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Kinetics of the α - β Phase Transformation in Seeded Si_3N_4 Ceramics

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Abstract:

The α - β phase transformation in Si_3N_4 was studied for seeded samples using an Y_2O_3 - Al_2O_3 mixture as a sintering aid. The concentration of β -seeds varied from 0 to 5 wt.%. The results showed that α - β phase transformation followed the first-order reaction. The calculated activation energy for seeded samples was in the range from 348 to 378 KJ/mol, indicating boundary reaction as the rate limiting step.

Keywords: Seeded Si_3N_4 , Phase Transition, Hot-Pressing.

1. Introduction

Good performances of Si_3N_4 based ceramics are based on a strong covalent nature of the Si-N atomic bond, which induces extremely low self-diffusivities of Si and N atoms [1]. Solid state sintering below the decomposition temperature of Si_3N_4 is therefore practically impossible, and one or more metal oxides are commonly used as sintering aids to promote densification. Silicate liquid of a low melting point, formed via a reaction between the additives and surface SiO_2 adsorbed on silicon nitride powder, acts as a mass transport medium and enhances the diffusivity of atoms during sintering [2]. Apart from densification, another phenomenon *i.e.* α - β phase transformation in silicon nitride takes place at elevated temperatures via the liquid phase, too. The α - Si_3N_4 phase is thermodynamically unstable during hot pressing showing a tendency to transform irreversibly into the more stable β - Si_3N_4 . The transformation is a reconstructive process that involves the breaking and reforming of Si-N bonds [3]. It is known that α -particles dissolve into existing silicate liquid and thereafter precipitate as β - Si_3N_4 . In the case when seeds are added, the as formed β - Si_3N_4 precipitates on the preexisting β -seeds, as mentioned before, which act as centers of crystallization. In connection with this it is expected that the rate of the transformation process will be affected by seeds concentration. In addition, the developed microstructure is also expected to differ. Namely, it is known that the α - β transformation exhibits an important influence on the grain growth process because the grain growth rate during the transformation is higher than after completion of the phase transformation. The majority of the Si_3N_4 elongated grains are formed during the transformation process [4].

The phase transformation in silicon nitride ceramics has been studied in related ceramics, however, the obtained results regarding the rate limiting process strongly depend on the system studied [5,6]. In the present investigation the phase transformation of α into β - Si_3N_4 was studied as a function of the seed content and heating time and to the best of our knowledge, there are no data in the literature on the activation energy of the process in the

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case when β - Si_3N_4 seeds are present in the reacting mixture. Rate constants and activation energies were calculated for compositions with different β - Si_3N_4 seed contents in the presence of Y_2O_3 - Al_2O_3 mixture as a sintering aid. In addition, the effect on microstructure development was connected to the phase transformation data.

2. Experimental procedure

In this work β - Si_3N_4 seeds were synthesized by the powder bed technique instead of the more expensive gas pressure one [7]. The seeds were prepared by heating a mixture of 8.27 wt.% Y_2O_3 , 4.40 wt.% SiO_2 and 87.33 wt.% α - Si_3N_4 in a flowing nitrogen atmosphere. The powder mixture was cold pressed into cylindrically shaped compacts covered with silicon nitride and boron nitride powder mixture and fired at 1850 °C. The sintered compacts were crushed and screened. The screened powder was chemically treated according to the method developed by Hirao [8]. In order to disrupt the agglomerates extensive acid treatment was combined with powerful sonication.

Seeded samples were prepared starting from a commercial α - Si_3N_4 powder (H.C.Stark, LC-12 SX), Al_2O_3 (Alcoa-Chemicals) and Y_2O_3 (H.C.Starck) with mass ratio 3:7 as sintering aids and β - Si_3N_4 seeds in the concentration of 0, 1, 3, and 5 wt.%.

