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MATERIALS ENGINEERING | RESEARCH ARTICLE

Effect of colemanite on properties of traditional mullite zirconia composite

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Abstract: In this study, mullite zirconia composites are synthesized via reaction sintering method by using zircon, kaolinite and alumina mixtures including colemanite ($Ca_2B_6O_{11}5H_2O$) (7 wt.%). In mullite zirconia composites, the effect of colemanite additive on mineralogical, thermal, microstructure and mechanical properties and also on formation are studied. Mixtures are sintered at 1,450, 1,500 and 1,550°C for 5 h. in air. The resulting sintered materials are characterized in terms of bulk density, DTA, X-ray diffraction (XRD), SEM and mechanical properties such as flexural strength and elastic modulus. Various effects of colemanite addition on the composites are observed with regard to thermal, mineralogical and mechanical properties. Both DTA and XRD analyses show that colemanite addition in mullite zirconia composite reduces the reaction temperature. Zircon alone in the mixture resulted in a 1,550°C reaction temperature, whereas the compositions including colemanite is attenuated to 1,450°C. While zircon exists up to 1,550°C in the mixtures free of colemanite, it decays at 1,450°C due to 7 wt.% colemanite addition. Composites comprising of 7 wt.% colemanite exhibit a higher density, flexural strength (σ) and elastic modulus (E). Microstructural characterization of the sintered samples through scanning electron microscope indicate mullite and zirconia are the two main phases. Homogenously distributed round-shaped ZrO_2 grains and irregularly shaped mullite grains are observed, which fundamantally constitute the microstructure.

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PUBLIC INTEREST STATEMENT

Particularly mullite zirconia composites are materials with important technological applications due to their good properties such as toughness, chemical stability, and high-creep resistance. In practice they are employed in the glass industry and where high chemical and corrosion resistance are required.

Although there are common studies that investigate the mullite zirconia composite synthesis through conventional reaction sintering and also the effect of various contributions to such synthesis zircon-alumina or zircon-alumina-kaolinite mixtures, there are no substantial studies on the effect of boron additions to such raw material mixtures. This study primarily bears a separate importance on that account. In addition, this study has three main objectives. These are; (1) to observe the effect of colemanite addition to kaolinite, alumina, and zircon mixture synthesized from conventional raw materials, (2) to contribute to scientific literature concerning studies on mullite zirconia with colemanite, a boron mineral, and (3) to form a new reference and field of interest.

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Subjects: Composites; Materials Processing; Materials Science

Keywords: A. composite materials; B. colemanite; C. mullite zirconia composite; D. reaction sintering

1. Introduction

In this work, the mullite zirconia composite was prepared by mixing alumina, kaolinite and zircon powders with colemanite in various compositions in order to study mineralogical thermal, micro-structure and mechanical behaviour of mullite zirconia composites.

Albeit possessing excellent properties such as low thermal expansion coefficient, low thermal conductivity, high temperature strength and phase stability at high temperatures, mullite by itself suffers from its low fracture toughness (2 MPa m$^{1/2}$) and difficulties in sintering to full density. In order to improve its fracture toughness and sinterability, other ceramics such as zirconia, silicon carbide and alumina have been introduced (Bradecki & Jonas, 2010; Hemra & Aungkavattana, 2014; Zaki, Ewais, & Rashad, 2009). Among these composites, mullite zirconia is considered as one of the most popular, because ZrO_2 enhances thermomechanical properties of mullite via transformation and microcrack toughening mechanisms, owing to its high room temperature, strength and fracture toughness (Ashrafi, Emadi, & Foroushani, 2015).

Partially stabilized zirconia (with oxides such as yttria (Y_2O_3), ceria (CeO_2), magnesia (MgO) and calcium oxide (CaO)) is one of the most excellent candidates in a mullite matrix ceramic matrix composites (CMC), due to its high room temperature strength and toughness enhancing the thermo-mechanical properties of mullite via transformation toughening and microcrack toughening mechanisms (Hemra & Aungkavattana, 2014).

