Reduction of Chromium from $\text{Al}_2\text{O}_3\text{--CaO--SiO}_2\text{--CrO}_x$ Slags by Carbon Dissolved in Liquid Iron

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The goal of this work is to investigate the reduction of chromium from a quaternary slag by carbon dissolved in liquid steel. Laboratory scale experiments were conducted to study the reduction of chromium oxides in the slag by carbon dissolved in the melt. These experiments were made under different conditions of slag basicity and amount of added carbon. Thermodynamic calculations based on Double Sublattice model were applied using the commercial software Thermo-Calc, with the IRSID database. The results obtained showed good correlation with practical and calculated results, making it possible to predict equilibrium conditions of the system and to determine the activities of chromium oxides in the slag.

KEY WORDS: thermodynamics; slags; chromium recovery.

1. Introduction

A big effort has been done to understand the behavior of chromium in slag. Chromium in slag is important essentially for the production of stainless steels and also Ferro-chromium because the processes require the reduction of chromium present in slags. Consequently, the understanding of chromium oxides activities in slag is necessary to control the process. The present work uses computational thermodynamics as a tool to analyze such systems.

The analysis of thermodynamic equilibrium of slags has been the object of study for many years, as much as for theoretical models as for the study of experimental data due to its great importance for the development of metallurgical processes.

Mathematical models for studying and mapping of chemical compositions and relationships of thermodynamic equilibrium have been developed by several studies.^{1–25)} Since the 1950s^{1,2)} these models have been detailed and perfected.

The main results of the thermodynamic slag models determine the phases predicted by the equilibrium. The phase diagrams and the activity of all the components can be determined from these models, as well as the entropies and partial molar entropy.

In addition to establishing thermodynamic properties, it is eventually necessary to validate the resulting data of the mathematical models with experimental data. The main validation objective is to verify the model applicability and reproducibility for the entire composition range of interest for specific study.

A critical analysis of the progress in theoretical studies on slag modeling was done by Jiang *et al.*³⁾ comparing models derived from physical parameters, thermodynamic parameters and structural slag models. Structural models of slag

(such as the double sub-lattice model) present good correlation with real results of measured parameters in slags.

One of the first and main thermodynamic slag models was the Flood and Grjotheim²⁾ model, from which derives an entire research line in slag modeling. The development of this model resulted in the Double Sub-lattice³⁾ model, which was finally perfected to the Double Sub-lattice model with the presence of oxisulphides,⁴⁾ considering the formation and the interaction between cationic and anionic cells.

The Quasi-chemical model and its modifications and improvements also stand out as a model for other software also used for thermodynamic calculations of slag equilibrium (*i.e.* Factsage). The original Quasi-chemical model was described by Pelton.⁶⁾ Developments of this model for ionic liquids were described by Pelton *et al.*^{6–8)} and Chartrand *et al.*⁹⁾ in subsequent works. These studies showed the expansion of the original model for binary solutions,⁷⁾ followed by its generalization for the case of systems containing multi-component solutions;⁸⁾ this model is still been applied for specific cases of solid solutions in which the number of lattices and coordination numbers remain constant. Next, an expansion of the Quasi-chemical model was developed for the treatment of solutions involving double sub-lattice.⁹⁾ The organization of short distance of the closer pair of neighbors was treated for liquid solutions, considering the neighbors' interaction of second order. Finally a simplification was established¹⁰⁾ with the use of the quadruplet approach to simultaneously treat the first and the second sub-lattice of closer neighbors.

2. Objective

The objective of this work is to investigate the reduction of chromium from a quaternary slag by carbon dissolved in

liquid steel.

3. Methodology

The slags of this work are in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system. These slags were reduced by the carbon present in liquid iron.

3.1. Preparation of the Synthetic Slag

The slags used for the experiments have two distinct chemical compositions: one with basicity 0.5 and the other with basicity 1.0. The basicity calculation was based on the following expression:

$$B = \frac{\text{wt\%CaO} + \text{wt\%MgO}}{\text{wt\%Al}_2\text{O}_3 + \text{wt\%SiO}_2} \dots\dots\dots (1)$$

Laboratory reagents of analytical purity were used for the preparation of these slags. The slags were pre-melted in a vertical laboratory furnace using platinum crucibles. After cooling, the slags were ground up.

