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Synthesis of Si_3N_4-celsian composite materials

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Abstract

The synthesis of Si_3N_4-celsian composite materials was studied in this paper. To obtain celsian, two different types of additives were used. In the first case the appropriate mixture of $BaCO_3$, Al_2O_3 and SiO_2 was added to Si_3N_4, while in the second case a Ba-A-zeolite, previously heated at 850°C, was used as an additive. Mixtures of Si_3N_4 and the sintering aids were homogenized in a vibratory mill in the presence of isopropanol. The green bodies were pressurelessly sintered in nitrogen atmosphere at temperatures of 1650–1750°C. Densification degree was followed, as well as microstructural changes, as a function of the sintering conditions and the additive used. Reaction of BAS formation was followed by X-ray analysis during the heating up period. It was found that with 10% zeolite as a sintering aid, full densification was achieved at 1750°C but with the same amount of oxide mixture, only 96% TD was attained. Phase changes were followed also during cooling down the samples from sintering temperature. Two crystalline phases, β-Si_3N_4 and hexacelsian, were present in both types of sintered samples. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Si_3N_4/celsian ceramic matrix composites are promising materials for high temperature engineering application, because BAS easily crystallizes from the melt during cooling, which improves high temperature properties. The composites can easily be produced [1] by pressureless sintering, exhibit very good mechanical properties and are economically acceptable, too.

Celsian ($BaAl_2Si_2O_8$–BAS) as a sintering aid to Si_3N_4 can be prepared from different sources. Besides from the mixture of BAS forming oxides, BaO, Al_2O_3, SiO_2 [2,3,4], celsian can be obtained starting from $BaCO_3$ [5] or $BaSO_4$ [6] and kaolin. Amorphous precursors to celsian have also been produced [7]. One of the latter possibilities is the ion exchange and thermal processing of zeolites, which was used in this work to produce celsian in the sintered bodies.

Although monoclinic phase of BAS is preferred to hexacelsian [4,7] due to its stability and low coefficient of thermal expansion, it was shown [1], that in some cases undesirable properties of hexacelsian do not dominate the overall composites properties.

The aim of this work was to study the possibility of using A-zeolite for producing dense Si_3N_4/celsian ceramic composites. The conventional route of celsian preparation from oxides was also studied for comparison.

2. Experimental

Starting powders used for the experimental work were α-Si_3N_4 (UBE10), $BaCO_3$ ("Zorka"-Šabac, Yugoslavia), Al_2O_3 (Alcoa, A-16), SiO_2 (Merck) and A-zeolite (Oldridge). Two different sources for producing celsian in the sintered body were used

Route 1. conventional mixing of $BaAl_2Si_2O_8$-forming powders ($BaCO_3$, Al_2O_3 and SiO_2)-additive NV.

Route 2. ion exchange of A-zeolite-additive BaA.

Homogenization of $BaCO_3$, Al_2O_3 and SiO_2 powders, was performed in vibratory mill, in isopropanol, for 2 min. Dried powder mixture was used as the additive NV.

The ion-exchange procedure involved suspension of 20 g A-zeolite powder into 250 ml of 0.5 M $BaCl_2$; stirring the suspension, and thereafter heating at 80°C with reflux condenser. This procedure was repeated eight times to ensure complete substitution of Ba for Na [8]. After each exchange step, the product was

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washed with distilled water until negative reaction for chlorides was obtained. The dried powder was heated at 800–850°C for 1 h to obtain an amorphous powder the composition of which corresponded to celsian-$BaAl_2Si_2O_8$ (additive-BaA).

Prepared additives were homogenized with Si_3N_4 powder in isopropanol in vibratory mill. Compositions with 10, 20 and 30% of additives were prepared. Green pellets were obtained by applying isostatic pressing at 300 MPa. Sintering was carried out in a nitrogen atmosphere in the temperature range 1650–1750°C for 1–8 h. Heating rate was 43°C/min, while cooling rate was very high in the first 5 min (~100°C/min), followed by significantly lower cooling rate (as the furnace itself was cooled down). During heating up a hold time of 3 h was chosen at 1150°C, according to TGA data, to allow for carbonate decomposition.