Usually, mullite zirconia composites can be obtained by various methods such as direct powder compact of mullite and zirconia, reaction sintering of alumina, silica and zirconia; reaction sintering of alumina, kaolinite and zircon (Bei-yue, Ying, Shao-gang, & Yu-chun, 2010; Bradecki & Jonas, 2010; Colm, 1983; Conville, Lee, & Sharp, 1998). In addition; mullite zirconia composites have been fabricated by various methods such as spark plasma sintering (Khmelev, 2014), laser floating zone directional solidification method (Carvalho, Oliveira, Silva, & Costa, 2014), sol–gel (Wei, Kao, & Lo, 1996) and reaction sintering (Ebadzadeh & Ghasemi, 2000). Among these methods, reaction sintering has been proved to be an inexpensive and simple method to obtain mullite zirconia composites with enhanced mechanical properties.

Distinctive approach of this study can be summarized in two aspects:

(1) While in similar studies in the literature the starting raw materials are zircon and alumina, this study not only dwells on zircon and alumina, but also studies the effects of kaolinite as well.

(2) In literature, there is no mullite zirconia composite synthesis by using boron additives to our knowledge. Accordingly, boron containing additive is used in mullite zirconia composite synthesis for the first time.

The main objective of the present work is to obtain a dense CMC comprised of mullite as the continuous matrix, from inexpensive starting raw materials. As mentioned earlier, complete formation of mullite during the reaction sintering of zircon-alumina mixtures takes place at temperatures higher than 1,600°C, which can be a struggle in the industry. Therefore, another goal of the study is to make a contribution to scientific literature concerning studies on sintering of mullite zirconia composites at lower temperatures by taking advantage of colemanite ($Ca_2B_6O_{11}5H_2O$).

2. Materials and methods

Zircon ($ZrSiO_4$, Johnsen Matthey, Sereltas, Istanbul), kaolinite ($Al_2Si_2O_5(OH)_4$, Kutahya Porselen, Kutahya), alumina (Al_2O_3, BDH Limited Poole, Germany) and colemanite ($Ca_2B_6O_{11}5H_2O$, Eti Mining

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Table 1. Chemical composition of starting raw materials (wt.%)				
Constituent	**Zircon**	**Kaolinite**	**Alumina**	**Colemanite**
SiO_2	29.96	53.01	0.02	5.54
ZrO_2	64.08	–	–	–
Al_2O_3	0.02	32.56	95.86	0.10
CaO	0.11	0.12	0.49	28.96
B_2O_3	–	–	–	35.69
MgO	0.03	0.04	0.02	1.80
Fe_2O_3	0.07	1.16	0.04	0.05
K_2O	0.04	0.13	0.01	0.02
Na_2O	0.11	0.09	0.04	0.05
TiO_2	0.22	0.30	0.01	–
MnO	–	–	–	0.01
SrO	0.07	–	–	0.85
HfO_2	1.10	–	–	–
P_2O_5	1.15	–	–	–
Loss of temperature	1.18	12.57	2.90	24.77

Company, Turkey) were used as starting materials. The chemical composition of raw materials used in this study was analysed by X-ray fluorescence and shown in Table 1. Two different mixtures were prepared. The weight % amounts of raw materials in ZM (additive-free mixture) and ZMC (mixture containing colemanite) compositions are given in Table 2. The mixtures were ball milled for 6 h using zirconia balls as grinding media in ethyl alcohol as a medium. After drying, the mixtures were uniaxial pressed into cylindrical pellets (20 mm diameter) applying 2 tons of pressure for density and microstructure analyses; and rectangular rods with the size of 7.5 mm × 5 mm × 55 mm were prepared for flexural strength and elastic modulus measurements. The pressed specimens were sintered 1,450, 1,500 and 1,550°C for 5 h at a heating rate of 5°C min^{-1}. Density of sintered composites was determined by the Archimedes' method. The crystalline phase formed was investigated by X-ray diffraction (XRD, Rigaku, MiniFlex) at 10–40° and a scanning speed of 2° (2θ) per minute. To understand the sintering behaviour of composites, thermo-differential analysis was performed in 25–1,500°C temperature range. Differential thermal analysis (DTA) was carried out with a 10°C min^{-1} heating rate in air (Netzsch STA 449 F3 Jupiter TG-DTA-DSC device).

