JOURNAL OF MATERIALS SCIENCE 9 (1974) 223–228

Elastic moduli measurements of some cubic transition metal carbides and alloyed carbides

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Polycrystalline elastic moduli have been determined for TiC, TiC-26% VC, VC-22% TiC and VC using a composite resonator. Carbon to metal ratios were in all cases close to 0.84. Room temperature moduli variations with alloy composition are discussed and by comparison with other data the order of magnitude of modulus variation with carbon content is determined for TiC. The temperature dependence of Young's modulus for TiC and VC are determined in the range 20 to 1600°C. Correlations are sought with hardness data.

1. Introduction

A number of experiments have been reported over a long period of time in which Young's moduli have been determined for several of the cubic carbides [1, 2]. In the case of $TiC_{0.91}$ the complete set of elastic constants has been determined as a function of temperature between 4.2 and 298 K [3]. Making use of previous work as far as possible, the present paper sets out, with the aid of new elasticity data, to determine how moduli of elasticity depend upon carbon concentration, alloy composition and temperature in the titanium and vanadium based carbides. Furthermore, reference is made to plastic behaviour through the property of hardness to see whether plastic and elastic effects can be correlated. The high temperature compressive strengths and room temperature hardnesses of $TiC_{0.84}$, $VC_{0.84}$ and several of their mutual alloys have been studied by Hollox [4] and Hollox *et al* [5]. The most significant finding of this work was that alloying in this way produces striking increases in the high temperature flow stress. To facilitate correlations and maintain uniformity of approach between the hardness work on alloys and the elastic results presented here, carbon compositions and alloys have been chosen to correspond closely to ones used in [4] and [5].

2. Experimental

The carbide specimens were prepared using the floating zone technique previously described by Packer and Murray [6]. General growth and purity conditions are presented in Table I. In all cases, polycrystalline single phase specimens free from major inclusions were grown.

Room temperature dynamic elastic moduli were measured using a composite resonator assembly. The experimental set-up consists essentially of two identical piezoelectric crystals and a specimen section. The operating principle and mathematical analysis of the method have been fully described by Marx [10]. For the Young's moduli measurements, the piezoelectric crystals were cut to oscillate at approximately 100 kHz in a longitudinal direction. Shear moduli were measured on the same specimen sections, using shear crystals oscillating at approximately 195 kHz.

The Young's moduli and shear moduli were then determined in the usual way using the expressions [11]

$$E = (\lambda_l f_l)^2 \rho, \; G = (\lambda_s f_s)^2 \rho \qquad (1)$$

where ρ is the density, λ the wavelength, f the resonant frequency and the subscripts l and s refer to longitudinal and shear waves, respectively. In general, specimen lengths could not be cut to match exactly the resonant frequency of the piezocrystals and the specimen frequency (f_S) was calculated using the relationship, also derived by Marx [10]

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TABLE I General growth and purity conditions of the specimens

Carbides	TiC	TiC-26%VC	VC-22%TiC	VC
C-M ratio	0.84	0.84	0.835	0.83
Density ($g\ cm^{-3}$)	4.72	4.96	5.43	5.62
Grain size average (mm)	0.717	0.513	0.120	2.4
Impurities* (ppm)				
W	7	200	70	7
Cr	<1	3	20	30
Zone speed ($cm\ h^{-1}$)	7.5	7.5	7.0	6.5

*From previous work of Packer and Murray [7], W was shown by spectroscopic analysis to be the greatest impurity; therefore, all other elements were expected to be present in quantities below the value of W. (Semi-quantitative electron probe microanalysis confirmed this assumption.) Shacklette and Williams [8] reported high Cr levels for our VC single crystal specimens. Since it was not possible to analyse for Cr with the electron probe, this element was also analysed spectroscopically.

