Synthesis of "*in situ*" reinforced silicon nitride composites

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Abstract: The objective of this work was to investigate the effect of two different sintering additives (CeO_2 and $Y_2O_3 + Al_2O_3$), sintering time and amount of β-Si_3N_4 seeds on the densification, mechanical properties and microstructure of self-reinforced Si_3N_4 based composites obtained by pressureless sintering. Preparation of β-Si_3N_4 seeds, also obtained by a pressureless sintering procedure, is described. Samples without seeds were prepared for comparison. The results imply that self-reinforced silicon nitride based composites with densities close to the theoretical values and with fracture toughness of 9.3 MPa m$^{1/2}$ can be obtained using a presureless sintering procedure.

Keywords: β-Si_3N_4 seeds, additive, pressureless sintering, self-reinforced composites, densification, fracture toughness.

INTRODUCTION

Silicon nitrides as a group of materials with attractive combinations of properties has generated substantial attention of ceramic research groups worldwide for more than three decades. They have high strength over a wide temperature range, good thermal shock resistance, and strong wear and corrosion resistance, which make them suitable for use in automotive, petrochemical, metallurgical and chemical industries.

As a result of its covalent bonding and low diffusivity, Si_3N_4 cannot be densified by solid state sintering. Sintering additives, which create a liquid-phase at high temperatures, allow mass transport through a solution repreciptation-process which leads finally to full densification. They react with the SiO_2 adhered on the particle surface to form a silicate phase, which is liquid at the sintering temperature.[1] Liquid phase sintering can be subdivided into three stage: (*i*) particle rearrangement by the development of capillary forces among the particles due to the formation of an eutectic melt consisting of the used additives and SiO_2 on the Si_3N_4 surface, (*ii*) Solution of α-Si_3N_4, the diffusion of Si and N through the liquid phase and repreciptation of

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β-Si$_3$N$_4$ nuclei,[2] followed by β-Si$_3$N$_4$ coarsening,[3] and (*iii*) the coalescence of the β-Si$_3$N$_4$ crystals which is of limited importance due to the low volume diffusion in Si$_3$N$_4$. Although it is well known that densification is assisted by a liquid-phase, its role varies depending on the composition, type and concentration of additives while the properties of the sintered material strongly depend on the morphology of the silicon nitride grains and the character of the intergranular phase.[4]

Today, most silicon nitride ceramics are prepared using α-rich Si$_3$N$_4$ powders. In silicon nitride ceramics, the microstructure is similar to whisker-reinforced ceramic composites, with large rod like β-Si$_3$N$_4$ grains as the reinforcing agents.

By incorporating a controlled amount of elongated β-Si$_3$N$_4$ single-crystal particles into the ceramics, the toughening mechanisms, such as crack deflection and/or bridging *via* interfacial debonding at elongated seeds, are activated. Therefore, the seeding method provides an effective way to improve the fracture resistance while retaining high strength if the size, content and distribution of the elongated β-Si$_3$N$_4$ single-crystal particles are carefully regulated.[5–7]

Ceramics based on Si$_3$N$_4$ obtained by gas pressure sintering or by hot pressing have rather high fabrication costs. For wide use, fabrication of these materials, by a low cost procedure, such as pressureless sintering, is mandatory. This work describes a preliminary attempt to produce silicon nitride in the beta form as seed particles, as well as to synthesize self-reinforced Si$_3$N$_4$ composites using the pressureless sintering procedure. The obtained results show that with carefully controlled preparation of the starting powder mixtures, very good results can be obtained as far as the mechanical properties are concerned.

<div align="center">EXPERIMENTAL</div>

Synthesis of β-Si$_3$N$_4$ seeds

Silicon nitride in the α-form (H.C. Starck LC12-SX) was homogenized with an additive mixture consisting of 4.4 wt % Y$_2$O$_3$ (H.C. Starck P7/88) and 8.3 wt % SiO$_2$ (Merck), in a vibratory mill for 2 h using 2-propanol as the mixing medium. The powder mixture was dried, passed through a 40 mesh sieve, and thereafter hydraulically compacted at a uniaxial pressure of 50 MPa. Subsequently, it was isostatically compacted under a pressure of 250 MPa. Particles of β-Si$_3$N$_4$ seeds were grown by heating this powder mixture in a graphite resistance furnace (Astro 606, Model No. 1000-3060) at 1850 ºC for 2 h under flowing nitrogen. The specimens were placed in a powder bed (50 % BN and 50 % Si$_3$N$_4$) in a graphite crucible. The powder bed technique was used to prevent thermal decomposition of Si$_3$N$_4$. The sintered samples were crushed (to about 3 – 4 mm), and thereafter pulverised. The screened powder was then subjected to four different and successive acid rinse treatments.[8]

