ISSN 1982-9345

ACIARIA
STEELMAKING
45º SEMINÁRIO DE ACIARIA - INTERNACIONAL
45TH STEELMAKING SEMINAR - INTERNATIONAL

Tema: Eletric Steelworks

THERMODYNAMIC EVALUATION OF THE SLAGS OF THE FeO-CaO-SiO_2-CrO_x-MgO SYSTEM AT 1,873 K*

Nestor Cezar Heck[1]
Julio Morales Pereira[2]
Antônio Cezar Faria Vilela[3]

Abstract

Aim of the present work is to continue the theoretical evaluation of the slags of the fundamental system CaO-SiO_2-CrO_x-MgO (Ca-O-Cr-Si-Mg quinary system) at the temperature of 1,873 [K], with the help of a computational thermodynamic tool. Driving force for this and the previous research works is the understanding of chromium losses from the molten bath into the slag. Especially motivating is the presence of solid phases in the slag, since they may prevent refractory degradation and help in the production of foaming slags. Nevertheless, Cr-bearing solid phases can lead to Cr losses, being therefore detrimental. Determination of the states of thermodynamic equilibrium for this system using a slag with fixed composition as a start material were made using MgO amount as variable. Results show the impact of the MgO content on the equilibrium phases (molten metal, liquid slag, solids) and their composition for this system.

Keywords: Slags; Ca-O-Si-Cr-Mg; Chromium losses; Computational thermodynamics.

[1] *Dr., Mining, Materials and Metallurgy Engineering Post-Graduate Program (PPGE3M), Computational Thermodynamic Res. Group, NTCm, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, Rio Grande do Sul, Brazil.*

[2] *Dr., Researcher, PPGE3M, Iron and steelmaking Laboratory (Lasid), UFRGS, Porto Alegre, Rio Grande do Sul, Brazil.*

[3] *Dr., PPGE3M, Iron and steelmaking Laboratory (Lasid), UFRGS, Porto Alegre, Rio Grande do Sul, Brazil.*

** Contribuição técnica ao 45º Seminário de Aciaria – Internacional, 25 a 28 de maio de 2014, Porto Alegre, RS, Brasil.*

1 INTRODUÇÃO

Having first been produced only 100 years ago, about a hundred chromium stainless steels are now widely used as construction materials when corrosion resisting metals at room or high temperatures are needed.

Unfortunately, during the production of these alloys, chromium losses are observed, especially as ions dissolved in the liquid (slag) or as minerals (solid phases) dispersed in slag.

Slags – as pointed out by Rosenqvist [1] – are used and may be studied under entirely different conditions: from reducing to strongly oxidizing environments. While changes in oxygen pressure do *not* noticeably affect the 'white' oxides SiO_2, Al_2O_3, CaO, and MgO, this is not the case when dealing with slags containing chromium, manganese, titanium, and iron oxides; changes occur due to the fact that these metal-oxide systems exhibit different valences.

Chromium, in particular, is a multivalent element; experimentally it was already demonstrated that this metal can show *several* oxidation states [2]. The most common oxidation state within a large temperature-composition range is Cr^{3+}; yet, several oxidation states are possible: Cr^{2+}, Cr^{3+}, Cr^{6+}, and probably Cr^{4+} and Cr^{5+} as well. Under strongly reducing conditions, and at high temperatures, however, substantial proportion of chromium is present in the *divalent* state [3].

Degterov and Pelton [4-6] examined closely the inclusion of chromium oxides data in a wide database of optimized thermodynamic properties of oxide systems (this database is now part of *FactSage* databases – the computational thermodynamic tool used in the present work). The CaO-rich part of the system CaO-CrO-Cr_2O_3-SiO_2 (*i.e.*, compositions within the CaO-Ca_2SiO_4-$CaCr_2O_4$ 'triangle') in air is an exception and was not considered in the *FactSage* databases optimization [6] (bearing in mind the reducing conditions present in the simulations of the current work, this fact is of minor significance).

Beside chromium losses, also refractory integrity is of concern: MgO refractories in slag line areas show a general tendency to dissolve when slags with low MgO content are used.