The flexural strength (σ, MPa) and elastic modulus (E, GPa) of composites were measured by using Instron 5581 device. In the tests, 2 kN load cell that moved at a rate of 0.5 mm min^{-1} was used. Microstructure analysis was carried out with Scanned Electron Microscope (SEM, Jeol JSM 50-CF).

Table 2. Mixtures (wt.%)		
	ZM	**ZMC**
Zircon	30	40
Kaolinite	25	10
Alumina	45	43
Colemanite	–	7

Table 3. Density of mullite zirconia composites as function of colemanite content and sintering temperature

| Temperature (°C)	Density of ZM (g cm⁻³)	Density of ZMC (g cm⁻³)
1,450	2.17	3.13
1,500	2.26	3.26
1,550	3.11	3.39

3. Results and discussion

3.1. Crystalline phases and densities

The bulk density of mullite zirconia composites sintered at 1,450–1,550°C temperature range for 2 h were estimated as a function of colemanite content and sintering temperature, as shown in Table 3. Difference in compositions showed a tremendous effect on bulk density, which increased with the sintering temperature. The presence of colemanite promoted the densification significantly. The maximum density was obtained when the sintering temperature was increased up to 1,550°C. The maximum density is 3.39 g cm⁻³ for ZMC. For the ZM specimens, the results showed that the density increases when the sintering temperature is increased. High-density values in the mixtures containing colemanite result from temporary liquid phase formations occurred during sintering.

Diffractograms of as sintered composites were shown in Figures 1 and 2 presenting at 10–40° of 2θ. Mullite as the main phase, t-ZrO$_2$ and m-ZrO$_2$ phase of zirconia and some corundum and zircon phases were detected.

Zircon, corundum, m-ZrO$_2$ and mullite phases observed in XRD patterns belonging to ZM mixture sintered at 1,450°C showed that zircon was partially decomposed and alumina played a significant role in mullite formation. At temperatures of 1,500 and 1,550°C, corundum phase disappeared, yet zircon remained partially unreacted.

However, no phases were observed other than mullite and zirconia in any of the XRD patterns of ZMC mixtures sintered at 1,450, 1,500 and 1,550°C (Figure 2). Figure 2 indicates further evidence in case of introducing colemanite dissociation of zircon and formation of mullite and zirconia. Moreover, employing colemanite in the mixtures favours the reaction between alumina, zircon and kaolinite

Figure 1. XRD paterns for additive-free mixture (ZM) sintered at a temperature of 1,450, 1,500 and 1,550°C.

