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Synthesis and Kinetics of Nano-Mullite *via* Micro-Boiling Method

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Synthesis and activation energy of nano-mullite by micro-boiling method using aluminum nitrate and silica sol as starting materials were studied. Results show that mullite of 3:1 of Al/Si molar ratio begin to form at 854 °C and mullitization is finished at 1200 °C and its mean size is 31.7 nm, grain size distribution is homogenous (20-50 nm), Al_2O_3 content is 59.8 mol %, activation energy is 634.52 ± 28.90 KJ mol^{-1}, appears characteristics of acicular and the interlocking continuous network structure. The activation energy of synthesizing mullite will gradually decrease with increase of Al/Si molar ratio from 3:1 to 6:1.

Keywords: Nano-mullite, Micro-boiling, Activation energy, Additive.

INTRODUCTION

Mullite is the only stable compounds in the Al-Si binary system and has good physicals, chemical and mechanical properties, such as low thermal conductivity, low thermal expansion, low dielectric constant, excellent optical performance, good thermal shock and stress resistance, high resistance to chemical erosion properties, high creep resistance *etc*.[1-4]. So it is considered as a candidate for advanced materials, used in a wide range, such as heat exchanger, filters, packaging material, windows and other fields[1-7]. There are many methods of synthesizing nano-mullite such as coprecipitation method, hydrothermal method and sol-gel method, *etc*. But micro-boiling method of synthesizing nano-mullite has not yet been reported.

The formula of mullite is $Al^{VI}_2[Al^{IV}_{2+2x}Si_{2-2x}]O_{10-x}$ (where x, about 0.2-0.9, is the number of oxygen vacancies) and the x value is 0.2-0.4 (Al/Si molar ratio is between 3:1 and 6:1) for thermal dynamic stability range of mullite, the others are metastable mullite[8-12]. In the paper, synthesis and kinetics of nano-mullite by micro-boiling method using aluminum nitrate and silica sol as starting materials and the effect of different Si/Al molar ratio on kinetics for thermal dynamic stability range are researched.

EXPERIMENTAL

Aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] and silica sol (SiO_2 content of 30 %, particle size is 10-20 nm) are used as main starting materials in the synthesizing mullite experiments.

Preparing aluminum nitrate and silica sol solutions: 1 mol L^{-1} aluminum nitrate solution and 1 mol L^{-1} silica sol solution can be obtained by putting 375.13 g aluminum nitrate and 200 g silica sol into 1000 mL volumetric flask with the deionized water, repectively. It is noted that 0.2 mol L^{-1} aluminum nitrate and 0.2 mol L^{-1} silicon sol solutions diluted by above the aluminum nitrate solution and silica sol solution, respectively will be used in the experiments.

Preparation of mullite precursor with different Al/Si molar ratio: Mullite precursor of Al/Si molar ratio of 3 can be prepared by micro-boiling method. Put 150 mL aluminum nitrate solution of 0.2 mol L^{-1} into 500 mL three-necked flask, then place the flask on the heating stage with the controlled temperature. Add slowly (about 10 mL h^{-1}) 100 mL silica sol solution of 0.2 mol L^{-1} into the flask after heating micro-boiling for 4 h. Subsequently pour the solution into a beaker and dry in an oven at 100 °C for 24 h. Finally, grind the dried samples into powders as mullite precursor M1.

Mullite precursor M2, M3 and M4 of the Al/Si molar ratios of 4:1, 5:1 and 6:1 can be prepared according to the above method.

Sintering experiments: Put the precursors in an electric furnace and calcine them at 1000, 1100, 1200 and 1300 °C with heating rate of 4 °C min^{-1} for soaking 0.5 h and then the calcined samples can be obtained after cooling to room temperature in the furnace.

Thermal analysis and activation energy: Using SDT Q600 made by TA company in the United States carry out the thermal analysis and research the activation energy of synthesizing mullite.

Thermogravimetric/differential scanning calorimetry (TG/DSC) test. Put 10 mg M1 into corundum crucible and heat up to 1260 °C at the conditions of 10 mL min^{-1} nitrogen flow rate and 40 °C min^{-1} heating rate.

