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RETENTION, RECOVERY AND RECYCLING OF METAL VALUES FROM HIGH ALLOYED STEEL SLAGS

RETENCJA, ODZYSK I RECYCLING METALU Z ŻUŻLI WYSOKOSTOPOWYCH STALI

The work was carried out in four parallel directions. The thermodynamic activities of oxides of Cr in steel slags were determined by slag-gas equilibration technique. The ratio of $\text{Cr}^{2+}/\text{Cr}^{3+}$ in $\text{CaO-MgO(-FeO)-AlO}_3\text{-SiO}_2\text{-CrO}_x$ system slags was measured by X-ray absorption near edge spectra (XANES). High-temperature mass spectrometry method was also used to obtain the distribution of chromium oxides. A mathematical correlation was established for estimating the ratio of $\text{Cr}^{2+}/\text{Cr}^{3+}$ as a function of temperature, partial pressure of oxygen and slag basicity. Laboratory investigations of the decarburization of high alloy steels under controlled oxygen potentials have been carried out to retain Cr in the steel phase. A mathematical model has been developed for the decarburization process with controlled oxygen partial pressure. Experimental and theoretical investigations have been carried out in optimizing the Mo-additions to steel in the EAF practice in Uddeholm Tooling AB. Substantial saving of Mo as well as less emissions of Mo-bearing dust are indicated in the study. A salt extraction process was developed to extract the metal values from steel slags. Successful extractions, followed by electrolysis indicate that this could be a viable route towards recovery of metals from metallurgical slags.

Keywords: retention, recovery, recycling, slag, chromium steel, decarburization

Praca była realizowana w czterech równoległych kierunkach. Termodynamiczne aktywności tlenków Cr w żużlu zostały określone w stanie równowagi żużel-gaz. Stosunek $\text{Cr}^{2+}/\text{Cr}^{3+}$ w żużlach $\text{CaO-MgO(-FeO)-AlO}_3\text{-SiO}_2\text{-CrO}_x$ mierzono metodą absorpcji promieniowania rentgenowskiego w pobliżu krawędzi widm (XANES). W celu uzyskania rozdziału tlenków chromu wykorzystano wysokotemperaturową spektrometrię masową. Korelację matematyczną ustalono do oceny stosunku $\text{Cr}^{2+}/\text{Cr}^{3+}$, jako funkcji temperatury, ciśnienia parcjalego tlenu i zasadowości żużla. Badania laboratoryjne odwęglania stali wysokostopowych, kontrolowanego przez potencjał tlenowy przeprowadzono, aby pozostawić Cr w stali. Model matematyczny został opracowany dla procesu odwęglania z kontrolą parcjalego ciśnienia tlenu. Eksperymentalne i teoretyczne badania zostały przeprowadzone przez optymalizację dodatku Mo do stali w procesie EAF w Uddeholm Tooling AB. Znaczne oszczędności Mo, a także mniejsza emisja pyłu zawierającego Mo są wskazane w badaniu. Proces ekstrakcji soli został stworzony, aby wyodrębnić metal z żużli stalowniczych. Udana ekstrakcja, a następnie elektroliza, wskazują, że mogłaby to być opłacalna droga do odzysku metali z żużli metalurgicznych.

1. Introduction

With the increasing constraints on the steel industry with respect to the energy and environmental optimization, eco-steel production has received high priority in Sweden, as exemplified by the national effort supported by Swedish Environmental Research Foundation (MISTRA) and the Swedish Steel Producers Association (Jernkontoret). New strategies for retaining the dissolved elements in the steel bath within specified intervals, especially in the case of high alloy steel production, has been one of the targets in this great effort. It is realized that drastic changes in steel processes towards environ-

mental improvements could not be easily accommodated. Modifications of existing processes and design of new process steps can only be enabled using process fundamentals which would lead to a win-win situation due to environmental as well as economic advantages. It is common knowledge that alloying elements like Cr and V form stable oxides and recovery of these metals in the element form is energy-intensive. A simple mass-balance consideration would reveal that

- 1) It would be useful if these elements can be retained in the steel, minimizing the loss of the same to the slag or dust, referred to in this project as “**Retention**”,

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- 2) Recovery of the elements from the slag and dust phases in a suitable form needs to be enabled so that these valuable metals can be reused in the steelmaking cycle, referred to in this project as **“Recovery”** and
- 3) The recovered metals as well as the rest products (slag and the dust) could be recycled, referred to in this project as **“Recycling”**.

