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Synthesis and alumina leaching mechanism of calcium sulphoaluminate

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Abstract: Calcium sulphoaluminate ($3CaO\cdot3Al_2O_3\cdot CaSO_4$, abbreviated as C_4A_3S) was synthesized by sintering at 1375 °C for 2 h with analytically pure carbonate calcium, alumina and dihydrate calcium sulfate. The crystal structure of C_4A_3S was characterized by XRD, SEM and TEM. Alumina leaching properties in Na_2CO_3 solution were studied, and the leaching mechanism was investigated by means of Raman spectrum and XRD. The results show that C_4A_3S has porous morphology. The polycrystallines and single crystals coexist in C_4A_3S and grow along different directions. The alumina leaching rate of C_4A_3S is 98.41%, which is higher than that of $12CaO\cdot7Al_2O_3$ under the optimal condition. The aluminum and sulfur elements exist in the leaching solution in the form of $Al(OH)_4^-$ and SO_4^{2-}, respectively, and the calcium exists as $CaCO_3$ in the leaching residues.

Key words: calcium sulphoaluminate; synthesis; alumina; leaching

1 Introduction

With the continuous improvement of the global industrial production, alumina industry has been rapidly developed [1]. The alumina production of China increased to 5125 million tons in 2014 from 700 million tons in 2004 [2]. The ore grade decreases because of the sharp and increasing demand of bauxite. It’s meaningful to study the use of non bauxite resources (such as red mud, fly ash, and iron-bearing bauxite) in the production of alumina [3]. So, the comprehensive utilization of the low grade ore, fly ash and solid waste has become research hotpots [4−7].

At present, for low grade ore, red mud and fly ash whose A/S (Al_2O_3/SiO_2, mass rate) is less than or equal to 3, the lime sintering method has many advantages, such as high alumina leaching rate, low level of secondary reaction, dry sintering process without alkali [8,9]. The main aluminum phase of lime sinter process is $12CaO\cdot7Al_2O_3$ whose alumina leaching property is excellent [10]. However, it also owns a lot of shortcomings, such as large consumption of calcium oxide, large material flow, considerable amount of slag, and small burning temperature range. Based on our previous study, the alumina leaching rate can reach 95% in the process of treating fly ash with lime sintering process, but the main phase of the clinker is C_4A_3S but not $12CaO\cdot7Al_2O_3$, which is consistent with the research of GOODBOY [11]. He found that C_4A_3S clinker has a good alumina leaching property. It substitutes $12CaO\cdot7Al_2O_3$ as the main phase while the C/A (molar rate between CaO and Al_2O_3) decreases from 1.71 to 1.33, and a high alumina leaching property is achieved under the condition of low calcium and aluminum. The source of sulfur of the process is calcium sulfate, which is the desulfurization residue obtained during the burning of pulverized coal. Therefore, it is very important to study the synthesis and the alumina leaching of C_4A_3S. At present, the researches on C_4A_3S are mainly focused on the cement, because C_4A_3S is the main component of the sulfate cement clinker and it has a fast hydration and good sulfur retention characteristics [12−14]. The formation of C_4A_3S is hindered with the increase of the concentration of additives, such as P_2O_5 and Cr_2O_3 [15]. The use of phosphorus gypsum can significantly reduce

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the temperature and time of the formation of C_4A_3S compared with the use of gypsum [16]. LI et al [17] found that the optimal temperature range of formation of C_4A_3S with C_3S and $CaSO_4$ was 1150−1350 °C, and the corresponding optimum holding time was 1−6 h. It was also found that the holding time decreased with the increase of the sintering temperature. The reaction equation is

$$3Ca_3Al_2O_6+CaSO_4 \longrightarrow Ca_4Al_6O_{12}(SO_4)+6CaO \quad (1)$$

The formation mechanism [18] and the thermodynamics [19] and kinetics of C_4A_3S [20] were researched, and the formation reaction of C_4A_3S was determined as

$$CaSO_4+3CaO+3Al_2O_3 \longrightarrow 3CaO\cdot3Al_2O_3\cdot CaSO_4 \quad (2)$$

Therefore, the researches on the formation and hydration of C_4A_3S are widely reported, but the alumina leaching properties and mechanism are rarely reported. In order to eliminate the influence of other impurities, the pure C_4A_3S was synthesized by adding calcium sulfate as the source of sulfur in this work. The structure of C_4A_3S was characterized, and the alumina leaching behavior and mechanism were studied to provide a theoretical basis for the treatment of low sulfur grade raw materials with lime sintering process.

