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THE SLAG-MATTE BOUNDARY IN THE Fe-O-S-SiO_2(sat) SYSTEM AT 1200 °C

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Synopsis: The Fe-O-S-SiO_2 system is one of the most basic systems in non-ferrous pyrometallurgy. This system can exist in two states: as a slag or oxysulphide. Despite its importance, the system has not been extensively studied except at iron saturation. This investigation was undertaken to examine the silica-saturated system under controlled oxygen and sulphur partial pressures in the range 10^{-9}-10^{-12} and 10^{-1}-$10^{-2.75}$ atm, respectively. The equilibrium products were characterised as slag or oxysulphide by microscopic examination and analysed to determine their composition. The conditions for formation of slag and oxysulphide were determined and the variation of composition of the slag and oxysulphide was determined as a function of the oxygen and sulphur partial pressures. The predominance area diagram of the system was constructed by combining the results with those of previous workers.

Keywords: oxysulphide, Fe-O-S-SiO_2 system, oxygen partial pressure, sulphur partial pressure, predominance area diagram.

1. Introduction

The Fe-O-S-SiO_2 system is a fundamental one in non-ferrous pyrometallurgy, because it is the basis of fayalite slags and iron sulphide-based mattes. The silica-saturated Fe-S-O-SiO_2 system has four components and, according to the phase rule, if the temperature and the partial pressures of oxygen and sulphur are fixed, two phases can co-exist, one condensed phase and gas. Because iron can form FeS, FeO and Fe_2O_3, it is possible for the condensed phase to be present either as a solution of FeO, Fe_2O_3 and SiO_2 containing dissolved FeS (a slag) or an iron sulphide solution containing dissolved FeO, Fe_2O_3 and SiO_2, which is frequently referred to as oxysulphide.

The silica-free Fe-O-S has been extensively investigated. Hilty and Crafts [1] determined the composition of oxysulphide in equilibrium with iron and established the phase diagram. Bog and Rosenqvist [2] determined the composition of oxysulphide as a function of oxygen and sulphur potential. Stofko *et al.* [3] measured the solubility of oxygen in the system and found that at magnetite saturation the solubility of oxygen was 15.5% at 1200 °C. Ol'Shanskii [4] and Yazawa and Kameda [5], [6], [7], [8] found that mixtures of FeS and FeO could form homogeneous melts but that the addition of SiO_2 to the melt produced a miscibility gap. In a large part of system, FeS was soluble in iron silicate liquid to only a limited extent and excess FeS formed an immiscible sulphide-rich liquid. MacLean [9] studied the liquid phase relations in the FeS-FeO-Fe_3O_4-SiO_2 system and found that iron silicate melts co-existed with iron sulphide melts over a wide range. MacLean combined his results with those of the earlier studies to construct the phase diagram of the FeO-FeS-SiO_2 system at iron-saturation. The aim of the present study was to determine experimentally the conditions for formation of slag and oxysulphide matte in the silica-saturated Fe-S-O-SiO_2 system at 1200 °C at oxygen and sulphur partial pressures common in non-ferrous smelting systems and the composition of the slag and matte within the slag and oxysulphide fields and at equilibrium.

2. Experimental Procedures

The experimental approach used was to react about 2 g iron chips in a silica crucible with a gaseous atmosphere of controlled oxygen and sulphur potential and allow the system to come to equilibrium. The melt was then quenched in air and water and characterised to determine whether it was in the slag or oxysulphide state, and its elemental composition. A vertical tube (internal diameter 40 mm) furnace heated by silicon carbide elements was used. The silica crucible containing the iron was suspended from a Pythagoras tube of 12 mm internal diameter into the constant temperature zone of the furnace. A gas mixture of CO, CO_2 and SO_2 was introduced into the mouth of the crucible through this tube which was also used to raise and lower the reaction crucible. The temperature within the reaction crucible was accurately measured and controlled to within ±3.5 °C at 1200 °C.

The sulphur and oxygen potentials in the furnace were controlled using of mixtures of SO_2, CO and CO_2. Deoxidised nitrogen was used for flushing the work tube. Gibbs free energy minimisation calculations were performed to determine the proportions of these gases required to produce the desired sulphur and oxygen potentials. The flow rates of the gases were controlled and measured using conventional capillary flow meters and constant-pressure head "bubblers" upstream of the flow meters. All the gases were dried using calcium chloride and magnesium perchlorate and the nitrogen was deoxidized by passing it through a small horizontal tube furnace containing copper wire at 600 °C.

After the reaction period, the atmosphere was changed to nitrogen and the reaction crucible was raised rapidly out of the furnace, removed from its holder and quenched in water. The reaction crucible was then cut length-wise using a diamond saw, mounted in Bakelite and polished for microscopic examination.

