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Effect of nanosized titanium and silicon carbides on synthesis and consolidation of titanium silicon carbide during spark plasma sintering

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Abstract. Using spark plasma sintering method, at temperature $T = 1400^\circ\text{C}$ and load of 30 MPa samples of composite material $\text{Ti}_3\text{SiC}_2/\text{TiC}$ were obtained. Before SPS powder mixtures with molar ratio $3\text{Ti}-1.25\text{SiC}-0.75\text{C}$ with addition of up to 4% wt of nanopowders of titanium carbide or silicon carbide were mechanically activated in a planetary mill. Material structure was studied using X-ray structural analysis, hardness and fracture toughness was evaluated on basis of Vicker's indentation results. It was established that introduction of nanocarbides up to 1% wt significantly reduces contents of Ti_3SiC_2 , and further on practically has no influence on phase composition. Increase of isothermal time from 5 to 15 min leads to an increase in the Ti_xSi_y secondary phases to 11–14%. Introduction of nano-TiC and nano-SiC into mixtures increases crack fracture toughness to $7.06-7.55 \text{ MPa}\cdot\text{m}^{1/2}$ for samples after 5 min of SPS and practically does not change it after 15 min of SPS.

1. Introduction.

Composite materials on of oxygen-free compounds are widely enough known and are used in production of wear-resistant parts for extreme (temperature, environment) operational conditions. Ti–Si–C composition is most promising system due to number of advantages over other systems. Optimal elemental contents of such composition during high-temperature consolidation provides for formation of multi-phase system, consisting mainly from titanium silicon carbide Ti_3SiC_2 and titanium carbide TiC. Carbides are widely used as basis for tungstenless hard alloys, in carbidic steels, wear-resistant materials, as they have high hardness, wear resistance, resistance to acids, alkali, temperature up to 1000°C [1, 2]. Disadvantage of traditional ceramics is low resistance to damage. In this aspect materials on basis of laminate compound – titanium silicon carbide are of interest, which has quasi-plasticity feature, i.e. is able to restrict crack propagation effectively [1, 3]. Addition of additional phase-forming elements, improving complex of properties of wear-resistant materials is a relevant objective [3–6].

The purpose of the work was to study evolution of phase composition during spark plasma sintering of Ti–SiC–C powder composition, supplemented with nanosized powders of silicon carbide and titanium carbide, and evaluation of Vickers hardness depending to contents of secondary phases.

2. Methods of experimentation and analysis.

For synthesis of titanium silicon carbide powders of titanium TPP-7, silicon carbide with fraction less $10 \mu\text{m}$ and graphite S-1. To increase hardness and wear resistance comparing to soft titanium silicon carbide obtained by reaction sintering of the source powders, 0.5–4.0% wt of nanosized powders of silicon carbide and titanium carbide were added. Powder mixtures were treated in planetary mill



SAND under following conditions: 1) ratio of drum angular velocity to cuvette angular velocity $k = -0.39$; 2) ratio of planetary rotation radius to cuvette radius $n = 2.7$; 3) drum rotation frequency 280 min^{-1} ; 4) cuvette rotation frequency 620 min^{-1} . To reduce milling of foreign material from the equipment titanium cuvettes were used, to prevent oxidation of the components mechanical activation (MA) was performed under vacuum. As grinding bodies titanium cylinders diameter 10 mm, height 10 mm were used. Ratio of masses of grinding bodies and material processed was 7.5:1.

Consolidation of powder mixtures was performed by spark plasma sintering method using SPS 1050b unit (Dr. Sinter, Japan) at temperature 1400°C , holding time for 5 and 15 min [2, 3].

Phase composition was analyzed on a XRD-6000 (Shimadzu) X-ray diffractometer in $\lambda\text{-Cu}$ radiation using Rietveld full-profile analysis. Structural analysis was performed using an Axiovert 40MAT (Carl Zeiss) optical microscope.

Vickers hardness was determined by indenting samples by diamond pyramid under load of 30 kg, and calculated per formula

$$H_v = \frac{18187.74 \cdot P}{a^2} \quad (1)$$

where P is the load, kg; a is the indentation diagonal, μm .

Crack resistance was evaluated per Evans formula [7]:

$$K_{IC} = 0.16 \cdot \left(\frac{c}{a}\right)^{-1.5} \cdot (H_v \cdot a)^{0.5} \quad (2)$$

where c is the mean length from center of impression to tip of crack obtained during indentation, μm ; a is the $\frac{1}{2}$ length of indentation diagonal, μm ; H_v is the Vicker's hardness, GPa.

3. Discussion of results.

Analysis of shrinkage during sintering shows that addition both of silicon carbide and titanium carbide in quantity up to 2% reduces shrinkage, and in greater quantity – increases it again (figure 1). Increase of holding time even greater emphasizes differences in shrinkage. For 1–2% of additives increase of holding time practically has no influence on shrinkage, while for other compositions holding time of 15 minutes increases it by 10–12%.

