VOD PROCESS – A THEORETICAL THERMODYNAMIC ANALYSIS[1]

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Abstract

The basic processes for the production of stainless steels are divided basically into two families: the one which makes use of argon and that which makes use of vacuum. The VOD process was developed in the sixties and of the vacuum processes is the world's most used. Among the main advantages of this reactor are: (i) the low consumption of argon; and (ii) low nitrogen pick-up (for there is no transfer of liquid steel, since the ladle containing the steel goes directly from LF to the VOD unit). Because of this, the objective of this work focuses on a detailed analysis of the phenomena which occurs in this reactor during the step of refining stainless steel. The chemical composition of the steel, particularly the evolution of the elements C and Cr in the molten metal along the oxidation step under vacuum is studied by means of a computational thermodynamic tool.
Key words: VOD; Stainless steel; Computational thermodynamics.

ANÁLISE TEÓRICA-TERMODINÂMICA DO PROCESSO VOD

Resumo

Os processos básicos para a produção de aços inoxidáveis se dividem basicamente em duas famílias: a que faz uso de argônio e a que faz uso de vácuo. O processo VOD foi desenvolvido nos anos sessenta e, dos processos a vácuo, é o mais utilizado no mundo. Dentre as maiores vantagens do uso deste reator estão: (i) o baixo consumo de argônio; e (ii) o baixo *pick-up* de nitrogênio (pois não há transbordo de aço líquido, uma vez que a panela contendo o aço vai diretamente à unidade de VOD). Por causa disso, o objetivo deste trabalho se concentra na análise detalhada de alguns dos fenômenos que transcorrem neste reator durante a etapa de refino do aço inoxidável. A composição química do aço, especialmente a evolução dos elementos C e Cr no metal líquido ao longo das etapas de oxidação sob vácuo é estudada por meio da ferramenta termodinâmica computacional.
Palavras-chave: VOD; Aço inoxidável; Termodinâmica computacional.

1 INTRODUCTION

The corrosion resistance of alloys of iron with high chromium content – known as stainless steels – is a property worthy of note, which makes them very desirable in different applications of the modern world. They are divided into different families, depending on the phases of iron present in the alloy, and among them, the most important is that of austenitic alloys.

The content of carbon is critical in austenitic stainless steels, for high values of this element in these materials lead to the formation of carbides of the type $Cr_{23}C_6$ in the grain boundaries when the metal temperature is increased to a range where this intermetallic phase containing chromium precipitates. The regions near the grain boundaries lose, then, this metal for precipitates.

If reduction is dramatic, to the point that the regions adjacent to the new phase present levels of chromium below the required for passivation, these places come to exhibit behavior similar to that of common steel, and without capacity to undergo passivation, lose their corrosion resistance.

Because of difficulties in obtaining a chromium alloy with low carbon content, a solution to achieve a low level of this element in the steel can be the forced reduction of its content in the steel shop, by Equation 1.

$$\underline{C} + 1/2\ O_2(g) = CO(g) \qquad (1)$$

However, it can not be made by oxidative refining in normal conditions, because the affinity of chromium by the dissolved oxygen is also high. In a very simplified mode, oxidation of the chrome alloy may be represented by Equation 2.

$$2\ \underline{Cr} + 3/2\ O_2(g) = Cr_2O_3(s) \qquad (2)$$
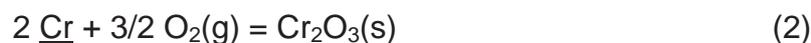
From Equation 3, obtained by combining the decarburization Equation 1 with the oxidation of chromium (Equation 2), we find that the balance will shift in favor of decarburization and the protection of chromium by lowering the partial pressure of CO (g) (Equation 3).

$$3\ \underline{C} + Cr_2O_3(s) = 2\ \underline{Cr} + 3\ CO(g) \qquad (3)$$

To the industry, then fell the duty to develop, on the basis of thermodynamics, techniques capable of producing stainless steel alloys of high chromium content and simultaneously low-carbon. Thus, the processes of the type AOD (Argon Oxygen Decarburization) or VOD (Vacuum Oxygen Decarburization) can be explained.

The AOD process is based on the simultaneous injection of argon and oxygen through tuyères and specially designed lance. The use of argon in large-scale aims to reduce the partial pressure of CO(g) (resulting from the carbon-oxygen reaction) and stir the molten metal bath.

