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BORON CARBIDE COATINGS : CORRELATION BETWEEN MECHANICAL PROPERTIES AND LPCVD PARAMETERS VALUES

J. REY⁽¹⁾, G. MALE*, Ph. KAPSA** and J.L. LOUBET**

Coating Development, Pôle de Productique, 74, rue des Acieries, F-42000 Saint Etienne, France

**I.M.P. CNRS, BP. 5, ODEILLO, F-66120 Font Romeu, France*

***Ecole Centrale de Lyon, Laboratoire de Technologie des Surfaces, CNRS UA-855, 36, avenue Guy de Collongue, BP. 163, F-69131 Ecully Cedex, France*

Résumé : Des dépôts de carbure de bore ont été élaborés par L.P.C.V.D. Leurs caractéristiques (taille de grain, composition, texture) varient fortement avec la température du substrat et la composition du mélange gazeux. L'effet de ces deux paramètres sur la microdureté, le comportement élastoplastique et le module d'YOUNG ont été déterminés par des tests d'indentation instrumentés. Les variations des caractéristiques sont analysées.

Abstract : Boron carbide coatings have been prepared by L.P.C.V.D. Their characteristics (i.e. grain size, composition, texture) depend heavily on the substrate temperature and gas mixture composition. The effects of these two parameters on microhardness, elastoplastic behavior and YOUNG's modulus, have been determined by indentation tests and are discussed in terms of variations in the coating characteristics.

1 - INTRODUCTION

Boron carbide is a ceramic known for its microhardness, wear and impact resistance, neutron absorption property and chemical inertness [1, 2]. It is often used in the form of powders or sintered components. Given its properties, it could be used as a coating to protect materials from severe environments.

Over the last few years, several works have been devoted to C.V.D. boron carbide coatings. The more recent one deal with the experimental study of the B-C-Cl-H system at room pressure [3] or at low pressures [4, 5, 6].

Apart from microhardness results, few mechanical property measurements of the coatings have been reported [7]. But, to find the right coating to protect a given material requires knowledge both of the specific properties of the deposited solid and of the correlations between these properties and the deposition conditions.

This is specially true for boron carbide layers whose characteristics heavily depend on C.V.D. conditions [3, 8]. Besides chemical protection, it seems that the most important uses of these coatings concern friction in dry conditions [9], as their mechanical properties directly appear through the performance of the coated materials.

Moreover, the properties of the material as a coating are often different from its properties as a bulk material, because of the absence of porosity and impurities and the possible existence of preferential crystallographic orientations. It is therefore important to study and compare both.

The indentation test is particularly well adapted to these measurements. Besides microhardness determination, the method, which analyses an indentation curve (i.e. load versus indentation depth), allows a YOUNG's modulus value of the coating to be calculated and its elastoplastic behavior to be quantified [10, 11].

(1) Present address : S.E.P., Le Haillan, B.P. 37, 33165 SAINT MEDARD EN JALLES Cedex, France

In this work, the dependence of these three properties on the variations in deposition conditions is studied, and correlated to the coating characteristics : microstructure, composition and texture.

2 - SAMPLE PREPARATION

Boron carbide coatings were prepared on WC-Co cemented carbides which were first coated with a titanium carbide layer. This layer, 4 microns thick, heavily limits boron diffusion from the gas phase to the cemented carbide. The substrate surface thus becomes practically inert /12, 13/.

The coatings were obtained by the L.P.C.V.D. process, from $\text{BCl}_3\text{-CH}_4\text{-H}_2$ gas mixtures, using a cold wall reactor (silica tube of 30 mm diameter).

The parameter values were chosen with reference to the results of preliminary experimental studies /6, 8/. By increasing R, the flow rates ratio ($R = [100 \times \text{CH}_4 \text{ flow}] / [(\text{CH}_4 + \text{BCl}_3) \text{ flow}]$), which represents the relative carbon content in the gas mixture, various compositions can be obtained under set conditions. These belongs successively to a " B_{50}C_2 " boron-rich tetragonal solid solution, a " B_{50}C_2 " + " B_{13}C_2 " co-deposition area, " B_{13}C_2 " rhombohedral solid solution and a " B_{13}C_2 " + X co-deposition area. The rich-in carbon X phase has not been isolated and defined until now.

Table I : Processing conditions and nature of phases obtained.