Aim of the present work is to evaluate theoretically the effects of MgO content in slags of the system FeO-CaO-SiO_2-CrO_x-MgO in contact with a Fe-Cr-Ni bath. Apart from the former work, here oxygen pressure is not imposed to the system, instead, is a result from an equilibrium calculation. The main subject has a direct relationship with two important topics: (i) chromium losses from molten metal into the slag; and (ii) refractory degradation – both are significant during the production of stainless steels.

Yet, it must be kept in mind that all considerations presented here will be limited to the thermodynamic equilibrium aspects. While recognizing that kinetics may be equally important, the thermodynamic approach, still, establishes the direction and the *limiting* conditions for the chemical reactions.

2 METHODOLOGY

The equilibrium state for every system under study in the present work was determined by the 'Gibbs energy minimization method' using the *Equilib* module of the *FactSage* software (version 6.4) – this software is described elsewhere by Bale *et al.* [7].

** Contribuição técnica ao 45º Seminário de Aciaria – Internacional, 25 a 28 de maio de 2014, Porto Alegre, RS, Brasil.*

The following three databases were employed:

- FSstel - FactSage steel intermetallic compounds and alloy solutions;
- FToxid - FACT oxide compounds and solutions;
- FactPS - FactSage general compound database.

Output of *Equilib* module of *FactSage* show results where oxides in the slag are grouped as the 'compounds' CaO, CrO, Cr_2O_3, etc. This is only a formalism; the model actually treats the slag phase as a mixture (solution) phase containing dissolved ions.

Focus of this work is located in the study of the slag ability to absorb Cr (the chief metal for the stainless steels) presented in the metal bath – a fact that reduces Cr yield and makes the steel being produced more costly.

To verify this, simulations with the aim to determine the equilibrium between metal and slag were conducted, under the constraint of keeping the metal chemical composition (18 wt.% Cr and 8 wt.% Ni) constant at any condition. A practical way to achieve this with the software used is by specifying the *chemical potential* of Cr and Ni in the molten bath. Hence, the amount of Cr or Ni necessary to reach the desired content was automatically controlled by the software.

Simulation itself was done adding 250 kg SiO_2 plus 250 kg CaO and 0-55 kg MgO to 42 t of molten metal (1:75 'slag' to molten metal ratio). The oxide composition corresponded at most to 45 wt.% CaO, 45 wt.% SiO_2 and 10 wt.% MgO (*nominal* binary capacity: 1; see *results* later).

3 RESULTS AND DISCUSSION

3.1 Equilibrium Atmosphere

Thermodynamics tells us that a simple iron-chromium alloy with ~20 wt.% Cr is in the liquid state at 1873 [K], and dissolves the element oxygen insofar as the oxygen pressure in the system atmosphere increases (Sievert's law). For approximately 1.8×10^{-12} [atm] ($\log pO_2 = -11.75$) and higher pressures, presence of the solid phase eskolaite (Cr_2O_3) – a very potent refractory component, which 'stiffens' the slag – can be observed at equilibrium state of the system, meaning that this is the highest O_2 partial pressure that can be attained before chromium oxidation starts [8].

In the present work, the equilibrium oxygen partial pressure refers to a more complex Fe - 18 wt.% Cr - 8 wt.% Ni molten alloy, in the presence of a CaO - SiO_2 - MgO slag, *i.e.*, it is a quite complex situation. As a result, the logarithm of the determined values varied somewhat from about -11.6 to -12.0, as a function of the MgO amount present in the system, Figure 1. Consequently, increasing the MgO content decreases the *equilibrium* pO_2 pressure, making the system more susceptible to Cr oxidation.

Noteworthy, these figures correspond to the theoretical partial pressures at the Fe-Cr-Ni metal / slag interface. The top slag is in contact with the atmosphere (O_2 at 0.21 [atm]) which is far more oxidant in comparison with the equilibrium values. For a viscous slag, the oxygen dissolution is, of course, limited to volumes near the surface by mass transport constraints. For low viscosity slags, or for those slags which are partially or fully stirred, however, this might not be quite the case.

