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RECYCLING OF LIGHT WEIGHT B_4C BASED COMPOSITES

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Abstract: *Recycling of light weight B_4C based composites by thermal processing use is the object of present work.*
At firs, for recycling the next compounds, formed during heat treatment at temperatures over 1150°C in oxidize surrounding, have influence on the aging time and as result, on spontaneous disintegration of composite. At second, for recycling after heat treatment at temperature under 1500°C this high wear resistant but brittle material don't have metallic binder phase and the chemical structure consists only from refractory ceramic compounds.
From these starting materials after spontaneous disintegration, disintegration and attrition milling or/and mixing with new added binder metal content (Al, Cu, C) were received the new light weight composites. For manufacturing the SHS process with subsequent high pressure and heat treatment was used.
The testing results show, that this light weight composite has lowest friction coefficient and highest dray sliding wear resistant in system of steel-composite with comparison of light weight on base of coarse grained boron carbide composite

1. INTRODUCTION

It is known (Mikli, et al., 2001, 2002) that for hard materials recycling the mechanical, so called disintegration milling can be used. Material refining depends on milling time. After 8 passes of disintegration milling the grain size can be reduced down to 300-400 μm during processing. By this the particles volume of metal from work pieces of installation in powder mixture as impurities increase. For characterize of impact-milled WC-Co powder particles the image analysis methods was used.
For fine grained TiC powder milling (Letunovitš et al., 2000) the attrition milling was used. The balls to powder weight ratio were chosen 3:1, 5:1 and 10:1. The attrition milling was carried out at 500, 800, 1400 and 2500 rpm for 2, 4, 6, 8, 10 and 12 hours. By this the milling has been done in methanol media. The particle mean size was decreased in maximal from 62μm in initial condition down to 0.85 μm after attrition milling. After time 12 hours of attrition milling the maximal specific surface area was increased up to 40 m^2/g. The cermets manufactured on fine grained TiC base have better mechanical and tribological properties then coarse grained have. Unfortunately, these processes have very large duration and the powder milling have different impurities by relative large micro grain size.
For B_4C and Al based composites recycling (Kommel, et al., (2002, 2003) the heat treatment at different temperatures and regimes were used. He was shown, that during heat treatment, depending on temperatures, regimes and surroundings, from boron carbide and aluminum alloy base cermets the structure and chemical composition change. For example the aluminum carbide (Al_4C_3), boron aluminum carbide (Al_3BC), aluminum boron carbon ($Al_4C_4B_x$), aluminum boron carbide ($Al_8B_4C_7$), aluminum nitride (AlN), boron nitride (BN) and also aluminum oxide (Al_2O_3) refractory compounds can be formed in binder phase of composites. The wear testing results show (Kommel et al., 2004) that these refractory compounds controlled wearing mechanism and wear rate of composites.
The material compositions, depending on temperature, have different conditions: composite, cermet (metal-ceramic) and ceramic. By this above 1150°C the small amounts of different compounds in composite can be formed. The recycling of B_4C/Al composites is based on high temperature heat treatment resulting in binary and ternary chemical composition formation, which is leading to the spontaneous disintegration of composites.
Recycled materials are becoming increasingly important as industry responds to public demands. Recent developments are concentrated in the sustained utilization of existing resources and recycling of materials. The potential savings in terms of energy and capital are obvious. The savings in terms of environmental impact are also increasingly important.
One of the ways to recycle old materials is to produce the powdered materials from worn products.
The present article summarizes the recycling method for light weight boron carbide (B_4C) based cermets produced by self-propagating high-temperature synthesis (SHS), and gives the comparing overview about the structure and properties of the primary and recycled composites.
The SHS or combustion synthesis is an attractive advanced technology for the synthesis of a wide variety of advanced materials. This technique uses the formation of initial compounds from reactant substances to develop exothermic reactions which in turn generates enough energy to initiate the formation of compounds from the mixture of reactants. The reaction becomes self-propagating and a combustion wave travels through the reactants completely converting them to the final product.
The recent investigations (Kommel, et al. 2003) of the B_4C/Al cermets produced by SHS-technique show that different compositions, such as Al_4C_3, Al_3BC, BN, $Al_8B_4C_7$, $Al_4C_4B_x$, AlN, AlB_2 and Al_2O_3 in binder phase of the composites were formed from initial boron carbide and aluminum powders as a result of the SHS-process and heat treatment temperature level.
Study will cover innovative research work, advances in ongoing research, and general industrial practices from recycling of light weight composites. Reports of work in other fields, including optimization of physical, aqueous, and thermal processing of serapes and waste; environmental and economic impacts; material selection and design based on recyclability; life-cycle analysis of materials; properties; and application of recovered materials.
The structure, mechanical- and tribological properties investigation of recycled from light weight B_4C based cermets, after their using in different mechanisms, is the aim of present work.

