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Multiphase Forming in Lightweight Composites during SHS Reaction

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Multiphase microstructures in lightweight composites were formed during self-propagating high temperature synthesis (SHS) reaction under pressure with followed heat treatment. The purpose of multiphase microstructure modelling in composites is an intensification of their functional properties. For this the composites were produced on base of chemical high active superhard refractory advanced ceramic materials such as boron carbide and cubic boron nitride powders. For primary binder phase the metals (aluminum, titanium, iron, chromium, rhenium, nickel) and carbon with different proportions were used. The attrition milling of mechanical activation technique was used in this study. Depending on chemical composition and grain size the ignition temperature (from room temperature up to ~2000 °C) and SHS reaction rates were very different. For phase state investigation the X-ray and field emission scanning electron microscopy techniques were used. Test results show, that these new phases – boron aluminum carbide and ultrafine titanium carbonitride have very large influence on composites microstructure and properties evolution. The hardness of materials was increased meanwhile the dry sliding wear and hydroerosion wear were decreased. The increased concentration of boron carbide and cubic boron nitride safeguarded the good wear resistance properties but materials with this composition were very hard to machinability.

Keywords: self-propagating high temperature synthesis, lightweight composite, boron carbide, cubic boron nitride.

1. INTRODUCTION

Diamond is the hardest material known [1]. Its carbon atoms form very short covalent bonds. Unfortunately, the diamond cannot be used to cut of steels without ruining. Ultra-hard advanced ceramic materials are used everywhere for drills and precision instruments manufacturing [2]. The advanced ceramic material, such as cubic boron nitride (c-BN) as a diamond substitute can be used for cut of steels and alloys. The cubic boron nitride (c-BN) has uppermost mechanical, physical and chemical properties [3, 4]. This advanced ceramics is made synthetically under very high temperature and high pressure [5]. Contrary, such new advanced hard material as rhenium diboride (ReB_2) is made in a simple process without applying pressure [6]. The hardness of rhenium diboride is equivalent to c-BN. But c-BN possesses, like diamond, excellent high hardness and elastic modulus [2]. The density of c-BN is $\rho = 2.52\ \mathrm{g{\cdot}cm^{-3}}$ which is lower that density of diamond ($\rho = 3.515\ \mathrm{g{\cdot}cm^{-3}}$) [1]. The hardness testing by diamond-pyramids show that c-BN has Vicker's hardness of 49.5 GPa and Knoop's hardness of 27.00 GPa, respectively. It has a low coefficient of friction (μ), which depends on crystallite orientation and has $\mu = 0.12$ for {100}; $\mu = 0.075$ for {110} and $\mu = 0.05 – 0.07$ for {111} and not different for wear direction, respectively. The temperature conductivity coefficient (α) of c-BN decrease up to 3 time (from $\alpha = 2.8$ to $\alpha = 1.0\ \mathrm{m^2{\cdot}s^{-1}}$) by increase (from 300 K up to 600 K) of temperature. Midst of the all advanced materials the c-BN has highest heat transfer (λ) coefficient. The coefficient of thermal expansion of this advanced ceramic is lowest at room temperature and increases significantly (up to ~5 times) by temperature increase up to 1600 °C. Boron carbide (B_4C) is an advanced ceramic material [7] like diamond and cubic boron nitride. Unfortunately, it is even more expensive then diamond and the choice of metallic alloy binder for composite manufacturing from this advanced ceramics is severely limited. It is well known, that the following requirements must be satisfied: a – sufficient wettability by metal or alloy; b – high adhesion of metal binder to c-BN or B_4C crystal surface; c – poor reactivity of binder phase with the ceramics; d – possibility to control the level of reaction on phase increase in the absence of its removal; e – minimal difference in the coefficients of thermal expansion of the phases and so on.

