



Proceedings of the
Fourth International

Slag Valorisation Symposium Zero Waste

15-17 April 2015
Leuven, Belgium

Editors Annelies Malfliet and Yiannis Pontikes

KU LEUVEN

PHASE RELATIONS IN THE SYSTEM $\text{CaO-SiO}_2\text{-Nd}_2\text{O}_3$ AT 1600 °C

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Introduction

The increasing demands for rare earth based materials, which are widely used in electronic devices, has raised the needs of the efficient use of rare earths to minimize environmental impacts, solve supply risk of critical raw materials, and minimize the “balance problem”.¹⁻⁵ In particular, attentions have been drawn on recycling of rare earth elements from enriched waste streams. Hydrometallurgy, which has shown potential in this specific area, suffers from large amounts of chemicals needed and difficulties in dismantling, separation, and processing steps when applied for rare-earth containing batteries and magnets. Therefore, pyrometallurgical methods have been developed as an alternative in which low environmental and economic impacts are their main advantages. In these processes, slags play an important role. As rare earth elements typically have more stable oxides than base metals, they can be separated from the base metal by adding appropriate flux material to the system. Efficient fluxing requires not only a suitable flux material but also knowledge of the phase relationships in the slag systems.

In this work, CaO-SiO_2 are used as flux material. Phase relations of rare earth oxide Nd_2O_3 in the chosen system will be investigated. The obtained information also allows estimating distributions of rare earths in the slag phases, which is useful for their extraction.

Experiment

In the present study, phase relations and solutions of the oxide system were studied using the quenching technique. Samples were prepared from powder of CaO (obtained by calcination of CaCO_3 , 99.99 %, Chempur), SiO_2 (99.9 %, Merck Millipore) and Nd_2O_3 (99.99 %, Chempur). These oxide powders were weighed using an analytical balance with 0.01 mg accuracy and mixed. 20 mg of the powder mixture was put in closed shallow-bottomed envelopes made by folding 0.1 mm thick Pt-

20 % Rh foil. Then, the envelopes were placed in a protection alumina crucible. These crucibles were positioned with a Pt-20 % Rh/Mo wire in the hot zone of a vertical tube furnace with MoSi₂ heating elements. The hot zone was measured to be within 2 cm with 1 °C in error. The furnace temperature was monitored within 1 °C by a type B (Pt-6 % Rh) thermocouple. The samples were then heated in the furnace under Argon atmosphere, and kept at the desired temperature for a specific time before quenching in cold water. Fast cooling rate is assumed due to the small size of the slag sample and its container.

The quenched samples were mounted in resin, grinded and polished. For microstructure and phase composition analysis, the samples were carbon coated, and analysed by electron probe micro-analysis (EPMA, JEOL JXA-8530F) using standardised wavelength dispersive spectroscopy (WDS) and operated at 15 kV-5 nA. The average accuracy of EPMA measurements is within $\pm 1\%$. The contents of expected contaminations, Mo, Rh and Pt, were measured to be less than 0.1 wt.%. The presence of liquid phase in the samples was verified by a Field Emission Gun Electron Microscope FEI-Nova Nanosem 450 using electron backscatter diffraction (EBSD) in low vacuum at 20 kV.

The equilibration time was determined by comparing the amount of Nd₂O₃ dissolved in the glass phase after different equilibration times. After performing this experiment, it was concluded that 24 h dwelling time was sufficient for the equilibrium.

Results and discussion

Experiments were carried out using the previously described system. The obtained results were used to determine the ternary diagram and the phases that exist at 1600 °C. Only the phase relations in the Ca₃SiO₅(C3S)-SiO₂-Nd₂O₃ pseudo ternary system are presented in Figure 1. These data will be used to optimize the ternary system using FactSage in future work.

For the conducted experiments, evolution of the microstructure is expected to be completed before quenching. Only samples that consist of at least 2 homogeneous phases in equilibrium with each other are useable to construct the isothermal section. Some typical microstructures that can be observed by EPMA-WDS in the quenched samples are shown in Figure 2.