With the industrial expansion of progressing countries like China and India and consequent increase in the prices of the alloying elements, there is a strong economic motivation for the recovery of metal values from slags and dust. For example, in the production of high alloy steel of 1 ton at Uddeholm Tooling AB, Hagförs, Sweden [1], the amount of Mo per ton of steel is about 13 kg. The slag contains 0.4 kg Mo and the dust, about 1 kg. Apart from the fact that there is a strong economic motivation, about SEK 500 for Mo per ton steel produced which is lost in the slag and the dust, this amount of Mo ends up in the environment. The situation is similar even in the case of Cr, Nb and V. Design of suitable process steps towards retention, recovery and recycling of these metal values is the primary motivation of the project.

2. Experimental methods

The strategy adopted in the present project has been tailored primarily to the EAF practice of Uddeholm

Tooling AB, Sweden[2]. The present project approach consists of four essential components, *viz.*

2.1. Thermodynamic studies of Cr-bearing slags

The objective of present investigation is to measure thermodynamic activity of chromium, or vanadium oxide in $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-CrO}_x(\text{VO}_x)$ melt by using the gas equilibrium technique. The P_{O_2} was controlled by the mixture of $\text{CO-CO}_2\text{-Ar}$. The present division has the necessary instrumentation as well as experience in such measurements [3]. The principle of gas-slag equilibration method is to equilibrate the slag sample kept in a Pt crucible with the above-mentioned gas mixture, so that the oxygen partial pressure was predetermined. From a knowledge of the thermodynamic activity of Cr in Cr-Pt alloy and the oxygen partial pressure in the gas stream, it is possible to calculate the thermodynamic activity of chromium oxide in the slag. A similar procedure is applicable for vanadium. The oxygen pressures used were $10^{-8}, 10^{-9}, 10^{-10}$ bar and experiments were carried out at 1823, 1873 and 1923K. The gas-cleaning train used and the experimental apparatus are presented in Figure 1 and 2 respectively. By preliminary experiments, it was found that the equilibrium between the slag and gas phases could be attained after 14 h; consequently, all the equilibration experiments were carried out at a safe limit of 20 h. The slags were then quenched in argon atmosphere and analyzed.

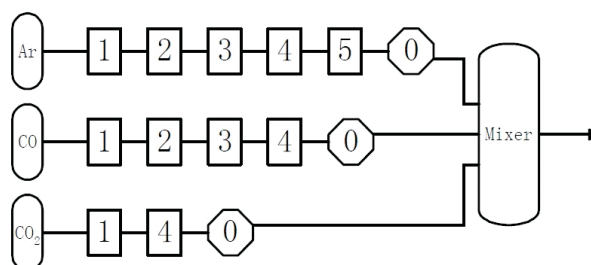


Fig. 1. Schematic graph of gas cleaning system

0 – flowmeter; 1 – silica gel; 2 – magnesium perchlorate; 3 – ascarite; 4 – copper turnings; 5 – magnesium chips

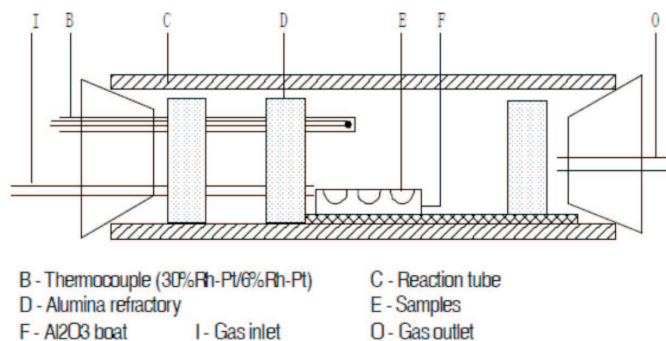


Fig. 2. Schematic arrangement of furnace

2.2. Retention of Cr in steel melt using oxygen partial pressure control

In the case of the decarburization of alloy steels especially stainless steels the oxidation of carbon is carried out by blowing O₂Ar mixture (AOD process) into the steel melt. While at the initial stages carbon is preferentially oxidized at later stages as the oxygen potential of the bath increases elements with strong affinity to oxygen for example Cr will be oxidized and lost to the slag phase. In order to minimize this loss, it was proposed in the present work to use O₂CO₂(-Ar) gas mixtures with high oxygen contents at the beginning of blowing and high CO₂ contents at the finishing stages.

