

THE OXIDATION AND REDUCTION OF CHROMIUM OF STAINLESS STEELS IN AN ELETRIC ARC FURNACE

Received – Prispjelo: 2010-06-22
Accepted – Prihvaćeno: 2010-09-30
Preliminary Note – Prethodno priopćenje

The oxidation of chromium during the elaboration of stainless steels occurs with oxygen in solution blown in the melt and with oxides in the slag. A higher content of silicon in the furnace charge decreases the extent of oxidation of chromium, however, the efficient reduction of chromium from the slag is of essential importance for a minimal loss of chromium. In this survey, the theory of the oxidation of chromium, its reduction from the slag and the conditions for the formation of foaming slag are discussed

Key words: manufacturing austenitic stainless steel, electric arc furnace, chromium oxidation, slag reduction, foaming slag

Oksidacija i redukcija kroma kod nehrđajućeg čelika u elektro-lučnoj peći. Prilikom izrade nehrđajućeg čelika u elektro-lučnoj peći dođe do oksidacije kroma zbog upuhavanja kisika i zbog oksida u troskii. Viši sadržaj silicija u ulošku smanjuje oksidaciju kroma. Za smanjenje gubitaka kroma potrebno je smanjiti i količinu kroma u troski. U ovom radu se predstavlja teorija oksidacije kroma, njegova redukcija iz troske i uvjeti za formiranje pjenjene troske.

Gljučne riječi: proizvodnja austenitnog nehrđajućeg čelika, elektro-lučna peć, oksidacija kroma, redukcija troske, pjenjenje troske

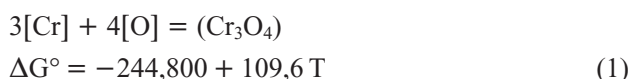
INTRODUCTION

More than 97 % of chromium is lost by the melting of steels from scrap in the electric arc furnace (EAF). The oxidation of chromium occurs during the melting, and to an even greater extent, it occurs during the blowing in of oxygen aimed to decrease the content of carbon in the bath of EAF. A high content of chromium increases the crusting of the slag, decreases its reactivity and impairs the formation of the foaming slag and the slag reduction during the process of steel elaboration. Stainless slags with high content of chromium oxide can't be recycled or used.

OXIDATION OF CHROMIUM

The oxidation of chromium with oxygen in solution in the melt occurs parallel to the oxidation of other elements, e.g., carbon, aluminium, silicon and manganese and it depends on the temperature and the activity of these elements and oxygen.

The standard free energy of oxidation (ΔG°) of these elements is given by the following relations [1]:



B. Arh, F. Tehovnik, Institute of Metals and Technology, Ljubljana, Slovenia

The equilibrium constant is for every of these reactions deduced from the change of standard free energy and it is written for the oxidation of chromium as:

$$\lg K_1 = \frac{53,521}{T} - 23,96$$

and

$$K_1 = \frac{a_{\text{Cr}_3\text{O}_4}}{a_{\text{Cr}}^3 \cdot a_{\text{O}}^4} = \frac{a_{\text{Cr}_3\text{O}_4}}{f_{\text{Cr}}^3 \cdot f_{\text{O}}^4 \cdot w_{\text{Cr}}^3 \cdot w_{\text{O}}^4} \quad (3)$$

with: $a_{\text{Cr}_2\text{O}_3}$, a_{Cr} , a_{O} – activity of (Cr_2O_3) , $[\text{Cr}]$, $[\text{O}]$; f_{Cr} , f_{O} – activity coefficient for Cr and O, $w_{\text{Cr}}/\%$, $w_{\text{O}}/\%$ – mass content of Cr and O in the steel melt.

At high content of chromium in the melt the activity of oxygen and of carbon is lower, as both interaction coefficients are negative. The effect of chromium on the content and the activity of oxygen in the melt at the temperature of 1600 °C is shown in Figure 1 [2].

The dependences were calculated using the equation valid for a content of 9 % chromium and more in the steel bath (equation 4)[2]. It is evident, that at high content chromium the solubility of oxygen in the melt is greater (Figure 1).

