REDUCTION OF CHROMIUM OXIDES FROM THE SLAG AT PRODUCTION OF ALLOYED STEELS

SOCHA Ladislav[1], ADOLF Zdeněk[1], BAŽAN Jiří[1], MACHOVČÁK Pavel[2]

[1]VSB - Technical University of Ostrava, FMME, Department of Metallurgy and Foundry, Ostrava, Czech Republic, EU,
ladislav.socha@vsb.cz, zdenek.adolf@vsb.cz, jiri.bazan@vsb.cz
[2]VÍTKOVICE HEAVY MACHINERY a.s., Ostrava, Czech Republic, EU, pavel.machovcak@vitkovice.cz

Abstract

In the steel industry, requirements for production optimization by the help of decreasing of energy and economical demands are increasing at the production of alloyed steels in the EAF. During the treatment of alloyed steel charging in the EAF containing chromium, its loss by oxidation and by the transition into slag happens. Chromium oxidation in the EAF happens during particular technological operations, however in different intensity. The main part of chromium loss from the melting happens during the oxidation period in which oxygen is blown with the aim of ensuring of basic refining reactions and melting decarbonisation. The chromium transition and its increase in the form of chromium oxides in the slag influences its properties which is shown by the creation of slag crust with the high viscosity which decreases the slag reactivity and prevents it from creation of foam slag during production of steel in the EAF. In the presenting paper, basic possibilities of Cr_2O_3 reduction from the slag at using of various reduction agents, application ways and technology modification of melting are given together with the proposal of theoretical calculation of consumption of chosen refining agents presenting silicon and aluminium for the conditions of steelwork VHM a.s.

Keywords: Slag mode, slag creation, slag reduction, high-alloyed steels, electric arc furnace

1. INTRODUCTION

Chromium content in the high-alloyed steels is generally between 8 to 30 wt. %. During the melting of steel charging containing chromium, its loss by the oxidation and transition into slag at the steel production in the electric arc furnace (hereinafter EAF) occurs. The first losses already occur during the charging melting in the EAF but the main part of the chromium loss from the melt occur during the oxidation phase when oxygen is blown with the aim of ensuring of basic refining reactions and melting decarbonisation. The high content of chromium in the slag influences it is properties which is shown by the creation of slag crust with the high viscosity which decreases the slag reactivity and prevents it from creation of foam slag during steel production in the EAF [1, 2]. In this presenting paper, basic possibilities of reduction of chromium oxides from the slag at usage of various reduction agents, application ways and technology modification of melting at production of high alloyed steels in the EAF are given.

2. REDUCTION OF CHROMIUM OXIDES FROM THE SLAG AT PRODUCTION OF HIGH-ALLOYED STEELS

Efficient reduction of chromium oxides from the slag at production of high-alloyed steels depends on the choice of suitable reduction agent and applied technology of reduction during the steel treatment in the EAF. Applied technology and a suitable reduction agent should ensure the high degree of reduction of chromium oxide from the slag. However, the choice of reduction agent depends on the equipment and technology possibilities of the running EAF. *Silicon, carbon, aluminium and calcium carbide* belong between the used reduction agents. Several technologies were developed and applied in the plant conditions but it is necessary to minimize the losses in the period of melting and primarily during the oxidation period for the efficient reduction [1].

The first step for controlled reduction of chromium oxides or control over the chromium content in the melt is the usage of steel charging or ferroalloys (*FeSi*) with a high contest of silicon, namely at ensuring its content 0.3 wt. % after charging melting. Silicon decreases the rate of chromium oxidation at low temperatures which can be used during the charging melting when the carbon is an efficient reduction agent at sufficient concentration and higher temperatures. In the following oxidation phase, reduction of chromium oxides with the silicon in the melt continues [1, 3]. Reduction of chromium oxides with silicon takes place according to the following chemical reaction:

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

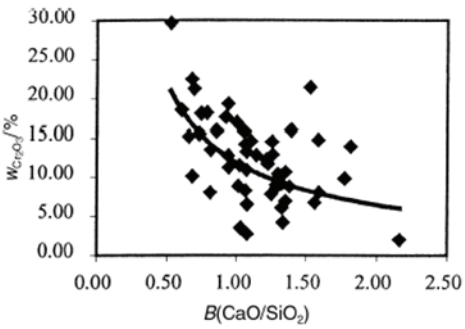

Fig. 1 Influence of slag basicity on the Cr_2O_3 content in the slag

The results of reduction of chromium oxides are oxides in case of silicon and aluminium which decrease the slag alkalinity and it leads to the necessity of lime addition and to the increase of slag amount in the EAF. Basicity or alkalinity presents an important parameter influencing the reduction of chromium oxides from the slag. Higher slag basicity positively influences the reduction of chromium oxides from the slag, as you can see in **Fig. 1**. According to the results of in **Fig. 1**, slag basicity should be in the range from B = 1.4 to 1.8 [1, 4].

