EVALUATION OF THE ROLE OF SLAG CHEMISTRY AND CHEMICAL INTERACTION IN EAF FOR STAINLESS STEEL PRODUCTION

Blazenko Korousic, Institute for Metals and Technology, Ljubljana, Slovenia
Joze Triplat, Acroni d.o.o. Jesenice, Slovenia,
and **Alojz Rozman**, Metal Ravne, Ravne na Koroskem, Slovenia

Abstract:

One of the most significant problems in the production of stainless steels is the optimization of conditions in the electric arc furnace (EAF) to prevent the heavy oxidation of Cr. Since in the making of stainless steels the behaviour of Cr is of fundamental importance, researchers from many parts of the world have been involved in studies investigating the mechanism for oxidation of Cr to Cr2O3 by air or/and slag oxides present in the EAF.
In an attempt to control Cr oxidation, slag chemistry and processing parameters (melt temperature, holdig time and slag chemistry) have been investigated using 90- and 50-ton EAF. Many samples of stainless steels (mostly AISI 304, AISI 316 and AISI D3) and slags were analysed to determine the role of the different reactions between the Cr2O3, FeO and the like in the slag, as well as between Al, Si, Mn, Cr and C in the melt. Experiments were conducted during the meltdown stage and the prolonged heating time prior to tilting. Finally, an analysis, based on the thermodynamically considerations was done.

Key words:
Stainless steels, oxidation, slags, activity, modeling

1 Introduction

Stainless steels are melted almost exclusively in electric furnaces. During the last decades there has been an increasing demand among stainless steel producers to optimize metallurgical processes, and to understand more exactly the factors affecting oxidation rate of some elements during the melting of row materials in electric furnaces. Chromium oxidation during the meltdown is critical, and dissolved silicon content in the melt should be sufficient to protect chromium from oxidation. During charging and other early stages of melting, surface oxidation of steel scrap occurs. This layer supplemented by additions of oxygen bearing components as well as slag components included in alloys (e.g. Cr2O3 in FeCrHC) contribute to an intensive oxidation of other elements after liquefaction of the metallic charge.
The study presented in this article is based on the previous research work [1,4]. Its purpose was to simulate the melting EAF process in order to control and optimize the present practice, and finally to enable a reduction of the costs for different melting route by stainless steels production. In this paper, we apply the thermodynamics of the reactions of oxidation/reduction of high-chromium steels. A comparison between modeling simulations and industrial data from a 90- and 50-ton EAFs is presented.

2 Characteristics of the melting stainless steel in EAF

The electric arc furnace has developed over the years towards a high efficiency melting machine. The melting of stainless steels in an electric arc furnace, has been favoured in last years with the help of oxygen injection, which oxidize beside carbon

also chromium, silicon and other elements. Normally, in the usual practice, lime and dolomite (or MgO) are put in the bucket, which during the melting period assists in the slag formation and in the elimination of phosphorus and sulphur. In order to create advantageous conditions for refractory wear, the total charged amount of CaO + MgO may vary from 40 to 60 kg/ton steel. During the melting period (when 95 – 100 % of charged metallic material is melted), the main problem is how to control oxidation reactions in order to reduce the costs and electric energy, and to increase the productivity.

Studies of the underlying slag and melt chemistry and the process parameters have been made in order to developed improved practice [3,4]. However, the existing wide variations in practice indicate that many questions about the processes in EAF require clarification.

Process parameters like slag additions, melt chemistry, power input per ton, melt temperature after downmelt vary considerably. Scrap charges for a specific grade of stainless steel may vary considerably in the start concentration of chromium, nickel, manganese and silicon. Practical experience have shown that some differences between the charge consistency from low alloyed scrap + Cr-bearing alloys and remelting practice of high alloyed Cr-bearing charge materials exists, indicating importance of role of chemical composition of the melt, the slag, temperature and time of the furnace period.

