STUDY OF SLAG REGIME OF HIGH- ALLOYED STEELS UNDER LABORATORY CONDITIONS

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Abstract

In the presented paper, the results of laboratory experiments aimed at the study of chromium and the behaviour of its oxides, together with its reduction mechanism with the aid of silicon and carbon, are given. Experimental heats were aimed at the proposal of a theoretical calculation of consumption of chosen reduction agents, a reduction study under laboratory conditions at the application of alloyed steel with a chromium content of ca. 9 wt. %, 13 wt. % and 18 wt. %, at temperatures of 1 600 °C and 1 650 °C, together with the change in the amount of reduction agents and the reduction period. The results will be used to verify the results obtained during half-operational and operational experiments that will imitate the operational conditions in the EAF.

Keywords: Slag reduction, chromium slag, high alloyed steels, laboratory experiments

1. INTRODUCTION

In the production of high-alloyed steels, the cost of raw materials represents an essential part of total production costs. Chromium is not only one of the main ingredients in the production of high-alloyed steels, but it also makes up a large part of the cost of raw materials [1, 2]. During steel charge melting in the EAF, chromium is partly lost due to its oxidation and transition into slag. A high chromium content in the slag affects its properties, which results in the creation of slag crust with high viscosity, reducing slag reactivity and preventing the formation of foaming slag during steelmaking in the EAF [3, 4].

In the production of high-alloyed steels, optimized slag regime is therefore very important for ensuring the production of steel while minimising costs. In addition, slag regime optimisation can also influence energy consumption and material balance in the EAF. In the production of high-alloyed steels, the effective reduction of chromium oxides from the slag depends on the choice of a suitable reducing agent (reductant) and the applied reduction technology during steel processing in the EAF. The used reducing agents include: silicon, carbon, aluminium and calcium carbide [5, 6].

This paper presents the results of laboratory experiments aimed at studying the behaviour of chromium and its oxides, as well as the mechanism of its reduction using carbon and silicon. Experimental heats were focused on verifying the theoretical calculation of consumption of the selected reducing agents, studying the reduction under laboratory conditions in the application of alloyed steel with a content of about 9 to 18 wt. % of chromium, at temperatures of 1 600 and 1 650 °C, while changing the amount of reducing agents and reduction time. The aim of these experiments was to verify the basic options of Cr_2O_3 reduction from slag when using various reductants.

2. CHARACTERISTICS OF THE LABORATORY EXPERIMENTS

Laboratory experiments were carried out in the application of three different charges representing high- alloyed steel, containing about 9 to 18 wt. % of chromium, and slag containing about 12 to 24 wt. % of Cr_2O_3. The basic chemical composition of the high-alloyed steel and slag used for the laboratory experiments is given in **Table 1** and **Table 2**.

Table 1 Chemical composition of high-alloyed steels A, B and C used for the laboratory experiments

Steel type	**Steel chemical composition (wt. %)**							
	C	**Mn**	**Si**	**P**	**S**	**Cr**	**Ni**	**Mo**
A	0.08	0.48	0.30	0.015	0.002	**8.65**	0.28	0.93
B	0.02	0.62	0.31	0.023	0.003	**12.16**	4.1	0.42
C	0.04	1.57	0.58	0.017	0.003	**17.44**	10.2	0.07

Table 2 Chemical composition of slags A, B and C containing Cr_2O_3, used for the laboratory experiments

Slag type	**Slag chemical composition (wt. %)**							
	CaO	**SiO_2**	**Al_2O_3**	**MnO**	**MgO**	**Cr_2O_3**	**FeO**	**V_2O_5**
A	6.1	21.6	9.0	6.4	×××	**23.9**	×××	0.9
B	8.2	28.6	5.0	3.8	35.7	**11.5**	4.9	0.16
C	18.19	20.42	6.18	3.09	35.2	**17.7**	5.21	×××

Two reducing agents were selected to reduce slags with Cr_2O_3: anthracite and ferrosilicon. The chemical composition of the two reducing agents is given in **Table 3**.