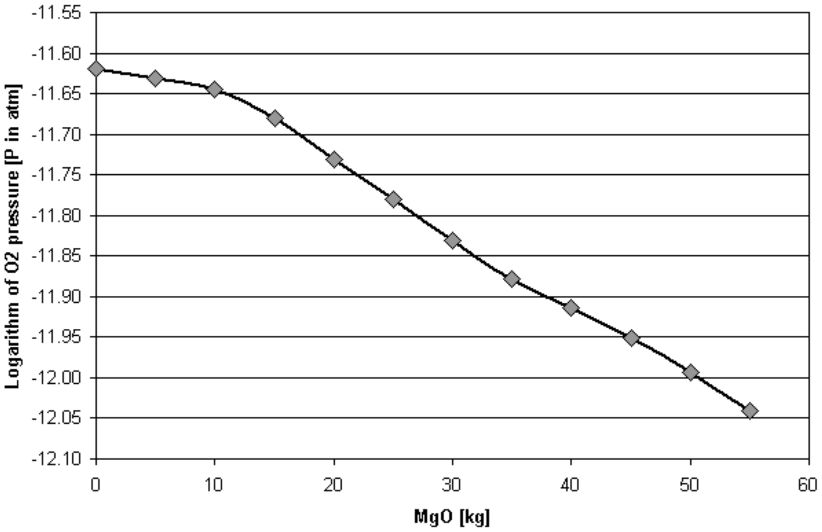

Figure 1. Equilibrium O_2 pressures at 1873 [K] as a function of MgO amount.

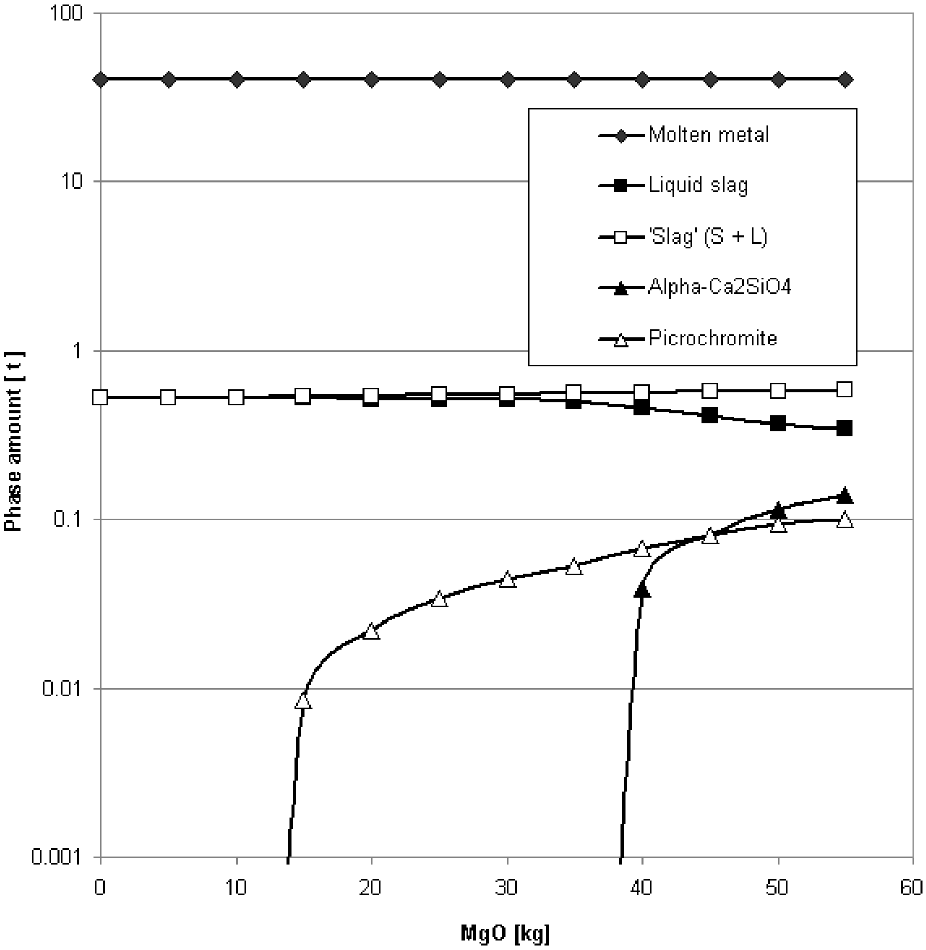

Figure 2. Phase amount at equilibrium at 1873 [K] as a function of MgO amount; the term 'slag' denotes the summation of liquid slag plus the solid phases Ca_2SiO_4 and picrochromite.

