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Effect of Milling Time on Mechanical Properties of Anorthite Obtained by Thermal Transformation of Ca-LTA Zeolite

Mia Omerašević^{1*)}, Zvezdana Baščarević², Radojka Vujasin¹, Aleksandar Devečerski¹, Dušan Bučevac¹

¹Department of Materials Science, Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, 11000, Belgrade, Serbia

²Institute for Multidisciplinary Research, University of Belgrade, 11000, Belgrade, Serbia

Abstract:

Anorthite ceramics was fabricated from calcium exchanged Na-LTA zeolite. The powder compacts of Ca-LTA zeolite were sintered at different temperatures ranging between 1100 and 1400°C. It was found that the temperature of 1100°C was sufficiently high to trigger formation of anorthite which stayed stable even at temperature as high as 1400°C. The highest relative density and the lowest open porosity were measured in samples sintered at 1200°C for 3 h. The effect of milling time of Ca-LTA zeolite precursor on density, microstructure and mechanical properties of samples sintered at 1200°C for 3 h was investigated. The particle size refinement appeared to be beneficial in accelerating densification process and improving mechanical properties. The density, compressive strength and hardness of anorthite ceramics obtained from non-milled precursor were measured to be 70.5 %TD, 64 MPa and 1.45 GPa, respectively. On the other side the anorthite ceramics obtained from 24-hour-long milled zeolite precursor had density of 83.9 %TD, compressive strength of 101 MPa and hardness of 3.44 GPa.

Keywords: Ca-LTA; Ball milling; Sintering; Thermal transformation; Anorthite.

1. Introduction

Anorthite is a calcium member of plagioclase feldspar family. This calcium aluminosilicate ($\text{CaAl}_2\text{Si}_2\text{O}_8$) occurs in nature as white or grayish, brittle, glassy crystals [1]. Chemically it is the most nearly related to celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$), and crystallographically most similar to albite ($\text{NaAlSi}_3\text{O}_8$) and orthoclase (KAlSi_3O_8). Its unit cell is primitive, with a 14Å *c*-axis; the *c*-axis is twice that of albite [2]. Anorthite crystals usually occur as euhedral (well-formed with sharp) and tabular crystals [3,4]. The theoretical composition of anorthite is 20.2 % CaO, 36.6 % Al_2O_3 and 43.2 % SiO_2 on a weight basis. According to the CaO– Al_2O_3 – SiO_2 phase diagram, pure anorthite has a melting point of 1553°C [5], which makes the solid-state synthesis of pure anorthite quite difficult at relatively low temperatures. Its theoretical density is about 2.76 g/cm³ [6] and it has triclinic crystal structure. Anorthite is material with good combination of physical properties, such as a very low thermal expansion coefficient, a high thermal shock resistance, a high creep resistance at high temperatures and a low dielectric constant [7–9]. These properties make it an important

*) Corresponding author: mia@vinca.rs

technical ceramic material for producing wall tiles, floor tiles and porcelain [8] as well as insulation parts of near space hypersonic speed aircraft [10–13]. In addition, anorthite is promising material for LTCC (Low temperature co-fired ceramic) substrates owing to coefficient of thermal expansion and dielectric constant which are lower than those of alumina [14]. Anorthite can be easily synthesized starting from mixture of commercial powders of Al_2O_3 , SiO_2 and CaO . However, in order to prepare low-cost ceramics, different low-cost sources of Al, Si and Ca have been commonly used. The most frequently used starting materials are kaolin, quartz, calcite, marble powder, gypsum, $\text{Ca}(\text{OH})_2$, etc. These starting materials have been processed by employing different methods such as sintering of powder mixtures, mechanochemical treatments and sol-gel procedures [15–17]. In recent years, a great deal of research has been devoted to the development of new technical ceramics, using raw materials instead of industrial chemicals due to the lower price of raw materials available [18,19]. Kaolin, as a good source of silicon and aluminium [20] has been reported as a proper starting, raw material for production of anorthite ceramics owing to its abundances and relatively low price. Most of the studies have investigated the effect of kaolin properties and sintering aids on anorthite densification [8,16,21,22].

