

REDUCTION OF CHROMIUM OXIDES WITH CALCIUM CARBIDE DURING THE STAINLESS STEELMAKING PROCESS

Received – Priljeno: 2014-06-05

Accepted – Prihvaćeno: 2014-10-20

Preliminary Note – Prethodno priopćenje

An efficient reduction of chromium from slag requires an appropriate reduction agent for the given steelmaking technology. The usual slag reduction praxis consists of carbon injections and additions of ferrosilicon and aluminum. Reduction of chromium containing slags with calcium carbide is an appealing alternative. Calcium carbide is a strong reduction agent that unlike ferrosilicon and aluminum also provides the possibility of foaming slag formation. Experimental work regarding chromium slag reduction with calcium carbide towards usual slag reduction praxis is described in this work. The results show that higher reduction rates in the stage of refining period of the melt and higher level of overall chromium reduction from slag can be reached with the blowing of CaC_2 .

Key words: electric arc furnace (EAF), stainless steel, chromium oxide, slag reduction, calcium carbide

INTRODUCTION

Stainless have relatively high chromium contents, but very low carbon contents, typically around 0,03 wt% C. Carbon can be removed by oxidation, but as carbon is oxidized to very low levels, its activity drops rapidly, which makes chromium oxidation favorable [1]. Chromium oxidation occurs during stainless steelmaking when chromium reacts with oxygen dissolved in steel, gaseous oxygen and oxides present in the slag. The reaction of Cr with dissolved oxygen is considered to be the main oxidation mechanism. Oxidation of chromium by dissolved oxygen may start simultaneously with oxidation of other elements such as C, Al, Si and Mn [2].

STAINLESS SLAGS

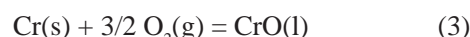
Many authors have studied the form of chromium oxides in the slag [2 – 4], it was suggested that the form of chromium oxides are CrO and $\text{CrO}_{1,5}$ (Cr_2O_3) oxide. Chromium is found in the slag as two and three valence ions. In slags the non-stoichiometric quantity of CrO_x depends on the temperature, on the slag's basicity and on the content of chromium oxides in equilibrium with the metallic chromium [5]. The carbon–chromium equilibrium is assumed during the decarburization of steel and can be expressed as follows [6]:



$$\Delta G^\circ (1\ 873\ \text{K}) = 173\ \text{kJ}$$

$$K = \frac{a_{\text{CrO}_{1,5}}^2 a_{\text{C}}^3}{a_{\text{Cr}}^2 a_{\text{CO}}^3} \quad (2)$$

Toker et al. [7] used the Gibbs standard free energy change for the formation of $\text{CrO}(\text{l})$ as follows:



$$\Delta G^\circ (1\ 938 - 2\ 023\ \text{K}) = -334\ 218 + 63,18\ \text{T} / \text{J}$$

In practice EAF slags are not necessarily saturated with chromium oxides so the values of the activity coefficients of CrO and $\text{CrO}_{1,5}$ in slag are significant, and depend on the composition of the slag [8].

The stainless steel slag in the EAF consists mostly of CaO , MgO , Al_2O_3 and SiO_2 . Relevant phase diagram at 5 wt% Al_2O_3 is shown in Figure 1 [9]. Slag with higher activity improves the reduction of chromium from the slag and increases the yield of chromium. Pretorius et al. [10] and Pei et al. [11] found that the activity coef-

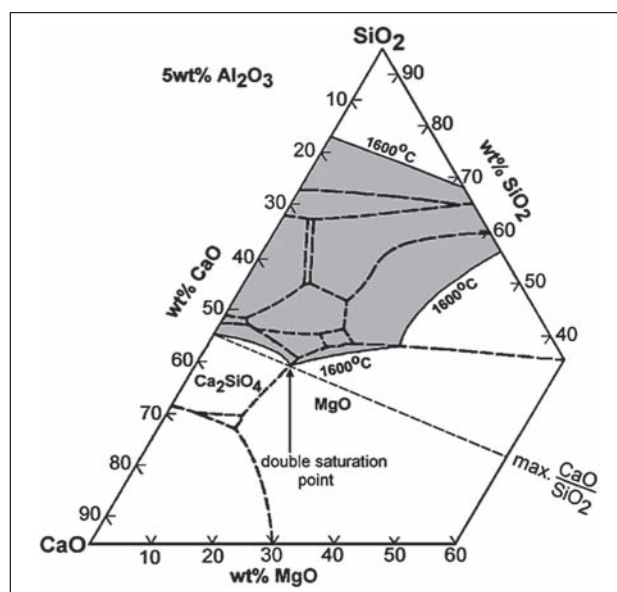


Figure 1 Liquid region at 1 600 °C in $\text{CaO-SiO}_2\text{-MgO-5 wt\% Al}_2\text{O}_3$ [9]