2. EXPERIMENTAL

In this work for recycling light weight wear resistant B_4C and Al-base cermet thermal processing technology was worked up and used. This cermet starting materials were 50 wt. % B_4C, and 50 wt. % aluminum alloy powder ASD-4. The aluminum alloy powder ASD-4 contains 96 wt. % pure aluminum. This cermet was produced from mixed boron carbide and aluminum alloy powders by self-propagating high-temperature synthesis (SHS) with hot pressing at 130-150 MPa and step-by-step heat treatment. The temperature of heat treatment (Kommel, et al., 2002) has essential effect on microstructure, chemical composition, mechanical- and tribological properties of cermet.

For recycling the cermets, after their use in different mechanisms, were subjected to additional heat treatment in oxidizing environment at temperature over 1150 °C and up to 1500°C. This was led to the formation of binary and ternary carbides and borides. The formation of these causes the spontaneous disintegration of material. Then the material was refined disintegration and attrition milling use. Refined material was mixed with new binder phase metals (Al, Cu) and carbon (C). This powder mixture as starting material was used for new composite manufacturing by SHS-process with subsequent pressing and heat treatment at 1050°C during 2 hours in zirconium oxide (ZrO_2). The zirconium oxide was used as catalyst. For comparison this material was double heat treated in TiC powder at 1460°C in vacuum.

The structural investigations of composites were performed using optical microscope Nikon CX, scanning electron microscopes JEOL JSM-840A, and Gemini LEO Supra-35.

X-ray diffraction technique (Bruker AXS D5005 analyzer) was used to analyze the chemical composition of recycled materials. Dry sliding tests were carried out with a block-on-ring cermet-steel tribosystem. B_4C/Al cermet specimens/blocks were pressed with load of 150 N against a rotating steel disc. Calculated sliding speed was approximately 2.3 m/s. All experiments were carried out in air at room temperature (20°C) and under atmospheric pressure. Universal hardness of composites was measured using Zwick Z2.5/TS1S testing machine according to the standard DIN 50359. Also Vickers hardness tests have been performed.

3. RESULTS

3.1 Recycling mechanism of composite

Composite recycling mechanism investigation show that the spontaneous disintegration takes place in the regions with different of new chemical compounds. The SEM investigation shows that the compounds were formed on base of such elements as Co, Cu, Si, Zr, Ti, Fe, Al, C and O. These areas of testing on SEM picture (Fig.1) are shown.

In region N1 the large grains of B_4C is shown. Around these grains with measures 7-10 μm the thin layer of Al_3BC was formed. The region N2 contain very large amount of chemical elements and compounds also. In this region were grains who take part in spontaneous disintegration of composite (Fig. 2).

This region contain all chemical elements (C, O, Co, Cu, Al, Si, Zr, Ti, Fe) of starting materials of powder mixture and from work piece of disintegration mill and attrition mill also. The chemical content of composite in region N2 on Fig. 3 is shown. As result the binary and ternary chemical compositions were formed. The thickness of these planes about 200 nm and length over 1 μm. This compounds forming duration depends from heat treatment temperature, time and level.

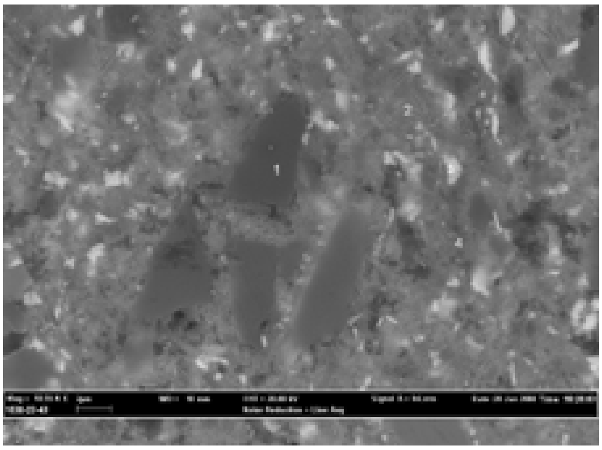

Fig. 1. The microstructure testing regions of recycled composite are shown on SEM picture.

Fig. 2. On SEM picture of composite the chemical compounds, which were formed during high temperature heat treatment is shown. They have influence on mechanical properties relaxation, and spontaneous disintegration of composite.

