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XPS study of the cBN–TiC system

E. Benko[a,]*, T.L. Barr[b], S. Hardcastle[c], E. Hoppe[b], A. Bernasik[d], J. Morgiel[e]

[a]*Institute of Metal Cutting, 37A Wrocławska Str., 30-011 Cracow, Poland*
[b]*Materials Department and Laboratory for Surface Studies, University of Wisconsin, Milwaukee, WI 53201, USA*
[c]*Advanced Analysis Facility, University of Wisconsin, Milwaukee, WI 53201, USA*
[d]*University of Mining and Metallurgy, Surface Spectroscopy Laboratory, 23 Reymonta Str., 30-059 Cracow, Poland*
[e]*Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta Str., 32-050 Cracow, Poland*

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Abstract

Sintered cubic boron nitride is widely used in various industrial applications because of its extreme wear and corrosion resistance, thermal and electrical properties. In order to obtain composite materials with these optimal properties it is important to elucidate whether chemical reactions occur at boron nitride/bonding phase interfaces. Some of these systems were then subjected to physical and thermal alteration This paper summarizes theoretical and experimental studies on the cBN–TiC 1:1 molar ratio. From theoretical calculations it follows that TiC reacts with boron nitride forming two new phases, TiB_2 and TiN. Experimentally CBN–TiC composites were prepared by hot pressing, and the samples were subsequently heat treated. The samples were characterized after heat treatment using transmission electron microscopy and X-ray diffraction. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: cBN; TiC; XRD; XPS; TEM

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1. Introduction

A cubic boron nitride (cBN) sintered compact has a wide range of potential applications such as cutting tools, structural materials and heat sink materials because of its good thermal conductivity and superior hardness, surpassed only by diamond . Metals of the IV–VI groups of the periodic table of elements or their compounds are most frequently used as binding additives to produce cBN compact [1–7].

One of the most important criterion for choosing the binding phase for sintering of the composites is the chemical reaction occurring at the BN-binding material interface. Formation of new phases on the BN-binding material interface can provide composite materials with good mechanical properties. Knowledge of the mechanisms of the reactions taking place at the BN-binding phase interface is also interesting from a technological point of view.

The main goal of this paper is to elucidate the nature of the interactions between the binding material, in this case TiC, and boron nitride.

2. Chemical equilibria in the BN–TiC system

Calculations of phase equilibria for the BN–TiC system were carried out using the VCS (Villars, Cruise, Smith) algorithm [8], i.e. an algorithm belonging to the so called stoichiometric algorithms.

In this procedure, the Gibbs energy of the reaction mixture is minimized, subject to side conditions of elemental abundance and non-negativity of the mole numbers. Reaction-extent variables derived from the transformation of the mass balance equations are the unknowns of the function being minimized; details of the procedure can be found elsewhere.

In the calculations of chemical equilibria the following components have been taken into account: B(g), B_2(g), N_2(g), BN(g), Ti(g), C(g), CB(g), CN(g), CN_2(g), C_2(g), C_2N(g), C_2N_2(g), C_3(g), NCN(g), C_4N_2(g), C_5(g), C_4(g), TiB_2(s), TiN(s), B(l), Ti(l), TiN(l), CB_4(l), TiC(l), TiB_2(l), TiB_2(s), TiB(s), TiN(s), Tiα(s), Tiβ(s), BN(s),

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* Corresponding author. Fax: +48-1233-9490.
E-mail address: ewa.benko@ios.krakow.pl (E. Benko).

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B(s), TiB(s), C(s), TiC(s), CB_4(s), $TiC_{0.8}N_{0.2}$ (where g, l, s denote gas, liquid, and solid respectively) [9].

For the BN:TiC molar ratio equal to 1:1 and at 1400°C, four phases co-exist in the system at constant pressure: BN(s), $TiC_{0.8}N_{0.2}$(s); TiB_2(s), C (s).

Under low pressure three solid phases co-exist in the system: TiB_2, C and $TiC_{0.8}N_{0.2}$ in molar amounts 0.50, 0.60 and 0.50 mol respectively, as well as gaseous nitrogen at the amount of 0.45 mol. At pressures higher than 1×10^{-1} Pa four solid phases co-exist in the system: TiB_2, C, $TiC_{0.8}N_{0.2}$, and BN in the molar amounts of 0.09, 0.27, 0.90 and 0.82 respectively.

