Spark plasma sintering of Si₃N₄-YAG nanocomposite

P V Andreev¹, E Ye Rostokina¹, L S Alekseeva², A A Murashov², M S Boldin² and S S Balabanov¹

¹G.G. Devyatyk Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Nizhny Novgorod, 603951, Russia
²Physical-Technical Research Institute, Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, 603950, Russia

*Corresponding author: andreev@phys.unn.ru

Abstract. Spark plasma sintering (SPS) of mixtures based on silicon nitride nanopowders (Si₃N₄) was considered. A method for creating a mixture based on nanosized Si₃N₄ and a sintering additive of yttrium-aluminum garnet (YAG, Al₃Y₃O₁₂) was developed. The precursor of the sintering additive was formed by the method of spray drying using a mixture of colloidal solutions of Al₅(NO₃)₃(OH)₁₂ and Y(OH)₃(CH₃COO). The produced mixture samples were studied by X-ray diffraction analysis and SEM. The kinetics of the SPS of the prepared mixtures was studied. The effect of preliminary annealing (up to 1000 °C) of the mixture on the formation of the YAG sintering additive have been considered, as well as the method of reactive synthesis of the sintering additive in the SPS process. It was found out that sintering of the annealed mixture does not allow forming high density ceramics. As a result of reactive sintering, ceramics based on Si₂N₂O were formed.

1. Introduction

Ceramics based on silicon nitride Si₃N₄ due to its physical and mechanical properties, such as high strength and hardness, bending strength, corrosion resistance, which in addition to refractoriness provides a number of advantages as a material for both cutting and machining tools, and for critical engine components in the automobile and aircraft industries [1]–[8].

Sintering of pure Si₃N₄ is difficult because of its covalent nature, which causes the slowing down of diffusion processes, particularly the processes of viscous flow, affecting the mass transfer and densification during sintering. For this reason, in the main modern methods of sintering ceramics Si₃N₄, activating additives are used, which at high temperatures form a liquid phase at the grain boundaries of the main component and contribute to the consolidation of ceramics.

Recently, ceramics with an ultrafine grain structure, including those based on Si₃N₄, have become increasingly popular for researchers [9]. In some cases, the reduction in grain size has a positive effect on the mechanical characteristics of ceramics. Among the sintering methods, in this case, preference is given to the method of spark plasma sintering (SPS). SPS allows compacting mixtures in the high-speed modes of heating, which does not lead to significant growth of crystalline grains during sintering and allows you to form an ultra-fine grained structure in ceramics.

The aim of the study was to investigate the possibility of fabrication of ceramics based on an ultrafine grained Si₃N₄-YAG mixture using the SPS method.

2. Materials and Methods
The objects of study were powder mixtures based on Si$_3$N$_4$ produced by "abcr GmbH" (Germany) with a particle size of up to 15 nm. The application of the sintering additive by spray drying is based on a mixture of Al$_5$(NO$_3$)$_3$(OH)$_{12}$ and Y(OH)$_2$(CH$_3$COO) colloid solutions with Si$_3$N$_4$ powder. The water suspension contained 52.5% wt. of Si$_3$N$_4$-YAG in conversion to solid phase. To stabilize the suspension, 1.5% wt. ammonium polyacrylate was added. After mixing in a planetary mill, the suspension was dried by spray drying at 150 °C.

The obtained mixture was annealed in four stages at temperatures of 300, 500, 800, 1000 °C for 2-8 hours with dispersion in an agate mortar between stages. The purpose of the annealing was to complete the YAG synthesis with the formation of sintering additive layer on the surface of Si$_3$N$_4$ particles.

The SPS was performed on DR. SINTER model SPS-625 equipment. Sintering was performed at a pressure of P = 70 MPa, the heating rate was V = 100 °C/min. To study the reactive synthesis of the sintering additive SPS was also carried out for the initial mixtures without preliminary annealing.

The crystal structure of the samples was studied by X-ray diffraction analysis using a Shimadzu XRD-7000 X-ray diffractometer. The microstructure of the powders was investigated by scanning electron microscopy using a JEOL JSM-6490 instrument. The density of sintered samples was measured by hydrostatic weighing in distilled water using Sartorius CPA scales.

