Research Article

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Evolution of physicochemical properties of quick lime at converter-smelting temperature

Abstract: The volume stability caused by the hydration of f-CaO is one of the main obstacles to the comprehensive utilization of steel-making slag. In view of the f-CaO produced by incomplete dissolution of lime, it is necessary to strengthen the dissolution behavior of lime in the converter process. The reactivity of lime determines the dissolution efficiency and is closely related to its microstructure. The experimental results show that the reactivity and porosity of quick lime decrease and the average diameter of pore increases with an increase in temperature. The CaO crystals gradually grow up under the action of grain boundary migration. When the temperature increased from 1,350 to 1,600°C, the lime reactivity decreased from 237.60 to 40.60 mL, the porosity decreased from 30.55 to 15.91%, the average pore diameter increased from 159.10 to 1471.80 nm, and the average CaO particle size increased from 0.33 to 9.61 µm. The results indicate that reactivity is decreased because of the deformation and growth of CaO crystals and the decrease in porosity in reactive lime. This will cause an obstacle to the dissolution of lime and is not conducive to the control of f-CaO in slag.

Keywords: quick lime, reactivity, CaO crystal, porosity, f-CaO

1 Introduction

The steel-making slag is an inevitable product of steel production, which accounts for about 15–20% of steel output [1]. About 90% of steel enterprises conduct production in a long process dominated by blast furnace-converter, which supports China’s large-scale steel production [2]. China is a big steel output country, with an annual output of 900 million tons of crude steel and 100 million tons of steel slag in 2018. In view of protecting the environment, reducing pollutant emissions, and promoting ecological progress, the environmental protection tax law of the People’s Republic of China was adopted on December 25, 2016 and implemented on January 1, 2018. It stipulates that smelting slag, fly ash, slag, and other solid wastes (including semi-solid and liquid wastes) shall be taxed at 25 yuan per ton. However, the environmental protection tax will be temporarily exempted if the taxpayer’s comprehensive utilization of solid waste meets national and local environmental protection standards. It is imperative to enhance the utilization of steel slag.

The obstacles to the comprehensive utilization of steel slag are mainly the disintegration caused by the crystal transformation of dicalcium silicate, the volume instability caused by f-CaO hydration, and the dissolution of heavy metal elements, among which the influence of volume instability is the most important [3,4]. The lime is the most important slag-making raw material for the steel-making process. The particle size of lime is generally 10–50 mm, and the addition amount is 20–40 kg/t. The mass content of CaO in steel slag is about 40%, and there are some white or brown spot-like substances in slag, namely f-CaO, which will cause volume instability because of digestion and dissolution of alkali metal ions [5–7]. On the basis of the testing results of 28 converter-slag samples obtained from 25 iron and steel enterprises in China, Xu and Huang [8] found that f-CaO existed in slag in two different forms: one is that f-CaO distributed around dicalcium silicate with a size of about 50 µm, which is derived from incompletely dissolved reactive lime; the other is that the f-CaO covering the calcium
The silicate phase, with the size of about 5 µm, which is derived from the decomposition of the calcium silicate during the high temperature cooling process of slag. The f-CaO produced by the decomposition of tricalcium silicate can be controlled by adjusting the cooling mode of steel slag. However, for the larger size of f-CaO because of incomplete dissolution of lime, it is necessary to enhance the dissolution behavior of lime in the converter process. Therefore, the study on the fast dissolution of lime in slag has been widely researched. The dissolution rate of lime is not only affected by the composition of slag, but also controlled by the properties of lime itself [9].

The slagging process is determined by the reactivity of lime, whereas the reactivity is closely related to its microstructure. When the quick-lime particles are charged into a converter, a dense layer of $2\text{CaO} \cdot \text{SiO}_2$ is formed quickly on the surface of the lime particles and continuously or intermittently covered the lime particles. It will impede the further dissolution of the lime [10–13]. If the lime wrapped in $2\text{CaO} \cdot \text{SiO}_2$ layer cannot be dissolved further for a long time at the steel-making temperature, the internal structure will change subsequently. Thus, the dissolution behavior of lime will be affected. The evolution behaviors of both reactivity and microstructure of the quick lime calcinated at different temperatures were investigated in this paper to reveal the relationship between the size of CaO crystal and the lime reactivity.

