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Properties of durable mullite bodies manufactured from waste clay-diatomite

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ABSTRACT

Durable mullite bodies have been fabricated using diatom frustules from diatomite powder as the Si source and Al-nitrate as the Al precursor, resulting in fibrous pore morphology. The hard mullite ceramics prepared by mold pressing without additives showed high compressive strength (up to 133 MPa when sintered at 1500 °C). The diatomite-nitrate samples were sintered at three temperatures (1300, 1400, and 1500 °C) for 2 hours. XRPD analysis of the sintered samples showed that the crystalline mineral phases mainly comprise mullite, cristobalite, and corundum. SEM results indicate the presence of rod-like mullite grains measuring 5 μm in length and 500 nm in diameter (aspect ratio 1:10). XRPD analysis of the samples sintered at 1300 °C demonstrated good thermo-mechanical stability and the formation of new hard phases (mullite, corundum, and cristobalite), making the analyzed diatomaceous earth suitable to produce various types of ceramic, construction, and thermal insulating materials.

Keywords: diatomaceous earth, mullite bodies, synthesis, phase change, eco-friendly materials.

1. Introduction

Demand for various applications such as fire-resistant insulation, refractory, filtration, catalyst support, absorption, bio scaffolds, and tissue engineering, ranks ceramic materials as one of the leading functional and structural materials in various branches of industry. Refractories work together in a harsh environment to form a cohesive shield that absorbs and dissipates heat from the outer layers to the inner layers, maintaining structural integrity (Pletnev et al. 2018). Similarly, the good mechanical properties formed by the ceramic whiskers that impinge on each other and pores contribute to high thermo mechanical stability, enabling applications such as refractories, furnace furniture, catalyst substrates, furnace tubes, and heat shields (Lima et al. 2022)

Unlike non-oxide ceramics, which demand a high cost of production (non-oxidizing atmosphere and extremely high sintering temperature), mullite ($3Al_2O_3{\cdot}2SiO_2$) can be synthesized using eco-friendly, natural materials under air, at much lower temperature and consolidation techniques thus reducing energy consumption. In such a way, consolidation techniques operate at lower temperatures due to a transient liquid phase accelerating a grain boundary/surface diffusion and mass transport (L. Dong et al. 2016).

Diatomite, or diatomaceous earth, is of sedimentary origin and consists mainly of an accumulation of the skeletons formed as a protective covering of the diatoms (Ivanov and Belyakov 2008; Inglethorpe 1993; Ilia, Stamatakis, and Perraki 2009). The skeletons are essentially eukaryotic unicellular microalgae composed of amorphous hydrated or opaline silica, while alumina originates from clay minerals such as illite, kaolinite, and minerals from micas group (muscovite), and organic matters (Reka, Pavlovski, and Makreski 2017). When heated at high temperatures, the diatomite undergoes a series of reactions, forming mullite, cristobalite, and impurity-containing silica-rich liquid phase. In stoichiometric 3:2 mullite ($3Al_2O_3.2SiO_2$), the amount of silica present is lower than that found in diatomite. The excess silica in diatomite converts to cristobalite and silica-rich liquid phase (Sahnoune et al. 2008).

In this study, mullite and mullite-based ceramic composites were prepared, using waste clay-diatomite (a by-product of mining) with aluminum nitrate to synthesize rod-like mullite grains by a simple preparation method. In our case an Al-source was introduced into diatomaceous earth particles in the form of a solution allowing its infiltration into all free space, remaining thus in the channels of diatomaceous earth during sintering. The solution of Al-nitrate envelops the exterior and interior of diatomite particles providing this way a larger contact surface between starting components and thus much higher reactivity during the stirring process. According to literature data, source of aluminum is usually introduced in diatomaceous earth via mechanical milling . No additives were used to promote the growth of mullite whiskers. The phase composition, mechanical properties (compressive strength), microstructure, and grain size distribution of the obtained mullite compacts were investigated.

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2. Experimental procedure

Diatom frustules were purchased from the surface coal mine Baroševac, Kolubara, Serbia. Aluminum nitrate nona hydrate ($Al(NO_3)_3 \cdot 9H_2O$, thermo scientific 99 % purity) was used as an Al precursor. The mixture, based on the mullite composition, was wet-mixed using a magnetic stirrer for 3 h at 70 °C. The obtained mixture was dried for 24 hours. The dried precursor powder mixture was pressed into compacts without any binder using a steel mold at uniaxial load of 2 MPa, loaded in alumina crucibles, put into an air furnace and heated to different temperatures (1300–1500 °C) for 2 h and a heating and cooling rate interval of 5 °C/min.