3.2 Condensed Phases

Figure 2 shows all the condensed phases present in the equilibrium state at 1873 [K] as a function of MgO amount present in the heterogeneous system.

** Contribuição técnica ao 45º Seminário de Aciaria – Internacional, 25 a 28 de maio de 2014, Porto Alegre, RS, Brasil.*

As it can be easily seen, at no point of the MgO range the oxide phase eskolaite (Cr_2O_3) could be found. This can be seen as a positive aspect, since Cr contained in solid phases is more difficult to recover due to kinetic reasons (reduction reactions can take place only at the solid / slag interface of the solid particle). However, spinel – *picrochromite* or *magnesiochromite* ($MgO \cdot Cr_2O_3$) – precipitates very early, at the beginning of the MgO range, and is as well a solid phase bearing chromium *i.e.* it behaves to some extent like Cr_2O_3 and has the same drawbacks of that oxide phase.

On the other hand, the precipitation of $2CaO \cdot SiO_2$ was expected – since this phase can be found already in the 'pure' pseudoternary CaO-SiO_2-MgO system.

The amount of liquid phase (slag) decreases at the end of the MgO range. However, as is usually the case, if all phases floating over the molten metal are to be considered as 'slag', it is apparent from Figure 2 that a slight amount increase takes place. Solid to liquid ratio (S/L) of the 'slag' than reaches a maximum of ~0.7 at 55 [kg] MgO.

3.3 Molten Metal

Concerning the Fe-Cr-Ni molten metal, it is clear that the proposed method of controlling the Cr and Ni contents by the thermodynamic tool was very effective, Figure 3.

Silicon, instead, was not added into the system, but it can be found in the molten metal originating from the slag phase.

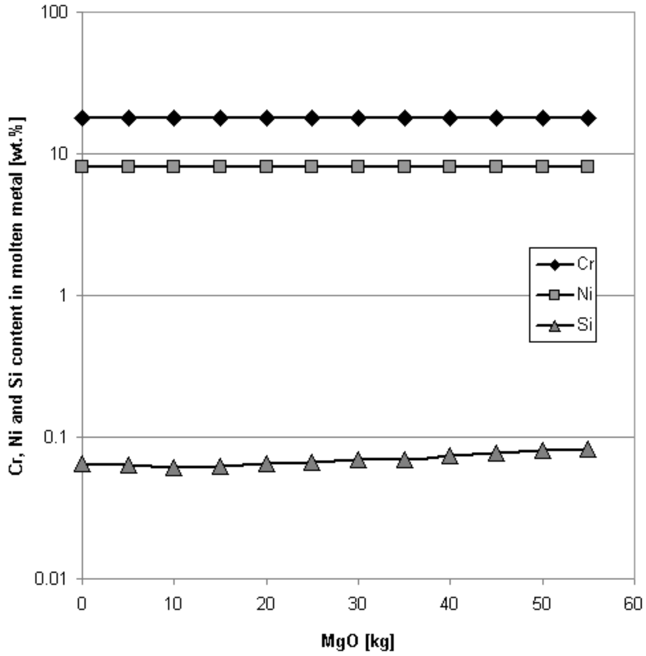

Figure 3. Equilibrium liquid metal phase composition representing the stainless steel at 1873 [K] as a function of MgO content; only major constituents dissolved in the molten bath are displayed.

3.4 Liquid Slag

The constituents of the liquid oxide phase (slag) where analyzed and their relative amount can be seen in the Figure 4.

As expected, SiO_2 and CaO make up the major part of the slag; yet, despite the equal amounts of SiO_2 and CaO used as input, there is a clear inequity between

---

them which can be primarily related to the Si content of the molten metal phase. Considering only the liquid slag, binary basicity is *circa* 1.3.

