

# Multifunctional hetero-modulus composites in the $B_4C$ –BN–TiC–SiC–C system

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Received 14 January 2010; received in revised form 1 January 2011; accepted 14 January 2011

Available online 8 May 2011

## Abstract

Experiments have been carried out to develop multifunctional composites with improved properties and structure for use in air turbines, ballistic armor, cutting tools and atomic reactors. For optimization of the sintering process, microstructure improvement and increased plasticity we used MgO,  $Y_2O_3$  additives. The composites contained carbon fiber (S-242  $L_{av} = 370 \mu\text{m}$ ,  $d = 13 \mu\text{m}$ ) the carbide stoichiometric composition was maintained. Sintering was by hot pressing (25 MPa) in vacuum in the interval of 1800–1900 °C with dwell time 5–7 min. Structural analysis proved the homogeneous structure of the composite. The properties satisfy ISO standards. In summary,  $H_v = 24 \text{ GPa}$ , compressive strength = 2300 MPa, HRA = 94, bending strength = 500–600 MPa.

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## 1. Introduction

The purpose of the work was to prepare hetero-modulus composites of improved structure on the basis of carbides and borides in a multi-component system. The contribution of these materials can be multifunctional, for use in different fields, e.g., for work in high temperature units.

For the research a series of composites on the basis of boron carbide, boron nitride, silicon<sup>1–3</sup> and titanium carbides were chosen, the composition of which is given in Table 1. In order to intensify the process of densification a small addition of magnesium and yttrium oxides was introduced into the mixtures of composites; boron nitride was also used to increase ductility.<sup>4,5</sup> As well as possessing favorable mechanical properties these composites can satisfy the demanding requirements of operation in conditions of high temperature and thermal shock. Selection of the components in the composites was based on the fact that they represent mixtures with highly refractory and wear resistant properties. In addition, their thermodynamic characteristics suggested that there would be intensive interaction among the components of composites during hot pressing, particularly: during high temperature heating under pressure the substructures of boron carbide, boron nitride and titanium carbide would change

and the crystal lattice of a new substance, titanium diboride<sup>6</sup> of unique properties would be formed. In this case, the formation of titanium diboride and material compaction happens simultaneously, in a short time, which in our opinion would promote the formation of a fine grain structure of the composite and a respective increase of strength.

## 2. Experimental

Commercial powders of hexagonal boron nitride, boron carbide and SiC were used. These had BET specific surface areas of 1.7, 1.3 and 0.91 m<sup>2</sup>/g, respectively. The carbon source was carbon fiber – DONACARBO S “ASHLAND-SUEDCHEMIE-KERNFEST GMBH” production: S 242 brand, fiber diameter  $d = 13 \mu\text{m}$ , length  $l = 370 \mu\text{m}$ . Titanium carbide prepared by self-propagating high temperature synthesis<sup>3</sup> was used. Its chemical composition, in mass% was: C – bound 19.88, C – free 0.15, oxygen – 0.02. Titanium carbide was preliminarily milled in a vibro-mill, in alcohol medium. The specific surface of the received powder was 4–5 m<sup>2</sup>/g.

Each composition given in Table 1 was made up and ground together in a vibro-mill using an alcohol medium for 5–6 h. After evaporating the alcohol from the mixture it was hot pressed in graphite moulds. 25 MPa pressure was applied in vacuum at 1800–1900 °C with a 5–7 min dwell at the maximum temperature.

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Table 1  
Initial chemical composition of composite charges, mass%.

Index of composite	B <sub>4</sub> C	BN	TiC	SiC	Y <sub>2</sub> O <sub>3</sub>	MgO	C-fiber
K <sub>1</sub>	10	20	35	28	1.5	0.5	5
K <sub>2</sub>	–	20	30	43	1.5	0.5	5
K <sub>3</sub>	50	–	20	23	1.5	0.5	5
K <sub>4</sub>	20	10	35	28	1.5	0.5	5

The final compositions and microstructure of the hot pressed composites were investigated by X-ray diffraction and microscopy of polished sections. Standard methods were used to determine the following properties of the composites: density, thermal conductivity, coefficient of thermal expansion, Rockwell A and Vickers hardness, microhardness, compressive strength, bend strength and electrical resistivity.