Table 3 Basic chemical composition of anthracite and ferrosilicon (reducing agent)

Anthracite - chemical composition (wt. %)				
C	**S**	**Moisture**	**Ashes**	**Elusiveness**
90.08	0.97	5.82	6.80	3.12
Ferrosilicon - chemical composition (wt. %)				
Si	**S**	**P**	**Mn**	**C**
73.5	0.01	0.03	0.28	0.06

A theoretical calculation of the consumption of the selected reducing agents was carried out prior to heating in the laboratory. For the calculation itself, it is necessary to know the following parameters that represent the values obtained from the operating conditions:

- *chemical composition of chromium-alloyed steel,*
- *oxygen activity in the melt* $a_{[O]}$*,*
- *chemical composition of the slag containing* Cr_2O_3*,*
- *mass of metal and slag.*

In addition to basic oxides, the slag contains the easily reducible oxides FeO, MnO and Cr_2O_3. Reducing agents anthracite and ferrosilicon are advantageously used to reduce easily reducible oxides, especially Cr_2O_3. Reactions of carbon or silicon with oxygen contained in easily reducible oxides in the slag occur according to the following general equations (1) and (2):

$$(Cr_2O_3) + 3C_{(s)} = 2[Cr] + 3CO_{(g)} \qquad (1)$$

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

The theoretical amount of consumed reducing agents was calculated from the chemical composition of the slag presented in **Table 2**. Calculations were made assuming 100 % reduction of Cr_2O_3 oxides and the remaining easily reducible oxides FeO, MnO from the slag. For the application of anthracite and ferrosilicon, we determined theoretical quantities for each type of slag as given in **Table 4** [7].

Table 4 The determined theoretical amount of reducing agent for various types of steel and slag

Reducing agent	**Type of slag in the steel production (g·100 g of slag^{-1})**		
	Steel and slag A	**Steel and slag B**	**Steel and slag C**
Anthracite	15.15	4.65	5.99
Ferrosilicon	24.67	6.70	8.63

Laboratory experiments took place in an induction furnace which was connected to a GV 22 high frequency generator. For the experimental laboratory heating, we assembled a block that was placed inside the inductor, which is shown in **Figure 1**.

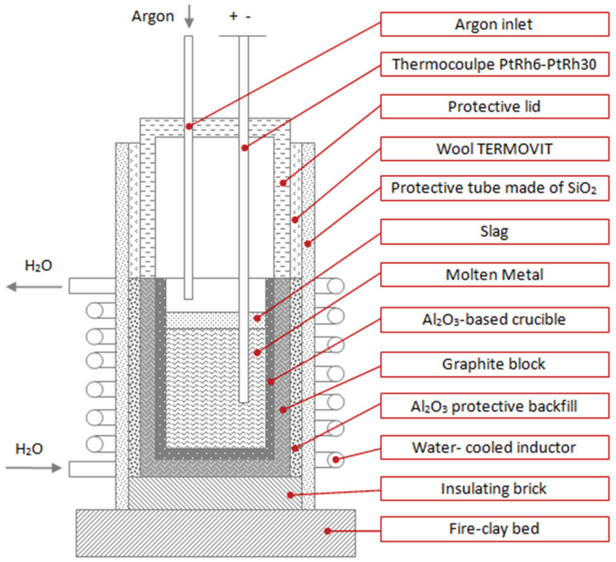


Figure 1 Schematic sectional view of the working block

The working block was composed 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 the graphite block was filled with a protective powdery Al_2O_3 backfill. The protective tube was sealed with TERMOVIT refractory wool. Al_2O_3-based crucible was inserted into the hollow graphite block. The working space was closed using a magnesite lid fitted with an opening to supply the inert gas argon. During the melt, this inert gas was fed to the block from a pressure cylinder at a constant flow rate of 0.5 l·min^{-1}. In addition to the gas inlet, the lid also comprised a thermocouple, type B (PtRh6-PtRh30), for conducting continuous temperature measurements.

