PROCESSING OF MULLITE AND MULLITE-BASED CERAMIC COMPOSITES FROM METAL WASTES AND BY-PRODUCTS OF MINING

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Abstract

The present work is part of a wide investigation on processing of mullite and mullite-based ceramic composites from Al metal wastes and waste by-products of mining tin ores with high kaolinite content. The Al wastes were dissolved in acid solution, mixed with aqueous suspension of kaolinite and precipitated the oxy-hydroxide using two alkaline bases. Kaolinite and α-alumina mixtures were also used to compare the results. Porous mullite and mullite-based composites (52-45 vol %) can be obtained by firing some precursors at 1500-1600 ºC for 120-30 min. They have interesting potential applications, such as ceramic substrates, refractories, filters and thermal barriers. The method has implications for the recovery and recycling of Al wastes, besides the application of waste by-products of mining as valuable raw ceramic materials.

Keywords: Processing, Mullite, Ceramics, Composites, Alumina, Wastes, Porosity

INTRODUCTION

Mullite ($3Al_2O_3 \cdot 2SiO_2$ and composition 72 wt% Al_2O_3 and 28 wt% SiO_2) is one of the most commonly found crystalline phases in industrial ceramics [1-7]. This material shows excellent properties: low thermal expansion coefficient, very high-transmittance in the mid-IR range, high-temperature strength, creep resistance, good chemical and thermal stability, with retention of mechanical properties to elevated temperature and stability in oxidative atmospheres. This ceramic material and its composites are important for high-temperature engineering applications as structural advanced materials, besides electronic and optic applications [2-3,6]. Mullite can be found only as scarce mineral phase at the Mull Island (Scotland), the origin of its name [2]. However, it is produced by thermal decomposition of aluminosilicates and hydroxialuminosilicates (for instance, kyanite, kaolinite, pyrophyllite, etc.) [1,4,9], raw clays containing mixtures of these silicates [1,10], and by thermal reaction of SiO_2 (silica) and Al_2O_3 (alumina) mixtures [3,6,11]. In the last case, a very high temperature (1700 ºC) and long periods of heating are required for obtaining dense sintered mullite materials because the high activation energy for Al and Si bulk diffusion in the mullite lattice [1,6]. The preparation of mullite powders have been extensively described in the literature [1-3,6,7,12]. The high-cost of some raw materials and chemicals, besides some limitations (use of organic solvents, inert amospheres, etc.) are not appropriate for a large-scale production. The use of clays containing Si and Al is the most attractive way for mullite preparation at relatively low cost.

Kaolinite ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$) produces mullite by heating, being similar to that of silica-alumina diphasic precursors [1]. However, the mixing level of Al and Si in the structure is not sufficient to prevent the segregation by heating of amorphous silica and a transient alumina or alumina-type spinel (980 ºC). Crystallization of cristobalite and mullite is produced as increasing heating temperature (>1200 ºC). Mullite can be produced at higher temperatures (>1300 ºC) by reaction-sintering of mixtures of kaolinite and alumina in a $3Al_2O_3 \cdot 2SiO_2$ proportion [1-3,5-8,13-15]. An interesting alternative is the use of cheaper and low-cost Al-Si precursors, such as wastes, and new chemical processing routes.

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The present research focus on the processing of mullite and mullite-based ceramic composites from metal wastes and by-products of mining. In previous works [16-18], the basic features of a mullite chemical processing was described. On the other hand, mining of tin ores by gravel pump or by dredging produces a stable mineral suspension containing very fine particles as a waste, the so-called tin tailing slurry [19]. The very fine clay particles in the slurry sometimes settle to a compact sediment and water can be recycled. In a precedent paper [20], it was demonstrated that this kind of solid wastes shows a high content of kaolinite. In the present paper, it is also examined the use of this kind of by-products or wastes as a raw material for the fabrication of mullite ceramics.