Preparation of mixtures and sintering

Two starting powder mixtures, the first containing α-Si$_3$N$_4$ (H.C. Starck LC12-SX) with 10 wt %, CeO$_2$ (Merck) as a sintering additive, Table I, and the second one containing α-Si$_3$N$_4$ (H.C. Starck LC12-SX) with an additive mixture of 7 wt % Y$_2$O$_3$ (H.C. Starck P7/88) and 3 wt % Al$_2$O$_3$ (Alcoa A16), Table II, were used in this study. To these starting powder mixtures, β-Si$_3$N$_4$ seeds were added in the amount of 1, 3 and 5 wt %. Samples without seeds were prepared for comparison, Tables I and II.

The powder mixtures were homogenized in a vibratory mill for 2 h and thereafter in an attritor for 6 h, in a polyethylene tube with stirrer. Si$_3$N$_4$ balls were used as the milling media. The slurries of ceramic powders in 2-propanol were dried and passed through a 40 mesh sieve. Green pellets were obtained by hydraulic prepressing under a pressure of 50 MPa which were then isostatically compacted under a pressure of 350 MPa.

TABLE I. Starting powder composition of the materials with CeO_2 additive

| Sample | Additive composition/wt % | Amount of β-Si_3N_4/wt % |
	CeO_2	
Y	10	Non seeded
3	10	1
4	10	3
8	10	5

Sintering of the green pellets was performed in a graphite resistance furnace. Specimens were placed in a powder bed in a graphite crucible and heated at 1800 °C for 1, 2, 4 and 6 h. The composition with no seeds added was sintered under the same conditions.

TABLE II. Starting powder composition of the materials with a mixture of $Y_2O_3 + Al_2O_3$ additive

| Sample | Additive composition/wt % | | Amount of β-Si_3N_4/wt % |
	Y_2O_3	Al_2O_3	
X	7	3	Non seeded
1	7	3	1
2	7	3	3
6	7	3	5

Phase identification of the sintered samples was performed by X-ray diffraction analysis (XRD, Siemens Instrument of the D-500 type). XRD measurement was made on the surface of the sintered samples. Bulk densities were measured by the Archimedes method. The polished surfaces were indented using a pyramid Vickers indenter. Fracture toughness was determined from ten Vickers indents for each sample. A load of 30 kg was used for indentation. The sintered samples were polished and etched for obaservation of the microstructure and crack behavior using scanning electron microscopy (SEM, JSM-5300, JEOL). Chemical etching was done with molten NaOH.

RESULTS AND DISCUSSION

Silicon nitride seeds in the beta form are usually obtained by a gas pressure sintering procedure at 1800 °C.[9–11] The composition of our starting powder mixture was adjusted in order to enable preparation of β-Si_3N_4 seeds under flowing nitrogen.
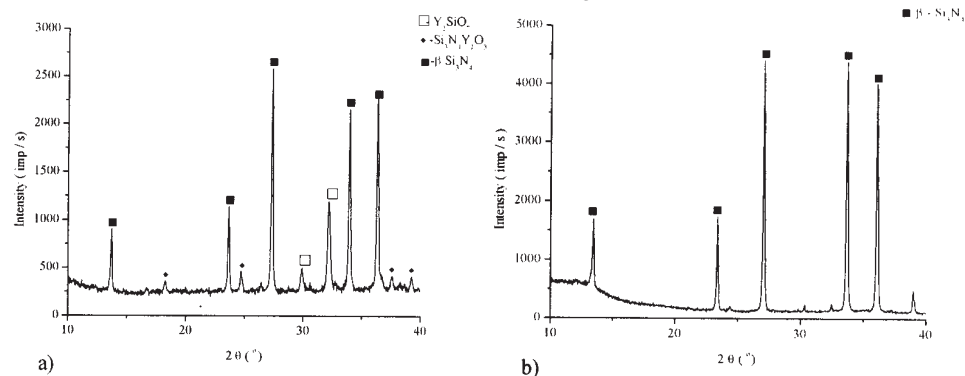

Fig. 1. X-Ray patterns of the obtained powder of the seeds before, a) and after acid rinse treatment, b).

