THE OXIDATION AND REDUCTION OF CHROMIUM DURING THE ELABORATION OF STAINLESS STEELS IN AN ELECTRIC ARC FURNACE

OKSIDACIJA IN REDUKCIJA KROMA IZ ŽLINDRE MED IZDELAVO NERJAVNIH JEKEL V ELEKTROOBLOČNI PEČI

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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. The loss of chromium during the steel bath processing increases the production costs and generates problems because of the high content of chromium oxide in the slag. A higher content of silicon in the furnace charge decreases the extent of the oxidation of chromium; however, the efficient reduction of chromium from the slag is very important 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: electric arc furnace, chromium oxidation, foaming slag, slag reduction, stainless steel

Oksidacija kroma med izdelavo nerjavnih jekel poteka zaradi topnega kisika v talini, vpihanega kisika in zaradi oksidov v žlindri. Izguba kroma med izdelavo nerjavnega jekla v EOP nima za posledico samo višji materialni strošek, ampak tudi določene operativne posege zaradi prekomerne količine kromovega oksida v žlindri. Večja vsebnost silicija v založenem legiranem vložku zadrži oksidacijo kroma med njegovim taljenjem, vendar je le učinkovita redukcija žlindre po oksidaciji taline ključnega pomena za minimalno izgubo kroma. V prispevku bomo predstavili predvsem teoretične osnove oksidacije kroma, redukcijo kroma iz žlindre in pogoje za tvorbo peneče se žlindre pri izdelavi nerjavnih jekel v elektroobločni peči.

Ključne besede: elektroobločna peč, oksidacija kroma, peneča se žlindra, redukcija žlindre, nerjavna jekla

1 INTRODUCTION

The content of chromium in austenite stainless steels is generally in the range from 16 % to 24 %. More than 97 % of the chromium is lost during the melting of steels from scrap in an 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 at decreasing the content of carbon in the bath. A smaller part of chromium is also oxidised while discharging the melt from the 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 a high content of chromium oxide cannot be recycled or used, and are for this reason also an ecological problem.

2 OXIDATION OF CHROMIUM IN THE MELT

The oxidation of chromium with oxygen in solution in the melt occurs in parallel with 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 the oxygen. The standard free energy of oxidation ($\Delta G°$) for these elements is given by the following relations[1]:

$$3[Cr] + 4[O] = (Cr_3O_4) \quad \Delta G° = -244.800 + 109.6 \, T \quad (1)$$

$$[C] + [O] = CO_{(g)} \quad \Delta G° = -5.600 - 9.37 \, T \quad (2)$$

$$[Si] + 2[O] = (SiO_2) \quad \Delta G° = -139.070 + 53.09 \, T \quad (3)$$

$$2[Al] + 3[O] = (Al_2O_3) \quad \Delta G° = -286.900 + 89.05 \, T \quad (4)$$

$$[Mn] + [O] = (MnO) \quad \Delta G° = -57.530 + 24.73 \, T \quad (5)$$

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

$$\lg K_1 = \frac{53.521}{T} - 23.96 \quad (6)$$

and

$$K_1 = \frac{a_{Cr3O4}}{a_{Cr}^3 \cdot a_O^4} = \frac{a_{Cr3O4}}{f_{Cr}^3 \cdot f_O^4 \cdot w_{Cr}^3 \cdot w_O^4} \quad (7)$$

with a_{Cr2O3}, a_{Cr}, a_O being the activity of (Cr_2O_3), $[Cr]$, $[O]$; f_{Cr}, f_O being the activity coefficient for Cr and O, and $w_{Cr}/\%$, $w_o/\%$ being the mass fractions of Cr and O in the steel melt.

The equation giving the content of oxygen in solution in the steel bath of known composition (T304L) as a function of the temperature and the activity of chromium oxide is:

$$w_o/\% = \left[\frac{a_{Cr3O4}}{K_1 \cdot f_{Cr}^3 \cdot f_O^4 \cdot w_{Cr}^3} \right]^{1/4} \quad (8)$$
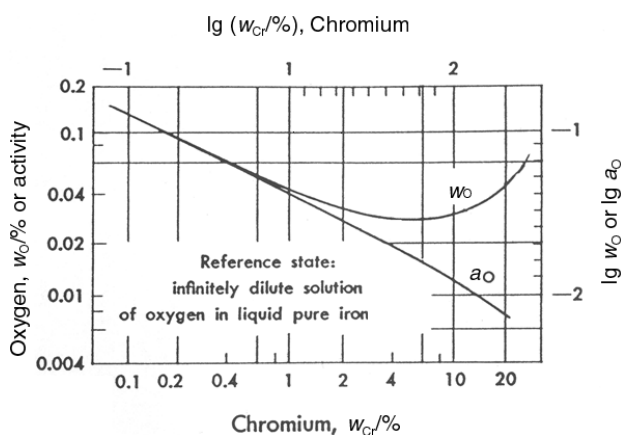
Figure 1: Effect of chromium on the activity and the content of oxygen in the system Fe-Cr at 1873 K [2]
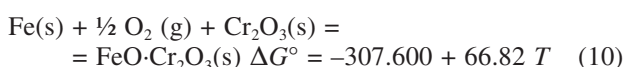**Slika 1:** Vpliv kroma na aktivnost in vsebnost kisika v sistemu Fe-Cr pri 1873 K [2]

Figure 2: Equilibrium between chromium and oxygen in the steel melt saturated with pure solid Cr_2O_3 and $FeO \cdot Cr_2O_3$ [4]
Slika 2: Ravnotežje med kromom in kisikom v tekočem železu, nasičenem s čistim trdnim Cr_2O_3 in $FeO \cdot Cr_2O_3$ [4]