Thermodynamic calculations were carried out to examine the possibilities of the effect of decarburization using CO₂.

Experiment series 1: In this series a steel melt containing pre-determined amounts of Cr and C was decarburized with oxygen and CO₂ blowing respectively.

Experiment series 2: In this series steel melts were exposed to gas mixtures with different oxygen partial pressures; viz. pure O₂, 75%volO₂25%volCO₂, 50%volO₂50%volCO₂, 25%volO₂75%volCO₂ and pure CO₂. The samples are withdrawn at different time intervals and the C as well as Cr contents are analyzed. The amounts of Cr and C in the melt as well as the temperature are varied. The aim of these experiments is to determine the mass transfer effects of reducing the oxygen partial pressure during decarburization.

Model development: If the oxygen partial pressure is to be continuously decreased during the decarburization process it is essential that a mathematical model that could predict the decarburization and the Cr loss by oxidation is developed.

2.3. Minimization of metal losses in dusts by process modification

In the addition of alloying elements losses are encountered especially in slag and dust. Minimization of the loss of these metals from dust is very important from environmental as well as economic view points as dust processing requires additional process steps. Once again the EAF practice in Uddeholm Tooling AB had been taken up for investigation.

An analysis of the dust samples at Uddeholm Tooling AB, EAF practice reveals that the total amount of Mo lost amounts to 72.64 kg/heat, 60.94 ton/year, 32 million EUR/year. Similar is the situation with respect to Cr slag losses. Total amount of Cr lost is 27.9 kg/heat, 14054 ton/year, .2 million EUR/year. This part of the present work was focused on Mo losses in the dust. Plant trials were conducted and samples of steel slag and dust

were collected systematically at the various stages of the process during regular campaigns over nearly two weeks. The measurements to increase the Mo yield were conducted and promising results have been obtained.

2.4. Extraction of metal values by using a salt extraction process

Despite the precautions taken in process optimization in view of the thermodynamic and kinetic constraints valuable metals are always lost in the slag. Chromium in stainless steel making slag can be usually 24% according to information from Outokumpu Avesta [5] and could go up to as high as 8%. The presence of such metals apart from the economic losses, poses a serious challenge to the recycling of the slags. The present group has been devoted to developing new process concept in this respect by extracting the metal values by a molten salt phase.

For the extraction of valuable metals in steelmaking slags a salt extraction process has been designed by the present group. In this process the slag is treated with a salt melt of suitable composition and fluxes are added in order to extract the metals into this melt. The salt phase can be electrolyzed or if necessary leached to extract the valuable metals in aqueous phase. The results have been encouraging and a patent application has been approved. The process parameters are currently being examined for optimization.

3. Results and discussion

The results obtained so far are summarized in the following sections.

3.1. Thermodynamic studies of Cr bearing slags

As part of the present project, thermodynamic activity measurements of the low Cr-containing slags by gas-slag equilibration method were carried out.

3.1.1. Activity of CrO in Cr-slugs

2 different slag compositions with varying amounts of chromium oxide have been investigated in the present work. The work at this stage was restricted to low Cr contents and the slag consisted of CaO, MgO, Al₂O₃ and SiO₂ apart from CrO_x. The Pt crucibles were analyzed after the experiment and the Cr content of the alloy in equilibrium with the slag was determined. The amount of chromium oxide retained by the slag was found to be strongly dependent on the slag chemistry, above all, the basicity. The thermodynamic activity of chromium oxide

was calculated utilizing the thermodynamic information from the PtCr system reported by Pretorius and Muan[4] It is well known that Cr exists as Cr^{2+} and Cr^{3+} in slags In the present work the amount of chromium oxide is very low Further, the slag is in equilibrium with PtCr alloy at low oxygen partial pressures in the gas phase. Hence, all Cr in the slag was assumed to be in the divalent state. This is supported by the measurements of Forssbacka and Holappa [5] as well as the experiments conducted in the present laboratory by independent technique. The relationship between the chromium oxide content for the slag compositions investigated in the present work and the thermodynamic activity of CrO is presented in Figure 3.

