Study of the influence of temperature and reducing agents on the chromium content in slag in the air atmosphere

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Summary

The paper presents the results of laboratory experiments of the reduction of chromium and its oxides from slag using carbon and silicon reducing agents. The study of chromium reduction from molten slag to molten steel was carried out for slag originating from the production of stainless steel with an average elemental content of 0.16 wt. % C, 16.25 wt. % Cr, 5.00 wt. % Ni and 1.05 wt. % Mo. Based on the literature studies experiments on chromium reduction from slag with high Cr_2O_3 content (16 wt. %) were designed, implemented, described and subsequently evaluated. The reduction was carried out using a reducing agent of carbon in the form of anthracite and silicon in the form of ferroalloy FeSi. The atmospheric conditions and pressure were used for experiments. The temperature of the slag was raised by an oxy-fuel burner and the carbon and silicon reducing agents were applied on the surface of the molten steel. The experiments confirmed the possibility of reducing up to 62 % of chromium from the molten slag back into the stainless steel melt.

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

1. Introduction

In stainless steel production, reducing production and energy costs is essential to ensure the competitiveness of metallurgical companies. The production of stainless steel is inherently related to the production of slag, which is nowadays largely disposed of in landfills. In the first quarter of 2021, more than 14.5 million tonnes of stainless steel were produced worldwide ¹. Considering that 270 – 335 kg of slag is produced per tonne of stainless steel, 3.9 – 4.8 million tonnes of slag was produced in just a short period 1Q 2021 ². In doing so, there is a strong drive by manufacturing companies to minimise production costs, reduce environmental impact and ultimately reduce their carbon footprint. ³. Research of the thermal reduction of chromium from slag has been published by many authors ^{3, 4, 5, 6, 7, 8, 9}. Most of the experimental work was performed only on a laboratory condition and has not been transferred to the practice of large industrial companies ¹⁰.

When the melt is produced from alloyed chromium waste (hereafter referred to as Cr waste) in an electric arc furnace (hereafter referred to as EAF), chromium is oxidized and lost to the slag in the form of chromium oxide. The loss of chromium from the melt into the slag is up to 97 wt. % if alloyed waste is used. Oxidation of chromium takes place during smelting and to an even greater extent during the process of carbon reduction in the melt by oxygen injection. A minor part of the chromium is oxidised during casting from the EAF into the casting pan^{11, 12, 13, 14, 15}.

Inclusion complexes containing chromium oxides are complicated in that chromium occurs in 3 powers, Cr^{2+} , Cr^{3+} and Cr^{6+} , depending on the partial pressure, temperature and chemical composition of the slag. Bivalent and trivalent chromium is found in stainless steel slags ¹⁵. The aim of the production companies is to use the maximum potential of the slags, so today, reduction with silicon, aluminium or calcium is used already during the melting process, which leads to a reduction of the chromium content in the slag. Another option is to reduce the chromium activity and convert the chromium into stable spinel bonds. Commonly used compounds for spinel bond formation are Al_2O_3 and MgO⁴.

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In metallurgical aggregates, reducing additives that have a higher affinity for oxygen than chromium is used to reduce chromium from slag to melt. These are mainly carbon, silicon and aluminium. Slag reducing additives need to have a large reaction surface to produce more intense and faster reduction reactions. For example, the author ¹⁶ ports the use of aluminium with a granule size of 1 - 2 mm with a dosing rate of 50 kg.min⁻¹ for a total dose of 10 kg.t⁻¹ Al per tonne of steel. The flow of production technology, and in particular the dosage of aluminium and carbon, at BGH company in the production of stainless steels is presented in the Figure 1. The Figure 1 shows the period of blowing oxygen, heating gas, electrical input, blowing pulverized carbon, lime and aluminium.