For this reason, and by equal content of carbon, the content of oxygen is higher in the bath with chromium than in the bath without this element.

$$\log[w_{\text{Cr}}^{3/4} \cdot (f_{\text{O}} \cdot w_{\text{O}})] = -13380 / T + 5,99 \quad (4)$$

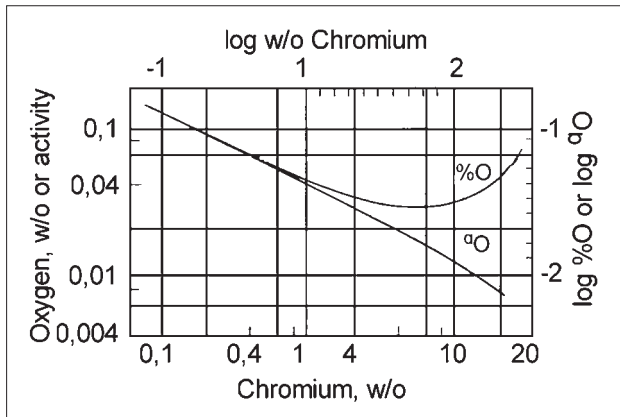


Figure 1 Effect of chromium on the activity and the content of oxygen in the system Fe-C at 1873 K [2]

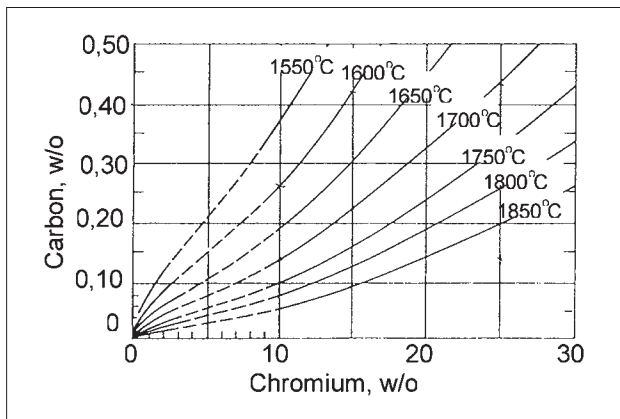
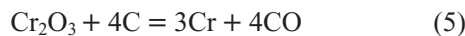


Figure 2 Thermodynamical equilibrium between C and Cr for different temperature and the pressure of $p_{CO} = 1$ bar [2]

Carbon, with an over critical content, delays the oxidation of chromium [2]. The equilibrium between chromium and carbon was for the pressure of $p_{CO} = 1$ bar and different temperature in Figure 2 determined applying the following relations and considering the coefficient of interaction of first order:



$$\log[(Cr)^{3/4} \cdot P_{CO}/a_C] = -11520/T + 7,64 \quad (6)$$

REDUCTION OF CHROMIUM

The efficient reduction of the furnace slag depends on the selection of the suitable reductant dependent on the used procedure and the control of the furnace slag which should ensure a high level of reduction of chromium oxide from the slag and should not contaminate the melt.

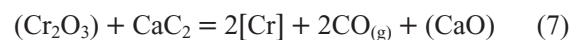
The importance is, the decrease of chromium losses during the oxidative melting with the blowing in of different reductants. The first measure for the control of the content of Cr_2O_3 is the use of a charge and alloys (FeSi) with a high content of silicon ensuring the content of 0,3 % Si after the melting of the charge. During the discharge, the reduction of chromium oxides is continued

with silicon in solution. However, for an efficient reduction of Cr_2O_3 is necessary with blowing of carbon in to slag. The blowing of carbon is carried out with parallel blowing in of oxygen [3].

The reduction of chromium oxide is more efficient on conditions of:

- high activity of Cr_2O_3 by increased basicity,
- high activity of carbon, $a_c = 1$ at the blowing in of carbon,
- low partial pressure,
- low activity of chromium in the metallic phase,
- high temperature.

Beside the used technology for the reduction with silicon and aluminium and the blowing in of carbon, the use of blowing in of calcium carbide was reported also [4]. When this carbide reacts with oxides in the slag, the product of the reaction are chromium, lime and carbon monoxide. CaO has the function of non metallic addition for the formation of the slag, while carbon monoxide improves the slag foaming in comparison to the blowing in of carbon powder. The reduction of chromium oxide with calcium carbide (CaC_2) proceeds according to the reaction:



The change of Gibbs free energy in dependence on temperature for the reactions of chromium oxide with silicon, carbon and calcium carbide are shown in Figure 3. It is clear that the reduction of chromium with carbon is more efficient by high temperature, therefore in practice it is performed with the parallel blowing in of oxygen. The reaction between silicon and chromium oxide is not strongly temperature dependent and occurs, for this reason, also at lower temperature. The suitability of calcium carbide as reductant is shown by the reaction between this carbide and chromium oxide, which has a lower Gibbs energy in the temperature range of 1550 to 1700 °C.

