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Producing composite materials based on ZrB_2, ZrB_2-SiC

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Abstract. The effect of mechanical treatment by planetary ball milling on the properties of hot pressed ZrB_2 - SiC ceramics was studied. It has been shown that material densification after mechanical treatment is finished at initial stages of sintering process. Addition of SiC causes a substantial increase in density of the sample to 99% of the theoretical powder containing 20% of silicon carbide, in comparison with samples ZrB2 density not exceeding 76%. It has been shown that all defects which were accumulated during mechanical treatment anneal in hot pressure process and there are no any changes of CDD values in sintered ceramics.

1. Introduction

High-melting compounds are the main part of the materials utilized in high-temperature technologies for heat protection of aerospace machinery and in electronics. Between high melting point materials, ZrB_2-based ceramic composites are the point of special interest. ZrB_2 ceramics with SiC addition demonstrate high thermochemical stability, including outstanding resistance to oxidation under high and ultra-high temperatures [1].

ZrB2-SiC composites are being produced via sintering process under high pressure and temperature of 2000 °C [2,4]. Strong covalent bond in ZrB2 leads to low atoms diffusibility, thus making its processing more complicated. As all the substances with covalent bond, zirconium diboride demonstrates lack of concentration and defect mobility of the lattice cell. Low velocity of the diffusion-viscous flow necessitates activation of consolidation via crystal structure imperfection decrease, diffusion processes acceleration and alleviation of the plastic deformation during baking process. Mechanical treatment of the powders in high-energy mills stays one of the most effective methods for baking temperature reduce and superdense microcrystalline structure production of high-melting compounds without application of activating additives which usually have negative effect on the thermal properties of the material [3].

The aim of this work was to investigate the influence of mechanical treatment of ZrB_2-SiC powder system on the structure of the produced ceramic composites.

2. Experiment

ZrB_2 (d_{50} =2.5μm)-SiC(d_{50} = 4.2 μm) powder blends with silicon carbide content of 10%, 15% and 20% (v/v) were used. The blends were mechanically treated in planetary mill with grinding bodies' centrifugal acceleration of 30 g (where *g* is gravitational acceleration). Treatment time was from 1 to 20 minutes.

Ceramic composites sintering was performed at a temperature of 1800 °C and at a pressure of 75 MPa. Time of isothermal exposure was 30 minutes. Phase composition and crystal lattice parameters were studied by means of XRD analysis with CuK_{α} irradiation. Scanning electron microscope observations operated at 20-30 kV were used to average grain size using Tescan VEGA-3SBH. Specific surface area was investigated with BET method.

3. Results and Discussion

Dependence of the specific surface area from the duration of mechanical treatment of ZrB_2 and ZrB_2-SiC powders in planetary mill is plotted in Figure 1. Before the mechanical treatment specific surface area of the powders was not differ. Maximum surface area (7.6 m^2/g) was found for ZnB_2 powder. After the mechanical treatment during 20 minutes it was reduced to 5.9 m^2/g. These results don't differ significantly from ones for ZrB_2-SiC powders (7 m^2/g and 5.8 m^2/g before and after the treatment, respectively). Thus, for all the investigated powder systems the reduce of surface area with increase of the mechanical treatment time was found.

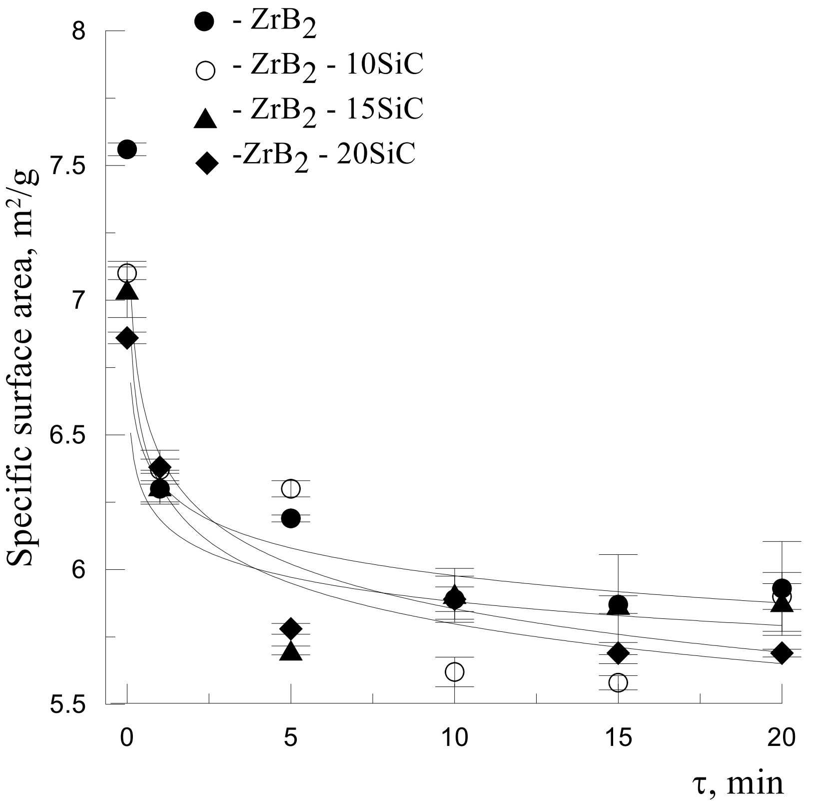

Figure 1. The influence of the mechanical treatment time on BET surface area for ZrB_2 and ZrB_2-SiC powder systems.

Changes of the powder morphology with mechanical treatment duration are shown in Figure 2 and Figure 3 using ZrB_2 - 20%SiC powder system. After 20 minutes of the mechanical treatment, formation of the aggregates with size of 15 μm was observed.

