Slags in ferroalloys production—review of present knowledge

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Ferroalloys like FeCr and FeMn are mostly produced in submerged electric arc furnaces. Typical for these processes is that the amount of slag is quite high. The role of slag for the process is thus very essential and specific chemical, physical and electrical properties are required. Slags in FeCr process are Al_2O_3-MgO-SiO_2 based with minor contents of CaO and CrO_x. Slags in FeMn process are principally similar originating from silicate minerals but can have quite a large composition range depending on the manganese ore and its gangue minerals. Characteristic for FeMn process is that the slag is rich in manganese oxide up to above 30%. A common feature is that the 'ore oxides', CrO_x and MnO_x in slag are not only divalent oxides but also containing some higher valent of Cr^{3+} and Mn^{3+}, respectively. In FeMn production conditions the slag consists mainly Mn^{2+}. This is a clear difference from CrO_x containing slags in which both two and three valent coexists in slags in FeCr process conditions. Oxidation state of the slag depends on the ambient oxygen partial pressure and temperature in the examined process. Thermodynamics of slags in ferroalloys production are discussed in terms of phase diagrams, activities and oxidation state of chromium and manganese oxides. Further, slag properties influencing reduction kinetics and furnace operation i.e. viscosity and electrical resistivity are discussed.

Keywords: review, slags, ferroalloys, ferrochromium, ferromanganese, thermodynamics, physical properties.

Introduction

Stainless steel consumption is steadily growing with 5 per cent per year in average, thus giving an impact for increasing production of ferrochrome. FeCr production (HC FeCr, 52 per cent Cr) has now reached the level of 5 Mton/year[1]. Production of Mn alloys, FeMn and SiMn exceeds 6 Mton/year contributing to manganese content of 4–4.5 Mton/year but is growing slowly following the trend of the global steel production which is increasing in the long-term, although highly fluctuating around 1–2 per cent/year. Manganese and silicon bearing ferroalloys (FeMn, FeSi, SiMn) are typical additives used in carbon steels as well as in low and high alloyed steels. In addition, 'minor alloys' (FeNi, FeMo, FeW etc.) and microalloys (FeV, FeTi, FeNb, FeB, FeAl) are produced and used to make different steel grades with desired properties. As the processes for these alloys are quite diverse and specific they are not discussed here. Concerning silicon alloys slag properties are essential in refining processes but in FeSi production the basic idea is just to reduce pure SiO_2 in submerged arc furnace. Consequently, the focus of this article is in slags of FeCr and FeMn processes.

Submerged-arc furnaces are used to smelt chromite and manganese ores into respectively ferrochrome and ferromanganese (containing silicon and carbon) as well as associated slags by the use of a suitable carbonaceous reductant (coke, anthracite, char). The slag is created in the process from gangue material associated with the ores as well as fluxes added to the burden. The fluxes are added to assist in the smelting by affecting the activities of the oxides in the slag, melting temperatures of the slag, its viscosity and electrical conductivity. Slags in FeCr process are Al_2O_3-MgO-SiO_2 based with minor contents of CaO and CrO_x. Slags in FeMn process are principally similar originating from silicate minerals but can have quite large composition range depending on the manganese ore and its gangue minerals. Chromium content of FeCr slags is typically 5 to 10 per cent of which a significant part is as metallic particles dispersed in the slag. Characteristic for FeMn process is that the slag is rich in manganese oxide up to above 30%. A common feature is that both Cr and Mn are present in two different valent states in the process conditions, namely Cr^{2+}/Cr^{3+} and Mn^{2+}/Mn^{3+}, respectively. Oxidation state of chromium and manganese depends on the local oxygen partial pressure and temperature of the slags.

A successful operation to a large extent depends on the metal recovery. For example, high chromium recovery would be beneficial in saving raw materials and energy as well as in reducing eventual chromium pollution from chromium containing slag and wastes. The knowledge of the thermodynamic properties of slags, including activities and phase relations will definitely help to evaluate the equilibrium distribution, to promote process modelling and, further, to better understand the process to achieve a higher recovery of metal from the slags.

Even though volume of work can be found in the literature on the chromium and manganese properties in the metallurgical slag, some fundamental nature and behaviour in general still need to be clarified. In this paper, the available information on the oxide activities and the phase relations in the slag, the metal recovery, and some other

properties like viscosity and electrical conductivity were summarized and discussed. The aim was to provide a guided metallurgical knowledge and, further, to establish practical implications to the process operation and control for ferroalloy production.

Thermodynamic properties of chromium bearing slag

A quantitative evaluation of the thermodynamic properties and roles of chromium oxides in silicate melts, and hence of the chromium distributions between slag and alloys, requires a knowledge of the activity—composition relations of chromium oxides as well as the phase relations in the slag. Chromium oxide containing slags have been investigated at temperatures corresponding to FeCr and stainless steel processes under different oxygen partial pressures ranging from a very strong reducing atmosphere to ambient air.

