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Improvement of Boron Carbide Mechanical Properties in B_4C-TiB_2 and B_4C-ZrB_2 Systems

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ABSTRACT

Experimental works have been conducted the objective of which was to improve mechanical properties of boron carbide by introduction of doping elements into the system. Titanium and Zirconium were selected as doping elements, which were introduced into the system in the form of TiB_2 and ZrB_2. Four types of boron carbide-titanium and zirconium mixture with various titanium and zirconium diboride content were used in experiments. Optimal process parameters, as well as doping elements concentration, necessary to provide required high mechanical parameters in the composite were defined.

Keywords: Boron Carbide; Titanium Diboride; Hot Pressing; Composite; Doping; Zirconium Diboride

1. Introduction

Due to outstanding features of its basic component—oron, boron carbide (B_4C), finds wide application in various fields, and in particular, thanks to its unique nuclear features it is widely used in control rods of nuclear power plants, as neutron absorbing material, as hard material (9.35 by Moos scale) it finds application in abrasive and finishing materials [1-3], in nozzles of sand-blasting and gas-jet facilities. Boron carbide preserves its hardness at high temperatures, which enables to use it at temperatures up to 2000˚C [4,5].

2. Main Part

However, despite its outstanding features, considered above, boron carbide, due to its fragility cannot be used as a constructive material. It is explained by its crystal structure (rhombohedral, comprising three B_4C molecules [6,7] or hexagonal, comprising nine B_4C molecules [5,8-14]) (see **Figure 1**) and strength of covalent bonds in the crystal lattice [4,15]. Besides low impact elasticity, boron carbide is characterized with low mechanical bending strength.

One of the ways to increase impact elasticity is to dope boron carbide with metal elements, which provides the growth of free electron fraction in boron carbide. In this work impact elasticity growth was achieved by introduction of titanium and zirconium diborides additives into B-C system.

3. Experimental

Samples of pure boron carbide as well as samples of containing titanium and zirconium diborides were prepared. Boron carbide powder produced by German company H.C.Stark was used in experiment. Boron carbide powder specifications are presented in **Table 1**.

Quantities of powders were selected in such way that

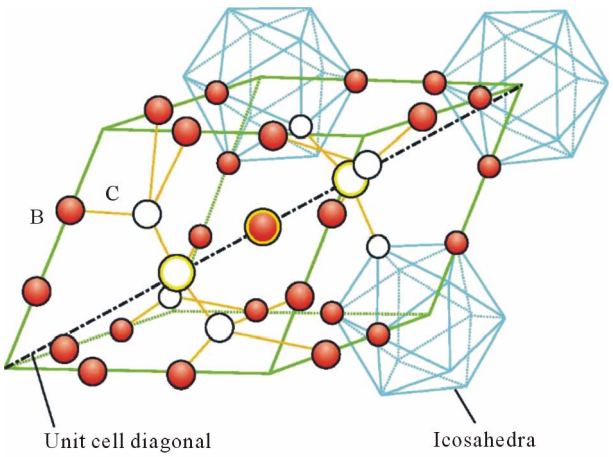


Figure 1. Crystal structure of boron carbide.

doping metal weight portion in the composite made 1%, 3% and 5% which is equivalent to 1.45, 4.35 and 7.25 wt% of titanium diboride and 2.35, 7.05 and 11.75 wt% of zirconium diboride. Fine-grained graphite, type APB, with inner surface covered with graphite foil "Sigraflex" was used for press moulds. The powders were pressed by hot pressing method in vacuum at 2150˚C - 2200˚C temperature and 20 - 25 MPa pressure, pressing duration at final temperature was 5 - 8 min.

In order to determine each property, the separate composition cylinders with dimensions Ø70 × 5.7 mm were pressed and various size samples were cut out to measure water absorption, open porosity, density, impact elasticity, thermal expansion coefficient, compressive and bending resistance. Samples surfaces were processed with fine grain diamond grinding wheel.

