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Modelling of Al, Si, Mn and Ti partition between slag and Fe-Ni alloys

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The modelling work presented here concerns Ni-bearing steels produced by Imphy Ugine Précision. In such grades, the contents of elements such as silicon or titanium must be precisely controlled by slag/metal treatments. The slag phase is described by IRSID slag model that has been slightly revised in order to better fit recent SiO_2 activity measurements in the low SiO_2 content domain of the $CaO-Al_2O_3-CaO$ system. The metallic alloys are described by the unified interaction parameter model (UIPM). In this formalism, the interaction coefficients, giving the effect of nickel on Al, Si, Mn and Ti activities, have been determined by electrochemical measurements and/or extracted from industrial data on slag/metal treatments concerning a wide range of alloy compositions:

$$e_{Si}^{Ni} = -\frac{146.5}{T} + 0.089$$

$$e_{Mn}^{Ni} = 0.0064$$

$$e_{Al}^{Ni} = -\frac{488.2}{T} + 0.253$$

$$e_{Ti}^{Ni} = -\frac{688}{T} + 0.337 \text{ and } r_{Ti}^{Ni} = 0.0006$$

Keywords: slag, Ni alloyed steels, activities, interaction coefficient

Introduction

Imphy Ugine Précision (IUP) has a unique know-how in the production of very elaborate Ni high alloyed steels. These high quality products are processed through its VOD-VAD (vacuum oxygen decarburization-vacuum argon degassing) unit allowing long stirring treatments under vacuum.

Thermodynamic modelling has been proved to be particularly useful to Imphy Ugine Précision in the development of these alloys. Two typical examples of such a contribution are given in this paper with alloys for shadow masks and alloys for frames of high definition colour TV sets.

This modelling is based on IRSID model for the slag phase and on unified interaction parameter model (UIPM) for the metallic liquid phase. The extension of this latter model to high Ni alloyed steels has required electrochemical measurements but has also beneficiated from careful examination of industrial data on slag/metal treatments.

Thermodynamic models

Metallic phase model

In this paper, the properties of the Ni-bearing alloys are described by the unified interaction parameter model (UIPM). In this formalism, the activity of the element i is given by the relation:

$$a_i = f_i \cdot [\%i] \qquad [1]$$

where f_i is the activity coefficient and $[\%i]$ the mass per cent i. $\log(f_i)$ is developed as a first or a second degree polynomial, function of the mass per cent of the different solutes:

$$\log(f_i) = \sum_j e_i^j \cdot [\%j] + \sum_{j,k} r_i^{jk} \cdot [\%j] \cdot [\%k] \qquad [2]$$

Experiments have been conducted to measure the coefficients relative to the effect of Ni on Al, Si and Mn activities. For each element i=Al, Si and Mn quaternary alloys Fe-36% Ni-O-i have been synthesized in an induction vacuum furnace by continuous addition of element i in an initially oxidized Fe-36% Ni liquid alloy. The oxygen activity measurement by an electrochemical probe associated with the content of the alloy in component i allows the determination of its activity coefficient. Indeed, if K is the solubility product associated with the reaction:

$$x \cdot i + y \cdot O = i_x O_y \qquad [3]$$

at equilibrium, the activity coefficient of i is:

$$\log(f_i) = \frac{1}{x}\left(\log K - \log\left([\%i] \cdot a_O^y\right)\right) \qquad [4]$$

The nickel contribution to that activity coefficient can be characterized by the definition of a partial activity coefficient f_i^{Ni}:

$$\log\left(f_i^{Ni}\right) = \frac{1}{x}\left(\log K - \log\left([\%i] \cdot a_O^y\right)\right) - e_i^O \cdot [\%O] - e_i^i \cdot [\%i] \qquad [5]$$

After each addition, a waiting time of at least 3 minutes is observed before sampling and oxygen activity measurement. Measures are corrected to take into account (a) the presence of oxides that have not had time to float out (b) oxygen probe polarization. The error on the temperature measurements is about 3°C.

Solubility product and activity coefficients e_i^O and e_i^i values are taken from Rist *et al.*[1].

Figure 1 gives an example for aluminium of the experimental results along with the experimental uncertainty.

