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Activation energy for mullitization of gel fibres obtained from aluminum isopropoxide

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Abstract. **Gel fibres of mullite precursor were prepared from an aqueous solution of aluminum nitrate (AN), aluminum isopropoxide (AIP) and tetraethylorthosilicate (TEOS). A 4:1 molar ratio of aluminum isopropoxide and aluminum nitrate was optimized to obtain spinnable precursor sol for synthesis of fibres. Thermogravimetry–differential scanning calorimetry (TG–DSC), Fourier transform infrared (FTIR) spectra and X-ray diffraction (XRD) analyses were used to characterize properties of the gel and ceramic fibres. The precursor gel completely transformed to mullite at 1200 °C. The activation energy of mullite crystallization was 993·5 kJ/mol by the Kissinger equation.**

Keywords. **Mullite; fibres; sol–gel method; activation energy.**

1. Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) has been recognized as an outstanding ceramic material, for its high temperature strength, creep resistance, thermal and chemical stability, low thermal expansion coefficient and good dielectric properties (Schneider *et al* 2008; Tan *et al* 2010). An important potential application of mullite is as fibre reinforcement. In the Al_2O_3–SiO_2 system, only mullite exists as the stable compound, which occupies the structure of edges-shared AlO_6 octahedron chains parallel to *c*-axis bounded by aluminum and/or silicon tetrahedron (Esther *et al* 2007; Tan *et al* 2010).

Main processes for the manufacture of ceramic fibres can be classified as melt-spinning processes and sol–gel spinning processes (Zhang *et al* 2009). Usually, the melt-spinning method was adopted for the synthesis of ceramic fibres with low melting point. So, the method was not suitable for the preparation of mullite fibres.

Many successful processes have been reported in the preparation of mullite fibres by the sol–gel method (Okada *et al* 1998; Chen and Gu 2009; Tan *et al* 2010). Continuous mullite fibres can be obtained using aluminum isopropoxide (AIP) as Al source, with smooth surface and dense microstructure, for AIP polymerization was responsible for the appropriate spinning viscosity (Chen and Gu 2009). Since the expensive AIP was involved in the synthesis process of mullite fibres, the process limits to its widespread applications. In order to reduce the amount of AIP, aluminum nitrate was added in preparation of precursor gel.

The activation energy of mullitization has been reported by many workers, but the value may be affected by raw materials category. Some reported that mullitization occurs by nucleation-growth mechanisms. There are, however, different opinions on the rate-controlling step of mullitization (Okada 2008). The activation energies values of mullitization occurs by nucleation-growth which was smaller than the value by rate-controlling (Okada 2008). According to the value of activation energy, mullitization mechanisms can be obtained.

In this work, gel fibres of mullite precursor were prepared from an aqueous solution of aluminum nitrate (AN), AIP and tetraethylorthosilicate (TEOS). And the mullitization behaviour of the mullite precursor gel fibres was determined by non-isothermal experiments, by the analysis of differential scanning calorimetry (DSC) data for samples heated at different heating rates.

2. Experimental

2.1 *Preparation of samples*

Starting materials used were AN (Chemical grade, Xi'an reagent factory, Xi'an, China), AIP (Chemical grade, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and TEOS (Chemical grade, Tianjin Kermel Chemistry Co. Ltd., Tianjin, China).

Mullite precursor solution was prepared by mixing H_2O, aluminum nitrate, AIP and TEOS were stirred vigorously at room temperature until clear solution was observed. Then the precursor solution was concentrated to obtain spinning

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sol in water bath (80 °C). The sol fibres were prepared by pulling a thin glass rod slowly from the sol after immersing. Then the sol fibres were dried at 60°C for 24 h in an oven. The gel fibres were then sintered at various temperatures between 800, 1000 and 1200 °C for 1 h, with a heating rate of 2 °C/min.

