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Boron Carbide Based Composites Manufacturing and Recycling Features

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This paper presents the study of multiphase lightweight boron carbide based composites manufacturing and recycling features via powder metallurgy technology. The manufacturing process includes self-propagating high-temperature synthesis (SHS) followed by a hot densification at liquid-state of aluminum binder phase. For composite properties optimization the heat treatment in vacuum at different conditions was used. Additional heat treatment in oxidizing environment was used for spontaneous disintegration and recycling of the investigated material.

Keywords: powder technology, SHS, boron carbide, spontaneous disintegration, recycling, sliding wear.

1. INTRODUCTION

Cermets are the materials with heterogeneous compositions of one or several ceramic phases with metals and alloys. The nonmetallic additives increase the hardness, wear resistance, and heat-resistance of composites. The metallic phase combines the hard particles into one composite material and provides strength and plasticity of cermets. Therefore, the properties of cermets depend on metal and ceramic phase properties, their proportion, and adhesion between initial components [1].

Self-Propagating High-Temperature Synthesis (SHS) is an attractive advanced technology for the synthesis of a wide variety of advanced materials, including powders and near net-shape products formed from ceramics, intermetallics, composites and functionally graded materials, by exploiting the heat-energy released by the exothermic reaction of raw materials via a self-sustaining combustion wave which propagates from one end of the specimen to the other. When compared with traditional technologies, remarkable savings in energy, time and equipment, and novel forms of equilibrium and non-equilibrium phases and high-purity products can result from using SHS [2].

It is known, that the development and using of new wear resistant lightweight cermets on the base of boron carbide is actual because of their excellent properties such as low density, high wear resistance, elastic modulus and hardness. Conventional production methods used to fabricate these materials, such as powder metallurgy, are usually energy, time, and capital consuming, hence reducing cost efficiency, due to the significantly high strength and melting temperature of initial materials [2]. Self-propagating high-temperature synthesis (SHS), which has been used in present study, provides an economical and energy efficient process route for the preparation of composites [3].

Objective of this project is to synthesize by the SHS technology the cermets based on boron carbide B4C and aluminum Al powders, as well as to consider the recycling features of sintered cermets.

Sintered boron carbide/aluminum cermets were subjected to the heat treatment at different conditions to establish the optimal processing parameters for unlubricated sliding against steel. With this purpose in addition to wear and friction tests the evaluations of mechanical properties, microstructural analysis, X-ray diffraction analysis, electron-optical investigations of the microstructures and wear surfaces of the samples were performed.

2. EXPERIMENTAL

2.1. Initial materials

Boron carbide B4C powders with different mean grain size and aluminum Al powder ASD-4 (96 % Al) have been used as raw materials for B4C/Al-cermets sintering. The initial boron carbide B4C powder contained also graphite C in small quantity.

Two groups of initial boron carbide B4C powder were used: coarse-grained powder with grain size in range of 4.2 – 74.7 μm (average 17.3 μm) and fine-grained powder with average grain size of 1.24 μm. The particle size of boron carbide is a dominant parameter that determines self-propagating sintering reaction rate and temperature of SHS-process. By decreasing of particle size the sintering time and residual aluminum content in cermet reduce substantially [4]. The reduction in the particle size is also known to exhibit a beneficial effect in improving the mechanical strength [5].

Boron carbide B4C powder grinding, activation and mixing with binder metal phase (aluminum) were carried out in attritor. The powder was milled during 6 hours at rotation speed of rotor 800 min^{-1} (linear speed 3.73 m/s). As a result the average grain size of boron carbide B4C powder have been reduced more than 13 times and the mean size of 1.24 μm and surface area of about 25 m^2/g obtained.

2.2. Samples preparation

Metal/ceramic material of B_4C/Al composition has been manufactured using SHS-technology. Following stages includes the manufacturing process of B_4C/Al cermets from initial boron carbide B_4C powder and aluminum alloy powder: preparation of powder charge;

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powder charge placement into the steel container and its vibration compaction; heating of container with the powder charge (SHS-process initialization) under pressing; removal of container.

The powder charge was mixed from boron carbide and aluminum powders in following proportion: aluminum – 46 – 48 wt.%, boron carbide – the rest.