Numerical values assessed through our experiments are reported in Table I.

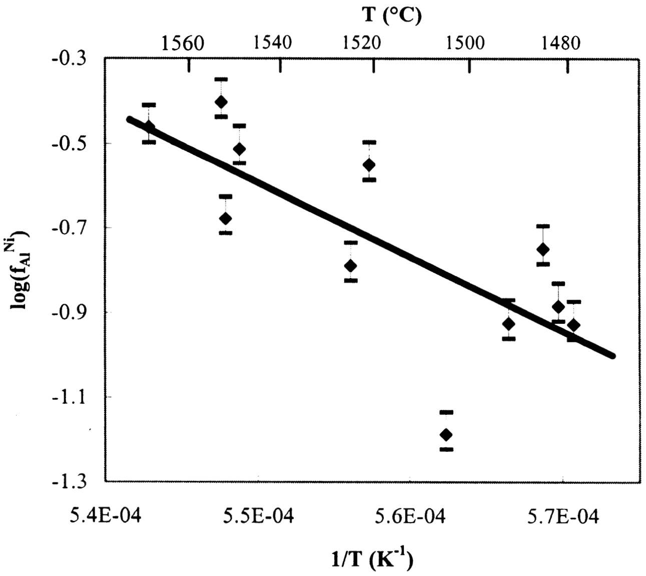

Figure 1. Experimental determination of the partial activity coefficient f_{Al}^{Ni} for a 36% Ni alloy as a function of temperature

Table I
Experimental values of the interaction coefficients and partial activity coefficients for a 36% Ni alloy

i	e_i^{Ni}	f_i^{Ni} 1540°C	f_i^{Ni} 1600°C
Si	-146.5/T+0.089	2	2.4
Mn	0.0064	1.7	1.7
Al	-488.2/T+0.253	0.25	0.53

Slag modelling

The properties of metallurgical slags are described by the IRSID slag model. This model, based on statistical thermodynamics, gives a precise description of the different slag properties: component activities, phase diagrams, sulphur capacities, etc. The composition domain for which the model has been validated is as follows: SiO_2-TiO_2-Ti_2O_3-Cr_2O_3-CrO-Al_2O_3-Fe_2O_3-FeO-MnO-MgO-CaO with CaF_2 contents up to 10–20 per cent and sulphur contents less than a few per cent.

In order to obtain a better fit with recent experimental data on SiO_2 activities in the system SiO_2-Al_2O_3-CaO, the values of the parameters of the slag model have been slightly revised.

Experimental data

SiO_2 activity data available for the system SiO_2-Al_2O_3-CaO originate from Kay and Taylor[3], Rein and Chipman[4] and Ozturk and Fruehan[5] as well as from the more recent work of Suito *et al.*[6–10]. The initial assessment of IRSID slag model was based on Rein and Chipman's work. The experimental technique is always based on the measurement of slag/metal Si equilibrium partition but, depending on the experiments, the oxygen activity can be determined:

- by equilibrium between a CO atmosphere and a C-saturated metal[3–5]. The SiO_2 activity is evaluated from metal Si contents through the reaction: $Si(l) + 2CO(g) \rightarrow SiO_2(s) + C_{graphite}$
- in a non C saturated metal, from a measurement of the metal oxygen content or by using slag/metal nitrogen partition[6–10].

IRSID model modification is partly based on Ozturk and Fruehan's[5] data that are the only direct determinations of silica activities at low SiO_2 contents. Nevertheless, these experimental data have been re-evaluated, in agreement with their authors. Indeed, they used activity/composition relationships for C saturated liquid iron proposed by Chunlin and Guojin[11] that under-estimate the Si activity (and, as a consequence, SiO_2 activity) by a factor of 5 when compared to the estimation issued from thermodynamic data classically used at IRSID. Therefore, we have used only the reevaluated data as they are presented on Figure 2.

Parameter re-assessment

IRSID slag model parameters are all binary parameters[12]. The parameters relative to the three limiting binaries SiO_2-CaO, SiO_2-Al_2O_3 and CaO-Al_2O_3 have an effect on SiO_2 activities in the ternary SiO_2-Al_2O_3-CaO. It has been shown that a slight modification of the SiO_2-CaO binary parameters, as reported in Table II, was sufficient to satisfactorily modify these activity values.