Oxygen and nitrogen are also expected to be present. Billingham [9] has reported that for VC, levels of a few thousand ppm O_2 and a few hundred ppm N_2 are present. Similar impurity contents are also expected here for oxygen and nitrogen.

$$f_S m_S = f_T m_T - f_D m_D \tag{2}$$

where f_T and f_D are the resonant frequencies of the total and piezocrystal assemblies respectively, and the m's are their respective masses. The elastic anisotropy of the carbides is small and, therefore, little error is introduced by assuming the polycrystalline specimens to be isotropic. For example, TiC is among the most elastically isotropic of materials with estimated values for anisotropy factor A [$= 2c_{44}/(c_{11} - c_{12})$] ranging between 0.9 to 1.18 [12]. The bulk moduli and Poisson's ratio can thus be determined by using the well-known relationships [13]

$$K = \frac{E}{3(3G - E)}, \nu = \frac{E}{2G} - 1. \tag{3}$$

Temperature coefficients of the Young's moduli were determined between 20 and 1600° C. For these experiments a carbide buffer rod was used to isolate the piezoelectric crystals from the heated specimen sections. In this case f_D and m_D in Equation 2 refer to the frequency and mass of the piezocrystals and rod combination thermal buffer (measured after slicing off the specimen section). Fractional variations in frequency can be readily measured in this way and related to fractional modulus variations through the expansion coefficient, α, by

$$E_T/E_{RT} = (1 + \alpha \Delta T)^{-1} (f_{ST}/f_S)^2 \tag{4}$$

where E_{RT} and f_S are the Young's modulus and resonant frequency of the specimen at the reference temperature (room temperature or 20° C), E_T and f_{ST} are the same quantities at any other temperature, ΔT is the difference between the measured and reference temperature, and α is the coefficient of linear expansion over the measured temperature range.

The most reliable results were obtained when buffer and specimen sections were grown in one operation, thus avoiding unnecessary bonds in the resonating system. This requirement involved zone-melting carbide rods approximately 35 cm long. Because it was not feasible to grow oriented single crystals of such great length, polycrystalline samples were studied.

Debye temperatures can be calculated from the elastic data. Anderson [14] has shown that the Debye temperature, θ, is related to the average sound velocity, v_m by the equation

$$\theta = \frac{h}{k} \left[\frac{3q\,Np}{4\pi M}\right]^{1/3} v_m \tag{5}$$

where q is the number of atoms in the molecule, M is the molecular weight, h is Planck's constant, k is Boltzman's constant, and N is Avogadro's number. Anderson showed that by using the Voigt-Reuss-Hill [15] approximation for elastic moduli in a polycrystalline solid the average sound velocity for shear, v_s, and longitudinal, v_l, waves are

$$v_m = \sqrt{(G_H/\rho)},\ v_l = \sqrt{\{(K_H + \tfrac{4}{3} G_H)/\rho\}} \tag{6}$$

where the subscript H denotes Hill's average of the Voigt-Reuss relationship [11]. The average sound velocity is taken to be

$$v_m = \tfrac{1}{3}\left(\frac{2}{v_s^3} + \frac{1}{v_l^3}\right)^{1/3} \tag{7}$$

3. Results and discussion

Room temperature elastic moduli and Debye temperature determinations for TiC, TiC-26VC, VC-22TiC, and VC are presented in Table II. Also presented in Table II are the moduli and Debye

TABLE II Values for elastic moduli, Poisson's ratio and Debye temperature for some cubic transition metal carbides