### 3. Results and discussion

SEM images of mixtures before and after sintering are shown in figure 1. The images show spherical particles forming agglomerates of Si$_3$N$_4$ particles and sintering additives.

![SEM images of the mixture based on Si$_3$N$_4$ nanopowder and YAG precursor before annealing (a) and after annealing (b).](image)

**Figure 1.** SEM images of the mixture based on Si$_3$N$_4$ nanopowder and YAG precursor before annealing (a) and after annealing (b).

The temperature dependences of shrinkage for sintering of the analyzed mixtures are presented in figure 2. The value of the α-Si$_3$N$_4$-YAG composite density (91.5-8.5% wt.) is accepted as $\rho_0$. The sintering kinetics of the studied samples differs significantly. The sample, which is not preliminary annealed, has a characteristic step on the shrinkage curve at about 1370 °C, typical for reactive sintering. The intensive shrinkage stage for this sample is completed at temperatures about 1700 °C. The use of preliminary annealing for the mixture leads to a shift in the intensive shrinkage stage to lower temperatures by ~ 300 °C. Further heating above $T = 1270 °C$ causes melting and decomposition of the sample.
X-ray diffraction patterns of the considered mixtures and ceramics samples prepared of them by the method of SPS are presented in figure 3.

As shown in the X-ray diffraction patterns in figure 3, we can conclude that the process of annealing of the originally amorphous mixture does not lead to the formation of a significant volume of rather coarse crystallites. Most likely, particles of mixed yttrium and aluminum oxides of various stoichiometry are formed during annealing, as is proven by a small number of low-intensity diffraction peaks. It is interesting that at the following SPS, intensive peak growth did not occur, but crystallites of one of SiO₂
modifications were found. As mentioned, the synthesis was stopped at about 1100 °C. Experiments have shown that heating the mixture above 1200 °C leads to intense melting of the sample accompanied by a sharp increase in pressure and subsequent break of the mold. This is probably due to the process of intense formation of the SiO₂ crystalline phase, which has a lower melting point than Si₃N₄.

During the reactive sintering of the initial mixture without preliminarily annealing, intensive growth of Si₂N₂O crystallites occurred, which may be associated with a high content of adsorbed oxygen in the mixture. It is also should be noted that a small fraction of β-Si₃N₄ was formed.

4. Conclusion
Therefore, oxygen adsorbed on the surface of Si₃N₄ particles has an effect on the sintering of the nanocomposites. In this case, the mixture preliminarily annealed in air leads to the formation of a mixture, the sintering of which is impossible - the sample melts intensively at a temperature of about 1200 °C. Reactive sintering allows obtaining a ceramic sample, but the Si₂N₂O phase is formed, as well as a small proportion of β-Si₃N₄. The method we have considered can be used for synthesis of ceramics based on Si₂N₂O with β-Si₃N₄ particles as a reinforcing additive.

Acknowledgments
The reported study was funded by RFBR, project number 19-33-60084.

References
[1] Knoch H and Heinrich J 1980 Materwiss. Werksttech. 11 361
[2] Ziegler G, Heinrich J, and Wötting G 1987 J. Mater. Sci. 22 3041
[3] Pyzik A J and Carroll D F 1994 Annu. Rev. Mater. Sci. 24 189
[4] Riley F L 2000 J. Am. Ceram. Soc. 83 245
[5] Richerson D W 2006 Proceedings of the ASME Turbo Expo (Barcelona) vol 2 (ASME) pp 241–254
[6] Hampshire S 2007 J. Achiev. Mater. Manuf. Eng. 24 43
[7] Bocanegra-Bernal M H and Matovic B 2010 Mater. Sci. Eng. A 527 1314
[8] Klemm H J. Am. Ceram. Soc. 93 1501
[9] Perevislov S N, Lukyanova O A, Lysenkov A S, Kim K A, and Vysotin A IOP Conf. Ser. Mater. Sci. Eng. 848 012068