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The structural change of diphasic mullite gel studied by XRD and IR spectrum analysis

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Abstract

A systematic study on the structural change of diphasic mullite gel with heat treatment was carried out by combination of XRD and IR analysis. Aluminium ions are prevalently hexacoordinated in the as-received gel. After heated at high temperatures, part of them transforms to tetrahedral coordination. Phase segregation occurs at ≈1000 °C, resulting in the formation of γ-Al_2O_3 (containing 9–11 wt.% SiO_2) and almost pure amorphous silica. Mullite forms at ≈1250 °C by reaction between (δ,θ)-Al_2O_3 and amorphous silica. The incorporation of SiO_2 into γ-Al_2O_3 raises the transformation temperature of γ-Al_2O_3→(δ,θ)-Al_2O_3, the formation of pure amorphous silica and mullite render Si-O bands in IR spectrum shift stepwisely towards higher wave numbers.

Keywords: Mullite; IR spectroscopy; Phase development; Sol-gel processes; X-ray methods

1. Introduction

Mullite is becoming increasingly important in electronic, optical and high-temperature structural applications, because of its low dielectric constant, good transparency for mid-infrared light and excellent creep resistance.[1] During recent decades, there has been considerable interest in preparing mullite by sol-gel method.[2–12] According to the short-range atomic arrangement, mullite gel can be classified into monophasic and diphasic gel.[5] In monophasic gel, SiO_2 and Al_2O_3 are mixed on a molecular level, where mullite forms from totally amorphous state by a nucleation-controlled process at 980 °C.[5] In diphasic gel only a nano-scaled mixing of SiO_2 and Al_2O_3 is achieved, mullite forms through a diffusion-controlled reaction between an intermediate cubic phase (γ-Al_2O_3 or Al–Si spinel) and amorphous silica at over 1200 °C.[5–6,13]

At present, some controversy exists concerning the nature of the intermediate phase formed in diphasic mullite gel. Schneider and Sanz claim that it is virtually γ-Al_2O_3, although possibly incorporated with minor amount of SiO_2.[10,12–14] Whereas many other researchers argue that the intermediate phase is an Al–Si spinel, whose composition varies from $6Al_2O_3{\cdot}SiO_2$, $2Al_2O_3{\cdot}SiO_2$, $3Al_2O_3{\cdot}2SiO_2$ to $2Al_2O_3{\cdot}3SiO_2$, depending on the results of different researchers.[3,15–19]

In the present work, IR analysis and XRD were used to monitor the thermo-chemical and structural changes of a diphasic mullite gel prepared by hydrolysis-coprecipitation method. Analysis of the IR spectra correlated with study of XRD results has allowed determination of the mullitization process.

2. Experimental procedure

$Si(OC_2H_5)_4$ and $AlCl_3{\cdot}6H_2O$ were used as starting materials during powder preparation. First, $Si(OC_2H_5)_4$ (TEOS) was prehydrolysed overnight at room temperature in an alcohol-water solution before mixed with $AlCl_3{\cdot}6H_2O$. Afterwards, the TEOS and $AlCl_3$ mixture solution was kept at 70 °C for one hour under vigorous stirring and then precipitated by slowly adding 4 N ammoniated water. The precipitate was washed free of Cl^- anion with distilled water, followed by rinsing with

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hot ethanol and drying at 110 °C. The resulting mullite precursor was designated as hydrolysis-coprecipitated powder (HCP).

Al_2O_3 and SiO_2 gels were also separately prepared following the same experimental procedure as HCP. Those Al_2O_3 and SiO_2 gels heated at the same temperature were mixed together with agate mortar and pestle in proportion corresponding to stoichiometric mullite composition. The resulting powder mixture was referred to as alumina-silica powder (ASP).

The structural evolution of HCP and ASP with heat treatment was monitored by the following techniques. Crystalline phases were identified by XRD using monochromized CuKα radiation. Infrared absorption spectra were recorded from 400 to 2000 cm^{-1} with samples prepared by KBr pellet method. Specific surface area was determined by BET method using nitrogen as absorptant gas. Finally, the powder was observed with TEM to characterise its morphological evolution with temperature.

