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Mechanism of mechanical–chemical synergistic activation for preparation of mullite ceramics from high-alumina coal fly ash

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ABSTRACT

High-alumina coal fly ash (HAFA) is a special solid waste due to the existence of more than 45% alumina and 35% silica, which can be applied to prepare Al-Si series ceramics if the impurities can be removed and the Al/Si mass ratio can exceed 2.55 (Mullite: $3Al_2O_3.2SiO_2$). In this work, a new mechanical–chemical synergistic activation–desilication process is proposed, and the contents of different impurities can be lowered up to less than 1%, and the Al/Si mass ratio can be elevated from 1.26 to 2.71. Especially, the mechanism of this process is investigated in detail. The analysis of the mechanism shows that the decrease of $Q^4(3Al)$ and the increase of $Q^4(0Al)$, $Q^4(1Al)$, and $Q^4(2Al)$ improve amorphous silicate reactivity through synergistic activation, and the exposed amorphous Si-O-/Si-O-Si can be removed by OH- during the desilication process (desilicated ratio > 55%), which help the fine mullite to exhibit excellent properties (bulk density > 2.85 g/cm^3, apparent porosity < 0.5%) during the sintering process. Finally, this process not only decreases the pollution but also alleviates the shortage of Al/Si resources and promotes the clean development of coal-fired power generation.

1. Introduction

High-alumina coal fly ash (HAFA), which consists of silicon-aluminium glass, mullite, corundum, unburned carbon residue and little impurities, is generated mainly by coal-fired power plants in Inner Mongolia, China. Approximately 30 million tons of HAFA is emitted annually [1], which can not only cause serious pollution of water, atmosphere, and soil [2–4] but also prevent the clean development of coal-fired power generation. On the other hand, it is regarded as a special resource because this material contains 40–50% alumina, 35–45% silica, and a small amount of Ga/Li [5,6]. At present, HAFA is widely used to produce building materials [7–9] and to extract alumina [10–12]. The preparation of Al-Si series ceramic [13–16] is investigated recently with its increasing demand because of the characteristic of composition and mineral phase, which not only alleviates the scarcity of bauxite but also resolves the environmental problems. However, a low Al/Si (Al_2O_3/SiO_2) mass ratio (approximately 1) and the existence of impurities play a negative role on the quality of HAFA [17,18]. Therefore, the deep removal of amorphous silica and impurities is necessary.

Biological process, physical mineral process and chemical treatment are the main methods during the desilication process [19]. During the biological desilication, bacteria and fungus are used to decompose the aluminosilicate in bauxite. Groudeva's results [20] show that bacillus circulans can decompose the aluminosilicate of different bauxite efficiently, and the desilicated ratios range from 12.5%~73.6%. Selective grinding [21], gravity separation [22] and flotation [23] are the main physical desilicated methods for the bauxite. Wei's investigation [24] indicates that the Al/Si ratio of bauxite can be elevated to above 6.2 according to its special hardness / density and surface properties between Si-rich minerals and Al-rich minerals. Alkali dissolution and high temperature roasting are the main chemical treatment. Li's results [25] show that the Si-rich minerals (kaolinite) in bauxite is transferred to amorphous phase under 1050–1100 °C, which can be dissolved easily in the alkali solution, and the desilicated ratio reaches to 55.61%. In the above three methods for bauxite, physical mineral process and chemical treatment have been applied in the alumina extraction from bauxite. However, the physical mineral process cannot be applied in the desilication of HAFA due to its encapsulated structure and homogeneity of physical properties. Therefore, chemical treatment is the best method for the desilication of HAFA.

In the traditional predesilication process, the amorphous silicate is

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dissolved in dilute alkali solution due to its high reactivity, but the Al/Si mass ratio is only elevated to 1.70 approximately [26–28]. In terms of the low Al/Si mass ratio and high content of impurities in HAFA, lots of mechanisms have been investigated. Du [29] has studied the thermodynamic stability of amorphous silica and sodalite, and the results show that the standard Gibbs energies of reaction between NaOH and amorphous silica(ΔG^0_{AS}) under low temperature (< 100 °C) is negative value, which indicate its high reactivity. But theΔG^0 of sodalite formation in dilute alkali solution is lower thanΔG^0_{AS}, which prevent the deep desilication. He [30] and Liu [31] has investigated the kinetics study of predesilication reaction, and the results indicate that the predesilication process follows a shrinking unreacted core model of decreasing particle size. The apparent predesilication reaction rate in the earlier stage is predominantly controlled by chemical reaction, and its rate in the later stage is controlled by internal diffusion. Therefore, in order to avoid the formation of zeolite and promote the desilication rate, a new synergistic activation (milling–acid activation)–deep desilication–formation–sintering method to prepare mullite ceramics is proposed [32], and the amorphous silica and impurities are removed efficiently. However, the mechanisms of synergistic activation and deep desilication have not been investigated in detail, which plays a positive role on the improvement of technology.

In this work, based on the previous study, the reaction model is established, and the changes of coordination bond, pore structure, mineral phase, morphology, and the occurrence regularity of elements and phases in the whole process have been studied to reveal the mechanism.

2. Materials and methods

2.1. Materials

Analytical regents were hydrochloric acid (Beijing Chemical Works, 36 wt%–38 wt%) and NaOH (Beijing Chemical Works, > 96 wt%).

HAFA was generated from the coal-fired power plant in Inner Mongolia, China.