### 3. Results and discussion

X-ray structural analysis of the densified samples was carried out (Fig. 1). For the K<sub>1</sub> and K<sub>2</sub> samples hot pressed at 1800 °C, X-ray analysis has not been done because of their very poor structure and mechanical properties. Simply boiling these samples in water prior to density measurement caused them partially to decay to powder. It was therefore decided to exclude them from further investigation.

A general conclusion of the XRD investigation is that TiB<sub>2</sub> was formed in all cases. More detailed conclusions are as follows.

At X-ray diffraction pattern for K<sub>1</sub> hot pressed at 1900 °C showed the following reflections. TiB<sub>2</sub>  $d_{hkl}$  – 3.23; 2.62; 2.03 (100); 1.612; 1.509 Å.  $\alpha$ -SiC,  $d_{hkl}$  – 2.62; 2.51; 2.353; 2.17; 1.538 (100) Å. C-carbon  $d_{hkl}$  – 3.37 (100); 2.133; 1.682 Å. B<sub>4</sub>C,  $d_{hkl}$  – 4.02; 2.573 Å. BN,  $d_{hkl}$  – 3.33 (100); 2.17; 1.817; 1.670 Å. Close inspection of the diffraction pattern shows that under the effect of titanium carbide and with the support of carbon, the boron carbide was almost completely consumed in the formation of titanium diboride; at the same time the carbon content in the mixture stayed unchanged because of its freeing from titanium carbide. The final boron carbide phase content in material was determined only as 1–2 mass %. As to boron nitride its content in the initial composition was 20 mass %; it reacts less with titanium carbide and its mass share in the product is mainly unchanged.

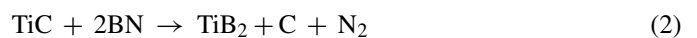
The X-ray diffraction pattern of the K<sub>2</sub> 1900 °C sample also showed TiB<sub>2</sub> phase formation and the following species. TiB<sub>2</sub>,  $d_{hkl}$  – 3.23; 2.62.2.033 (100); 1.612; 1.516 Å.  $\alpha$ -SiC,  $d_{hkl}$  – 2.61–2.62; 2.52; 2.17; 1.955; 1.539 (100) Å. TiC,  $d_{hkl}$  – 2.48; 2.170 (100) overlapped with  $\alpha$ -SiC; 2.145; 1.516 Å. C-carbon,  $d_{hkl}$  – 3.337 (100); 1.682; 1.54 Å. BN,  $d_{hkl}$  – 3.33 (100); 2.17; (coincided with  $\alpha$ -SiC); 1.955 (coincided with  $\alpha$ -SiC); 1.817 Å. B<sub>4</sub>C does not appear in the initial K<sub>2</sub> composition, therefore titanium carbide and carbon are acting on boron nitride resulting in the formation of well defined peaks of titanium diboride, which dominates the phase composition together with  $\alpha$ -SiC. The reflections of carbon are maintained here, too. The TiC and BN contents in the original are 30 and 20 mass %, respectively,

and because of the reaction between them, the TiB<sub>2</sub> formation in material has sharply decreased.

In contrast to K<sub>2</sub>, B<sub>4</sub>C was present in the initial K<sub>3</sub> content in great amounts. Here an interesting phenomenon is noticed. TiC has almost entirely decomposed the initial B<sub>4</sub>C of composition of 50 mass% with the formation of TiB<sub>2</sub>. The boron carbide phase is only weakly manifested in the X-ray diffraction pattern: B<sub>4</sub>C,  $d_{hkl}$  – 3.79; 2.57; 2.30; 1.82 Å. Titanium carbide has been completely spent in the process of titanium diboride formation. TiB<sub>2</sub> maximums here also prove its dominating phase content in the material: TiB<sub>2</sub>,  $d_{hkl}$  – 3.22; 2.62; 2.032 (100); 1.51 Å. Silicon carbide with sharply expressed reflexes is entirely maintained in composition. SiC,  $d_{hkl}$  – 2.63; 2.59; 2.52 (100); 2.36; 2.17; 1.54; 1.81 Å. Carbon phase content is not high in it which is conditioned with the composition. C,  $d_{hkl}$  – 3.363 (100); 3.348; 2.132; 2.036; 1.811, 1.675; 1.54 Å.

