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CBN-metal/metal nitride composites

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Abstract

Theoretical and experimental studies of cubic BN mixed with various metals and metal nitrides in the molar ratio 1:1 and 2:1 are reported. Theoretical calculations show that all investigated phases react with cubic BN forming new phases at 1400 and 1627°C. Experimental cBN-phase composites were prepared by high pressure hot pressing. Additionally, studies of the phase composition, morphology as well as of the mechanical properties of the superhard materials obtained have been carried out. Of all materials studied, composites containing a titanium binding phase show the best mechanical properties.

Keywords: cBN

1. Introduction

Boron nitride is a chemical compound that can exist in two forms; cubic and hexagonal. The hexagonal form is widely applied for fabrication of refractory materials whereas the cubic form is used to produce composite materials. Owing to their unique physico-mechanical properties these materials are frequently applied in machine engineering as cutting blades that are especially useful for processing of quenched steel and cast iron.

As a binding phase of these composites, metals (VI-VI groups of the periodic table) or their compounds are most frequently used [1–3]. Chemical reactions between the activators and boron nitride occur, resulting in the formation of some new phases. The prediction of the final products of the reactions taking place during sintering as well as the elucidation of its mechanism is of crucial importance in the selection of the appropriate binding phase.

Titanium, chromium, tantalum and their compounds are most commonly used as binders in sintering technology [2–10].

2. Thermochemical analysis of the phenomena taking place in the BN-phase system

For the calculations of the equilibria compositions of the BN-phase systems the VCS algorithm has been used [11]. This algorithm belongs to a group of so-called stoichiometric algorithms, where stoichiometric coefficients of chemical reactions via which the system reaches the equilibrium state are taken into account. The algorithm requires that its user merely lists chemical compounds that can co-exist in the equilibrium state together with their standard thermochemical potentials of formation. The knowledge of the number and types of independent reactions is not necessary for the calculations.

The algorithm is based on minimization of the thermodynamical potential of the whole reacting mixture [Eq. (1)]; this potential is expressed by reaction-extent variables related to the number of moles by Eq. (2).

$$g = \sum_{i=1}^{N} n_i \cdot \mu_i = (\min) \tag{1}$$

g - thermodynamical potential of the whole reacting system,
n_i - number of moles of the i-component,

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μ_i - chemical potential of the *i*-component,
N - number of components.

$$n_i = n_i^0 + \sum_j^R \gamma_{ij} \cdot \xi_j \quad i = 1, 2, \ldots N' \tag{2}$$

n_i^o - starting number of moles of the *i*-component,
γ_{ij} - stoichiometric coefficient of the *i*-component in *j*-reaction,
ξ_j - reaction-extent variable of *j*-reaction,
R - number of independent reactions
N' - number of components minus the inert ones ($N' < N$)

Thus in the VCS algorithm the non-linear function of many variables g is minimized:

$$g = \min$$

where x- is a vector of many variables.

The equilibria compositions in the following systems have been calculated: BN–Ti, BN–Zr, BN–Hf, BN–CrN, BN–Ta, BN–Nb, BN–Cr, BN–Mo, BN–Al, BN–TiH_2, BN–TiN for the molar ratios BN : metal equal to 1:1, 1:2 in a wide range of pressure ($1.3 \cdot 10^{-3}$–$1 \cdot 10^8$ Pa) and temperature (27–2427°C). The data needed for the calculations (e.g. Standard thermodynamical potentials of formation) have been taken from the appropriate tables [11,12]. It has been found from the calculations that all the phases mentioned above react with boron nitride forming new phases. Metals from IV and V groups, Al and TiH_2 react with BN in wide temperature and pressure ranges forming either one phase (metal boride) or two two-component phases: metals boride and nitride. Metals from the VI group of the periodic table form only one new phase -metal boride. The type and number of new phases formed depends on pressure and temperature.

According to the calculations of chemical equilibria in the BN–TiN systems, TiN reacts with boron nitride in a very wide range of temperature and pressure. One new phase is formed, namely titanium boride , whose content strictly depends on the parameters of the process. Typical diagrams of chemical equilibria in the BN–TiH_2 and BN–TiN systems at 1400°C are shown in Figs. 1 and 2.

