

Phase formation in the SiC-Al₂O₃-ZrO₂ system during hot pressing by the method of electroconsolidation

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The composition changes in the electroconsolidation of powdered ceramic materials based on SiC with Al₂O₃ and ZrO₂ contents are considered. Analyzed possible mechanisms of decrease of compaction ability due to chemical reactions and phase composition changes. The influence of nanodispersed powders on the formation of a eutectic composition during liquid-phase sintering and compaction of a material is shown. The nanocomposite material based on β-SiC, satisfying the requirements of a polyfunctional material obtained.

Keywords: nanocomposite, liquid-phase sintering, compaction, electroconsolidation.

Рассмотрены изменения состава при электроконсолидации порошковых керамических материалов на основе SiC с добавкой Al₂O₃ и ZrO₂. Проанализированы возможные механизмы ухудшения уплотняемости вследствие протекания химических реакций и изменения фазового состава. Показано влияние нанодисперсных порошков на образование эвтектического состава при жидкофазном спекании и уплотняемость материала. Получен наноконпозиционный материал на основе β-SiC, удовлетворяющий требованиям полифункционального материала.

Фазоутворення в системі SiC-Al₂O₃-ZrO₂ при гарячому пресуванні методом електроконсолідації. *Р.В. Вовк, М.В. Кислиця, М. Рукі*

Розглянуто зміни складу при електроконсолідації порошкових керамічних матеріалів на основі SiC з добавкою Al₂O₃ та ZrO₂. Проаналізовані можливі механізми погіршення ущільнюваності внаслідок протікання хімічних реакцій і зміни фазового складу. Показано вплив нанодисперсних порошків на утворення евтектичного складу при рідкофазному спіканні і ущільнення матеріалу. Отримано наноконпозиційний матеріал на основі β-SiC, що задовольняє вимогам поліфункціонального матеріалу.

1. Introduction

Composite tool materials are widely used for the processing of high-hard, difficult-to-work alloys of metals and other materials, possessing mechanical characteristics that are significantly superior to hard alloys. Silicon carbide is an excellent basis for the manufacture of superhard, heat-resistant cutting tools, but it is difficult to sinter [1-2]. The

solution to this problem is to use different methods of activation: the introduction of additives, the use of nanoscale powders, intensive methods of consolidation [3]. Highly active compaction techniques, such as FAST (Field-activated Sintering Technology), SPS (Spark Plasma Sintering), as well as the use of nano-sized powders, allows to obtain composite materials with a fine structure [4-5], but on the other hand entails inevitable

changes composition, due to increased chemical activity [6]. It should also be noted that the use of special structuring techniques, including using the features of the morphology of the defective ensemble and the use of extreme external influences [7–9], can play a crucial role in the development of technologies for producing newer multifunctional materials. The purpose of this work is to research the manifestation of high chemical activity of nanopowder materials during electroconsolidation and optimization of sintering regimes based on obtained data for creating nanostructured composite materials with high physico-mechanical properties.

2. Experimental

Powders of Al_2O_3 and ZrO_2 , possessing high hardness, chemical and heat resistance, which is necessary both for the tool material and in demand in other industries, were used as an additive. Nanopowders with an average crystallite size of about 50–100 nm were used. Structure researches were performed using MIRA3 TESCAN electron microscope. Structural and phase researches of the samples were carried out on an X-ray diffractometer DRON-4-07 in $\text{Cu-K}\alpha$ radiation. Determination of microhardness and crack resistance of the obtained samples was carried out using a microhardness tester NEXUS 4504.

Raman spectroscopy showed the predominance of the phase of cubic SiC (3C) with transverse and longitudinal modes and the presence of a small amount of 6H-SiC phase. Also, free carbon C is present in the composition. Based on this nano-SiC powder and additives of nanopowders of Al and Zr oxides, batch was prepared for further compaction by electroconsolidation.

Based on the results of X-ray phase analysis, the charge consists of a mixture of Al_2O_3 with parameters $a = 4.760 \text{ \AA}$; $c = 12.993 \text{ \AA}$ and SiC-3C with the lattice parameter $a = 4.359 \text{ \AA}$. The size of the coherent scattering region practically coincides and is 82.7 nm and 87.7 nm, respectively. Both Al_2O_3 and SiC are in the nanostructured state. On the diffractogram (Fig. 1), there are additional lines from the Vaseline used for the binding of powders, the width of the lines is not affected.

The compaction of ceramic samples from the powder batch was carried out on an original hot-pressing unit with alternating current passing through the mold and the sample itself [10].

