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STRUCTURE AND PROPERTIES MODIFICATIONS IN BORON NITRIDE. PART II: HARDNESS MODIFICATION INDUCED BY THE POLYMORPHIC TRANSFORMATIONS

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Caracteristicile structurale ale varietăţilor polimorfe ale nitrurii de bor examinate în Partea I a lucrării sunt folosite în Partea II pentru a calcula duritatea teoretică ce se modifică dramatic când nitrura de bor hibridizată sp^2 se transformă în nitrură de bor hibridizată sp^3. In calculul durităţii teoretice au fost luate în considerare pe lângă varietăţile polimorfe masive de nitrură de bor şi varietăţile moderne nanostructurate, în speţă nanotuburile de BN multi-strat pentru care distanţa interstrat a fost considerată ca având acelaşi rol structural ca şi distanţa interplane din grafit. S-a obţinut o foarte bună concordanţă între durităţile experimentale raportate pentru BN şi cele calculate din date cristalochimice. Un calcul pas cu pas al durităţii teoretice a permis să se discearnă care sunt factorii de control atât pentru duritatea produsă de acţiunea legăturilor covalente cât şi pentru duritatea produsă de forţele de legătură van der Waals în varietăţile polimorfe de BN hibridizate sp^2 . S-a demonstrat pe această cale că acţiunea forţelor covalente produce o duritate mai mare în varietăţile polimorfe de BN hibridizate sp^3 spre exemplu în cBN decât în cele hibridizate sp^2 spre exemplu în nanotuburile de nitrură de bor, raportul durităţilor Mohs teoretice fiind 1,2 iar al celor Vickers 1,76. Explicaţia acestui fapt a fost găsită în prevalenţa creşterii numărului de legături covalente faţă de efectul exercitat asupra durităţii de creşterea lungimii acestor legături în structurile hibridizate sp^3 .

The structural features of boron nitride polymorphs examined in Part I of this paper are used in Part II for calculating the theoretical hardness that changes dramatically when the sp^2 bonded BN polymorphs transform into sp^3 bonded BN polymorphs.. The modern BN nanotubes were also considered in this hardness calculation by taking into account multi-wall nanotubes for which the interwall spacing was considered to play the same structural role as the interlayer spacing in graphite. A good agreement was obtained between the experimentally reported hardness for BN and the theoretical hardness calculated from the crystallochemical features for each BN polymorph. A step by step calculation of the theoretical hardness has permitted to disclose the control factors for the hardness promoted by the covalent bonds as well as for the hardness promoted by the van der Waals bond in sp^2 hybridized BN polymorphs. The action of the covalent bonds was proved to promote a higher hardness in sp^3 BN polymorphs such as cBN than in sp^2 BN polymorphs such as BN nanotubes (theoretical hardness ratio =1.2 on Mohs scale and 1.76 on Vickers scale). An explanation was given based on the prevalence of the role played by the increase of the number of covalent bonds over the role played by the increase of the bond length in the sp^3 structures.

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1. Introduction

The main boron nitride polymorphs have an extremely different hardness on which their application is based, namely 1.65 Mohs hardeness for hBN and 37000 up to 40000 MPa (depending on the grain size) for the Vickers hardness of cBN as reported by Novikov et al. [1]. If the Mohs scratch hardness for hBN (white graphite) is converted into Vickers penetration hardness one obtains a value equal to 131 MPa, that is about 300 times lower than the penetration hardness of cBN (borazone).

This huge discrepancy between the hBN and cBN hardness is of course to be ascribed to the crystallochemical differences previously specified in Part I of this paper. A quantitative examination of the influence exerted on hardness by each of the factors that define the specific structure of various BN polymorphs has been undertaken in what follows by calculating a theoretical hardness.

