

Increase of chromium yield by slag reduction during production of chromium steels

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Abstract. The paper is focused on the evaluation of the course of Cr₂O₃ reduction from slag to alloyed steel under laboratory conditions. The experiments were aimed at the evaluation of increase in the chromium content in the melt together with the studying the behaviour of Cr₂O₃ and the mechanism of reduction by means of three reducing agents. Anthracite, ferrosilicon and mixtures of anthracite and ferrosilicon belong among the selected reducing agents. The experimental melts were focused on the proposal of a theoretical calculation of the consumption of selected reducing agents, study of reduction under laboratory conditions at application of alloyed steel with content of chromium of 12.16 wt. %, temperatures of 1600 °C and 1650 °C, together with the change of amount of reducing agents and reduction time. The results indicated in the paper constitute basic information on the possibilities of Cr₂O₃ reduction from slag; they will be used for verification of results in the pilot plant and operation experiments which will simulate operating conditions in the electric arc furnace.

1 Introduction

In general, the content of chromium in alloyed steels ranges from 8 to 30 wt. %. During melting of a steel charge containing chromium during steel production in an electric arc furnace, chromium is lost through oxidation, being transferred into slag. Primary losses already occur during the charge melting in the EAF; the main proportion of chromium, however, is lost from the melt during the oxidation period in which oxygen is blown to ensure essential refining reactions and decarbonisation of the melt [1, 2, 3, 4].

A high content of chromium in the slag affects its properties, which is apparent from the creation of high-viscose slag crust, which reduces the reactivity of the slag and prevents the formation of foamy slag during steel production in the EAF. Efficient reduction of chromium oxides from the slag during production of alloyed steels depends on the selection of a suitable reducing agent and the reduction technology applied during processing of steel in the EAF. The applied technology and suitable reducing agent should provide for a high degree of chromium oxide reduction from the slag. However, selection of the reducing agent depends on the equipment and technological capacities of the EAF operated. The reducing agents used include: silicon, carbon and calcium carbide. Under



operating conditions, several technologies have been developed and applied; for an efficient reduction of chromium losses in the melt, however, it is necessary to minimize losses as early as during the melting period, and particularly within the oxidation period [5, 6, 7, 8].

The paper states the results of laboratory experiments focused on the study of behaviour of chrome and its oxides, as well as the mechanism of its reduction by means of *anthracite*, *ferrosilicon* and *mixtures of anthracite and ferrosilicon*. The experimental melts were aimed at the proposal of the theoretical calculation of the consumption of selected reducing agents, the study of reduction under laboratory conditions together with a change in the amount of reducing agents and reduction time. The objective of the experiments was the verification of the basic possibilities of Cr_2O_3 reduction from slag with the use of various reducing agents.

2 Characteristics of the experiments

The laboratory experiments were implemented with the application of a charge representing alloyed steel containing 12.16 wt. % Cr and slag containing approx. 11.5 wt. % Cr_2O_3 . These samples were taken after melting of the charge and short oxidation with oxygen from the EAF under operating conditions. The basic chemical composition of the alloyed steel and slag used is indicated in **table 1** and **table 2**.

Table 1. Production chemical composition of chromium-alloyed steel taken from the EAF.

Chemical composition of steel (wt. %)							
C	Mn	Si	P	S	Cr	Ni	Mo
0.02	0.62	0.31	0.023	0.003	12.16	4.1	0.42

Table 2. Chemical composition of slag containing Cr_2O_3 taken from the EAF.

Chemical composition of slag (wt. %)							
CaO	SiO ₂	Al ₂ O ₃	MnO	MgO	Cr ₂ O ₃	FeO	V ₂ O ₅
8.2	28.6	5.0	3.8	35.7	11.5	4.9	0.16

Three reducing agents: anthracite, ferrosilicon and a mixture of anthracite and ferrosilicon in the proportion 1:1 were chosen for the reduction of slags containing Cr_2O_3 . Chemical composition of particular reducing agents is given in **table 3**.

Table 3. Chemical composition of reducing agent: *anthracite*, *ferrosilicon* and mixture of *anthracite and ferrosilicon (1:1)*.

Anthracite – C (wt. %)				
C	S	Humidity	Ash	Volatility
90.08	0.97	5.82	6.80	3.12
Ferrosilicon – FeSi (wt. %)				
Si	S	P	Mn	C
73.5	0.01	0.03	0.28	0.06

Before the laboratory melts, the consumption of the selected reducing agents was calculated theoretically. For the actual calculation, it is necessary to know the following parameters representing values acquired under operating conditions: *chemical composition of the chromium-alloyed steel*, *oxygen activity in the melt $a_{[O]}$* , *chemical composition of slag containing Cr_2O_3* , *metal and slag weight*.

