

NANOSCALE COMPOSITES BASED ON Al_2O_3 AND SiC PREPARED BY ELECTROCONSOLIDATION METHOD

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Abstract. In the paper, preparation and characteristics of nanoscale composites based on mixtures of Al_2O_3 with additions of SiC up to 50 wt % are described. In the experiments, electroconsolidation of powdered ceramic materials was performed in different proportions at temperatures between $T_{sint} = 1400$ and 1800 °C during 2, 3 or 4 minutes. The sintered samples were analyzed in the terms of grain growth, grain dispersion and material densification related to the sintering parameters (time and temperature) and proportion of powders. One of the most important findings was that the nanodispersed SiC supported better densification. It was demonstrated that the prolonged sintering time caused decrease of small dispersed particles, while larger particles increased in number. The obtained density of sintered material was higher than that recently reported, but achieved at substantially lower energy consumption and cheaper equipment.

Keywords: nanocomposite, sintering, compaction, electroconsolidation, densification.

Introduction

Composite tool materials are widely used for processing high-hard, hard-to-process metal alloys and other materials. The most recent researches are focused on mainly on WC-based composites [1] gradient composites [2], nano-composites [3] or micro-nano-composites [4], as well as graphene platelets reinforcing [5] or graphene multilayer reinforcing [6]. Despite their obvious advantages over hard alloys, composites are inferior to them in strength and crack resistance, which narrows the field of their application.

It was demonstrated that composite materials obtained from nanopowders from the refractory compounds, such as Al_2O_3 and SiC, had higher mechanical characteristics, especially if they were obtained by such highly effective methods as FAST, SPS or others [7]. Thermal conductivity of Al_2O_3 -SiC nanocomposites proved to be very advantageous, especially in certain sintering conditions [8]. Intensive compaction methods (electroconsolidation), as well as the use of nanoscale particles of various powders, made it possible to obtain composite materials with a fine structure, but on the other hand, entail unavoidable changes in composition, due to increased chemical activity [9].

Materials and methods

Nanopowders SiC and Al_2O_3 with an average size of crystallites about 50-100 nm were used as raw materials for sample production. Their analysis results are shown in Fig. 1. Table 1 presents the composition of chosen samples and characteristics of the sintering process.

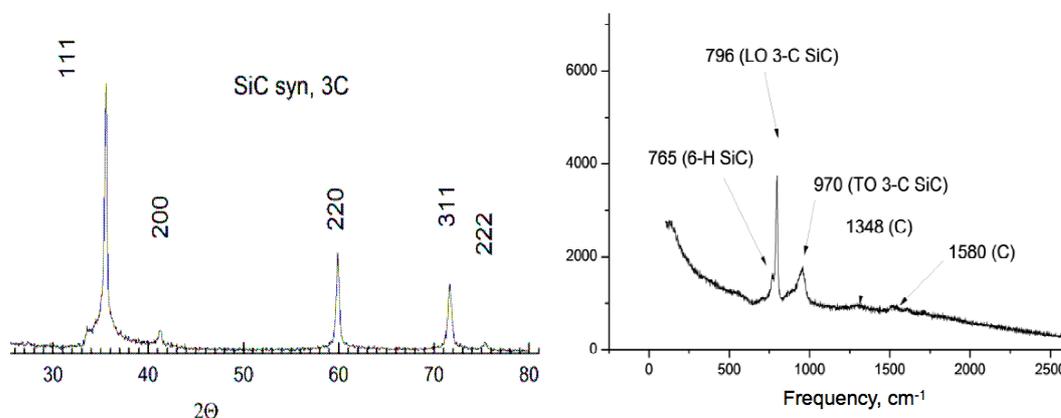


Fig. 1. Diffractogram (left) and Raman spectrum (right) of the initial SiC nanopowder