The composition of the slags aimed at 20% of Cr_2O_3 , basicities of 0.5 and 1.0 and melting point below 1600°C . The possible liquidus temperatures were estimated in order to choose the slag composition, to guarantee complete slag melting during the experiments.

Ternary diagrams were used to estimate the *liquidus* temperatures of the produced slags. The available diagrams in the literature²⁶⁾ do not present $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system projection, therefore the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ diagram was chosen and later, the $\text{CaO-SiO}_2\text{-Cr}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ systems were used, to infer the Cr_2O_3 influence in the *liquidus* temperature. The $\text{Cr}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-MgO}$ systems were also considered to evaluate the slag *liquidus* temperature.²⁶⁾

From these data, it was possible to choose the slag chemical compositions. The chemical compositions used are presented in **Table 1**.

3.2. Description of the Experimental Apparatus

A vertical laboratory furnace was used, heated by electrical resistance with nominal heating capacity up to 1700°C .

A tube of 99.7% alumina was used as retort. The tube was 808 mm in length, 69 mm external diameter and 9 mm thickness. A stainless steel flange was set up in the extremities of the tube, allowing control of the atmosphere inside the furnace. Inside the tube, the crucible was held and positioned by a support made of refractory material during the experiments. The height of the crucible inside the furnace was defined according to the reading of the furnace thermal profile; in other words, in the region of the highest temperatures. **Figure 1** presents a schematic diagram of this assembly.

3.3. Experiments of Reduction of Cr Present in the Slag

For each one of the experiments, loads of approximately

350 g of steel SAE 1020 were prepared. The slag reducing agent was loaded, together with the steel, in the cold charge. These charges were prepared in alumina crucibles. The chemical composition of the steel can be seen in **Table 2**.

Carbon was used as a reducing agent. Carbon was added in the form 98% purity graphite.

In each test, the retort was initially purged with argon and from that point onwards a continuous flow of argon maintained inert atmosphere inside the retort. Next, the crucible containing the metallic load was introduced into the furnace at 900°C ; the temperature was raised to $10^\circ\text{C}/\text{min}$ up to 1600°C . This temperature was held for 60 minutes in order to stabilize the bath temperature.

The experimental procedure consisted of adding pre-melted synthetic slag to the metallic bath of steel SAE 1020 with the reducing agent dissolved, and in the removal of steel samples for analysis of chemical composition in defined intervals.

The slag amount used in all tests maintained the relationship of 1:20 slag/metal, which resulted in approximately 20 g of slag per run. For the slag addition directly onto the melted bath, the whole slag mass was put on a boat-shaped alumina crucible. Soon afterwards a tube of stainless steel was introduced in the furnace reaching close to the bath level. The slag was transferred to the surface of the metallic bath. At the end of this operation, the stainless steel tube was removed from the furnace. After the slag meltdown the countdown began for the removal of samples. The intervals for sample removals were: 0.5, 1, 1.5, 2, 3, 5, 8, 11, 14 and 17 minutes.

Vacuum sealed quartz samplers were used. The samples obtained weighed about 6 g.

The tests used two slag basicities, with the reducing agent added in stoichiometric proportion to the chromium oxide present in the slag and with 20% of excess of reducing agent. The stoichiometry was calculated according to Eq. (2). The tests are shown in **Table 3**.

Fig. 1. Schematic diagram of the experimental apparatus.

Table 2. Chemical composition of the used steel (mass %).

C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu
0.16	0.10	0.38	0.012	0.008	0.02	0.01	0.01	0.015	0.11

Table 1. Chemical composition of the used slags (mass %).

Basicity	CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Cr ₂ O ₃ (%)	Estimated liquidus (°C)
0.5	26.7	43.3	10.0	20.0	1600°C
1.0	40.0	30.0	10.0	20.0	1300°C

Table 3. Systematic tests.

Test	Amount of C	Basicity
CS05	Stoichiometric	0.5
CE05	20% excess	0.5
CE10	20% excess	1.0

Fig. 2. Concentration variations of C, Si and Cr as function of time for CS05.

Fig. 3. Concentration variations of C, Si and Cr as function of time for CE05.

Fig. 4. Concentration variation of C, Si and Cr as function of time for CE10.

