

IN-SITU STUDIES ON THE CRYSTALLIZATION OF CaO-SiO₂-CaF₂-CeO₂ SYSTEM BY A CONFOCAL LASER SCANNING MICROSCOPE

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Abstract

The recovery of rare earth elements from metallurgical slags containing rare earths is an important topic. The crystallization behavior of CaO-SiO₂-CaF₂-CeO₂ system with CeO₂ content range from 12 to 16 mass pct and a constant CaO/SiO₂ ratio of 1 has been examined by using a confocal laser scanning microscope (CLSM). Diagram of continuous cooling transformation and that of isothermal (time temperature) transformation for the slag have been constructed to characterize the solidification behavior of the slag with cooling rates between 3.125 and 100 K/minutes and temperature between 1373 and 1598 K. Depending on the CeO₂ content in the slag, the primary crystalline phase of CaO-SiO₂-CaF₂-CeO₂ system precipitates with elongated needle-like or short and rod-like crystals. The XRD analyses of crystalline phase of solidified slags confirm that the primary crystalline phase is a rare earth-rich phase Ca₂Ce₈O₂(SiO₄)₆, which contains no fluoride.

Introduction

Bayan Obo of China has the largest iron-rare earth-niobium deposit in the world, in which 71 elements and 170 minerals have been detected. Up to 1980s, it has been mined merely as an iron ore. Currently, to utilize the rare earth resources of the Bayan Obo ore, the concentrates of iron and rare earth are separated with applications of various mineral processing techniques, including low and high intensity magnetic separation, anti-flotation and flotation processes. However, only approximately 10 mass pct of rare earths can be recovered, while most of the rare earth minerals remain in the tailings and/or flow into blast furnace (BF) slags generated by using Bayan Obo ore. Since 1950s, effort has been attempted on recovering rare earth elements from the BF slags and tailings. Xu [1] found that the main rare earth containing phase in the BF slags and tailings is Cefluosil, i.e. 7[(Ca, Ce, Nd, La, Pr)₂SiO₄](F, O)₁₀, which precipitates as a rod-like crystal during cooling of the BF slag with 12.6 pct REO content. To recover rare earth from Bayan Obo tailings, Jiang et al. [2] proposed a reduction method and Ding et al. [3] a melting process respectively, for separating iron and rare earth of the melts generated in the processes. To efficiently separate rare earths from molten slags, it is significantly important to understand the crystallization behavior of rare earth phase during the slag solidification. By using a confocal laser scanning microscope with high temperature heating system (CLSM), this paper focuses on

the *in-situ* observation of the crystallization and solidification behavior of the CaO-SiO₂-CaF₂-CeO₂ system, which is relevant to the recovery of rare earth from Bayan Obo tailings and BF slag generated by using Bayan Obo ore.

Experimentals

A. Materials and Sample Preparation

The BF and the direct reduction slags generated by using Bayan Obo ore contain 13 to 39 mass pct CaO, 11 to 35 mass pct SiO₂, 3 to 18 mass pct REO, 10 to 36 mass pct CaF₂ and minor impurities, such as FeO, MgO, Al₂O₃ [1-4]. To mimic these slags, chemistry of the slag in the present CLSM test was designed as in table I

Table I The Chemical Composition of Experimentally Synthesized Slag (mass pct)

	CaO	SiO ₂	CeO ₂	CaF ₂
A	32	32	16	20
B	34	34	12	20

Synthetic slags were prepared from the chemical reagents, i.e. CaO (obtained by calcination of CaCO₃, 99.9%, analytically pure, Aladdin Industrial Corporation), SiO₂ (99.9%, analytically pure, Aladdin Industrial Corporation), CeO₂ (99%, analytically pure, Baotou Steel Rare-Earth Hi-Tech Co.) and CaF₂ (99.9%, analytically pure, Aladdin Industrial Corporation). These chemical powders were dried for 8 hours at 393 K under 0.08 MPa in a vacuum chamber and then weighed by using an analytical balance with 0.1 mg accuracy. The powders were mixed by an auto mixer (200 r/min) for 45 minutes to obtain a homogeneous sample. The mixture was further pressed to form a disc pellet with 6 mg weight for the following CLSM test.

