An Assessment of the Ca-Fe-O System

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The Ca-Fe-O system is studied with an emphasis on the slag system CaO-FeO-Fe₂O₃. The compound-energy model is used with ionic species for all solid solution phases. The liquid is described with a special two-sublattice model. The parameters in the models are assessed in order to give an accurate description of the thermodynamic properties of the system, in accordance with all consistent experimental data. The system is described in the temperature range of 298.15 to 2000 K.

I. INTRODUCTION

The CaO-FeO-Fe₂O₃ system is of central importance for steelmaking and has been studied experimentally many times with an emphasis on various aspects. The purpose of the present study was to attempt to fit all of the experimental information by applying thermodynamic models to the individual phases and then to obtain the phase diagram and thermochemical properties by computer calculation. The hope was to obtain a more reliable phase diagram and, in addition, more reliable descriptions of the thermodynamic properties of the phases, in particular, the liquid. The numerous studies of the Fe-O system will not be covered here because that system is discussed in a parallel work. A metallic phase can exist inside the CaO-FeO-Fe₂O₃ triangle, and it is thus necessary to extend the assessment to include the Fe and Ca corners. The very scarce information available on the Ca-Fe and Ca-CaO systems has been used in order to have a reasonable description of these two binaries as a basis for assessing CaO-FeO-Fe₂O₃.

A special notation is generally used when discussing these oxide systems and will be used here. CaO is denoted by C, FeO by W, and Fe₂O₃ by F. All stoichiometric oxide phases and solutions based upon them will be denoted by combinations of these three components.

II. SELECTED EXPERIMENTAL DATA

A. Ca-Fe

Sponseller and Flinn[21] have investigated the solubility of Ca in liquid Fe in equilibrium with liquid Ca. This must be done in a pressurized system to avoid losing Ca by boiling. No information on the mutual solubility in the solid phases could be found. Thus, the same regular interaction parameter as in the liquid was used for the face-centered cubic (fcc) and body-centered cubic (bcc) phases.

B. Ca-CaO

Above 50 pct oxygen, the Ca-O system is unknown. In the range of 0 to 50 pct oxygen, some information is given by Bevan and Richardson.[3] No solubility data for the solid phases could be found. Thus, the same regular interaction parameter as in the liquid was used in the fcc and bcc phases.

C. CaO-Fe₂O₃

Experimental information on the CaO-Fe₂O₃ system has been obtained by studies in air and in a pure oxygen atmosphere at 1 atm by Phillips and Muan.[4] That information is not on the real binary CaO-Fe₂O₃ system, as there will be a significant fraction of Fe⁺² present in the liquid, but these isopotential sections fall to a large degree fairly close to the true binary side. Phillips and Muan[4] conducted experiments with the quenching technique under controlled oxygen pressure. When the results were presented, they gave the composition of the liquid in only some of the cases. The results at the two oxygen potentials were presented as diagrams resembling binary ones. They show three intermediary compounds, C₂F, CF, and CF₂. Two of them, CF and CF₂, melt incongruently, and C₂F melts congruently at both potentials. Some pieces of information on the liquid composition at 1 atm O₂ will be used in the present assessment.

King[5] gave values on entropy and heat capacity at 298 K for CF and C₂F. In a recent revision of thermodynamic data of oxides, Kubaschewski[6] gave ΔH₂₉₈ for CF and C₂F and heat of fusion for C₂F, which melts congruently. In addition, he gave expressions for the heat capacity of CF and C₂F as series expansions of T. Thermodynamic information on the third ternary compound, CF₂, could not be found, but there is some information on its stable range of temperature.[4,7]

Electromotive force (emf) measurements on CF and C₂F at some temperatures were conducted by Rezukhina and Baginska.[8] Bonnickson[9] measured the enthalpy content of CF and C₂F at some temperatures relative to 298 K. He also measured the same quantity for the liquid with the composition of the two stoichiometric compounds. All of this information was used in the assessment.

D. Liquid

The liquid phase in the CaO-FeO-Fe₂O₃ system and its phase relations have been studied under controlled oxygen potentials by several authors.