In K<sub>4</sub> the initial 20 mass% content of B<sub>4</sub>C was almost entirely used up in the formation of TiB<sub>2</sub>, whilst BN has been partially maintained: BN,  $d_{hkl}$  – 2.17; 1.816; 1.673 Å. TiB<sub>2</sub>,  $d_{hkl}$  – 3.23; 2.625; 2.030 (100); 1.612; 1.51 Å. SiC,  $d_{hkl}$  – 2.615; 2.520 (100); 2.370; 2.17; 1.67; 1.539 Å. C-carbon,  $d_{hkl}$  – 3.363 (100); 3.348; 2.127; 1.673; 1.539. B<sub>4</sub>C,  $d_{hkl}$  – 4.02; 3.77; 2.81; 2.563; 2.37; 2.02; 1.816; 1.505 Å.

During hot pressing of these materials the following chemical reactions may take place:



Energy-wise, if the initial composition contains B<sub>4</sub>C and BN simultaneously, Table 1, the chemical reaction proceeds according the first equation overall, but the TiC action, is liable to proceeds preferentially relative to B<sub>4</sub>C and then relative to BN.

In the case of compositions K<sub>2</sub> and K<sub>3</sub> chemical reaction proceeds according Schemes (2) and (3), respectively.

Comparison of micrographs in Fig. 2 with the X-ray analysis showed that the material consists of the following phases: silicon carbide (K<sub>1</sub>–K<sub>4</sub>), titanium diboride (K<sub>1</sub>–K<sub>4</sub>), titanium carbide (K<sub>2</sub>), boron carbide (K<sub>3</sub>, K<sub>4</sub>), boron nitride (K<sub>1</sub>, K<sub>4</sub>). As to grain dimensions the average dimension of silicon carbide is 10–12  $\mu\text{m}$ , with some individual grains being of 16–20  $\mu\text{m}$ . Such a great size of the grains is caused by the initial sizes of the grains of this component which were in the range 2–20  $\mu\text{m}$  and which resulted in low values for some of the mechanical characteristics. The main mass of titanium diboride grains is 2–3  $\mu\text{m}$ , with some individual grains 4–6  $\mu\text{m}$ , the titanium carbide grain