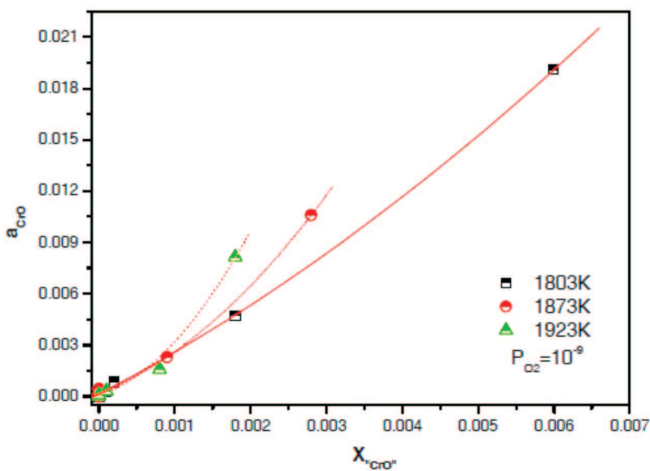


Fig. 3. Thermodynamic activity of CrO as a function of content of CrO_x in the slag

As can be seen the activity of CrO shows a positive deviation from Raoult's law in agreement with results reported earlier. The values at slightly higher Cr contents could be affected by slight increase in the Cr^{3+} contents of the slags

From the present results an expression for the amount of Cr in the slag as a function of the oxygen partial pressure and basicity was worked out and was given below:

$$\log(\%Cr)_{slag} = 4.488 + \frac{16907.82}{T} + 2.555 \times \log[Cr]_{alloy} + 1.589 \times \log(P_{O_2}) - 8.483 \times \log B \quad (1)$$

Where 'B' is the basicity defined as

$$B = \frac{wt\%CaO + wt\%MgO}{wt\%SiO_2 + wt\%Al_2O_3} \quad (2)$$

This expression can be valuable in assessing the amount of Cr lost in the slag under given basicity and

oxygen partial pressure if the activity of Cr in steel is known

3.1.2. Cr valence states

The distributions of CrO and $CrO_{1.5}$ in the $CaOSiO_2-CrO_x$ and $CaOMgO(FeO) Al_2O_3SiO_2CrO_x$ slag systems were measured in the present study by gasslag equilibrium method and by hightemperature Knudsen cellmass spectrometry respectively The results indicate that ratio $X_{CrO}/X_{CrO_{1.5}}$ increases with the increasing temperature, decreasing oxygen partial pressure and slag basicity. Combining the results obtained in present study and selected literature values a mathematical expression of $X_{CrO}/X_{CrO_{1.5}}$ ratio described as function of temperature, oxygen partial pressure and slag basicity was built up and is presented in equation (2).

$$\log\left(\frac{X_{CrO}}{X_{CrO_{1.5}}}\right) = -\frac{11534}{T} - 0.25 \cdot \log(P_{O_2}) - 0.203 \cdot \log(B) + 5.74 \quad (3)$$

where T is temperature in K, P_{O_2} is oxygen partial pressure in Pa and B refers to basicity defined as $(\%CaO + \%MgO)/(\%Al_2O_3 + \%SiO_2)$ The correlation is compared with the experimental results from the present as well as earlier works in Figure 4 It is seen that the correlation is satisfactory