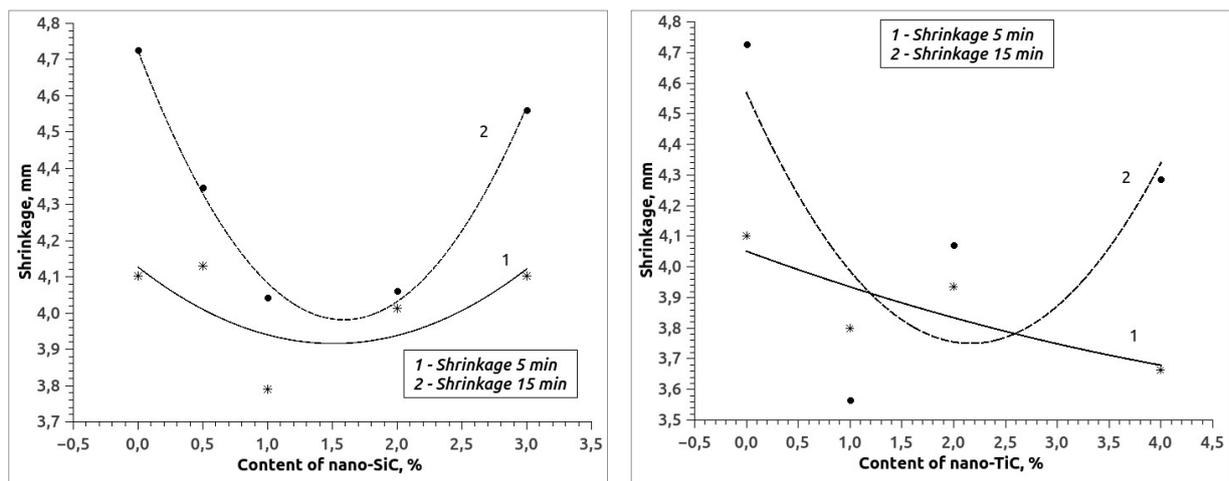


Figure 1. Effect of (a) nano-SiC and (b) nano-TiC additives on the shrinkage at SPS.

All compositions after SPS consist mainly from titanium silicon carbide, but introduction of nanosized additives somehow reduces its content: from 80 % for composition without additives to 65 for sample with 4% SiC. Probably carbides nanopowders inhibit not only shrinkage, but also synthesis of the compounds during reaction sintering. Figure 2 shows dependencies of content of Ti_3SiC_2 and TiC phases on contents of TiC and SiC nanosized powders during spark plasma sintering at

$T = 1400^{\circ}\text{C}$. Obviously, introduction of up to 1% wt nanocarbitides significantly reduces contents of ternary compound, and further on does not practically influence phase composition. Independently to what additive is doped to mixtures nano-TiC or nano-SiC, phase composition in studied range of 1–4% wt stays stable.

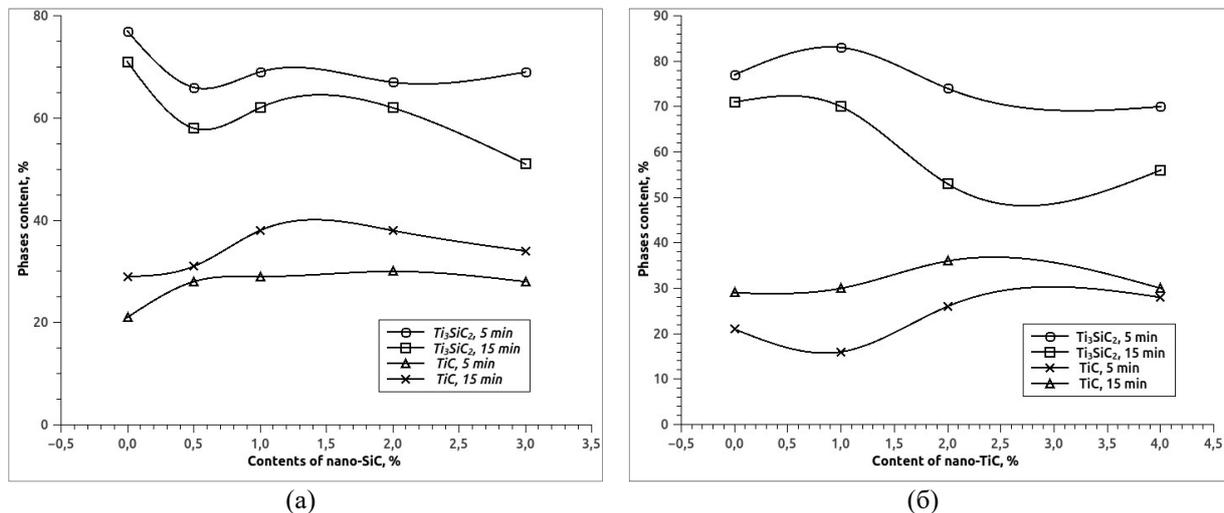


Figure 2. Phase composition dependence at SPS of mixtures with different content of (a) nano-SiC and (b) nano-TiC additives.