Constant conditions for this study	
Pressure(mbar)	10
H ₂ flow (l/h)	7
BCl ₄ flow (l/h)	1.5

Variable conditions : coating set 1								
Temperature (K)	1293							
CH ₄ flow (l/h)	0.08	1.23	1.36	1.54	1.83	2.25	2.66	3.04
R	5	45	47.5	50	55	60	64	67
Phase (X-Rays)	"B ₅₀ C ₂ "	"B ₅₀ C ₂ " + "B ₁₃ C ₂ "		"B ₁₃ C ₂ "				"B ₁₃ C ₂ " + X

Variable conditions : coating set 2						
Temperature(K)	1223	1293	1333	1373	1423	1473
CH ₄ flow (l/h)	1.5					
R	50					
Phase (X-Rays)	"B ₁₃ C ₂ "					"B ₁₃ C ₂ " + X

A first set of samples was prepared with various R values, for a substrate temperature of 1293 K. and another set. with various substrate temperatures for R = 50, so that, the

rhombohedral solid solution has been mainly studied (table I). All coatings were about 50 microns thick. The experimental points are set out on the diagram (fig. 1) proposed by LARTIGUE /8/.

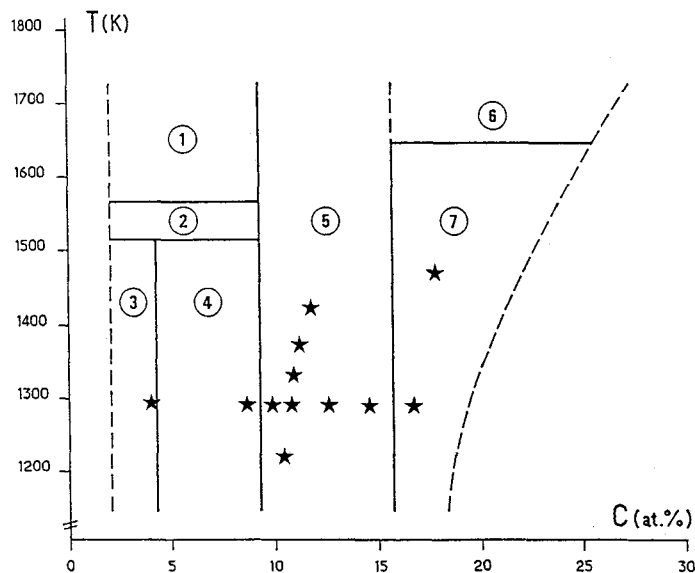


Fig. 1 : Deposit temperature / carbon atomic concentration diagram from LARTIGUE /8/. Location of experimental points of this study are plotted (stars).

- 1) $B_B + "B_{13}C_2"$
- 2) $B_B + "B_{13}C_2" + B_{50}C_2$
- 3) $B_{50}C_2$
- 4) $B_{50}C_2 + "B_{13}C_2"$
- 5) $"B_{13}C_2"$
- 6) $"B_{13}C_2" + C$
- 7) $"B_{13}C_2" + X$

3 - GOATINGS CHARACTERIZATION

3.1. Elementary composition

The analysis was made by Glow Discharge Optical Spectroscopy (2), following a previously described method /14/. The curve in figure 2 shows that the coating composition is strongly dependent on that of the gas mixture. The relation seems to be linear in the rhombohedral phase area (5 and 7 on fig. 1). Then, to further understanding, variations in the mechanical properties were plotted against the composition of the solid.

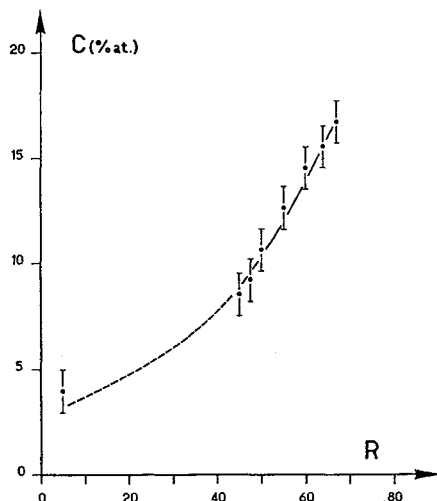


Fig. 2 : Carbon concentration of deposits (C) versus R.
T = 1293 K.

The composition of the coating seems to depend little on substrate temperature (fig. 3). However, an increase in temperature does help the dissociation of CH_4 which is the limiting step at low temperatures /5/, so the carbon concentration of the coating slightly increases. Only the layer deposited at 1473 K has a rich in carbon composition which belongs to the " B_{13}C_2 " + X area. This phenomenon seems to be related to a change in the kinetic law /8/.