Chromium–oxygen system

In order to understand the complexity of chromium containing slags it is useful to examine the basic diagram of Cr-O system, as shown in Figure 1[2]. At low temperatures Cr has stable oxides of which most common is Cr_2O_3 (Cr^{3+}) but oxides with higher oxidation state (Cr^{6+}) can form under high oxygen partial pressure. Lower valent oxides are stable only at high temperatures, Cr_3O_4 exists above 1650°C and divalent oxide CrO forms above 1665°C. When cooling down it disproportionates to metallic Cr and Cr_2O_3:

$$3CrO = Cr + Cr_2O_3 \qquad [1]$$

As seen in Figure 1 liquid 'CrO' is formed at low oxygen partial pressure, e.g. in equilibrium with metallic chromium or ferrochrome. It has a rather wide non-stoichiometric composition range. The oxygen partial pressure at the eutectic point is inferred to be of the order of 10^{-12} atm[2].

Activities of chromium oxides in slag

The available activity data in the literature are still very limited, especially for the slag systems under the conditions
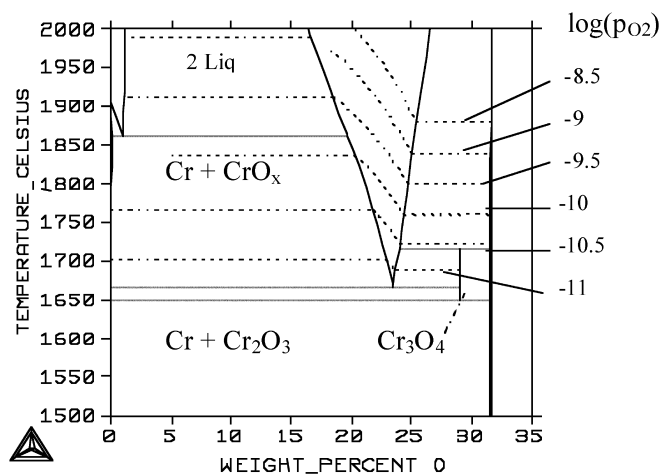

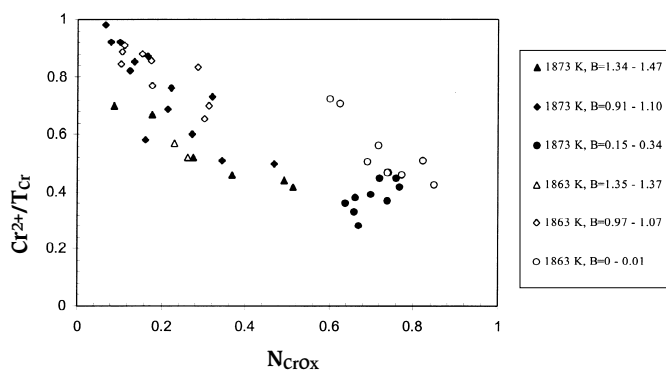**Figure 1. Equilibrium relations in Cr-Cr₂O₃ system[2]**

Figure 2. Oxidation state of chromium in CaO-SiO₂-CrOx slag system in equilibrium with metallic chromium[5]
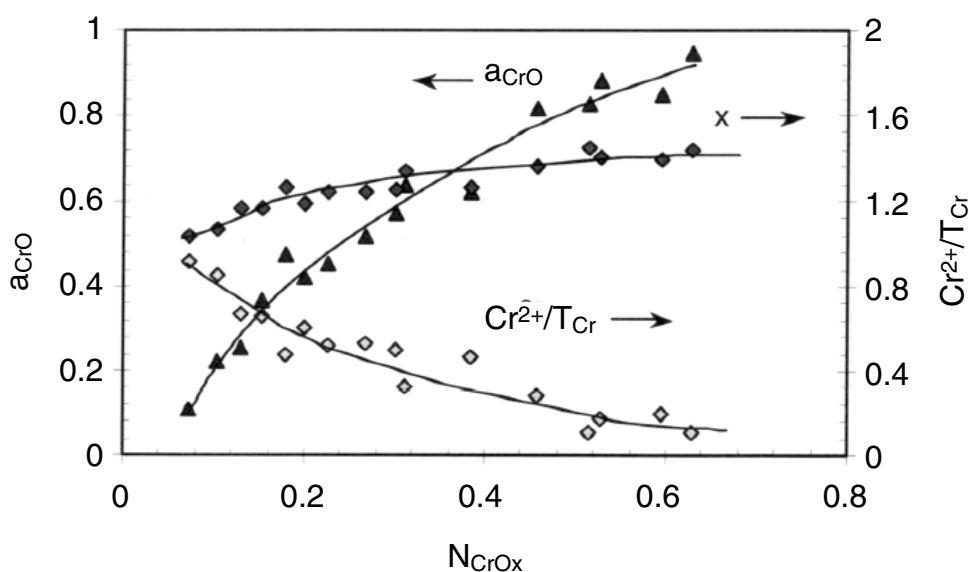