Another aluminosilicates, worth of our attention, are zeolites which are also considered as inexpensive materials. The wide application of zeolites over the past 40 years has motivated research associated with their thermal stability and thermally induced phase transformation [23,24]. The phase transformation is usually a multiple step process which consists of a thermal treatment that destroys the zeolite structure causing formation of an amorphous phase, and subsequent recrystallization into structurally new phase with higher density than that of the starting zeolite structure [25–29]. Dimitrijevic et al. [26] were pioneers in the synthesis of anorthite from zeolite as precursor. Thermal transformation of two types of zeolite LTA and FAU which were previously exchanged with Ca^{2+} cations was studied. It was found that Ca-LTA form of zeolite transforms into anorthite powder at approximately 1050°C . Chandrasekhar and Pramada [30] used similar approach. In their study, zeolite (A and X) which was synthesized from metakaolin using hydrothermal method was exchanged with Ca^{2+} cations and subsequently sintered at various temperatures. The process was quite complex as it involved synthesis of zeolite and subsequent ion exchange. Furthermore, the obtained anorthite was normally accompanied by amorphous phase which deteriorates mechanical properties of anorthite.

Therefore, the present study was focused on syntheses of anorthite using commercial Na-LTA zeolite. The Ca^{2+} exchanged Na-LTA, i.e., Ca-LTA was used as precursor for anorthite. The effect of milling time on microstructure and mechanical properties of sintered samples was investigated. The results showed that the variation of milling time is an effective way to modify microstructure and further improve mechanical properties of anorthite obtained from zeolite.

2. Materials and Experimental Procedures

Sodium form of LTA ($\text{Si}/\text{Al} = 1.00$) zeolite manufactured by Union Carbide Co. was used as the starting material. Fully exchanged Ca^{2+} form of LTA zeolite was prepared by treating Na-LTA zeolite with CaCl_2 solution as previously described by Firor and Seff [31]. The chemical compositions of exchanged samples were analyzed using a Perkin-Elmer 700 atomic absorption spectrophotometer. Loss on ignition was measured as weight loss during DTA/TG analysis which was carried out up to 1000°C in air using a TA SDT Model 2090 thermobalance. The obtained Ca-LTA zeolite was milled for different periods of time in a plastic jars using Al_2O_3 balls as a milling media and distilled water as a liquid vehicle. Milling time was 0, 3, 6, 12 and 24 h. The powders were dried, sieved and uniaxially pressed under pressure of 60 MPa to obtain compacts with a diameter of 10 mm and height of ~ 8 mm.

Powder compacts of non-milled powder were heat treated at 1100, 1200, 1300 and 1400°C for 3h in the air in order to determine the optimum sintering temperature. The heating rate was 5 °C/min. The compacts made of powders milled for different periods of time were sintered at the optimum sintering temperature (1200°C) for 3 h. The phase composition was investigated by X-ray powder diffraction (XRPD). XRPD patterns were obtained on a Rigaku Ultima IV diffractometer, using a Cu tube operated at 40 kV and 40 mA. The diffraction data of samples were collected in 2θ range of 10 to 50° using a count time of 1.0s and a step size of 0.02°, for routine phase analysis. Bulk density and open porosity were determined by the Archimedes' method using water as immersion liquid. Particle size distribution was determined using Horiba LA-910 Particle Size Analyzer. The microstructure analysis of anorthite samples was conducted using VEGA TS 5130 MM scanning electron microscope (SEM). Prior to SEM analyses, the samples were coated with 15 nm layer of gold. Room-temperature compressive test of six samples was carried out by using 1185 Instron-type testing machine at a strain rate of 2 mm/min. The average value was calculated. Two end surfaces of the cylindrical samples were carefully ground to make surfaces parallel. Vickers hardness was measured by indentation method using Vickers indenter. Sample hardness was estimated by measuring the diagonal length of the five indents made by 5 kg load.

3. Results and Discussion

As mentioned before, the starting material for anorthite fabrication was Ca^{2+} exchanged Na-LTA zeolite. The chemical composition of exchanged zeolite (Ca-LTA) is presented in Tab I. It is evident that Na^+ cations, which were initially present in LTA framework, are completely exchanged for Ca^{2+} after the treatment of Na-LTA with CaCl_2 .

Tab. I Chemical composition of a) Na-LTA b) Ca-LTA zeolite (oxide wt.%).