Powder charge vibration compaction was performed during approximately for 2 minutes. The heating of container with the powder charge in vacuum furnace up to temperature of about 850 °C initiates the SHS-process. SHS-process proceeds as exothermic reaction, i.e. with heat releasing, and the process temperature increase up to 1100 – 1150 °C. The SHS-process has been performed under pressing strength of about 130 – 150 MPa for better densification. After sintering the plate of manufactured material was cut into samples, which then were machined by diamond grinding.

For the strength properties improving additional heat treatment of the synthesized cermets is required [4, 6, 7]. Different heat treatment regimes were used for composite properties optimization. The temperature of heat treatment varies in range from 1150 °C to 1500 °C. It is known, that boron carbide B_4C in temperature interval of 300 – 2300 °C is very chemical attractive with metals and as a result the forming of refractory compounds occur [8]. Earlier performed experiments [4, 6, 7] allow concluding that forming of hard refractory carbides in structure of cermets promotes increasing of wear resistance.

It was be found that spontaneous disintegration of the cermets heat-treated in oxidizing surrounding at temperatures above 1300 °C occurs. This material after spontaneous disintegration was additionally subjected to attrition and disintegration milling, mixing with powders of binder metals (aluminum Al – 41.4 wt.%, copper Cu – 4.3 wt.%) and small amount of graphite C. The obtained powder mixture was then used for the new composites manufacturing by SHS process as it described above. The recycled composite was subjected to the heat treatment at temperature of 1080 °C in zirconium oxide ZrO_2 powder.

In Table 1 are presented the reference designations for tested samples that are used further for simplification in current paper.

Table 1. Designations and characteristics of the samples

Sample symbol	Parameter	
	Initial B4C-powder mean grain size, μm	Heat treatment conditions
N1	17.3	1080 °C, vacuum
N2	1.24	1470 °C, vacuum, ZrO_2
N3	1.24	1080 °C, vacuum, ZrO_2
N4	recycled material	1080 °C, vacuum, ZrO_2

2.3. Characterization and testing

In present study mechanical properties of the synthesized cermets were studied by data obtained from using universal hardness tester Zwick Z 2.5/TS1S and according to the standard DIN 50359. Microhardness of B_4C/Al cermets has been measured according to ASTM E384-89 standard test method. Buehler Micromet-2001 tester and Vickers diamond indenter were used for microhardness evaluating under different test loads. Up to 10 measurements of each phase have been performed for mean value evaluating.

Tribological properties studies included wear resistance determining of the material in unlubricated sliding against steel and friction coefficient measurements. Dry sliding friction experiments were performed on a block-on-ring contact geometry. The following test conditions have been used: room temperature, atmospheric pressure, normal load of 82 N (in static state), sliding velocity of 2.19 m/s (disk rotation speed of 235 min^{-1}), sliding distances of 2 km, 4 km, 6 km and 8 km. The specimens mass was reweighed after each sliding distances with accuracy 10^{-4} g. The wear of steel disc was not measured. The coefficient of friction in the dry sliding condition was obtained as the ratio of the frictional force to the contact force. The frictional force values were continuously determined using a dynamometer.

Microstructural studies of B_4C/Al cermets before and after wear experiments have been performed using several complementary analytical techniques. Optical microscopy (Neophot 32 microscope), EDX and SEM (JEOL JSM-840A microscope) were used to examine qualitatively the surface morphology of cermets. X-ray diffraction technique (Bruker AXS D5005 analyzer) was used to analyze the chemical composition of investigated materials.

The primary and the recycled materials were tested in the same conditions, and obtained experimental data was compared to estimate the reuse possibilities and validity of boron carbide/aluminum composites.

2.3.1. Recycling mechanism

Recycling mechanism of the cermets is based on spontaneous disintegration. It was discovered that spontaneous disintegration is occurred in result of additional heat treatment in oxidizing environment.