Homogenization of α - Si_3N_4 powder and additive was performed in a vibro mill (Fritsch Pulverisette 9) for 2 h, using isopropanol as the mixing medium. Homogenization of seeds with previous mixtures was carried out in an attritor, in isopropanol, for another 6 h. After drying, the powders were pressed into cylindrical bars of 16 mm in diameter. The pellets were hot pressed in a graphite furnace (Astro) in the temperature range from 1500 to 1700 °C under 40 MPa in flowing nitrogen for 1-6 h. The density of as sintered samples was measured by the Archimedes method. Theoretical density (TD) calculated by rule of mixture is 3.29 g/cm³. The achieved sintered densities were above 98 % of TD. The phase transformation degree and the identification of the phases present was assessed using X-ray diffraction (Siemens Crystalloflex device, D-500). The relative amounts of α and β -phase were measured on the basis of diffraction peak intensities, and calculated by applying the Gazzara and Messier method [9]:

$$\beta - \text{Si}_3\text{N}_4 (\text{wt}\%) = \frac{I_{\beta(101)} + I_{\beta(210)}}{[I_{\alpha(102)} + I_{\alpha(210)} + I_{\beta(101)} + I_{\beta(210)}]} \quad (1)$$

where $I_{\beta(101)}$ and $I_{\beta(210)}$ are the diffraction intensities of the (101) and (210) planes of β - Si_3N_4 and $I_{\alpha(102)}$ and $I_{\alpha(210)}$ represent the intensities of (102) and (201) planes of α - Si_3N_4 .

Microstructural characterization was carried out by scanning electron microscopy (SEM-JEOL-5300) on polished and etched samples.

3. Results and discussion

The basic unit of Si_3N_4 is the SiN_4 tetrahedron (Fig. 1). A silicon atom is at the centre of a tetrahedron, with four nitrogen atoms at each corner. The SiN_4 tetrahedra are joined by sharing corners in such a manner that each nitrogen is common to three tetrahedra. Thus nitrogen has three silicon atoms as neighbors. The structural difference between α - and β - Si_3N_4 can be explained by different arrangements of Si-N layers. The basic units are linked together to form puckered six-membered rings which surround large holes. These basal planes form the building blocks for the structures of α and β - Si_3N_4 . The α - Si_3N_4 structure is formed by stacking the basal planes in such an order that the unit cell dimensions, α - and β - Si_3N_4 structures are related by $a_\alpha \approx a_\beta$ [10].

The basic processes through which phase transformation is completed are: (i) dissolution of α - Si_3N_4 particles, (ii) diffusion through the liquid phase and (iii) precipitation of dissolved Si_3N_4 predominantly on preexisting β -seeds. Since the α - β transformation is influenced by the degree of local supersaturation in the liquid phase [11] the reaction at α - Si_3N_4 /liquid interface and diffusion through the melt are basic steps of the phase transformation. After solution of α -grains in a liquid phase they transform into the β -phase, which precipitates as mentioned, predominantly on the β -seeds. The degree of this reaction was calculated by determining the amount of unreacted α - Si_3N_4 phase.

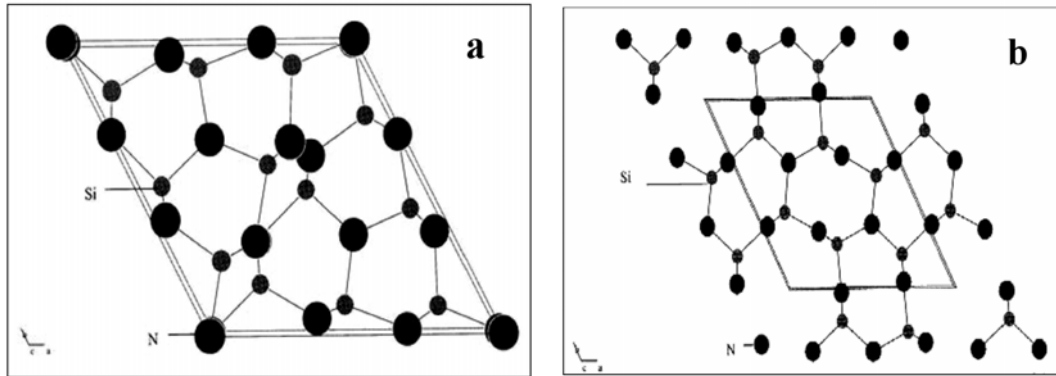


Fig. 1. Crystal structures of: (a) α - Si_3N_4 and (b) β - Si_3N_4 [12].

Fig. 2 summarizes the influence of heating time on the phase transformation at 1700 °C for different seed concentrations. The rate of transformation, as seen from Fig. 2, increased with increasing seed content in the samples. In samples without seeds, α - Si_3N_4 can still be detected even after 6 h of hot pressing at 1700 °C. However, in the samples with 5 wt.% seeds there was no evidence of α - Si_3N_4 , even after the shortest heating time.