After heat treatment, which was discribed in the Experimental part of this paper, the obtained products were analyzed using various techniques. The X-ray patterns of the obtained seed powder before and after acid rinse treatment are shown in Figs. 1a and b. Fig. 1b clearly shows that removal of Y–silicates was succesful. The large elongated rod-like grains which can be seen in the SEM micrograph belong to β-Si_3N_4 seeds (Fig. 2).
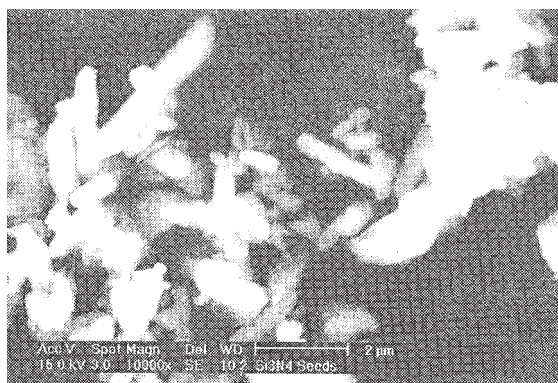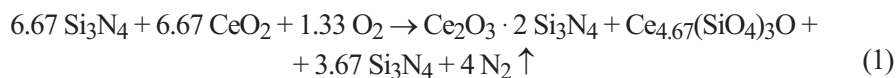

Fig. 2. SEM Photograph of an acid rinse treated powder.

Affter sintering of the composites, phase transformation, densification and properties were followed, as mentioned before.

The results show that transformation of α to β-Si_3N_4 was complete for all samples for both sintering additives and all sintering times. All patterns had the peaks of β-Si_3N_4 as the major crystalline phase. The secondary crystalline phase is cerium orthosilicate $Ce_{4.67}(SiO_4)_3O$ for samples containing CeO_2 (Fig. 3a). Commercial Si_3N_4 powder particles are covered with a SiO_2 film. It is known that the Ce^{3+} ions found at high temperatures in the Ce–Si–Al–O–N system change to Ce^{4+} and the evolved oxygen reacts with Si_3N_4 to form SiO_2.[12] At temperatures above 1400 ºC,[12,13] the SiO_2 adhered to the surface of the Si_3N_4 particles reacts with the additive, in this case, CeO_2 to form a liquid phase. During cooling from the sintering temperature, the liquid phase crystallizes giving a secondary crystalline phase (Fig. 3a), which in this case was detected as cerium orthosilicate, $Ce_{4.67}(SiO_4)_3O$.

Mah *et al.*[12] claim that additional oxygen may be supplied from the Si_3N_4 powder, as metntioned, and therefore the following equation is one of the possible chemical reactions

$$6.67\ Si_3N_4 + 6.67\ CeO_2 + 1.33\ O_2 \rightarrow Ce_2O_3 \cdot 2\ Si_3N_4 + Ce_{4.67}(SiO_4)_3O +$$
$$+ 3.67\ Si_3N_4 + 4\ N_2 \uparrow \qquad (1)$$

which could explain the apperarence of $Ce_{4.67}(SiO_4)_3O$ in Fig. 3a.

Samples containing a mixture of $Y_2O_3 + Al_2O_3$ as the additive showed the presence of the Y-silicates, Y_2SiO_7 and $Y_5(SiO_4)_3N$, N-apatite as secondary crystalline phases (Fig. 3 b). Jack[13] in his early papers describes that during hot-pressing at temperatures up to 1800 ºC, Y_2O_3 reacts with α-Si_3N_4 to give an "H" phase or $Y_5(SiO_4)_3N$, N-apatite. Thus, the same considerations should apply equally to pressureless sintering except, of course, that the rates
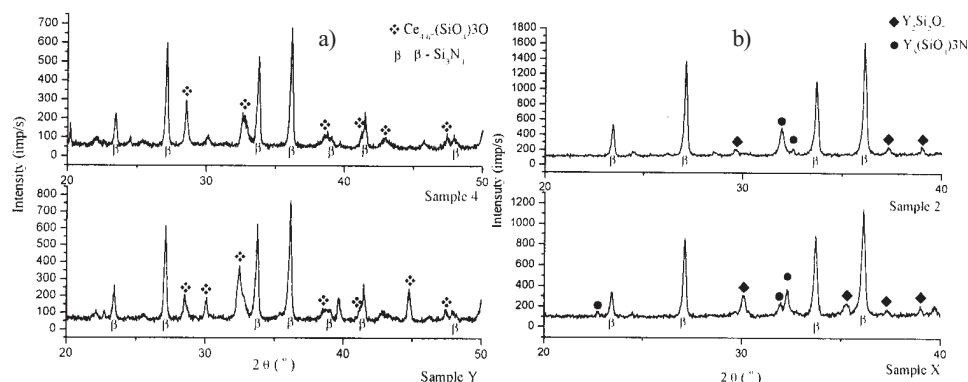
Fig. 3. XRD Patterns of samples sintered with CeO$_2$, a) and a mixture of Y$_2$O$_3$ + Al$_2$O$_3$ as a sintering additive, b).