Density of the samples made about 96% of theoretical value. X-ray-structural analysis was done using DRON-3 diffractometer. X-ray pattern clearly shows boron carbide and titanium diboride sharply drawn peaks. **Figure 2** presents diffraction patterns of boron carbide and titanium diboride, while **Figures 3** and **4** present X-ray patterns of boron carbide doped with titanium and zirconium, respectively.

Diffraction patters prove that chemical interaction of boron carbide and doping compound does not give some new phase. The material is two phased which is also proved with electron microscope research.

Figures 5 and **6** present the results of electron microscope research. Test was performed on scanning microscope SEM Cam Scan. The surfaces are not but the figures clearly show that material consists of two phases—

Table 1. Boron carbide powder specifications.

Boron carbide	Grade HP
B:C Ratio	3.8 - 3.9
Boron content, wt%	77.1
C, wt%	21.8 min
N, wt%	0.7 max
O, wt%	1 max
Fe, wt%	0.05 max
Si, wt%	0.15 max
Al, wt%	0.05 max
Other	0.5
Specific Surface, m^2/g	10
Green Density, g/cm^3	1.5
PSD 90%, um	6.2
PSD 50%, um	2.9
PSD 10%, um	0.9

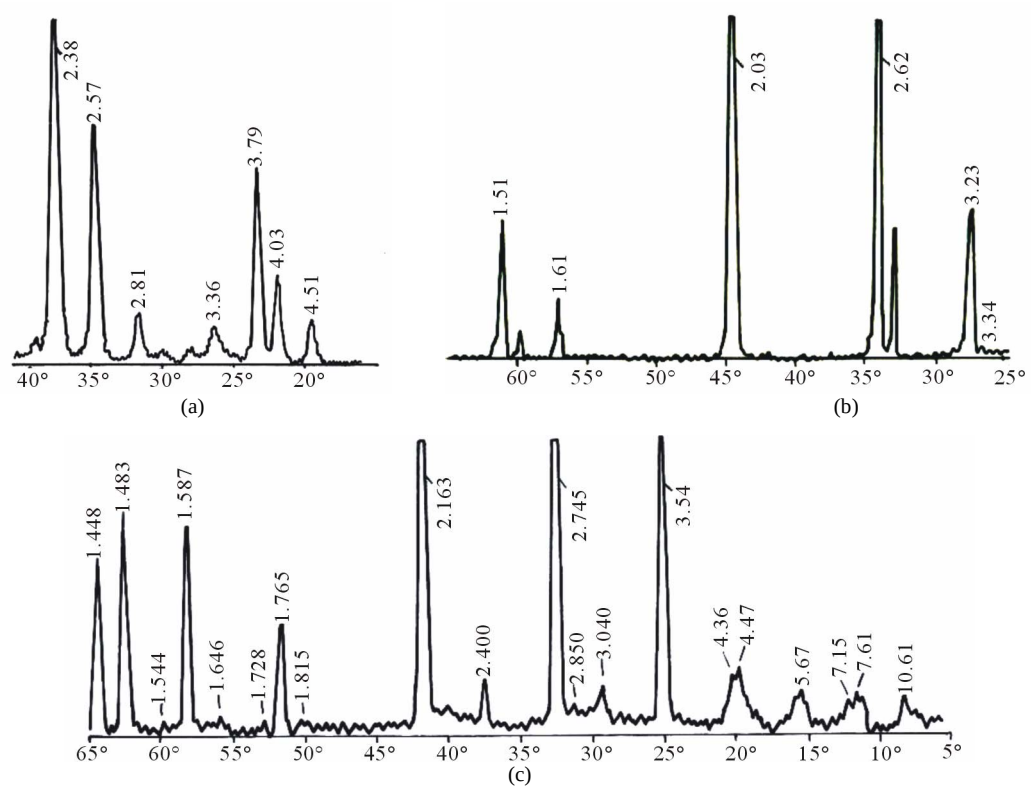


Figure 2. X-ray of (a) boron carbide, (b) titanium diboride and (c) zirconium diboride.