3. Results and discussions

Fig. 1 A shows the phase evolution of HCP gel with heat treatment. The XRD pattern of the as-received gel exhibits reflections of bayerite. After heating at 600 °C, the gel transforms to a totally amorphous state. Further heating leads to the formation of γ-Al_2O_3 at 920 °C and (δ,θ)-Al_2O_3 at 1150 °C. However, till then SiO_2 consistently remains amorphous. At 1250 °C, mullite reflections have become dominant in the XRD pattern, together with two weak reflections of residual (δ,θ)-Al_2O_3. At 1350 °C, only mullite is detected in the powder, although the XRD pattern is not presented here.

Fig. 1 B summarizes the XRD data of ASP powder. Since Al_2O_3 and SiO_2 gels have been heated separately before mixing, the present XRD results should reflect the independent crystallization behaviors of Al_2O_3 and SiO_2. As can be seen, SiO_2 remains amorphous at the whole studied temperature range, bayerite exists in the as-received powder and transforms to γ-Al_2O_3 and (δ,θ)-Al_2O_3 successively at 600 and 920 °C.

A comparison between Fig. 1A and B finds that the crystallization temperatures of γ-Al_2O_3 and (δ,θ)-Al_2O_3 in HCP are much higher than that in ASP. Such phenomena have also been observed in the works of other researchers,[12,13,20] and are ascribed to the stabilization of transition Al_2O_3 by substitutional Si.[20]

The structural change occurring in HCP on firing was monitored by infrared spectrum analysis (IR), as shown in Fig. 2A. The absorption band at 1640 cm^{-1} is induced by absorbed water, the dimension of which decreases with increasing temperature and water removal. Because of the lack of tetrahedrally coordinated Al ion (Al^{IV}) in the as-received HCP gel,[13,21–24] the Al^{IV}–O band at 830 cm^{-1} is hardly discernable, whereas a strong Al^{VI}–O

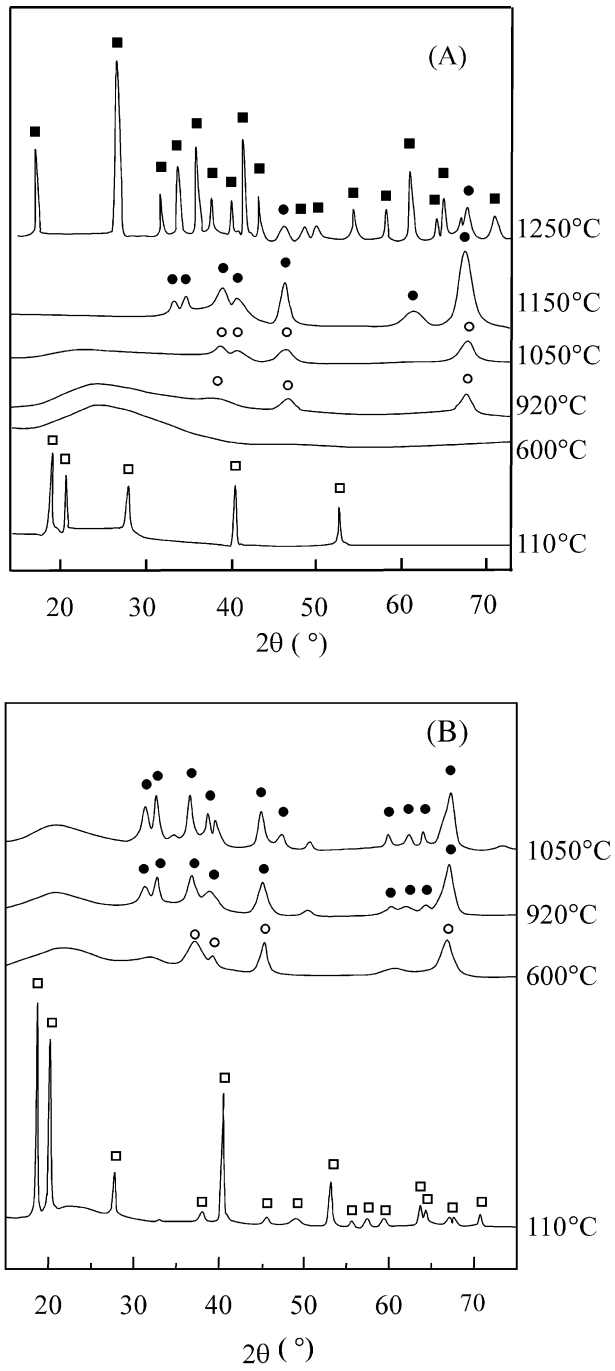

Fig. 1. X-ray diffractograms of HCP (A) and ASP (B) powders undergoing heat treatment at various temperatures. (□: bayerite, ○: γ-Al_2O_3; ●: (δ,θ)-Al_2O_3; ■: mullite).