3   Experimental

The scrap charge mix of row materials in steelwork ACRONI plant used for making stainless steels AISI 304 and AISI 316 can be divided in the two groups:

- **Group A:** Si contents (0.3-0.6 wt. %) – the most common practice ,
- **Group B:** Al contents (0.03 – 0.6 wt.%) – remelting stainless scrap contaminated with Al-bearing steels (small percentage of the entire charge numbers).

In order to study how input materials for charge mix influence on oxidation/reduction reactions, the trials on a production basis were made, starting with charges with high Si+Al contents, variable slag additions and melt temperature. At various times in last period of the EAF process, slag and metal samples have been taken and steel temperature was measured in various stages of the EAF process.

The averages melt composition for both groups after charge downmelt from some plant trials are summarized in **table 1**.

Figure 1 presents the correlation between Al- and Si-content in *'the first probe'* after the meltdown at the average melt temperature of 1580 °C. The presented data show that aluminium is the most effectively element in complex aluminium-silicon-manganese carbon-chromium system. In all analysed charges where aluminium content of the bath was over 0.04%, minimum silicon, manganese and chromium oxidation during the meltdown was observed. Oxygen blowing is common practice to oxidize both aluminium and silicon and this oxidizing phase of the process in EAF (the critical effect of initial temperature and the rate of oxygen injection) is fairly well understood.

It is common practice that during aluminium removal an extra amounts of CaO+MgO in the furnace is added, providing control of the optimal slag fluidity, but the slag weight increases rapidly. From the data shown in **Figure 1**, it is apparent that the reaction oxidation is determined by reaction between aluminium, silicon and oxygen. The measured Cr-content in *'the first probe'* (upper part of the diagram) should be compared with Cr-start values in the charge mix. As can be seen, the yield of Cr

resulted from the Cr-oxidation (Cr→ Cr2O3) is nearly 100%, for the Si-content over 0.25% and Al-content over 0.03% respectively.

In **Figure 2,** can be seen that the Cr-oxidation rate (ΔCr) at the end of meltdown follows approximately the thermodynamical conditions for the reaction [Si] + 2[O] = SiO2 (continuous line drawn in this figure). It should be noted that the scatter of the results is very high, indicating the influence of the process factors as the melt temperature, slag chemistry, metal chemistry an the like.

In order to evaluate the reactions between the melt and the slag at the end of downmelt stage and before the tapping, slag samples were taken. If a steel AISI 304 type is taken as an example, **Table 2** shows the slag chemistry in EAF after the meltdown.

In order to decrease the chromium losses during holding melt in the EAF, a normal way of the reducing the Cr2O3 content in the slag is carbon blowing or the proceeding slag reduction with Si. The collected data have shown (see **Figure 3**) that the reduction of Cr2O3 in the slag vary widely depending of the many factors.

4   Modeling of the elements oxidation

Let us present in short a thermodinamically model that was designed to introduce the improved EAF practice, as well as to optimize conditions for the melting of the stainless steels in EAF regarding Cr losses and refractory wear. Considerable variations in the start contents of charge naturally give an irregular and less predictable result, related to a specific plant and production program. It is not very interesting whether it is theoretically correct or not, the main thing is that it works. Below is briefly described an expedient model for the prediction of the elements oxidation in EAF.

The reaction mechanism for the oxidation of Cr may be proposed via the oxygen activity concept. For a given metal – slag system may be assumed that the oxygen activity at equilibrium is fixed for each corresponding reaction.

$$a_O = \sqrt[3]{\frac{a_{Al2O3}}{a_{Al}^2 * K_{Al}}} = \sqrt{\frac{a_{SiO2}}{a_{Si} * K_{Si}}} = \frac{a_{MnO}}{a_{Mn} * K_{Mn}} = \frac{p_{CO}}{a_C * K_C} = \sqrt[3]{\frac{a_{Cr2O3}}{a_{Cr}^2 * K_{Cr}}} \quad \textbf{En. 1}$$

At start of the oxidation process, the slag oxide activities may be assumed as hypothetical values (for example for a_{Al2O3}=1 and for a_{SiO2}=0.01 an so on). The activity of the elements as Al, Si, Mn, C and Cr will be calculated according known thermodynamical procedures[2]. The total CO-pressure is taken as constant, (for example 1 bar). The melt temperature loss factor takes the furnace geometry into account and is being used to calculate a new the temperature value during a time step of about 10 seconds.