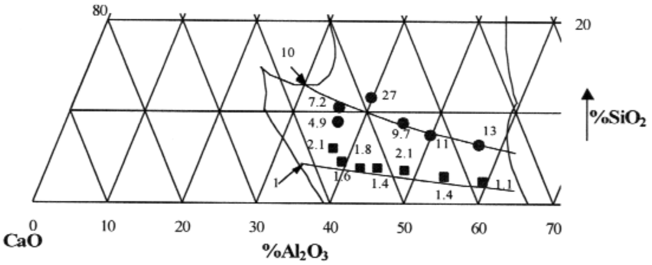

Figure 2. Experimental values of SiO_2 activities (*10^4) at 1600° of the SiO_2-Al_2-O_3-CaO system at low SiO_2 contents (Ozturk and Fruehan[5] reevaluated results). Two symbols have been used in order to distinguish values lower and higher than 5.10^{-4}

Table II
Initial and modified values of IRSID slag model parameters relative to the SiO_2-CaO binary (cal.mol^{-1})

	Formation energy	Interaction energy
Initial parameters	-12500	$-4500+7500X_{SiO2}$(*)
Modified parameters	$-11100-2000X_{SiO2}$	$-4500+8900X_{SiO2}$

(*) X_{SiO2} is the mole fraction of SiO_2.

Table III
Experimental SiO_2 activities compared to activities calculated with IRSID slag model and by correlations proposed by different authors

	Temperature (°C)	$\%SiO_2$	$\%Al_2O_3$	%CaO	Experimental data		Slag model		Correlation	
					Rein and Chipman[4]	Ozturk and Fruehan[5(*)]	Inital	Modifié	Ohta and Suito[9,10]	Banya[13]
Lime saturated	1600	2.0	38.0	60.0			8.1E-06	3.2E-05	1.2E-04	2.4E-04
	1600	2.0	33.7	60.0		2.2E-04	4.0E-05	1.3E-04	2.0E-04	1.1E-03
	1600	10.9	29.1	60.0	1.0E-04	6.4E-04	1.3E-04	3.2E-04	3.6E-04	2.9E-03
Ca aluminate saturated	1600	2.2	60.0	37.8		1.4E-04	1.3E-03	4.2E-03	2.8E-03	2.6E-04
	1600	5.9	60.0	34.1		9.8E-04	1.2E-02	2.4E-02	6.7E-03	9.8E-04
	1600	7.6	60.0	32.4	1.0E-03		2.3E-02	4.0E-02	1.0E-02	1.5E-03

(*) These data have been reevaluated (see text). The uncertainty on SiO_2 activity determination is at least equal to 200%

