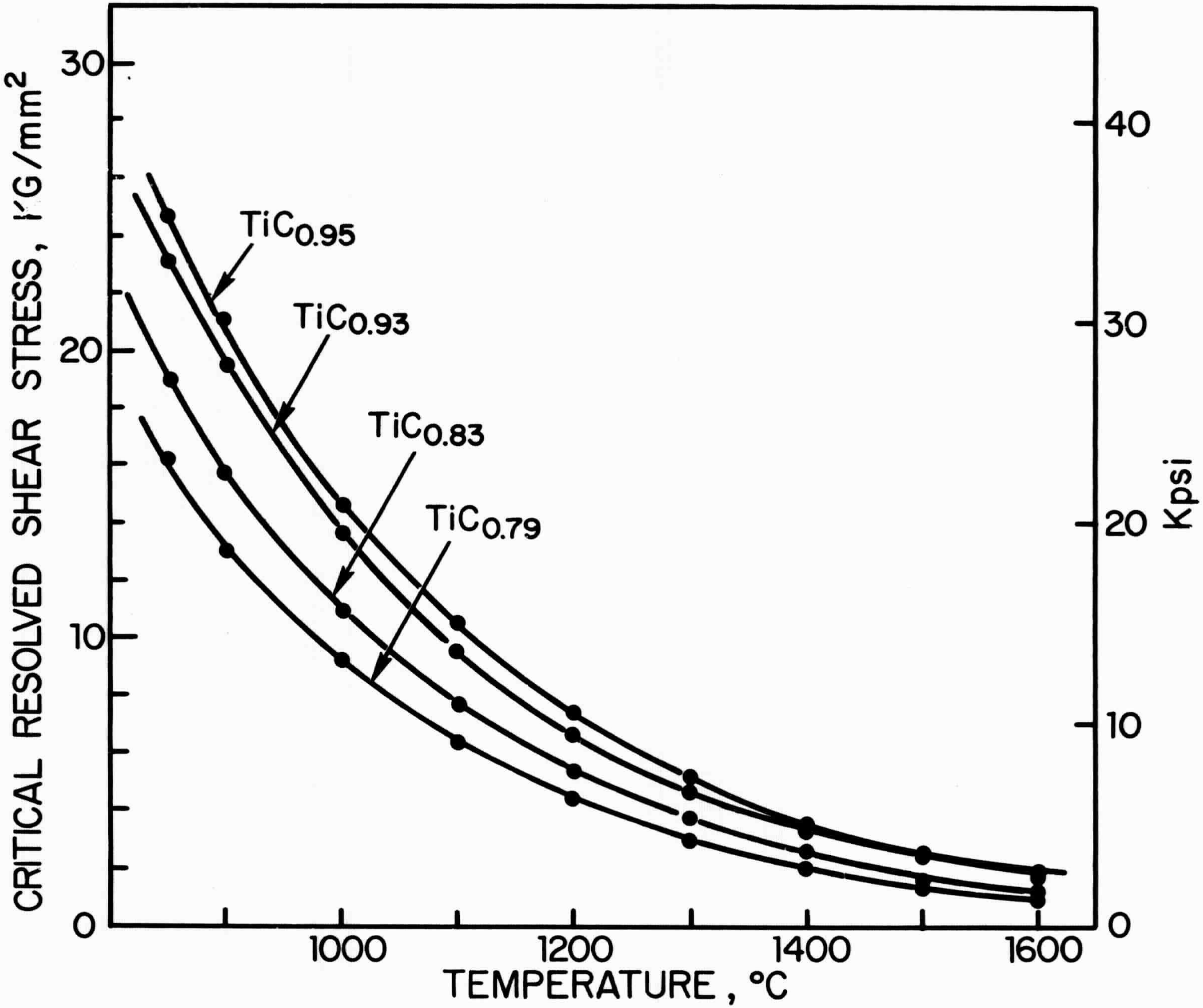


Figure 4. The temperature dependence of the yield strength of TiC as a function of carbon content (after Williams[22]).

upon surface condition[19], the maximum reported value being 800,000 p.s.i. Failure occurs by cleavage on {100} planes, and is initiated at surface or internal defects, although the possibility that microcracks are produced by dislocation interactions cannot be completely eliminated.

Plastic deformation occurs readily at testing temperatures above 800°-900°C. Slip lines corresponding to deformation on {111} planes are observed[19,22], and analysis of dislocation Burgers vectors indicate a $< 1\bar{1}0 >$ slip direction[23]. Slip on this system suggests that TiC is more appropriately considered as a fcc metal rather than a 'rocksalt' structure ionic compound.

Above the brittle-to-ductile transition temperature, the strength decreases rapidly. For example, the critical resolved shear stress for slip $\tau_c$, in $TiC_{0.95}$ decreases from about 22 $Kg/mm^2$ at 900°C, to 2 $Kg/mm^2$ at 1600°C, Fig. 4. This variation with temperature may be described by:

$$\tau_c = A \exp(-BT) \qquad \text{Eq. 3.1}$$

where A and B are constants. Relationships similar to this have been observed in other materials, for example MgO[24] and LiF[25], but temperature dependences of this form have not been related to the physical mechanisms controlling the strength.

The data can be presented in a manner more conducive to interpretation if the critical resolved shear stress is considered as a measure of the stress required to give a critical dislocation velocity. Stein and Low[26] have shown that the temperature dependence of the yield strength of silicon-iron is similar to that of the stress to produce a constant dislocation

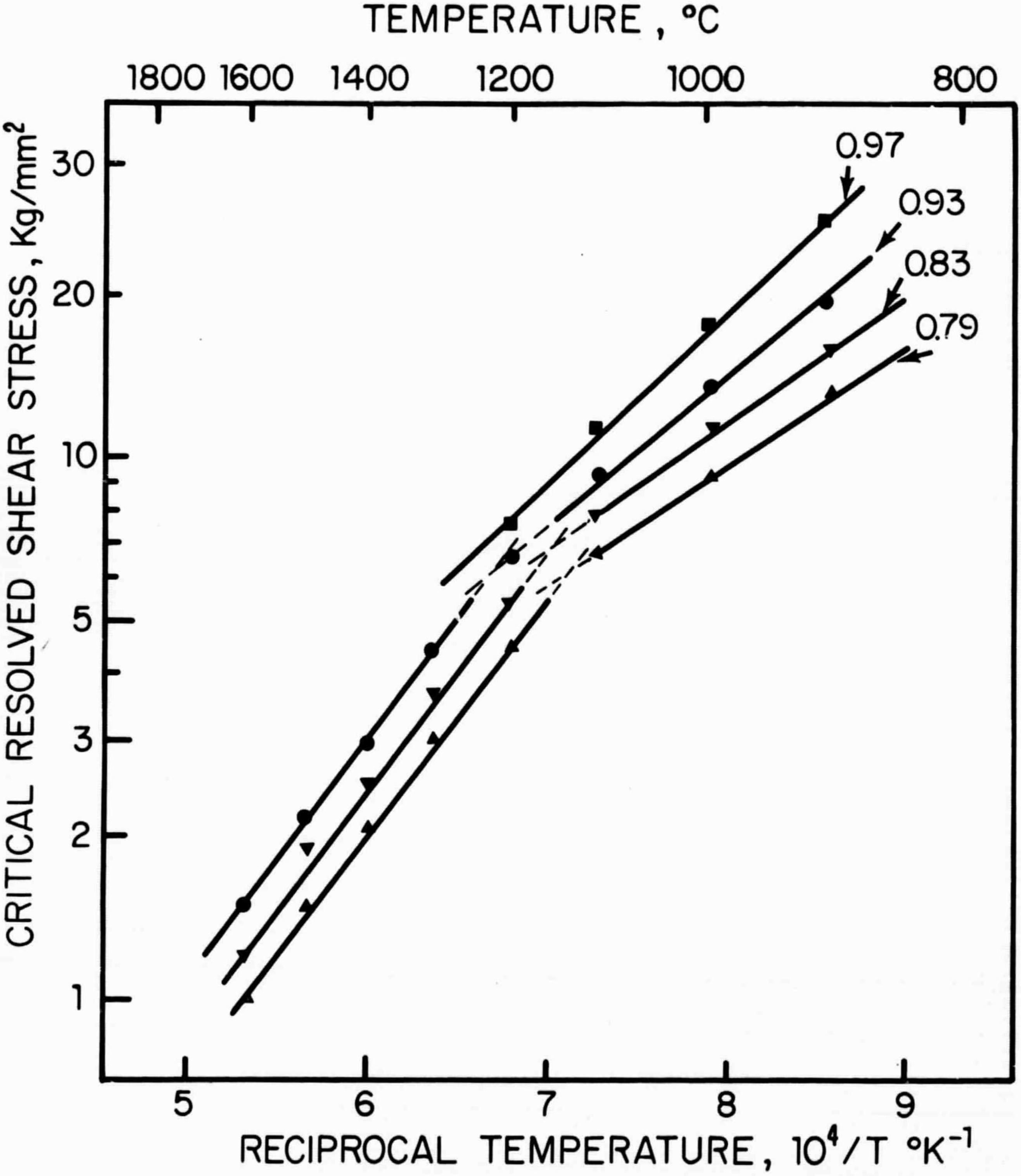


Figure 5. The temperature dependence of the yield stress of TiC (after Williams[22]). The change in slope - close to 0.475 $T_m$ - corresponds to a change in the mechanism controlling the deformation. The data for $TiC_{0.97}$ are taken from Hollox and Smallman[23].

velocity. Chaudhuri et al.[27] indicate that the variation in dislocation velocity v with temperature in semiconductors has the form:

$$v \propto \tau_c^{\ m} \exp(-U/kT)$$

where U is the activation energy for dislocation motion, k is Boltzmann's constant and m is a parameter defining the stress sensitivity. Consequently, for a constant dislocation velocity:

$$\tau_c^{\ m} \propto \exp U/kT.$$

Williams[20] has suggested that such a relationship is applicable to the deformation of TiC. As shown in Fig. 5, there is a change in slope of this function, for example at about 1150°C in $TiC_{0.83}$, suggesting that there is a change in the mechanism governing the deformation behavior. Using a value of m measured from the strain rate sensitivity of the critical resolved shear stress, namely:

$$\tau_c \propto (\dot{\epsilon})^{1/m}$$

Williams concluded that the activation energy for flow above the "critical temperature" is about 3.0 eV. Below this temperature, the activation energy appears to be dependent on carbon content, and has a range of values from about 1.7 to 2.3 eV.

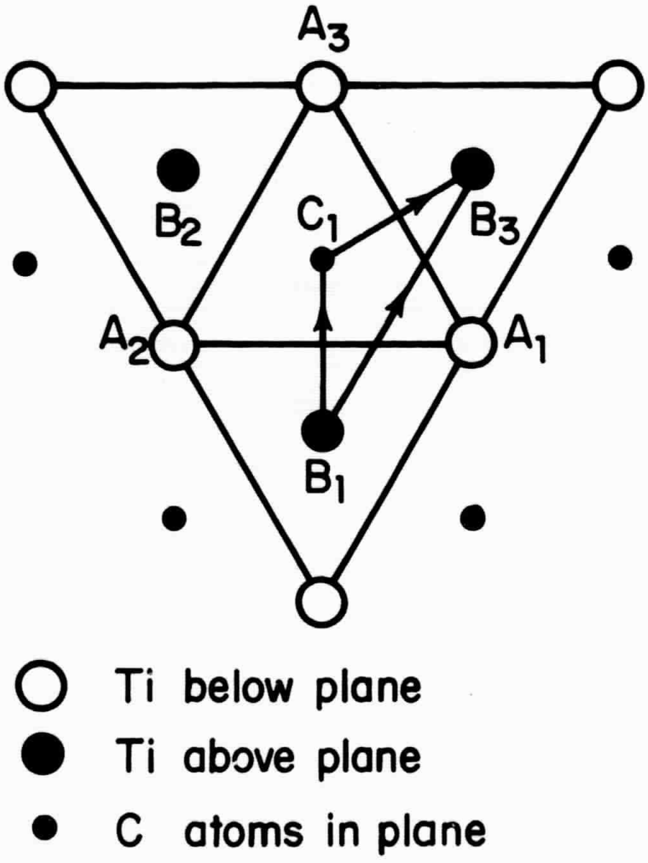


Figure 6. The slip plane of TiC (after Rowcliffe[28]).

Determination of the activation energies for flow from these relationships is difficult for a number of reasons. For example, the variation in strength shown in Fig. 4 is in good agreement with that described by Eq. 3.1. Consequently, the linear regions in Fig. 5 are approximations to a curve, and errors may arise in measuring the slopes. Moreover, it is necessary to assume that the activation energy is independent of stress, and that the value of m is independent of temperature. Experimental verifications of the validity of these assumptions have not been made for TiC.

