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Research Article

Mullite whiskers prepared by molten salt method using Si powders

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Abstract: Mullite whiskers were prepared from Si powders in molten $Al_2(SO_4)_3$-Na_2SO_4 mixture salts with different Al/Si molar ratio (*R*) of raw materials. The resulting mullite whiskers, had been investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and infrared spectroscopy analysis (FT-IR). Mullite phase was obtained in molten salts when the temperature reached at 850 ℃. SEM and EDS results revealed that two kinds of microstructures were formed in the final product, Al-rich mullite pellets and clusters of tiny mullite crystals, and the content of Al-rich mullite pellets increased with the higher Al/Si molar ratio (*R*) adopted in raw materials. A new oxidation-dissolution mechanism was proposed to explain mullite whiskers growth. According to thermodynamic analysis, mullite phase might be spontaneously formed as the temperature reached the decomposition temperature of aluminum sulfate (1023 K).

Key words: chemical preparation; whiskers; mullite; infrared spectroscopy

1 Introduction

Mullite is an attractive potential engineering ceramic because it has high strength and high creep resistance at both low and high temperatures, a low thermal expansion coefficient and good chemical and thermal stability. Mullite whiskers have attracted attention as a possible reinforcement for high temperature structure materials. Various processing routes have been reported for the preparation of mullite whiskers such as sol-gel [1,2], high-energy ball milling process [3-5], internal crystallization method [6] and thermal decomposition of minerals [7]. However, these conventional synthesis methods have apparent shortcomings that the reactive system needs providing higher crystallization temperature and longer crystallization time. As a new ceramic powder synthesis method, molten salt synthesis has been employed to synthesize ceramic powders because it decreases reaction temperature and gives powders of homogeneous morphology [8]. Mullite whiskers formation in molten salts system has been extensively studied [9-13]. But earlier studies focused on utilizing SiO_2 as raw material, there was no report about the preparation of mullite whiskers from Si powders by molten salt synthesis.

In this paper, mullite whiskers were prepared in $Al_2(SO_4)_3$-Na_2SO_4 mixture molten salts using Si powders. The morphology of mullite whiskers prepared by firing mixture powders with different

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Al/Si molar ratios (*R*) were investigated, and the oxidation-dissolution mechanism was proposed to explain the reactive process.

2 Experimental procedures

As raw materials, aluminum sulfate hydrate [$Al_2(SO_4)_3 \cdot 18H_2O$, AR], sodium sulfate [$Na_2SO_4$, AR] and Si powders (AR) (Xi'an Chemical Reagent Factory) were used. The mean particle size of Si powders was 30 μm.

Aluminum sulfate hydrate was placed in a microwave oven and heated with high fire for 10 min to remove intra-molecular water. Aluminum sulfate and Si powders were weighed accurately according to the different Al/Si molar ratio (*R*). The weight of sodium sulfate was equal to the total weight of aluminum sulfate and Si powders. The mixture was grinded in a ceramic mortar for 30 min, then heated to the sintering temperature for 1 h and cooled down to room temperature in air. The samples were washed with 95 ℃ water to remove the sulfate. Finally, white mullite powders were obtained after filtration, washing and drying. While the Al/Si molar ratio *R* was 3, two samples were obtained at different sintering temperature 850 ℃ and 900 ℃ with 1 h holding time, named as sample S1 (*R*=3, 850 ℃) and sample S2 (*R*=3, 900 ℃). When the sintering temperature was constant (900 ℃), another three samples were got with different Al/Si molar ratio (*R*=3.5, 4.5 and 5.5), named as S3 (*R*=3.5, 900 ℃), S4 (*R*=4.5, 900 ℃) and S5 (*R*=5.5, 900 ℃).

Crystalline phase and morphology of the samples were measured by X-ray diffractometer (XRD, D/MAX-RA) and scanning electronic microscope (SEM, S-2700) equipped with an energy dispersive spectrometer (EDS, INCA-350), respectively. Infrared spectroscopy (IR) studies were performed with infrared spectrometer (AVATAR 360 FT-IR, Nicolet) in the wavenumber range of 4000-400 cm^{-1}.