Under laboratory conditions, a total of 48 relevant heatings were carried out. The laboratory experiments were implemented as follows: First of all, a steel charge was added in the amount of 200 to 300 g. After melting and tempering the steel charge to a temperature of 1 650 °C, steel samples were taken. The obtained sample served for determining the initial chromium content in the steel. Crashed reduced slag - containing Cr_2O_3 in an amount of 10 wt. % to the steel weight - was added subsequently. This slag comprised 10 wt. % of CaF_2 to ensure the fluidity of the reducing slag. The selected reducing agent, anthracite or ferrosilicon, was added 60 seconds after adding the slag. The addition of the reducing agents was carried out in two variants:

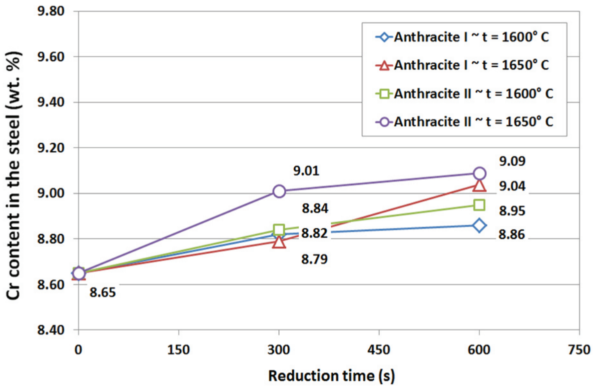
- *Variant I - corresponding to the theoretical amount providing 100 % reduction of Cr_2O_3 oxides from the slag;*
- *Variant II - corresponding to double the theoretical amount providing reduction of Cr_2O_3 oxides from the slag.*

The total time of the reducing agents' activity was fixed at 600 seconds. During the experiments, steel samples were taken in order to determine the content of chromium - in the middle of the experiment after 300 seconds, and at the end of the experiment after 600 seconds. After completion of the experiments, each steel sample was analysed to determine the efficiency of the reduction process under laboratory conditions.

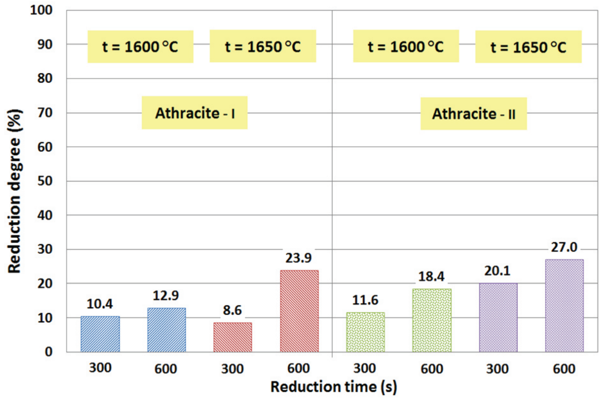
3. EVALUATION OF ACHIEVED RESULTS

The course of Cr_2O_3 reduction from the slag into the high-alloyed steel under laboratory conditions was evaluated in several steps. First, the evaluation focused on the increase in chromium content in the steel, the degree of reduction using the two reducing agents, the influence of changes in the amount of reducing agents, and temperatures of 1 600 and 1 650 °C was carried out.

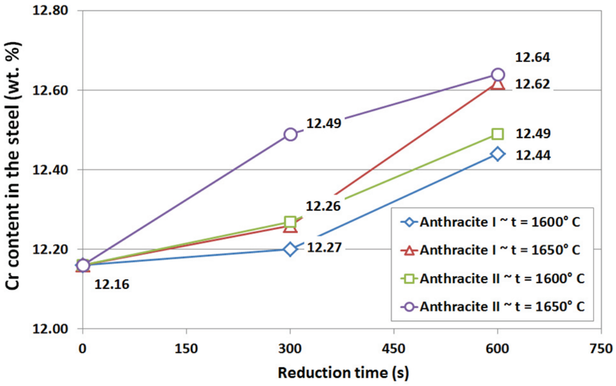
For anthracite, the results regarding the course of changes in chromium content in the steel are given in **Figure 2a** to **Figure 2c**, the achieved degrees of reduction are shown in **Figure 3a** to **Figure 3c**.



