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Microstructure and mullitization of aluminosilicate matrix in Nextel 720/aluminosilicate composites prepared by LPCVI at 550°C

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Abstract

Nextel 720/aluminosilicate composites were prepared by low pressure chemical vapor infiltration (LPCVI) at 550 °C using $AlCl_3$–$SiCl_4$–CO_2–H_2 precursor system. The microstructure and mullitization of the aluminosilicate matrix were monitored by SEM, DTA and XRD. The matrix consisted of concentric muti-layers like the annual tree rings and contained some isolated alumina particles and pores. The phase composition of the matrix was composed of an amorphous silica, γ-Al_2O_3, Al–Si spinel, an amorphous monophasic mixture (in which Al^{3+} and Si^{4+} were mixed at the molecular level), and an amorphous diphasic mixture (in which Al^{3+} and Si^{4+} were mixed at a nanometer scale). The mullitization of the matrix included three stages. Complex mullitization process and inhomogeneous microstructure of the matrix suggested that $AlCl_3$ and $SiCl_4$ were not molecularly mixed.

Keywords: Microstructure; Mullitization; Aluminosilicate; LPCVI

1. Introduction

Nextel 720 fibers reinforced mullite matrix composites have been considered as potential candidates for ceramic shingles in combustion chambers of aircraft engines and hot gas particulate filters in advanced coal-based power generation system [1–3]. Because grain growth of Nextel 720 fiber at 1300 °C and above resulted in the decrease of the strength [4], sol–gel, EPD and other methods with low mullitization temperature were selected to prepare Nextel 720/mullite composites [5–9]. The present authors proposed a two-step method to fabricate Nextel 720/mullite composite [10]: the first step was to fabricate Nextel 720/aluminosilicate composites by LPCVI at 550 °C using the $AlCl_3$–$SiCl_4$–CO_2–H_2 precursor system; the second step was to convert the aluminosilicate matrix into mullite matrix by heat-treatment at 1260 °C. Since LPCVI and subsequent heat-treatment were employed to prepare the composites at relatively low temperature so as to avoid the strength degradation of Nextel 720 fiber, it would be a useful piece of work to investigate the microstructure and mullitization of the aluminosilicate matrix.

2. Experimental procedure

3D preform woven from continuous Nextel 720 fibers (3M Corporation) was chosen for this project. Nextel 720/aluminosilicate composites were prepared by LPCVI at 550 °C using the $AlCl_3$–$SiCl_4$–CO_2–H_2 precursor system. The reaction chamber of the horizontal hot wall LPCVI reactor consisted of an alumina tube, with an inside diameter of 5.0 cm and a length of 48 cm, sealed at both ends by a pair of stainless steel flanges with compression O-ring fittings. The temperature and total pressure in the reaction chamber were fixed at 550 °C and 10^4 Pa. The stoichiometry of the input $AlCl_3$ mol/$SiCl_4$ mol ratio was fixed at 3/1. All reactant gases were mixed just before introduction into the hot wall reactor. The $AlCl_3$ evaporator was maintained at

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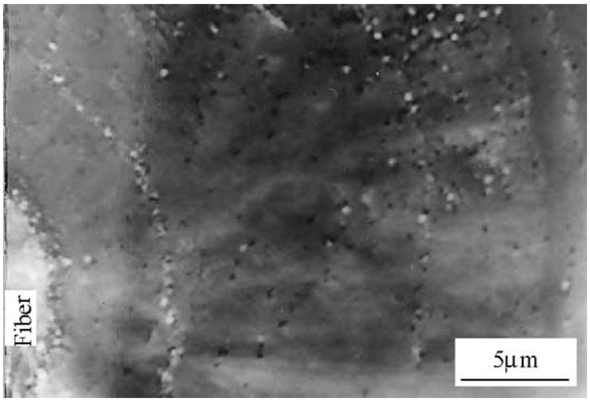

Fig. 1. SEM micrograph of the matrix of the Nextel 720/aluminosilicate composite.

130 °C in an oil bath source tank. The gas lines from the $AlCl_3$ evaporator to the reactor were heated to 200 °C to prevent $AlCl_3$ from condensing. The $SiCl_4$ bubbler was immersed in a refrigerated bath and $SiCl_4$ vapor pressure was controlled by the bath temperature (0–20 °C).

The aluminosilicate powders scraped off the surface of the as-prepared Nextel 720/aluminosilicate composites were heat-treated in air atmosphere at temperatures in the range of 820–1350 °C for 0.5 h. Phase transformation of the aluminosilicate powders was studied using differential thermal analysis (DTA, NETZSCH STA409). Phase identification of all powders was examined by X-ray diffraction (XRD, Rigaku D/MAX-3C). The microstructure of the as-prepared aluminosilicate matrix was observed by scanning electron microscopy (SEM, JEOL JXA-840).