Densification was followed by measuring densities using Archimedes method. Theoretical density was calculated using the rule of mixture (β-Si3N4-3.19 g/cm^3 + BAS-3.29 g/cm^3). Phase analysis was done with Siemens–Kristalloflex apparatus, with CuK_α radiation and microstructures were observed under SEM, using a Philips XL30. Hardness and fracture toughness of obtained dense samples were measured by indentation method under 10 kg load, for 10 s loading time. Ten indents were made at each point.

3. Results and discussion

Sintering of studied composites takes place in the presence of transcient liquid phase. Liquid phase is formed during heating enabling both the $\alpha \rightarrow \beta$ transformation and densification of Si_3N_4 to occur. During cooling, however, the liquid crystallizes as hexacelsian, giving a crystalline grain boundary phase [1].

Phase transformation of α-Si_3N_4 takes place via a liquid phase, whereby β-Si_3N_4 precipitates. According to our results in Table 1, α-phase content decreases with increasing additive amount, sintering temperature and time. It is evident that α-phase disappears at 1700°C after 4 and 8 h for samples containing 30 and 20% of BaA, respectively. On the other hand, with samples containing 20 and 30% of NV additive, α-phase was detected in samples heated under the same conditions. These results suggest that the increasing amount of additive i.e. the liquid phase, enabled complete conversion of α into β-Si_3N_4, in samples containing BaA.

Table 1
$\alpha/\alpha+\beta$ As vs additive amount, temperature, time and the type of additive

Sample	Sintering conditions (T,t)			
	1650°C-4 h	1700°C-4 h	1700°C-8 h	1750°C-4 h
30% NV	40.8	17.2	10.0	—
30% BaA	27.4	0	0	—
20% NV	43.2	29.4	—	—
10% NV	—	—	—	0

Densification curves vs isothermal heating time for samples with 10% of sintering aids (Fig. 1), show that there is a remarkable difference in densification degree between the additive NV and BaA. Moreover, densification rate at 1750°C is higher for the system containing Ba-A-zeolite, (which is usually among other parameters the consequence of a larger amount of liquid in the system, as will be discussed).

During sintering of studied composites, in the heating up period, reaction of BAS formation takes place. This process differs to a great extent, depending on the additive used. Bearing in mind that both additives should give the same overall chemical composition (in both cases the same amount of excess silica is present, introduced via starting Si_3N_4 powder), the processes taking place during heating should be discussed. Namely, with NV additive, reactions leading to BAS formation take place during heating among additive constituents. The mechanism of BAS formation from $BaCO_3$, Al_2O_3 and SiO_2 was studied in detail [7,9]. Formation of BAS was also studied in the presence of Si_3N_4 [10,11] and it was shown that BAS formed via the intermediate appearance of Ba-silicates.

Our results on BAS formation were obtained by heating the α-Si_3N_4 samples with BaA and NV additives in the temperature range 760–1200°C in nitrogen atmosphere. The X-ray results showed that, hexacelsian started forming at 760°C from BaA amorphous powder; the relative intensities of its diffraction lines are rather low. In samples with NV additive, however, besides α-Si_3N_4 and Al_2O_3, Ba-silicates ($BaO.SiO_2$, $2BaO.3SiO_2$) were found. At 900°C the relative intensities of hexacelsian diffraction lines with samples containing BaA increase while in samples with NV additive, hexacelsian was first observed (with Al_2O_3 and $Ba_5Si_8O_{21}$). Strong hexacelsian diffraction lines (d[Å]-7.78, 3.94, 3.87, 2.96, 2.64, 2.58, 2.30, 2.27-ASTM, No.12-726) in NV samples

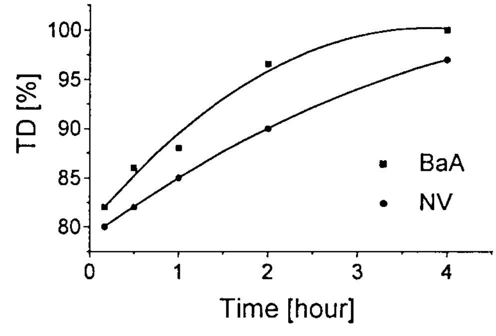

Fig. 1. Sintered density vs isothermal heating time, 1750°C, 10% additives.

appeared at 1160°C and 1200°C with small amount of alumina (d[Å]-3.47, 2.37, 2.07, 1.59-ASTM, No.10-173) and $Ba_2Si_3O_8$ (d[Å]-3.67, 2.76-ASTM, No.27-1035). In samples with zeolite however, only crystalline hexacelsian d[Å]-7.80, 3.95, 3.88, 2.97, 2.64, 2.59, 2.31, 2.26, 2.20-ASTM, No.12-726) and α-Si_3N_4 were observed at 1160–1200°C. The reaction of hexacelsian formation is obviously incomplete at 1160°C in samples containing NV.