In **Figure 4,** we present the computer simulation results for a case when the oxygen activity changes in equilibrium with various Al-, Si-, Mn-, C- and Cr-concentrations by 1600 °C. Initially, the melt composition of: 1%C, 0.6%Si, 1.2%Mn, 19%Cr, 810%Ni, 0.5%Mo and 0.6%Al is selected

So for this melt composition by 1600 °C, it may be assumed that by practical oxygen blowing rate about 24(Nm³/min), the oxygen activity at the beginning of the oxidation process will be determined obviously by the reaction:

$$2[Al]+3[O]=Al_2O_3 \qquad\qquad \textbf{En. 2}$$

During the Al-oxidation, the melt temperature increases from initially 1500 to 1680 °C, while activities of slag oxides also changes and oxidation direction flips from left

to right side. In case of the equilibrium, when oxygen activity reaches the equilibrium oxygen activity determined with silicon, start Si-oxidation (decreasing index of basicity). According to **Equation 1** this procedure continues, often simultaneously with the C- reaction, Mn – reaction and finally Cr - reaction. It is important to note, that the beginning of oxidation reactions depends on the temporary oxide-activity and of the melt/slag temperature.

Figure 5 shows the variation of the Si, Mn, C and Cr after the meltdown of stainless steel (AISI 304) with

- the initially composition: 1%C, 0.58%Si, 1.02%Mn, 19%Cr and 8.5%Ni,
- the slag activities $a_{SiO2}=0.1$ and $a_{MnO}=0.03$ and $a_{Cr2O3}=0.07$, and by
- the initially melt temperature about 1540 °

We have applied this model on the remelting practice of ledeburitic steels in EAF (for example type AISI D3) and become aware that use of this model enables better understanding of the oxidation Cr and V, and optimization of standard melting practice by changing the slag constituents, metallic mix content and amounts of the slag constituents in EAF.

In **Figure 6,** it is shown, that the improved technology applied in 50-ton EAF, during the melting of the ledeburitic steel with initially analysis **1.55 %C, 12.5%Cr** gives better Cr – yield. It was good agreement between predicted and measured data with smaller deviations in chemical analysis, which may be explained by better control chemical composition of the slag and the melt temperature control.

5 Conclusions

In this paper, an oxygen activity model was applied to explain the effect of the melt chemical composition and the slag, and second other process parameters on oxidation behaviour of some elements during meltdown in EAF furnace. The optimized process gives a better prediction and control of the melt chemical composition. Moreover, it enables savings on the alloying elements, with respect to the usual industrial data. The paper demonstrates that a relatively simple approach can be very useful in understanding melting processes in EAF where we are relatively far from thermodynamic conditions.

6 References

1. K.J.Filar,J.P.Bartos and G.H.Geiger:
   Chromium Recovery During the Manufacture of Stainless Steels,
   Journal of Metals, May 1968, pp. 51-55
2. Michael H:
   Oxygen activities in Cr-containing Fe and Ni-based melts,
   Steel Research 60, No.6, 1989, pp.
3. M.Görnerup,H.Jacobsson:
   Foaming Slag-Practice in Electric Stainless Steelmaking,
   Electric Furnace Conference Proceedings, 1997, pp.57-68
4. K.Gustafsson and R.Vikman:
   Chromium recovery from stainless steel EAF slag by carbon injection,
   4th European Electric Steel Congress, November 3-6, Madrid, Spain, 1992