4. Results and Discussion

The results of the alloy elements variation against the reaction time are shown in **Figs. 2 to 4**.

In general, it can be seen that the carbon and silicon content initially decrease, while the chromium concentration grows. The chromium incorporation speed decreases in the proportion that the amount of available chromium in the slag decreases.

Ternary diagrams were used to verify that the slag was always completely liquid during the test.

Fig. 5. Concentration variation of Cr in the steel as function of the time in the tests CE05 and CE10.

Fig. 6. Cr content variation in the steel as function of time in the tests CS05 with slag basicity 0.5 (tests CS05 and CE05).

4.1. Influence of Slag Basicity

By establishing the reducing agent as a fixed parameter, the effect of the slag basicity can be observed in the chromium recovery. The data stratification for this comparison is shown in **Fig. 5**.

By comparing the different slag basicities, a greater chromium recovery is observed for the tests with lower slag basicity.

In general, steels with chromium content between 0.3% to 3.0% have properties for high performance applications in mechanical construction.^{27,28)} Therefore, the secondary refining processes of these steels use high basicity slags for better control of the microinclusions present in the steel.^{29,30)} Hence, a specific evaluation of the system in question is necessary not only to optimize the chromium recovery but also to not affect the specified characteristics for the final product.

4.2. Effect of the Amount of Reducing Agent

In order to evaluate the influence of the reducing agent amount, the slag basicity was fixed. **Figure 6** shows the chromium content curves in the steel as function of time for the tests.

By comparing the curves, a greater chromium recovery is observed when excess carbon was applied.

4.3. Thermodynamics of the System

Considering the system involving iron, carbon, silicon, chromium and oxygen, the following is a list of equations for the reduction of chromium oxides present in the slag by carbon dissolved in the metallic bath, where the notation

between parentheses means dissolved elements in the slag and the underlined means dissolved elements in the metallic bath:

In order to determine which of these reactions are thermodynamically spontaneous at test temperature, it is necessary to calculate the ΔG° of the reactions.

ΔG° of each equation was initially determined at 1873 K,

Table 4. Values of ΔG° 1873 for the reactions involved in the reduction reactions of the slag chromium oxides.

Reaction	ΔH° (cal)	$-\Delta S^\circ$ (cal/K)	ΔG°_{1873} (cal)
$2 (\text{Cr}_2\text{O}_3) + 3 \underline{\text{Si}} = 4 \underline{\text{Cr}} + 3 (\text{SiO}_2)$	-114.220	4.56	-106.924
$2 (\text{Cr}_2\text{O}_3) + \underline{\text{Si}} = 4 (\text{CrO}) + (\text{SiO}_2)$	-3.820	-16.30	-29.900
$2 (\text{CrO}) + \underline{\text{Si}} = 2 \underline{\text{Cr}} + (\text{SiO}_2)$	-55.200	10.42	-38.528
$2 (\text{Cr}_2\text{O}_3) + 3 \underline{\text{C}} = 4 \underline{\text{Cr}} + 3 \text{CO}_2$	247.190	-118.61	57.414
$(\text{Cr}_2\text{O}_3) + 3 \underline{\text{C}} = 2 \underline{\text{Cr}} + 3 \text{CO}$	183.310	-120.61	-9.666
$2 (\text{Cr}_2\text{O}_3) + \underline{\text{C}} = 4 (\text{CrO}) + \text{CO}_2$	116.650	-57.35	24.890
$(\text{Cr}_2\text{O}_3) + \underline{\text{C}} = 2 (\text{CrO}) + \text{CO}$	78.230	-49.10	-330
$2 (\text{CrO}) + \underline{\text{C}} = 2 \underline{\text{Cr}} + \text{CO}_2$	65.270	-30.63	16.262
$(\text{CrO}) + \underline{\text{C}} = \underline{\text{Cr}} + \text{CO}$	52.540	-35.75	-4.660
$(\text{Cr}_2\text{O}_3) + 3 \text{CO} = 2 \underline{\text{Cr}} + 3 \text{CO}_2$	63.880	2.00	67.080
$(\text{CrO}) + \text{CO} = \underline{\text{Cr}} + \text{CO}_2$	12.730	5.12	20.922
$(\text{Cr}_2\text{O}_3) + 3 \underline{\text{Fe}} = 2 \underline{\text{Cr}} + 3 (\text{FeO})$	81.730	-20.62	48.738
$(\text{Cr}_2\text{O}_3) + \underline{\text{Fe}} = 2 (\text{CrO}) + (\text{FeO})$	44.370	-16.23	18.402
$(\text{CrO}) + \underline{\text{Fe}} = \underline{\text{Cr}} + (\text{FeO})$	18.680	-2.87	14.088
$(\text{SiO}_2) + \underline{\text{C}} = \underline{\text{Si}} + \text{CO}_2$	187.620	-61.42	89.348
$(\text{SiO}_2) + 2 \underline{\text{C}} = \underline{\text{Si}} + 2 \text{CO}$	160.280	-81.92	29.208
$(\text{SiO}_2) + 2 \text{CO} = \underline{\text{Si}} + 2 \text{CO}_2$	147.810	-20.55	114.930

