Use of Electro-Slag Refining for Novel \textit{in-situ} Allying Process in Steel

Somnath Basu, and Deepoo Kumar

\textbf{Abstract}— Alloying elements having higher oxygen affinity than iron are susceptible to oxidation loss during refining of alloy steel. This problem is more severe while processing high alloy steels, like stainless steel and tool steel. Earlier workers have attempted to introduce reactive alloying elements in the ESR mould, in order to minimise the magnitude of oxidation loss. The present authors investigated \textit{in-situ} reduction of $\text{Cr}_2\text{O}_3$ and subsequent Cr pick-up in the liquid steel using a laboratory-scale ESR facility. It was observed that $\text{Cr}_2\text{O}_3$ in the ESR slag could be reduced by Al addition to the mould, leading to enrichment of the steel with Cr. The findings suggest a possibility of \textit{in-situ} alloying during electro-slag refining of a leaner composition, and also prevention of oxidation loss while processing steels with higher Cr concentration. The resulting increase in $\text{Al}_2\text{O}_3$ concentration in the slag did not cause any hindrance to ESR operation.

\textbf{Keywords}— Alloying element, Alumino-thermic reduction, Electro-slag refining, Ferro-alloy.

\section*{I. INTRODUCTION}

Addition of ferroalloys to the liquid steel, mostly during secondary refining stage, is the established process for introduction of alloying elements like Mn, Cr, V and Ti. High cost of ferro-alloys leads to significant price escalation of the steel thus produced. Production of the ferro-alloys, in turn, consumes mineral resources, energy, time and effort, which leads to high prices of the ferro-alloys. Major savings may be achieved if the alloying elements can be added directly in the form of the corresponding ores. This is the major motivation behind the present work, which may lead to significant savings while producing alloy steel grades.

The ability of electro-slag refining (ESR) process to produce clean steel with high internal soundness is well established. An ingot of the feedstock (to be refined) having the desired overall chemical composition is made into an electrode, which is melted by resistive heating through a slag pool. The resulting droplets solidify at the bottom of the pool to generate the refined ingot. The present work aims to explore the feasibility of reducing oxide ore(s) of some of the elements, in order to enable \textit{in-situ} alloying of the steel while carrying out electro-slag refining.

Somnath Basu is with the Indian Institute of Technology Bombay, Mumbai, INDIA (corresponding author’s e-mail: somnathbasu@iitb.ac.in).

Deepoo Kumar was with Indian Institute of Technology Bombay. He is now with Larsen & Toubro Ltd., Hazira, INDIA (e-mail: deepoo.iitb@gmail.com).

\section*{II. EXPERIMENTAL PROCEDURE}

\subsection*{A. ESR Setup}

A laboratory-scale ESR equipment, illustrated in Fig. 1, was used to carry out refining of the steel electrodes. A direct current (DC) motor was used for vertical motion of the electrode. The synthetic flux was preheated to remove the moisture, which might otherwise induce hydrogen entrapment. The electrically conducting liquid slag pool, generated by melting of the added flux, ensures continuity of the process through resistive heating. Details of the equipment have been reported in a recent publication [1].

Austenitic stainless steel of 18-8 type (18 mass% nominal Cr content) and plain carbon steel containing 0.3% C were selected as the electrode materials. This allowed a wide range of Cr concentration to be investigated.

Fig. 1 Schematic diagram of the electro-slag refining equipment

\subsection*{B. Slag Selection}

$\text{CaF}_2$, $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ were the principle constituents of the slag used in the ESR. Small concentrations of $\text{CaO}$, $\text{MgO}$, $\text{FeO}$, $\text{Cr}_2\text{O}_3$, etc. were also present as minor constituents. Specific quantities of reagent grade $\text{CaF}_2$, alumina and silica powder were pre-fused using a graphite crucible in an induction furnace. The resulting flux, after cooling and crushing, was preheated at 900°C for at least 4 hours before use in order to eliminate moisture to the extent possible. Each experiment required addition of 750 – 800 gm of the dry flux for refining 6 – 8 kg of steel. Tables I and II present that initial
Chemical compositions of the steel and slag used in the present work.