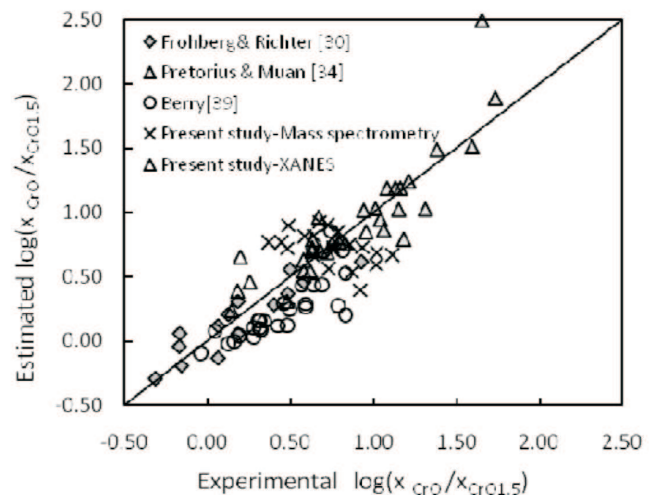


Fig. 4. Comparisons between experimental and estimated $X_{CrO}/X_{CrO_{1.5}}$

Equation (2) can be utilized in estimating the chromium oxidation level in slags in industrial practice. With a knowledge of basicity oxygen partial pressure prevailing as well as temperature of the process the extent of Cr(III) in the slag can be estimated This information is considered to be useful in process control

3.2. Retention of Cr in steel melt using oxygen partial pressure control

Retention of reactive metals like Cr requires lower oxygen partial pressures, higher temperatures and /or higher thermodynamic activities of the oxide in the slag. During decarburization, the competition between carbon and the reactive metals is an important factor in determining the loss of these metals to the slag.

Preliminary laboratory experiments at 500 g scale using an induction furnace were carried out with Fe-Cr melts. The gases, O_2 or CO_2 were blown through the sample. A schematic diagram of the experimental setup is presented in Figure 5. Samples were taken periodically in order to analyze the C and Cr contents.

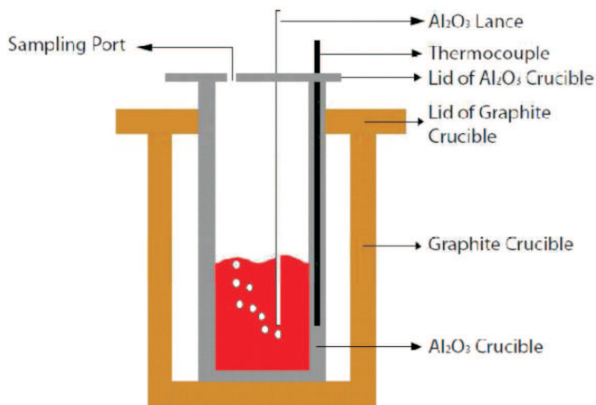


Fig. 5. A schematic diagram of the induction furnace experiments

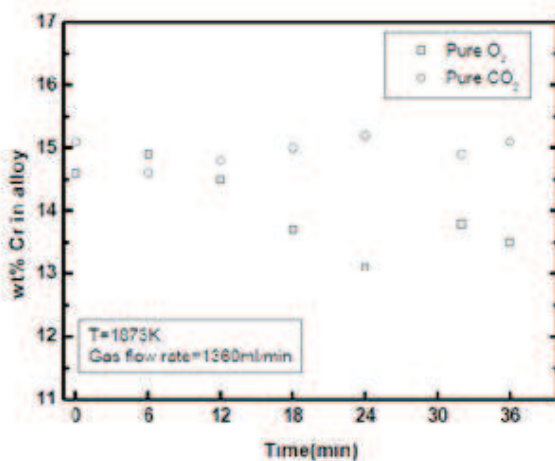


Fig. 6. Effect of gas composition on the Cr loss of high carbon alloy

Experiments were carried out to explore the effect of composition of the injected gas on oxidation of the FeCr-C melts having high (approximately 3 mass%) as well as low (0.25-0.3 mass%) carbon contents with the

chromium range of 118155 mass%. Figure 6 shows the variation of Cr content with time for gas injection at different gas flow rates and injected gas compositions at high carbon level. Although initial chromium content was different, it is still evident that the rate of Cr loss decreases with increasing CO_2 content in the injected gas. Figure 7 shows the change in carbon content with injection time at a gas flow rate of 136 Nml/min for melts having high carbon contents. It can be seen that carbon content in the melt decreases. At this gas flow rate, the decarburization is much faster when blowing with pure CO_2 .

