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### New Superhard Ternary Borides in Composite Materials

Zachary Zachariev Institute of Polymers, Bulgarian Academy of Sciences Bulgaria

#### 1. Introduction

Superhard substances are those a hardness above 20 GPa, i.e. higher than that of corundum (Kislii et al.,1988) or with a Vickers hardness Hv exceeding 40 GPa (Sologenko&Gregorianz, 2005). The ten utmost non-metal substances and refractory compounds form a "hardness pyramid" (Kislii et al.,1988) diamond being on top, followed by cubic-boron nitride and boron carbide.

Metal-like ones form a similar pyramid, the transition metal borides occupying its top. However, the maximum hardness found for them is inferior to that of the non-metal substances. The interest in borides is due to their extraordinary hardness (up to 1873 °C) as compared to other refractory compounds.

The hardest boride ( $B_{12}C_3$ ) is used as a wear resistant polycrystalline material, armor tiles, nuclear industry, etc. (Anderson, 2002).However, applications are restricted by its high brittleness due to the strong covalent bonds in its crystal lattice. It has been established (Zakhariev&Radev, 1988) that superhard ternary compounds based on boron carbide with dissolved IV-VI group metals ( $B_{12-n}C_3Me_n$ ) can be obtained by sintering CMC composite materials without pressure.

Sintering of TiB<sub>2</sub>-MeC-Me systems with no pressure applied is a new trend in the field of superhard boride composite materials. The binding metal (e.g. Ni or Co) in TiB<sub>2</sub>-Me system reacts with the boride and forms a low-melting phase (Lecrivan&Provost, 1968); (Fitzer, 1973). The growing interest in borides comes from their high-temperature behavior: high melting point, hardness, wear resistance and chemical inertness. These allows using them to produce cathodes for electrolytic aluminium, first wall coatings and neutron absorbers for nuclear technology, valve components in cool liquefaction plants and crucible materials for metal evaporation.

Studies on the TiB<sub>2</sub>-TiC and TiB<sub>2</sub>-TaC systems show that the carbides inhibits the grain growth of the boride phase (Murata et al., 1967).The TiB<sub>2</sub>-MeC-Me materials have the following advantages as compared with the binary systems mentioned (Petzow&Telle, 1984): application of hot pressing is not necessary, the grain growth is completely inhibited, the mechanical properties are improved due to the small grain size (about 1µm) (Zakhariev et al., 1993).

WC-Co is the source material in the field of the metal-working whereas superhard ternary boride (WCoB) coating entails a sharp rise in wear resistance of the composite materials (Zakhariev et al., 1987). The micro hardness of synthetic polycrystalline WCoB amounts to

4650 κgf/mm<sup>2</sup> (Zakhariev et al., 1986) which explains the increased service tool - life of the WC-Co instruments. Similar ternary compounds are MoCoB and WFeB with the same orthorhombic unit cells (Jeitschko, 1968).

Combining borides (B<sub>4</sub>C, TiB<sub>2</sub> et al) with carbides (MeC, WC-Co et al) allows their chemical interactions upon heating, the building up of eutectics etc. This can result in densification of the composite material without applying of any additional pressure as well as in enhanced physico-mechanical properties due to the arising of superhard ternary compounds (B<sub>12</sub>,  ${}_{n}C_{3}Me_{n}$ , (Ti,W)<sub>2</sub>B, WCoB) (Zachariev, 2001).

Under thermochemical treatment of steels (Fe-C) with a transition metal borides (ZrB<sub>2</sub>, TiB<sub>2</sub>, CrB2) (Zakhariev et all., 1970) it appears a ternary compound (Fe,Me)<sub>2</sub>B of considerable hardness 20-23 GPa. The layer it has built up combines the advantages of consecutive metalizing and boronizing layers thus bringing about the enhanced resistance to wear and corrosion of the metal-matrix composite (MMC) system.

Similar properties with respect to corrosion and wear have another complex boride (synthesized  $Mo_2FeB_2$  with ferrous binder), known as "new hard alloy" (Komai et al., 1989). The ternary boride  $Cr_xFe_yB_z$  ( $Cr_3Fe_{80}B_{17}$ ) also shows unique properties which have been utilized in several amorphous materials for corrosion applications.

