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Letter

Hardness and elastic properties of $Ti(C_x N_{1-x})$, $Zr(C_x N_{1-x})$ and $Hf(C_x N_{1-x})$

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Abstract

Here we report for the first time *experimental* results of the nanohardness and elastic properties (Young's modulus, shear modulus, bulk modulus) of well-characterised complete series of bulk Ti, Zr and Hf carbonitrides, $Ti(C_xN_{1-x})$, $Ti(C_xN_{1-x})_{0.81}$, $Zr(C_xN_{1-x})$ and $Hf(C_xN_{1-x})$, as a function of the carbon/nitrogen ratio measured by continuous nano-indentation test and an ultrasonic technique. A correlation between elastic constants and porosity of TiC and TiN was obtained and used to correct elastic constants for the zero-porosity state. Recently, band structure calculations for transition metal carbonitrides yielded a maximum of the shear modulus of Ti and Hf carbonitrides at a valence electron concentration (VEC) of ≈ 8.4 and ≈ 8.2 , respectively. These results were used to explain the hardness maximum of carbonitrides, which was considered as a success of theoretical material design. For the stoichiometric carbonitrides we indeed found—though much weaker than predicted—the maximum at $[C]/([C]+[N])\approx 0.6-0.8$ (VEC $\approx 8.4-8.2$) of the shear modulus, but neither the nanohardness nor the microhardness show a corresponding maximum. Thus the conclusion of a correlation of hardness and shear modulus is inapplicable for this type of hard materials. © 2000 Published by Elsevier Science S.A.

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1. Introduction

Transition metal carbonitrides, especially Ti(C,N), have attracted considerable interest because of their unique combination of physical properties such as high melting temperature, high hardness, high electrical and thermal conductivities and metallic lustre [1] and are widely used for cutting tools and wear-resistant coatings [2].

Though hardness is not an exactly specified physical quantity, it is one of the most important properties for the application of many materials. Microhardness data of Ti(C,N), Zr(C,N) and Hf(C,N) have been reported [3–7] as a function of the [C]/([C]+[N]) ratio. Results on well-characterised specimens [3] show that the hardness of the carbonitrides increases monotonously with increasing [C]/([C]+[N]) ratio with a load of 0.98 N, which is in accordance with data reported for 0.48 N [4]. Others [5]

show a minimum hardness at a valence electron concentration (VEC) at ≈ 8.5 but their samples were not dense. On the contrary, a compilation [6] on bulk samples reports a maximum hardness for VEC of ≈ 8.4 and a study [7] of thin films shows a maximum at VEC of ≈ 8.5 with extremely high absolute values—about twice as high as for bulk samples.

Recently, Jhi et al. [8] proposed an electronic mechanism of the hardness enhancement by band structure calculations in these transition metal carbonitrides. The hardness maximum was explained by the calculated maximum of the shear modulus, c_{44} , for VEC \approx 8.4 for Ti(C_xN_{1-x}) and \approx 8.2 for Hf(C_xN_{1-x}) assuming a correlation between hardness and shear modulus. No experimental data for a direct comparison of their calculated data had been available.

In view of our microhardness data [3] obtained with extremely carefully prepared and characterised samples not showing such a maximum, and of the contradiction in microhardness data as well as the lack of experimental data for the shear modulus, we investigated series of well-

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characterised carbonitrides, $Ti(C_xN_{1-x})$, $Zr(C_xN_{1-x})$, $Hf(C_xN_{1-x})$ and $Ti(C_xN_{1-x})_{0.81}$, for nanohardness and elastic properties such as Young's modulus *E*, shear modulus *G* and bulk modulus *B*.

2. Experimental

A variety of different compositions were adjusted by hot-pressing carbide, carbonitride and nitride powders. Chemical analysis for nitrogen and carbon was done by Dumas gas chromatography (GC) [9].

The samples were polycrystalline with an average grain size of $5-20 \ \mu m$ and prepared with various porosities for obtaining an extrapolation function to zero porosity. The porosity was determined by comparison of the theoretical density (from lattice parameters and composition) with the density determined by the Archimedes technique at room temperature in which the sample is suspended in a liquid of known density versus temperature.

Continuous nano-indentation tests were performed with a Berkovich indenter on well-polished samples with a maximum depth of indent of 300 nm, a rate of indentation of 15 nm/s, a holding time at the maximum load of 15 s, and a rate of unloading of 1.5 mN/s. The temperature of the sample was kept at 25°C. For every sample, 10 indents were made and average values were calculated with an improved method [10].

Ultrasonic wave velocity measurements were performed in pulse-echo mode [11], in which the time of an acoustic wave to travel back and forth along a sample (in the range of 0.9-7.3 mm) is determined. Therefore the samples were lapped and polished to a parallelism of better than a few μ m.