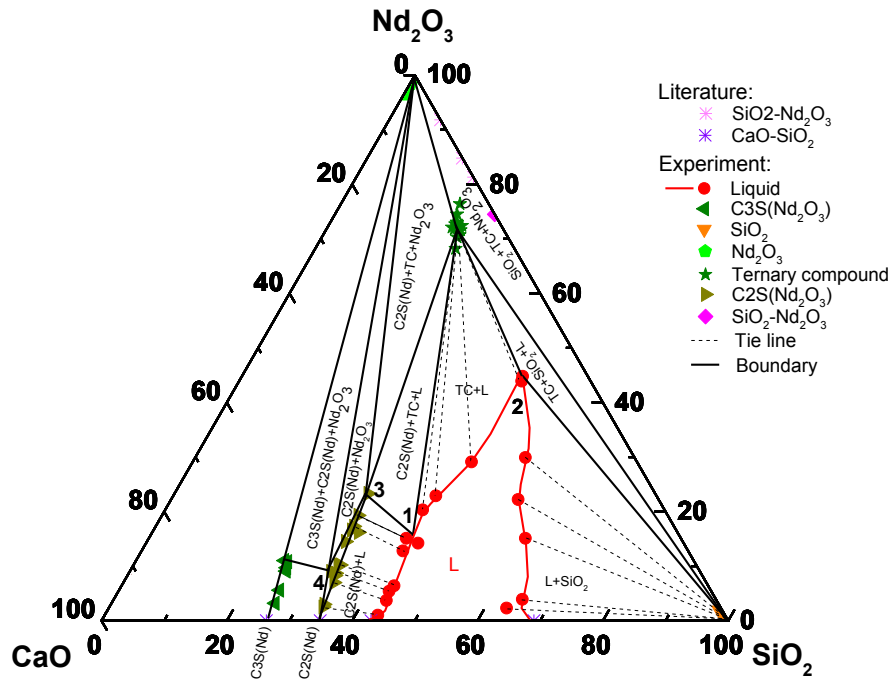


Figure 1: Isothermal section of $\text{CaO-SiO}_2\text{-Nd}_2\text{O}_3$ phase diagram and tie lines at 1600 °C (in wt.%). Phase relation of the pseudo system $\text{CaO-C3S-Nd}_2\text{O}_3$ has been omitted for clarity.

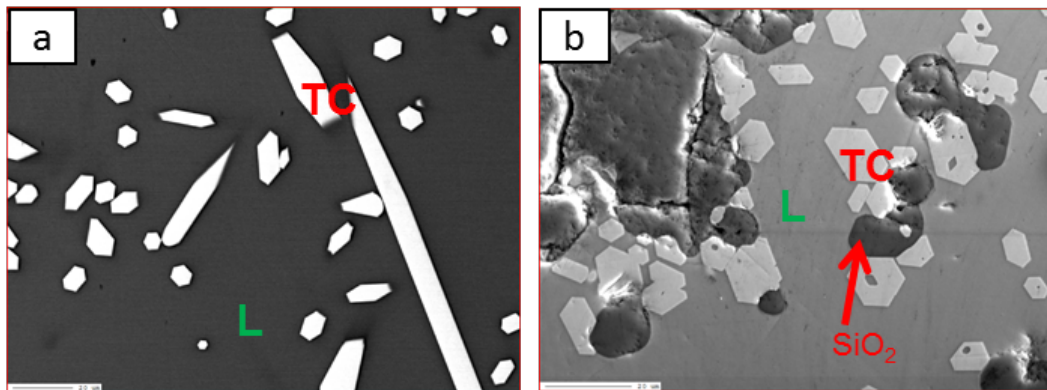


Figure 2: BSE image a) one solid phase in equilibrium with one liquid phase, b) two solid phases in equilibrium with one liquid phase.

The shape of phase boundaries allows the liquid and solid phases to be distinguished. However, when a rounded shaped solid solution, which can also be falsely judged as

liquid, is in equilibrium with liquid and/or solid phase, EBSD is required to classify the phase. As shown in Figure 3, the difference of Kikuchi patterns between the crystalline and amorphous phases can be detected using EBSD technique. With the combination of EPMA and EBSD, the solid solution phase and its solubility data can be determined.