2.2 *Characterization techniques*

The viscosity measurement of sol was carried out at room temperature by using a NDJ-8 viscometer (Shanghai Fangrui Instrument Co., Ltd, Shanghai, China) at a shear rate 3 r/min. For the gel fibres, thermal behaviour was measured by thermogravimetry–differential scanning calorimetry (TG/DSC) instruments (SDT Q600, TA Instrument, America) at a heating rate of 5, 10, 15 and 20 °C/min in flowing air, and Fourier transform infrared (FTIR) spectra was recorded on 6700 Infrared Spectrometer (Nicolet Magna, America) with the samples as KBr pellets. X-ray diffraction analysis was carried out on a DX-2500 X-ray diffractometer (XRD, Dandong Fangyuan, Dandong, China) using CuKα radiation, and a step width of 0·05°/s. Microstructure feature was observed under a JSM-6390LV scanning electron microscope (SEM) instrument (JEOL, Japan). All tests were done at room temperature.

3. Results and discussion

3.1 *Characterization of precursors*

Some properties of the sols prepared with different amounts of AIP are shown in table 1. The spinning sol could be obtained when the ratio of AIP and AN was 5:1 and 4:1, respectively. AIP has not participated in hydrolysis and condensation polymerization reaction without adding AN, the sols have no spinnablity (Chen and Gu 2009). The acidic solution can be obtained by adding AN, then the M–OH monomer (where M is defined as metal Al or Si) was obtained, when the hydrolysis of AIP or TEOS took place. The polymer chains of M–O–M and M–OH–M were present while the condensation polymerization of M–OH monomer took place (Chen and Gu 2009). So, the spinnable sols were obtained.

Table 1. Effects of AIP and AN ratio on sols spinnable property*.

Sol	AIP:AN (mol)	Appearance of sol	Spinnability of sol
1	5:1	Transparent	Preferable
2	4:1	Transparent	Preferable
3	3:1	Transparent	Able
4	2:1	Transparent	Unable

*AIP, aluminum isopropoxide; AN, aluminum nitrate.

The spinnability of the sol was remarkably dependent on the added content of AN. With the increase of the content of AN, the sol spinnability reduced because pH value of sol decreased. As a result, the content of polymer chains (M–O–M and M–OH–M) decreased in precursor sol (Shojaie-Bahaabad *et al* 2008). The sol did not have spinnability, with a 2:1 ratio of AIP and AN.

According to the cost and spinnability of precursor sol, the sol (Tan *et al* 2010) was suitable for fibres preparation, when the molar ratio of AIP and AN was 4:1 in the sol. When the viscosity of sol (Tan *et al* 2010) was about 8602 mPa s, long gel fibres were obtained having 20 cm length. The length and diameter of fibres were influenced by viscosity and surface tension of spinning sol, speed of hand drawing and so on. Further research about these factors is being carried out.

TG/DSC curves of the mullite precursor gel are shown in figure 1, with a heating rate of 10 °C/min. DSC curve of the gel fibres exhibited two endothermic peaks at about 160 °C and 300 °C, and two exothermic peaks at about 500 °C and 983 °C. The two endothermic peaks are assigned to dehydration of the residual water and decomposition of hydroxides in the gel fibres, whereas two exothermic peaks are assigned to decomposition of organic component and crystallization of mullite, respectively. TG curve of the gel fibres showed weight loss around 43 wt% at 400 °C, while almost no further weight loss appeared with increasing temperatures.

In the above thermal analysis, the most interesting phenomenon is the intensity of the exothermic peak at 983 °C. Sharp 983 °C exothermic peak indicated better homogeneity of the Al and Si components at a molecular scale (Lee *et al* 2002; Douy 2006), which will be beneficial for obtaining mullite phase at lower temperature.

FTIR spectra of mullite precursor gel and calcined fibre are shown in figure 2. As can be seen, the band at 1636 cm^{-1} is assigned to the OH bending mode. The band at 1384 cm^{-1} and 1353, 1384 cm^{-1} are assigned to the CH_2, CH_3 stretching modes, respectively, which were obtained because AIP and TEOS hydrolyzed. The bands observed at 970 cm^{-1} and 560 cm^{-1} correspond to Al–O bonding modes. The band observed at 830 cm^{-1} and 430 cm^{-1} corresponds to O–Si–O stretching mode and bonding modes, respectively.

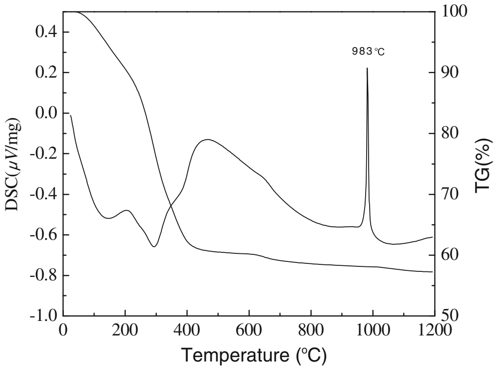

Figure 1. TG and DSC curves of mullite precursor gel fibres.