The VOD process, on the other hand, relies basically in the lowering of the *total* system pressure in a vacuum tank. The tank, plus vapor ejection systems (for evacuation of the atmosphere), the ladle with porous plug in its lower part (through which argon is injected to ensure, by convection, adequate exposure of the metal bath to the surface under vacuum) ensures the correct process utilization. The elimination of carbon, by the combined action of oxygen and vacuum, basically occurs in two stages: the *oxygen blowing* (through a special lance) and *deep vacuum* stages. The third and final stage is characterized by a stage where the chromium contained in the slag is reduced by the action of elements added to the bath such as Si and Mn.

Clearly, then, is by lowering the pressure – whatever the technique – that the oxidation of chromium dissolved in the alloy can be *limited*.

The family of processes that makes use of argon to promote decarburization of the bath is composed of many alternative techniques and was the first to be discovered and used. The processes using vacuum for this purpose are more recent and their production, added, is less than that of the previous family – of these, the process VOD is the most frequently used.

The rapid acceptance of the AOD process by a majority of worldwide stainless producers is indicative of its capability to economically produce high quality product from least cost charge materials. Hot metal (pig iron) supply means high start carbon and silicon levels and favors a high blowing rate converter or converter/vacuum systems. Also grades that require ultra-low sulfur levels would tend to favor converter processes. A disadvantage is high argon costs, which would tend to support converter/vacuum or vacuum rather than converter-only processes.

Among the main advantages in using VOD are the low consumption of argon and low nitrogen pick-up (for there is no transfer of liquid steel, since the ladle containing the steel goes directly from LF to the VOD unit). Some disadvantages can be cited, among them are: high consumption of refractories, and less flexibility in the use of cheaper raw materials. However, despite the drawbacks, this reactor is still very important in the production of stainless steels.[1]

The major advantages of 'converter' equipment relative to 'vacuum' are ease of maintenance and slag handling ability. The major advantage of vacuum equipment is the ability to reach lower levels of carbon and nitrogen without excessive argon consumption.[1]

In spite of a large amount of changes in these two main types of processes, a *third* category can be highlighted: Converter/Vacuum Processes. Essentially, any type of converter which can be used to supply the VOD (including the AOD) can be integrated in this category. Obviously, this category *combines* the two basic ideas mentioned in a single process and tries to use the inherent advantages that each of these routes presents separately.

All things considered, choosing the most practical and economic process route for stainless steelmaking depends on many factors and is far outside of the scope of the present work.

This study focuses on a detailed analysis of the phenomena that occur in some of the VOD process stages during the refining of stainless steel by means of a computational thermodynamic tool. The work focuses especially on the evolution of the elements C and Cr dissolved in the liquid metal or, in the case of chromium, also in oxidized form of eskolaite.

2 THERMODYNAMIC ANALYSIS

The core for the thermodynamic analysis of the VOD process described in this paper is based in the works of Kho et al.,[2] and Swinbourne, et al.[3] recently published. They were used both as a sort of general guide to the simulation, and as a reference point to evaluate the results and even to reflect on the differences and similarities between these works.

Swinbourne et al.,[3] especially in the second work, follow, in turn, the steps taken by Ding et al.[4] These authors present an algorithm for the calculation and simulation of the VOD process and solve numerically the complex systems of nonlinear equations of the simulation.

In those works above cited, the authors Swinbourne et al.[3] used a computational thermodynamic software named *HSC Chemistry*. This software has limitations that are not present in the *FactSage* software used in this study, such as the need for introduction of activity coefficients for solutes in the two liquid phases: the metal bath and slag phase.

In addition, two modes of execution of the simulation process were used: 'closed' and 'open'. The first of these options is used systematically in thermodynamic softwares for processes simulation. In it, the input matter in the system, at the beginning of the simulation, is maintained while the software searches for a thermodynamic equilibrium state of the system. The 'open' mode (recently introduced into the software FactSage) consists in the possibility of elimination of some chemical species keeping, for example, a particular system pressure setting. This feature denotes an 'open system' in which matter can cross the system boundary. Some analyses were made in this mode of execution.

In this study, only the two first stages of VOD process – in which carbon is removed by oxidation in a vacuum – were analyzed, i.e.:

- oxygen blowing stage; and
- deep degassing stage.

The *reduction stage* was not simulated in this introductory work.

3 SIMULATION METHODOLOGY

3.1 Software

The application used in this work is called FactSage, version 6.2; it has been described in the literature by Bale et al.[5]

The following databases allow performing the simulation:

- Fact53 - FactSage compound database (2010);
- FToxid - FACT oxide compounds (2010);
- FSstel - FactSage steel intermetallic compound and alloy solutions (2010).