At present, no complete interpretation of these activation energies is available. The gradual transition between brittleness and an increasing strain at failure as the testing temperature is raised suggest that diffusion is important for the thermally activated motion of dislocations, and on this basis, Rowcliffe[28] has applied Kronberg's[29] synchroshear process to the deformation behavior of TiC. He points out that a unit of slip from $B_1$ to $B_3$, Fig. 6, would require a large lattice expansion normal to the slip plane. If the carbon atom at $C_1$ can move at the same time as the titanium atom moves to $C_1$, however, the unit displacement $B_1$ to $B_3$ can be accomplished by movements of partial dislocations by slip from $B_1$ to $C_1$ and $C_1$ to $B_3$. This motion cannot be described by a single shear vector and may require the diffusion of carbon atoms into tetrahedral or octahedral vacant sites in order that deformation may take place.

If this mechanism is applicable to TiC, then the activation energy for dislocation motion should be close to that expected for carbon diffusion in TiC. The self-diffusion energy for carbon in TiC is not known with any certainty at present. Many of the reported results have been obtained on sintered and polycrystalline material, in which case, surface or grain boundary diffusion may have been an important influence. In layer-growth experiments, values of 2.7 eV and 5.1 eV have been reported for the activation energy for carbon and titanium diffusion respectively in TiC[30,31]. These results do not relate to a specific composition, and are average values for diffusion through a range of compositions of TiC. More recently, Sarian[32] has reported that the activation energy for carbon diffusion in TiC is about 5.0 eV, the results being obtained using accurate radiotracer techniques. This result is particularly interesting since it is contrary to the previously held view, confirmed for example in the isomorphous compound UC[33], that carbon was likely to have a considerably lower activation energy for diffusion than titanium, consistent with its smaller size, interstitial position, and the presence of a large number of vacancies in its sublattice.

There is, therefore, little correlation between the activation energies measured from the temperature dependence of the critical resolved shear stress below the 'critical temperature,' 1.7-2.3 eV, and those for self-diffusion of carbon, 2.7 eV[30,31] or 5.0 eV[32]. One reason for this may be that a diffusion mechanism within the stress field or core of the dislocation may have to be considered. Williams[20] has associated the similarity between the activation energy for the deformation processes in $TiC_{0.83}$ above about 1150°C, 3.0 eV, with that for 'pipe-diffusion' deduced from the annealing of dislocation dipoles[34], 3.4 eV.

However, titanium self-diffusion does influence the mechanical behavior of TiC above about 0.5 $T_m$. At these temperatures, Keihn and Kebler[35] have shown that the creep rate of TiC is governed by an activation energy of between 5.0 eV and 7.0 eV, and this has been confirmed by Brizes[36]. These values are in fair agreement with the self-diffusion energy for titanium in TiC measured in layer-growth experiments, 5.1 eV[31], and from dislocation loop annealing, 5.25 eV[34]. As is established for metals[37], this correlation is consistent with the rate controlling process in steady state creep being the diffusion of metal vacancies. It is possible, therefore, that the mechanical behavior of TiC above the critical temperatures shown in Fig. 5 is controlled by titanium diffusion. Some other mechanism, which may involve carbon diffusion may control behavior below 0.5 $T_m$.

### 3.1.2. Dislocation structures in TiC.

It has been mentioned that the deformation characteristics of TiC are similar to those of a fcc metal. Dislocation structures are consistent with a high stacking-fault energy similar to that in, for example, aluminum. Neither fringe contrast nor dissociation of dislocations into partials has been observed in transmission electron metallography[23] although partial dislocations[38] may exist within the width of the dislocation image,

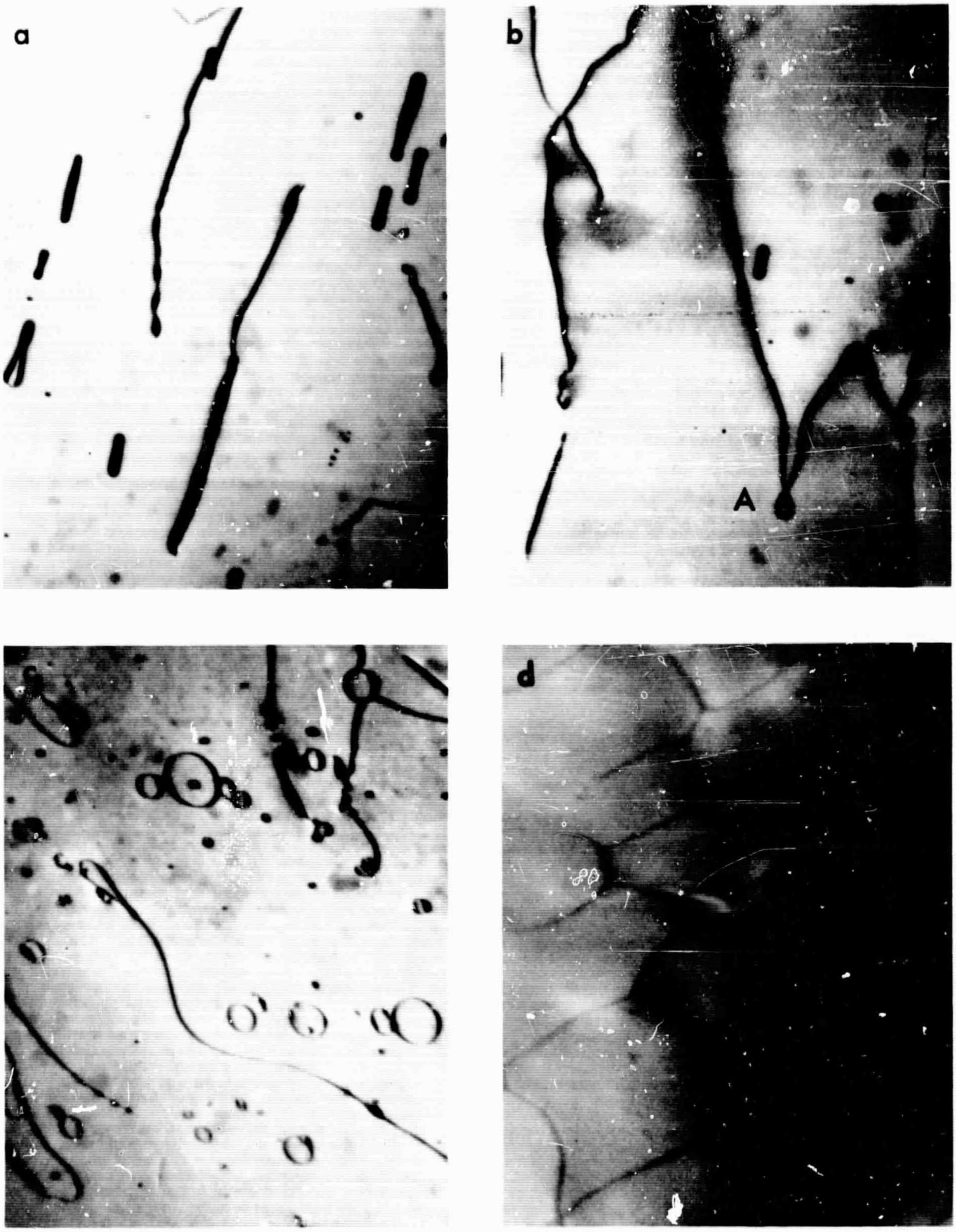


Fig. 7. Dislocation structures in TiC. (a) Early stage of deformation showing elongated dislocation loops, (b) annealing of an elongated loop, A, by pipe-diffusion along dislocation cores, (c) formation of vacancy dislocation loops on annealing at 1300°C, (d) final annealed structure - a hexagonal dislocation network as observed in fcc metals (after Hollox and Smallman[23]).

~ 100 Å[39]. The observation of elongated dislocation loops (dipoles) in the early stages of deformation, Fig. 7(a), and of cell structures in more heavily deformed samples, is also consistent with an ease of cross-slip. The strongly directional atomic bonding in TiC probably accounts for its high stacking-fault energy, since the hexagonal symmetry of stacking faults in the fcc structure would require different bond directions. An alternative explanation relies on the observation that metals with a filled d-band have a lower stacking-fault energy than those with partially filled bands[40,41]. The latter case is applicable to TiC, but no estimate of the stacking-fault energy has been made on this basis for any material, and the value of this parameter is not known.

Annealing of plastically-deformed TiC is accompanied by coalescence of vacancy dislocation loops[23]. The initial stages appear to be associated with the formation of trails of small loops, Fig. 7(b), produced from dislocation dipoles. The final stages involve the formation of a hexagonal network of dislocations, Fig. 7(d), similar to those observed in fcc metals.

When crystals of $TiC_{0.97}$ are compressed in the cube orientation, the resolved shear stress for slip is equal on all $\{111\} < 1\bar{1}0 >$ slip systems, and parabolic hardening is observed (although three stage hardening may be expected in other orientations when single slip is favored). The dislocation density $\rho$ increases linearly with strain, $\epsilon$:

$$\rho = (8.6 \times 10^{10})\epsilon/\mathrm{cm}^2$$

and work hardening represented by the variation of flow stress $\tau_f$ with dislocation density given by:

$$\tau_f = \tau_i + k(\rho)^{1/2}$$

where k is a constant, this behavior[23] being typical of several other materials.

The $\tau_i$ term may be interpreted as the stress required to move a dislocation in a dislocation-free lattice or the lattice-friction (Peierls) stress. Despite averaging over many thin foils, there are some errors in determining the dislocation density in inhomogeneously deformed single crystals. However, values of $\tau_i$ have been determined[23] and agree closely with the values of the observed critical resolved shear stress for slip at the same temperature. This result suggests that a high lattice friction stress is the source of the strength of this material.

### 3.1.3. Effects of carbon-to-metal ratio.

Vacancies have been commonly recognized as a cause of hardening in crystal lattices. For example, the yield strength of quenched aluminum is greater than annealed aluminum[42,43], and non-stoichiometric $TiO_{2-x}$ is stronger than the stoichiometric composition[44]. Both these observations are explained by interactions between dislocations and isolated or clustered vacancies [44,45,46]. However, in TiC the critical resolved shear stress for slip at 900°C decreases linearly from about 22 $Kg/mm^2$ for $TiC_{0.95}$ to about 12 $Kg/mm^2$ for $TiC_{0.79}$[22], Fig. 8. This decrease in strength with increasing carbon vacancy concentration may be attributed to a decrease in the contribution made by carbon atoms to cohesion in TiC. The nature of

