

Effect of Additive on Hydration Resistance of Sintered CaO

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Abstract: CaO was mixed with various additives, such as Al₂O₃, Cr₂O₃, CuO, Fe₂O₃, MgO, SrO, SiO₂, TiO₂, ZrO₂ and La₂O₃, and then the mixing powders were sintered at 1400°C for 2h in air. The effect of additives on hydration resistance of sintered CaO was studied. The growth of grain in the sintered samples was observed on the samples containing Cr₂O₃, Fe₂O₃, CuO and La₂O₃. However, the grain growth in the sintered samples with other additives. The relative densities of these samples containing Cr₂O₃, Fe₂O₃, CuO, La₂O₃ and TiO₂ showed the value exceeding 90% and that of the samples containing other additives exhibited less than 90%. A remarkable improvement in hydration resistance was found with the samples containing CuO, Fe₂O₃, La₂O₃ and Cr₂O₃, the weight gain after 2 days being about one hundred-fiftieth of the sample containing ZrO₂. On the samples containing Al₂O₃ and TiO₂, the hydration resistance was also improved mostly. However, no pronounced improvement in hydration resistance was found on the samples containing ZrO₂, SiO₂, MgO and SrO. And also, the sintered CaO without additives, after 12 h of hydration time, was broken due to hydration reaction between CaO and moisture.

Key words: Hydration resistance, Calcium oxide, Sintered body, Additive.

1. Introduction

Calcium oxide (CaO) is an attractive refractory material at high temperature, because of their thermodynamically excellent stability at high temperature. Then, the crucible constructed with CaO has been used to melt metals and alloys, such as iron, platinum and stainless steel, etc.[1]. However, the uses have been restricted in a dry atmosphere. Because the CaO crucible is broken to occur rapidly the volume expansion due to the hydration reaction between CaO and moisture in atmosphere, *i.e.*, the reaction of $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$. Therefore, the improvement of the hydration resistance of CaO is one of the important problems to be solved. In order to improve the problems, two effective methods have been proposed and reported; increasing the sintering density by either hot-pressing green body or adding various additives [2-5]. However, the sintering by hot-pressing is required to be done at high temperature and under high pressure. Consequently, we had much attention for preparing the sintered body with high density by adding other additives expect conventional additives reported, such as CuO and La₂O₃.

In the present work, CaO was mixed with either CuO, La₂O₃ or various additives and then sintered at 1400°C for 2h. The samples obtained were placed at 25°C under P_{H₂O} of 3.0kPa. The effect of additives on hydration resistance of the

sintered bodies was studied by measuring the weight gain due to the hydration reaction of CaO.

2. Experimental

2.1 Preparation of sintered body

Commercial calcium carbonate (CaCO₃, purity: 98%, average particle size: 1.0 μm) was used as a starting powder. Al₂O₃, Cr₂O₃, CuO, Fe₂O₃, MgO, SrO, SiO₂, TiO₂, ZrO₂ and La₂O₃ were selected as the additives to have probably the effect for hydration resistance. These additives were added with the weight ratio (additive/CaCO₃) of 0.05 and then mixed by wet ball-milling at the rotation rate of 30 rpm. After the mixed powders were calcined at 900°C for 3h, they were uniaxially pressed under 10MPa. The green bodies obtained were isostatically cold-pressed under 22.4MPa and then sintered at 1400°C for 2h in air with the heating rate of 10°C/min, the size of sintered bodies being approximately φ 8.3mm x 3.7mm.

The microstructures of sintered samples before and after hydration tests were observed by scanning electron microscopy (SEM) after gold coating. The average sizes of the grains on the sintered samples were evaluated by the linear-intercept method on the polished surface after sintering, which was carried out by counting 100 grains for each sample. In order to measure the view point of the additives in sintered samples, energy dispersive X-ray analysis (EDX) was carried

out at their surfaces.

2.2 Hydration test

Water was introduced at the bottom of desiccator, which has been purified by distillation. After soaking the desiccator in water bath, the temperature in desiccator was kept at $25 \pm 1^\circ\text{C}$. The partial pressure of water vapor condense in desiccator, " PH_2O ", was approximately 3.0kPa. The sintered samples were inserted into the baggage with mesh made from a nylon and then they were angled into desiccator. The hydration resistance

was evaluated by measuring the weight gain due to the hydration reaction of CaO, *i.e.*, the reaction of $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$.

3. Results and Discussion

3.1 Characterization of sintered body

The sintered samples containing various additives were obtained by sintering the green bodies at 1400°C for 2h in air. Fig. 1(a), (b), (c) and (d) show typical SEM-micrographs of the surface of the sintered samples containing TiO_2 , Cr_2O_3 , Fe_2O_3 and La_2O_3 , respectively.