The self-propagating high-temperature synthesis (SHS) reaction [8 – 13], also called as solid state combustion, uses the formation of initial compounds from reactant substances to develop exothermic reactions, which in turn generates enough energy to initiate the formation of initial compounds from the mixture of reactants. The SHS reaction parameters depend on the particle size, stoichiometry of the reactants, pellet size and green density, gas or mechanical pressure and in summary are very relevant. The reaction becomes self-propagating and a combustion waves move through the reactants converting them to the final product. Usually for the better densification of composite the SHS reactant can be densified under high pressure [14 – 15] at liquid state of binder metal or alloy [16 – 19]. The recent investigations [20 – 22] show that during SHS under nitrogen (N) gaseous pressure is possible to form TiB_2-TiC particles in steel matrix of composites. The interface reactions [23 – 28] between phases during processing have the large influences on mechanical properties of composites. Such effects can be received by addition of new ceramics to facilitate the formation mechanism.

The present study focuses on the new refractory phases forming under different processing parameters and their influence on composite properties are described.

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2. EXPERIMENTAL

In order to study the effects of the preparation of multiphase composition on microstructure, only two types of hard particles were used – cubic boron nitride (c-BN) and boron carbide (B_4C). The c-BN with a percentage of 25 wt.% and mean crystallite size of 20 µm. The binder phase was composed from iron (Fe – 29 wt.%), titanium (Ti – 20 wt.%), Nickel (Ni – 9 wt.%), chromium (Cr – 12 wt.%) and carbon (C – 5 wt.%) powders. The B4C with a percentage of from 25 wt.% to 75 wt.% was added to aluminum alloy binder. The powders of listed materials were mixed and compacted by vibration in steel containers. To initiate the reaction bonding process the containers were heated in a furnace. Spontaneous ignition starts at temperature of about 1150 °C and increased up to 1200 °C – 2000 °C. The ignition temperatures and self-propagating rates depend on the chemical composition and grain size. When SHS reaction was completed and binder metal was in a liquid state, the pulse pressure under forging hammer was applied to achieve better densification. The deformed containers were cooled in an air and then the raft composites were cut off. The synthesized samples were subjected to the heat treatment in different environmental conditions and in vacuum at the operating temperature range of 700 °C – 1500 °C for 15 min – 30 min.

The microstructure of the diamond grinded samples was characterized with an optical light microscope (OLM) Nikon CX. The field emission scanning electron microscope (FE SEM) ZEISS ULTRA-55 enables to study the microstructure. The different detectors of secondary (SEs) and backscattered (BSEs) electrons were used. For formed phases content study the X-ray diffraction (XRD) patterns were recorded on each stage of processing by X-ray analyzer Bruker AXS D5005. For the X-ray diffraction patterns study the 1997 JCPDS – International Centre for Diffraction Data programmer was used. The instrumented microindentation performance using Zwick Z2.5/TS1S installation according to the EVS-EN ISO 14577-1:2003 Standard was used to quantify the mechanical properties of the composites. The microhardness of composite and phases was measured using Buehler Mikromet-2001 tester at load of 0.01 kg and 0.05 kg during 12.5 s of dwell or indentation time. The three-point bending tests were performed according to EVS-EN ISO 3327 Standard using Instron-8515 testing installation with personal computer. The block-on-ring scheme was used to study resistance to dry sliding wear of composites against carbon steel ring in air at atmospheric pressure and room temperature according ASTM-B 611-85. The normal load of 82 N, linear sliding speed of 2.2 $m \cdot s^{-1}$ and sliding distance up to 8 km were the tribological testing conditions. Hydroerosion resistance of the composites was tested in the sodium solution slurry at test time of 150 h.