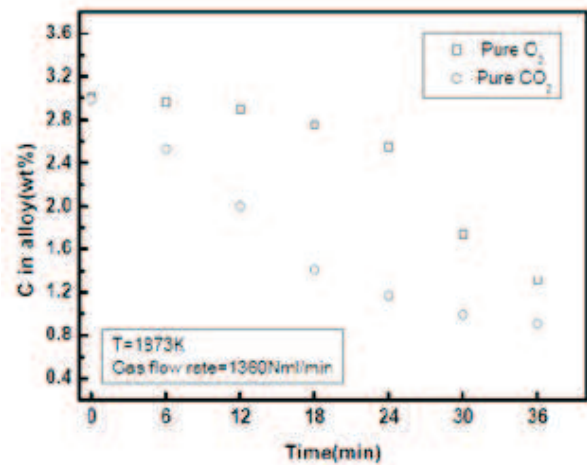


Fig. 7. Effect of gas composition on the decarburization rate of high C alloy

3.3. Minimization of metal losses in dust by process modification

Plant trials were conducted in the EAF at Uddeholm Tooling AB, in collaboration with Dr Nzotta [1], in order to investigate the Mo losses in the slag and dust. A mass balance for Mo worked out from the results is shown in Figure 8.

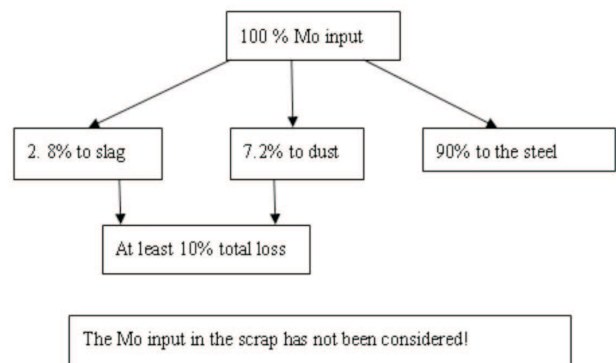


Fig. 8. Mo mass balance in EAF practice at UTAB

The present investigation focuses on the evaporation of MoO_3 from various stabilizing sources during continuous heating of the materials from room temperature up to 1300°C by thermogravimetric analysis (TGA). The results from the nonisothermal TGA investigations of the mixtures of MgO , CaO and CaCO_3 with MoO_3 are presented in Fig. 9. It can be seen that in the case of mixtures of MoO_3 with CaO or MgO only a minor part of MoO_3 (wt loss was about 1.8%) evaporated below 1373 K .

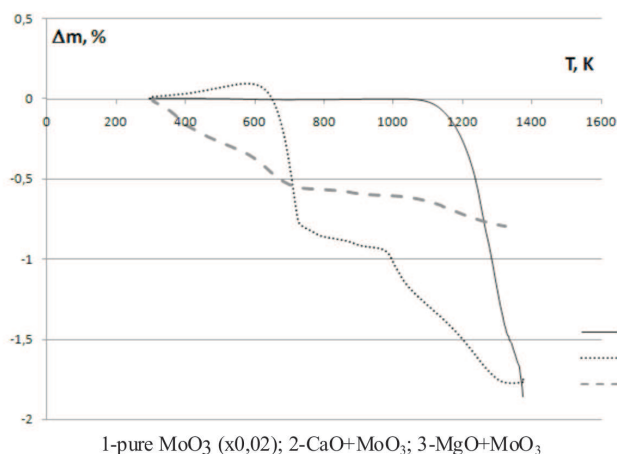


Fig. 9. The mass changes for MgMoO_4 and CaMoO_4 precursors by TGA studies

The evaporation rate of pure MoO_3 was studied by TGA and compared with the evaporation rates from mixtures of MoO_3 with CaO , CaCO_3 , MgO . MoO_3 can be stabilized by mixing with CaO , MgO or CaCO_3 and heating the mixtures as the result of appropriate molybdates formation. In the case of CaMoO_4 and MgMoO_4 the decomposition rate is increased with increasing temperature and the evaporation rate of MoO_3 would be proportional to the equilibrium partial pressures of MoO_3 . Liquid steel treatments with different sources of Mo in a small induction furnace in argon atmosphere showed the Mo yield in the case of MoO_3+C was similar to that of CaMoO_4+C and also $\text{MoO}_3+\text{CaO}+\text{C}$ mixtures. $\text{CaO}+\text{MoO}_3$ mixture can be used instead of CaMoO_4 as the Mo yield is approximately the same. The lowest Mo yield is found for $\text{MgO}+\text{MoO}_3$ mixture. Fast evaporation of MoO_3 from the mixture with $\text{MgO}+\text{C}$ was found to be the reason for very low yield for this mixture. Further work towards stabilization of molybdenum oxide is currently in progress.

