



Roles of impurities on sintering structure and thermal strength of CaO-containing carbon pellet and the CaO sintering kinetic analysis

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ABSTRACT

CaO containing carbon pellet (CCCP) for calcium carbide production was proposed in this work. The occurrence of impurities in both pulverized char and carbide slag is normally inevitable. This study is to examine the effects of the inorganic oxides on the microstructure and thermal strength of CCCP. Three different CCCPs of Ca(OH)₂ + raw char (CRC), carbide slag + raw char (CSRC) and Ca(OH)₂ + demineralized char with various impurities were prepared for the purpose of comparison. The results showed that the order of thermal strength of three kinds of CCCPs was as follows: Ca(OH)₂ + raw char (CRC) > carbide slag + raw char (CSRC) > Ca(OH)₂ + demineralized char (CDC). Four kinds of oxides (i.e. SiO₂, Al₂O₃, Fe₂O₃ and MgO) as impurities could all possibly react with CaO to form low-melting eutectic matters to different extents, thus resulting in the decrease in the stability of CaO pellet. The presence of CaF₂ in the demineralized char has caused over-sintered CaO grains and reduced the thermal strength of CDC. Meantime, the isothermal and non-isothermal experiments have revealed that the CaO grain sintering process could be well expressed by the model of “porous body sintering”.

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1. Introduction

To alleviate the problems related to the discharge of carbide slag, a technology process using the carbide slag to prepare CaO containing carbon pellet (CCCP) for calcium carbide production was recently proposed [1], as is shown in Fig. 1. CCCP was prepared by co-molding the pulverized char and purified carbide slag in order to partially substitute for pure CaO for calcium carbide production in a submerged arc furnace system where the bulky CaO and char (5–30 mm) particles are fed through a moving bed reactor. The submerged arc furnace, a kind of traditional “moving-bed” reactor, required the bulky char and CaO particles to have sound thermal strength at high temperatures, so that the permeability among the large particles in the moving bed could allow the CO and other gases to travel through the bed materials without creating high back pressure [2]. Therefore, the newly-developed CCCP must hold satisfied thermal strength for being possibly used in the current arc furnace system featuring moving bed reactor.

Impurities in CCCP can come from both pulverized char and carbide slag, and the impurities originally in char and natural limestone might migrate into the recycled carbide slag. After the co-molding process of carbide slag and pulverized char, various mineral matter particles and Ca(OH)₂ particles together could form low-temperature eutectic matters during the calcination process [3]. Consequently, the stability of CCCP would be significantly reduced by the eutectic matters with low-melting points, resulting in the decrease in the thermal strength of CCCP.

According to our previous results, Ca₂(PO₄)₃ produced from Ca(OH)₂ and H₃PO₄ reactions could improve the sintering degree of CaO particles [4], thus increasing the thermal strength of CCCP. However, extremely high contents of Ca₂(PO₄)₃ could play negative roles on the thermal strength of CCCP by over-sintering CaO particles [1]. The impurities in the pellets may directly (e.g. forming eutectic matters) and/or indirectly (e.g. interrupting the sintering process) affect the thermal strength, for which the exact reasons still remain unknown.

The strength of a pellet is dependent on interface structures among particles; therefore it is desirable to study the effects of impurities on the interface structure of particles. The two main components (char and CaO particles) in CCCP have very high melting points. Because char and CaO are not mutually soluble materials, CaO (melting point 2570 °C) was the main sintering body in the mixture. And the thermal strength of CCCP mainly depended on the CaO sintered structure/

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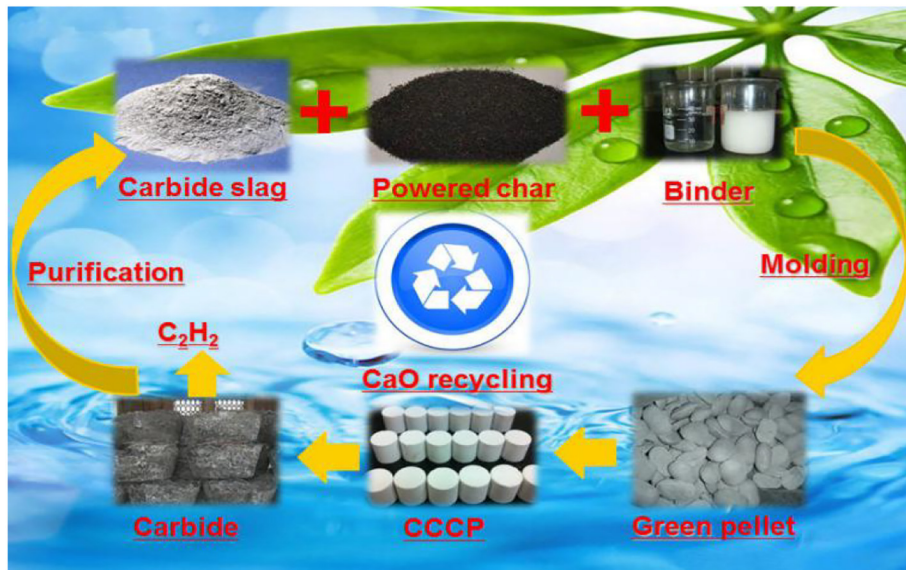


Fig. 1. Proposed utilization process of carbide slag and char powers.

degree. The pulverized char as part of CCCP would be involved in the CaO sintering processes, hence affecting the eventual thermal strength of CCCP.