Table 1

Composition of chosen samples and characteristics of the sintering process

Sample	Composition	T_{sints} , °C	t , min	P , MPa	Morphology
AS0-6	pure Al ₂ O ₃	1600	3	35	micro
as15-6	Al ₂ O ₃ + 15 wt % SiC	1600	2	35	micro - nano
as15-4	Al ₂ O ₃ + 15 wt % SiC	1400	2	35	micro - nano
as15-7	Al ₂ O ₃ + 15 wt % SiC	1700	2	35	micro - nano
AS15-4	Al ₂ O ₃ + 15 wt % SiC	1700	3	35	micro - micro
AS15-7	Al ₂ O ₃ + 15 wt % SiC	1700	3	35	micro - nano
AS15-6	Al ₂ O ₃ + 15 wt % SiC	1600	3	35	micro - micro
as50-7	Al ₂ O ₃ + 50 wt % SiC	1700	4	35	nano - nano
as10-5	Al ₂ O ₃ + 10 wt % SiC	1500	4	35	nano - nano
as50-6	Al ₂ O ₃ + 50 wt % SiC	1600	4	35	nano - nano

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. These phases have similar density and differ slightly in physical characteristics [10]. Also, free carbon C was present in the composition.

Based on this SiC nanopowder and additives of nanopowders of aluminum oxide, the batch was prepared for further compaction by electroconsolidation. The mixture #1 was prepared out of Al₂O₃ nanopowder with SiC-3C phase, while in the mixture #2, SiC-6H phase was used. The samples sintered out of mixture #1 were marked with small letters 'as', while the ones sintered out of mixture #2 with capital letters 'AS.' From the results of the X-ray phase analysis it can be stated that the initial mixture consisted of powder Al₂O₃ 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 coincided and was 82.7 nm and 87.7 nm, respectively.

The compaction of ceramic samples from the powder batch was carried out using an original hot-pressing unit with alternating current passing through the mold and the sample itself [11]. The method can be classified as a Spark Plasma Sintering unit [12], but with some modifications [13]. The main difference was in the way of generating the electrical field, which was not pulse current typical for SPS technology, but a conventional AC power frequency without additional special equipment like pulse generators. Electroconsolidation was performed at different temperatures between $T_{sint} = 1400$ and 1800 °C. Sintering temperatures were registered using tungsten-rhenium thermocouple BP-5/20 with sensitivity 11.4 $\mu\text{V/K}$ and maximal error $\pm 0.5 \%$ of actually measured temperature. Before the experiments, the thermocouple was calibrated using optical pyrometer.

In the measurement, the following devices were applied. For the microstructure, atomic force microscopy (AFM) was applied in semi-contact mode, dual-beam scanning electron microscopy (SEM) and field emission scanning microscopy (FESEM). The AFM device Ntegra Aura provided non-linearity below 0.2 % and the noise level below 0.06 nm, a dual-beam scanning electron microscope (SEM) combined with focused ion beam (FIB) instrument Quanta 200 3D provided resolution 50 nm at 30 kV, and the field-emission SEM device Nova NanoSEM ensured high resolution of 1.8 nm at 3 kV. X-ray phase analysis was performed with the diffractometer Shimadzu XRD-6000, CuK α -radiation of $\lambda = 1.54187 \text{ \AA}$, a graphite monochromator was placed before the counter, continuous scanning θ - 2θ at scanning speed $1.2 \text{ }^\circ \cdot \text{min}^{-1}$, angle range $2\theta = 5.0$ - 100.0 ° with step 0.02 ° . In the phase analysis, database ASTM (American Society for Testing Materials) was referred.

Results and discussion

Concerning the grain growth during sintering, it is well known that with the reduction of sintering temperature and sintering time the grain growth is suppressed [14]. During the compaction of ceramics out of pure Al₂O₃ without any additions at temperatures 1600-1700 °C, average grain size is ca. 20 μm , as it is seen in Fig. 2. From the perspective of grain size dependent mechanical properties, it is quite large value.

