

In-situ Observation of the Precipitation Behavior of a Dy₂O₃ Containing Slag System

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Abstract An experimental investigation of the precipitation behavior of the Dy₂O₃ containing slag during cooling was carried out in this work. The slag with composition 45 wt% SiO₂—49 wt% CaO—6 wt% Dy₂O₃ was equilibrated at 1673, 1773 and 1873 K for 24 h in an argon atmosphere, and then quenched in water to determine the phase relations. The composition and microstructure of the equilibrated phases of the systems were determined by EPMA/WDS. The precipitation behavior of the REEs containing phases during cooling was studied by using an in-situ confocal scanning laser microscope (CLSM) observation technique combined with an infrared imaging furnace heating (IIF). Data resulting from this work aims to support further investigation on separation of rare earths from metallurgical slags.

Keywords In-situ observation · Rare earth · Precipitation · Recovery

Introduction

The rare earth elements (REEs), including dysprosium, are increasingly valuable because of their limited known exploitable deposits in the earth's crust [1], and because of their significant role in permanent magnets, lamp phosphors, rechargeable NiMH batteries, catalysts and other applications [2–4]. The recycling of Dy doped permanent magnets in electric vehicles and wind turbines is considered

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as part of the solution for a more green and sustainable future [5, 6]. As the largest rare-earth volume is used in permanent magnets, it is urgent to recover dysprosium, neodymium and other valuable metals from the end of life magnets. This work focuses on the REEs recovery from the slags by pyrometallurgical route, which is employed for REEs recovery as an alternative or combination with hydrometallurgical processing. However, research on the presence of rare-earth metals in slags as part of a recycling scheme has been fairly limited up to now [7, 8]. In this respect, this work aims to investigate precipitation behavior of the Dy_2O_3 - SiO_2 - CaO ternary system during cooling and to optimize the cooling process for high REEs recovery.

Experimental Method

Slags were prepared by mixing reagent-grade oxides CaO (obtained by calcination of CaCO_3 , 99.99%, Chempur), SiO_2 (99.9%, Merck Millipore) and Dy_2O_3 (99.99%, Chempur) with the composition 45 wt% SiO_2 , 49 wt% CaO and 6 wt% Dy_2O_3 . The mixtures were respectively melted at 1673, 1773 and 1873 K for 24 h in an argon atmosphere, and then quenched in water. The schematic set-up of the quenching experiments is shown in Fig. 1.

The microstructure and phase composition analysis of the quenched samples were investigated using an Electron Probe Micro Analyzer coupled with Wavelength Dispersive Spectroscopy (EPMA/WDS, JEOL JXA-8530F). A quantitative analysis using standards at an acceleration voltage of 15 kV and a probe current of 15 nA was performed. The slag samples were mounted in resin, grinded, well polished and Pt coated before the EPMA/WDS analysis. The CSLM-IIF was used to observe the precipitation behavior of the slag in situ. The CSLM sample was selected from the 1873 K quenched samples. The slag sample was charged into a Pt-20%Rh crucible placed on the sample holder in the heating chamber. The CSLM chamber was evacuated and flushed with argon three times before the slag sample was heated to the desired temperature while a constant Ar stream was maintained continuously during the experiments. Then the slag sample was cooled to solidify temperature at a predefined cooling rate then quench to room temperature for later microscope analysis. The temperature profile during the CSLM test is shown in Fig. 2. The laser scanned images of this cooling process were captured and used for further investigation.