The theoretical amount of reducing agents consumed was calculated from the given chemical composition of the slag as indicated in **table 1**. The actual calculations were performed on the

assumption of 100 % reduction of Cr_2O_3 oxides and remaining easily reducible FeO , MnO oxides from the slag. The calculated theoretical amount for particular reducing agents for 100 g of slag is given in **table 4**.

Table 4. Theoretical amount of reducing agents calculated according to the chemical composition of slag.

Reduction agent ($\text{g}\cdot 100\text{g slag}^{-1}$)		
Anthracite	Ferrosilicon	Anthracite + Ferrosilicon
4.65	6.70	2.32+3.35

For the laboratory experiments, an induction furnace was used, connected to a high-frequency generator GV 22. For the actual experimental laboratory melts, a block was assembled and located inside the inductor, as illustrated in **figure. 1**.

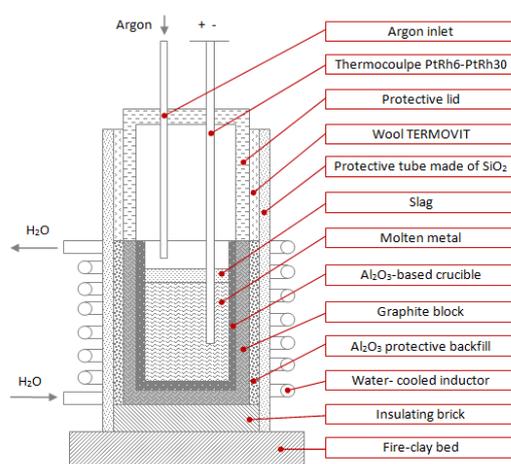


Figure 1. Schematic sectional view of the working block.

The working block consisted of a protective tube made of SiO_2 and a hollow graphite block for indirect heating of the charge. The gap between the protective tube and graphite block was filled with a protective filling of Al_2O_3 dust. The protective tube was sealed with fire-resistant TERMOVIT wool. The Al_2O_3 -based working crucible was inserted in the hollow graphite block. The working space was closed with a magnesite lid with an inlet hole of argon inert gas. During melting, the inert gas was fed to the block from a pressure cylinder with a constant flow of $0.5 \text{ l}\cdot\text{min}^{-1}$. Besides the argon inlet, there was also a thermocouple of type B located here to continuously measure temperature.

In total, 16 relevant melts were executed under laboratory conditions. The laboratory experiments proceeded in the following way: firstly, a steel charge was added within the range of 200 to 300 g. After the steel charge had been melted and tempered at the temperature of $1600 \text{ }^\circ\text{C}$ or $1650 \text{ }^\circ\text{C}$, a steel sample was taken. The obtained sample was used to determine the initial content of chromium in the steel. Subsequently, crushed reducing slag containing Cr_2O_3 was added to the steel weight in the amount of 10 wt. %. To this slag 10 wt. % of metallurgical spar CaF_2 was added to ensure fluidity of the reducing slag. 60 seconds after addition of the reducing slag the selected reducing agent, *anthracite* or *ferrosilicon* or *a mixture of anthracite and ferrosilicon*, was added. Additions of the reducing agents were executed in two variants:

- *variant I* – corresponding to the 1×theoretical amount providing for 100 % reduction of Cr_2O_3 oxides from the slag;
- *variant II* – corresponding to the 2×theoretical amount providing for reduction of Cr_2O_3 oxides from the slag.

The overall acting time of reducing agents was determined at 600 s. During the experiments, samples of steel were taken to determine the chromium content. The steel samples were taken in the middle of the experiment at 300 s and at its end at 600 s. Upon completion of the experiments, the individual steel samples were analysed to ascertain efficiency under laboratory conditions.

3 Results and discussion

Assessment of the Cr_2O_3 reduction from slag to alloyed steel under laboratory conditions was implemented in several stages. Firstly, evaluation of the course of increase in the chromium content in the steel was executed together with evaluation of the degree of reduction by means of three reducing agents, change in the amount of reducing agents and temperatures of 1600 °C and 1650 °C. The resulting course of the change in chromium content is indicated in **figure 2a** and **figure 2b**, the achieved degrees of reduction in **figure 3a** and **figure 3b** and complex evaluation of the degrees of reduction in **figure 4a** and **figure 4b**.