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

The dependences were calculated using an equation valid for a content of 9 % chromium and more in the steel bath (eq. 9)[2,3]. It is evident that for a high content of chromium the solubility of oxygen in the melt is greater (**Figure 1**). For this reason, and with an equal content of carbon, the content of oxygen is higher in the bath with chromium than in the bath without this element.

$$\lg[w_{Cr}^{3/4} \cdot (f_O \cdot w_O)] = -13380/T + 5{,}99 \qquad (9)$$

Chromium is a relatively strong deoxidiser. With a higher content of chromium, the oxidation products consist of iron-chromium spinels of the type $FeO \cdot Cr_2O_3$. The transition from spinel to the saturation with Cr_2O_3 in the system Fe–O–Cr occurs when the critical content of chromium is exceeded[4].

$$Fe(s) + \tfrac{1}{2} O_2 (g) + Cr_2O_3(s) =$$
$$= FeO \cdot Cr_2O_3(s) \; \Delta G° = -307.600 + 66.82 \, T \quad (10)$$

In **Figure 2** the equilibrium between $FeO.Cr_2O_3$ and oxygen is shown for both a low and a high content of chromium in the bath. The critical content of chromium is shown for different temperatures when the equilibrium oxide phase changes from $FeO \cdot Cr_2O_3$ to Cr_2O_3. The phase $FeO \cdot Cr_2O_3$ in equilibrium with the Fe–Cr melt is changed to Cr_2O_3 when the actual content of chromium in the bath increases above the critical content. Pure Cr_2O_3 is the phase in equilibrium with the Fe–Cr bath for more than 7 % Cr in the bath.

The activity of Cr_2O_3 and of $FeO \cdot Cr_2O_3$ in the $FeO \cdot Cr_2O_3$ solid solution in equilibrium with the Fe–Cr melt decreases when decreasing the content of chromium below the $w_{Cr \, critical}$.

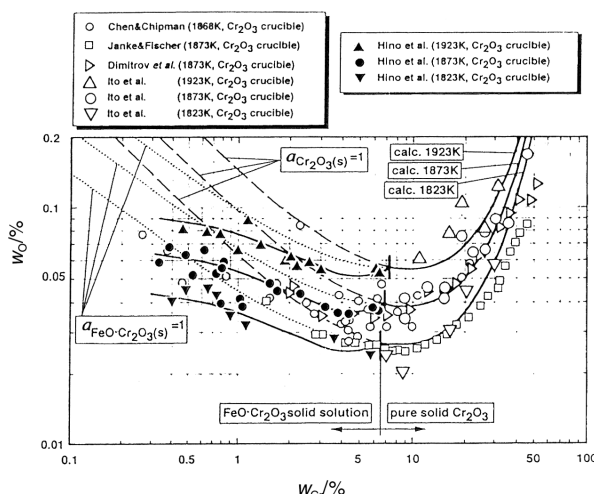In addition to the thermodynamic activity of different elements in the melt, the connection temperature-activity

of chromium oxide in the slag is of great importance, since this effect is significantly greater at lower temperatures. The activity of Cr_2O_3 depends on the alkalinity of the slag and on the content of CaO and SiO_2. The dependence of the free enthalpy of oxidation of chromium, silicon and carbon on the temperature shows that, according to the affinity for oxygen in solution, silicon lies between carbon and chromium and, for this reason, it is oxidised first and its oxidation delays the oxidation of chromium.

The deoxidation of the Fe-Cr melt with silicon is shown in **Figure 3**[5] as the equilibrium of the contents of chromium and oxygen in the bath at 1600 °C in dependence of the silicon content. The initial content of oxygen in the Fe-Cr melt before the addition of silicon is shown by the upper dashed line, which represents the equilibrium Fe-Cr/Cr_2O_3 or Fe-Cr/$FeO \cdot Cr_2O_3$ for the content of $w_{Si}/\% = 0$. The addition of silicon lowers the content of oxygen by a constant amount of chromium.
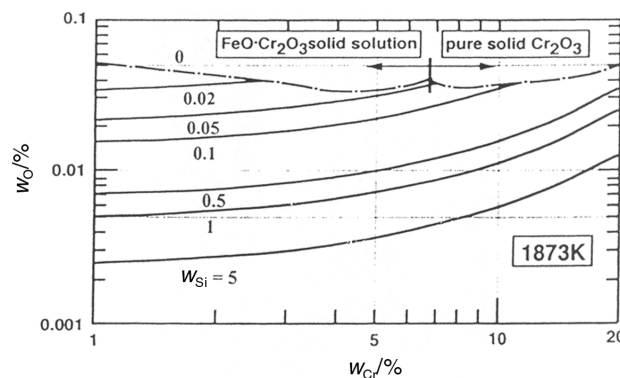

Figure 3: Equilibrium between the contents of chromium and oxygen in the steel bath at 1873 K for different contents of silicon[5]
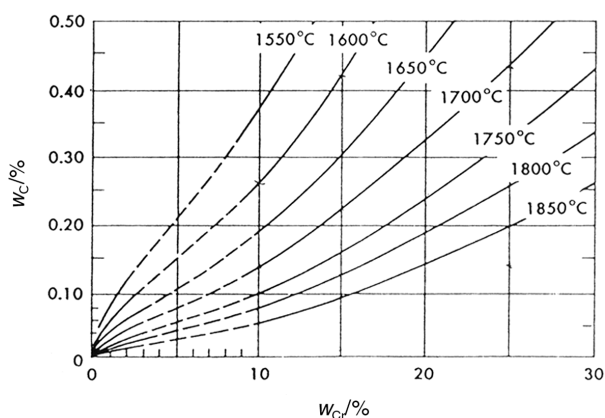**Slika 3:** Ravnotežje med vsebnostjo kroma in kisika v tekočem železu v odvisnosti od vsebnosti silicija pri 1873 K [5]

Figure 4: Thermodynamic equilibrium between carbon and chromium for different temperatures and a pressure of $p_{co} = 1$ bar [2]