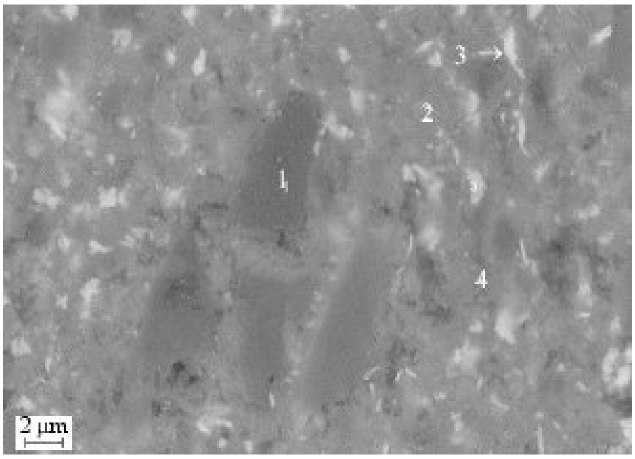

Fig. 1. SEM micrograph of cermet microstructure

Four different regions can be visually observed in the microstructure of cermet, that is illustrated in Fig. 1: dark-gray colored grains of hard phase (boron carbide B_4C) with microhardness up to 3800 HV0.05 (Region 1), flake-shaped structural formations in Region 2, light colored areas of second hard phase (Region 3, 1500 HV0.05), and light-gray colored areas of binder phase (Region 4, 700 HV0.05). The marks of spontaneous disintegration of cermet are presented in Fig. 1 (see Region 2). In region 2 of the SEM-image expressed in Fig. 1 are the flakes of cermets material which trend to fall out from the sample. These flakes are about 200 nm in width and up to 1 μm in length (see Fig. 2).

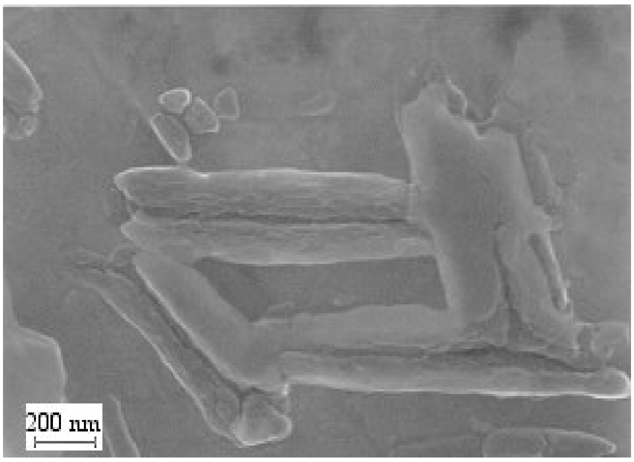

Fig. 2. SEM micrograph of the cermet microstructure in Region 2

In Fig. 2 are presented the structural formations in the cermet’s microstructure that was subjected to additional heating in oxidizing atmosphere. It should be noted, that no evidence of such flake-shaped formations was observed before additional heat treatment.

The EDX analysis of the microstructure in region illustrated in Fig. 2 suggests that large amount of different chemical elements concentrated in this area (see Fig. 3).

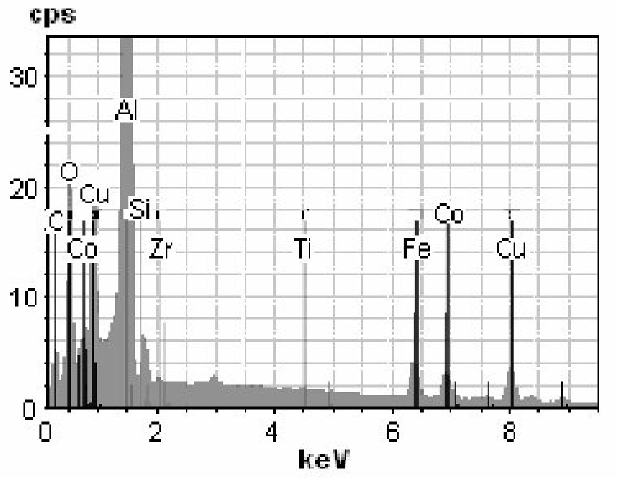

Fig. 3. EDX patterns of the recycled cermet in Region 2

2.3.2. Mechanical properties

Universal hardness of B_4C/Al cermets has been measured according to standard DIN 50359 and using Zwick Z 2.5/TS1S testing machine at load value of 100 N and standard load application time of 7.5 s. The results of universal hardness measuring are present in Fig. 4.

