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PHASE EQUILIBRIA STUDY OF THE CaO-“Fe_2O_3”-SiO_2 SYSTEM IN AIR TO SUPPORT IRON SINTERING PROCESS OPTIMISATION

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Abstract

Phase equilibria studies of the CaO-Fe_2O_3-SiO_2 system in air from 1200°C to 1260°C have been carried out at Fe-rich region with particular focus on the phase chemistry of Silico-Ferrite of Calcium (SFC) phase and associated equilibria. The measurements have been made possible through the use of a modified experimental technique involving high temperature equilibration, rapid quenching followed by electron probe X-ray micro analysis (EPMA). The compositions and temperatures determining the limits of the primary phase field of the SFC phase have been determined for the first time. Isothermal sections for 1220°C, 1240°C, 1255°C and 1260°C have been measured and the liquidus in the SFC primary phase field has also been determined.

Introduction

The system CaO-FeO-Fe_2O_3-SiO_2 forms the basis for the description of the chemical behaviour of slags encountered in a wide range of metallurgical ferrous and non-ferrous processing systems. One of the important features of the system is that the phases present and the phase equilibria are dependent on not only bulk composition and temperature but also on the effective oxygen partial pressure of the system. At the one extreme, at low oxygen partial pressures, the system is limited by equilibrium with metallic iron; even under these conditions the iron species in the liquid oxide phase are present in both ferrous, Fe^{2+} and ferric, Fe^{3+} states [1]. The proportions of ferric iron in these slags increase with increasing oxygen partial pressure and decreasing temperature [2].

The CaO-FeO_x-SiO_2 system (see Figure 1) [3, 4] can be characterised by two low melting temperature regions; one at relatively high silica concentrations, the other at low silica concentrations approaching the CaO-FeO_x pseudo-binary join. Most experimental studies of the system have been undertaken to define the phase assemblages formed and the liquidus in the silica-rich region of the phase diagram. This silica-rich region is of direct relevance to steelmaking and non-ferrous, fayalitic smelting slags. The low-silica region is of interest to non-ferrous, “calcium ferrite” converter slags and ironmaking.

It is the iron-rich, low-silica corner of the system that is of particular interest to ironmaking practice. The majority of iron ore fines used in primary metal production are agglomerated into

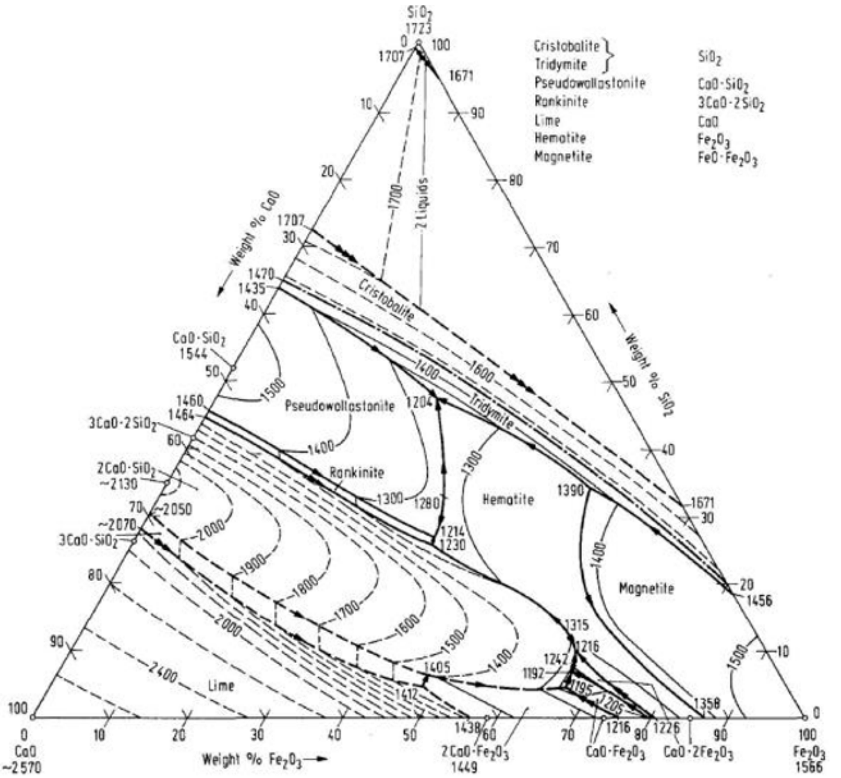

Figure 1. SiO_2-Fe_2O_3-CaO ternary phase diagram in air [3], [4].