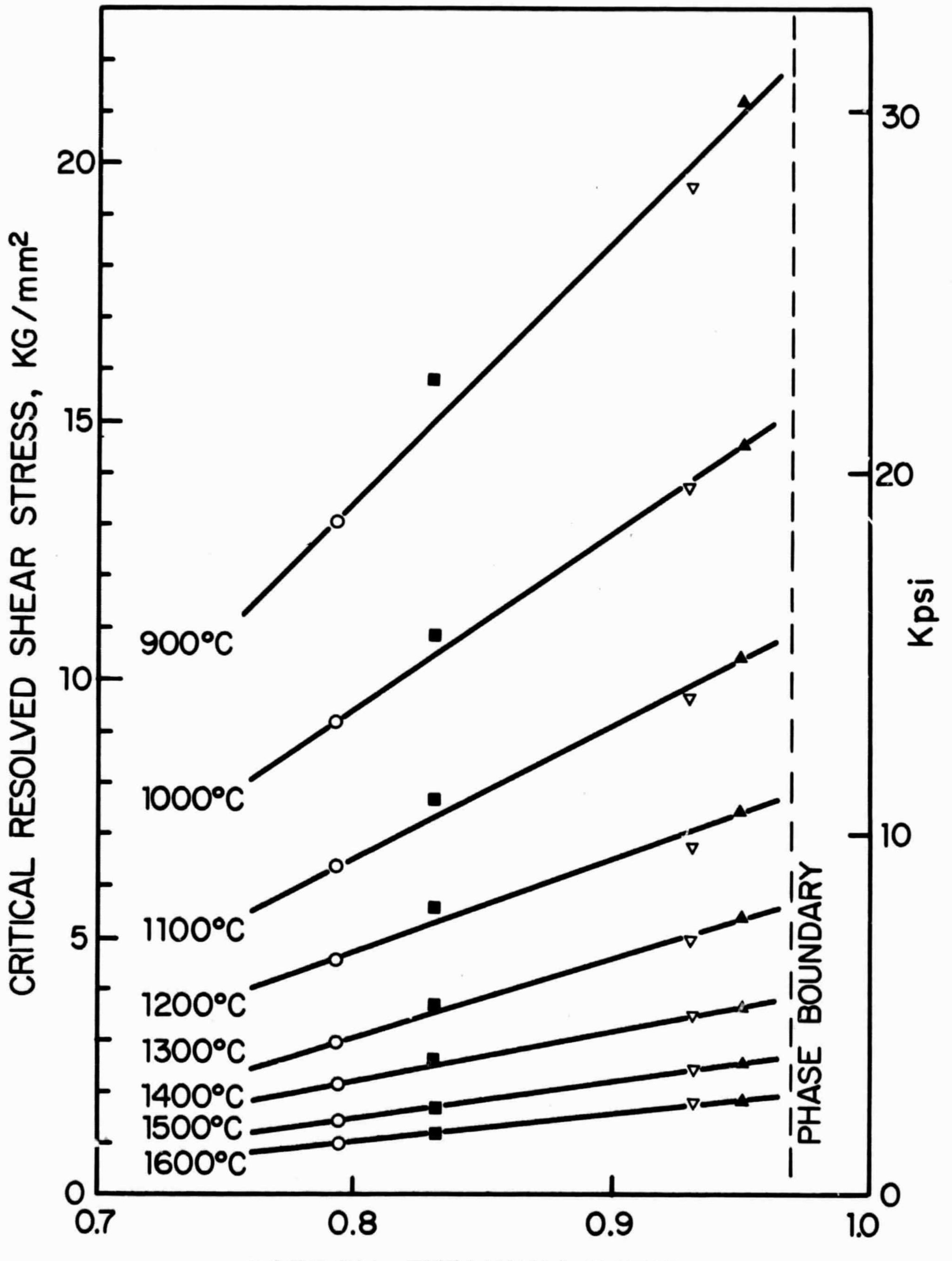


**Figure** 8. The critical resolved shear stress for slip in TiC as a function of carbon content (after Williams[22]).

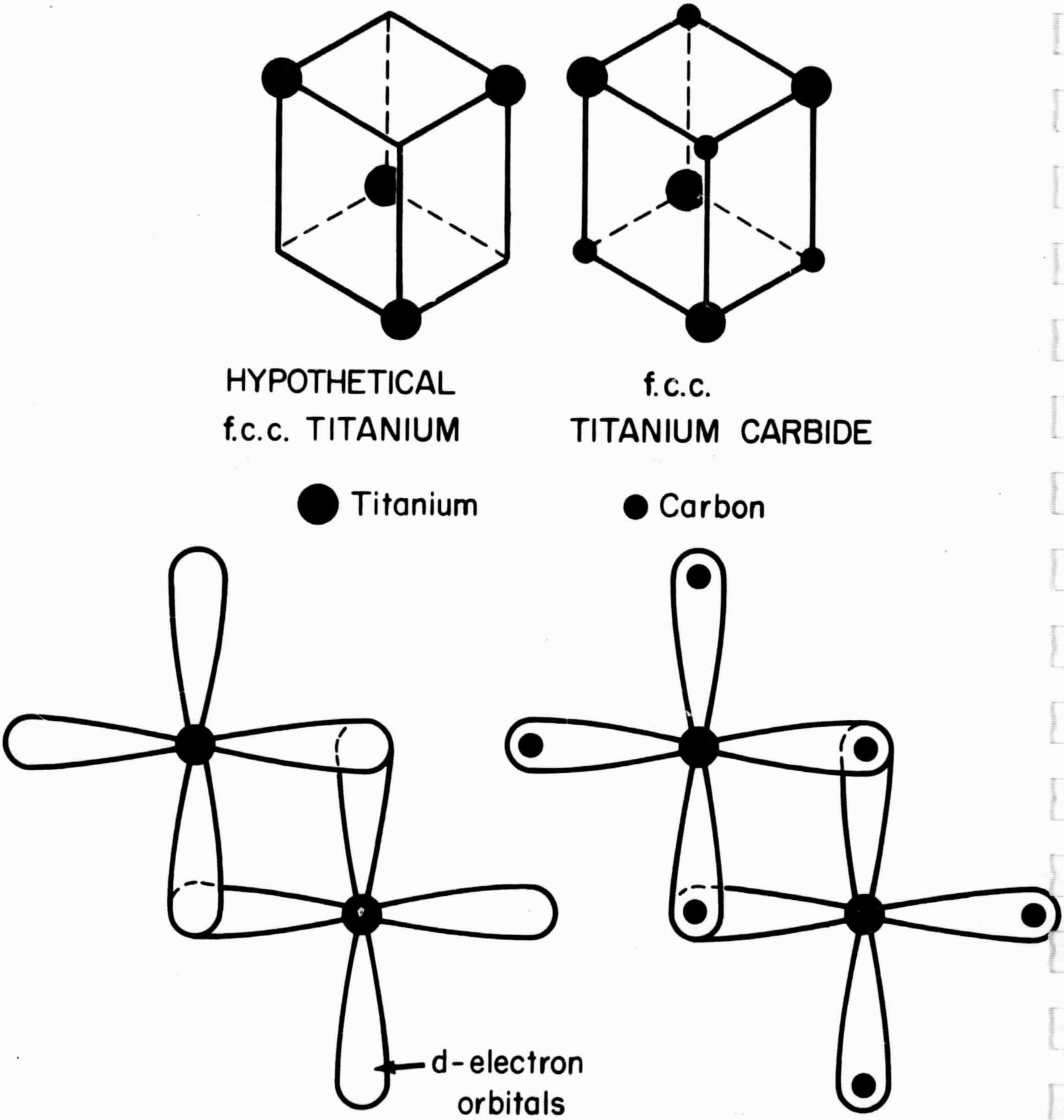


**Figure 9.** Schematic representation of the bonding between $\pi$-oriented 3-d functions in TiC compared with that of hypothetical fcc titanium. This illustrates the position of carbon atoms in the overlap region between orbitals on neighboring atoms (after Lye[10])

the electronic interactions between constituent atoms in the lattice has been deduced from studies of the band structure of this material. Lye[47] has shown that the predominant contribution to the bonding is from covalent metal-metal bonds, the strength of which increases with carbon content because (i) the carbon atoms donate electrons to crystal states derived from metal atom wave functions and 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, Fig. 9. A decrease in the brittle-to-ductile transition temperature might also be expected as carbon content is reduced, but such an effect has not been conclusively demonstrated. However, it may be significant that Williams[22] observed ductile behavior in $TiC_{0.95}$ at 800°C, while Hollox and Smallman[23] showed that the transition in $TiC_{0.97}$ occurred at about 900°C.

Changes in carbon content do not appear to have any influence on dislocation structures in TiC, but the annealing kinetics are changed[23]. Dislocation loop densities as a function of isochronal annealing temperature for $TiC_{0.97}$ and $TiC_{0.88}$ are shown in Fig. 10. Initially, the loop density increases due to the break-up of dipoles, but then decreases as these loops grow and coalesce. The "self-diffusion temperature," $T_D$, (defined as the temperature at which loops disappear completely in a fifteen minute anneal) is about 1400°C for $TiC_{0.97}$, and 1270°C for $TiC_{0.88}$. As is observed in fcc metals, $T_D = 0.475\ T_m$[34] (where $T_m$ is the absolute melting point). The activation energy for the annealing process is 5.25 eV for $TiC_{0.97}$ and

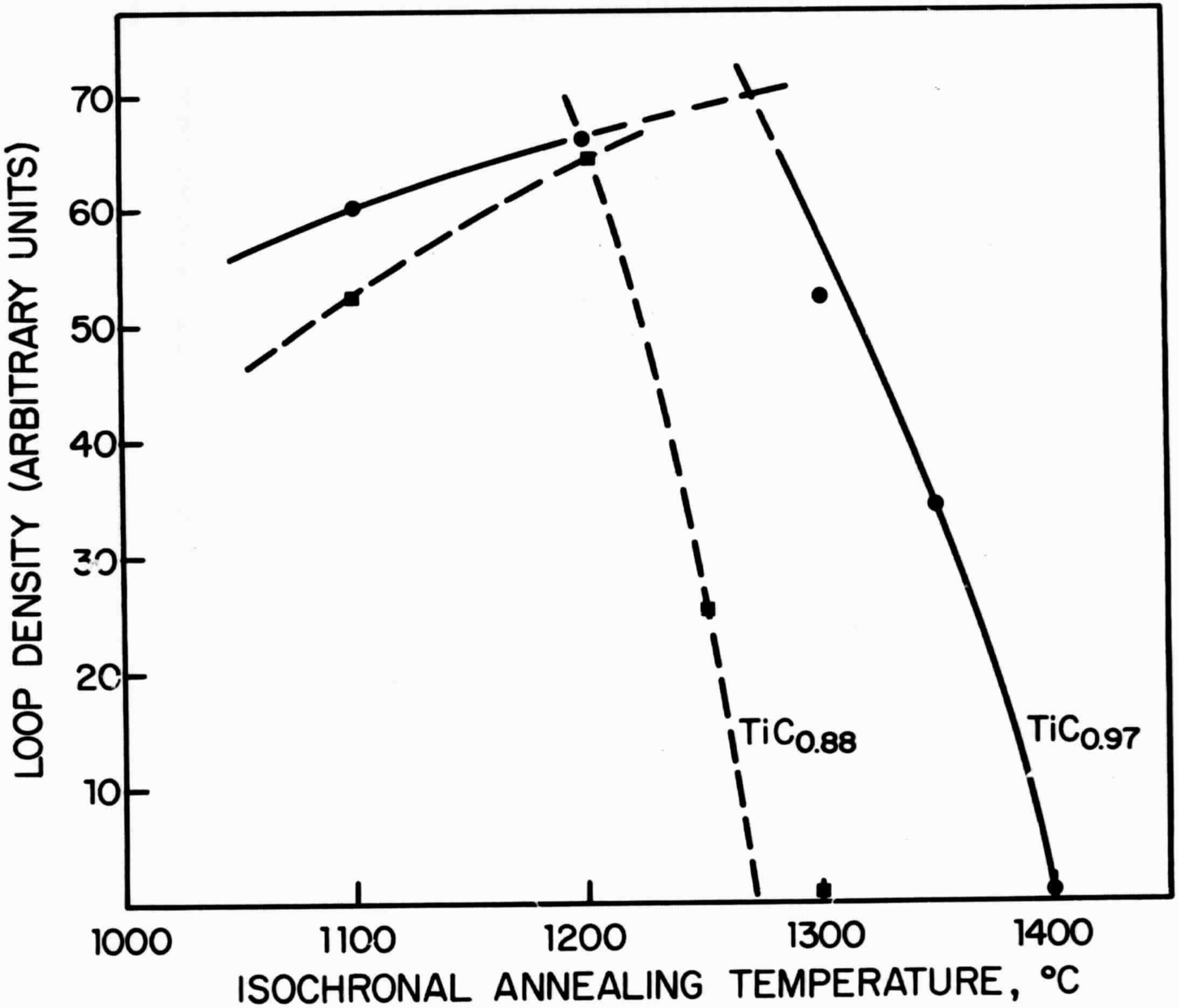


Figure 10. Variation in dislocation loop density as a function of isochronal annealing temperature in TiC (after Hollox and Smallman[23]).

4.88 eV for $TiC_{0.88}$, in good agreement with the reported value of the activation energy for the diffusion of titanium atoms in TiC, 5.1 eV[31]. It is significant to note that the "self-diffusion temperatures," 0.475 $T_m$, are close to the values of the critical temperatures observed for the change in the mechanism controlling the strength, supporting the view that deformation at higher temperatures is influenced by titanium diffusion.

### 3.2. Zirconium carbide.

Williams[22] has shown that $ZrC_{0.88}$ is stronger than all TiC compositions between $TiC_{0.79}$ and $TiC_{0.95}$, and this has been confirmed by Lee and Haggerty[48]. The latter investigators also measured the strength of $ZrC_{0.90}$ as a function of crystal orientation, and induced slip on $\{111\} < 1\bar{1}0 >$, $\{110\} < 1\bar{1}0 >$ and $\{001\} < 1\bar{1}0 >$ systems when the crystal orientation was chosen such that the Schmidt factor favored slip on these systems. One surprising observation which has not been explained so far is that the critical resolved shear stress for slip on $\{110\} < 1\bar{1}0 >$ appears to be slightly lower than that for slip on $\{111\} < 1\bar{1}0 >$, Fig. 11.

