CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 56 (2017) 185–195

Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

Novel design of ferronickel smelting slag by utilizing red mud as a fluxing agent: Thermochemical computations and experimental confirmation

Hyun Sik Park[a], Min Chul Ha[a], Min Seok Kim[a], Jung Ho Heo[b], Joo Hyun Park[b,*]

[a] Resource Recovery Research Center, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 34132, Republic of Korea
[b] Department of Materials Engineering, Hanyang University, Ansan 426-791, Republic of Korea

ARTICLE INFO

Keywords:
Ferronickel slag
Metallurgical flux
Melting temperature
Red mud
Olivine
Spinel

ABSTRACT

The effect of red mud on the melting behavior of ferronickel slag was investigated in a laboratory-scale horizontal tube furnace. Melting and softening of slag samples fluxed with different amounts of red mud were examined by an *in-situ* visualization technique in the temperature ranges from 1673 K to 1823 K. FactSage™ 7.0 was used to perform thermodynamic calculations of the multi-component system of ferronickel slag and red mud. The liquid phase area was extended to lower temperatures by adding red mud, and this implied that red mud was an excellent flux. The primary solid phase field was confirmed to be dependent on the red mud content from X-ray diffraction measurements. Microscopic observations using a scanning electron microscope (SEM-EDX) confirmed that the primary solid phase changed from olivine to spinel with the addition of red mud.

1. Introduction

Ferronickel smelting in a submerged arc furnace (SAF) is an energy intensive process performed at a high temperature range of 1773–1873 K. During the smelting process of sapolitic nickel laterite ore having a nickel content of 2.2–2.3%, a large quantity of ferronickel slag is produced that accounts for 97% of the ore charge. To achieve a ferronickel grade of 15–20% Ni, 80–85 MW of electrical energy is used to produce the rate of 150 t/h of slag and 21 t/h of ferronickel [1]. Unreduced components, which consist mostly of MgO, SiO_2 and some FeO, are removed from the furnace in a liquid slag form by a tapping operation. Forsterite (Mg_2SiO_4)-based slag containing approximately 10% FeO requires a typical process temperature of 1873 K due to the high melting temperature.

In a metallurgical process, flux is a medium that decreases melting and operating temperatures while increasing the fluidity of the liquid slag. Burnt lime (CaO) and fluorspar (CaF_2) are examples of fluxing materials used for ironmaking, steel refining and continuous casting processes. Oxide systems based on the $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}CaF_2$ cover most of the slag composition in ferrous metallurgy. Crucial operating factors for ironmaking and steelmaking slags include the basicity (practically the CaO/SiO_2 ratio), viscosity and impurity levels. These physicochemical properties are extensively controlled by the fluxes. Raw materials for metallurgical fluxes such as limestone, dolomite and fluorspar are abundant in nature and are supplied to steel mills at relatively low prices.

In the copper smelting process, silica is supplied as a fluxing material with copper concentrate to remove iron oxide (FeO) generated from sulfide oxidation. The $FeO\text{-}SiO_2$ binary slag forms a eutectic area at 25–38% SiO_2 that has a melting temperature below 1478 K. The fayalitic (Fe_2SiO_4) slag, which has a low viscosity (0.1 Pa s) at 1723 K [2], facilitates easy separation of slag from molten mattes. Recently, copper smelters have actively utilized recycled raw materials as a fluxing agent. Various recycled glass cullets are ground and fed to the copper smelting process as a partial replacement for the silica flux.

Applying industrial wastes to the ferrous and non-ferrous metallurgical processes is advantageous because they can remarkably reduce the production cost. In addition, the consumption of recycled materials can ultimately minimize the environmental risks and the waste management costs. Therefore, we investigated waste materials that can be effectively used in the ferronickel smelting process. Prerequisites for potential fluxing materials are that the materials are non-recyclable, have a low transportation cost and provide excellent performance as a flux.

Red mud is a bauxite residue produced from the Bayer process. Its application to construction material has been very limited due to its fine particle sizes ($< 50\ \mu m$) and high alkalinity due to the residual sodium hydroxide solution [3]. Concentrated radioactive elements and heavy metals that are contained in red mud also increase concerns related to the utilization of red mud. There have been attempts to recover valuable elements (Al, Na, Fe, Ti, V) and rare earth elements from red mud [4,5]. However, the extractions were only successful at

* Corresponding author.
E-mail address: basicity@hanyang.ac.kr (J.H. Park).

http://dx.doi.org/10.1016/j.calphad.2017.01.006
Received 22 November 2016; Received in revised form 9 January 2017; Accepted 24 January 2017
0364-5916/

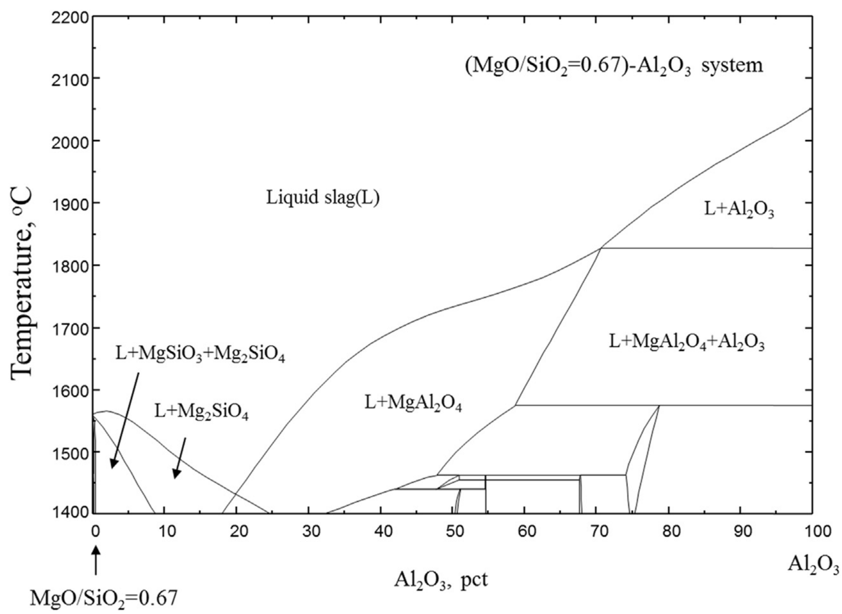

Fig. 1. Phase diagram of the MgO - SiO_2 - Al_2O_3 ternary system as a function of Al_2O_3 content (FactSage™ 7.0).

laboratory scales, and none of them have been commercially successful.