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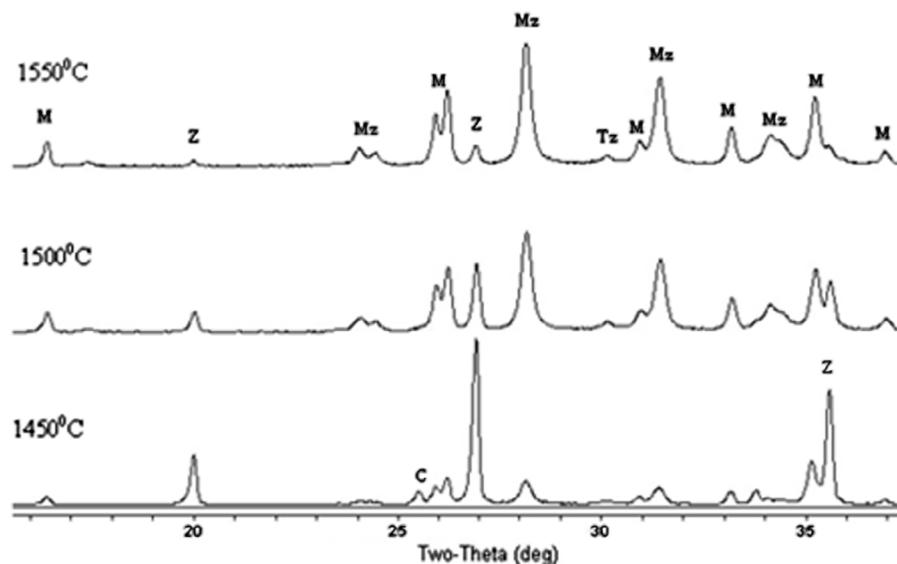
Figure 2. XRD paterns for mixture containing colemanite (ZMC) sintered at a temperature of 1,450, 1,500 and 1,550°C.
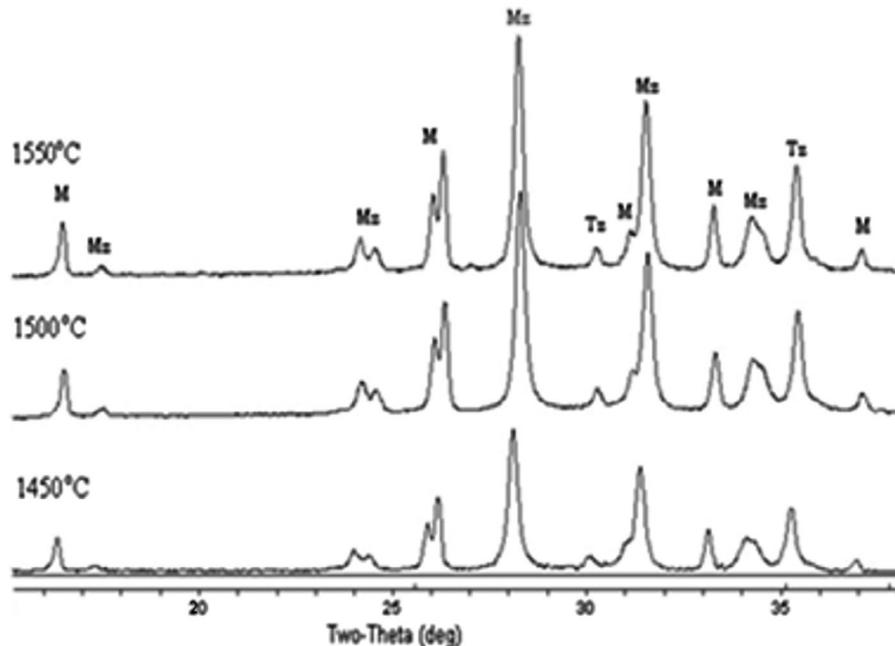
(Figure 2) correspondingly altering the temperatures where disssocation of zircon and formation of ZrO_2 take place, towards a lower range.

Zirconia is an allotropic ceramic which has different crystal structures at different temperature ranges and undergoes the following allotropic transformations (Ewais, 2007):

$$\text{Monoclinic} \xrightarrow{1170°C} \text{Tetragonal} \xrightarrow{2370°C} \text{Cubic}$$

The monoclinic zirconia is stable at room temperature. However, in the XRD pattern of mixtures sintered for different temperatures, monoclinic and tetragonal peaks were observed together. The zirconia produced by reaction is initially in the tetragonal form, which is expected to transform to monoclinic zirconia upon cooling. It has been reported that presence of silica significantly impedes the conversion of tetragonal zirconia to monoclinic zirconia (Zhao, Huang, Wang, Huang, & Guo, 2003).

3.2. DTA analysis

DTA curves of the samples with codes ZM and ZMC are given, respectively, in Figures 3 and 4. In comparison to DTA curves, it is observed that the mixtures have different endothermic and exothermic reactions and similar reactions take place at different temperatures. In ZM mixture, endothermic peaks, which arise at temperatures between 180 and 558°C, have resulted from vapourization in H_2O and OH groups in kaolinite. This reaction, which usually occurs around 540°C when low heating rates applied (Garrido, Aglietti, Martorello, Camerucci, & Cavalieri, 2006; Tokgöz, 2008; Wachtman, Cannon, & Matthewson, 2009), is observed at 558°C, believed to be emanating from various factors such as high heating rate, impurity content, and grain size. Common endothermic reactions are triggered by the presence of kaolinite, which is the common ingredient in both compositions. Along with this, there are also physical water losses of kaolinite in the ZMC mixture at temperatures up to 650°C. An exothermic peak in pure kaolinite minerals at temperatures around <1,000°C (generally around 980°C) was observed at a temperature of 1,008°C in the ZM mixture (Figure 4). Such a peak is believed to exist due to decomposition of metakaolin to crystal $Si_3Al_4O_{12}$ (or γ-Al_2O_3) and to amorphous SiO_2 phases (Garrido et al., 2006; Tokgöz, 2008; Wachtman et al., 2009).

