

CHROMIUM REDUCTION FROM HIGH CHROMIUM SLAG WITH REDUCING AGENTS OF C AND SI IN AN ATMOSPHERIC INDUCTION MELTING FURNACE USING AN OXYGEN/FUEL BURNER

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Abstract

The presented work presents the proposal, accomplishment and consequent evaluation of experiments based on the theoretical calculation and its comparison to the actually achieved level of chromium reduction from slag. The aim is reduction of chromium from slag with a high content of Cr₂O₃ with reducing agents of carbon in the form of anthracite and silicon in the form of ferroalloy FeSi. Experimental meltings in an atmospheric induction melting furnace were performed with an oxygen/fuel burner which was designed and produced for these experiments. Medium element contents in the melt during reduction were 16 % of Cr, 5 % of Ni and 1 % of Mo. The technology for chromium reduction from the slag was designed and experimentally performed with the aim of its transferability to the large metallurgical aggregate of intensified electric arc furnace.

Keywords: Stainless steel, slag, chromium, carbon, silicon

1. INTRODUCTION

During the production of melt from alloyed chromium waste (hereafter referred to as Cr waste) in an intensified electric arc furnace (hereafter referred to as EAF), oxidation of chromium and its loss to the slag in the form of Cr₂O₃ occurs. According to the used Cr waste, the losses are in the range of 30-60 %, when the slag contains up to 13-15 % of Cr₂O₃. Reverse reduction of chromium from the slag to the melt in EAF is difficult and particularly time-consuming and subsequently also energetically-consuming. For this reason, experimental meltings were performed. They were aimed at reducing chromium from the slag back to the melt with a reducing agent of carbon in the form of anthracite and silicon in the form of a ferroalloy. Reduction of chromium with silicon and carbon is performed according to chemical reactions (1) and (2) [1] [2]



From the thermodynamic point of view, reverse reduction of chromium from the slag to the melt depends on temperature, the chemical composition of the slag and the chemical composition of the melt. The author [3] presents the thermodynamic reactions of balance (3) shown below

$$\log(\%Cr)_{\substack{slag \\ exp.}} = 4.887 - \frac{8866}{T} + 0.340 \log[\%Cr] - 0.178 \log[\%Si] - 1.721 \log B \quad (3)$$

where B is slag basicity expressed by the relation (4)

$$B = \frac{CaO}{SiO_2} \quad (4)$$

nevertheless, according to the author [3] there is a significant difference between the calculated equilibrium states and the actual data from industrial practice. For this reason, the author presents the thermodynamic equation (5) obtained from statistical evaluation of data from industrial practice.

$$\log(\%Cr)_{\frac{slag}{ind.}} = 1.118 + \frac{949}{T} - 0.550\log[\%Cr] - 0.154\log[\%Si] - 0.508\log B, \quad (5)$$

where B is slag basicity expressed by the relation (6)

$$B = \frac{CaO+MgO}{SiO_2} \quad (6)$$

Temperature dependence of Gibbs energies for chromium reduction with calcium carbide, carbon and silicon is presented by [1] in **Figure 1**. It follows from the figure that with increasing temperature, the effect of reduction of calcium carbide (CaC₂) and carbon decreases, and reduction with silicon is not so much temperature dependent. Experimental meltings of Cr reduction from the slag to the melt are described in next chapter.

