LIQUID IRON DEOXIDATION BY ALUMINUM: A BRIEF REVIEW OF EXPERIMENTAL DATA AND THERMODYNAMIC DESCRIPTION

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Abstract

The iron-oxygen-aluminum equilibrium has been a subject of interest for many years due to its importance in the steel industry. A great percentage of all flat rolled steel is aluminum killed "AK" (deoxidized) low-carbon steel, not only because of the low soluble oxygen contents that can be achieved but also because of the importance of the residual aluminum in forming aluminum nitride that is one of the main tools used to achieve crystallographic texture adequate for forming. The behavior both of oxygen and of aluminum in liquid iron are relatively well understood and quantified, as is the free energy of formation of alumina. Nonetheless, the Fe-Al-O behavior at liquid iron temperatures is not fully understood and considerable controversy still prevails. Thus, the objectives of this work are (a) to critically review the experimental work and assessments performed mainly on the Al-Fe-O–Al_2O_3 equilibrium, (b) to evaluate the current models used to describe this equilibrium and (c) to present a recommendation about the data, based on its evaluated reliability and consistency.
Keywords: Steel; Deoxidation; Thermodynamics; Al-Fe-O system; CALPHAD.

DESOXIDAÇÃO DO FERRO LÍQUIDO POR ALUMÍNIO: UMA BREVE REVISÃO DOS DADOS EXPERIMENTAIS E DESCRIÇÕES TERMODINÂMICAS

Resumo

O sistema ferro-oxigênio alumino tem sido investigado há muitos anos em função de sua importância para a indústria do aço. Uma grande fração de todo o aço plano produzido é de aço de baixo carbono acalmado ao alumínio, não apenas pelo baixo conteúdo de oxigênio residual em solução que pode ser obtido, mas, também, pela importância do alumínio residual na formação de AlN, importante no controle de estrutura e textura obtidas. Tanto o comportamento do oxigênio como o do alumínio no ferro líquido são relativamente bem compreendidos e quantificados, assim como a propriedades termodinâmicas da alumina. Entretanto, há discrepâncias significativas na quantificação do comportamento do sistema Fe-Al-O na temperatura do aço líquido, havendo, ainda, bastante controvérsia com respeito a equilíbrios importantes neste sistema. Assim, o objetivo deste trabalho é (a) realizar uma revisão crítica dos experimentos e avaliações termodinâmicas principalmente do equilíbrio Al-Fe-O–Al_2O_3 (b) avaliar os métodos atualmente usados para descrever este equilíbrio e (c) apresentar recomendações sobre os dados, com base em sua confiabilidade e consistência.
Palavras-chave: Aço; Desoxidação; Termodinâmica; Sistema Al-Fe-O; CALPHAD.

1 INTRODUCTION

The iron-oxygen-aluminum equilibrium has been a subject of interest for many years due to its importance to the steel industry. A great percentage of all flat rolled steel is aluminum killed "AK" (deoxidized) low-carbon steel, not only because of the low soluble oxygen contents that can be achieved but also because of the importance of the residual aluminum in forming aluminum nitride that is one of the main tools used to achieve crystallographic texture adequate for forming [1]. For many years, aluminum has also been an important alloying addition at relatively high levels in steels used for nitriding, such as Nitralloy® or W.Nr. 1.8550 (about 1% Al). High Mn-Al steels (such as 20Mn23AlV, 23%Mn,

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2%Al) [2] are used for electrical purposes and, in recent years, the prospect of producing lower density steels for the automotive industry through the use of significant additions of aluminum has been the subject of many studies [3,4]. Aluminum usage for deoxidation in typical flat products mill making "standard" steels ranges from 1.3 to 2kg/t, which represents a significant part of the alloy addition costs in these plants [5].

The behavior of oxygen in liquid iron is relatively well understood and quantified, as is the behavior of aluminum in iron. Even though the Gibbs Energy of formation of the aluminum oxides is also well established, the understanding of the Al-Fe-O equilibrium in liquid steel has been studied in detail since at least 1950 [6] until the last decade [7] and considerable controversy still prevails. Two of the main reasons for this are that the measurement of the Al-Fe-O equilibria at steelmaking temperatures involves extremely low oxygen potentials and the difficulties in the chemical analysis of the true content of oxygen dissolved in the alloy. Thus, the objectives of this work are (a) to critically review the experimental work and assessments performed mainly on the Al-Fe-O –Al_2O_3 equilibrium, (b) to evaluate the current models used to describe this equilibrium and (c) to present a recommendation about the data, based on its evaluated reliability and consistency.