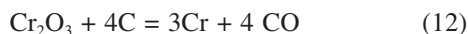**Slika 4:** Termodinamično ravnotežje med ogljikom in kromom v odvisnosti od temperature pri tlaku $p_{co} = 1$ bar [2]

The deoxidation power of silicon is lower with a higher content of chromium, e.g., by the addition of 1 % of silicon, the content of oxygen in the Fe + 5 % Cr bath is lowered from 350 μg/g to approximately 73 μg/g and for Fe + 18 % Cr it is lowered from 450 μg/g to 110 μg/g. For this reason, a low content of oxygen cannot be achieved with the addition of silicon alone. The oxidation-reduction equation for silicon and chromium is:

$$2Cr_2O_3 + 3[Si] = 4[Cr] + 3SiO_2 \qquad (11)$$

The thermodynamics indicates that the content of silicon in the melt is proportional to the activity of SiO_2 in the slag; thus, the content of silicon in the melt is higher with a higher content of SiO_2 in the slag. The thermodynamics of the relations content of Cr_2O_3 in the slag, the content of chromium and silicon in the melt, the melt temperature and the activity of SiO_2 in the slag were investigated by McCoy and Langerberg[6]. The results of these investigations show that the loss of chromium is higher with a low content of silicon in the melt and with a higher bath temperature[6].

Furthermore, 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 the different temperatures in **Figure 4**, determined by applying the following relations and considering the coefficient of interaction of the first order:

$$Cr_2O_3 + 4C = 3Cr + 4 CO \qquad (12)$$

$$\lg[(Cr)^{3/4} \cdot p_{CO}/a_C] = -11520/T + 7.64 \qquad (13)$$

2.1 Stainless slags

The behaviour of chromium oxides (CrO_x) in metallurgical slags is complex because of the existence of ions with several valences and of the high melting temperature of the slags containing chromium[7]. In slags the non-stoichiometric quantity of CrO_x depends on the

temperature, on the slag's alkalinity and on the content of chromium oxides in equilibrium with the metallic chromium. For the mixture of Cr_2O_3 with the other components of the slag in contact with metallic chromium at high temperature, the equilibrium of the oxides is:

$$2CrO_{1.5} + Cr = 3CrO \qquad (14)$$

Chromium is found in the slag as two- and three-valence ions. The activity of CrO and $CrO_{1.5}$ increases with the increase of the total content of CrO_x and the basicity. In **Figure 5** the activity of CrO and $CrO_{1.5}$ in the system $CaO–SiO_2–CrO_x$ at 1873 K is shown. At higher temperature, the activity is lower and the content of the bivalent chromium in the slag is increased. In contrast, with increased basicity the activity of chromium oxides is increased and the content of bivalent chromium in the slag is diminished (**Figure 6**). A greater activity of chromium oxides in the slag is found with greater alkalinity, a higher ratio of CaO/MgO and a lower temperature. The lower content of MgO in the slag increases the activity of the chromium oxides in the slag up to a limit; however, it does not affect the oxidation state and, as a result, the content of Cr^{2+} and Cr^{3+}. Small additions of Al_2O_3 affect the activity of CrO_x, while larger amounts have little effect. Slag with greater
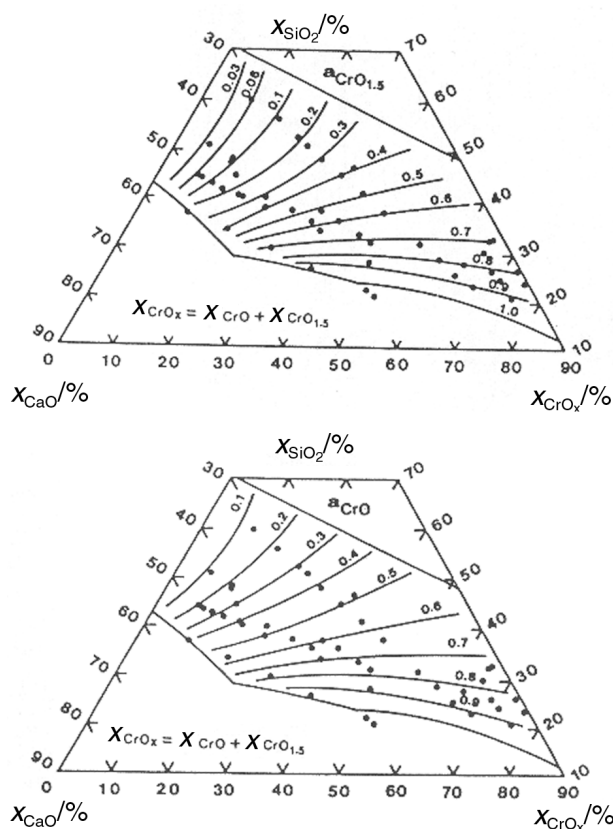

Figure 5: Iso-activity diagrams for $CrO_{1.5}$ and CrO in the CaO-SiO_2-CrO_x quasi-ternary system at 1873 K [7]

Slika 5: Izoaktivnostni diagram molskih deležev (x/%) $CrO_{1.5}$ in CrO v CaO-SiO_2-CrO_x v kvasiternarnem sistemu pri temperaturi 1873 K [7]