Oxidation of Al and Si in EAF during melting AISI 304
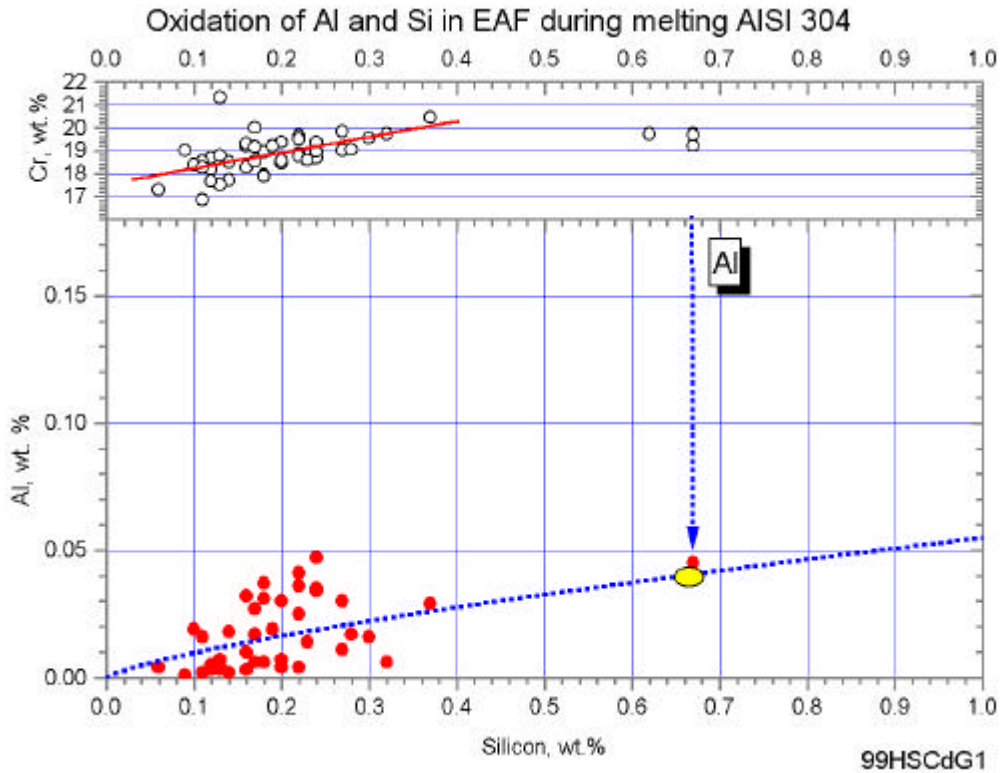
Figure 1 Correlation between the measured Al-, Si- and Cr contents in the melt after downmelt (first probe in EAF) for AISI 304 steels.