3. Results and discussion

The nanohardness is shown in Fig. 1a–d as a function of [C]/([C]+[N]) ratio and VEC together with previously measured microhardness data [3] for comparison. They correspond closely to each other in their compositional dependence—a monotonous increase with increasing [C]/([C]+[N]) ratio (with decreasing VEC), but without a maximum in between. The carbides, [C]/([C]+[N])=1 (right), show the highest hardness. For Zr(C,N) and especially for Hf(C,N) a significant positive deviation from linearity of the addition rule can be observed. The



Fig. 1. Nanohardness (\blacktriangle) and microhardness (\bullet) for (a) Ti(C_xN_{1-x}), (b) Ti(C_xN_{1-x})_{0.81}, (c) Zr(C_xN_{1-x}) and (d) Hf(C_xN_{1-x}) as a function of the [C]/([C]+[N]) ratio as well as of the valence electron concentration (VEC). For stoichiometric carbonitrides the two functions are practically parallel. No maximum between the nitride ([C]/([C]+[N])=0 and the carbide [C]/([C]+[N])=1 exists. There is an increasing trend from Ti over Zr to Hf carbonitrides for a positive deviation from the mixing rule.

nanohardness is higher than the corresponding microhardness due to cracks at higher loads, which additionally expands the indentation and yields a larger indentation area, and thus a lower hardness value.

The reported hardness maximum [6] is most probably due to the inhomogeneity of the samples (the sample preparation and characterisation have not been communicated). Thus, in fact two-phase mixtures had most probably been investigated which are known to show higher hardness than a gross-compositionally equal single-phase material because of the precipitation hardening effect. Data from thin films [7] are not representative for bulk data because they are influenced by their inherent properties such as high dislocation densities and stress. Thus thin-film samples often show twice as high hardness than bulk samples, e.g., for TiN values of up to almost 50 GPa have been reported [7], which is only to a minor extent attributable to the much lower load used for measuring thin films (see Fig. 1).

There are no experimental data for a comparison of hardness with elastic properties. The only systematic study of elastic properties of carbonitrides was done by Ivanov et al. [12] but their samples were substoichiometric around $Ti(C,N)_{\approx 0.92}$ and highly porous (up to 18.6%), and a correction for the high porosity was not performed. From these data a detailed function of the Young's modulus with [C]/[N] ratio for Ti(C,N) cannot be obtained because of the uncertainty in the extrapolation function for the correction of porosities [11].

Fig. 2a,b shows the porosity dependence of Young's modulus (E), shear modulus (G) and bulk modulus (B) of TiC and TiN. From these data, we obtained elastic constants for zero porosity by correlations between elastic constants and porosities of TiC and TiN:

• For TiC:

$$E(0) = E(P) + 6.1P + 0.52P^2$$
(1)

$$G(0) = G(P) + 2.5P + 0.22P^{2}$$
⁽²⁾

$$B(0) = B(P) + 2.7P + 0.39P^2$$
(3)

 $E(0) = 445 \text{ GPa}, \quad G(0) = 187 \text{ GPa}, \quad B(0) = 242 \text{ GPa}$

• For TiN:

$$E(0) = E(P) + 7.0P + 0.38P^2$$
(4)

$$G(0) = G(P) + 3.5P + 0.14P^2$$
(5)

$$B(0) = B(P) + 2.5P + 0.41P^2$$
(6)

 $E(0) = 463 \text{ GPa}, \quad G(0) = 189 \text{ GPa}, \quad B(0) = 277 \text{ GPa}$

where E(0), G(0) and B(0) are the elastic data for the zero-porosity state, E(P), G(P) and B(P) are the measured data and P is the porosity in percent.

Since bulk carbonitrides cannot be prepared in zeroporosity state (usually, the higher the nitrogen content the larger the porosity) these correction functions are very important in order to compare experimental data with data from theoretical considerations. It is clear that the extrapolation function should be obtained with samples as close as possible to zero porosity.

In order to obtain elastic properties of the carbonitrides for the zero-porosity state, the mixing rule was used, that is

$$M(0)_{MeC_xN_{1-x}} = M(P)_{MeC_xN_{1-x}} + x^*(aP + bP^2) + (1-x)^*(cP + dP^2)$$
(7)



Fig. 2. Dependency of the Young's modulus $E(\blacktriangle)$, the shear modulus $G(\blacklozenge)$ and the bulk modulus $B(\blacksquare)$ on the porosity for (a) TiC and (b) TiN. TiC can be prepared with almost zero-porosity, whereas TiN cannot. The functions for TiC and TiN are almost identical (see text for polynomial expressions), a mixing rule of these were applied to correct the measured data of all carbonitrides in order to obtain data for zero porosity.

where $M(P)_{MeC_xN_{1-x}}$ is the measured Young's modulus (E), the shear modulus (G) and the bulk modulus (B), respectively, P is the porosity of the carbonitride $Me(C_xN_{1-x})$, x is the composition [C]/([C]+[N]) and a, b, c, d are the factors (unit, GPa) of the polynomial equations (Eqs. (1–6; a, b of TiC and c, d of TiN) for E, G and B, respectively. Since the porosity dependencies of the elastic properties are almost identical for TiC and TiN the mixing-rule treatment of the data gives only a small correction, which should, however, not be neglected.