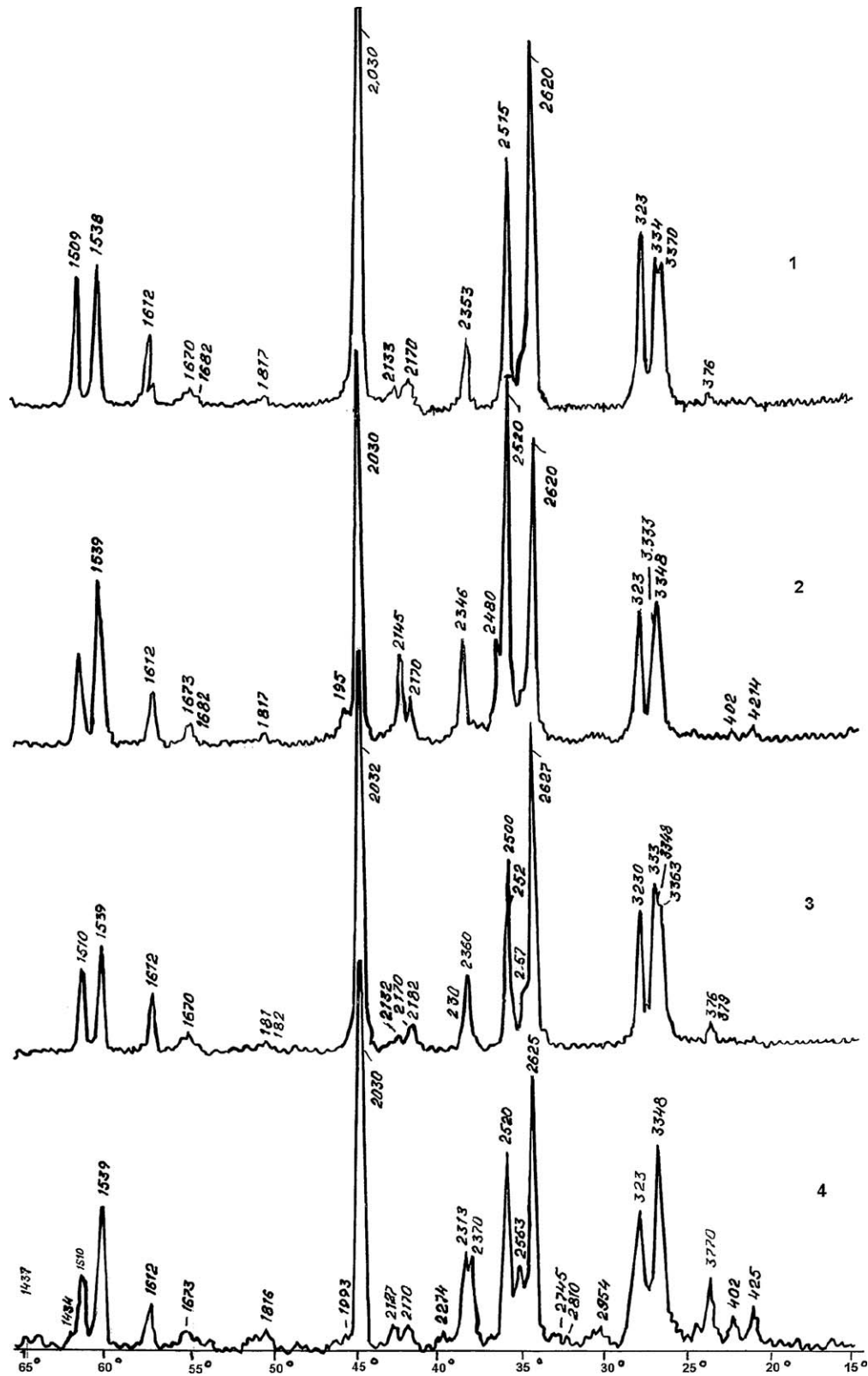
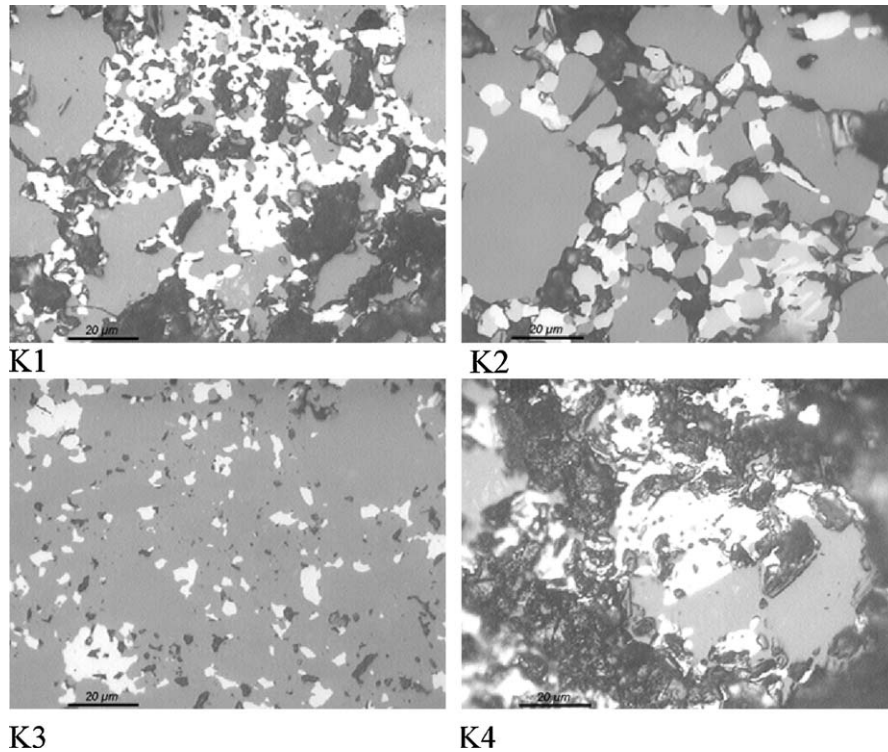