Results and Discussion

In consideration of slags containing lower rare earths content, a suitable cooling trajectory can enrich the rare earths in the liquid phase. The slag sample quenched from 1873 K was selected for the CLSM observation. It was remelted in the heating

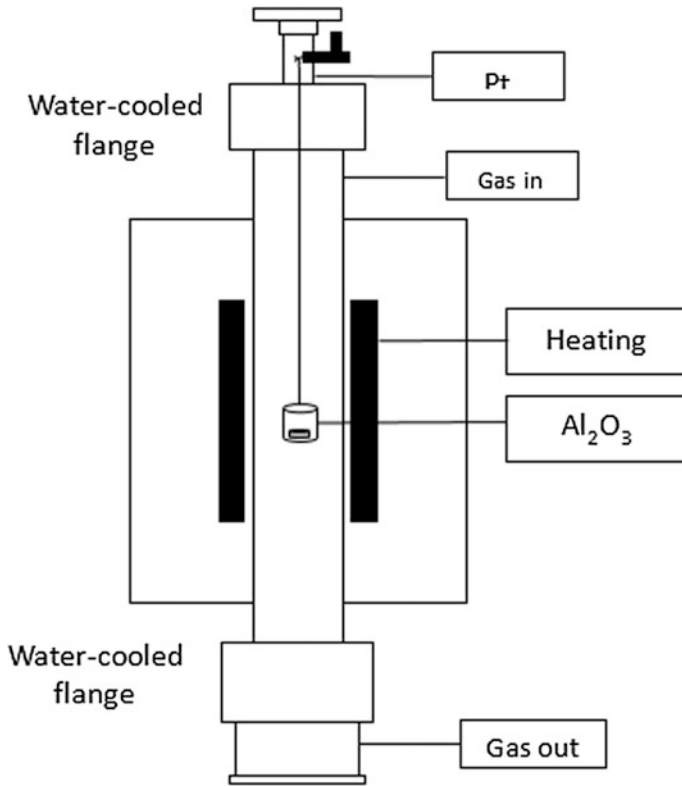
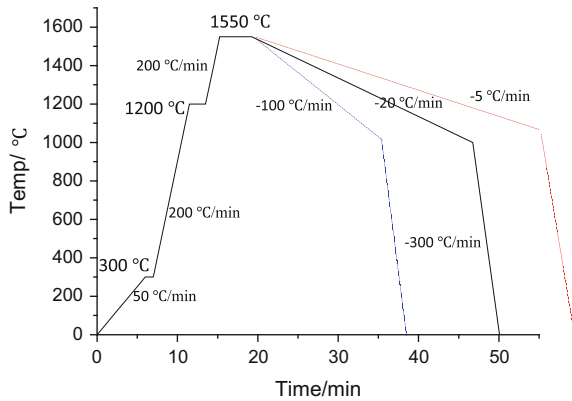


Fig. 1 Schematic representation of the equilibration furnace

Fig. 2 Temperature profile during CSLM tests



chamber at 1550 °C and then cooled under different cooling rate at 5, 20 and 100 °C/min, respectively. The images were recorded to show the precipitation and solidification process during cooling from 1550 °C through CSLM observation of which some snapshots are listed in Fig. 3. The composition and microstructure of the precipitates are further confirmed by EPMA/WDS with the back scattering electron (BSE) images of the equilibrated samples from 1873, 1773 and 1673 K as are shown in Fig. 4. The presence of Ca_2SiO_4 and Dy_2O_3 is determined at 1773 and 1673 K by quantification analysis through EPMA/WDS. The eutectic reaction proceeds as $\text{L} \rightarrow (\text{Ca,Dy})_2\text{SiO}_4 + \text{Dy}_2\text{O}_3$ during cooling from above 1773 K. In the $(\text{Ca,Dy})_2\text{SiO}_4$ solid solution, the solubility of Dy_2O_3 is given as 10.52 wt% at 1773 K and 5.61 wt% at 1673 K from the quantification results. It shows the C_2S phase at higher temperature shows higher Dy_2O_3 solubility. The substitution of Dy^{3+} at Ca^{2+} site in C_2S phase leads to the formation of $(\text{Ca,Dy})_2\text{SiO}_4$ solid solution, resulting cation vacancies or oxygen interstitials to maintain charge balance in this structure. Below 1673 K, the solubility of Dy_2O_3 in C_2S may be lower or even almost negligible.

