Sintering Property and Hydration Resistance of CaO-Y_2O_3 Composite Materials

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Abstract. A preparation method of CaO-Y_2O_3 composite materials and its sintering property and hydration resistance were investigated in this paper. The CaO-Y_2O_3 core-shell structure powders were obtained by precipitation, after calcination, pressing and sintering the CaO-Y_2O_3 composite materials were prepared. The obtained powders and composite materials were characterized by crystalline phase formation, thermodynamic property, density, hydration resistance and microstructural analysis. The results showed that the prepared CaO-Y_2O_3 core-shell structure powders had good coating property, the sintering property and hydration resistance of composite materials were excellent. As the molar ratio Ca to Y was 1:1, the relative bulk density was 95.68%, the apparent porosity was 1.28%, and the hydration weight gain rate of the sample after 21 days in the atmospheric environment was 0.45%.

Keywords: CaO-Y_2O_3 composite materials; precipitation; hydration resistance; sintering property.

1. Introduction

With the development of super clean steel and superalloy, the ordinary refractories are difficult to meet the requirements of ultra-pure smelting. Taking into the account the free Gibbs energy of formation of oxides, Y_2O_3 and CaO presented the first and the second negative value among all metallic oxides respectively [1]. Moreover, Y_2O_3 and CaO possess a unique combination of properties such as high refractoriness, low vapor pressure and good corrosion resistance, and the latter has the ability of removal of O, N, S and inclusions from the molten metal [2,3]. In view of the excellent properties above, Y_2O_3 and CaO are regarded as the ideal candidate materials for melting of super clean steel and superalloy. However, the poor sintering property of Y_2O_3 and hydration resistance of CaO are the limited factors in metallurgical industry application. Therefore, it is extremely essential and urgent to improve the sintering properties of Y_2O_3 and hydration resistance of CaO materials.

The densification sintering temperature of Y_2O_3 is usually higher than 1800°C, generally, ultrafine powders are used as raw materials to realize densification sintering of Y_2O_3 by hot pressing sintering and plasma sintering [4,5], which processes consume a lot of energy and need higher equipment requirements. At present, the main methods to improve the hydration resistance of CaO are induction of additives [6-8], high temperature calcination [9] and surface treatment [10-13], which can improve the hydration resistance of CaO to a certain extent, however, the problem of CaO hydration has not been completely solved.

Therefore, in the present work, a novel way was proposed to prepare the CaO-Y_2O_3 composite materials, which CaO core particles were coated by a stable Y_2O_3 shell layer to prevent the hydration of CaO, and to improve the sintering properties of Y_2O_3 by interactions of the core and the shell.

2. Experimental Procedures

$CaCO_3$ powders (Nanjing Xianfeng Nanomaterials Technology Co., Ltd., the particle size 40-80 nm), AR grade yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$), ammonium bicarbonate, citric acid ammonia, anhydrous ethanol and ammonia were used as the raw materials to prepare CaO-Y_2O_3 composite powders. All chemical materials were supplied from Sinopharm Chemical Reagent Co., Ltd., China.

CaO-Y_2O_3 composite powders were prepared by precipitation. Firstly, 0.05 mol yttrium nitrate was dissolved in deionized water to prepare 100 ml yttrium nitrate solution with concentration 0.5 mol/l, a certain amount of $CaCO_3$ powders (molar ratio of Ca to Y was 3:2, 1:1, 1:2, 1:4, 1:6 respectively) and 0.6% dispersant citric acid ammonia (based on the mass of $CaCO_3$) were added into 150 ml ammonium bicarbonate solution with concentration 1.5 mol/l. Next, at room temperature, the yttrium nitrate solution was slowly and evenly dropped into the ammonium bicarbonate solution at a rate of 5 ml/min by a peristaltic pump. The ultimate pH value of solution was adjusted to around 9 by ammonia. The whole process of precipitation was under the condition of magnetic stirring. After precipitation, the slurry was stirred for another 30 min. Then the precipitate was filtered off and washed three times with ethanol. Finally, the precursors were dried at 120°C for 24 h, then the dried precursors were put into the muff furnace and calcined at the selected temperature for 2 h.