Photomicrographs were taken of all the samples at a magnification of 200 and electron microprobe analyses were performed on selected samples to identify the species in the microstructures and their compositions. The mineralogical composition of the quenched melts was determined by covering each photomicrograph with a transparent plastic sheet with a 1 mm by 1 mm grid drawn on it. Each photomicrograph was thereby divided into about 2200 small squares of equal area. The number of squares corresponding to each species was next counted and this was used to obtain the fractional area occupied by each species in the sample. The area fractions were then converted to mass per cent of the various species. By combining the results for the average composition of each species and the amount of each species, the bulk elemental composition of each sample was calculated. The analyses were performed in this manner because the quantity of sample recovered from an experiment was small and usually contaminated with silica from the crucible. The elemental analyses were used to calculate the composition in terms of FeO, Fe_2O_3, FeS and SiO_2.

3. Results

The time required for equilibrium to be attained was determined by carrying out a series of experiments at partial pressures of oxygen and sulphur of $10^{-10.5}$ and $10^{-2.0}$ atm, respectively, for different times up to 40 hours. The composition of the melts remained constant from 6 hours onwards and, accordingly, all subsequent runs were carried out for 10 hours to ensure they were at equilibrium.

A series of experiments was then performed in which the oxygen and sulphur partial pressures were systematically varied over the range $p_{O2} = 10^{-9.0}$ to $10^{-12.0}$ atm and $p_{S2} = 10^{-1.0}$ to $10^{-2.75}$ atm. The photomicrographs of the quenched samples revealed two types of microstructure, one with a light matrix phase and the other with a dark matrix phase. The electron microprobe analyses indicated that the light phase was nearly pure FeS and that the dark phase was nearly pure fayalite ($2FeO.SiO_2$). The samples classified into the two types of microstructure are shown in Figure 1 and it is clear that there is a sharp division according to the oxygen and sulphur partial pressures.

The variation of the sulphur content of the melts at constant partial pressure of sulphur and oxygen are shown in Figs. 2 and 3, respectively. There is clearly a discontinuity in the sulphur concentration and this corresponds to the boundary in Figure 1 between the two microstructure types. This indicates that the melt existed in two distinct states during the experiment and that the microstructures do not only reflect conditions during solidification; the open triangles in Figure 1 correspond to the slag state at 1200 °C while the closed squares correspond to the oxysulphide state.

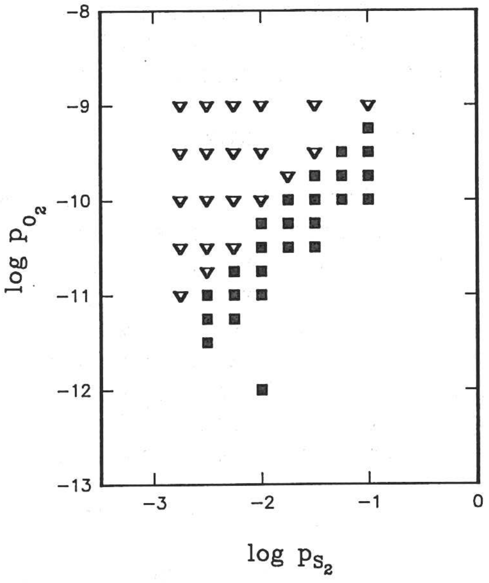

Figure 1: Classification of quenched melts according to nature of the matrix phase. Open triangles indicate fayalite matrix and closed squares indicate iron sulphide matrix.

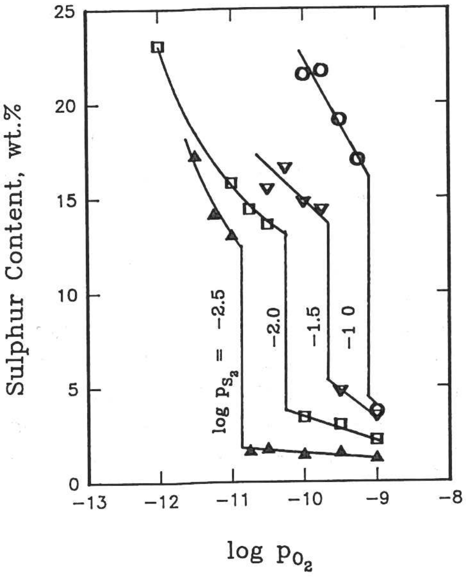

Figure 2: The effect of oxygen partial pressure on the sulphur content of the melts at constant sulphur partial pressure.

