Densification and Improvement of Slaking Resistance of Calcia Clinker by Addition of ZrO₂

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Key-words: Lime refractory, ZrO₂, Additive, Sintering, Slaking resistance

1. Introduction

Lime has long been considered to be an attractive refractory for application in metallurgical and ceramics industries because of the global abundance of limestone, as well as its advantages of high melting temperature, low vapor pressure, and thermodynamic stability in the presence of carbon.1)-3) However, the application of CaO as a refractory is inhibited due to the drawback that it is easily slaked when exposed to water vapor. As a principle subject in the application of CaO as a refractory, the prevention of slaking has been studied since the 1940s. In the manufacture of superpure steel, CaO refractory shows advantages of dephosphorization and desulfurization in secondary steelmaking, which led to studies on improvement of slaking resistance in recent years.4)-6)

To improve the slaking resistance of CaO materials, the adoption of other oxide additives is one of the simple methods available, and some oxides have proved effective for this purpose.7),8) The slaking resistance of CaO materials is usually improved by the promotion of densification via the formation of a liquid phase when some other oxides are doped, but the formation of low melting compounds deteriorates the refractory quality of CaO materials, which does not suit the requirement of high-temperature refining. Therefore, studies on improving CaO slaking resistance without significantly deteriorating the advantages of CaO refractory have become very important.

Since ZrO₂ does not form a low-melting-temperature compound with CaO,9) the advantage of the high refractory quality of lime could be retained if the slaking resistance of lime refractory can be improved by the addition of ZrO₂. This has constantly attracted researchers to study the addition of ZrO₂ for improving the slaking resistance of CaO refractory.10)-13) Owing to the various material conditions and sintering temperatures used, different conclusions regarding the effect of ZrO₂ additive have been drawn. The significant problem in all of the above works is that the effect of ZrO₂ was simply studied by adding a certain amount of ZrO₂ at a fixed temperature. No studies on the effect of ZrO₂ were carried out for various contents and temperatures.

CaO clinker was sintered from CaCO₃ powder (with purity of more than 98%) at 1300-1600°C by the addition of ZrO₂ to 1% (molar ratio). ZrO₂ reacted with CaO to form CaZrO₃ at all temperatures. The formed CaZrO₃ was mainly located between CaO grains when the sample was sintered at a lower temperature (1300°C), whereas it was mainly located within CaO grains when the sample was sintered at higher temperatures (above 1400°C). The growth of CaO grains was inhibited by the addition of ZrO₂, resulting in poor densification when the sample was sintered at a lower temperature (1300°C). When the sintering temperature was raised, grain growth and densification were promoted and the relative density of the clinker reached a maximum at 1500°C. The slaking test showed a better slaking resistance when the clinker was sintered at 1400-1600°C by the addition of ZrO₂.

[Received March 25, 2002; Accepted August 9, 2002]

Table 1. Compositions of Starting Materials of CaCO₃ (mass%)

<table>
<thead>
<tr>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>FeO</th>
<th>TiO₂</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.12</td>
<td>0.52</td>
<td>0.15</td>
<td>0.23</td>
<td>0.07</td>
<td>0.04</td>
<td>43.87</td>
</tr>
</tbody>
</table>
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lyses as well as a slaking test. Bulk density was measured in kerosene using Archimedes’ principle. The relative density was calculated by comparing bulk density as the fraction of the theoretical density that was calculated from a fractional summation of the theoretical densities of cubic CaO (3.346 × 10³ kg/m³) and hexagonal CaZrO₃ (4.611 × 10³ kg/m³). Phase compositions were analyzed by X-ray diffraction (Cu target, 30 kV and 30 mA). The lattice constant was measured for samples both cooled in a furnace and quenched in air. The microstructure was observed by SEM on the polished surface after etching in methanol picric solution. A linear intercept method was used for the determination of the grain size. The distribution of added ZrO₂ and the compositions of different grains were examined by EPMA. The slaking test was conducted on the sintered body at 70°C in 90% humidity for 96 h.

3. Results

3.1 Densification

Figure 1 is the comparison of densification of the clinkers sintered from the two different starting materials. For the sample sintered from reagent-grade CaCO₃, the relative density increased when the temperature was raised to 1600°C. It was below 90% when the sample was sintered at 1300°C, while for the sample sintered from the Yabashi CaCO₃, the relative density exceeded 95% when the sample was sintered at 1300°C. Increase of temperature only slightly promoted densification, and the relative density passed a maximum at 1500°C. This result indicates that the impurities influenced the densification of the clinker.

Figure 2 shows the effect of ZrO₂ content on densification at different temperatures. It is observed that the relative density decreased with an increase of ZrO₂ content at 1300°C. The relative density was 95.4% at 1300°C without ZrO₂, which decreased to 92.5% by the addition of 1.0% ZrO₂. However, the relative densities increased by the addition of ZrO₂ when the sample was sintered at higher temperatures (1400–1600°C), and a small amount of ZrO₂ (less than 0.3%) seems to be more effective. The relative density of the sample without ZrO₂ was 96.8% at 1500°C, which increased to 98.3% by the addition of 0.3% ZrO₂. The relative density reached 99% when 1.0% ZrO₂ was added at the same temperature. Additionally, the maximal relative densities were achieved at 1500°C for all samples with and without ZrO₂.