EXPERIMENTAL

Waste washing solid by-products of mining granitic tin-bearing alluvial sands containing cassiterite (SnO_2) with minor valuable mineral components (ilmenite, tantalite and others), were used [20]. The kaolinite content was high, 60 wt %, with 15 wt % potassium mica (illite), < 10 wt % potassium feldspar (microcline), < 15 wt % quartz and the presence of amorphous iron oxides. The main components were (in wt %) 48.30 SiO_2 and 32.00 Al_2O_3, 5.13 Fe_2O_3, 2.43 K_2O, and 10.30 wt % weight loss by heating at 1000 ºC. This sample, sample W, shows a particle size < 2 µm, 74.75 wt % with < 1.12 µm, 30.45 wt %. Commercial kaolin powder, sample A (Poveda, Guadalajara, Spain), with kaolinite content > 90 wt% and quartz (*ca.* 10 wt %) was also used as raw material. This sample shows a particle size < 2 µm, 45.4 wt %. The main components were (in wt %) 47.98 SiO_2 and 38.10 Al_2O_3 and 12.26 wt % weight loss by heating at 1000 ºC.

Several aluminium alloys used in the manufacture of can beverages, foils and aeronautics were examined as raw materials. For the present study, waste shavings of 2024 alloy (92 wt % Al) were selected. These Al shavings were dissolved using an aqueous solution of HCl (35 vol %). After reaction, the resultant cold solution was filtered. It was thoroughly mixed with aqueous suspension of kaolinite in a stoichiometric molar ratio of mullite $3Al_2O_3 2SiO_2$. The aluminium hydroxide was precipitated under controlled conditions [18] from the aluminium in solution using concentrated ammonia (ammonium hydroxide) or hexamethylenediamine (HMDA), a low-cost chemical used in the manufacture of synthetic textile fibres. The washed and wet solid was dried at 110 ºC. The resultant powder is designed mullite precursor KAH. The product obtained using HMDA was gently ground and thermally pretreated at 300 ºC for times longer than 60 min, under nitrogen flow, to eliminate the remaining diamine. The resultant powder is designed mullite precursor KAD. However, sample W was found adverse in this chemical processing route, being associated to the presence of amorphous iron oxide. Addition of aluminium oxide was an alternative for the fabrication of mullite [1,13-15]. A powdered alumina (99 wt % Al_2O_3) with particle size < 63 µm, 66 wt %, was selected. After ball milling [21], this powder shows < 63 µm, 90 wt %. An aqueous suspension in deionized water of kaolin sample W was prepared and pH adjusted by addition of HCl. After vigorous mixing of sample W and ground alumina in a stoichiometric molar ratio of mullite, the wet solid product was dried at 110 ºC. The resultant powder is mullite precursor KWM. To compare all the results, kaolin sample A was also mixed with that alumina powder under the same conditions, resulting the mullite precursor KAM.

Thermal treatments of cylindrical uniaxial cold-pressed samples at 500 MPa were performed in air using a furnace at 10 ºC/min, from 1200-1600 ºC. Thermal analysis were performed in air, at a heating rate of 10 ºC/min, using a Setaram equipment, Model 92. X-Ray powder diffraction (XRD) diagrams were obtained with a Siemens D-501 diffractometer. Scanning electron microscopy (SEM) observations in fractured samples were carried out using a JEOL JSM-5400 microscope. Bulk density (BD) and apparent porosity (AP) were measured in sintered samples by Archimedes' method using deionized water. Intrusion porosimetry was performed using a Fisons 4000 equipment.

RESULTS AND DISCUSSION

In the case of KAH and KAD kaolinite and quartz were observed by XRD as crystalline phases besides an amorphous phase. It is assumed that the Al oxy-hydroxides produced in the precipitation and drying are the main components of this amorphous phase. Additional results by short-range techniques [16] confirmed this assumption. In contrast,

powdered KWM and KAM samples showed α-alumina, kaolinite and quartz. The particles were found mixed uniformly, as observed by SEM, in the case of KWM and KAM. Differences were observed by SEM in KAH sample, with formation of globular gelified structures around kaolinite particles. Finally, a fibrous morphology was observed by SEM in KAD sample, being associated to the effect of the diamine in the chemical precipitation process as described above.