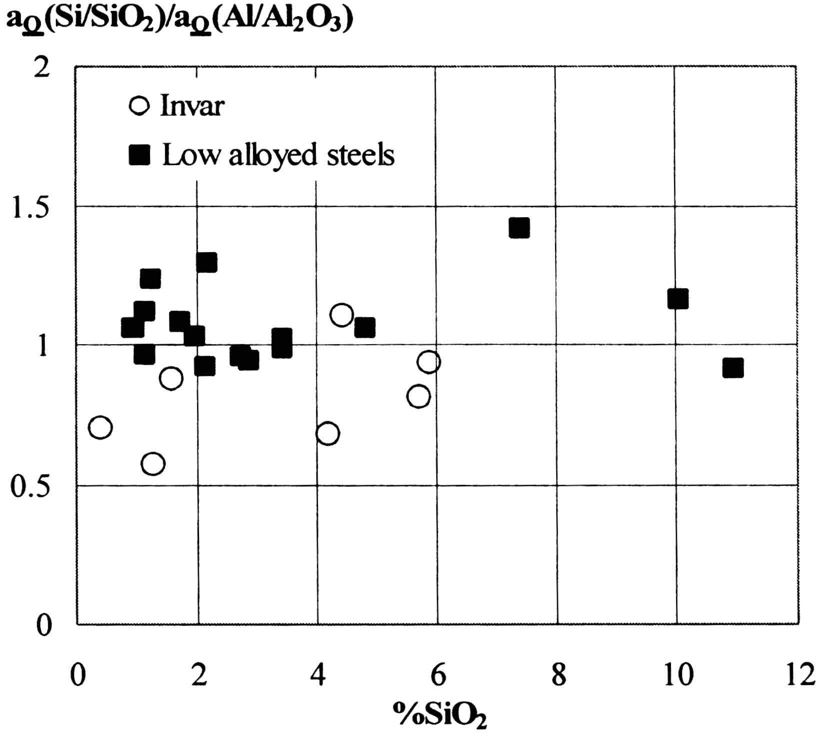

Figure 3. Ratio between oxygen activity values given by the oxide/deoxidizer couples Al/Al_2O_3 and SiO_2 for low-alloyed and Invar steel grades

Table III compares the available experimental data to the predictions delivered by the initial and the modified IRSID model, as well as by correlations proposed by various other authors[10,13]. Comparison has been done for slags with a given CaO content near lime saturation and for slag with a given Al_2O_3 content near Ca aluminates saturation.

At 1600°C, Ozturk and Fruehan's[5] data, in agreement with the correlation proposed by Ohta and Suito[10], show that Rein and Chipman's[4] work leads an underestimation of SiO_2 activities for lime-saturated slags at low SiO_2 contents. The modification of IRSID slag model that was initially well fitted to Rein and Chipman's data in this composition domain, now provides predictions close to Ozturk and Fruehan's and Ohta and Suito's data.

In the Ca-aluminates saturated slags, the model predictions are in better agreement with Ohta and Suito's correlation than with Ozturk and Fruehan's data.

Slag/metal reactions

Si partition

Si content control of Invar steels (Fe-36 per cent Ni) appears to be of utmost importance for shadow masks production line productivity. Indeed, too high silicon contents of the metal provoke clogging problems on these chemical etching lines. Therefore, elaboration of these grades must be performed with $CaO\text{-}Al_2O_3$ based slags, whose silica content must be controlled.

Information delivered by the thermodynamic model on a possible deviation from equilibrium of the silicon content will be given by comparing the oxygen activity computed through the reaction:

$$\underline{Si} + 2\underline{O} = SiO_2 \qquad [6]$$

to that given by the equivalent reaction for the main deoxidizer, i.e. aluminium.

The good estimation of the silica activities delivered by this model is demonstrated on Figure 3. On this Figure, we have plotted data concerning Invar grades and points relative to low-alloyed carbon steels elaborated in the vacuum tank degasser of the AG der Dillinger Hüttenwerke. In both cases, $CaO-Al_2O_3-SiO_2$ slags, close to lime saturation and with low SiO_2 contents, have been used. The Figure clearly shows that the vacuum treatment that has been used for the elaboration of this grade has reached a situation of slag/metal equilibrium.

Titanium partition

The Ti content control of Gammaphy grade (Fe-42 per cent Ni), used for the production of TV set frames, is crucial because of the effect of this element on the alloy thermal expansion. Here, too, modelling is useful to define the most appropriate slag/metal treatment. A large set of industrial data on slag/metal treatments has been used to propose a description of the Ti activity in the UIPM formalism using a 1st and a 2nd order interaction coefficient:

$$e_{Ti}^{Ni} = -\frac{688}{T} + 0.337 \text{ and } r_{Ti}^{Ni} = 0.0006 \qquad [7]$$

Since most of these treatments consist in long stirring treatments under vacuum, it appears legitimate to assume that, in these conditions, a state of chemical equilibrium has been reached. The accuracy of the temperature measurements for these industrial data is supposed to be around ±10°C.

These interaction coefficients give, for a Fe 36 per cent Ni alloy, a value of 0.2 for f_{Ti}^{Ni} at 1550°C close to the value of 0.29 proposed by Kawashita and Suito for a similar alloy composition (30 per cent Ni) but far from the value of 42 calculated with the expression proposed by Wada and Pehlke. Let us note, however, that this latter expression has been established for alloys with Ni contents lower than 20 per cent.