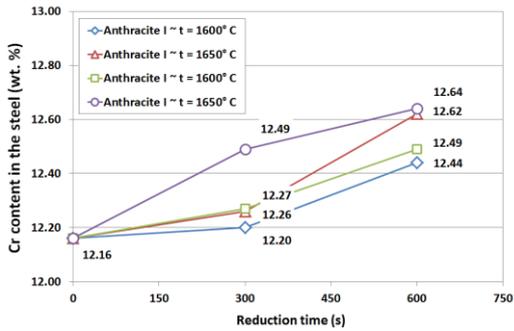
By comparing the results regarding the increase in chromium content at the application of three reducing agents from **figure 2** it was found that at *variant I* an increase in chromium content was in the range of 12.44 to 12.80 wt. %, which represents the degree of slag reduction according to the **figure 3** in the range of 31.80 % to 81.40 %. In the case of *variant II*, the increase of chromium content was in the range of 12.49 wt. % to 12.85 wt. %. It represents the degree of slag reduction in the range of 41.90 % to 87.70 %.

It is obvious from the results in the **figure 2a** to **figure 4b** that the highest increase in the chromium content of 0.69 wt. %, together with the achieved degree of reduction of 87.7 %, was found when the *mixture anthracite and ferrosilicon* was used in the proportion 1:1 together with the double the theoretical amount of reducing agent applied and at the experiment temperature of 1650 °C. In the contrary, the lowest increase in the chromium content of 0.28 wt. %, together with the achieved degree of reduction of 31.8 %, was found when *anthracite* was used, the theoretical amount of reducing agent applied and at the experiment temperature of 1600 °C.

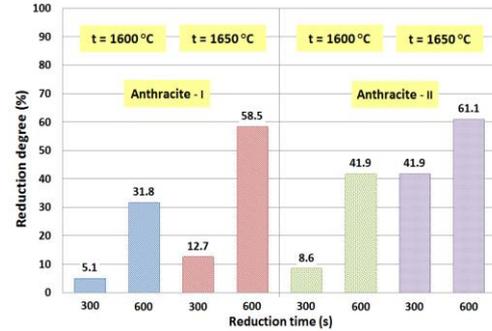
Comparing the results from **figure 2a** to **figure 4b** with a view to the individual reducing agents, it can be stated that *the mixture of anthracite and ferrosilicon* seems to be more efficient. In the case of the *mixture of anthracite and ferrosilicon*, better results were achieved, with regard to both the chromium content increase in the range of 0.15 wt. % to 0.21 wt. % and the achieved degree of reduction being in the range of 19 % to 26 %. These results are valid at application of the double the theoretical amount of reducing agent and at the experiment temperature 1650 °C.

In addition to the reducing agents, the effect of an increase in the theoretical amount of reducing agents providing for reduction of Cr_2O_3 oxides from the slag was also tested. In this case, the application of *variant II* with the 2× theoretical amount of reducing agent resulted in an increase in the chromium content in steel together with an increase in the degree of reduction, as evident from **figure 2a** to **figure 4b**.

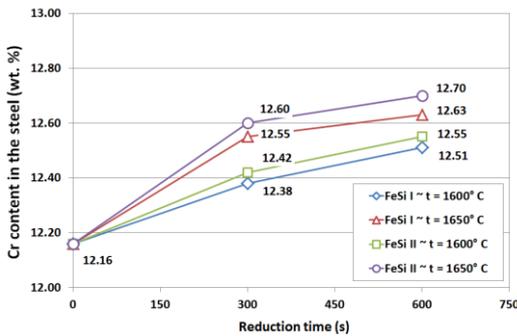
A temperature increase from 1600 °C to 1650 °C had a positive influence on the efficiency of Cr_2O_3 reduction from the slag. The increase in the theoretical amount of reducing agent and extension of the reduction time from 300 s to 600 s had a similar effect, as it is evident from **figure 2a** to **figure 4b**.



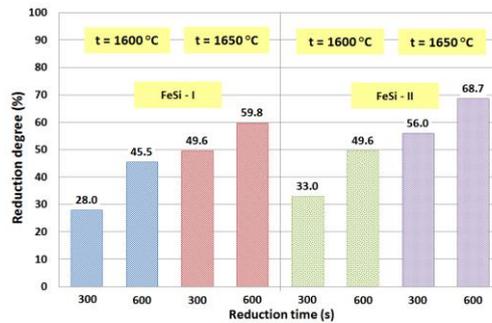
a) reducing agent anthracite and variants I and II