The activation energy of synthesizing mullite can be determined by non-isothermal method. DSC curves are used to obtain peak temperature (Tp) at different heating rates (β) of 10, 20, 30 and 40 °C min^{-1} with different Al/Si molar ratio for the precursors, respectively. Then the activation energy (E) can be determined by formula (1).

$$\ln(\beta/Tp^2) = -E/(R\cdot Tp) + C \quad (1)$$

where C is constant; R is the universal gas constant.

Phase composition and microstructure: The phase composition and grain size of calcined samples can be analyzed by using PANalytical X'Pert Pro X-ray diffraction (XRD) under the condition of 40 KV voltage, 40 Am current and copper target. The microstructure and morphology of sintered samples are observed through the LEO 1530 field emission electron scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

TG/DSC: The TG/DSC curves of M1 calcined at a heating rate of 20 °C min^{-1} are shown in Fig. 1. The curves show that there are four endothermic peaks at about 100, 200, 240 and 400 °C and two exothermic peaks at about 854 and 920 °C, respectively. These endothermic peaks companying with decrease of weight are attributed to dehydration of the absorbed water, crystallization water and decomposition in the heating process. The exothermic peak with no changing weight at about 854 °C is caused by forming mullite and Al-Si spinel ($2Al_2O_3{\cdot}3SiO_2$) reacted between aluminum hydroxide and the amorphous silica. The exothermic peak with no changing weight at about 920 °C is generated by forming mullite through Al-Si spinel[12-14]. The temperature of forming mullite is agreed well with data of 850-1350 °C reported by several researchers[13,14].

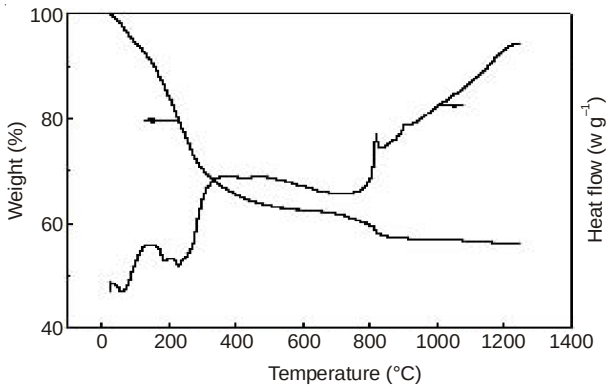

Fig. 1. TG/DSC curves of sample M1 during heating process

The main chemical reactions of forming mullite can be simplified as the following eqns. 2-5[13-17], although the actual reactions are complex. First, generating aluminum hydroxide by hydrolysis reaction of aluminium nitrate then forming mullite and Al-Si spinel reacted between aluminum hydroxide and silica. Finally, Al-Si spinel transform into mullite with increasing temperature again.

$$Al(NO_3)_3 + 3H_2O = Al(OH)_3 + 3HNO_3 \quad (2)$$

$$6Al(OH)_3 + 2SiO_2 = 3Al_2O_3{\cdot}2SiO_2 + 9H_2O \quad (3)$$

$$4Al(OH)_3 + 3SiO_2 = 2Al_2O_3{\cdot}3SiO_2 + 6H_2O \quad (4)$$

$$3(2Al_2O_3{\cdot}3SiO_2) = 2(3Al_2O_3{\cdot}2SiO_2) + 5SiO_2 \quad (5)$$

Sintering experiments: XRD patterns of M1 calcined at 1000, 1100, 1200 and 1300 °C are shown in Fig. 2. Mullite is obtained at 1000 °C. At 1100 °C, amounts of mullite increase and a very small amount of SiO_2 is appeared. At 1200 °C, whole crystal phase is mullite and at 1300 °C, phase composition is not change. So, it can be concluded that mullitization should be finished at 1200 °C. Mullitization temperature is considered to be an important criterion in the assessment of the mixing scale of the Al and Si components. Temperatures of complete mullitization at 1600-1700 °C for mixing alumina and silica particles in the micrometre size range and at 1000-1200 °C for the mixing scale at molecular level[6]. So we conjecture that the mixing scale of synthesizing mullite by micro-boililng method should be at molecular level.