Precursor	Oxides				LOI
	SiO_2	Al_2O_3	Na_2O	CaO	
Na-LTA	39.05	29.36	17.88	/	13.71
Ca-LTA	38.23	30.45	/	17.20	15.10

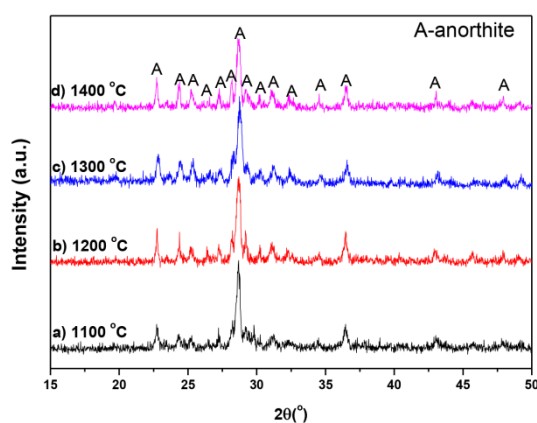


Fig. 1. XRPD patterns of samples obtained from Ca-LTA zeolite precursor thermally treated at 1100-1400°C for 3 h.

The obtained Ca-LTA (non-milled powder) was compacted and sintered at temperatures ranging from 1100 to 1400°C in order to obtain anorthite ceramics. The XRPD patterns presented in Fig. 1 show the phase composition of crushed pellets sintered at different temperatures. It can be seen that the temperature of 1100°C is sufficient to allow formation of anorthite which stayed stable even at temperature as high as 1400°C. This is in a good agreement with the research conducted by Chandrasekhar and Pramada [30] and Dimitrijevic et al. [26] which showed that in the case of zeolite Ca-LTA, the maximum crystallinity was observed after heat treatment at 1150°C.

Tab. II Density of anorthite ceramics obtained after sintering of non-milled zeolite powder at temperature ranging from 1100 to 1400°C.

Sample	Open porosity (%)	Density (g cm ⁻³)	Relative density (%TD)
Ca-LTA– 1100	12.43	1.020	36.96
Ca-LTA– 1200	6.85	1.947	70.54
Ca-LTA– 1300	7.89	1.766	63.98
Ca-LTA– 1400	7.12	1.898	68.77

In this work, the first step was determination of the optimum sintering temperature, i.e., the temperature at which maximum density was achieved. Tab. II shows the effect of sintering temperature on relative density and open porosity of anorthite ceramics obtained from non-milled zeolite powder. As can be seen, the highest relative density and the lowest open porosity were measured in samples sintered at 1200°C which will be designated as the optimum sintering temperature. Further increase of sintering temperature was followed by a decrease of the bulk density.

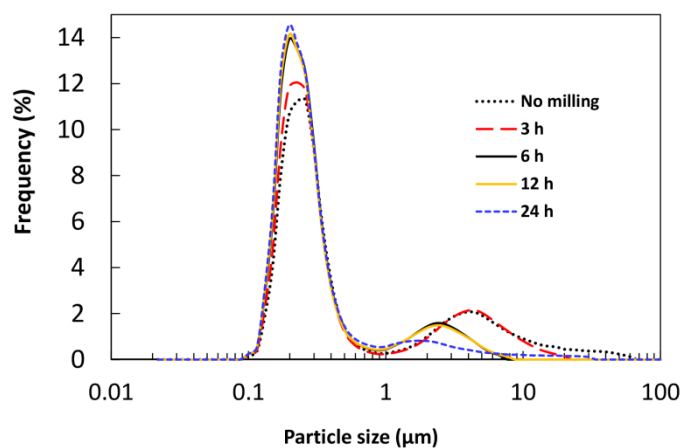


Fig. 2. Particle size distribution of Ca-LTA zeolite powders milled for different periods of time.

It is well known that the reduction in particle size normally increases the driving force for sintering. Therefore, it is expected that the milling of zeolite powder will further improve the density of sintered compacts. The effect of milling time on particle size of Ca-LTA zeolite powders is presented in Fig. 2. In order to quantify particle size distribution, the milled powder agglomerates were dispersed in water to break the particle–particle interactive forces. Fig. 2 shows that non-milled zeolite has a bimodal particle size distribution. The first peak is located between 0.2 and 0.3 μm whereas the second peak is located around 4 μm. Prolonged milling was found to be effective in breaking large particles. As can be seen, the peak located at 4 μm almost disappeared after 24-hour-long milling. At the same time the fraction of fine