The phase liquid iron takes account of the concept 'associates'.[6]

3.2 Phases and Chemical Species

Several stoichiometric compounds and three solution phases were used in the present simulation for the determination of the equilibrium state. They are listed bellow using common or chemical names followed by the FactSage nomenclature – when helpful, for the sake of clearness.

Compounds (which are, at the same time, solid phases):

$Mg_2SiO_4(s)$	FToxid (forsterite);	$Ca_2SiO_4(s_2)$	FToxid (alpha-prime)
$Cr_2O_3(s)$	FSstel (solid);	$Ca_2SiO_4(s)$	FToxid (olivine)
$Ca_2SiO_4(s_3)$	FToxid (alpha);	$(MgO)(Cr_2O_3)(s)$	FACT (chromite)

The gas phase had the following gaseous constituents:

$$SiO; O_2; Mn; CO; CO_2$$

Solutions (apart from the gas phase):

Liquid steel	FSstel-LIQU
Slag	FToxid-SLAGA

3.3 Temperatures and Pressures

The temperatures used in the present study were: 1,600°C, 1,700°C and 1,800ºC, most of the results shown were run at a temperature of 1,600ºC.

The pressure had a fundamental role in the simulation. With a fixed value, the pressure on the reactor had the following values: 100 kPa and 10 kPa. In the stage *deep degassing* its value varied in order to simulate properly the VOD second process step.

3.4 Input Substances and Amounts

Oxygen for decarburization, is provided with the step of 0.1 kg, ranging from 0 kg to 20 kg at the end.

Other substances and respective used amounts are given in Table 1.

Table 1. Input amounts (for open and closed systems)

Gas [kg]	Slag [kg]	Metal [kg]
O 0-20, step 0.1	CaO 6	Fe 718
	SiO_2 1.5	Cr 164
	MgO 3	Ni 105
		Mn 5.5
		Si 2
		C 5

4 SIMULATION RESULTS

Some selected results are given in the following sections. All results stemming from the cited work of Swinbourne et al.[3] are presented with the single purpose of scientific comparison and are denoted by the word 'Paper'.

4.1 The Oxygen Blowing Stage

The basis for modeling the oxygen blowing stage of the VOD process was 1 t of metal (steel) and all quantities of species given in Table 1.

The amount of oxygen given varied between 0 kg and 20 kg; 201 determinations were performed in total. However, in the 'open' mode, substances from the gas phase were removed from system after each step, and 0.1 kg of oxygen was added to the reactor for the next step.

The temperature was assumed to be constant at 1,600ºC to simplify the simulation, although it is known that the temperature does increase during the oxygen blow.

The calculated carbon and chromium contents of the steel are given in Figures 1 and 2 at atmospheric pressure (~100 kPa). Carbon, chromium, silicon and manganese contents of the steel are given in Figures 3, 4 and 5 at the lowest pressure likely to occur during the oxygen blow (~10 kPa).

It can be seen, by comparison between the two pressures, that the carbon content is dramatically affected by the system pressure, as expected.