Fukatsu et al. (Fukatsu, 1967) have shown that the wear resistance of hard alloys increases with the increasing of their hardness provided all other conditions are the same.

The present paper, based mainly on research done by the author and associated colleagues, aims at a concise unification of the results on new superhard boride composites in view of their practical applications.

#### 2. Experimental methods

The carbides  $(B_{12}C_3, TiB_2 \text{ and } Me^{IV-VI}C \text{ produced by "ESK-Kempten", "Merck" and "Ventron Alfa Products", respectively) were homogenized in a Frisch planetary mill, pressed at 200 MPa and then sintered at 1700 - 2250°C in a Degussa furnace with graphite heater in argon atmosphere.$ 

The hardness was determined using a "Leitz-Durimet" hardness tester with loads of  $HV_{0.5}$  to  $HV_1$  and a "Carl Zeiss" micrometer with indentation load 30-100 g. Compound hardness as a function of indentation load has been traced.

An automated DRON-3 diffractometer, with CuKa radiation was used to investigate the structure of the materials under study. Their morphology was characterized by scanning electron spectroscopy (SEM) on a JSM 840 apparatus equipped with a Link QK 200 dispersive X-ray analyzer.

The initial TiB<sub>2</sub> powder (type PIII; Ti-68.6, B-27.3, TiO<sub>2</sub>-3.9, Co-0.2 wt.%) was prepared under industrial conditions using a technology developed in the Institute of problems in Materials Science, Kiev. The chemical analysis of another initial TiB<sub>2</sub> Koch-Light powder showed Ti-68.8 and B-31.2 wt.%. The powders TiB<sub>2</sub> were milled 75-120 min using hard-alloys bodies and vessels of WC-Co (K10) in the Fritsch planetary mill with acetone serving as a medium. The polycrystalline samples of the ternary boride WCoB were obtained by crystallization from a cobalt-rich melts of the corresponding powdery components at 1600 °C according to (Petrov&Will, 1981).

Standard WC-Co cutting plates K10 (92 wt.%WC, 6%Co and 2 wt.% TaNbC) were packed separately in Borozar-HM (powdery product, 325 mesh) and  $B_4C$  (F220 technical grade, ESK-Kempten) and heated at 1000-1400 °C for 30-120 min in an inert medium (argon). The

heating was carried out in a large-scale Bor 6-CM-3 installation for deposition of boride coating on K10 plates.

For simultaneous boron-zirkonizing (or boron-chromizing) of steel samples by powdery borides  $ZrB_2$  (CrB<sub>2</sub>) and some activators were used the heating occurring at 950-1050 °C in argon atmosphere.

Obtaining the superhard boron-metallizing layer on steel tools or parts of them requires their coating in a patented paste (commercial paste "Zahobor-P"). The technology is very simple: a coat of the paste is applied over the working surfaces of machine tools and parts. The metal surfaces thus coated are dried and then subjected to heat-treatment. Additional procedures, staff and equipment are not required.

#### 3. Results and discussion

#### 3.1 Ternary B<sub>12-n</sub>C<sub>3</sub>Me<sub>n</sub> borides in CMC-composite B<sub>12</sub>C<sub>3</sub> + Me<sub>x</sub>B<sub>y</sub>

It is obvious that a sintering of  $B_{12}C_3$  is only possible at temperatures above 2100°C, i.e. close to the melting point of boron carbide (2447°C). SEM of a fracture surface of  $B_{12}C_3$  (10 wt %) +  $W_2B_5$  material sintered at 2150°C and a grain size of 2-7 µm is shown in Fig.1. With larger magnifications (2000x), a thin eutectic binder is visible at the grain boundaries.



Fig. 1. SEM of the fracture surface of  $B_{12}C_3 + 10 \text{ wt}\%W_2B_5$  composite material (sintered at 2150°C; 20 min)

An eutectic resulting from interaction between the two carbides ( $B_4C + WC \rightarrow W_2B_5 + C$ ) does not seem unexpected when taking into account the eutectic character of the ternary diagrams B-C-Me <sup>IV-VI</sup> (Schouler et al.,1983) and the quasi-binary systems  $B_4C$ -MeB<sub>2</sub> (Portnoi& Samsonov,1960).