Many other features of the mechanical behavior of ZrC are similar to that of TiC. Lee and Haggerty[48] have shown that the stacking-fault energy is high, and that the steady-state creep rate of single crystal ZrC is governed by an activation energy of about 4.8 eV. This value is slightly lower than that expected for the diffusion of zirconium in ZrC (5.7 eV)[31], but is in fair agreement with the hypothesis that metal atom diffusion is controlling the high temperature deformation process. No information

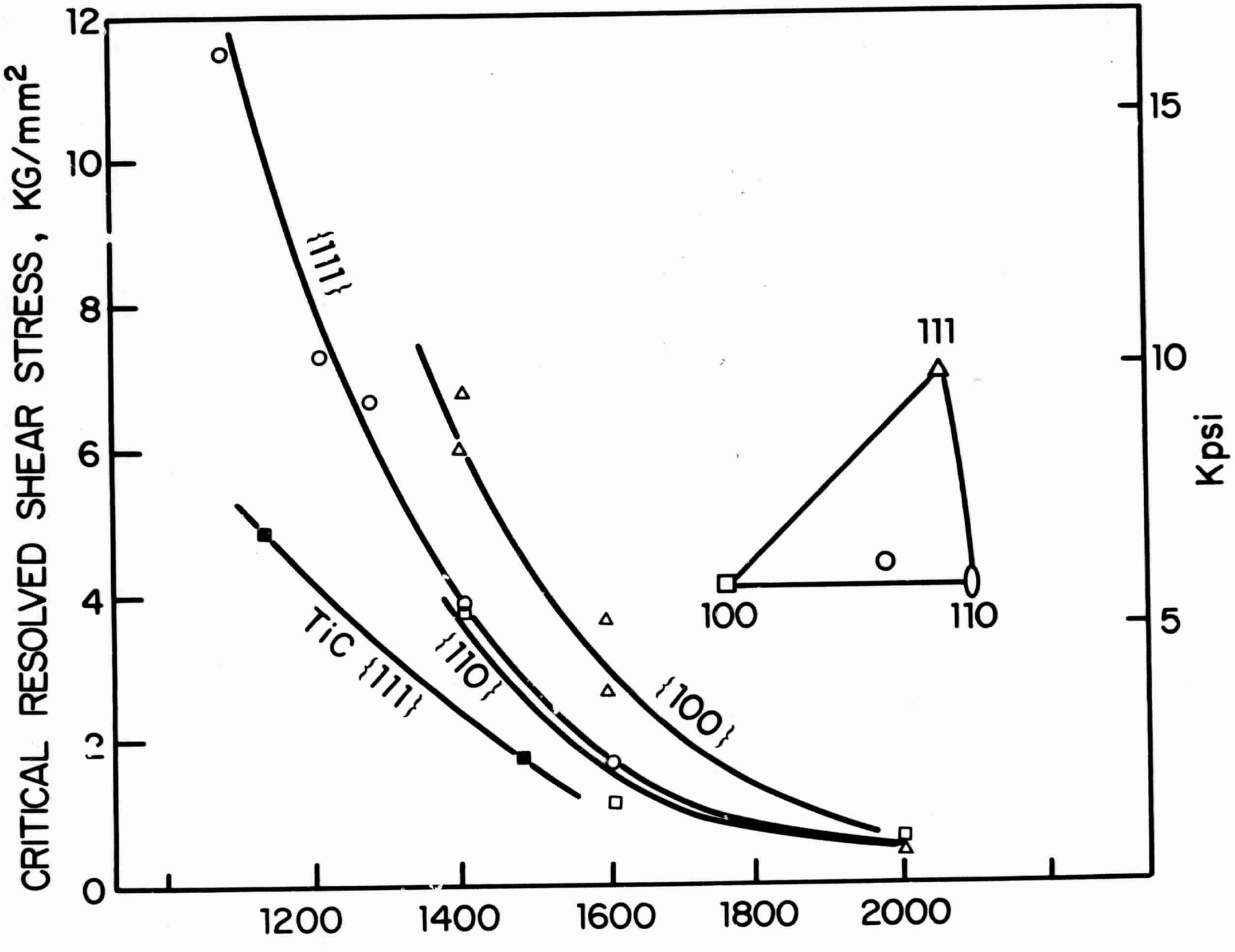


Figure 11. Variation in critical resolved shear stress for slip on different systems in ZrC (after Lee and Haggerty[48]).

on the variation in strength or the brittle-to-ductile transition temperature with carbon content is available at present.

### 3.3. Hafnium carbide.

HfC has been the least investigated of the carbides because of its limited availability. For example, no information on the slip system or brittle-to-ductile transition temperature has yet been obtained. The work that has been performed has utilized material containing a few percent of zirconium, so that a comparison of the behavior of this material with other purer carbides is of limited value. Brizes[36] has reported that such HfC is ductile at about 1600°C, and that the temperature dependence of the yield strength has a form different from that of the other Group IV carbides, but he believes this may be due to the impurity content. Adams and Beall[49] have investigated the properties of a number of hafnium-carbon alloys. Their results suggest that microhardness increases with carbon content in the HfC phase, as observed in TiC.

## 4. Mechanical Behavior of Group V Carbides.

### 4.1. Vanadium carbide.

It has been mentioned that "cubic" VC is more correctly described as a series of ordered compounds[15] although the composition ranges over which it should be described as a single ordered phase, two coexisting ordered phases, or even a disordered carbide are not known. However, the mechanical behavior will be markedly affected by carbon content as the

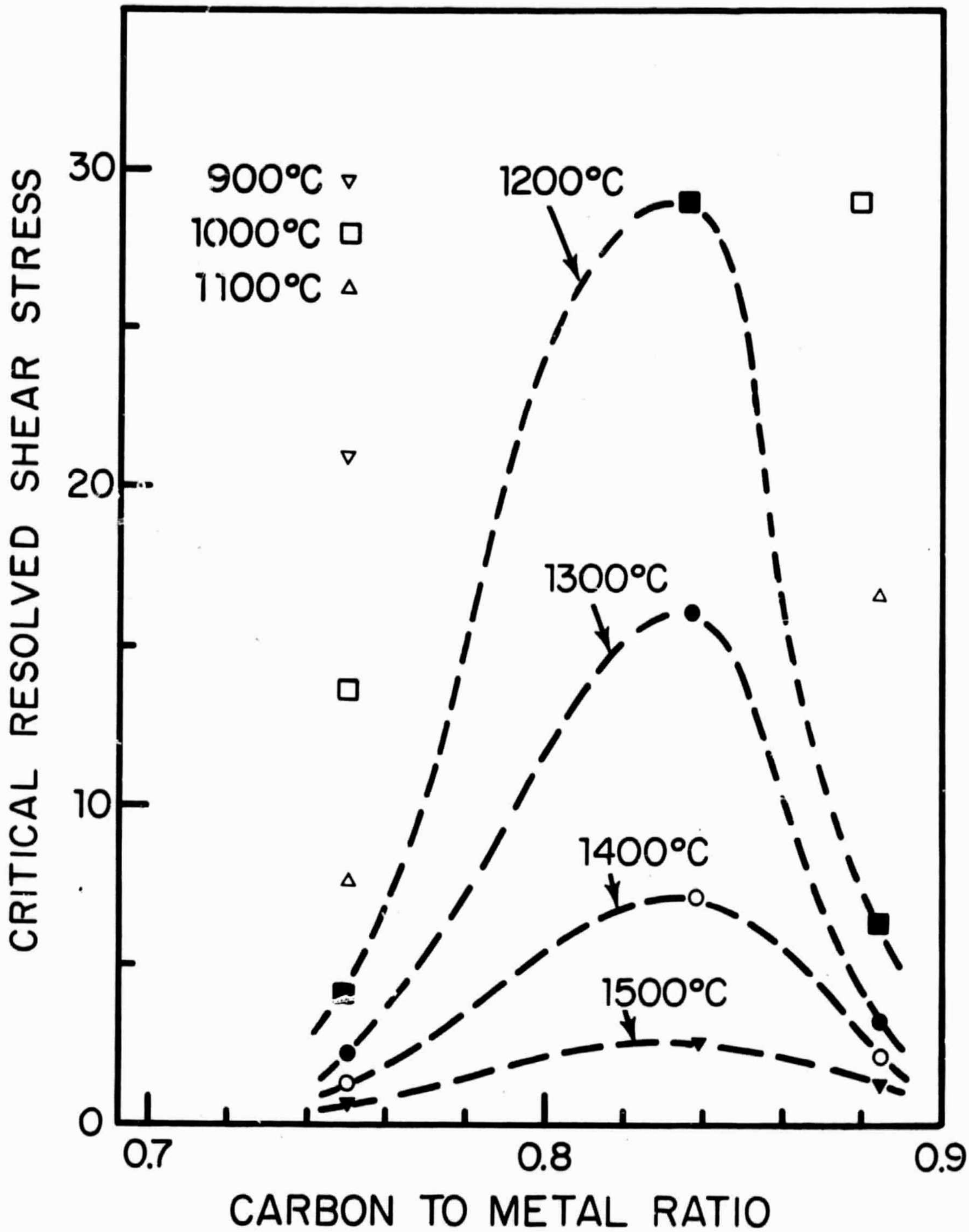


Figure 12. The critical resolved shear stress for slip in VC as a function of carbon content.

structural resistance to dislocation motion is altered. In fact, the yield strength passes through a maximum as carbon content is increased, Fig. 12, the strength of $VC_{0.84}$ ($V_6C_5$) being higher than that of either $VC_{0.88}$ ($V_8C_7$) or $VC_{0.75}$[50]. $VC_{0.84}$ ($V_6C_5$) and $VC_{0.88}$ ($V_8C_7$) both exhibit a similar form for the temperature dependence of their yield strength, Fig. 13. Above the brittle-to-ductile transition temperatures, the strength appears to be governed by one thermally activated process. However, two thermally activated processes control the deformation behavior of $VC_{0.75}$, Fig. 13, and so this material appears to behave in a similar manner to the "disordered" carbide, TiC.

Consistent with its greater strength, the brittle-to-ductile transition temperature of $VC_{0.84}$ ($V_6C_5$) is the highest of the three compositions. Both $VC_{0.84}$ ($V_6C_5$) and $VC_{0.88}$ ($V_8C_7$) are ordered compounds at low temperatures. One consequence of ordering in $VC_{0.84}$ is that crystals exhibit a colored domain pattern when viewed in polarized light, corresponding to the several possible orientations of the anisotropic superlattice within the metal lattice[15,51]. Metallographic observations, Fig. 14, suggest that disordering of the compound occurs at some temperature between 1250°C and 1300°C, close to the brittle-to-ductile transition temperature[52]. Disordering may also be related to the onset of ductility at 1100°C in $VC_{0.88}$. Volkava et al.[53] have observed a break at 1120°C in the relationship between enthalpy and temperature in $VC_{0.92}$. This composition is more correctly represented as $VC_{0.89}$ plus excess graphite, and this break may therefore correspond to an order-disorder transition in the carbide. The precise role of ordering in inhibiting dislocation motion, however, has not yet been interpreted.