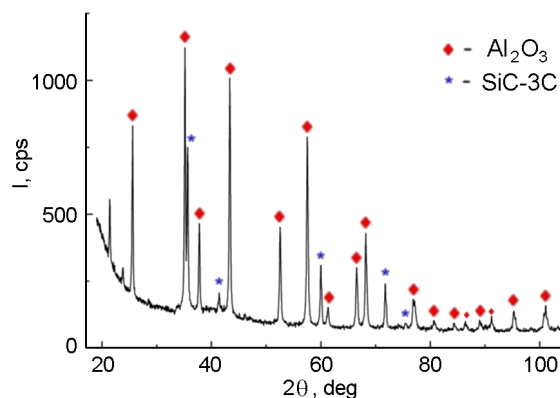


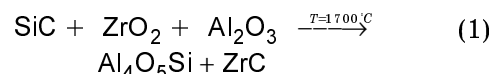
Fig. 1. Diffractogram of the initial powders

3. Results and discussion

The results of X-ray researches of the samples are shown in Fig. 2 and Tabl. 1. Based on the results of X-ray phase analysis, it became known that when nanopowder mixtures of SiC, Al_2O_3 and ZrO_2 are consolidated at the temperature $T_{sint} = 1600 \text{ }^\circ\text{C}$, the phase composition does not change. Sample №1 is made of Al_2O_3 and various modifications of SiC: 3C (cubic), H (hexagonal) and SiC-IV (Si_7C_7).

When the sintering temperature increases up to $1800 \text{ }^\circ\text{C}$, a phase of sillimanite (Al_2O_3) (SiO_2) with a low hardness and density (sample №3) is formed in the sample with the same composition, which negatively affects the mechanical properties of the final product. At this temperature, it is highly undesirable to increase the sintering time for more than a few minutes, since according to the researches [11], in the sillimanite there are intra-structural rearrangements and decomposition into mullite, which is accompanied by an increase in volume by 7.2 % and a decrease in density to 3.02 g/cm^3 .

It was found that the presence of zirconium dioxide in the initial composition reduces the temperature of formation of sillimanite to $1700 \text{ }^\circ\text{C}$ (sample №4), while the entire ZrO_2 (about 10% by weight) decomposes to form ZrC.



As is known from [12], a mixture of Al_2O_3 and ZrO_2 in equal proportions at a temperature of $1860 \text{ }^\circ\text{C}$ forms a liquid phase, the presence of which, during consolidation, facilitates the compaction of the base material. But a large amount of a liquid phase activating additive can lead to an increase in porosity due to its displacement

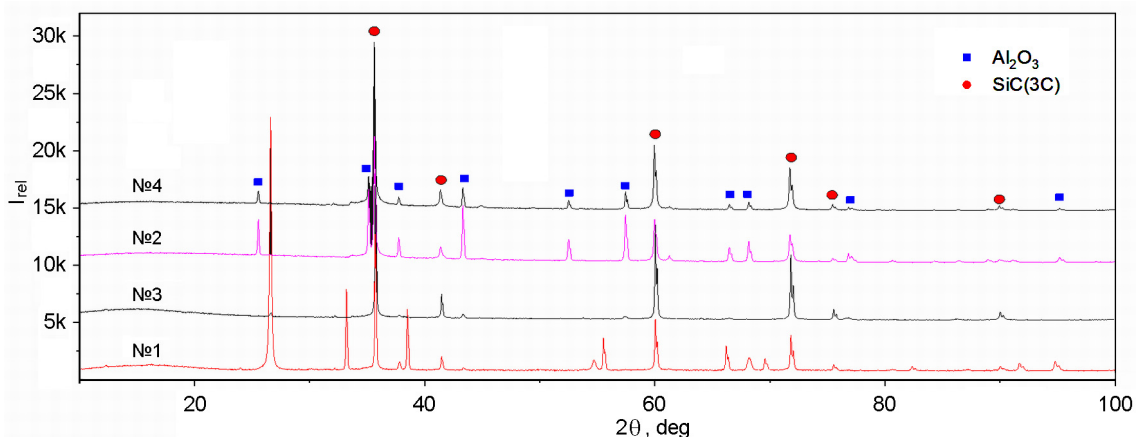
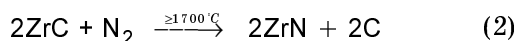


Fig. 2. Diffractogram of samples of ceramics based on SiC with additives Al_2O_3 and ZrO_2 ; №1 – SiC + 20 wt.% Al_2O_3 , $T_{\text{sint}} = 1600$ °C; №2 – SiC + 50 wt.% Al_2O_3 , $T_{\text{sint}} = 1700$ °C; №3 – SiC + 20 wt.% Al_2O_3 , $T_{\text{sint}} = 1800$ °C; №4 – SiC + 12 wt.% Al_2O_3 + 8% ZrO_2 , $T_{\text{sint}} = 1700$ °C.

from the compacted volume. In Fig. 3 shows the structure of the ceramic (sample №4 composition), pressed at a temperature of 1860 °C and a sintering time of 4 minutes (a) and traces of liquid phase separation on the mold parts (b). Their gold metallic luster is clearly visible, which seems to indicate the presence of ZrN zirconium nitride formed during the reaction [13]:



Despite the data from the sources mentioned above that the eutectic of Al_2O_3 - ZrO_2 has a melting point of 1860 °C, using the nanoscale powders of these oxides (50 nm), the presence of the liquid phase was observed when pressed already at 1700 °C (sample №4). The reason for this, apparently, is the large chemical activity of nano-dispersed materials compared with microdispersed materials.