Fig. 1. X-ray diffraction patterns of hot pressed composites. (1) K<sub>1</sub> – 1900 °C; (2) K<sub>2</sub> – 1900 °C; (3) K<sub>3</sub> – 1800 °C; (4) K<sub>4</sub> – 1800 °C.

size is 2–4 μm, whilst boron carbide and boron nitride grain sizes do not exceed 3–4 μm.

The physical–mechanical properties of the materials have also been measured. The results are presented in Table 2.

The study of samples densified at 1800 °C showed that for the K<sub>1</sub> and K<sub>2</sub> composites this temperature was not enough, as mentioned above, this being indicated by significant porosity and low mechanical strength, respectively:  $W = 13.4$  and  $8.5\%$ ;

Fig. 2. Microstructure of composite materials K<sub>1</sub>–K<sub>4</sub>.Table 2  
Physical–mechanical characteristics of composites.

Index of composite	Density, $\rho$ (g/cm <sup>3</sup> )	Open porosity, $W$ (%)	Thermal conductivity, $\lambda$ (cal/cm deg s)	Coefficient of thermal expansion $\alpha \times 10^{-6}$ K	Hardness, HRA	Hardness, $H_v$	Micro-hardness (MPa)	$\sigma_{comp}$ (MPa)	$\sigma_{bend}$ (MPa)
K <sub>1</sub> 1900 °C	4.43	0	0.11	5.07	87.5	–	21,800	1594	214
K <sub>2</sub> 1900 °C	3.77	0	0.11	4.82	87.0	–	24,800	1801	192
K <sub>3</sub> 1800 °C	3.23	0	0.18	4.03	91.5	–	28,500	2135	427
K <sub>4</sub> 1800 °C	3.30	0	0.12	4.53	94.5	23.2	30,800	2340	577

$\sigma_{comp}$  = 176 MPa and 234 MPa. The K<sub>3</sub> and K<sub>4</sub> composites pressed at 1800 °C had zero porosity and the mechanical properties were high, too. Increasing the processing temperature to 1900 °C reduced the porosity of K<sub>1</sub> and K<sub>2</sub>; the mechanical properties were improved but, all the same, are low compared to those of K<sub>3</sub> and K<sub>4</sub> (Table 2). In our opinion, the high boron nitride content in K<sub>1</sub> and K<sub>2</sub> composites (20 mass %) requires a higher temperature for densification. The porosity of K<sub>3</sub> and K<sub>4</sub> composites densified at 1800 °C is equal to zero, so the density increases and the mechanical characteristics increase respectively.

The K<sub>4</sub> composite is characterized with the highest physical–mechanical properties among the researched samples: HRA = 94.5;  $\alpha_{comp}$  = 2340 MPa;  $\alpha_{bend}$  = 577 MPa; thermal expansion coefficient  $\alpha$  =  $4.53 \times 10^6$  K<sup>-1</sup>, which points to its thermal stability. This is conditioned by the components in the composite and at the same time by the existence of a fine dispersion of diboride formed in the process of densification. At the same time a small amount of boron carbide

did not enter the reaction and the correlation of silicon carbide and boron nitride positively influences the composite microstructure and respectively, its physical and mechanical properties.

Fig. 3 presents the results of Vickers hardness testing of the K<sub>4</sub> composite.

As it is seen from the figure at load 10 N the imprint shape is sharp, and no cracking is observed.<sup>7,8</sup> The indenter penetrates into the material for about 14 μm. At 50 N loading energy dissipation is observed around the imprint which decreased the imprint outline sharpness, but cracking is not observed. The indenter penetrated the material for 28 μm. Here, the plastic property of the material is able to respond to the load so that it does not form a crack.