CaO sintering in CCCP belongs to the category of “solid sintering process” [5] that consists of three continuous stages based on the observation on the grain growth and pore evolution [6]. Firstly, the initial sintering necks among the particles started to form and grow while the shrink of particles led to the increase in density of the sintered body [7,8]. During the second stage, the sintering neck continued to grow, and the pores formed due to the gas release created the boundary structures surrounding the grains. The grain boundary might then move around inside the CCCP body because of the phenomena of crystal diffusion [9,10], resulting in the gas pore coalescence and forming the solitary pore structure. The sintered body became further densified, and the relative density reached 90%. At the third stage, the sizes of sintered grains were clearly larger than the first and second stages, and the relative density could reach as high as 95% [11].

Some impurities in the char and/or CaO may hinder the migration of grain boundary by pinning effects during the sintering process, which could suppress the grain growth, refine the grain size, and thus possibly improve the strength of sintered body [11]. At the same time, the existence of second phase due to the impurities also potentially inhibited the growth of grain boundary [12,13].

Generally, the smaller grain size for sintered body is, the higher strength of sintered material is. When grain size is very small, it would require high forces to fracture the inter-granular structure [14]. The high strength shown by the small grains essentially resulted from the increase in the amount of sintering necks [15]. The controlling growth of CaO grains is thus very critical for improving the strength of pellets, especially for the thermal strength.

According to Brook model for grain growth kinetics [16,17], the growth of grains can be expressed by the following equation at constant temperatures:

$$G^n - G_0^n = Kt \quad (1)$$

where, G and G_0 were grain sizes at time t and 0, respectively. According to different diffusion mechanisms, the range of n value was changing from 1 to 4. For the kinetic constant $K = Ae^{(-\frac{Q}{RT})}$, A was the ratio constant related with atom transition, and Q was the apparent activation energy of grain growth. T and R were kelvin (K) degree and gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) respectively.

When n is 2, the driving force of grain growth is the chemical gradient resulted from the curvature radius of grain boundary, belonging to the classic growth kinetics. The relation between the rate of growth (dG/dt) and radius can be expressed as following:

$$\frac{dG}{dt} = \frac{k}{G} \rightarrow G^2 - G_0^2 = \frac{k}{2}t \quad (2)$$

where, G_0 was the grain size at the initial stage ($t = 0$); when $G \gg G_0$, G^2 was proportional to time t .

When the pore hindered the growth of grain, the growth kinetic process consisted of two phases, that is, grain and pore [18], belonging to the porous body sintered kinetic model where the value of n is 3 [19]. The migration rate of pore was inversely proportional to the pore size (r) that was in positive relationship with the grain size (G), as following:

$$\frac{dG}{dt} = \frac{k}{G} \times \frac{k'}{r} = \frac{k}{G} \times \frac{k''}{G} \rightarrow G^3 - G_0^3 = \frac{kk''}{3}t \quad (3)$$

When $G \gg G_0$, G^3 was proportional to time t . The sintering process in CaO pellet for this study was examined by using the sintered kinetic model mentioned above.

Although carbide slag or char was purified by using various physical methods [20,21]. The impurities would be never completely eliminated. The impurity could hinder the sintering of CaO particle [22] as well as improve the hydration resistance of CaO-ceramics [23], thus affecting the structure and strength of CaO pellets. This work is to examine the effects of the impurity contents and types on the microstructure and thermal strength of CCCP, especially for the change in sintered structure. The sintered kinetic model for CaO grain growth in pellet was also studied.

2. Experimental

2.1. Samples

The pulverized char (1–100 μm) and carbide slag (1–110 μm) were from Inner Mongolia Province. To reduce mineral matters from the pulverized char and carbide slag, the char was washed by a mixed acids (HCl and HF mixture) [24], while the carbide slag was purified by a water cyclone [20,21]. Finally, the two kinds of materials after being demineralized were dried for 12 h at 100 $^\circ\text{C}$ before use, and their chemical compositions were listed in Tables 1 and 2. Ash (from char oxidation at low temperature) and carbide slag compositions were characterized

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