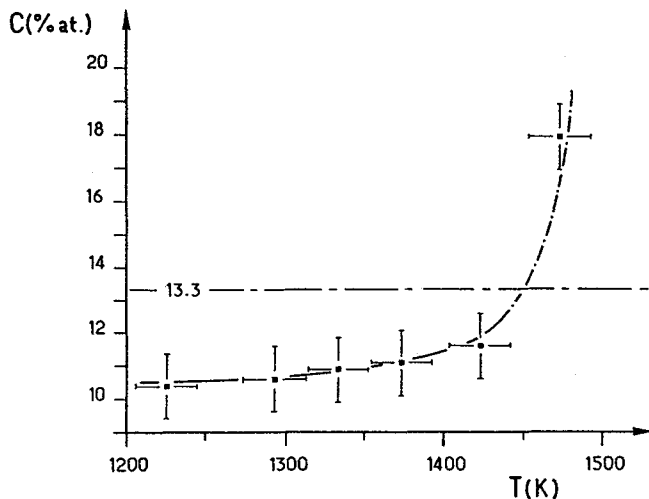


Fig. 3 : Carbon concentration of deposits (C) versus temperature (T). R = 50.

3.2. Surface morphology

The L.P.C.V.D. boron carbide microstructure (particularly the rhomboedral phase) cannot be easily revealed by the usual metallographic methods /8/. However, a good image of the variation in layer microstructure can be obtained by observing the surface morphology.

Generally, an increase in the CH_4 content in the gas mixture, and consequently in the carbon content of the coating, induces a decrease in the grain size (fig. 4b, 4c, 4d). The " B_{50}C_2 " tetragonal phase grows particularly as a well crystallized coating, with a crystal size equal to 10 microns or more (fig. 4a). In the rhombohedral solid solution, the microstructure is rather amorphous for high carbon concentrations. An increase in the substrate temperature favours crystallization of the coating in the " B_{13}C_2 " area (fig. 4a, 4b, 4c). However, for temperatures higher than 1423 K, the trend is again towards an amorphous state.

3.3. Texture

Coating methods, the L.P.V.C.D., often bring about preferential crystallographic orientations in the deposited materials. For boron carbide layers, this effect depends on the deposition conditions. Qualitative information has been obtained from experiments with an X-Ray texture camera /15/. The method is based on the exploitation of intensity spectra measured on negatives obtained from the intersection of diffraction cores and a cylindrical sensitive film. Boron carbide has a low adsorption coefficient, detection sensitivity was increased by using a 10° incident beam angle.

A comparison of a conventional X-Ray diffraction pattern of the " B_{50}C_2 " coating and the corresponding powder one, shows the existence of preferential orientations. However, the method described above could not be successfully carried out in this case, because the high crystallization of these coatings induces selective spacial diffractions leading to additional series of dots on the sensitive film.

In B_{13}C_2 rhomboedra, the c-axis (i.e. [111] direction) is made up of a C-B-C. chain on which the strongest atomic bonds are located. Therefore, under mechanical stresses, the influence of this crystallographic axis is predominant and, during the indentation test, its orientation, with regard to such a directional test, will affect the material behavior. The coating anisotropy will be more significant in this case if it is represented by angle (α_c) between the c-axis and the layer surface.

