THERMODYNAMIC EVALUATION OF THE SLAGS OF THE $CaO\text{-}SiO_2\text{-}CrO_x\text{-}MgO$ SYSTEM AT 1873K [1]

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Abstract

The production of high quality stainless steel with material and energy efficiency requires a good slag practice. Aim of the present work is to evaluate theoretically, with the help of computational thermodynamics, the slags of the system $CaO\text{-}SiO_2\text{-}CrO_x\text{-}MgO$ (Ca-O-Cr-Si-Mg quinary system) at the temperature of 1873K. Driving force for this research work is the prevention of chromium losses from the molten bath into the slag. Especially motivating compositions are: dicalcium silicate and/or MgO-saturated slags. They are aimed at two important issues: the prevention of refractory degradation and the production of foaming slags. Isothermal phase diagram for this system were made having oxygen partial pressures as variable. They are quite seldom in the literature but show, with greater emphasis, the impact of the oxygen potential on the equilibrium state for this system.

Keywords: Slags; Ca-O-Si-Cr-Mg; Chromium losses; Thermodynamics

ANÁLISE TERMODINÂMICA DAS ESCÓRIAS DO SISTEMA $CaO\text{-}SiO_2\text{-}CrO_x\text{-}MgO$ À 1.873K

Resumo

A produção de aço inoxidável de alta qualidade com eficiência de materiais e energia requer uma boa prática no trato da escória. Objetivo do presente trabalho é avaliar, teoricamente, com o auxílio da termodinâmica computacional, as escórias do sistema $CaO\text{-}SiO_2\text{-}MgO\text{-}CRO_X$ (sistema quinário Ca-O-Cr-Si-Mg) à temperatura de 1.873K. A força motriz desta pesquisa está na prevenção das perdas de cromo do banho para a escória. Composições especialmente motivadoras são: escórias saturada em silicato dicálcico e/ou em MgO. Elas focam duas questões importantes: a prevenção da degradação de refratários e a produção de escórias espumantes. Diagramas de fase isotérmicos, para este sistema, foram feitos tendo pressões parciais de oxigênio como variável. Eles são raramente vistos na literatura, mas mostram, com grande ênfase, o impacto do potencial de oxigênio no estado de equilíbrio para esse sistema.

Palavras-chave: Escórias; Ca-O-Si-Cr-Mg; Perdas de cromo; Termodinâmica

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1 INTRODUCTION

Chromium stainless steels have been widely used as construction materials when corrosion resisting materials at room or high temperatures are needed.

Unfortunately, during the production of these alloys, chromium losses are observed, especially as ions dissolved in the slag or as constituent of the slag minerals.

As pointed out by Rosenqvist,(1) slags are used – and may be studied – under completely different conditions: from reducing to strongly oxidizing conditions. Changes in oxygen pressure do *not* noticeably affect the “white” oxides SiO_2, Al_2O_3, CaO, and MgO but this is not the case when dealing with slags containing manganese, chromium, titanium, and iron oxides. Changes may occur due to the existence of different valencies in these metal-oxide systems.

Chromium is multivalent and it was demonstrated experimentally that this metal can show *several* oxidation states.(2)

The most common oxidation state within a large temperature-composition range is the 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 proportions of the chromium is present in the divalent state.(3)

In a series of three articles Degterov and Pelton(4-6) examined closely the inclusion of chromium oxides 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). Nevertheless, the CaO-rich part of the system $CaO\text{-}CrO\text{-}Cr_2O_3\text{-}SiO_2$ (*i.e.*, compositions within the $CaO\text{-}Ca_2SiO_4\text{-}CaCr_2O_4$ ‘triangle’) in air was not considered in the *FactSage* databases optimization [6]. Bearing in mind the conditions used in the present simulations, this fact is of less significance.

Aim of the present work is to evaluate theoretically the effects of periclase addition into slags of the system $CaO\text{-}SiO_2\text{-}CrO_x$. It correlates with two important issues: chromium losses to the slag and refractory degradation.

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 does, however, establish the direction and the *limiting* conditions for the 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 6.1) – this software is described elsewhere by BALE et al.(7)

The following three databases were employed:

- FSstel - FactSage steel intermetallic compounds and alloy solutions [2009];
- FToxid - FACT oxide compounds and solutions [2009];
- FACT53 - FactSage compound database [2009].