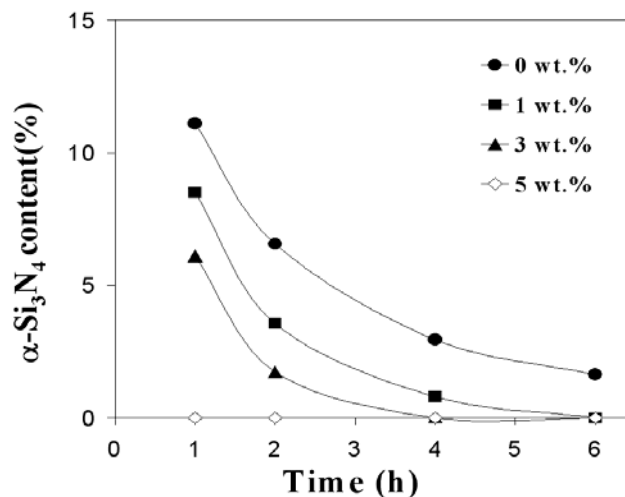


Fig. 2. α -phase content vs. isothermal heating time.

The phase transformation kinetics was studied in the temperature range from 1500 to 1600 °C, for all compositions. After a shorter heating time, ranging from 15 to 90 min, the amounts of retained α -phase are significant which enabled following of the concentration decrease of the reactant.

Bowen [13] has shown that the α - β phase transformation in silicon nitride without seeds, in the temperature range from 1425-1750 °C, follows the first order equation:

$$\frac{d\alpha}{dt} = -k\alpha \quad (2)$$

that after integration becomes:

$$\ln \alpha = -kt + 4.605 \quad (3)$$

in which α is α -Si₃N₄ content, k is the rate constant and t is the hot-pressing time. According to equation (3), the rate constant for a corresponding temperature is obtained from the slope of the straight line. The relation between the rate constant and temperature is given by equation:

$$\ln k = \ln A - \frac{Ea}{R} \cdot \frac{1}{T} \quad (4)$$

when A is a pre-exponential constant and R is the general gases constant, T is the absolute temperature and Ea is the activation energy.