The increase in the sintering temperature always entails the activation of processes, in particular chemical reactions (for mixtures of Al_2O_3 -SiC it is SiO, Al_2O , CO),

which can justify the compaction of the material [14]



It was found that the density and decrease of the mechanical properties of Al_2O_3 -SiC composites were increased when the consolidation temperature increased above 1600 °C. Analysis of samples of Al_2O_3 + 15% SiC ceramics compacted at a temperature of $T_{\text{sint}} = 1700$ °C (Fig. 4) showed the presence of SiO_2 formed during sintering. Presumably, the reduction of compaction ability is mainly due to excess of the percolation limit. The presence of the SiO_2 phase can also be the reason for the decrease of the compaction ability due to the formation of gases inside closed pores that are formed at high temperatures during similar reactions [15]:



Increasing the dispersion of the powder increases the defectiveness of its crystal lattice and the excess energy reserve. The increase in the surface layer with a distorted grating promotes the flow of surface diffu-

Table 1.

Phase name	Formula	Spatial group	Sample			
			№1	№2	№3	№4
Moissanite (3C)	Si C	216: F-43m	•	•	•	•
Corundum	Al_2O_3	167: R-3c,hex-1	•	•	•	•
Moissanite (H)	CSi	186: P63mc	•	•		
SiC-IV	C_7Si_7	160: R3m,hex-1	•	•		
Sillimanite	$\text{Al}_2\text{O}_5\text{Si}$	62: Pbnm			•	•
ZrC	CZr	225: Fm-3m				•

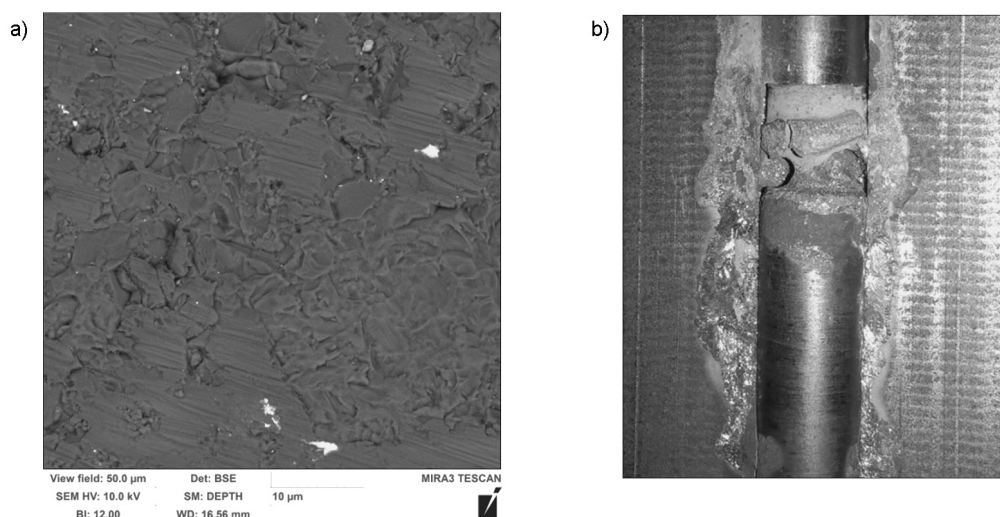


Fig. 3. The structure of the ceramics ($ZrO_2 + Al_2O_3$) + 80% SiC, $T = 1860$ °C, $\tau = 4$ min. (a) and traces of liquid phase separation on the mold parts (b).