Output of *Equilib* module of *FactSage* will show results where oxides 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 containing dissolved ions.

Caution is needed when selecting candidate phases which may take part in the equilibrium state. The application may suggest phases which are inadequate. One example is the phase CrO_2(s) contained in the database FACT53; when this phase is selected, results are inconsistent. This phase can take part of the equilibrium state only when pressure is higher than that of atmospheric pressure.(8)

Some problems were experienced with the *Phase diagram* module of this software; perhaps related with some equilibrium conditions or set of phases.

3 RESULTS AND DISCUSSION

3.1 Cr and Fe-Cr Alloys in Contact with Oxygen

This topic serves as an introduction to the study of slag systems containing chromium and therefore underscores the importance and promotes understanding of the role oxygen potential has in this system establishing a basic line of reference.

Thermodynamics tells us (without the limitations imposed by the kinetics) that pure solid chromium at a temperature of 1873K dissolves the element oxygen insofar as the oxygen pressure in the system atmosphere increases (Sievert's law). For ~$1x10^{-12}$ atm and higher pressures, the presence of solid phase eskolaite (Cr_2O_3) – a corundum type phase Me_2O_3 – can be observed in the system; by increasing the pressure further, the solid metal melts – always keeping itself in equilibrium with Cr_2O_3 (Figure 1), Cr/(Cr+Fe)=1.

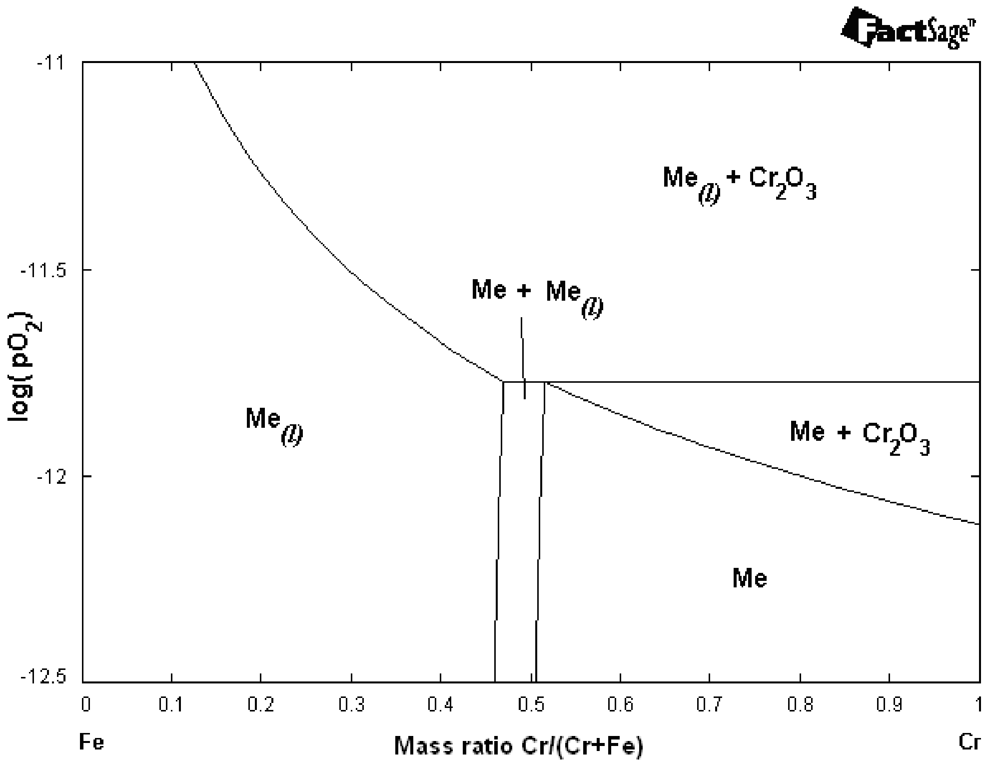

Figure 1. Phase diagram for the system Fe-Cr in the presence of a gas phase containing oxygen under several pressures at 1873K; at this temperature, eskolaite, Cr_2O_3, is a solid phase.