Figs. 3a–d shows the elastic constants of $Ti(C_x N_{1-x})$, $Ti(C_x N_{1-x})_{0.81}$, $Zr(C_x N_{1-x})$ and $Hf(C_x N_{1-x})$ as a function of the [C]/([C]+[N]) ratio and VEC. For stoichiometric

Ti($C_x N_{1-x}$) the shear modulus has a slight maximum of 196 GPa at [C]/([C]+[N]) \approx 0.6–0.7 (VEC \approx 8.4–8.3). This is in good agreement with the results on the shear modulus c_{44} obtained by Jhi et al. [8] using ab initio pseudopotential calculations which is ca. 190 GPa at the maximum (for cubic isotropic polycrystalline materials c_{44} is identical to *G*, so that a direct comparison is possible). The calculated data on the left and right of the maximum are, however, much smaller (at the boundaries: $c_{44} \approx$ 175 GPa for TiC and \approx 155 GPa for TiN) and the measured maximum is thus much weaker. The shear modulus of the substoichiometric carbonitride Ti($C_x N_{1-x}$)_{0.81} increases with increasing [C]/([C]+[N]) ratio (decreasing VEC) and



Fig. 3. Young's modulus $E(\blacktriangle)$, shear modulus $G(\blacklozenge)$ and bulk modulus $B(\blacksquare)$ for (a) $Ti(C_xN_{1-x})$, (b) $Ti(C_xN_{1-x})_{0.81}$, (c) $Zr(C_xN_{1-x})$ and (d) $Hf(C_xN_{1-x})$ as a function of the [C]/([C]+[N]) ratio as well as of the valence electron concentration (VEC). A weak maximum in *G* for all stoichiometric carbonitrides was found supporting the calculations for $Ti(C_xN_{1-x})$ and $Zr(C_xN_{1-x})$ of Jhi et al. [8]. The bulk modulus *B* of $Ti(C_xN_{1-x})$ shows a negative curvature opposed to what was found theoretically [13].

the compound with the highest VEC, which is $TiN_{0.81}$ (VEC=8.1) shows the lowest shear modulus, in contrast to what is implied by the calculations. The bulk modulus of $Ti(C_xN_{1-x})$ shows a slight negative deviation form the mixing rule $B_{Ti(C_xN_{1-x})} = xB_{TiC} + (1-x)B_{TiN}$. This is just opposed to the findings of Jhi and Ihm [13], who found a

opposed to the findings of Jhi and Ihm [13], who found a positive deviation for most of the different structure types considered. The maximum in the experimental shear modulus of

The maximum in the experimental shear modulus of $Zr(C_xN_{1-x})$ and $Hf(C_xN_{1-x})$ is more pronounced than in $Ti(C_xN_{1-x})$ and these two compounds show a maximum in the Young's modulus, too, whereas the data for the bulk modulus, especially of $Zr(C_xN_{1-x})$, are too much scattered for a quantitative analysis. The calculations of Jhi et al. [8] for $Hf(C_xN_{1-x})$ again shows good agreement with our results with respect to the location of the maximum of the shear modulus at $VEC \approx 8.2$ and absolute values, but again the maximum is much weaker. Hence, as in the case of TiC and TiN, theoretical data for the boundary compounds HfC and HfN are in substantial disagreement with measured data.

In conclusion, we found that our nanohardness data are in full accordance with microhardness data and do not show a maximum for these compounds. Thus, the conclusion of a correlation between shear modulus and hardness, used to explain the hardness of carbonitrides [8], from which also the success of theoretical material design was concluded [14], is not appropriate. This may be due to the fact that the hardness is not an easy-to-define physical quantity. Within an indentation test, a variety of material properties, such as dislocation movement and viscous material flow, influence the results significantly, so that a direct correlation between a physical quantity like the shear modulus and a result, from an atomistic point of view, from a complicated hardness test method is obviously not possible. This is certainly true for at least the carbonitrides investigated in this study and other binary carbides and nitrides [15], of which the microhardness does not show the theoretically proposed maximum at VEC \approx 8.4. For example a VEC of 8.4 corresponds to a 12% vacancy concentration for TiN, which means TiN_{0.88}, but the maximum hardness was found at TiN_{0.67} [16] (VEC \approx 7.4, 33% vacancy concentration).

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