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A study of the development of crystal shape of mullite prepared from $Al(OH)_3$ and kaolinite gangue

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Granular and needle-like crystals were observed in mullite made from $Al(OH)_3$ and kaolinite gangue using SEM and EDS. It's found that the granular mullite crystals are in the $Al(OH)_3$ pseudomorphs but the needle-like mullite crystals are in the gangue pseudomorphs. The differences of crystal shape of mullite come from the secondary mullitization based on the difference between the original shape of the Al_2O_3 crystallites and mullite crystallites in the pseudomorphs. With increases in the sintering temperature and additions of $MgCO_3$, the differences of shape of mullite crystals become small.

Key words: Crystal shape, Mullite, $Al(OH)_3$, Kaolinite.

Introduction

Mullite is an important material for both traditional and advanced ceramics because of its favorable thermal and mechanical properties [1-15]. Very often Al_2O_3 (or $Al(OH)_3$) and kaolin are used as raw materials to prepare dense and porous ceramics [5-15]. However, most of the studies have been on the content and crystal size of mullite [5-13]. Only a few were on the shape of mullite crystals [14, 15]. Chen et al prepared mullite from kaolinite with a mean size of 1.7 μm and alumina particles with a mean size of 0.3 μm, and found the addition of alumina reduced the size of mullite grains and their aspect ratio [14]. Sainz *et al* prepared mullite from kaolinite with d50 = 3 μm and α-$Al_2O_3$with d50 = 0.5 μm, and observed that elongated and equiaxed grains of mullite coexisted [15]. However these papers did not explain the reasons for the difference of the shape of mullite crystals very clearly. Based on our study we think that the different shape of mullite crystals in the same compacts results from the shape difference between the crystallites in the grains from Al_2O_3 (or $Al(OH)_3$) and kaolinite. This communication will address some of the results.

Experimental

The starting materials were $Al(OH)_3$, kaolinite gangue and $MgCO_3$. $MgCO_3$ was an additive. The chemical compositions of starting materials are listed in Table 1. The average particle sizes of $Al(OH)_3$, kaolinite gangue and $MgCO_3$ measured by a laser particle size analyzer (Matersizer 2000) were 54.3 μm, 42.3 μm and 16.2 μm, respectively.

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Table 1. Chemical compositions of $Al(OH)_3$, kaolinite gangue and $MgCO_3$ (wt%)

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ignition loss
$Al(OH)_3$	64.86	0.08	0.06	0.04	0.02	0.04	0.01	34.44
Kaolinite gangue	36.48	44.52	0.21	0.15	0.15	0.084	0.028	17.89
$MgCO_3$	0.19	0.05	0.02	0.04	42.69	-	-	57.06

Powder mixtures consisted of 54.3 wt% $Al(OH)_3$ and 45.7 wt% kaolinite gangue which is consistent with a stoichiometric mullite proportion of Al_2O_3 to SiO_2. The amounts of $MgCO_3$ added to the starting powders were 0, 1.76, 2.93 and 3.51 wt% based on our early research [12]. The starting powders were mixed for 4 h in polyurethane pots using alumina balls. The milled powders were pressed in cylinders with a height of 36 mm and diameter of 36 mm at a pressure of about 100 MPa and the green compacts after drying at 110 °C were heated at 1500 °C for 180 minutes in an electric furnace. Additionally, the green compacts prepared from the milled powder with 2.93 wt% $MgCO_3$ were also heated at 1400 °C and 1600 °C for 180 minutes in an electric furnace.

For the investigation of crystal shapes, a scanning electron microscope with EDAX (Nova NanoSEM 400, FEI) and another scanning electron microscope with EDAX (Philips XL30) were used. Samples were embedded in resin and polished with diamond paste, and then etched by a 40 wt% HF solution. The liquid phase contents in samples were calculated from the Equilib Mode of the Al_2O_3-SiO_2-MgO-CaO-Fe_2O_3 system by FactSage 5.5 thermochemical software. This FactSage software has been introduced in detail by Bale *et al* [16].

Results and Discussion

The mullite crystal shapes and EDS analysis of the samples (with different $MgCO_3$ additions) sintered at 1500 °C are shown in Fig. 1. The mullite crystal shape of the samples (containing 2.93 wt% $MgCO_3$) sintered at different temperatures are given in Fig. 2. In these two figures, two mullite crystals with different shapes are observed. One shape is needle-like and the other is granular even though they have almost the same chemical composition. They were located at difference areas in the compacts.

