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

André Luiz Vasconcellos da Costa e Silva[1]
Roberto Ribeiro de Avillez[2]
Flávio Beneduce[3]

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, ferramenta importante no controle de estrutura e textura obtidas. O sistema Fe-O é relativamente bem compreendido e quantificado, da mesma forma que o sistema Fe-Al. Entretanto, há discrepâncias significativas na quantificação do comportamento do sistema Fe-Al-O havendo, ainda, bastante controvérsia com respeito a equilíbrios importantes. 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; Sistema Fe-Al-O; Termodinâmica, CALPHAD

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

Abstract

The iron-oxygen-aluminum equilibrium has been a subject of interest for many years for 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 of oxygen in liquid iron is relatively well understood and quantified, as is the behavior of aluminum in iron. Nonetheless, the Fe-Al-O system is not fully understood and considerable controversy still prevails. Thus, the objectives of this work is (a) to critically review the experimental work and assessments performed mainly of 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 of the data, based on its reliability and consistency.
Keywords: Steel; Deoxidation; Fe-Al-O system; Thermodynamics; CALPHAD.

[1]   PhD, Professor, EEIMVR-UFF, Volta Redonda, RJ, Brasil.
[2]   PhD, Professor, DEQM, PUC-RIO, Rio de Janeiro, RJ, Brasil.
[3]   Doutor, Escola Politécnica, USP, São Paulo, SP, Brasil.

1 INTRODUCTION

The iron-oxygen-aluminum equilibrium has been a subject of interest for many years for 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 [1] . For many years, aluminum has also been an important alloying addition in 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, 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 steel products mill making "standard" steels ranges from 1.3 to 2kg/t , which represents a significant part of the alloy addition costs [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 reasons is that the measurement of the Al-Fe-O equilibria at steelmaking temperatures involves extremely low oxygen potentials and difficulties in the chemical analysis of the true content of oxygen dissolved in the alloy [8]. Thus, the objectives of this work is (a) to critically review the experimental work and assessments performed mainly of the Al-Fe-O–Al_2O_3 equilibrium, (b) evaluate the current models used to describe this equilibrium and (c) to present a recommendation of the data, based on its evaluated reliability and consistency.

2 EVALUATION OF AVAILABLE DATA

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].

Table 1. Most important sources of error in determination of equilibrium with Al2O3 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.	[6]
Analytical techniques for aluminum in iron	In the high oxygen range (in special when hercynite becomes stable, the expected aluminum contents are very low.	[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 opportunity for equilibrium to be reached with oxides other than Al_2O_3.	[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.	[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.	[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.	[9]
Insufficient time to equilibration	The time to equilibration depends on the amount of material used in the experiment.	[6,10]

2.2 Thermodynamic Modeling

Most of the modeling work describing this equilibrium has been based on Wagner's dilute solution formalism in which different order interaction parameters are used to improve the description. Several authors (for instance [11-20]) have discussed the limitations of the formalism. For this reason, the works of St Pierre [20], among others, in which mathematical descriptions for the solubility curve of alumina in iron are discussed based on interaction coefficients are not discussed here.

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 1.
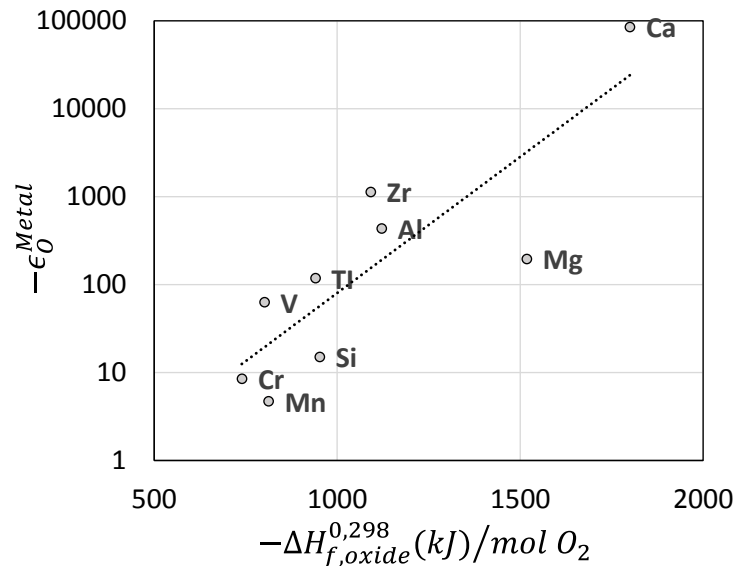
Figure 1. First order interaction coefficient ϵ_O^{Metal} versus enthalpy change for the formation of the metal oxide, per mol of O_2. Interactions coefficients from (13) except for Ca and Mg, calculated according [21] from e_O^{Metal} given by [22]. Enthalpies from [23].