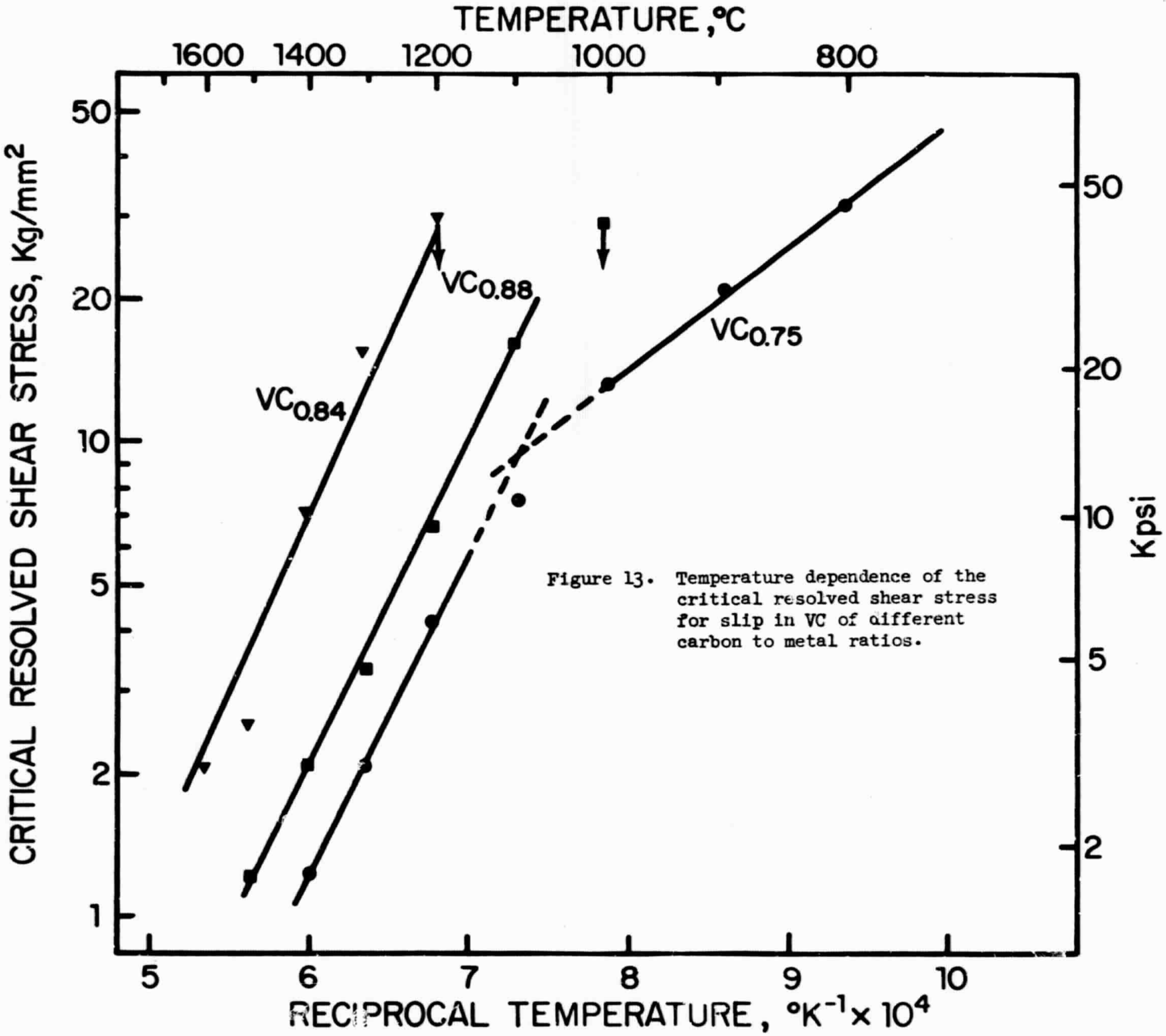
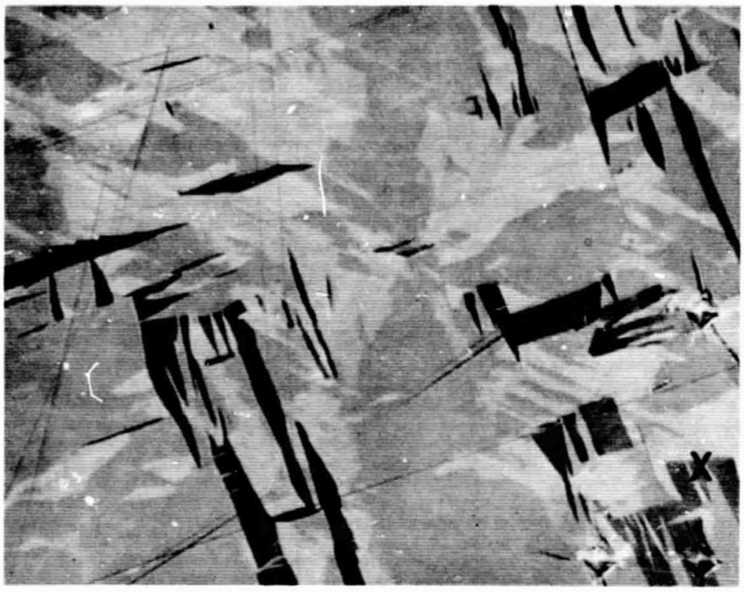


Figure 13. Temperature dependence of the critical resolved shear stress for slip in VC of different carbon to metal ratios.



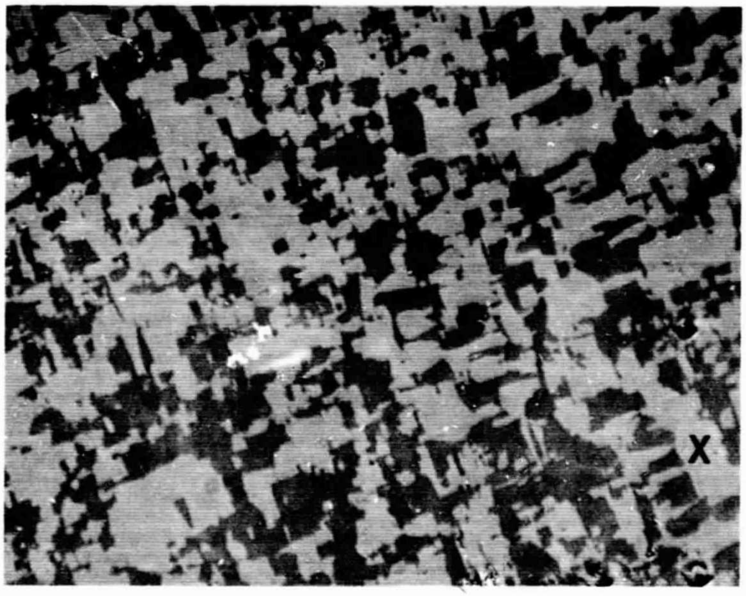


Figure 14. The change in domain structure of $VC_{0.84}$ after an anneal at 1300°C. The upper micrograph shows the structure before annealing, and the lower one the final structure. No change is observed in a similar anneal at 1250°C. These observations are consistent with disordering of the carbon superlattice between 1250° and 1300°C (after Hollox and Venables[52]).

## 4.2. Niobium carbide

Of the group V carbides, much less is known about the behavior of NbC than VC or TaC. Williams[22] has shown that single crystals of $NbC_{0.76}$ exhibit greater strength than either $ZrC_{0.88}$ or $TiC_{0.95}$. Kelly and Rowcliffe[54] have shown that hot pressed $NbC_{0.95}$ is stronger than $NbC_{0.88}$ of similar density, indicating an increasing strength with carbon content over this composition range between 1500° and 2000°C. Brizes[36] has reported that the high temperature creep rate is governed by diffusion of the metal species, consistent with the behavior of other carbides.

## 4.3. Tantalum carbide.

Except for some measurements of high temperature creep rate[36] TaC single crystals have not been studied. However, a considerable emphasis has been placed on studying polycrystalline and sintered specimens of this carbide because of its high melting point, which is exceeded only by the less available carbide HfC. This work is difficult to evaluate and a lack of specimen characterization may be responsible for the confusion in the literature.

Some of the properties reported for TaC are shown in Fig. 15. Santoro[55] has shown a maximum in the microhardness and a minimum in the room temperature rupture strength at about $TaC_{0.83}$. He correlated these trends with several other physical properties in the material, notably the melting point maximum in this phase, Fig. 2. There is no simple explanation for such conflicting mechanical properties, although a microhardness

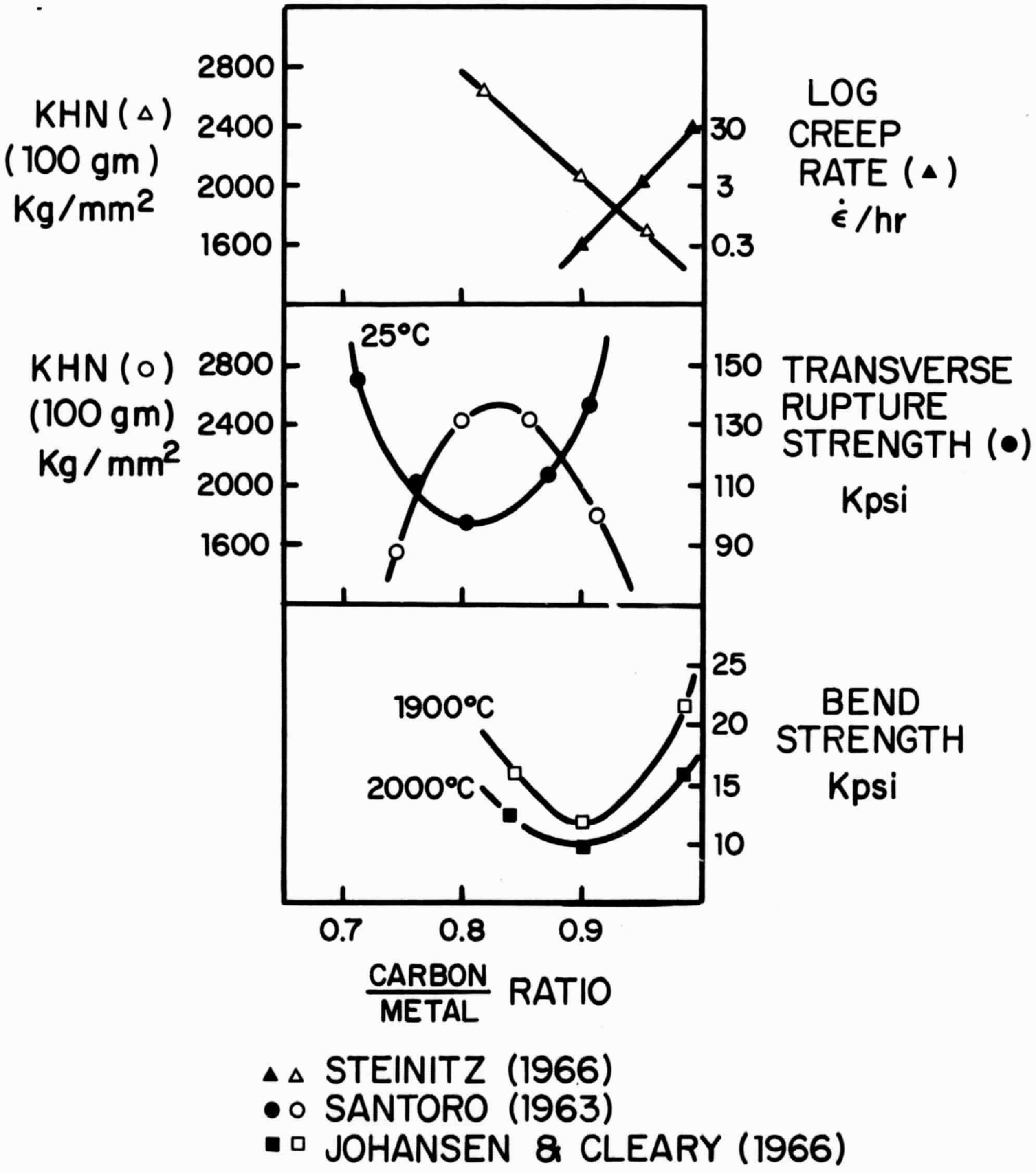


Figure 15. Mechanical properties of tantalum carbides as a function of carbon content.

measurement is probably more meaningful since it implies measurement of the internal material properties, rather than the properties of the grain boundaries as in room temperature tensile measurements. However, measurements of the bend strength of TaC at high temperatures by Johansen and Cleary[56] support the trend shown by the room temperature tensile measurements[55], although these investigators placed the minimum strength at about $TaC_{0.9}$. In addition, they showed that the brittle-to-ductile transition temperature increased linearly with increasing carbon content from compositions with the TaC + $Ta_2C$ two-phase field across the TaC region to the two-phase TaC + C field. If compositions within the TaC single phase region only are considered, which would appear more justifiable, then these data indicate a minimum in the transition temperature corresponding exactly with that of the bending strength.

The most recently reported data[57] indicate that the room temperature hardness decreased and the creep rate at high temperatures increased with carbon content over the composition range $TaC_{0.8}$ to $TaC_{1.0}$, in contrast to the previous results[55,56]. Steinitz[57] suggested that this decrease in strength with increasing carbon content was due to dislocation-vacancy interactions.

All these investigations have utilized TaC produced either by hot pressing with 4% Co as a binder[56,57] or by carburization of Ta wires[55]. Although fully dense, and apparently of constant radial composition, the latter showed a large variation in grain size. It would seem that with these specifications, the material lacked metallurgical integrity and that an examination of the properties of TaC single crystals might help to evaluate the mechanical behavior of this carbide.

## 5. Effect of Alloying Additions on Mechanical Behavior of Carbides.

### 5.1. Binary carbide alloys.

A very limited amount of work has been performed on binary alloys between carbides. Several microhardness studies have been reported, and although a control of metal:metal ratio was maintained, no control of carbon content was attempted. This may account for some of the discrepancies between the results of various investigators[1,58-60]. One result which may be significant, however, is that a maximum hardness has been observed at TaC-20% HfC, corresponding to the melting point maximum in this system[60].

Single crystals of binary carbides have been prepared only recently[61] and studies of their mechanical behavior are still at an early stage[50]. Preliminary results for some TiC-VC alloys, however, Fig. 16, are particularly interesting because: (i) the alloys show considerably higher strength than the parent carbides; (ii) the temperature dependence of the yield strength of the VC-25 a/o TiC and VC-50 a/o TiC compounds appear to be different in form from that of TiC-25 a/o VC and the pure carbides; (iii) there is some evidence for a small amount of ductility (~ 1%) at about 1000°C in VC-25 a/o TiC.