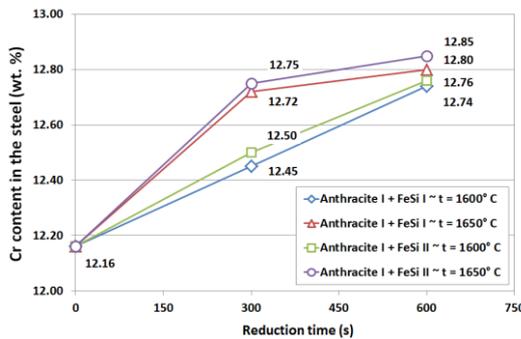
a) reducing agent anthracite and variants I and II



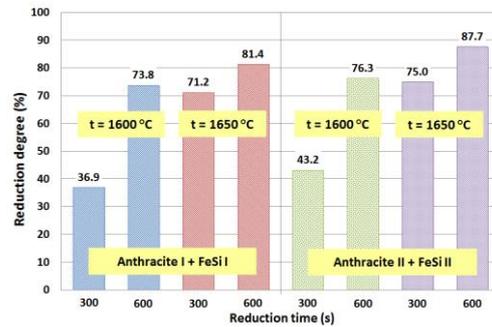
b) reducing agent ferrosilicon and variants I and II



b) reducing agent ferrosilicon and variants I and II



c) reducing agent anthracite + ferrosilicon and variants I and II



c) reducing agent anthracite + ferrosilicon and variants I and II

Figure 2. Changes in chromium content in the metal when using the reducing agent.

Figure 3. The degree of reduction of Cr₂O₃ oxides from the slag when using the reducing agent.

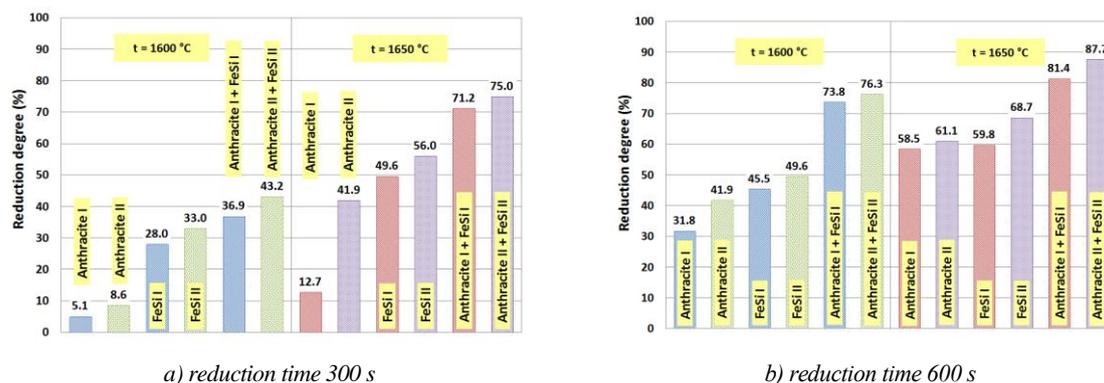


Figure 4. Aggregate comparison of achieved degrees of reduction in Cr_2O_3 oxides when using the reducing agent.

4 Conclusions

Pursuant to the results achieved by means of the laboratory experiments, it is possible to state:

- trend of reduction of Cr_2O_3 oxides to steel at different efficiency was verified at all three reducing agents;
- the mixture of anthracite and ferrosilicon in the proportion 1:1 seems to be more efficient reducing agent than separately used ferrosilicon and anthracite;
- in the case of steel with the Cr content 12.16 wt. % and Cr_2O_3 11.5 wt. % in the slag, the reducing agents can be ordered in the following sequence from the best: the mixture of anthracite and ferrosilicon, ferrosilicon and anthracite;
- with the usage of the mixture of ferrosilicon and anthracite in the proportion 1:1, together with the application of the double the theoretical amount of reducing agent and the temperature 1650 °C the efficiency of Cr_2O_3 reduction to 87.7 % was achieved;
- the increase of temperature from 1600 °C to 1650 °C had a positive influence on the efficiency of Cr_2O_3 reduction from slag;
- in addition to temperature increase, the increase in theoretical amount of reducing agent together with the extension of reduction time from 300 s to 600 s has also a positive influence on reduction efficiency;
- it can be also assumed that with the increase in Cr_2O_3 content in the slag a higher viscosity of slag connected with the crust creation can occur which decreases the reduction efficiency. This assumption will be verify with the subsequent series of experiments;
- in the subsequent series of experiments, the possibility of combination of various reducing agents at application of steel with various content of Cr and Cr_2O_3 in the slag under similar laboratory conditions will be verify which will be a part of following papers.

The acquired laboratory findings will subsequently be used during the half-operational and operational experiments that will imitate the operating conditions in the EAF with the aim of designing and testing new technology for the reduction of chromium oxides from the slag using selected reducing agent.

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