Carbide	E	K	G	ν	$\theta_{298\ \mathrm{K}}$	Ref.
TiC	4.570	2.401	1.938	0.1828	947	16
$TiC_{0.91}$	4.500	2.422	1.886	0.1928	943	3
TiC	4.369	2.420	1.822	0.1991	921	17
$TiC_{0.84}$	3.998	2.33	1.642	0.215	884	
TiC-26VC	3.807	2.254	1.562	0.2185	855	
VC-22TiC	3.918	2.361	1.601	0.2235	846	
$VC_{0.84}$	4.154	2.230	1.746	0.1896	855	18
$VC_{0.83}$	3.840	2.347	1.544	0.2273	822	
$ZrC_{0.94}$	4.061	2.231	1.697	0.1966	708	3
ZrC	3.717	1.699	1.637	0.1352	643	16
*$NbC_{0.97}$	5.102	2.965	2.137	0.21	—†	19
*$NbC_{0.964}$	4.884	3.003	1.987	0.229	740	20

Note: E, K and G in units of ($\times\ 10^{12}$ dyn cm^{-2}).
*Elastic constants not available – value obtained by conversion.
†Density not available.

temperatures determined from measurements reported by other authors.

To enable meaningful comparison between the polycrystalline elastic moduli obtained from this work and the single crystal values obtained by other authors, the modified averaging method suggested by Hill [15] for the Voigt [21] and Reuss [22] approximations have been employed. The values for ZrC and NbC are included to enable comparisons to be made with carbides within the same periodic groups.

In general, the elastic moduli and Debye temperatures evaluated in this work are in good agreement, where comparison can be made, with values computed from single crystal data. Although it is assumed in the computation that the crystal grains are equiaxed, in reality the grain structure is columnar and some preferred orientation is expected with long axes of grains directed about ⟨110⟩ [7]. Fortunately ⟨110⟩ elastic properties of cubic crystals have values near to the average for those of ⟨100⟩ and ⟨111⟩ orientations and, furthermore, we have already noted the high elastic isotropy of carbides. The systematic errors for the averaged elastic constants are small therefore and estimated to be less than 3%.

A little can be said about the effect of carbon concentration on Young's modulus by making comparison with earlier work. The most meaningful comparison that can be made is for TiC, since only in this carbide has the carbon content been reported for an elastic study. By comparing, (Table II), Chang and Graham's [3] value for TiC and that determined here, it can be seen that the values of the moduli decrease with decreasing carbon content. The Debye temperatures computed from the moduli show the same trend. These findings support the idea that for TiC the bond strength is decreased as carbon is removed from the lattice.

The finding that Young's modulus decreases as carbon content decreases is in agreement with Toth's [2] low temperature specific heat experiments. Toth found that the Debye temperature decreases with carbon content indicating that the lattice becomes less "stiff". It may also be significant that the decrease of 12% in Young's modulus between $TiC_{0.91}$ and $TiC_{0.84}$ is equal within experimental error to the percentage fall in hardness observed by Williams [23] between the same limits of carbon content.

The variation of elastic moduli with alloying of TiC and VC is shown in Fig. 1. From the figure it can be seen that TiC-26VC has lower modulus values than VC and that VC-22TiC has higher modulus values, suggesting that bond strengths vary in a complicated way. For the alloys furthermore, the hardness shows a quite different trend.

Shown in Fig. 1 are room temperature microhardnesses obtained by Hollox *et al* [5] as a function of alloy composition. The microhardness trends clearly do not follow those of the moduli. Although there does seem to be a stronger correlation between Debye temperature and hardness, it should be pointed out that there is some doubt about the hardness shown for

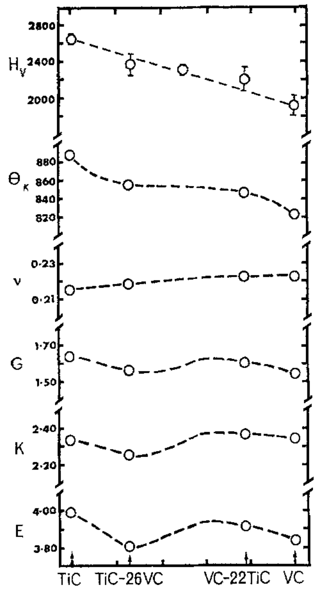

Figure 1 Room temperature elastic moduli and Debye temperatures for TiC, VC and their mutual alloys. Also shown are room temperature hardnesses reported by Hollox *et al* [5]. Moduli values in units of 10^{12} dyn cm^{-2} hardness in units of deg mm^{-2}.