Figure 3. Activity of CrO and oxidation state of chromium in CaO-SiO₂-MgO-Al₂O₃-CrOx slag at 1873 K in equilibrium with metallic chromium, standard state-pure liquid CrO
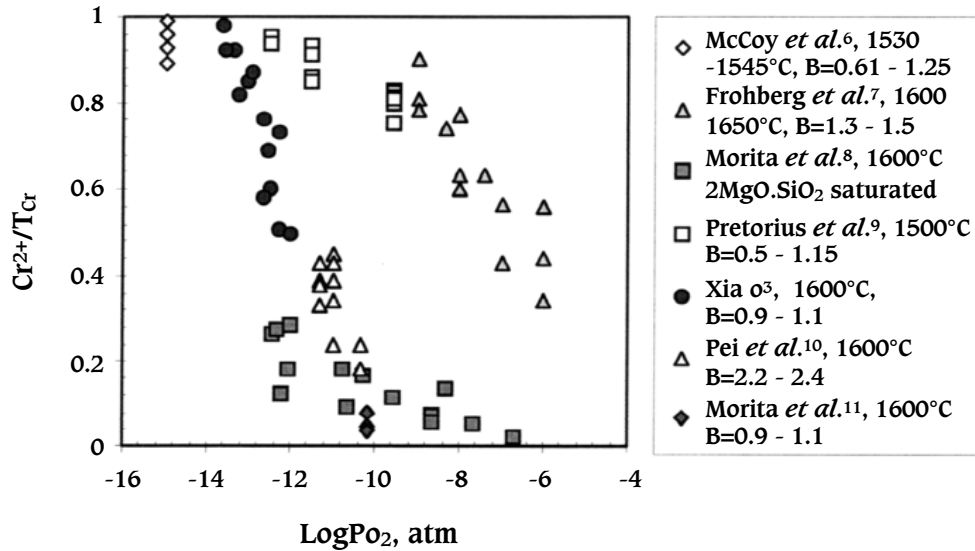
MOLTEN SLAGS FLUXES AND SALTS

Figure 4. The effect of oxygen partial pressure on the oxidation state of chromium in slag from different researchers

for FeCr production. In most cases the slags were equilibrated with Cr metal or Cr alloy, only in few cases the ambient Po_2 was controlled by the gas phase only. Xiao and Holappa[3–5] studied chromium containing slags equilibrated with metallic chromium crucible at 1500–1600°C. The oxidation state of chromium in CaO-SiO_2-CrO_x based slag was evaluated by wet chemical method, and activities of CrO and $CrO_{1.5}$ were determined by the electromotive force method. The effects of temperature, slag basicity, as well as additions of MgO and Al_2O_3 were investigated. The divalent chromium fraction increased but the activities of chromium oxides decreased with temperature. The higher the slag basicity, the higher the activities of chromium oxides.

Figure 2 shows that the divalent chromium fraction in the slag decreases with increasing basicity and total CrO_x. The index of x changes from a value slightly above 1.0 to a value almost 1.5. By partially substituting MgO for CaO, the activities of CrO and $CrO_{1.5}$ decreased, the oxidation state of chromium in the slag did not change significantly. Increasing Al_2O_3 content to 10 mol% resulted in a lower divalent chromium fraction and higher activities of chromium oxides. A further increase in the Al_2O_3 content to 20 mol% did not cause obvious change. The CaO-SiO_2-MgO-Al_2O_3-CrO_x slags with a low melting point in relation to FeCr production were also investigated. The basic composition of the Cr-free slag was: (CaO) = 10 mol%, (SiO_2) = 40 mol%, (MgO) = 35 mol% and (Al_2O_3) = 15 mol%. The CrOx varied from about 7.5 mol% to saturation. The results of the activities of the chromium oxides are presented in Figure 3. It can be seen that the solubility of CrO_x in the slag is about 60 mol%, if the slag is in equilibrium with metallic chromium. In this slag system, the slag is more acidic, the slag basicity is less than 1.0, and the effect of MgO and Al_2O_3 co-existence is incorporated.

In general, in silicate slags in equilibrium with Fe-Cr-O (unsaturated) melts or in silica saturated slag systems under low oxygen partial pressure, both Cr^{2+} and Cr^{3+} are present in all slags, and an equilibrium exists between these two valences depending on the equilibrium oxygen partial pressure, slag composition and temperature. It was found that the ratio of Cr^{2+}/Cr^{3+} in the slag increased with higher temperature, lower oxygen partial pressure and lower slag

basicity. In order to compare the available data in literature, some of the experimental results from different researchers were selected and compared under specific conditions in Figure 4. Due to the difference in experimental methods, conditions as well as the slag analysing methods, there seems to exist a great discrepancy in the oxidation state of chromium in the slag.

Figure 5 shows a comparison of the activities of CrO. A general consistency of the activity values can be observed from the figure. The agreed conclusion is that increasing the slag basicity will increase the activity of chromium oxides. Also, temperature has a weak lowering effect on the activity of CrO. The activity coefficients of CrO and $CrO_{1.5}$ increased with increasing oxygen partial pressure and CaO content in the melts.
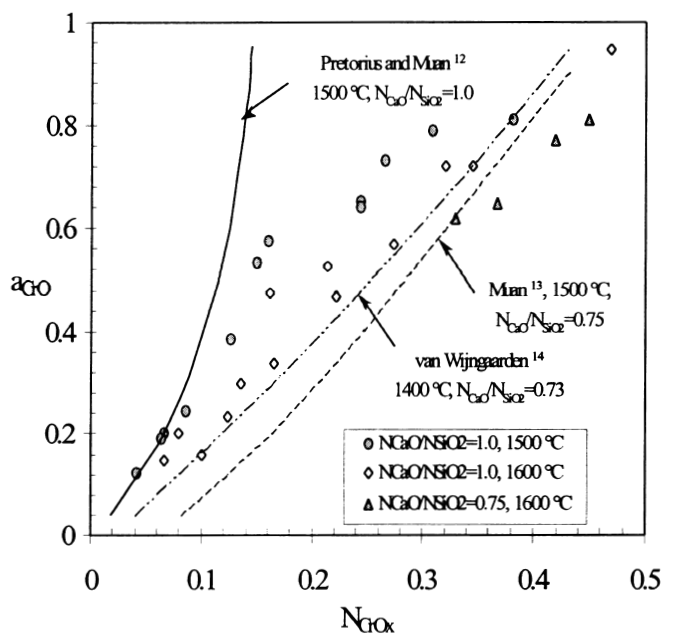