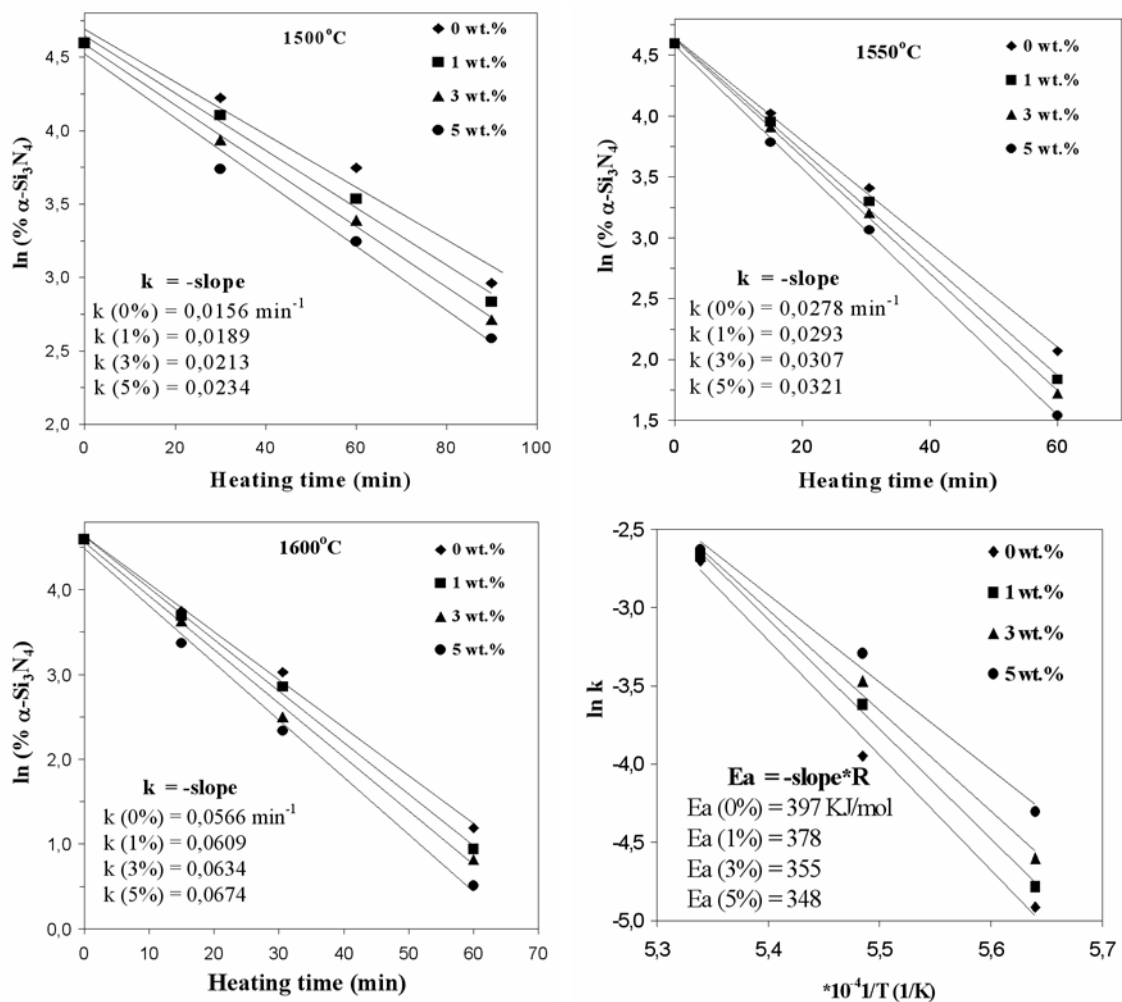


Fig. 3. The rate constants for different amount of seeds at (a) 1500 °C, (b) 1550 °C (c) 1600 °C and (d) the activation energies.

The rate constant k was calculated for each of our compositions at three different temperatures (Fig. 3a, 3b and 3c). The activation energies (Ea), for different seed

concentrations, were determined from the slope of $\ln k$ vs. $1/T$ function as given in Fig. 3d. The curves were obtained by using 3 points i.e., three measurements at each temperature. The linear dependence of $\ln \alpha$ vs. hot-pressing time t for our results (Fig. 3) confirms the assumption of the first order reaction for α - β transformation.

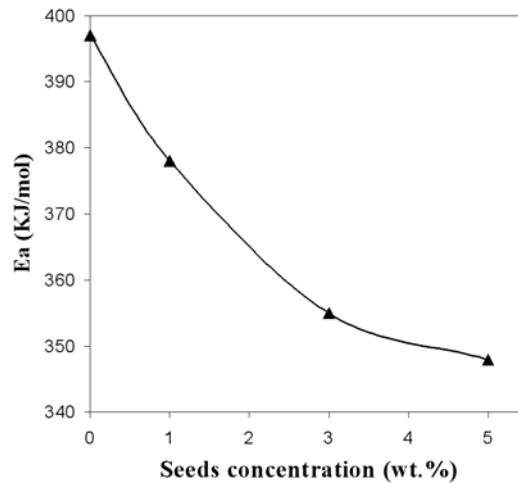


Fig. 4. Activation energy as a function of seeds concentration.

From the obtained results it is obvious that the rate constant increases while the activation energy decreases with the increase of seed concentration (Fig. 3). Large amounts of seeds, which are favorable crystallization centers, beneficially affect the transformation that can be completed at a lower temperature with a lower energy consumption. In our system, for samples with 5 wt.% seeds, the activation energy is 348 KJ/mol (Fig. 4).