Technology of carbon blowing to the slag is used for limitation of range of chromium oxidation because it is economically more favourable than reduction with silicon or aluminium. Reduction of chromium oxides with carbon is realized in the plant conditions by the carbon blowing which reacts with oxides in the slag at creation of carbon monoxide supporting creation of foam slag. However, a high slag temperature is necessary for efficient reduction of chromium oxides at carbon blowing. That is why carbon blowing is realized at parallel oxygen blowing in the oxidation phase. Reduction of chromium oxides with carbon takes place according to the following equation:

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

Technology of calcium carbide blowing is used except of technology using silicon, aluminium of carbon blowing as a reduction agent [1, 4]. Calcium carbide reacts with the oxides in the slag and the products of these reactions are chromium, calcium monoxide and carbon monoxide. Lime is a slag-making addition supporting slag creation. Carbon monoxide improves the creation of foam slag in comparison with blowing of carbon powder. Reduction of chromium oxides with the calcium carbide takes place according to the following equation:

$$(Cr_2O_3) + CaC_2 = 2[Cr] + 2CO_2 + (CaO) \qquad (3)$$

It is appropriate to use individual reduction agents under definite conditions which can be defined by the help of change of Gibbs free energy depending on temperature for reactions of chromium oxides with silicon, carbon or calcium carbide, as you can see in **Fig. 2**.

It is obvious from **Fig. 2** that reduction of chromium oxides with carbon is more efficient at high temperature. In practise, this technology is used at oxygen blowing during oxidation phase. It follows from the curve of reduction of chromium oxide with silicon that the reaction is independent on temperature and it takes place even at low temperatures. In practise, it is appropriate to use this reduction agent already during charging melting in the EAF. The suitability of application of calcium carbide as a reduction agent according to the obtained lower values of Gibbs energy up to 1550 ° C to 1700 ° C follows also from **Fig. 2** [1, 4].

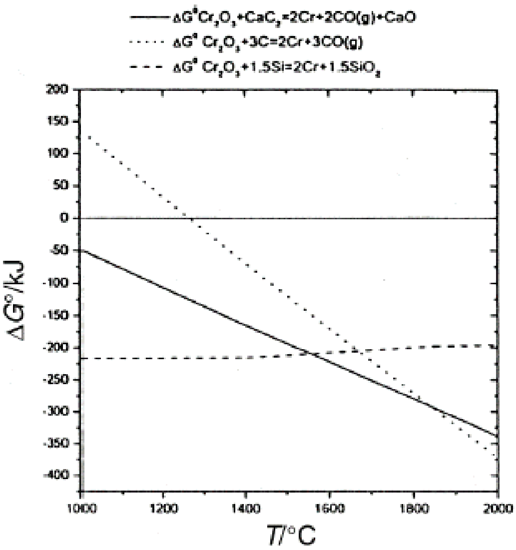

Fig. 2 Temperature dependence of Gibbs free energy for reduction of chromium oxides with reduction agents

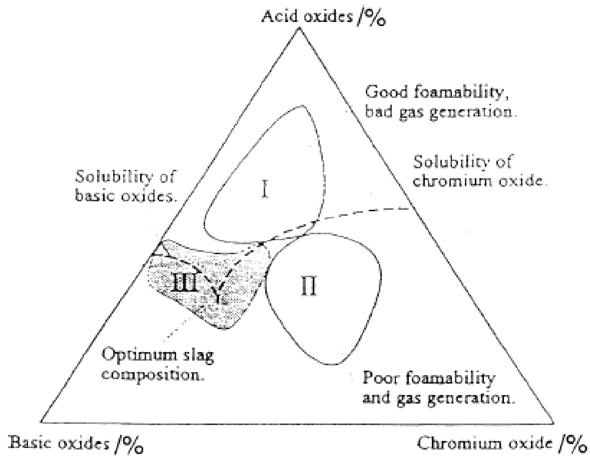

Fig. 3 Areas of three-phase diagram with different areas of activity of foaming / reduction

Technology of foam slag is one of the possibilities, how to reduce chromium oxides from the slag at melt treatment in the EAF which is commonly used at production of carbon or low-alloyed steels in the EAF. However, utilization of this technology at production of alloyed steels is limited because of the high viscosity of slag containing a big portion of chromium oxides which negatively influences the slag foaming [1, 5].

