Preparation of Si₃N₄-YAG mixtures for the spark plasma sintering method

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Abstract. In order to obtain ceramics based on Si₃N₄ with improved physical and mechanical properties, methods of creating composites for their subsequent consolidation by the spark plasma sintering method were investigated. Four different methods of producing mixtures based on the Si₃N₄ and Al₃Y₃O₁₂ (YAG) precursor were considered in order to obtain a homogeneous distribution of the YAG sintering additive on the surface of the Si₃N₄ particles. It is shown that the YAG and Y-Si-Al-O-N phases are formed by co-precipitation, deposition in a gelatin matrix and Pecini methods. The spray drying method does not lead to the formation of the YAG phase. This may indicate a high homogeneity of the YAG coating on the surface of the Si₃N₄ particles, preventing the growth of crystalline particles.

1. Introduction
Sintering of pure Si₃N₄ is complicated by its covalent nature. For this reason, the main modern methods of sintering Si₃N₄ ceramics use activation additives, which at high temperatures form a liquid phase at the grain boundaries of the main component and promote consolidation of ceramics. Binary and triple eutectic compounds based on the Y₂O₃–Al₂O₃ are widely used as sintering additives [1]–[6]. The additives increase the density of ceramic samples, but adversely affect the properties of the completed ceramic samples due to the fact that the sintering additive forms an amorphous phase [7], [8].

Different ways of precipitation from solutions are used for the preparation of Si₃N₄ mixtures with uniformly distributed sintering additives, to achieve a more homogeneous and finer microstructure of ceramics than mechanical mixing. [9]–[15]. Our preliminary studies have also shown the high efficiency of precipitation methods for the implementation of the technological process. [16], [17].

The purpose of presented research is optimization of the technology of Si₃N₄ high-strength ceramics fabrication by the method of spark plasma sintering (SPS). Various methods of the synthesis of composites based on Si₃N₄ powder and yttrium aluminum garnet (YAG, Al₃Y₃O₁₂) precursor are presented. The phase composition and microstructure of the obtained samples were studied.

2. Materials and methods
Mixtures based on silicon nitride with YAG precursors, synthesized by various methods were used as the object of study. Silicon nitride powder (Si₃N₄) produced by AlfaAesar GmbH & Co KG (Germany)
with a particle size of up to 44 microns was used as a raw material. The composition of the mixtures was chosen based on the expected ratio of Si₃N₄-YAG equal to 91.5–8.5% wt.

The method of co-precipitation (1) is the joint deposition of yttrium and aluminum hydroxide from solutions of the corresponding nitrates Y(NO₃)₃ and Al(NO₃)₃. Silicon nitride powder was added to an aqueous solution of nitrates at room temperature with continuous stirring. Aqueous solution of ammonia was added to the obtained suspension by drops until pH = 8 with continuous stirring. The resulting mixture was dried at 80 °C.

The Pechini method (2) included the production of citrate gels from solutions of nitrates Y(NO₃)₃ and Al(NO₃)₃ with the addition of citric acid (CA). To the aqueous solution of yttrium and aluminum nitrate the CA solution was added in such an amount that the molar ratio of CA to the total content of nitrate ions was 1 to 1. Silicon nitride powder was added to the gel obtained at the previous stage with continuous stirring. The resulting mixture was dried with continuous stirring to the condition of a thick gel. Then the gel was annealed at 350 and then 500 °C for 2 hours.

The precipitation in the gelatin matrix (3) was the creation of a thick gel based on gelatin. Gelatin was added to a hot (80 °C) solution of yttrium and aluminum nitrate (at the rate of ~ 2 g per 1 g of the output product) and kept at this temperature for 2 hours with continuous stirring. Powder of silicon nitride was added to the obtained solution. The produced mixture was cooled to 4 °C until the formation of a gel, then cut into 3-5 mm pieces. The cut gel was covered with an aqueous ammonia solution and kept for 24 hours at 4 °C. After that, the gel was washed first with distilled water, then with ethanol. After that, the gel was dried at 100 °C for 8 hours.

The deposition of the sintering additive by spray drying (4) is based on a mixture of Al₃(NO₃)₁₂(OH)₁₂ and Y(OH)₂(CH₃COO) colloidal solutions with Si₃N₄ powder. The aqueous suspension contained 52.5% wt. Si₃N₄-YAG in the conversion to the solid phase, for stabilization purposes an additional 1.5% wt. of ammonium polyacrylate was introduced. After mixing in a planetary mill, the suspension was spray dried at 150 °C.

As a result, four mixtures were obtained with the YAG precursor distributed over the surface of Si₃N₄ particles. To form YAG, the powders were annealed in stages at 300, 500, 800 and 1000 °C for 2-6 hours with dispersion in an agate mortar between the stages.

The obtained mixtures were studied by scanning electron microscopy using a JEOL JSM-6490 instrument and X-ray diffraction analysis on a Shimadzu XRD-7000 diffractometer.

3. Results and discussion

X-ray diffraction studies of mixtures right after synthesis showed the presence of crystalline phases α-Si₃N₄ and β-Si₃N₄, regardless of the method of preparation. Diffraction patterns of the mixture samples annealed at 1000 °C are shown in Figure 1. The crystal phase composition of the mixtures obtained by methods 1-3 is identical and contains the crystal phases of YAG and Y-Si-Al-O-N in addition to the initial phases α-Si₃N₄ and β-Si₃N₄. The mixture obtained by method 4 (spray drying) differs because it does not contain the YAG crystal phase. This may indicate a more homogeneous deposition of the sintering additive precursor on the Si₃N₄ particles.

Researches carried out on a scanning electron microscope also did not show significant differences in the structure of mixtures prepared by methods 1-3, both before and after annealing. However, the structure of the mixture prepared by the spray drying method (4) contains spherical particles 5-100 microns in size. SEM images of mixtures obtained by the deposition method in the gelatin matrix (3) and the spray drying method (4) are shown in Figure 2.
4. Conclusion

Four methods for fabrication of Si₃N₄-YAG mixtures by applying a sintering additive precursor to the surface of Si₃N₄ particles were considered. The phase composition of the mixtures after the oxide phase formation during annealing was studied. The appearance of the Y-Si-Al-O-N phase in the samples of the mixtures obtained by all considered methods has been shown. The YAG phase is characteristic of the mixtures synthesized by co-precipitation, Pechini and precipitation in gelatin matrix methods. The YAG phase (Al₅Y₃O₁₂) was not formed in the mixture obtained by the spray drying method. This may indicate a high homogeneity of the mixture. Particularly, the absence of large agglomerates of the precursor phase and its predominant formation as a coating on the surface of the silicon nitride particles, therefore the formation of YAG crystalline grains do not occur during annealing.

In summary, the spray drying method is a promising method of fabrication Si₃N₄-based mixtures for sintering ceramics with increased physical and mechanical characteristics.
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