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Preparation and Phase Transformation of Mullite-Zirconia from Boehmite and Algerian Halloysite

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In this work, mullite-zirconia composite were fabricated by reaction sintering of Algerian halloysite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, boehmite $\text{Al}(\text{OOH})$, and zirconia (ZrO_2) powder using conventional heating. The appropriate amount of the three raw powders was ball milled for 5 h and sintered between 1250 and 1650 °C for 2 h. A scanning electron microscope was used to characterize the microstructure of sintered samples. A dilatometer and X-ray diffractometer were used to analyze the formation and transformation of phases. It is found that for the addition of zirconia up to 20wt.% the zirconia phase retains its tetragonal structure. The formation of primary mullite in all samples was complete at 1220 °C. The cristobalite started to form at 1350 °C, and disappeared at 1500 °C in the samples of mullite, and at 1450 °C when ZrO_2 was added. The zircon compound ZrSiO_4 started to form at 1350 °C and completely disappeared at 1550 °C. The increase in ZrO_2 ratio promoted the formation of grains with a spherical shape.

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1. Introduction

Mullite is one of the basal ceramic materials traditionally used for refractories and is attractive because of its high melting point, thermal expansion coefficient and low thermal conductivity [1, 2], and excellent electrical insulating capability [3]. However, mullite ceramics exhibit both low strength and fracture toughness at room temperature. It is, therefore, necessary to use reinforced mullite ceramics with particles or fibers to produce composites with superior properties [1]. Many methods have been used to prepare mullite such as sintering, sol-gel [4], and coprecipitation. However, the high cost associated with these methods made it unattractive for commercial applications. Synthesis of mullite from clay [5] remains an economical way to prepare mullite with desired properties [6]. It is also well known that the reactivity of halloysite clay changes as it undergoes these thermal transitions. The rate of mullite formation depends on the temperature of the reaction. Mullite- ZrO_2 composites have been prepared through many processes [7] including sintering of mixed mullite and ZrO_2 powders, reaction sintering of zircon and alumina is a well-established method for producing mullite-zirconia ceramics. The zircon dissociates at high temperature and the ZrO_2 and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ form.

The addition of ZrO_2 promotes densification and retards grain growth of mullite phase in mullite-zirconia composites [8]. In this work, we synthesized mullite-zirconia composite through reaction sintering of Algerian halloysite, boehmite, and ZrO_2 and investigated the phase transformation of the composite.

2. Material and experimental procedure

Algerian raw halloysite (from Djabal Debagh), boehmite, and zirconia were used in this investigation. The powder mixtures were prepared to obtain 80/20mullite/ ZrO_2 composites, and this is named HB20Z. In order to prepare a homogeneous mixture of halloysite, boehmite and zirconia, the ball milling technique was used [9]. This technique was used to develop many advanced materials including compounds as oxide-dispersion-strengthened compounds of composites and nanocomposites. The mixture of the raw powders was charged into cylindrical zirconia vials together with 15 zirconia balls. The water was added to the mixture at a ratio of 2:1. The experiments were performed in a high-energy planetary ball mill (Fritsch P6) and were carried out at room temperature with a rotation speed of 250 rpm. Finally, the milled mixture was dried at 150 °C for 24 h, then compacted at 75 MPa by using the uniaxial press. The present phases and their transformations were characterized by a high resolution diffractometer MRD, PANalytical (ISM), of a wavelength equal to 1.5418 Å. The scanning electron microscope (SEM) was used to characterize the microstructure of sintered samples. Dilatometry experiments performed on samples were heated from room temperature up to 1600 °C, at heating rates of 5 °C/min by using NETZSCH (Dil 402C) equipment.

3. Results and discussion

Figure 1 shows linear shrinkage of halloysite-boehmite-zirconia (sample HB20Z) mixture heated at a rate of 0.5 °C/min. This shrinkage curve shows reactions that could take place during heating and are discussed below. Relative expansion at a temperature inferior that 150 °C is due to the evaporation of adsorbed water, and the rate of evaporation is maximal at around

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90 °C. A relative shrinkage starts at 467 °C and ends at 636 °C, where the rate of shrinkage is maximal at 567 °C. This shrinkage is due to the dehydration of the halloysite which transforms to metahalloysite. A third relative shrinkage is a result of the transformation of metahalloysite to spinel (Al-Si), where the rate of shrinkage is maximal at 980 °C [10], and also the transformation of spinel phase (Al-Si) to silica in the form of cristobalite and primary mullite at 1239 °C and this reaction ends at a temperature lower than 1400 °C. A relative shrinkage starts at 1354 °C and ends at 1460 °C, where the rate of shrinkage is maximal at 1412 °C. The shrinkage is due to the formation of $ZrSiO_4$ from ZrO_2 and SiO_2 [11]. Finally, the secondary mullite (which results from the reaction of the added Al_2O_3 with SiO_2 remaining from the formation of primary mullite) formed at a temperature above 1501 °C.

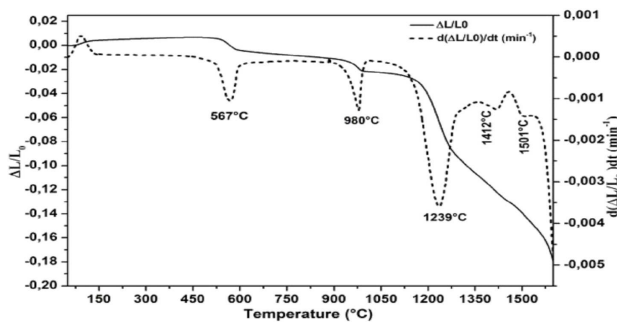


Fig. 1. Dilatometry studies on unfired halloysite-boehmite-zirconia samples.