will be correspondingly lower than for hot-pressing. The simultaneous presence of Y$_2$SiO$_7$ can be explained in a way that this Y-silicate lies on the same join with N-apatite and that they both belong to the compatibility triangle Si$_3$N$_{4e}$ Y$_2$SiO$_7$ Y$_5$(SiO$_4$)$_3$N.

The effect of the concentration of seed particles on the relative density of specimens sintered with different additives for various times are shown in Figs. 4a and b. Theoretical density was calculated from the rule of mixtures. Samples containing CeO$_2$ as an additive denoted as Y, 3 and 4 achieved full density after 4 h (Fig. 4a). For all soaking times, samples with 5 wt % of seed particles have significantly lower densities than those with 0, 1 and 3 wt % seed particles.

The effect of the amount of seed particles on the relative density of samples sintered with an additive mixture of Y$_2$O$_3$ + Al$_2$O$_3$ *versus* sintering time is shown in Fig. 4b. Full densification was achieved after a soaking time of only 2 h for the sample without seed particles, denoted as X. Seeding with β-Si$_3$N$_4$ particles slightly hinders densification. Hirao *et al.*[7] also observed that seeding with single crystal particles of β-Si$_3$N$_4$ hinders densification, as shown in Fig. 4b, and they achieved full density only after 6 h at 1850 °C. However, all our samples were sintered to nearly full density (99 % of the theoretical density) after 4 h, (Fig. 4b). The sample with 1 wt % of β-seeds was sintered to nearly full density (99 % of the theoretical density) after only 2 h. Seeding with 5 wt % seed particles caused a decrease of the sintered density because of steric hindrance, as is shown in Figs. 4a and b.[14] The obtained results show that the Y$_2$O$_3$ + Al$_2$O$_3$ mixture is more efective as an additive than CeO$_2$, under our experimental conditions.

The SEM micrographs of chemically ethced surfaces of samples with 3 wt % β-Si$_3$N$_4$ seeds containing CeO$_2$, as well as the mixture of Y$_2$O$_3$ + Al$_2$O$_3$, after sintering at 1800 °C for 4 h, are shown in Figs. 5a and b, respectively. Both samples, as expected, exhibit a bimodal microstructure composed of small matrix grains and large rod-like grains 1–2 μm in diameter and 5–10 μm long, with a high aspect ratio. The large rod-like grains, morphologically correspond to the grains developed from the seed particles during sintering. A much finer and more uniform microstructure can be seen in the non-seeded sample.
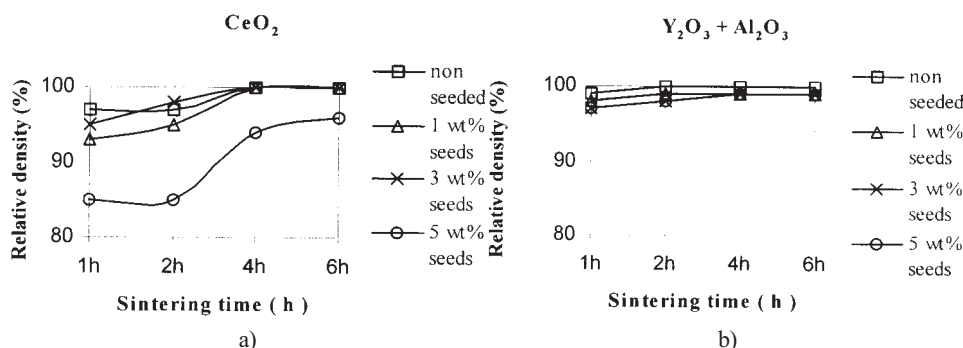
Fig. 4. Efect of sintering time and amount of seed particles on the relative density of silicon nitride sintered at 1800 °C with CeO_2 a), or with a mixture of $Y_2O_3 + Al_2O_3$ as a sintering additive, b).