2 REVIEW OF PREVIOUS WORK

2.1 Possible Sources of Error in Experimental Work

When evaluating the various publications dealing with the equilibrium with Al_2O_3 in the iron rich corner of the Al-Fe-O system it is interesting to review the various possible sources of experimental errors, as summarized in

Table 1, most of which have been discussed during the years since the pioneering work of Hilty and Crafts [6].

2.2 Thermodynamic Modeling and the Interaction Between the Solutes

It has been observed for quite some time [10] that for strong deoxidants in iron, the equilibrium Henryan activity curves show significant discrepancies from the equilibrium plots of concentration, as schematically shown in Figure 1 for the chromium oxygen equilibrium in liquid iron at 1600°C.

Most of the modeling work describing this equilibrium has been based on Wagner's dilute solution formalism [11]. In this formalism, interaction parameters are used to account for deviations from Henry's law caused by deviation from extremely dilute solutions and by the interaction between the solutes in the liquid phase. Several authors have discussed the limitations of this formalism (see, for instance [12-14]). Fruehan [15] has probably been the first author to call the attention to these limitations specifically in the Fe-Al-O system, albeit he mentions the fact that Lupis and Elliott [16] had already addressed the general aspects of the problem.

An evident conclusion of these remarks and discussions is that the dilute solution formalism predictions increasingly deviate from reality as the solutes significantly depart from dilute solution.

Later, Pelton and Bale [17] proposed an alternative approach to Wagner's formalism, and currently, with the solution models used in computational thermodynamics, these limitations can be completely eliminated [18,19]. For this reason, the works of St. Pierre [20] and others, in which the effects of the different interaction coefficients on the shape of the solubility curve of alumina are discussed, are not reviewed here.

Table 1. Most important sources of error in determination of equilibrium with Al_2O_3 in Fe rich alloys

Source of error	Comment	First Discussed by
Analytical techniques for oxygen in iron	The expected minimum values are lower than 10ppm of oxygen.	Hilty and Crafts [6]
Analytical techniques for aluminum in iron	In the high oxygen range (in special when hercynite becomes stable), the expected aluminum contents in the liquid are very low.	Hilty and Crafts [6]
Equilibrium achieved with oxide other than Al_2O_3 without knowledge of the authors	Due to the reactivity of aluminum and of oxygen, many experimental setups/procedures create opportunities for equilibrium to be reached with oxides other than Al_2O_3.	Hilty and Crafts [6]
Contamination of sample due to atmosphere or refractories	In some experiments when the authors expect to closely control the oxygen potential inside the furnace (as opposed to simply measure the results) secondary reactions and purity issues may affect the results.	Hilty and Crafts [6]
Presence of primary particles floating in the melt	If the experiment is conducted as a deoxidation experiment, Al_2O_3 formed during the experiment might not float completely out of the melt and result in error. Should not be confused with secondary Al_2O_3 that will precipitate as the sample cools but represents Al and O that were in solution at the experiment temperature.	Hilty and Crafts [6]
Nucleation of alumina in the melt	Depending on the type of experiment (adding Al to an oxidized melt or dissolving Al_2O_3, for instance), nucleation can be a barrier to equilibrium.	Schenk et al. [8], Rohde et al. [9]
Time for equilibration	The time for equilibration depends on many factors including size of samples, agitation, etc.	Hilty and Crafts [6], Kang et al. [7]

One important and unfortunate fact is that, to date, there is no way to predict to which extent the formalism can be accurately applied in a given system.

However, not surprisingly, when the Wagner dilute solution formalism is used, the values of the interaction coefficients do express, somehow, the affinity between the deoxidizer and oxygen, as shown in Figure 2. This indicates that the interaction coefficients do have some physicochemical significance.

One important effect of the use of interaction coefficients is that, when the interaction between oxygen and deoxidant is sufficiently strong, the equilibrium composition curve passes through a minimum, discussed by many authors [14,20]. Kuo [21], for instance, has shown that the position and value of this minimum depend strongly on the value of the interaction coefficient e_O^{Al}.