3 Results and discussion

3.1 Na_2SO_4-$Al_2(SO_4)_3$ phase diagram analysis

The corresponding Na_2SO_4-$Al_2(SO_4)_3$ phase diagram is shown in Fig. 1 [14]. The phase diagram of the molten salts system consists of eight areas which correspond

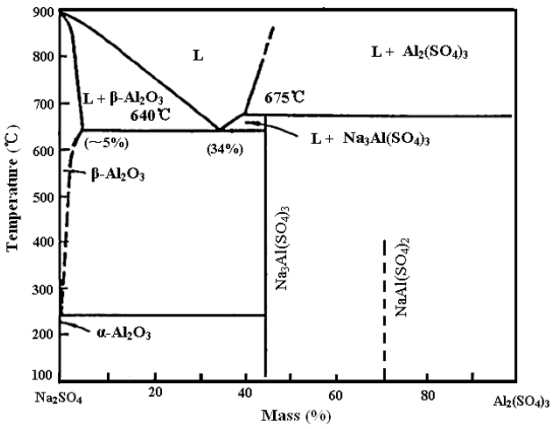

Fig. 1 Phase diagram of system Na_2SO_4-$Al_2(SO_4)_3$.

to different materials α-Al_2O_3, β-Al_2O_3, L+β-Al_2O_3, L, L+$Al_2(SO_4)_3$, $NaAl(SO_4)_2$, $Na_3Al(SO_4)_3$ and L+$Na_3Al(SO_4)_3$, respectively. Furthermore, it can be seen that the eutectic melt form at 640 ℃ in mixture molten salt system of 34% mass fraction aluminum sulfate. Aluminum sulfate and sodium sulfate could melt each other with any ratio when the temperature up to 900 ℃. Therefore, it is important and indispensable to investigate Na_2SO_4-$Al_2(SO_4)_3$ quantitative system at 900 ℃ for mullite whiskers synthesis.

3.2 XRD analysis

The XRD patterns of samples S1 and S2 are shown in Fig. 2. Mullite phase is the main composition of the product, and diffraction peaks of Si and γ-Al_2O_3 are also observed in the final samples, indicating that mullite phase form in molten salts as the temperature reached 850 ℃. Moreover, the content of Si in the product decreases with increasing the sintering

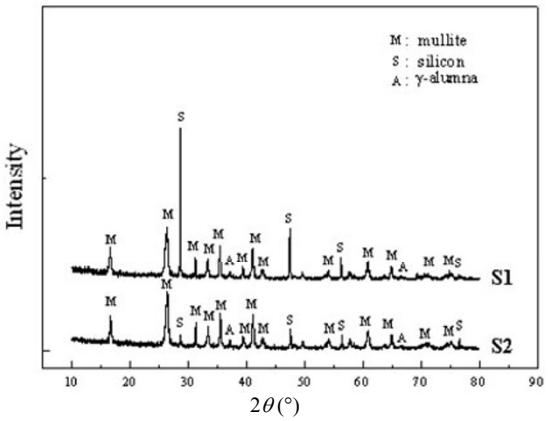

Fig. 2 X-ray diffraction pattern of samples S1 (*R*=3, 850 ℃) and S2 (*R*=3, 900 ℃).

temperature. Therefore, we selected higher temperature (900 ℃) to study the effect of different Al/Si molar ratio *R* on composition of samples S2, S3, S4 and S5.

Figure 3 shows the XRD patterns of samples S2, S3, S4 and S5 prepared for 1 h holding time at 900 ℃with different *R* values in the raw mixture salts. There exist the diffraction peaks corresponding to mullite, Si and γ-Al_2O_3 in sample S2, indicating that the product is a tri-phase composite consisting of major phase mullite, minor phase Si and tiny phase γ-Al_2O_3. However, with the increase of *R* value, the content of residual Si in the final product gradually decreases, simultaneously forms a new compound $Al_{1.7}O_{2.85}Si_{0.15}$ (PDF#290086). When the Al/Si molar ratio is up to 3.5, the peaks ascribed to residual Si are not observed in sample S3. The diffraction intensity of compound $Al_{1.7}O_{2.85}Si_{0.15}$ increases gradually with *R* value increasing, demonstrating Al-rich molten salt is benefit for the $Al_{1.7}O_{2.85}Si_{0.15}$ formation.