porous, reactive but physically strong, lump material for feed into the iron blast furnace using the Dwight Lloyd moving grate sintering process [5]. The feed to the process consists of typically, iron ore fines and return sinter fines, limestone and dolomite flux, and fine coke. As the charge progresses through the process air is drawn through the porous bed and the charge is heated through combustion of the coke in the bed. The charge then experiences a range of temperatures and gas conditions as the combustion and the heat fronts progress through the bed.

The production of high quality iron ore sinter is an important factor in achieving high productivity, and high thermal and chemical efficiencies in modern blast furnace practice. Control of sinter microstructure is the key factor in attaining optimum physical and chemical properties. Research reports and literature available to date [6] have suggested the formation of a particular phases namely Silico-Ferrite of Calcium (SFC) and/or Silico-Ferrite of Calcium and Aluminium (SFCA) during the sinter making play a dominate role in determining the sinter microstructure, and the metallurgical properties of iron ore sinter, such as, reducibility, mechanical strength and soften temperature. There is strong experimental and anecdotal evidence to suggest that SFC and SFCA are formed through crystallisation from the liquid phase, however, inspection of the liquidus surfaces for the $CaO-Fe_2O_3-SiO_2$ system in air, see Figure 1 [1, 2] shows no primary phase field for these compounds. Iron-rich, low-silica corner of the diagram consists of primary phase field of magnetite, Fe_3O_4; hematite, Fe_2O_3; calcium oxide, CaO; calcium di-ferrite, $CaO.2Fe_2O_3$; monocalcium ferrite, $CaO.Fe_2O_3$; di-calcium ferrite, $2CaO.Fe_2O_3$. The lack of experimental data also means that current thermodynamic databases do not include the SFC and SFCA phases.

The SFC phase has been found [7] to be stable of the system $CaO-Fe_2O_3-SiO_2$ in air; and its crystal structure reported has been confirmed [8] by X-ray powder diffraction studies. Isothermal phase equilibria studies [9] for temperatures in the range at 1240ºC to 1270ºC have been undertaken for the iron-rich corner of the phase diagram. In this study it was found that the SFC phase was stable up to 1252ºC in air and to melt incongruently at higher temperature to form hematite and liquid. The compositional range of SFC was measured by electron probe microanalysis and reported to be between 3.9wt% and 6.8wt% SiO_2. The experiments involved the equilibration of (3.5g) pellitised, synthetic chemical mixtures supported by Pt foil in air and quenching into water. The samples were then examined using optical microscopy, EPMA and XRD analysis. Using this technique it was not possible to measure the compositions of the coexisting solid and liquid phases. The results have provided a valuable initial guide to the phases present in the sub-system $CaO-FeO-Fe_2O_3-SiO_2$ in the composition ranges of interest to iron ore sintering, however, the compositions of all the phases observed were not reported. It was clear that using this technique it was not possible to retain the liquid present at temperature as a glass phase on cooling to room temperature in these low-SiO_2 liquids; this meant it was not possible to accurately determine the liquidus surface in the high-iron region of the system or the conjugate phase relations between solid and liquid solutions.

The aim of present study is to accurately determine the slag liquidus compositions and the solid/liquid phases that coexist at equilibrium with focus on the SFC primary phase field. Particular efforts have been put on addressing the issue of quenching high-fluidity, low-SiO_2 liquid.

Experimental

Over a number of years experimental procedures for phase equilibrium measurements have been developed by the Pyrometallurgy Research Laboratory (PYROSEARCH) at the University of Queensland [10]. The technique involves high temperature equilibration of a synthetic oxide sample in a controlled gas atmosphere. The sample is then rapidly quenched so that the phase assemblage present at high temperature remains unaltered. The quenched sample is mounted in epoxy resin, polished for metallographic examination and microanalysis, and the compositions of the crystalline solid phases are measured by electron probe X-ray microanalysis (EPMA) with wavelength dispersive detectors (WDD).