2 Experiment

2.1 Raw materials of limestone

The raw material used in this experiment is limestone provided by a large steel enterprise in China, which is calcined to a quick lime in the laboratory. The composition of limestone was determined by XRF analysis. As shown in Table 1, the limestone contains 98.55% CaCO$_3$ and a small amount of MgO, SiO$_2$, and other components. Combined with the analysis results of the limestone X-ray diffractometer (type PHILIPS-Xpertpro) (Figure 1a), calcite (CaCO$_3$) is the only mineral phase. The microstructure of limestone was observed by scanning electron microscope (SEM, Zeiss-ASIN EVO10, Zeiss, Germany). As shown in Figure 2, limestone mainly consists of CaCO$_3$ crystal with obvious crystal structure, which is about 10 µm in size.

2.2 Preparation of the quick-lime samples

The preparation of reactive lime was divided into the crushing process and the limestone calcination. The limestone was broken with a jaw crusher, and 20–25 mm limestone particles were sifted out with a sieve. The remaining large blocks of limestone were further broken to make full use of the raw materials. The broken limestone particles were washed with water and dried in an oven at 200°C for 3 h. The cooled samples were placed in a dried vessel for

| Table 1: Chemical composition of limestone, wt% |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| SiO$_2$         | Al$_2$O$_3$     | Fe$_2$O$_3$     | CaO             | MgO             | CO$_2$          |
| 0.35            | 0.47            | 0.10            | 55.24           | 0.19            | 43.65           |

Figure 1: Mineral compositions of the raw materials. (a) Lime obtained at 1,350°C for 10 min and (b) limestone.

Figure 2: Microstructure of limestone sample.
For the calcination of limestone, 100 g of clean limestone particles (20–25 mm) were charged in the basket (diameter 50 mm, height 75 mm) made by molybdenum wire (φ 0.5 mm). When the furnace temperature was up to 1,350°C under the atmosphere of high purity N₂, the basket was put into the carbon-tube furnace. After holding for 10 min, the sample was taken out of the furnace using a molybdenum wire hook. The obtained lime (L0) was placed in a clean metal container and cooled to room temperature. Then it was put into an airtight container with desiccants.

The heating system used for sample preparation is a carbon-tube furnace (25 kW, 1,650°C), the cover and bottom parts of which are water-cooled, and the middle part is made of refractory materials. A double platinum-rhodium thermocouple is equipped to monitor the temperature in the furnace [14–16]. The high purity N₂ was introduced into the carbon-tube furnace as a protective gas to avoid the oxidation of carbon pipe, and the decomposition of limestone can be promoted because the CO₂ generated by the decomposition process was taken away by N₂.

According to the test results, the reactivity degree of the L0 is 346.20 mL, which is high quality reactive lime. According to Figure 1b, the calcined products are mainly composed of CaO and contain a small amount of undecomposed CaCO₃. According to the microscopic morphology of the calcined products (Figure 3), the quick lime is mainly composed of cubes with particle size of 3–5 µm, which consist of smaller CaO crystals, about 0.22 µm. The interior of crystals is loose and porous with a porosity of 36.09%. The pore diameter is small, with an average pore size of 94.90 nm.

2.3 Heating procedure of quick lime and analytical methods

The 100 g lime sample is put into a basket (diameter 50 mm and height 80 mm) made by molybdenum wire (φ 0.5 mm). After the carbon tube furnace is heated to the target temperature (1,350, 1,400, 1,450, 1,500, 1,550, and 1,600°C) under the atmosphere of high purity N₂, the basket containing samples was put into the isothermal zone of the furnace for 25 min, and then directly taken out from the furnace. The samples were placed in a metal plate for air cooling to room temperature and collected. The corresponding sample number was L1–L6.