Data in Tabl.1 show that the systems containing 4th Period metals, such as  $B_{12}C_3$ -TiB<sub>2</sub> (VB<sub>2</sub>,CrB<sub>2</sub>) have the lowest T<sub>eut</sub> (2150-2200 °C) as compared with the other ones (B<sub>12</sub>C<sub>3</sub>-ZrB<sub>2</sub> /NbB<sub>2</sub> and B<sub>12</sub>C<sub>3</sub>-HfB<sub>2</sub>/ TaC), which is of importance for the assessment of the sintering temperature of composites.

MeB <sub>2</sub> in eutectic, %					
Compounds	T <sub>m</sub> ,°C	ΔH,KJ/mol	vol.	Mol	T <sub>eut</sub> , °C
B <sub>12</sub> C <sub>3</sub>	2447	70,0			
TiB <sub>2</sub>	3217	280,0	20,0	26	2197
ZrB <sub>2</sub>	3247	314,0	20,0	24	2277
HfB <sub>2</sub>	3347	335,0	23,0	22	2377
VB <sub>2</sub>	2747	142,4	35,0	46	2167
NbB <sub>2</sub>	2997	174,6	35,6	36	2247
TaB <sub>2</sub>	3097	217,7	27,0	32	2367
CrB2	2217	125,6	63,0	70	2147

Table 1. Melting point and Eutectic temperature of composite system B<sub>12</sub>C<sub>3</sub>-MeB<sub>2</sub>

Due to the  $Me_xB_y$  particles it creates, appearance of the eutectic leads to brittle boron carbide becoming stronger. This results in a significant decrease in brittleness of the recrystallized composite and an increase in its crack-resistance. Measured by the indentation method, the critical coefficient of stress intensity (KIc) is in differently oriented eutectics ( $B_{12}C_3$ -MeB<sub>2</sub>) ranges from 6-12 MPa to 2.5-3.5 MPa depending on their components. This result indicates that the use of eutectics as a new class of CMC composite materials resistant under extreme conditions is promising.

The microhardness values of a ternary phase  $B_{12-n}C_3Me_n$  borides in composite  $B_{12}C_3 + Me_xB_y$ , as compared to hot-pressed pure boron carbide, and the values obtained by other authors are presented in Table 2. The data show that the boron carbide hardness in the ternary borides phases is much higher than that of pure boron carbide and other composites based on  $B_{12}C_3$ , *c*-BN and c-BC<sub>2</sub>N.

This sharp increase in hardness seems to be due to dissolution of the transition metals in the crystal lattice of boron carbide. During the chemical interaction of the two carbides the boron needed for the reaction comes from the boron carbide lattice.

Since from the investigations of Lipp et al. (Lipp&Schwetz, 1975) it is known that the homogeneity region of  $B_{4+x}C$  has no substantial effect on its hardness, the only reason for the sharp increase in boron carbide hardness should be the formation of new superhard ternary compounds with the formula  $B_{12-n}C_3Me_n$  (Fig. 2).

These compounds do not differ essentially from the ternary compounds  $B_{12}C_{3-n}Me_n$  (predicted by Lipp &Roder, 1966 and proved to Okada et al., 1990). The difference is that with the latter compounds, the replacement of *Co* (at. Radius 0.91 Å) by the larger element Al (at. radius 1.43 Å) leads to a considerable increase in the size of the unit cell in the direction of the hexagonal C- axis and of the lattice volume (Table 3). In our case, just the opposite happens. The volume shows no substantial change, whereas the lattice parameter *c* decreases (see Table 3).

This is attributed to an increase in carbon content in the homogeneity region of the boron carbide, which is due to elimination of boron from the compound. The decrease in the

parameter *c*o, while the crystal lattice volume remains unchanged, indicates that the metal atoms are incorporated most probably in the icosahedron B2 and B1 sites.