The influence of Si-content on the Cr-oxidation rate in EAF
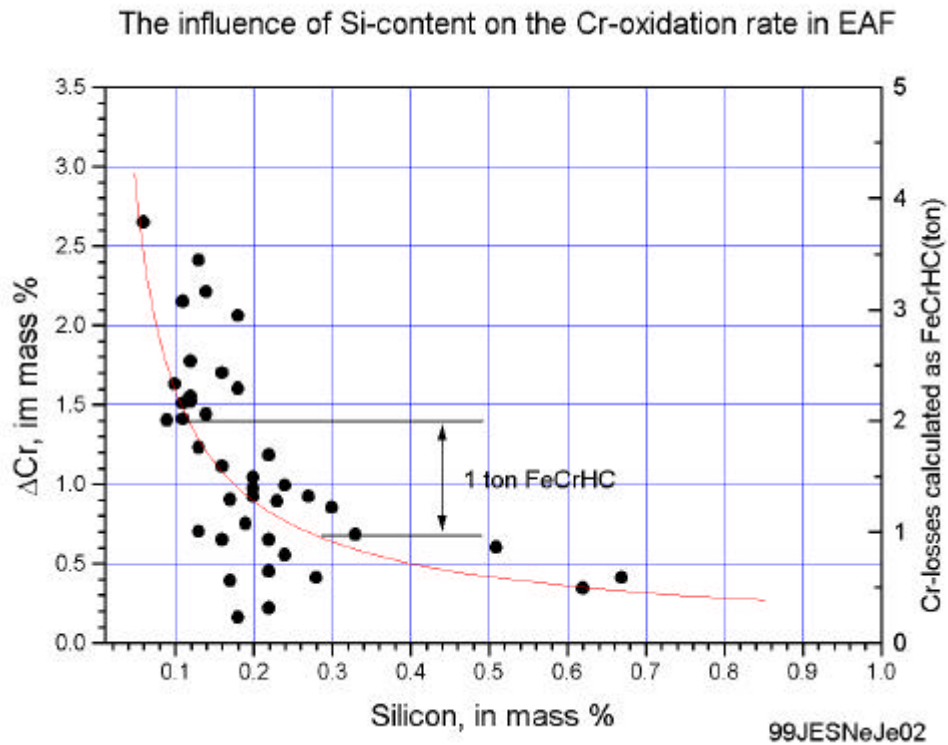
Figure 2 The influence of silicon content in the melt in the first probe in EAF on the oxidation rate of chromium in AISI 304 steels.
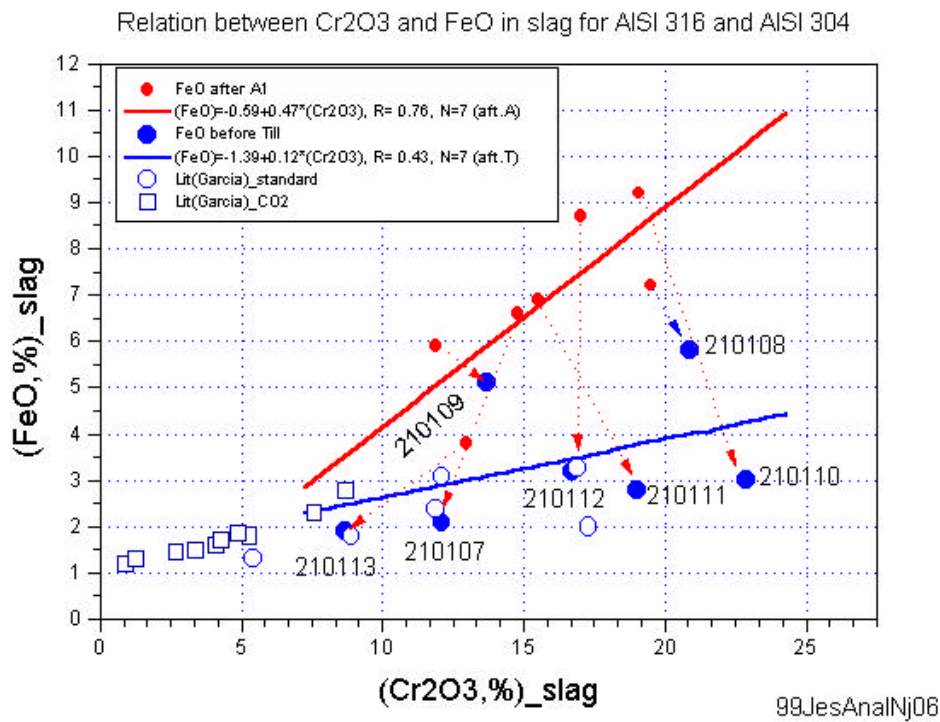
Figure 3 The relation between the FeO- and Cr2O3-content in slag after the meltdown and before tapping into the transfer ladle (AISI 304 steels).