Figure 1: Typical stainless steels production process at BGH with aluminium and carbon dosing ¹⁶

The author ¹⁷ states that at the beginning of the oxidation period the silicon content in the melt must be 0.3 wt. % Si. The reason for this is the preferential oxidation of silicon over chromium, thus preventing chromium loss to the slag. The back-reduction of chromium by silicon and carbon follows the chemical reactions (1) and (2) below, according to the authors ¹⁸ and ¹⁹.

$$Cr_2O_3 + 1.5Si = 2Cr + 1.5SiO_2,$$
 (1)

$$Cr_2O_3 + 3C = 2Cr + 3CO_{(g)}.$$
 (2)

From a thermodynamic point of view, the back-reduction of chromium from slag to melt is dependent on temperature, the chemical composition of the slag and the chemical composition of the melt. The author ²⁰ presents below the thermodynamic equilibrium reactions (3),

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

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

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

However, according to the author ²⁰, 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 a statistical evaluation of data from industrial practice.

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

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

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

The author ²⁰ presented that from theoretical formulas (3) and (4) and from formulas obtained from practice (5) and (6) it follows that very important aspects for the reduction of chromium from slag to melt are temperature, chemical composition of melt and chemical composition of slag. The temperature dependence of the Gibbs energy for the reduction of chromium by calcium carbide, carbon and silicon is presented by the author ¹⁸ using the graph in Figure 2. Figure 2 shows that the effect of reduction of chromium from slag, by calcium carbide (CaC₂) and carbon, increases with increasing temperature, and that reduction by silicon is not so temperature dependent. Experimental melt reduction of Cr from slag to melt is also described.



Figure 2: Temperature dependence of Gibbs energy for the reduction of chromium with calcium carbide, carbon and silicon ¹⁸

Based on a literature review describing the relationship of chromium reduction from slag to melt, a design and experimental verification of Cr reduction from slag to melt was performed. Due to the complexity of the experiments, the effect of the content of reducing agents at a constant melt temperature was investigated in the first phase. The aim of the laboratory experiment was to verify the possibility of Cr_2O_3 reduction from slag using carbon and silicon agents.

2. Experimental materials and methods

The experimental melts were carried out on an atmospheric induction melting furnace (INDUCTOTHERM EUROPE LTD, Worcestershire, England) with a nominal melt weight of 1750 kg (hereafter referred to as AIF), frequency 1200 Hz, power input 600 kW. An oxygen-fuelled 1M200 burner (Linde AG, Deutschland), hereafter referred to as KPH, fed by oxygen and propane-butane, was used to heat the slag.

Chromium reduction experiments from slag were performed for a melt with the chemical composition shown in the Table 1. The experiments were carried out in an AIF containing a crucible made of dry Al_2O_3 based asphyxiant. The chemical composition of the externally supplied slag for the experiments is presented in the Table 2. The slag used had a granulometry of about 20 – 50 mm.

Table 1: Chemical composition of melt quality 16Cr5Ni1Mo (wt. %)

| | С | Mn | Si | Р | S | Ni | Cr | Мо |
|------------|------|------|------|-------|-------|------|-------|------|
| 16Cr5Ni1Mo | 0.20 | 0.36 | 0.33 | 0.015 | 0.005 | 4.83 | 16.03 | 1.04 |

| | - | | - | | - | | - | - |
|------------|------|------|------|-------|-------|------|-------|------|
| 16Cr5Ni1Mo | 0.20 | 0.36 | 0.33 | 0.015 | 0.005 | 4.83 | 16.03 | 1.04 |
| | | | | | | | | |

| | С | S | Fe | FeO | Fe ₂ O ₃ | MnO | | V_2O_5 | TiO ₂ |
|-------------------|------|-------|-------|------|--------------------------------|------|-------|----------|------------------|
| Component content | 0.12 | 0.034 | 12.95 | 0.01 | 0.47 | 2.97 | 15.87 | 0.21 | 3.12 |

Table 2: Chemical composition of slag (wt. %)