Initial Material (weight %)	HV1	HV05	Reference
$B_{12}C_3 + W_2B_5$ (10; 50)	50; 58	53* ; 77**	(Zakhariev, 1988)
$B_{12}C_3 + CrB_2$ (10)	56	77**	(Zachariev, 2001)
$B_{12}C_3 + VB_2$ (10)	43	52	(Zachariev, 2001)
B <sub>12</sub> C <sub>3</sub> +Ti (7)		63	(Makarenko et al. ,1977)
$B_{12}C_3 + Zr$ (10)	-	60	(Makarenko et al.,1977)
$B_{12}C_3 + A1 (50)$	25	_	(Lipp & Roder ,1966)
B <sub>48</sub> C <sub>2</sub> Al <sub>3</sub> - crystal	30.5	-	(Okada et al., 1990)
$B_{12}C_3 + TiB_2 (10;20)$	-	45 ; 55	(Nishiyama , 1985)
B <sub>12</sub> C <sub>3</sub> +TiB <sub>2</sub> (10;25)	-	30 ; 34	(Telle & Petzow ,1987)
$B_{12}C_3$ +Ti $B_2$ (10)+ $W_2B_5$ (5)	-	37 ; 42	(Telle & Petzow ,1987)
c-BC <sub>2</sub> N	-	76	(Solozhenko , 2001)
B12C3-HP "pure"	34	30 ; 38 ; 30	(Lipp &Schwetz , 1975)

 $^{*}$  - Length of pyramid diagonal indentation [µm]: \* 4.4; \*\* 3.15

Table 2. Microhardness (GPa) of  $B_{12-n}C_3$  Me<sub>n</sub> from the initial materials  $B_{12}C_3$  + Me<sub>x</sub>B<sub>y</sub> and other composites



Fig. 2. Non-metal hardness pyramid with the new ternary boride phase B<sub>12-n</sub>C<sub>3</sub>Me<sub>n</sub>

Compounds	$C_{o}[Å]$	a <sub>o</sub> [Å]	Volume [nm <sup>3</sup> ]	Reference	
B <sub>11</sub> C <sub>3</sub> W	12,078	5,601	0,32757	(Zachariev, 2001)	
B <sub>11</sub> C <sub>3</sub> W	12,024	5.604	0,32697	(Zachariev, 2001)	
B <sub>11</sub> C <sub>3</sub> W	12,054	5,606	0,32802	(Zachariev, 2001)	
B <sub>11</sub> C <sub>3</sub> Ti (10 – 20%)	12,06-12,07	5,607		(Zachariev, 2001)	
B <sub>11</sub> C <sub>3</sub> V (10-20%)	12,02-12,05	5,605	-	(Zachariev, 2001)	
B <sub>12</sub> C <sub>2</sub> Al	12,39	5,65	0,34252	(Lipp & Roder , 1966)	
B <sub>12</sub> (C,Si) <sub>3</sub>	12,1-12,4	5,60	0,3286-	(Kislii at all. , 1988)	
B <sub>13</sub> C <sub>2</sub>	12,19	5,67	0,33938	(Thevenot & Bouchacour, 1979)	
B <sub>12</sub> C <sub>3</sub> (initial ESK)	12,12	5,60	0,32915	(Lipp & Schvetz , 1975)	

Table 3. Parameters of the crystal lattice of the ternary metal borides compounds  $C_0[\text{Å}]$ ,  $a_0[\text{Å}]$ ; V[nm<sup>3</sup>]

Due to the strongly extended lattice during the incorporation of Al and Si into the C-C-C axis, the phases  $B_{12}C_2A1$ ,  $B_{48}C_2Al_3$  and  $B_{12}C_2Si$  have a microhardness (HV1 = 25 – 30.5 GPa) even lower that that of pure boron carbide (Table 2).

A novel superhard phase c-BC<sub>2</sub>N was synthesized using the laser-heated diamond anvil cell with a hardness Hv=76 GPa [Solozhenko, 2001] (Tabl.2).

The hardness (50-77GPa) of the new ternary borides is much higher than that of "pure" boron carbide sintered by hot pressing (Tabl.2). It is equal to that of cubic boron nitride (i.e. next to diamond) and even of some polycrystalline diamonds of the type "Carbonado" and "CB". However, the price of the new boride is several orders of magnitude lower.

We have developed an original method to obtain articles of boron carbide composite, in which the hot-pressing stage is avoided. The new superhard boron carbide has already found several applications: in the production of armor plates to protect people and machines from bullets and shrapnel (Fig. 3 and Fig. 4), for protection against neutron radiation in nuclear power plants as well as in nuclear therapy of tumours.