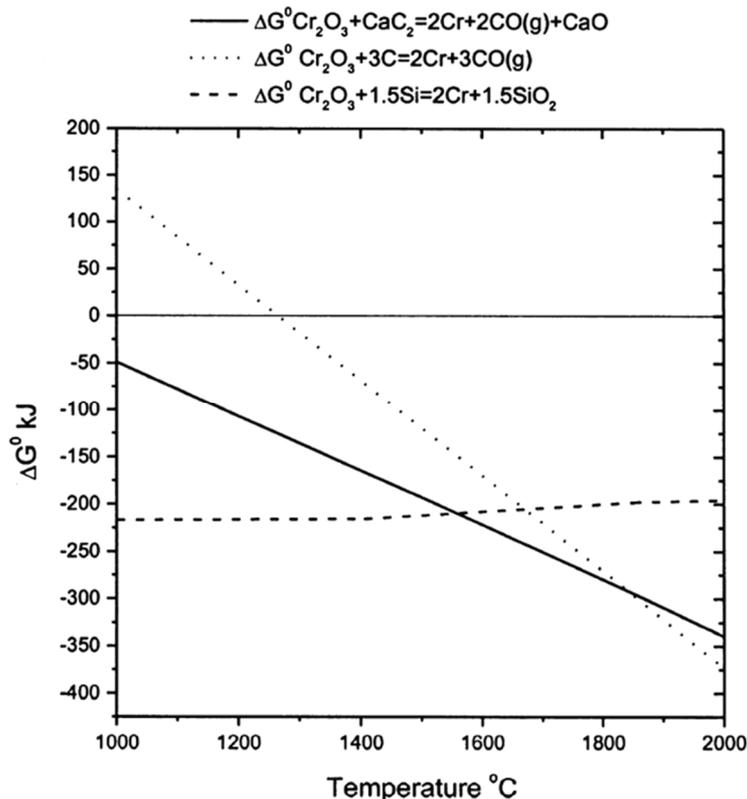


Figure 1 Temperature dependence of Gibbs energies for chromium reduction with calcium carbide, carbon and silicon

2. CHROMIUM REDUCTION FROM THE SLAG

Experimental meltings were performed in pilot conditions of the company MATERIAL AND METALLURGICAL RESEARCH Ltd. (hereafter referred to as MMR) in an atmospheric induction melting furnace (hereafter referred to as IF) with an oxygen/fuel burner (hereafter referred to as OFB) simulating conditions in the EAF in the company of VÍTKOVICE HEAVY MACHINERY a.s. (hereafter referred to as VHM), see **Figure 2**. Propane-butane cylinders and oxygen distribution in MMR were used as a source of gas. The melt surface was covered with Sibral insulation blocks laid down on the top part of the crucible of IF, see **Figure 2**.

A total of 5 series of experiments on the melted steel of X4CrNiMo16-5-1 quality were performed. The standardized chemical composition of X4CrNiMo16-5-1 quality is presented in **Table 1**. The chemical

composition was modified to the conditions in EAF and in **Table 1** it is labelled as X4CrNiMo16-5-1EAF. This chemical composition was fundamental for the experiments in MMR.

Table 1 Chemical composition of standardized X4CrNiMo16-5-1 quality for experiments identical to the chemistry in EAF in VHM (weight %)

		C	Mn	Si	P	S	Ni	Cr	Mo	V	N
Standard	min.	-	-	-	-	-	4.00	15.00	0.80	-	0.0200
	max.	0.06	1.50	0.70	0.040	0.030	6.00	17.00	1.50	-	-
Experiments in MMR (X4CrNiMo16-5-1EAF)	min.	0.15	0.25	0.25	-	-	4.50	15.00	0.90	-	-
	max.	0.20	0.35	0.35	0.025	0.020	5.50	16.50	1.20	0.10	-

For a full transfer of the production technology - from pilot experiments performed in MMR to the metallurgical aggregate of EAF in VHM - batch raw materials, alloying and slag-forming agents and reducing agents of C and FeSi from the company VHM were used for experimental meltings in MMR. Since a molten ingot from the previous experiment was used for each experiment, the input conditions are not completely identical.

In the newly produced IF crucible for the batch weight of 1750 kg, 1000 kg of batch and alloying additives as total were used for each series of experiments. Immediately before its full melting, slag with a weight of 45 kg (4.5 % of the melt weight) was added on the surface. The chemical composition of the slag externally added for experiments is presented in **Table 2**. To improve melting and covering of the melt surface, the slag was manually crushed in MMR from a granulation of ca. 250-300 mm, to a granulation of ca. 20-50 mm, see **Figure 3**. The slag immediately after the addition of the last dose is presented in **Figure 4**.