The difference of shape of mullite crystals in the same compact may result from the secondary mullitization based on the different shapes of Al_2O_3 crystallites and primary mullite crystallites in the pseudomorphs of $Al(OH)_3$ and gangue, respectively. The mechanism of formation of mullite from $Al(OH)_3$ and gangue can be described as follows:

1) At low temperature, $Al(OH)_3$ is decomposed to form Al_2O_3 crystallites whose shape is granular, and kaolinite gangue is decomposed to form SiO_2 and primary mullite whose shape is needle-like.

2) After decomposition the particle contours of $Al(OH)_3$ and gangue are kept. The contours of $Al(OH)_3$ and gangue particles are called $Al(OH)_3$ pseudomorphs which consist of Al_2O_3 crystallites with a granular shape, and gangue pseudomorphs which consist of mullite crystallites with a needle-like shape, respectively. The secondary mullitization takes place by diffusion and a chemical reaction. As shown in Fig. 3, SiO_4^{4-} diffuses from gangue pseudomorphs into $Al(OH)_3$ pseudomorphs and reacts with Al_2O_3 crystallites to form mullite, retaining the shape of the Al_2O_3 crystallites. At the same time, Al^{3+} diffuses from $Al(OH)_3$ pseudomorphs into gangue pseudomorphs and reacts with SiO_2 to form mullite which precipitates on the primary mullite. This is the reason why there are two types of shape of mullite crystal in the same compacts made of $Al(OH)_3$ and gangue particles.

3) With increases in temperature and the amount of $MgCO_3$ in the compacts, the liquid content increases (Fig. 4) and the diffusion and reaction are improved. After the reaction between Al_2O_3 crystallite and SiO_4^{4-} finishes, the crystal growth becomes an important process, the smaller mullite crystallites with a granular shape disappear and the larger mullite crystallites grow and become prism-like. At same time the mullite crystals in the gangue pseudomorphs grow and become larger, gradually. Then, the difference of the shape of mullite crystals in the same compact becomes smaller.

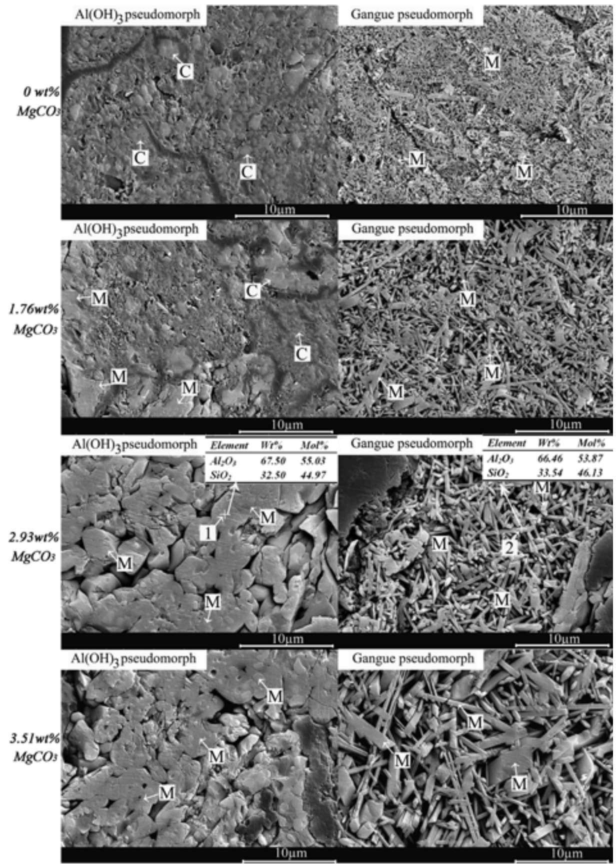

Fig. 1. Mullite shapes in pseudomorphs and EDS analysis of samples (with different $MgCO_3$ addition) sintered at 1500 °C. C, corundum; M, mullite.