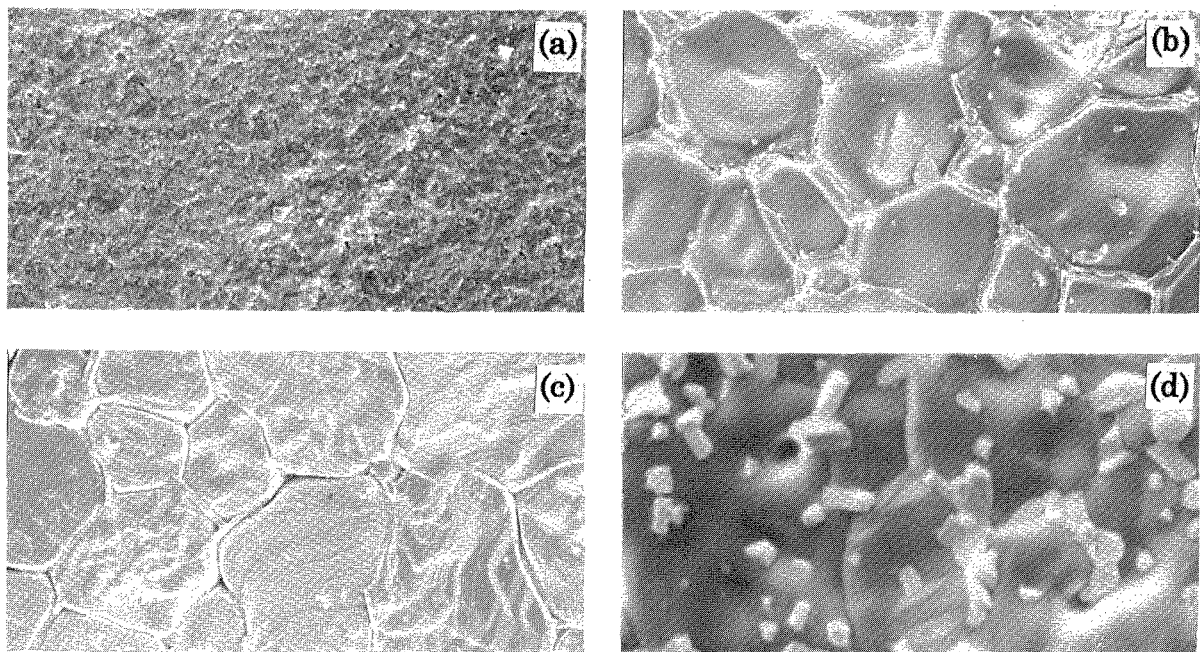


Fig. 1 SEM-micrographs of the surface of sintered samples containing various additives: (a) TiO_2 , (b) Cr_2O_3 , (c) Fe_2O_3 and (d) La_2O_3 .

Table 1 The results of XRD measurements.

| Additive | Al_2O_3 | Cr_2O_3 | CuO | Fe_2O_3 | La_2O_3 | MgO | SrO | SiO_2 | TiO_2 | ZrO_2 |
|---------------|------------------------------------|---------------------------|---------------------------|------------------------------------|-------------------------|--------------|--------------|---------------------------|------------------------------------|------------------|
| Crystal phase | CaO + | CaO + | CaO + | CaO + | CaO + | CaO | CaO | CaO + | CaO + | CaO + |
| | $\text{Ca}_3\text{Al}_2\text{O}_6$ | Ca_2CrO_4 | Ca_2CuO_3 | $\text{Ca}_2\text{Fe}_2\text{O}_5$ | La_2O_3 | | | Ca_3SiO_5 | $\text{Ca}_3\text{Ti}_2\text{O}_7$ | CaZrO_3 |

Table 2 The relative densities of the samples heated at 1400°C for 2h.

| Additive | Al_2O_3 | Cr_2O_3 | CuO | Fe_2O_3 | La_2O_3 | MgO | SrO | SiO_2 | TiO_2 | ZrO_2 |
|---------------------|-------------------------|-------------------------|--------------|-------------------------|-------------------------|--------------|--------------|----------------|----------------|----------------|
| Relative density(%) | 88 | 93 | 93 | 96 | 94 | 86 | 86 | 88 | 97 | 87 |

In the case of sample containing TiO_2 , the grains with average size of $5.0 \mu\text{m}$ were observed, similar to that of the samples containing Al_2O_3 , MgO , SrO , SiO_2 and ZrO_2 . However, the grain of the samples containing Cr_2O_3 and Fe_2O_3 consisted of the average size of $50 \mu\text{m}$ and even the phase considered due to liquid-phase sintering was observed at grain boundaries, similar to those on the sample containing CuO . In the case of the samples containing La_2O_3 , the average size of grains was approximately $50 \mu\text{m}$, whereas the addition of La_2O_3 was formed with the deposition of fine particles at the surface. From SEM observations, it was found that a remarkable growth of grain in sintered samples caused by the addition of Cr_2O_3 , Fe_2O_3 , CuO and La_2O_3 .