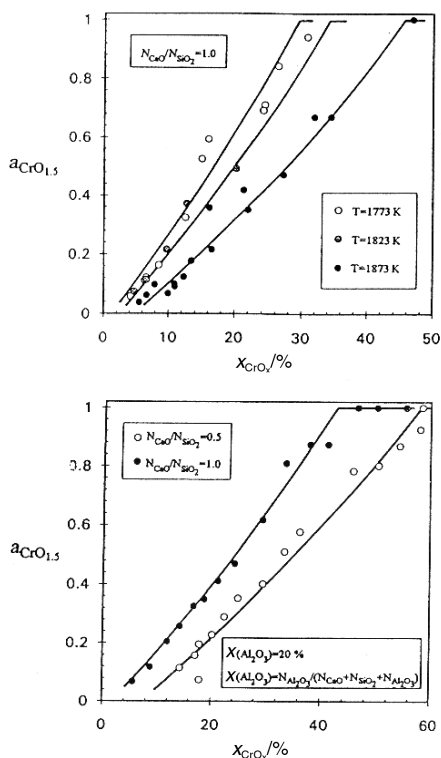**Figure 6:** Effect of temperature on the activity of $CrO_{1,5}$ in the system $CaO-SiO_2-CrO_x$ and the effect of slag basicity on the activity of $CrO_{1,5}$ in the system $CaO-SiO_2-Al_2O_3-CrO_x$ at 1873 K [7]
Slika 6: Vpliv temperature na aktivnost $CrO_{1,5}$ v sistemu $CaO-SiO_2-CrO_x$ in vpliv bazičnosti žlindre na aktivnost $CrO_{1,5}$ v sistemu $CaO-SiO_2-Al_2O_3-CrO_x$ pri temperaturi 1873 K [7]

activity improves the reduction of chromium from the slag and increases the yield of chromium during the elaboration of stainless steels.

The stainless slag in the EAF consists mostly of CaO, MgO, Al_2O_3 and SiO_2[8]. The optimal composition in the
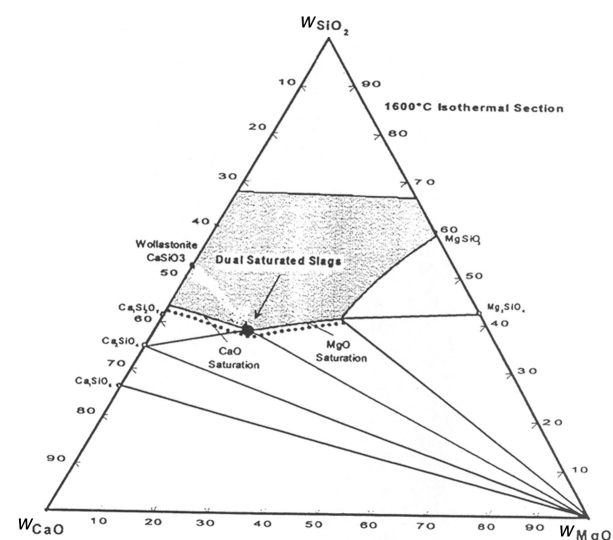

Figure 7: Isothermal section of the system $CaO-MgO-SiO_2$ at 1600 °C [9]
Slika 7: Izotermični prerez sistema $CaO-MgO-SiO_2$ pri 1600 °C [9]

system, $CaO–MgO–SiO_2$, shown in **Figure 7**, is the saturation with CaO and MgO[9], which is the necessary condition for a minimal content of Cr_2O_3 in the liquid slag and it is acceptable for the resistance of the refractory lining, also. The solubility of CrO_x in these slags is small. During the blowing of oxygen in the bath, the elements are oxidised according to their affinity to oxygen and their activity in the melt. Al and Si have a greater affinity for oxygen; however, chromium is also oxidised due to its greater activity. If CrO_x is absorbed in the molten slag, the equilibrium conditions change after the blowing of oxygen and the chromium is returned in the bath on the condition that there is a sufficient content of silicon. In the presence of chromium in the solid phase ($MgCrO_4$, $CaCrO_4$), the slag is rigid and the return of chromium in the bath is lower, also in the case of a higher content of silicon in the bath.

3 REDUCTION OF CHROMIUM FROM THE SLAG

Several procedures were developed for the reduction of chromium from the slag during the elaboration of the steel in the furnace and during the discharge in the ladle using silicon and aluminium. It is, however, very important that the loss of chromium is minimised during the oxidation melting and blowing of different reductants. In **Figure 8 and 9** the equilibrium curves are shown for the oxidation of chromium with respect to the reactivity of silicon, carbon, aluminium and manganese
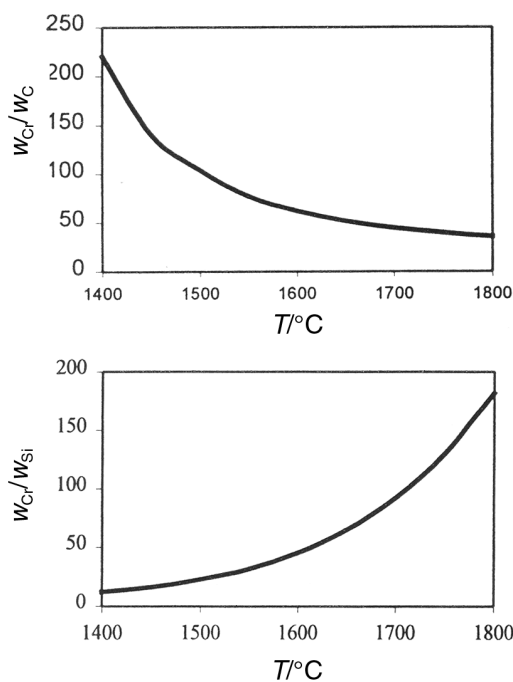