3. RESULTS AND DISCUSSION

The SHS processed raft composite contains (Fig. 1) large c-BN crystallites (black color) and metallic alloy (white grey color) binder phase. Homogenous distribution of ceramic phase crystallites is a characteristic feature of as-synthesized by SHS process lightweight composite materials. The microhardness of phases is indicated. Figure 2 shows the magnified SEM micrograph of the binder phase of c-BN based composite. Depending on followed to SHS process, the heat treatment temperature of obtained multiphase composites show different microstructures and properties. By use of the FE SEM investigation was revealed, that during processing the new secondary ultrafine hard phase (grey color) was formed (see Fig. 2). The spherical inclusions have maximal diameter about of 600 nm only. The measurement of this microhardness was not possible by Mikromet-2001 use as the size of particles is so small. By one of X-ray investigation was established, that the microstructure contains hard (7300 $HV_{0.05}$) c-BN crystallites and between large c-BN grains the steel $C_{0.14}Fe_{1.86}$ binder phase with in situ ultrafine-grained $C_{0.7}N_{0.3}Ti$ secondary hard phase. The c-BN grains are in the wide range of sizes from 2 µm to 50 µm (Fig. 1), while TiCN particles are from 50 nm to 600 nm in diameter (Fig. 2).

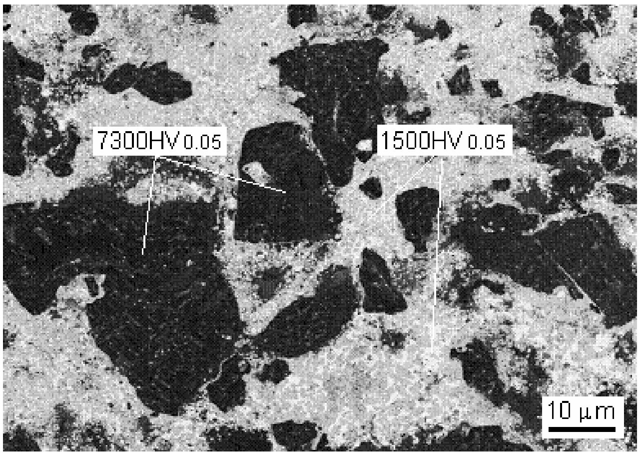

Fig. 1. SHS processed raft c-BN-based composite with microhardness indication

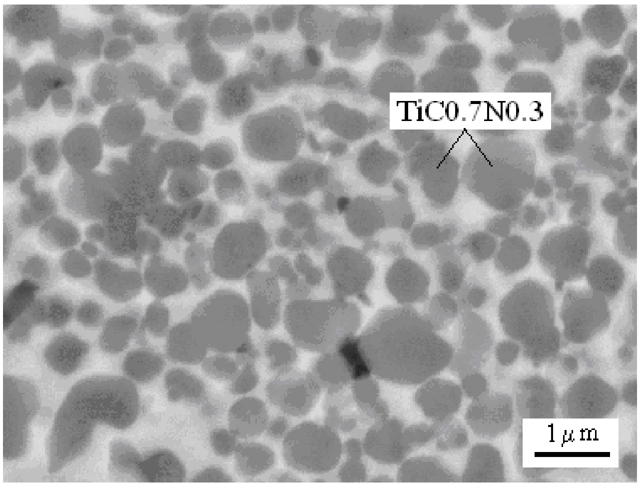

Fig. 2. Microstructure of binder phase with indication of ultrafine precipitated of stoichiometry titanium carbonitrides

The transition zone is about of one micrometer in thick and surrounds partially the large c-BN grains. This transition zone contains large quantity of titanium (Ti), nitrogen (N) and carbon (C). The titanium (Ti) content took increase in this zone up to maximal value on distance of 1 μm from surface of c-BN grain. There is an increase in nitrogen content up to maximum in the transition zone and then a decrease in N content one micrometer away from a c-BN grain surface. As it was shown in SEM investigations, these spherical particles contain more titanium with decreased content in chromium and iron. By this near large c-BN grain surface the Ti, C and N concentration is highest. It means that in result of diffusion via solid-state sintering during the SHS process the N combines with Ti to form the titanium carbonitride (TiCN), which is found in the hardened steel binder phase. The chromium (Cr) content increases slightly at the c-BN grain surface and then immediately decreases in the binder phase. As well, there is Fe and Ni content increase in the transition zone. However, the amount of Ni decreases slightly and amount of Fe and Cr increases at a short distance (about 1 μm) from the c-BN grain surface. This increase of Fe and Cr took place in the binder phase after transition zone when the Ni content took decrease. There is an increase in Ti content and Fe and Cr contents decrease in the binder phase. The approximate estimation gives the TiCN nano grains quantity of about 26 wt.% within the metallic binder. The binder phase is Fe-Cr-Ni stainless steel and contains Fe25Cr11Ni0.3C in wt%. TiCN particles have been nucleated and grown during SHS process. Depending on the start metals of binder there can be formed also such compound as FeO, AlB_2 and Fe_2B.