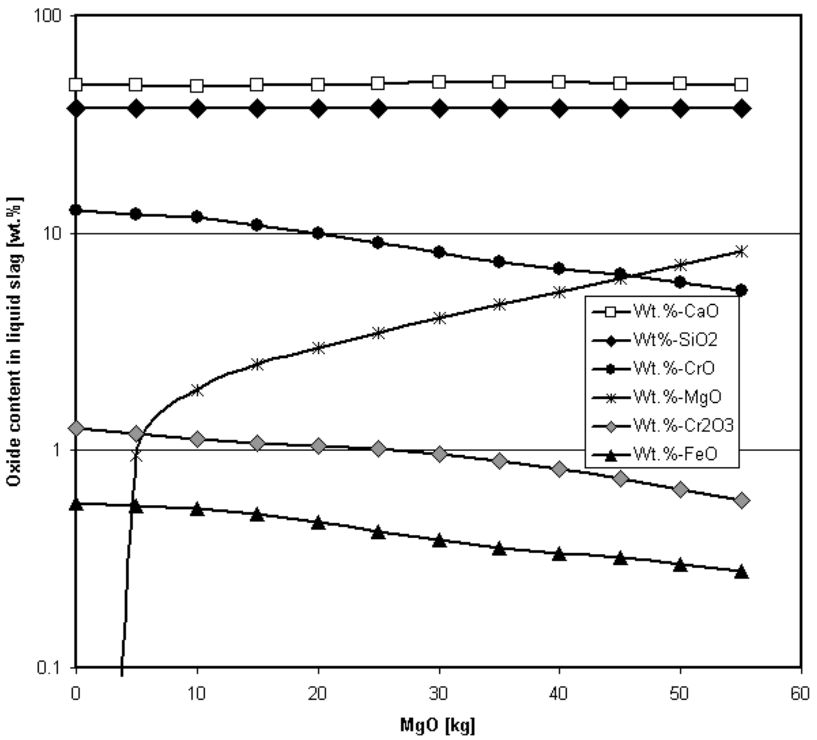

Figure 4. Equilibrium liquid slag composition in terms of oxide ‘compounds’ (the slag model actually treats the slag phase as a mixture – or solution – phase containing dissolved ions); only major constituents are displayed.

Among the Cr-bearing constituents, CrO (associated to Cr^{2+}) surpasses Cr_2O_3 (associated to Cr^{3+}) in an order of magnitude (decade) due to the prevailing reducing conditions. Same reasoning can be applied to the FeO and Fe_2O_3 constituents (only FeO reaches the scale range displayed).

Apart from silicon and calcium oxides, the amount of all other constituents shows a natural decline as a function of MgO addition (wt.% MgO reaches the second place in the range at the end of scale).

3.5 Cr Distribution

In addition to the Cr-bearing constituent distribution in the slag, the Cr amount in the slag and in picrochromite was computed. The choice to present the mass content in Cr of the slag and spinel takes into consideration the very practical nature of this information.

When necessary, the relative amount (wt.%) of Cr in both phases can be computed from the given figures, taking as basis for the analysis the respective phase amount given in Figure 2.

** Contribuição técnica ao 45º Seminário de Aciaria – Internacional, 25 a 28 de maio de 2014, Porto Alegre, RS, Brasil.*

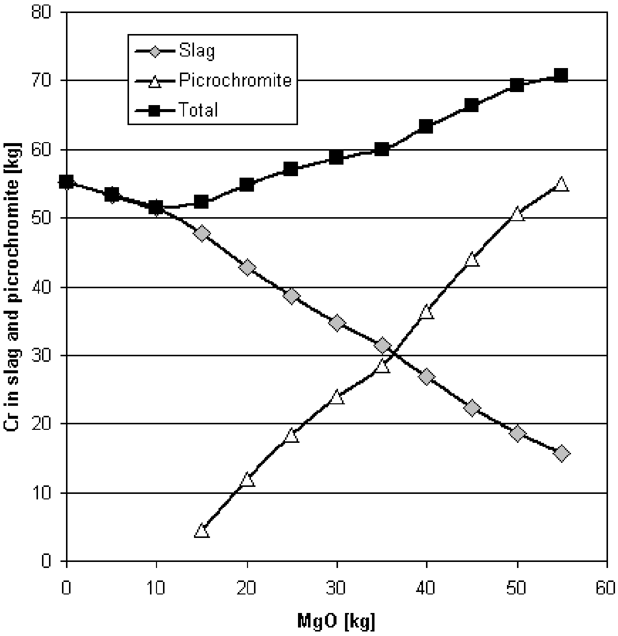

Figure 5. Amount of Cr present in the liquid slag and in picrochromite at 1.873 [K]; total Cr amount of the system is also presented as a function of MgO.