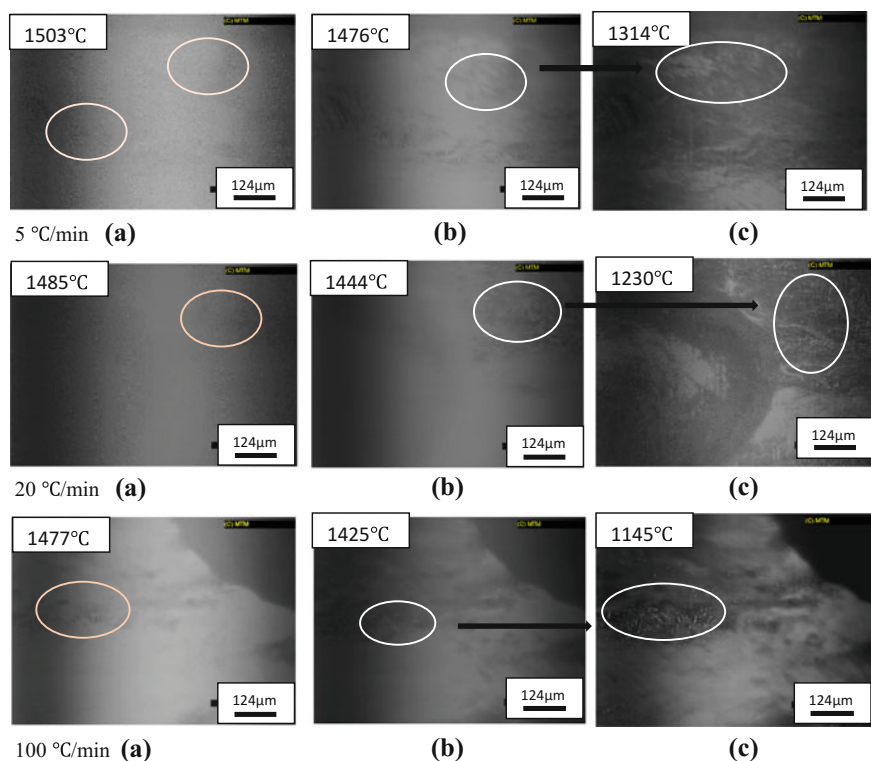


Fig. 3 In situ observation of precipitation behavior of the 45 wt% SiO_2 –49 wt% CaO –6 wt% Dy_2O_3 slag sample at different cooling rate with 5, 20, 100 °C/min: **a** first precipitate (C_2S) appears **b** second type of precipitate appears (Dy_2O_3) **c** complete solidification