starting from the thermodynamic compilation data made by Turkdogan.³¹⁾ The obtained results for the calculations of ΔG° at 1873 K are shown in **Table 4**.

The henryan activity was used for elements in diluted solution *e.g.* for carbon, chromium and silicon dissolved in the steel. The raoultian activity was adopted for oxides present in slag and for liquid iron. The Eqs. (20) to (36) present ΔG expressions for Eqs. (3) to (19), where:

$\Delta G_{(n)}$ = Gibbs free energy of the equation n.

R = gas constant

T = temperature (K) = 1873 K

$$\Delta G_{(3)} = \Delta G_{(3)}^0 + RT \ln \frac{a_{\text{SiO}_2}^3 \cdot h_{\text{Cr}}^4}{a_{\text{Cr}_2\text{O}_3}^2 \cdot h_{\text{Si}}^3} \dots\dots\dots (20)$$

$$\Delta G_{(4)} = \Delta G_{(4)}^0 + RT \ln \frac{a_{\text{SiO}_2} \cdot a_{\text{CrO}}^4}{a_{\text{Cr}_2\text{O}_3}^2 \cdot h_{\text{Si}}^3} \dots\dots\dots (21)$$

$$\Delta G_{(5)} = \Delta G_{(5)}^0 + RT \ln \frac{a_{\text{SiO}_2} \cdot h_{\text{Cr}}^2}{a_{\text{CrO}}^2 \cdot h_{\text{Si}}^3} \dots\dots\dots (22)$$

$$\Delta G_{(6)} = \Delta G_{(6)}^0 + RT \ln \frac{P_{\text{CO}_2}^3 \cdot h_{\text{Cr}}^4}{a_{\text{Cr}_2\text{O}_3}^2 \cdot h_{\text{C}}^3} \dots\dots\dots (23)$$

$$\Delta G_{(7)} = \Delta G_{(7)}^0 + RT \ln \frac{P_{\text{CO}}^3 \cdot h_{\text{Cr}}^2}{a_{\text{Cr}_2\text{O}_3} \cdot h_{\text{C}}^3} \dots\dots\dots (24)$$

$$\Delta G_{(8)} = \Delta G_{(8)}^0 + RT \ln \frac{P_{\text{CO}_2} \cdot a_{\text{CrO}}^4}{a_{\text{Cr}_2\text{O}_3}^2 \cdot h_{\text{C}}^3} \dots\dots\dots (25)$$

$$\Delta G_{(9)} = \Delta G_{(9)}^0 + RT \ln \frac{P_{\text{CO}} \cdot a_{\text{CrO}}^2}{a_{\text{Cr}_2\text{O}_3} \cdot h_{\text{C}}^3} \dots\dots\dots (26)$$

$$\Delta G_{(10)} = \Delta G_{(10)}^0 + RT \ln \frac{P_{\text{CO}_2} \cdot h_{\text{Cr}}^2}{a_{\text{CrO}}^2 \cdot h_{\text{C}}^3} \dots\dots\dots (27)$$

$$\Delta G_{(11)} = \Delta G_{(11)}^0 + RT \ln \frac{P_{\text{CO}} \cdot h_{\text{Cr}}}{a_{\text{CrO}} \cdot h_{\text{C}}} \dots\dots\dots (28)$$