Typical diagrams of chemical equilibria at 1400^0C are shown in Fig. 1.

3. Experimental

3.1. Substrate materials

Two types of TiC+BN samples were prepared, namely powdered and layered samples.

Powdered samples in the form of the 1:1 molar ratio mixture of boron nitride (ABN–300, De Beers, 3–5 μm grains size) and titanium carbide (H.C. Starck, 3–5 μm grains size) were mechanically mixed in ethyl alcohol and pressed into pellets of 6 mm diameter at 10^2 Pa. Then the sintered material was thermally treated at 1400°C for 2 h in vacuum.

The layered TiC+cBN samples were prepared using two PVD techniques: magnetron sputtering method and arc evaporation technique. Then the layered samples were heated at 1400 and 1600°C for 2 h.

The BN plates were obtained during direct transformation of hexagonal boron nitride powder at high temperature (2800°C) and pressure (9GPa). The chemical composition of cBN was found to be C-0.04, Ca-0.05, Si-0.02, Mg-0.002, Mg-0.004 at. %. The resulting disks were 6 mm in diameter and 1 mm high. The surface was mechanically ground and polished using diamond micron powder of various grit sizes in order to obtain the surface of the desired roughness. Prior to the deposition, BN substrates were cleaned ultrasonically in three steps: acetone, trichloroethylene and propyl alcohol for 15 min each.

3.2. X-ray diffraction studies

Two types of samples were investigated:

1. Powdered samples 1:1 BN:TiC ratio thermally heated at 1400°C.
2. Samples of cBN layered with TiC thermally heated at 1400 and 1600°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 [7]. Filtered CuK_α radiation was used.

3.3. TEM studies

The microstructure observations of the BN–TiC powdered samples were performed with a Philips type CM-20 TWIN (200 kV) transmission electron microscope. Thin foils were prepared by dimpling and ion milled with a Gatan 600 DuoMill.

3.4. Studies of the reactions occurring in the BN–Ti system by X-ray photoelectron spectroscopy

XPS studies were generally performed on a Hewlett-Packard (HP) 5950A, spectrometer with a high-resolution

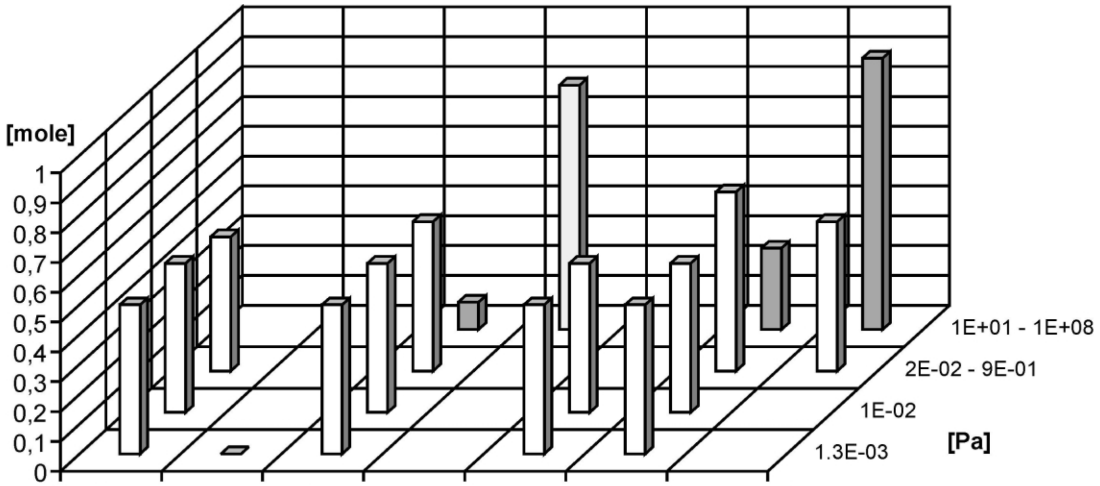

Fig. 1. Diagram of chemical equilibria at 1400°C in the 1:1 cBN:TiC molar ratio system.