Our data further show that, full conversion of amorphous Ba-A-zeolite into hexacelsian took place below 1160°C. Moreover, starting from amorphous BaA powder both hexacelsian and monoclinic celsian appeared at 1250°C. The following diffraction lines of monoclinic celsian were detected: d[Å]-6.46, 4.57, 3.79, 3.54, 3.46, 3.34, 2.50, 2.01, 1.79-ASTM, No.19-90. The relative intensities of celsian difraction lines increased with increasing temperature while those of hexacelsian decreased, indicating that hexacelsian→celsian conversion takes place. It should be recalled that in this temperature range, according to BaO-Al_2O_3-SiO_2 phase diagram [12] the monoclinic phase appears to be thermodynamically stable.

From the BaO–Al_2O_3–SiO_2 phase diagram [12] and the X-ray data, it can be concluded that during heating up period, phase compositions of the two studied systems at 1200°C effectively lie in different regions; "low-melting" region (BAS–SiO_2 line)—BaA additive, and "high-melting" region (BAS–Al_2O_3–Ba-silicate)—NV additive. Since the eutectic temperature between monoclinic BAS and SiO_2 is located at 1307°C [13], liquid phase forms at this temperature in BaA samples. Below sintering temperature total amount of additive converted into liquid. On the other hand, in samples obtained by route 1, reaction of hexacelsian formation takes place among the constituents of the liquid phase. Until the reaction is over, the amount of liquid phase will be lower as compared to route 2 which explaines higher densification degree and faster $\alpha \rightarrow \beta$ phase transition of Si_3N_4 with samples containing zeolite, because the amount of liquid is one of the parameters affecting both processes.

With prolonged heating time, the differences in densification degree get smaller. Differences in densification degree also diminish with increased quantity of additives (Fig. 2), i.e. with a higher amount of liquid the processes taking place are enhanced leading to faster equilibration. Dense samples could be produced under given experimental conditions, even at 1650°C (Fig. 3) if the amount of sintering aids was increased up to 30%.

X-ray pattern of sintered samples at 1750°C for 4 h, show the presence of β-Si_3N_4 and hexacelsian (which crystallized from the melt during cooling) in both materials. The relative intensities of hexacelsian diffraction lines (d[Å]-3.91, 2.97, 2.27, 1.96-ASTM, No.12-726) in materials prepared with zeolite are, however, twice

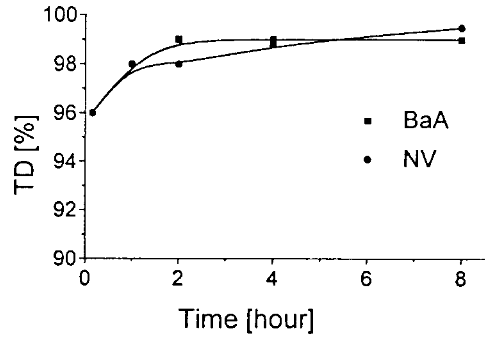

Fig. 2. Densification degree vs isothermal heating time, 1700°C, 20% additives.

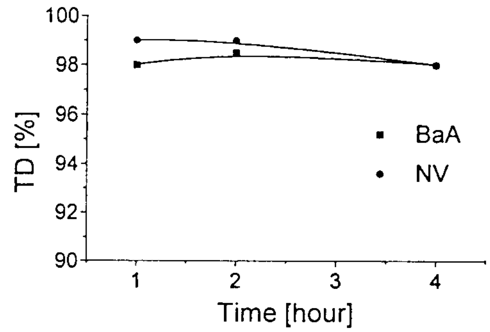

Fig. 3. Densification degree vs isothermal heating time, 1650°C, 30% additives.