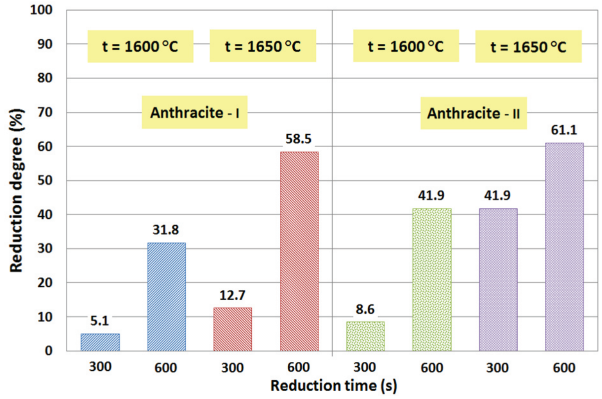
a) Steel A, reducing agent anthracite, variants I and II



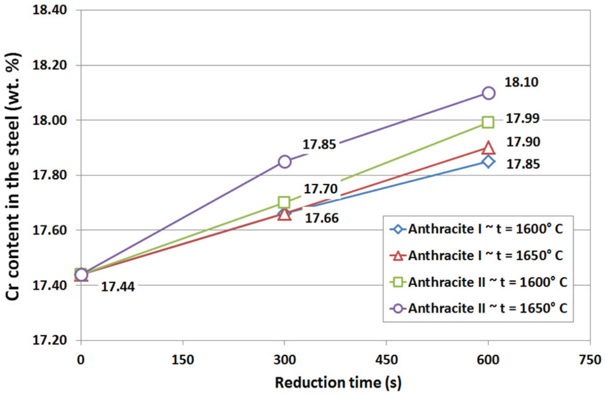
a) Slag A, reducing agent anthracite, variants I and II



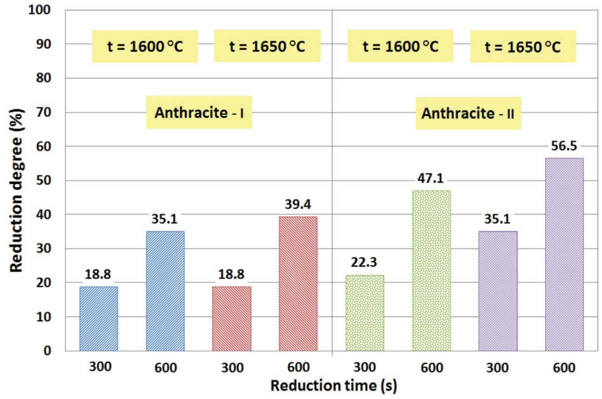
b) Steel B, reducing agent anthracite, variants I and II



b) Slag B, reducing agent anthracite, variants I and II



c) Steel C, reducing agent anthracite, variants I and II

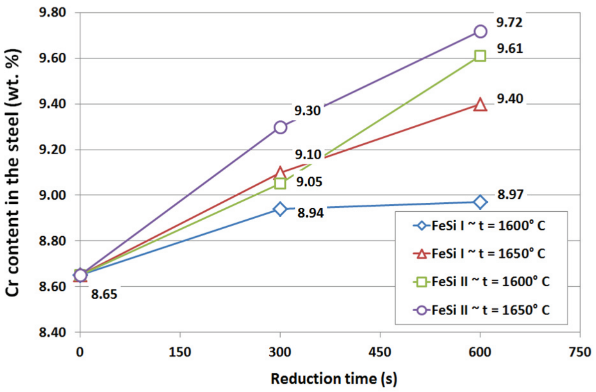


c) Slag C, reducing agent anthracite, variants I and II

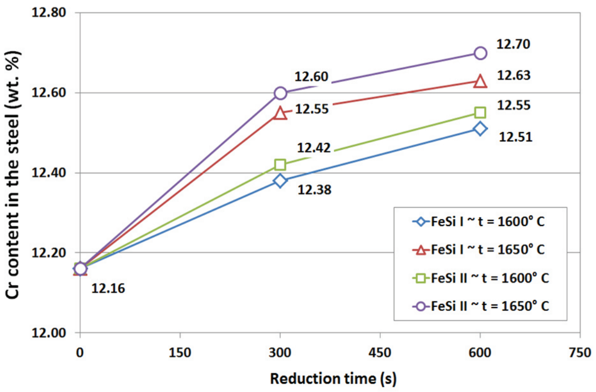
Figure 2 Changes in chromium content in the metal when using anthracite as the reducing agent

