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Formation at low temperature with low shrinkage of polymer/Al/Al_2O_3 derived mullite

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Abstract

The active filler controlled pyrolysis of polymer has been used to synthesize mullite from Al/Al_2O_3-filled siloxane. This monolith has been compared to mullite synthesized in the same conditions from Al-filled and Al_2O_3-filled siloxanes. Due to the presence of transition alumina and to a finer scale of mixing of the mullite precursors provided from the active Al-filler, the initial mullitization temperature was lowered in the two first systems (1200–1250°C) in comparison to the last one (1400°C). However, the improved microstructure obtained with the Al/Al_2O_3-filled mixture indicates that this system has advantages of low temperature and shrinkage, and low defect mullite, in comparison to mullite obtained from Al-filled and Al_2O_3-filled siloxanes. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Numerous searches have been devoted to the ceramic synthesis, via active filler pyrolysis, of polymer. The filler may react with the product of the pyrolysis, and thus limit the shrinkage [1–7]. The advantages of the method are: possibility of complex shapes, homogeneity improvement and moderate processing temperature due to the high reactivity of amorphous silica (SiO_2) yielded by the polymer. In this work, mullite monoliths are processed, associating the reaction-bonding of Al powders with the pyrolysis of the silica polymer precursor.

2. Experimental

Polydimethylsiloxane (NH2000, Hüls) was used as a silica precursor. Aluminum (A1183, Cerac) and α-Al_2O_3 (CR1-AS1, 500wt-ppm MgO-doped alumina, Baikowski) with particle sizes of 0.8 and 1 μm, respectively, were used as fillers. Suitable polymer/filler ratios, with respect to stoichiometric 3/2 mullite, were determined for the three compositions: polymer/Al/α-Al_2O_3 (62/19/19 vol.%, PAAO), polymer/Al (65/35 vol.%, PA) and polymer/α-Al_2O_3 (59/41 vol.%, PAO). Powder mixtures were processed in propanol-2/acetone (75/25 vol%). The residue was granulated and then uniaxially pressed (15 MPa) to yield samples with porosity of 3–7%. The heat-treatment was performed up to 1550°C (3 h). Differential thermal analysis (DTA), thermogravimetry and dilatometry were used to monitor the associated phase, mass and dimensional changes during the reaction. Products were identified by X-ray diffraction, and characterized by Hg porosimetry. Microstructure was observed both by scanning and transmission electron microscopes.

3. Results and discussion

3.1. Thermoanalytical characterization

The oxidation sequences of the PAO are fully similar to those of the polydimethylsiloxane one. The mass loss is of −5.5% and is only due to the pyrolysis of the

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polymer. Degradation and oxidation of the polymer start at temperature above 200°C and are completed at 800°C.

In the case of the siloxane/Al/Al_2O_3 system, the reaction steps are significantly different (Fig. 1). The mass loss due to the degradation of the polymer is progressively compensated, between 350 and 700°C, by a mass increase due to the oxidation of Al, in solid state, to alumina. After a hold at 700°C for 2 h, the PAAO sample shows another mass gain in the range 700–900°C, due to the oxidation of Al in liquid state. The mixture is fully oxidized at 1400°C after a soaking time at 1100°C (2 h). By DTA, the two exothermic peaks, typical of the degradation/oxidation of the polymer, appear respectively at 280 and 550°C. The oxidation process of Al is evidenced at first by a sharp exothermic peak at 600°C, where oxidation of solid Al particles takes place. After a soaking time at 700°C (2 h), the process accelerates with an oxidation peak at 810°C. The rupture of the oxide scale under the thermal expansion of the melt results in a rapid oxidation of Al in liquid state [8]. The two weak endothermic peaks at 660 and 1410°C correspond effectively to the melting of Al metal and free Si metal respectively. The melting peak of Si is absent in the case of the PAO system and thus the presence of free Si is correlated here to the consumption of the oxygen, from the polymer, by the oxidation of Al.

In the case of the PA system the mixture is fully oxidized only at 1550°C despite a soaking time at 1100°C (10 h).

3.2. Phase development

The phase development of the PAAO mixture on heating is shown in Fig. 2. After 3 h at 1100°C, the present phases are α-Al_2O_3, an amorphous phase (identified by a small diffuse hump at $2\theta = 20°$) and traces of transition alumina (γ, θ and δ). Mullitization begins after 3 h at 1200°C along with the crystallization of cristobalite which is maximum at 1250°C. At 1300°C, due to the consumption of transition alumina with mullite formation, only the stable α-Al_2O_3 phase is still present as a source of alumina. On further heating to 1550°C, the main crystalline phase is mullite.