There are present universal hardness (*HU*) and plastic hardness (HU_{plast}) of B_4C/Al-cermets. It refers to a permanent deformation of the material in response to an applied force. The part will be deformed and the deformation will remain after the load is removed. As opposed to elastic deformation or hardness where the material springs back to its original shape.

The B_4C/Al cermets synthesized from fine-grained boron carbide powder have

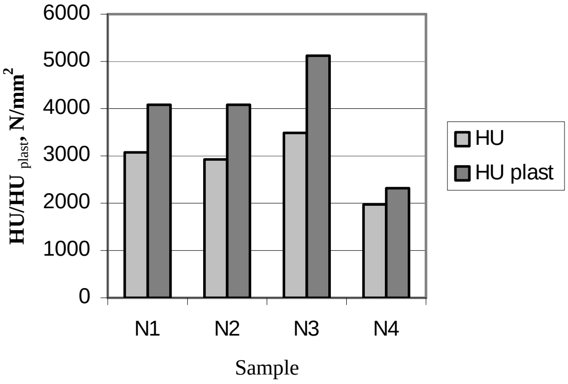

Fig. 4. Universal hardness of B_4C/Al-cermets

Elastic characteristics of material can be obtained from universal hardness tests. In Fig. 5 are present the values of indentation elastic modulus Y_{hu} for B_4C/Al-cermets.

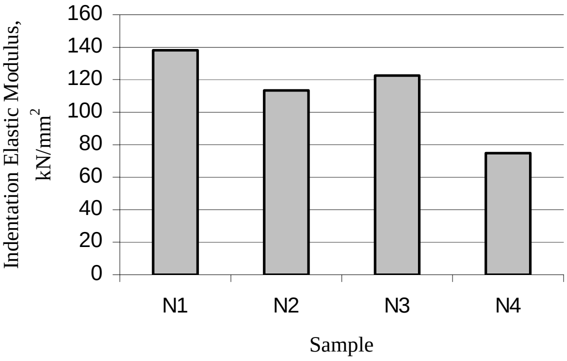

Fig. 5. Indentation elastic modulus of B_4C/Al-cermets

The indentation elastic modulus Y_{hu} is comparable with the modulus of elasticity (Young’s modulus) E of the material [8]. The relatively low elastic properties of investigated materials do not ensure that deformation can take place under stress without rupture occurring, resulting in delamination and galling.

2.3.3. Tribological properties

The sliding friction tests were carried out in open air and under atmospheric pressure according to block-on-ring tribosystem, where the B_4C/Al-block was pressed with normal force of 85 N against rotating steel disc (linear speed 2.19 m/s). The mass loss was determined every 2 km up to 8 km of sliding distance. In Fig. 6 are presented the dry sliding tests results, namely the average values of wear rate and steady-state friction coefficient.

The values of wear rate presented in Fig. 6 are the mean values of wear rate obtained after 8 km of sliding distance. The results obtained are comparable with those obtained in the same conditions of the WC-Co and TiC-NiMo composites, but the density of B_4C/Al cermets is well lower (about 2.5 g/cm^3) [9].

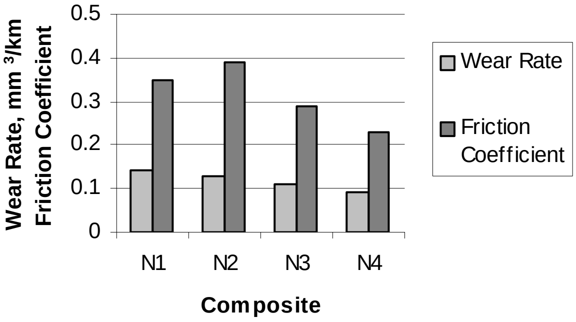

Fig. 6. Wear rate and friction coefficient for boron carbide/aluminum cermets

The performed dry sliding friction tests for B_4C/Al samples fabricated from coarse and fine powders composite produced friction coefficients averaging between 0.30 and 0.40. The friction coefficient values do not oscillated widely and after 2 – 3 minutes of breaking-in remained stabile during whole test (about 60 minutes).

For the recycled composite the value of the friction coefficient oscillates at value of 0.24.