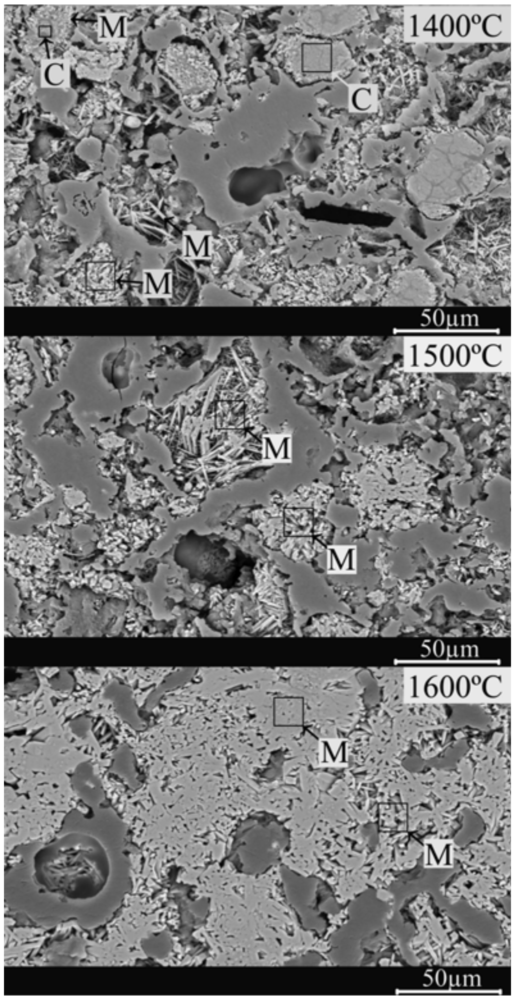

Fig. 2. Mullite shapes of samples (containing 2.93 wt% $MgCO_3$) sintered at different temperatures. C, corundum; M, mullite.

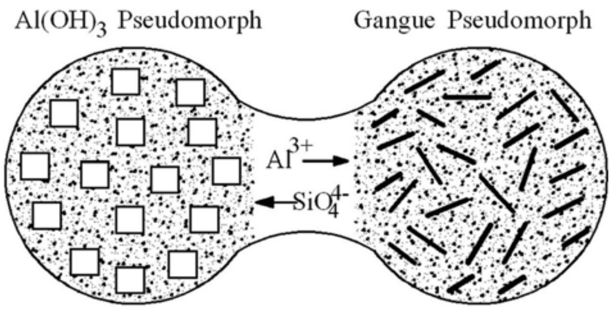

Fig. 3. Sketch map of the reaction between kaolinite and $Al(OH)_3$ pseudomorphs.

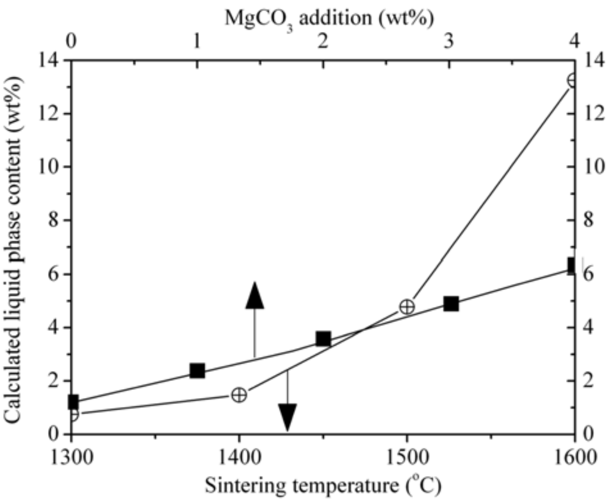

Fig. 4. Variations of liquid phase content with $MgCO_3$ additions (at 1500 °C) and sintering temperature (containing 2.93 wt% $MgCO_3$).

Conclusions

Granular and needle-like crystal coexisting in mullite prepared from $Al(OH)_3$ and kaolinite gangue were observed. The granular mullite crystals were in $Al(OH)_3$ pseudomorphs but the needle-like mullite crystals were in gangue pseudomorphs. The two different mullite crystal shapes retain the original shape of Al_2O_3 and primary mullite crystallites in pseudomorphs, because the formation and growth are based on the Al_2O_3 crystallites which are granular in $Al(OH)_3$ pseudomorphs and the primary mullite crystallites which are needle-like in gangue pseudomorphs. With increases in sintering temperature and the addition of $MgCO_3$ the differences of shape of mullite crystals become small.

Acknowledgements

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