XRD measurements were carried out for all sintered samples, of which the results were summarized in Table 1. The crystal phase of the samples containing MgO and SrO gave only CaO , due to the formation of solid solution. For other additives except La_2O_3 , the phase of complex oxides formed by the reaction between additive and CaO were detected in addition to CaO . The addition of La_2O_3 resulted in two phases of La_2O_3 and CaO .

In complex oxides detected by XRD measurements (see Table 1), it has been known that CaCrO_4 , Ca_2CuO_3 and $\text{Ca}_2\text{Fe}_2\text{O}_5$ consist of liquid phase at 1400°C and above [6-8]. On the base of the formation of liquid phase described above, the phase observed at grain boundaries seems to be due to the deposition of complex oxides through their liquid phase which was in good agreement with the chemical composition detected by EDX measurements (see Fig. 1(b) and (c)). The fine particles observed on the surface of the sample containing La_2O_3 were suggested to be La_2O_3 , which agreed with the results of XRD and EDX measurements (see Fig. 1(d)).

In Table 2, the relative densities of all samples are shown. The relative densities of sintered samples were calculated with theoretical one (3.37 g/cm^3) of CaO . The relative density of sample containing TiO_2 was highest than that of the samples containing other additives, the value of relative density being 97%. In the case of the samples containing Cr_2O_3 , CuO , Fe_2O_3 and La_2O_3 , the relative densities showed the value exceeding 90%. For other additives expect them described above, the densities gave the value in the range of 86 to 88%.

From these results, it was found that the samples with a high density were obtained to be prepared through liquid phase of complex oxides at 1400°C .

3.2 Hydration resistance

The hydration tests were carried out at $25 \pm 1^\circ\text{C}$ under the partial pressure, $P_{\text{H}_2\text{O}}$, of approximately 3.0kPa. The weight gain per the initial weight of the original samples was measured as a function of hydration time on the samples containing various additives. In Fig. 2, the results of hydration tests are shown. A remarkable improvement in hydration resistance was found with the samples containing CuO , Fe_2O_3 , La_2O_3 and Cr_2O_3 . The weight gain in these cases was about one hundred-fiftieth of the sample containing ZrO_2 after 2 days. On comparison of the weight gain after 10 days, the gain with hydration time was also found to be improved mostly on the samples containing Al_2O_3 and TiO_2 , which was slightly higher than those on the samples containing additives with the effect of hydration resistance. No pronounced improvement in hydration resistance was found on the samples containing ZrO_2 , SiO_2 , MgO and SrO .

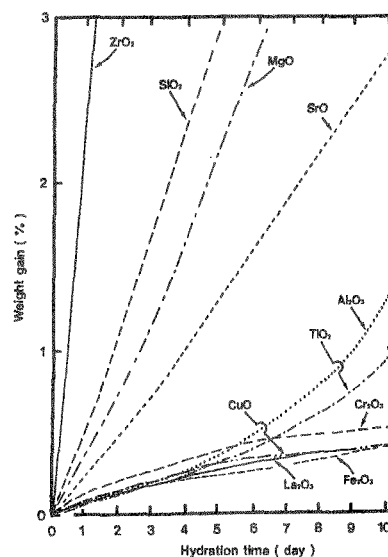


Fig. 2 The changes of weight gain of sintered samples with hydration time.

And also, the sintered CaO without additives (relative density: 95%), after 12 h of hydration times, was broken due to the hydration reaction between CaO and moisture.

After hydration for 10 days, typical SEM-micrographs of the surface of the sintered samples containing TiO_2 , Cr_2O_3 , Fe_2O_3 and La_2O_3 are shown in Fig. 3(a), (b), (c) and (d), respectively. The cracks and the expanded grains were observed on the surface of either sample. From the XRD measurement, these samples after hydration for 10 days gave the diffraction peaks of both CaO and