The powders calcined were uniaxially pressed into the pellets with a diameter of 10 mm and thickness of 10 mm at 100 MPa. The samples were heated at 1600°C for 3 h.

The phase compositions of powders were determined by X-ray diffraction (XRD). Thermal analysis of the precursor was measured by thermogravimetric/differential scanning calorimetry (TG/DSC) at a heating rate of $5°C\cdot min^{-1}$ in air. The micrographs of the calcined powders and the fracture surface of the sintered pellets were detected via field emission scanning electron microscope (FESEM), and its components and distribution of elements were analyzed by using the incidental energy disperse spectroscopy (EDS).

The bulk density and apparent porosity of the sintered samples were measured according to the Archimedes principle using kerosene as the medium. The hydration resistance test on the samples was carried out in indoor natural atmosphere for 21 days. The hydration resistance of samples was characterized by the weight gain rate.

3. Experimental results and discussion

The XRD patterns of the raw material nano $CaCO_3$ and as-synthesized precursors were showed in Fig. 1. It can be seen that only $CaCO_3$ phase in as-synthesized precursors was detected, and the intensity of the diffraction peak of $CaCO_3$ decreased greatly with the decrease of Ca/Y molar ratio. The XRD results indicated that the precipitate of yttrium was amorphous. The intensity of the diffraction of $CaCO_3$ decreased with increasing precipitate of yttrium, especially the $CaCO_3$ particles were coated by the amorphous precipitate.

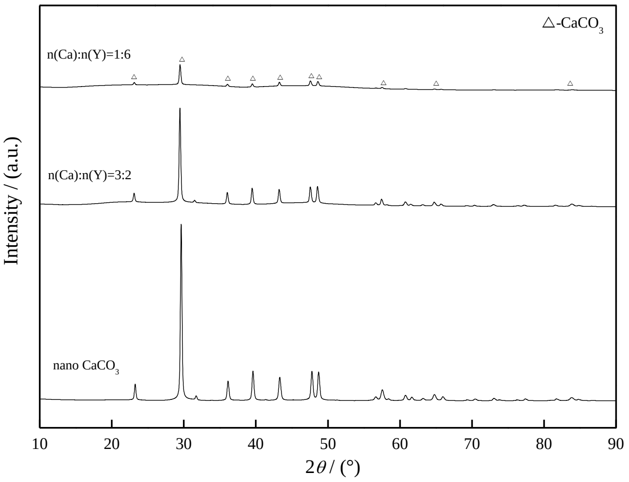
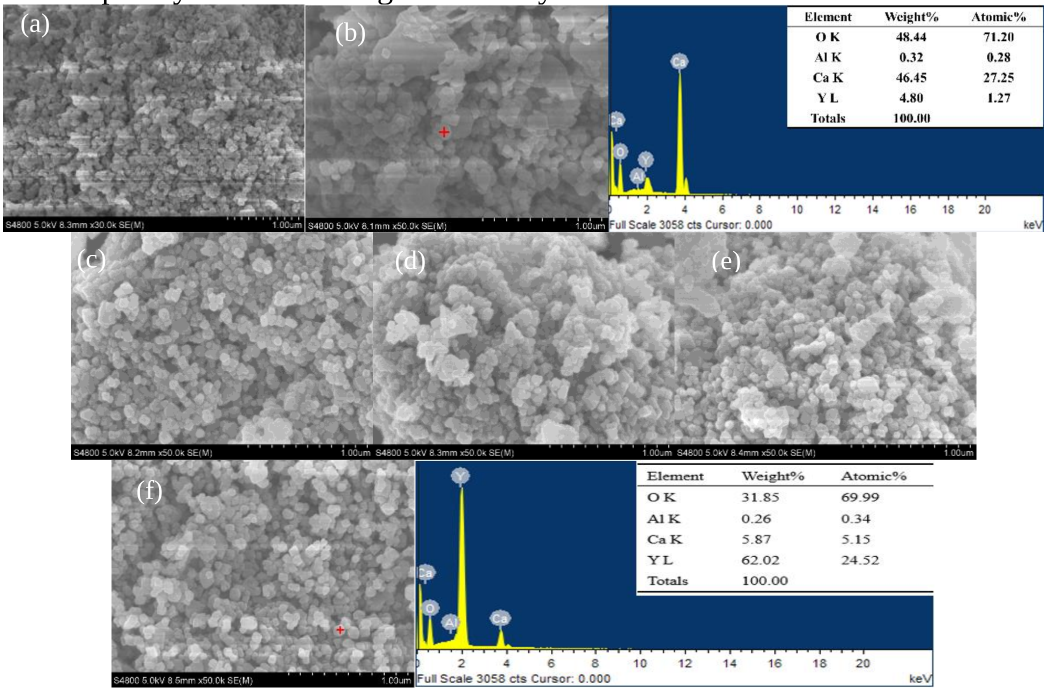


