Liquidus Surface of “Lime Ferrite” Slags at Intermediate Oxygen Potentials

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“Lime ferrite” slag with limited silica content has proven to be a valuable choice in the modern processes of copper smelting and converting due to several advantages that this slag offers compared to classical silicate slags. Nevertheless the liquidus surface of this slag has been experimentally measured only at low oxygen potentials such as in equilibrium with iron or near it and in air. Although most of the smelting and converting processes that use this slag occur at intermediate oxygen potentials, the liquidus surface of this slag is not known at these conditions and the effect of oxygen potential and silica has not been correctly understood. This has brought some confusion in literature as well as in the industrial practice. In this work the liquidus surface of the calcium ferrite slags has been quantified by the means of a new thermophysicochemical model and a new type of liquidus surface diagrams which are very convenient for any industrial process that uses calcium ferrite slags. These diagrams can be easily used to select the lowest liquidus temperature of calcium ferrite slags at a minimum cost and can help design several fluxing strategies in copper smelting and converting processes. The effect of the oxygen potential and silica is also quantified and important industrially related conclusions are drawn.

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1. Introduction

The “Lime Ferrite” slag that often is also called “Calcium Ferrite” slag, was proposed about two decades ago¹ as a new slag for modern copper smelting processes and especially for copper continuous converting. It contains CaO, Fe₂O₃ and FeO as major components and silica, copper oxide etc. as minor ones. This slag has proven to be a valuable choice in the modern processes of copper smelting and converting due to several advantages that this slag offers such as its lower viscosity and higher solubility of magnetite compared to classical silicate slags. This slag has been successfully used for several years by Mitsubishi continuous converting process.² However, the liquidus surface of this slag has been experimentally measured only at low oxygen potentials such as in equilibrium with iron or near it and in air. Although most of the smelting and converting processes that use this slag occur at intermediate oxygen potentials, the liquidus surface of this slag is not known at these conditions and the effect of oxygen potential, silica and copper oxide has not been correctly understood. Their effects have usually been generalized without taking into account the specific combination of the process conditions such as the slag composition, oxygen potentials, primary phases and minor components. This has brought some confusion in the literature as well as in the industrial practice.

Following the previous work on the quantification of the liquidus surface of several other slags³–¹⁶ the purpose of this work is to quantify the liquidus surface of calcium ferrite slags at intermediate oxygen potentials through a new thermophysicochemical model and a new type of liquidus surface diagrams which is very convenient for any industrial process that uses calcium ferrite slags.

A new thermophysicochemical model that reflects the physicochemical structure of the slags has been developed in conjunction with FLOGEN™ software package¹⁶ and will be published elsewhere. The strongest point of the model is that it does not fit the experimental data but on the contrary predicts them at intermediate oxygen potentials within the experimental uncertainty. In other words it has its own independence from the experimental data.

The partial pressures of oxygen throughout the article are given as dimensionless ones defined by \( p_{O_2} = (P_{O_2})/(101325 \text{ Pa}) \).

2. Validation of Model Predictions

The model predictions are validated against the existing data of Acuna and Yazawa,¹⁷ at several temperatures and oxygen potentials.

Figure 1 shows a comparison of the model predictions with

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Fig. 1 Comparison of model predictions (solid and dashed lines) with the experimental data of Acuna and Yazawa (full black circle) at iron saturation and various temperatures.
the data of Acuna and Yazawa at iron saturation at different temperatures while Fig. 2 compares the model predictions with the data of the same authors at log($P_{O_2}$) of $-10.59$ and $-8.59$ at 1573 K. As it can be seen from both figures the model predictions agree very well with the experimental data.

The new model describes even better the data of Tsukihashi\(^{18}\) and Takeda \textit{et al.}\(^{19,20}\) compared to the previous publication\(^7\).

The model predictions on the copper solubility and distribution between copper and calcium ferrite slag are also in good agreement with the data of Yazawa and Takeda\(^{21}\) and Takeda\(^{19}\).

3. New Type of Multicomponent Phase Diagrams

A new type of multicomponent phase diagrams has been presented in this work in order to effectively quantify the liquidus surface of lime ferrite slags. This new type of diagrams is a two dimensional representation of a multi-components system in the form of SiO\(_2\) versus Fe/CaO ratio at any oxygen partial pressure and any content of minor components. These kinds of diagrams, both in polythermal or isothermal forms, are very convenient for any industrial process that uses calcium ferrite slags. They can directly give the effect of silica, iron, lime, oxygen potential etc. on the liquidus surface of the lime-ferrite slag at any oxygen potential and minor components.

4. Effect of Oxygen Potential

4.1 Polythermal projection diagrams

Figures 3 and 4 give the liquidus surface of lime ferrite slag at the oxygen partial pressures of $10^{-7}$ and $10^{-6}$. As it can be seen, in these diagrams, at this particular set of conditions, only three primary precipitate areas are present. They are magnetite, Ca\(_2\)SiO\(_4\)' and Ca\(_2\)Fe\(_5\)O\(_8\). The following important conclusions can be drawn from these diagrams:

- An increase of the oxygen partial pressure increases the slag liquidus temperature in the magnetite saturation area and consequently increases the risk of magnetite precipitation.
- An increase of the oxygen potential increases the liquidus temperature in the Ca\(_2\)Fe\(_5\)O\(_8\) precipitation area and increases the risk of the precipitation of this phase.