The composition of the liquid in its one-phase field as a function of the oxygen potential was studied by Gurry...
and Darken,[10] who analyzed CaO-FeO-Fe$_2$O$_3$ melts equilibrated in various atmospheres at 1873 K. Hara et al.[11] and Larson and Chipman[12] measured the distribution of iron on Fe$^{2+}$ and Fe$^{3+}$ ions at several fixed CaO contents and oxygen potentials at 1773 and 1823 K, respectively. Hara et al.[11] declared in their article that their measurements showed considerable differences, at low CaO content, with Larson and Chipman[12] and with a study by Timucin and Morris.[13]

The previously mentioned investigation by Phillips and Muan[4] also gives some information on the liquid one-phase field as well as equilibria between the liquid and one or two solid phases.

Takeda et al.[14] quenched samples equilibrated with CO$_2$-CO mixtures. Oxygen isobars and liquid isotherms at 1473 and 1573 K of the CaO-FeO-Fe$_2$O$_3$ system were presented. This work gives information on two- and three-phase equilibria involving the liquid.

Two-phase equilibria between the liquid and one solid phase were also studied by Takeda et al.,[14] Timucin and Morris,[15] and in another investigation, by Phillips and Muan.[16] Some data from the investigations by Larson and Chipman[12] and Hara et al.[11] also apply here. All information from the second investigation by Phillips and Muan,[16] except for the invariant points, was omitted from the present assessment since no information was given on the oxygen potential.

All of these investigations on the liquid phase will be used in the present assessment.

E. Wüstite-Lime

Due to the large deviation of wüstite from the ideal composition, FeO, samples with an average composition falling in the FeO-CaO section generally contain some metallic Fe phase and sometimes contain an oxide phase from the center of the CaO-FeO-Fe$_2$O$_3$ system, CWF, CW$_3$F, CW$_4$F$_4$, and even C$_2$F. Nevertheless, experimental results are often represented in a phase diagram which looks like a binary diagram.

The section CaO-FeO has been investigated by several authors. Two alternative shapes have been suggested by Schürrmann and Kraume[17] and by Abbattista et al.[18]

Schürmann and Kraume[17] conducted thermal analysis, isothermal holding tests, and microscopic examinations. They found eutectic-like structures in their samples and therefore concluded that a eutectic four-phase reaction, where liquid transforms into C$_2$F, wüstite, and metallic iron, takes place.

Abbattista et al.[18] determined the oxygen potential of the solid solution (Fe, Ca)O in equilibrium with metallic iron and C$_2$F. They found a much higher solubility of CaO in wüstite than Schürmann and Kraume[17] and suggested a diagram with a point of minimum on the liquidus and a four-phase reaction where wüstite and lime transform into C$_2$F and iron.

Other investigations, supporting Schürmann and Kraume[17] concerning the low CaO solubility in wüstite, have been reported by Perrot[19] and Aubry et al.[20] However, Abbattista et al.'s alternative is supported by an earlier study by Allen and Snow[21] and a recent investigation of the phase relations in the system by Bergman and Song.[22] They suggested that the eutectic-like structure observed by Schürmann and Kraume[17] probably was the result of the decomposition of wüstite into C$_2$F and metallic iron, which occurs after the four-phase reaction suggested by Abbattista et al.[18]

According to Abbattista et al.,[18] a very high cooling rate is required in this system in order to conserve the state established at higher temperatures. That might be the reason for the discrepancy between various measurements. The data from Schürmann and Kraume,[17] Perrot,[19] and Aubry et al.[20] concerning the solubility of CaO in wüstite will therefore not be included in the present assessment.

Using a galvanic cell, Björkman[23] measured the oxygen potential for the solid phases, all in equilibrium with metallic Fe. These measurements were consistent with Abbattista et al.[18] and will be used in the present assessment.

F. Magnetite

The information on the solubility of CaO in magnetite is scarce. Berggren[24] gives the CaO content in magnetite in equilibrium with different ferrites at known temperatures and oxygen potentials. Phase equilibria where magnetite participates will be taken from several articles already mentioned,[4,11,12,14,15]

G. Ternary Compounds

The phase relations in the CaO-FeO-Fe$_2$O$_3$ system have been studied in several works concerned with quasi-binary sections. Phases have been located at the W-CF and WF-CF$_2$ sections or close to them (see the dotted lines in Figure 1). All phases suggested in various articles are shown. Only four of the ternary phases, CWF, CW$\_3$F, CW$\_4$F$_4$, and CW$\_4$F$_8$, will be included in the present assessment. Their existence seems to be well documented,