3.4. Extraction of metal values by using a salt extraction process

A salt extraction process was designed to extract the metal values from slag rests. Attention was mainly focused on Cr in the slag. The flow sheet for the ex-

traction part of Cr from the slag is presented in Figure 10. Experiments were conducted with Cr slags from Uddeholm Tooling AB by extracting the Cr values by NaCl/KCl melts at 1023 K at different time intervals. The investigations were carried out in order to optimize the process parameters for dissolution of slag/chromite in the eutectic salt mixtures of NaCl/KCl containing a patented flux AlCl_3 . Based on the optimized conditions, lab-scale investigations of electrolysis were carried out applying a cell voltage of 2.8 V . Ferrochrome was recovered as the cathode deposit.

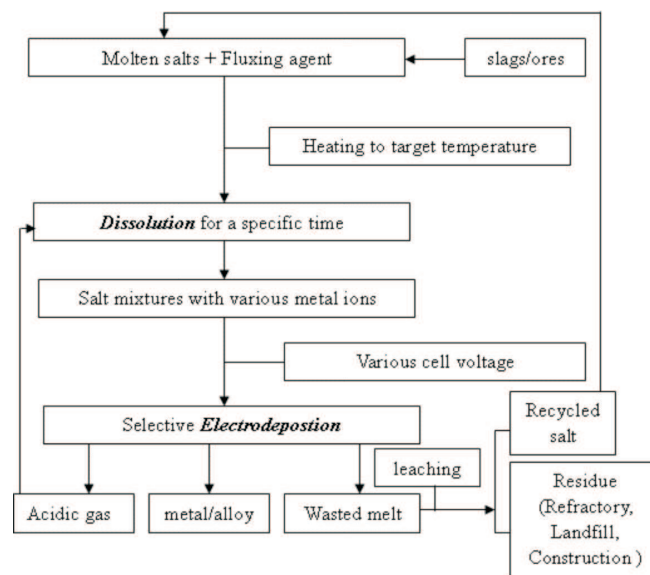


Fig. 10. Schematic diagram of Salt Extraction Process

The theoretical decomposition voltage plotted in Figure 11 can give the deposition trend as follows: $\text{CrCl}_3 > \text{FeCl}_2 > \text{MnCl}_2 > \text{AlCl}_3 > \text{MgCl}_2 > \text{NaCl} > \text{CaCl}_2 > \text{KCl}$. It shows that Fe and Cr will deposit first. Taking account of the higher cell voltage requirement and the lower content of Mn^{2+} and Mg^{2+} in salt phase, under a cell voltage of 28 V , ferrochromium alloy is likely to be the main product. It should be noted that the electrodeposition of metals can be affected by a number of factors, even in pure molten salt systems, as for example, over voltage, current density, current efficiency, bath electric conductivity, the nature and surface of the cathode material, and distance between electrodes, etc. In the present work, several electrolysis tests on EAF slag/chromite are being carried out with promising results.

A typical photograph of the cathode product after electrolysis of the slag is shown in Figure 12 (a). The deposit consists of Fe-Cr alloy with a low amount of oxygen and salt mixtures with some undissolved slag. After removing the adhered product and washing the cathode with ethanol, a typical SEM image of the deposited product could be obtained, which is shown in

Fig. 12 (b). A dendritelike structure of the crystal deposit could be observed in this figure. Further EDS analysis of the dendritic crystal shows that it consists of Fe and Cr along with low content of oxygen (below 10%) and a small amount of Ca, Na, K and Cl. It should be noted that the oxygen content in this EDS analysis is not accurate. The present experiments show clearly that ferrochrome can be recovered from the slag by the combined extraction-electrolysis process. XRD results of the adhered substances on the cathode confirm the formation of Fe-Cr, as shown in Fig. 12 (c). The cathode products consist mainly of FeCr, inclusions of NaCl and KCl from the electrolyte apart minor levels of other impurities.