Preparation of oxide mixtures

The starting mixtures were made from CaO (99.98 wt% purity), Fe_2O_3 (99.98 wt% purity), SiO_2 (99.98 wt% purity). Mixtures of selected bulk compositions were prepared by weighing the high purity powders, mixing them thoroughly using an agate mortar and pestle then compacted to produce a pellet weighing around 0.2 gram.

To ensure that the specimen could be cooled rapidly following equilibration the pellet was supported initially on a platinum wire formed into a spiral shape (see Figure 2a). During equilibration, the sample became partially molten and flowed into the gaps between the spirals and was held onto the wire by the surface tension (See Figure 2b). In this way on quenching the sample the liquid slag phase was the first phase to come in direct contact with the quenching medium (water). This results in very high quenching rate and minimizes the extent of crystallisation of the liquid during the quenching process. It was found that platinum, under the conditions investigated, did not dissolve in or contaminate the slag samples.

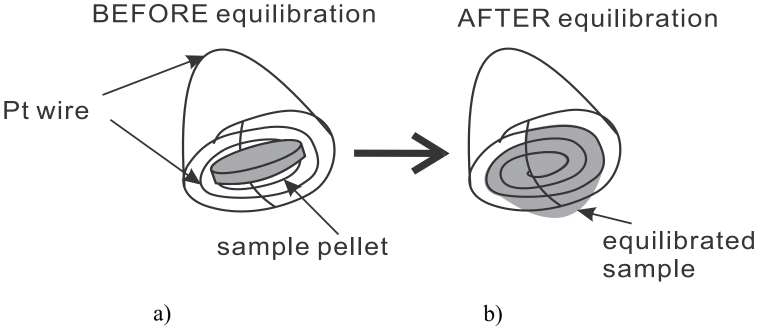

Figure 2 Sample a) before and b) after equilibration

High temperature equilibration technique

All equilibration experiments were conducted in a vertical impervious re-crystalized alumina, reaction tube in electrical resistance-heated furnaces. The sample was introduced from the bottom of the vertical tube furnace and suspended by a sample holder constructed using Pt wire. The experiment commenced by raising the sample into the uniform temperature hot zone of the furnace. After the equilibration, the specimen was rapidly quenched by dropping it directly into the iced water. The samples were mounted in epoxy resin, polished using conventional metallographic polishing techniques and carbon coated for subsequent electron probe X-ray micro-analysis (EPMA).

To monitor the actual temperature of the sample, a working thermocouple of 6-30 wt% Rh/Pt was placed in a re-crystallised alumina thermocouple sheath immediately adjacent to the sample. It is estimated that the overall absolute temperature accuracy of the experiment is within 5^{o}C.

Analysis technique and selection of measurement points

The rapid quenching technique successfully retains phase assemblages present at the equilibration temperatures. The compositions of various phases were measured using JEOL

8200L EPMA with wavelength dispersive detectors (JEOL is a trademark of Japan Electron Optics Ltd., Tokyo). A 15-kV accelerating voltage and 15 nA probe current were selected for the micro-analyzer operation. The standards (Charles M. Taylor, Stanford, CA) used in the EPMA measurements were as follows: wollastonite ($CaSiO_3$) for Ca and Si, hematite (Fe_2O_3) for Fe. The Duncumb–Philibert correction based on atomic number, absorption, and fluorescence (ZAF correction, supplied by JEOL) was applied. The accuracy of compositions measured was expected to be within 1wt%. Only the Me-cations concentrations were measured with EPMA; the corresponding oxidation states were assigned.