Figure 8: Effect of temperature on the ratio w_{Cr}/w_{Si} and w_{Cr}/w_C in the steel bath with 18 % Cr [10]
Slika 8: Vpliv temperature na razmerji masnih deležev w_{Cr}/w_{Si} in w_{Cr}/w_C v talinah jekel z 18 % Cr [10]
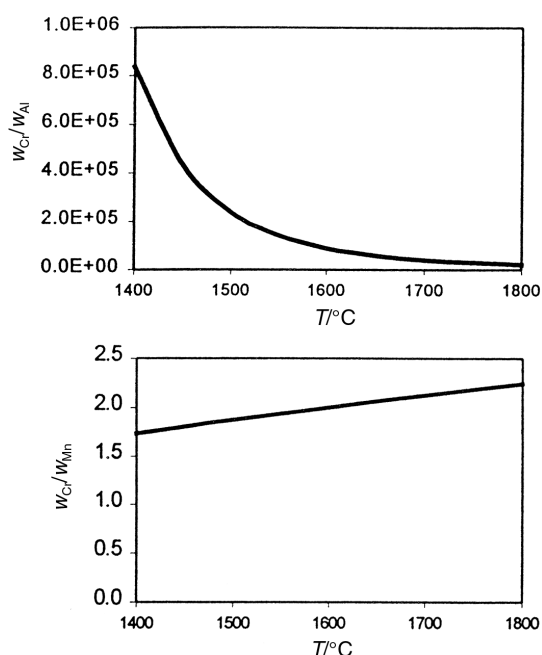
Figure 9: Effect of temperature on the ratio w_{Cr}/w_{Al} and w_{Cr}/w_{Mn} in the steel melt with 18 % Cr [10]

Slika 9: Vpliv temperature na razmerji masnih deležev w_{Cr}/w_{Al} in w_{Cr}/w_{Mn} v talinah jekel z 18 % Cr [10]

Figure 10: Effect of slag basicity on the content of Cr_2O_3 in the slag[11]
Slika 10: Učinek bazičnosti žlindre na vsebnost Cr_2O_3 v žlindri[11]

at the temperature of the elaboration of the steel T304L[10].

The thermodynamics of the relation w_{Cr}/w_{Si} in the melt with 18 % Cr shows that with a temperature of approximately 1500 °C the oxidation of silicon starts at 0.2 % Si and at 1700 °C at 0.4 % Si. Thus, at 1500 °C a content of 0.2 % Si in the melt already arrests the oxidation of chromium, while at higher temperatures a greater content of silicon is required. The ratio of w_{Cr}/w_C for 18 % Cr in the melt shows that the reactivity of the chromium increases with the temperature. For this reason, at higher temperatures a lower equilibrium content of carbon impairs the oxidation of chromium. **Figure 9** shows that the affinity of aluminium for oxygen is very high and that its activity decreases with increasing temperature. The activity of manganese is not affected by the temperature and in stainless steels with 2 % Mn the behaviour of manganese is different from that of chromium, carbon, aluminium and silicon.

Silicon impairs the oxidation of chromium at low temperatures, thus, during the melting of the charge, while carbon is efficient in this role and with sufficient concentration, at higher temperatures. The blowing in of the oxygen at high temperature (>1550 °C) increases the oxidation of carbon and strongly decreases the oxidation of chromium.

The slag basicity (($CaO+MgO$)/($SiO_2+Al_2O_3$)) has a strong effect on the reduction of chromium oxides, and with a higher basicity the content of chromium oxide in the slag is lower. The activity of SiO_2 and Al_2O_3 is also
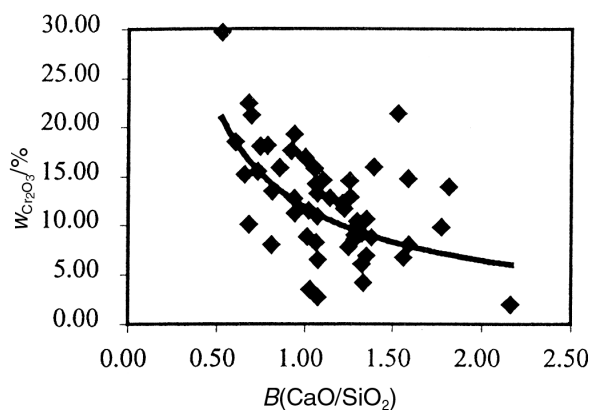
lower, while the activity of CrO_x is higher. All these levels of activity increase the rate of reduction of chromium oxide from the slag (**Figure 10**)[11]. According to this figure, the basicity should be approximately at the level of $B = 1.8$.

The efficient reduction of the furnace slag depends on the selection of a 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 selection of the reductant depends on the furnace and the raffination practice.

However, of special importance is the decrease of the chromium losses during the oxidative melting with the blowing in of the 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 a 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.
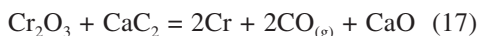
For a decrease of the chromium oxidation, the injection of carbon is widely used because it is economically more suited than the reduction with Si and Al. These two elements are bound to form oxides, thereby decreasing the slag basicity, which requires the further addition of lime, resulting in the increase of the slag volume. With slag reduction as a result of the blowing in of carbon, carbon monoxide is formed, which is necessary for the formation of the foaming slag. However, for an efficient reduction of Cr_2O_3 with the blowing in of carbon, a high slag temperature is also necessary. For this reason, the blowing in of carbon is carried out with the parallel blowing in of oxygen. The reduction of chromium oxide with Si and C occurs by the reactions:

$$(Cr_2O_3) + 1{,}5\ [Si] = 2\ [Cr] + 1{,}5\ (SiO_2) \qquad (15)$$

$$(Cr_2O_3) + 3C_{(S)} = 2[Cr] + 3CO_{(g)} \qquad (16)$$

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

- a high activity of Cr_2O_3 with increased alkalinity,
- a high activity of carbon, $a_c = 1$ during the blowing in of carbon,
- a low partial pressure,
- a low activity of chromium in the metallic phase,
- a high temperature.

Besides the used technology for the reduction with silicon and aluminium and the blowing in of carbon, the use of the blowing in of calcium carbide was reported also[12]. When this carbide reacts with oxides in the slag, the products of the reaction are chromium, lime and carbon monoxide. CaO has the function of a 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:

$$Cr_2O_3 + CaC_2 = 2Cr + 2CO_{(g)} + CaO \quad (17)$$

The change of Gibbs free energy with temperature for the reactions of chromium oxide with silicon, carbon and calcium carbide are shown in **Figure 11**. It is clear that the reduction of chromium with carbon is more efficient at 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 temperatures. The suitability of calcium carbide as a reductant is shown by the reaction between this carbide and chromium oxide, which has a lower Gibbs energy in the temperature range of 1550 °C to 1700 °C.