X-ray monochromator, using an Al K_α (1476 eV) anode at an irradiation power of 600 W. General calibration produced a binding energy scale specified by Au ($4f_{7/2} = 83.8 \pm 0.05$ at a linewidth of < 1.0 eV. The charging shifts produced by the insulating samples were removed by a combination of electron flood gun adjustments and fixing the C1s binding energy of the hydrocarbon part of the adventitious carbon line at 284.6 eV [10]. The photoelectron peaks for Ti(2p), B(1s), O(1s), N(1s), C(1s) of the investigated samples (BN + TiC) were examined in order to characterize the chemical interactions between BN and TiC. For calibration XPS was also carried out on standard samples of Ti, TiN, TiB, BN, TiC and TiB_2. The satellites were included automatically in the synthesis.

The samples were also sputtered with 2.5 keV argon ions to determine the chemical state of the substrate and interfacial features of the deposited film as a function of depth.

The data curve fitted a Shirley background subtraction, using a 2 points box curve fitting program with a Gaussian/Lorentzian product function.

4. Results and discussion

4.1. X-ray diffraction study

In the powdered 1:1 BN:TiC molar ratio samples heat treated at 1400°C at 1.3×10^{-3}Pa (2 h) two new phases formed, TiB_2 and $TiC_{0.8}N_{0.2}$. This has been compared with calculated equilibrium composition. In the cBN samples layered with TiC, heat treated at 1400 and 1600°C under 1.3×10^{-3} Pa (2 h), only one new phase formed, namely TiB_2. This is caused by the fact that the layer is too thin and it is sufficient only to form TiB_2 which is created in the vicinity of BN.

4.2. TEM study

Observations of cBN sintered with TiC showed that BN grains are separated by the material composed of micron sized crystallites (Fig. 2). The irregular shape of some boundaries in Fig. 2 is due to the roughness of the surfaces limiting BN crystallites, their inclination with respect to the beam direction as well as significant thickness of the thin film at the observation point. At thinner points, as in Fig. 3a, the boundaries between fine-crystalline material and BN grains were more regular. Analysis of the electron diffraction patterns (Fig. 3b–d) concluded that the fine crystallites at the boundary are of TiB_2 whereas the bigger grains inside are TiC-type. In several cases the electron diffraction of single reflections are close to the central one. This corresponds to the presence of the phases whose unit cell was of 0.7–0.8 nm in size which may indicate the formation of the ternary Ti(BC) or Ti(NC) compound. However, their small size made it impossible to keep them in the visual field for unequivocal identification.

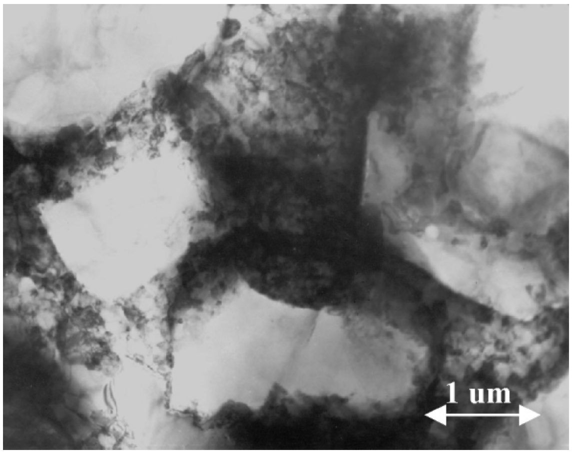

Fig. 2. Microstructure of cBN sintered with TiC.

4.3. X-ray photoelectron spectroscopy

The following samples have been investigated:

Sample 1. BN + TiC powder heat-treated at 1400°C.
Sample 2. TiC layer deposited onto cBN by magnetron sputtering and thermally treated at 1600°C.
Sample 3. TiC layer deposited onto cBN by magnetron sputtering and thermally treated at 1400°C.
Sample 4. TiC layer deposited onto cBN using PVD method and thermally treated at 1400°C.

Since the spectra of samples 2 and 3 are similar the spectrum corresponding to sample 2 will be discussed in detail.