### Table I
**Initial Chemical Composition of the Steel Electrodes**

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Stainless Steel</th>
<th>Medium C Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.05</td>
<td>0.30</td>
</tr>
<tr>
<td>Mn</td>
<td>–</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr</td>
<td>18.02</td>
<td>0.23</td>
</tr>
<tr>
<td>Si</td>
<td>–</td>
<td>0.45</td>
</tr>
<tr>
<td>Ni</td>
<td>8.06</td>
<td>–</td>
</tr>
<tr>
<td>Al</td>
<td>–</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

### Table II
**Initial Chemical Composition of the Flux Used**

<table>
<thead>
<tr>
<th>Flux #1</th>
<th>Flux #2</th>
<th>Flux #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF₂</td>
<td>55.90</td>
<td>54.16</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>30.61</td>
<td>35.77</td>
</tr>
<tr>
<td>SiO₂</td>
<td>13.40</td>
<td>9.85</td>
</tr>
<tr>
<td>CaO+MgO</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.085</td>
<td>0.099</td>
</tr>
<tr>
<td>Fe₀</td>
<td>0.80</td>
<td>–</td>
</tr>
</tbody>
</table>

### C. Solute Enrichment in Steel

Controlled amount of dry Cr₂O₃ powder was added to the starting flux before supplying to electroslag refining. Cr₂O₃ was also added to the molten slag at specified instants after start of refining, as a means of additional chromium input. Dry copper rods were dipped into the slag pool from the top for collecting slag samples, maintaining precaution to avoid short-circuiting between the mould wall and top electrode. The solidified ingot was machined and steel samples were collected from different locations. Since the melting rate in any particular experiment was roughly constant during the process, the distance from the bottom of the ingot could be correlated linearly with the time of melting and re-solidification.

### III. Results

#### A. Addition of Cr₂O₃

The authors have indicated in a recent publication the initial objectives starting this work [1]. It started with electro-slag refining of an austenitic stainless steel ingot in air. Cr was expected to undergo aerioal oxidation due to its higher oxygen affinity than Fe. However, no significant decrease in Cr content could be observed. On the contrary, the Cr₂O₃ concentration in the slag decreased with progress of refining.

The most likely explanation for this anomaly would be in-situ aluminothermic reduction of Cr₂O₃ in the ESR slag pool. Addition of aluminium to the melt pool is normally made for scavenging the oxygen picked up from the atmosphere. This Al may reduce Cr₂O₃ present in the slag, leading to increase in Cr content in the solidified ingot.

\[
2 \{Al\}_{(l)} + (Cr₂O₃)_{slag} = (Al₂O₃)_{slag} + 2 \{Cr\}_{in\ steel}
\]

\[\Delta G^o = -538608 - 14.22T \text{ J mol}^{-1}\]

It is noteworthy that a recent work of Seethraman et al. has highlighted the evaporation of chromium oxide from liquid slag under oxidising atmosphere, at temperature above 1800K [2]. The possibility of a similar mechanism cannot be ruled out, though this alone would contribute to much lesser decrease in the Cr₂O₃ concentration in slag.

These observations led to the idea of chromium enrichment in the solidifying steel by deliberate reduction of excess Cr₂O₃ in slag with Al. The first set of experiments was carried out on plain carbon steel. Fig. 3 shows the variation of Cr concentration in the metal and Cr₂O₃ concentration in the slag. Once the initial melt-down occurred, excess Cr₂O₃ was added to the slag after approximately 30% of the refining duration was over. It can be seen from the figure that this led to the Cr₂O₃ concentration reaching a local maximum of 9 – 10 mass% within 2 min of addition of Cr₂O₃ powder. This delay might have resulted from the kinetics of dissolution of solid Cr₂O₃ in the slag pool. Cr content in the steel showed similar trend, though there was a gap between the sampling instants of steel and slag.