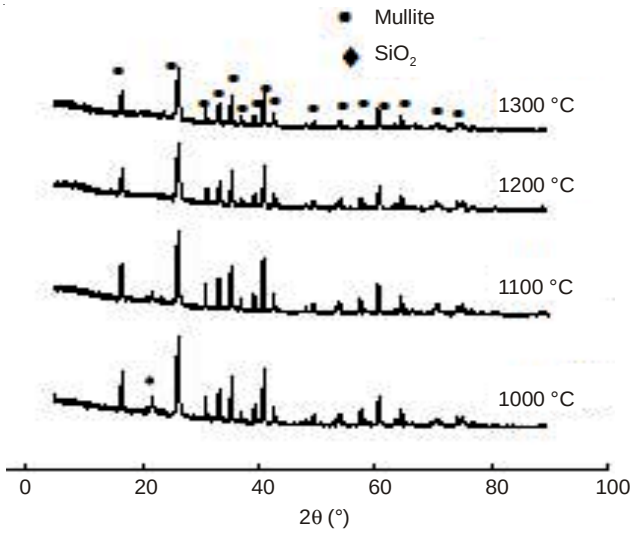

Fig. 2. XRD patterns of samples M1 calcined at 1000-1300 °C

XRD and SEM: XRD patterns of M1 is shown in Fig. 3. Fig. 3 shows that pure mullite sintered at 1200 °C can be gained. From XRD patterns and Ban and Okada formula (6)[18], we can gain that Al_2O_3 content of mullite is 59.8 mol %. The results is much the same as stoichiometric mullite (Al_2O_3 content is 60 mol %). It proves that mullite synthesized by micro-boiling method is pure.

$$Al_2O_3 = 44.17 \times I(220)/I(111) + 27.6 \quad (6)$$

where I(220) and I(111) are the diffraction peak intensities of crystal face (220) and (111), respectively in mullite. The average grain size of mullite basing on the statistical analysis through the formula (7) is 31.7 nm, grain size distribution is most between 20.3 and 51.5 nm, which is consistent with the results observed by the SEM in Fig. 4. Fig. 4 shows that mullite appears characteristics of acicular and uniform particle size distribution (mainly about 20-50 nm) and the interlocking continuous network structure. This structure will improve mechanical properties of mullite.