When the metal phase is an *alloy* of Fe and Cr, the oxygen pressure – or its chemical potential – affects the results in a certain degree (remaining of Figure 1).

For Fe-Cr alloys with Cr content from 7-8% to around 50 wt.% Cr, the metal phase (at a temperature of 1873K) melts – even though partially. For alloys containing higher concentrations, only solid metal will be present at equilibrium. In all cases, though, the general behavior is similar to that described for pure chromium.

On the other side, it is known that for Fe-Cr alloys with Cr contents lower than 8.7 wt.%, an increase in the oxygen pressure produces slightly different results. This is because Fe eventually oxidizes concurrently with Cr producing the spinel phase $FeO{\cdot}Cr_2O_3$, instead of 'pure' eskolaite.

The atmosphere on the whole becomes slowly less aggressive for alloys with lower levels of chromium. For instance, as shown in Figure 1, an atmosphere whose logarithm of the oxygen pressure equals to -11.5 is able to oxidize pure chromium – but is not sufficiently oxidizing for a plain Fe-Cr alloy with 20wt.% chromium. This information is relevant since the Cr content in stainless steels is limited to values around 20 wt.%. This lies on the fact that the metal iron is nobler than chromium.

In a real solid metal the dissolution of oxygen is, of course, limited to volumes near the surface by mass transport constraints. For those alloys which are partially or fully in the liquid state, however, this may not be quite the case.

3.2 CaO-SiO_2 Base Slag

A simple binary slag of the CaO-SiO_2 system, which becomes a CaO-SiO_2-CrO_x (Ca-Si-O-Cr quaternary system) slag in contact with the metal chromium, alters these results to a certain extent – as it will be seen subsequently. This case represents better the situation encountered when using a metallic crucible of pure chromium containing a CaO-SiO_2 slag (it has been used experimentally, for instance, by Xiao and Holappa(9)). Very important, the experimental results are considered to be consistent and will be employed to anticipate the practical utilization of Fe-Cr alloys. In that case it is considered that, essentially, it is 'just' the *activity* of Cr which will experience a change.

A slag of binary basicity CaO/SiO_2 near 1.2 (45.5 wt.% SiO_2) is quite interesting for the possibility of presenting the so-called double or 'dual saturation' – as will be explained later – and it was chosen, consequently, for the initial part of this work.

Determinations of the equilibrium state of the system were effected in an unusual way. Instead of using varying temperatures for a constant pressure, the temperature was set to 1873K while the system pressure (pO_2) was chosen as variable. This reflects a situation closer to reality, namely: that of the existence of a (relatively) fixed furnace temperature, with a variable oxygen *potential* (in a real furnace it varies from that which establishes itself at the atmosphere/slag interface to the one existing at the slag/metal interface).

Furthermore, it was a careful choice to present the mass content in Cr of the slags, instead of the Cr-oxides activities – as is usual – taking into account the very practical nature of this information.

The results of simulations can be seen in Figure 2.

It is apparent from the diagram that a slag phase will form in the equilibrium state for a considerable oxygen pressure range. Nevertheless, *metallic* Cr can be found in thermodynamic equilibrium with the slag only for pressures *lower* than approximately ~7×10^{-13}; otherwise it will oxidize completely to *eskolaite*, Cr_2O_3.

From these results, three facts can be highlighted: (i) in presence of a CaO-SiO_2 slag the metal chromium will oxidize in a range of pressures where it usually was stable and in equilibrium with O_2 (ii) slag dissolves the chromium metal to a considerable extent – content increases with the increase of oxygen pressure – even there where metallic Cr *is* a stable phase, (iii) for pressures higher than that quoted as the limit between Cr and Cr_2O_3, Cr content in slag remains high, although, paradoxically, it diminishes as the oxygen pressure increases. In this case it can be said, too, that the solubility of *chromium oxide* in slag reduces.