3. Identification of the phases formed after sintering of cubic boron nitride (cBN) with the additions of metals and nitrides

In order to verify experimentally the results of theoretical calculations model studies have been carried out. In these studies BN–Ti, BN–Zr, BN–Hf, BN–CrN, BN–Ta, BN–Nb, BN–Cr, BN–Mo, BN–Al, BN–TiH_2, BN–TiN compounds[1] of 3–5 μm grain size were mixed with the cBN powders[2] (3–5 μm grain size) in the molar ratio 1:1 and 2:1. The mixtures were than sintered in the pressure range of $1.3 \cdot 10^{-3}$–$1 \cdot 10^7$Pa at 1400 and 1627°C for 2 h. For high pressure sintering of pre-pressed pellets, a PH0044 press equipped with a Bridgman cavity chamber (15 mm diameter) was used.

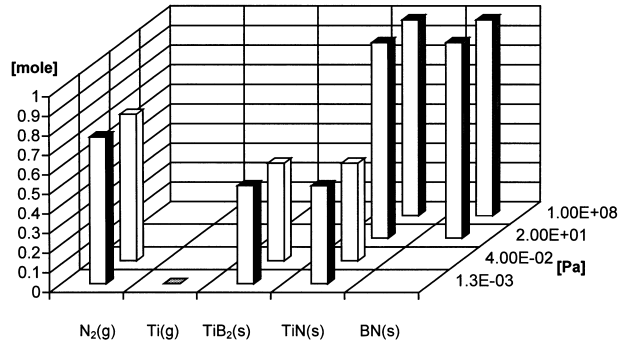

Fig. 1. Calculated equilibrium compositions for 1:1 molar BN:TiH_2 mixture at 1400°C.

X-ray diffraction studies have been carried out using a Philips 1710 diffractometer. X-ray diffraction pattern identifications were done using a APD-3.5B computer program based on the selected diffraction Data-JCPDS. Filtered CuKα, CoK_α, NiK_α, and FeK_α radiation were used in the studies.

The results of X-ray diffraction studies indicate good agreement of the experimental data with the calculated equilibrium compositions for both molar ratios studied.

Fig. 3 shows a comparison between calculations and experiments for the BN–TiH_2 system.

4. TEM studies of cBN sintered with metals, and metal nitrides

Phase distribution in the sintered materials was studied by transmission electron microscopy. Sinters in which the BN:phase molar ratio was equal to 1:1 and 9:1 were prepared at $T = 1750$°C under $p = 7.0$ GPa for 3 min. After high pressure sintering the samples were additionally thermally treated at various temperatures in vacuum ($p = 3 \cdot 10^{-3}$ Pa).

Observations of microstructure of cBN sintered with metals were carried out using a Philips CM20 TWIN (200 kV) transmission electron microscope. Thin films of the samples were obtained using a Gatan 600 Duo-Mill ion drill.

The BN–TiH_2 sample was thermally treated at 900°C for 1 h. TEM observations have shown that the sinters exhibit a compact structure and the binder is evenly

[1] Supplied by de Beers, Germany.
[2] Supplied by MS Stark, Germany.

distributed in its whole volume. The BN grains which constitute the matrix are ca. 2 μm in size and within them single, loose grains of 0.5–2 μm occur. Electron diffraction studies have shown that in both cases these are grains of cBN. This has been also corroborated by microanalysis studies. Inside the BN grains one can observe a great number of twins and dislocations, which give a characteristic contrast in the form of a system of parallel strips and microtwins. In this material, polycrystalline areas adjacent to the BN grains have been also observed whose size is of several microns. The distance between them is more than ten microns. At higher magnification one can see that the polycrystalline areas are formed by grains free from defects ca. 0.5–2 μm in size, which in smaller parts are formed by casually oriented grains ca. 0.1 μm in size. Electron diffraction from these areas has shown that these grains are of TiN. Application of the diffraction contrast has made it possible to establish that at the interface with the BN grains there exists a layer of columnar grains of 0.1–0.2 μm in diameter and ca. 0.5 μm in length (Fig. 4) or — more rarely — a layer of equiaxial grains of comparable size.

Electron diffraction from these layers show that this is a TiB_2 hexagonal structure. The layer of polycrystalline TiN grains adheres directly to these grains.

In the sample after thermal treatment fine-crystallites have been observed close to the BN surface. Polycrystals of TiN have been identified. At the interfaces one can observe the formation of thin layers of columnar grains and similar crystallographic orientation (Fig. 5). Microanalysis studies have shown that this layer is formed mainly by titanium boride.