Fig. 1 XRD patterns of raw material nano $CaCO_3$ and as-synthesized precursors

Fig. 2 showed the SEM images and EDS analysis of raw material nano $CaCO_3$ and as-synthesized precursors. The size of raw material $CaCO_3$ powders was about 40-80 nm, which was smaller than that of as-synthesized precursors. And the existence of Y elemental peaks proved the information of yttrium precipitate coating around the surfaces of the $CaCO_3$ particles from the Fig. 2(b), 2(f). The results above confirmed that the $CaCO_3$ particles had been coated with yttrium precipitate, and it was coated more completely with increasing content of yttrium.



Element	Weight%	Atomic%
O K	48.44	71.20
Al K	0.32	0.28
Ca K	46.45	27.25
Y L	4.80	1.27
Totals	100.00	

Element	Weight%	Atomic%
O K	31.85	69.99
Al K	0.26	0.34
Ca K	5.87	5.15
Y L	62.02	24.52
Totals	100.00	

Fig. 2 SEM images and EDS analysis of raw material nano $CaCO_3$ and as-synthesized precursors (a) nano $CaCO_3$; (b) n(Ca):n(Y)=3:2; (c) n(Ca):n(Y)=1:1; (d) n(Ca):n(Y)=1:2; (e) n(Ca):n(Y)=1:4; (f) n(Ca):n(Y)=1:6

Fig. 3 showed the TG-DSC curves of the precursor which the molar ratio of Ca to Y was 3:2. During the process from room temperature to 1200℃, it can be divided into four stages. The first stage was from room temperature to 270℃, the mass loss was 9.76%, which was due to the evaporation of absorbed water and release of bound water. The mass loss in the second stage from 270℃ to 600℃ was 13.70%, which was caused by the decomposition of yttrium precipitant. The third stage was from 600℃ to 720℃, 20.54% mass loss was due to the decomposition of nano $CaCO_3$. And Two large endothermic peaks were detected in the DSC curve correspondingly. The last stage related to the crystallization of the Y_2O_3 crystals.

From the results above, the calcination temperature of the precursor should not be lower than 726°C. Considering some impurity ions such as $NH_4^+$and $NO_3^-$are difficult to remove by washing with water or alcohol, while they can be removed by volatilization at high temperature. So the calcination of precursors was set 800℃ in the present work.

The XRD patterns of powders calcinated at 800℃ for 2 h were shown in Fig. 4. For the five specimens, there was no obvious change between them, except that peak shape of yttrium oxide gradually became sharp with the decrease of Ca/Y molar ratio. It also can be found that the intensity of the diffraction peak of calcium oxide was very weak. The K value of calcium oxide is very small compared to yttrium oxide, which is less than half of the K value of yttrium oxide, this may be one reason for the low intensity of the characteristic diffraction peak of calcium oxide in the samples. Moreover, the Y_2O_3 coating on CaO particles may be another reason.

Fig. 5 showed the relative bulk density and apparent porosity of the samples with different ratio of raw materials. It can be concluded that Y_2O_3 had an appreciable effect on the density of samples. The relative bulk density generally decreased with increasing content of Y_2O_3 except the sample which molar ratio of Ca to Y was 1:1. The trend of apparent porosity was contrary. It's well known that CaO and Y_2O_3, especially Y_2O_3, are difficult to sintered. The melting point of CaO and Y_2O_3 is high, and there isn't a binary compound between them. However, the solid solution between them caused the lattice distortion of each other, reduced the activation energy of grain growth, and consequentially promoted the sintering property. In the present work, as the molar ratio of Ca to Y was 1:1, the density of sample was the highest, its relative bulk density was 95.68%, and apparent porosity was 1.28%.