2. Theoretical considerations for calculating the hardness modification in BN polymorphic transformations

To this purpose a relationship proposed by Povarennykh [2] for calculating the theoretical Mohs hardness for minerals was adopted (eq.1). We have preferred this relationship instead of the largely used semi-empirical relationship (eq. 2) proposed in [3] for calculating the bulk elastic modulus B_o at zero Kelvin for carbon solids. Indeed, if one considers both properties,- hardness and elastic modulus,- as a reflection of the interatomic forces acting in a specific crystallochemical structure, a more pronounced detailedness of the involved factors is desirable, and this is the case for eq.(1).

$$H_M = K.w.\beta.\alpha.\gamma / d^2 \quad (1)$$

$$B_o=(Nc/4)(1972-220)\lambda d^{-3.5} \quad (2)$$

Indeed by letting aside factor d (= the interatomic spacing) that is common to both equations, one sees that eq (2) involves two crystallochemical factors (N_c = the coordination number and λ = an empirical ionicity factor), whilst eq.(1) involves five crystallochemical factors whose significance will be given together with the results on hardness calculation.

Because the penetration hardness is the modern way to measure this property of materials, in what follows we have transformed the Mohs calculated theoretical hardness H_M obtained by applying eq.(1) into Vickers penetration hardness H_V.

The conversion relationship between H_M and H_V we have applied in our calculations is defined by eq. (3) proposed by Kruschow [4]. It correlates with very good results the hardness of minerals up to corundum (H_M =9) as illustrated in Table 2 reproduced from [5].

$$H_M = 0.7 (H_V)^{1/3} \quad \text{or} \quad H_V = 2.91545 (H_M)^3 \quad (3)$$

(where H_V is expressed in kgf/mm^2 or in daN/mm^2 ; the values obtained for H_V in daN/mm^2 may be further converted into MPa by multiplication by 10).

Table 1

Calculated Mohs hardness according to Kruschow conversion relationship for the ten standard minerals

H_M	Talc	Gypsum	Calcite	Fluorite	Apatite	Orthoclase	Quartz	Topaz	Corundum	Diamond
Mohs scale	1	2	3	4	5	6	7	8	9	10
Calculated from H_V	0.9	2.3	3.3	4.0	5.7	6.5	7.3	7.9	8.9	15.1

A remarkable feature revealed in Table 1 is the fact that the Mohs hardness calculated for diamond from experimental penetration hardness data is 15 and not 10 as originally ascribed by Mohs. For the purpose of this paper this fact is of special significance because the upper range of the new Mohs scale comprises the synthetic superabrasives including boron nitride.

3. Selection of the factors involved in hardness calculation for BN

The values of the factors involved in eq. (1) for calculating the theoretical hardness have been selected according to the crystallochemical features previously specified for the BN polymorphs in Part I of this paper. To make clear the way of selection, the significance of each factor is briefly outlined in what follows as indicated in [6]:

- factor K reflects the effect exerted on hardness by the intensity of the strong atomic bonds. It depends on the share of participation of the covalent bond (%cov.) which at its turn depends on the difference in electronegativity E between the constitutive atomic species in the compound, and also on the state of hybridization of the atomic orbitals.
- factor β expresses the weakening of the atomic bond due to the negative electrical charge of the valence electrons non-participating to the chemical bond. It is equal to 1 except for the case when transition metals exist in the composition of the compound..
- factor w is the product of the valences involved in the strong atomic bond.
- factor α takes into account the effect of the repulsion interatomic forces. It is strongly dependent on the ratio of the valences w_{cat} / w_{an} .
- factor γ reflects the increase in hardness when the compressibility of the crystal decreases. It increases when the coordination number z in the crystal lattice increases
- factor d represents the interatomic spacing (in A^o) in the direction of the chemical bond. It decreases when the bond energy increases.

For factors K, α and γ whose derivation is not straightforward we have indicated in Table 2 the steps to be taken. For deriving factor K we have specified in

Table 2 only the electronegativity E (in kcal/ g.at.) of the elements in the second period (including boron and nitrogen) which are of interest for this paper. The electronegativity E was considered according to the definition of Pauling [7].