Figure 5. Comparison of a_{CrO} in silicate slag from different researchers

Phase diagrams of slag systems containing chromium oxides

More than 35 phase relation diagrams were available to demonstrate the thermodynamic properties of chromium containing oxides systems. It seems that the phase relations of the metallurgical chromium oxide systems have been broadly investigated from monometric Cr-O system to multicomponent oxide systems of Fe, Cr, Ca, Mg, Al and Si. The monometric, binary and ternary systems were investigated systematically, mainly in air atmosphere, and a few systems were studied in equilibrium with metallic chromium. An important system concerning FeCr production is the quasi-ternary MgO-SiO_2-CrO_x. The diagrams in air and in equilibrium with metallic Cr were presented in Slag Atlas[15]. The diagram of the system in equilibrium with metallic Cr shows the low liquidus area at lower slag basicity (SiO_2 around 60%) than the corresponding system with CaO. Both diagrams were given as ternaries with Cr_2O_3 which is, evidently, not relevant for the Cr metal equilibrium, due to the significant amount of CrO in slag.

As to the quaternary chromium containing oxide systems, only Ca-Mg-Si-Cr-O system was reported in the literature[16]. The quinary Ca-Mg-Al-Si-Cr-O system was only studied in air atmosphere, and the chromite spinel phase was the primary interest[17]. Based on the information, the most important features of the liquidus surface of chromium oxide containing silicate systems are the larger liquid miscibility gaps and the dominance of the chromite spinel stability area. Subsolidus relations of special interest are those involving spinel phases. The oxygen potential of the gas phase is an important parameter in chromium oxide containing systems, as the oxidation state of chromium has powerful influence on phase diagrams and physical properties of slags as well.

Recovery of metal from slag

The basic slag system for FeCr production is MgO-Al_2O_3-SiO_2-CrO_x. In general, furnace atmosphere, temperature, charge (mineralogical) composition, size and type of the furnace are all factors influencing the chromium loss. In general, the chromium loss from an open furnace is significant for runs of several hours duration at 1500 to 1700°C. For a closed furnace under similar conditions, however, the loss is considered to be negligible.

Among others, McCoy and Philbrook[6] and Maeda et al.[18] studied chromium recovery from chromium-containing slags. Chromium recovery from ferrochrome slag can reach high values of 90–99 per cent within a reasonable time. Most of the chromium left in high carbon ferrochrome slag was found to exist as undissolved chromite. Eric and Akyuzlu[19] investigated the slag/metal equilibrium in FeCr production conditions. They indicated that the chromium content of the slag decreases with increasing slag basicity, and this effect was stronger at relatively low basicity. The chromium content of the slag decreased rapidly as the basicity increased. The temperature and slag composition would have an effect on chromium partition. The recovery of chromium is enhanced by the presence of Al_2O_3 in the slag. The presence of MgO leads to the formation of a spinel phase which has a very low solubility in basic melts. The addition of MgO greatly enhances the recovery of chromium in basic melts with a basicity ratio larger than 0.80.

It is concluded that increasing slag basicity is an effective way of reducing the loss of chromium to the slag when the basicity is relatively low. The beneficial effect levels off significantly, however, when the basicity exceeds 1.4. But adding lime has also severe drawbacks; it increases slag volume which causes extra losses, and it raises up electrical conductivity which can be detrimental for the furnace operation.

Physical properties of chromium oxide containing slags

Viscosity and electrical conductivity are the physical properties with the closest relation to the practical operation of a submerged arc furnace for FeCr production. Downing and Urban[20] investigated the effect of chromic oxide content on the electrical conductivity of the synthetic slag containing 30 wt% Al_2O_3, 30 wt% MgO, 20 wt% SiO_2 and 20 wt% CaO, in the temperature range of 1430 to 1700°C. They concluded that Cr_2O_3 additions increase the resistivity of the slag, i.e. decrease the electrical conductivity. Rennie et al.[21] studied effects of Cr_2O_3, Fe_2O_3 and CaO on the viscosity and electrical conductivity of the FeCr slags containing 45 wt% SiO_2 and MgO/Al_2O_3=4/3 or 3/4 with melting points of 1519°C or 1554°C, respectively. Kato and Minowa[22] measured viscosity and electrical conductivity in the slag system of 43 mol% CaO, 43 mol% SiO_2, 14 mol% Al_2O_3 with additions of (0.68, 1.38, 2.45 mol%) Cr_2O_3 at temperatures of 1400–1500°C. High viscosity values were obtained and the conductivity was improved by Cr_2O_3 addition which is an extraordinary behaviour and cannot be explained by the application of the ionic conduction.