Additionally, the amount of the solid phase eskolaite (Cr_2O_3) was shown in order to give a clear idea of the Cr lost from steel and that is not taking part of the slag.
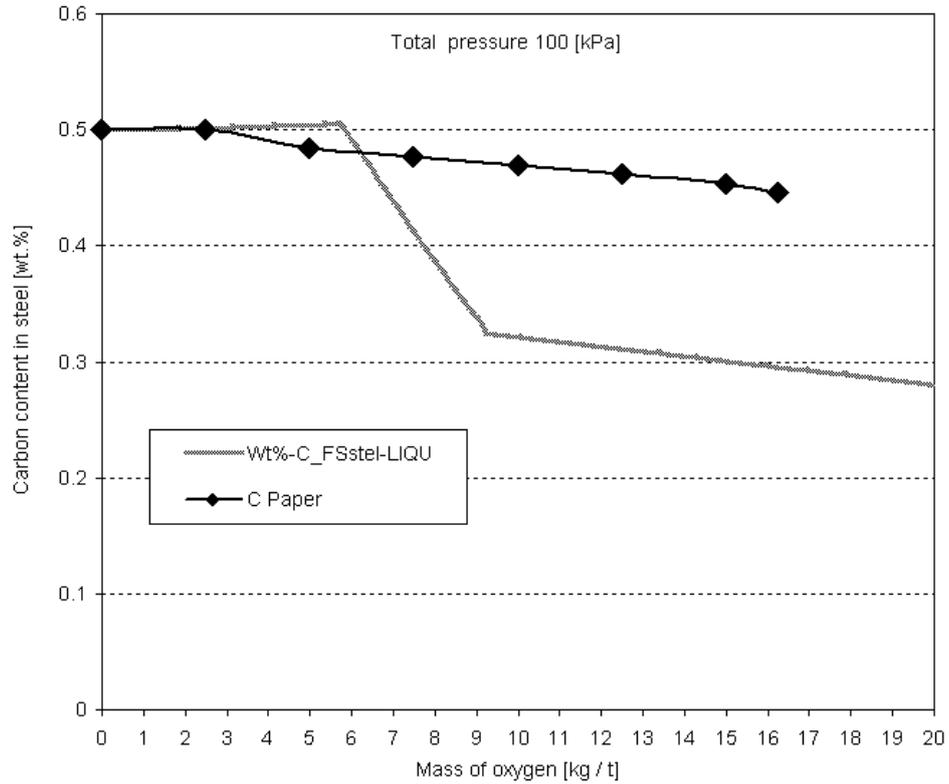
Figure 1. Carbon content in liquid steel as a function of the mass of oxygen; results from this work are compared with those from Swinbourne et al.[3] 'C Paper'; pressure: 100 kPa.
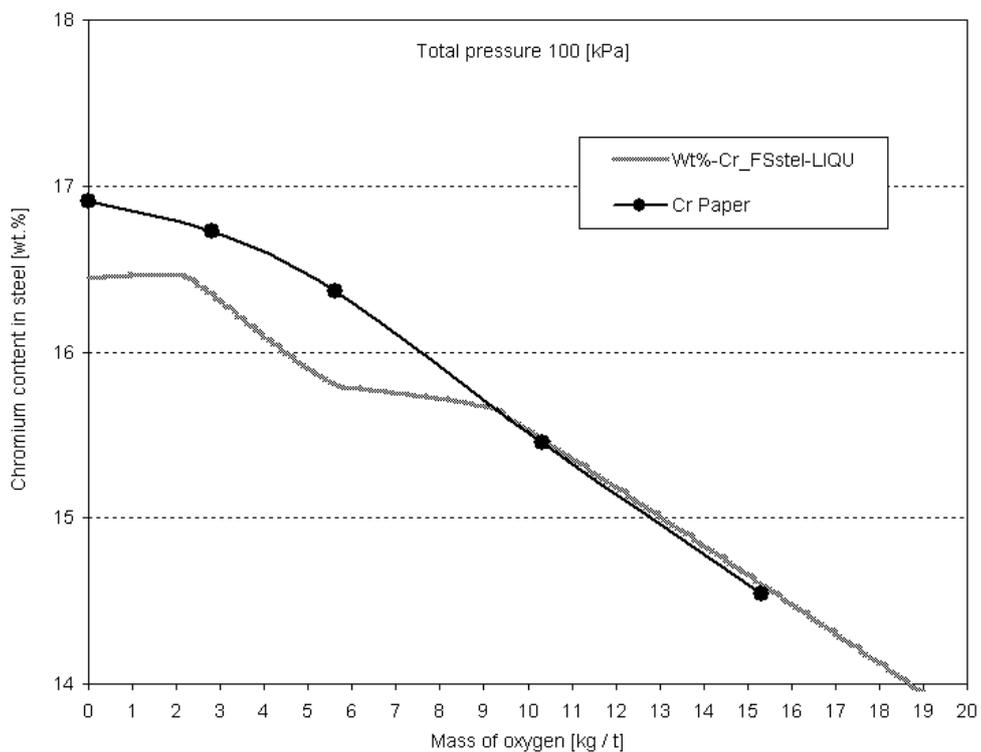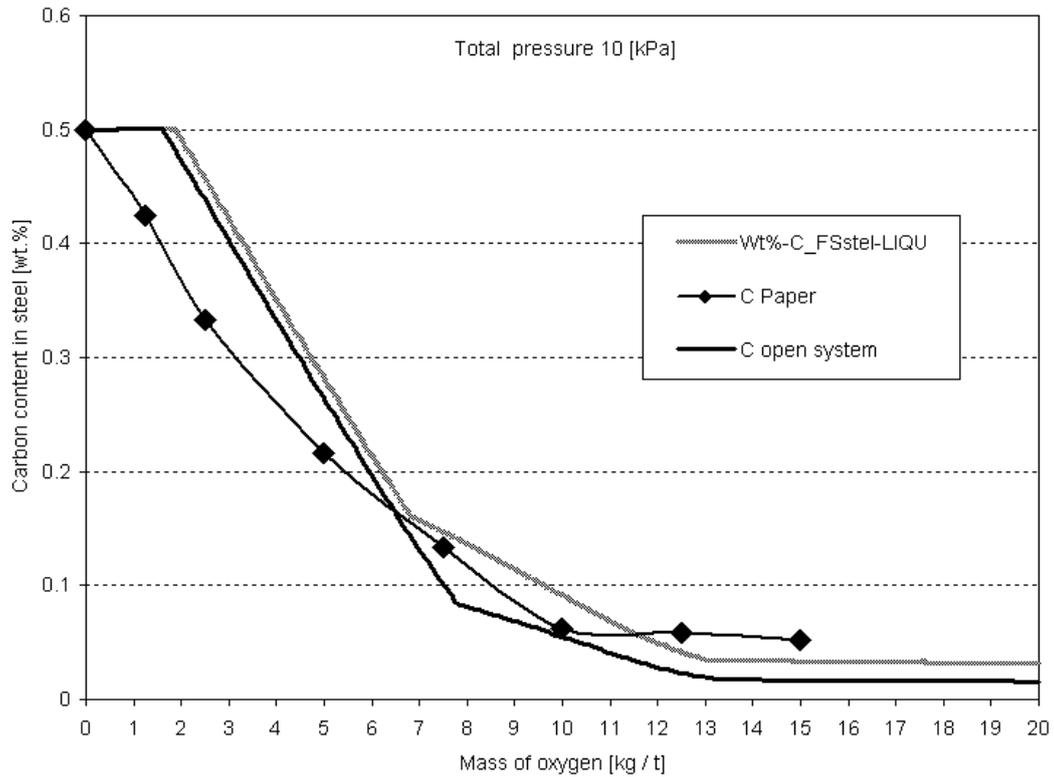