Table 2

Steps in the derivation of factors K, α and γ in eq. (1)

3 a. Derivation of factor K

Element	Li	Be	B	C	N	O	F
E, Kcal/g.at	125	210	290	370	450	530	605
ΔE, Kcal/g.at	550	180	170	160	150	140	0
% cov.	0	75.0	77.5	80.0	82.0	84.0	100

K (for % cov. =0)	1	1	1	1	1	1	1	1
K (for %cov. = 100)	1.000 s	1.732 p^3	1.932 sp	1.991 sp^2	2.000 sp^3	2.694 dsp^2	2.923 d^2sp^3	2.983 d^4sp
K (for 0<%cov.< 100)	values obtained by linear interpolation							

3 b. Derivation of factor α

Valency ratio w_{cat} / w_{an}	1/1	2/2	3/3	4/4	5/5	6/6	2/1	3/1	3/2	4/2	5/2	6/2
factor α	13.60	4.82	2.65	1.72	1.25	0.94	8.00	5.75	3.90	2.25	1.40	1.00

3 c. Derivation of factor γ

z	3	4	5*	6	7*	8	9*	10*	12
factor γ	0.46	0.65	0.83*	1.00	1.16*	1.30	1.35*	1.38*	1.42

* interpolated values

4. Special case for hardness calculation: the boron nitride nanotubes

A special configuration for the sp^2 bonded boron nitride may result when a nanometric sized hexagonal layer is folded to make up a cylindrical nano-body or a nanotube. Such BN nanotubes have been theoretically predicted [8-10] and experimentally observed [11] to have interesting mechanical and electrical properties. They have been documented to have superior properties than carbon nanotubes at least in some respects: higher resistance to oxidation in air up to 900^o C, better thermal conductivity and especially stable electronic properties. Indeed BN nanotubes are wide gap semiconductors (band gap ~ 5.5 eV) whose electronic properties are independent of tube diameter and number of layers (for multi-wall BN nanotubes). As depicted in Fig. 1, depending on the synthesis conditions the nanotubes may be either single-wall consisting of a single grapheme layer, or multi-wall consisting of several (up to ~40) graphene layers. Each type organizes itself during the synthesis in a self-assemblage as depicted in Fig. 1. Single wall nanotubes assemble themselves in compact bundles, whilst multi-wall nanotubes insert one in another like Russian dolls.

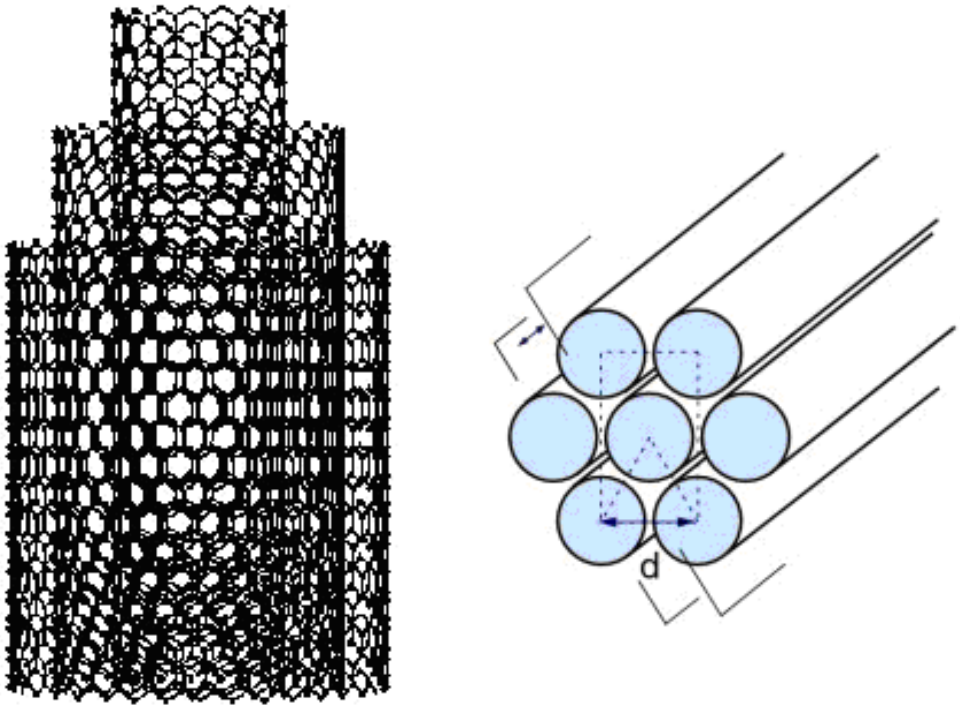

Fig.1. Self-assemblages of nanotubes
a. multi-wall nanotubes inserted one in another
b. single-wall nanotubes compacted in bundles