3.3 FT-IR analysis

FT-IR spectra of the samples S2, S3, S4 and S5 are shown in Fig. 4. The absorption peaks of sample S2 at 3426 cm^{-1} and 1619 cm^{-1} are assigned to absorbed water from environment [15,16], and that at 1143 cm^{-1}, 838 cm^{-1}, 619 cm^{-1} and 536 cm^{-1} are assigned to mullite. The absorption peak at 1143 cm^{-1} is attributed to the Si-O-Si stretching vibration of SiO_4, and three absorption peaks at 838 cm^{-1}, 619 cm^{-1} and 536 cm^{-1} are attributed to the vibration of tetrahedral and octahedral coordination Al-O bonds. The spectra of samples S3, S4 and S5 display that they have similar absorption wavelength compared with sample S2, and the observed frequencies are listed in Table 1. Two absorption bands centring at 1500 cm^{-1} and 426 cm^{-1} are observed for the sample S2, which were not reported in any public information. These absorption peaks may be ascribed to the vibration of Al-O-Si of $Al_{1.7}O_{2.85}Si_{0.15}$. Moreover, the intensity of these absorption peaks increases with the *R* values increasing. Because the Al/Si molar ratio of mullite is 3 : 1, and excessive aluminum sulfate will lead to residual γ-Al_2O_3 remained in the final product, the Al-rich phase $Al_{1.7}O_{2.85}Si_{0.15}$ may be formed in the mixture

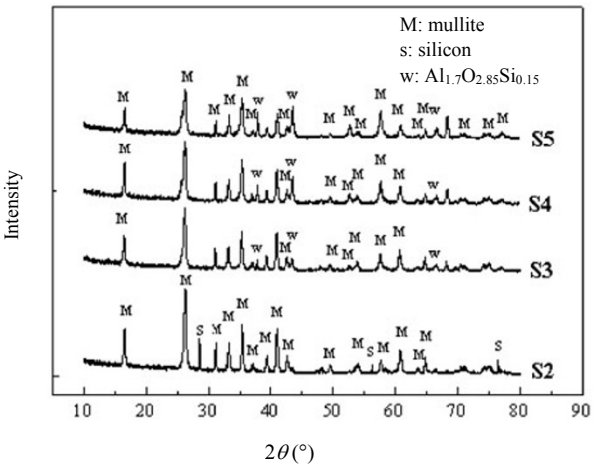

Fig. 3 X-ray diffraction patterns of samples S2, S3, S4 and S5 prepared at 900 ℃ with different *R*

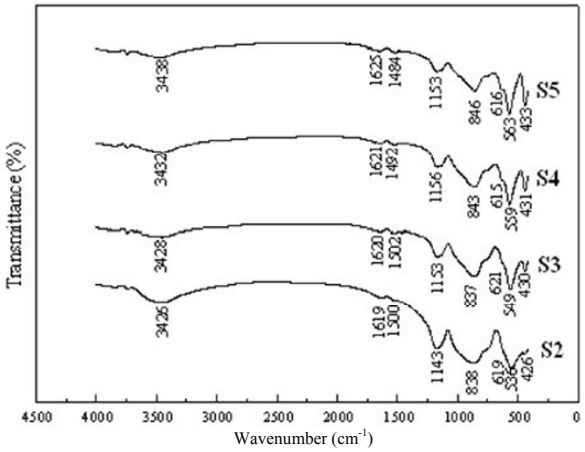

Fig. 4 FT-IR spectra of the samples S2, S3, S4 and S5 that prepared with different *R* values.