The results are given in Figure 5. After a short decline at the beginning of the MgO addition, the *total* Cr amount in the slag plus spinel rises steadily as a function of MgO amount. An increase of about 30 wt.% Cr is to be found at the end of the MgO scale.

This can be directly related to the rising content of picrochromite in the system, once the amount present in the liquid slag declines both by the diminishing amount as well as because of the smaller CrO and Cr_2O_3 content.

This trend is particularly of concern taking into consideration the nature of the spinel phase: as a solid, it imposes kinetic-related problems in the recovery of the chromium it bears.

4 CONCLUSIONS

From the analysis of the obtained data, the fundamental importance of MgO content in the system is highlighted – side by side with the (system) oxygen partial pressure (here: as a free variable) and slag basicity (here: binary basicity is equal to *unity*) as already shown in the previous works.

Results show, that a plain $CaO\text{-}SiO_2$ base slag in contact with a molten iron metal containing 18 wt.% Cr (plus 8 wt.% Ni) tends to absorb a great quantity of this costly metal from the melt (*rate* is, however, dependent on the local conditions). Cr solubility limit in the slag decreases, though, the more MgO is added to the system.

Seen alone, one can say that a slag with limited solubility can be seen as a major barrier to inhibit the loss of chromium from bath to the slag; however, as results show, it must be kept in mind that precipitation of Cr-bearing compounds completely hinders this positive effect. And, as they demonstrate, apart from the very beginning, the amount of chromium lost from steel into the slag plus solid phases increases as the MgO content rises.

MgO amount interferes with the solubility of Cr_2O_3 in the slag so that the primary chromium saturation phase changes from eskolaite (Cr_2O_3) to spinel ($MgO\cdot Cr_2O_3$).

** Contribuição técnica ao 45º Seminário de Aciaria – Internacional, 25 a 28 de maio de 2014, Porto Alegre, RS, Brasil.*

For the used conditions, this precipitation occurs very early, much before the precipitation of $2CaO{\cdot}SiO_2$.

In addition to all results, at the ‘top’ portion of the slag inside the furnace – where values of oxygen potential are higher – there is a tendency for formation of solid phases containing Cr (eskolaite and spinel – picrochromite or magnesiochromite). This phenomenon can acts as a real drain for chromium dissolved in the slag and must be seen as a serious obstacle to its recovery.

Summarizing, the information presented in this work can be of value both for the understanding of the conditions where loss of chromium occurs, during the production of stainless steels, as well as for planning future possible countermeasures.

REFERENCES

1 Rosenqvist T. Principles of extractive metallurgy. Tokyo: MacGraw-Hill; 1974.
2 Xiao Y, Holappa L, Reuter MA. Oxidation state and activities of chromium oxides in CaO-SiO2-CrOx slag system. Metallurgical and Materials Transactions B, 2002;33:595-603.
3 Villiers JPR, Muan A. Liquidus-solidus phase relations in the system CaO-CrO-Cr_2O_3-SiO_2. Phase Equilibria. 1992;75:1333-41.
4 Degterov S, Pelton AD. Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the CrO-Cr_2O_3, CrO-Cr_2O_3-Al_2O_3, and CrO-Cr_2O_3-CaO systems. Journal of Phase Equilibria. 1996;17(6):476-87.
5 Degterov S, Pelton AD. Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the CrO-Cr_2O_3-SiO_2 and CrO-Cr_2O_3-SiO_2-Al_2O_3 systems. Journal of Phase Equilibria. 1996;17(6):488-94.
6 Degterov S, Pelton AD. Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the CrO-Cr2O3-SiO2-CaO system. Metallurgical and Materials Transactions B. 1997;28:235-42.
7 Bale CW, Chartrand P, Degterov SA, Eriksson G, Hack K, Ben Mahfoud R, *et al*. FactSage termochemical software and databases. Calphad. 2002;26(2):189-228.
8 Heck NC, Klug JL, Vilela ACF. Thermodynamic evaluation of the slags of the CaO-SiO2-CrOx-MgO system at 1873 K. In: 66th ABM Congress Proceedings; 18th-22nd July 2011; São Paulo, Brazil. São Paulo: ABM; 2011.