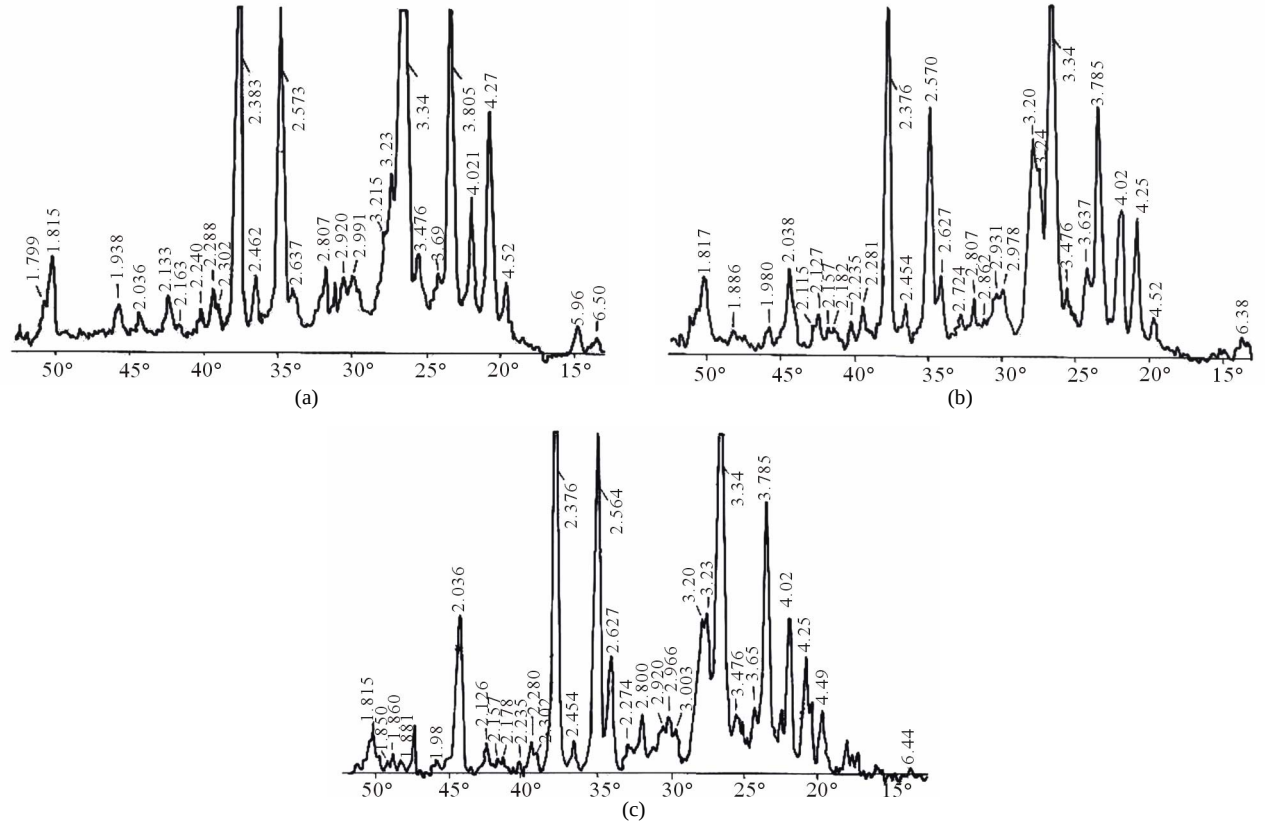


Figure 3. X-ray of boron carbide doped with titanium diboride: (a) 1% Ti; (b) 3% Ti; (c) 5% Ti.