The reactivity of samples was determined according to YB/T105-2005. The microstructure of the samples was observed by an SEM (German Zeiss, Zeiss-ASINEVO10), and the configuration of spectrometer (EDS, OxfordX-Max80) was used to determine the composition of microzone. X-ray diffraction (X-ray powder diffractometer, Dutch PANalytical analysis instruments, XPertPRO MPD) was used to determine the mineral phases. The porosity and average pore size of the samples were determined by mercury injection instrument (AutoPoreIV9510), and the mean particle size of the CaO crystal was determined by IPP software (image-proplus6.0). The maximum pressure of the mercury injector is 414 MPa, and the aperture measurement range was 0.003–1,000 µm.

3 Results

3.1 Microstructure of heat-treated lime

According to the XRD analysis results of the samples (Figure 1a), the reactive lime raw material L0, which had been calcined at high temperature, was composed of calcite (CaCO₃) and calcium oxide (CaO), and CaO is the dominant mineral of L0. However, when samples were treated at high temperature for 25 min (Figure 4), only CaO was detected by the XRD analysis. It was shown that the limestone was completely decomposed and the sample was only composed of CaO.

Combined with the microstructure of reactive lime raw materials L0 (Figure 3), it can be seen from the microscopic morphology of the samples (Figure 5) that the cube formed by the CaO microcylinder (CaO crystal) gradually disappeared after heat treatment. The cube structure still maintained in L1 sample, and only a small trace of the cube structure was retained in L2 sample. For the

![Figure 3: Microstructure of calcined lime.](image-url)
L3 sample, the cube basically disappeared, and the small CaO microcylinder gradually merged and grew. The cubes almost completely disappeared in the L4 samples and were replaced by adjacent CaO column, which had fused and grew up. The cubes completely disappeared in L5 and L6 samples, and the CaO columns evolved into large granular crystals.

The shape and size of the CaO column in the sample changed significantly with the increase in temperature. As shown in Figures 3 and 6, it can be seen that the long CaO-column in the quick lime (L0) gradually changed from thin strip to thick columnar, and finally to round CaO crystal through crystal fusion. The length of CaO column is about 0.5 µm and the average particle size is 0.22 µm in sample L0. At 1,450°C, the length of the CaO column is about 1–2 µm, and the average particle size increased to 0.87 µm. For the sample L6, the interface between some of the CaO columns gradually disappeared, and the shape of the CaO crystal changed from a strip to a pie with a diameter of 7–12 µm. At this time, the average particle size of the crystal was the largest, which was 9.61 µm.

The change in temperature has an important effect on the pore distribution and pore size of lime sample. As shown in Figure 3, the CaO column in L0 was dispersed with fine (average pore size 94.90 nm) and numerous pores, and the porosity is up to 36.09%. According to Figure 5(a), after treatment at 1,350°C for 25 min, the pores in the CaO column decreased (30.55%) and the pore diameter (159.10 nm) increased. When the temperature increased, the fusion between the poles was further strengthened, and the small pores merged into larger pores.

According to Figure 5(f), after the treatment at 1,600°C, not only the number of pores in sample L6 significantly decreased, but also the pore diameter significantly increased, with the average diameter up to 1471.80 nm. An aperture with a diameter of about 2,000 nm has been found in this field.

### 3.2 Properties of quick lime after heating treatment

The changes in lime reactivity, porosity, average particle size, and pore size distribution with heating temperature are shown in Figure 6. When the temperature increased, the lime reactivity decreased, but the decline rate was decreasing. After heating at 1,350°C for 25 min, the reactivity of the samples decreased from 346.20 to 237.60 mL. With an increase in temperature, the reactivity of the samples kept decreasing. When the temperature increased to 1,550°C, the lime reactivity further decreased to 42.50 mL, which is only 12.28% of L0. When the temperature increased to 1,600°C, the reactivity degree of lime was 40.60 mL (L6), slightly lower than that of L5 sample.