Venables[18] has shown that the VC-25 a/o TiC alloys are two-phase, one of which is ordered. The details of this phase separation are not fully understood, but the fine scale precipitation of a hard ordered phase in a

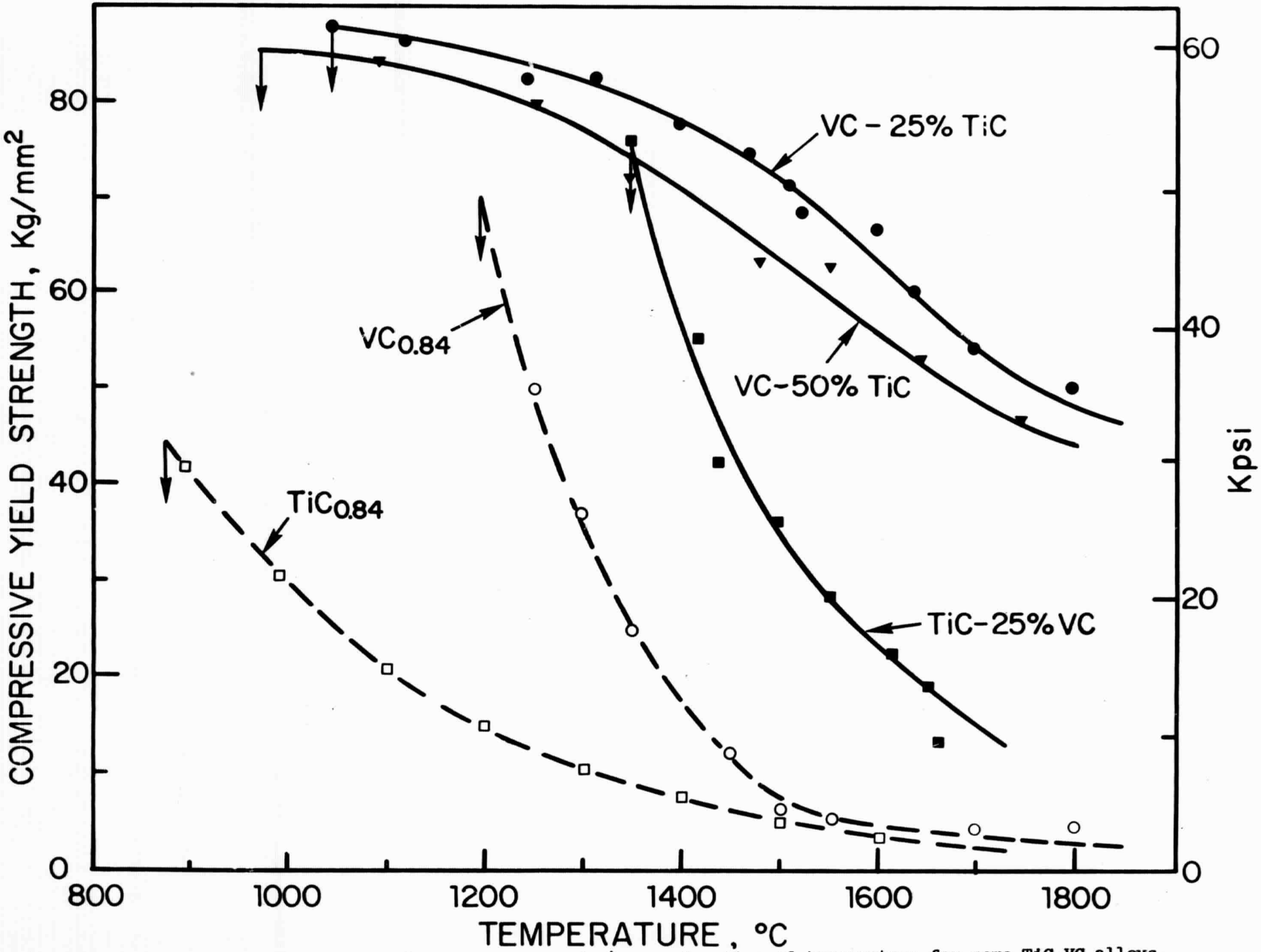


Figure 16. The yield strength (< 001 > compression) as a function of temperature for some TiC-VC alloys, compared with that of $TiC_{0.84}$ and $VC_{0.84}$.

"ductile" matrix may explain the mechanical behavior of this alloy[18]. The results have yet to be interpreted, but it is likely that they are dependent on stoichiometry. This factor and thermal history may significantly influence the mechanical behavior of these alloys.

### 5.2. Effect of boron on the structure and properties of TiC and VC.

It has been shown that boron significantly increases the strength of TiC and VC. For example, Williams[62] observed a tenfold increase in strength at 1600°C of TiC crystals after heating them in contact with boron powder at 2000°C, Fig. 17. Similarly, the critical resolved shear stress of boron-doped $VC_{0.84}$ is about 19 Kg/mm$^2$ (27,000 p.s.i.) compared with 3 Kg/mm$^2$ (4,200 p.s.i.) in the undoped carbide of the same composition, Fig. 17[52]. In both of these cases, increased strength has been associated with the formation of boride precipitates. Williams[62] suggested that the precipitates which form on {111} planes of TiC are $TiB_2$, and this has been confirmed by Venables[63] who has also shown that dislocation nodes are important in acting as nucleation sites for this precipitation. When VC is doped with boron by diffusion at 1800°C for 1 hour, precipitates form on {111} planes in the surface layers, where a high concentration of boron would be expected, but the plane of precipitation changes to {100} with increasing distance from the surface, Fig. 18[52]. The composition of the precipitates has not been conclusively established, although the presence of boron has been demonstrated in both types[52] by means of an alpharadiograph technique[64-67]. The identical structures of $TiB_2$ and $VB_2$ and the similar

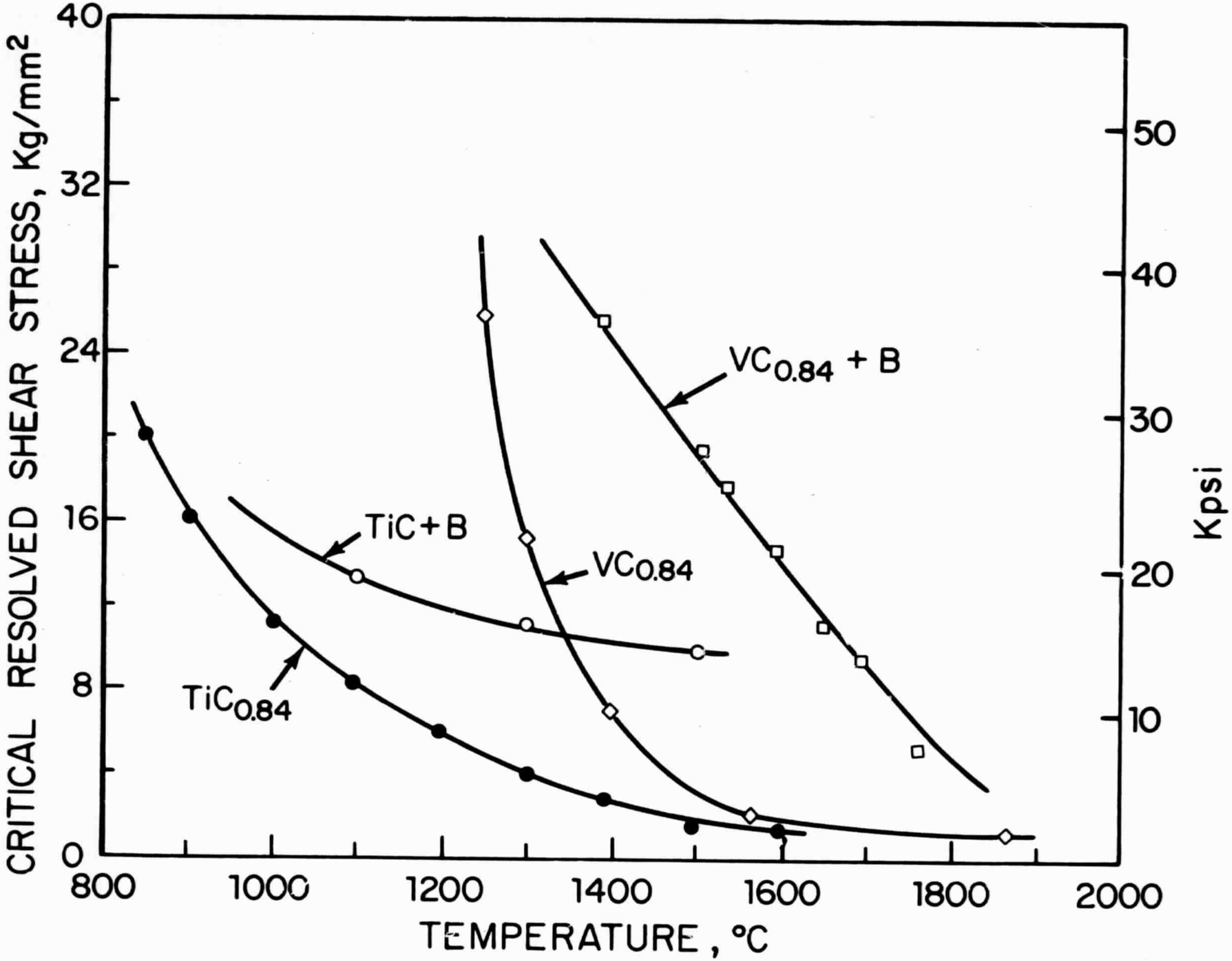


Figure 17. The critical resolved shear stress for slip as a function of temperature in boron-doped TiC (after Williams[62]) and $VC_{0.84}$ (after Hollox and Venables[52]).

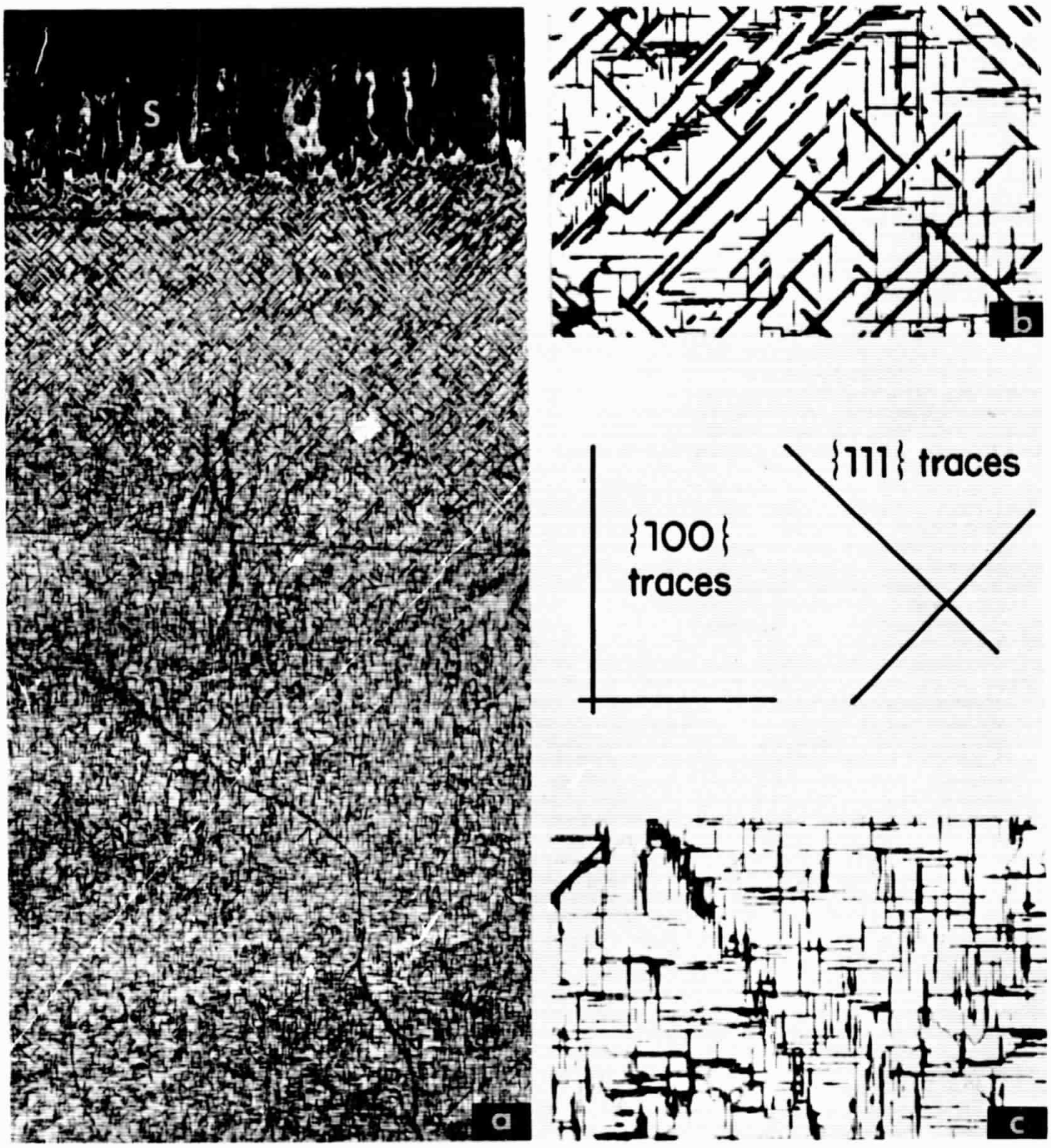


Figure 18. A {100} section through a sample of boron-doped $VC_{0.84}$. In the surface layers where a high concentration of boron is expected, precipitates form on {111} planes (b), but the plane of precipitation changes to {100} with increasing distance from the surface (c) (after Hollox and Venables[52]).