Table 1 FT-IR frequency assignments of as-prepared samples S2, S3, S4 and S5

S2	S3	S4	S5	Assignments
3426 m & br	3428 m & br	3432 m & br	3438 m & br	v (-OH)
1619 w	1620 w	1621 w	1625 w	v (-OH)
1500 vw	1502 w	1492 w	1484 w	v(Al-O-Si)
1143 s	1153 s	1156 s	1153 s	v (Si-O-Si)
838 s & br	837 s & br	843 s & br	846 s & br	v (Al-O of AlO_4)
619 vw	621 vw	615 vw	616 vw	v (Al-O of AlO_6)
536 s	549 s	559 s	563 s	v (Al-O of AlO_6)
426 vw	430 w	431 m	433 s	v (Al-O-Si)

s: strong; m: medium; w: weak; vw: very weak; br: broad.

molten salts.

3.4 SEM analysis

Figure 5 is representative SEM images of mullite whiskers prepared at 900 ℃ for 1 h with different *R* values. The images show the needle-like appearances of mullite whiskers clusters with diameters in the range of 100-200 nm and lengths in the range of 2-5 μm. And the micrographs also reveal the presence of two kinds of particles: plate-like crystals and clusters of smaller angular crystals [10]. When the *R* value is 3 (Fig. 4(a)), the product obtained is almost clusters of smaller angular crystals. It can be seen that the amount of plate-like crystals increases with increasing the *R* value, because excessive aluminum sulfate leads to Al-rich mullite pellets formed in the final product. This is further supported by the absorption intensity increasing in FT-IR spectra and the XRD data.

The corresponding EDS spectrum of the sample S3 shown in Fig. 6(a) indicates that the clusters of mullite tiny-crystal mainly consist of O, Al, Si. Moreover, the quantitative analysis shows that their average atomic ratio approximates to $O:Al:Si \approx 13:6:2$. While the Al/Si molar ratio (*R*) of raw materials increases, the content of Al-rich mullite pellets improves in the final product. We selected the area of pellets and measured EDS-surface-scanning spectrum of the sample S5 (Fig. 6(b)). It can be seen that O (43.2%) and Al (46.24%) are the main elements, and the content of element Si is 0.86%. Therefore, the EDS results are consistent with FT-IR and XRD analysis, demonstrating Al-rich molten salts is benefit for plate-like microstructure formation. A small amount of Na and S measured in Fig. 6 is originated from Na_2SO_4 of raw materials.

3.5 Formation mechanism of mullite whiskers

The growth mechanism of mullite whiskers can be explained by oxidation-dissolution process as described in Fig. 7. Firstly, Si powders contacted with molten salts ($Al_2(SO_4)_3$ and Na_2SO_4) were formed in the interface of solid and liquid, and free Al-cations formed in the liquid before decomposition of $Al_2(SO_4)_3$, which transformed to amorphous γ-Al_2O_3 above 700 ℃ according to the reaction (1). Subsequently, due to the strong oxidation of SO_3, the SiO_2 coating was formed through the reaction (2) and covered on the surface of Si powders. Then, the new formed SiO_2 coating can be etched by molten salts according to reaction (3) and mullite nuclei were formed in this