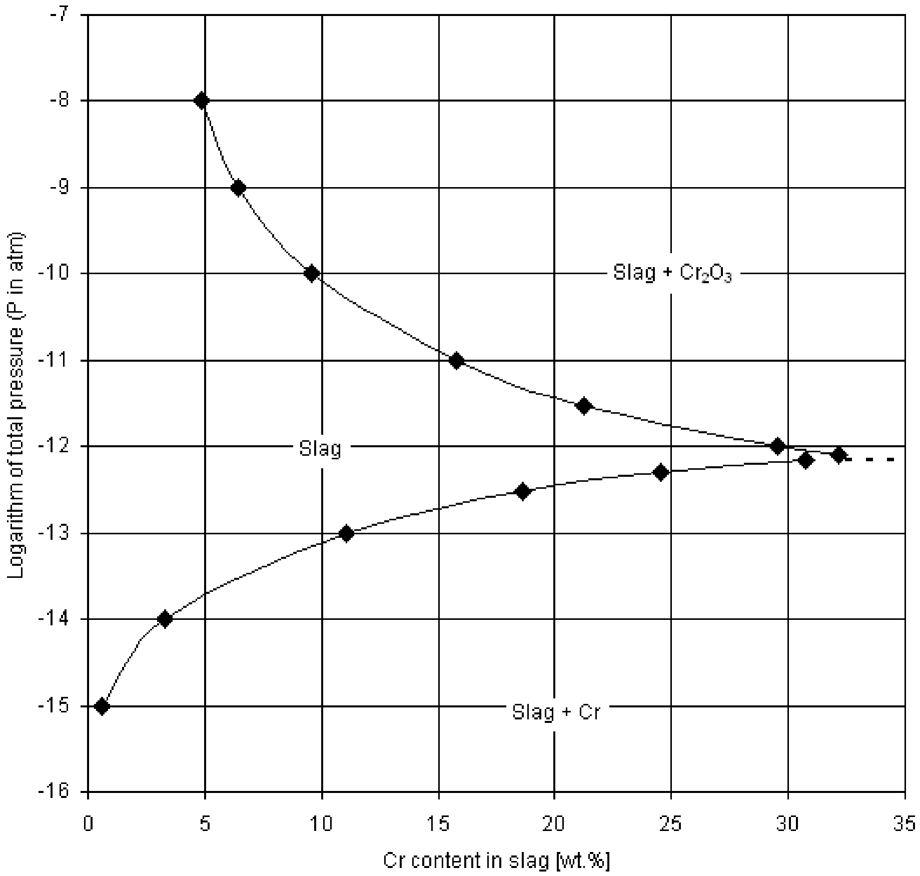

Figure 2. Chromium saturation content in CaO-SiO_2 base slag with basicity B=1.2 in the presence of a gaseous phase containing oxygen under several pressures at 1873K.

It is of great importance to recognize that, in an experimental system containing (i) chromium metal, (ii) a binary CaO-SiO_2 slag and (iii) an atmosphere rich in oxygen, the oxygen potential of the whole system tends to *stabilize* in a value which corresponds to the partial pressure abovementioned, approximately $7x10^{-13}$ [atm], provided the metal chromium remains in the system. This fact is being highlighted owing to the similarity that exists between that situation at the metal/slag interface of the electric arc furnace and the one here described.

In order to evaluate the binary basicity influence on the solubility of Cr in the slag, new simulations were performed. The results show that slags with binary basicities smaller than 1.2 have a higher solubility for chromium for a particular oxygen pressure, and are detrimental to the purpose of avoiding the loss of chromium to the slag (Figure 3). The general behavior, however, follows that presented by slags with basicity B=C/S=1.2.