On the other hand, when analyzing the Fe-Ca-O system, Hillert et al. [22] considered that the apparent interaction, expressed by the Wagner interaction coefficient,
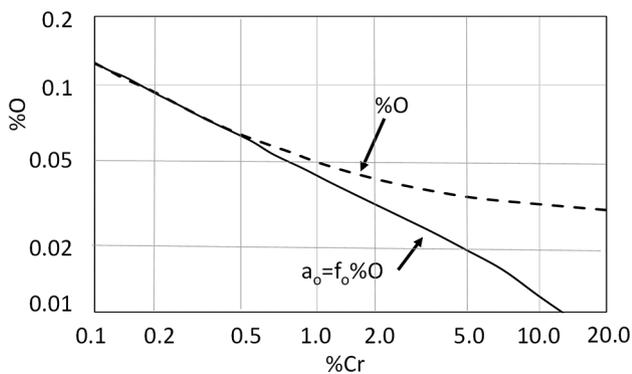
Figure 1. Discrepancy between oxygen and chromium Henryan activities and chemical composition in equilibrium with oxide, as proposed in 1949 by Chipman [10] for the chromium-oxygen equilibrium at 1595°C in iron (The notation used by Chipman, a_o instead of h_o was preserved).
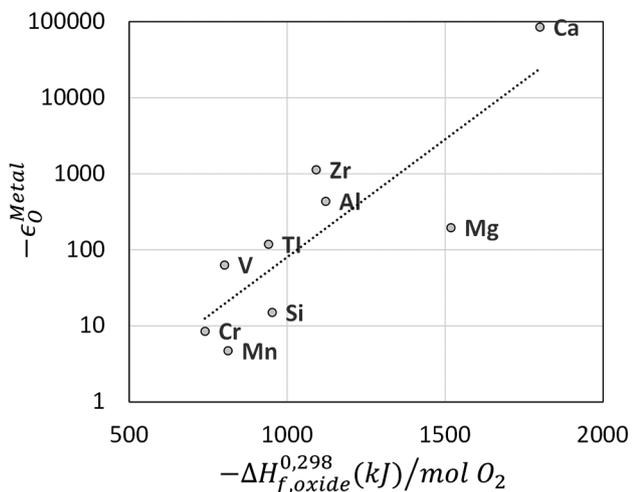
Figure 2. First order interaction coefficient ε_O^{Metal} versus enthalpy change for the formation of the metal oxide, per mol of O_2. Interactions coefficients from [13] except for Ca and Mg, calculated according [23] from e_O^{Metal} given by [24]. Enthalpies from [25].

was excessive. Later Hillert and Selleby [26] proposed that this was due to "a serious systematic error" on the experimental determination of the oxide solubilities. By relating the sub-lattice model equations for regular solutions to the dilute solution formalism, they calculated ε_O^{Al} from the information on the Fe-O and Fe-Al binary systems, together with the free energy of formation of Al_2O_3. They suggested that the interaction coefficient in the Fe-Al-O system should be $e_O^{Al} = -0.11$ at 1600°C, a value much lower than the values determined experimentally by most authors, as will be discussed in the next section.

2.3 Review of Experimental Work

In this section, the experimental work on the Fe-Al-O-Al_2O_3 equilibrium is reviewed following as much as possible their chronological order, to emphasize how the different sources of error identified in Table 1 were dealt with by different authors as they learned from previous works. The possible sources of errors listed in Table 1 are highlighted in the context of each work reviewed.

Hilty and Crafts [6] were probably the first authors to have access to reliable analytical techniques for measuring the content of Al and O present in steel. Since their results deviated too much from the theoretically calculated values, they speculated that the deviation was due to achievement of equilibrium with other oxides instead of pure Al_2O_3. In the discussion of this paper, Chipman proposed that this oxide could be hercynite, $FeO.Al_2O_3$. Also in the discussion, both J. Elliott and N.A. Gokcen speculate that an additional source of oxygen might be contaminating the atmosphere. Furthermore, the authors reported that they have observed extensive reaction between the crucible (that was supposed to be pure Al_2O_3) and the melt. It is conceivable that lower stability oxides might have been present in the raw material they have used for making the crucible, which, as observed in other experiments, can be a significant source of oxygen and affect the possibility of reaching equilibrium [27].

At their time, Hilty and Crafts estimated the precision of vacuum fusion analysis of oxygen at 10 ppm, which, for their results, was not relevant, due to the possible equilibrium with hercynite and not alumina. The estimated precision of their colorimetric method for aluminum was better than 1 ppm. Therefore, at this time, the question of the precision and limitation of the analytical method was only applicable to oxygen.