The composites on boron carbide based and with aluminum alloy binder in different concentrations have another new phases forming mechanism. In this case the boron aluminum carbide was formed between the boron carbide grains (Fig. 3). To investigate mechanical properties of composites the instrumented microindentation method was chosen.

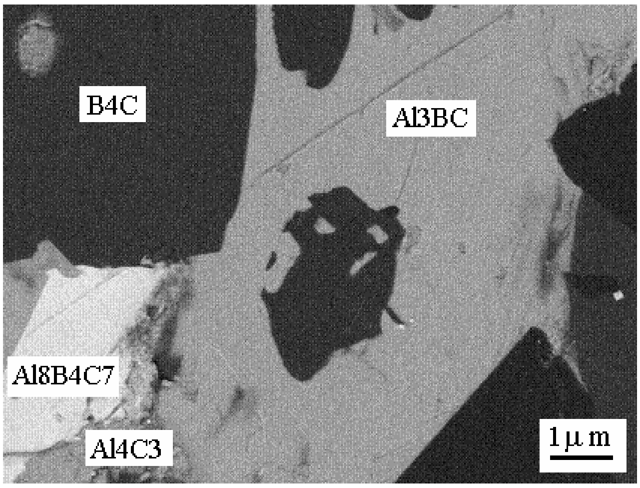

Fig. 3. The mechanism boron aluminum carbide (Al_3BC) forming in composite binder phase during SHS reaction is presented

Because of small size (about 600 nm) of the second hard phase, the microhardness measurement of TiCN spherical particles was not possible on Mikromet 2001. The micro-hardness of the binder phase is not uniform over the composite surface. There are porous and soft inclusions which contain graphite. As a result, the density of composite was about 4.5 g/cm^3. The mean microhardness of binder phase is 1500 $HV_{0.05}$ and micro-hardness of the soft dross inclusions is about 900 $HV_{0.05}$. The Vicker's hardness under load of 10 kg was 945 HV_{10}. The large c-BN grains have a very high micro-hardness of ~7300 $HV_{0.05}$ that is revealed with diamond microhardness. Measured indentation (universal) hardness was H_{IT} 100 / / 7.5 / 15 / 30 = 5650 N/mm^2 and Martens hardness was HM_s 100 / 7.5 / 15 = 8500 N/mm^2. The indentation modulus was increased to E_{IT} 100 / 7.5 / 20 / 30 = 196000 N/mm^2 with relation of W_{elast} to W_{total} equal to η_{IT} 100 / 7.5 / 20 = 28 %. The composite has relaxation of 2.15 % and creep of 2.18 %.