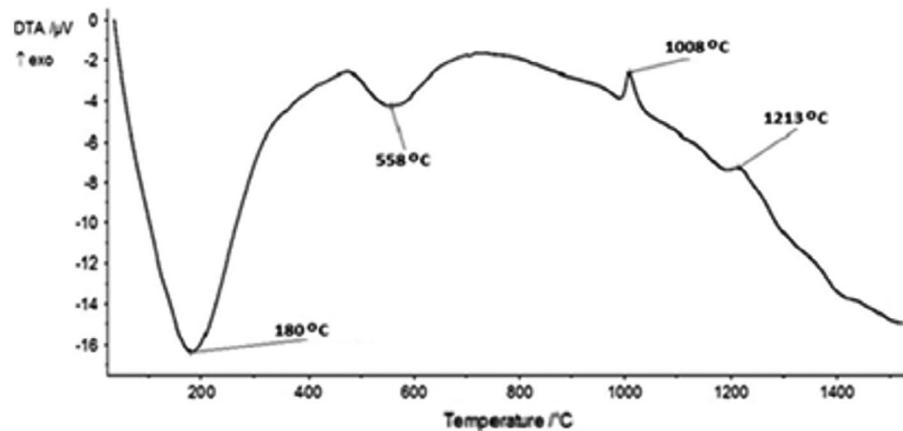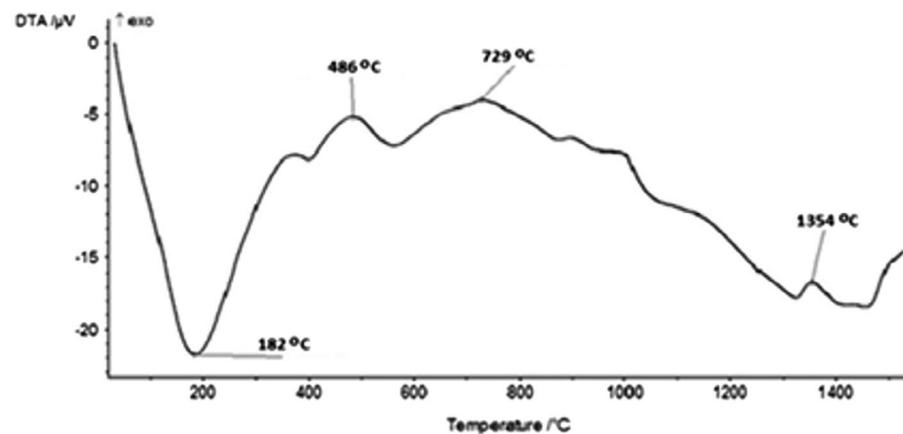**Figure 3. TG/DTA curve of additive-free mixture (ZM).**

Figure 4. TG/DTA curve of mixture containing colemanite (ZMC).

In the DTA curve of the ZMC mixture, before the exothermic peak at 729°C, there is a very small shaped and marked endothermic region observed in temperatures of 700°C (650–720°C). This peak is probably related to the decomposition of anhydrous colemanite to amorphous CaO and amorphous B_2O_3 (Figure 4).

$$Ca_2B_6O_{11} \xrightarrow{\leq 700°C} 2CaO\ (amorphous) + 3B_2O_3\ (amorphous)$$

$$2CaO\ (amorphous) + 3B_2O_3\ (amorphous) \xrightarrow{\leq 729°C} CaOB_2O_3 + CaO_2B_2O_3$$

Taking the DTA curves into account, a liquid phase seems to exist up to 1,000°C for ZMC compositions. This liquid phase results in an exothermic peak at 1,008°C in the ZM mixture to lower temperatures. In the DTA curve, since a strong peak and an observable temperature in the ZM mixture is not observed, this is thought to be caused by the conflict of endothermic (melting) and crystal formation temperatures. This case causes this temperature region to be seen as a wide and misshaped curve in the DTA plot.