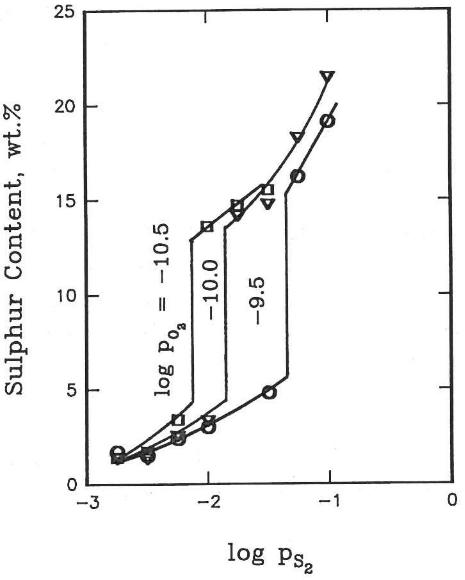

Figure 3: The effect of sulphur partial pressure on the sulphur content of melts at constant oxygen partial pressure.

The variation of the slag composition with change in sulphur partial pressure is shown in Fig. 4 at an oxygen partial pressure of 10^{-10} atm. The trends are similar at other oxygen partial pressures investigated and indicate that the FeS content increases with increasing sulphur partial pressure, while the SiO_2 and FeO contents decrease.

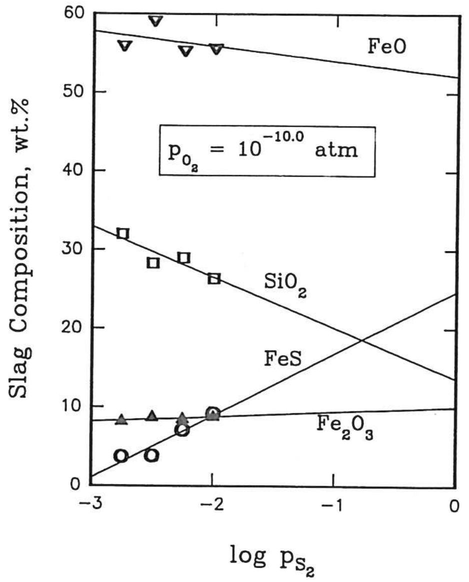

Figure 4: Effect of sulphur partial pressure of sulphur on the slag composition at oxygen partial pressure of 10^{-10} atm.

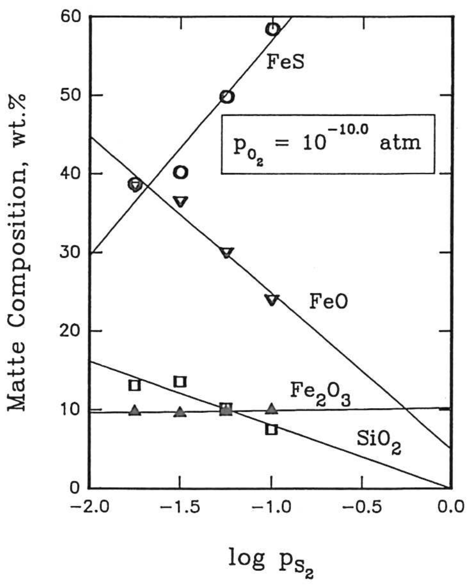

Figure 5: Effect of sulphur partial pressure on the composition of oxysulphide at oxygen partial pressure of 10^{-10} atm.

If the oxysulphide is considered as a solution of Fe, S, O and SiO_2, the oxygen concentration varied from 7.5 to 12.0% over the range investigated. The oxysulphide may also be considered as a solution of FeO, Fe_2O_3, FeS and SiO_2 and the variation in concentration of these species with sulphur partial pressure is shown in Figure 5 at a partial pressure of oxygen of 10^{-10} atm. Similar trends are exhibited at the other oxygen partial pressures investigated and these indicate that silica and FeO solubilities decrease as the sulphur concentration increases.

4. Predominance Area Diagram

The discontinuities in the curves in Figures 2 and 3 provide a means of accurately determining the oxygen and sulphur partial pressures at which slag and oxysulphide can co-exist. These can then be used to construct the boundary between slag and oxysulphide on the predominance area diagram for the Fe-O-S-SiO_2 (sat) system. This is shown as the section OP in Figure 6. Other lines have also been drawn in the figure to complete the predominance diagram over the range of oxygen and sulphur partial pressures of practical interest. The line HY is given by

$$\log p_{S2} = -5.08 + 2 \log a_{FeS} \tag{1}$$

which represents the equilibrium of the reaction [10]:

$$Fe(s) + 1/2\ S_2(g) = FeS(\ell);\ \Delta G^\circ = -116{,}273 + 30.33\ T\ \text{Joule} \tag{2}$$

The activity of FeS in FeS melts in equilibrium with solid iron is 0.68 according to Nagamori *et al.* [11] Although this value was obtained for the oxygen-free system, it is reasonable to assume that the oxygen content of FeS would be negligible below oxygen partial pressures of 10^{-13} atm.