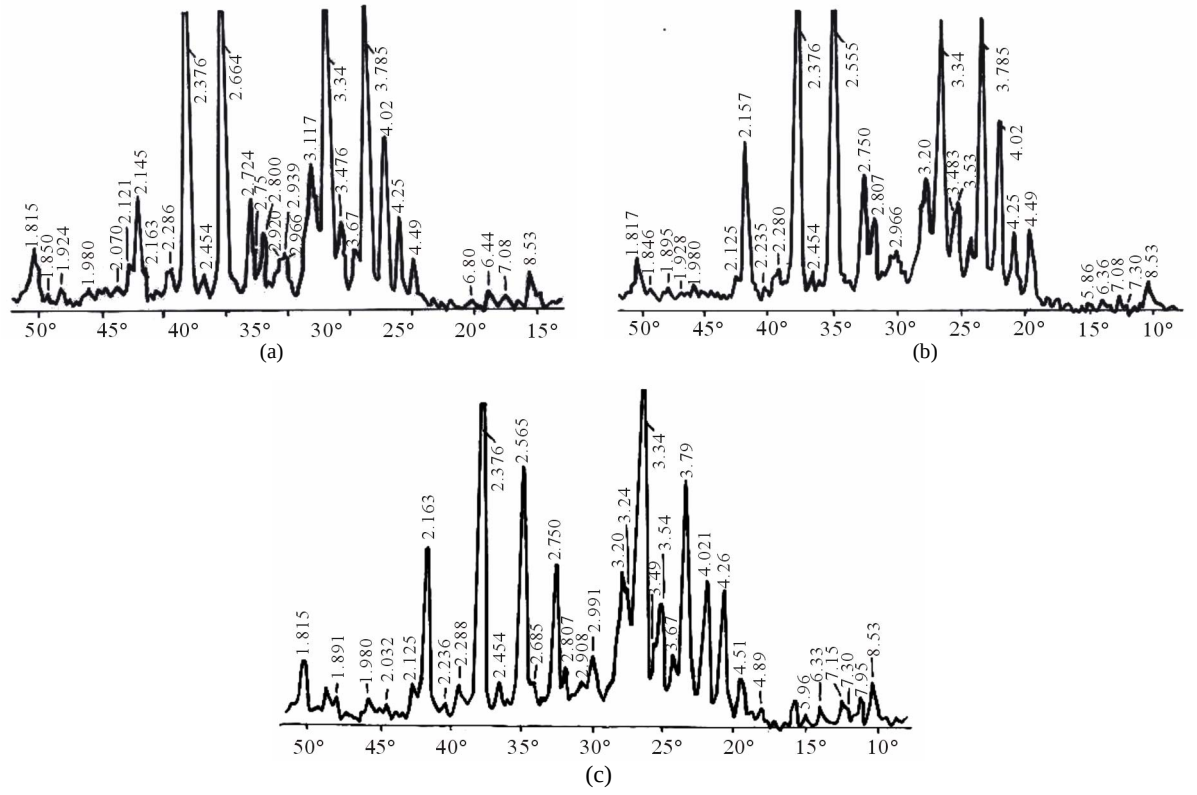
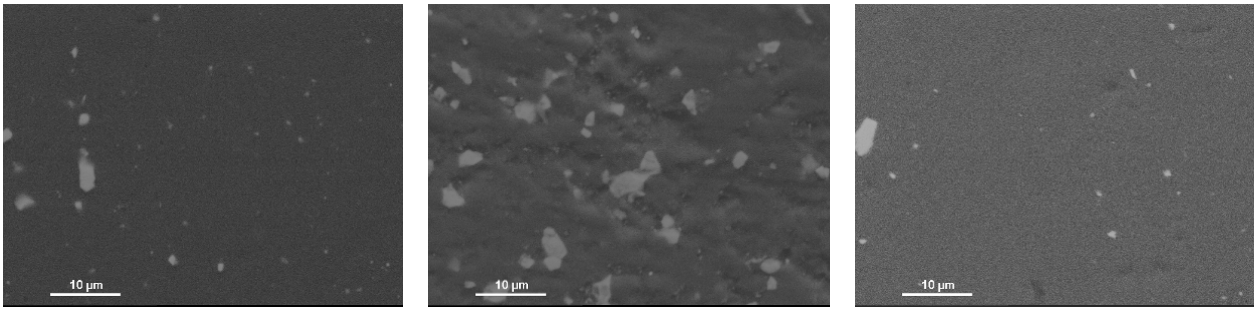