B. Experimental set-up and Procedure

Firstly, samples were heated to 473 K at the heating rate of 200 K/min and maintained for 1 minute to evaporate water in materials, and then heated up to 1773 K at the heating rate of 200 K/min and held for 3 minutes to eliminate the bubbles and homogenize the melts. Figure 2(a) and (b) show the respective cooling history for investigating the continuous cooling transformation (CCT) and isothermal (time temperature) transformation (TTT) of the slags.

The crystallization and solidification behavior of rare earths-bearing slags was *in-situ* observed by using a CSLM equipped with an infrared furnace (VL2000DX; Lasertec Corporation, Yokohama, Japan). The present experimental set-up is schematically shown in Figure 1. Slag sample was put in a Pt crucible placed on a sample holder inside the CSLM heating chamber. Before heating the sample, the CSLM chamber was evacuated and flushed with argon gas (Ar > 99%) for three times and then a constant Ar stream (0.2L/min) was maintained during the experiments. The moisture and oxygen in argon gas were removed by a purifier.

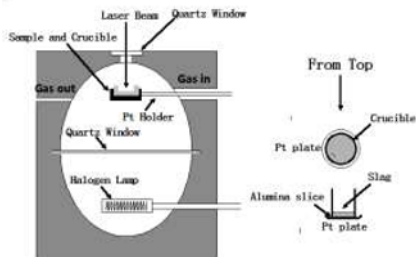


Figure 1. Schematic representation of CSLM experimental set-up.

The temperature calibration was conducted by using pure copper (melting point: 1356K) and pure nickel (melting point: 1726 K) as references. The heating and cooling processes were controlled. Firstly, samples were heated to 473 K at the heating rate of 200 K/min and maintained for 1 minute to evaporate water in materials, and then heated up to 1773 K at the heating rate of 200 K/min, the temperature was held for 3 minutes to eliminate the bubbles and homogenize the melts. Figure 2(a) and 2(b) show the respective cooling history for investigating the continuous cooling transformation (CCT) and isothermal transformation (TTT) of the slags. For the CCT study (Figure 2(a)), after the slag had melted and homogenized at 1773 K, it was cooled to 1623 K at the cooling rate of 500 K/min and held for 1 minute, then cooled to 1373 K at the various cooling rate ranged from 3.125 K/min to 100 K/min, followed by quenching the slag to room temperature. For the measurement of the TTT diagram, after the same heating process as that for CCT study, the slag sample was rapidly cooled at the cooling rate of 2000 K/s to the distinct temperatures ranged from 1373 K to 1598 K and maintained at the respective temperature for 5 minutes, followed by quenching the slag, as shown in Figure 2(b).

The crystallization and solidification of slag samples were *in-situ* observed and recorded. The obtained images were extracted from a series of CLSM video sequences at a rate of 5 frames per second. These images were used for further investigation, such as estimation of number, size and volume of the precipitates, determination of the on-set precipitation temperature for constructing the CCT and TTT diagram. Furthermore, the cooled samples were examined using scanning electron microscope (QUANTA 400, FEI) and X-ray diffraction (D8 ADVANCE, BRUKER).