Figure 2. Chromium content in liquid steel as a function of the mass of oxygen; results from this work are compared with those from Swinbourne et al.[3] 'Cr Paper'; pressure: 100 kPa.

Figure 3. Carbon content in liquid steel as a function of the mass of oxygen; results from this work are compared with those from Swinbourne et al.[3] 'C Paper'; pressure: 10 kPa;, C content determined by the 'open' mode are additionally given 'C open system'.
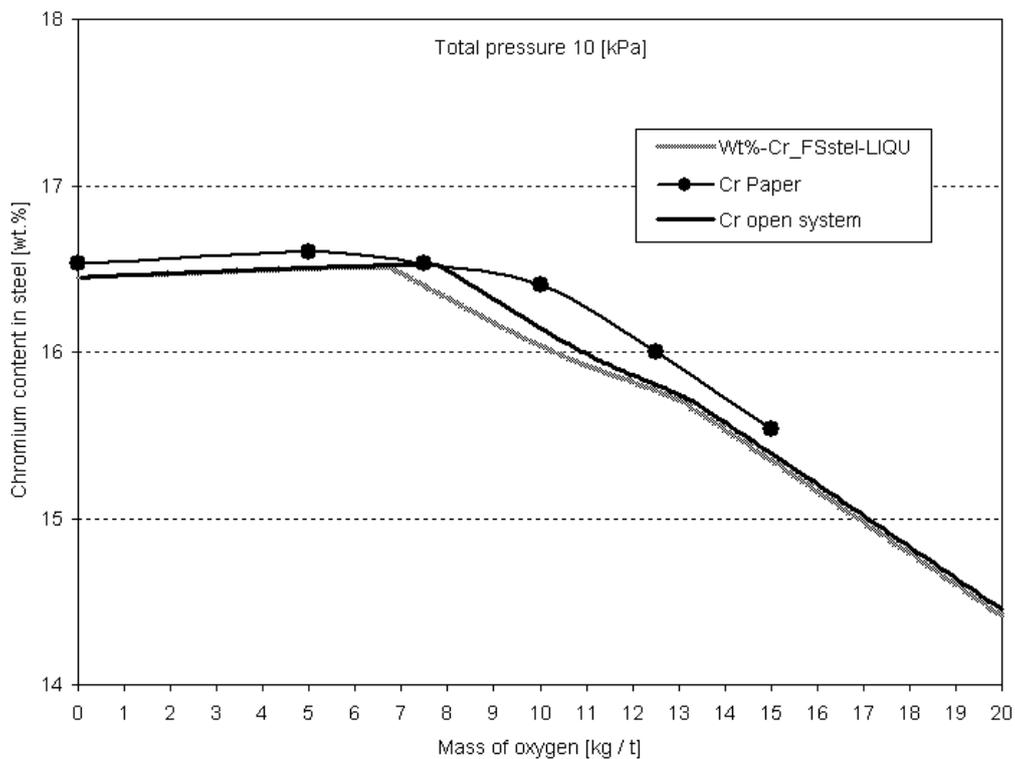