2.2. Experimental

The experimental process is shown in Fig. 1. HAFA was milled in order to diminish the particle size and destroy the structure of encapsulation in the milling activation process. The impurities in the mechanical activated HAFA (MHAFA) were leached with hydrochloric acid, and the active Al in the aluminosilicate glass phase was also leached in order to increase the reactivity of amorphous silicate. The acid treated HAFA (CHAFA) was mixed with alkali solution in order to leach the amorphous silicate absolutely. The fine mullite grains in desilicated HAFA (DHAFA) are grown to rod-like mullite by agglomeration. All the above processes have been optimized [32], and the optimal conditions are presented as follows:

The reduction of HAFA particle size was performed by ball milling using the planetary ball mill and steel ball as grinding media. The constant parameters were considered as following: pulp concentration: weight ratio between the HAFA and the grinding media used with a constant value of 1.20; rotation rate: 300 r/min; milling time: 120 min. After the milling process, the particle size (d90) is decreased from 170 μm to 11 μm approximately.

Hydrochloric acid leaching of the milled HAFA was carried out under the optimal following conditions: T = 80 °C, L/S = 5, t = 90 min, C = 6 mol/L. After the acid treatment, the samples are washed by deionized water. The reactivity of acid treated HAFA can be analyzed by efficient desilicated ratio (EDR) [32] under the determined conditions: T = 80 °C, L/S = 20, alkali concentration: 1 mol/L, t = 3 min. The leaching ratios of active Al and Fe can reach to 2.5% and 55%, which leads to a high reactivity of amorphous phase (EDR > 11%).

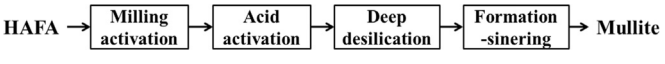

Fig. 1. Schematic diagram.

CHAFA was reacted with alkali solution to remove the amorphous silicate. The desilicated ratio is considered as an important parameter, which can achieve to 60% under the optimal following conditions: T = 90 °C to 95 °C, L/S = 5, C = 5.5 mol/L, t = 90 min.

2.3. Characterization

Chemical composition was examined by an X-ray fluorescence spectrometer (AXIOS-MAX, 50kv, 60 mA). The phase compositions of the sintered samples were examined with an X-ray diffractometer (Empyrean, CuKα, 40 kv, 40 mA) in a 2θ range from 5° to 90°. The concentration of ions was determined using inductively coupled plasma optical emission spectrometer (Thermo Fisher Scientific, iCAP 6300), which ranges from 165 nm to782nm in wavelength (± 0.1 nm). The morphology of the samples was detected by a scanning electron microscope (SEM, FEI MLA Quant 250) under the BSE model at an acceleration of 25 kV. Compositions of different regions on the sample were analyzed by energy-dispersive X-ray spectroscopy (EDS, EDAX). The analyzed samples were mixed with resin (samples: resin = 1:15) for 24 h at the room temperature, and then were grinded and polish on the optical polishing lathe. The particle size was analyzed by Malvern Mastersizer Hydro 2000MU (Malvern Instruments Ltd.).

N_2 adsorption was measured using Quantachrome Autosorb-1 at 77 K. Each sample was degassed under vacuum at 573 K for 3 h before measurement. The specific surface areas were calculated from N_2 adsorption data that ranged from P/P0 = 0.05–0.30 according to the BET method. Pore size distributions were obtained by analyzing the desorption branch according to the Barrett–Joyner–Halenda method.

The solid-state ^{29}Si MAS NMR spectra of the powders were obtained on Bruker AVANCEIII 400 (PROBHD 4 mm MAS BB/BB), with a zirconia sample cell of 4 mm o.d. and pulse program of HDPEC with a relaxation delay of 5 s. The resonant frequencies of H and Si are 399.16 and 79.30 MHz, respectively. The 29Si chemical shifts are referenced to Q8M8 (trimethylsiyl, d(29Si) = 11.72 ppm). Deconvolution of the 29Si MAS spectra was performed using the Origin85 software.

The distribution of different elements in HAFA is analyzed by electron microprobe (JEOL, JXA-8230, 20 kV, 20 nA), and the beam spot diameter is 5 μm. The analytical error of the sample is 1% approximately.

2.4. Properties of HAFA

The chemical compositions of different treated HAFA are shown in Table 1, and the physical properties, and mineral phases of HAFA are shown in Table 2 and Fig. 2.

Mullite/corundum and amorphous aluminosilicate are the main phases in HAFA (Fig. 2). The bulge between 10° and 30° indicates the amorphous phase. The combustion temperature when high-alumina coal is burned in a pulverized coal-fired boiler is approximately 1300 °C, which is equal to the formation temperature of mullite. Thus, a large amount of mullite is formed from aluminium and silica in high-alumina coal. Amorphous-phase materials are wrapped on the mullite surface because of quenching. Table 1 shows that the contents of Al_2O_3

Table 1
Chemical compositions of high-alumina coal fly ash (wt%).

Sample	Al_2O_3	SiO_2	Fe_2O_3	CaO	Na_2O	MgO	TiO_2	LOI
HAFA	50.64	40.21	1.97	2.51	0.00	0.00	3.27	2.78
AHAFA	48.17	47.42	0.84	0.52	0.00	0.00	1.02	2.95
DHAFA	69.61	25.64	0.73	0.29	0.00	0.00	2.71	3.88