It is characteristic for slags containing iron and chromium oxides, that on the boundary between the slag
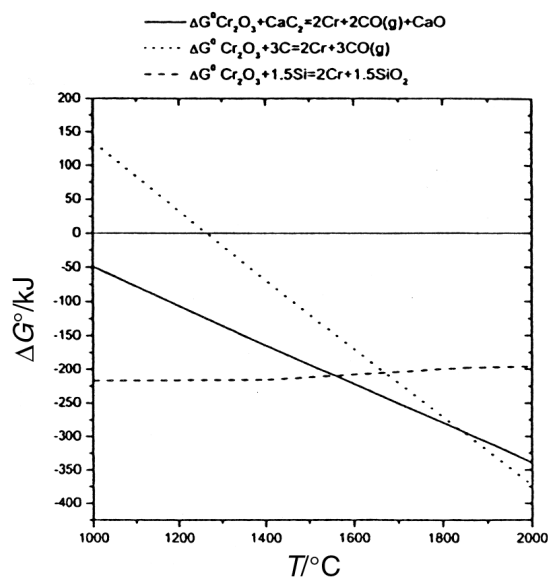

Figure 12: Content of FeO and Cr_2O_3 with respect to time at 1600 °C and 1650 °C [13]
Slika 12: Vsebnosti FeO in Cr_2O_3 v žlindri v odvisnosti od časa pri temperaturi 1600 °C in 1650 °C [13]

and the carbon the reduction starts immediately and without any incubation period, while the reduction of Cr_2O_3 has an incubation period and is slower than the reduction of FeO[13]. The reduction of Cr_2O_3 begins only after the reduction of a considerable amount of FeO (**Figure 12**).

In **Figure 13** the ratio $\ln(w_{Cr}/w_{Cro})$ with respect to time is shown for a slag with a different content of FeO with (%Cr) as the total content of chromium in the slag and with (Cr_o) as the reduced chromium in the slag at the time t[13]. The slope of the curves for the content of 5 % or 10 % of FeO shows that the reduced part of Cr_2O_3 is greater with a higher content of FeO in the slag. For a content of FeO = 0.5 % the incubation for the reduction becomes longer and the Cr_2O_3 reduction time is lengthened.

3.1 Foaming slag

The formation of foaming slag is a process dependent on a sufficient evolution of gases 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

Figure 11: Temperature dependence of Gibbs free energy for the reduction of chromium with calcium carbide, silicon and carbon[12]
Slika 11: Temperaturna odvisnost Gibbsove proste energije za redukcijo kroma s kalcijevim karbidom, z ogljikom in s silicijem[12]
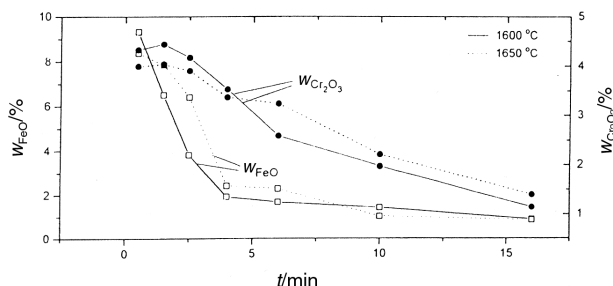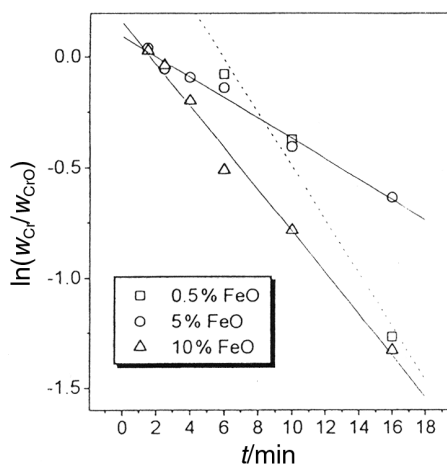

Figure 13: The kinetics of the reduction of chromium oxides for a different content of FeO in the slag and the slag alkalinity of $CaO/SiO_2 = 1.15$ [13]
Slika 13: Redukcija kromovega oksida v odvisnosti od vsebnosti FeO pri bazičnosti žlindre $CaO/SiO_2 = 1,15$ [13]

to maintain sufficient foaming. If the viscosity is too great, the foaming cannot occur, or occurs with insufficient intensity.

The foaming characteristics are improved with the lowering of the surface tension (σ) and density (ρ) and with the increase in the slag viscosity (η)[14]. The foaming stability and the foaming index (Σ) are determined from the average size of the bubbles (D_b).

$$\Sigma = 115 \, \eta \, /(\, \sigma \cdot \rho)^{0,5} \qquad (18)$$

$$\Sigma = \eta^{1,2}/(\, \sigma^{0,2} \cdot \rho \cdot D_b^{0,9}) \qquad (19)$$

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 the viscosity. An optimised slag is not entirely liquid; however, it is saturated with CaO (Ca_2SiO_4) and MgO. The particles in suspension act as nuclei for gas bubbles and enable the formation of a large number of small bubbles.

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

$$\eta_e = \eta(1-1,35\theta)^{-5/2} \qquad (20)$$

With: η_e – the effective slag viscosity

η – the viscosity of the liquid gas without particles in suspension

θ – the volume share of the solid phase in the slag

In **Figure 14** the dependence between the foaming index and the relative effective slag viscosity is shown[15]. If the relative effective slag viscosity is increased, the time of the presence of bubbles in the slag is lengthened, the foaming stability is increased and the foaming time is lengthened, also. As shown in **Figure 15**, the optimal quantity of solid particles is at the point G. Away from this point the slag becomes too crusty and the index of foaming is decreased.