It should be noted that during SPS, except for main phases of Ti_3SiC_2 and TiC, secondary phases of titanium silicide Ti_xSi_y are observed. In largest quantity (up to 11–14%) they are found during SPS for 15 min for all compositions. During SPS for 5 min their contents does not exceed 1–3%. Obviously, this is determined by increase of role of diffusion mass transfer at increase of high temperature consolidation time. In majority of cases the researchers showed that already at 1200°C shell structures from Ti_5Si_3 and TiC are formed on surface of titanium particles, and further on with temperature increase, due to interaction of Ti_5Si_3 and TiC titanium silicon carbide Ti_3SiC_2 is formed. On the other side, mechanism of phase composition change depending on content of additives and SPS duration at 1400°C is complex enough and is possibly determined by several important processes. During heating not only reaction sintering takes place, but at high temperature partial decomposition of titanium silicon carbide is possible, leading to increase of titanium carbide share at 1400°C [8]. Wei-Kong Pang and I.M. Low [9], on basis of refinement of Ti_3SiC_2 phase transformations determined by thermal decomposition during vacuum annealing, showed that increase of TiC_x as result of Ti_3SiC_2 decomposition was observed during temperature increase from 1200 to 1500°C . That is, Ti_3SiC_2 originally decomposes very slowly to TiC_x at 1200°C through sublimation of Si and Ti, because their vapor pressure exceeds pressure in vacuum furnace. Consequently speed of Ti_3SiC_2 decomposition to TiC_x significantly increases.

All samples after SPS are characterized by 3–5% porosity. Microstructure of one of compositions is shown in figure 3. The material consists of titanium silicon carbide grains (dark phase) and titanium carbide grains (bright phase). Titanium silicon carbide grains are bigger than titanium carbide grains due to greater growth speed during spark plasma sintering.

Figure 4 shows the dependence of the Vickers hardness on the content of nano-TiC and nano-SiC additives. From the results obtained it follows that composites obtained with nano-SiC additives have slightly greater hardness, as there is a greater titanium carbide content in SPS-consolidated samples. At the same time, in samples made from mixtures with addition of nano-TiC, the TiC content is lower, and consequently Vickers hardness is lower.

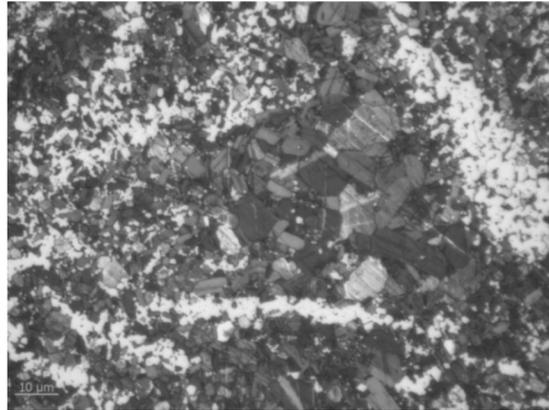


Figure 3. Microstructure of Ti-SiC-C + 2% nano-TiC composition.

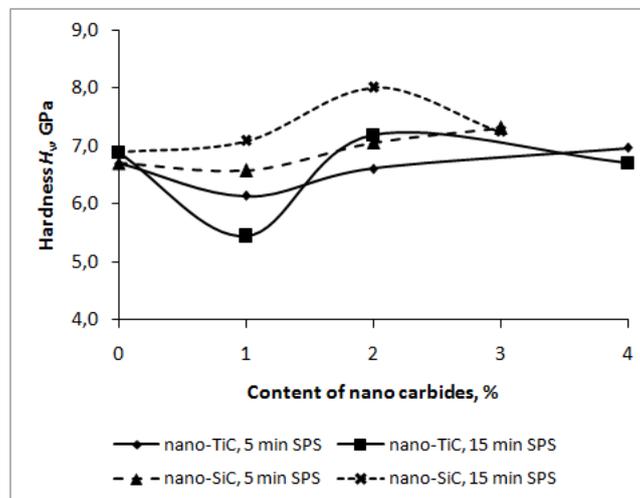


Figure 4. Effect of nano-TiC and nano-SiC additives on the Vickers hardness of the composite material.

Fracture toughness calculated per Evans for material without nanocarbide additives after SPS for 5 and 15 min was 6.58 and $6.28 \text{ MPa} \cdot \text{m}^{1/2}$. Introduction of nano-TiC and nano-SiC into mixtures increases crack resistance to 7.06 – $7.55 \text{ MPa} \cdot \text{m}^{1/2}$ for samples after 5-min SPS and practically does not change it after SPS for 15 min.

4. Conclusions

Using spark plasma sintering method at 1400°C under a load of 30 MPa , $\text{Ti}_3\text{SiC}_2/\text{TiC}$ composite material samples were obtained. The addition of nano-TiC or nano-SiC powders up to 1% wt, prior to consolidation, significantly reduces the Ti_3SiC_2 content, and further on (up to 4% wt) practically does not affect the phase composition. The increase in the isothermal holding time from 5 to 15 min leads to an increase in the content of Ti_xSi_y secondary phases up to 11 – 14% . Introduction of nano-TiC and nano-SiC into mixtures increases the fracture toughness to 7.06 – $7.55 \text{ MPa} \cdot \text{m}^{1/2}$ for samples after 5-min SPS and practically does not change it after 15-min SPS.

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