Figure 2 shows XRD spectra of two samples (HB00Z and HB20Z) sintered at various temperatures between 1250 and 1650 °C for 2 h. It is clear that mullite started to form below 1250 °C (primary mullite that forms from spinel). On the other hand, the cristobalite begins to form from amorphous SiO_2 near 1300 °C and vanishes at 1500 °C in the sample of HB00Z. While for the HB20Z samples, the cristobalite disappeared at 1500 °C. Zircon ($ZrSiO_4$) starts to appear at 1350 °C (sample HB20Z) and dissolves to give ZrO_2 and SiO_2 after 1550 °C [12]. It has been reported that zircon forms from the reaction of zirconia with silica at 1300 and 1400 °C [11]. Also, it is known that pure zircon usually dissociates at higher temperature (over 1675 °C), whereas in the presence of impurities, zircon dissociates at temperature below 1675 °C [13]. Monoclinic ZrO_2 starts below 1250 °C, and ZrO_2 stabilization in the amorphous matrix is lost, giving rise to m- ZrO_2 formation with increase of sintering temperature.

Figure 3 shows the scanning electron microstructure of polished and thermally etched surface of two samples sintered at 1600 °C for 2 h. As expected with the X-ray analysis, the microstructure of two samples shows a mullite-zirconia composite for sample HB20Z and only mullite for sample HB00Z. We note a homogeneous microstructure with a uniformly distributed porosity. All samples

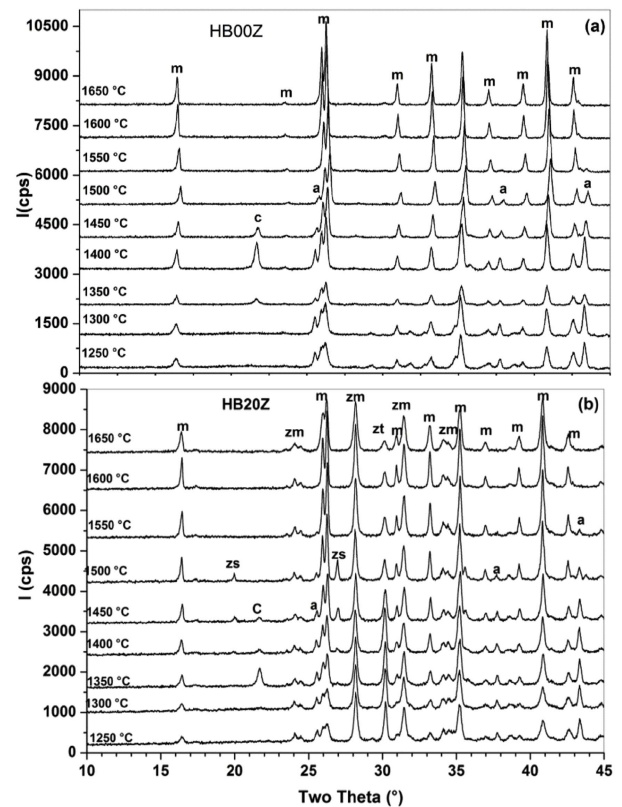


Fig. 2. XRD patterns of (a) HB00Z and (b) HB20Z samples treated at shown temperatures for 2 h: m — mullite; zs — zircon; zm — monoclinic zirconia; zt — tetragonal zirconia; a — α -alumina; c — cristobalite.

are composed of irregularly large shaped mullite grains (Fig. 3a), and round shaped zirconia grains (Fig. 3b) which are distributed both intergranularly and intragranularly. Intergranular zirconia is localized especially in a triple point of the mullite/mullite particles or at the vicinity of the pores. The ZrO_2 formed intergranular, isolated particles.

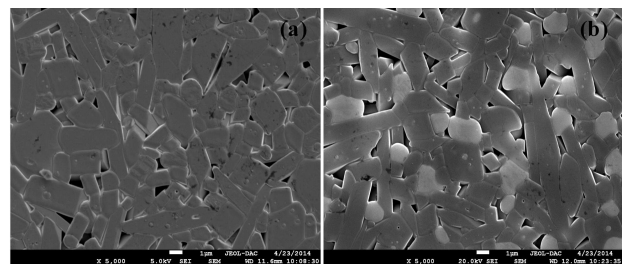


Fig. 3. Micrographs (SEM) of fractured surface of sample sintered at 1600 for 2 h: (a) HB00Z and (b) HB20Z.

4. Conclusion

Algerian halloysite and boehmite were suitable raw materials for the synthesis of mullite- ZrO_2 composites through reaction sintering. Phase transformation and

sintering behavior of the developed composites were investigated. It was found that mullite was the dominant phase present in the sintered samples and also concluded that the zirconia phase retained its tetragonal and monoclinic structure. The formation of primary mullite in all samples was complete at 1350 °C. The cristobalite started to form at 1300 °C, and disappeared at 1500 °C in the samples of mullite, and at 1450 °C when ZrO₂ was added. The zircon compound ZrSiO₄ began to form at 1350 °C and completely disappeared at 1550 °C in the sample of HB20Z. Also, the addition of ZrO₂ promoted densification and retarded grain growth of the mullite phase.

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