Figure 4. X-ray of boron carbide doped with zirconium diboride: (a) 1% Zr; (b) 3% Zr; (c) 5% Zr.

boron carbide (basic phase) and doping additive. The latter is located as small inclusions at the boundaries of boron carbide grains. The patterns clearly show distinct phase boundaries and strong bonding between phases; around doping element grains the decrease of pores is observed.

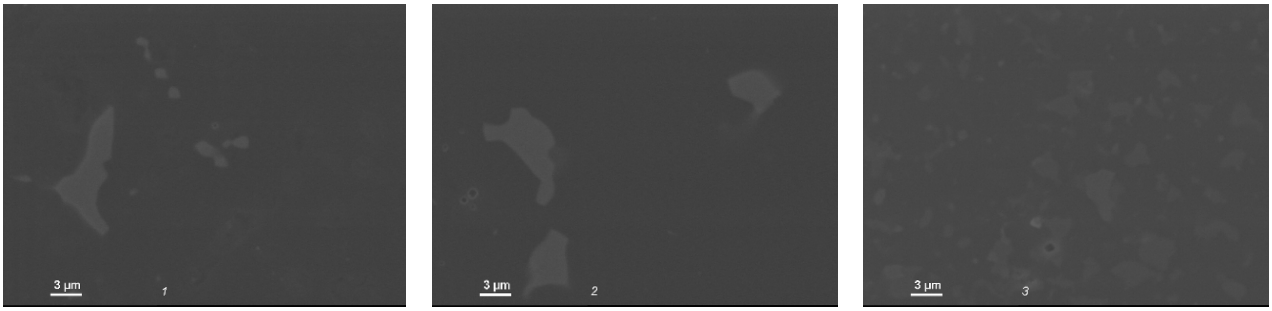
Besides, the samples were tested for bending strength and compressive resistance, their thermal expansion coefficients, hardness, microhardness and impact elasticity were measured. The obtained results are presented in **Table 2**.

It is seen from **Table 2** that when doped with titanium and zirconium diborides, mechanical properties of boron carbide increased. Especially remarkable is the increase of mechanical compressive strength and impact elasticity. The increase of impact elasticity is the main purpose of



(a) (b) (c)

Figure 5. Electron microscope patterns in B-C-Ti system; 2000-fold magnification: (a) Ti—1 wt%; (b) Ti—3 wt%; (c) Ti—5 wt%.



(a) (b) (c)

Figure 6. Electron microscope patterns of B-C-Zr system; 3000-fold magnification: (a) Zr—1 wt%; (b) Zr—3 wt%; (c) Zr—5 wt%.

Table 2. The results of samples testing.

Specification	B_4C	B-C-T, 1% Ti	B-C-T, 3% Ti	B-C-T, 5% Ti	B-C-Zr, 1% Zr	B-C-Zr, 3% Zr	B-C-Zr, 5% Zr
Water absorption, %	1.8	0.07	0.07	0.09	0.25	0.08	0.09
Porosity, %	10	0	0	0	0	0.27	0.27
Density, g/cm^3	2.2	2.58	2.65	2.65	2.61	2.61	2.67
Thermal expansion coefficient, 1/grad.10^{-6} (800˚C)	4.90	3.75	4.53	4.55	4.80	4.75	4.78
Flexural Strength, MPa	221	316	275	357	272	197	221
Compressive strength, MPa	400	-	791	-	969	657	785
Hardness, HRA	89	-	97.5	-	-	-	-
Hardness HV, GPa	28.0	-	-	-	30.7	33.1	31.0
Microhardness HV, (0.05 kg), kg/mm^2 (0.5 N)	2646.7	-	-	-	2902.7	3130.7	2926.4
Microhardness HV, (0.02 kg), kg/mm^2 (0.2 N)	4570	-	5120	-	-	-	-
Young Modulus, GPa	304.1	-	-	-	184.2	211.6	395.7
Impact elasticity, kJ/m^2	4.33	-	7.11	-	11.33	7.33	6.81