(hexacoordinated Al ion) band is observed at 560 cm^{-1}. With increasing temperature, the Al^{IV}–O band at 830 cm^{-1} expands continuously, due to an increase in Al^{IV} number.[4,24–26] At 920 °C, the intensities of the two Al–O bands have become comparable. They overlap into one broad band stretching from 500 to 900 cm^{-1}, which remains almost intact until mullite formation at 1350 °C, where it evolves into three separated components at 560 cm^{-1}(Al^{VI}–O), 740 cm^{-1}(Al^{IV}–O) and 830 cm^{-1}(Al^{IV}–

O). In contrast, the IR spectrum of ASP always shows clearly distinguishable Al^{VI}–O and Al^{IV}–O bands (Fig. 2B). The overlapping of Al–O band in Fig. 2A probably indicates a more disordered Al^{VI} and Al^{IV} distribution in HCP, due to the substitution of Si for Al in transition Al_2O_3.

Going parallel with the variations of Al–O bands, radical changes in the Si–O bands have taken place. Following crystallization of γ-Al_2O_3 at 1050 °C and mullite at 1350 °C, the Si–O band at about 1100 cm^{-1} shows a stepwise shift to higher wave number as illustrated by the dashed lines in Fig. 2A. Concurrently, another Si–O band near 470 cm^{-1} also slightly shifts to higher wave number. In addition, at 1050–1150 °C, both the Si–O bands show the typical wave numbers and shapes of their counterparts in the IR spectrum of pure amorphous SiO_2 (see Fig. 2B). This indicates that at the above temperature range the amorphous SiO_2 in HCP powder is almost composed of pure SiO_2.

Fig. 2B shows that heat treatment hardly brings any change to the Si–O bands in the IR spectrum of ASP gel. Therefore, it can be deduced that the IR spectrum of pure amorphous SiO_2 is insensitive to heat treatment at temperature range from 110 to 1050 °C. In the light of that, the radical changes of Si–O bands in Fig. 2A at 920–1050 °C can not be exclusively attributed to heat treatment itself alone, some more significant reasons must exist.

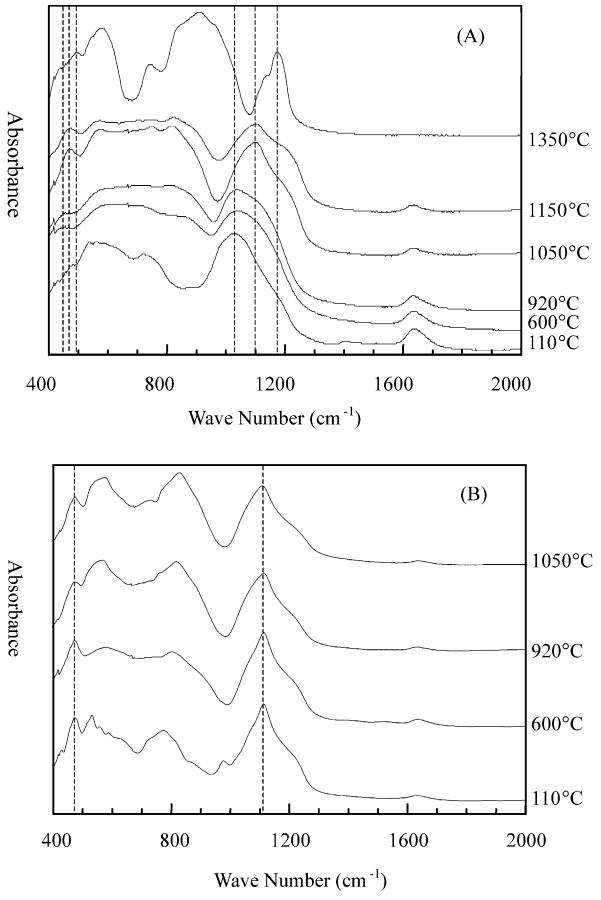

Fig. 2. Infra-red spectra of HCP (A) and ASP (B) powders heat treated at various temperatures.