XPS results for individual samples are collected in Tables 1–3. These tables give photoelectron binding energy values of the appropriate elements. Based on these values individual chemical compounds present on the surface of the samples have been identified in accordance with literature data given in Table 4 [10,11]. The tables show relative intensities of the lines corresponding to the elements studied as well as the relative intensities of the lines due to various compounds of the same element. These values enabled quantitative analysis of the samples.

Analysis of the spectra of sample 1 has shown that on the surface of this sample the following compounds are present: TiC, TiN, TiO_2 [10,11].

The carbon 1s spectrum indicates the presence of carbon as TiC (Fig. 4). The intensity of the strongest C1s line corresponding to this compound is almost 3.5 less than the most intense C1s line. The presence of TiC cannot be excluded when the $Ti2p_{3/2}$ spectrum is considered (Fig. 5). Location of the line due to TiC in this spectrum overlaps with that originating from TiO. The

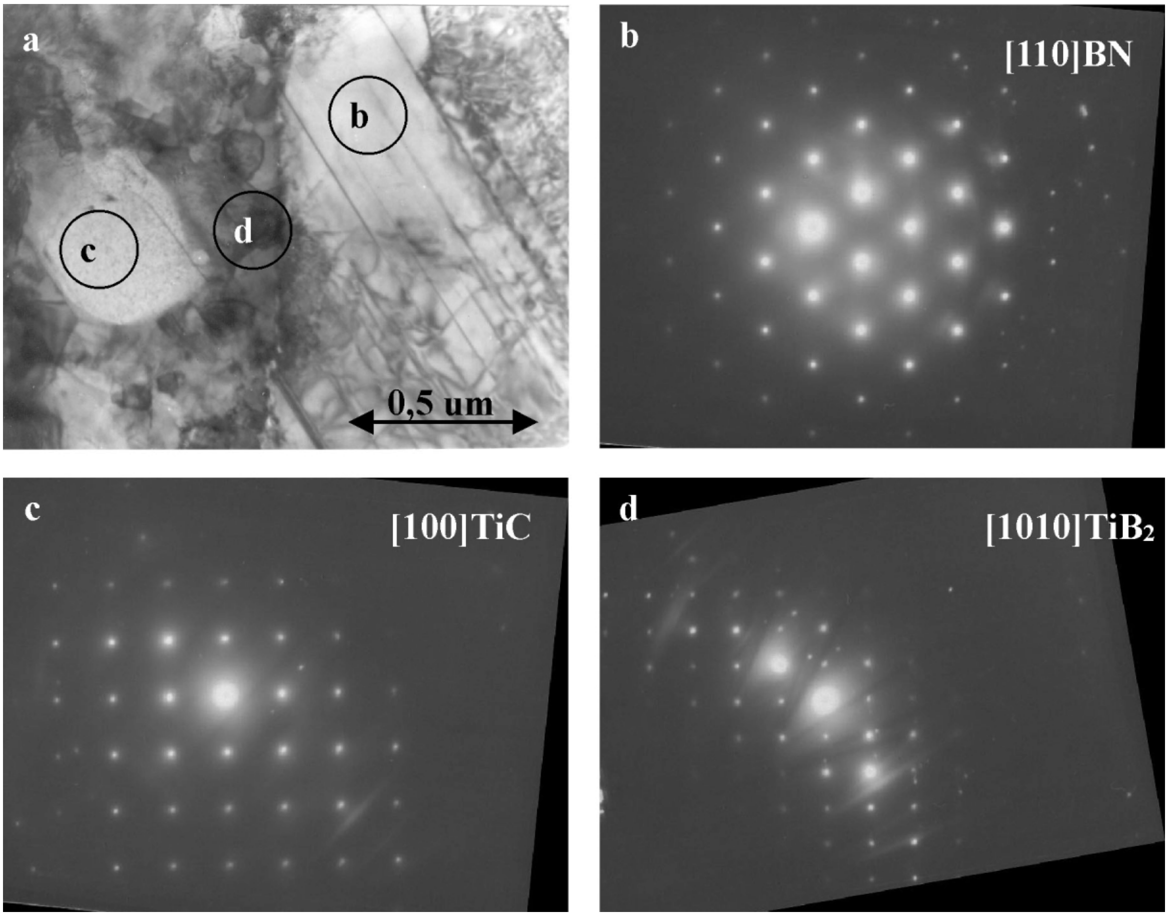

Fig. 3. Boundary between the fine-crystalline area of cBN sintered with TiC (a) and electron diffractions from the points marked in the microstructure (identical constant for b, c, d).