Slag foaming containing chromium oxides is decreased because of the lower content of iron oxide and higher content of chromium oxide in the slag. Solid particles of chromium oxides in the slag lead to the high melt temperature and to the growth of slag viscosity which decreases the foaming of the slag.

Ensuring of foaming in the slags with high content of Cr_2O_3 in the EAF is a very demanding task, especially for creation of sufficient amount of gas bubbles.

The creation of a foam slag and reduction possibilities confirm that the area of stable foaming for a slag containing chromium oxides is small and it is schematic given in **Fig. 3** [1, 5]:

- *area I - low basicity with a high viscosity of slag and with a good foaming. Unfortunately, creation of gas bubbles is very small. Poor foaming without required benefit is the total result,*
- *area II - shows the slag composition after a poorly controlled oxidation. Slag shows high basicity and it has a higher content of solid particles Cr_2O_3. High viscosity and the share of solid particles decrease the kinetics of creation of gas bubbles,*
- *area III - presents the optimum composition of slag. Basicity is high and conditions for creation of gas bubbles are optimal. Solid particles of CaO and Cr_2O_3 increase the viscosity and foaming index.*

The reduction of chromium oxide during slag foaming in the EAF occurs according to the following equations [1, 5]:

$$(CrO_{1,5}) + \frac{3}{4}[Si] = [Cr] + \frac{3}{4}(SiO_2) \tag{4}$$

$$(CrO) + \frac{3}{4}[Si] = [Cr] + \frac{3}{4}(SiO_2) \tag{5}$$

$$(CrO) + xC = xCO + [Cr] \tag{6}$$

3. PROPOSAL OF THEORETICAL DETERMINATION OF SILICON AND ALUMINIUM CONSUMPTION AT REDUCTION OF SLAGS CONTAINING Cr_2O_3

On the basis of increasing demand for steels alloyed with chromium, proposal of technology of chromium oxides reduction from the slag into the metal melt in the production aggregate presenting the intensified EAF no. 5 is preparing. At first, theoretical calculation of consumption of chosen reduction agents presenting silicon and aluminium was made for the proper proposal of technology of reduction of chromium oxides during the heat.

The calculation course is given below and it focuses on the theoretical silicon and aluminium consumption at reduction of chromium oxides and other easily reducible oxides from the slag. It is necessary to know the following parameters which present the average values obtained from the realized heats in the company VÍTKOVICE HEAVY MACHINERY a. s. [6]:

- *chemical composition of two melts with diverse chromium content in the EAF (see* **Table 1***),*
- *oxygen activity in the melt: $a_{[O]}$ = 80 to 100 ppm,*
- *chemical composition of slag with the diverse content of Cr_2O_3 taken from the EAF (see* **Table 2***),*
- *metal weight: 60,000 kg,*
- *slag weight: 3,000 kg (i.e. 5 % of metal weight).*

Table 1 Average chemical composition of alloyed melt in the EAF

Chemical composition of alloyed melt with the medium content of chromium (wt. %)							
C	**Mn**	**Si**	**P**	**S**	**Cu**	**Ni**	**Cr**
0.50	0.30	0.10	0.02	0.02	0.15	0.23	**8.5**
Chemical composition of alloyed melt with the high content of chromium (wt. %)							
C	**Mn**	**Si**	**P**	**S**	**Cu**	**Ni**	**Cr**
0.60	0.40	0.06	0.02	0.02	0.15	9.0	**16.0**

Table 2 Average chemical composition of the slag in the EAF at the end of oxidation phase

Chemical composition of the slag (wt. %) with the medium content of the chromium the melt						
CaO	**Al_2O_3**	**FeO**	**MnO**	**MgO**	**SiO_2**	**Cr_2O_3**
28	10	15	5	8	8	**20**
Chemical composition of the slag (wt. %) with the high content of chromium in the melt						
CaO	**Al_2O_3**	**FeO**	**MnO**	**MgO**	**SiO_2**	**Cr_2O_3**
26	4	18	8	10	6	**25**

FeO, MnO a Cr_2O_3 belong among the easily reducible oxides. Subsequently, weight calculation of particular oxides and in them contained oxygen in 3,000 kg of slag was carried out from the given chemical composition of slag in **Table 2**, namely for both types of melts and slags, as it is obvious from **Table 3** and **Table 4**.