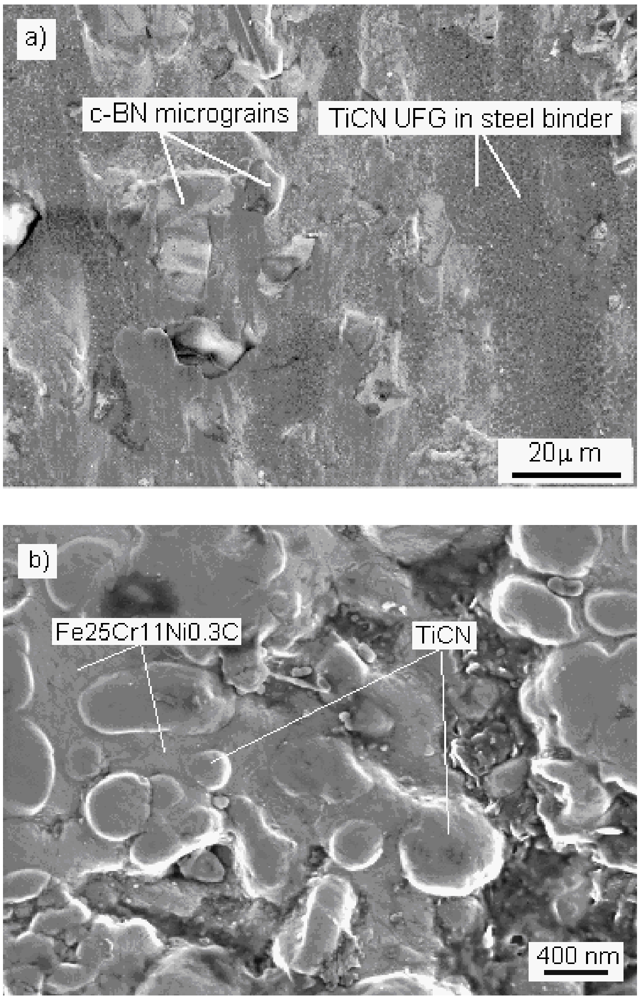

Fig. 4. Wear surface of composite under dry sliding with phase's indication (a) and stainless steel binder with in situ TiCN particles (b)

As it was measured, the weight loss of composite under dry sliding on distance of 4 km increases from 0.8 mg to 6.1 mg with a normal load increased from 40 N to 320 N in the first series and from 0.8 mg to 3.9 mg in the second series. Fig. 4 represents the wear surface of composite (a) and binder phase of composite (b) in dependence on normal load. It can be supposed that only the large c-BN particles contact with the steel ring while sliding under a load of 40 N (Fig. 4). An increase in the load causes breaking of the large B_4C grains and an increase in wear rate (Fig. 5). The composite has two hard phases, micro size c-BN and nano size TiCN in stainless