Fracture toughness as a function of the amount of seed particles for samples sintered with CeO_2 and a mixture of $Y_2O_3 + Al_2O_3$ are given in Figs. 6a and b, respectively. The sample without seed particles, denoted as Y, sintered for 1 and 2 h has higher values of fracture toughness than the seeded samples (Fig. 6a). After sintering for 4 h, however, the
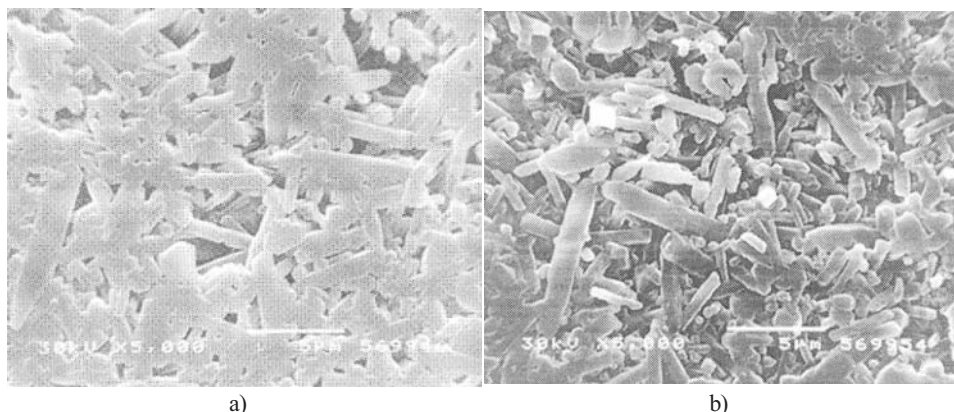

Fig. 5. Microstructures of samples with CeO_2, a) and a mixture of Y_2O_3 and Al_2O_3, b), with 3 wt % β-seeds, sintered at 1800 °C for 4 h.

sample without seeds has a relatively low fracture toughness of 6.4 MPa m$^{1/2}$. By addition of 3 wt % of seed particles, the maximum value of fracture toughness, 8.4 MPa m$^{1/2}$, was achievbed (denoted as 4 in Table I) after sintering for 4 h. However, the sample with 5 wt % of seed particles, denoted as 8, shows a much lower fracture toughness of 5.2 MPa m$^{1/2}$ even after sintering for 6 h. Fracture toughness as a function of the amount of seed particles for samples sintered with a mixture of $Y_2O_3 + Al_2O_3$ is shown in Fig. 6b. With the short sintering time of 1 h, the sample without seeds, denoted as X, has, as in the previous case, a higher fracture toughness than the seeded samples (Fig. 6b). By adding seeds and prolonging the sintering time, the fracture toughness increases and a maximum value of 9.3 MPa m$^{1/2}$ is achieved for the sample with 3 wt % of β-seeds, denoted as 2, sintered for 4 h. The toughness increases with sintering time, which is obviously connected with grain coarsen-
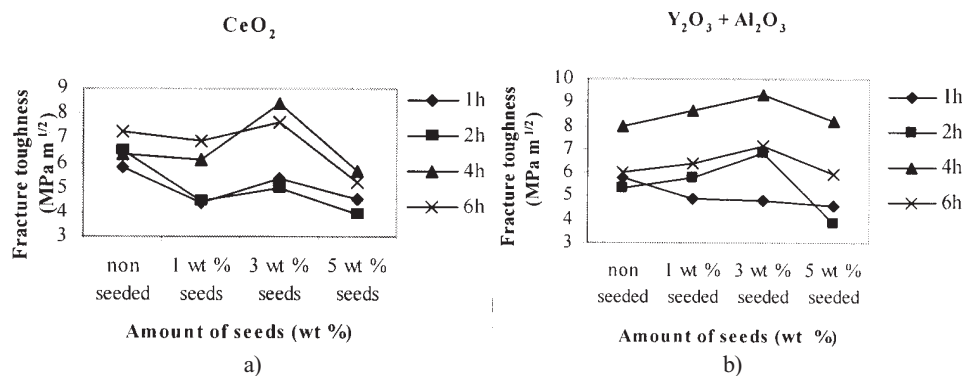
Fig. 6. Efect of sintering time and amount of seed particles on the fracture toughness for silicon nitride sintered at 1800 ℃ with CeO_2, a) or with a mixture of $Y_2O_3 + Al_2O_3$ b).