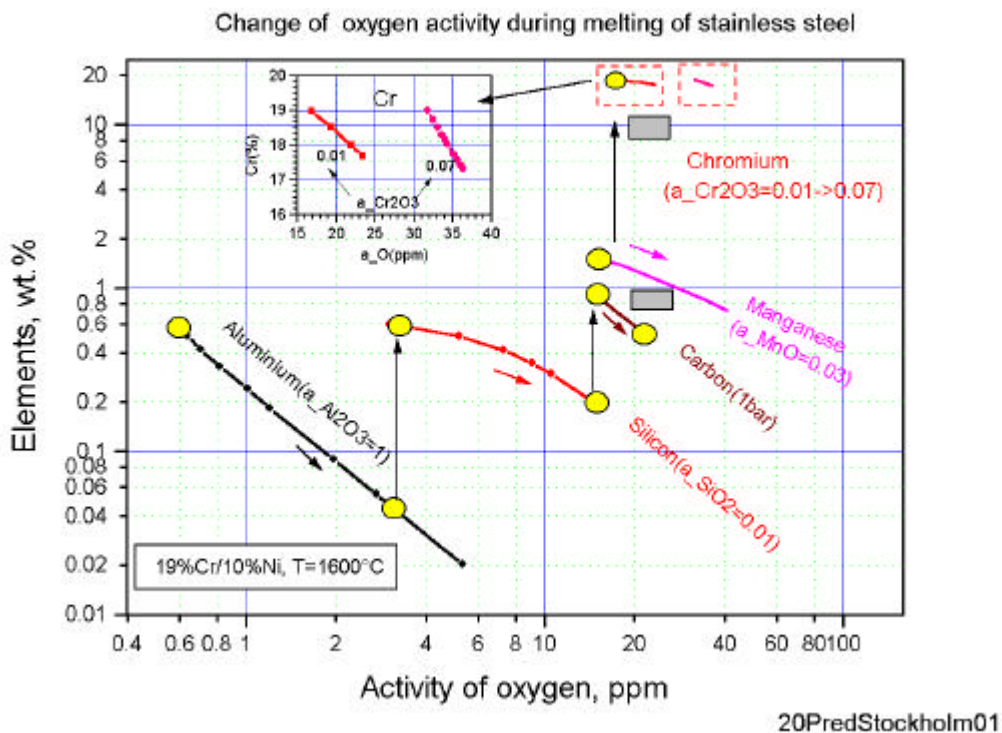
Figure 4 Calculated oxygen activity in equilibrium by isoactivity/isothermal state for various elements content by 1600 °C.
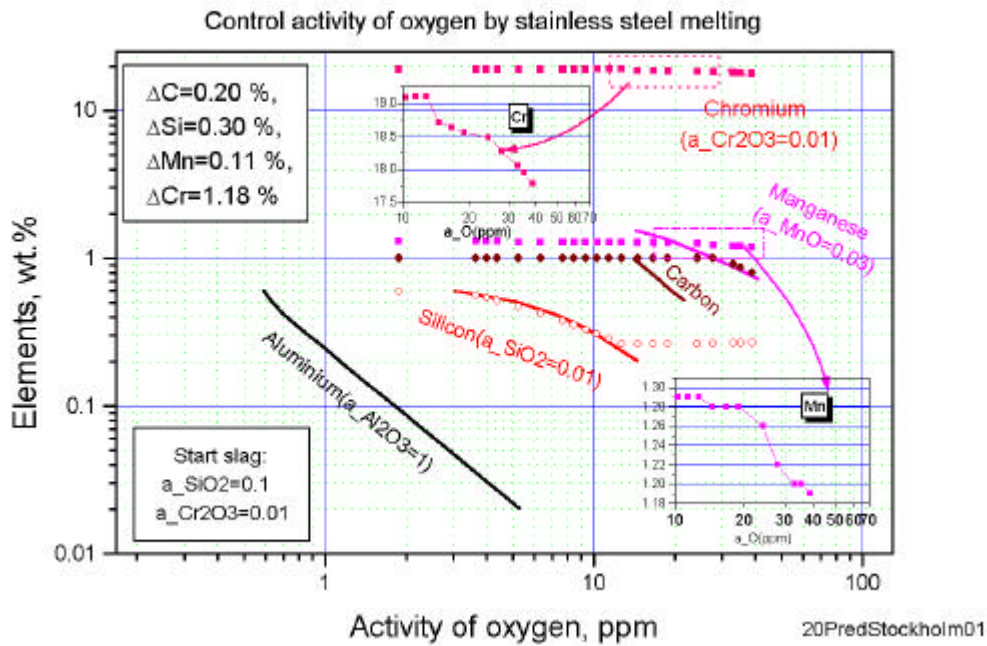
Figure 5 Computer simulation of the change equilibrium content of Si, Mn, C and Cr during meltdown in EAF for AISI 304 steel.
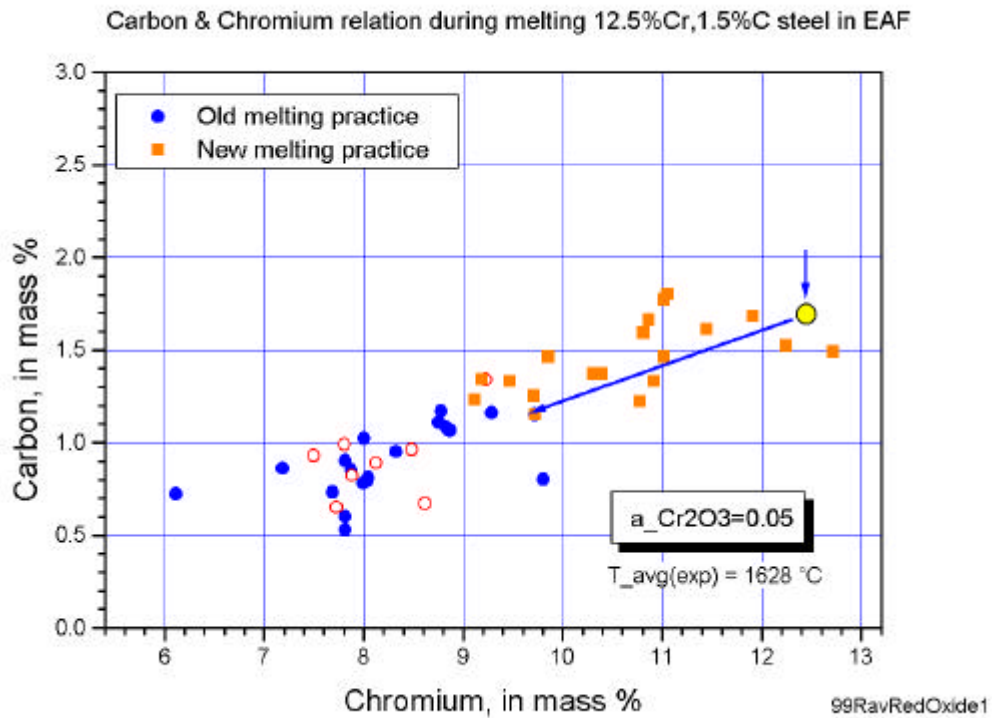