The exothermic peak at 1,213°C observed in DTA curves of ZM mixture is related to (primary) mullite formation as a result of a reaction between $Si_3Al_4O_{12}$ (or γ-Al_2O_3) phases and amorphous silica. In ZMC mixture unlike ZM mixture exothermic reaction has occurred at 1,354°C. This reaction is related to mullite formation as a result of reaction with silica components from decomposed zircon and aluminium oxide in the composition.

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3.3. Microstructures

The SEM micrographs addressing to ZM and ZMC samples (Figures 5 and 6, respectively). Composites prepared from ZM and ZMC mixtures showed similar microstructure evolution with temperature. All specimens present large pores and high porosity at lower sintering temperatures and appeared to be dense microstructures with increasing sintering temperature. Mullite is observed to be constituting the matrix phase, while zirconia is equiaxed and dispersed between mullite grains (intergranular grain).

In ZM mixture a highly porous microstructure with homogeneously distributed small pores was observed at 1,450°C (Figure 5(a)). Sintering at 1,500°C tremendously changed the microstructure (Figure 5(b)).

Intergranular ZrO_2 grains also appeared as agglomerates with pores located between them. Previous studies using special XRD techniques, revealed that intragranular particles are tetragonal ZrO_2, whereas the intergranular ZrO_2 is mainly monoclinic (Garrido et al., 2006). In ZM composites sintered at 1,550°C, the growth of intergranular ZrO_2 grains mainly located around the pores (Figure 5(c)) was significant.

SEM studies indicate that colemanite additive promotes the grain growth of ZrO_2 at 1,500–1,550°C (Figure 6(b) and (c)). This result can be correlated to the generation of transitory liquid phase, by higher sintering temperature that favours the grain growth. At 1,550°C, the microstructure showed a dense mullite matrix where it is possible to notice the development of grain boundaries. Mullite grains were well developed in the dense matrix and some of them showed a change from rounded to slightly elongated shape (Figure 6(c)).

3.4. Mechanical characterization

Elastic modulus (*E*, GPa) and flexural strength (σ, MPa) values of compositions sintered at 1,450, 1,500 and 1,550°C are given together in Figure 7. The average and standard errors of RT flexural strength correspond to at least five tests for each growth rate. The decrease in viscosity of the glassy grain-boundary phase plays an important role in the high temperature mechanical properties