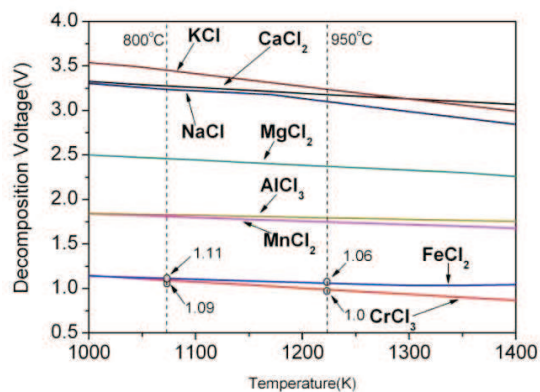


Fig. 11. The theoretical decomposition voltage of different metal chlorides

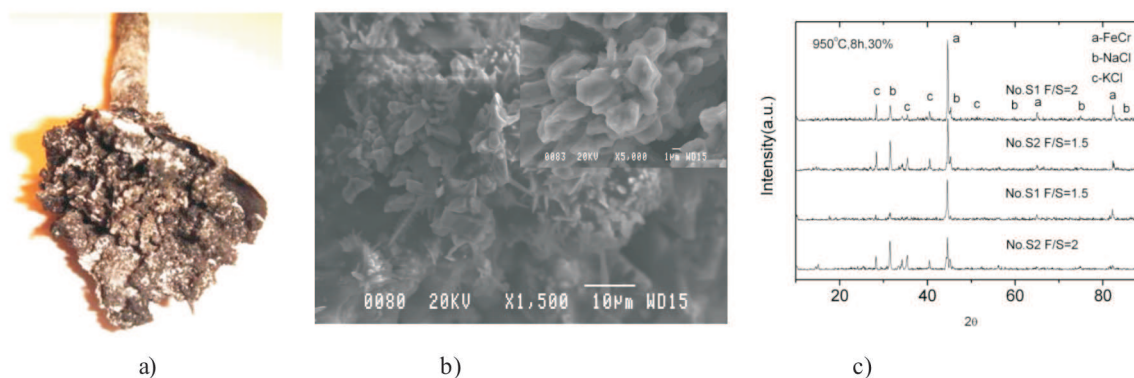


Fig. 12. Analysis of the cathode deposit after salt extraction and electrolysis (a) Cathode deposit product photo; (b) SEM analysis; (c) XRD analysis of the cathode deposit with different flux/slag ratio

4. Conclusions

4.1 Thermodynamic activities of chromium oxides in slags were measured by gaslag equilibration method. Activity of chromium oxide shows positive deviation from ideality; it decreases with increasing temperature and decreasing content of chromium oxide in slag and oxygen partial pressure. The oxidation states of CrO_x containing slag have been studied.

A mathematical correlation was established for estimating the ratio of $\text{Cr}^{2+}/\text{Cr}^{3+}$ as a function of temperature, partial pressure of oxygen, and slag basicity.

4.2 The second part *viz.* decarburization under controlled oxygen partial pressure was dealt with both theoretically and experimentally. A theoretical generic model describing the mass transfer phenomena between rising gas bubbles and a metal bath has been developed by the present authors to predict the composition change in the melt as a consequence of blowing different oxidant gases. The experimental results also indicate that the crosses

can be significantly lowered by replacing the oxygen with CO_2 in the injected gas specifically for FeCrC melts with carbon levels higher than about 0.8 mass%.

4.3 In the third part of the project *viz.* modification of the Mo precursor additions in EAF, theoretical assessment of Mo additions and plant trials are being carried out. Synthesis of stable Mo compounds from low-grade Mo sources were carried out. Liquid steel treatments with different sources of Mo in a small induction furnace in argon atmosphere showed the Mo yield could be increased by using proper Mo source.

4.4 In the fourth part *viz.* salt extraction of valuable metals from slags, successful extraction of Cr and Mo using suitable fluxes have been carried out. The electrolysis of the extract to get Fe-Cr has also been demonstrated.

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