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CRYSTALLIZATION BEHAVIOR OF MOLTEN BLAST FURNACE SLAG USING CONFOCAL SCANNING LASER MICROSCOPE

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Abstract

Extracting perovskite from high titanium-bearing blast furnace (BF) slag is a green and potential method to recover the second titanium resource. The non-isothermal crystallization process of perovskite in synthesized high titanium-bearing slag was studied in situ by confocal scanning laser microscope (CSLM) with cooling rate of 20 K/min. The results showed that perovskite was the primary phase formed during cooling process in the titanium-bearing synthesized slag (TiO_2=23%). Perovskite started to precipitate at 1719 K and finally presented an orthogonal straight lines morphology.

Introduction

China has abundant titanium resources, 92.4% of which is vanadium-titanium bearing magnetite, deposited mostly around the Panzhihua-Xichang area in the southwestern part of China. At present, smelting the iron concentrate ores in blast furnace is the main process to use these resources. However, titanium resource is not used effectively through BF process because the 54% of titanium in the raw ores finally ends up in blast furnace slag (TiO_2=22-23 mass %) and it is hard to extract titanium from the high titanium-bearing BF slag [1]. Moreover, the high titanium-bearing BF slag is unsuited to be cement [2]. As a result, more than 60 million tons of slag has been stacked in the open from the beginning of BF smelting, which not only brings environmental pollution but also wastes resources. How to extract the valuable secondary titanium resources and use waste slag is a serious problem in China.

The comprehensive utilization of titanium-bearing BF slag has aroused wide concern since 1980 but none of the proposed techniques is easy to be put into industrial and commercial use [3-12]. However, green extractive process of titanium component shows a bright prospect [1,12-14]. In this technique, making titanium gather in perovskite crystals and making these grow up to big sizes is essential for following mineral separation [15]. Many researches on kinetics of precipitation and crystal growth process of perovskite phase have been done [13,16-17] but the crystallization process of perovskite was rarely reported.

In this work, the non-isothermal crystallization process of perovskite in synthesized high titanium-bearing slag based on the industrial slag (the composition is shown in **Table I**) was studied by confocal scanning laser microscope (CSLM) in order to provide information for extracting titanium from slag. Compared with the conventional methods of studying crystallization, such as quenching followed by microscopy, or hot-stage microscopy, CSLM is a new advanced technology which has higher resolution and enables real time in-situ observation of high temperature (up to 1973 K) transient phenomena [19-20]. The CSLM has not been used extensively for studying the complex melting and solidification behavior of slag.

Table I. The main chemical composition of the industrial slag and the experimental synthesized slag (mass %).

	TiO_2	CaO	SiO_2	Al_2O_3	MgO	MoO_3	Total
Industrial slag	22.34	26.96	24.21	14.35	8.32	0	96.18
Aim composition	23	28.8	26.2	14	8	0	100
XRF analyzed composition	22.65	28.68	25.47	14.21	7.54	1.45	100

*In XRF result, the minor impurities (Fe, K, P, Cr, Sr, Zr, Nb) were ignored and the major species were normalized to give a total of 100%. It was assumed that MoO_3 had little effect on the experiments.

Experimental

The synthesized slag was prepared by pre-melting 100 g chemical reagent powder mixture, with the aim composition as shown in **Table I**. The powders used were reagent grade CaO (98 pct), MgO (98 pct), SiO_2 (99 pct), TiO_2 (99 pct) and Al_2O_3 (98 pct). The chemical reagent powders were dried at 373 K for 6h.The mixed powder was put into a molybdenum crucible (50 mm in inner diameter and 80 mm in height) and melted under an argon atmosphere at 1773 K for 1h in $MoSi_2$ furnace so that the slag was homogenized. After melting, the slag was quenched in water and was cut into a small slag sample in a wafer shape of 7 mm in diameter and 3 mm in height for running the experiment. The slag was also analyzed by X-Ray fluoroscopy, and the result in **Table I** showed that there was small deviation from the aim composition.