On loading to 100 N only the area of the indentation is increased. The material maintains its plasticity and no cracking appears, though the indenter penetrates the material for 55 μm. These results suggest that the K<sub>4</sub> composition would withstand operation in impact loading conditions.

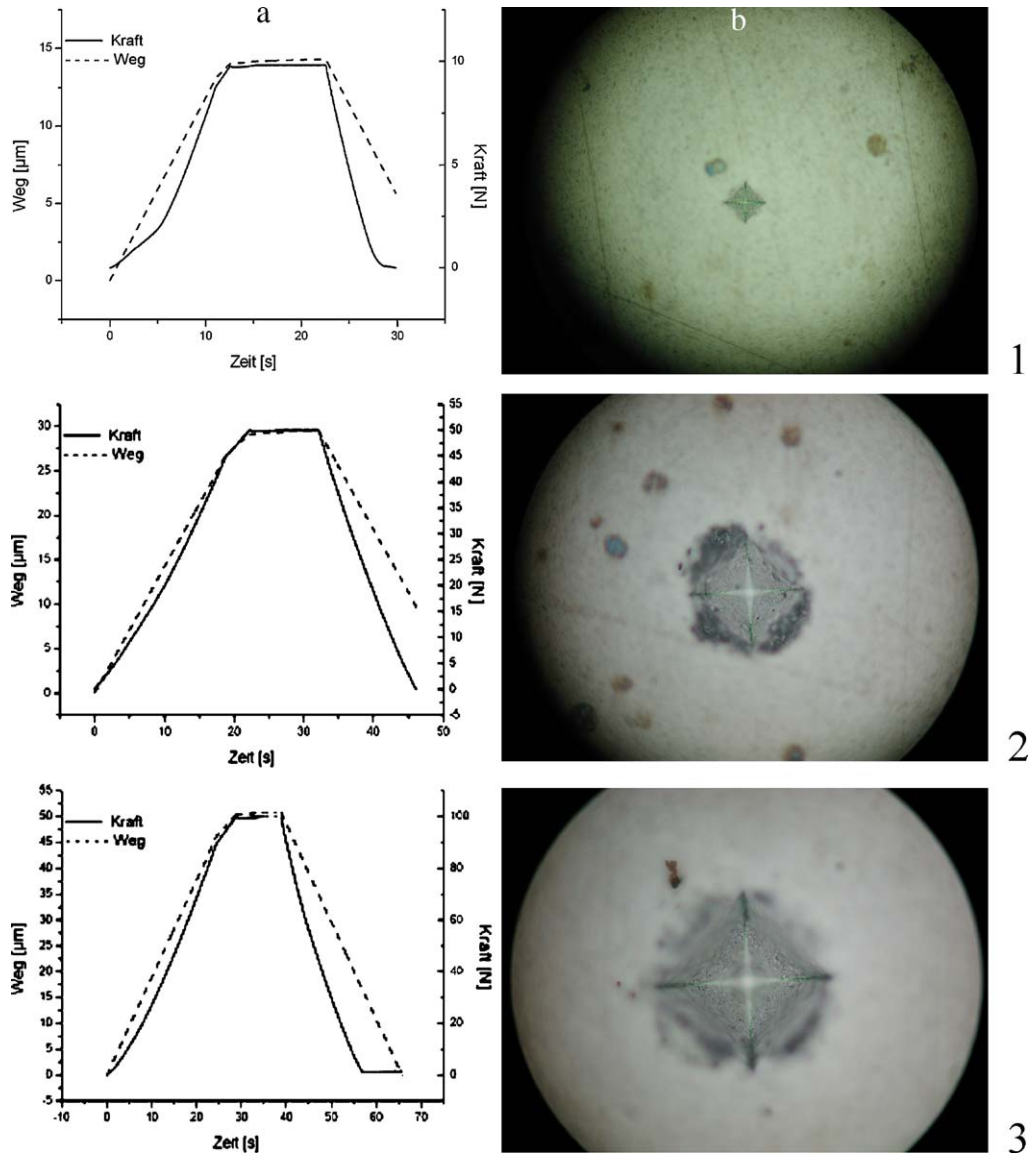


Fig. 3.  $H_V$  data of the composite with indenter at 10, 50 and 100 N loading. (a) Relation of indenter loading on the sample and its displacement with time, (b) indenter imprint,  $\times 500$  lens. (1) Load – 10 N; (2) load – 50 N; (3) load – 100 N.