Figure 4. Chromium content in liquid steel as a function of the mass of oxygen; results from this work are compared with those from Swinbourne et al.[3] 'Cr Paper'; pressure: 10 kPa; C content determined by the 'open' mode are additionally given 'Cr open system'.
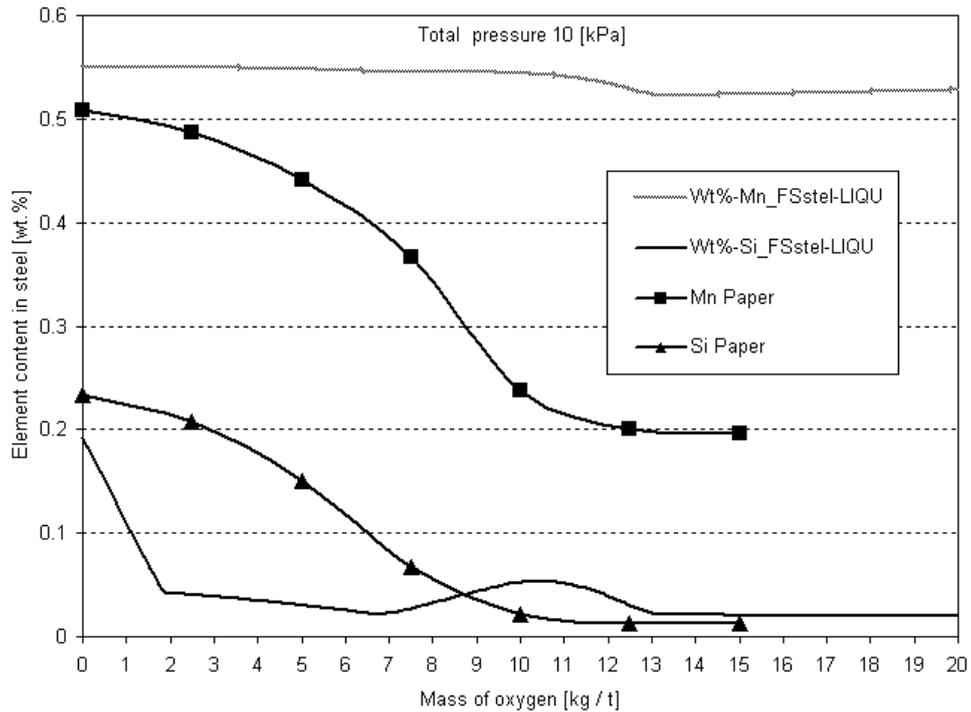
Figure 5. Manganese and silicon contents in liquid steel as a function of the mass of oxygen; results from this work are compared with those from Swinbourne et al.[3] 'Mn and Si Paper'; pressure: 10 kPa.
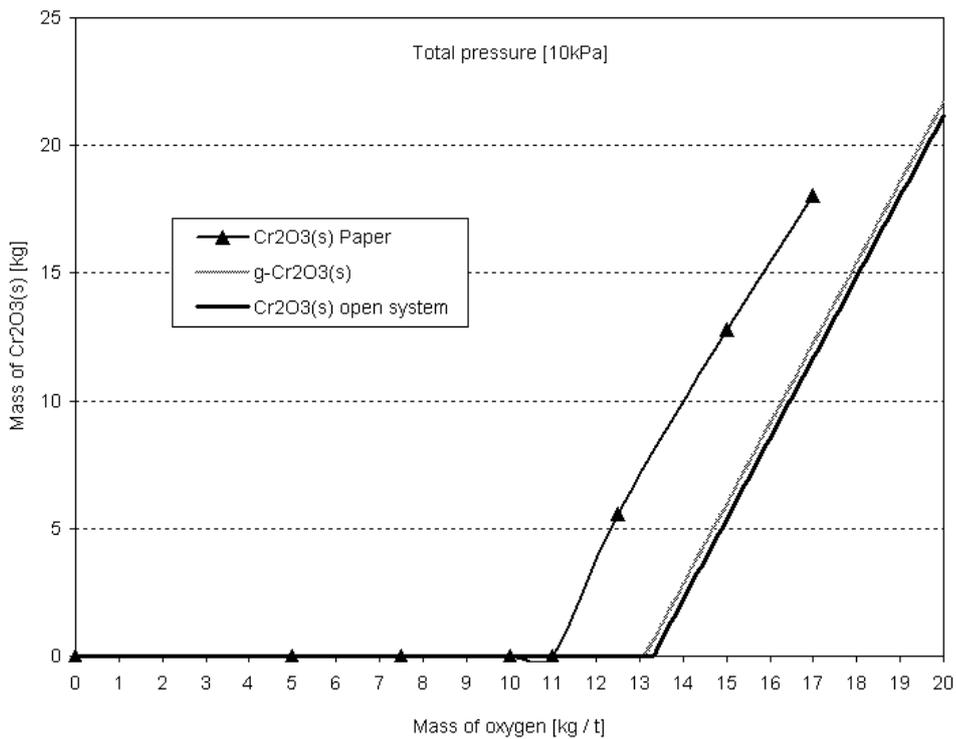

