

The utilization of metallurgical slags by means of oxidation in the liquid state

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Abstract: In the present contribution, the concept of the slag utilization based on transformation of non-magnetic wüstite (FeO) to magnetic magnetite (Fe₃O₄) using an oxidizing atmosphere is proposed. In order to verify the feasibility of the proposed way of slag utilization, experiments were performed on the ternary CaO-FeO-SiO₂ and quaternary CaO-FeO-SiO₂-MnO slag systems, accompanied by thermodynamic and kinetic modelling.

The kinetic studies of the oxidation of FeO in liquid synthetic slags were carried out using thermogravimetric technique (TGA) and nucleation / crystal growth of the precipitated phase by confocal scanning laser microscopy (CSLM). Air was used as an oxidizing atmosphere. TGA results indicated that, during the first 10-15 min of oxidation, 80-90% of FeO in the slag was oxidized. CSLM images showed that crystals grew and agglomerated on the liquid slag surface, reaching 50 µm in length in some cases. Different shapes of crystals were observed at different experimental temperatures. A kinetic analysis of the TGA results indicated that the oxidation process consists of three distinct steps, i.e., nucleation of magnetite/manganese ferrite from the slag, followed by a chemical reaction-controlled stage and later, the diffusion of oxygen through the product layer.

Precipitated phases were analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD analysis confirmed the presence of magnetite and manganese ferrite in the product layer.

Keywords: Slag utilization, oxidation, kinetic studies, CSLM

1. Introduction

Through production of iron and steel, large amounts of industrial wastes and by-products are generated. Efficient recycling of these materials is of increasing interest worldwide for the sustainability in processes with respect to increasing raw material costs and waste reduction. For example, slag from the first stage of Electric Arc Furnace (EAF) in the Swedish and Ukrainian steelmaking industries contains a significant amount of FeO (up to 30 mass %). It is important to maximize the amount of iron that is recovered from the slag so that the remaining portion can be used for more civil engineering purposes. In order to find a practical solution, joint efforts were made at the Royal Institute of Technology, Sweden (as a part of the Eco-steelmaking national project in Sweden) and National Metallurgical Academy of Ukraine. A sustainable approach to utilize steelmaking slag components based on transformation of non-magnetic iron monoxide (or wüstite) to magnetite by oxidation has been proposed by the current authors [1]. This allows selective recovery of iron-bearing and non-iron-bearing slag constituents for the specific purposes. From the technological point

of view, pre-treated slag can be processed using a magnetic method wherein iron oxides transformed to a magnetic form are separated for further utilization. The rest of the slag (non-magnetic) could be effectively used in production of cement binder or in other applications. Magnetic products may be recycled in steel industry or utilized in electronic industry if sufficient purity could be achieved..

In this study, the ternary CaO-FeO-SiO₂ and quaternary CaO-FeO-SiO₂-MnO slag systems were examined to verify the feasibility of the proposed way of slag utilization. Results were further investigated along with thermodynamic and kinetic modelling.

2. Thermodynamic analysis

The phase equilibria for the slag systems containing iron oxides have been studied by Turkdogan [2], Bodsworth and Bell [3], Kongoli and Yazawa [4]. Muan and Osborn [5] reported the phase diagrams of the FeO-MnO system in a low oxygen partial pressure and the FeO-MnO-SiO₂ system in CO₂/H₂ and air atmospheres. A structural model for binary silicate systems including MnO-SiO₂ and CaO-SiO₂ as well as thermodynamics of Fe₃O₄-Mn₃O₄ spinels are presented in work of Pelton et al [6]. Pownceby et al [7] analysed the effects of basicity on the phase equilibria of Fe₂O₃-CaO-SiO₂ in air at 1513–1573K. Sun and Jahanshahi [8] summarized measurements of redox equilibria in slags involving Fe, Mn, Ti, and V transition metals, and kinetics of CO-CO₂ reactions with slags.

The present work investigated the oxidation of the ternary CaO-FeO-SiO₂ and quaternary CaO-FeO-SiO₂-MnO slag systems in air. The oxidation paths for studied slags were estimated by using stability phase diagrams prior to the experiments. The calculations were performed by using FactSage 6.1. Figure 1 shows temperature vs. partial pressure of oxygen in the system 27.5%CaO-30%FeO-27.5%SiO₂-15%MnO.