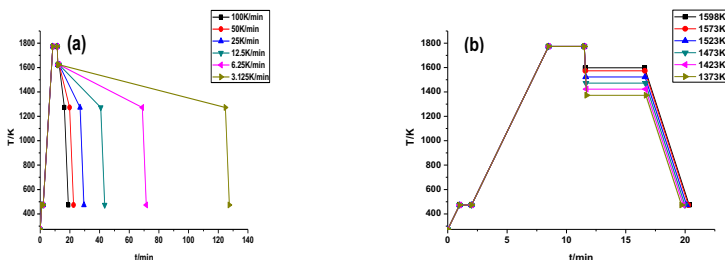


Figure 2. The thermal history of the CSLM test for (a) CCT and (b) TTT studies

Results and Discussion

A. Crystallization Process and Crystals Morphology of CaO-SiO₂-CaF₂-CeO₂ Slag

Since the molten slag was transparent, by maintaining the focus of the CLSM on the bottom of the crucible the on-sets of the crystallization were detected by the appearance and growth of a new phase in the slags. Figure 3 illustrates a representative melting and crystallization process of the slag A with 16 mass pct CeO₂ content. The slag started to sinter at around 1200 K (Figure 3(a)). The start of the melting was observed at around 1363 K with generation of a large number

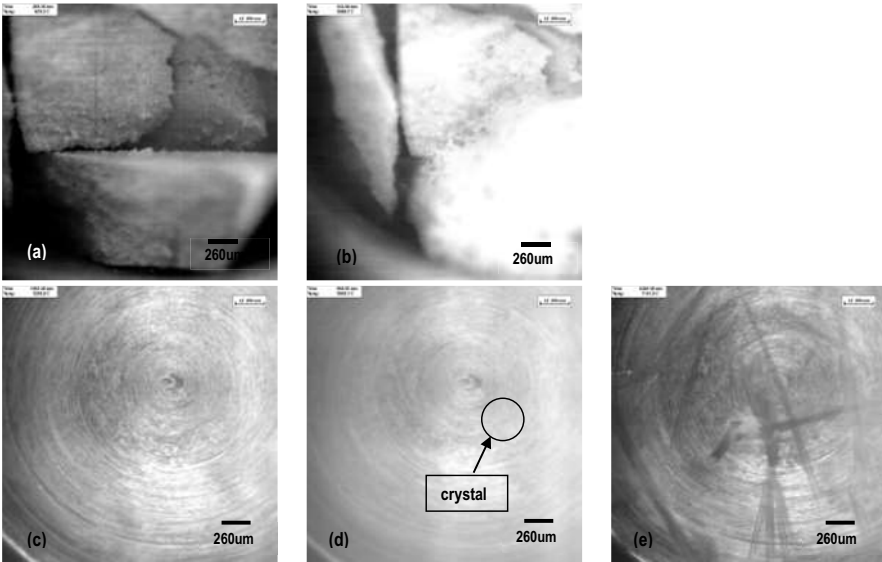


Figure 3. *In-situ* observation of melting and crystallization process for slag A using a CLSM. (a) beginning to sinter; (b) liquid appears; (c) transparent liquid slag; (d) on-set of a primary phase precipitation; (e) fast growth of the crystals

of gas bubbles (Figure 3(b)), and the slag became liquid at 1662 K, where the bottom of the crucible can be seen clearly as in Figure 3(c) due to the transparency of the liquid slag at high temperature. The sample was continuously heated up to 1773 K to ensure a fully liquid state. After holding for 3 minutes the slag was cooled down with a cooling rate of 6.25 K/min for *in-situ* observation of the solid phase precipitation. The primary phase with an elongated needle-like crystal precipitated at around 1445 K (Figure 3(d)) and the newly formed precipitate grew with further decreasing temperature (Figure 3(e)).

Figure 4 shows the representative CLSM images for the crystallization of slag B with 12 mass pct CeO₂ content at the cooling rate of 3.125 K/min. Compared to the crystallization of slag A, the following three crystallization characteristics were identified. Firstly, a multiple number of the crystals precipitated in the beginning of slag solidification (Figure 4(a)), whereas only a limited

number of crystals appeared in slag A at the initial crystallization stage (Figure 3(d)). Secondly, instead of the crystals with elongated needle-like shape in slag A (Figure 3(e)), the short and rod-like crystals were seen in slag B (Figure 4(b)). Thirdly, the rod-like crystals were aligned in parallel (Figure 4(b)). Comparing with the two kinds of crystals, it is obvious that the elongated needle-like crystals in slag A are much longer than the rod-like crystals in slag B.