the work. The mentioned phenomenon is presumably conditioned with the increase of free electrons' share in boron carbide which is caused with metal solubility increase. The latter process provides the increase of elasticity preserving covalent type bonds. Only in such a case may high hardness be preserved which is clearly seen in the Table.

Figure 7 presents in diagram form the conditions and results of hardness test by Vikers method of boron carbide doped with zirconium diboride (3% Zn), while **Figure 8** presents optical microscope patterns of the same sample **(b)** and boron carbide **(a)** surfaces after hardness testing. As shown in **Figure 7** under 0.5 N loading indenter is implanted in material for 1.35 mcm. Test continued for 27 sec. In this case imprint form is clear, with well-defined edges (**Figure 8(b)**), cracks are not observed, accordingly, there happens no energy dissipation [16,17]. Here is noticed elastic property of material (**Table 2**) to endure loading so that not generate cracks and not turn loading energy into dissipation phenomena. The unalloyed boron carbide pressed with the same technological mode at 2150˚C is characterized with more porosity than doped one (**Figure 8(a)**). The imprint shows lateral cracks in right upper and lower corners. In spite of equal loading (0.5 N) the imprint form is not clear compared to the sample doped with zirconium diboride. Energy dissipation is explicit which decreased to some extent the sharpness of imprint contours.

Figure 9 presents polished and contaminated surface **(a)** of boron carbide sample doped with zirconium diboride (3% Zr) and the same sample after testing for microhardness **(b)**. The sample was contaminated with 0% water solution of $NaNO_3$ for 15 seconds.

The figures show that matrix as well as second phase grain dimension is of micron size which is one of the preconditions of high mechanical strength. Zirconium diboride (white grains) is equally apportioned in matrix which creates dispersive strengthened composite material. This enables significant improvement of ceramic composite decomposition elasticity (Kic), also of strength (**Table 2**) and wear resistance.

In large grains (35 - 40 mcm, **Figure 9(b)**) on the whole diameter of the imprint the cracks appear. In small