Figure 6. Eskolaite amount as a function of the mass of oxygen; results from this work are compared with those from Swinbourne et al.[3] 'Cr2O3(s) Paper'; pressure: 10 kPa; Cr_2O_3 content determined by the 'open' mode is additionally given: 'Cr2O3(s) open system'.
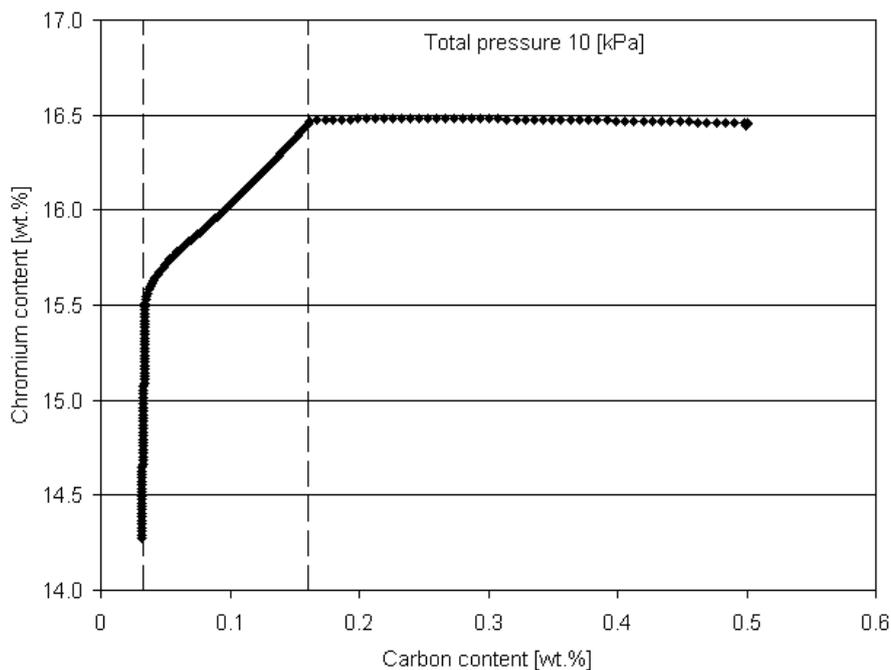
Figure 7. 'Critical carbon' determined for 1,600ºC and 10 kPa.

An analysis of the 'critical C' (from the point of view of *thermodynamics*, is the carbon content which could be achieved during the production of a Fe-Cr alloy, without great losses of chromium) was not carried out in the work of Swinbourne et al.[3] Due to its importance, it was analyzed here and the result can be seen in Figure 7.

In accordance with thermodynamics, the 'critical carbon' is influenced by both pressure and temperature – it decreases with *increasing* temperature and *reduced* pressure (which are thus favorable effects). For the conditions of the discussed system – temperature of 1,600ºC and system pressure of 10 kPa – the 'critical carbon' (in spite of a small drop of chromium content in 0.16 wt.%) has the value of 0.03 wt.% C.

4.2 Deep Degassing Stage

Following the HSC model for deep degassing stage of VOD, the masses of species in slag, steel and solid Cr_2O_3 at 16.4 kg of oxygen addition – the endpoint of the oxygen blow used by Ding et al.[4] – were taken again in the present work as input quantities.

The temperature was taken as 1,600ºC, and the system pressure was used as the variable in the simulation.