The porosity of the treated samples decreased with increase in temperature. The porosity of the active lime sample was 36.09% (L0), which was reduced from 36.09 to 30.55–15.91% respectively after heat treatment from 1,350 to 1,600°C. The porosity of sample L6 is only 44.08% of L0, as shown in Figure 6. It indicated that temperature has a significant effect on the pore diameter of lime sample. Combined with Figure 3, it can be seen that the L0 has dispersed pores with an average pore size of 94.90 nm. When the reactive lime was heated at 1,350°C for 25 min, the average pore size of pores in the sample increased to 159.10 nm. In addition, the average pore size gradually increased with the increase in temperature. When the temperature increased from 1,500 to 1,550°C, the average pore size of lime increased significantly. However, the increase amplitude decreases sharply when the temperature was higher than 1,550°C. When the temperature increased to 1,600°C, the average pore diameter in the sample further increased to 1471.80 nm, an increase of 1450.90% compared with the reactive lime L0. At the same time, temperature also has a great influence on the average particle size of CaO grains. The average particle size of CaO grains in sample L0 was 0.22 µm. When the temperature was 1,600°C, the average CaO grain size of the prepared sample L6 increased to 9.61 µm. The average particle size of L6 sample is 44 times that of L0 samples.
4 Discussions

The reactivity of quick lime is an important chemical property for application in ferrous metallurgy and also the main index to measure the quality. According to YB/T105-2005, the lime samples were crushed into 1–5 mm particles. Then 50 g particles were put into 40 ± 1°C deionized water (2,000 mL) with stirring device. The slaking reaction is a solid/liquid reaction and controlled by the porosity of the lime sample. According to Figure 6, when the temperature increased, the lime reactivity decreased from 346.20 to 40.60 mL, and the porosity maintained the

Figure 5: Microstructures of samples treated at different temperatures. (a) 1,350°C, 25 min; (b) 1,400°C, 25 min; (c) 1,450°C, 25 min; (d) 1,500°C, 25 min; (e) 1,550°C, 25 min; (f) 1,600°C, 25 min.
same trend, from 36.09 to 15.91%, whereas the change in porosity depends on the microstructure of the lime samples.

As shown in Figure 3, the CaO columns in sample L0 are adjacent to each other with a large number of pores with an average pore size of 94.90 nm. As shown in Figure 5, the microstructure unit of the lime sample, CaO crystal, also changed in shape and size with temperature changing. The microstructure of lime sample is changed through the grain boundary migration among the CaO crystals. As can be seen from Figure 5(a), the newly formed CaO grains are fine, curve, and have many grain boundaries, which mean that it has high grain boundary energy. As the lower the energy it has, the more stable it will be, the newly formed CaO grain will spontaneously reduce the grain boundary area, reduce its own energy and become more stable under the condition of high temperature calcination.

The schematic diagram of the growing process of CaO crystal is shown in Figure 7. CaO crystal is generated first on the surface of CaCO$_3$ crystal. The grains begin to fuse and gradually grow up, and then micropores appear (Figure 7(c)) with the calcining process going on. Subsequently, the original grain boundary of CaO gradually disappeared (Figure 7(d)), the shapes of CaO grains change from the initial thin strip to a round cake, and the pore size also increased. In the end, the round grains with a length and width of about 10 µm are formed, and pores with an aperture of 1–2 µm also appear at the same time. According to Figure 7(a)–(e), the original grain boundary completely disappeared, CaO grain continued to fuse and grow up, and a new grain boundary with lower energy is formed finally. The CaO grain boundary migration rate in the lime samples is controlled mainly by grain boundary migration driver during the heating process [17,18].