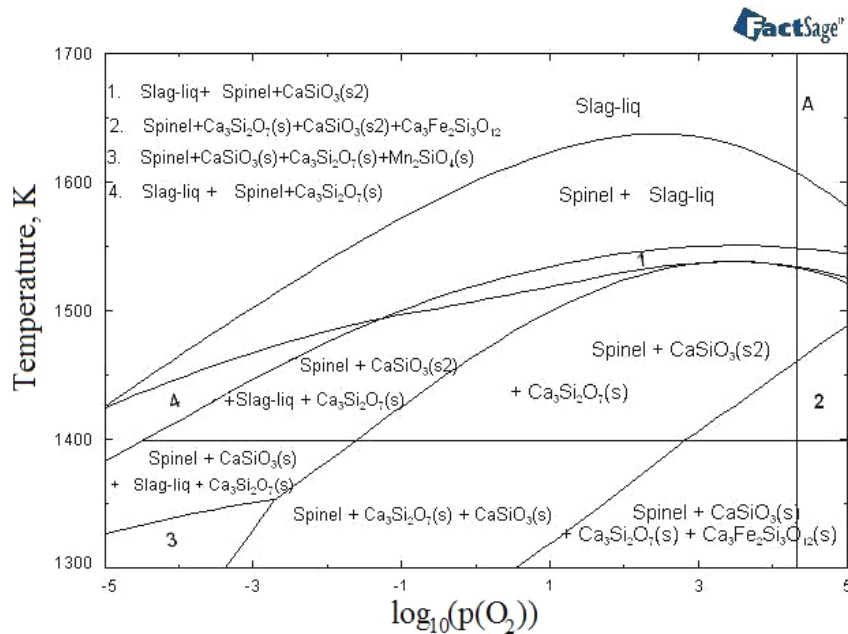


Fig. 1 Temperature-partial pressure of oxygen phase diagram of the quaternary 27.5%CaO-30%FeO-27.5%SiO₂-15%MnO system calculated by FactSage 6.1 where a line marked (A) corresponds to the partial pressure of oxygen in air. $P(O_2)$ is presented in Pa

At the low partial pressure of oxygen ($\log_{10}(P_{O_2})=-5$) and above 1430 K, the slag is completely molten (see Figure 1). With the introduction of the oxidant gas, viz. air, Fe in the slag changed its valence and different phases precipitated depending upon the temperature. From Figure 1, only spinel may be thermodynamically obtained from the liquid slag in the temperature range of 1548-1607 K. The main constituents of the spinel above are manganese ferrite and magnetite [9]. From this diagram, it is easy to predict that to obtain manganese ferrite or magnetite as a final product after slag oxidation in air, it is necessary to work in the temperature range 1548-1607 K.

Before conducting experiments, similar type of thermodynamic calculations was performed for all the experimental slag compositions. The experimental conditions (temperature and partial pressure of oxygen) were then chosen.

3. Experimental

3.1 Sample preparation

For slag preparation, CaO powder with a purity of 99.9%, SiO₂ powder with a purity of 99.5% and MnO powder with a purity of 99.5% were supplied by Sigma Aldrich Chemie (Germany). SiO₂ powder was dried for 24 hours at 1073K and CaO powder at 1273K for 2 hours in an Ar atmosphere prior to mixing. FeO (wüstite) was synthesized and examined by X-ray Diffraction (XRD). The details of the synthesis were described in earlier work [10]. Appropriate amounts of these powders were mixed well. Chemical compositions of studied slags are presented in Table 1.

Table 1 Chemical composition of the slags studied

№	Composition (mass %)			
	CaO	SiO ₂	FeO	MnO
1	26.0	44.0	30.0	-
2	31.0	39.0	30.0	-
3	35.0	35.0	30.0	-
4	40.0	40.0	20.0	-
5	37.5	37.5	25.0	-
6	21.0	34.0	30.0	15.0
7	27.5	27.5	30.0	15.0
8	33.0	22.0	30.0	15.0
9	31.0	29.5	27.9	11.5
10	27.4	34.0	27.3	11.1
11	21.9	37.0	29.5	11.5
12	28.8	28.7	26.5	15.8

3.2 Experimental techniques adopted

Oxidation of liquid synthetic slags was investigated by the TGA using SETARAM TAG 92 (France) and by CSLM (Lasertec 1LM21H, Japan). The experimental assembly with the gas cleaning system was described in details in the earlier publication [11].