According to Figure 1, there are three primary phases: SiO_2 , C2S(N) solid solution and a ternary compound (TC). Nd_2O_3 dissolves in $3\text{CaO} \cdot \text{SiO}_2$ (C3S) and $2\text{CaO} \cdot \text{SiO}_2$ (C2S), and its solubility limit is 11 wt.% and 23.3 wt.% Nd_2O_3 , respectively. The ternary compound has been reported to have the formula of $\text{Ca}_{2+x}\text{Nd}_{8-x}(\text{SiO}_4)_6\text{O}_{2-0.5x}$ and suggested $x = 0$ at 1600°C ⁶. In another publication⁷, the present authors showed that the solubility of Ca in the ternary compound, in equilibrium with liquid, is $x = 0.49$ at 1600°C using XRD single crystal technique. However, in the present work, a range in composition of the ternary compound was observed. Therefore, further study needs to be done to confirm the presence of the ternary solid solution.

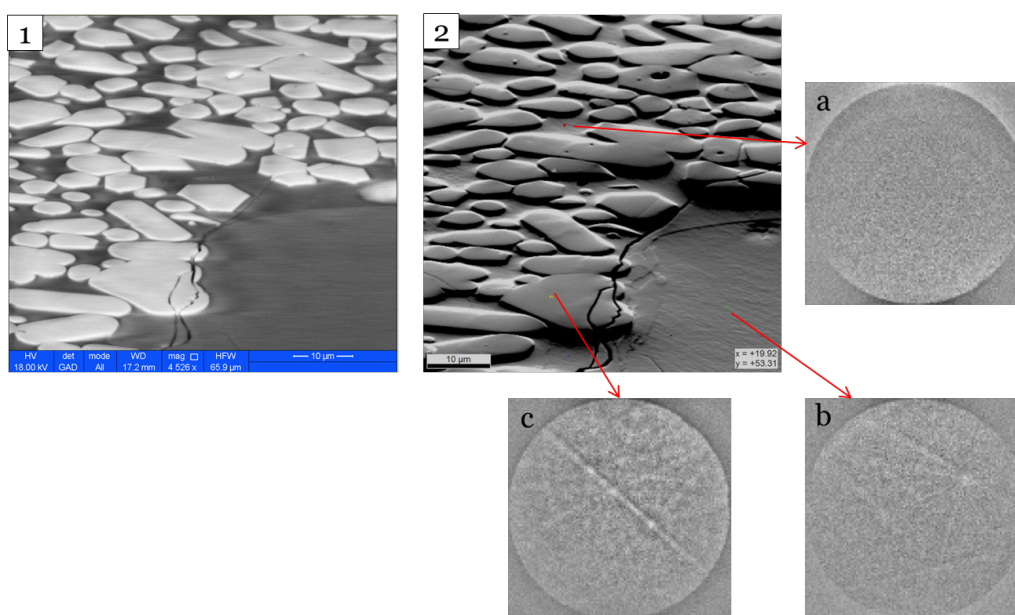


Figure 3: EBSD images 1) BSE image, 2) SE image; Kikuchi pattern of a) liquid phase, b) solid solution phase, and c) solid phase.

The present study is the first to report on the solid-liquid phase diagram at 1600°C in the condensed system. The liquidus is displayed by a red line in Figure 1. The solubility of Nd_2O_3 in the liquid phase at the temperature is high, up to nearly

45 wt.%. The tie-lines between liquid and C2S, SiO₂, and TC in three two-phase regions are also indicated. The amount of liquid at any point along these tie-lines can be determined by the Lever rule. Points 1 and 2 represent the composition of liquid in equilibrium with 2 solid phases, namely, solid solution C2S(Nd₂O₃) and TC or SiO₂ and TC. Point 3 and 4 represent the composition of solid solution C2S(Nd₂O₃) in equilibrium with two other phases: Nd₂O₃ and TC; and Nd₂O₃ and solid solution C3S(Nd₂O₃). All four points lie on the three-phase boundaries.

Conclusion

The isothermal section in the Ca₃SiO₅-SiO₂-Nd₂O₃ pseudo ternary system at 1600 °C has been constructed. The investigated phase relations will be used for optimizing thermodynamic database and separation of Nd₂O₃ from the slag. The combination of EPMA-WDS and Nanosem-EBSD provides crucial evidence for the classification of the amorphous phase and for the determination of solubility data of the solid solutions.

Acknowledgments

The authors acknowledge the support from the Hercules Foundation (project no. ZW09-09) in the use of the FEG-EPMA system.

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