Table 2: Chemical composition of slag (wt. %) (continuing)

| CaO | SiO ₂ | P_2O_5 | Al ₂ O ₃ | MgO | CaF ₂ | Na₂O | Zn | K ₂ O | BaO | Nb ₂ O ₅ |
|-------|------------------|----------|--------------------------------|------|------------------|------|------|------------------|------|--------------------------------|
| 24.63 | 21.27 | 0.01 | 8.94 | 8.72 | 0.01 | 0.01 | 0.01 | 0.04 | 0.01 | 0.47 |

Slag weighing 45 kg and the slag forming additive MgO, was introduced to the surface of the 1000 kg steel melt. Then KPH was switched on for full and rapid melting of the slag. After melting the slag in about 20 min and heating the melt to 1650 °C, a sample of metal and slag was taken for chemical analysis. Then the reducing additive C weighing 1.7 kg was dosed in the form of anthracite with a granulometry of 1-3 mm. Together with the reducing additive Si in the form of FeSi with a granulometry of 1-3 mm weighing 3.9 kg. The Si and C additives together formed a so-called single reduction batch. In the first experiment, 1x reduction dose was introduced, in the second experiment 2x reduction dose, in the third experiment 3x reduction dose, in the fourth experiment 4x reduction dose and in the fifth experiment 5x reduction dose.

For the sixth experiment, a 3-fold reduction dose was introduced, first only Si was dosed and only after metal and slag sampling (after 10 min) was C dosed. For the seventh experiment, a 3x multiple reduction dose was introduced, containing C and Si at the same time. But during the seventh experiment, the Si content in the melt was twice that of the previous experiments and was 0.6 wt. % Si.

Reducing additives were introduced to the slag surface while the oxy-fuel burner was on. They were then mixed with the slag by external mixing. Slag sampling for chemical analysis and melt temperature measurements were carried out after 5 minutes, for a total of 30 minutes after the first reduction charge was introduced.

After the completion of each set of experiments, the steel melt was poured from the AIF to the pouring ladle and subsequently under protective argon atmosphere a V2A ingot was poured.

3. Results

Change of Cr₂O₃ content in slag is presented in Figure 3. It shows that the highest reducing power was at three times the reducing dose. A total of 53 wt. % Cr was reduced from the slag, i.e. 1.94 kg Cr, see Figure 4 and Table 3. Based on the findings, further experiments were carried out with a triple reduction dose, where the very best result was achieved by successive dosing of Si followed by C in the sixth experimental melt, where 62 wt.% Cr was reduced.



Figure 3: Change of Cr₂O₃ content in slag for all experimental melts



Figure 4: Total change of Cr content in slag in all experimental melts

Table3: Change of chemical composition and weight of Cr_2O_3 and Cr in slag during individual experiments

| | Unito | | | Expe | rimenta | l melts | | |
|--|---------|--------|--------|--------|---------|---------|--------|--------|
| | Units | 1. | 2. | 3. | 4. | 5. | 6. | 7. |
| Multiplication of the reduction dose of Si and C | [1] | 1x | 2x | Зx | 4x | 5x | 3x* | 3x** |
| Si content in the melt | [wt. %] | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 | 0.60 |
| Slag weight | [kg] | 45 | 45 | 45 | 45 | 45 | 45 | 45 |
| Change of Cr. O. content in alog | [wt. %] | -1.50 | -1.70 | -6.30 | -0.80 | -0.90 | -6.90 | -3.20 |
| Change of Cr ₂ O ₃ content in stag | [kg] | -0.68 | -0.77 | -2.84 | -0.36 | -0.41 | -3.11 | -1.44 |
| Change of Cr content in alog | [kg] | -0.46 | -0.52 | -1.94 | -0.25 | -0.28 | -2.12 | -0.99 |
| | [wt. %] | -10.42 | -10.69 | -53.85 | -10.81 | -16.36 | -62.16 | -57.14 |

Note: * initially only Si was dosed and after 10 min C was dosed. ** the melt had a different Si content in the melt compared to the other melts.