Platinum crucibles with a 10.0 mm inner diameter and a height of 8.0 mm were used as containers for the slag samples during the TGA investigations. Platinum containers were made from platinum foil (supplied by Alfa Aesar, Germany) with 0.1 mm thickness and 99.99% purity. In all the experiments, the same level of slag in the crucible was maintained so that the results are comparable. In order to ensure homogeneity, the slags were premelted in purified argon atmosphere. The slag samples were soaked at the experimental temperature for at least 30 min before the oxidant gas was introduced. No mass change was noticed during the heating period. Ar was then replaced by air, at a rate of

400 ml/min. This was above the starvation rate, which was determined during preliminary trials. All the experiments were conducted in an isothermal mode for the duration of 1800 sec. The weight and the temperature of the samples were recorded every 1 sec.

In the experimental setup for the CSLM investigations used, a cylindrical platinum crucible containing approximately 0.030 g of slag was placed on a high-density alumina crucible. The whole sample was set on a platinum sampler pan, which was connected to the thermocouple. The temperature calibration for the crucible holder was performed beforehand. At the beginning of each experiment, the CSLM chamber was evacuated for 10 min and was then purged with argon gas for 20 min at a rate of 200 ml/min. Each slag sample in the Pt-crucible was then heated at the CSLM hot stage in an Ar atmosphere. The sample was initially heated to 1700K and maintained for 20 minutes until it completely melted. The sample was then slowly (5 K/min) cooled down to desired temperatures. The atmosphere in the heating chamber was then switched from Ar to air.

After the experiments, the samples were cooled in the furnace in an argon atmosphere at maximum possible rates (40 K/min for TGA and 74 K/sec for CSLM). Obtained samples were analyzed by XRD and SEM.

4. Results

4.1 Thermogravimetric results

Typical experimental curves for the isothermal weight gain during oxidation at different temperatures are presented in Figure 2. In this figure, two horizontal solid lines indicate the theoretical levels corresponding to complete oxidation of FeO in the slag to magnetite and to hematite. The characteristics of the curves demonstrate that during 10-15 min of the experiment, the oxidation level of 80-90% was reached.

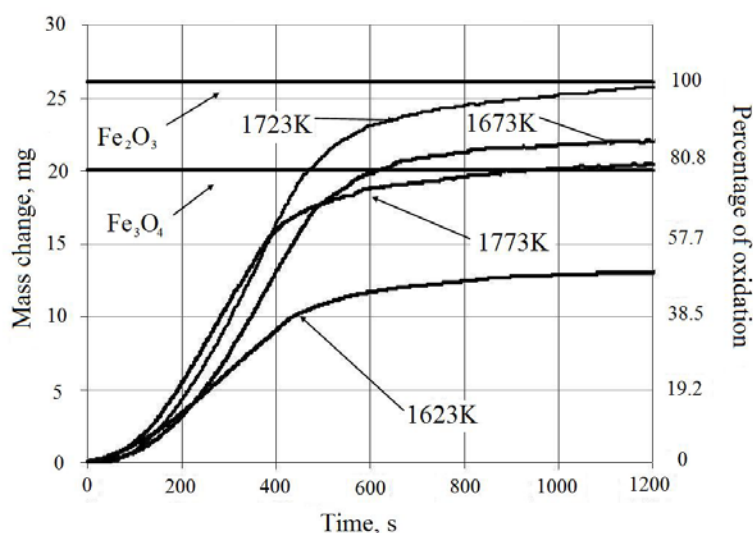


Fig. 2 The isothermal mass changes for the composition: 25% FeO; 37.5% CaO; 37.5% SiO₂ at different temperatures. Horizontal lines indicate oxidation levels corresponding theoretically to magnetite and hematite levels

It can be seen in Figure 2 that an increase of temperature in the range 1623-1723 K caused the progressive mass gain induced by oxidation. The maximum oxidation level achieved also increased for all the slags studied with rise in temperature. The unique oxidation behavior was observed 1773 K; oxidation proceeded rapidly in the early stage but slowed down at the later stage. The final weight gain (i.e., oxidation level achieved) was below the theoretical levels at 1673 K and 1723 K. The divergence of the oxidation behavior at 1773 K from the lower temperature experiments can be explained with the liquid formation along with magnetite [10].

4.2 CSLM results

Typical CSLM images of the crystal growth on the liquid slag surface during oxidation are presented in Figure 3.