The XRD patterns of heat-treated compacts were scanned by Rigaku Ultima IV using Cu Kα radiation and operating at 40 kV and 40 mA in the 2θ range between 5° and 90° with a step of 0.02° and a scan rate of 5°/min. The apparent density and open porosity of sintered mullite samples were determined by the Archimedes method. Linear shrinkage was calculated by measuring the diameter of the samples before and after heat treatment. A Tescan Mira 3 XMU FESEM was used for the morphological characterization of synthesized powders. Before the FESEM analysis, the powders were coated with Au using a Polaron SC502 sputter coater. The mechanical stability of sintered cylindrical mullite ceramics, i.e., 7.4 mm to 8.6 mm in diameter and 15.4 mm to17.4 mm in height, was evaluated by compressive testing in a Universal testing machine Instron 1185 using test Instrument Explorer software. Briefly, cylindrical samples were compressed with a testing speed of 1 mm/min until fracture occurred. The compressive strength was obtained from the quotient of maximum force and cross-sectional area of the test least four replicas were tested for each sample.

3. Results and discussion

In terms of chemical composition, diatomite is composed of very high silica content, moderately high Al2O3, small percentage alkaline and alkaline-earth element oxides along with Fe2O3 present in the diatomite powder and vitreous part which promote the viscous flow at lower sintering temperature favoring mullite formation (Saponjic et al. 2024).

During sintering, several phase transformations occur in the minerals present in the starting powder mixture, and the ultimate phases obtained are mainly mullite and a glassy phase (XRPD, Figure 1). The selection of sintering temperatures (1300–1500 °C) was compromise between the composition phases and the mechanical properties of analyzed compacts. At a temperature of 1300 ºC and 1400 ºC, for 2h the main peaks belong to the mullite phase (ICDD NO. 01-088-2049), cristobalite SiO2 (ICDD PDF No. 01-071-6248), corundum α-Al2O3 (ICDD PDF No. 00-046-1212) and quartz SiO2-Q (at 2θ = 26.5°, INSET in Fig.1, PDF No.01-089-8936).

When sintering, diatomite, a liquid phase first forms on the surfaces of quartz grains (Saponjic et al. 2024) due to transformation of quartz to cristobalite which acts as precursors in the mullite formation by reacting with α-Al2O3. As predicted by the SiO2–Al2O3 phase (Akhtar, Rehman, and Bergström 2010) the crystallization of mullite, as it is an equilibrium phase, from aluminum-silicate glass is not particularly surprising. It is already known that crystallization of cristobalite preferentially from silicate glasses even below 1400 °C can be largely affected by the presence of even low amounts of alkalis (Galotta et al. 2021). According to Zheng et al., the phase transition temperature from opal to cristobalite is reduced about 200 °C, because the alkali ions (Na+, likewise with other alkalis present in starting diatomite) would partly broke down the Si-O-Si chains of opal and occupy interspaces of the mesh structure, finally facilitating the formation of crystalline silica phase with high temperature process (Ren et al. 2014; Zheng et al. 2018).

Above 1400 °C, the increase in the intensity of mullite peaks implies an increased amount of mullite phase and better crystallinity. After 2 h at 1500 °C, the peaks of cristobalite (1, inset Figure 1) and corundum (2, inset Figure 1) disappeared, and pure mullite bodies were obtained (Figure 1).