particles increased causing the increase in intensity as well as small shift of peak located between 0.2 and 0.3 μm towards smaller particle sizes. Statistical parameters such as D10, D50, D90 and mean particle size which are generated from a particle size distribution given in Fig. 2 are listed in Tab. III. As can be seen, all parameters decrease with an increase of milling time. It is important to note a large decrease of D90 parameter. Namely, non-milled sample has D90 = 5.994 μm whereas D90 of sample milled for 24 h reaches value of only 0.976 μm indicating that 90 % of particles have diameter up to 0.976 μm . Furthermore, the mean particle size of non-milled sample is 2.351 μm whereas the mean particle size of sample milled for 24 h is considerably smaller reaching value of only 0.554 μm . Thus, it can be concluded that 24 hour-long milling is an effective way of reducing the particle size of Ca-LTA zeolite powder.

Tab. III Parameters generated from a particle size distribution analysis.

Milling time (h)	D10 (μm)	D50 (median value) (μm)	D90 (μm)	D _{mean} (μm)
0	0.160	0.268	5.994	2.351
3	0.156	0.251	4.477	1.330
6	0.151	0.229	1.722	0.690
12	0.150	0.227	1.680	0.556
24	0.149	0.223	0.976	0.554

The effect of milling time on density and open porosity of samples sintered at 1200 °C for 3h was shown in Fig. 3. It is evident that powder milling shows positive effect on density which continuously increases with an increase of milling time. This is expected knowing that the particle refinement and consequent increase of specific surface of powder improves driving force for sintering and therefore accelerate sintering process, i.e., densification. It is important to stress that 24 hour-long milling caused an increase in density from 70.54 to 83.98 %TD which is an increase of 19 %. The increase in density is followed by the decrease in open porosity which was especially pronounced in samples obtained from powders milled for 3 and 6 h. The open porosity of sample obtained from powder milled for 6 h is only 3 %. The decrease in porosity with milling time was also confirmed by microstructural observation.

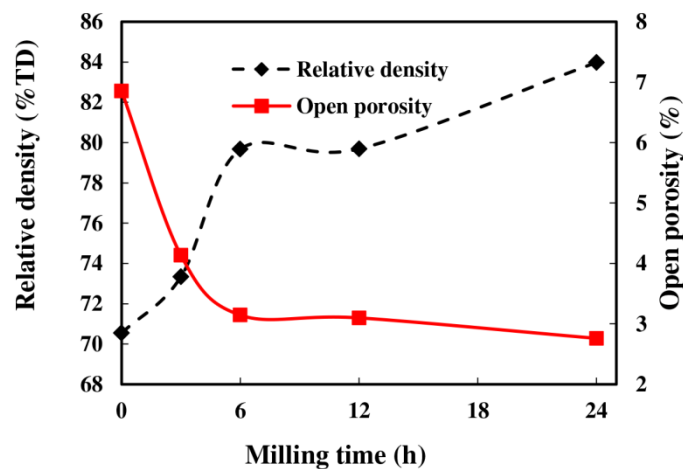


Fig. 3. Effect of milling time of precursor Ca-LTA zeolite on density and open porosity of anorthite sintered at 1200°C for 3 h.

The micrographs of polished surfaces of sintered samples are presented in Fig. 4. It clearly shows the decrease of porosity as well as the decrease of pore size with milling time as a result of reduction of particle size and consequently improved driving force for sintering of starting powder. It is also important to point out the difference in size and shape of the pores in samples obtained from powders milled for different periods of time. Fig. 4a shows that pores in non-milled sample are very often connected making large, elongated pores consisting of several predominantly spherical pores. It is believed that these elongated pores, which can be over 40 microns in length, are responsible for low compressive strength and Vickers hardness of these samples, which will be discussed in the following section. On the other side, the pores in sample obtained from powder milled for 24 h (Fig. 4e) are mostly insulated, with diameter below 5 microns.