After the work of Hilty and Crafts, Gokcen and Chipman [28] performed experiments under carefully controlled H_2/H_2O atmospheres and pure alumina crucibles (no information on exact purity or source) to try to control sources of oxygen contamination. Through careful analysis of all measurable data and consistency checks with thermodynamic values, they were able to measure equilibrium with Al_2O_3 and to estimate the interaction coefficient of Al and O in liquid iron. They showed how their precision in oxygen analysis of ±5ppm affected the results and the estimated
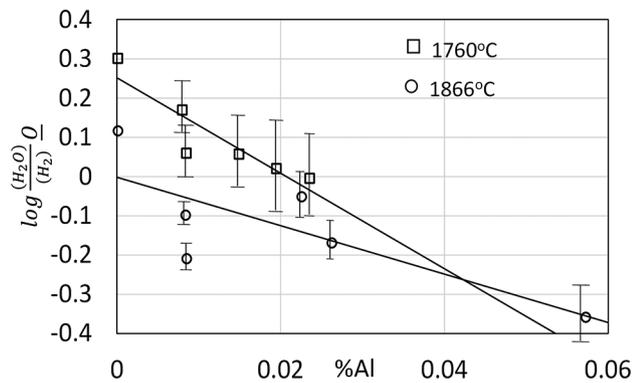
Figure 3. Experimental values measured by [28] of $log \dfrac{(H_2O)}{(H_2)} Q$ in equilibrium with Fe-Al-O in Al_2O_3 crucibles. The bars indicate an uncertainty of 10 ppm in the oxygen analysis. The slope of the lines represent the interaction coefficient e_O^{Al}. The graph emphasizes the importance of the accuracy of chemical analysis mentioned in section 2.1.

interaction coefficient. They also indicated clearly that oxygen and aluminum interact in solution in liquid iron (Figure 3). Their result is consistent with the observations supported by measurements, and reported since that time, for many other deoxidants in iron (such as Cr, V, C [10]). At that time, Chipman [10] proposed a simple physicochemical model for this interaction, in which the deoxidizer would have more ability than iron to *"share electrons with the oxygen atoms, thus…tying up oxygen and reducing its activity"*.

Later, D'Entremont et al. [29] revisited the problem, including in their experiments melts with high aluminum contents. In order to avoid errors in oxygen analysis caused by aluminum vaporization during vacuum fusion analysis, they decided on a different analytical technique. Thus, they took the alumina present at room temperature in the solidified sample as representative of the Al and O present in the steel at the experiment temperature. By doing that, they assumed that the solubility of alumina in steel at room temperature is negligible and that no alumina was present in the liquid steel at the experiment temperature. In their experiments they used purified argon (including a step in which argon was passed through a bed of magnesium chips at 550°C for final removal of oxygen) and thus avoided oxygen contamination by the atmosphere.

Their results were consistent with the previous measurements for alloys with low aluminum content [28] and resulted in much lower estimates for the interaction coefficients than those shown in Figure 3. Their recommended value was $e_O^{Al} = -1.0$ at 1600°C, obtained by extrapolation. However, their temperature error was reported to be 20°C. They observed the minimum oxygen content in the range of 0.2-0.5% Al, depending on the temperature. Interestingly, as they cover the complete binary Fe-Al, their results indicated that the solubility of oxygen in iron in equilibrium with alumina would, after the minimum, pass through a maximum and then decrease at compositions close to pure aluminum as the solvent.

The various works of Chipman and collaborators were performed in induction furnaces, so convection was extensive and the liquid can be assumed homogeneous. There is little spread in the results in the range of low aluminum (before the minimum in oxygen is reached) while this spread apparently increases when one passes this minimum. It is difficult to ascribe the spread specifically to any of the experimental error sources discussed in each case. If, for instance, alumina particles were not properly removed from the liquid, this difficulty should also be experienced at lower aluminum values. It is probable that the variations were caused by a combination of the factors and it can be speculated that the preparation and analysis techniques might have played a significant role, in special when the oxygen and aluminum contents were on the higher range.

Schenk et al. [8] studied the equilibrium with alumina as well as the precipitation kinetics of alumina inclusions in Fe-Al-O alloys. They used purified argon and alumina crucibles to control oxygen contamination. Their analytical methods could only determine Al and O with "satisfactory accuracy" above 10 ppm. Their experiments, however, were mostly performed on conditions in which nucleation barriers for the formation of alumina were present. Fewer experiments were performed under conditions in which Al_2O_3 would dissolve in steel to establish equilibrium. They proposed a value $e_O^{Al} = -0.22$ at 1600°C and the occurrence of the minimum oxygen value at around 2% Al.