It was concluded that additions of CaO and Fe_2O_3 decrease the viscosity and increase the electrical conductivity of the slags. The viscosity increases with the addition of 7% Cr_2O_3, but decreases for higher content of 12% when the temperature is above the liquidus
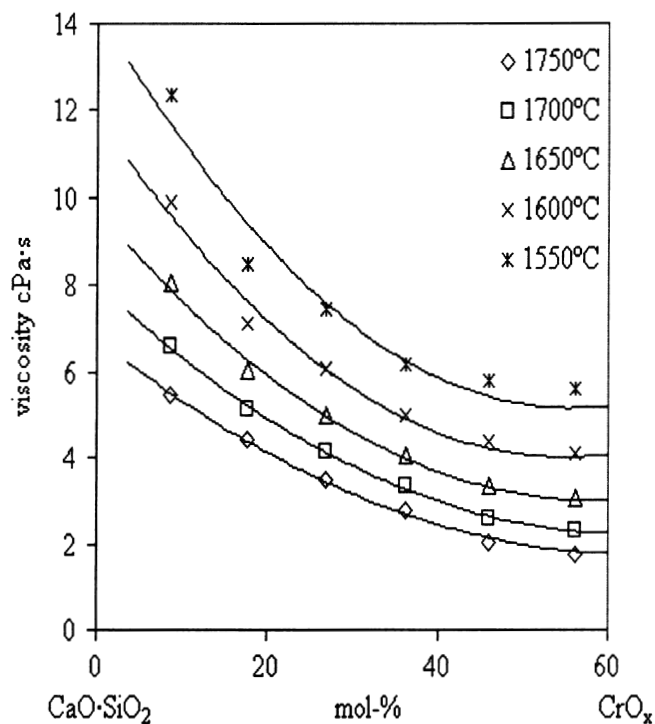
Figure 6. The effect of CrO_x addition on the viscocity of $CaO \cdot SiO_2$ melt (Forsbacka[24])

temperature. Cr_2O_3 additions decrease the electrical conductivity for the temperature below the liquidus temperature, but increase for the temperature above.

Recently, Forsbacka et al.[23] measured the viscosities of the slag system of SiO_2-MgO-Al_2O_3-CaO with the compositions near to FeCr process in the temperature range of 1600 to 1750°C. The results were assessed to the Iida model for viscosity and gave reasonable relations in the studied composition and temperature region. The current paper by Forsbacka and Holappa presents results of viscosity measurements when CaO-SiO_2-CrO_x slag was in contact with metallic Cr[24]. The results show that addition of CrO_x (with relatively high CrO fraction) decreases the viscosity, as shown in Figure 6. A similar effect is assumed in FeCr type slags too.

Electrical conductivities of Al_2O_3-MgO-SiO_2-Cr_2O_3 slags have been summarized in Slag Atlas[15]. In general, electrical conductivity decreases with increasing temperature. The effect of Cr oxide seems to be complex showing a slight maximum in some of the systems discussed. The presence of two-valent CrO can further complicate the phenomenon.

In general, because of the technical diffculties in high temperature measurement and the high melting points of the slags, the viscosity and the electrical conductivity in the slags containing chromium oxides are not studied systematically. Further research in this field is very much in need, especially under well controlled atmosphere due to the complex structure of chromium containing slags.

Thermodynamic properties of manganese bearing slag

Most of the high carbon ferromanganese is produced in submerged arc furnaces. The feeding charges are manganese ores, carbonaceous reductants and fluxes (quartzite and limestone). In the upper part of the furnace, the solid state reduction occurs and the higher oxides of manganese are reduced to MnO with up-stream CO gas. The FeMn alloy and slag are formed at the high temperature zone in bottom of the furnace. Depending on the type of furnace operation the slag of a typical ferromanganese operation can either be labeled as 'high slag' or 'discard slag' operation[25]. 'Discard slag' practice produces slags with MnO contents around 8 to 12%. The slag is produced by silica and other basic oxides associated with the ores. The components of the slag are ca. 2 to 8 % MgO, 4 to 10% Al_2O_3, ca. 35% CaO and ca. 31% SiO_2. A high basicity, i.e. high CaO and MgO contents ensure that MnO is released from the silica lattice and hence increases the recovery which lies around 70 to 75%. In high slag practise less coke and less energy are required to produce a slag that contains more than 25% MnO. Little or no basic fluxes are added. Correspondingly, the recovery of manganese is less than for 'discard slag' practice. Typical slag analysis for the other compounds are ca. 2 to 5% MgO, 10 to 30% Al_2O_3, ca. 15% CaO and ca. 27% SiO_2. These slags are usually used in silicomanganese production, increasing the overall manganese recovery. These silicomanganese slags form the basis for creating silicomanganese (ca. 65% Mn and ca. 15% Si) and typically have the following composition: ca. 4 % MgO, ca. 7% Al_2O_3, ca. 21% CaO and ca. 50% SiO_2.