Other possible applications will use the large capacity for neutron absorption by the investigated CMC- composites. The cross-sections of neutron absorption are as follows: boron carbide –  $1,98.10^{-2}$  barn, tungsten boride ( $W_2B_5$ ) –  $2,14.10^{-1}$  barn, the proposed CMC material  $B_4C + W_2B_5 - 3,18.10^{-1}$  barn. The latter has been successfully tested in the nuclear power plant in Kozloduy, Bulgaria for 14 months.

#### 3.2 Ternary (Ti,W)B<sub>2</sub> boride in CMC-composite materials TiB<sub>2</sub>-WC-Co

The milled TiB<sub>2</sub>-WC powders containing up to 1 wt. % cobalt are sintered in order to obtain two-phase cermets, i.e. to avoid crystallization of the brittle ternary phases WCoB and W<sub>2</sub>CoB<sub>2</sub>. The ternary phases were found in sintered samples which are obtained from initial

mixtures containing 2 to 10 wt. % Co. The densification of the alloys during the sintering began above 1100 °C. Increasing the temperature, the decomposition of WC causes formation of facets on the grain surfaces. During the isothermal sintering above 1700 °C to 1850 °C,  $\beta$ -WB and (Ti,W)B<sub>2</sub> solid solutions were precipitated on the TiB<sub>2</sub> nuclei. The microstructure of the initial powder TiB<sub>2</sub> +TiO<sub>2</sub>+ 18.64WC + 1Co is characterized by homogeneous distribution of fine TiB<sub>2</sub> grains (4.4 µm). The presence of the (Ti,W)B<sub>2</sub> -phase seems to be more pronounced now as the latter is not restricted to the periphery of TiB<sub>2</sub> (the Koch-Light sample) entire grains of it being observed (Fig. 5). Some of the boride crystals have partially lost their boron through the eutectic Co-WCoB film (TiB<sub>2</sub>: a=3.018; c=3.209Å). The eutectic built up seems uniformly distributed remaining all but invisible with a thickness of less than 0.4 µm. The size of the pores is 1-3 µm.



Fig. 3. Protective ceramic equipment



Fig. 4. Composite boroncarbide ceramic plates on armored vehicle (Company Rafael - Israel)



Fig. 5. The microstructure of TiB<sub>2</sub>- WB – (Ti,W)B<sub>2</sub> composite; x 1600

The mechanical properties of the  $TiB_2$ -WB-Co composite materials under study have exhibited a very high hardness combined with a high strength.

Small amounts of the binding metal (cobalt – 1%) considerably decrease the sintering temperature. This is due to reactions which yield eutectics. The same binding metal allows densification of the alloys during sintering without pressure application.

As a general rule, introducing small amounts of the binding metal (1 wt-% with colalt) in  $TiB_2$ -WB system considerably decreases the sintering temperature considerably without any resort to pressure while yielding a very high hardness 50.6 GPa (92.3 HRA) (Fig.6 and Tabl.4) of the ternary phase (Ti,W)B<sub>2</sub>.



Fig. 6. Metal-like hardness pyramid with the new superhard ternary phases CoWB and  $(Ti,W)B_2$ 

The difference in hardness between of the two composite materials (Tabl.4) seems to come from more ternary  $(Ti,W)B_2$  being present in the initial powder  $TiB_2$  (PIII), due to contamination of the latter with  $TiO_2$ .

Initial milled	Specific surface	ce Experimental	Relative	Hardness N	/licrohardness
powder[wt%]	area [m²/g]	density[g/cm <sup>3</sup> ]	density[%]	RockwellA	Hµ0.1 [GPa]
TiB <sub>2</sub> (Koch-Light)	2.58	5.22	98.30	91.3	33.83
+ 20.25WC+0.75Co					
TiB <sub>2</sub> (PIII)+18.64WC	3.53	5.09	98.80	92.3	50.6
+ 1 Co+ 3.9TiO2					
		1			

Table 4. Properties of TiB<sub>2</sub>-WB-Co sintered in Ar at 1850 °C, 120 min

#### 3.3 Ternary WCoB boride in MMC-composite materials WC(TiC)-Co

For the sintered ternary polycrystalline tungsten-cobalt boride WCoB chemical analysis gave: W-  $66.3\pm 6$  + Co-  $24.7\pm 2$  + B-  $6\pm 3$  wt.% while X-ray studies showed that it is orthorhombic WCoB (ordered PbCl<sub>2</sub> structure, Type E-TiNiSi), a=5.724Å; b=3.240Å; c=6.632Å.