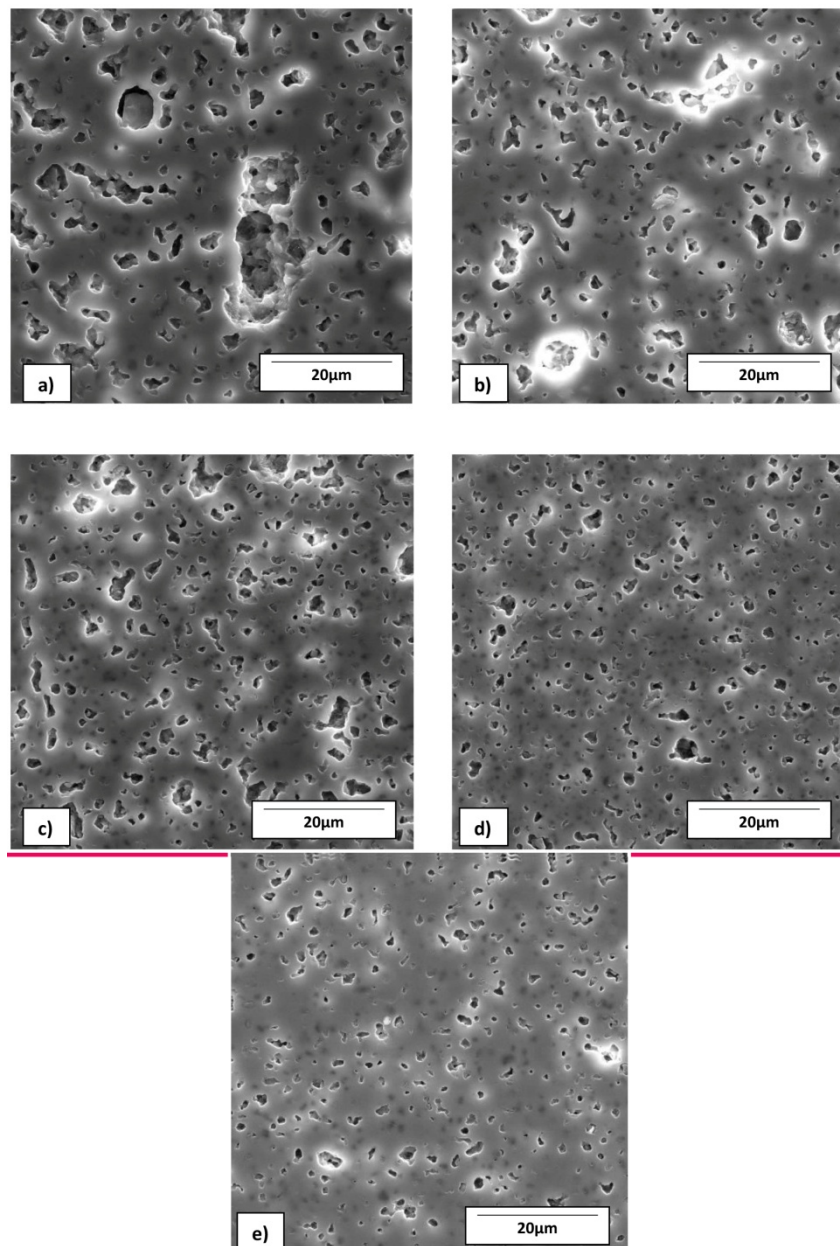


Fig. 4. SEM micrographs of polished surfaces of anorthite samples sintered at 1200°C for 3h obtained from Ca-LTA precursor milled for: a) 0 b) 3 c) 6 d) 12 and e) 24 h.

3.1. Mechanical properties

It can be seen from Fig. 5 that the increase of milling time results in the increase of both hardness and compressive strength. Positive effect of milling time on mechanical properties is attributed to the increased density of samples obtained from milled powders (Fig. 3). It is well known that hardness as well as compressive strength is strongly affected by density, i.e., porosity. The highest values of hardness (3.44 GPa) and compressive strength (101 MPa) are measured in samples made of precursor Ca-LTA which was milled for 24 h. These values are much higher than those have been reported so far in the literature for anorthite obtained by pressureless sintering in air [8].

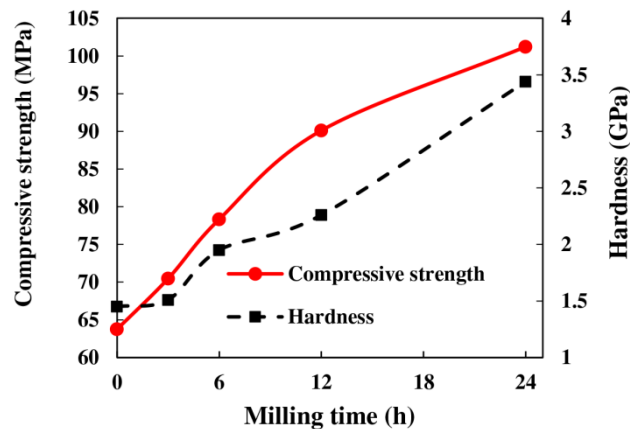


Fig. 5. Influence of milling time of precursors (Ca-LTA) on hardness and compressive strength of anorthite samples sintered at 1200°C for 3 h.