Table 1
Sample 1. BN + TiC powder heat-treated at 1400°C

Element line	Binding energy, eV	Relative intensity of the element line	Relative intensity of the compound line	Compound
Ti 2p 3/2	455.3		0.68	TiO, TiC
	456.3	0.19	0.24	TiN
	459.1		0.09	TiO_2
B 1s	190.9		0.62	BN
	192.3	0.06	0.38	B–O, B_2O_3
N 1s	396.5		0.09	TiN
	398.1		0.58	BN
	399.2		0.21	
	400.6	0.12	0.12	
O 1s	530.6		0.33	Ti–O
	532.2		0.47	B–O
	533.4	0.28	0.21	B_2O_3
C 1s	281.9		0.16	TiC
	284.6		0.58	C
	285.9		0.18	C–O
	288.4	0.35	0.08	C=O

nitrogen N1s spectrum shows the presence of BN and TiN (Fig. 6). For both these compounds B1s (Fig. 7) and $Ti2p_{3/2}$ (Fig. 4) spectra have also been recorded.

Table 2
Sample 2. TiC layer deposited onto cBN by magnetron sputtering and thermally treated at 1600°C

Element line	Binding energy, eV	Relative intensity of the element line	Relative intensity of the compound line	Compound
Ti 2p 3/2	454.2		0.25	TiB_2
	455.2	0.15	0.14	TiO
	458.5		0.61	TiO_2
B 1s	187.7		0.67	TiB_2
	191.6	0.09	0.33	B–O
O 1s	530.3		0.51	
	531.7	0.60	0.49	
C 1s	284.6		0.84	C
	288.2	0.16	0.16	

The photoelectron spectra obtained for samples 2 and 4 are similar. The following compounds may be present on the surface of these samples: TiB_2, TiO_2.Thus TiO_2 content is much higher than for the sample 1; the relative intensity of the $Ti2p_{3/2}$ line of this compound is about 0.6 whereas in the case of the sample 1 its value is about 0.09. Moreover, samples 2 and 4 record higher

Table 3
Sample 4. TiC layer deposited onto cBN using PVD method and thermally treated at 1400°C

Element line	Binding energy, eV	Relative intensity of the element line	Relative intensity of the compound line	Compound
Ti 2p 3/2	454.2		0.29	TiB_2
	455.3	0.25	0.09	TiO
	458.5		0.62	TiO_2
B 1s	187.4		0.81	TiB_2
	191.8	0.12	0.19	B–O
O 1s	530.2		0.49	Ti–O
	531.4	0.57	0.51	
C 1s	284.6		0.91	C
	288.4	0.06	0.09	

Table 4
Photoelectron binding energy of the elements studied (C1s = 284.6) [10]

	Ti $2p_{3/2}$	N 1s	B 1s	C 1s	O 1s
Ti met	453.0				
	453.6				
TiO	454.9				529.8
	455.7				
TiO_2	458.3				529.6
	458.4				529.9
	458.7				
TiN	455.6	396.7			
TiC				281.3	
				281.3	
				281.5	
TiN_X		396.3			
TiB_2	454.3		187.0		
			187.3		
BN		397.9	189.8		
		398.0	190.2		
		398.8	190.5		
B_2O_3			191.8		532.8
			192.9		533.0
			193.1		
			193.4		
B_4C			186.3		
B met			187.1		

concentrations of oxygen but are lower in carbon (Fig. 8).

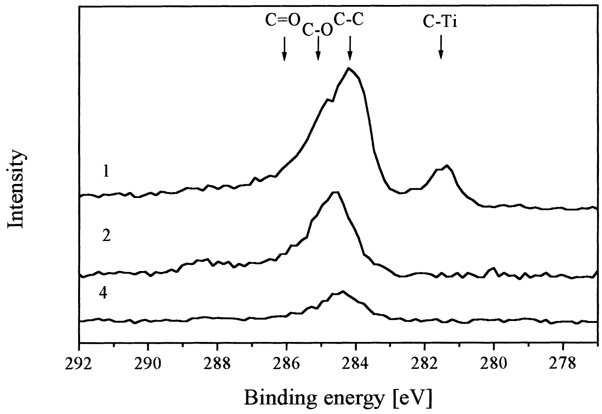

Fig. 4. XPS spectra of the carbon 1s regions measured for the sample nos. 1, 2 and 4. Arrows indicate different chemical environments of carbon.