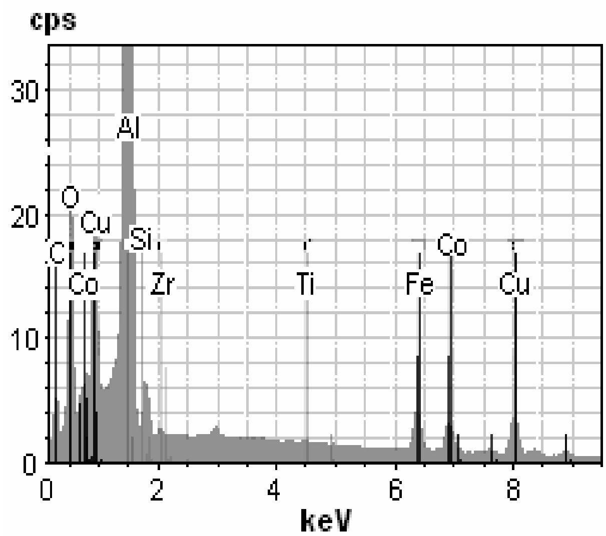

Fig. 3. Chemical elements content of composite in region of N2 is shown.

By heat treatment temperature increase up to 1150°C the relaxation of composite staring and during next 2-3 ears the mechanical properties decrease. At this temperature in material aluminum carbide (Al_4C_3) forming took place. For mechanical properties, such as hardness increase the new heat treatment required only.

Heated at temperatures 1300-1500°C composite spontaneous disintegration took place during next 2-3 months after heat treatment. In this material the aluminum nitride (AlN), aluminum boron carbide ($Al_8B_4C_7$), and aluminum boron (AlB_2) were formed, and by this the aluminum content was decreased in composite down to zero. Less than 1150 °C heat treatment temperature the composite contain free aluminum content and the aging hardening of composite took place. Regions N3 and N4 contain the aluminum content. In region N3 (white grains on picture Fig. 1) the aluminum (Al), copper (Cu) and tungsten (W) based carbides, and aluminum oxide (Al_2O_3) were formed. Opposite in region N4 (grey key image on the Fig. 1) contain the aluminum oxide (Al_2O_3) and copper (Cu) only. These regions (N1, N3, and N4) are thermal stabile and don't take part in spontaneous disintegration of light weight composites and cermets.

3.2. Recycled composite structure and properties

New composite (N1), manufactured from spontaneous disintegrated cermets after attrition milling contain in mixture the milled power of recycled composite and as new binder Al -41.4 wt.%; Cu – 4.3 wt.%; C – 4.3 wt.%, and WC-NiCo – impurities from attrition mill work pieces and balls. After spontaneous disintegration and attrition milling during 3-4 h and the material was heat treated at 1080 °C in zirconium oxide (composite N1) and (composite N2) double heat treated in TiC powder at 1460°C during 0.5 h in vacuum.

Composites N3 and N4 were manufactured from initial or starting composite after their heat treatment at 1500°C, disintegration and attrition milling. Binder metal content of new recycled composite contain 50 wt. % Al. Heat treatment regimes were identical as for composites N1 and N2. After SHS-processing this material was heat treated at 1080°C in ZrO_2 granules at 4 h. Material (N3) was double heat treated at 1460°C during 30 minutes.

The material (N1) has hard phase (B_4C) with mean grain size about 5 μm (Fig. 4), with microhardness 3400HV0.05 and binder phase with mean microhardness of 520HV0.05 and 360HV0.05 in different regions of testing. The new hard phase region (light areas on Fig. 4) has microhardness over 2000HV0.05 and after heat treatment at 1460°C in vacuum the microhardness was decreased down to 1800HV0.05.

Materials N3 and N4 manufactured from heat treated at 1500°C in vacuum composite, disintegration refining and attrition milling has ultra fine grained hard phase and the grains microhardness measuring was impossible. Were defined the areas of different grain/phase regions only.

Microstructure testing results of recycled composite show that structures is different by comparison with initial composite structure. This composite don't have large grains of boron carbide (Fig. 4, and 5). In binder metal phase of aluminum the new refractory compounds were formed. These phases forming are identical with phases forming in staring composite and depend from heat treatment temperature. Unfortunately, during disintegration and attrition milling the mixture was appending different impurities during processing. These impurities were aluminum borate ($Al_4B_2O_9/2Al_2O_3$-B_2O_3), tungsten carbide (WC), titanium carbide (TiC) and wuestite (FeO).