Figure 5. Microstructure of ZM mixture sintered at a temperature of 1,450°C (a), 1,500°C (b) and 1,550°C (c).
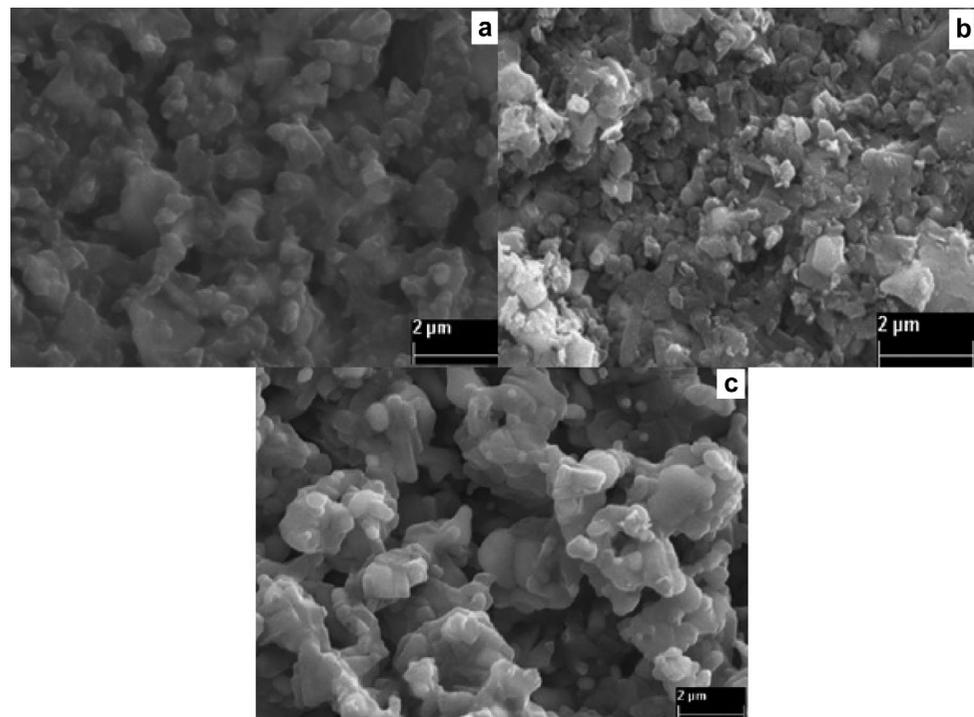
Figure 6. Microstructure of ZMC mixture sintered at a temperature of 1,450°C (a), 1,500°C (b) and 1,550°C (c).
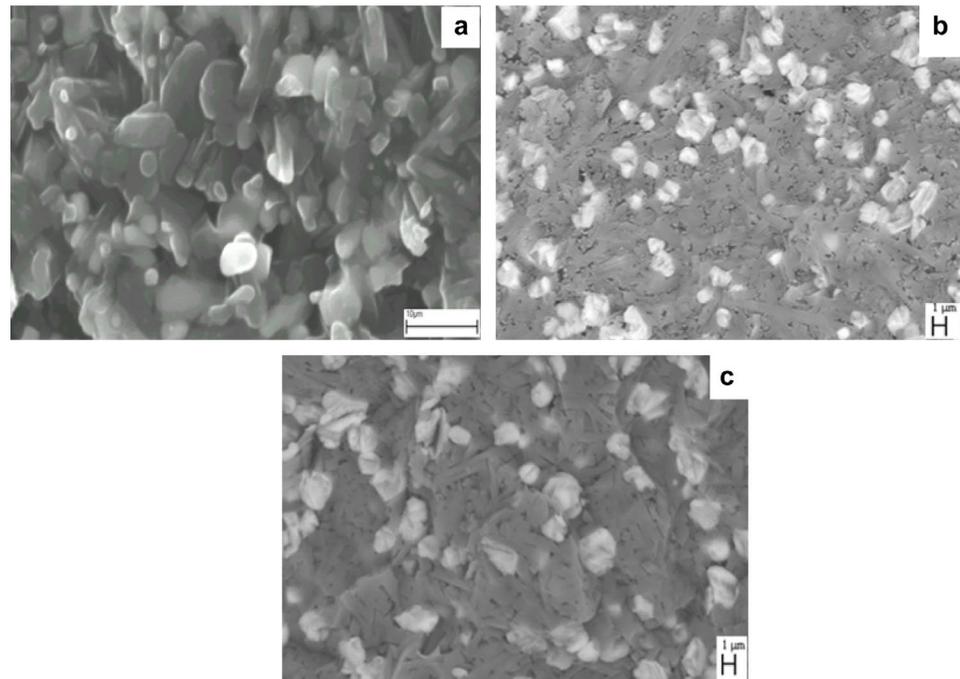
(Carvalho et al., 2014). According to Figure 7, flexural strength and elastic modulus increase along with the higher sintering temperatures. The maximum flexural strength was 293 MPa for ZMC sintered at 1,550°C. Smilarly, the maximum elastic modulus was 142 GPa for ZMC sintered at 1,550°C.

Considering flexural strength and elastic module values, it is possible to say that colemanite is an effective additive for zirconia–mullite ceramics synthesized with traditional zircon, kaolinite and/or alumina mixture powders. As a result of 3-point bending tests, it may be inferred that flexural strength and elastic module values hit their maximum for ZM compositions sintered at 1,550°C while this pinnacle is observed for the ZM specimens sintering temperature is 1,400°C.

Mechanical properties of the materials obtained are compared with the data reported in literature for dense mullite zirconia materials obtained by different processing routes. From this it can be clearly observed that the results obtained by this processing route are comparable. And the properties are sometimes better than the ones obtained by traditional routes like slip casting (Prusty, Mishra, Mohapatra, & Singh, 2012; Rendtorff et al., 2016), uniaxial pressing and pressure-less sintering (Das & Banerjee, 2000; Garrido et al., 2006), SPS sintering of high energy powders milled drily 1,300°C (Rendtorff, Suarez, Sakka, & Aglietti, 2014). The advantage of the mechanic activation is also observed (Ashrafi et al., 2015).