$$\Delta G_{(12)} = \Delta G_{(12)}^0 + RT \ln \frac{P_{\text{CO}_2}^3 \cdot h_{\text{Cr}}^2}{a_{\text{Cr}_2\text{O}_3} \cdot P_{\text{CO}}^3} \dots\dots\dots (29)$$

$$\Delta G_{(13)} = \Delta G_{(13)}^0 + RT \ln \frac{P_{\text{CO}_2} \cdot h_{\text{Cr}}}{a_{\text{CrO}} \cdot P_{\text{CO}}} \dots\dots\dots (30)$$

$$\Delta G_{(14)} = \Delta G_{(14)}^0 + RT \ln \frac{a_{\text{FeO}}^3 \cdot h_{\text{Cr}}^2}{a_{\text{Cr}_2\text{O}_3} \cdot a_{\text{Fe}}^3} \dots\dots\dots (31)$$

$$\Delta G_{(15)} = \Delta G_{(15)}^0 + RT \ln \frac{a_{\text{FeO}} \cdot a_{\text{CrO}}^2}{a_{\text{Cr}_2\text{O}_3} \cdot a_{\text{Fe}}} \dots\dots\dots (32)$$

$$\Delta G_{(16)} = \Delta G_{(16)}^0 + RT \ln \frac{a_{\text{FeO}} \cdot h_{\text{Cr}}}{a_{\text{CrO}} \cdot a_{\text{Fe}}} \dots\dots\dots (33)$$

$$\Delta G_{(17)} = \Delta G_{(17)}^0 + RT \ln \frac{P_{\text{CO}_2} \cdot h_{\text{Si}}}{a_{\text{SiO}_2} \cdot h_{\text{C}}} \dots\dots\dots (34)$$

$$\Delta G_{(18)} = \Delta G_{(18)}^0 + RT \ln \frac{P_{\text{CO}}^2 \cdot h_{\text{Si}}}{a_{\text{SiO}_2} \cdot h_{\text{C}}^2} \dots\dots\dots (35)$$

$$\Delta G_{(19)} = \Delta G_{(19)}^0 + RT \ln \frac{P_{CO_2}^2 \cdot h_{Si}}{a_{SiO_2} \cdot P_{CO}^2} \dots\dots\dots (36)$$

To calculate the $\Delta G_{(n)}$ of each reaction, it was then necessary to obtain data regarding the following variables:

- Henryan activities of dissolved carbon, chromium and silicon.
- Raoultian activities of the SiO_2 , Cr_2O_3 , CrO and FeO in the slag.
- Partial pressures of CO and CO_2 in the gaseous phase.

The Henryan activity for dissolved carbon, chromium and silicon in and their activity coefficients with interaction coefficients of the first order were calculated according to the data of Sigworth and Elliot.³²⁾

The calculation results of the activity coefficients and the Henryan activities for the final conditions found in the experiments are shown in **Table 5**.

The Double Sub-Lattice model for liquid oxysulphides⁵⁾ was applied to determine the activities of the elements present in the slag and partial pressure of the gases involved in the reactions. **Table 6** shows the conditions used for each test.

These calculations were made using the SLAG module of the Thermo-Calc software, through the minimization of the free energy of the system. An L version was used whose database for slags is IRSID.³³⁾ Initially, the mass and chemical composition data, and bath temperature were supplied for each experiment. Next, the slag additions were computed and the software calculated the conditions of minimum free energy for the system, which represents the thermodynamic equilibrium.³⁴⁾

The values obtained for the activities of the elements present in slag and partial pressures of gases involved in the equilibrium are presented in **Table 7**.

Once the activities of all of the elements involved in the

system equilibrium are defined, it is possible to calculate the $\Delta G_{(n)}$ for each of the reactions from 3 to 19. **Table 8** presents the calculation results of ΔG for each of the tests.

From these results of Gibbs' free energy, it is observed that the reactions that occur spontaneously in the system are the same for all tests.

Considering the Gibbs free energies for the described reactions, one can suppose that reduction of Cr_2O_3 should occur in two stages: firstly the CrO is formed and soon after the chromium is dissolved into the bath. According to this hypothesis, CrO is the corresponding intermediate phase formed during Cr_2O_3 reduction. Under equilibrium conditions, this phase would supposedly have a very low activity, given its low concentration in the slag. Consequently the reactions that consume CrO would cease and therefore the bath would reach equilibrium.