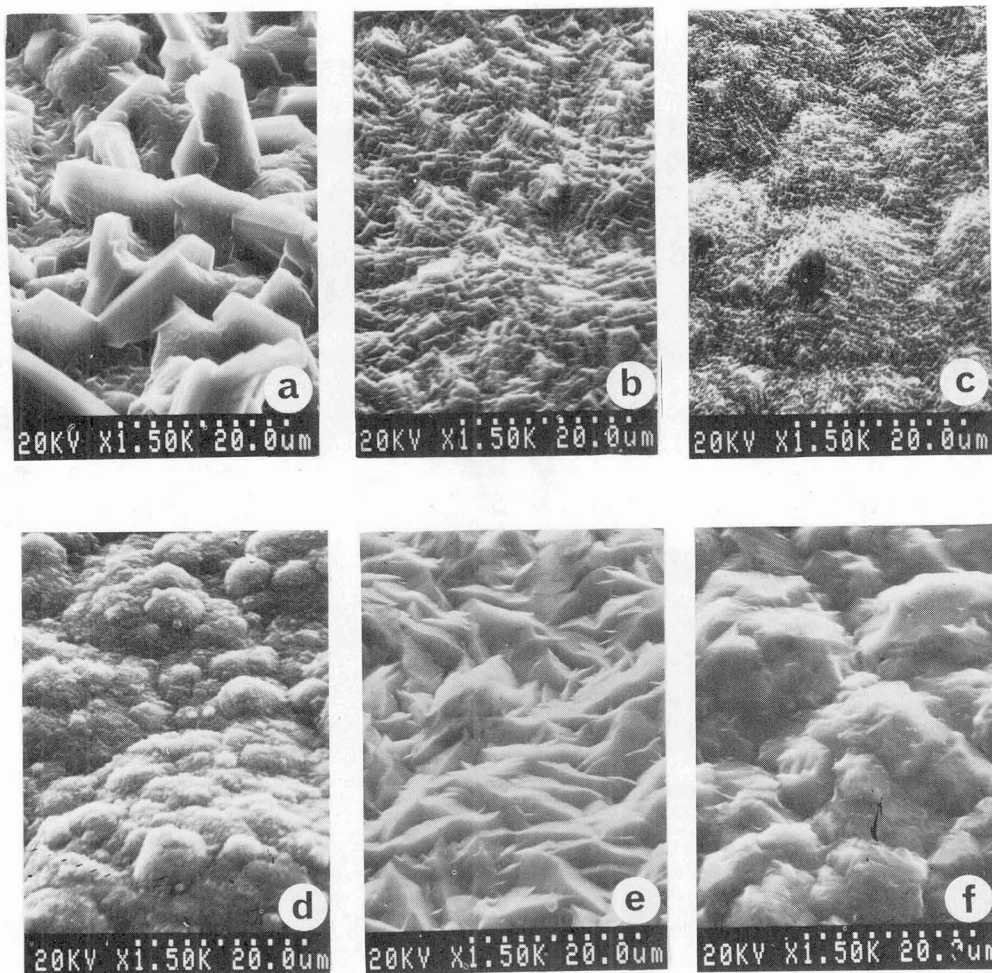


Fig. 4 : Surface morphology of coatings :

Quadratic phase : a) " $B_{50}C_2$ ",

Rhombohedral phase : b) $R = 55 - T = 1293$ K, c) $R = 60 - T = 1293$ K, d) $R = 67 - T = 1293$ K, e) $R = 50 - T = 1373$ K, f) $R = 50 - T = 1423$ K.

The results obtained with coatings in the rhomboedral area show a strong influence of the gas phase composition.

For R values equal or lower than 55 (i.e. for coating carbon content equal or lower than 13,3 at. %, $B_{13}C_2$ composition), (332) planes are oriented parallel to the layer surface because of an α_c value of 72° .

For higher R values (i.e. for the carbon rich part of the solid solution), a perpendicular orientation of the c -axis is detected. However, for the highest carbon content, the coating appears to be nearly isotropic, corresponding to the small grain size and only slight crystallization shown on a conventional X-Ray diffraction pattern.

The influence of the substrate temperature is important too. The (332) orientation ($\alpha_c = 72^\circ$) was observed for low temperatures too ($R = 50$). From 1573 K, an additional orientation according to (111) planes ($\alpha_c = 11^\circ$) appears. At 1423 K, a (211) orientation ($\alpha_c = 58^\circ$) takes the place of the (332) one. The texture of the coating deposited at 1478 K is nearly isotropic

as for the coating obtained at 1293 K with R equal to 67 which has the nearest elementary composition. The most significant patterns are shown in figure 5.