The electric resistance for K series material was studied in the range 20–300 °C, using the electric resistance cell given in Ref. [9]. Fig. 4 presents curves showing the relation between resistivity ( $\rho$ ) and temperature of the researched material which shows that the “ $\rho-T$ ” relation is rectilinear in the 100–300 °C temperature interval and slightly changes stepwise in measurements at 20–100 °C. The latter may be caused by adsorbed humidity on sample surface at room temperature, which is lost at 100 °C and higher temperatures. The slope of the “ $\rho-T$ ” plots shows a near zero value of temperature coefficient of the resistance for the K-3 materials whilst for K-1, K-2 and K-4 samples the slope is  $((1.0-3.5) \times 10^{-3} \Omega/k)$ .

According to the experimentally received values of temperature coefficient of electric resistance and resistance of samples their rank order according to increasing value is: K-3 > K-4 > K-1 > K-2.

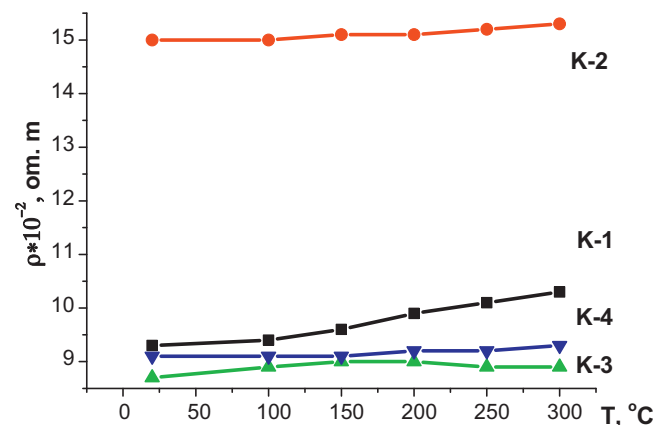


Fig. 4. Temperature relation of electric resistance of K series materials.

#### 4. Conclusion

X-ray analysis has proved that in compositions containing boron carbide, titanium carbide and carbon, the presence of titanium carbide at high temperatures leads to the decomposition of boron carbide to form titanium diboride. When boron nitride is low in the initial composition, TiC and C mainly react with B<sub>4</sub>C. In the composition where there is no B<sub>4</sub>C but only BN, TiC and C cause this to react and decompose it with the formation of TiB<sub>2</sub>, but in this case the decomposition is partial with less effectiveness than in the case of B<sub>4</sub>C. The K<sub>4</sub> composite is marked out with the best physical and mechanical properties. This is caused by the particular components in the final composite and at the same time, with the existence of a fine dispersion of diboride formed in the process of densification. At the same time, the relation of both boron carbide and boron nitride being involved in the reaction has a positive effect on the composite microstructure.

Micrographs (Fig. 2) of the composites investigated show that the basic phase of the composites is silicon carbide, the grain size of which in K<sub>1</sub> and K<sub>2</sub> composition samples is greater compared to K<sub>3</sub> and K<sub>4</sub> samples. The grains of titanium diboride created in the sintering process are smaller than silicon carbide grains.

The range of composites produced, because of their excellent physical and mechanical properties, can be used at high temperatures and are suitable for operation in conditions of wear, thermal exposure and air-thermal shocks.

#### Acknowledgements

We express our gratitude to the department of Keramische Werkstoffe und Bauteile of Bremen University and to Prof. Dr.-Ing. Georg Grathwohl for the support rendered in scientific experiments.

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