$$D_{hkl} = k\lambda/(B_{hkl}\cos\theta) \quad (7)$$

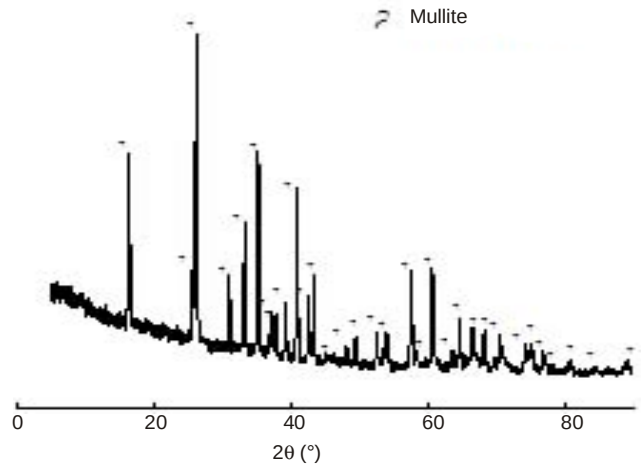

Fig. 3. XRD pattern of sample M1 sintered at 1200 °C

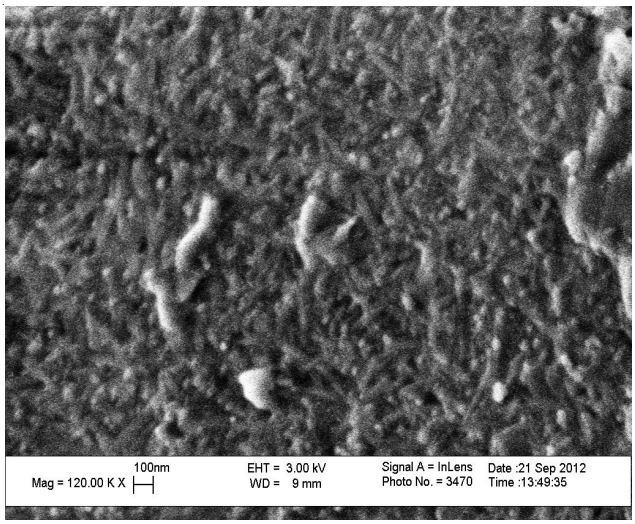

Fig. 4. SEM micrograph of sample sintered at 1200 °C

where D_{hkl} is average size of crystal face (hkl) on the normal direction, nm; K is the shape factor, 0.89; B_{hkl} is half width of the diffraction peak high, rad; λ is diffraction angle, rad; λ is wavelength of X-ray, 0.154056 nm.

Activation energy

Al/Si molar ratio of 3:1: The DSC curves of M1 calcined at different heating rates are shown in the Fig. 5. The curves show that the exothermic peaks temperature (Tp) are 844, 854, 854 and 866 °C at heating rate (β) of 10, 20, 30 and 40 °C min^{-1}, respectively.

From relationship between 1/Tp and $\ln(\beta/Tp^2)$ shown in Fig. 6, we gain that slop K is -76314.94917 ± 3476.41535 and then get that E is 634.52 ± 28.90 KJ mol^{-1} through the K = -E/R. Main mechanism of forming mullite is diffusion-controlled mechanism if activation energy[18-23] is 600-1200 KJ mol^{-1}. So mullitization processes of M1 should be controlled by diffusion mechanism and low E value shows that diffusion path length of forming mullite is very short, that is to say that the mixing scale of Al and Si is very high.

Different Al/Si molar ratio: The DSC curves of M1, M2, M3 and M4 are shown in Fig. 7. The exothermic peaks temperature (Tp) are 859, 858, 856 and 854 °C at the Al/Si molar ratio of 3:1, 4:1, 5:1 and 6:1 under condition of 20 °C min^{-1},