the intensities of the same diffraction lines found in material with NV.This suggests that the conditions for hexacelsian crystallization from these two liquids during cooling are not the same. Some Al_2O_3 may be incorporated into "β-Si_3N_4" during heating. This may be expected to occur to a higher extent in samples sintered in the presence of unreacted BAS (NV). Hwang et al. [14] also found a higher lattice parameter of β-SiAlON in samples sintered in the presence of unreacted mixture of BAS forming oxides, as compared to previously synthesized BAS as an additive to Si_3N_4. The fact that Al_2O_3 from the liquid phase entered Si_3N_4 lattice is evident from Table 2 when comparing the values of interplanar distance "*d*" (for β-Si_3N_4) for the two samples sintered under the same conditions. These data show higher concentrations of alumina in the β-Si_3N_4 lattice, for NV samples. As a result of Al_2O_3 dissolution in the β-Si_3N_4 lattice, the viscosity of the remaining liquid phase will increase. During cooling, as reported [2,3] hexacelsian crystallizes from the melt. Higher viscosity of the liquid phase in NV system, retards crystallization [15] during cooling, which was found according to our data (Table 2), also.

The increased viscosity of the liquid in NV samples, as known, retards densification. Therefore, the results obtained in Fig. 1 can be explained to be a consequence of both a lower amount and higher viscosity of this liquid.

Table 2
Interplanar spacing "*d*" [Å] for (200), (101), (210) and (202) reflexions of β-Si_3N_4 vs temperature, time and type and amount of additives

Mass % of additives	1650°C –4 h	1700°C –4 h	1700°C –8 h	1750°C –8 h
10				
BaA				3.79, 3.28, 2.66, 2.17,
NV				3.82, 3.30, 2.67, 2.19
20				
BaA			3.79, 3.28, 2.65, 2.17	
NV		3.81, 3.29, 2.66, 2.18	3.82, 3.31, 2.67, 2.19	
30				
BaA	3.81, 3.30, 2.66, 2.19	3.81, 3.30, 2.66, 2.20	3.81, 3.31, 2.66, 2.18	
NV	3.82, 3.31, 2.67, 2.20	3.82, 3.30, 2.66, 2.20	3.82, 3.31, 2.66, 2.19	

SEM micrographs of sintered composite materials are given in Fig. 4. At 1750°C for 4 h, dense material was obtained only with additive BaA. Differences in microstructure between the two materials are obvious, after 4 h isothermal heating time, (Fig. 4). Elongated grains of β-Si_3N_4 can be seen in NV material [Fig. 4(a)]. On the other hand less elongated grains of β-Si_3N_4 can be seen in the sample sintered with Ba-A-zeolite [Fig. 4(b)]. These differences in microstructure could be explained on the basis of liquid viscosity effect [16], on the aspect ratio of Si_3N_4 grains. Namely, Si_3N_4 grains, grown in viscous liquids exhibit higher aspect ratio which is the case for samples containing NV (Fig. 4).

After prolonged heating, dense materials were obtained with both additives, at 1750°C for 8 h. Microstructures (Fig. 5) consisted of elongated Si_3N_4 grains with submicron sized hexacelsian particles, which are very homogeneously distributed throughout the bulk. The two microstructures [Figs. 5(a) and 5(b)] do not seem to be much different after long term annealing.

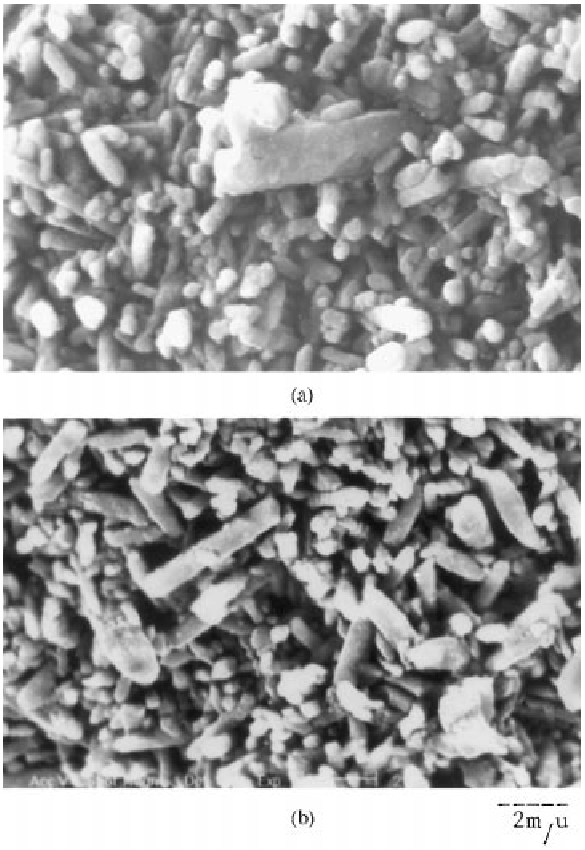

Fig. 4. SEM micrographs of samples with (a) BaA, and (b) with NV, 1750°C, 4 h.