When the interaction is sufficiently strong, the composition curve passes through a minimum discussed by many authors [14,20]. Kuo [24] has shown that the position and value of this minimum depend strongly on the value of the interaction coefficient e_O^{Al}.

2.3 Experimental Data

Figure 2 presents a summary of all experimental data and the results of calculations using two thermodynamic databases with Thermo-calc. SLAG3 [30] which uses the free energies compiled by Gaye [31] and the interaction coefficients of Sigworth and Elliott [32] converted as proposed by Hillert [33] and TCFE7 [29] which uses data of preliminary unpublished work by Selleby and Mao. This data is supported by the hypothesis of a systematic error in the experimental data, proposed by Hillert and Selleby [34] based on the observations during their Fe-Ca-O assessment [35]. The large scatter of experimental data reflects the experimental difficulties mentioned in Table 1.

* Contribuição técnica ao 70º Congresso Anual da ABM – Internacional e ao 15º ENEMET - Encontro Nacional de Estudantes de Engenharia Metalúrgica, de Materiais e de Minas, parte integrante da ABM Week, realizada de 17 a 21 de agosto de 2015, Rio de Janeiro, RJ, Brasil.
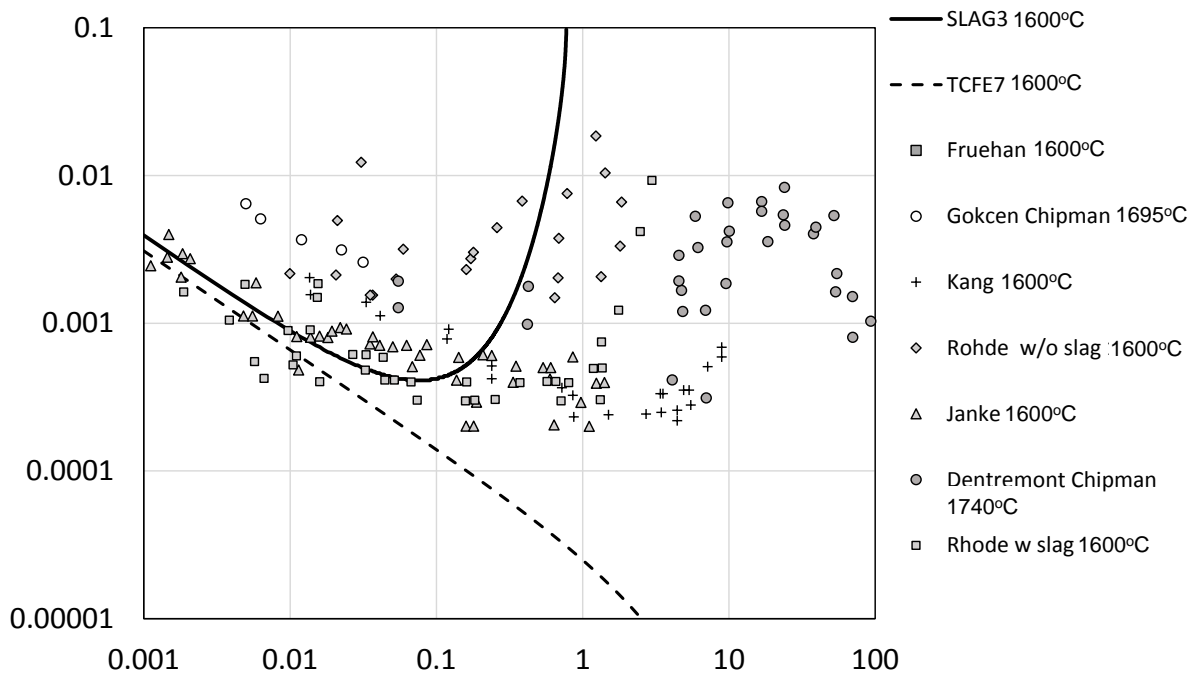
1926

Figure 2. Compilation of experimental data discussed in the text. Data is not at the same temperature in some cases. SLAG3 model agreement to data is good for values up to approximately 0.24% Al. References to the Figure data: Fruehan 1600C [15] Gokcen Chipman 1695C [25] Kang 1600C [7] Rohde 1600C [26] Janke 1600C [27] D'Entremont Chipman 1740C [28]. TCFE7 1600C [29] SLAG3 1600C [30].

3. DISCUSSION

Figure 2 indicates 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 Janke and Fischer [27] as well as Kang and co-workers [7]. The values of Janke and Fischer, based on EMF measurements, need some correction due to the presently accepted values for the $Cr-Cr_2O_3$ equilibrium [36]. Apparently, the values calculated by SLAG3, are a reasonable prediction up to around 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. Furthermore, Wasai et al. [10] studied the three phase equilibrium liquid iron, Al_2O_3 and $FeO.Al_2O_3$ and compared with previous experimental data. They observed that the oxygen content increases in the low aluminum content region, as already previously noted by Gustafsson and Melberg [13], with substantial deviation from the usually accepted solubility product. They also argued that the dilute solution model is not appropriate since the experimental curve is concave.