Several large WCoB crystals (dimensions of 1x1.5x3 mm) are shown in Fig.7-1.

The dependence of the compound hardness on the indentation load was plotted. In this way, the straight line of Meyer and the line of microhardness (Fig.7-2) were obtained. Obviously, within the range of indentor loads used (below 100 gf), the microhardness gradually decreased with increasing loading. Hence, the microhardness value for WCoB depends on the loading. This correlation is due mainly to plastic deformation, which was observed in our case at a low indentation load (less than 50 gf).

The  $\{001\}$  and  $\{100\}$  faces of WCoB showed a reticular anisotropy of microhardness in directions *c* and *b*.

The hardness of the ternary compound,  $H\mu 50 = 4650 \pm 230$  kgf.mm<sup>-2</sup>, is associated mainly with the type and the distribution of bonds in it and corresponds to the usual high hardness of the transition metal borides. Gilman (Gilman, 1970) is of the opinion that this hardness is due for the most part to overlapping of themetal-nonmetal bonds during the shearing of the dislocations. Within the framework of this model  $H\mu$ =-2 $\Delta$ H<sub>f</sub>/V<sub>m</sub>, where  $\Delta$ H<sub>f</sub> denotes the heat of formation of borides (kcal mol<sup>-1</sup>) and V<sub>m</sub> is the molecular volume (cm<sup>3</sup>).Thereupon, after converting 4650 kgf.mm<sup>-2</sup> into 5.45 kcal.cm<sup>-3</sup> (the value of H $\mu$ ) and 30.758 Å<sup>3</sup> into 18.5 cm<sup>3</sup>.mol<sup>-1</sup> (the value of V<sub>m</sub>), one obtains for WCoB  $\Delta$ H<sub>f</sub> = 100.5 kcal mol<sup>-1</sup>. Comparison of the heat of formation of WCoB with that of TiB<sub>2</sub> (77.4 kcal mol<sup>-1</sup>) confirms the increase in hardness of the compound with rising heat of formation.



Fig. 7-1. Ternary polycristals WCoB

Fig. 7-2. Dependence of Hµ on the indentor loading for WCoB

Formation of WCoB upon the WC(TiC)-Co matrix during thermo-chemical treatment could result from interaction of the type WC + TiB<sub>2</sub> + Co  $\rightarrow$  WCoB + TiC + CoB.

TiB<sub>2</sub> most probably participates in the coating formation as a donor of boron which diffuses into the samples and interacts with the cobalt and the tungsten carbide. A similar mechanism is proposed in order to explain the formation of boride coatings on iron and steel during thermo-chemical treatment with other boronizing agents (boron and B<sub>4</sub>C). The concentration of WCoB in the diffusion layer depends on the composition of the initial alloys and the experimental conditions of thermal treatment 950-1100 °C (Fig.8).



Fig. 8. The phase composition us depth through the diffusion layer formed on a WC-Co:  $\Delta$ -950 °C; O-1000 °C; x-1050 °C;  $\Box$ -1100 °C; --WCoB; -.-WC

The presence of the ternary orthorhombic compound WCoB in the surface layer of carbide alloys enhances their wear resistance in metal-cutting. The enhancement seems to follow from the increase in their hardness (Fig. 9. The difference in phase composition of the diffusion layers obtained using the two powders affects the layer hardness. The use of Borozar-HM (base TiB<sub>2</sub>) leads to the formation of WCoB only in the diffusion layer, whereas in the case of B<sub>4</sub>C the ternary boride W<sub>2</sub>CoB<sub>2</sub>, which is richer in boron, prevails. This can be explained on the basis of the Co-W-B phase diagram (Stadelmaier, 1967) taking into account the boron content (i.e. the transfer of boron from boron carbide). The termo-chemical treatment with Borozar-HM of the cutting alloy results in the formation on its surface of superhard layers whose hardness exceeds that of the layers obtained with B<sub>4</sub>C. The maximum hardness value 23.4 GPa was found for layer with Borozar-HM at 1200 °C, which is assigned to the formation at this temperature of a single-phase ternary WCoB layer.