In comparison, in the case of PA, the oxidation of Al at 1200°C provides transition alumina together with the α-Al_2O_3 phase. The sample begins to mullitize at 1250°C. The subsequent heat treatment, up to 1550°C, yields mullite with no excess alumina. Concerning the PAO system, the phase evolution shows that the crystallization of cristobalite is maximum at 1350°C. At 1400°C three phases coexist: the beginning of mullite formation is evidenced and α-Al_2O_3 and cristobalite are present. At 1550°C the PAO sample consists mainly of mullite and only traces of α-Al_2O_3 are left.

In the PAAO and PA systems, beyond α-Al_2O_3 and the amorphous silica, the mullite precursor mixture includes transition alumina yielded by Al oxidation. Thus, the beginning of mullite formation through the PAAO and PA mixtures was achieved at temperatures as low as 1200–1250°C. In the case of PAO the mullite precursors mixture consists of stable α-Al_2O_3 and amorphous silica yielded by the polymer, thus the mullitization of the mixture starts at 1400°C, a temperature which is characteristic of an inhomogeneous mixture. The difference in mullitization temperature indicates

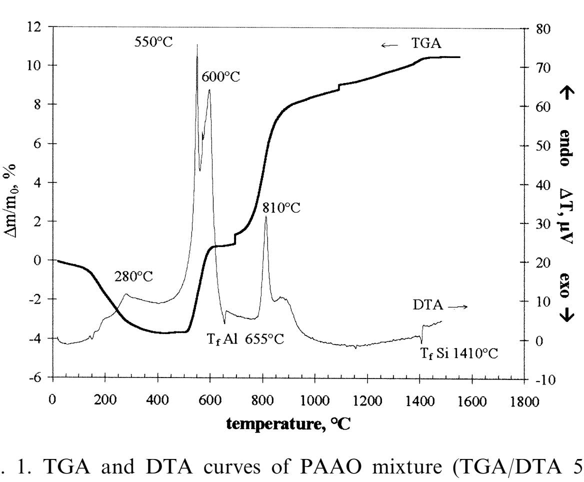

Fig. 1. TGA and DTA curves of PAAO mixture (TGA/DTA 5°C min^{-1}).

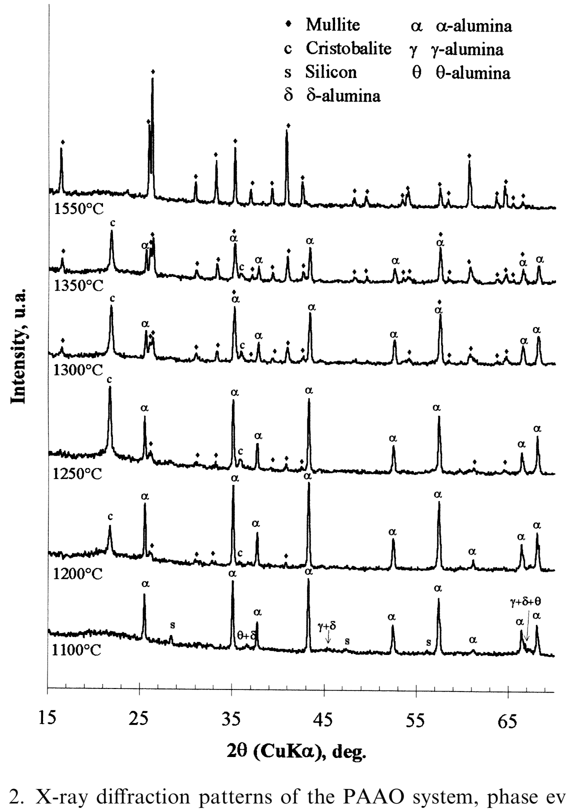

Fig. 2. X-ray diffraction patterns of the PAAO system, phase evolution during heat treatment.

that the scale of mixing of the mullite precursors provided by the PAAO and PA systems was finer than in the PAO one. The lower temperature of mullitization for the PAAO and PA samples, together with the presence of transition alumina at 1100–1200°C, may be indicative of a dual mechanism of mullitization including on one part, the formation of mullite directly from the reaction between transition Al_2O_3 and the glassy silica phase, and on the other part, the crystallization of mullite through the transient individual crystallization of cristobalite and α-Al_2O_3.

3.3. Dilatometry

Dimensional changes are shown in Fig. 3. Up to 400°C, all the mixtures are expanding, followed up to 700°C by a subsequent shrinkage that is caused primarily by the degradation/oxidation of the polymer.