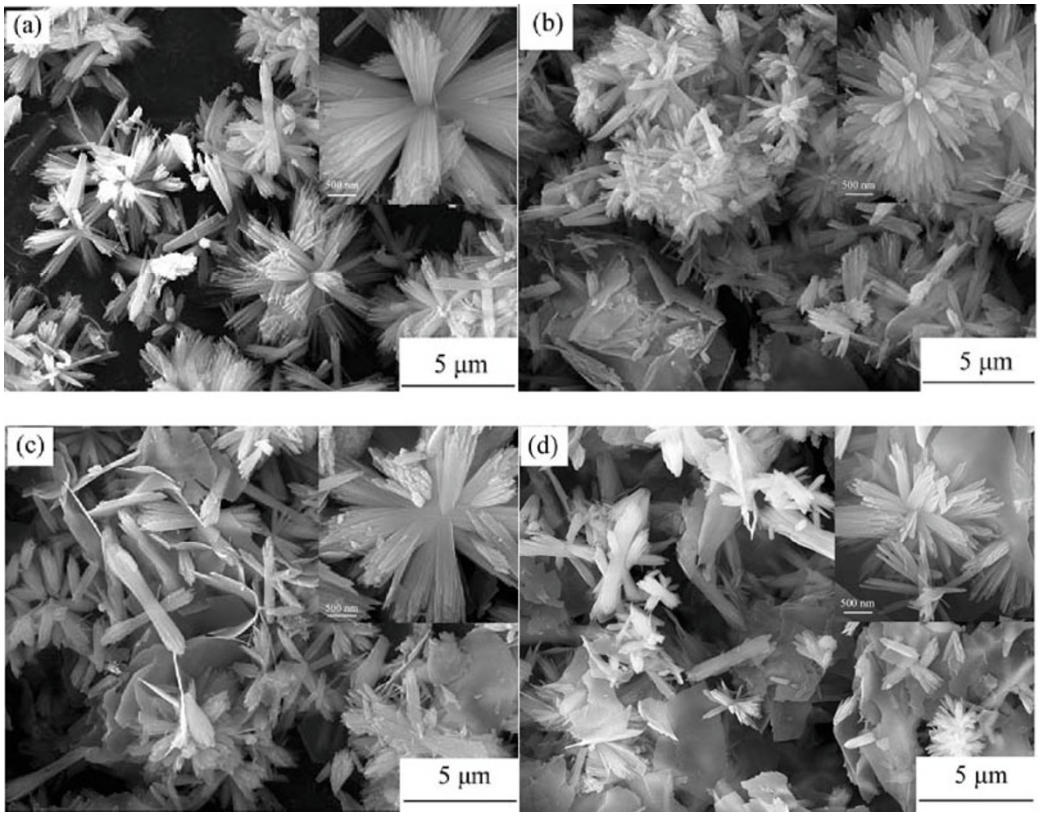

Fig. 5 SEM micrographs of samples S2 (a), S3 (b), S4 (c) and S5 (d) prepared at 900 ℃ for 1 h.