Ternary borides are useful in drawing plain wire and metalworking where a superhard layer of them is formed by diffusion on the main material consisting of carbide – cobalt alloys WC (TiC) – Co.

Layers of this kind improve the performance of nozzles, turning-lathes and other devices used in drawing and cutting of metal articles such as wire, rods, pipes, plates (Fig.10).



Fig. 9. Dependence of the boride layer hardness on the temperature of matrix (K10, WC-Co-10%) treatment with Borozar-HM (TiB<sub>2</sub>) and B<sub>4</sub>C



Fig. 10. Comparative diagram (VB) of the wear in steel working of various types of coated cutting tools:  $\Box$  – WCoB+ TiC-Al<sub>2</sub>O<sub>3</sub> deposited on Sm 336 plate (Gabrovo, Bulgaria); X- TiC-Al<sub>2</sub>O<sub>3</sub> deposited on Cp 1 –V04 (Hertel, Germany); O- TiC-Al<sub>2</sub>O<sub>3</sub>-TiN deposited on GC 415 plate (Coromant, Sweden) ;  $\Delta$ - WCoB + TiC-Al<sub>2</sub>O<sub>3</sub> on Sm334 plate (Gabrovo, Bulgaria)

#### 3.4 Ternary (Fe,Zr)<sub>2</sub>B boride in MMC- composite material (Fe-C matrix)

The thermochemical treatment with  $ZrB_2$  ( $CrB_2$ ,  $TiB_2$ ) and activators on steels yields a diffusion layer with a thickness between 50 µm and 1 mm. Our investigation of  $ZrB_2$  (KBF<sub>4</sub> having been used as a activator) were carried out over the temperature range 1000-1100 °C for 4 h. The diffusion layer obtained at 1050 °C was of a two-zone nature: zone "A" and the underlying (in the direction of the sample centre) zone "B" (Fig .11(A) and Fig.11 (B), respectively). The photograph of the polished section in Fig.11(A) shows that zone "b" consist of needle-like crystals characteristic for the gas transport of boron. Zone "B", which is situated above layer b-d, has a different structure with small grain size and a very high microhardness (3575-2438 kg.mm<sup>-2</sup> (Fig. 11(B)).



Fig. 11. The two-zone diffusion layer on Armco-iron treated with  $ZrB_2$  and  $KBF_4(3wt.\%)$ : A - boronized zone (Fe<sub>2</sub>B) ; B - upper superhard (Fe<sub>2</sub>Zr)<sub>2</sub>B - ZrO<sub>2</sub> zone; x 600

For the zones below the zirconium a greater microhardness (as compared with that of "pure" Fe<sub>2</sub>B) has been detected by microprobe analysis. It might be due to replacement of some iron atoms of the Fe<sub>2</sub>B-phase by zirconium ones. This is also indicated by the change in lattice parameters of the underlying iron boride.

The ternary boride (Fe,Zr)<sub>2</sub>B enhances the wear- and heat resistance of the steels coated.

With boron-chromizing, the ternary boride (Fe,Cr)<sub>2</sub>B imparts additionally augmented resistance to corrosion (Fig.12).

The microstructure of the boron-chromium layer obtained on steel C45 with Zahobor paste is presented in Fig.13. X-ray microanalysis has shown that black grains of chromium- iron boride (Fe,Cr)<sub>2</sub>B contain 14-50 wt.%Cr.

Boron-metalizing with paste during hardening of steel is a new process resulting in a surface layer with a high wear resistance and stability with respect to oxidation and corrosion, minimum time and cost losses needed. The proces carried out with pastes for boronization and boronmetalization leads to products of higher hardness, i.e. durability (twice as long as in cases of nitration and cementation), a higher stability towards high temperatures and a higher corrosion resistance.