degree of atomic mismatch between these compounds and the parent carbides therefore suggests that the precipitates on {111} planes of VC are probably $VB_2$. It is also reasonable to suggest that the precipitates on {100} planes are one of the lower borides of vanadium, since they appear in the more boron deficient regions of the sample. In order of increasing boron content, these borides are: (i) $V_3B_2$ (tetragonal, $U_3Si_2$-type structure), (ii) VB (orthorhombic CrB type-structure), and (iii) $V_3B_4$ (orthorhombic $Mn_3B_4$-type-structure)[68]. Consequently a different plane of precipitation may be the result of a change in composition and structure of the precipitate, although no crystallographic relationship has been suggested by considering the atomic arrangements in these structures. In addition, more than one phase may precipitate on the same crystallographic plane. Precipitates having hexagonal structures tend to lie on {111} planes in fcc metals, while those with cubic or tetragonal symmetry favor {100}, since Young's modulus is generally lowest in $< 001 >$ and strain energy is therefore a minimum[69].

## 6. Discussion.

From the previous sections, it is apparent that comparatively little work has been performed on well-characterized carbides, and at present there is only a limited understanding of the mechanical behavior of these materials. Techniques for growing single crystals of these materials have been developed only in recent years[61,71-73]. Moreover, with the exception of WC in which the slip system has been determined[74-76], deformation studies have been confined to determining the basic deformation mechanisms of cubic carbides. Temperature, carbon-to-metal ratio, purity, structure and microstructure all have important effects on the properties of these carbides, and their relative behavior with respect to these variables will now be discussed.

### 6.1. Effects of temperature.

At low temperatures, the carbides are hard and brittle, but become relatively soft and ductile at high temperatures. Above about 0.5 $T_m$, the creep behavior appears to be governed by metal atom diffusion. Further work to clarify the nature of the thermally activated mechanisms controlling dislocation motion between these extremes is clearly necessary. In particular, measurement of such parameters as the activation volume and activation energy involved in the flow processes using the methods derived by Conrad et al.[77] would contribute significantly to an understanding of the mechanical behavior. Brizes[36] has utilized changes in strain rate to measure the activation volume as a function of temperature in a number of carbides. Although these measurements only apply above 0.5 $T_m$, the results are in agreement with a Peierls mechanism controlling the strength. Activation energies for flow processes are also very conveniently measured in creep tests[37,78], and it would be informative if these could be performed above and below 0.5 $T_m$ on the same carbide by one investigator. Correlations of energies measured from the variation in critical resolved shear stress with temperature and the self-diffusion energies for metal and carbon diffusion in the carbides must be regarded as tentative until a more definitive interpretation of dislocation motion is available, and until more accurate measurements of the diffusion energies are available, particularly as a function of carbon content and temperature in single crystal material.

Temperature is an important parameter when comparing the properties of the different cubic carbides. For example, over the temperature range 800°-1200°C, the yield strength of three compositions of VC is higher than that of TiC of equivalent stoichiometry, yet the room temperature hardnesses are consistently lower. These results confirm Westbrook's[79] observation that the microhardness of an unspecified composition of VC was less than that of TiC at room temperature, but greater at 1000°C, Fig. 19. The present measurements of high temperature yield strength suggest that a second cross-over in the relative strength or hardness of TiC and VC may occur at about 1200°C, Fig. 20, although $VC_{0.84}$ appears to be an exception to this generalization. Thus, the simple concept that the harder a material at room temperature the stronger it will be at high temperatures cannot be applied.

Gilman[80] has shown a dependence of microhardness on the elastic constant $c_{44}$ in a group of materials of similar structure. This appears to be obeyed in the carbides, the microhardness decreasing with $c_{44}$, Table 1. Quantitative correlations are difficult, since the microhardness is a function of load[50], time, environment[84] and orientation of the indenter with respect to the slip planes[20]. The data in Table 1 clearly indicate that room

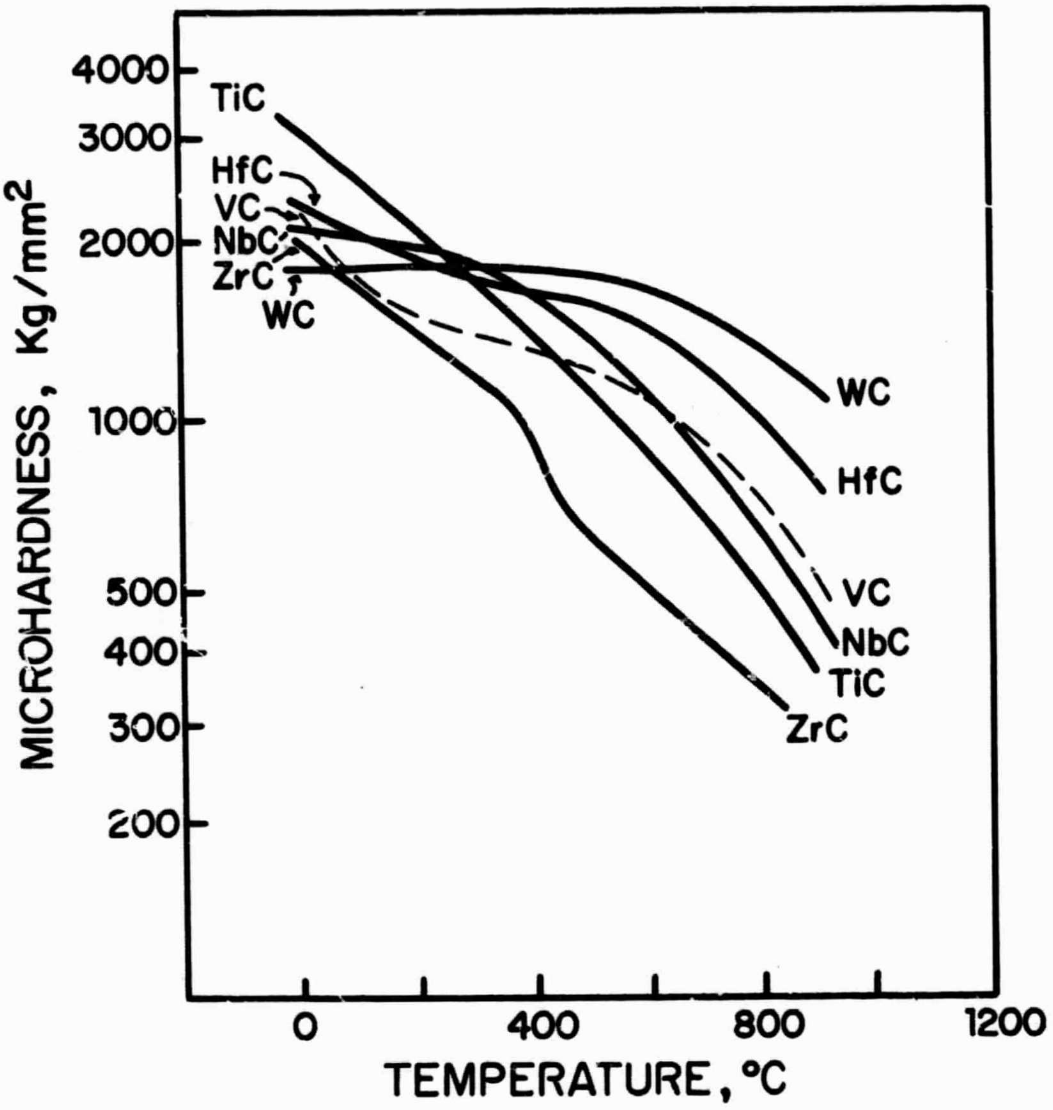


Figure 19. Microhardness of carbides as a function of temperature (after Westbrook[79]).

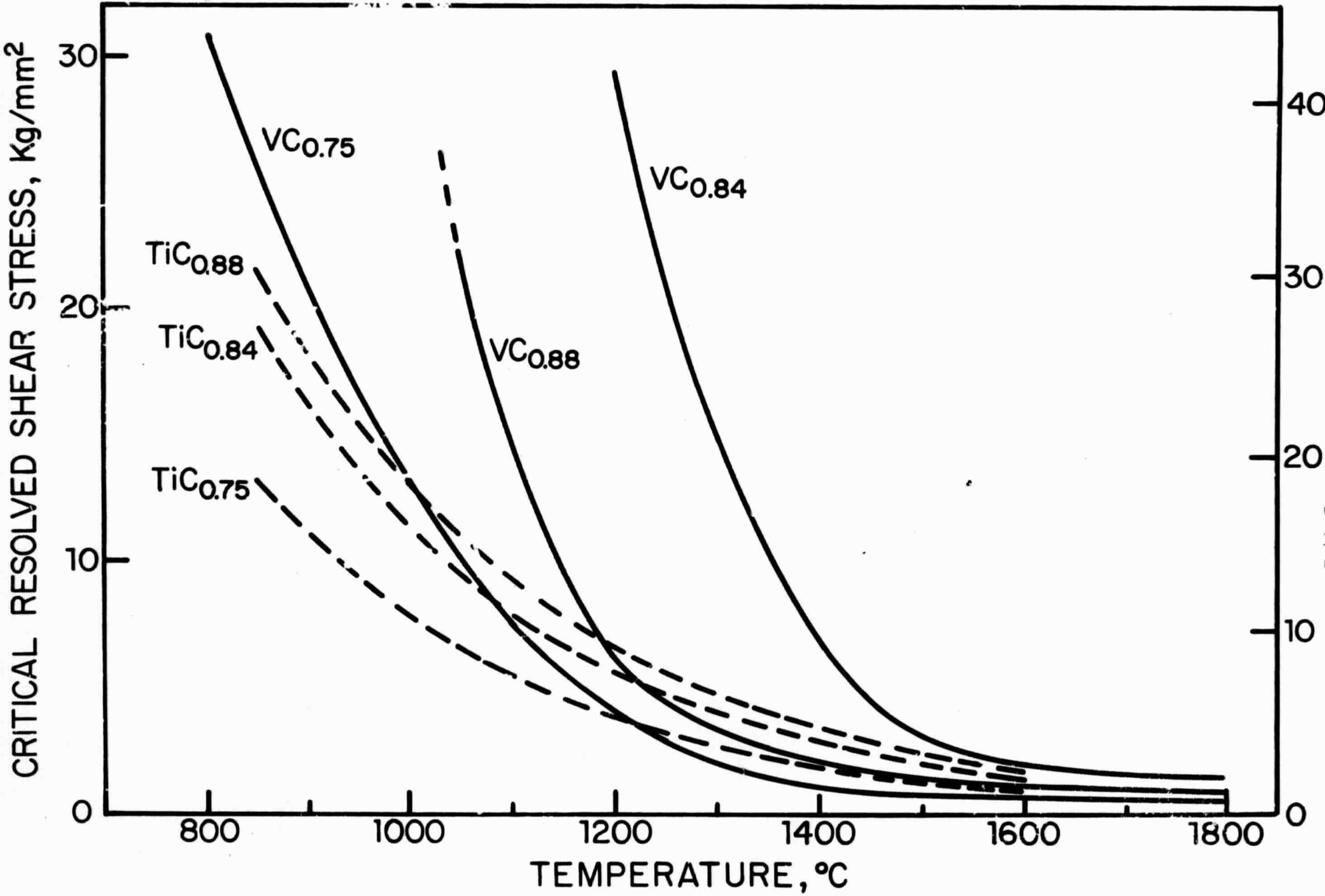


Figure 20. Comparison between the temperature dependence of the critical resolved shear stress for slip in TiC and VC of equivalent carbon to metal ratio.

| | $c_{44}$ $10^{12}$ dyn-cm | MELTING POINT (2) °C | HARDNESS KHN Kg/mm$^2$ |
|---|---|---|---|
| $TiC_{0.91}$ | 1.788 (81) | > 3000 | ~ 3600 (36) |
| $ZrC_{0.94}$ | 1.593 (81) | 3300 | ~ 2300 (36) |
| $VC_{0.84}$ | 1.55 (82) | 2650 | ~ 2000 (50) |
| $TaC_{0.99}$ | 0. 97 (83) | > 3500 | ~ 1800 (57) |

Table 1. Hardness of refractory carbides as a function of melting point and $c_{44}$. (Figures in parentheses are reference numbers.)

temperature hardness is not related to melting point. The complex variation shown by the microhardness as a function of temperature, Fig. 19, suggests that the temperature dependence of the elastic constants plays an important role in determining the mechanical behavior of the carbides. It is interesting to note that if these correlations are valid, then the hardness of UC should increase with temperature over the range 0°-300°C. In this cubic carbide, a positive temperature coefficient for the elastic constants[85] is exhibited over this temperature range.