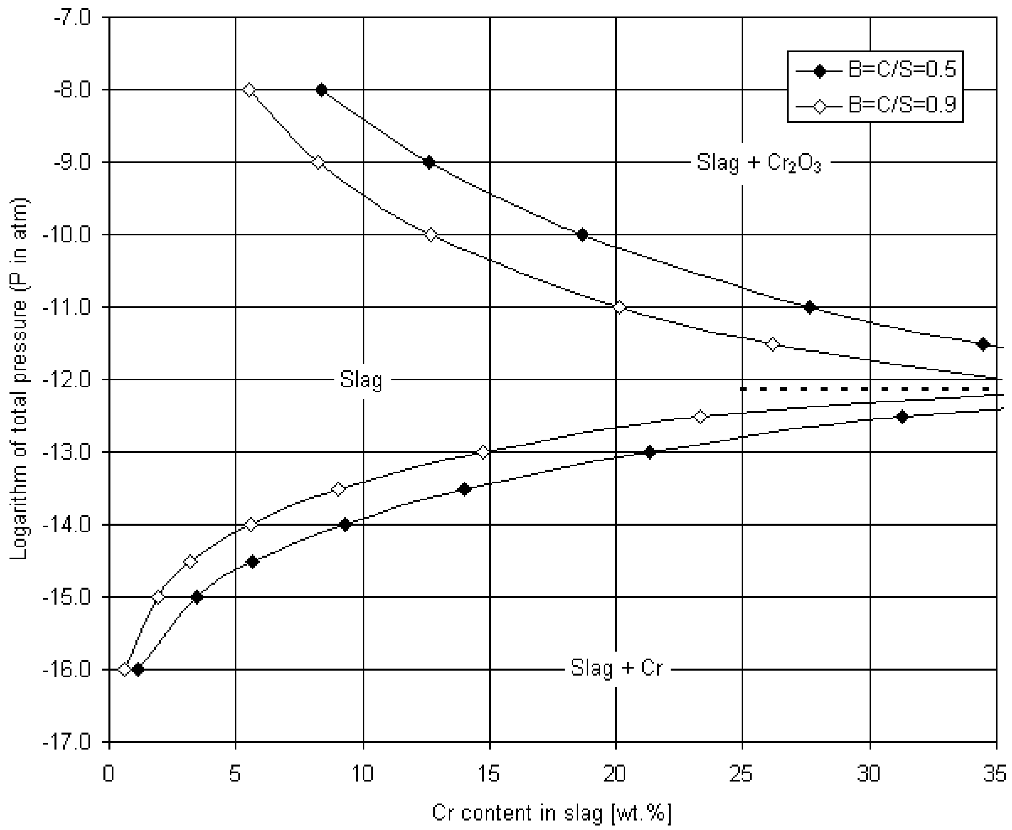

Figure 3. Chromium saturation content in $CaO-SiO_2$ base slags with basicities B=0.5 and 0.9 in the presence of a gaseous phase containing oxygen under several pressures at 1873K.

3.3 $CaO-SiO_2$-MgO Base Slag

The importance of magnesium oxide in this work can be related to the large use of MgO-based refractory materials for inner walls and linings of metallurgical vessels or ladles – *e.g.* EAF and LF – which can take contact with the slag. Another source of MgO is dolomite – a calcium magnesium carbonate. This mineral can be added with the charge at some points of the process during the fusion of stainless steel scrap.

Concerning the presence of MgO, the simplest system of relevance is that depicted by the $CaO-SiO_2$-MgO pseudoternary system. An isothermal section of this system at 1873K, showing phases in the equilibrium state, can be seen in Figure 4.

As mentioned earlier, the use of slag with binary basicity around 1.2 (up to approximately 1.5) is advantageous because, when MgO is added to the system, these slags may present a ‘dual saturation’ – both with periclase, MgO, and with dicalcium silicate, C_2S, ($2\ CaO{\cdot}SiO_2$). The saturation on the first of these solid phases prevents the attack on the refractory material of the furnace (and its consequences), while the second would provide the solid cores which will act as gas nucleation sites required to generate a foamy slag in the furnace – both items are pointed out by Pretorius and Nunnington as requirements for an ‘optimum foaming slag’.(10)