Once the equilibrium equations are defined and the activities of the elements present in the phases of the system calculated, it was possible to make the final equilibrium calculations for the conditions of each experiment. These calculations were done using the Double Sub-Lattice model for liquid oxysulphides,⁵⁾ defined in the Thermo-Calc software as Kapoor-Frohberg-Gaye model for liquid oxides.³⁵⁾

The calculations development was carried out directly using Thermo-Calc. The SLAG (IRSID in the Thermo-Calc L version) database was used which is a compilation of slag

Table 7. Calculated values for element activities in the slag and partial pressure of gases.

Test	a_{FeO}	a_{SiO_2}	$a_{Cr_2O_3}$	a_{CrO}	P_{CO}	P_{CO_2}
CS05	9.543E-02	5.089E-01	1.222E-03	3.697E-14	9.893E-01	1.075E-02
CE05	8.928E-02	5.056E-01	9.948E-04	3.448E-14	9.899E-01	1.007E-02
CE10	6.858E-02	1.456E-01	4.552E-04	2.660E-14	9.922E-01	7.757E-03

Table 5. Activity coefficients and Henryan activities calculated for the test conditions.

Test	f_C	h_C	f_{Si}	h_{Si}	f_{Cr}	h_{Cr}
CS05	1.01	0.10	1.06	0.06	0.97	0.45
CE05	1.03	0.16	1.08	0.06	0.96	0.46
CE10	1.04	0.09	1.09	0.20	0.98	0.20

Table 6. Initial values used for the equilibrium calculation of each experiment.

	Unity	CS05	CE05	CE10
b(Fe)	g	354.96	354.98	302.95
w(C)	mass %	0.0028	0.0030	0.0033
w(Si)	mass %	0.0010	0.0010	0.0010
w(Cr)	mass %	0.00010	0.00010	0.00010
w(Al)	mass %	0.00015	0.00015	0.00015
N(CaO)	mols	0.0833	0.0833	0.1070
N(SiO_2)	mols	0.1261	0.1261	0.0749
N(Cr_2O_3)	mols	0.0230	0.0230	0.0197
N(Al_2O_3)	mols	0.0172	0.0172	0.0147

Table 8. Values of ΔG calculated for each experiment.

	CS05	CE05	CE10
$\Delta G_{(3)}$	-45.844	-44.044	-77.561
$\Delta G_{(4)}$	-432.682	-432.236	-439.144
$\Delta G_{(5)}$	193.403	194.080	180.776
$\Delta G_{(6)}$	70.126	66.337	63.600
$\Delta G_{(7)}$	34.571	30.553	34.211
$\Delta G_{(8)}$	-394.015	-395.431	-392.080
$\Delta G_{(9)}$	-197.155	-198.572	-195.220
$\Delta G_{(10)}$	232.070	230.884	227.840
$\Delta G_{(11)}$	115.871	114.570	114.724
$\Delta G_{(12)}$	35.554	35.785	29.389
$\Delta G_{(13)}$	116.199	116.314	113.116
$\Delta G_{(14)}$	41.577	41.803	35.402
$\Delta G_{(15)}$	-195.556	-195.558	-195.559
$\Delta G_{(16)}$	117.487	117.600	114.401
$\Delta G_{(17)}$	73.225	71.362	81.622
$\Delta G_{(18)}$	38.339	35.060	48.671
$\Delta G_{(19)}$	73.553	73.106	80.015

Fig. 7. Comparison between chromium content obtained experimentally and the equilibrium value calculated by the slag model of basicity 0.5 using stoichiometric carbon as reducing agent.

Fig. 8. Comparison between the chromium content obtained experimentally and the equilibrium value calculated by the slag model of basicity 0.5 using 20% excess stoichiometric carbon as reducing agent.

data in equilibrium with liquid iron done by IRSID.³⁶⁾

Curves of chromium content as a function of time for experimental and calculated results were plotted in the same figures in order to establish a comparison. The calculated chromium content is represented by a horizontal line. The experimental values are presented as a function of time so that the tendency of chromium stability at the end of the experiments can be observed. The experimental results are presented with error bars of around 0.02%, due to the errors of method of chemical analysis used to determine the chromium concentration in steel.