Fig. 12. Corrosion resistance in 10%H<sub>2</sub>SO<sub>4</sub> of boron-chromium (Zahobor paste MD10, MD30, MD50); boronizing with Ekabor-Paste (Eka-Germany); subsequently boronized electrolyte chromium (B/Cr); boro-aluminizing (B/Al) layers deposited on C45 and chrom-nickel steel (X18H9T)



Fig. 13. Microstructure of boron-chromium layer deposited on C45 steel by Zahobor paste (MD30); X600

Table 5 shows the results of x-ray phase analysis of the layers as well as data on their thickness and microhardness. Obviously, the highest hardness corresponds to borchromium layer obtained using Zahobor (MD30).

Paste	Phase composition	Thickness, µm	Нµ 30, GPa	Нµ50, GPa
Zahobor – Bulgaria	CrB, (Fe,Cr) <sub>2</sub> B	150	20.4	18.6
Ekabor- Germany	Fe <sub>2</sub> B	160	15.6	15

Table 5. X-ray phase analysis, thickness and microhardness of the diffusion layers with pastes on C45

On the basis of these results it may be inferred that doping of the layers with chromium, which leads to the appearance of  $(Fe,Cr)_2B$  phase increases significantly their microhardness. The phase composition of the diffusion layers determines their microhardness, i.e. their wear resistance. Hence, we may predict an even higher wear resistance of our boron-chromium layers. Indeed, the results on their wear resistance correlate with those on their microhardness (Fig.14). The most stable Zahobor (MD30) layer is more than twice as stable as the boronized one according to the fifty-hours-test.



Fig. 14. Wear resistance of the boron-chrominized (5-MD30), boronized (4-Ekabor), boronaluminized (2- B/Al), electrodeposited chromium (3) layers and base chromium-nickel steel

The positive effect from boron-chromizing is illustrated on Fig.15 and Fig.16 for landholder's steel instruments treated with the "Zahobor"-paste and used in the Netherlands.

The paste is suitable for treatment of steel machine tools and parts of large dimensions, e.g. metal stamps, hammering press matrices, guides, rolls for wiredrawing, steel pulleys, steel belt conveyor rolls, ploughshares, tracks, extruder screws and other similar machine parts, subjected to wear and corrosion. Machine tools, instruments and parts with larger design tolerances as regards cross-section dimensions are especially suitable for boron-metalizing.



Fig. 15. Boronized parts have been used for 6 ha



Fig. 16. The knifes "Tortella" - Italy boronized with paste "ZAHOBOR"

#### 4. Conclusion

Sintering without applying a pressure is a new trend in the field of superhard boride materials. The present paper deals with the microhardness of some boride CMC and MMC composite materials ( $B_{12}C_3 + Me_xB_y$ ,  $TiB_2 + WB + Co$ , WCoB + WC-Co,  $(Fe,Me)_2B + Fe-C)$  obtained in this way.

It is shown that the transition metal dissolves in the crystal lattice of  $B_{12}C_3$  building up new superhard ternary borides  $B_{12 - n}C_3Me_n$  with a hardness of 50 - 77 GPa. The latter values exceed considerably the hardness of pure  $B_{12}C_3$  and coincide with those for cubic-BN and some synthetic diamonds of the type "CB" or "Carbonado ACPK".

Another example is the composite material  $TiB_2$  - WB, where the surface of its grains proves enriched of tungsten to  $(Ti,W)B_2$ , this leading to an extremely high value of 50.6 GPa.

The hardness of the ternary boride WCoB amounts to 38 - 43 GPa depending on the indentor loading. Presipitate in the form of a boronizing coating upon the carbide cutting tools, WCoB- phase increase their tool-life.

Thermochemical treatment of steels with  $ZrB_2$  (TiB<sub>2</sub> or CrB<sub>2</sub>) leeds to form a diffusion layer with superhard ternary phases (Fe,Me)<sub>2</sub>B. This phases improve the wear- and corrosion resistance of the steels.

In comparison with other metal- like refractory compounds, the superhardness of the materials studied points to new applications in industry. In this field of view, include my own researches, is make an attempt to unification of the scientific results and to show the perspectives about using of the obtaining superhard ternary composite (CMC and MMC) materials.

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Composite materials, often shortened to composites, are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure. The aim of this book is to provide comprehensive reference and text on composite materials and structures. This book will cover aspects of design, production, manufacturing, exploitation and maintenance of composite materials. The scope of the book covers scientific, technological and practical concepts concerning research, development and realization of composites.

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