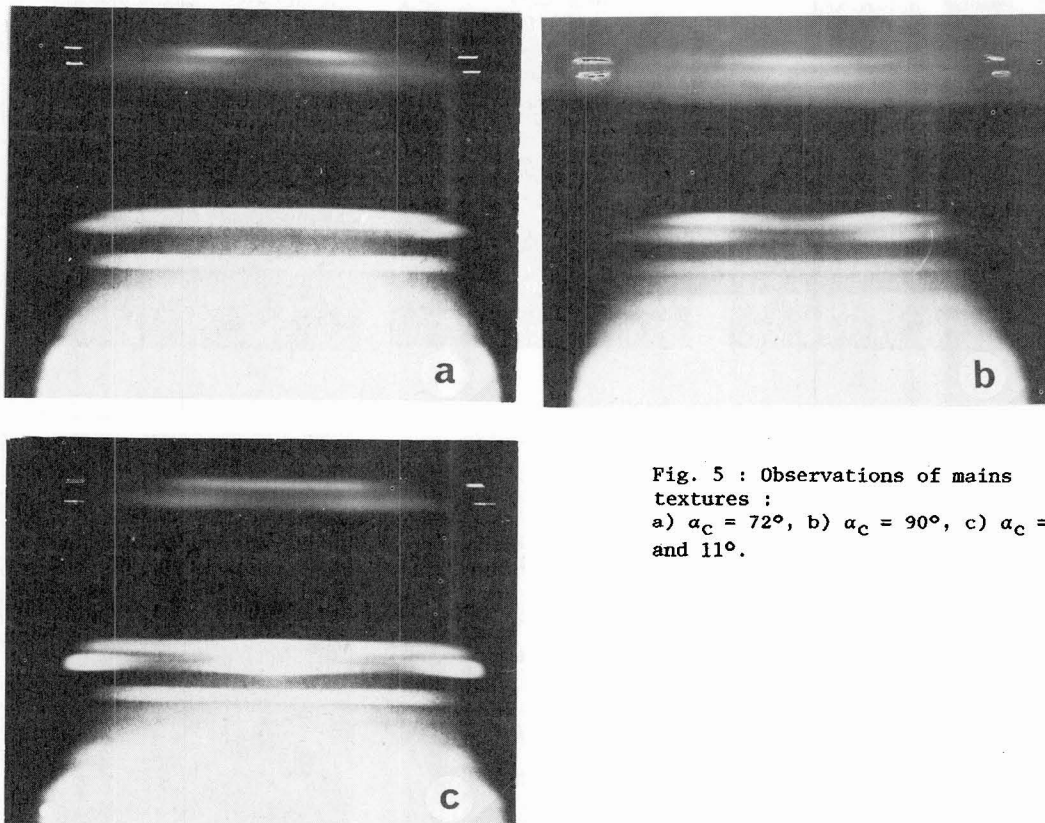


Fig. 5 : Observations of mains textures ;
 a) $\alpha_C = 72^\circ$, b) $\alpha_C = 90^\circ$, c) $\alpha_C = 58$
 and 11° .

4 - DETERMINATION OF MECHANICAL PROPERTIES BY INDENTATION

4.1. Experimental details

Vickers microhardness is measured on an automatic cycle O.P.L. tester. Five measurements are performed on each surface with 1 and 2 N loads. Before the indentation tests the surfaces are polished with diamond paste to obtain a total roughness of less than 0.25 microns. Measurements are performed at least three weeks after polishing.

The elastoplasticity index and YOUNG'S modulus are estimated from the load-depth curves using LOUBET's model /10, 11/.

Figure 6 shows the evolution of the load applied to the indenter (P) with the penetration depth (h). Interpretation of these curves is based on measurements of h_R , h_R' and h_T , respectively the residual depth of indentation, the abscissa of the point of intersection between the h-axis and the tangent to the unloading curve at point B, the maximum depth under load.

In this study, the maximum load applied was limited to 2 N to avoid crack formation which make the test unworkable. The maximum depth reached for our tests was about 2 microns for a 40 micron thick layer (thickness after polishing). In this case, the effect of the substrate nature is eliminated and the test concerns the layer alone. The penetration speed is fixed during each test at 0.1 micron per second. For our study, the indenter is supposed to be rigid.

4.2. Microhardness measurements

The effect of the carbon content of the deposit on microhardness is illustrated the figure 7. LARTIGUE's results /8/, obtained under similar conditions are also plotted on the same figure.

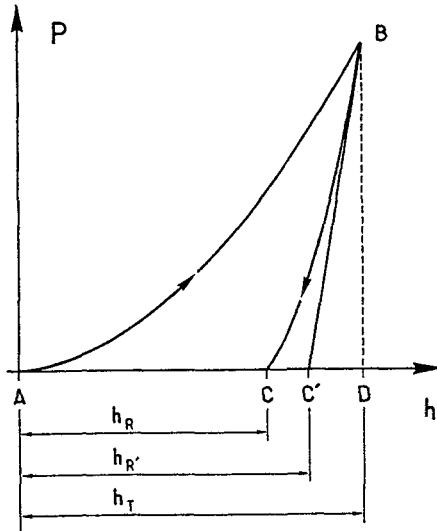


Fig. 6 : Indentation curve : load (P) versus penetration depth (h).