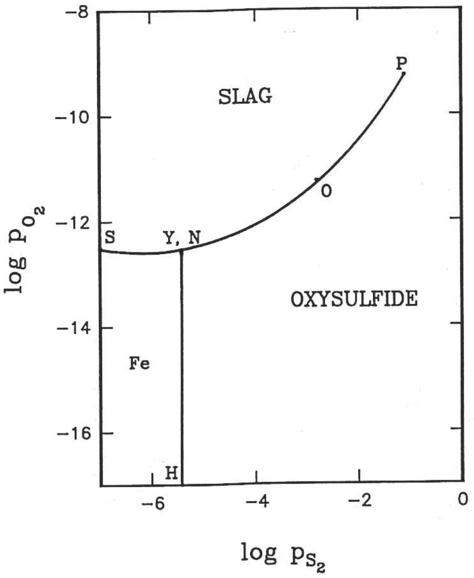

Figure 6: Predominance area diagram of the Fe-S-O-SiO_2(sat) system at 1200 °C.

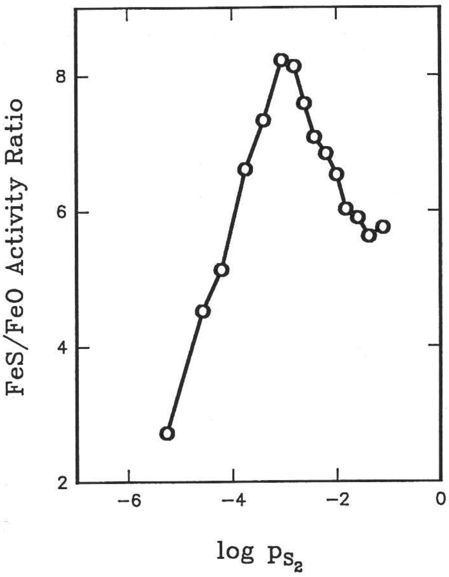

Figure 7: Variation of the ratio of activities of FeS and FeO along the line YOP in Figure 6.

The line SY represents the equilibrium between solid iron and FeO [12]:

$$Fe(s) + 1/2\ O_2(g) = FeO(\ell);\ \Delta G^\circ = -231{,}984 + 45.54\ T\ \text{Joule} \tag{3}$$

Therefore,

$$\log p_{O2} = -11.71 + 2 \log a_{FeO} \tag{4}$$

Schuhmann and Ensio [13] determined the activity of FeO to be 0.41 in fayalite slags saturated with both silica and iron. This value was used to locate point S on the assumption that FeO activity is not affected by sulphur at partial pressure s of sulphur below 10^{-7} atm. Yazawa [14] obtained the activities of FeS and FeO in iron- and-silica saturated slag in equilibrium with oxysulphide at 1200 °C to be 0.66 and 0.30, respectively. These values were used to locate point Y. The smooth curve SYO was obtained by joining points S, Y and O with a smooth curve to join with the experimentally determined curve OP.

The curve SYOP represents the equilibrium between slag and oxysulphide as a function of oxygen and sulphur partial pressures, obtained by combining Eqns. (2) and (3):

$$FeO(\ell) + 1/2\ S_2(g) = FeS(\ell) + 1/2\ O_2(g);\ \ \Delta G^\circ = 115{,}711 - 15.21\ T\ \text{Joule} \tag{5}$$

The curve is given by the relation:

$$\log p_{S_2} = 6.62 + 2 \log \left(\frac{a_{FeS}}{a_{FeO}}\right) + \log p_{O_2} \tag{6}$$

The variation of the activity ratio of FeS-to-FeO for the section YOP is shown in Figure 7. Clearly, the sulphur content of slag and oxysulphide has a marked effect on the activities of FeO and FeS.

5. Conclusions

This investigation has shown that silica has a high solubility in oxysulphide and that the solubility of silica and oxygen decrease as the sulphur content of oxysulphide increases. There is a discontinuity in composition of the melt at a unique series of oxygen and sulphur partial pressures and this represents the division between the oxysulphide and slag states of the Fe-O-S-SiO_2(sat) system. The predominance area diagram of the system was constructed by combining the experimentally determined boundary with data from previous investigators. The ratio of the activity of FeS-to-FeO along the boundary varies between about 2.7 and 8.2 and this indicates that sulphur in slag has a marked effect on the activity of FeO.

6. References

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