The microstructure of polycrystalline materials is mainly composed of grain and grain boundary. When the grain boundary is driven by a large enough force, the grain-boundary migration will occur, accompanied by the growth of grains and the shrinkage of adjacent grains. It means that the growth of grains is based on the consumption of adjacent grains, so as to realize the process of microstructures evolution of the recrystallization and grain growth. The essence of grain boundary migration is to shrink the lattice position of grain surface and break the atom away from the lattice to form a vacancy. The detached atom moves to the surface of the grown grain to form a new lattice and fill the vacancy on the surface of the grown grain.

The driving force required for the grain boundary migration is the free energy difference between adjacent grains on both sides of the grain boundary. When the free energy difference is large enough, the grain boundary will move toward the grain with large free energy. The grain with high free energy will gradually shrink in the process of grain boundary migration, whereas the grain with small free energy will gradually grow up. The free energy of the whole system reduces in the process of grain boundary migration. The driving force of grain boundary migration can be provided theoretically by the gradient of any thermodynamic variable (temperature, pressure, etc.) in a polycrystalline system. Grain boundary mobility is a quantitative characterization of grain boundary migration ability of the important performance parameters of the grain boundary.

As the driving force, the surface energy is used to provide the driving force for grain boundary migration by constructing a curved grain boundary and using the surface energy difference on both sides of the grain boundary. Based on the grain boundary migration, the relationship between the average grain size, heating time $T$, and the heating time $t$ is shown in equation (1) [19]:

$$R^2 = R_0^2 + tA_0 \exp \left( -\frac{\Delta H}{kT} \right).$$

where, $R_0$ is the average initial grain size before heating, $\Delta H$ is the activation enthalpy, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $A_0 = 4\gamma_b m_0$ is the generalized mobility constant, and $m_0$ is the mobility constant independent of temperature.

The equation (1) means that the particle size and calcination temperature of CaO crystal show an
exponential increase in trend. Because L0 was calcined for 10 min at 1,350°C, the sintering phenomenon was not serious. However, when calcination continued in the carbon-tube furnace, a large number of small CaO particles would subsequently migrate into crystallization. In the early stage of calcining, the temperature increases rapidly, and the grain boundary energy of CaO increases, whereas the average diameter of CaO is small. Therefore, the migration rate of grain boundary is large. The surrounding small particles of CaO grain are fused to grow up to consume the excess grain-boundary energy. The growth rate of CaO grain increased rapidly with the increase in temperature. As can be seen from Figure 5, at 1,350°C, CaO grain has many small grains that have not yet fused and grown. These are CaO grains generated by continued decomposition of undecomposed CaCO3. When the temperature rises to 1,600°C, the transmission speed of heat to the inside of the reactive lime becomes faster because of the high temperature. Thus, the CaO is generated from undecomposed CaCO3 at higher temperature, and its grain boundary energy is large and the average particle size is small. CaO growth rate is large simultaneously, and so it grows up immediately by fusing the surrounding small CaO particles. Then the small particles of CaO grain are eliminated, and grains grow into a pie shape, the length and width of which are about 10 μm. This explains the correspondence between the particle size and temperature of CaO crystal.

When the temperature increases, the reactivity and porosity of reactive lime decreased, whereas the average diameter of pores and the average particle size of CaO grain increased. When the temperature increased from 1,350 to 1,600°C, the lime reactivity degree decreased from 237.60 to 40.60 mL, the porosity decreased from 30.55 to 15.91%, the average pore diameter increased from 159.10 to 1471.80 nm, and the average CaO particle size increased from 0.33 to 9.61 μm.

The microstructure of reactive lime changed significantly with the change in temperature. The migration of grain boundaries between CaO crystals causes the growth of CaO crystals. With the increase in temperature, the size of CaO crystal increased exponentially, and the pores become larger because of diffusion and integration with the grain boundary migration. When the reactive lime sample was heated at 1,600°C for 25 min, the CaO crystals in the reactive lime grew from a cylinder with an average diameter of 0.22 μm to a cake with a diameter of 7–12 mm, and the average pore diameter changed from 94.90 to 2 μm.

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