Rohde et al. [9] also investigated the Al-O equilibrium in iron. Their experiments were performed in a Tammann furnace, where convection is limited. To try to circumvent this limitation they have stirred the melt with argon injection, and, at an intermediate point in some of their experiments, "rinsed" the metal with the injection of a small amount of a $CaO-Al_2O_3$ slag to help remove inclusions from the liquid. Their analysis indicate that, indeed, some Al_2O_3 particles were removed. After the slag was introduced, the activity of Al_2O_3 was not unity in these slags. One could argue that this could influence the equilibrium, even considering the presence of the pure Al_2O_3 crucible. It is also possible that this played a significant role on the scatter of their results (Figure 4 presents their result with slag separated from the results without slag).

More recently, Suito et al. [30] performed similar experiments: instead of argon agitation however, they have used an alumina rod to stir the bath but also used calcium aluminate slags for rinsing. When they corrected Schenk's results for the activity of alumina in the aluminate slags they claim to find good agreement with their results in the high aluminum range. Furthermore, they found reasonable agreement with the thermodynamic calculated equilibrium values when the data of [31] was used for the interaction coefficients. They also performed a variety of experimental cycles to determine the nucleation supersaturation as well as the equilibrium conditions. Suito and co-workers did a detailed SEM evaluation after the different equilibration cycles to decide whether they were able to eliminate all
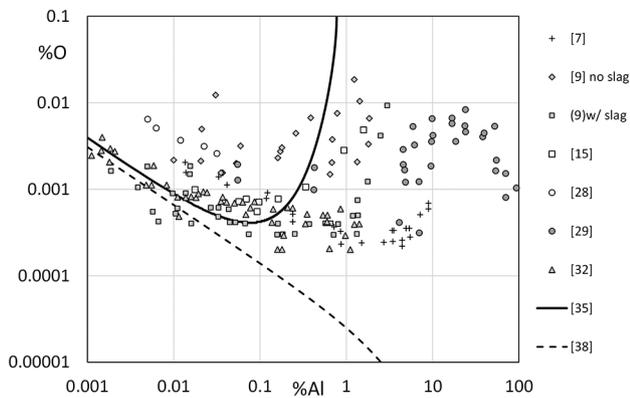
Figure 4. Plot of %Al vs %O in steel in equilibrium with Al_2O_3. Compilation of experimental data discussed in the text. Data is not at the same temperature in some cases. Solid and dashed lines were calculated with the SLAG3 [32] and TCFE7 [33] models, respectively. SLAG3 model [32] agreement to data is good for values up to approximately 0.24% Al.

primary alumina inclusions and they were convinced that this had occurred in their experiments.

Fruehan [15] experimental technique differed significantly from other authors in the use of the neutron activation technique for the oxygen analysis. This was due to the concern with Al effects on the fusion analysis of oxygen first mentioned by D'Entremont et al. [29]. Fruehan emphasizes that the samples analyzed were free of "entrapped" non-metallic inclusions. By this he probably meant large oxide particles, possibly primary deoxidation products. He also followed the reaction using EMF measurements with very good results, in agreement with the assumption that oxygen did not affect the activity of the aluminum. Nonetheless for exact calculations, the results should be corrected to the presently accepted value for the Cr/Cr_2O_3 equilibrium [34], since this mixture was used as reference in his electrolytic cell.

Based on his experimental data Fruehan proposed a value of $e_O^{Al} = -0.39$. Later, Kuo [25], however, proposed $e_O^{Al} = -0.75$ using Fruehan data, the thermodynamic data of hercinite and the assumption that the minimum oxygen in the hercynite solubility curve must be at the intersection with the alumina solubility curve. So, further uncertainties were introduced in the analysis of Kuo.

Janke and Fischer [35] also used EMF measurements to determine the deoxidation equilibrium in the Fe-Al-O system with good results. However, their total oxygen analysis, which were too high in their own evaluation, did not allow for a good estimation of e_O^{Al}.

Cho and Suito [36] performed equilibration experiments between iron and CaO-Al_2O_3-SiO_2 slags, derived the equilibrium constant for the aluminum deoxidation reaction and proposed a value of $e_O^{Al} = -6.83$ at 1600°C. Their experiments were focused on the low aluminum range, away from the minimum of the %Alx%O curve.