![Progressive decrease in Cr₂O₃ concentration in the slag during electro-slag refining of a plain carbon steel](image-url)

Fig. 2  Progressive decrease in Cr₂O₃ concentration in the slag during electro-slag refining of a plain carbon steel

http://dx.doi.org/10.15242/IIE.E0514553
structure in the final product through ESR of alternately
reports are available in public domain on in-situ reduction of
ferroalloys during electroslag refining [8]. However, very few
Cores reported the manufacture of microalloyed steel
through addition of C, Al and Fe-Ti. Even earlier, Medina and
al. [5] as well as Maity et al. [6], [7] on compositional
modifications during electroslag remelting of low alloy steel
through addition of C, Al and Fe-Ti. Even earlier, Medina and
Cores reported the manufacture of microalloyed steel
containing Ti, Nb and V by addition of the corresponding
ferroalloys during electroslag refining [8]. However, very few
reports are available in public domain on in-situ reduction of
oxide minerals and consequent alloying of steel. In that
respect, the present work opens up new possibilities for
carrying out alloying in steel with reduced need of ferro-
alloys. This promises to offer significant reduction in cost as
well as energy consumption and emission of greenhouse gases
since lesser amount of ferro-alloys would need to be
produced.

IV. CONCLUSION

It was possible to increase the Cr concentration in steel
during electro-slag refining by alumina-thermic reduction of
Cr₂O₃ from the slag. Similar attempts were made to recover Ti
from TiO₂, but with limited success. The relative oxygen
affinity of the alloying element of interest appears to be the
deciding factor. This opens up possibility of enriching steel
grades with alloying elements like Cr and Mn, and possibly V
as well, by in-situ reduction of the corresponding oxides
added to the slag.

ACKNOWLEDGMENT

The authors wish to thank Indian Institute of Technology Bombay for providing the facilities and the opportunity to
carry out this work. We also thank our colleagues and students
for chipping in with ideas and moral support.

REFERENCES

Steelmaking, Jamshedpur, 2013, paper SMTO-3.
vaporization of chromium from thin slag films at steelmaking
characteristics of functionally graded steels produced by electroslag
http://dx.doi.org/10.1007/s11661-005-0020-8
behavior of functionally graded steels produced by electroslag
http://dx.doi.org/10.1007/BF02586133
on microstructure and compressive yield strength of as cast ESR Fe-
http://dx.doi.org/10.1179/174328405X20969
strength steel by electroslag remelting: Effect of inoculation of titanium on
the microstructures and mechanical properties,” ISIJ Intl., vol. 46, 2006,
pp. 1361-1370. http://dx.doi.org/10.2355/isijinternational.46.1361
of ultrahigh strength low alloy steel through electroslag refining
http://dx.doi.org/10.2355/isijinternational.49.902
manufacturing of microalloyed steels by the electroslag remelting
http://dx.doi.org/10.2355/isijinternational.33.1244

Fig. 3 Variation in Cr content in the steel upon Cr₂O₃ addition to
slag during electro-slag refining of a plain carbon steel

Mohandesi and co-workers had produced composite
structure in the final product through ESR of alternately
welded austenitic stainless steel and low carbon steel
electrodes [3], [4], Substantial work was done by Baligidad et
al. [5] as well as Maity et al. [6], [7] on compositional
modifications during electroslag remelting of low alloy steel
through addition of C, Al and Fe-Ti. Even earlier, Medina and
Cores reported the manufacture of microalloyed steel
containing Ti, Nb and V by addition of the corresponding
ferroalloys during electroslag refining [8]. However, very few
reports are available in public domain on in-situ reduction of

Fig. 4 Influence of Cr₂O₃ addition to ESR slag upon Cr content in
the steel, indicating transfer of chromium from slag to steel