For mechanical properties testing the recycled composites (N1-N4) were used. The mechanical properties testing show, that spontaneous disintegrated of composites (N1, and N2) indentation work is higher on 1.75 times but universal-, plastic- and Vickers hardness are low up to 2 times with comparison of composites N3 and N4. The indentation modulus and ratio of elasticity have identical level for all recycled composites. By this the mean indentation module of recycled composites was lower up to two times then the in initial condition light weight boron carbide based cermets have. Ratio of elasticity of recycled composites doesn't decrease with comparison of cermets.

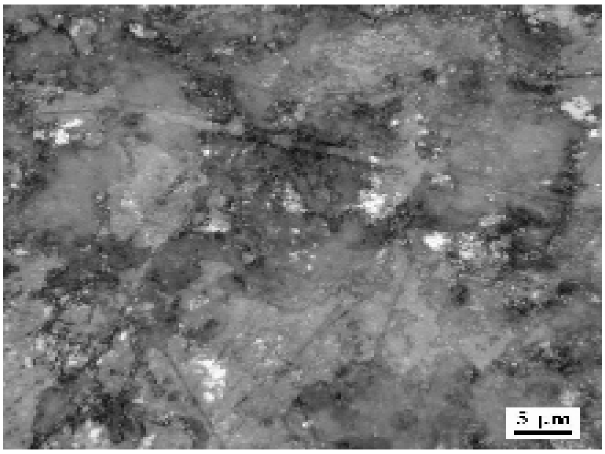

Fig. 4. Recycled composite microstructure is shown. The new refractory phases (light) are formed.

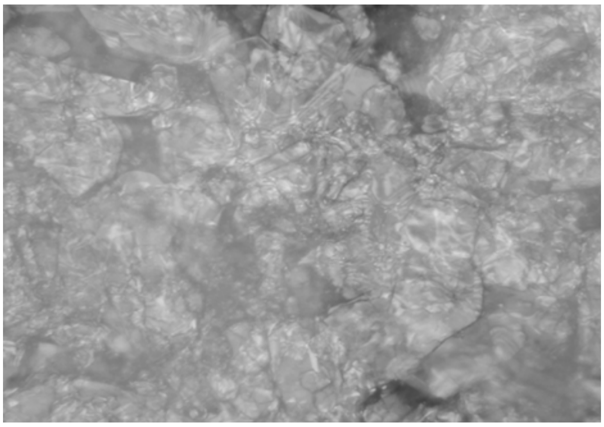

Fig. 5. Microstructure of recycled composite with low friction coefficient is shown.

The volume dry sliding wear resistant and friction coefficient of recycled composites have opportunity distribution. These properties are higher up to 20-30% with comparison of primary cermets after thermal hardening processing. The dry sliding in system of block-on-ring testing results were: N1=0.14mm^3/km; N2= 0.13mm^3/km; N3= 0.11mm^3/km; and N4= 0.09mm^3/km. the lowest friction coefficient has composite N4=0.23 in this study. This parameter is lower down to two times for comparison of primary light weight cermet.

The hydroerosion wear in sodium solution of these composites are different and don't have identical distribution with hardness of recycled composites. This parameter of composites depends from heat treatment temperature, surrounding and regime. By heat treatment temperature increases the wearing loss increase in many times. Exactly this increasing is high after heat treatment at 1460°C in vacuum, up to 2-3 times for recycled composites N2 and N4 accordingly. The hydroerosion wear testing results were: N1=0.08g/h; N2=0.014g/h; N3=0.001g/h; and N4=0.003 g/h.

4. CONCLUSIONS:

1. The given experimental results show that the thermal recycling of boron carbide based cermets/composites is possible.
2. The mechanism of thermal recycling of composite starting after heat treatment at temperature higher then 1150°C.
3. At temperature 1150°C the binary and ternary chemical carbides forming took place on base of boron carbide and aluminum or the chemical compounds formed from these elements.
4. The recycling process starting in region in which the concentration of chemical elements or chemical compounds number is maximal.
5. During refining of primary composite in disintegrator and/or in attrition mills the materials of these installations as impurities increase in the powder mixture and those impurities have influence on SHS process parameters and properties of recycled composites.
6. Recycled materials wear rate is lower then the primary composites have.
7. Friction coefficient decreases are identical as wear rate decrease, but don't have correlation with hardness of recycled composite.
8. Hydroerosion wear or weight loss in sodium solution during testing time 48 h depend on aluminum content in composite and decrease in result of heat treatment temperature increase.
9. The hard phase grains microhardness was decreased lightly in result their thinning during milling and during thermal processing by SHS and heat treatment in result of chemical reaction or as solute phase forming in binder of composite.
10. The heat treatment in TiC power have influence on run out of aluminum content from boron carbide-aluminum based composite and/or cermet.

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