Table 2 The chemical composition of the slag externally added for experiments of Cr reduction from the slag (weight %)

Element	C	S	Fe	FeO	Fe ₂ O ₃	MnO	Cr ₂ O ₃	V ₂ O ₅	TiO ₂	CaO
Content	0.12	0.034	12.95	0.01	0.47	2.97	15.87	0.21	3.12	24.63
Element	SiO ₂	P ₂ O ₅	Al ₂ O ₃	MgO	CaF ₂	Na ₂ O	Zn	K ₂ O	BaO	Nb ₂ O ₅
Content	21.27	0.01	8.94	8.72	0.01	0.01	0.01	0.04	0.01	0.47



Figure 2 Atmospheric induction melting furnace with an oxygen/fuel burner during experimental melting with the crucible covered with Sibril insulation blocks



Figure 3 Granulation of 20-50 mm slag for experiments after manual crushing



Figure 4 The slag on the melt surface immediately after the addition of the last dose from 45 kg

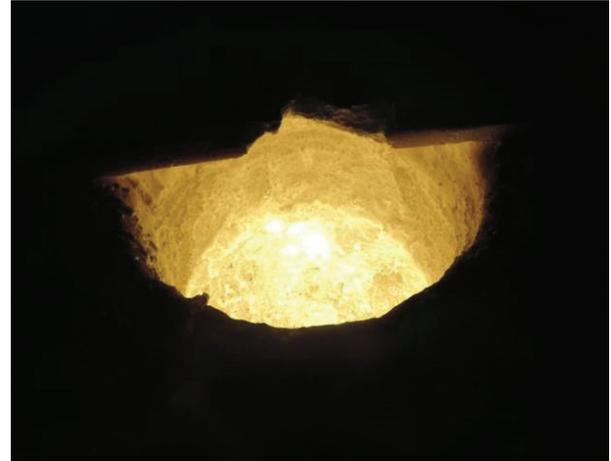


Figure 5 Molten slag in IF crucible

Immediately after the addition of the slag on the melt surface, the slag-forming agent Topex with a high content of MgO was added. This additive is standardly used in EAF in VHM to increase the operational life of the furnace lining. Topex granulation was 20-30 mm. Subsequently, Topex in the crucible was mixed together with the slag and then OFB for full and fast melting of the slag was started. When the slag was melted after ca. 20 min, see **Figure 5**, and the melt was heated to a temperature of 1650 °C, a so-called zero sample of the metal and of the slag was taken for chemical analysis.

One reducing dose consisted of 1.7 kg of C and 3.9 kg of Si. These elements were added in the form of anthracite with granulation of 1-3 mm and ferro-silicon FeSi with granulation of 1-3 mm, and one dose of reducing agents was formed by them together. This dose was multiplied for each additional experiment. 1x for the first set, 2x for the second set, 3x for the third set, 4x for the fourth set and 5x for the fifth set of experiments. One dose of reducing agents of C and FeSi was added on the surface in each set of experiments when the input to the oxygen/fuel burner was on. This dose was added on the surface of the slag and was inserted into the whole volume of the slag by vigorous mixing. Five minutes after the reducing dose was added, partial melting of the reducing agents was visible and first samples of the metal and slag were taken for chemical analysis.

Subsequently, the temperature of the melt was measured every 5 minutes within 20 minutes of the addition of the first reducing dose and then samples of the metal and slag were taken for chemical analysis. When each set of the experiments was finished, the melt was poured from IF into a ladle and then, in the atmospheric foundry field, the melt under an argon protective atmosphere was cast from the bottom to a V2A ingot mould.

3. EVALUATION OF CHROMIUM REDUCTION FROM THE SLAG

During the evaluation of changes in chromium content in the melt, see **Figure 6**, and changes Cr₂O₃ content in the slag, see **Figure 7**, it can be seen that the highest reducing capability was found for the dose with 3x higher content of C and FeSi. Altogether, 53 % of Cr was reduced from the slag, see **Figure 8**. If we add the total change in Cr content in the melt in the 3rd experiment before and after reduction, the result is a Cr content 8.42 kg higher, see **Figure 9**, but the chromium content in the slag fell by 1.94 kg of Cr only, see **Figure 9**. It can be seen from **Figure 8**, **Figure 9** and **Table 3** that in the 1st, 4th and also 5th experiment, the chromium content both in the slag and in the melt decreased. In the 2nd and 3rd experiment, the Cr content disproportionately increased compared to its decrease in the slag. To maintain the same initial conditions regarding the Cr content in the melt before the addition of the slag, alloying of the slag to the required content was performed. Based on this fact, the IF crucible was destroyed. Penetration of the metal, probably chromium, which penetrates the lining during the experiments and this way is uncontrollably returned to the melt.