Three major oxide components of red mud are Fe_2O_3, Al_2O_3 and SiO_2, and these account for 90% of the total weight. If red mud is fluxed to ferronickel slag, the MgO-Fe_tO-Al_2O_3-SiO_2 oxide system will appear. The strong reducing atmosphere in SAF due to the presence of carbon will reduce Fe_2O_3 to FeO and Fe, which will finally contribute to the recovery of iron source. In addition, SiO_2 in red mud will increase the silica to magnesia ratio, which in turn increases the operational flexibility. Most importantly, the effect of Al_2O_3 content in the MgO-Al_2O_3-SiO_2 ternary slag system was predicted using FactSage™ 7.0 as shown in Fig. 1. At a conventional smelting composition (MgO/SiO_2=0.67), alumina addition consistently decreased the melting temperature of forsterite from 1830 K to 1638 K up to a composition of 20% Al_2O_3. The temperature gap of 130 K between forsterite and the ternary eutectic point implies that red mud may possibly be used in the smelting process to significantly reduce energy consumption. A life cycle assessment showed that 10% ferronickel embodied energy can be saved when the process temperature is decreased by 100 K [6]. The effect of minor components in red mud such as CaO, Na_2O and TiO_2 were assumed to be negligible considering their small quantity and neutrality. That is, the fluxing effect of basic oxides (CaO and Na_2O) is offset due to the presence of acidic oxide (TiO_2) in the red mud.

The MgO-Fe_tO-Al_2O_3-SiO_2 quaternary slag system was studied by Jak and Hayes using thermodynamic modelling of ferronickel smelting slags [7]. In their study, the high liquidus temperature was attributed to the extensive solid solutions between Mg_2SiO_4 and Fe_2SiO_4. Increasing the FeO concentration in the silica primary phase field rapidly decreased the slag viscosity, while the addition of Al_2O_3 increased the viscosity of the liquid slags [7]. According to the MgO-Al_2O_3-SiO_2 ternary phase diagram [8], the addition of Al_2O_3 into a MgO-SiO_2 binary system decreased the liquidus temperatures in the olivine primary phase field. Moreover, FeO is known to be a basic oxide that lowers both the melting temperature and viscosity of the slags [9]. The effect of FeO/SiO_2 ratio as well as the influence of Al_2O_3 in copper smelting slag was also investigated by one of the present authors [2]. FeO and Al_2O_3 addition decreased the melting temperature of the slag to some extent, which in turn decreased the viscosity. Thus, it can be expected that an adequate amount of red mud will considerably reduce the melting temperature of ferronickel slag, which should enable low temperature and energy-saving operation in the smelting process.

In the present study, the melting behavior of ferronickel slags fluxed with red mud was investigated by an *in-situ* visualization technique in a temperature range of 1673 K to 1823 K. The pseudo-binary phase diagram of the projected ferronickel slag and red mud flux was derived using thermochemical computing software, FactSage™7.0, which has been successfully used in ferrous and non-ferrous metallurgical systems [10–14]. For example, the phase diagram of the CaO-SiO_2-Al_2O_3-MgO-Fe_tO system, which is of interest in the present study, has been fully predicted at any temperature under wide oxygen potential range [15,16]. All these major oxide components have been fully optimized and evaluated together at all compositions. All available data for binary, ternary and quaternary sub-systems have been fully optimized [15,16]. These calculations were confirmed through the melting behavior of the composite samples. Phase analysis was carried out by X-ray diffraction, which assisted with phase change in the complex system. Morphological changes in the samples were investigated, which clearly demonstrated compound formation after the addition of red mud.

2. Experimental procedure

Ferronickel slag from a local smelter and the red mud supplied by a regional Bayer process in Korea were used for the present experimental investigation. The chemical compositions of the air-cooled slag from Société du Nickel de Nouvelle Calédonie et Corée (SNNC) and dry, stacked red mud from the KC corporation are shown in Table 1. This quantitative compositional analysis was carried out by X-ray fluorescence spectroscopy (XRF-1800, Shimadzu, Kyoto, Japan). Particle sizes were adjusted by sieving raw materials under 100 µm. To investigate the effect of red mud addition, composite pellet samples that were 12 mm in diameter were prepared at the compositional ratios shown in Table 2. Spherical pellets were obtained by hand rolling with drops of distilled water. Pellets were dried at 473 K for 48 h to eliminate potential physisorbed residual moisture.

A schematic of the experimental apparatus is shown in Fig. 2. The horizontal tube furnace was heated using Super-Kanthal ($MoSi_2$) elements, which formed a 125 mm hot zone. Inside the furnace there was a graphite substrate connected to a graphite rod, which enabled sample movement in and out of the hot zone. Solid graphite substrate was selected because it simulates reduction conditions in the smelting process, but the contact area of the substrate was minimal due to the spherical shape of the pellets.