Figures 7 to 9 present the comparison between the experimental results of chromium content in steel as a function of time and the equilibrium concentration calculated. One can observe that 20 to 25 minutes is not enough to reach the equilibrium, consequently the final concentration of chromium would be a little higher than the presented in these Figures.

By comparing the results obtained experimentally and the calculated ones, one can observe a discrepancy between the calculated values and those obtained in the laboratory.

A probable source of experimental error concerns the steel sampling which uses immersion samples. The bath in the laboratory piece-of-equipment had a mass of approximately 350 g and was initially in contact with about 17.5 g of slag. This slag initially contained approximately 20% of Cr_2O_3 and was the main chromium source of the system. When taking the steel sample, it is possible that a small amount of slag has been joined to the sampler external wall of the sampler. If this loss of slag mass occurs in the first samples, the chromium of this removed slag would no longer be in the system; therefore it would not be recovered by the steel. A loss of about 3.5 g of slag, in the first two samples, could cause a variation of about 0.07% in the total chromium recovered by the steel.

Another probable source of error in the results is related to the variation of bath mass during sampling. Considering that each removed sample from the bath has approximately 3 g of mass, approximately 30 g of the original 350 g of the bath were removed by the end of the experiment. Considering that hypothetically half of the total chromium was incorporated before the removal of the samples, variation of approximately 0.02% in the final chromium content would be observed.

The thermodynamic calculation does not consider varia-

Fig. 9. Comparison between the chromium content obtained experimentally and the equilibrium value calculated by the slag model of basicity 1.0 using 20% excess carbon as reducing agent.

tion in the system total mass; therefore it does not consider the chromium concentration effect due to the reduction of the total bath mass.

Thermodynamic calculation also did not consider manganese presence in the metallic bath. According to Sigworth and Elliot,³²⁾ manganese increases silicon activity in the bath, as long as the $e_{\text{Si}}^{\text{Mn}}$ interaction parameter is 0.02, and reduces carbon activity, as e_{C}^{Mn} is equal to -0.012 , increasing the dissolved carbon content in the bath. By virtue of this C content increase, there is another increase in the silicon activity, as long as the interaction coefficient e_{Si}^{C} is 0.18. Increasing silicon activity in the metallic bath favors Cr_2O_3 and CrO reduction, moving the equilibria towards the formation of more reduced chromium species. Hence, the presence of the manganese dissolved in the bath can change the system equilibrium and could increase the chromium recovered for the bath.

The activity coefficients of FeO and MnO are influenced by the Cr_2O_3 content in the slag. Jo and Kim³⁷⁾ studies show that the Cr_2O_3 content in the slag quickly initially increases the γ_{FeO} . On the other hand, the γ_{MnO} decreases abruptly with the Cr_2O_3 increase in the slag, up to around 5%, remaining practically constant after this level. Also, increasing slag basicity decreases γ_{FeO} .³⁷⁾

5. Conclusions

- (1) Based on the Double Sub-lattice model and also

using the IRSID database of Thermo-Calc, an approach tried to study the behavior of a quaternary slags $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-CrO}_x$ under reducing conditions. The experimental and calculated results presented a difference inferior to 10%. Thermodynamic calculations also allowed the determination of chromium oxides present in the slag.

(2) The increasing of the reducing agent amount causes the increasing in the chromium recovery from the slag.

(3) Cr_2O_3 is the main chromium oxide present in the studied slags under low oxygen potential established due to the reducing conditions.

(4) The increasing of the slag basicity causes a decrease in chromium recovery. The decrease in chromium recovery was a consequence of the reduction in chromium oxide activity in the slag.