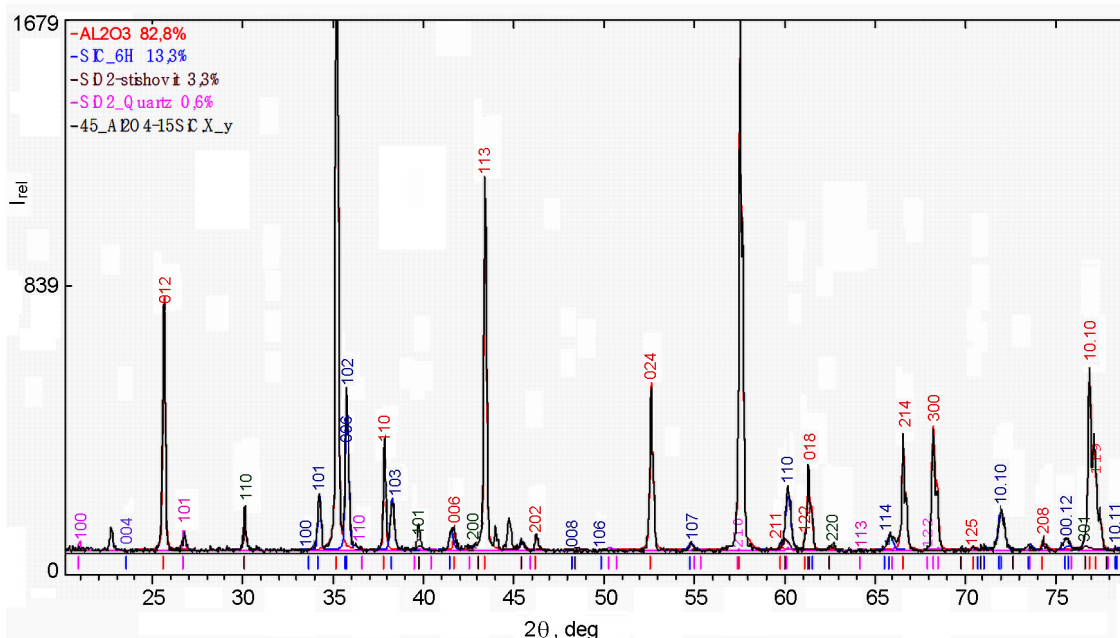


Fig. 4. Diffractogram of samples of ceramics $Al_2O_3 + 15\%$ SiC, $T_{sint} = 1700$ °C, $\tau = 3$ min.

sion and mass transfer. This approach refers to physical methods of activation of sintering. Earlier in the literature it was noted that the melting point of metal powders, whose particle size is about hundreds of nanometers, is reduced by 150-200 °C. Sintering of SiC in the presence of the $Al_2O_3-ZrO_2$ liquid phase at a temperature of $T_{sint} = 1700$ °C made it possible to obtain a ceramics with microhardness $H_V = 21.0$ GPa, crack resistance $K_{IC} = 4-4.5$ $MPa \cdot m^{1/2}$ and density 99%.

Fig. 5 shows the fractogram of the fracture of the obtained composite. The fracture, as can be seen, is transcrystalline,

which indicates a rather high strength at the interphase boundaries. Despite the fact that the density is very high, there are areas where, apparently, the liquid phase does not completely envelop the grains of silicon carbide, forming a kind of "shell". This may be the result of not enough high-quality mixing of nanopowders in the original mixture, which can also explain the not very high value of crack resistance. It is obvious that by applying better mixing, such defects can be avoided and crack resistance can be significantly improved.

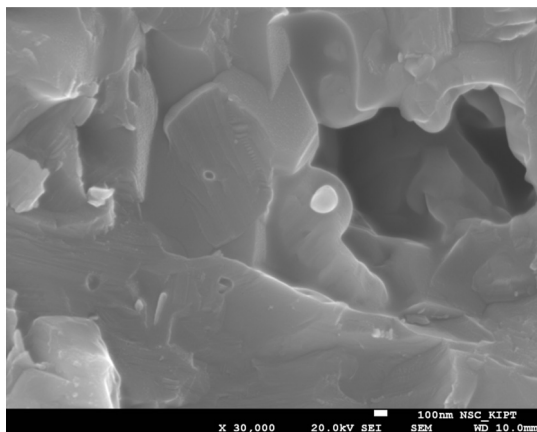


Fig. 5. Fractogram of the SiC-Al₂O₃-ZrO₂ composite fracture at a temperature of $T_{sint} = 1700$ °C, pressure $P = 30$ MPa, sintering time 3 min.

4. Conclusions

The production of composite materials with high mechanical properties by the consolidation of powder materials is associated with the solution of a number of complex problems. On the one hand, the increase in the sintering temperature promotes a more active flow of intergranular diffusion and their sintering, on the other hand it activates the formation of by-products, which negatively affects the density and hardness of the material. When choosing the optimal parameters for compaction of composite materials from nanosized powders, special attention should also be paid to their increased activity. But on the other hand, this feature of nanopowders can give a positive effect in liquid-phase sintering, reducing the temperature of formation of the eutectic mixture. Thus, the use of nanodispersed powders made it possible to perform consolidation at lower temperatures and to obtain

a composite material based on SiC with high mechanical properties ($H_V = 21.0$ GPa, $K_{IC} = 4-4.5$ MPa·m^{1/2}).

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