Another reason for low compressive strength of anorthite obtained from non-milled precursor is the presence of thin and long cracks. As shown in Fig. 6a, the length of these cracks can be more than 30 μm whereas the width is up to 5 μm . The long cracks were not observed in anorthite sample obtained from 24-hour-milled precursor (Fig. 6b) indicating that one of the crucial benefits of milling is elimination of long crack. The presence of these cracks causes substantial stress concentration at their tips which can easily initiate crack propagation even under relatively small external loads.

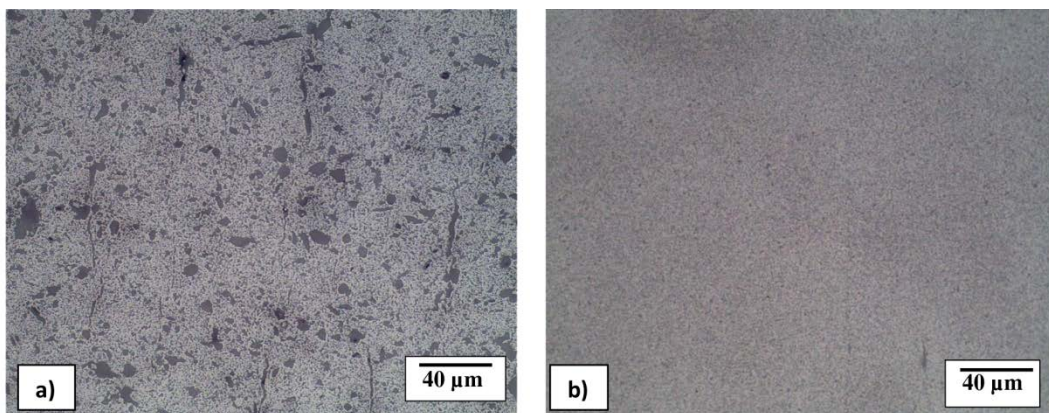


Fig. 6. Optical micrographs of polished surface of anorthite ceramics sintered at 1200°C for 3 h obtained from Ca-LTA precursor: a) non-milled and b) milled for 24 h.

SEM micrographs of fracture surfaces of sintered anorthite samples obtained from non-milled powder and powder milled for 24 h are presented in Fig. 7. The large cracks which were observed in Fig. 6a were not observed in Fig. 7a. This implies that the fracture of samples takes place along these elongated cracks. Therefore, the surface of elongated cracks can be seen at the fracture surface shown in Fig. 7a. Unlike elongated cracks, the big pores are observed at the fracture surface presented in Fig. 7a (denoted by arrows). As discussed, milling of precursor Ca-LTA powder was beneficial for elimination of these large pores. As Fig. 7b confirms, large pores ($\geq 10 \mu\text{m}$) are not detected in sample obtained from 24-hour-milled precursor. It is evident that 24-hour-long milling was sufficient to increase the driving force for sintering to the level necessary for elimination of large pores responsible for premature fracture. Furthermore, the analysis of fracture surfaces presented in Fig. 7 indicates that crack propagates either through the grains (transgranularly) or along the grain boundaries (intergranularly). These two mechanisms of crack propagation are typical for brittle materials [32] such as anorthite ceramics. Fig. 8, which is taken under high magnification (15000x), points out that transgranular crack propagation is dominant in sample obtained from from Ca-LTA precursor milled for 24 h.

