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Research paper

# Mullite-zirconia composites prepared from halloysite reaction sintered with boehmite and zirconia

A. Raghdi[a], M. Heraiz[a], F. Sahnoune[a], N. Saheb[b,*]

[a] Physics and Chemistry of Materials Lab, Department of Physics, University Mohamed Boudiaf of M'sila, 28000 M'sila, Algeria
[b] Department of Mechanical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

In this study, Algerian halloysite, a naturally occurring clay mineral, was used as low-cost precursor for the production of mullite-zirconia composites. The halloysite was reaction sintered with boehmite and zirconia in the temperature range 1250–1650 °C for 2 h. Differential thermal analysis (DTA), thermogravimetry (TG), dilatometry, high temperature X-ray diffraction (XRD), and scanning electron microscopy (SEM) complementary techniques were used to characterize the prepared materials. The influence of $ZrO_2$ content on the microstructure, densification, hardness, and coefficient of linear thermal expansion of the composites was investigated. Algerian halloysite was found suitable material for the synthesis of low-cost mullite based composites. All prepared samples exhibited same phase transformations that ended at 1550 °C with the formation of monolithic mullite in halloysite-boehmite mixture and mullite-zirconia composites in halloysite-boehmite-zirconia mixture. The composite materials showed higher values of hardness and coefficient of linear thermal expansion compared with monolithic mullite. The composite containing 10% $ZrO_2$ possessed the highest hardness value of 13.5 GPa. The composite containing 30% $ZrO_2$ possessed the lowest value of linear coefficient of thermal expansion of $7.5725 \times 10^{-6} K^{-1}$ between 200 and 1500 °C.

## 1. Introduction

The occurrence of mullite in nature is so rare because it is the result of reaction between alumino-silicate minerals at high temperatures (Manfredini and Manuskova, 2012). Fortunately, low-cost mullite and mullite based advanced ceramics can be easily produced by simple heat treatment of clay minerals such as kaolinite (Sahnoune et al., 2008a,b) and halloysite (Harabi et al., 2014). Mullite is an attractive advanced ceramic material for structural and functional applications because of its excellent thermal, optical, and mechanical properties as well as stability under severe environments (Heraiz et al., 2013). However, the low fracture toughness of mullite limited its wide use in many applications (Rezaie et al., 1999). As a result, a second phase such as zirconia is usually added to mullite to produce composites that have improved properties (Sahnoune et al., 2011). Over the past years, researchers used various starting raw materials and different processing methods to synthesize mullite-zirconia composites (Schneider et al., 1994; Park et al., 2005; Belhouchet et al., 2007, 2009). Because of its low cost, reaction sintering remained the most attractive method for the preparation of mullite containing ceramic matrix composites. In this process, chemical reaction between the starting minerals and/or raw materials as well as densification have been attained in a one-step simple heat treatment (Yangyun and Brook, 1985). This inexpensive method was used to prepare mullite based ceramics (Alves et al., 2016, 2017) as well as mullite-alumina (Heraiz et al., 2013), zirconia-mullite (Chandra et al., 2015), and alumina-mullite (Medeiros et al., 2016) composites.

Alves et al. (2016) synthesized mullite based ceramics by reactive sintering of kaolin clay and kaolin waste mixtures. They reported the formation of mullite and glass phases in kaolin waste processed ceramics sintered at 1550 °C. In another study, Alves et al. (2017) followed a low-cost preparation method to synthesize mullite-based ceramics by reaction sintering kaolin and 25 wt% mica-rich kaolin waste. They reported the formation of mullite containing 1.2 wt% quartz after firing at 1500 °C. Algerian kaolin and boehmite were found suitable raw materials for the synthesis of $Al_2O_3$ containing mullite through reaction sintering (Heraiz et al., 2013). Chandra et al. (2015) prepared dense zirconia-mullite composites by reaction sintering zircon flour and reactive alumina with different proportions of MgO and CaO additives. They concluded that MgO facilitated the formation of mullite and zirconia. In another work, alumina-mullite composites were prepared via reactive sintering of a mixture of kaolinite clay mineral

* Corresponding author.
*E-mail address:* nouari@kfupm.edu.sa (N. Saheb).