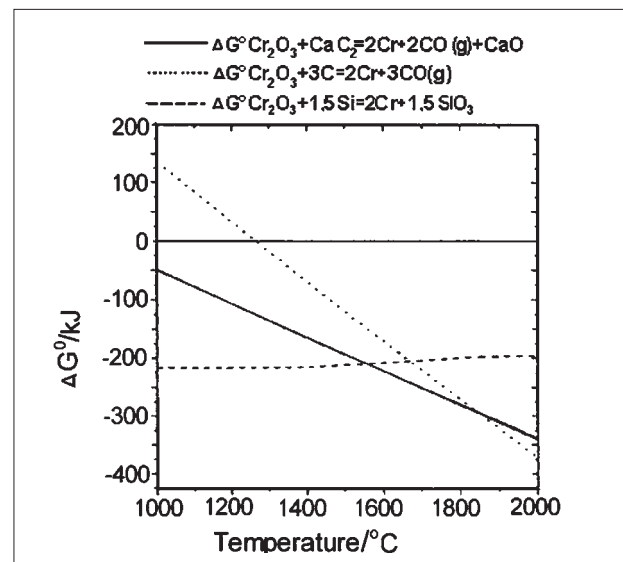


Figure 3 Temperature dependence of Gibbs free energy for the reduction of Cr with CaC_2 , Si and C [4].

It is characteristic for slags containing iron and chromium oxides, that on the boundary slag – carbon the reduction starts immediately and without incubation period, while the reduction of Cr_2O_3 has an incubation period and it is slower than the reduction of FeO [5].

FOAMING SLAG

The formation of the foaming slag is process dependent on a sufficient evolution of gasses in a slag with a proper viscosity which should not be too small, as a determined time of presence of gas bubbles in the slag is necessary to maintain a sufficient foaming. If the viscosity is too great, that the foaming could not occur, or occurs with insufficient intensity.

The foaming characteristics are improved with the lowering of surface tension (σ) and density (ρ) and with the increase of slag viscosity (μ) [6]. The foaming stability, also foaming index (Σ) is determined by the average size of bubbles (D_b).

$$\Sigma = 115\eta / (\sigma \cdot \rho)^{0.5} \quad (8)$$

$$\Sigma = \eta^{1.2} / (\sigma^{0.2} \cdot \rho \cdot D_b^{0.9}) \quad (9)$$

D_b is the increase of volume due to the arising CO bubbles in the slag. Small bubbles are of special importance for the slag stability. The presence in the slag of a suspension of different solid phases has a stronger effect on the foaming than the slag surface tension or viscosity. Optimal slag are not entirely liquid, however, they are saturated with CaO (Ca_2SiO_4) and MgO . Particles in suspension act as nuclea for gas bubbles and enable the formation of a great number of small bubbles.

In Figure 4 the dependence between the foaming index and the relative effective slag viscosity is shown [7].

For the effect of particles in suspension on the slag viscosity, the following relation was developed:

$$\mu_e = \mu(1 - 1,35\theta)^{-5/2} \quad (10)$$

With: μ_e – effective slag viscosity
 μ – viscosity of the liquid gas without particles in suspension
 θ – volume share of the solid phase in the slag

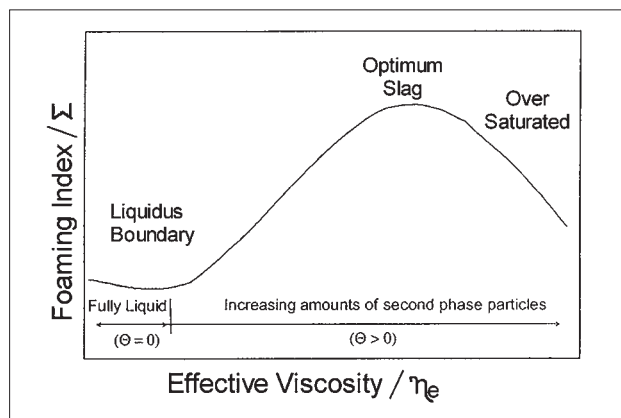


Figure 4 Foaming index in dependence of the effective slag viscosity [7].

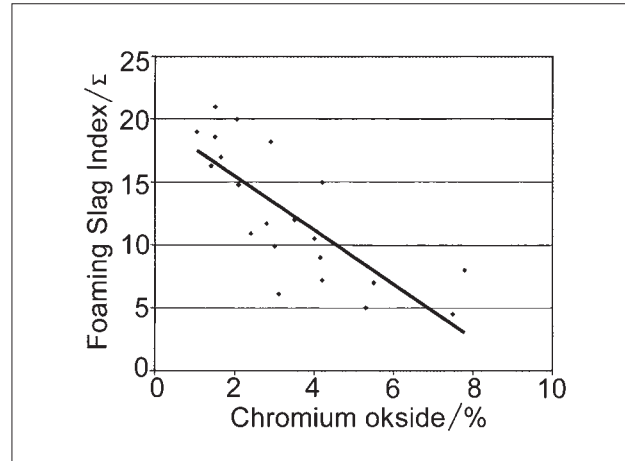


Figure 5 Content of Cr_2O_3 in the slag after discharge of the furnace in dependence of the slag foaming index [8].