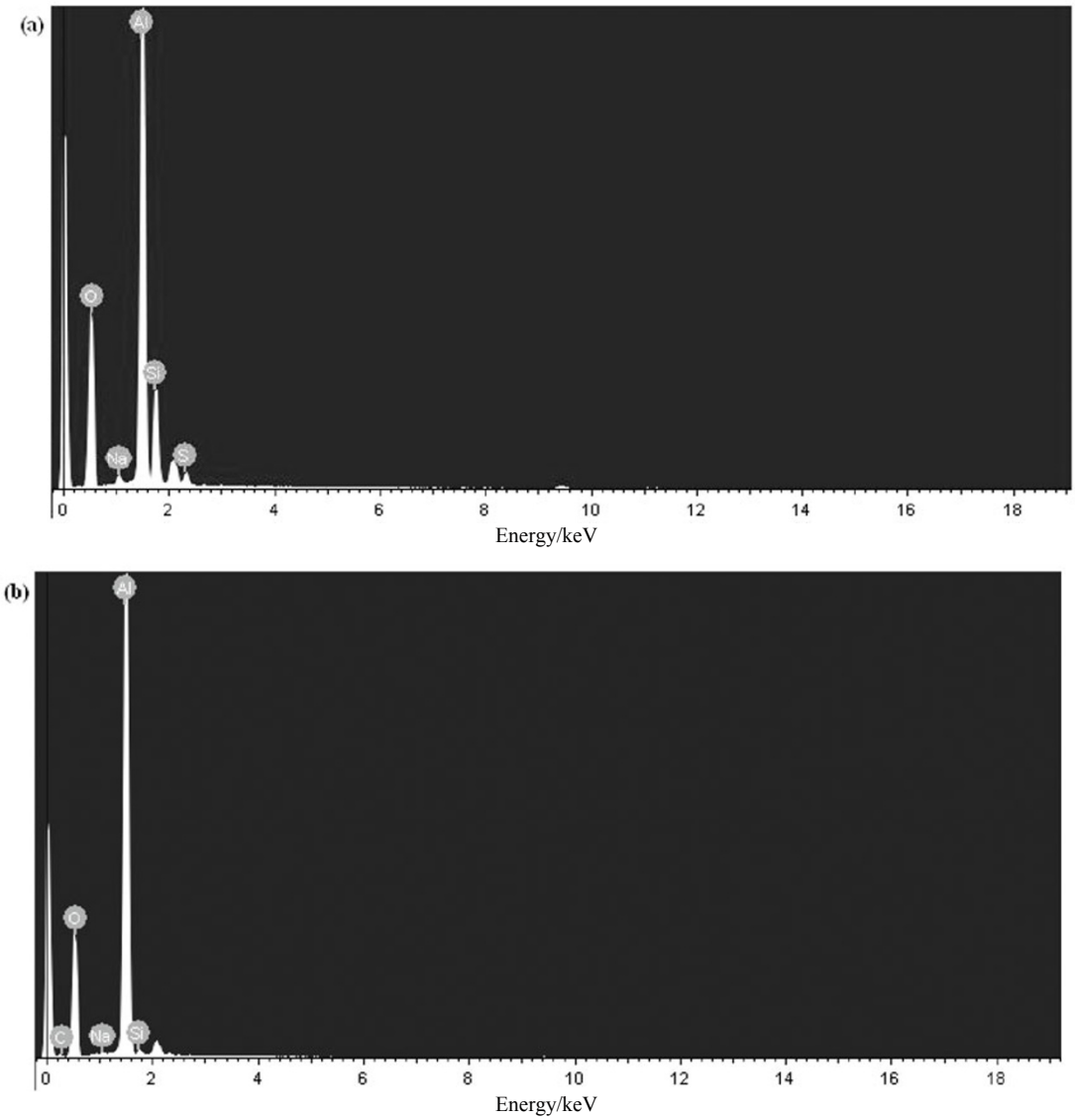

Fig. 6 EDS spectrum of samples S3 (a) and S5 (b).

process. At the same time, free Si substrate was exposed to molten salts system and the oxidation reaction would follow. By repeating this oxidation-dissolution cycle, the active Si has been etched completely and the inert mullite whiskers has been grown continuously. This repeated oxidation-dissolution mechanism is different from the commonly accepted mechanism of mullite whiskers formation [13], raw material Si powders could be oxidized by SO_3 which originated from the decomposition of $Al_2(SO_4)_3$. Thus, mullite nuclei form in the mixture molten salts and mullite whiskers could grow continuously depending on oxidation-dissolution cycle.

$$Al_2(SO_4)_3 \longrightarrow \gamma\text{-}Al_2O_3+3SO_3 \quad (1)$$

$$Si+2SO_3 \longrightarrow SiO_2+2SO_2 \quad (2)$$

$$3\gamma\text{-}Al_2O_3+2SiO_2 \longrightarrow 3Al_2O_3\cdot 2SiO_2 \text{ (mullite)} \quad (3)$$

From thermodynamic point of view, one reaction could be estimated qualitatively according to the change free energy (ΔG) of this reaction. Thus, we calculated the effect of temperature on free energy change of reactions (1), (2) and (3), which are shown in Fig. 8. The data of G are obtained from Reference [17]. As far as chemical equilibrium is concerned, the smaller the value of ΔG, the larger the equilibrium constant k is, and the more the products are when equilibrium state is attained. Therefore, the reaction (1) can not process in the lower temperature range ($\Delta G > 0$), the reaction would start extremely vigorous when the temperature was reaching at 1023 K ($\Delta G < 0$). It is found that the free energy change of reactions (2) and (3) are negative in the whole temperature range, which indicated that reactions are spontaneous. From the