Industrial results for aluminum deoxidation agree well with the values calculated using SLAG3. For higher aluminum steels, such as Nitralloy and similar material, Al analysis is scarce or absent in the literature. The parallel of high aluminum nickel based superalloys cannot be used since these are normally dynamically deoxidized by carbon under vacuum [37], so that the Al-O-Al_2O_3 equilibrium is never approached. Recently Paek [38] reported the industrial results of Yin, of 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,

* Contribuição técnica ao 70º Congresso Anual da ABM – Internacional e ao 15º ENEMET - Encontro Nacional de Estudantes de Engenharia Metalúrgica, de Materiais e de Minas, parte integrante da ABM Week, realizada de 17 a 21 de agosto de 2015, Rio de Janeiro, RJ, Brasil.

1927

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, when 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 show considerable discrepancy. This is probably related to the high affinity of the two solutes and the related experimental difficulties. However, it seems clear that there is indeed a strong interaction between the two solutes in the liquid and that this leads 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 [22] or that in SLAG3 is sufficiently accurate for the deoxidation of steels (low aluminum steels and relatively low soluble oxygen in the steel after deoxidation).

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 within the theoretical framework [34] 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 [38], by preventing the achievement of equilibrium in industrial conditions. This, however, does not limit the need to a correct understanding of the equilibrium in this very important system.

Acknowledgements

REFERENCES

1   Llewellyn DT, Hudd RC. Steels: Metallurgy and Applications. Woburn, MA, USA: Butterworth-Heinemann; 1998.
2   Wang Q, Sun M, Qiu S, Tian Z, Zhu G, Wang L, et al. Study on Mold Slag with High Al2O3 Content for High Aluminum Steel. Metall Mater Trans B. 2014 Apr;45(2):540–6.
3   Rana R. Low-Density Steels. JOM. 2014 Sep;66(9):1730–3.
4   Zuazo I, Hallstedt B, Lindahl B, Selleby M, Soler M, Etienne A, et al. Low-Density Steels: Complex Metallurgy for Automotive Applications. JOM. 2014 Sep;66(9):1747–58.
5   Costa e Silva A, Ågren J, Clavaguera-Mora MT, Djurovic D, Gomez-Acebo T, Lee B-J, et al. Applications of computational thermodynamics — the extension from phase equilibrium to phase transformations and other properties. Calphad. 2007 Mar;31(1):53–74.
6   Hilty DC, Crafts W. The solubility of oxygen in liquid iron containing aluminum. Trans AIME. 1950;188(414):181–204.

Contribuição técnica ao 70º Congresso Anual da ABM – Internacional e ao 15º ENEMET - Encontro Nacional de Estudantes de Engenharia Metalúrgica, de Materiais e de Minas, parte integrante da ABM Week, realizada de 17 a 21 de agosto de 2015, Rio de Janeiro, RJ, Brasil.

1928

7   Kang Y, Thunman M, Sichen D, Morohoshi T, Mizukami K, Morita K. Aluminum deoxidation equilibrium of molten iron-aluminum alloy with wide aluminum composition range at 1 873 K. ISIJ Int. 2009;49(10):1483–9.

8   Physical Chemistry of Steelmaking Committee. Basic Open Hearth Steelmaking, edited by the staff of Alloys of Iron Research and T.S. Washburn, B.M. Larsen, and J.S. Marsh; Frank T. Sisco, consulting editor. New York, NY: AIME; 1944.

9   Schenk H, Steinmetz E, Mehta K. Equilibrium and kinetics of the precipitation of alumina in the system iron-oxygen-aluminium at 1600C. Arch Fuer Eisenhuettenwesen. 1970;41(2):131–8.

10   Wasai K, Mukai K, Fuchiwaki H, Yoshida A. Determination of Aluminum and Oxygen Contents in Liquid Iron in Equilibrium with .ALPHA.-Alumina and Hercynite. ISIJ International, 39(8), pp.760–766; 1999

11   Chipman J. Another Look at the Problem of Steel Deoxidation. Met Prog. 1949; (August): 211–21.

12   Pelton AD. The Polynimial Representation of Thermodynamic Properties in Dilute Solutions. Metall Mater Trans B. 1997; 28B (October):869–76.

13   Lupis CHP. Chemical Thermodynamics of Materials. New York: North-Holland; 1983.

14   Gustafsson S, Melberg P-O. On the free energy interaction between some strong deoxidizers, especially calcium and oxygen in liquid iron. Scand J Metall. 1980;9:111–6.