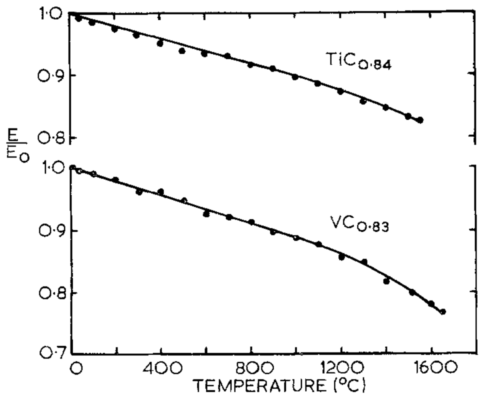

Figure 2 Young's modulus ratio versus temperature for TiC and VC.

$TiC_{0.85}$. Rowcliffe and Hollox [24] report a hardness of 2000 kg mm^{-2} for $TiC_{0.80}$ under nearly identical conditions. Whilst it is expected that the hardness of $TiC_{0.80}$ should be lower than that of $TiC_{0.85}$, the small difference in carbon concentration cannot account for a difference in hardness of 600 kg mm^{-2} [23]. Taking the lower of these two values would put the hardness of $TiC_{0.84}$ lower than that for TiC-25% VC. Other experiments by Jangg *et al* [25] tend to confirm that hardness has a maximum near TiC 30% VC.

It seems that there is a situation in which elastic moduli and Debye temperature can be simply correlated to hardness through varying carbon composition in TiC_x, but not through varying alloy composition. One explanation for this situation (based on hardness being controlled only by the Peierls stress) is that only the mean bond strength varies with carbon concentration, whereas the spacial distribution of bonds is affected by alloying.

Fig. 2 shows a plot of the modulus ratios for TiC and VC. Up to 1000° C the internal friction peaks are sufficiently small [26] that within experimental error the dynamic modulus can be taken as equal to the unrelaxed or Hookean modulus. Above room temperature the Young's modulus is linearly related to the temperature until at some high temperature the data departs from linearity. Temperature coefficients and the extent of the linear regions of the reduced Young's modulus for TiC and VC are given in Table III. The values shown in Table III are in general agreement with those of other workers who have studied similar materials. For example, Martin and Costa [27] who studied TaC using a micro-flexural technique determined a value of -10^{-4} K^{-1} in the linear region extending to 800°C. Sarian [28], using the low temperature data of Chang and Graham for $TiC_{0.91}$ and $ZrC_{0.94}$, determined a temperature coefficient of -1.0×10^{-4} K^{-1} for both materials. Hall [29] also using a dynamic resonance technique in his early study of UC determined values of -1.3 and -1.1×10^{-4} K^{-1} for both hyper- and hypo-stoichiometric UC, respectively.

The only other relevant work reported on the temperature dependence of elastic moduli in cubic carbides is that of Spinner [30] on TiC. However, his specimens had a quoted porosity of 28% and the stoichiometry was not reported. Although porosity affects the absolute values of the elastic moduli, Coble and Kingery [31] have shown that in the linear region the temperature coefficient is not affected. Thus, the reported

TABLE III Temperature coefficients and linear region of the reduced Young's modulus

Carbide	$-\frac{1}{E_0}\frac{dE}{dT}$ (°C × 10^{-4})	Linearity limit (°C)
TiC	1.06	850
VC	1.11	1050

findings of Spinner for the temperature coefficient of the Young's modulus to 950° C, namely $-1.04 \pm 0.03 \times 10^{-4}$ K^{-1}, is in excellent agreement with the value of -1.06×10^{-4} K^{-1} obtained here for TiC. It is interesting to make further comparison with Spinner's work. Spinner's results deviate from linearity at 950° C. In the present work, a specimen of $TiC_{0.97}$ containing a higher percentage of free carbon showed a deviation from linearity at approximately 1050° C. Single phase $TiC_{0.84}$ was found to deviate at 850° C, as shown in Fig. 2. These results indicate that the temperature at which the data depart from linearity is a function of the carbon content and increases as the carbon content increases. This suggests that Spinner's specimen was intermediate in carbon between $TiC_{0.84}$ and $TiC_{0.97}$.