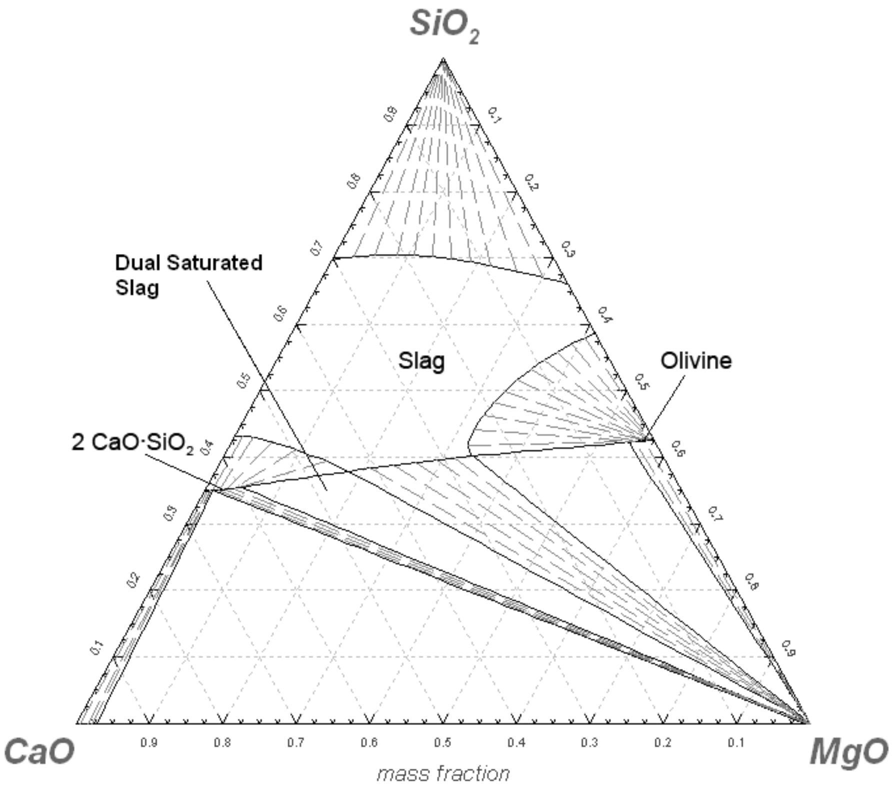

Figure 4. CaO-SiO_2-MgO phase diagram; isothermal section at 1873K; dicalcium silicate is represented as a solid solution phase (as well as olivine and CaO); white fields without indication are ternary phase fields (no gaseous phase present).

The presence of chromium in this case can be imagined as forming a pseudoquaternary system CaO-MgO-SiO_2-Cr_2O_3 (actually a quinary system Ca-Si-O-Cr-Mg).

To study the relationship between chromium and MgO one can start with a pseudobinary CaO-SiO_2 slag. To begin the simulations, the basicity B=C/S=1.3 was chosen. Slags with this basicity, once enough MgO is added, are capable to reach the ‘dual saturation’ field of the pseudoternary system CaO-MgO-SiO_2. Departing from a composition in which slag is the only condensed phase, they go through the intermediate biphasic (C_2S-slag) region and reach finally the ‘dual saturation’ field of the pseudoternary system CaO-MgO-SiO_2.

It is clear from the results that the addition of MgO to a CaO-SiO_2 slag of B=1.3 containing chromium, in equilibrium with Cr_2O_3, will produce a continuous decrease in the solubility of chromium oxide because the primary chromium saturation phase changes from eskolaite (Cr_2O_3) to spinel – *picrochromite* or *magnesiochromite* (MgO·Cr_2O_3) (Figure 5). At the end of the MgO intended addition, the solubility is at its minimum point and the ‘dual saturation’ ternary phase field turns into a quaternary phase field (with spinel precipitation).

Some simulations were effected, in order to verify the influence of oxygen potential in this pseudoquaternary system. For this we have chosen the most favorable condition – the composition which shows the lowest solubility of chromium in the slag – to perform the simulations. Having the pseudoternary CaO-SiO_2-MgO system as reference, the most favorable conditions correspond to: (i) the ‘dual saturation’ field – for the basicity B=1.3 – and (ii) ~30wt.% MgO – for B=0.9.