Manganese @ oxygen system

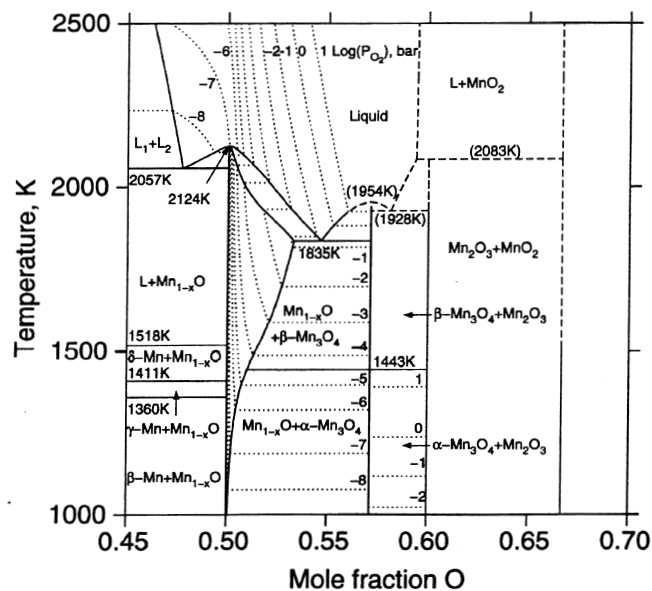A part of the manganese-oxygen phase diagram is shown in Figure 7[26]. It has similarities with the Cr-O system

Figure 7. Assessed Mn-O system (Grundy et al.[26])

including several oxides manganosite ($Mn_{1-x}O$), hausmanite (Mn_3O_4), bixbyite (Mn_2O_3) and pyrolusite (MnO_2) depending on oxygen partial pressure and equilibrium temperature of the system. The lowest oxide $Mn_{1-x}O$ has a very large non-stoichiometric region over which x gets values from ca. 0.11 in air to ca. 0.0004 in equilibrium with metallic Mn, corresponding to $P_{O_2} \approx 10^{-14}$ at 1600°C[26]. As a consequence, manganese oxide in FeMn production conditions consists, almost completely, of Mn^{2+} and only of a minute fraction of Mn^{3+}. This is a clear difference from CrO_x containing slags in which both two and three valent forms are abundantly present in slags in FeCr process conditions.

Activities of manganese oxides in slag

Activities of MnO in slags have been studied since the 1950s by e.g. Turkdogan and Pearson[27], Abraham et al.[28], and Rankin and See[29]. The data for CaO-SiO_2-MnO system published in Slag Atlas[15] is from Abraham et al.[28]. Activity data for FeMn slags were modelled by applying neural nets by Cengizler et al.[30] at 1500°C for slag compositions lying in the range of MnO 5–40%, CaO 4–35%, MgO 0.3–38%, SiO_2 25–60% and Al_2O_3 2.5–7%. In general it can be concluded that activity coefficient of MnO in liquid slag region varies on both sides of unity. In acid slags $\gamma_{MnO} < 1$, whereas in basic slags $\gamma_{MnO} > 1$. It also increases with increasing MnO content.

Phase diagrams of manganese containing oxide systems

Phase diagrams of manganese containing oxide systems have often been studied since early sixties. The binary MnO_x-SiO_2 system was studied by Glasser[31] at low oxygen partial pressure from 10^{-10} atm at 1130°C to 10^{-6} atm at 1555°C, and by Muan[32] in air. The phase diagrams of the CaO-MnO_x-SiO_2 system at low oxygen partial pressure were investigated by Glasser[33,34] The oxygen potential of 10^{-6} atm was used to control the manganese in divalent state. The low melting 'valley' (1600°C liquidus) goes roughly from 67–43 wt% SiO_2 in the CaO-SiO_2 binary to 52–19 wt% SiO_2 in the MnO-SiO_2 binary. Replacement of MgO for CaO results in higher liquidus temperature and
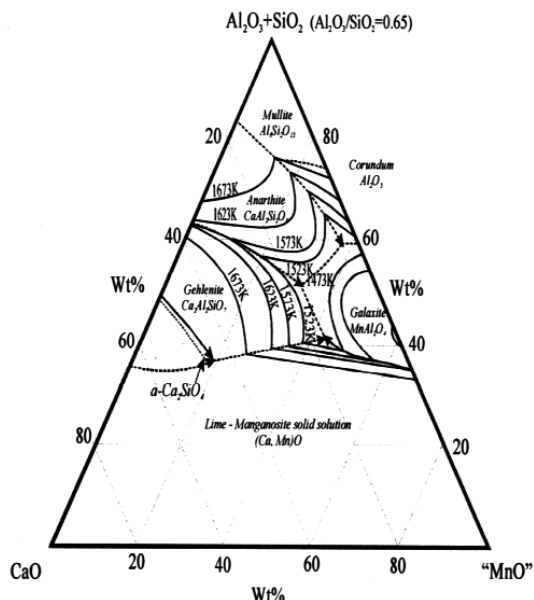
Figure 8. Liquidus lines for CaO-Al₂O₃-SiO₂-MnO system in equilibrium with Mn/Si alloy (redrawn from Roghani et al.[35])

Figure 9. MnO content in multicomponent slag in equilibrium with FeMn alloys with 10 per cent iron[40]

narrower low melting area in the MgO-MnO$_x$-SiO$_2$ system[34]. Recently, Roghani et al.[35] made a quite comprehensive investigation on phase equilibria in the 'MnO'-CaO-(Al$_2$O$_3$ + SiO$_2$) system by equilibrating slags with Mn-Si alloy at 1100 to 1550°C. An example diagram is shown in Figure 8. Typical slags in manganese alloy production are in the region of triple valley point upwards from 'Galaxite'.