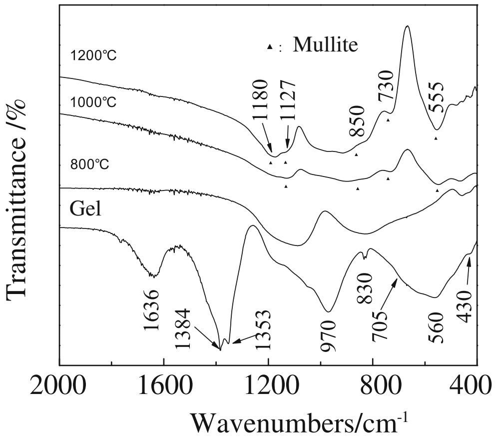

Figure 2. FT–IR spectra of mullite precursor gel fibres and fibres heated at 800, 1000 and 1200°C for 1 h.

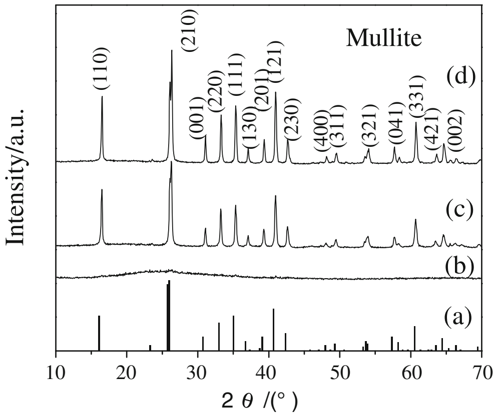

Figure 3. XRD patterns of (**a**) JCPDS Card #15-0776, mullite, and mullite precursor gel fibres heated at (**b**) 800, (**c**) 1000 and (**d**) 1200°C for 1 h.

The band at 560 cm^{-1} has a shoulder around 705 cm^{-1}, which is may be assigned to the (Si, Al)–O–(Si, Al) linkages bending modes. This assignment is in agreement with the proposed (Si, Al)–O–(Si, Al) bending mode for the band at 737 cm^{-1} in mullite (Beran *et al* 2001). The polymer chains of Si–O–Si, Al–O–Al and Al–O–Si were obtained by hydrolysis and condensation polymerization of AIP and TEOS.

The bands at 1636 cm^{-1} and 1383 cm^{-1} were not detected from the specimen which was calcined at 800°C. The result indicated that organic substance and water had evaporated.

The spectra of mullite are clearly observed in the gel calcined at 1000°C and 1200°C, and show bands at 1100–1200 cm^{-1} due to AlO_4 and SiO_4 species. In the region 800–900 cm^{-1}, they are mainly associated with AlO_4 and AlO_6 species; at 730 cm^{-1}, it is due to AlO_4 species; and at 550 cm^{-1}, it is corresponding to AlO_6 species (Song 1998). The infrared spectra show that the formation of mullite begins at 1000 °C.

When the chemical composition of mullite is rich in Al_2O_3, the 1127 cm^{-1} peak is stronger than the 1180 cm^{-1} peak in intensity. As can be seen, in the sample sintered at 1000 °C, the 1127 cm^{-1} peak was stronger than that at 1180 cm^{-1}. But in the sample sintered at 1200 °C, the 1127 cm^{-1} peak was weaker than that at 1180 cm^{-1}. This fact suggests the initial formation of an Al_2O_3-rich mullite and reflects the change in chemical composition of mullite.

X-ray diffraction patterns of JCPDS Card #15-0776 and the mullite precursor gel fibres heated at 800, 1000 and 1200 °C are shown in figure 3. Only amorphous phase was present when fibres were sintered at 800 °C. Mullite phase was obtained in the samples sintered at 1000 °C, while only mullite phase was observed at 1200 °C. XRD peak lines of fibres were not nearly shifted compared with JCPDS Card #15-0776. From the DSC and XRD analysis results, it can be concluded that mullitization of the gel occurred at temperature of about 1000 °C.