As mentioned previously, due to the high fluidity of low SiO_2 liquid, it is impossible to obtained well-quenched liquid phase across the whole sample even when the open support method was used. Mounted samples were examined carefully under the electron microscope at high magnifications and well quenched areas were selected when carrying out the EPMA measurement for the liquid phase. Following example is given. A micrograph of a sample containing hematite-SFC-liquid three phase equilibrium phase assemblage is shown in Figure 3. It consists of large crystalline hematite and SFC grains surrounded by a liquid phase. Within the liquid phase and at the interface of liquid and solids, clusters of fine needle-shaped microcrystalline phases were observed; these phases were believed to have precipitated out of the liquid during quenching (e.g. region A). It is generally found that better quenching was obtained at the edges of the sample where direct contact with quenching media was expected. Measurement of the liquid composition should then be carried out on the well quenched areas, such as B, rather than those of type A, where there is the presence of microcrystalline precipitates. The direct observation of the phase assemblage makes it possible to distinguish phases that were present at the equilibration temperature. In this sense the present technique is superior to the use of XRD, although the latter can provide useful information on the crystal structures and confirm the individual phases present. The cracks in the sample have formed after cooling as evidenced by the continuity of the crack position across the phase boundaries between solid and (liquid) glass phases, and the solid/solid interface boundaries.

The following phases have been identified in the range of compositions investigated: liquid (L), silicoferrite of calcium solid solution (SFC); hematite, H, (Fe_2O_3); dicalcium silicate, C_2S, ($2CaO.SiO_2$); calcium diferrite, CF_2, ($CaO.2Fe_2O_3$) and calcium monoferrite, CF, ($CaO.Fe_2O_3$).

Liquidus between 1200°C to 1260°C

The liquidus of the iron-rich corner of the CaO-Fe_2O_3-SiO_2 system in air deduced from the results of the present investigation is shown in Figure 4. The eutectic and peritectic temperatures on the CaO-“Fe_2O_3” binary system in air were taken from previously studies by Liu et al. [11]. The CF and CF_2 phases melt incongruently and form a binary eutectic at 1205°C. This eutectic reaction extends into SiO_2-containing system and a peritectic reaction involving C_2S, CF and CF_2 phases occurs at 1192°C and approximately 4.2wt%SiO_2. The eutectic liquidus temperature continues to decrease with increasing silica concentration; at 1192°C and 4.4wt% SiO_2 the eutectic reaction is between C_2S and CF_2. The temperature continues to decrease until the ternary eutectic point involving C_2S-CF_2-SFC is reached at 1185°C and 6wt% SiO_2.

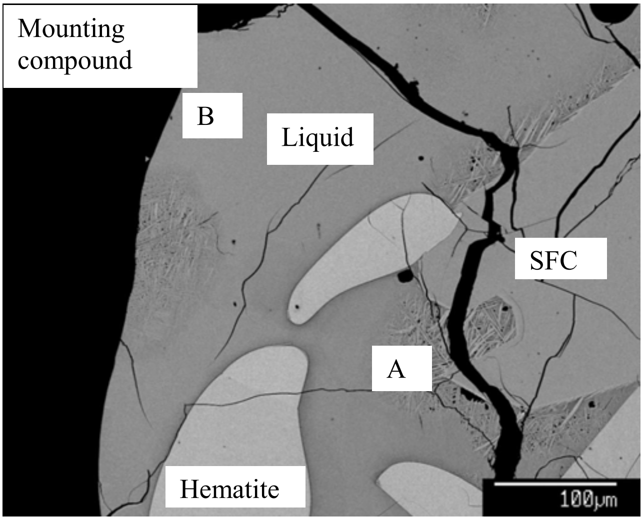

Figure 3 Example of microstructures observed (in backscattered electron mode) in the CaO-"Fe_2O_3"-SiO_2 system in air at 1240ºC showing the hematite-liquid-SFC phases in equilibrium.

The primary phase field of the SFC solid solution (labelled as "S") was found to exist in a narrow range of compositions between 4-8.5 wt% SiO_2. The SFC field is bounded by the primary phase fields of hematite (labelled as "H"), calcium di-ferrite (labelled as "CF_2") and di-calcium silicate (labelled as "C_2S"). The points abcd on Figure 4 mark the limits of the SFC primary phase field. The point a) marks the coexistence of the SFC-CF_2-H phases; point b) marks the coexistence of the C_2S-CF_2-SFC phases; at point c) the phases C_2S-SFC-H are present and at point d) SFC and H. Point d) represents the maximum temperature at which SFC can exist; above this temperature only liquid and hematite are present. The dashed lines marking the particular temperatures indicate the estimated positions of these isotherms.