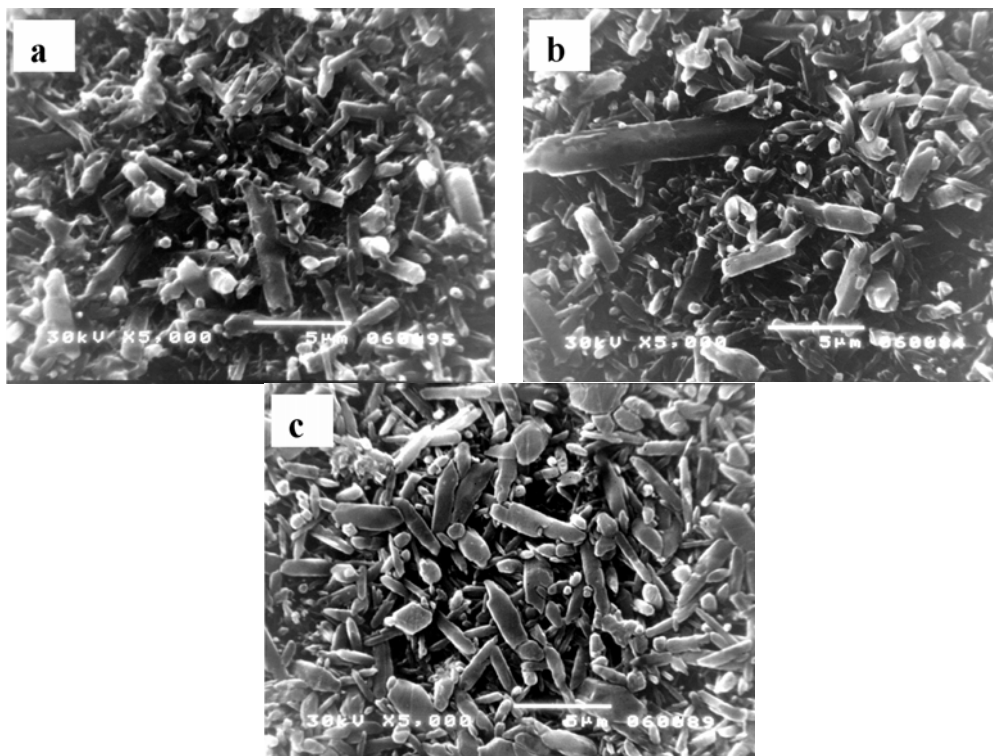


Fig. 5. SEM images of seeded samples sintered at 1600°C for 1 h, with (a) 1 wt.%, (b) 3 wt.% and (c) 5 wt. % seeds.

The results of the activation energy of the phase transformation differ in the literature. It is shown [13] that the value differs for different additives which form the liquid phase. Bowen [13] calculated the activation energy for Si_3N_4 without seeds, in the presence of $\text{Y}_2\text{O}_3/\text{MgO}$ sintering additive, as 500 KJ/mol. Hampshire and Jack [14] reported that the value of activation energy for transformation in the presence of Y_2O_3 , was close to Si-N chemical bond energy, being of 435 ± 38 KJ/mol [5]. Our results for non-seeded Si_3N_4 of 397 KJ/mol are close to this value and confirm the reconstructive nature of the studied transformation. Since the activation energy value for non-seeded samples is close to the Si-N bond energy, the results point out that a boundary reaction is the rate limiting step during the phase transformation. It may be added that the liquid phase on the basis of $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ provides a good vehicle for mass transport being of relatively low viscosity. The results (Tab.1) on the densification degree, being higher than the transformation degree for the same samples, are in accordance to the above made statement indicating, also, that the boundary reaction is the rate controlling step in the $\alpha\text{-}\beta$ phase transformation.

It was mentioned above that the phase transformation affects to a great extent the grain growth process. The variations in microstructure for specimens sintered at 1600 and 1700 °C with 1, 3 and 5 wt.% seeds are shown in Figs. 5 and 6. In contrast to the non-seeded samples [15], which exhibit a relatively uniform microstructure with mostly small and equiaxed grains, the seeded specimens exhibit a bimodal microstructure with elongated Si_3N_4 grains embedded in a matrix of finer grains. It should also be noticed that in specimens sintered at 1600 °C the presence of rounded shape grains indicate, also the remaining α -phase as was confirmed by XRD.