Figure 7. Elastic modulus (*E*) and flexural strength (*σ*) of compositions sintered at 1,450, 1,500 and 1,550°C.

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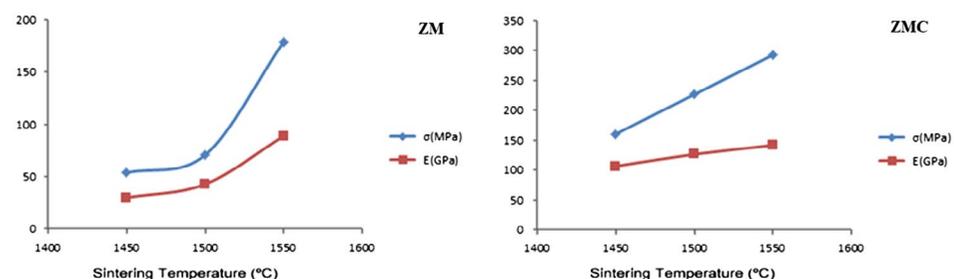
4. Conclusions

The present experimental results indicate that the addition of colemanite to mullite zirconia composites prepared from alumina, zircon and kaolinite mixture leads to a change in sintering reaction, densification and phase evolution.

Sintering of polycrystalline composites are governed by diffusion, a thermally activated process that can place in different paths in the solid, where various mechanisms play significant role: lattice, grain boundary and surface diffusion. The density is also influenced by phase transformation of monoclinic to tetragonal zirconia above 1,170°C during heating. The density results present that the elimination of pores, simultaneous grain growth with grain boundary diffusion and lattice diffusion are the predominant mechanism in the densifications of material at high temperatures (Moazzam Hossen, Chowdhury, Gafur, Abdul Hakim, & Nasrin, 2014). The density of the composites varied between 2.17 and 3.39 g cm^{-3}. The microstructure of all composites is composed of irregularly shaped mullite grains, and round-shaped zirconia grains which are distributed homogenously.

Colemanite addition reduces the decomposition temperature of zircon thereby enables mullite zirconia composite synthesis at much lower temperatures, compared to the batches without colemanite (ZM). The zircon phase is not detected in the mixture of ZMC sintered below 1,500°C, while the mixture of ZM zircon peaks appear at high sintering temperature (e.g. 1,550°C).

The t-ZrO$_2$ and m-ZrO$_2$ phases are observed for each mixture. The reason for the dominance of monoclinic zirconia phase in XRD analysis is either due to the large size of the tetragonal zircon particles and/or dissolving of impurities such as CaO, B$_2$O$_3$, Al$_2$O$_3$ in mullite structure rather than the zircon structure. However, the t-ZrO$_2$ phase predominated when sintered at 1,500–1,550°C, which caused the mechanical strength to drastically increase with respect to increasing sintering temperature, especially for ZMC mixture sintered at 1,550°C. The maximum mechanical strength was 293 MPa and the maximum elastic modulus was 142 GPa.

The Ca, B and colemanite containing some impurities have had an effect of reducing the temperatures of the decomposition of zircon and to increase the reaction capability of the amorphous silicate phase (dissolving strength). Impurities not only decrease dissociation temperature of zircon but also increase fluidity of the formed amorphous phase (silicate glass). As impurities dissolve in amorphous silicate phase, and alumina decreases dissolving limit in silicate phase; mullite phases include high impurity. As impurities dissolve in mullite and/or zirconia body, at grain boundaries in amorphous/amorphous phase or composite body does not include inclusion phases (undesirable compounds), resistance is not affected negatively.

The DTA curves of mixtures have shown endo and exothermic peaks. The exothermic peak of temperature at 1,213°C observed in DTA curves of ZM mixture is related to (primary) mullite formation as a result of a reaction between Si$_3$Al$_4$O$_{12}$ (or γ-Al$_2$O$_3$) phases and amorphous silica. In ZMC mixture, mullite occurs at a temperature quite lower that 1,354°C. This reaction is related to mullite formation as a result of reaction with silica components from decomposed zircon and aluminium oxide in the composition.

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