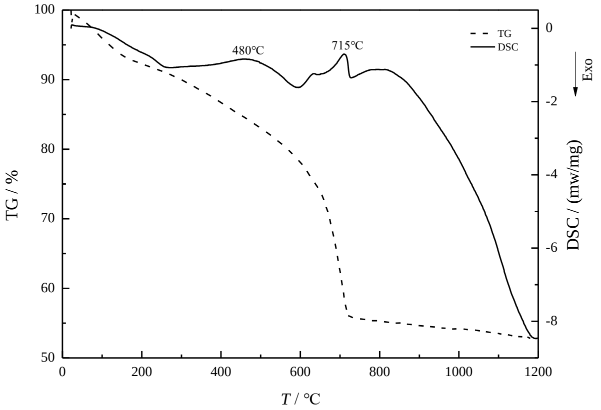


Fig. 3 TG-DSC curves of the as-synthesized precursors n(Ca):n(Y)=3:2

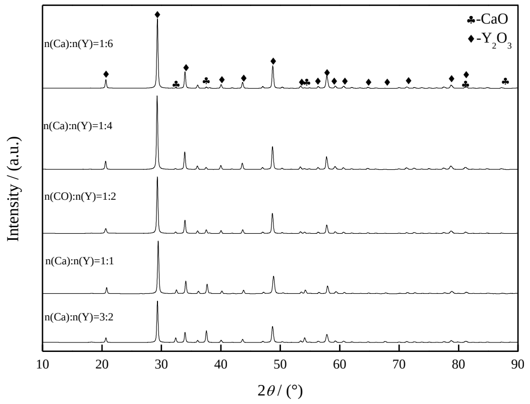


Fig. 4 XRD patterns of calcinated powders

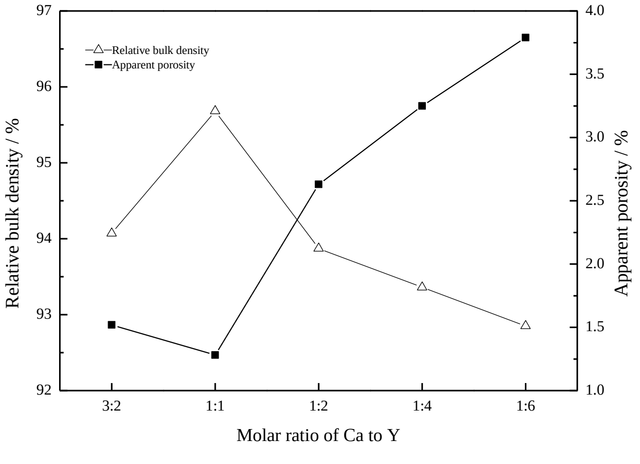


Fig. 5 Density and porosity of the samples

The Cross-sectional SEM images and EDS mapping of the sintered samples were shown in Fig. 6. It can clearly be seen that the density of all samples was high, and the density of samples with low content of Y_2O_3 was higher than that of high content samples, which indicated that the content of Y_2O_3 affected the density of samples greatly. From the Fig. 6(a), the morphology of CaO and Y_2O_3 were irregular particles, the size of CaO particles was about 30 μm, and they were surrounded by the smaller Y_2O_3 particles. The interactions (solid solution) of the CaO core and Y_2O_3 shell layer promoted the sintering property, and it was helpful to improve the hydration of samples.