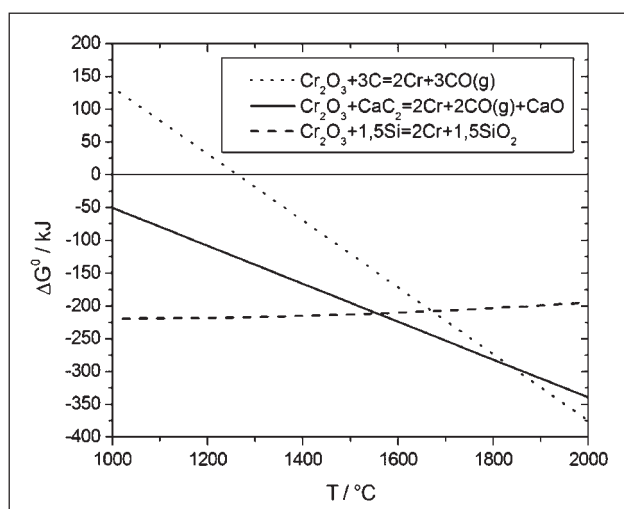


Figure 2 Temperature dependence of Gibbs energy for chromium reduction with calcium carbide, carbon and silicon [13]

ficients of CrO and $\text{CrO}_{1,5}$ in the slag increase with increasing slag basicity, although both define basicity a little differently.

Figure 2 shows that at 1 600 °C the maximum basicity of the slag is obtained at the point where the slag is double saturated with Ca_2SiO_4 and MgO . In practice, the slag may also be saturated with $\text{MgO}\cdot\text{Cr}_2\text{O}_3$ and $\text{CaO}\cdot\text{Cr}_2\text{O}_3$. Guo et al. [12] examined quenched slag samples and mainly observed idiomorphic crystals of $\text{MgO}\cdot\text{Cr}_2\text{O}_3$. They stated that crystals of $(\text{Ca},\text{Mg})_2\text{SiO}_4$ were sometimes also seen and the presence of $\text{MgO}\cdot(\text{Cr},\text{Al})_2\text{O}_3$ spinel confirmed early during melting of the steel scrap and heating of the charged material.

REDUCTION OF CHROMIUM

Besides the used technology for the reduction with silicon or aluminum and the carbon blowing, the use of blowing of calcium carbide was also reported [13]. When calcium 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 slag formation, while carbon monoxide improves 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 following reaction [14]:



The change of Gibbs free energy with temperature for the reactions of chromium oxide with silicon, carbon and calcium carbide are shown in Figure 2.

It is clear that the reduction of chromium with carbon is more efficient at high temperatures; therefore, in practice it is performed with the parallel blowing of oxygen. The reaction between silicon and chromium oxide is not strongly temperature dependent and also occurs at lower temperatures. The suitability of calcium

carbide as a reduction agent is shown by the reaction between the calcium carbide and chromium oxide, which has a lower Gibbs energy in the temperature range of 1 550 °C to 1 700 °C.

The aim of the investigation was to determine the effect of the CaC_2 injections on the reduction and decrease of the final chromium oxide concentration in the slag during stainless steel production in EAF.

EXPERIMENTAL PROCEDURE

Production of stainless steel is carried out by technology used in EAF, VOD and LF devices. We have made the experimental work on the UHP electrical furnace, with central bottom tapping and, charge capacity of 85 t. In this trial set different austenitic stainless steel grades were produced. The experimental data collection consisted from 39 charges using standard praxis of reduction (reduction with ferrosilicon and carbon powder) and from series of 10 charges where technology reduction with ferrosilicon in combination with injection of CaC_2 was used. The experiments were carried out using MEFOS portable powder dispenser and injection equipment. Analysis of the melt and the slag were made after melting metals (EAFs1), after reduction of slag (EAFs2) and after tapping of the melt from the furnace (EAFsT).

RESULTS AND DISCUSSION

Results of the slag analysis and rate of reduction of chromium after different stages of stainless steel production are shown in Figures 3 and 4. The content of Cr_2O_3 in slag decreases from 14,8 % to 12,6 % and to 8,2 % after tapping in charges without CaC_2 . In charges with CaC_2 slag reduction, Cr_2O_3 content in slag decreases from 12,1 % to 8,3 % and to 5,4 % after tapping.

Average reduction rate of chromium from slags in furnace without CaC_2 is 13,2 %, and 40,6 % between the tapping of the melt from furnace. When CaC_2 was injected, the reduction rate of chromium from slags in the furnace during reduction period was 41,9 % and was 32,3 % at tapping. The overall reduction of slag in EAF without CaC_2 was 47,8 % and with CaC_2 was 52,8 %.