Figure 4 shows that the two models used here, Irsid model to predict TiO_2 activities of the slag phase and UIPM for the metal, are precise and quite versatile. Indeed, the figure contains, as mentioned before, data relative to a very wide range of metal composition:

- Ni free grades (low alloyed steels and ferritic stainless steels containing 12 or 18 per cent chromium)
- Cr free grades (Gammaphy alloys with 42 per cent nickel)
- alloys containing both chromium and nickel (25–65 per cent Ni and 16–22 per cent chromium).

Even though these alloys have all been produced with $TiO_x-Al_2O_3-CaO$ based slags, the compositions of these slags also differ quite a lot from one grade to the other: the ratio CaO/Al_2O_3 varies from 0.6 to 4, TiO_2 varies from a few per cent fractions to 15 per cent; SiO_2 from 0 to 25 per cent, MgO from 3 to 20 per cent and CaF_2 from 0 to 7 per cent.

Conclusion

The models presented in this paper have been proved to be useful to precisely monitor slag/metal treatment for the production of high quality Ni alloyed steels. Their development has required careful experimental studies, in particular, to determine the activities in Invar alloys, but has also greatly beneficiated from industrial data obtained in well stirred reactors such as the VOD-VAD unit of IUP.

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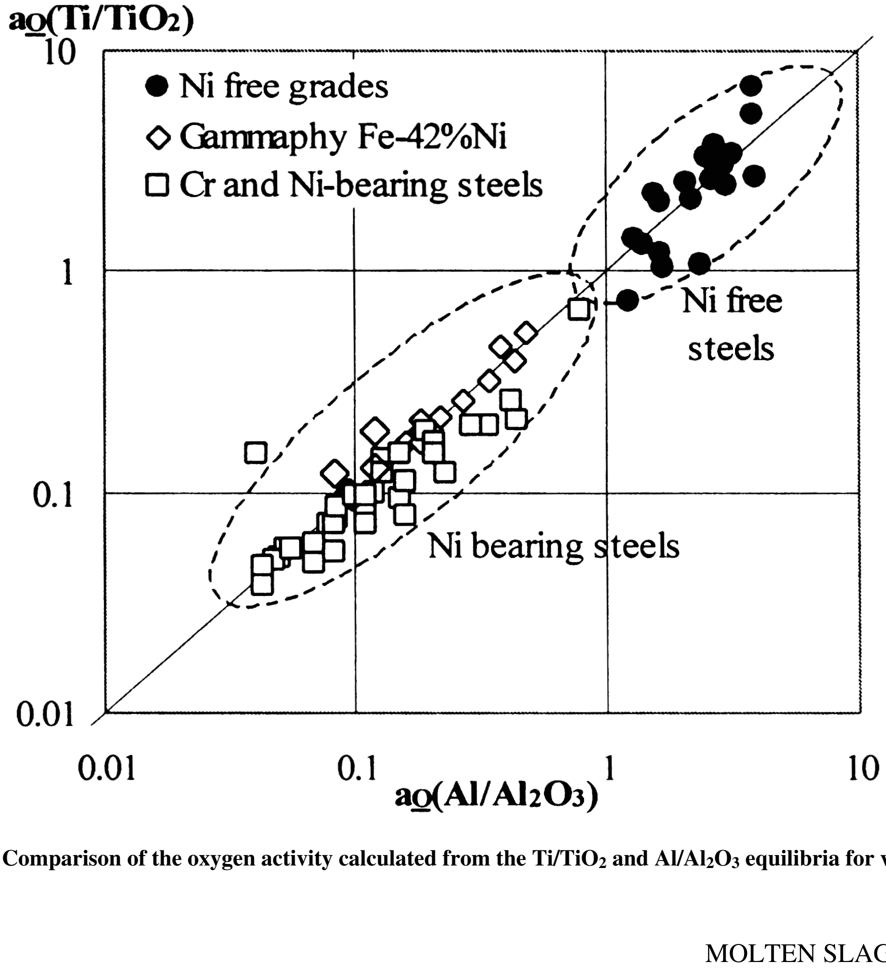

Figure 4. Comparison of the oxygen activity calculated from the Ti/TiO_2 and Al/Al_2O_3 equilibria for various steel grades

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