As an example of higher temperature effect, the changes of relative density with time at a constant temperature 1500°C are shown in Fig. 3. For the sample without ZrO₂, the relative density was 95% when the sample was heated to 1500°C, and it increased to 96.8% when the time was raised to 2 h. It is evident that the densification was still in progress. When ZrO₂ was doped, the time necessary for completion of sintering was shortened. The relative density was 97.3% for the sample with 0.3% ZrO₂ after heating for 1 h, which changed little when the time was increased to 2 h. When 1% ZrO₂ was doped, a slight promotion in density was observed when the sintering time was increased from 0 to 2 h. This result implies that the shrinkage of the compact, or the full densification of CaO clinker, was enhanced by the addition of ZrO₂.

3.2 Phase composition and microstructure

Figure 4 shows the XRD patterns for CaO sintered by the addition of 1% ZrO₂. ZrO₂ reacted with CaO to form CaZrO₃ at all temperatures. There was little change of the CaZrO₃ amount with the increase of temperature. The lattice constant of CaO sintered at 1500°C without ZrO₂ was 0.4793 nm (the theoretical value is 0.4813 nm), which did not change after ZrO₂ was added, even for the sample quenched in air.

Figure 5 shows the microstructures of the clinkers sintered at 1500°C by the addition of various amounts of ZrO₂. Coarse CaO grains, with irregular grain boundaries and pores predominantly located within the individual grains, were observed when the clinker was sintered without ZrO₂. This microstructure indicates the occurrence of discontinuous or abnormal grain growth. The addition of ZrO₂ led to the formation of a uniform microstructure, with an evident decrease in both pore size and number. When 0.3% ZrO₂ was doped, an appreciably homogenous microstructure was observed. Further increase of ZrO₂ content to 1% led to a
noticeably dense microstructure, with an evident decrease in grain size. The grain size increased with the increase of temperature for all samples (as shown in Fig. 6). With increasing ZrO₂ amount, the grain size decreased. These results indicate that grain growth of CaO was inhibited by the addition of ZrO₂.

The microstructures of the samples sintered at a lower temperature (1300°C) and a higher temperature (1600°C) are shown in Fig. 7. The results of spot analysis and map scanning (within the square region in Fig. 7(c)) are shown in Table 2 and Fig. 8. At a lower temperature (1300°C), the formed CaZrO₃ was predominantly located between CaO grains, with an evident decrease of grain size and increase of pore numbers between grains (Fig. 6(b)). At a higher temperature (1600°C), the formed CaZrO₃ was homogenously dispersed in the entire microstructure. It was also observed (from Fig. 8) that MgO, TiO₂ and FeO were uniformly dispersed, which implies that these impurities formed a solid solution with CaO. SiO₂ and Al₂O₃ were mainly in the liquid phase that was observed in the sample sintered at 1300°C without ZrO₂. When ZrO₂ was added, some of it entered into the liquid phase, and a part of SiO₂ was observed to coexist with free CaZrO₃.

### 3.3 Improvement of slaking resistance

Figure 9 shows the slaking results of CaO sintered at 1400–1600°C by the addition of ZrO₂. The mass gains are found to decrease with the increase of ZrO₂ content, and the addition of a small amount of ZrO₂ was found to be more effective. The mass gain was 5.8% for the sample without ZrO₂ sintered at 1500°C and was about 4.7 and 4.1% for the samples with 0.3 and 1% ZrO₂, respectively. When the sintering temperature was raised, the slaking resistance improved. The mass gain reached a minimum for all samples sintered at 1600°C, and was only 3.6% for the sample sintered at 1600°C by the addition of 1% ZrO₂.

### 4. Discussion

#### 4.1 Effect of ZrO₂ on densification

Discontinuous grain growth or secondary recrystallization is a common phenomenon that occurs on the sintering of pure oxide ceramics, giving rise to nonuniform microstructures that are enhanced with the increase of temperature. Consequently, the pores are readily entrapped and the densification is inhibited due to the excessively high grain growth rate. In the present work, the formation of a liquid phase by the reaction of CaO with impurities of Al₂O₃ and other oxides can be controlled by the addition of ZrO₂.
SiO₂ around 1200°C enhanced the abnormal grain growth further. Because of the excessively high grain growth rate, the relative density had only a slight elevation with the increase of sintering temperature, and it decreased when the sintering temperature was raised to 1600°C.