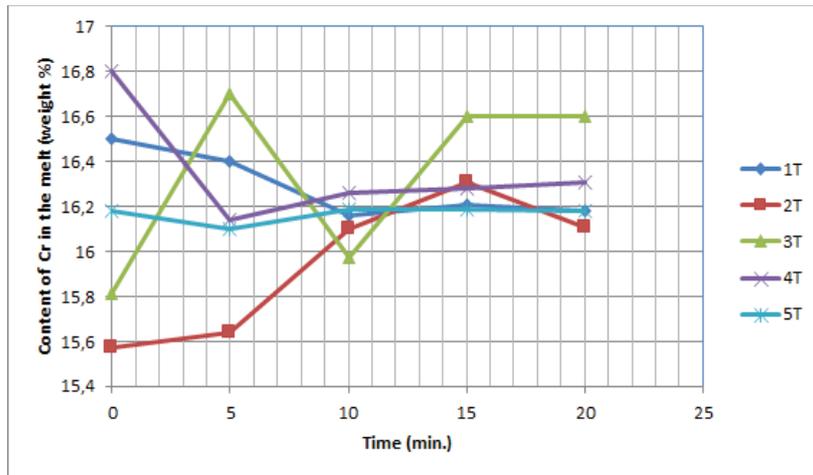


Figure 6 Time course of Cr content in the melt for all experiments

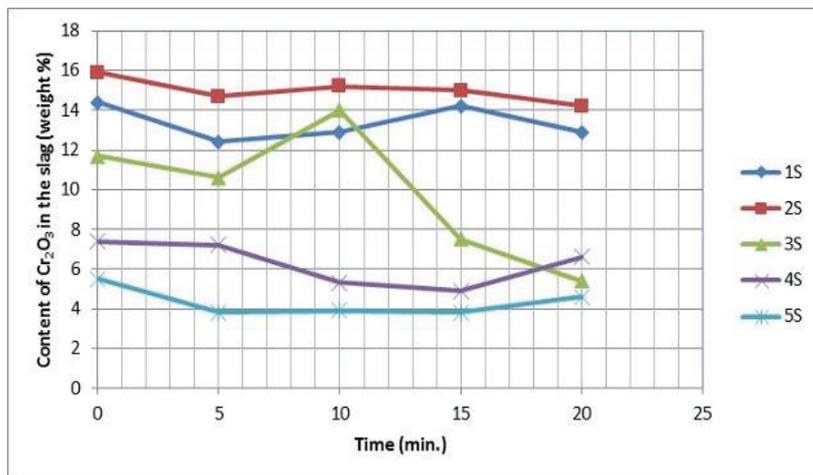


Figure 7 Time course of Cr₂O₃ content in the slag for all experiments

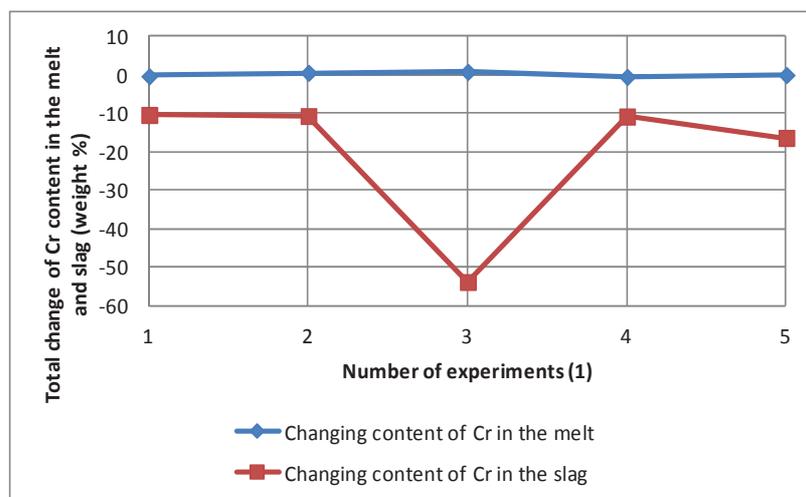


Figure 8 Total change of Cr content in the melt and slag for all experiments (weigh %)