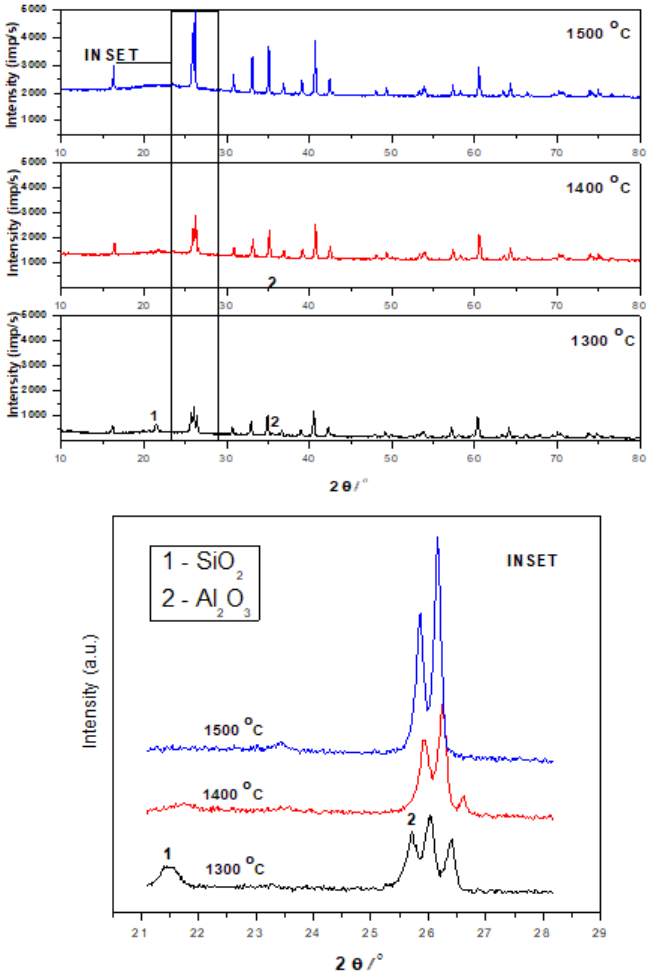

Fig. 1. XRD diagrams of the obtained compacts sintered from 1300 °C to 1500 °C for 2h.

The temperature of mullite appearance is significantly lowered below 1200 °C due to the eutectic reactions, which promote the formation of the liquid phase in the presence of admixture of Al2O3 and alkali earth oxides in starting diatomaceous earth. As mentioned by Rana et al. (Rana, Aiko, and Pask 1982a) and Dong et al. (L. Dong et al. 2016), the temperature at which mullitization occurred is decreased by 200 °C due to using amorphous bio silica as a Si precursor, which forms a liquid phase below 1000 °C (Akhtar, Vasiliev, and Bergström 2009; Rana, Aiko, and Pask 1982b).

Percentage of each phase is calculated using Powder cell program (Kraus and Nolze 1996), and results are given in Table 1. All the structure information was taken from American Mineralogist Crystal Data Structure Base (AMCDSB) (Downs and Hall-Wallace 2003). The values of crystallite size and lattice parameter of samples sintered at different temperatures for 2 h are presented in Table 1. As expected, with an increase in sintering temperature, the average crystallite size is increased due to accelerated diffusion at higher temperature. Increased atomic diffusivity at high temperature also caused the increase of the lattice parameter with temperature, confirming ordering of structure with thermal treatment. Unlike crystallite size, the internal strain of samples, which was estimated from the slope of Williamson-Hall plots, slightly is decreased with increasing sintering temperature. Internal strain is caused by defects like impurity atoms, self-interstitials or vacancies (Völkl 1994) so we can presume that this decrease is a result

of an ordering of atomic arrangement during sintering process and goes together with grain growth.

Table 1. Lattice parameters (a, b, c), amount of crystalline phases (%), crystallite size, and lattice strain of mullite sintered at different temperatures for **2h**.

Sintering temperature (°C)	mullite cristobalite corundum quartz (%)	a (Å) b (Å) c (Å)	Crystallite size (nm)	Lattice strain (%)
1300	70.3 11.9 5.1 12.8	7.5714(2) 7.7241(5) 2.8987(5)	40 ± 0.4	0.000996
1400	78.3 12.1 4.3 5.3	7.5549(1) 7.7059(3) 2.8933(7)	44 ± 0.3	0.000845
1500	99.0; /; /; 1.0	7.5535(4) 7.7016(3) 2.8914(5)	70 ± 0.3	0.000732

The results shown in Table 2 indicate that the starting powders, sintered at 1400 and 1500 °C, yield a hard and reliable material. Shows the linear sintering shrinkage, open porosity, and compressive strength of samples sintered at different temperatures. The linear shrinkage is significant (16,52 %) and nearly keeps a constant value of 24 % when the samples are sintered below 1500 °C. In contrast to literature data, where the source of aluminum is introduced via mechanical milling in diatomaceous earth, in our case an Al-source in the form of a solution allowed its penetration in all free space in diatomaceous earth particles and remains in the channels of diatomaceous earth (Ersoy et al. 2022; Y. Dong et al. 2008; 2010; 2011; Behera and Bhattacharyya 2021). During the stirring process, this liquid solution of Al-nitrate envelops the exterior and interior of diatomite particles, providing a higher reactivity of diatomaceous earth and source of Al because the contact surface is much larger contrary to literature data (Sahnoune et al. 2008; L. Dong et al. 2016). It leads to enhanced densification and higher values of compressive strength.

Table 2. Linear shrinkage, open porosity, and compressive strength of mullite bodies.