5. Mechanical properties of BN-phase alloys

Studies of the BN-phase composites prepared via high-pressure and high-temperature sintering have been focused on the following measurements:

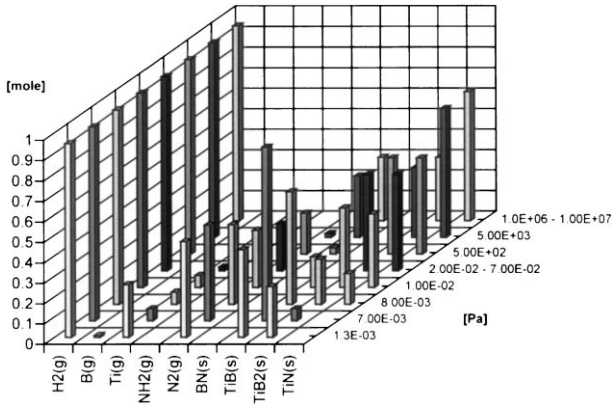

Fig. 2. Calculated equilibrium compositions for 1:1 molar BN:TiN mixture at 1400°C.

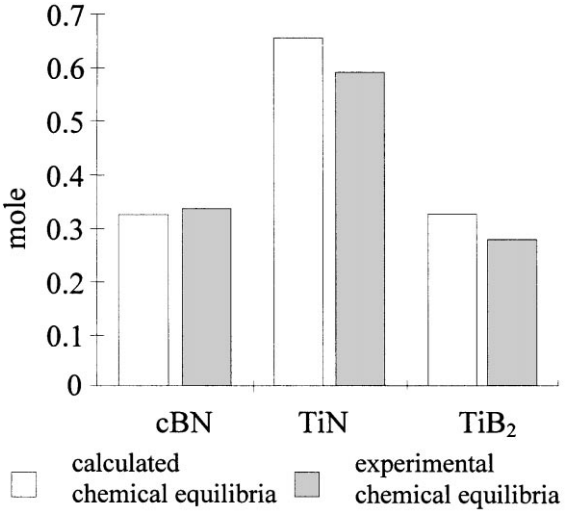

Fig. 3. Quantitative diagram of equilibrium composition for 2:1 molar cBN: TiH_2 mixture ($T = 1400$°C, $p = 3 \times 10^5$ Pa).

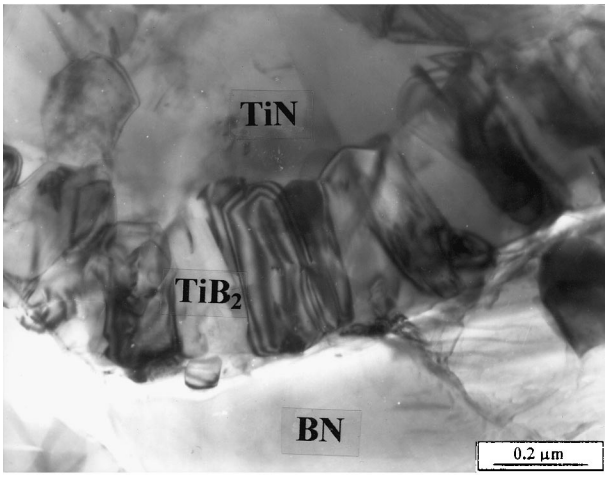

Fig. 4. TEM micrograph showing columnar layer of TiB_2 grains between the TiN and cBN.

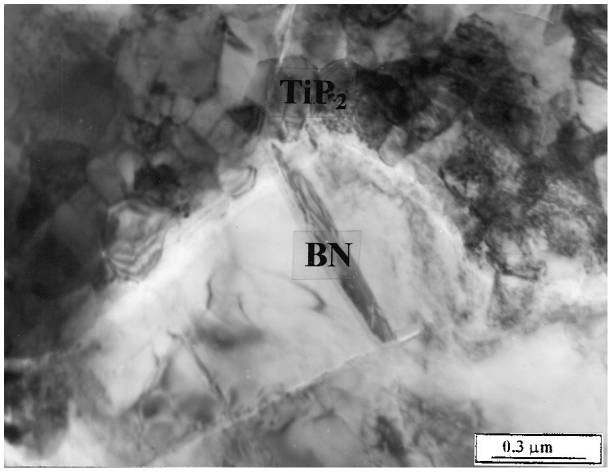

Fig. 5. Columnar layer of TiB_2 grains on the cBN surface.

1. hardness;
2. elastic modulus obtained from the measurement of the velocity of ultrasonic waves through the sample.