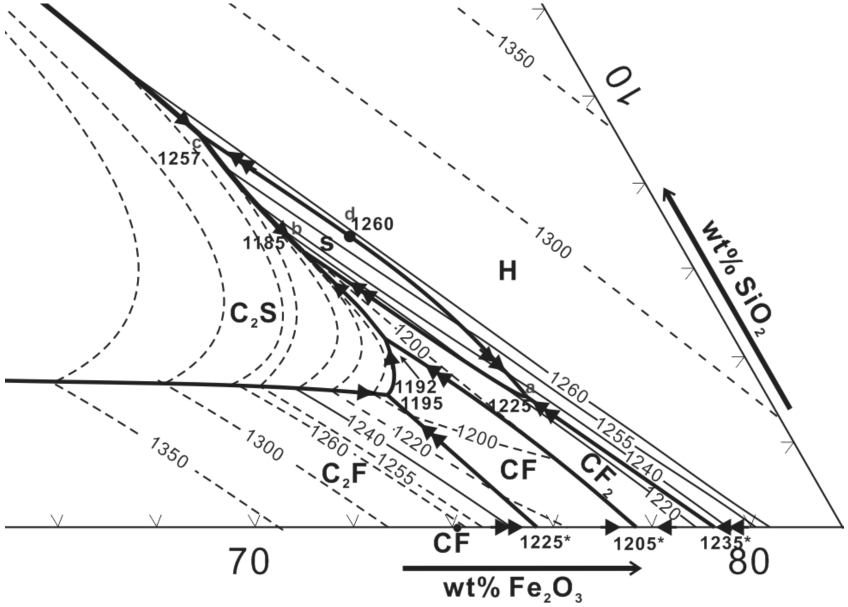

Figure 4. Estimated liquidus of $CaO-Fe_2O_3-SiO_2$ system in air including the SFC primary phase field based on the results of the present study and binary data reported by [11]. Legend: H = Hematite (Fe_2O_3), SFC = SFC solid solution, L = Liquid, C_2S = Dicalcium silicate ($2CaO.SiO_2$), C_2F = Di-calcium ferrite ($2CaO. Fe_2O_3$), CF = Calcium monoferrite ($CaO.Fe_2O_3$) and CF_2 = Calcium diferrite ($CaO.2Fe_2O_3$). Temperatures in ºC.

Liquidus

The liquidus obtained in the present study for the $CaO-Fe_2O_3-SiO_2$ system, shown in Figure 4, differs from that of Phillips and Muan [3], which has been the accepted diagram for this system to date. The SFC phase did not appear on the previous versions of the liquidus. The present study provides information on the limits of the SFC primary phase field. This information is essential to identify the compositions and temperatures in which this phase will form from the liquid.
The narrow region over which the SFC phase can be formed helps to explain why the presence of this SFC primary phase field was not recognised in the earlier investigations.

Summary

Phase equilibria in the CaO-“Fe_2O_3”-SiO_2 ternary system in air have been determined between 1200ºC to 1260ºC with the focus on identifying the limits of stability of the SFC phase. Particular attention has been paid to minimizing the experimental uncertainties including:

- Developing special experimental techniques to address the challenges in quenching the low-SiO_2, high-fluidity liquid encountered in iron-rich compositions.
- Confirmation of attainment of equilibrium

- Area selection for composition measurement using EPMA.

The major findings and results of the present study are summarised as follows

- Isothermal sections in the CaO-Fe_2O_3-SiO_2 system in air have been constructed for 1220ºC, 1240ºC, 1255ºC and 1260ºC.
- The primary phase field of SFC and the liquidus between 1200ºC to 1260ºC of CaO-"Fe_2O_3"-SiO_2 system at Fe-rich side have been determined and constructed for the first time.
- The SFC solid solution was found to be stable below 1255ºC in air and melt incongruently to form hematite and liquid above this temperature.
- The substitution mechanism of SFC solid solution was found to be in good agreement with the reaction $Si^{4+} + Ca^{2+} = 2Fe^{3+}$
- The SFC primary phase field was found to exist over a narrow range of compositions bounded by the primary phase fields of hematite (Fe_2O_3), dicalcium silicate ($2CaO.SiO_2$) and calcium diferrite ($CaO.2Fe_2O_3$).

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