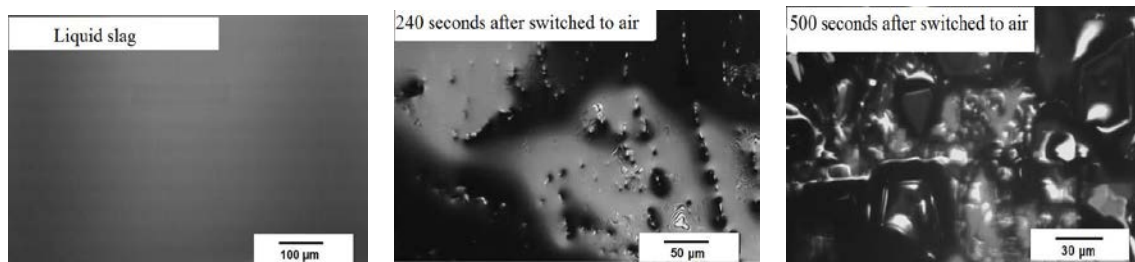


Fig. 3 Successive CSLM images showing crystal precipitation in a CaO-FeO-SiO₂ slag as a result of oxidation at 1593K

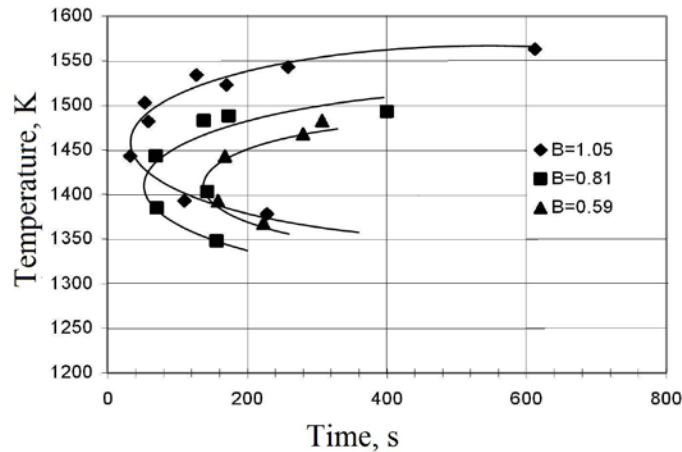


Fig. 4 TTT diagram for the quaternary CaO-FeO-SiO₂-MnO system. B- basicity ($B = \text{CaO}/\text{SiO}_2$), samples № 9-11, Table 1

The time until observable crystal precipitation took place was measured through *in-situ* visualization from CSLM video recording at various temperatures. A corresponding TTT diagram with average data was then constructed as shown in Figure 4. A single TTT nose was found and the precipitated particles at the gas/liquid interface were found to grow and agglomerate. Different types of crystals were observed in a size range of 1-50 µm. For the Mn-containing slags below 1473K, crystals had a shape similar to that presented in Figure 3, whereas above 1473K, crystals had complicated geometry. At higher temperatures, crystals were larger in comparison to those found at lower temperatures.

With time, the crystals grew and agglomerated.

4.3 XRD and SEM results

Precipitated phases were analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD analysis confirmed the presence of magnetite/hematite in the oxidized CaO-FeO-SiO₂ slags and manganese ferrite/magnetite in the oxidized CaO-FeO-SiO₂-MnO slags. From the SEM analysis of the samples treated in TGA, the top layer of the sample was found to be porous. The diameter of the pores obtained from the SEM micrographs was about $2.5 \cdot 10^{-6}$ m.

5. Discussion

During the TGA studies, the isothermal mass change curves showed differences in slopes at different stages of oxidation indicating a change in mechanism as the reaction progressed. Oxidation may take place by steps, starting first with an incubation period (corresponding to the initial oxygen dissolution in the slag), then, the chemical reaction rate-controlling step (corresponding to a linear part of the slope), and finally, diffusion of iron/manganese/oxygen rate-controlling step (corresponding to the parabolic part of the slope). The detailed analysis of the suggested oxidation mechanism was described in earlier publications [9-10].

With the onset of the oxidation process, the oxygen molecules impinge on the slag surface leading to the oxidation of FeO in the slag. Reaction (1-3) would be occurring at the gas/slag interface.



The thermograms show an incubation period, which is likely to correspond to the initial dissolution of oxygen in the slag as the oxidant gas is let in. To describe this incubation period, an Avrami-type of equation was used:

$$1-X = \exp(-K_N t^n) \quad (4)$$

where X is the reacted fraction, K_N is a constant (can be determined graphically), and t is the time and n is the growth exponent.

For the quaternary slag system, an initial incubation period was relatively short (less than 10 seconds). It was, therefore, assumed that the initial incubation was negligible.

At the initial stage, the effect of the product layer formed is less significant and chemical reaction would be the rate-controlling step. The main equation corresponding to the chemical reaction control step can be expressed as:

$$\frac{\Delta m}{A} = \Omega \exp\left(\frac{-\Delta E_a}{RT}\right)t \quad (5)$$

where Ω is a pre-exponential term; ΔE_a is the Arrhenius activation energy, t is the time, A is the surface area, Δm is the mass change.