In the present experiment, the crystallization behavior was observed in-situ through a confocal scanning laser microscope (CSLM) with an infrared furnace (Lasertec, VL2000DX). The melting and solidification of the synthesized slag sample took place in a platinum crucible (8 mm in inner diameter and a height of 5 mm) under an argon atmosphere in the CSLM (Ar>99.999%). The moisture and oxygen were removed by purifier provided with the CSLM. The infrared furnace was evacuated and back-filled with argon three times before heating. The temperature schedule in the experiment is shown in **Figure 1.** The experiment focussed on the crystallization process of slag from 1723 K to 1373 K at cooling rate of 20 K/min. The temperature accuracy was confirmed by melting experiments of pure copper (melting point: 1356 K) and pure nickel (melting point: 1726 K).

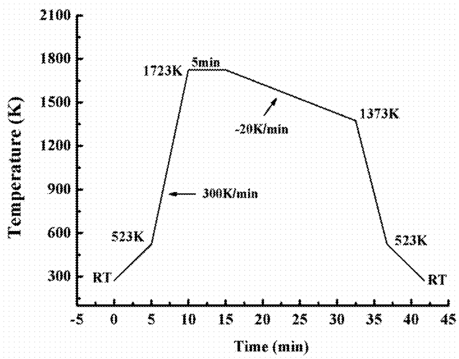

Figure 1. Temperature profile of the CSLM experiment.

After the CSLM experiment, the images captured and digitized from the video recordings of experiment were analyzed to obtain information on the crystallization process of slag. In addition, the quenched sample was examined by X-ray Diffraction (D/max 2500PC).

Results and Discussion

The surface of liquid slag fluctuated because of surface tension driven flow. So the crystals moved in and out of the viewing field with the moving liquid slag. **Figure 2** shows the crystallization process of slag at a cooling rate of 20 K/min. The slag remained totally liquid above 1723 K and the liquid phase presented as bright white field**.** The pictures a, b and c in **Figure 2** were of a different location because the movement of the slag. Pictures c to h are for the same location.

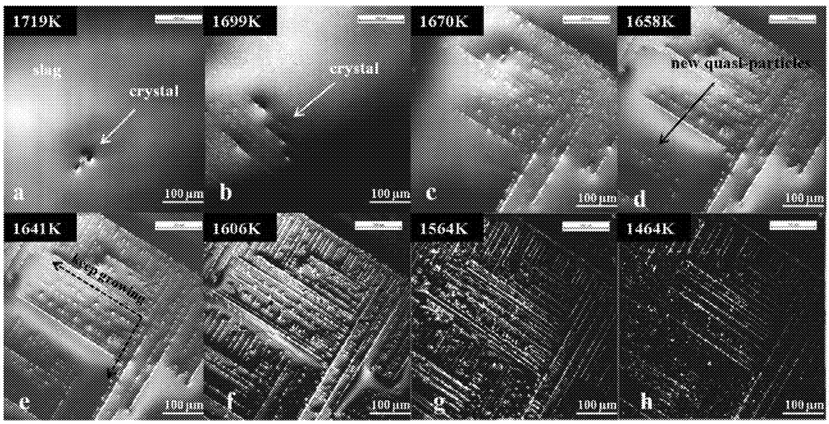

Figure 2. The CSLM images of crystallization process of slag cooled at 20 K/min.

The primary phase precipitates as three quasi-particles at 1719 K (**Fig.2(a))** Then larger pieces of crystals appear below 1703 K. The crystals present mutually perpendicular closely-spaced straight lines which consist of the quasi-particles. As the temperature decreases, crystals keep growing and extending in mutually perpendicular directions in a way that new quasi-particles precipitate one by one in alignment, forming closely-spaced structure – presumably made up of dendrites (**Fig.2(b-h)**). Meanwhile, crystals keep coarsening and the amount of liquid phase reduces gradually with decreasing temperature. It is shown that the dendrites present orthogonal straight lines morphology at the cooling rate of 20 K/min. The dendrites grow in a way that new dendrites precipitate successively in orthogonal directions.