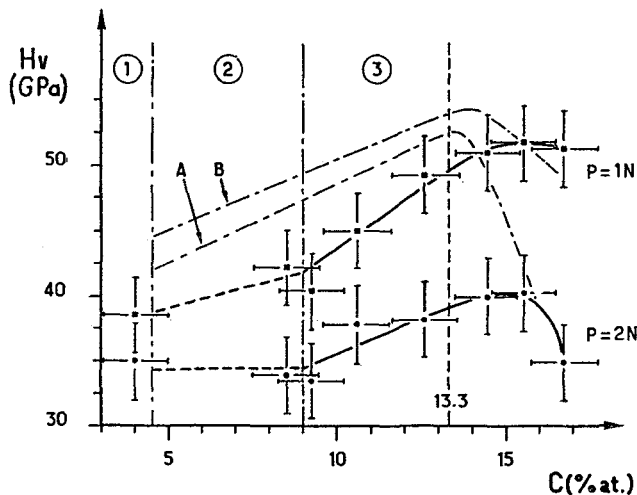


Fig. 7 : Vickers microhardness (Hv) versus the carbon concentration (C). T = 1293 K.
----- from LARTIGUE /8/
with 1 N load,
curve A : T = 1343 K,
curve B : T = 1598 K

- 1) "B₅₀C₂"
- 2) "B₅₀C₂" + "B₁₃C₂"
- 3) "B₁₃C₂"

The measured hardness first increases with the carbon concentration, as observed in the case of melted carbides by BOUCHACOURT /16/ and of layers obtained by CVD at 1800°C by MIHARA /7/. After the increase, a decrease is observed in a two phases field, (B₄C + C) for layers obtained at high temperatures and ("B₁₃C₂" + X) for our layers and LARTIGUE's. Differences in concentrations corresponding to the maximum hardness in these last two cases (fig. 7) can be explained by some differences in the processing conditions (graphite substrate for example) and by errors in the compositions. The existence of a discontinuity or an extremum for the B₁₃C₂ composition has already been observed for other properties. It is often associated to the position of carbon atoms in the rhombohedral lattice /16/. In our case, it is not observed after 13.3 at % of C but it is possible that this is taken aback by the evolution of texture (c-axis becoming perpendicular to the surface) and by the decrease in the grain size. Otherwise, the quadratic phase ("B₅₀C₂") appears to be the least hard, but similar to layers with a composition closer to the rich in boron limit of the rhomboedral solid solution.

Figure 8 shows the evolution of hardness with the deposition temperature. A minimum value is observed for 1373 K for all indentation loads used. This is due to the microstructure. The minimum value is obtained for the maximum grain size. No effect of the texture is observed.

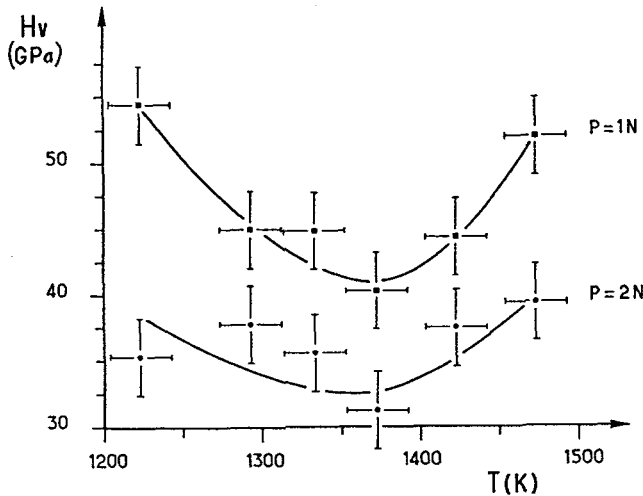


Fig. 8 : Vickers microhardness (H_v) versus the processing temperature (T). $R = 50$.

4.3. Elastoplastic behavior

This behavior is described by taking the value of the ratio between the residual depth after unloading (h_R) and the maximum depth at maximum load (h_T). Figure 9 shows the influence of the composition in the rhomboedral solid solution. The curve is in two parts separated by the $B_{13}C_2$ composition. First, independent of the composition, the index value then shows an extreme elastic behavior at the rich-in-carbon limit of the solid solution. At the other end, the " $B_{50}C_2$ " phase is the hardest. It seems to combine the effects of composition (modification of interatomic bondings) and texture, the c-axis first making an angle of 72° with the surface and then of 90° .