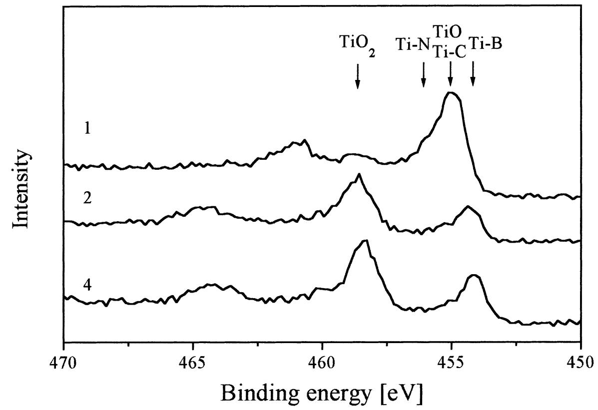

Fig. 5. XPS spectra of the titanium 2p regions measured for the sample nos. 1, 2 and 4. Arrows indicate position of the Ti $2p_{3/2}$ lines corresponding to different chemical environments of titanium.

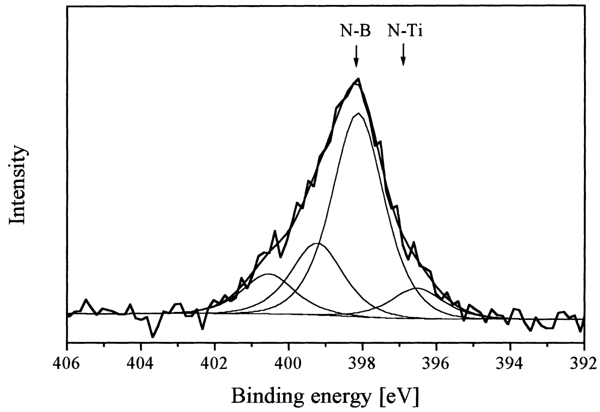

Fig. 6. XPS spectra of the nitrogen 1s regions measured for the sample no. 1 (BN + TiC powder heat-treated at 1400°C). Arrows indicate different chemical environments of nitrogen.

When surface compositions of samples 2 and 4 are compared it can be seen that the concentration of Ti on the surface of the sample 4 is higher than on the surface of the sample 2; however, the proportions of individual Ti compounds are very similar (Fig. 7). Lower concentrations of carbon are observed on the surface of

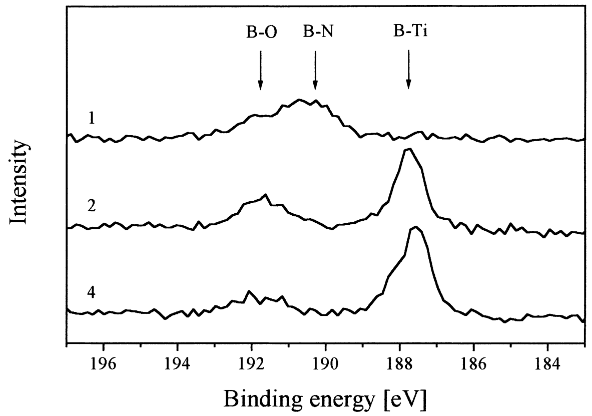

Fig. 7. XPS spectra of the boron 1s regions measured for the sample nos. 1, 2 and 4. Arrows indicate different chemical environments of boron.