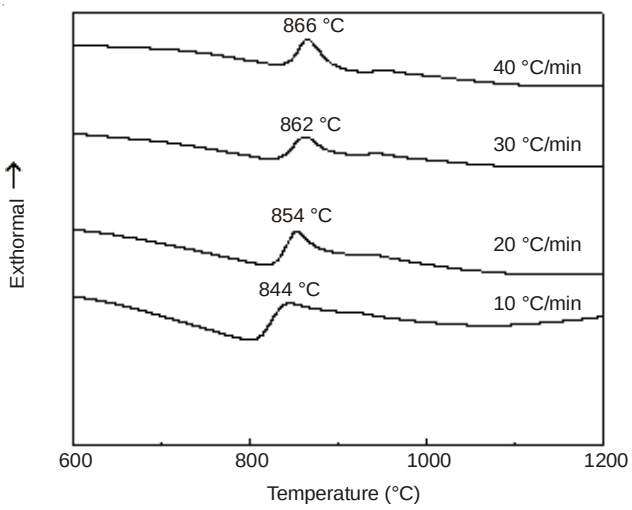

Fig. 5. DSC curves of synthesizing mullite at different heating rate

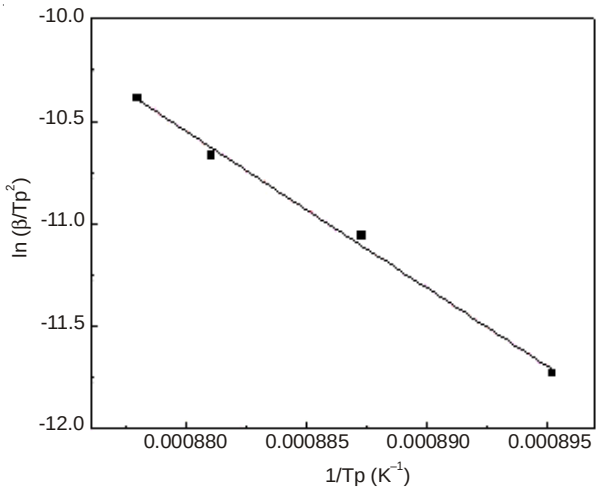

Fig. 6. Relationship between 1/Tp and $\ln(\beta/Tp^2)$

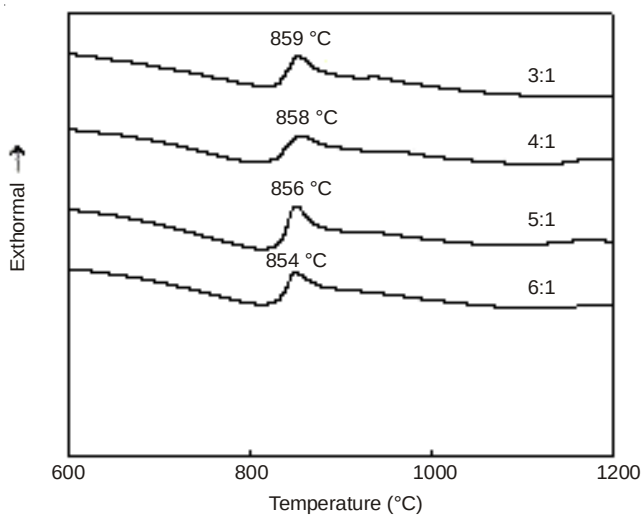

Fig. 7. DSC curves of synthesizing mullite at different molar ratio of Al/Si

respectively. It indicates the initial synthesizing mullite temperature slightly declines with the increase of Al/Si molar ratio between 3:1 and 6:1.

From relationship of M4 between 1/Tp and $\ln(\beta/Tp^2)$ shown in Fig. 8, it is found that the slop K is -61911.36235 ±

1732.39041 and then get that E is 514.73 ± 14.40 KJ mol^{-1} for 6:1 of Al/Si molar ratio through the K = -E/R. The E value is lower about 120 KJ mol^{-1} than the 3:1 of Al/Si molar ratio. It indicates that the activation energy of synthesizing mullite will gradually decrease with increase of Al/Si molar ratio, that is to say that Al/Si molar ratio has greatly effect on the activation energy of synthesizing mullite.

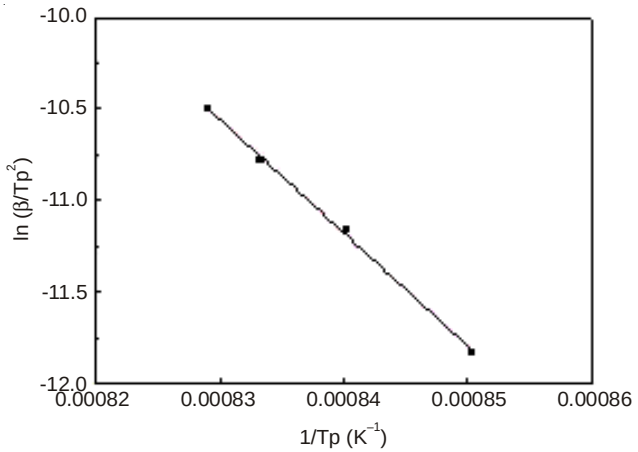

Fig. 8. Relationship between 1/Tp and $\ln(\beta/Tp^2)$

Conclusion

• Mullite could be synthesized by micro-boiling method using aluminum nitrate and silica sol as starting materials. Mullite of 3:1 of Al/Si molar ratio begins to form at 854 °C and complete mullitization is at 1200 °C and its mean size is 31.7 nm, grain size distribution is homogenous (20-50 nm), Al_2O_3 content is 59.8 mol %, activation energy is 634.52 ± 28.90 KJ mol^{-1}, appears characteristics of acicular and the interlocking continuous network structure. This structure improve the mechanical properties of mullite.

• Al/Si molar ratio has greatly effect on the activation energy of synthesizing mullite. With increase of Al/Si molar ratio, the activation energy of synthesizing mullite will gradually decrease to 514.73 ± 14.40 KJ mol^{-1} for 6:1 of Al/Si molar ratio from 634.52 ± 28.90 KJ mol^{-1} for 3:1 of Al/Si molar ratio.

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