The foaming slag increases the return of chromium from the slag (Figure 5) [8].

The foaming of stainless slag is different from that at the elaboration of carbon steels. The foaming capacity of stainless slags is decreased by low content of iron oxide and a high content of chromium oxide in the slag. Solid particles of chromium oxide in the slag with a high melting point increase the slag viscosity and impair the foaming. By low FeO content and by slow kinetics of reduction of chromium oxide, the addition of carbon, which increases the quantity of CO, does not fulfil the condition for an efficient foaming [9-11].

CONCLUSION

The content of silicon of 0,3 % and the addition of silicon decrease significantly the oxidation of chromium during the melting because silicon is oxidised as first. The decrease of oxydation of chromium with the addition of FeSi requires the addition of lime to maintain the right slag basicity.

Suitable reductant are ferrosilicon, aluminium, carbon and calcium carbide. The silicon and carbon are used the most. However, the blowing in of carbon powder is efficient at high bath temperature.

The alternative is the injection of calcium carbide in the slag, when as products CO and CaO are obtained. The advantage of calcium carbide is that it is efficient reductant for chromium oxide already by lower bath temperature.

The chemical composition and the basicity of the slags affects strongly the reduction of chromium oxides. For greater furnace slag basicity, the activity of SiO_2 and Al_2O_3 should be lower and the reduction of chromium oxide is greater. The basicity of 1,4 to 1,8 is optimal.

For the formation of the foaming slag an early presence of a sufficient volume of fluid slag is necessary. The final slags should be saturated with CaO and MgO (5-10 %) and have a viscosity suited for the formation of

the foaming process. The appropriate content of Si in the steel bath is necessary for the control of the ratio Cr/Cr₂O₃, since, the solid chromium oxide increases the viscosity of the slag and impairs the foaming. Further, the reactions should ensure the formation of small gas bubbles. The injection of carbon in the slag by high potential of oxygen in the bath, high content of FeO generates the formation of CO bubbles. For a stable foaming of stainless slags with low content of FeO it is necessary to maintain the generation of gas bubbles with the injection of carbon and iron oxide in the slag.

REFERENCES

- [1] J. Elliott: Physical Chemistry of Liquid Steel in Electric furnace Steelmaking, The Iron and Steel Society (Ed. By C.R. Taylor), 1985, 291.
- [2] J. Elliott, M. Gleiser: Thermochemistry for Steelmaking, The American iron and steel Institute, U.S.A., 1960.
- [3] D.C. Hilty and T.F. Kaveney: Stainless Steel Melting in Electric Furnace Steelmaking, The Iron and Steel Society, 1985, 143.
- [4] J. Björkqvall, S. Angström, L. Kallin: Reduction of chromium oxide containing slags using CaC₂ injection, 7 International conference on Molten slag fluxes and salts, 2004.
- [5] M. Görnerup: Studies of Slag Metallurgy in Stainless Steel-making, Doctoral thesis, Stockholm, 1997.
- [6] Y. Zhang and R.J. Fruehan; Effect of the bubble Size and Chemical Reaction on Slag Foaming, Met.Trans.B(26B), (1995), 803-812.
- [7] K. Ito: Slag Foaming in New Iron and Steelmaking Processes, Met.Trans.B (20B), (1989), 515-521.
- [8] R. Krump, et al.: Quantitative detection of foaming slag in EAF and its benefit..., 8th European Electric Steelmaking conference, 2005.
- [9] M. Torkar, M. Godec, M. Lamut: An investigation of brushed AISI 304 Stainless steel after corrosion testing, Materiali in tehnologije 42(2008)1, 39-43.
- [10] B. Arh, F. Tehovnik, J. Lamut, J. Triplat: Report of the research project, IMT, Ljubljana, 2007.
- [11] V. Marušič, D. Malovrh, M. Klinar, J. Triplat, M. Knap, J. Lamut: Partial oxidation and reduction of EAF stainless steel slag, 13 seminar on steel process metallurgy, NTF.OMM., Ljubljana, 2007, 89-95.

Note: The responsible for English language is A. Paulin, Ljubljana, Slovenia.