XRD analysis of the ZrB_2 powder and ZrB_2-SiC powder systems indicated no phase changes during the mechanical treatment. Only ZrB_2 reflections were marked in the XRD pattern of the ZnB_2 and ZrB_2-

SiC powder system containing 5% wt. of SiC. On the XRD patterns with higher concentration of SiC its reflections were distinguished.

With increase of the mechanical treatment time ZrB_2 reflection tailing was observed that may be a result of ZrB_2 dispersity rise. Calculations of the X-Ray coherent-scattering regions size demonstrated that with prolongation of the mechanical treatment time it was reduced from 46 to 37 nm (Figure 4). In that time, any changes in X-Ray coherent-scattering regions size with increase of SiC concentration were not observed.

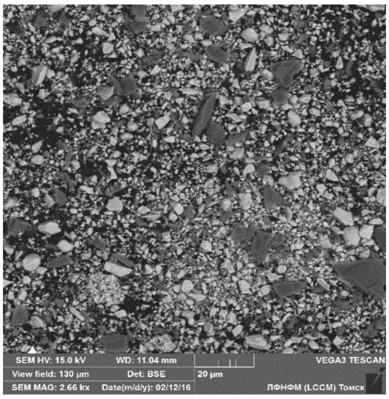

Figure 2. Original blend.

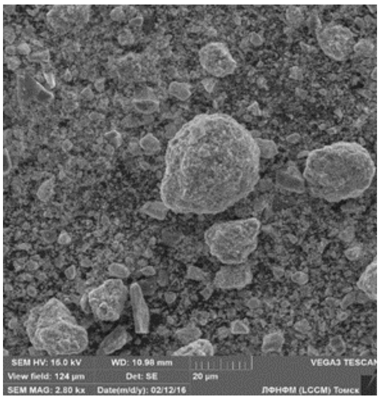

Figure 3. Changing of the powder morphology during the milling process after 20 minutes of the mechanical treatment.

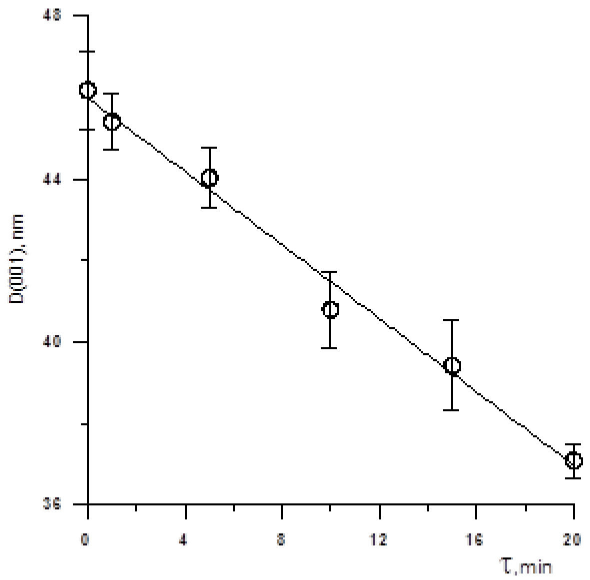

Figure 4. The influence of the mechanical treatment time on the coherent-scattering regions size of the ZrB_2 powders.

Phase structure analysis of the ZrB_2 ceramics and ZrB_2-SiC composite didn't show any differences from powders phase structure. Mechanical treatment influenced ZrB_2 X-Ray coherent-scattering

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regions size in consolidated materials. In ZrB_2 ceramics and ZrB_2-SiC composites produced from the powders, mechanically treated in planetary mill for 20 minutes, average ZrB_2 X-Ray coherent-scattering regions size was found of 85 nm, which is less than for non-treated powders (98 nm).

Mechanical treatment of the powders influenced density of the produced ZrB_2 ceramics and ZrB_2-SiC composites (Figure 5). For both ceramics and composites increases of the mechanical treatment time lead to the growth of density. However, the largest density was demonstrated by ZrB_2-SiC composites. Thus, relative density of ZrB_2 ceramics was less than 0.76, while for ZrB_2-SiC (80%/20% wt.) it was found at 0.98 (Figure 5).

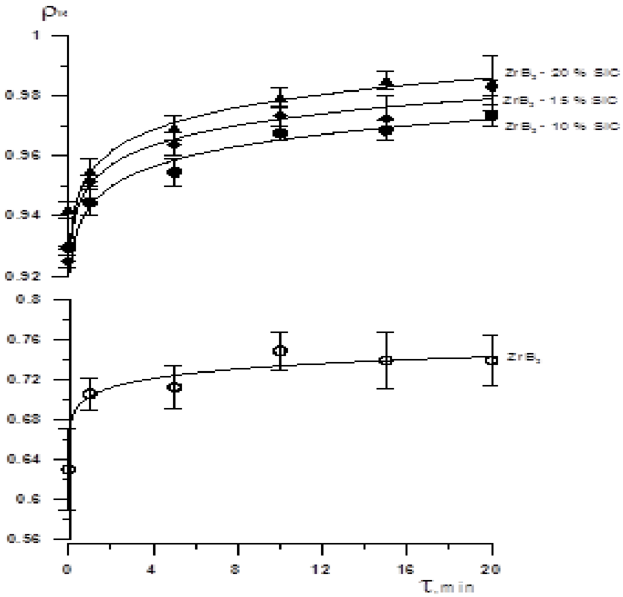

Figure 5. Influence of the mechanical treatment time on relative density of the hot pressured ceramics.

4. Summary
It was demonstrated that mechanical treatment of ZrB_2 and ZrB_2-SiC powders leads to the reduction of their specific area. That fact may be explained by agglomerates formation. Mechanical treatment of the ZrB_2-SiC powders increases density of the produced ceramic materials.

Acknowledgement
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