More recently, Kang et al. [7] performed a careful equilibration of iron-aluminum alloys with alumina crucibles

in a Tammann furnace. The alloys were prepared in advance by pre-melting iron and aluminum inside an Al_2O_3 crucible in an induction furnace under Ar-3 vol%H_2, to prevent oxygen contamination. Once prepared, 6 g of the alloy was placed inside an Al_2O_3 tube inserted into a mullite tube in a Tammann furnace previously flushed with Ar-3 vol%H_2 to avoid oxygen contamination. The equilibration time was one hour, which according to the authors was enough to reach the equilibrium. They carefully checked the premelted alloy samples to eliminate the primary Al_2O_3 inclusions. After the equilibration, they measured the aluminum and oxygen content using inductively coupled plasma atomic emission spectrometry (ICP-AES) and inert gas fusion infrared absorption spectroscopy, respectively. Their results show a lower amount of oxygen than all previously discussed experiments for higher Al content and a minimum around 2% Al. They did find a deviation toward higher oxygen values for low Al contents that they could not explain. They also expressed concern for a possible aluminum getter effect in the oxygen analysis, as pointed out by D'Entremont et al. [29]. They proposed a value of $e_O^{Al} = -0.174$ for the first order interaction parameter, and included a second order interaction parameter to describe their data.

3 DISCUSSION

Figure 4 presents a summary of all experimental data and the results of calculations using two thermodynamic databases with Thermo-Calc. SLAG3 [32] which uses the free energies compiled by Gaye [37] and the interaction coefficients of Sigworth and Elliott [31] converted as proposed by Hillert [38] and TCFE7 [33] which uses data of preliminary unpublished work by Selleby and Mao, performed in 2007 [33].

The results indicate that in the low aluminum region, where there is little deviation between Henryan activity and composition, the values calculated by TCFE7 and SLAG3 are quite close and agree well with the results of Fruehan [15]. Janke and Fischer [35] as well as Rohde and collaborators results, with slag rinsing [9]. Apparently, the values calculated by SLAG3, based on the dilute solution model are a reasonable prediction up to approximately 0.24%Al. The occurrence of a minimum in the curve of Figure 4 is not expected by the calculations of TCFE7 while most of the experimental data does show a minimum at some value of %Al. The various experimental values for this minimum differ significantly, however.

Industrial results for aluminum deoxidation agree well with the values calculated using SLAG3. For higher aluminum steels, such as Nitralloy and similar material, oxygen analysis is scarce or absent in the literature. The comparison with high aluminum nickel based superalloys is not applicable, since these are normally dynamically deoxidized by carbon under vacuum [26], so that the Al-O-Al_2O_3 equilibrium is never approached. Recently Paek et al. [39] reported

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the industrial results of Yin for total oxygen analysis in a Fe-1.2%Al steel slab. The value was in the range of 4~10 ppm (6 ppm in average), lower than expect by thermodynamic calculations. To elucidate this, Paek and co-workers have oxidized a Fe-9.06%Al alloy containing 1.76 ppm oxygen, by adding a controlled amount of Fe_2O_3. They have found that the oxygen content increased and after 1h and 2h reached the equilibrium values calculated by Kang and co-workers [7]. This confirms that the normal industrial practice used for high aluminum steels of adding this element as close to the end of the heat as possible is efficient, if, at this point, there is a lack of oxygen sources to dissolve back into the steel (via the use of stable refractories- both from the thermodynamic and kinetic point of view).

4 CONCLUSIONS

The experimental data for the equilibrium of Al and O dissolved in Fe with Al_2O_3 shows considerable discrepancy. This is probably related to the high affinity of the two solutes and the related experimental difficulties in measuring this equilibrium at steelmaking temperatures. However, it seems clear that there is a strong interaction between the two solutes in the liquid and that this leads indeed to the occurrence of a minimum in the curve that describes the equilibrium compositions at a constant temperature.

The values predicted by assessed thermodynamic data such as that given by JSPS [24] or that in SLAG3 are sufficiently accurate for the evaluation of the deoxidation of steels (low aluminum steels).

With the increasing interest in low density steels, electrical applications and nitriding alloys, in which one can expect the use of high aluminum contents, the controversy between experimental data and also with theoretical considerations [26] needs to be solved. The slow kinetics of dissolution of modern basic refractories in steels together with the favorable area/volume ratios and appropriate steelmaking practices certainly makes it possible to achieve relatively low total oxygen values with considerable aluminum contents, as reported by Paek et al. [39], by preventing the achievement of equilibrium in industrial conditions. This, however, does not limit the need for a correct understanding of the equilibrium in this very important system.

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