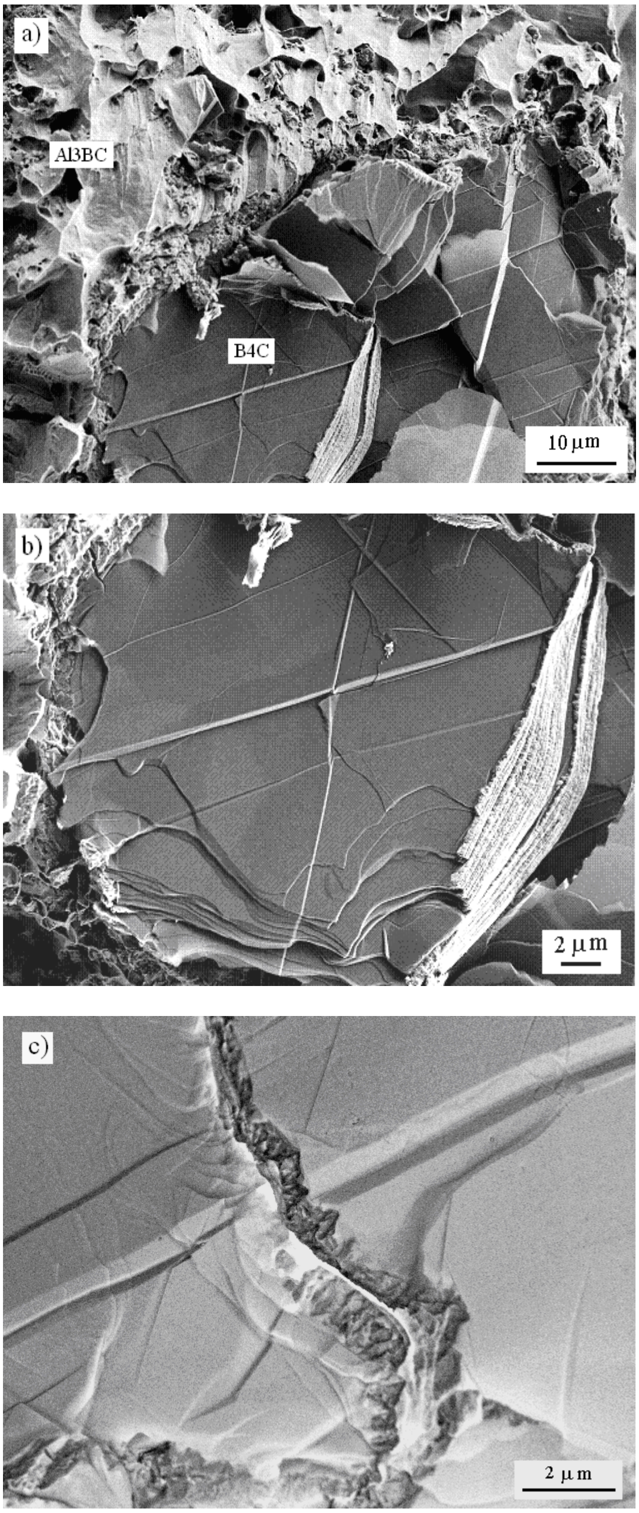

Fig. 5. The fractures are of boron carbide based composite (a), by atomic layers of boron carbide crystallite (b) and crystal fracture in cross-section to crystal (c)

steel. At the first series of tribological tests, the wear rate is higher than at the second test series. The wear coefficient decreases with normal load increasing from 180 N to 320 N. This value is lower as compared to the theoretical as the grain sizes are small and binder of raft composite is relative soft (~1500 $HV_{0.05}$) immediately after SHS processing.

The composite with such mechanical properties has low dry sliding friction coefficient revealed to ~0.23 and low wear rate which revealed to 0.09 mm^3/km. These results of tribological properties have been obtained on distance of 8 km under normal load of 150 N. Increase in a normal load leads to a proportional increase in wear rate. Low friction coefficient and low wear rate under relative low normal load point out that friction can occur only between the large c-BN grains and a counter body. Such wear mechanism is illustrated in Fig. 4, a. Also the c-BN-based composite has a high wear resistance to slurry erosion. Weight loss by slurry erosion in sodium solution during 150 h was only ~0.1 mg/h. The c-BN based composite has a higher wear resistance by slurry erosion as compared to WC-CoNi (VK-15) hard metals, TiC-Ni (TH30B) cermets and B_4C-Al composites.

The boron carbide based composite wear mechanism is differing from c-BN based composite (Fig. 5). The wear of boron carbide based composite took place as result of crystallites fracture by and as well as across atomic layers.

This wear mechanism via crystallite fracture increases the wear rate under dry sliding condition.

The hydroerosion wear in sodium solution was higher for this composite with compare to c-BN based composite. The composite primary hard phase of c-BN and secondary hard phase of TiCN as well as stainless steel binder have a very high oxidation resistance.

4. CONCLUSIONS

The summary is set up as follows:

- The structure and properties of composite depend on new chemical compounds which were formed during SHS and followed heat treatment processing.
- The hardness and internal connections between phases control the wear resistant properties of composites.
- The new ultrafine sized second hard phase ($TiC_{0.7}N_{0.3}$) in metallic steel binder of c-BN composite has been sintered. It increases significantly the wear resistance during dry sliding.
- The composite steel binder, hard c-BN phase and second hard TiCN phase have very high hydroerosion resistance.
- Increase in a normal load leads to a proportional increase in wear rate.
- The wear coefficient decreases by normal load increase when the TiCN ultrafine spherical particles involve in wear and the tribofilm formation took place and the friction mechanism changes as a result.
- The relatively low hydroerosion wear of the composite in sodium solution slurry means that all compounds have high erosion resistance.
- Is established, that the c-BN-based and with synthesized secondary ultrafine hard phase in stainless steel binder composites may be filling an important role as one of the key advanced materials for modern technologies in applications where lightweight and hardness as well as oxidation- and wear resistance are necessary.

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