The foaming slag has a positive effect in the EAF, since it decreases the electrodes radiation loss, decreases
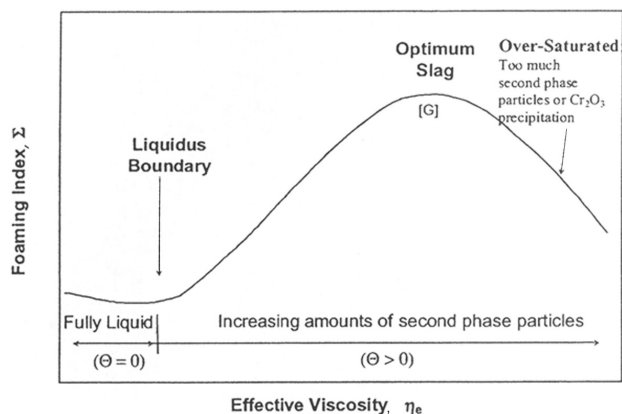

Figure 14: Foaming index versus the effective slag viscosity[15]
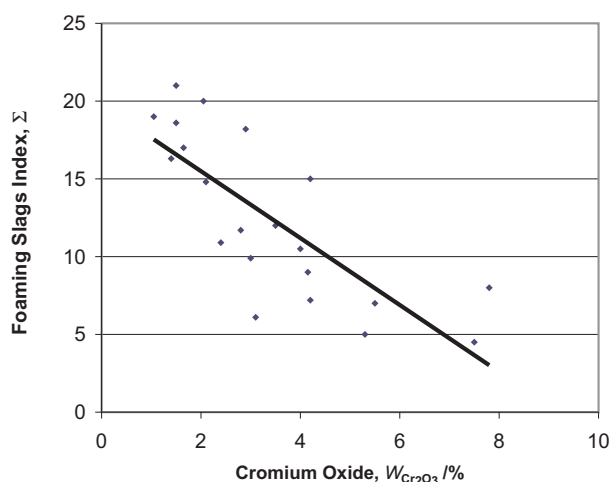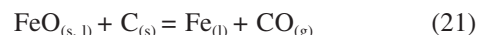**Slika 14:** Indeks penjenja v odvisnosti od efektivne viskoznosti žlinder[15]

Figure 15: Content of chromium oxide in the slag after discharge of the furnace in dependence of the slag foaming index[16].
Slika 15: Vsebnost kromovega oksida v žlindri po prebodu na peči v odvisnosti od indeksa penjenja žlindre[16]

the spraying of the slag on the lining and on the water panels, decreases the loss of electrodes and lowers the effect of variation of electrical tension with a longer electric arc[16]. It was found, also, that the foaming slag increases the return of chromium from the slag in the metallic bath (**Figure 15**).

By the elaboration of the carbon steels with FeO as major oxidation product (> 20 % of FeO in the slag), the propensity of the slag to foam is achieved simply with the blowing in of carbon in the slag. The base reaction for the formation of gas bubbles in the slag is:

$$FeO_{(s, \, l)} + C_{(s)} = Fe_{(l)} + CO_{(g)} \qquad (21)$$

The foaming of stainless slag is different from that during the elaboration of carbon steels. The foaming capacity of stainless slags is decreased by a 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. With a low FeO content and with 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[17].

The controlled formation of gas bubbles is very important for the formation of the foaming slag. During the elaboration of stainless steels, CO is produced, mainly with the carbon reduction of CrO_x and FeO_x. In stainless slags the Cr-O buffer appears at a much lower oxygen potential than the Fe-O buffer and, for this reason, chromium is oxidised before iron[18]. During the blowing in of oxygen in the melt CrO_x is formed as an oxidation product in place of FeO and for this reaction it is characteristic that:

- the solubility of CrO_x in the slag is low and it depends upon the ratio CaO/SiO_2 and the temperature,

- the share of reduction of CrO_x with carbon is small in comparison to the reduction of FeO. Consequently, the rate of formation of CO is small, since it forms mostly with the reduction of FeO.

In presence of FeO_x a greater quantity of CO is formed, and it can also be achieved with a greater degree of oxidation of the melt or the addition of FeO to the slag.

The second condition for the formation of the foaming slag is the proper slag fluidity. During the elaboration of stainless steels in the EAF the SiO_2 and Cr_2O_3 are the main oxidation products. SiO_2 is a flux component, while Cr_2O_3 is a component of the lining and it increases the rigidity of the slag. For this reason, the control of the Cr/Cr_2O_3 equilibrium in the melt is very important for achieving a foaming slag. The solubility of CrO_x in these slags is small ($< 5 \%$ CrO_x), and once the solubility is reached, the oxide CrO_x is precipitated.

If a moderate amount of secondary particles is available in the slag, the viscosity and thus the foaming index increases. However, at higher chromium contents, large solid particles destroy the bubble network and become detrimental to the slag's foamability. The data from the investigation shows that the Cr_2O_3 content should be kept lower than 16 % for the slag composition, temperature and oxygen potential used in the research[15].

The next parameter affecting the slag foaming is the temporal addition of additives during the elaboration of the steel in the furnace, since the composition of the slag is very important for the control of chromium and the achieving of the optimal degree of foaming. The formation of a fluid slag during the melting depends on the oxidation-reduction kinetics in the steel bath. An early fluid slag is achieved with the addition of wollastonite ($CaSiO_3$). The addition of MgO in the system CaO-SiO_2 increases the fluidity and decreases the

melting point of the slags up to a content of 15 % MgO, above this level periclase or spinel are precipitated.
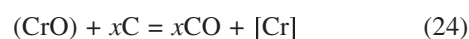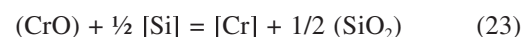
Considering the above analysis, it is understandable that achieving foaming in EAF slags rich in Cr_2O_3 is a difficult task, especially with regard to the formation of a sufficient quantity of gas bubbles. The investigation of the foaming and the reduction confirm that the area of stable foaming for EAF stainless slags is small[19]. This area and the area of the formation of gases are schematically shown in **Figure 16**.