A quinary system consisting of all major components in the slags for ferromanganese production was studied by Eric et al.[36] and Reuter et al.[37]. The slag compositions ranged from 5–30% MnO, 20–35% CaO, 5–15% MgO, 27–58% SiO$_2$, 5% Al$_2$O$_3$. It is clear that liquidus temperatures vary from 1300 to 1380°C. The results of neural net functions also demonstrate that liquidus temperatures increase with increasing basicity. Further, MnO additions first decrease the liquidus temperature and then increase it forming valleys in three dimensional plots. In general, the slag basicity ratio has a moderate positive effect on the liquidus temperature for the slags with up to 25 % MnO. For the slags containing 30% MnO, this effect is more significant. The variation of the liquidus temperature with CaO/MgO ratio depends to a large extent on the basicity and MnO content.

Recovery of metal from slag

Rankin[38] and Swinbourne et al.[39] investigated the equilibrium MnO content in ferromanganese and silicomanganese slags, respectively. They concluded that the distribution of Mn and Si decreased as the alumina content increased up to 20%. Olsen[40] and his group have carried out a comprehensive study on equilibrium content of MnO in high carbon FeMn process. The slags contained MnO, CaO, MgO, SiO$_2$ and Al$_2$O$_3$. The Al$_2$O$_3$/SiO$_2$ ratio was between 0.22–0.30. The effect of basicity and temperature on MnO content in slag in equilibrium with ferromanganese with 10 per cent Fe is shown in Figure 9.

Physical properties of manganese oxide containing slag

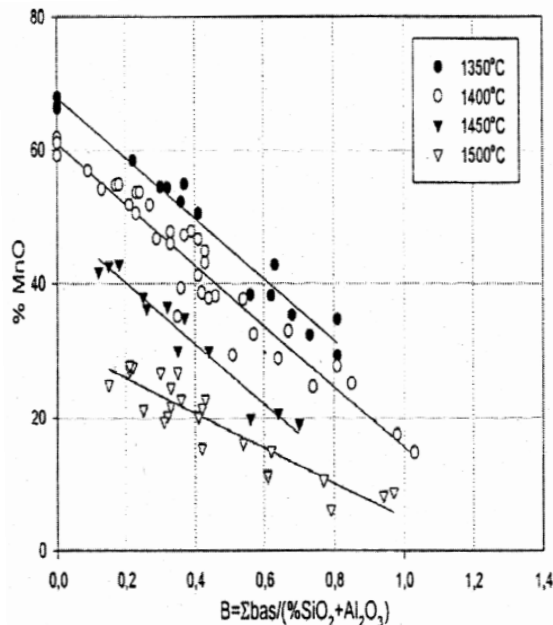Viscosities of several slags (from binary to quinary)

containing MnO have been presented in Slag Atlas[15]. Eric et al.[36] measured electrical conductivity of synthetic ferromanganese slags at 1425–1430°C. The slag compositions are in the range of: MnO 5-30%, CaO 20-35%, MgO 5-15%, SiO$_2$ 27–58% and Al$_2$O$_3$ 5%. Reuter et al.[37] modelled the slag system by neural nets. Recently, Seetharaman, Du and co-authors[41–42] have measured viscosities of various slag system, including CaO-SiO$_2$-MnO system. In most cases, MnO in slags seems to slightly decrease viscosity acting as a basic, non-bridging oxide.

Applications in ferroalloy production

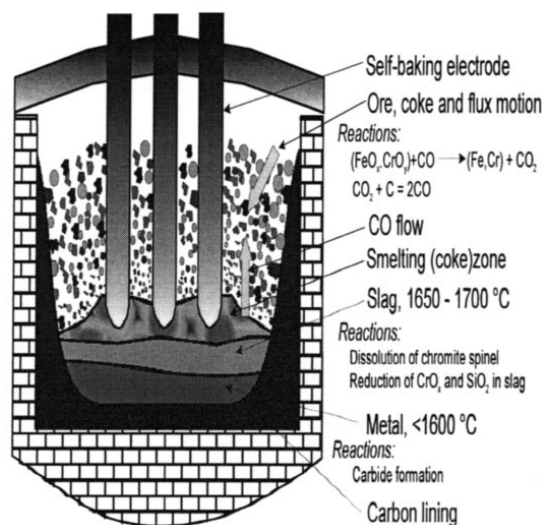The main feature of the reaction process for FeCr production is schematically illustrated in Figure 10. As the