Using liquid- and solid-state ^{27}Al and ^{29}Si NMR spectroscopy, Jayme and co-workers conducted systematic studies on the synthesis of monophasic mullite gel by slow hydrolysis of TEOS and $Al(NO_3)_3{\cdot}9H_2O$ in an aqueous solution.[22] They found that Si–O–Si bonds in silica network were broken by partially hydrolyzed aluminium cations and concurrently Si–O–Al bonds formed in situ, causing the shift of ^{29}Si NMR lines towards the lower field.[22,23] In the present case, although the diphasic gel is prepared at much higher hydrolysing speed, certain degree of Al solution in amorphous silica is still possible. The resulting changes in the Si–O bond strength and length may cause the shift of Si–O band towards a lower wave number, as shown in the IR spectrum of HCP gel heated below 1050 °C and reported by Hirata and Okada.[4,15] During heat treatment, phase segregation in HCP powder becomes significant at around 1000 °C as found by Schneider and Sanz.[12,13] First, γ-Al_2O_3 nucleates from the Al_2O_3 rich area derived from decomposed bayerite, followed by γ-Al_2O_3 grain growth and the liberation of Al ions from amorphous silica. With the progress of phase segregation, almost pure amorphous silica forms, resulting in the increase in Si–O wave number, as displayed in Fig. 2A. Later, mullite forms by reaction between amorphous silica and (δ,θ)-Al_2O_3, causing the Si–O bands further shift to higher wave numbers.

As mentioned in the introduction, there is much controversy and uncertainty about the identity and composition of the γ-Al_2O_3 formed in diphasic mullite gel prior to mullite crystallization. In the present work, HCP powders heated at 920 and 1050 °C were leached with 10 wt.% NaOH at 70 °C for 60 min to remove the amorphous phase. The residual crystalline γ-Al_2O_3 was washed with distilled water for 5 times and centrifuged. Only a trace amount of γ-Al_2O_3 is recovered from the powder heated at 920 °C, although a considerable amount is recovered from the other. The small γ-Al_2O_3 quantity contained in the former powder indicates that at 920 °C phase segregation in the gel is at its beginning stage.

The pre- and post-leaching IR spectra of the two mullite precursors are presented in Fig. 3. Despite the obvious differences between the pre-leaching spectra, the post-leaching ones are almost identical, where the 470 cm^{-1} Si–O band is completely eliminated, and the Si–O band near 1100 cm^{-1} is only left as flat shoulder. The SiO_2 contents in the post-leaching samples were measured by X-ray fluorescence semi-quantitative analysis. It is found that both samples contain 9–11 wt.% SiO_2, which is similar to the result of Okada,[15] who claimed that the intermediate crystalline phase in

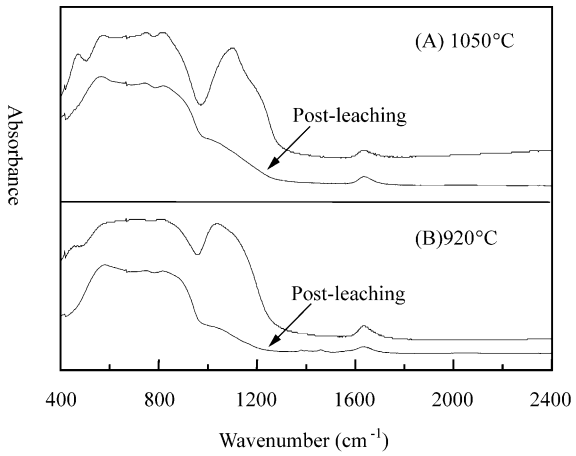

Fig. 3. Infrared spectra of pre- and post-leaching HCP powders calcined at 1050 °C (A) and 920 °C (B).

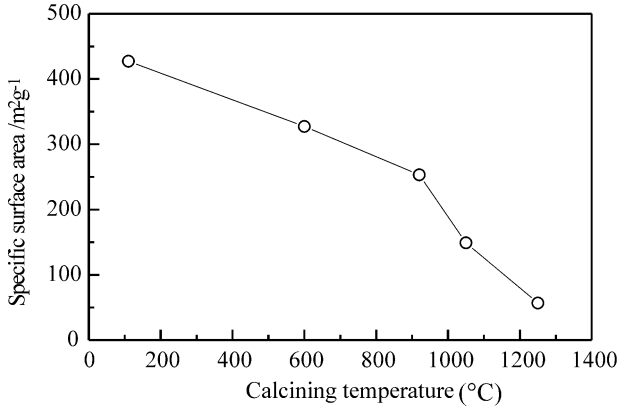

Fig. 4. BET specific surface area of HCP powder as a function of temperature.