Area I: A low basicity slag with a high viscosity gives a good foamability, according to Equation (18). Unfortunately, the gas generation is very small. The overall result of this is a poor foaming without any industrial interest.

Area II: This area shows the composition of the slag after a poorly controlled oxidation. The slag has a high viscosity and it has a large content of Cr_2O_3 solid particles. The great viscosity and the share of the solid phase in the slag decrease the kinetics of the formation of gases.

Area III: This part of the slag system is optimal. The basicity is high and the conditions for the formation of the CO gas are optimal. With particles of solid CaO and Cr_2O_3 the viscosity is increased and the index of foaming is increased, also.

The reduction of chromium oxide in the foaming occurs according to the following reactions[18]:

$$(CrO_{1,5}) + ¾ [Si] = [Cr] + ¾ (SiO_2) \qquad (22)$$

$$(CrO) + ½ [Si] = [Cr] + 1/2 (SiO_2) \qquad (23)$$

$$(CrO) + xC = xCO + [Cr] \qquad (24)$$

4 CONCLUDING REMARKS

During the elaboration of stainless steels in an EAF the loss of chromium is reduced with a decrease of the oxidation during the melting of the charge, the control of the blowing in of the oxygen by partial oxidation of the melt, with the slag composition and with efficient slag reduction.

The share of the oxidation of chromium depends on the composition of the charge, which may contain chromium oxides. During the melting, chromium is oxidised with other oxides present and with oxygen in the air. The dependence of the oxidation enthalpy on temperature shows that silicon and aluminium prevent the oxidation of chromium and that the sequence of oxidation depends on the activity of the element.

The 0.3 % content of silicon and the addition of silicon decrease significantly the oxidation of chromium during the melting because silicon is oxidised first and, in this way, the content of chromium in the slag is reduced. The oxidation of silicon is efficient during the melting and the heating of the charge and during the discharge of steel and slag from the furnace. The decrease of the oxidation of chromium with the addition
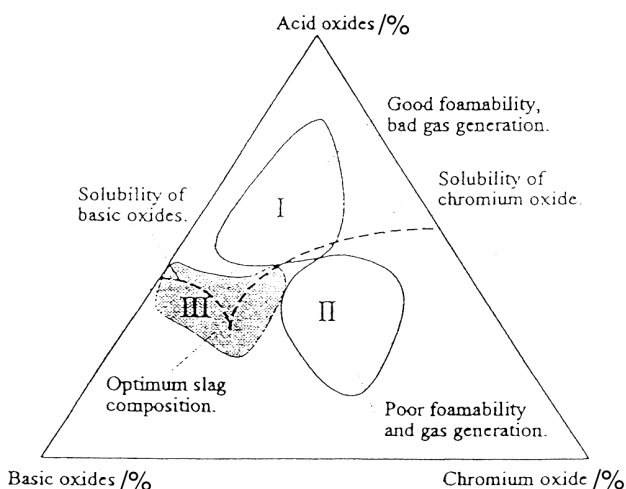

Figure 16: Areas of the tri-phase diagram with different activities of foaming/reduction[17]
Slika 16: Področja trifaznega diagrama s prikazom različnih lastnosti penjenja/redukcije[17]

of FeSi requires the addition of lime to maintain the right slag basicity (CaO/SiO_2). These additions increase the volume of the slag.

During the refining period the reducing conditions must be secured by controlling the C/O_{tot} injection ratio and the temperature of the blowing of oxygen. For this reason it is recommended that the blowing in of oxygen is carried out at a high temperature > 1600 °C, when the oxidation of carbon is strong and the oxidation of chromium is minimised.

After the charge was melted and the blowing in of oxygen stopped, a significant content of chromium oxides in the slag is obtained. The chromium is returned in the bath with the reduction of slag during the heating up and the raffination of the bath and during the discharge from the EAF. The selection of the reductant and the procedure of reduction are significant for achieving a maximal return of chromium and a minimal content of reductant in the melt.

Suitable reductants are ferrosilicon, aluminium, calcium carbide and carbon. However, silicon and carbon are used the most. A second possibility is the addition of ferrosilicon with parallel blowing in of carbon powder in the slag when CO and gas bubbles are formed. Both are necessary to obtain a foaming slag. However, the blowing in of carbon is efficient at a high bath temperature. The alternative is the injection of calcium carbide into the slag, when CO and CaO are obtained as products. The advantage of calcium carbide is that it is an efficient reductant for chromium oxide even at lower bath temperatures.

Good mixing between the steel and the slag during tapping provides excellent conditions for dissolving the silicon to reduce the Cr_2O_3 in the slag. The chemical composition and the basicity of the slags affect strongly the reduction of chromium oxides. For furnace slag, the lowering of chromium oxide depends also on the lowering of the activity of SiO_2 and Al_2O_3. For a higher slag basicity the activity of SiO_2 and Al_2O_3 is lower and the reduction of chromium oxide greater. An basicity of 1.4 to 1.8 is the optimum range.

For the formation of the foaming slag an early presence of a sufficient volume of fluid slag is necessary. The final slag should be saturated with CaO and MgO (5–10 %) and have a viscosity suitable 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/Cr_2O_3, since the solid chromium oxide increases the viscosity of the slag and impairs the foaming. Furthermore, the reactions should ensure the formation of small gas bubbles. The injection of carbon into the slag with a high potential of oxygen in the bath and a high content of FeO generates the formation of CO bubbles. For the stable foaming of stainless slags with a 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.

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