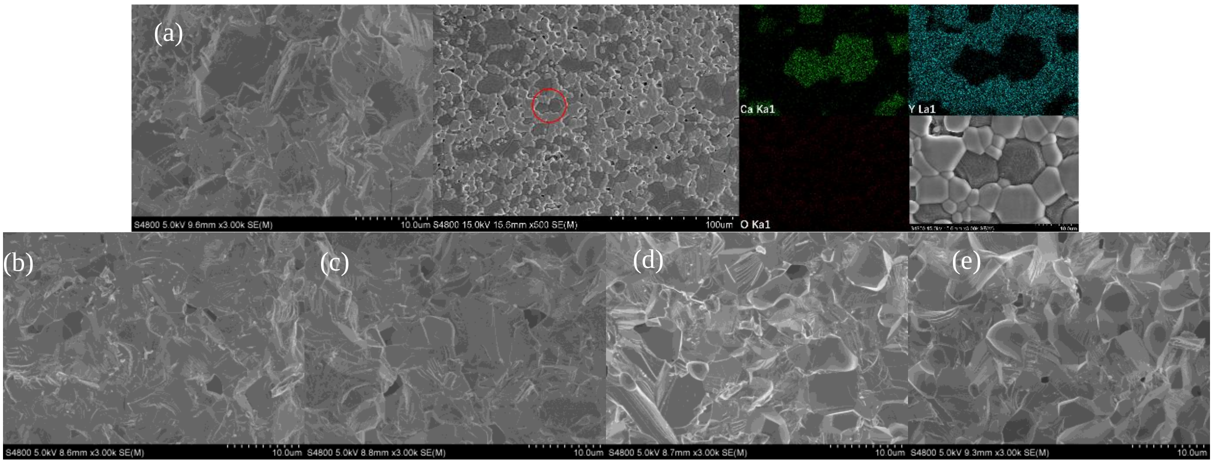


Fig. 6 Cross-sectional SEM images and EDS mapping of the sintered samples

(a) n(Ca):n(Y)=3:2; (b) n(Ca):n(Y)=1:1; (c) n(Ca):n(Y)=1:2; (d) n(Ca):n(Y)=1:4; (e) n(Ca):n(Y)=1:6

Fig. 7 showed the weight gain rate of sintered samples. As seen, the weight gain rate of pure CaO sample was 15.14%, and the sample was cracked in the test process. All CaO-Y_2O_3 composite materials presented good hydration resistance, which weight gain rate was less than one twenty-fourth of pure CaO sample. With increasing Ca/Y molar ratio, the weight gain rate decreased.

It was considered that the hydration process of CaO particle was happened from outside to inside based on the hydration mechanism of CaO material. It can be seen that the good hydration resistance of CaO-Y_2O_3 composite was due to the fact that the CaO particles was surrounded by smaller Y_2O_3 particles, the Y_2O_3 shell layer prevented the water in the air from contacting with CaO particles. Bulk density and apparent porosity were two important indicative parameters and had a direct impact on the hydration of CaO materials.

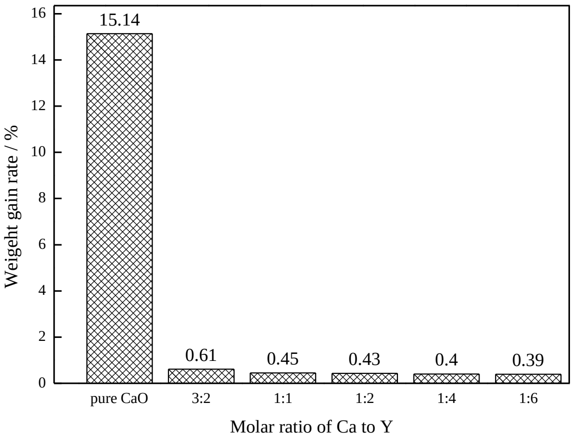


Fig. 7 Weight gain rate of the sintered samples

4. Summary

CaO-Y_2O_3 core-shell structure powders were successfully prepared by precipitation method, and then using the synthesized powders as raw material, the CaO-Y_2O_3 composite materials with excellent sintering property and hydration resistance were prepared. The Ca/Y molar ratio had the important effect on the properties of CaO-Y_2O_3 composite materials. The appropriate ratio of raw materials was helpful to promote the sintering property and ensured that the CaO particles were surrounded by Y_2O_3 particles completely. As the molar ratio Ca to Y was 1:1, the relative bulk density was 95.68%, the apparent porosity was 1.28%, and the hydration weight gain rate of the sample after 21 days in the atmospheric environment was 0.45%.

Acknowledgements

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