An analytical description of diffusion as the rate-controlling step is based on the concept that a porous solid product layer forms during the oxidation of liquid slag in air. The formation of such a product layer was confirmed during the current experiments in the case of the quaternary CaO-FeO-SiO₂-MnO system. The size of the pore was estimated to vary from $2 \cdot 10^{-6}$ m to $5 \cdot 10^{-6}$ m. From the Fick's diffusion law, the following equation was derived to describe diffusion rate-controlling step:

$$\left(\frac{m_o}{A}\right)^2 = \frac{2\rho_{MnFe_2O_4}\varepsilon M_o^2 D_o (C_o^s - C_o^i)}{M_{MnFe_2O_4}} t \quad (6)$$

where m_o is the mass of oxygen, M_o and $M_{MnFe_2O_4}$ are the molar mass of oxygen and manganese ferrite, respectively, $\rho_{MnFe_2O_4}$ is the manganese ferrite density, ε is the manganese ferrite fraction in the product layer, D_o represents the diffusion coefficient of oxygen, C_o^s and C_o^i are the oxygen potential at the top and the bottom of this product layer, t is the time, and A is the surface area.

From equations (4) – (6), a complete description of the oxidation process can be given. To validate this, a sample (30w%FeO-15w%MnO-27.5w%CaO-27.5w%SiO₂) in a temperature range of 1500K -1600K was considered as an example. Model simulations of the three rate-controlling steps were compared with the experimental results in Figure 5. In calculations, it was assumed that oxidation occurred by reaction (3). Density of MnFe₂O₄ is equal to 5.03 g/cm³ [12]. D_o of O₂ was estimated from experimental results and equation (6). The D_o was found to be equal to $0.2 \cdot 10^{-3}$ cm²/s, $0.3 \cdot 10^{-3}$ cm²/s, and $0.7 \cdot 10^{-3}$ cm²/s at temperatures of 1500K, 1550K, and 1600 K, respectively. These values are reasonable with respect to the mean free path estimated earlier, in comparison with the diffusion coefficient of oxygen in air at 1600 K, which is equal to $0.4 \cdot 10^{-4}$ cm²/s [13].

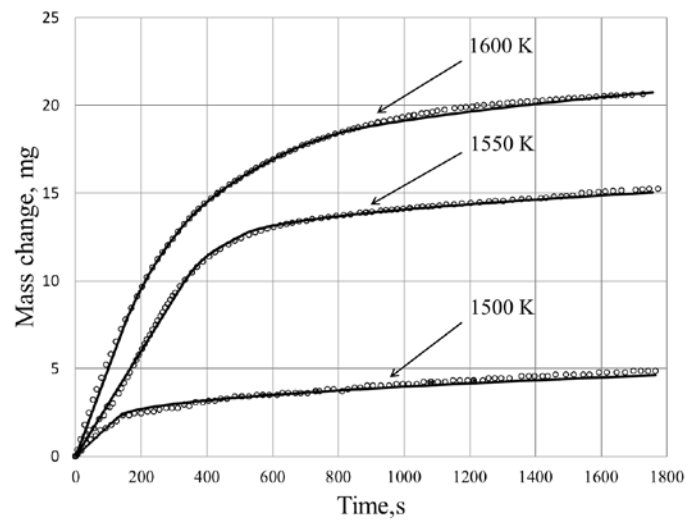


Fig.5 The calculated isothermal weight changes (solid curves) superimposed with experimental data points (circle) for the composition 30%FeO-15%MnO-27.5%CaO-27.5%SiO₂ through different temperatures

6. Conclusions

The oxidation of FeO in steelmaking slags towards selective recovery of iron has been investigated by TGA analysis and CSLM in synthetic ternary CaO-FeO-SiO₂ and quaternary CaO-FeO-SiO₂-MnO slags systems, accompanied by thermodynamic and kinetic modelling. The TGA experiments showed that, during 10-15 min, 80-90% of oxidation was achieved. An increase of temperature in the range 1623-1723K was found to cause an increase in the rate of the reaction. The real time CSLM analysis showed the crystal formation behaviors during oxidation of liquid slag. With time, the crystals grew and agglomerated, reaching, in some cases, 50 µm in length. Different types of crystals were observed at different temperatures. A TTT diagram was constructed based on CSLM results. The XRD analysis confirmed the presence of magnetite and manganese ferrite in the oxidized slag samples. The mechanism of the oxidation process was described by means of a theoretical model and good agreement with the experimental results was achieved

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