Table 3 Weight determination of observed oxides and oxygen for the steel with chromium content of 8.5 wt. %

Easily reducible oxides	Oxides content in the slag (wt. %)	Weight of oxides in the slag (kg)	Oxygen weight in the slag (kg)
FeO	15	450	100
MnO	5	150	33.8
Cr_2O_3	20	600	189.5

It is obvious from **Table 3** that the total weight of easily reducible oxides is 1,200 kg in case of steel with the chromium content 8.5 wt. %, when these oxides contain 323.3 kg of oxygen. Usage of reduction agent silicon or aluminium is expected for the reduction of easily reducible oxides and especially Cr_2O_3. The reaction of silicon or aluminium with oxygen contained in the easily reducible oxides in the slag takes place under following general equations:

$$Si + (Me_xO_y) = (SiO_2) + [Me] \tag{7}$$

$$Al + (Me_xO_y) = (Al_2O_3) + [Me] \tag{8}$$

282.9 kg of reduction agent silicon is needed for the reduction of 1,200 kg of easily reducible oxides, i.e. 323.3 kg of oxygen. In this way, 606.2 kg of SiO_2 is created in the slag. Subsequently, similar calculation was made, but with the usage of aluminium as a reduction agent, when 687 kg of Al_2O_3 is created in the slag.

Table 4 Determination of weight of observed oxides and oxygen for the steel with chromium content 16 wt. %

Easily reducible oxides	Content of oxides in the slag (wt. %)	Weight of oxides in the slag (kg)	Weight of oxygen in the slag (kg)
FeO	18	540	120
MnO	8	240	54.1
Cr_2O_3	25	750	236.8

In case of **Table 4** for steels with the chromium content 16 wt. %, the total weight of easily reducible oxides is 1530 kg, when these oxides contain 410.9 kg of oxygen. The usage of reduction agent silicon or aluminium is again expected for the reduction of easily reducible oxides and especially Cr_2O_3.

For the reduction of 1530 kg of easily reducible oxides, i.e. 410.9 kg of oxygen, 359.5 kg of reduction agent silicon is needed and 770.4 kg of SiO_2 is created in the slag. However, at the usage of aluminium as a reduction agent, 873.2 kg of Al_2O_3 is created in the slag.

On the basis of given calculations, calculation of change in weight and chemical composition for slags after reduction of oxides FeO, MnO, Cr_2O_3 was made, namely not only for both types of melts alloyed by chromium, but also according to the used reduction agent, as is given in **Table 5** and **Table 6**.

Table 5 Change in weight and chemical composition of slag for the steel with the chromium content 8.5 wt. %

Oxides	Original slag (old slag)		New slag - reduction with Si		New slag - reduction with Al	
	Chem. comp. (wt. %)	Weight (kg)	Weight (kg)	Chem. comp. (wt. %)	Weight (kg)	Chem. comp. (wt. %)
CaO	28	840	840	34.9	840	33.8
Al_2O_3	10	300	300	12.5	+ 687 = 987	39.7
FeO	15	450	0	0	0	0
MnO	5	150	0	0	0	0
MgO	8	240	240	10	240	9.6
SiO_2	8	240	+ 606 = 846	35.1	240	9.7
Cr_2O_3	20	600	0	0	0	0
Sum	**94**	**2820**	**2226**	**92.5**	**2307**	**92.8**
Other	6	180	180	7.5	180	7.2
Sum total	**100**	**3000**	**2406**	**100**	**2487**	**100**

It is obvious from **Table 5** that it came to the change in the weight and chemical composition of slag with the reduction of easily reducible oxides at the steel treatment with the chromium content 8.5 wt. % by the help of silicon or aluminium, which is manifested in the change in the basicity, too. The original basicity reached the values B_{OLD}= 3.5 and B_{NEW} = 1.0 at the application of silicon, however in case of reduction with aluminium, the basicity didn't change significantly and reached the values B_{OLD} = 3.5 a B_{NEW} = 3.48.

In case of **Table 6** it follows that the change in weight, chemical composition and basicity occurs again with the reduction of easily reducible oxides at the steel treatment with the chromium content 16 wt. % by the help of silicon. The original basicity reached values B_{OLD} = 4.3 and B_{NEW} = 0.8 at the application of silicon. In case of reduction with aluminium, basicity hardly ever changed and reached the values B_{OLD} = 4.3 a B_{NEW} = 4.32.