Figure 6 Computer simulation of the change equilibrium content of C and Cr during meltdown in EAF for an ledeburitic steel AISI D3 with initially composition: 12.5%Cr, 1.5%C .

List of Tables:

Table 1 Plant data from melt composition in EAF after completely fluid bath

Group	%C	%Si	%Mn	%Cr	%Ni	%Mo	%Al
Si-high	0.82	0.18	1.03	18.8	8.38	0.47	0.019
Al-high	0.75	0.67	1.45	19.5	8.52	0.60	0.55

Table 2 Plant data from slag chemistry in EAF (after the meltdown)

Heat No.	SiO_2	Cr_2O_3	V_2O_5	Al_2O_3	TiO_2	MgO	MnO	CaO	FeO	Temp[1]
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	°C
210107	12,90	15,50	0,26	6,90	0,48	9,79	1,80	42,00	6,90	**1568**
210108	14,50	19,50	0,22	6,90	0,89	10,80	2,30	38,70	7,20	**1586**
210109	10,70	11,90	0,19	11,40	0,90	12,00	1,40	44,70	5,90	**1587**
210110	11,50	19,10	0,20	4,30	0,61	7,09	2,20	43,30	9,20	**1561**
210111	8,90	14,80	0,20	4,80	0,59	5,42	1,90	37,90	6,60	**1584**
210112	10,40	17,00	0,32	8,00	1,06	5,98	2,40	39,90	8,70	**1624**
210113	15,60	13,00	0,22	7,00	0,93	6,97	2,00	48,60	3,80	**1574**

[1] Melt temperature