Figure 10. A schematic reaction diagram in submerged arc furnace for chromite smelting

raw material, natural chromite ore can be described with the following compounds: Fe_3O_4, iron chromite $FeO.Cr_2O_3$, picrochromite $MgO.Cr_2O_3$, $MgO.Al_2O_3$ pseudo-ternary spinel solid solutions coexisting with $(Cr,Al)_2O_3$. These compounds form a complicated spinel structural solid solution. Among these components, magnetite Fe_3O_4 can be easily reduced in the process, for example, by carbon. Normally the reduction takes place in stages: solid state reduction of chromite by coke and CO; chromite dissolution in the slag; reduction of chromium oxides in the slag by solid carbon and by carbon dissolved in the metal. According to the information in the phase diagrams, minimizing the MgO/CaO ratio in the slag will improve dissolution of chromite spinel, enable more complete chromium reduction, and further result in an improved chromium recovery. On the other hand, by lowering slag basicity in the furnace spinel dissolution and chromium recovery will also be enhanced. The most important factors in FeMn slags are the MnO content and the basicity ratio. A rather large range in the variation of furnace power may be expected with the change of the basicity ratio at MnO contents between 5% and 10%. As the MnO content of the slag increases in the range of 20–25% MnO, the variation in basicity ratio will have very little effect on the slag resistivity. Therefore the aimed power input could only be achieved by a substantial increase in the furnace current to maintain an economical smelting rate[25].

From thermodynamic standpoint, the equilibrium between slag and metal controls the metal recovery in the process. Thermodynamic activity data of chromium oxides or manganese oxide in the slags will provide very important knowledge to evaluate the equilibrium distribution. Maximum metal recovery could be achieved by optimized slag composition. Phase diagram helps to establish liquidus temperature of the slag, which determine the overall operating temperature and degree of overheat to the melt. The lower liquidus slag temperatures would need less power input. Based on the present study, the liquidus temperatures of FeCr slags may vary from 1550 to 1700°C depending on the composition. With increasing chromium oxides content in the slag, the liquidus temperature will be raised significantly. Regarding turbulence both in the furnace and during the tapping, small droplets of metal may entrap in the slag, high slag viscosity reduces the rate of this physical separation. An excessively viscous slag may produce operational difficulties during tapping, and even cause foaming in the furnace. From the view point of reaction kinetics, low viscosity would favour diffusion processes in the slag/metal interface reaction and allow the reaction to reach equilibrium rapidly. For FeMn production, the slags with 10 to 25% MnO and basicity from 0.55 to 1.1 are of low liquidus temperatures between 1310 and 1350°C. When the slags contain more than 25% MnO and have the basicity higher than 1.4, the liquidus temperature is increased. At low MnO and low SiO_2 region, the slag has a relative high liquidus temperature.

Electrical conductivity of the slag assists to determine electrode penetration and power input to the furnace. Normally more resistive slag allows deeper penetration, higher voltage operation and higher power inputs. Energy generation by electric resistance heating is controlled by the secondary voltage and electrical resistivity of burden and slag. The electrical resistivity of the burden is determined mainly by the thickness of the coke layer and type and size of the carbon reductant, i.e., low resistivity coke and high resistivity coal. The electrical resistivity of the slag will be determined by its composition. The FeCr and FeMn processes contain ore, flux additives, reducing agent, slag and metal alloy. Even though the carbon reducing agent is expected to supply the major part of the electrical current, the slag may still contribute considerably to the overall resistivity at the electrode-tip area. However, in the process the relative importance of the electrical conductivity of the slag is still in question.

Summary and conclusions

The fundamental knowledge of chromium and manganese bearing slags was reviewed and discussed, including the oxidation state of chromium and manganese, the activities of oxides, the phase diagrams, and the factors affecting the metal recovery from slags. The physical properties such as liquidus temperature, viscosity and electrical conductivity in the related slag systems and their industrial applications were discussed.

It can be concluded that under reducing conditions of FeCr and FeMn productions, divalent and trivalent chromium and manganese are the major existing forms. In FeCr production Cr^{2+} and Cr^{3+} coexist in the slags. However, only Mn^{2+} is present in the FeMn slags. Increasing slag basicity and Al_2O_3 content have positive effect on the activities of both CrO_x and MnO_x in the slags. The fraction of divalent chromium increases with increasing temperature, lowering oxygen potential and decreasing slag basicity. The activities of CrO and $CrO_{1.5}$ have positive deviation from ideal solution. Activity of MnO has both positive and negative deviation from ideal solution. In FeCr production, the addition of MgO into the slag greatly improves the recovery of chromium with a basicity ratio higher than 0.80. The recovery is also enhanced by the presence of Al_2O_3 in the slag. Increasing slag basicity increases the chromium recovery from the slags, but the effect will level off when the basicity is higher than 1.4. To minimize the chromium loss in the slags, it is also important to control the slag volume in practice while decreasing the chromium oxides concentration in the slags. The most important feature of the oxide phase diagrams is that the liquidus temperatures are affected significantly by system oxygen potential because of the possible different oxidation states of chromium and manganese. The results on the quaternary and quinary systems are still very limited, and require to be further studied especially under controlled oxygen partial pressures. Except the thermodynamic properties, the effect of slag composition on physical properties must be considered, in order to obtain an efficient process operation and furnace control.

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