Figure 3 illustrates the XRD patterns of the sample. As can be seen, perovskite is the main crystalline phase during experiments which coexists with another phase clinopyroxene - $CaMgSi_2O_6$. Besides, an amorphous peak is also present. In order to better understand the crystallization process, the equilibrium phases at different temperatures of the synthesized Ti-bearing slag were calculated by FactSage 6.2 shown in **Figure 4.** The liquidus temperature of the slag is 1705 K and perovskite is the primary phase during cooling process. There is small deviation between the theoretical calculation and experimental result. Combining the analytical and calculated results, it can be concluded that the crystals observed in CSLM experiments are perovskites, which crystallized along a specific path mentioned earlier. The growth process of perovskite is shown in **Figure 5.**

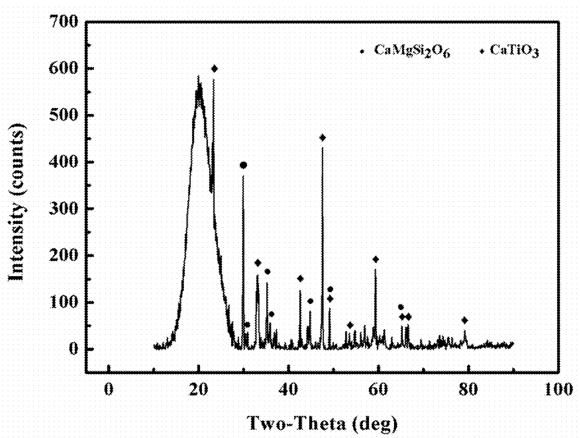

Figure 3. XRD patterns of the sample cooled at 20 K/min.

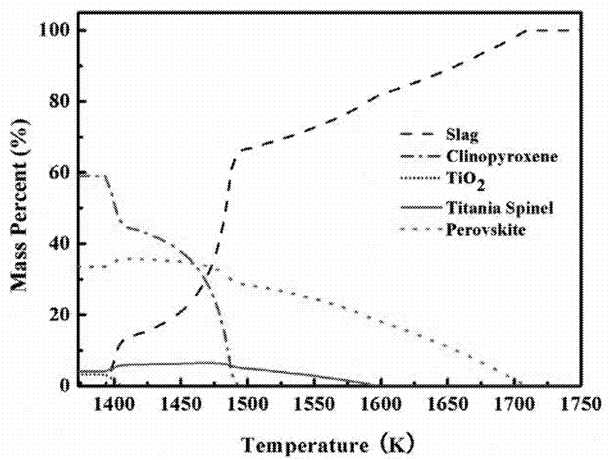

Figure 4. Theoretical isothermal phase composition of 28.8%CaO, 26.2%SiO_2, 14%Al_2O_3, 8%MgO, 23%TiO_2 slag during cooling.

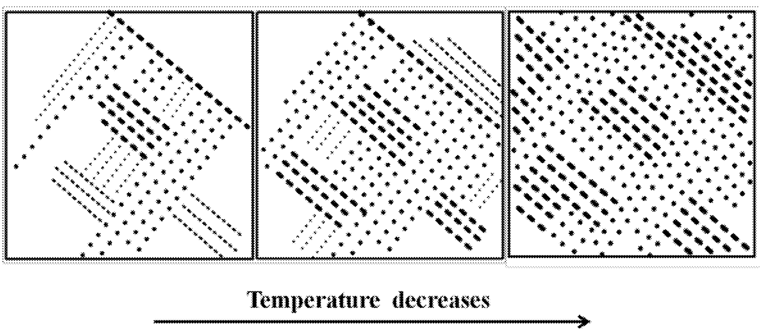

Figure 5. Schematic representation illustrating the growth process of perovskite during CSLM experiment at a cooling rate of 20 K/min.

Conclusions

Perovskite was the primary phase formed during cooling process of the Ti-bearing synthesized slag (TiO_2=23%) at cooling rate of 20 K/min. Perovskite started to precipitate at 1719 K and finally presented as orthogonal dendrites. Perovskite grew along a specific growth path with new dendrites precipitating successively.

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