3. Results and discussion

Fig. 1 shows a SEM micrograph of the cross-section of Nextel 720/aluminosilicate composites. Some isolated white particles and pores, at micrometer sized scale (0.1–0.7 μm), are present within the aluminosilicate matrix. Electron probe microanalysis indicates the white particles are alumina. The aluminosilicate matrix appears to consist of concentric muti-layers like the annual rings of a tree around the fiber core. Fig. 2 shows a SEM micrograph of the boundary within the aluminosilicate matrix. It indicates that the boundary actually is an interfacial layer with many 0.2–0.5 μm width pores. Accordingly, the microstructure of the matrix is inhomogeneous. These results allow us to draw the following conclusion: the gas species in LPCVI reaction chamber are not homogeneously mixed. Further investigation shows the mullitization of the inhomogeneous aluminosilicate matrix is complex.

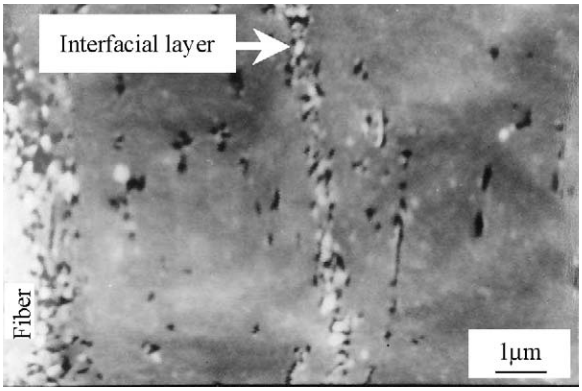

Fig. 2. SEM micrograph of the interfacial layer within the aluminosilicate matrix.

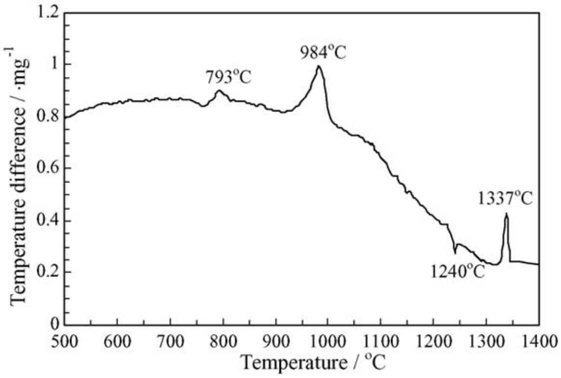

Fig. 3. DTA curve of the powder of the aluminosilicate matrix.

Fig. 3 shows a DTA curve for the aluminosilicate powders. There are two sharp exothermic peaks (i.e. at 984 and 1337 °C), one weak exothermic peak (i.e. at 793 °C) and one weak endothermic peak (i.e. at 1240 °C) in the DTA curve. The aluminosilicate powders were calcined in air atmosphere at temperatures in the range of 820–1350 °C for 0.5 h, that is at temperatures slightly higher than the first and last DTA peaks to determine the phase transformation.

Fig. 4 shows XRD patterns for the as-prepared and heat-treated aluminosilicate powders at different temperatures. EDS results in ref. [10] indicate that the aluminosilicate matrix is composed of 79.6 wt% Al_2O_3 and 20.4 wt% SiO_2. Fig. 4(a) indicates the aluminosilicate matrix is in the form of amorphous phase, γ-Al_2O_3 and an Al–Si spinel. The spinel phase has poorly defined X-ray diffraction pattern, which exhibits broad peaks very similar to those of γ-Al_2O_3. Therefore, it is difficult to distinguish γ-Al_2O_3 from Al–Si spinel (a solid solution between γ-Al_2O_3 and SiO_2) [11]. Despite the intensive investigations the spinel phase is not yet unanimously characterized. The basic disagreement is about the composition of the spinel phase. Owing to spinel-type structure the phase was called Al–Si spinel. Okada and Otsuka [12] and Jin et al. [13] proposed phase composition to be $6Al_2O_3{\cdot}SiO_2$. The amorphous phase was proposed to be amorphous silica and Al–O–Si mixture, which would be sustained by the following discussion.

Some δ-Al_2O_3 and a trace of mullite is present in 820 °C sample, which indicates the 793 °C peak may be attributed to the mullite and δ-Al_2O_3 formation. More mullite is