In the case of the ternary mixture PAAO, after the pyrolysis stage, there is no important dimensional change. Only a continuous shrinkage of about 1.5% is observed from 700 to 1300°C. Here, the dilatation associated with the oxidation of Al is not sufficient to compensate the shrinkage due to the sintering of amorphous SiO_2 with Al_2O_3. Finally, the total linear shrinkage, for a final pore volume of 20%, is of 3.6% for the siloxane/Al/Al_2O_3 system.

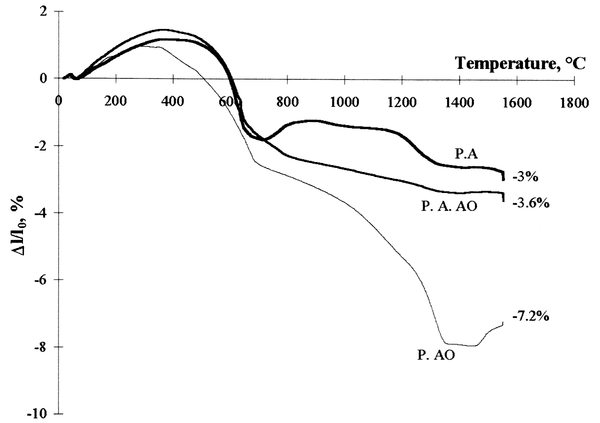

Fig. 3. Relative linear shrinkage of PAAO, PA, PAO compositions during oxidation and sintering under air.

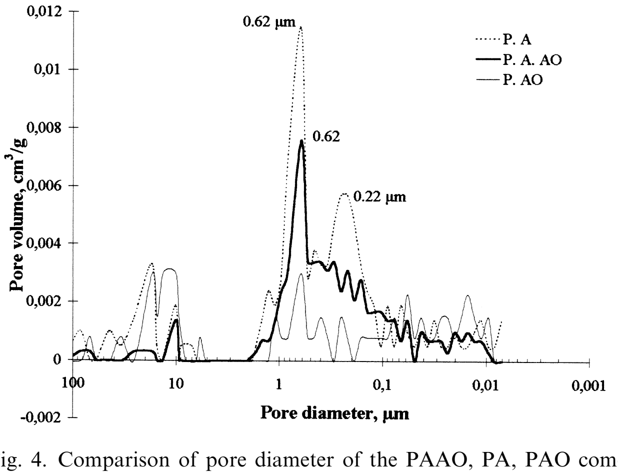

Fig. 4. Comparison of pore diameter of the PAAO, PA, PAO compositions.

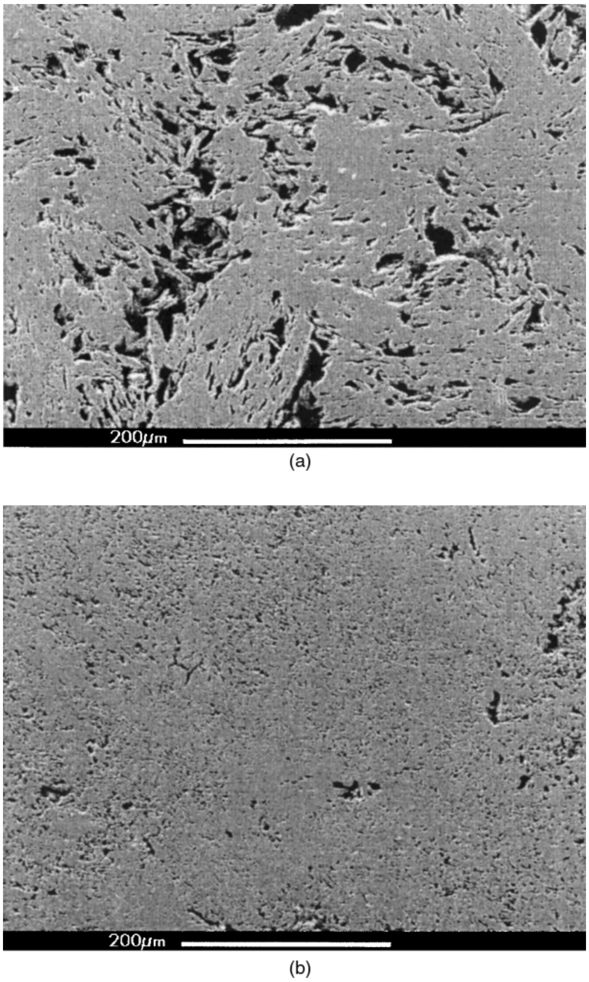

Fig. 5. SEM microstructures of (a) PA and (b) PAAO samples.