REFERENCES

- 1) H. Flood and A. Muan: *Acta Chem. Scand.*, **4** (1950), 395.
- 2) H. Flood and K. Grjotheim: *J. Iron Steel Inst.*, (1952), 64.
- 3) G. Jiang, K. Xu and S. Wei: *ISIJ Int.*, **33** (1993), 20.
- 4) H. Gaye and J. Welfringer: Proc. 2nd. Int. Symp. on Metallurgical Slags and Fluxes, Met. Soc. of AIME, Warrendale, PA, (1984), 357.
- 5) H. Gaye and J. Lehmann: Proc. 5th Int. Conf. Molten Slags Flux. Salts, The Iron Steel Soc., Warrendale, PA, (1997), 27.
- 6) A. D. Pelton: Adv. Phys. Chem. Proc. Met., Academic Press: San Diego, CA, (1997), 87.
- 7) A. D. Pelton, S. A. Degterov, G. Eriksson, C. Robelin and Y. Dessureault: *Metall. Mater. Trans.*, **31B** (2000), 651.
- 8) A. D. Pelton and P. Chartrand: *Metall. Mater. Trans.*, **32A** (2001), 1355.
- 9) P. Chartrand, A. D. Pelton: *Metall. Mater. Trans.*, **32A** (2001), 1397.
- 10) A. D. Pelton, P. Chartrand and G. Eriksson: *Metall. Mater. Trans.*, **32A** (2001), 1409.
- 11) I-H. Jung, S. A. Degterov and A. D. Pelton: *Metall. Mater. Trans.*, **35B** (2004), 493.
- 12) L. C. Oertel and A. Costa e Silva: *Calphad*, **3** (1999), 379.
- 13) H. Gaye, C. Gatellier, M. Nadif, P. V. Riboud, J. Saleil and M. Faral: *Rev. Metal.*, **84** (1987), 759.
- 14) C. Gatellier, H. Gaye, J. Lehmann, J. Bellot and M. Moncel: *Rev. Met.*, **3** (1992), 361.
- 15) G. Eriksson and A. D. Pelton: *Metall. Mater. Trans.*, **24B** (1993), 807.
- 16) K. Yamaguchi, S. Ueda and Y. Takeda: *Scand. J. Metall.*, **34** (2005), 164.
- 17) E. Jak, S. Degterov, P. C. Hayes and A. D. Pelton: *Can. Metall. Q.*, **37** (1998), 41.
- 18) O. Esin and V. Kozheurov: *Chem. Abst.*, **43** (1949), 2908.
- 19) J. Chipman, J. B. Gero and T. B. Winkler: *JOM*, **188** (1950), 341.
- 20) R. H. Rein and J. Chipman: *Trans. Met. Soc. AIME*, **233** (1965), 415.
- 21) J. F. Elliot, D. C. Lynch and T. B. Braun: *Metall. Trans.*, **6B** (1975), 495.
- 22) M. Blander: *Metall. Trans.*, **8B** (1977), 529.
- 23) M. A. Hillert: *Metall. Trans.*, **17A** (1986), 1878.
- 24) G. A. Haralampieva and I. M. Galabova: *Calphad*, **18** (1994), 245.
- 25) P. Herasymenko: *Trans. Faraday Soc.*, **34** (1938), 1245.
- 26) Slag Atlas, 2nd ed., Verlag Sathleisen GmbH, Düsseldorf, (1995), 21.
- 27) SAE Handbook, Society of Automotive Engineers Inc., Warrendale, PA, (2005), 1.13.
- 28) SAE Handbook, Society of Automotive Engineers Inc., Warrendale, PA, (2005), 1.18.
- 29) T. A. Engh: Principles of Metal Refining, McGraw Hill, London, (1992), 181.
- 30) K. Beskow, J. Jia, C. H. P. Lupis and D. Sichen: *Ironmaking Steelmaking*, **29** (2002), 427.
- 31) E. T. Turkdogan: Physical Chemistry of High Temperature Technology, Academic Press, New York, (1980), 1.
- 32) G. K. Sigworth and J. F. Elliot: *Met. Sci.*, **8** (1974), 298.
- 33) THERMO-CALC SOFTWARE AB. Available online: <http://www.thermocalc.se/Products/Databases_TCC_TCW.html#>. (02/11/2006).
- 34) TCC – THERMO-CALC SOFTWARE USER'S GUIDE – VERSION Q, Thermo-Calc Software AB, Stockholm, Sweden, 2004. Available online: <http://www.thermocalc.se/Download/Man_ex_TCC.html#>. (02/20/2006).
- 35) J-O. Andersson, T. Helander, L. Höglund, P. Shi and B. Sundman: *Calphad*, **26** (2002), 273.
- 36) B. Sundman, B. Jansson and J-O. Andersson: *Calphad*, **9** (1985), 153.
- 37) S-H. Jo and S-H. Kim: *Steel Res.*, **71** (2000), 281.