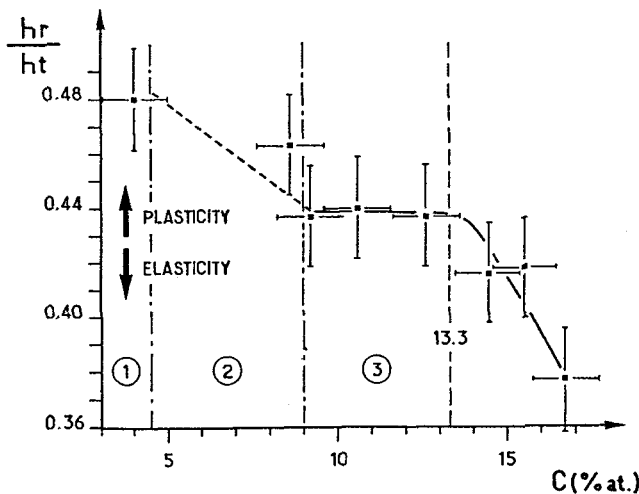


Fig. 9 : Elastoplasticity index (h_R/h_T) versus the carbon concentration (C). $T = 1293$ K.

- 1) " $B_{50}C_2$ ",
- 2) " $B_{50}C_2$ " + " $B_{13}C_2$ ",
- 3) " $B_{13}C_2$ ".

The effect of texture is clearly seen when the processing temperature changes while the composition is similar (fig. 10). The h_R/h_T ratio regularly increases with the temperature up to 1400 K. The preferential orientations are responsible for an elasticity increase at low

temperatures and for a plasticity increase at higher temperatures. This is simultaneous with the orientation of the c-axis parallel to the surface.

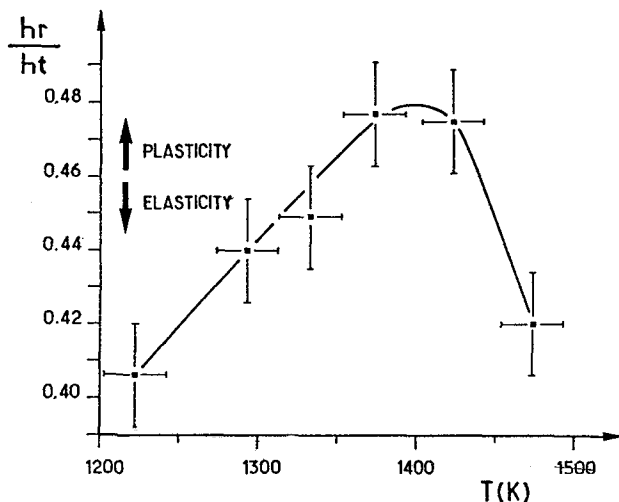


Fig. 10 : Elastoplasticity index (h_R/h_T) versus the processing temperature (T). R = 50.

For the layer prepared at 1473 K, the texture has no effect and the behavior of the rich-in-carbon solid solution already described is observed.

Elastoplasticity does not seem to be related to grain size.

4.4. YOUNG'S modulus

The YOUNG'S modulus may also be calculated from the unloading part of indentation curves /10, 11/ by the relation :

$$E = \frac{(1 - \nu^2) P_{\max} \sqrt{2\pi}}{2D (h_T - h_R)}$$

where P_{\max} is the maximum applied load,

D is the diagonal of the plastic indentation (optical measurement),

ν is the POISSON'S ratio.

For boron carbide, POISSON'S ratio is only known for massive B_4C (20 at % of C). Values obtained ranged from 0.143 to 0.188. Extrapolation of these values onto our coatings which are richer in boron is uncertain. Our calculations therefore concern the ratio $E/(1 - \nu^2)$ which is similar to E (the indenter is presumed to be rigid).

Figure 11 shows the strong influence of the composition on the elastic modulus. A maximum value of 475 GPa is obtained for the $B_{13}C_2$ stoichiometry. On both sides of this maximum, the value decreases by 25 %. The modulus of " $B_{50}C_2$ " (410 GPa) is slightly higher than that of " $B_{13}C_2$ ".

The calculation of YOUNG'S modulus is made from the beginning of the unloading curve during the elastic recovery of the indentation as shown on monocrystal /10/. It is normal that therefore the effects of texture and microstructure are not visible and that the major variation is due to composition changes and so to interatomic bonding in the solid solution.

The decrease in E obtained by BEAUVY /17/ for two rich in carbon compounds is thus confirmed by our results.