Figure 3 The degree of reduction of Cr_2O_3 oxides from the slag when using anthracite as the reducing agent

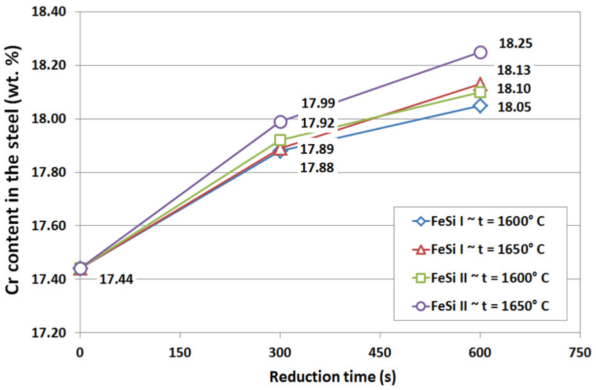
For ferrosilicon, the results regarding the course of changes in chromium content in the steel are given in **Figure 4a** to **Figure 4c**, the achieved degrees of reduction are shown in **Figure 5a** to **Figure 5c**.



a) Steel A, reducing agent FeSi, variants I and II

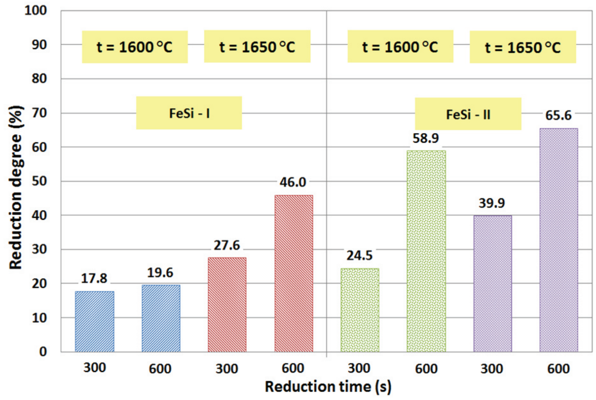


b) Steel B, reducing agent FeSi, variants I and II

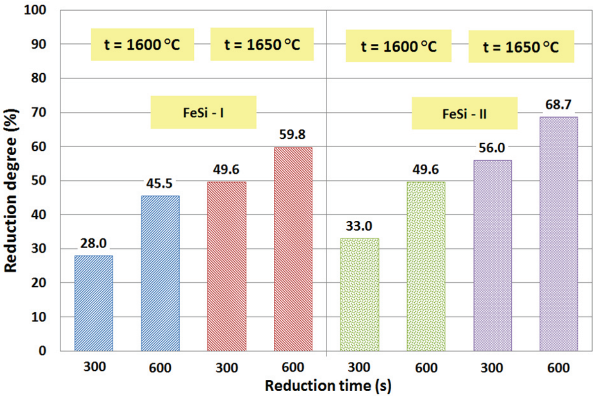


c) Steel C, reducing agent FeSi, variants I and II

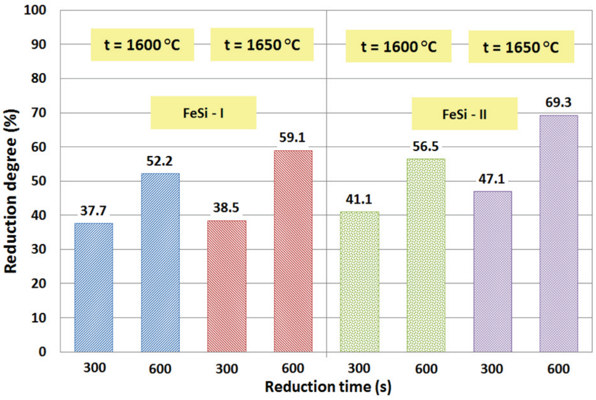
Figure 4 Changes in chromium content in the metal when using FeSi as the reducing agent



a) Slag A, reducing agent FeSi, variants I and II



b) Slag B, reducing agent FeSi, variants I and II



c) Slag C, reducing agent FeSi, variants I and II

Figure 5 The degree of reduction of Cr_2O_3 oxides from the slag when using FeSi as the reducing agent