The sharp exothermic Differential Thermal Analysis (DTA) peaks from metakaolinite thermal decomposition were observed at 995 and 994 °C in KAD and KAH samples, respectively. This peak appeared as low as 952 °C in KWM sample. This result can be attributed to a particle size effect, with differences in kaolin samples A and W, and presence of impurities [1]. The observation of this exothermic DTA peak at 980 °C has been attributed to the formation of either mullite nuclei or a transient alumina-type spinel (γ- Al_2O_3 solid solution) or both, because at DTA heating rates both mullite and spinel have the possibility of forming concurrently [1,6,9,21-23]. The formation of such an exothermic peak is most likely due to a release of energy, associated with the Al ion transformation to a more stable sixfold coordination, facilitating the formation of mullite with amorphous silica segregation [22,23]. The formation of primary mullite from metakaolinite thermal decomposition, was observed by XRD after heating the four prepared samples at 1300 °C. Further heating produced mullite by reaction. Mullite, quartz and unreacted α-alumina are observed in all the samples at 1500 °C for 120 min. Cristobalite, from amorphous silica crystallization is only observed in sample KAM.

Further heating produced the disappearance of quartz (impurity in samples A and W) and cristobalite, a decrease of α-alumina by reaction and an increase of secondary mullite formation, as deduced from XRD peak intensities. In samples KWM and KAD sintered at 1600 °C for 30 min, single-phase mullite was obtained. A mixture of mullite and unreacted α-alumina were observed in samples KAH and KAM, although in the last one as a residual phase. Its assumed that a similar reaction pathway, as previously observed [1-3,5-7,13,14], accounts for mullite formation using metakaolinite-alumina mixtures by reaction-sintering, such as mullite precursors KWM and KAM, but not

prepared by a chemical method as described in the present study (KAH and KAD). It should be noted that the reaction of formation of a secondary mullite is accelerated by effect of eutectic liquid formation in the silica-alumina binary system at *ca.* 1587 °C [6,11,13,14,24]. This effect seems more relevant in samples KWM (prepared with clay wastes) and KAH (prepared with Al shaving wastes), as deduced by the XRD results.

The evolution of BD and AP as increasing firing temperature follows a tendency to decrease the porosity and increase the bulk density. At 1600 °C for 30 min, KAM and KWM show similar bulk densities values (2.28 and 2.30 g/mL, respectively), but apparent porosity is lower in sample KWM (7.8 vol %). It is associated to the combination of single-phase mullite crystals and the presence of a glassy phase in the sample, which must be in higher proportion in KWM. Sample W contains more impurities than sample A (see Experimental), with presence of illite and microcline. These two phases contain alkaline elements which produce an increase of liquid phase (i.e. glassy phase) by progressive heating. In contrast, samples KAH and KAD at 1600 °C for 30 min show high porosity values: 35.3 vol % and 45.1 vol %, respectively. It could be associated to the chemical processing using two different alkaline bases.

CONCLUSIONS

Mullite and mullite-based ceramic composites have been obtained by reaction-sintering from four precursors after processing using two different waste sources: (a) Al alloy as shavings dissolved in acid solution and (b) waste washing by-products of mining tin ores with high kaolinite content. Mixtures of kaolinite and α-alumina were also used to compare the results. By firing at 1500-1600 °C for, at least, 30 min, the reaction-sintering between α-alumina and metakaolinite in the samples produced mullite and the disappearance of residual phases (quartz and cristobalite). The thermal behavior was affected by the presence of impurities in the kaolinite samples because amounts of liquid phase produce a progressive and enhanced sintering in some mullite precursors. Porous mullite and mullite-based composites, with values of 52-45 vol % can be obtained by firing some precursors at 1500-1600 °C for 120- 30 min.

Taking into account the present results, these mullite-based composites have potential applications as ceramic substrates, refractories, catalytic supports, isolating materials, filters and materials used at high-temperatures as thermal barriers. The method has implications for the recovery and recycling of Al wastes as an alternative of remelting, besides the application of waste by-products of mining as valuable raw ceramic materials for mullite preparation.

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