## 6.2. Effects of carbon-to-metal ratio.

The strength, brittle-to-ductile transition temperature, creep rate, microhardness and other mechanical properties are a function of carbon content in the carbides, although there is no simple description of these variations. In non-ordered carbides, dislocation motion is opposed only by the high Peierls stress, and hence the strength is related to the occupancy of the electron states responsible for cohesion in these materials. Lye[47] has suggested that the bonding contributions from carbon atoms increase the strength of TiC. However, in a different carbide, carbon atoms may contribute electrons to anti-bonding states so that the strength may decrease with increasing carbon content. This may apply to TaC, although Steinitz[57] has suggested that the decrease in strength with increasing carbon content is a result of dislocation-vacancy interactions. This view may not be correct since a similar relationship between strength and composition would also be expected for TiC. Dislocation-vacancy interactions may be more important in compounds which contain vacancies in the metal lattice, a particular example of which is TiO, which can exist over a range of composition from $TiO_{0.67}$ to $TiO_{1.25}$[8] and for which anomalous variations in strength have been observed[86] in oxygen-rich compositions. Some recent unconfirmed results also suggest that TiC and TiN can exist up to $TiC_{1.026}$ and $TiN_{1.054}$, respectively[87].

The maximum melting point composition in the MC phase may be expected to have an important influence on mechanical strength. This feature may be an indication of ordering or compound formation at low temperatures, as appears to be the case in VC. The most recently reported phase diagram[7] indicates that the maximum melting point in VC occurs close to $VC_{0.85}$, which suggests that the ordered carbide $V_6C_5$ may correspond to the maximum stability composition. Certainly this carbide has the highest strength of all the VC carbides yet examined, Fig. 13. However, this correlation does not appear to be general, since the melting point maximum reported in TiC does not correspond with any compound formation or ordering and does not appear to influence hardness or strength. Further examination of mechanical behavior, structure and phase equilibria in the carbides is clearly necessary.

### 6.3. Effects of additional elements.

The dramatic increase in strength produced by a small amount of boron in TiC and VC single crystals, Fig. 17, illustrates an important influence of chemical composition on the properties of the carbides. Boron is a common impurity in these materials and it may not have been as effectively removed from the sintered materials used in early studies as it would be in, for example, zone refined material[61]. In the presence of boron, a second phase having a different crystal structure is often formed. It is difficult to visualize a mechanism by which impurities in solid solution can significantly affect the properties of the carbides. This may be applicable to, for example, solutions of TiN and TiO in TiC, although considerable effects must be expected at appreciable quantities of these isomorphs. However, the impurity effects may be particularly important in polycrystalline samples and in sintered materials where equilibrium conditions may not be reached and where grain boundary segregation may occur. (Under hardness indentations, Cadoff et al.[88] have shown that polycrystalline TiC containing 45 a/o carbon and 5 a/o oxygen appears more brittle than pure TiC.)

Controlled alloying with boron can be used to improve high temperature strength of the carbides. The observations reported in Section 5.2 must be regarded as "casual" since no control of precipitate size to optimize these properties was attempted. However, from transmission electron metallography, Venables[63] has shown that the boride precipitates are nucleated at extrinsic dislocation nodes in TiC, Fig. 21, and has suggested that precipitate density and size, and hence the mechanical strength may be controlled by varying the dislocation node density prior to or during doping. Alternatively, it is possible that precipitate size and distribution may be controlled by quenching and ageing techniques similar to those applied to aluminum alloys[69].

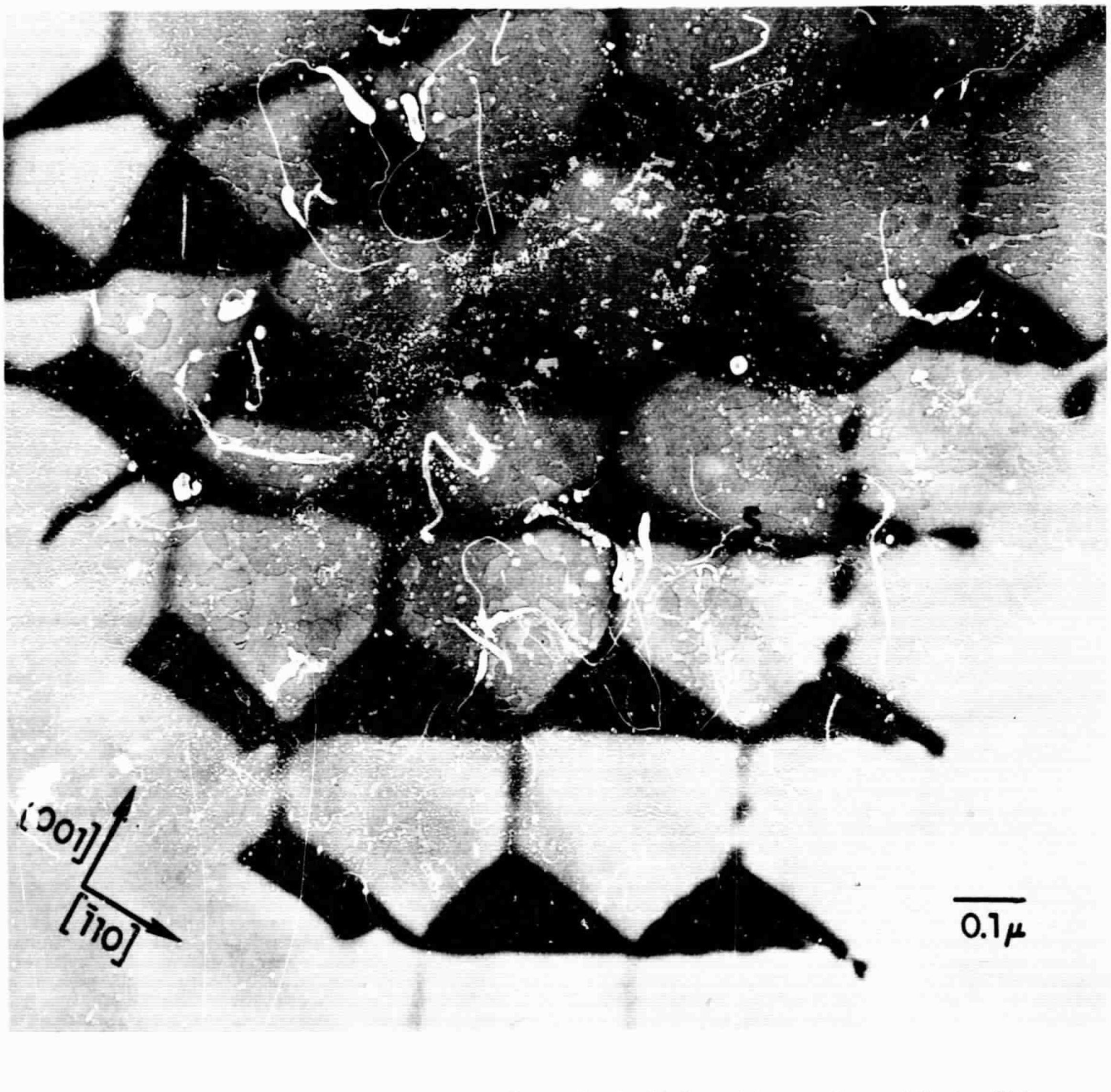


Figure 21. $TiB_2$ precipitates nucleated at dislocation nodes. Their diffraction contrasts resembles that of extrinsic stacking faults (after Venables[63]).

Alloying with elements in solid solution may also be applied to the carbides. In fact, the carbides appear to be a particularly appropriate field of study in which to relate electronic structure to mechanical behavior. Lye[10] has suggested that alloying may be expected to change the relative occupancy and the bond strength of the electron states which are responsible for cohesion in the carbides. By appropriate alloying, therefore, it may be possible to adjust the relative occupancy of bonding and anti-bonding electronic states such that differences in strength, ductility and brittle-to-ductile transition temperature may be produced. If a relatively ductile carbide could be develop by alloying it would be of extreme technological importance. A thermomechanical treatment involving prestrain of a ductile carbide solid solution - perhaps in some forming process - followed by controlled high temperature boron-doping, could provide extremely useful characteristics of mechanical behavior.

The electronic structure of the carbides may be controlled by alloying in solid solution with other carbides, nitrides or oxides. Although ordering may introduce complications to these studies, a concurrent investigation of both electronic and mechanical properties should provide valuable information on the fundamental properties of these materials. At present, however, much remains to be learned about phase equilibria in these systems. Current work suggests that the earlier observations of complete solid solubility between carbides, nitrides and oxides may be invalidated by the application of more sensitive experimental techniques to determine phase equilibria and to generally characterize these materials.

### 6.4. Crystal structure.

The presence of grain boundaries in a crystal imposes a barrier to slip propagation, and unless each grain conforms to the deformation of its neighbors, grain boundary separation will occur. Von Mises[89] determined that five independent slip systems were necessary for ductility in polycrystalline aggregates. As Groves and Kelly[90] have pointed out, most ceramic materials do not meet these requirements. The cubic oxide ceramics, for example MgO, deform by slip on $\{110\} < 1\bar{1}0 >$ systems. The number of independent slip systems is two and ductility is not observed in polycrystalline material until slip is activated on additional systems[91]. Since the predominant slip system[‡] is $\{111\} < 1\bar{1}0 >$ in the cubic carbides, five independent slip systems are available and ductility in polycrystalline form is expected at temperatures not far above the brittle-to-ductile transition temperature found in single crystals. The hexagonal carbides and other similar ceramics are likely to possess more limited ductility.

Ductility has been observed in a number of polycrystalline carbides. Recently, Kelly and Rowcliffe[54], have shown that hot-pressed $TiC_{0.75}$, $VC_{0.61}$, $NbC_{0.88}$, $NbC_{0.95}$, TaC and WC, all behave in a ductile manner in bending tests performed at above 0.5-0.6 $T_m$.

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[‡] Gillies and Lewis[92] have studied the line broadening which results from ball milling different carbides, and they conclude that the strain associated with TiC, ZrC and VC is similar to that observed in fcc metals, while that in TaC and NbC is similar to that found for the alkali halides and ionic oxides of the same structure. This suggests that $\{110\} < 1\bar{1}0 >$ slip may be important in TaC and NbC.

### 6.5. Microstructural details.

Optimizing the properties of carbides will require the use of fully dense materials since the yield strength of ceramics decreases exponentially with increasing porosity[93,94]. Porosity gives rise to increased brittleness since the pores act as crack nuclei at low temperatures and restrict grain boundary sliding at high temperatures[95].

Although the material should be fully dense, it may not be necessary to restrict the use of carbides to single crystal components, because these materials should be ductile in polycrystalline form. In fact, at 1500°C coarse grained TiC of about 2mm grain size has exhibited about 30% ductility, and a yield strength about ten times that of single crystals of the same composition at the same temperature[50]. It is well known that the yield strength and fracture strength of metals and ceramics increases as the grain size decreases. The behavior of TiC is likely to follow this pattern. In fact, the room temperature modulus of rupture of TiC has been shown to increase from about 31 $Kg/mm^2$ (44,000 p.s.i.) at a grain size of 12μ to 51 $Kg/mm^2$ (73,000 p.s.i.) when the grain size is 4μ[96]. This data cannot be accurately described by, for example, an Orowan-Petch analysis[97] because of the variation in porosity of intermediate grain sizes. However, it appears that fine grain, fully-dense, polycrystalline carbides could provide useful mechanical strength and ductility at high temperatures, and may therefore be of significant technological importance in the future[98].

It may not be the carbides or alloyed carbides of highest melting points (NbC, TaC, HfC) which will prove of greatest usefulness in applications where strength-to-density ratio is an important criterion for their utilization. These carbides are of considerably greater density than TiC, VC or TiC-VC alloys and would therefore be required to be considerably stronger to exhibit an equivalent strength-to-density ratio.

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