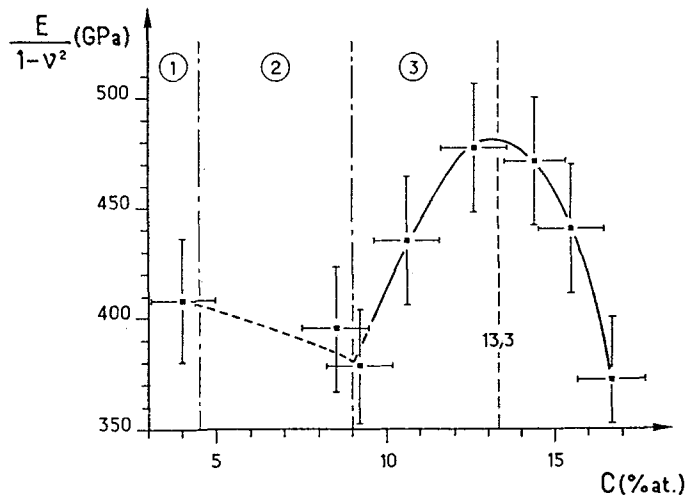


Fig. 11 : Variation of $E / (1 - \nu^2)$ ratio versus the carbon concentration (C).
T = 1293 K.

- 1) " $B_{50}C_2$ ",
- 2) " $B_{50}C_2$ " + " $B_{13}C_2$ ",
- 3) " $B_{13}C_2$ ".

However, the value obtained for the $B_{13}C_2$ stoichiometry (475 GPa) could be a maximum limit for these compounds, the non porous massive materials having a modulus, depending on authors, between 250 and 450 GPa.

The scatter observed for different processing temperatures (fig. 12) do not allow an exact curve to be plotted. The modulus increase between 1223 and 1423 K probably corresponds to the composition change observed (fig. 2) as the modulus is sensitive to this parameter. The value obtained at 1473 K, close to values for other temperatures with a much higher carbon concentration, agrees with the symmetry of curve figure 11.

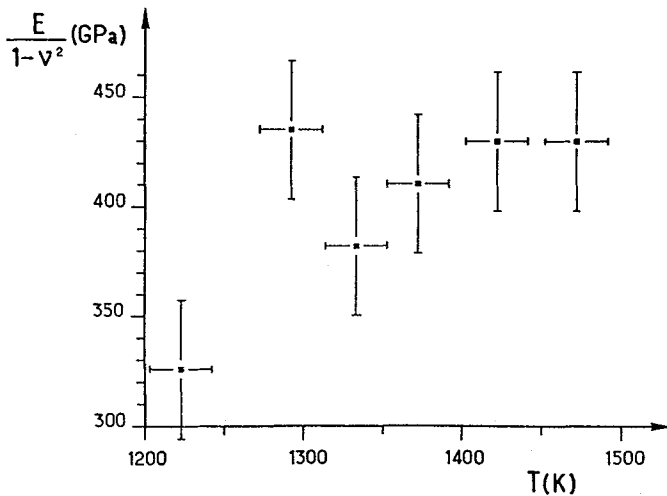


Fig. 12 : Variation of $E / (1 - \nu^2)$ ratio versus the processing temperature (T). R = 50.

5 - CONCLUSION

By using indentation technology the elastic behavior of carbides richer in boron than B_4C , classically characterized, can be investigated. The " $B_{50}C_2$ " compound was tested.

Coatings prepared by L.P.C.V.D. exhibit mechanical properties strongly related to their chemical, crystallographic and microstructural characteristics which are dependent on processing conditions more specially the gas mixture composition and the substrate temperature.

Hardness is more influenced by the grain size, while elastoplastic behavior is more related to the presence of preferential crystallographic directions. The composition of the solid solution and so interatomic bondings are important for both characteristics. YOUNG'S modulus changes can only be related to composition. This effect is similar to the effect observed on properties directly related to the electronic state of boron and carbon /16/. This characterization leads to the evaluation of an apparent elastic modulus which is probably inferior to the real one if we consider correction by ratio $1/(1 - \nu^2)$, and that the indenter is presumed to be rigid. The error then induced is difficult to estimate because of the lack of data from other techniques on the same materials.

The particular behavior of stoichiometric $B_{13}C_2$ (13.3 at % C) is pointed out, as already mentioned by BOUCHACOURT /16/. This seems to confirm the hypothesis that two mechanisms exist for the formation of the rhombohedral solid solutions on both sides of this composition.

Over and above their great hardness, well known for this material, the boron carbide coatings are also very rigid. They are therefore in an extreme position in the ceramic materials family /18/. Such characteristics are probably responsible for their good wear resistance in dry and abrasive conditions /9/.

The processing technology used give carbide coatings with characteristics which are of interest for protection in classical situations. This technology is also flexible enough to be adapted to other non-classical problems.

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