diphasic gel should have a $6Al_2O_3{\cdot}SiO_2$ composition, and to the result of Schneider.[12] The possible formation of Al–Si spinel with $2Al_2O_3{\cdot}SiO_2$, $2Al_2O_3{\cdot}3SiO_2$ or $3Al_2O_3{\cdot}2SiO_2$ composition is completely ruled out, because of the high SiO_2 content in these compounds.[16,18,19]

Fig. 4 reveals the evolution of the specific surface area of HCP gel with heat treatment. The as-received gel has a high specific surface area of 427 m^2/g. With increasing temperature, the specific surface area decreases steadily in a linear manner up to 920 °C, where an inflection point appears. Beyond the inflection point, the specific surface area drops sharply due to the increasing crystallinity of the powder.

HCP powders heated at different temperatures are observed by TEM, as demonstrated in Fig. 5. The powder heated at 600 °C is very fluffy and loosely agglomerated, showing a particle size smaller than 10 nm. The agglomerated morphology of the powder persists at 1250 °C, but the shape of the primary particles has changed from spherical to more irregular. After heat treatment at 1350 °C for three hours, many mullite particles have developed into a plate-like morphology.

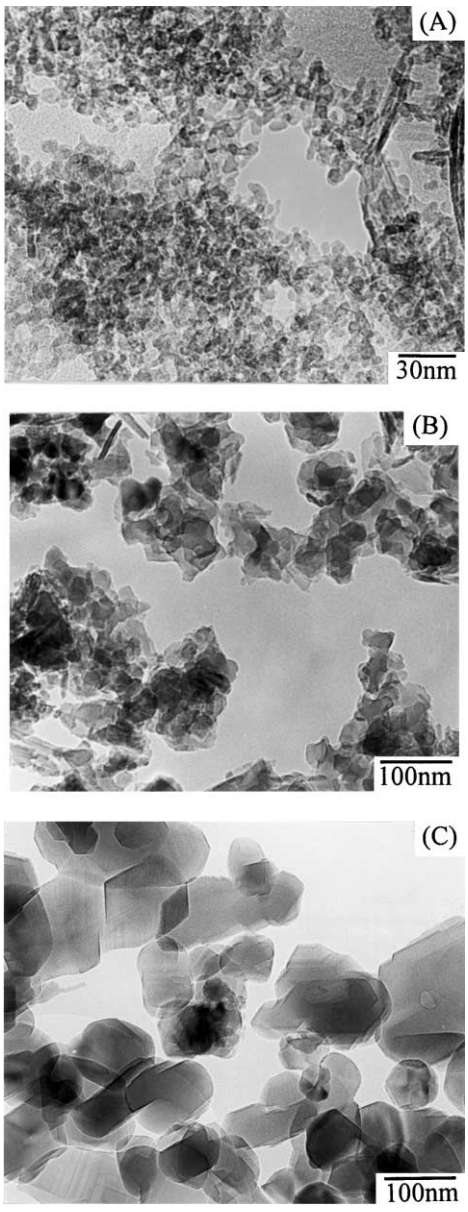

Fig. 5. TEM images of HCP powder heated at (A) 600 °C, (B) 1250 °C and (C) 1350 °C.

The powder shows an average size of about 80–100 nm and is well dispersed.

4. Conclusions

In the as received HCP gel, Al ions are prevalently octahedrally coordinated. At temperature below 920 °C, some of these octahedrally coordinated Al ions undergo a continuous transformation to tetrahedral coordination with heat treatment. At around 1000 °C, the Si–O bands in infrared spectrum show a stepwise increase towards higher wave numbers, due to a phase segregation happening within the gel. The phase segregation leads to the formation of γ-Al_2O_3 containing 9–11 wt.%

of SiO_2 and almost pure amorphous silica. The incorporation of SiO_2 in γ-Al_2O_3 results in the elevating of γ-$Al_2O_3 \rightarrow (\delta,\theta)$-$Al_2O_3$ transformation temperature. Mullite begins to form at 1250 °C by reaction between (δ,θ)-Al_2O_3 and amorphous silica, causing Si–O bands to shift further to higher wave numbers.

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