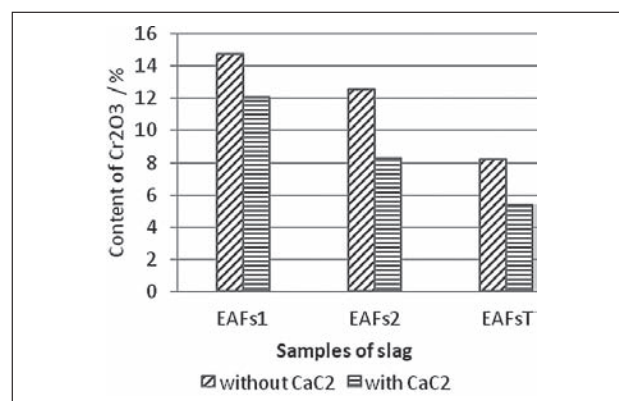


Figure 3 Average Cr_2O_3 content in slag

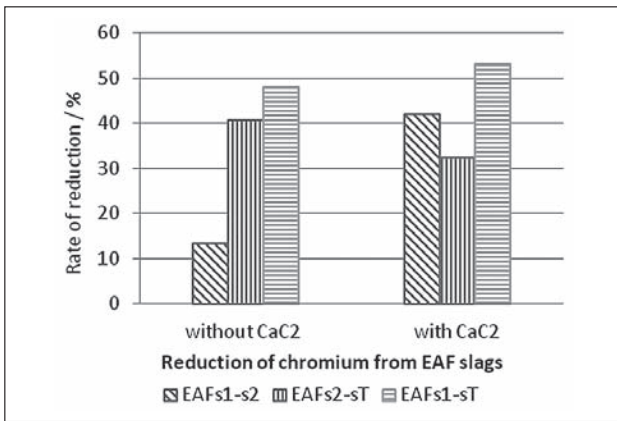


Figure 4 The rate of reduction of Cr₂O₃ from slags with respect to the way of reduction

The results of our trials of the slag reduction with CaC₂ (80 t EAF) are shown in Figure 5 as a function of the total amount of reduction agents supplied, the results are compared to the research performed by J. Björkvall et al. [13]. They have investigated the efficiency of the different reduction agents used including, carbon, calcium carbide, and a combination of carbon and Cr₂O₃ by different steel types.

Analysis of slags shows the presence of chromium spinels, slag matrix and droplets of iron. Mapping of chromite spinel crystals and the surrounding slag with iron droplets are shown in Figure 6.

CONCLUSION

According to the results, it can be concluded that the CaC₂ has proven to be a good reducing agent. In the standard slag reduction protocol, the reduction of chromium took place mainly between tapping of the melt on EAF (40,6 %), but when CaC₂ was blown the reduction of chromium slag had already reached the stage of the

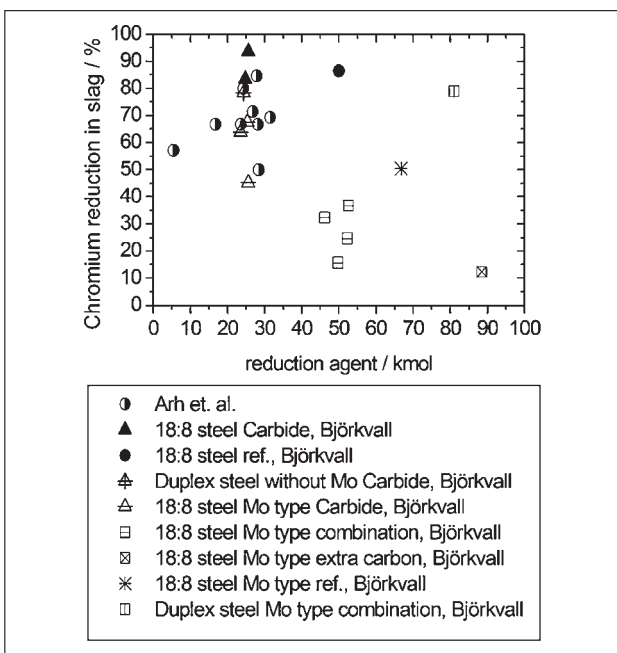


Figure 5 Chromium reduction in slag as a function of added reduction agent

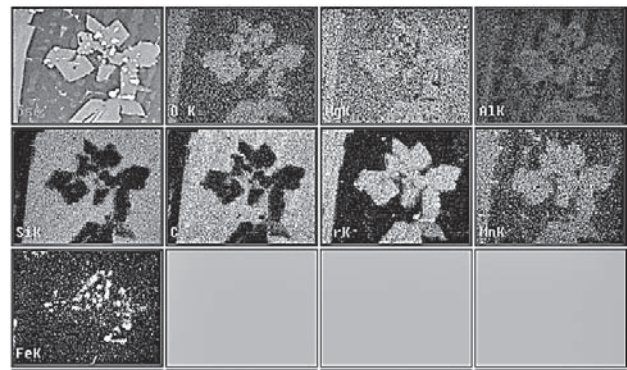


Figure 6 Mapping of chromite spinel and slag (SEM)

melt refining before tapping (41,9 %). The overall reduction of chromium from slag with CaC₂ blowing has reached a higher level, namely 52,8 % Cr₂O₃, compared to 47,8 % without CaC₂. Consequently the slag after tapping with blowing CaC₂ reached lower final average Cr₂O₃ content – 5,4 %, then in the standard process which had 8.2 % Cr₂O₃. The comparison of our work with others [13] has shown good agreement. The achieved reduction rate of Cr₂O₃ slag was from 50 to 85 % when roughly 30 kmol of reduction agent was added per charge. However a lot of operational challenges still need to be overcome for the routine use of CaC₂ in the EAF in the manufacture of stainless steel.

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Note: Responsible person for English translation T. Šušteršič, Medvode, Slovenia