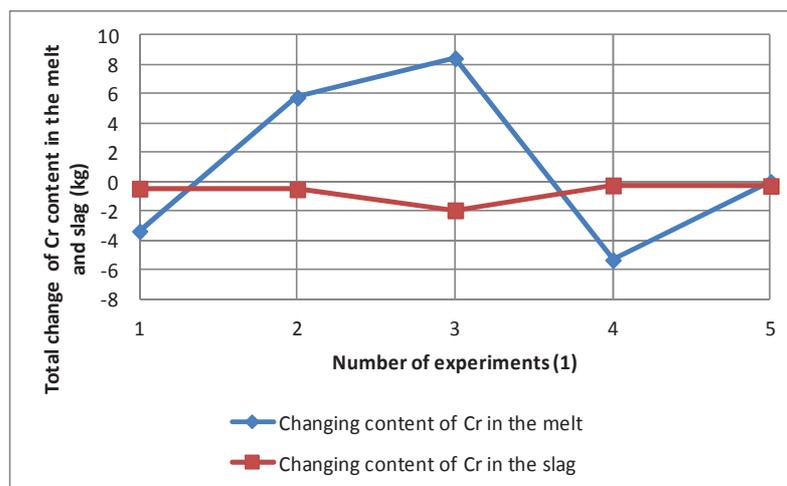


Figure 9 Total change of Cr content in the melt and slag for all experiments (kg)

Table 3 Changes in chemical composition and weight of Cr₂O₃ and Cr in the slag during individual experiments

	Units	Experiments				
		1.	2.	3.	4.	5.
Slag weight	(kg)	45.00	45.00	45.00	45.00	45.00
Changes of Cr ₂ O ₃ content in the whole volume of the slag	(%)	-1.50	-1.70	-6.30	-0.80	-0.90
	(kg)	-0.68	-0.77	-2.84	-0.36	-0.41
Changes of Cr content	(kg)	-0.46	-0.52	-1.94	-0.25	-0.28
	(%)	-10.42	-10.69	-53.85	-10.81	-16.36

The most important of the above-mentioned facts was the decrease in Cr₂O₃ content in the slag, which was highest in the 3rd experiment with the triple reducing dose of C and FeSi.

Optical evaluation of the slag's appearance was performed as well. This evaluation is indicative only, to discover trends, since due to the non-uniform initial chemical composition of the melt, the content of Cr₂O₃ in the slag after partial melting is influenced as well. It can be concluded from that the slag after the addition of reducing agents of C and FeSi in the 1st and 2nd experiment was fully liquid 20 minutes after the start, while in the 3rd experiment already after 10 to 15 minutes, and in the 4th and 5th experiments there was not enough time for it to liquefy due to the high content of reducing agents.

4. CONCLUSION

Experimental meltings for Cr reduction from slag were designed for the conditions at the company MATERIAL AND METALLURGICAL RESEARCH s.r.o. so that they are transferable to the intensified electric arc furnace (EAF) of the company VÍTKOVICE HEAVY MACHINERY a.s. The experimental meltings were performed for X4CrNiMo16-5-1 quality with a chemical composition corresponding to the composition in EAF during production from recyclable metal waste alloyed with chromium.

The evaluation of the change in the Cr₂O₃ content in the slag is clear but due to alternative saturation of the induction furnace crucible, the found Cr content in the melt varies. One batch of raw material was used for all the experiments. The initial conditions of the experiments, especially the chemical composition of the melt, were influenced by this raw material and as a result, the chemical composition of the slag after melting was influenced as well. Therefore, trends of the results were assessed as well.

It follows from the performed evaluation that the highest reducing ability was in the case of the reducing dose in the 3rd experiment, i.e. a triple dose of C (total 5.1 kg) and a triple dose of Si (total 11.7 kg) for 45 kg of slag, with highest 53 % reduction of Cr₂O₃ from the slag

Based on the performed experiments, the proposal, verification and consequent preparation of the technology "Chromium reduction from slag in an induction melting furnace with reducing agents of C and Si" were performed. The technology is a verified technology within the project with release sheet number OT-01/2015 and with result number QI-ISO-941-10-03.

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