5.1. Measurements of hardness

Hardness measurements are usually used in the studies of plasticity and cracking phenomena in superhard materials. For superhard materials based on cBN, determination of most mechanical properties is very difficult and often even impossible. Quite frequently hardness is the only mechanical property which can be determined with high accuracy. This measurement is rather complex [13]. In the hardness measurements the shape of the indenter plays an important role which significantly influences the hardness value [14]. Conical and spherical indenters cause stress around the indentation which results in brittle cracks, which frequently make an accurate measurements impossible [15]. For superhard materials, diamond indenters of Vickers's, Knoop's and Berkowicz's shape are used. They form square, rhomboid and triangular indentations respectively. Hardness of the materials determined by indenters of a different shape is different at the same indenter loading force. This is due to the different holding manner and different work necessary to cause the deformation of the material around the indentation. The deformation level of the brittle materials increases as the loading force increases. The deformation is higher when Vickers and Berkowiczs pyramids are used than with the Knoop's pyramid. In order to precisely determine the hardness of superhard materials, it is necessary to use the indenter that ensures the minimum deformation around the indentation. These requirements are met by the diamond Knoop's indenter. In the hardness measurements of sintered materials it is also important that the size of the indentation exceeds the grain size . This requirement is also met by the Knoop's indenter. Its diagonal is 2.8 times wider than that of the indentation made using the Vickers indenter at the same load. Additionally, the Knoop's indenter is more durable than the Vickers, whose top usually breaks during the measurements of superhard materials. Knoopãs parameters provide the information not only of the hardness of the sample but also of the elastic modulus of the material.

However, determination of the longitudinal elastic modulus based on the hardness indentation has turned out to be impossible in this case because after the hardness measurements, deformation of the indentation along the shorter diagonal occurred.

The results of the measurements of the samples of cBN sintered with different amounts of Ti, Zr ,Ta, Cr are presented in Table 1. For comparison in the Table the hardness of the standards of the tradenames — kiboryt (product of ISM-Ukraine) and Amborite (product of De Beers) has been included. From these measurements it has been found that the highest hardness is exhibited by the composites sintered with titanium. Hardness becomes lower as the elements are changed from IV to VI groups of the Periodic Table of the Elements.

Table 1
Young's modulus and hardness of the samples studied

Sample	Youngs modulus (GPa)	Hardness HK1[b] (GPa)
Kiboryt	820 ± 35	52.0
Amborite	490 ± 25	42.0
9cBN + 1TiH_2	340 ± 20	20.0
9cBN + 1TiH_2[a]	460 ± 20	40.0
9cBN + 1Zr	280 ± 15	20.0
9cBN + 1Zr[a]	350 ± 24	29.0
9cBN + 1Ta	315 ± 28	10.0
9cBN + 1Cr	280 ± 16	9.4
1cBN + 1TiN	270 ± 15	21.4
1cBN + 1TiN[a]	265 ± 16	20.07

[a] Samples after treatment at: $T = 900°C$, $p = 3 \cdot 10^{-3}$ Pa, $t = 1$ h.
[b] In the hardness measurements of the composites a constant stress of 9.81 N/mm^2 was applied. The numerals in the chemical formulae denote the number of moles of a given substance.

5.2. Determination of elastic modulus based on the velocity of the ultrasonic waves through the sample

Ultrasonic methods are now one of the main techniques used for the determination of the elastic constants of the materials. In the case of isotropic materials, which includes the studied superhard materials Young's modulus—E, and Poisson's ratio—ν are the constants of interest. In the case of superhard materials, elastic moduli can be considered as key parameters which characterize their properties as well as their possible use for given applications.

In the ultrasonic method elasticity moduli of the material are determined through on the measurements of velocity of the longitudinal ultrasonic waves—C_L and of the transverse waves—C_T. It is also necessary to know the density of the material—ϑ. The calculations are carried out according to the following equation:

$$E = \varphi C_T^2 \frac{3C_L^2 - 4C_T^2}{C_L^2 - C_T^2}$$

$$\nu = \left(\frac{C_T^2}{C_L^2} - \frac{1}{2}\right) / \left(\frac{C_T^2}{C_L^2} - 1\right)$$

where:

E - Young's modulus
ν - Poisson's ratio

C_L - velocity of the longitudinal wave
C_T - velocity of the transverse wave
φ - density of the material

The so-called broad-band ultrasonic heads have been applied which give very short pulses. Such heads allow the measurements of small samples (thickness of the order of several mm) [16].

The system used works together with a laboratory ultrasonic defectoscope UNIPAN 512 and with a digital oscilloscope which makes it possible to precisely determine the measurement of the difference in time between two successive pulses. The velocity of the longitudinal ultrasonic waves was determined as the quotient of the measured sample thickness and the transition time of the ultrasonic pulse through this thickness. The error in the measurement of the wave velocity resulted from the error in the sample thickness measurement (0.002 mm), and error in the measurement of the time during which the ultrasonic pulse passes through this thickness (0.002 μs) and was equal to $+/- 0.2\times10^3$ m/s. It constituted 1–2% of the measured velocity values.