ing and the creation of conditions for activating the grain bridging and pull out mechanisms (Fig. 7). An example of the interaction of a propagating crack with the β-Si_3N_4 grains pull-out is shown in Fig. 7. In this way, the improved fracture toughness in seeded samples is attributed to the two most frequently observed mechanisms: grain pull-out and crack bridging.
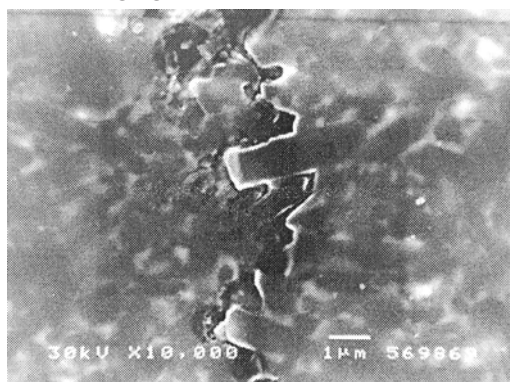

Fig. 7. Interaction of a propagating crack with β-Si_3N_4 grains: pull-out.

It seems, that under our conditions, there is an optimum amount of Si_3N_4 seeds *i.e.*, 3 wt %, beyond which the density and fracture toughness significantly decrease. The lower toughness after a long sintering time, 6 h, for both types of additives can be explained by inappropriate microstructural features. On the other hand, the lower fracture toughness for samples seeded with 5 wt % β-Si_3N_4 seeds compared with samples having lower seeds concentrations may be explained by the development of localised regions of compressive strain in the matrix around the β-crystals which besides densification may also have an influence on the fracture toughness.[15]

CONCLUSIONS

Rod line β-Si_3N_4 seeds were obtained from a mixture of α-Si_3N_4, SiO_2 and Y_2O_3. Using the powder bed technique, silicon nitride material possessing a bimodal micro-

structure was fabricated using pressureless sintering. After sintering different crystalline phases formed during cooling. The main crystalline phase for all samples is β-Si$_3$N$_4$, while a secondary crystalline phase is Ce$_{4.67}$(SiO$_4$)$_3$O for samples with CeO$_2$ and Y$_2$SiO$_7$ and Y$_5$(SiO$_4$)$_3$N for samples containing a mixture of Y$_2$O$_3$ + Al$_2$O$_3$. In these materials, for both type of additives samples with 3 wt % β-seeds exhibited the highest fracture toughness, 8.4 MPa m$^{1/2}$ with CeO$_2$, and 9.3 MPa m$^{1/2}$ with a mixture of Y$_2$O$_3$ + Al$_2$O$_3$, when sintered at 1800 ºC for 4 h. The full density was achieved after 4 h for samples with 0, 1 and 3 wt % β-seeds with CeO$_2$ and after 2 h for samples without seeds using a mixture of Y$_2$O$_3$ + Al$_2$O$_3$ as the additive. Increasing the amount of β-seeds up to 3 wt % for both types of additives positively affected the fracture toughness. However, addition of 5 wt % β-seeds for both type of additives resulted in a decrease in the fracture toughness and density. Microscopic studies of the crack paths in the self-reinforced Si$_3$N$_4$ ceramics reveal that pull-out and crack bridging are the two most frequently observed toughening mechanisms.

ИЗВОД

СИНТЕЗА "*in situ*" ОЈАЧАНИХ КОМПОЗИТА НА БАЗИ СИЛИЦИЈУМ НИТРИДА

АЛЕКСАНДРА ВУЧКОВИЋ[1], СНЕЖАНА БОШКОВИЋ[1] и ЉИЉАНА ЖИВКОВИЋ[2]

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Циљ овога рада био је испитивање утицаја два различита типа адитива (CeO$_2$ и Y$_2$O$_3$ + Al$_2$O$_3$), времена синтеровања и садржаја клица β-Si$_3$N$_4$ на денсификацију, механичке особине и мкроструктуру самоојачаног композитног материјала на бази Si$_3$N$_4$ добијеног синтеровањем без примене притиска. Припрема клица β-Si$_3$N$_4$, добијених, такође, без примене притиска детаљно је описана. Узорци без клица припремљени су ради поређења. Резултати указују да се самоојачани композитни материјал на бази Si$_3$N$_4$ са густинама блиским теоријским вредностима и жилавости од 9,3 MPa m$^{1/2}$ могу добити техником синтеровања без примене притиска.

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