Suppression of the grain growth with reduced sintering time or temperature, however, can have negative effects caused by impartial grain boundary diffusion. On the other hand, increasing percentage of SiC particles in the initial powder mixture can lead to the decrease of average grain size after sintering at the same temperature and time. It is seen in Fig. 3 that the composite microstructure remains essentially the same after addition SiC to Al_2O_3 . When micropowder SiC was used, the grain size was ca. $3\ \mu\text{m}$ after sintering at $T_{\text{sint}} = 1400\ \text{°C}$.

Based on the initial powder shapes, it can be stated that effective suppression can be achieved when the number of the reinforcing particles is 6 times larger than the number of the matrix particles. To achieve such a proportion, SiC percentage by weight can be increased, but it may lead to its undesirably high amount. On the other hand, application of finely dispersed powders leads to the same effect. It can be seen from Fig. 4 and 5 that the structure of composite with nanodispersed SiC remained essentially the same even after sintering at $T_{\text{sint}} = 1700\ \text{°C}$, but in addition, it had grains smaller than the sample AS15-4.

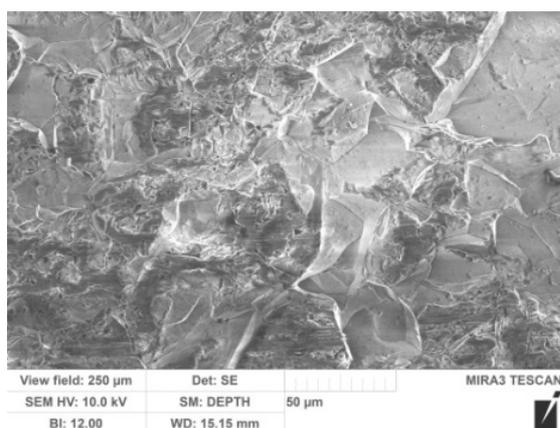


Fig. 2. Microstructure of the Al_2O_3 composite, sample AS0-6

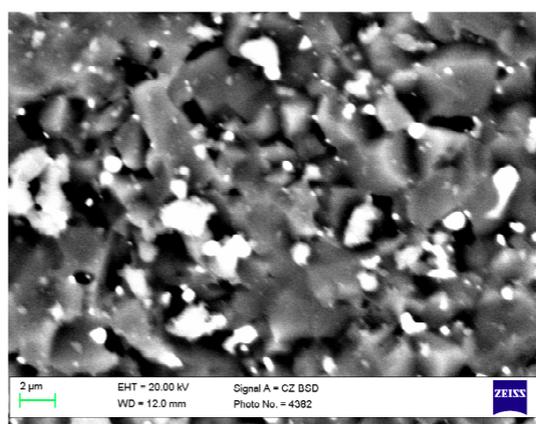


Fig. 3. Microstructure of the Al_2O_3 composite, sample AS15-4

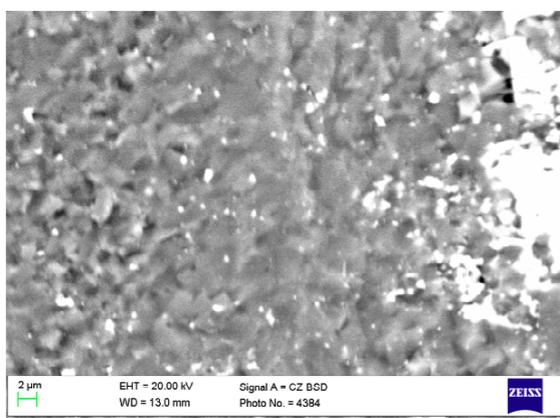


Fig. 4. Microstructure of the Al_2O_3 composite, sample as15-4