The carbon content of the steel as a function of system pressure is shown in Figure 7. The results are even lower than those from Kho et al.[2] Actual values are at least an order of magnitude higher than the equilibrium value at the pressures applied.

5 DISCUSSION

The chromium content of the metal determined by the two models, either at atmospheric pressure, and for the lower pressure, agrees fairly well. This is also the case when comparing carbon content. As for the Si and Mn, however, the results diverge from each other more substantially – even though the final content of Si of

the two models is close to the same value. The dissimilarity in the levels observed in other places – especially with the Mn – is probably due to differences in the model phase slag that is used in both applications.

This should also affect the amount of Cr of the steel that is lost in the form of eskolaite – since the results of the two models also differ significantly and chromium which is lost from the metal can be located both in the slag as in eskolaite. This chrome off the slag, in a solid phase is, for kinetic reasons, of reduced probability of return to the metallic phase by the action of reducing agents.

Regarding the results obtained with the method of determination denoted as 'open' in the present work, it can be said to be only slightly dissimilar from the results obtained with the traditional method.

In general, the results showed no effect of resistance-type diffusion or convection, as elements dissolved in the body of steel can react promptly with oxygen in atmosphere.

Especially this fact, it is known, led to the development of models capable of taking into account effects of diffusion and convection – but this topic is too away from the main discussion of this work.
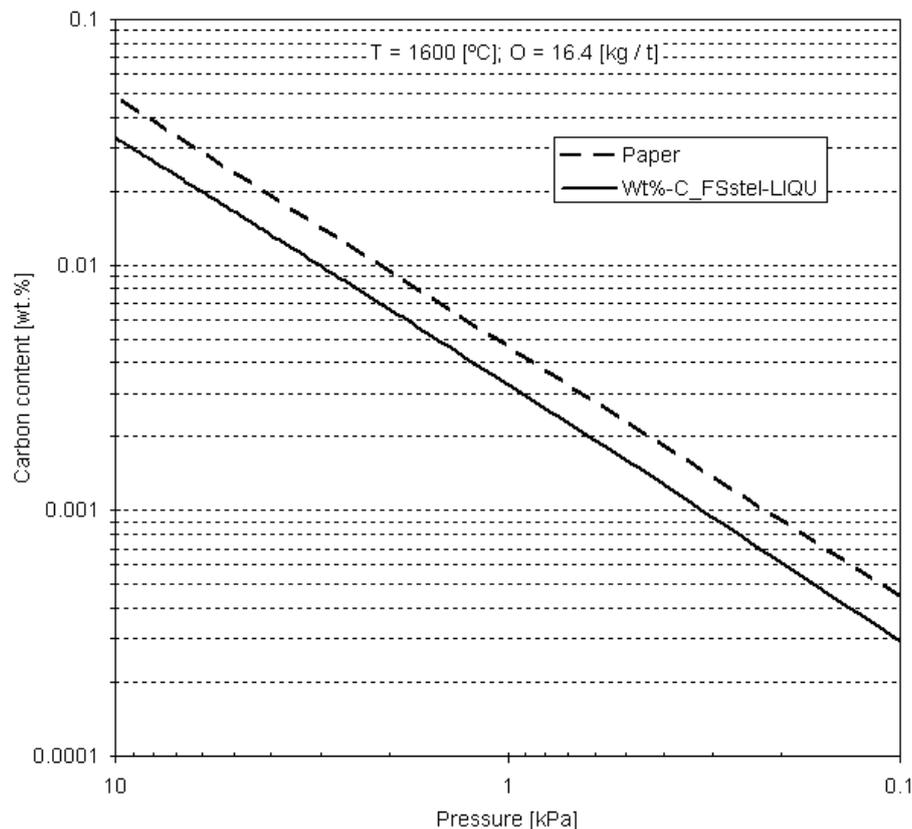

Figure 8. Equilibrium carbon content of steel as function of system pressure at 1,600ºC; results from this work are compared with those from Swinbourne et al.[3] 'Paper'.

6 CONCLUSIONS

Based on a number of simulations and comparisons with results published on the subject VOD process, it can be said that, for the compositions, temperatures and pressures tested, the thermodynamic software FactSage presents results that are comparable in many points to other commercial software using the same input and boundary conditions.

However, the approach taken by the technique of 'staged reactors' – for the reasons mentioned – is probably a more appropriated method for making process simulation than models that address more appropriately local phenomena – even with the option of a calculation system of the type 'open system'.

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