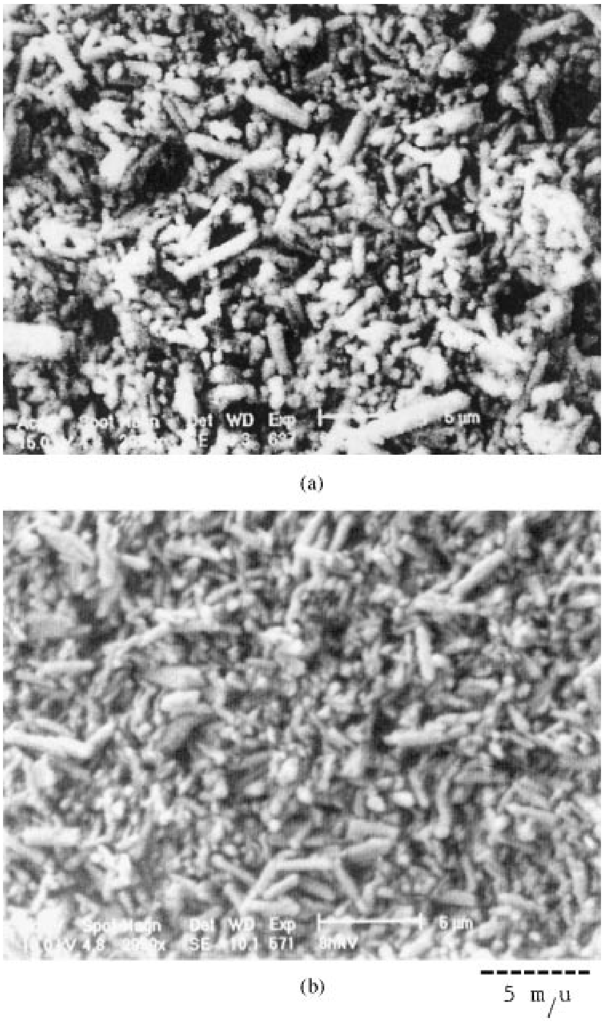

Fig. 5. SEM micrographs of samples with (a) BaA, and (b) with NV, 1750°C, 8 h, (elongated grains—β-Si_3N_4, small equiaxial grains-BAS).

Table 3
Fracture toughness and hardness obtained for different additive amounts

Additive amount	H_{V10} (GPa)	K_{Ic} (MPa m$^{1/2}$)	Sintering conditions (T,t)
10% BaA	12.7	5.20	1750°C-4 h
10%BaA	12.9	5.30	1750°C-8 h
10% NV	12.3	4.57	1750°C-4 h
10% NV	12.7	4.90	1750°C-8 h
20% BaA	11.8	4.97	1700°C-4 h
20% NV	11.9	3.95	1700°C-4 h
30% BaA	11.2	4.39	1700°C-4 h
30% NV	11.3	3.56	1700°C-4 h

Fracture toughness and hardness for materials obtained at 1700 and 1750°C, after 4 and 8 h heating time, containing 10–30% of additives are given in Table 3. It is evident that with decreasing additive amount, both NV and BaA, fracture toughness and the hardness increase. Measured values are in good agreement with the data published by K. Richardson et al. [1]. However, only small differences between samples with the two additives were found.

4. Conclusion

Fully dense ceramic composites Si_3N_4/celsian with good properties can be obtained by pressureless sintering using Ba-A zeolite as a source for BAS formation in the sintered body. Amorphous Ba-A-zeolite transforms during heating into hexacelsian as low as 760°C. Hexacelsian starts converting to celsian at 1250°C. Liquid phase needed for densification was formed between celsian and excess SiO_2. Compared to composites obtained by the mixing of BAS forming oxides, zeolite is less expensive. Another advantage of using zeolite is that it produces dense sintered bodies at 1750°C, after only 4 h heating time, with only 10 wt% of additive. The properties of materials with two different additives (NV and BaA) are not much different after prolonged heating (8 h) at 1750°C, except for the fracture toughness which is higher with BaA samples.

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