Mullite formed at 980 °C is always richer in alumina than the bulk precursor. It has been called 'tetragonal mullite' but in fact has an orthorhombic structure with cell parameters *a* and *b* being very close. By increasing the temperature, a progressive contraction of the *a*-parameter indicating a decrease of the alumina content, is generally observed and a composition very close to $3Al_2O_3{\cdot}2SiO_2$ is reached (Douy 2006).

The mullitization temperature was considered to be an important criterion in the assessment of the mixing scale of Al and Si components in the gels. When the scale of chemical homogeneity is at the atomic level, mullite formation is observed at about 980 °C (Leivo *et al* 2009). In contrast, when the scale of chemical homogeneity is in the nanometer range (the so-called diphasic precursors), formation of mullite is delayed due to temperatures higher than 1200 °C (Sales and Alarch 1996). Tkalcec *et al* (2005) obtained mullite phase at a sintering temperature of 1200–1300 °C using diphasic aluminosilicate gels. Temperatures in the range of 1600–1700 °C are required to achieve complete mullitization by mixing alumina and silica particles in the micrometer size range (Song 1998). The start transformation to mullite was obtained at 983 °C in this experiment. So, conclusion can be obtained that the Si and Al were mixed at a molecular level in the precursor gel.

SEM micrographs of mullite fibres calcined at 1200 °C are shown in figure 4. The diameter of these fibres is about 20 μm, with a smooth surface and uniform diameter.

When the gel fibres were dried and sintered, some gas could be produced for dehydration of the residual water and decomposition of hydroxides and organic component. Some micropores were formed in fibres in order to eliminate gas. After sintering at 1200 °C, the micropores were not observed because the fibre structure became dense.

3.2 *Activation energy*

The activation energy (E_a) of mullitization can be determined by isothermal or non-isothermal method. Under non-isothermal conditions, DSC or DTA curves were used to

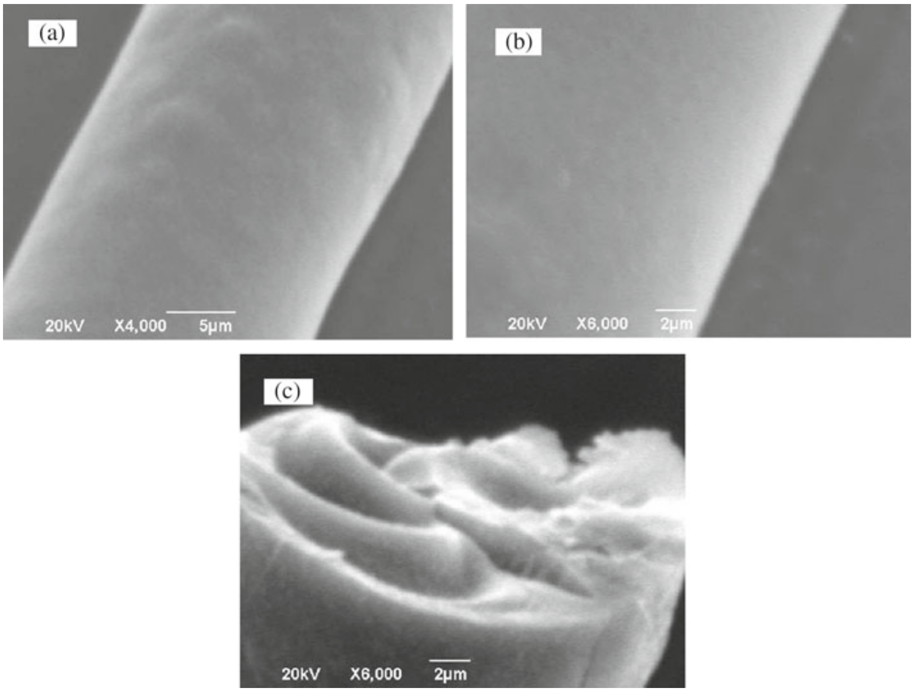

Figure 4. SEM microstructures of mullite fibres heated at 1200 °C for 1 h.