4.2 Isothermal diagrams

Figure 5 shows the influence of the oxygen potential on the liquid regions of lime ferrite slag at 1573 K. As can be seen the liquid region decreases considerably with the increase of oxygen partial pressure. This decrease is significant in the magnetite saturation area even for small changes of oxygen potentials and consequently the risk of magnetite precipitation increases considerably. This explains several problems encountered in the industrial practice with the magnetite precipitation. However, another effect is visible in the Ca\(_2\)SiO\(_4\)' saturation area where an increase of the oxygen potential slightly increases the liquid region.

4.3 Other diagrams

Figure 6 directly quantifies the effect of oxygen potential on the liquidus surface of lime-ferrite slags without silica and copper content. It can be seen that a decrease of oxygen...
potential decreases the liquidus temperature for this particular slag.

5. Effect of Silica

From Figs. 7 and 8 it can be seen that the effect of silica on the liquidus temperature of lime ferrite slags is different at different compositions and especially at different Fe/CaO ratios. This can also be gauged from Fig. 7 at an oxygen potential of \( \frac{10^7}{C_0} \). From this figure it can be seen that, at this particular set of conditions, at a Fe/CaO ratio of 2 silica decreases the liquidus temperature until about 3% and then increases it considerably. However, a completely different effect is noticed at a Fe/CaO ratio of 3 where it continuously increases the liquidus temperature. In the first case silica maybe beneficial for the smelting process in term of the liquidus temperature if this is necessary but not in the second case. It should be again noted that these conclusions are specific for the present set of conditions since other combinations of oxygen potentials and minor components may change these relationships.

The effect of silica on the liquidus temperature at an oxygen potential of \( \frac{10^6}{C_0} \) is given in Fig. 8. It can be seen that at these particular conditions a silica addition of 3% in the slag increases the liquid temperature for Fe/CaO ratios greater than about 2.5 and decreases it for Fe/CaO ratios less than 2.5. However, it is important to be mentioned that this effect should not be wrongly generalized since at different conditions the effect of silica might be different.

6. Effect of Cu2O

6.1 Polythermal projections diagrams

Figure 9 gives the liquidus surface of lime-ferrite slag at \( \frac{10^6}{C_0} \) and at copper saturation. It can be seen that in this case three primary phases are also present magnetite, \( \text{Ca}_2\text{SiO}_4 \), and \( \text{Ca}_3\text{Fe}_2\text{O}_5 \). The Cu2O content in the slag at the saturation
of a second phase varies according to composition and temperature. For instance at SiO$_2$=10% in the scope of this diagram the content of Cu$_2$O varies around 7 to 11%. The following points are worthy of note:

- A comparison of this figure with Fig. 4, given previously, shows that Cu$_2$O generally decreases the liquidus temperature of the calcium ferrite slag in the three saturation areas.
- The effect of copper oxide is not uniform and is very sensible to the oxygen partial pressure and temperature. For example, an increase of the oxygen potential and a decrease of temperature have considerable effects on the phase relationships since the copper content in the slag increases.

6.2 Isothermal diagrams

Figure 10 shows the influence of the copper oxide on the liquid regions of lime-ferrite slag at 1573 K. As it can be seen, in this particular set of conditions, the liquid region increases with the saturation of the slag with copper. This increase is more pronounced in the magnetite saturation area and consequently the risk of magnetite precipitation decreases. Copper also increases the liquid region of the slag at both Ca$_2$SiO$_4$' and Ca$_2$Fe$_2$O$_5$ saturation areas.

6.3 Other diagrams

Figure 11 shows a comparison of the liquidus temperature of silica-free lime ferrite slag at log($P_{O_2}$) = −6 at copper saturation and without copper saturation. It can be seen that the dissolution of copper in the slag decreases the slag liquidus temperature. The recent data of Takeda$^{22)}$ are also shown for comparison. It should also be mentioned that although the data of Takeda became available after the diagrams were constructed, the agreement is excellent.

7. Conclusions

The liquidus surface of the calcium ferrite slags has been quantified by the means of a new thermophysicochemical model. A new type of multicomponents liquidus surface diagrams was presented which is very convenient for any industrial process that uses calcium ferrite slags. These diagrams can be easily used to select the lowest liquidus temperature of calcium ferrite slags at a minimum cost and can help design the best fluxing strategies in copper smelting and converting processes. The effect of the oxygen potential, silica and copper oxide was also quantified and important industrially related conclusions are drawn. It was also reconfirmed that the effect of the oxygen potential, silica and copper oxide are not uniform and can be completely different at different combination of the slag composition, oxygen potentials and minor components. The confusion found in the literature and in the industrial practice was also clarified. For example it was found that the effect of silica and copper is not uniform and unidirectional but dependent on the oxygen potential and the precipitate phases as well as the effect of oxygen potential in itself is not uniform. The optimum composition of the slag depends on all these factors. The quantification of the effect of other minor components is ongoing research.

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