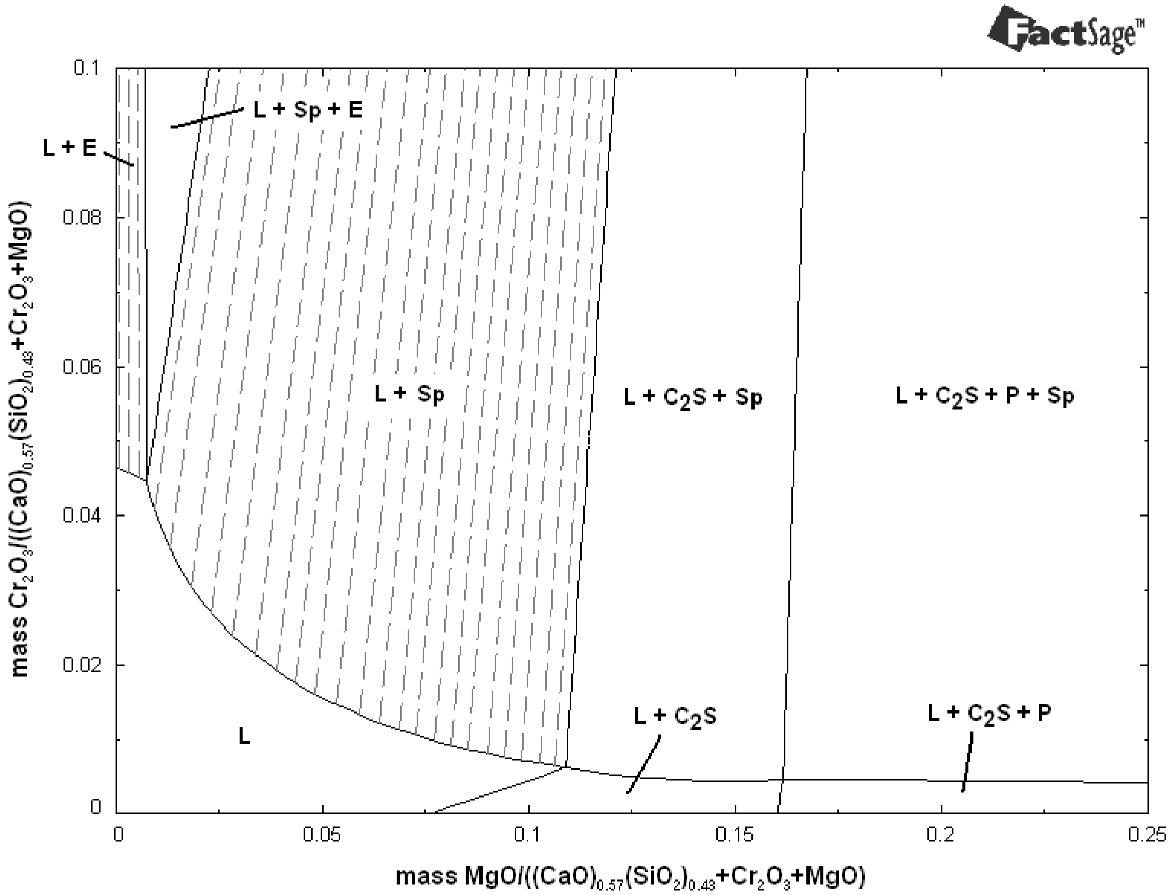

Figure 5. $CaO-SiO_2-MgO-Cr_2O_3$ phase diagram at 1873K; C/S=1.3; L=slag; C_2S=dicalcium silicate ($2\ CaO{\cdot}SiO_2$); P=periclase (MgO); Sp=spinel, picrochromite or magnesiochromite ($MgO{\cdot}Cr_2O_3$); pO_2=1atm.

Regarding the slag basicity (considering only those values of basicity tested, B=1.3 and 0.9), under the chosen circumstances, one can say that its influence is significantly smaller and may even be disregarded. Oxygen pressure however continues to have a notable influence on the saturation level (Figure 6).

4 CONCLUSIONS

From the analysis of the results the fundamental role and the great importance of *oxygen chemical potential* in the system is highlighted – side by side with the (system) composition and slag basicity – when trying to be aware of and at the same time to prevent the loss of chromium during the production of ferrous alloys containing this valuable metal.

A plain $CaO-SiO_2$ base slag in contact with Cr (or an alloy containing Cr, like stainless steel) tends to absorb a great quantity of this costly metal from the melt (*rate* is, however, dependent on the local conditions). It was already known that the chromium solubility limit for this slag system varied with basicity. Nevertheless, as it has been demonstrated, it also greatly depends on the oxygen partial pressure.

When MgO is added to the base slag there is a strong trend for lowering the level of chromium solubility limit. When the original ternary composition of the slag shows saturation in MgO and dicalcium silicate phases, the solubility limit will be minimal. Even in this situation, however, the oxygen pressure continues to have a notable influence on the saturation level.