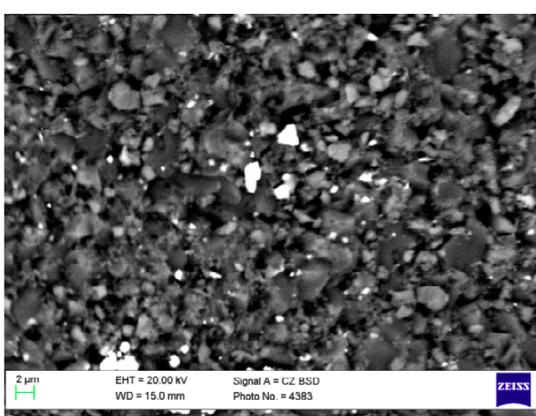


Fig. 5. Microstructure of the Al_2O_3 composite, sample as15-7

In case of nanosize materials, it is important to keep isothermal sintering time. In Fig. 6, there are structures of two samples obtained from the same initial mixture and at the same sintering parameters, but with different sintering time. It is seen that longer time caused decrease of small dispersed particles and increase of the number of larger particles. Moreover, the conformity of particle distribution became worse with longer time.

Concerning densification effects. The relative density ρ_{rel} was calculated using pycnometer measurements and theoretical values of density ρ (Al_2O_3) = $3.99\ \text{g/m}^3$ and ρ (SiC) = $3.21\ \text{g/m}^3$. Figure 7 shows graphs that demonstrate dependence of the obtained relative density on SiC content in Al_2O_3 -SiC materials sintered at different temperatures. It is noteworthy that the proposed method and

addition up to 15 wt % of SiC provided much higher density at temperatures 1400-1600 °C than 98.37 % for the recently reported material prepared by more energy-consuming two-step microwave sintering [15].

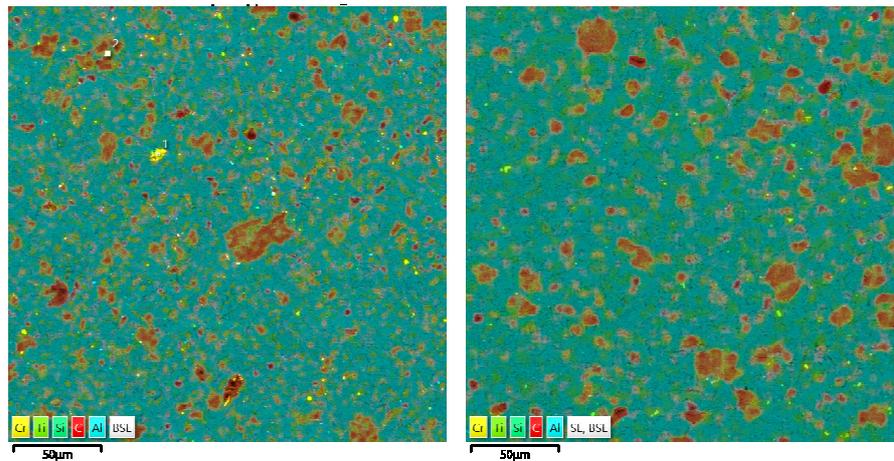


Fig. 6. Multilayer mapping of energy dispersion spectroscopy of Al_2O_3 -SiC composite sintered at $T_{sint} = 1500$ °C, during the time: $t = 3$ min (left) and $t = 10$ min (right)

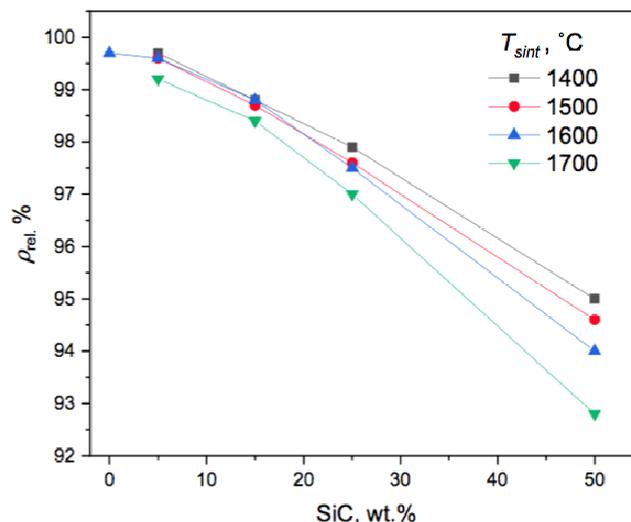


Fig. 7. Relative density of different Al_2O_3 -SiC proportions sintered at different temperatures