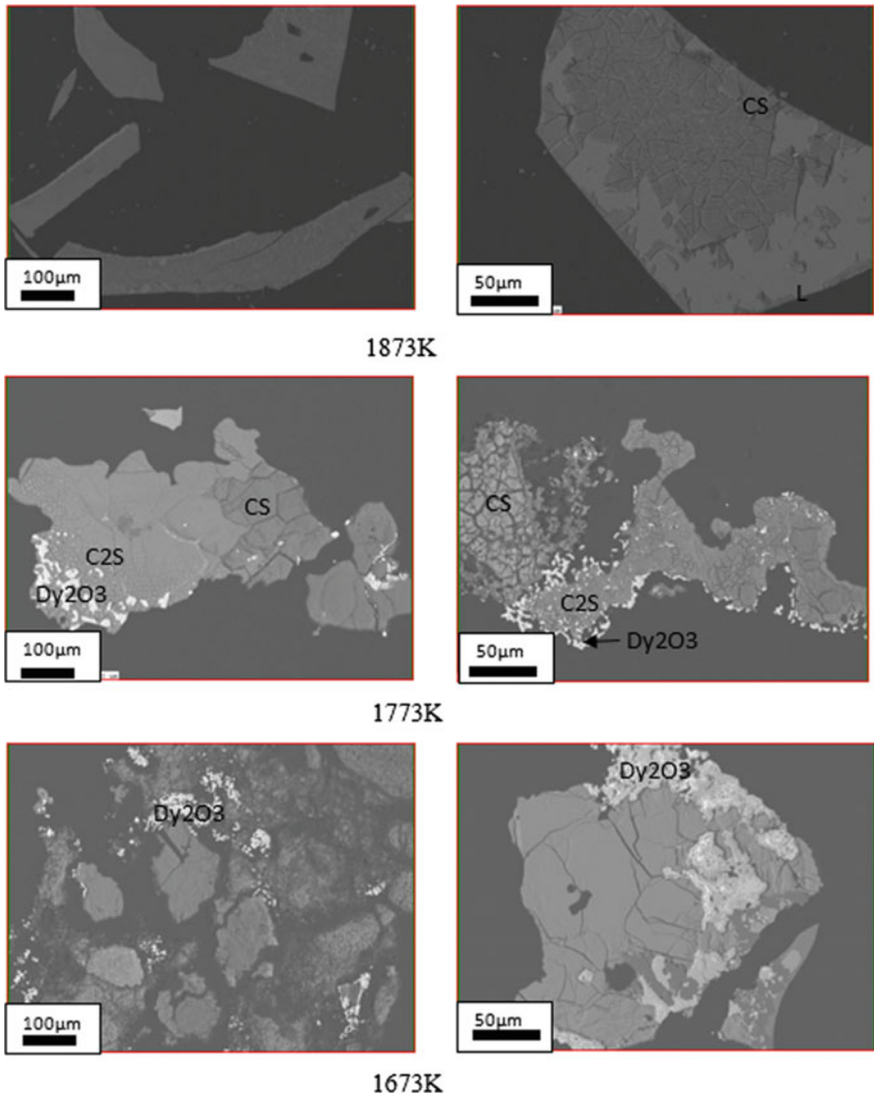
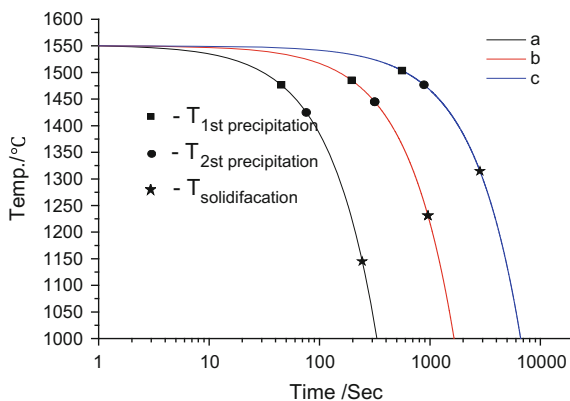


Fig. 4 BSE images of the quenched slag samples from equilibrium at 1873, 1773 and 1673 K

It is observed that the first precipitates shown in Fig. 3a were found to be $(Ca,Dy)_2SiO_4$ phase and another precipitation with bright color were analyzed to be Dy_2O_3 as shown in Fig. 3b. As the cooling proceeds, more Dy_2O_3 precipitated from C_2S phase. It is also found that the grain size of the precipitates (Dy_2O_3) increases with lower cooling rate. The precipitation and complete solidification temperatures were shown in Fig. 5 as a potential reference for the construction of a continuous cooling transformation (CCT) diagram.

Fig. 5 The precipitation and complete solidification temperatures during cooling with different cooling rate.

a: 100 °C/min **b:** 20 °C/min
c: 5 °C/min



Conclusion

The phase relations and precipitation behavior of $\text{Dy}_2\text{O}_3\text{-CaO-SiO}_2$ system during isothermal and continuous cooling experiments with different cooling rate were studied. As the eutectic reaction proceeds as $\text{L} \rightarrow (\text{Ca,Dy})_2\text{SiO}_4 + \text{Dy}_2\text{O}_3$ during cooling, it is possible to precipitate Dy_2O_3 from the Dy_2O_3 -containing slag system. A suitable cooling trajectory can enrich the rare earths with different grain size to satisfy the practical demands.

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