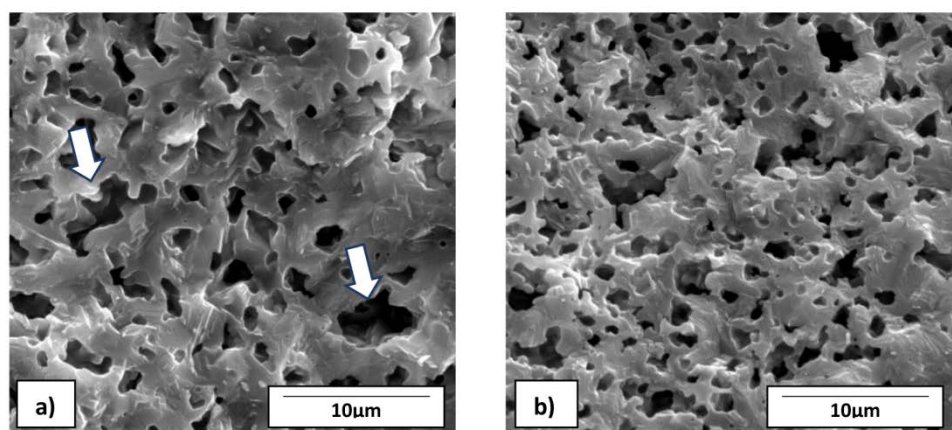


Fig. 7. Fracture surface of anorthite samples sintered at 1200°C for 3 h obtained from Ca-LTA precursor: a) non-milled and b) milled for 24 h.

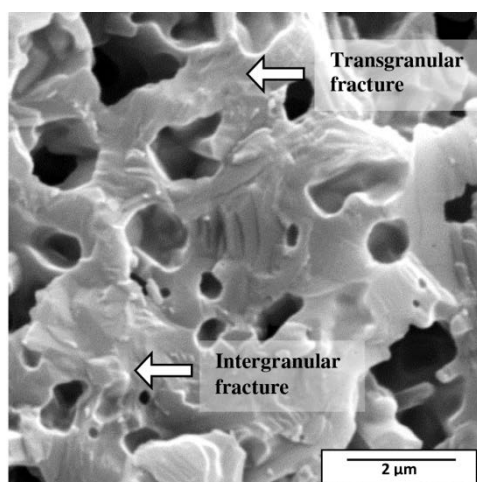


Fig. 8. Fracture surface of anorthite samples sintered at 1200°C for 3 h obtained from Ca-LTA precursor milled for 24 h (magnification 15000x). The arrows are showing transgranular and intergranular fracture.

4. Conclusion

Dense anorthite ceramics was obtained by sintering of Ca exchanged Na-LTA zeolite at 1200°C for 3 h. It was found that 24-hour-long ball milling of Ca-LTA precursor reduced D90 from 5.994 μm in non-milled to 0.976 μm in milled precursor. The particle size refinement appears to be beneficial in accelerating densification process and improving mechanical properties. Anorthite ceramics obtained from Ca-LTA precursor milled for 24 h had density of 83.9 %TD whereas the density of anorthite ceramics obtained from non-milled precursor was only 70.5 %TD. The increase in density was followed by the reduction in open porosity which decreased from 6.8 % in anorthite obtained from non-milled precursor to 2.8 % in samples obtained from precursor milled for 24 h. Accelerated densification contributed to an elimination of long cracks as well as large pores which improved compressive strength. 24-hour-long milling of Ca-LTA precursor improved compressive strength of sintered samples from 64 MPa in sample obtained from non-milled precursor to 101 MPa in sample obtained from milled precursor. At the same time hardness increased from 1.45 GPa in sample obtained from non-milled powder to 3.44 GPa in sample obtained from precursor milled for 24 h which was an increase of more than two times. The samples fractured predominantly transgranularly.

Acknowledgments

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5. References

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Сажетак: Анортитна керамика је добијена из калцијумом измењеног Na-LTA зеолита. Компакти праха Ca-LTA зеолита су синтеровани на различитим температурама у интервалу од 1100 до 1400°C. Утврђено је да је температура од 1100°C довољно висока да изазове формирање анортита који је остао стабилан чак и на температури од 1400°C. Највећа релативна густина и најмања отворена порозност измерена су у узорцима који су синтеровани 3 h на 1200°C. Испитиван је утицај времена млевења Ca-LTA зеолита као прекурсора на густину, микроструктуру и механичка својства узорака синтерованих на 1200°C током 3 h. Смањење величине честица Ca-LTA праха након млевења је убрзало процес згушњавања и побољшало механичка својства добијеног материјала. Измерене вредности густине, компресионе чврстоће и тврдоће анортитне керамике добијене од немлевеног прекурсора су 70,5 % теоријске густине, 64 MPa and 1,45 GPa, респективно. Са друге стране, код анортитне керамике добијене од прекурсора зеолита млевеног у трајању од 24 сата, постигнута је густина од 83,9 % теоријске густине, компресиона чврстоћа од 101 MPa и тврдоћа од 3,44 GPa.

Кључне речи: Ca-LTA, млевање куглама, синтеровање, термална трансформација, анортит.