It was found that irrespectively of the sintering temperature, increase of the SiC content caused decrease of the obtained bulk material density ρ_{rel} . That can be attributed to the possible mechanism, where SiC grain growth could prevent boundary mobility and subsequently suppress the densification process. In addition, it should be noted, that if it were porosity which caused worsened densification, the porosity value would decrease at higher temperatures. That was not the case, however, for the composites $\text{Al}_2\text{O}_3 - 25\%$ SiC and $\text{Al}_2\text{O}_3 - 50\%$ SiC. Hence, lower densities were the result of the carbon content or formation of glassy phases with lower density.

Concerning strength. Physical characteristics of the composites Al_2O_3 -SiC(nano) are closely connected with their porosity and grain sizes. For the mixture Al_2O_3 with 15 wt % SiC, bending strength increased from 500 up to 600 MPa with the increase of sintering temperature from 1660 °C up to 1700 °C. This fact proves better completion of grain boundary diffusion. According to the Griffith's theory, strength of the ceramics is dependent on the number of the existing defects, which in turn is proportional to the grain size. Hence, decrease of the grain sizes affects the increase of the polycrystalline materials.

It was confirmed by the fact that pure Al_2O_3 with largest grains performed the lowest bending strength, namely 250 MPa. It can be assumed, however, that apart from grain size, decreased strength in the Al_2O_3 composite may be caused by anisotropy of thermal expansion of the matrix grains [16].

Thus, ceramic composite strength increased because of the grain size reduction after introduction of nanodispersed SiC. However, since increase of the sintering temperature generated grain growth, it negatively affected the material strength. It was found also, that addition of SiC had positive effect on microhardness, up to 25 wt % of SiC. Further increase of SiC concentration caused decrease of microhardness [17].

The obtained properties suggest that Al₂O₃-SiC nanocomposites may be useful in such applications as cutting inserts for hardly machinable materials like Inconel 718 [18; 19]. Since nanodispersed additives could increase the probability of occurrence of transgranular fracture mode during the fracture at room temperature, but softening of grain boundary at elevated temperatures may decrease their original mechanical properties [20], it is planned to perform tests in high temperatures of real machining conditions.

Conclusions

Production of composite materials with high mechanical properties by the consolidation of powder materials requires solution of a number of complex problems. On the one hand, the increase of the sintering temperature and sintering time promotes more active grain boundary diffusion and consolidation. On the other hand, it affects negatively the structure and grain size, decreasing the strength and hardness of the material.

In case of aluminum oxide ceramics, it can be concluded as follows.

1. The certain addition of nanodispersed SiC helped keep the average grain size of several microns. While pure Al₂O₃ without any additions sintered at temperatures 1600-1700 °C had the average grain size ca. 20 μm, addition of micropowder SiC reduced the grain size down to ca. 3 μm.
2. Pure Al₂O₃ had the largest grains and performed the lowest bending strength, namely 250 MPa. When to Al₂O₃ were added 15 wt % of SiC nanopowder, the bending strength increased up to 600 MPa. Thus, the strength of Al₂O₃-SiC(nano) composites was 2.4 times higher than that of pure Al₂O₃.
3. The obtained density for the mixture Al₂O₃ with 5 wt % SiC was above 99 % and for the mixture Al₂O₃ with 15 wt % SiC it was 98.5-99.0 %, which was higher than that reported recently 98.37 % for the more energy-consuming two-step microwave sintering method.
4. From the perspective of better results at much lower energy consumption, the material obtained with this production technology may be considered greener and more environmentally friendly.

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