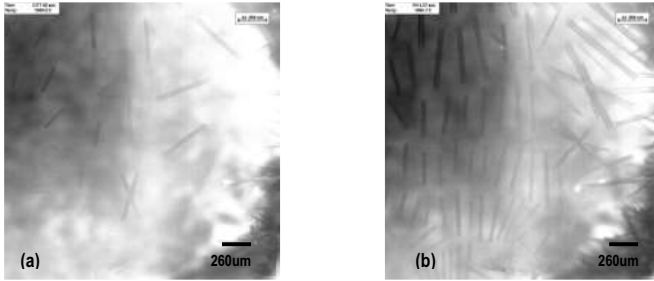


Figure 4. *In-situ* observations of the crystallization process for slag B using a CLSM. (a) a number of rod-like crystals precipitated in the beginning of slag cooling; (b) crystals grew and aligned in parallel.

B. Non-Isothermal and Isothermal Solidification Diagrams of 32 mass pct CaO - 32 mass pct SiO₂ - 20 mass pct CaF₂-16 mass pct CeO₂ Slag (Slag A)

To quantitatively understand slag solidification behavior, the on-set precipitation temperature as a function of time for sample A was plotted for the continuous cooling (CCT diagram in Figure 5(a)) and isothermal solidification (TTT diagram in Figure 5(b)) respectively. Due to the limitation of the CLSM resolution, the on-set precipitation temperature was defined as the temperature measured at the moment of the primary phase with 100 µm size. With increasing cooling rate from 3.125 to 100 K/min, the initial crystallization temperature decreased from 1460 to 1293 K (Figure 5(a)). For the isothermal solidification, on the other hand, the crystal incubation (or nucleation) time increased from 7.9 to 60.2 seconds as the isothermal solidification temperature increased from 1373 to 1598 K. These diagrams will provide a basis for selecting appropriate slag cooling rates and solidification temperature to optimize the recovery process of rare earth from Bayan Obo tailings and BF slag generated by using Bayan Obo ore.

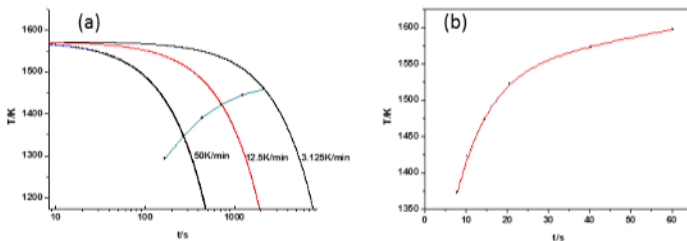


Figure 5. Continuous cooling and isothermal solidification behaviors of slag A. (a) CCT and (b) TTT diagrams

C. Analysis of Crystalline Phase of the Solidified Slags

In order to investigate the microstructure and phase composition of crystal, the samples after *in-situ* observation were examined for the isothermal experiments of Slag A and slag B at 1423K. Figure 6 (a) and (b), respectively, show morphology of the crystals on the slag A and slag B surface. The crystals in slag A are thick hexagonal prisms, while that of slag B are thin and tiny hexagonal prisms like the letter “H”. The “H”- like crystals were aligned in parallel, which is in an agreement with the *in-situ* CLSM observation (Fig. 4), while crystals on slag A surface is