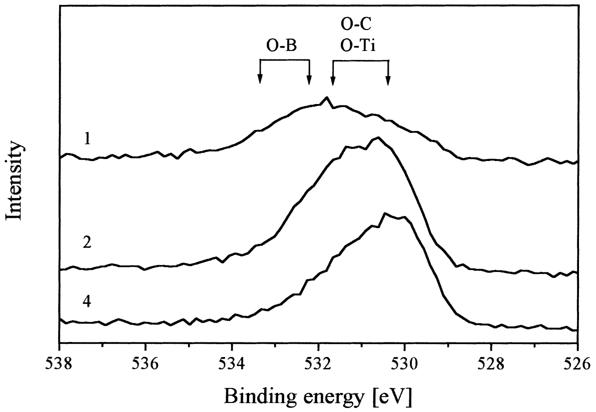

Fig. 8. XPS spectra of the oxygen 1s regions measured for the sample nos. 1, 2 and 4. Arrows indicate different chemical environments of oxygen.

sample 4. Concentrations of boron on the surface of both samples are comparable but for sample 4, a slightly higher concentration of TiB_2 has been recorded (Fig. 7).

Bombardment of the surface of the samples with argon ions results in decreasing the C1s intensities. This can be explained by removal of the adsorbed molecules from the surface. However, the most significant change is observed in Ti2p spectra. Shapes of these spectra make it impossible to conclude precisely which Ti compounds are present on the surface. When the spectra before and after argon ions bombardment are considered, one should expect higher concentrations of Ti^{3+} and lower concentrations of Ti^{4+} after argon ions bombardment. Additionally broadening of the spectral lines is expected which makes the interpretation of the spectra more difficult.

5. Conclusions

The XRD investigations performed confirmed formation of TiB_2 and $TiC_{0.8}N_{0.2}$ within the cBN + TiC powdered samples (1400°C treated) as was predicted by thermodynamic calculations.

TEM observation of the cBN–TiC compact showing compact structure and formation of TiB_2 at the BN–TiC interface. Analysis of the electron diffraction concluded that fine crystallites of TiB_2 formed at the boundary whereas the bigger grains inside are TiC-type. In several cases the electron diffraction of single reflections corresponds to the presence formation of the ternary Ti(BC) or Ti(NC) compound.

XRD studies of cBN with TiC layered samples show only formation of TiB_2. XPS analysis of 1400 and 1600°C treated cBN–TiC samples independently of the way of coating (magnetron sputtering method and arc evaporation technique) indicates that TiB_2 is the only compound formed. This can be explained by the low coating thickness that is sufficient only for the creation of TiB_2 which is formed first on the cBN surface.

Powdered cBN + TiC samples showed only TiN as a new phase. This can be explained by the limited XPS penetration depth (50 Å) and, as has been shown from the TEM studies, TiB_2 is formed at cBN surface, i.e. much deeper than the XPS analysis penetration of Ti.

XRD studies have also shown the formation of $TiC_{0.8}N_{0.2}$ as a new phase in the powdered cBN–TiC sample. Creation of this phase cannot be excluded judging by XPS results. More precise studies planned by the authors should solve this problem.

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References

[1] Hayashi, Katsura, Japanese Patent 95,172,91, 11 July 1995.
[2] Narita, Kenya Japanese Patent 9416476, 25 January 1992.
[3] Corrigan, Francis Raymont, European Patent 368,069, 16 May 1990.
[4] Toshiba Tungaloy Co., Jpn. Kokai Tokkyo Koho, Japanese Patent 81 29,650, 25 March 1981.
[5] Toshiba Tungaloy Co., Jpn. Kokai Tokkyo Koho Japanese Patent 84 78.528, 8 May 1984.
[6] Toshiba Tungaloy Co., Jpn. Kokai Tokkyo Koho Japanese Patent,81 29,648, 25 March 1981.
[7] Ueda, Fumihiro; Eto, Hiroyuki; Miyake, Masami, Japanese Patent,91,193,668, August 1991.
[8] W.P. Smith, R.W. Missen, Chemical Reaction Equilibrium Analysis; Theory and Algorithms, John Wiley & Sons, New York, 1982.

[9] D.R. Stull, M. Prophet, JANAF Thermochemical Tables, 2nd Edition, National Bureau of Standards (NSRDS-NBS37), Washington, DC, 1971.

[10] T.L. Barr, S. Seal, J. Vac. Sci. Technol. A13 (1995) 1239.

[11] D. Wagner, D.M. Bickham, NIST X-ray Photoelectron Spectroscopy Database, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, October 1989.