By comparing the results regarding the increase in chromium content for all grades of steels A, B and C from **Figure 2** and **Figure 4,** it was found that Variant I corresponded to an increase in chromium content in the range of 8.86 to 18.13 wt. %. According to **Figure 3** and **Figure 5**, this represents a degree of slag reduction in the range of 12.90 to 59.80 %. Based on the analysis of the results, we can say that the greatest increase in chromium content in the steel - in the range of 0.47 to 0.75 wt. %, with an achieved degree of reduction of 46.0 to 59.80 % - was found when using ferrosilicon, the theoretical amount of reducing agent and an experimental temperature of 1 650 °C, for all grades of steels A, B and C.

The results also indicate that the lowest increase in chromium content in the steel - in the range of 0.21 to 0.46 wt. %, with an achieved degree of reduction of 12.90 to 35.10 % - was found when using anthracite, the theoretical amount of reducing agent, and an experimental temperature of 1 600 °C, for all grades of steels A, B and C.

In Variant II, for all grades of steels A, B and C, the increase in chromium content ranged between 0.30 to 1.07 wt. %; this corresponds to a degree of reduction between 18.40 to 69.34 %. From the results for all grades of steels A, B and C, it can again be stated that the highest increase in chromium content in the steel - in the range of 0.54 to 1.07 wt. %, with an achieved degree of reduction of 65.50 to 69.34 % - was found when using ferrosilicon, double the theoretical amount of reducing agent, and an experimental temperature of 1 650 °C, for all grades of steels A, B and C.

In Variant II, the lowest increase in chromium content in the steel - in the range of 0.30 to 0.55 wt. %, with an achieved degree of reduction of 18.40 to 47.08 % - was found when using anthracite, double the theoretical amount of reducing agent, and an experimental temperature of 1 600 °C, for all grades of steels A, B and C.

When focusing on the results achieved in each variant, a comparison of **Figure 2** to **Figure 5** shows that the application of ferrosilicon as the reducing agent and a temperature of 1 650 °C leads to the highest increase in chromium content and degree of reduction when using double the theoretical amount of reducing agent. Better results were achieved in the case of ferrosilicon, both in the increase in chromium content by about 0.4 wt. %, and the higher degree of reduction by about 8 %, when comparing the best results.

According to **Figure 2** to **Figure 5**, the experiments also show that the increase in temperature from 1 600 to 1 650 °C and reduction time from 300 to 600 seconds supports the process of Cr_2O_3 reduction from the slag into the steel, when using both types of reducing agents, i.e. anthracite and ferrosilicon.

4. CONCLUSION

Under laboratory conditions, we carried out experiments to obtain information about the course of Cr_2O_3 reduction from the slag into the alloyed steel and about the increase in chromium content in the metal when using anthracite and ferrosilicon as reducing agents. Based on the experiments' results, it is possible to draw the following conclusions:

- *Identical trends in the reduction efficiency were observed for all three grades of high-alloyed steels A, B and □;*
- *Ferrosilicon seems to be a more effective reducing agent than anthracite;*
- *A higher degree of reduction was positively affected by increasing the temperature from 1 600 to 1 650 °C;*
- *In addition to higher temperatures, positive effects were also brought about by increasing the theoretical amount of reducing agent;*
- *Extension of the reduction time from 300 to 600 seconds has a positive effect on reduction efficiency;*
- *The achieved degrees of reduction are comparable for all steel grades under similar conditions;*
- *When using ferrosilicon as the reductant at a temperature of 1 650 °C and with double the theoretical amount of reductant, the achieved degree of reduction ranged between 66 and 69 %;*
- *The results also clearly show that different initial contents of* Cr_2O_3 *in the slag had no significant effect on the degree of reduction.*

The acquired laboratory findings will subsequently be used during the half-operational and operational experiments that will imitate the operating conditions in the EAF run in the steel plant VHM, a.s., with the aim of designing and testing new technology for the reduction of chromium oxides from the slag using carbon and silicon as reducing agents.

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