Sintering temperature (°C)	1300 °C	1400 °C	1500 °C
Linear shrinkage (%)	16,52	25,14	24
Open porosity (%)	51	31	21
Compressive strength (MPa)	12.03	83.67	133.24

So, the open porosity of ceramics is about 51 % when sintered at 1300 °C and is significantly reduced to 21 % when increasing the temperature to 1500 °C due to the densification of samples. Compared with literature data (L. Dong et al. 2016), where the high values of compressive strength (57.6 MPa at open porosity of 60 %) are mostly obtained due to the addition of aids for grain growth, the values in the present study are significantly improved for samples sintered at 1400 °C, 83.67 MPa and at 1500 °C, 133.24 MPa without additives.

A typical microstructure of sintered mullite bodies is shown in Figure 2. Observations were complemented by FESEM analysis, revealing the elongated mullite grains are embedded within mainly glassy phase. As expected, the average crystallite size increased from 1 μm (1400 °C) to 5 μm (1500 °C), with an increase in sintering temperature due to accelerated diffusion at high temperatures. It is worth noting finally, that anisotropic grain growth of rod-like mullite grains occurs by dissolution and reprecipitation through the liquid (or glass) phase (Hong and Messing 1999). In the liquid (or glass) phase multicomponent-assisted systems, the present cations reduce the viscosity of silica (glassy phase) by several orders of magnitude and thus facilitate diffusion of reacting species causing the low eutectic temperature below 1200 °C. Therefore, the alkali, alkali earth, iron, and titanium cations positively affect the mullite formation and grain growth, favoring anisotropic rather than equiaxial grain growth, resulting in rod-like mullite microstructure with significantly improved compressive strength. Close contact between the particles/grains hinders the grain growth, and elongated mullite grains/whiskers thicken after blocking the grain growth observed at higher temperatures (Ilić et al. 2014; Hong and Messing 1999).

4. Conclusions

This study demonstrated the possible eco-friendly, energy-saving, and inexpensive method for manufacturing mullite bodies using an industrial mineral, clay-waste diatomaceous earth, and Al-nitrate as raw materials without additives. Anisotropic growth, resulting in rod-like mullite grains, is favored by the presence of amorphous biosilica, alkali, and earth alkali cations, which reduce the viscosity of silica phase, facilitate the diffusion of reacting species and lower the eutectic temperature below 1200 °C. The present liquid phase enabled the formation of a ceramic composite with the following crystalline phases: mullite, cristobalite, and corundum at 1300 °C and pure mullite at 1500 °C. According to the XRD analysis and compressive strength, the temperature of 1500 °C appears to be proper for producing durable mullite refractories and insulators. Mullite compact sintered at 1500 °C exhibits the highest compressive strength, up to 133 MPa, due to the highest density and unique rod-like microstructure with grains of 5 μm in length. In line with the study's results, this combination of the starting raw materials opens the possibility of obtaining durable mullite ceramics.

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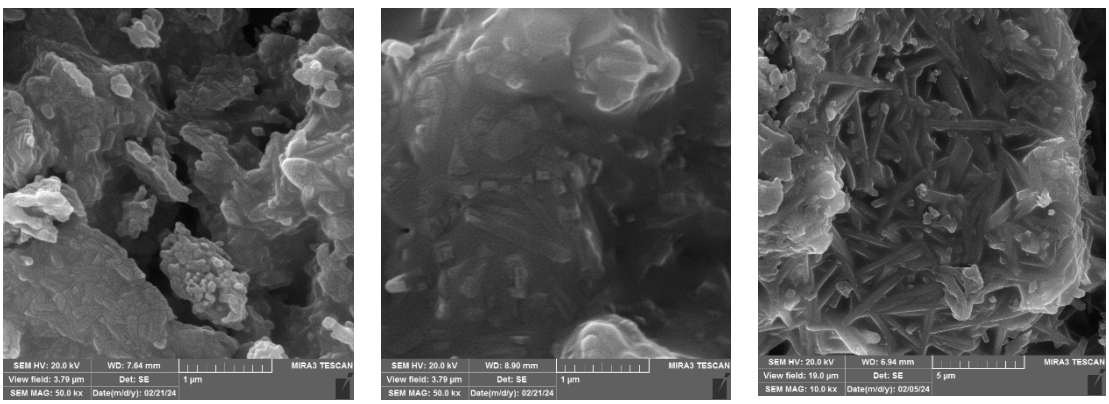

Fig. 2. SEM images of powder after sintering at different temperatures (1300, 1400 and 1500 °C, left to right) for 2h.-

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