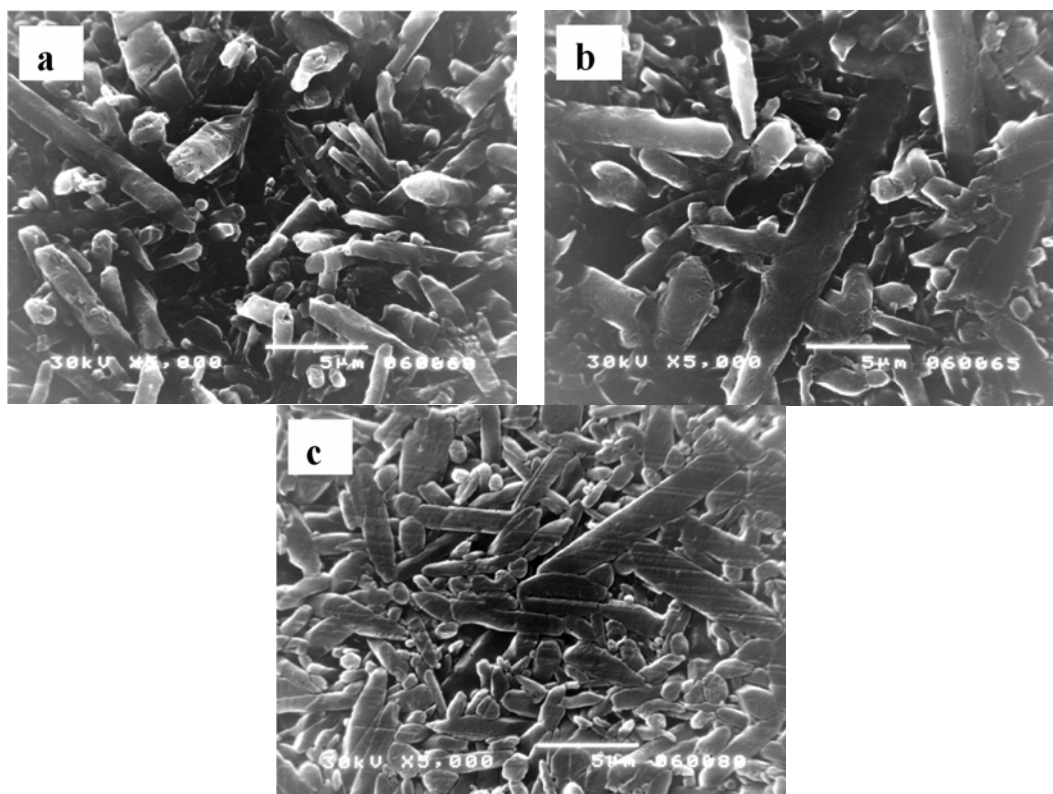


Fig. 6. SEM images of seeded samples sintered at 1700°C for 1 h, with (a) 1 wt.%, (b) 3 wt.% and c) 5 wt.% seeds.

The size of β - Si_3N_4 grains depends not only on the heating time but also on the seed content. If during transformation a large number of seeds were present this would mean a large number of centers of crystallization, which significantly accelerates phase transformation but not necessarily grain growth (Fig. 5). With increasing number of crystallization centers, the whole available amount of β - Si_3N_4 crystallizes on a larger number of centers inducing less β - Si_3N_4 deposited on each seed, which in turn, results in a smaller final grain size (Fig. 5c).

With further increase of the seed amount (5 wt.%), the grain diameter is decreased due to impingement of seeds, as well, which is more pronounced in specimens sintered at 1700 °C as can be seen in Fig. 6c. The appearance of β -grains with different aspect ratios in these compositions is also due to the broad size distribution of initial β -seeds. According to the observed microstructure it can be seen that the seeding allows the microstructural design and through optimization of the seed content the concentrations of elongated grains can be tailored. Microstructure development in seeded samples will be discussed in more detail elsewhere [16].

4. Conclusion

The effect of seed concentration on the phase transformation of self-reinforced silicon nitride ceramics was analyzed in the temperature range from 1500 to 1700 °C. It was proved that:

1. Introduced β - Si_3N_4 seeds accelerate α - β phase transformation, which was completed after only 1 h at 1700 °C in the presence of 5 wt.% seeds.
2. The α - β phase transformation obeys a first order reaction. The activation energy of 397 KJ/mol, for a non-seeded sample, is very close to the value of Si-N chemical bond energy.
3. With increasing seed concentration from 0-5 wt.%, the rate constant increases while the value of activation energy becomes lower. The lowest value of activation energy of 348 KJ/mol was obtained for the samples with 5 wt.% seeds. The values of activation energy for seeded samples from 378 to 348 KJ/mol indicate the grain boundary reaction as the rate limiting process.
4. An increased transformation rate does not imply increased growth of elongated seeds.

Acknowledgement

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Садржај: Проучавана је α - β фазна трансформација у Si_3N_4 керамици у присуству клица и адитива из Y_2O_3 - Al_2O_3 система. Концентрација β – клица је варирана од 0 до 5 теж.%. Резултати су показали да α - β фазна трансформација прати реакцију првог реда. Вредност активационе енергије за фазну трансформацију у узорцима са присуством клица је варирала од 348 до 378 KJ/mol, што указује да је брзина реакције на граници зрна одлучујући корак ове трансформације.

Кључне речи: Si_3N_4 клица, фазни прелаз, топло пресовање.