Table 6 Change in the weight and chemical composition of slag for the steel with the chromium content 16 wt. %

Oxides	Original slag (old slag)		New slag - reduction with Si		New slag - reduction with Al	
	Chem. comp. (wt. %)	Weight (kg)	Weight (kg)	Chem. comp. (wt. %)	Weight (kg)	Chem. comp. (wt. %)
CaO	26	780	780	34.8	780	33.3
Al_2O_3	4	120	120	5,4	+ 873 = 993	42.4
FeO	18	540	0	0	0	0
MnO	8	240	0	0	0	0
MgO	10	300	300	13.4	300	12.8
SiO_2	6	180	+ 770 = 950	42.4	180	7.7
Cr_2O_3	25	750	0	0	0	0
Sum	**97**	**2910**	**2150**	**96.0**	**2253**	**96.2**
Other	3	90	90	4	90	3.8
Sum total	**100**	**3000**	**2240**	**100**	**2343**	**100**

Except of basicity and slag composition change, also change in the weight and chemical composition of steel occurs, which is manifested in the increase of content of easily reducible elements in the melt. In case of melt with the chromium content 8.5 wt. %, following amount of elements was reduced:

- *weight of Cr from the slag: 410.5 kg,*
- *weight of Mn from the slag: 116.2 kg,*
- *weight of Fe from the slag: 350 kg.*

Increase of melt weight from $m_{OLD,SLAG}$ = 60,000 kg to $m_{NEW,SLAG}$ = 60,876.7 kg occurs with the reduction of slag. Change in chromium content in steel from 8.5 wt. % to 9.05 wt. % also occurs. It is obvious from the above mentioned calculation that a significant decrease of slag basicity occurs at reduction of slag containing Cr_2O_3 with silicon, not only at reduction of Cr_2O_3 but also of oxides FeO and MnO. In case of aluminium application, a significant change in the basicity doesn't occur but the content of Al_2O_3 in the slag increases. It can be also stated that the total weight of slag decreases from $m_{OLD,SLAG}$ = 3000 kg to $m_{NEW,SLAG}$= 2406 kg (reduction with silicon) or $m_{NEW,SLAG}$ = 2487 kg (reduction with aluminium).

In case of melt treatment with the chromium content 16 wt. %, basicity, slag composition, weight and chemical composition of steel also change which is manifested in the increase of content of reduced elements in the melt:

- *weight of Cr from the slag: 513 kg,*
- *weight of Mn from the slag: 186 kg,*
- *weight of Fe from the slag: 420 kg.*

Weight of the melt from $m_{OLD,SLAG}$ = 60,000 kg to $m_{NEW,SLAG}$ = 61,119 kg is increased with the reduction of slag. Content of chromium in the steel from 16 wt. % to 16.5 wt. % is changed again. It can be stated again that at the reduction of slag containing Cr_2O_3 with the silicon, a significant decrease of slag basicity occurs, not only at reduction of Cr_2O_3 but also of other oxides FeO and MnO. In case of aluminium application, basicity doesn't change significantly but the content of Al_2O_3 in the slag increases again. With the use of both reduction agents by the melt with the chromium content 16 wt. %, the slag weight will decrease again, from $m_{OLD,SLAG}$ = 3,000 kg to $m_{NEW,SLAG}$= 2,240 kg (reduction with silicon) or $m_{NEW,SLAG}$ = 2,343 kg (reduction with aluminium).

4. CONCLUSIONS

On the basis of increasing demand for steels alloyed with chromium, a technology proposal of reduction of chromium oxides from the slag into the metal melt is preparing, namely on the production aggregate presenting intensified EAF no. 5 in the company VÍTKOVICE HEAVY MACHINERY a.s. At first, a theoretical consumption calculation of chosen reduction agents presenting silicon and aluminium was made for the proper technology proposal. Obtained theoretical knowledge will be subsequently used during laboratory, pilot plant and plant experiments that will imitate the plant conditions of the EAF no. 5 aiming the suggestion and verification of the new technology of reduction of chromium oxides from the slag by the help of reduction agents presenting silicon, aluminium and carbon. The suggestion and testing of the unit prototype for the controlled slag reduction with the high content of chromium oxides and the setting of the kind, amount and way of application of the reduction agent to the slag surface are the research aim. In this way, energetic and economical demands of the production of high-chromium steels will be decreased, competitiveness of the engineering company in the market will increase and scientific-research cooperation of the production company with the important research institution presenting VSB-Technical University in Ostrava will be strengthened.

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