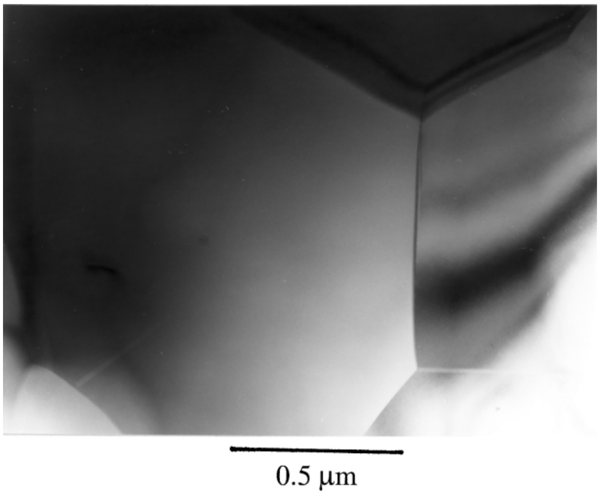

Fig. 6. TEM microstructure of PAAO sample.

Comparatively, the PA mixture presents a transition stage in the range 600–800°C, with a corresponding compensation of the shrinkage associated with pyrolysis of the polymer, by the volume expansion (+28%) due to oxidation of Al. In the temperature range 800–1200°C the weak shrinkage corresponds to the same behavior as that observed in the case of reaction-bonded alumina [8]. The final linear shrinkage, corresponding to a pore volume of about 30%, is of 3% for the PA system. In the case of the PAO system, the final linear shrinkage is of 7.2% for a final pore volume of about 18%.

In all of the materials, most sintering probably takes place by the viscous flow of the amorphous silica phase, a mechanism which has been already proposed for the sintering of mixture of amorphous SiO_2 with α-Al_2O_3 [9–11]. Therefore, densification starts above about 1000°C and occurs prior to mullitization. The crystallization of the amorphous SiO_2 to cristobalite at 1250°C is expected to decrease the sintering rates [12–14]. For the PAAO and PA composites, mullitization proceeds at low temperature, with a consecutive liquid-phase sintering being dominant via the eutectic in the Al_2O_3–SiO_2 system at about 1550°C.

3.4. Microstructure development

Two families of pores are evidenced by Hg porosimetry (Fig. 4): the pore size for the first class is in the range 10–100 μm and for the second in the range 0.01–1 μm. It seems that the amount of the second class of pores increases with the presence of Al in the initial mixture. The improvement obtained with the ternary system is shown on the SEM micrographs, where large pores, such as those present in the PA specimen (Fig. 5a) have been replaced by a fine-distributed pore network in the PAAO one (Fig. 5b). From the defect point of view, the PAAO seems to be a good system as it presents minimum macroporosity. The PAAO derived mullite consisted of equiaxed grains of about 1 μm in size which were primarily dislocation free (Fig. 6) contrary to the PAO system where the mullite grains revealed a high dislocation-density [5,6]. The granular-shaped mullite has been often correlated with the sparse existence of glassy phase in the grain boundaries [15,16]. The occurrence of a glassy thin film (about 1 nm in thickness), along certain grain boundaries was nevertheless confirmed by lattice fringe imaging [17]. Moreover, TEM micrographs show that in all of the materials a few triple-junctions are filled with residual glassy phase materials which is consistent with that expected for mullite materials sintered at a temperature (1550°C) near the eutectic one (1570±20°C) in the SiO_2–Al_2O_3 system [18]. The formation of nearly 3/2 mullite matrix grains was confirmed by EDS. The mullite appears as slightly Si-rich (Al/Si = 2.96). The composition of the glassy phase was 6,5 mol% Al_2O_3, 93 mol% SiO_2 with a very small quantity (about 0.5 mol%) of Na_2O+K_2O+MgO. This is very near the eutectic one (5 mol% of Al_2O_3) in the SiO_2–Al_2O_3 system [18] and is in good accordance with results obtained by Kleebe et al. [19] and Thalcec et al. [20].

4. Conclusion

The active filler controlled pyrolysis of polymer has been followed to synthesize 3/2 mullite from Al/Al_2O_3-filled polydimethylsiloxane (PAAO). This mullite with relatively low linear shrinkage has been compared to 3/2 mullite synthesized in the same conditions from Al-filled and Al_2O_3-filled siloxanes (PA and PAO systems respectively). Due to a finer scale of mixing of the mullite precursors provided from active Al filler, the temperature of mullitization was lowered in the PAAO and PA systems. However, the improved microstructure obtained with the PAAO mixture indicates that this ternary system seems to be the best compromise, for low temperature and shrinkage and low defect 3/2 mullite, between mullite obtained from Al-filled and Al_2O_3-filled siloxanes.

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