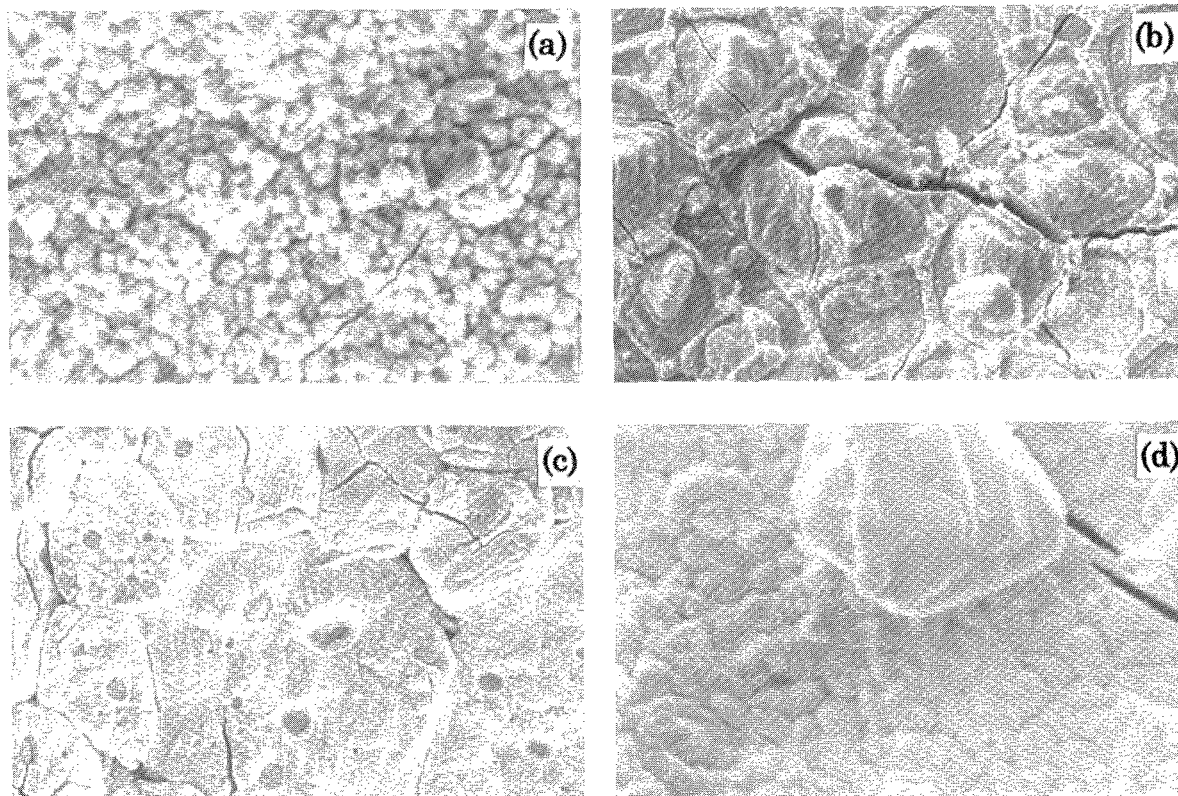


Fig. 3 SEM-micrographs of the surface of sintered samples after hydration for 10 days: (a) TiO₂, (b) Cr₂O₃, (c) Fe₂O₃ and (d) La₂O₃.

Ca(OH)₂. The occurrence of the cracks and the expanded grains seems to occur the volume expansion due to the hydration reaction between CaO and water, *i.e.*, the reaction of $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$. On the samples without hydration resistance, such as addition of ZrO₂, SiO₂, MgO and SrO, no shape of the sintered bodies was maintained with the volume expansion due to the hydration reaction. In other words, the sintered bodies with the size of $\phi 8.3\text{mm} \times 3.7\text{mm}$ were broken up to the granules with the size of approximately 1.0mm.

4. Conclusion

CaO was mixed with various additives and then sintered at 1400°C for 2h, the additives being Al₂O₃, Cr₂O₃, CuO, Fe₂O₃, MgO, SrO, SiO₂, TiO₂, ZrO₂ and La₂O₃. The effect of additives on hydration resistance of sintered samples was studied at 25°C under the partial pressure of water vapor of 3.0kPa.

The growth of grain in the sintered samples was observed on the samples containing Cr₂O₃, Fe₂O₃, CuO and La₂O₃. The relative densities in these cases and TiO₂ showed the value exceeding 90%. However, the density of the samples containing other additives exhibited less than 90%.

A remarkable improvement in hydration resistance was found with the samples containing

CuO, Fe₂O₃, La₂O₃ and Cr₂O₃, the weight gain being about one hundred-fiftieth of the sample containing ZrO₂ after 2 days. On the samples containing Al₂O₃ and TiO₂, the hydration resistance was also improved mostly. However, no pronounced improvement in hydration resistance was found on the samples containing ZrO₂, SiO₂, MgO and SrO.

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