What matters for the purpose of this paper is the tight packing of the nanotubes. Indeed the spacing between two adjacent nanotubes is almost equal to the spacing between the hexagonal layers in graphite or hBN (white graphite). It means that the nature of the chemical bonds in a self-assemblage of nanotubes remains the same as it was in bulk graphite or in bulk hBN. So by including the BN nanotubes in our calculations of the theoretical hardness we'll have to consider two types of chemical bonds, namely the covalent bond in the curved surface of the nanotube and the van der Waals bond acting between the nanotubes assembled in bundles or in multi-wall edifices. The length of each type of bond is reflected in a separate value of the interatomic spacing d that we have to introduce in eq.(1) for calculating the theoretical hardness.

On account of possessing two types of bonding the nanotubes are expected to behave as anisotropic bodies. This anisotropy is expected to be exhibited by the nanotubes because unlike the bulk substance (graphite or hBN) the nanotubes have an extremely high aspect ratio, their length being of the order of tens of microns whilst their diameter is of nanometric size..

5. Results

The values we have obtained for the theoretical hardness in BN polymorphs by means of eq. (1) are given in Table 3. In presenting the results we have taken a two steps approach. In the first step we have calculated the product K.β.w.α.γ and in the second step we have calculated the final value of the hardness by taking into account the influence of the length of the interatomic bond *d*. In this way it was possible to have a clearer distinction between the influences exerted on hardness by the various crystallochemical factors.

Concerning the value of *d* a new type of distinction was made in Table 3. For each sp^3 hybridized BN polymorph we have calculated a single hardness value by taking into account the length *d* of the covalent bond. For the sp^2 hybridized BN polymorphs in which two types of bonding exist we have calculated two hardness values, one of them taking into account the length *d* of the intralayer covalent bond, and the second one obtained by taking into account the length d_{002} of the interlayer van der Waals bond. The values for *d* expressing the length of the covalent bond in Table 3 have been taken from Table 1 in Part I of this paper.

The interlayer spacing d_{002} for the usual sp^2 bonded BN polymers (hBN, turbostratic BN, pyrolitic BN) are indicated in Table 3 by specifying the reference source for each of them. For BN nanotubes a very careful research performed on multi-wall BN nanotubes by Demczyk et al.[12] has indicated the value d_{002} being dependent on the number of tubes in the multi-wall assemblage. In Table 3 we have used the d_{002} values indicated in [13] for two-wall and for four-wall nanotubes, respectively. The reason for this dependence was ascribed in [12] to the need to maintain a low energy packing sequence for defect-free multi-wall nanotubes

Table 3

Results on the calculated theoretical hardness of BN polymorphs, expressed in H_M (Mohs scratch scale) and in H_V (Vickers penetration hardness in MPa)

a. isotropic hardness in sp^3 polymorphs produced by the covalent bonds

BN polymorph	% cov.	hybri-disation	K	β	w	α / w_{cat}/w_{an}	γ / z	K·β·w·α·γ	d, A° / $1/d^2$	H_M	H_V (MPa)
cBN stable	80	sp^3	1.8	1	3x3	2.65 / 3/3	0.65 / 4	27.9045	1.567 / 0.4072	**11.36**	**42,740**
wBN metastable	80	sp^3	1.8	1	3x3	2.65 / 3/3	0.65 / 4	27.9045	1.576 / 0.4026	**11.235**	**41,345**

b. anisotropic hardness in sp^2 polymorphs produced by the intralayer covalent bonds