The Young's modulus values have been estimated from the measured velocity of the longitudinal waves and the material density together with an assumed value of the Poisson's ratio.

In the calculations the following equation has been used:

$$E = \varphi C_L^2 \frac{(1+\nu)-(1-2\nu)}{1-\nu}$$

where:

E - estimated Young's modulus value of the sample
C_L - measured velocity of the longitudinal wave
φ - measured material density
$\nu = 0.11$ - assumed value of the Poisson's ratio

The approach applied is a significant simplification, but, in the case of large differences in Young's modulus values between the samples, the error made may be relatively small.

The Young's modulus values, obtained, should be treated as relative values which make it possible to compare the samples rather than the absolute values of this parameter. The results of the measurements are presented in Table 1.

The Young modulus values of the standard samples are different. For kiboryt it is equal to 820 whereas for Amborite it is equal to 490 GPa. The samples sintered with different metal additions show also different values of Young's modulus which is due to different chemical compositions of the samples. The highest values of Young's modulus have been obtained for the samples sintered with titanium (with low molar content of this metal).

This proves that the samples containing titanium are well sintered owing to the chemical reactions that occur at the BN–Ti interface. It has been found that after thermal treatment the Young's modulus of the samples containing titanium increased.

Generally, it can be stated that the studies have shown large differences in the velocity of the longitudinal ultrasonic waves as well as in Young's modulus among the samples. Hence, these parameters can be treated as a sensitive probe of the structure and quality of these materials. Substantial advantages of the ultrasonic method are that it is a non-destructive, fast and relatively inexpensive technique.

6. Conclusions

X-ray diffraction studies indicate good agreement between experimental and calculated equilibrium compositions for BN-Ti, BN–Zr, BN–Hf, BN–CrN, BN–Ta, BN–Nb, BN–Cr, BN–Mo, BN–Al, BN–TiH_2, BN–TiN systems, as predicted by the VCS method. The calculated and experimentally determined contents of coexisting phases agree within the experimental error. TEM observations of the cBN–TiH_2 samples showed compact structure and formation of TiB_2 and TiN at the cBN–TiH_2 interface and in the BN–TiN samples showed formation of TiB_2.

Hardness and Young modulus of the samples of BN-metal systems before and after thermal treatment differ significantly. Thus it can be stated that thermal annealing of cBN sintered with metals accompanied by formation of new phases results in an increase in mechanical strength of the material. Hardness and Young modulus of the samples of BN–TiN before and after thermal treatment showed only a small decrease probably related to the formation of titanium boride.

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References

[1] N.P. Venezar et al. Polucenie i Primienienie Sverhtverdyh Materialov. ISM USSR, Kiev, 1986.
[2] F.P. Bundy, H.P. Bovenkerk, H.M. Strong, R.H. Wentorf, J. Chem. Phys. 35 (2) (1961) 394.
[3] F.P. Bundy, J. Chem. Phys. 38 (3) (1963) 618–630.

[4] F.P. Bundy, J. Chem. Phys. 38 (3) (1963) 631–643.
[5] R. Berman, F. Simon, Z. Electrochem. 55 (5) (1955) 333–338.
[6] F.R. Corrigan, F.P. Bundy, J. Chem. Phys. 63 (9) (1975) 3812–3820.
[7] V.L. Solozhenko, Doklady Phys. Chem. AN SSSR 301 (1) (1988) 147–149.
[8] V.L. Solozhenko, High Press. Res. 7 (1991) 201.
[9] V.L. Solozhenko, Thermochim. Acta 218 (1993) 201.
[10] V.L. Solozhenko, Diamond and Related Materials 4 (1994) 1–4.
[11] W.P. Smith, R.W. Missen, Chemical Reaction Equilibrium Analysis: Theory and Algorithms, Wiley, New York, 1982.
[12] D.R. Stull, M. Prophet, IANAF Thermochemical Tables, 2nd Ed., National Bureau of Standards, NSRDS–NBS37, Washington, DC, 1971.
[13] N.V. Novikov [i in], Sverhtverdye Materialy, No. 5 (1983), 11.
[14] L. Ramquirt, J. Phys. Chem. Solids 3 (1979) 30.
[15] D.B. Marshall [i in.], Communications of the american ceramic society, 1982.
[16] S. Mackiewicz, W. Wojdowski, Biul. Inform. OBRN, VIS, 3, Warszawa, 1989.