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An optical assessment of the appearance of the slag was also performed. This evaluation is only indicative or trend. From Table 4 it can be concluded that the slag was, after the introduction of the reducing additives C and Si, fully liquid in experiments 1 and 2 after 20 minutes, in experiment 3 after 10 to 15 minutes, and in experiments 4 and 5 probably due to the large amount of reducing additives it did not fully liquefy.

| Table 4: | Comparison of the | e appearance of the co | ollected slag sa | amples for all e | experiments, a | after |
|----------|-------------------|------------------------|------------------|------------------|----------------|-------|
| cooling | - | | - | - | • | |

| Time of collection | Cr ₂ O ₃ content [v to the expen | wt. %] in the slag a riment number or I | nd appearance of multiplication of | of the slag sampl the reduction do | e taken according se of C and Si |
|--------------------|---|---|------------------------------------|---------------------------------------|----------------------------------|
| [min.] | 1. | 2. | 3. | 4. | 5. |
| 0 | 14,4 | 15,9 | 11,7 | 7,4 | 5,5 |
| 5 | 12,4 | 14,7 | 10,6 | 7,2 | 3,8 |
| 10 | 12,9 | 15,2 | 14,0 | 5,3 | 3,9 |
| 15 | 14,2 | 15,0 | 7,5 | 4,9 | 3,8 |
| 20 | 12,9 | 14,2 | 5,4 | 6,6 | 4,6 |

Conclusions

The paper presented the results of laboratory experiments of the reduction of chromium and its oxides from slag using carbon and silicon reducing agents. The 16Cr5Ni1Mo stainless steel was used. The atmospheric conditions and pressure were used for experiments. The temperature of the slag was raised by an oxy-fuel burner.

In can be concluded that changes of Cr_2O_3 content in the slag were clearly achieved. The evaluation shows that the highest reduction ability was obtained in the 6th experiment, i.e. a triple reduction dose, when Si (total 11.7 kg) was first applied on the melt surface and C (total 5.1 kg) was applied on the surface after 10 min for 45 kg of slag.

The industrial partner with whom it was cooperating at the time of the experiments seriously considered introducing this technology into production. Further experiments leading to higher Cr reduction from slag to melt are currently being proposed.

The most effective 6th experiment, at three times the reduction dose, showed:

• highest 62 wt. % reduction of Cr₂O₃ from slag,

• optical evaluation of the slag samples collected in Experiments 1 to 5 confirmed that the slag with triple reduction dose showed the highest fluidity. Therefore, the highest contact reaction area between the melt and the slag can be inferred.

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Studium termické redukce chromu ze strusky pomocí redukčních činidel v atmosféře vzduchu

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Souhrn

Článek prezentuje výsledky laboratorních experimentů redukce chromu a jeho oxidů ze strusky pomocí redukčních činidel uhlíku a křemíku. Studium redukce chrómu z roztavené strusky do taveniny oceli byla realizována pro strusku vznikající při výrobě korozivzdorné oceli o středním obsahu prvků 0,16 % C, 16,25 % Cr, 5,00 % Ni a 1,05 % Mo. Na základě rozboru problematiky byly navrženy, realizovány, popsány a následně vyhodnoceny experimenty redukce chrómu ze strusky o vysokém obsahu Cr₂O₃ (16 %) pomocí redukčních činidel uhlíku ve formě antracitu a křemíku ve formě feroslitiny FeSi. Experimenty byly provedeny v atmosférických podmínkách za intenzifikace teploty strusky pomocí kyslíko-palivového hořáku a současného působení redukčního činidla uhlíku a křemíku. Experimenty potvrdily možnost redukce až 62 % chrómu z roztavené strusky zpět do taveniny korozivzdorné oceli.

Klíčová slova: korozivzdorná ocel, struska, chrom, uhlík, křemík, ferosilicium.