BN polymorph	% cov.	hybri-disation	K	β	w	α / w_{cat}/w_{an}	γ / z	K·β·w·α·γ	d, A° / $1/d^2$	H_M	H_V (MPa)
hBN turbostratic pyrolitic nanotubes	80	sp^2	1.7928	1	3x3	2.65 / 3/3	0.46 / 3	19.6688	1.4457 / 0.4784	**9.41**	**24,293**

c. anisotropic hardness in sp^2 polymorphs produced by the intralayer van der Waals bonds

Polymorph	$K\cdot\beta\cdot w\cdot\alpha\cdot\gamma$	d_{002}, A°	reference	$1/d^2$	H_M	H_V (MPa)
hBN	19.6688	3.3306	[13]	0.0901	**1.770**	**162.0**
turbostratic	19.6688	3.4640	[14]	0.0833	**1.640**	**129.0**
Pyrolitic	19.6688	3.3972	[14]	0.0866	**1.700**	**143.0**
two-wall nanotubes	19.6688	3.7000	[12]	0.0730	**1.436**	**86.3**
two-wall nanotubes	19.6688	3.4000	[12]	0.0865	**1.701**	**143.0**

6. Discussion

The calculations in Table 3 permit to disclose the influence exerted on hardness by the different crystallochemical factors that characterize the structure of various BN polymorphs and also to have a quantitative insight in the hardness modification promoted by the polymorphic transformations in BN.

As seen in Table 3 for the sp^3 polymorphs a single set of hardness values has been calculated, namely the one promoted by the covalent bonds acting in the structure. For the sp^2 polymorphs two sets of hardness values have been calculated, one set promoted by the covalent bonds acting within the layers and the second set promoted by the weak van der Waals bonds acting between the layers. One expects the hardness promoted by the covalent bonds acting within the layers to manifest itself only if the sp^2 bonded product is highly anisotropic in such a way that the strong covalent bonds are put at work. This is the case for pyrolitic BN and even more important for BN nanotubes. For the remaining sp^2 bonded BN products such as polycrystalline hBN or turbostratic hBN one expects the hardness to be controlled by the weakest link, namely by the van der Waals bonding.

In this view we'll discus our results under two headings: (i) theoretical hardness promoted by the covalent bonds, and (ii) theoretical hardness promoted by the van der Waals bonds.

I. Concerning the theoretical hardness promoted by the covalent bonds

In a first instance we'll let aside the influence exerted on hardness by the interatomic spacing d in eq.(1), and we'll consider the influence of the five remaining crystallochemical factors ($K, w, \beta, \alpha,\gamma$) in eq. (1). In so doing a very interesting fact becomes obvious in Table 3 when one calculates the ($K. w. \beta. \alpha.\gamma$) product. The covalent bonds in sp^3 polymorphs (cBN and wBN) would result in a higher hardness than the hardness promoted by the covalent bonds in sp^2 polymorphs, such as hBN. Indeed the ratio of the ($K. w. \beta. \alpha.\gamma$) product in the above mentioned structures is 27.9045 / 19.6688 = 1.4187. As seen in Table 3 two factors contribute to this result, namely factor K and factor γ. The largest contribution is due to factor γ that decreases from 0.65 to 0.46 when the coordination number z drops from 4 (in sp^3 BN polymorphs) to 3 (in sp^2 BN polymorphs).

Also seen in Table 3 is the fact that this situation cannot be reversed even when the last crystallochemical factor *d* is taken into account. The discrepancy is attenuated but not eliminated. Indeed when the length of the covalent bond *d* in cBN, respectively in hBN is introduced in the total product ($K. w. \beta. \alpha.\gamma. 1/ d^2$) one obtains a ratio of the theoretical Mohs hardness H_M equal to 11.36 / 9.41 = 1.2072, and a ratio of the theoretical Vickers hardness H_V equal to 42740/ 24293 = 1.7593 This attenuation of the discrepancy is to be ascribed to the higher intralayer bond energy for sp^2 hybridized BN polymorphs (3.25 eV in Table 1 and consequently a shorter bond length as compared with the covalent bond energy in sp^3 BN polymorphs (1.52 eV in Table 1 of Part I of this paper).