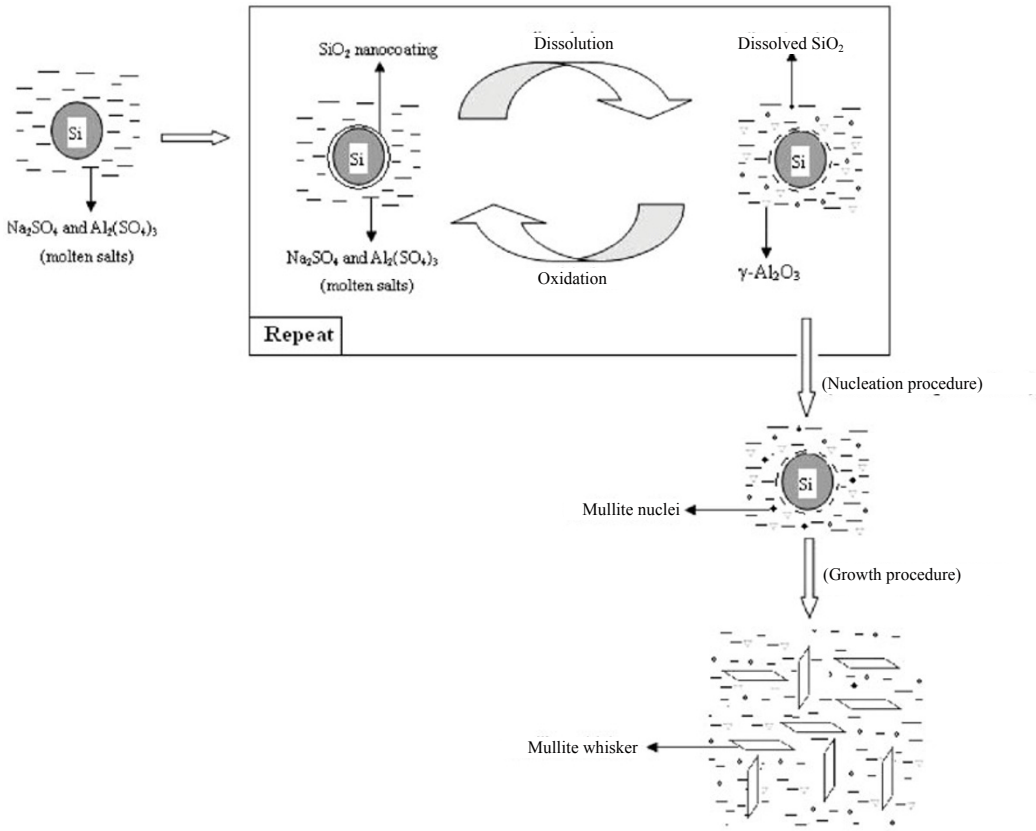

Fig. 7 Schematic illustration of growth process of mullite whiskers.

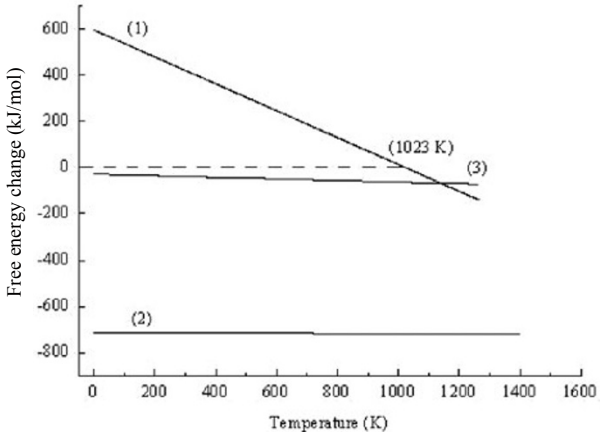

Fig. 8 Change of free energy ΔG for reactions (1), (2) and (3) depending on temperature.

temperature range of 0-1400 K, mullite whiskers form and grow controlled by reaction (1). This implies that mullite phase may spontaneously form once the temperature of the molten salts reaches the decomposition temperature of aluminum sulfate.

The mixture molten salts contact with solid-state Si powders, which is converted in a short period under these conditions especially when they are liquid mixed in a molecular level, which will shorten the diffusion paths, so that the reaction kinetics need not be considerated. This principle is applied in our investigations and the results are discussed in this paper.

4 Conclusions

Mullite whiskers were prepared from Si powders using molten $Al_2(SO_4)_3$-Na_2SO_4 salts method. XRD, FT-IR, SEM and EDS studies showed that Al-rich mullite pellets and clusters of tiny mullite crystals were formed in the final product. In addition, the content of Al-rich mullite pellets increases with the R of raw mixture salts increasing. A new oxidation-dissolution mechanism was proposed to explain mullite whiskers growth. Thermodynamic calculation indicated that mullite phase may be spontaneously formed as the temperature reached the decomposition temperature of aluminum sulfate (1023 K).

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