According to Spinner's results, the Young's modulus falls sharply above 1050° C. This he attributed to grain-boundary slip. The effect was not observed in the present series of experiments where grain boundaries were also present. Neither was such an effect observed by Speck and Miccioli [19] in low porosity sintered NbC. It seems likely, therefore, that the abrupt high temperature decrease in modulus is a property of the high porosity of Spinner's specimens. Further evidence for this point of view is found in the work of Shaffer and Jung [32], who compare data on fully dense polycrystalline SiC with data on less dense specimens, and find a similar rapid increase in temperature coefficient at high temperatures for the porous specimens.

The empirical equation proposed by Wachtman *et al* [33] to describe the temperature dependence of Young's modulus for several oxides is

$$E = E_0 - BT \exp(-T_0/T) \qquad (8)$$

where E_0 is the Young's modulus at 0 K and B and T_0 are constants. Anderson [34] derived Wachtman's equation and showed it fully describes the temperature dependence of elastic moduli of oxide compounds when the variation of Poisson's ratio with temperature is small. Anderson also showed that T_0 is connected to the Debye temperature and that B is connected to the Gruneisen constant. A fit has not been attempted here, since the low temperature region up to room temperature suggests that T_0 is close to room temperature. In the present work, B has been determined for TiC as 4.3×10^8 dyn cm^{-2} K^{-1}. T_0 can be obtained using the Young's modulus values at 0 K and room temperature determined by Chang and Graham namely 4.500 and 4.548×10^{12} dyn cm^{-2}. Substitution of these values into Wachtman's equation [8] gives a value for T_0 of 327 K. This value is close to that obtained for refractory oxides which together with the carbides also have high values of Debye temperature, θ_D. In the theoretical paper by Anderson [34] it was suggested that $T_D \simeq \theta_D/2$. However, the experimental values for T_0 and θ_D obtained by Wachtman *et al* [33] and Brenton *et al* [35], together with those determined here, suggest that T_0 is usually given better by $T_0 \simeq \theta_D/3$. Not enough data are available to compute T_0 for VC, but it is expected that it will have a value close to that for TiC.

4. Conclusions

1. The elastic moduli of TiC_x fall by 12% as carbon content is decreased from $TiC_{0.91}$ to $TiC_{0.84}$. A similar fall has previously been observed in hardness between the same carbon compositions.

2. The variation of elastic moduli with alloy composition in the TiC-VC system is not a linear function, and suggests that near TiC-26% VC the alloy binding energy may reach a minimum value whilst at TiC-60% VC it may reach a maximum value.

3. Alloy hardness does not follow the pattern of the elastic moduli. This departure suggests that in addition to binding energy there may be strong variations in the directionality of bonds with alloy composition. However, the situation is not clear since one set of hardness data [5] does correlate more closely with Debye temperature behaviour.

4. Temperature coefficients for Young's modulus in the linear region above room temperature have been verified to be close to -1×10^{-4} K^{-1} in both TiC and VC. Departures from linearity occur in the temperature range 850 to 1050° C and depend, in the case of TiC, on the carbon concentration.

Acknowledgements

This work forms part of a study of mechanical properties at high temperatures and was carried out under the general supervision of Professor D. Tabor, FRS. The authors are indebted to the Ministry of Defence (Procurement Executive) for financial support.

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Received 4 June and accepted 25 July 1973.