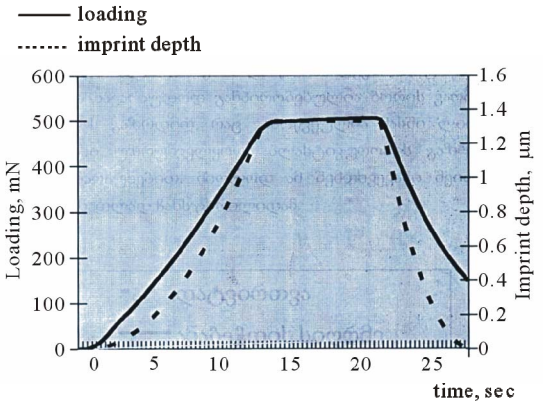
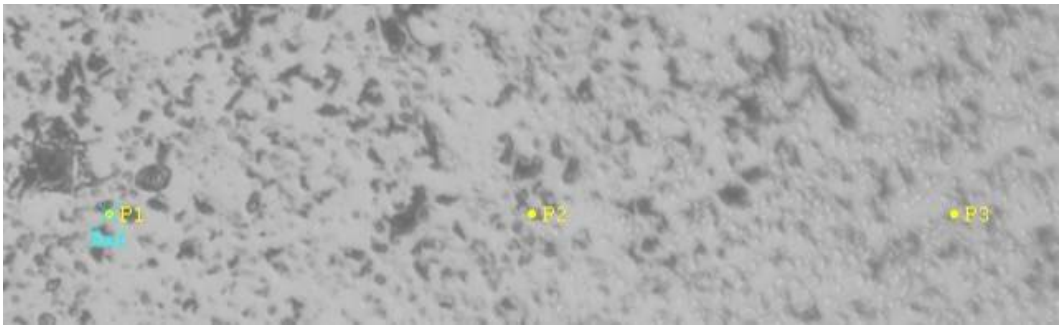
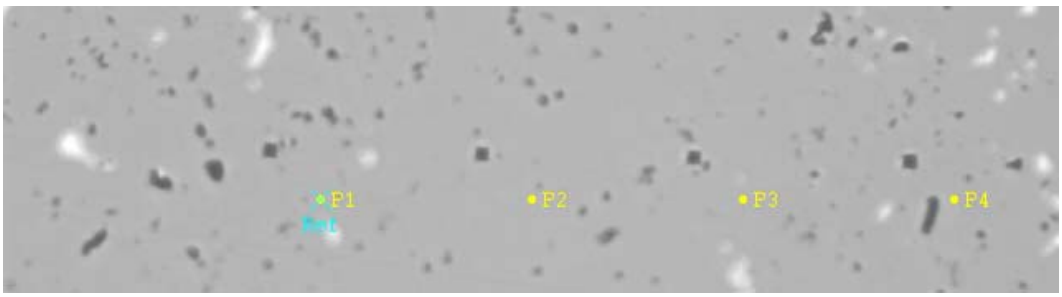


Figure 7. Time ratio of loading and imprint depth (3% Zr).

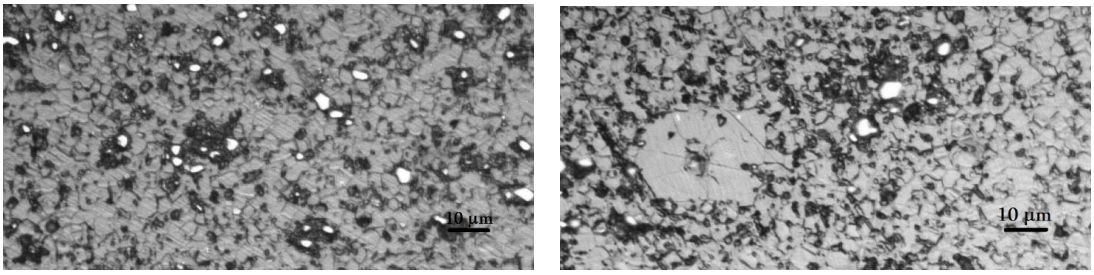


(a)



(b)

Figure 8. Optical microscope patters of unalloyed boron carbide and zirconium diboride doped (3% Zr) boron carbide after testing for hardness. Annealing temperature was 2150˚C.



(a) (b)

Figure 9. (a) Polished and contaminated surface of boron carbide sample doped with Zirconium diboride (3% Zr); (b) The same sample after testing for microhardness.

grains (2 - 4 mcm) cracks are not observed. The figure shows that the second phase is apportioned on matrix grain boundary, as well as, in grain (in large grain). At the same time around zirconium diboride inclusions cracks are not observed or crack avoids the inclusion which indicates that at doping the grain brittleness also decreases.

4. Conclusions

Composites B_4C-TiB_2 and B_4C-ZrB_2 with improved parameters are obtained. The above composites can be used when measuring refractory material hardness at temperatures up to 2000˚C. Besides, possibility of its application in nuclear engineering, in abrasive materials, etc. also extends.

Simultaneous increase of impact elasticity and hardness parameters provides important possibility to use this material as construction ceramics.

REFERENCES

[1] A. Sarukhanishvili, T. Cheishvili and Z. Kovziridze, "Theoretical Fundamentals of Composite Materials Receiving," Tbilisi, 2003, p. 170.