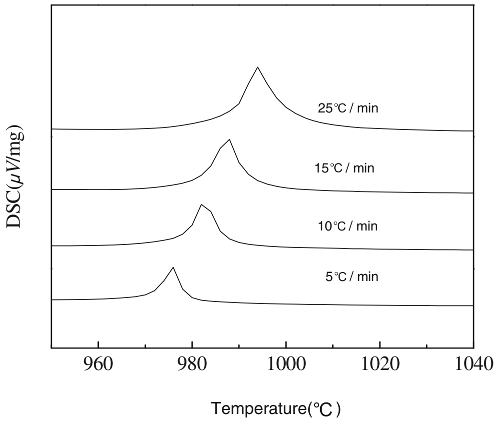

Figure 5. DSC curves of mullite precursor gel fibres at different heating rates.

obtain E_a values from peak temperature measurements at different heating rates. A non-isothermal method was experimentally easier than an isothermal method, but the accuracy of the resulting E_a value was generally strongly influenced by experimental conditions such as particle size, particle distribution, packing state, etc (Okada 2008; Tan *et al* 2010). In general, using larger sample sizes and faster heating rates may result in a reduction in the accuracy of activation energy (Okada *et al* 2003; Campos *et al* 2005).

Figure 5 shows thermograms obtained for DSC runs with heating rates of 5, 10, 15 and 20 °C/min for precursors. The exothermic peak, in the range of 976–994 °C, corresponds to mullite crystallization.

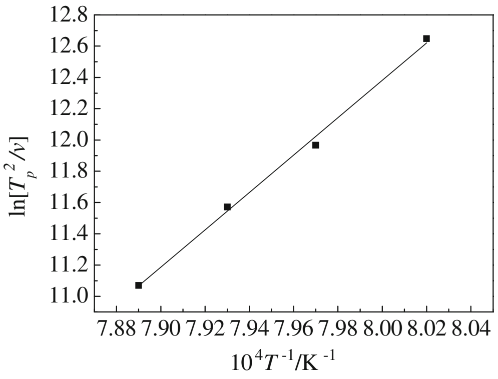

Figure 6. Activation energy plot for mullitization, according to (1).

Although many mathematical equations had been proposed for the calculations, the Kissinger equation (1) was most commonly used (Okada 2008).

$$\ln\left(\frac{T_p^2}{\nu}\right) = \ln\left(\frac{E_a}{R}\right) - \ln\phi + \frac{E_a}{RT_p}, \tag{1}$$

where T_p is the temperature of the exothermic peak top (crystallization temperature), ν the heating rate, E_a the activation energy, R the universal gas constant and ϕ the frequency factor (it is a constant dependent of the sample).

According to (1), by plotting of $\ln(T_p^2/\nu)$ vs $1/T_p$, the activation energy can be determined from the slope. As can be shown in figure 6, the value $E_a = 993{\cdot}5$ kJ/mol was determined.

Table 2. Activation energy of mullitization reported by different authors.

Authors	Starting materials	Activation energy (kJ/mol)
Lee *et al*	Monophasic gel	1394
Tkalcec *et al*	Diphasic gel	1119 ± 25
Okada *et al*	Monophasic gel	1202 ± 27
Tkalcec *et al*	Monophasic gel	1053 ± 51
Chen *et al* (2004)	Kaolinite $+\text{Al}_2\text{O}_3$	1182

The E_a values are consistent with the data reported by Tkalcec *et al* (1998) which obtained the value by isothermal differential scanning calorimetry using single-phase gel. But, E_a values are smaller than the other reported data listed in table 2, where data also were obtained using monophasic gel. This conflicting result can be explained as follows. The experimental conditions used by different authors are inconsistent, such as particle size, particle distribution, packing state, etc.

The nucleation-growth controls mullitization, when direct crystallization from an amorphous phase occurs in the low temperature range (900–1000 °C) and the E_a values are high (900–1400 kJ/mol). So, mullitization occurred by nucleation-growth mechanisms in this work, and the pathway of mullite formation was direct formation of Al-rich mullite at about 1000 °C.

4. Conclusions

Mullite gel fibres have been prepared using AN, AIP and TEOS as starting materials. The molar ratio of AIP and AN of 4:1 was optimal proportion to obtain spinnability of the sols. Only amorphous phase was present when fibres were sintered at 800 °C and complete mullitization temperature was at 1200 °C.

The activation energy for mullite formation in precursor gel fibres was determined by means of differential scanning calorimetry. The E_a value was 993·5 kJ/mol by Kissinger equation.

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