15   R J Fruehan. Activities in Liquid Fe-Al-O and Fe-Ti-O Alloys. Metall Trans. 1970; 1 (December) :3403–10.

16   Lupis CHP, Elliott JF . Generalized interaction coefficients. Acta Metall. 1966;14 (April): 529–38.

17   Pelton AD, Bale CW. A modified interaction parameter formalism for non-dilute solutions. Metall Trans A. 1986;17(7):1211–5.

18   Lukas HL, Fries SG, Sundman B. Computational Thermodynamics. Cambridge, UK: Cambridge University Press; 2007.

19   Pelton AD. Solution models. In: Sano N, Lu W-K, Riboud PV, Maeda M, editors. Advanced Physical Chemistry for Process Metallurgy. San Diego, CA: Academic Press; 1997. p. 87–116.

20   St . Pierre GR.The Solubility of Oxides in Molten Alloys. Metall Trans B. 1977;8B:215-217.

21   Lupis CHP, Elliot JF. Generalized interaction coefficients Part II Free energy terms and the quasi-chemical theory. Acta Metall. 1966;14:1019–32.

22   Hino,M., Ito K, editors. Thermodynamic data for Steelmaking, The 19th Committee for Steelmaking, JSPS. Tohoku University Press, Sendai; 2010.

23   Fruehan R, editor. Making, Shaping, and Treating of Steel, Steelmaking And Refining Volume. 11th Edition. Pittsburgh PA: AISE Steel Foundation; 1998.

24   Kuo C-G. The Calculation of Fe–Al–O Interaction Coefficient. J Alloys Compd. 2010 Apr;494(1-2):72–7.

25   Gokcen NA, Chipman J. Aluminum-Oxygen Equilibrium in Liquid Iron. Trans AIME. 1953;194:173–8.

26   Rohde LE, Choudhury A, Wahlster M. New investigations into the Aluminum-Oxygen equilibrium in iron melts. Arch Fuer Eisenhuettenwesen. 1971;42(3):165–74.

27   Janke D, Fischer WA. Deoxidation equilibrium of titanium, aluminum and zirconium in iron melts at 1600C. Arch Eisenhuttenwesen. 1976;47(4):195–8.

28   d'Entremont JC, Guernsey DL, Chipman J. Aluminum-Oxygen Interaction in Liquid Iron. Trans Metall Soc AIME. 1963;227:14–7.

29   TCAB. TCFE7 Database. Stockholm: TCAB; 2012.

30   TCAB. SLAG3 Database. Stockholm, Sweden: TCAB; 2012.

31   Gaye H, Welfringer J. Modelling of the thermodynamic properties of complex metallurgical slags. In: H. A. Fine DRG, editor. Second International Symposium on Metallurgical Slags and Fluxes. Lake Tahoe, Nevada: TMS-AIME; 1984. p. 357–75.

32   Sigworth GK, Elliott JF. The thermodynamics of liquid dilute iron alloys. Met Sci. 1974; 8:298–310.

* Contribuição técnica ao 70º Congresso Anual da ABM – Internacional e ao 15º ENEMET - Encontro Nacional de Estudantes de Engenharia Metalúrgica, de Materiais e de Minas, parte integrante da ABM Week, realizada de 17 a 21 de agosto de 2015, Rio de Janeiro, RJ, Brasil.

1929

33 Hillert M. A modified regular solution model for terminal solutions. Metall Trans A. 1986;17A(October):1878–9.

34 Hillert M, Selleby M. Solubility of CaO and Al2O3 in liquid Fe. Scand J Metall. 1990;19:23–5.

35 Hillert M, Selleby M, Sundman B. An assessment of the Ca-Fe-O system. Metall Trans A. 1990;21(10):2759–76.

36 Povoden E, Grundy AN, Gauckler LJ. Thermodynamic Reassessment of the Cr-O System in the Framework of Solid Oxide Fuel Cell (SOFC) Research. J Phase Equilibria Diffus. 2006 Aug 1;27(4):353–62.

37 Costa e Silva A. Refractories in Vacuum Induction Melting. M.A.Sc Thesis, Vancouver, Canada: University of British Columbia; 1979.

38 Paek M-K, Do, KH, Kang YB, Park J-H, Pak J-J. Inclusion Thermodynamics for High-Al High-Mn Advanced High Strength Steels. Proceeding of Clean Steel in Future – Prof Hae-Geon Lee Symposium. GIFT, POSTECH, May 31-June 1, 2012, Pohang, Korea: Postech; 2012.

* Contribuição técnica ao 70º Congresso Anual da ABM – Internacional e ao 15º ENEMET - Encontro Nacional de Estudantes de Engenharia Metalúrgica, de Materiais e de Minas, parte integrante da ABM Week, realizada de 17 a 21 de agosto de 2015, Rio de Janeiro, RJ, Brasil.

1930