What matters for the purpose of this paper is the fact that by taking into account all the six crystallochemical factors in eq. (1) the calculations in Table 3 show that during the polymorphic transformation hBN (sp^2) → cBN (sp^3) the hardness is modified on account of two main factors in the covalent bond : (i) the length of the bond increases (reflecting a decrease in the bond energy and this tends to diminish the hardness; (ii) the number of covalent bonds increases from 3 to 4 and this tends to increase the hardness. Our calculations in Table 3 show that increasing the number of covalent bonds during the (sp^2) → (sp^3) transformation has a stronger influence to increase the hardness promoted by the covalent bond as compared to the opposite action exerted by the decrease of the bond energy (reflected in a longer length of the bond) that tends to decrease the hardness.

The net result put in evidence by our calculations in Table 3 is a theoretical hardness promoted by the covalent bond that is necessarily higher in sp^3 bonded BN polymorphs than in sp^2 bonded BN polymorphs. The latter type of hardness manifests itself (as we have stated before) only in highly anisotropic sp^2 bonded BN polymorphs (pyrolitic BN or more impressively in BN nanotubes), when the products are stressed in such a way that the covalent bonds are put at work.

II. Concerning the theoretical hardness promoted by the van der Waals interlayer bonds

When the interlayer spacing d_{002} was introduced in eq.(1) far smaller values for the hardness H_M were obtained in Table 3 for the sp^2 hybridized BN polymorphs; these values were located at the bottom level of the Mohs hardness scale (see Table 1). These results are quite expectable if the interlayer spacing d_{002} is considered to reflect the far lower energy of the van der Waals bond in BN (0.052 eV in Table 1 of Part I of this paper). Slight variations for H_M have been obtained in Table 3 when the degree of order in the stacking sequence of the hexagonal layers was taken into consideration, as reflected by the variations in the interlayer spacing d_{002}. Indeed increasing the disorder in the turbostratic BN structure has resulted in a slightly lower value for H_M in Table 3. On the other side for well compacted multi-wall BN nanotubes an increase in the hardness promoted by the inter-wall van der Waals bonding was obtained in Table 3.

III. To conclude, one may say that the theoretical hardness values calculated in Table 3 are in very good agreement with the experimental hardness values reported

for hBN and cBN (mentioned in the Introduction of this paper). This is a proof that ec. (1) originally established for natural minerals [2] may be applied with good results for synthetic ceramic compounds such as BN. A remark is however necessary. The factors involved in eq. (1) that allow the calculation of a theoretical hardness are concerned only with the finest levels of the structure of a compound (interatomic forces, crystal lattice). Other factors that characterize the structure at a less fine level (grain size, grain orientation,) which are documented to have an influence on hardness are not considered in eq. (1).

But it is just this fact that matters for the purpose of this paper. Indeed only fine structure factors are involved both in the characterization of the theoretical hardness and in the specification of the mechanisms of the polymorphic transformations of BN. As a consequence eq. (1) proved to be a useful tool to account for the hardness modification of BN during its polymorphic transformation, as demonstrated in this paper.

7. Conclusions

1. A connection has been established between the factors involved in the structure characterization at fine levels (interatomic forces, crystal lattice) of various boron nitride polymorphs and the hardness modification during the polymorphic transformations of BN.

2. The theoretical hardness calculated by means of a relationship involving fine level crystallochemical factors has permitted to make a distinction between the hardness promoted by the van der Waals interlayer bonds manifested in usual sp^2 hybridized BN polymorphs (hBN, turbostratic BN) and the hardness promoted by the covalent bonds in highly anisotropic sp^2 modern BN polymorphs (multi-wall BN nanotubes)

3. A difference was noticed, expressed by a theoretical hardness ratio equal to 1.2 (on the Mohs scale) and equal to 1.76 (on the Vickers scale) when the covalent bond was acting in sp^3 hybridized BN polymorphs (such as cBN) or it was acting in highly anisotropic sp^2 hybridized BN polymorphs (such as multi-wall BN nanotubes).

4. A step by step calculation of the theoretical hardness has permitted to ascribe this difference to the change in the number of covalent bonds (from 4 to 3), this factor prevailing on the change in the bond energy (from 1,52 eV to 3.25 eV).

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