The temperature of the worn surfaces was also measured immediately after testing. Using a thermocouple the temperature of 150 – 170 °C has been recorded.

2.3.4. Microstructural investigations

Microstructural features of the samples are considered in following.

As a result of heat treatment the forming of hard refractory compounds (carbides, nitrides, borides) and skeleton of hard phase occurs. The use of XRD-technique allows to detect the forming of boron aluminum carbide Al_3BC and small amount of aluminum carbide Al_4C_3 as a result of heat treatment at temperature of 1080 °C, and no evidence of forming of complex carbide $Al_8B_4C_7$, aluminum boron AlB_2, and aluminum nitride AlN, which taken place at temperature of 1470 °C was observed [4, 7]. All of these phases tend to form large clusters of grains and result in lower strength regardless of which phase forms [10].

The structure of recycled cermet (sample N4) is present in Fig. 7.

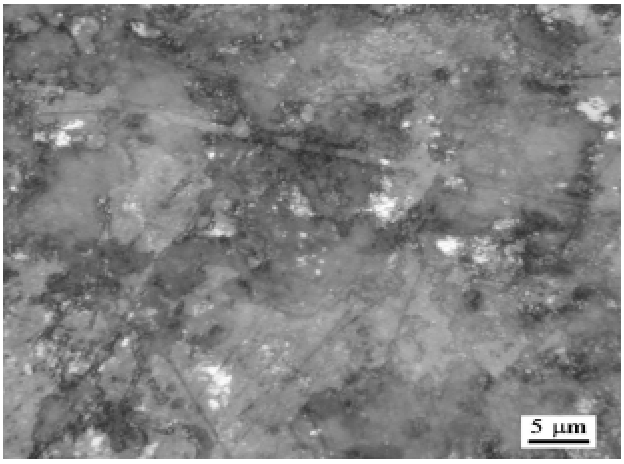

Fig. 7. Microstructure of the recycled cermet

It can be concluded that the microstructure of the recycled cermet is similar to that of the primary cermet. The main phases are the light-gray colored carcass of hard phase, dark-gray colored binder phase and light colored inclusions of second hard phase.

3. DISCUSSION

For strengthening of the B_4C-based composites it is necessary to use manufacturing and processing technologies which provide the fine-grain structure, improve carbide/binder bonding and do not allow forming a skeleton of hard phase. Furthermore, technologies must provide the absence of free graphite in structure, prevent the decarbonization of carbide and forming of complex chemical compounds [8].

It should be noted that the specific wear rates of all the B_4C/Al-composites, including recycled one, in this study were in order of 10^{-6} $mm^3/(Nm)$, which belong to a mild wear regime. This confirms the high wear resistance of considered materials in given conditions of dry sliding contact against steel.

The friction tests of present study produced friction coefficients averaging between 0.35 and 0.45 (see Fig. 3) and they remain constant throughout the test as the material wears and temperature increases, i.e. exhibited no fade with increasing temperature. The results of friction and wear of boron carbide/aluminum cermets published in [11] confirm this fact. The B_4C/Al-cermets showed friction coefficients that fell within the industry-accepted range for automotive brake materials [11]. The stable and relatively high friction coefficient is one among the main requirements for frictional materials.

The recycling process of the composites investigated in current study is based on heat treatment processing of materials. The additional heat treatment of B_4C/Al composites was realize in oxidizing environment at temperatures up to 1500 °C. This was led to the formation of binary and ternary borides and carbides in material's structure, which tend to form large clusters. The complex compounds formed in structure following the heat treatment promote spontaneous disintegration of composites. The refined material can be used further as raw material for composite preparation.

4. CONCLUSIONS

1. The SHS-process was used to synthesize the lightweight B_4C/Al composites. This manufacturing route has a number of benefits comparing to traditional powder metallurgy methods. Additional heat treatment of cermets allows to improve strength and tribological properties of the material.
2. An alternative route for boron carbide/aluminium cermets disintegration was found, that is able to reuse the material.
3. The B_4C/Al cermets demonstrate high wear resistance in dry sliding conditions in combination with stabile friction coefficient and low density.
4. The use of fine-grained initial boron carbide powder does not influence significantly on wear resistance of cermets, however, the strength properties increase.

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