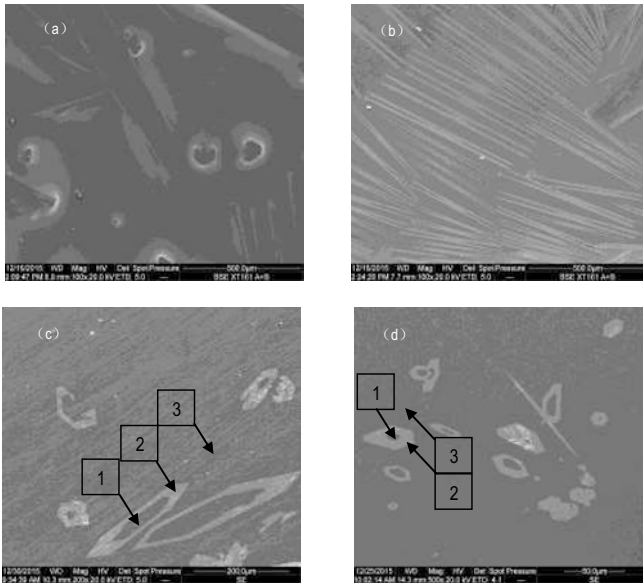


Figure 6. SEM photographs of the surface and polished surface. (a) surface of slag A, (b) surface of slag B, (c) cross section of slag A and (d) cross section of slag B

randomly directed. By cutting the slag sample perpendicular to the top slag surface, the crystals in both slag A and B show a hollow hexagonal prism shape (Figure 6(c) and (d)). However, the size of crystals in slag A is much bigger than that in slag B.

The phase compositions of crystals in slag A and B are analyzed by EDS as shown in table II. It is obvious that rare earths enriched in crystals of hexagonal prisms with hollow, while there are only 1 to 2 wt% rare earth in the slag matrix.

Table II. The Content of different locations by EDS (mole pct)

	Ca	Si	Ce	O	F
'1' of figure 6(c)	17.67	20.54	1.1	51.06	9.62
'2' of figure 6(c)	10.93	18.17	11.71	59.18	-
'3' of figure 6(c)	18.52	20.9	1.47	50.26	8.85
'1' of figure 6(d)	16.32	20.12	0.96	52.0	10.6
'2' of figure 6(d)	11.27	19.17	11.58	57.98	-
'3' of figure 6(d)	19.32	18.65	1.53	46.3	14.19

The primary crystalline phase observed in the CLSM test was identified with XRD analysis after high temperature experiment. 5 g of slag A sample were melted and then solidified with the same thermal history of the CLSM test. The obtained sample was characterized with X-Ray Diffraction and its characteristic pattern is shown in Figure 7. The primary crystalline phase was identified as a rare earth concentrated $\text{Ca}_2\text{Ce}_8\text{O}_2(\text{SiO}_4)_6$.

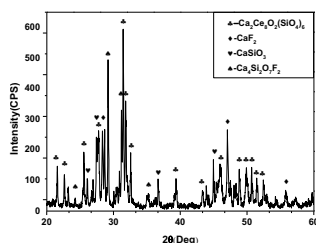


Figure 7. XRD patterns of the solidified slag A

Conclusion

The confocal scanning laser microscope (CSLM) was employed to study the crystallization behavior of $\text{CaO-SiO}_2\text{-CaF}_2\text{-CeO}_2$ slags with CeO_2 content ranged from 12 to 16 mass pct and a constant CaO/SiO_2 ratio of 1. CeO_2 content influences nucleation, growth and morphology of the primary crystals. With increasing CeO_2 content, shape of the primary precipitate changes from an elongated needle-like to a short and rod-like crystal. Furthermore, lowering CeO_2 content favors nucleation of the primary phase during solidification. The CCT and TTT curves for 32 mass pct CaO - 32 mass pct SiO_2 - 20 mass pct CaF_2 - 16 mass pct CeO_2 slag (Slag A) were determined to characterize the crystallization behavior of the slag with cooling rates between 3.125 and 100K/minutes and temperature between 1373 and 1598 K. The primary crystalline phase was identified as a rare earth concentrated $\text{Ca}_2\text{Ce}_8\text{O}_2(\text{SiO}_4)_6$.

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