[2] P. G. Karandikar, E. Evans, S. Wong and M. K. Aghajanian, "A Review of Ceramics for Armor Applicationism," *Advances in Ceramic Armor IV Ceramic Engineering and Science Proceedins*, Vol. 29, No. 6, 2008, pp. 163-174.

[3] J. G. Tao, H. Y. Jinb, Z. H. Jina, J. F. Yanga and G. J. Qiaoa, "An Investigation of the Mechanical Property and Thermal Shock Behavior of Machinable B4c/Bn Ceramic Composites," *Journal of Ceramic Proceeding Research*, Vol. 10, No. 1, 2009, pp. 113-116.

[4] V. V. Jemilinski, M. C. Kovalchenko and G. N. Makarenko, "Materials of Indenters for Measuring Hardness at High Temperatures," *Powder Metallurgy*, Vol. 12, No. 2, 1973, pp. 168-170.

[5] Y. Paderno, A. B. Lyachshenko, V. N. Paderno, V. B. Filipov and A. N. Martinenko, "Composite Materials on the Basis of Eutectics of B_4C-$Me^{V-VI}B2$ System," *III International Conference, Works of Conference*, Kiev, 13-17 September, 2004, pp. 449-450.

[6] F. Mauri, N. Vast and C. J. Pickard, "Atomic Structure of Icosahedral B4C Boron Carbide from a First Principles Analysis of NMR Spectra," *Physical Review Letters*, Vol. 87, No. 8, 2001, Article ID: 085506. doi:10.1103/PhysRevLett.87.085506

[7] V. D. Risovani, A. V. Zavarov, E. P. Klyuchkov and T. V. Guseva, "Boron in Nuclear Technique," State Scientific Center of Russian Federation, Scientific Research Institute of Nuclear Reactors, Dimitrovgrad, 2003, pp. 30-88.

[8] G. V. Samsonov, L. Y. Markovski, A. F. Zhigach and M. U. Valyashko, "Boron, Its Compounds and Alloys," Publisher of the Academy of Sciences of the Ukrainian SSR, Kiev, 1961, pp.158-194.

[9] A. A. Kurakevich, "Superhard Phases of Simple Materials and Double Compounds of B-C-N-O System: From Diamonds to Last Results," Superhard Materials No. 3, 2009, ISSN 0203-3119.

[10] R. Lazzari, N. Vast, J. M. Besson, S. Baroni and A. Dal Corso, "Atomic Structure and Vibrational Properties of Icosahedral B4C Boron Carbide," *Physical Review Letters*, Vol. 83, No. 16, 1999, pp. 3230-3233. doi:10.1103/PhysRevLett.83.3230

[11] F. Mauri, N. Vast and C. J. Pickard, "Atomic Structure of Icosahedral B4C Boron Carbide from a First Principles Analysis of NMR Spectra," *Physical Review Letters*, Vol. 87, No. 8, 2001. pp. 085506-1-085506-4.

[12] F. Thevenot, "Boron Carbide—A Comprehensive Review," *Journal of the European Ceramic Society*, Vol. 4, No. 4, 1990, pp. 205-225. doi:10.1016/0955-2219(90)90048-K

[13] B. U. Arabei and V. V. Chekunov, "Absorbing Materials for Control of Nuclear Reactors," Atomizdat, Moscow, 1965, pp. 61-62.

[14] K, Silver, "Processing of Nano-Sized Boron Carbide Powder," M.Sc. Thesis, School of Materials Science and Engineering, Georgia Institute of Technology, 2007.

[15] "Refractory Borides and Silicides," Naukova Dumka, Kiev, 1977.

[16] G. Grathwohl, "Under Critical Growth of Cracks," In: W. Kollenberg, Ed., *Technical Ceramic*, Vulkan Publisher, Essen, pp. 54-58.

[17] R. Kieffer and F. Benesovsky, "Hartmetalle," Springer-Verlag, Wien, New York, 1971, pp. s.45-s.103.