2 Experimental

2.1 Materials

The synthesis experiment of C_4A_3S was carried out with the analytically-pure reagents of carbonate calcium, alumina and dihydrate calcium sulfate.

The alumina leaching solution was prepared by analytically pure reagents of sodium carbonate and sodium hydroxide solution.

2.2 Experimental apparatus

Experimental apparatus: KSL-1700X-A2 box type high temperature sintering furnace, thermostatic water bath, SFM-1 planetary ball mill, planet type mixer.

Analytical apparatus: D/MAX-2500 X-ray diffraction analyzer of Rigaku made in Japan, S-4800-I scanning electron microscopy (SEM) of HITACHI made in Japan, JEM-2100 transmission electron microscopy (TEM) of JEOL made in Japan and Nicolet 6700 FT-Raman modules of Thermo Fisher made in America.

2.3 Synthesis of C_4A_3S

According to the formula of C_4A_3S, analytically pure carbonate calcium, alumina and dihydrate calcium sulfate were weighed at the rate of 3:3:1. They were mixed in the planetary mixer at the speed of 130 r/min for 2 h. The mixed material was sintered for 2 h at 1375 °C and then was taken out when the temperature below 200 °C. After sintering process, a portion of the sintered clinker was ground to less than 200 meshes (≤74 μm) for the use of XRD analysis and alumina leaching in the SFM-1 planetary ball mill at the speed of 250 r/min for 1 h. The scanning angle of XRD ranged from 10° to 80°, and the scanning speed was 2 (°)/min. Another part of the sintered sample was polished, corroded, sprayed with gold, and scanned by the SEM.

2.4 Alumina leaching of C_4A_3S

The leaching experiments of clinker were carried out in the constant temperature water bath, using flask as leaching container which was connected with the circulating cooling water. The experiments were performed under the following conditions: carbon alkali concentration (N_C) was 80 g/L, caustic concentration (N_K) was 10 g/L, leaching temperature ranged from 60 to 90 °C, leaching time ranged from 5 to 30 min, liquid to solid rate (L/S) was 10, and stirring speed was 400 r/min. The content of Al_2O_3 in the filtrate was analyzed by EDTA titration, and the content of SO_4^{2-} was analyzed by Barium sulfate gravimetric method. The alumina leaching rate was calculated according to

$$\eta_{AO}=\frac{C_{ls}\cdot V_{ls}-C_{cl}\cdot V_{cl}}{m\cdot w} \quad (3)$$

where C_{ls} is the alumina content in leaching solution, g/L; C_{cl} is the alumina content in correction liquor, g/L; V_{ls} is the volume of leaching solution, L; V_{cl} is the volume of correction liquor, L; m is the mass of C_4A_3S, g; w is the alumina mass fraction of C_4A_3S.

3 Results and discussion

3.1 Synthesis of C_4A_3S

A part of the sintered sample was analyzed by XRD. The XRD pattern is shown in Fig. 1. Another part of the sintered sample was scanned by the SEM. The result is shown in Fig. 2.

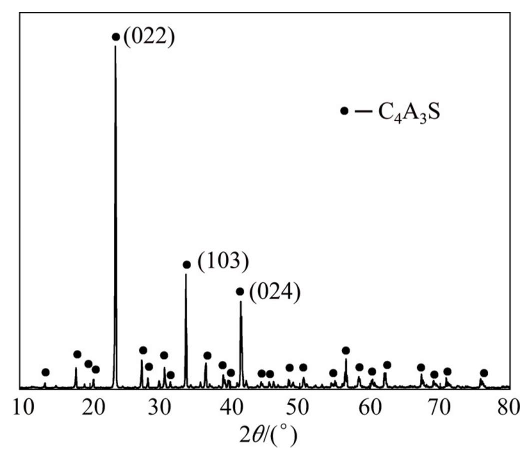

Fig. 1 XRD pattern of sintering clinker at 1375 °C for 2 h