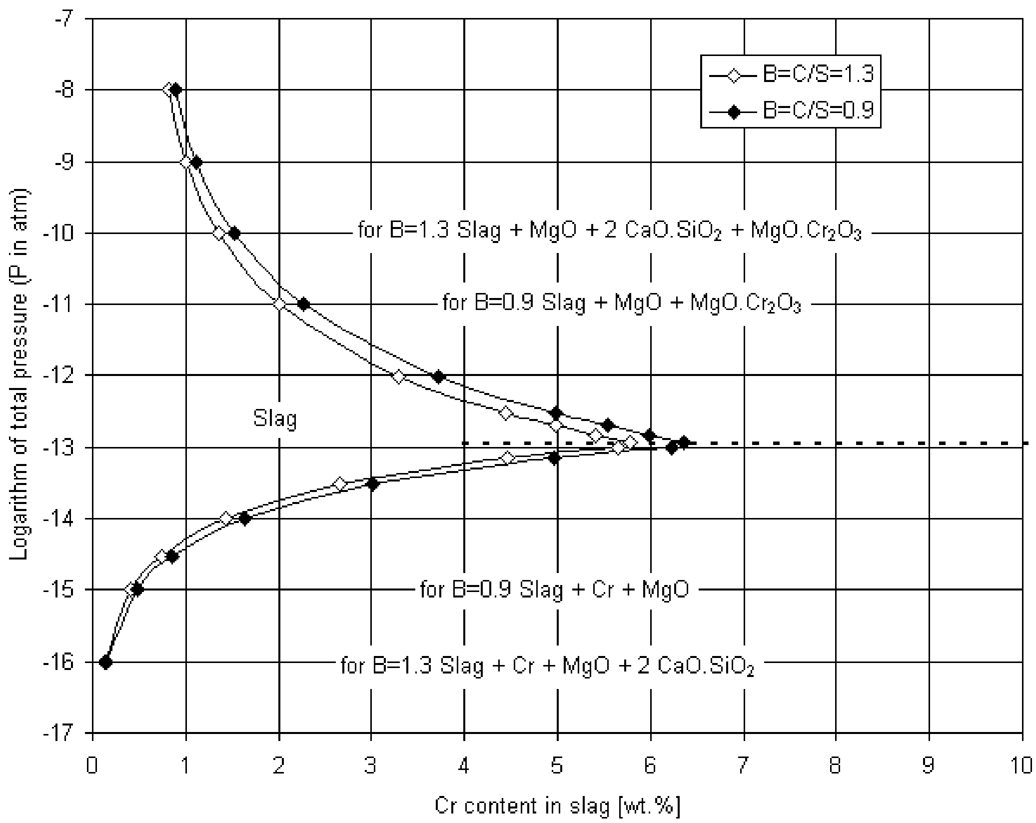

Figure 6. Chromium saturation content in CaO-SiO$_2$-MgO base slags with basicities B=0.9 and 1.3 in the presence of a gaseous phase containing oxygen under different pressures at a temperature of 1873K.

It is of value to note that the maximum level of saturation in chromium – for slags of all systems – also happens to be exactly the most likely condition to be met in practice, and is the same potential that establishes naturally in the bath/slag interface. Increasing the oxygen potential – as when, for example, an slag portion approaches the slag/atmosphere interface – the critical Cr concentration of the slag reduces – a fact which apparently is an advantage. But that is not true because, in this case, the already dissolved chromium in the slag transforms itself into a mineral compound (eskolaite and spinel, for example), which, at the same time, increases the 'slag' viscosity – now taken as a mixture of solid phases in a liquid – and hinders again Cr recovery.

Summarizing, one can say that a slag with limited solubility can always be seen as a major barrier to inhibit the loss of chromium from bath to the slag and is preferable to a slag with a high saturation limit. It must be kept in mind, though, that, at the 'top' portion of the slag in the furnace – where the values of oxygen potential are higher – independently of the slag type, there is always the tendency for formation of solid phases containing Cr (eskolaite and spinel – picrochromite or magnesiochromite). This phenomenon acts as a real drain for chromium dissolved in the slag and can be seen as a serious obstacle to its recovery.

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