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and aluminum hydroxide (Medeiros et al., 2016). The authors demonstrated the possibility of preparing low cost alumina-mullite composites with technological properties compatible with those of ceramics produced by companies with large operations in the international market of refractory products.

Furthermore, many researchers successfully synthesized mullite-zirconia composites via reaction sintering different starting materials. These include zircon and alumina mixtures (Torrecillas et al., 1993), Indian coastal zircon flour and calcined alumina with addition of yttria (Das et al., 1998), alumina, amorphous silica with the addition of stabilized zirconia (Lin, 1999), zircon and alumina derived from the oxidation of Al between 1200 and 1600 °C (Ebadzadeh, 2005), alumina and zircon powders together with acicular aluminum borate templates (Öztürk and Tür, 2007), alumina and zircon (Rendtorff et al., 2008), gibbsite, boehmite, and zircon powders (Belhouchet et al., 2009), zircon-alumina mixture (Ashrafi et al., 2015), and zircon, kaolinite and alumina mixtures with the addition of 7 wt% of colemanite (Aydın and Gören, 2016).

Halloysite "is a low-cost, natural material having many interesting properties that allow for versatile potential uses in a variety of domains e.g. as filler in polymers, carrier for the loading and controlled release of guest molecules, adsorbent for pollution remediation, and for the synthesis of functional materials" (Joussein et al., 2005; Yuan et al., 2015). Treated Algerian halloysite has been used as Pb(II) adsorbents (Kadi et al., 2012) and crystal violet adsorbents (Belkassa et al., 2013; Mahrez et al., 2015) from aqueous phases. In addition, it was found useful in removing copper(II) ions from aqueous solutions (Mellouk et al., 2009) and dyes from wastewaters (Bessaha et al., 2016). Algerian halloysite was also used to fabricate resistant porous membrane by solid-state reaction (Harabi et al., 2014). Traditionally, halloysites had been used as an alternative raw material to kaolinite for the production of ceramics (Churchman et al., 2016). Algerian kaolinite had been successfully used to synthesize mullite through reaction sintering it with high purity alumina (Sahnoune et al., 2008a,b). In addition, mullite-zirconia composites were produced by reaction sintering Algerian kaolin, α-$Al_2O_3$, and stabilized zirconia (3Y-TZP) (Sahnoune et al., 2010); and phase transformations in these composites had been investigated (Sahnoune et al., 2011). The objective of this work was to explore the possibility of using Algerian halloysite to synthesize low-cost millite-zirconia composites. The procedure involves heating pure gibbsite in air to obtain boehmite (Cesteros et al., 1999; Digne et al., 2002), and then reaction sintering Algerian halloysite with boehmite and zirconia to produce millite-zirconia composites. Complementary techniques were used to characterize and analyze phase transformations and sintering behavior. Additionally, the influence of $ZrO_2$ content on the microstructure, densification, hardness, and coefficient of linear thermal expansion of the composites was investigated.

## 2. Materials and methods

### 2.1. Starting materials

Algerian holloysite, a natural raw material from Djabal Debagh (Guelma, East Algeria), aluminum hydroxide ($Al(OH)_3$) obtained from VWR International S.A.S., and zirconium dioxide ($ZrO_2$) supplied by Biochem chemopharma, Georgia-USA, were used in this investigation. The gibbsite (aluminum hydroxide) was heat-treated at 400 °C to obtain boehmite (α-aluminum oxyhydroxide, α-AlOOH). Gibbsite and boehmite are the most common aluminum hydroxide and oxyhydroxide minerals in nature (Gitzen, 1970). They play important roles in the preparation of high purity alumina. In this work, boehmite was used as a source of alumina.