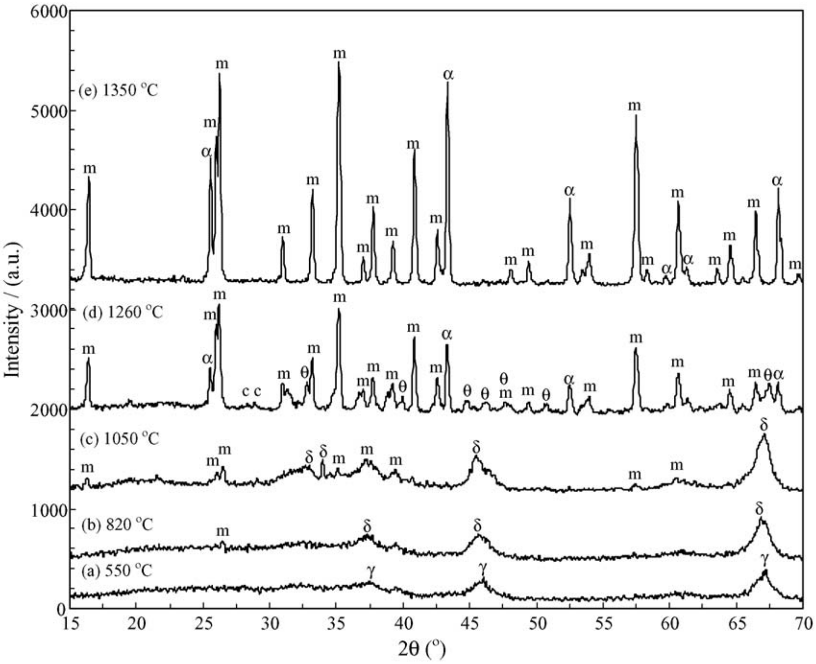

Fig. 4. XRD patterns for the aluminosilicate powders heat-treated at temperatures in the range of 820–1350 °C for 0.5 h (m: $3Al_2O_3{\cdot}2SiO_2$; α: α-Al_2O_3; δ: δ-Al_2O_3; γ: γ-Al_2O_3; θ: θ-Al_2O_3; c: cristobalite).

present in 1050 °C sample, which indicates the 1050 °C peak may be attributed to mullite formation. Some α-Al_2O_3, a significant amount of mullite and θ-Al_2O_3 are present in 1260 °C sample, which indicates the 1240 °C peak may be attributed to α-Al_2O_3 and θ-Al_2O_3 formation. The seeming presence of a bulge at $2\theta = 28$–30° in Fig. 4(d) could possibly indicate the presence of a trace amount of cristobalite. The strong exothermic peak at 1337 °C may be attributed to the reaction between cristobalite and alumina. Mullite and α-alumina are the ultimate phases in 1350 °C sample. Residual alumina is necessary to eliminate residual trace amount of glassy silica and enhance the creep resistance and the strength of the mullite matrix.

The mullite precursors prepared by all kinds of chemical methods are divided into two categories, based on the precursor chemical homogeneity and the resultant crystallization behavior [14]. In amorphous monophasic system, alumina and silica are molecularly mixed to form $[\text{Al–O–Si}]_n$ network structure, the mullitization occurs rapidly by a strong exothermic reaction at ~1000 °C. In contrast, in diphasic system, alumina- and silica-rich precursors are segregated at a scale of 1–100 nm, hence the mullitization occurs slowly by an exothermic reaction at temperatures typically in the range of 1150–1350 °C.

According to the above considerations, some of alumina and silica in the as-prepared aluminosilicate matrix are molecularly mixed to form amorphous monophasic mixture, whose mullitization occurs at 984 °C; some of alumina and silica in the as-prepared aluminosilicate matrix are mixed at the nanometer scale to form amorphous diphasic mixture, whose mullitization occurs at 1337 °C. The mullitization at 793 °C may result from the phase transformation of Al–Si spinel. The weak endothermic peak at 1240 °C may result from the phase transformation of the isolated alumina particles (see Fig. 2). All these results allow us to conclude that $AlCl_3$ and $SiCl_4$ were not homogeneously mixed in the present LPCVI experiments.

A number of reaction equations were given to analyze the homogeneous chemistry mechanism for $AlCl_3$–$SiCl_4$–CO_2–H_2 deposition above 1000 K in ref. [15]. However, ref. [16] reported that decomposition of $AlCl_3$ was impossible at 550 °C, the model between $AlCl_x$ and OH was unfit to the present LPCVI. The individual reaction between $AlCl_3$ or $SiCl_4$ and H_2O may be the major mechanism.

The inhomogeneous aluminosilicate matrix might result from two considerations: on the one hand, because of the quick hydrolysis, Al^{3+} and Si^{4+} had not enough time to diffuse and completely form $[\text{Al–O–Si}]_n$ network structure. On the other hand, because of the low temperature and short gas-lines, the $AlCl_3$ and $SiCl_4$ molecules had not been mixed homogeneously before reaction.

4. Conclusion

(1) The aluminosilicate matrix within Nextel 720/aluminosilicate composites prepared by LPCVI at 550 °C using $AlCl_3$–$SiCl_4$–CO_2–H_2 precursor system consist of concentric muti-layers like the annual tree rings and contains some isolated particles and pores.
(2) The phase composition of the aluminosilicate matrix is composed of an amorphous silica, γ-Al_2O_3, Al–Si

spinel, an amorphous monophasic mixture (in which Al^{3+} and Si^{4+} were mixed at a molecular level), and an amorphous diphasic mixture (in which Al^{3+} and Si^{4+} were mixed at a nanometer scale).

(3) The mullitization of the aluminosilicate matrix includes three stages. First stage is the mullitization of a Al–Si spinel at 793 °C; the second stage is the mullitization of an amorphous monophasic mixture at 984 °C; the third stage is the mullitization of an amorphous diphasic mixture at 1337 °C.

(4) Complex mullitization process and inhomogeneous microstructure of the aluminosilicate matrix suggested that $AlCl_3$ and $SiCl_4$ were not molecularly mixed during 550 °C LPCVI.

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