It is known that all of MgO, FeO, TiO₂ and ZrO₂ can form solid solutions with CaO. Since the radii of Mg²⁺, Fe³⁺ and Ti⁴⁺ cations are smaller than that of Zr⁴⁺ cation, Ca²⁺ cation is more easily substituted by Mg²⁺, Fe²⁺ and Ti⁺ cations. With the shrinkage of the lattice that occurred when MgO, FeO and TiO₂ formed a solid solution with CaO, the electrostatic force among the ions in CaO lattice increased and thus the substitution of Ca²⁺ cation by Zr⁴⁺ cation became difficult. Since there was no change in lattice constant and the dispersion of zirconium was not uniform (as shown in Fig. 8), it is considered that the added ZrO₂ did not form a solid solution with CaO. Therefore, the

**Table 2. Point Analysis of CaO Sintered at 1600°C by Addition of 1% ZrO₂ (mol%)**

<table>
<thead>
<tr>
<th>Position</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Ti</th>
<th>Zr</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
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<td>45.37</td>
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<td>0.02</td>
<td>0.03</td>
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<tr>
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<td>0.52</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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</tr>
<tr>
<td>3</td>
<td>19.92</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>18.94</td>
<td>61.02</td>
</tr>
<tr>
<td>4</td>
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<td>0.25</td>
<td>1.53</td>
<td>2.16</td>
<td>0.02</td>
<td>0.00</td>
<td>2.52</td>
<td>50.91</td>
</tr>
</tbody>
</table>

**Fig. 7.** SEM photographs of CaO clinkers sintered at a), b) 1300°C and c) 1600°C for 2 h. Sample a) was sintered without ZrO₂ while samples b) and c) were sintered with 1% ZrO₂. "L" represents the liquid phase.

**Fig. 8.** EPMA microscopy of CaO clinker sintered at 1600°C with 1% ZrO₂ addition. a) is the SEI photograph of the sample and b)–i) are the element scanning images.

**Fig. 9.** Effect of ZrO₂ content on improvement of slaking resistance.
addition of ZrO₂ could not enhance the growth of CaO grain by the formation of vacancies. On the contrary, the addition of ZrO₂ inhibited grain growth due to the following two reasons:

First, since a part of SiO₂ preferentially coexisted with free CaZrO₃, the amount of SiO₂ available for formation of the liquid phase decreased. Thus, the grain growth was inhibited due to the decrease of liquid phase.

Second, the formed CaZrO₃ acted as an inhibitor that restrained the grain growth of CaO by increasing the energy necessary for movement of the grain boundary, thus, the grain growth was restrained by the free CaZrO₃. This effect is enhanced with increasing the amount of ZrO₂.

Regarding the effect of grain growth inhibitor, different results were obtained when ZrO₂ was doped at different temperatures. At a lower temperature (1300°C), the driving force for grain growth was insufficient. When ZrO₂ was doped, the driving force decreased further to such a degree that the grain boundaries could not pass over the inhibitors (CaZrO₃). Thus, the formed CaZrO₃ was mainly located between CaO grains and the densification was inhibited. When the temperature was raised, the grain growth was promoted. Though the grain growth of CaO was inhibited by the addition of ZrO₂ at a higher temperature (above 1400°C), the driving force was adequate for the grain boundaries to pass over the CaZrO₃ grains. The decrease of grain size contributed to the escaping of pores. Thus, the formed CaZrO₃ was dispersed uniformly and the densification was promoted.

4.2 Improvement of slaking resistance

It is known that the slaking resistance of CaO clinker is related to the specific surface area that is determined by the microstructure, including the relative density, pore distribution and grain size. The sample with high density and large CaO grains is considered to be more slaking resistant. In previous works, ZrO₂ was added to low-density samples. The effect of ZrO₂ on inhibiting grain growth led to the densities being decreased further. Thus, it is impossible to improve the slaking resistance by the addition of ZrO₂. In Matsui and Fukuda’s work, a slaking test was conducted on the ground CaO particles. The decrease of grain size might play a dominant role in the increase of the specific surface area though the densification was promoted by the addition of ZrO₂. As a result, no obvious effect on the improvement of slaking resistance was obtained. In the present work, the slaking test was conducted on the sintered CaO clinker. The decrease of grain size played a dominant role in the decrease of the specific surface area though the grain size was decreased. Therefore, different from the former studies, slaking resistance of CaO clinker was improved by the promotion of relative density when ZrO₂ was doped. When the temperature was raised from 1500 to 1600°C, since large stable grains were formed, the slaking resistance improved though the relative density decreased slightly.

5. Conclusions

Based on the above results, the following conclusions were drawn in case of sintering of CaO clinker by the addition of ZrO₂:

1) ZrO₂ reacted with CaO to form CaZrO₃ that restrained the growth of CaO grain. As a result, the densification of CaO clinker was inhibited at a lower temperature (1300°C), while it was promoted at a higher temperature (above 1400°C). The relative density reached 99% when the clinker was sintered at 1500°C for 2 h by the addition of 1% ZrO₂.

2) The slaking resistance of CaO clinker with ZrO₂ addition was improved due to the promotion of densification when the sample was sintered at a temperature above 1400°C.

References