### 2.2. Processing of powders

The holloysite, boehmite, and zirconia were mixed to obtain 100/00 (wt%), 90/10, 80/20, 75/25, and 70/30 mullite/$ZrO_2$ composites, and were named HB00Z, HB10Z and HB20Z, HB25Z, and HB30Z, respectively. Each mixture "was charged into zirconia vials (250 ml in volume) together with 15 zirconia balls (10 mm in diameter), and water was added to the mixture at a ratio of 2:1. The ball milling experiments were performed in a high-energy planetary ball mill (Fritsch P6) and were carried out at room temperature at a rotation speed of 250 rev/min. The milled mixture was dried at 150 °C for 24 hours then compacted at a pressure of 75 MPa using a cold uniaxial press to produce cylindrical specimens of 13 mm diameter" (Sahnoune et al., 2008a,b, 2011). The compacted samples were reaction sintered in the temperature range 1250–1650 °C for 2 h.

### 2.3. Characterization and analysis

TG and DTA experiments were carried out using a LABSYS EVO DTA/DSC-TG SETARAM equipment. Dilatometry experiments were performed on unfired mixtures as well as samples sintered at 1600 °C for 2 h, using NETZSCH (Dil 402 C) equipment. TG/DTA and dilatometry experiments were performed from room temperature to 1600 °C using heating rates of 20 and 5 °C/min, respectively. A high-temperature diffractometer MRD, PANalytical (ISM), with CuKα radiation of a wavelength 0.15418 nm was used to characterize the raw powders as well as sintered samples. The bulk density of samples was measured by water immersion method using a KERN densimeter. Morphology of the halloysite powder and the microstructure of sintered samples were characterized using a JEOL scanning electron microscope (SEM) model JSM-7001F. A universal hardness-testing machine (Zwick-Roell, ZHV, Germany) was used to measure the Vickers hardness of the sintered samples. Conditions of a load of 500 g and a dwell time of 10 s were used.

The magnitude of the Vickers hardness was determined according to:

$$H_v = 1.854\frac{P}{d^2}$$

where $P$ is the applied load (in N) and $d$ is the diagonal length (in mm). Values for the reported hardness were the average of 10 readings.

## 3. Results and discussion

### 3.1. Characterization of raw materials

Typical scanning electron micrographs and particle size distribution of the halloysite powder are presented in Fig. 1. The majority of particles have platy or irregular shapes, Fig 1(a) and (b), respectively. The powder has a wide particle size distribution, Fig. 1(c), and the majority of particles have sizes around 10 and 50 μm. Although the most common reported morphology of halloysite was the elongated tubule and short tubular (Tan et al., 2016), spheroidal and platy particle shapes have all been widely reported (Joussein et al., 2005). The chemical composition of halloysite, $Al_2Si_2O_5(OH)_4$-$2H_2O$, as determined by X-ray fluorescence (XRF) is presented in Table 1. The halloysite contains approximately 44 and 38 wt% of $SiO_2$ and $Al_2O_3$, respectively. Other oxides are present in the form of impurities exception CaO.

In halloysite, a dioctahedral 1:1 clay mineral, the alumina octahedral sheet is bound to the silica tetrahedral sheet by covalent bonds, forming layers. "In the formation of the halloysite lattice, hydroxyl groups of one layer are bound to $O^{2-}$ ions of another layer by hydrogen bonds" (Kadi et al., 2012). Halloysite, a polymorph of kaolinite, has similar chemical constitution and crystal structure to kaolinite (Tan et al., 2015). The structural formula of halloysite is $Al_2(OH)_4Si_2O_5{\cdot}nH_2O$, where the value of n is equal to two for hydrated halloysite and zero for dehydrated halloysite (Joussein et al., 2005; Yuan et al., 2015). XRD spectra of raw halloysite and samples treated at