

# Use of Electro-Slag Refining for Novel *in-situ* Alloying Process in Steel

Somnath Basu, and Deepoo Kumar

**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 *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 *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.

**Keywords**— Alloying element, Alumino-thermic reduction, Electro-slag refining, Ferro-alloy.

## 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 *in-situ* alloying of the steel while carrying out electro-slag refining.

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## II. EXPERIMENTAL PROCEDURE

### 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.

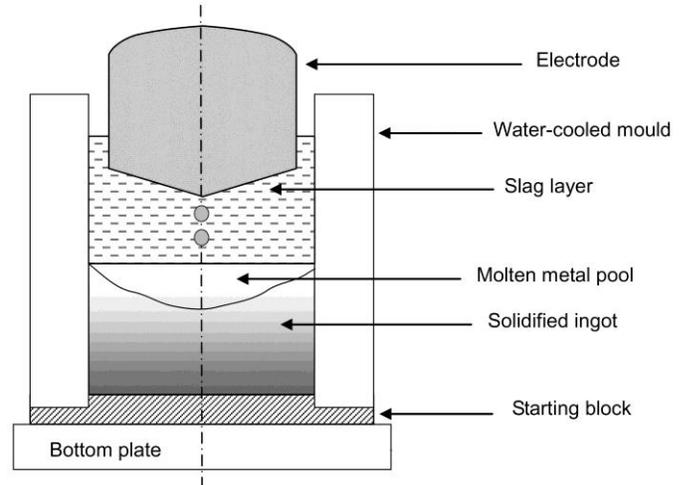


Fig. 1 Schematic diagram of the electro-slag refining equipment

### 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  $900^\circ\text{C}$  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

Electrode material	Stainless steel	Medium C steel
C	0.05	0.30
Mn	–	0.5
Cr	18.02	0.023
Si	–	0.45
Ni	8.06	–
Al	–	< 0.01

TABLE II  
INITIAL CHEMICAL COMPOSITION OF THE FLUX USED

	Flux #1	Flux #2	Flux #3
CaF <sub>2</sub>	55.90	54.16	63.48
Al <sub>2</sub> O <sub>3</sub>	30.61	35.77	25.28
SiO <sub>2</sub>	13.40	9.85	7.69
CaO+MgO	–	–	0.49
Cr <sub>2</sub> O <sub>3</sub>	0.085	0.099	1.38
Fe <sub>(l)</sub>	0.80	–	0.70

### C. Solute Enrichment in Steel

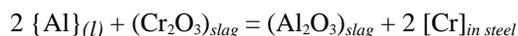
Controlled amount of dry Cr<sub>2</sub>O<sub>3</sub> powder was added to the starting flux before supplying to electroslag refining. Cr<sub>2</sub>O<sub>3</sub> was also added to the molten slag at specified instants after start of refining, as a means of additional chromium input. Dry copper rods were 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 Cr<sub>2</sub>O<sub>3</sub>

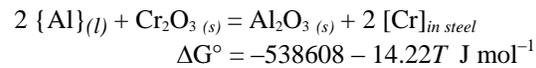
The authors have indicated in a recent publication the initial objectives starting this work [1]. It started with electro-slag refining of an austenitic stainless steel ingot in air. Cr was expected to undergo aerial oxidation due to its higher oxygen affinity than Fe. However, no significant decrease in Cr content could be observed. On the contrary, the Cr<sub>2</sub>O<sub>3</sub> concentration in the slag decreased with progress of refining.

The most likely explanation for this anomaly would be *in-situ* alumino-thermic reduction of Cr<sub>2</sub>O<sub>3</sub> 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 Cr<sub>2</sub>O<sub>3</sub> present in the slag, leading to increase in Cr content in the solidified ingot.



In the present set of experiment, the concentration of Cr<sub>2</sub>O<sub>3</sub> in the slag decreased from an initial level of 1.4 mass% to less

than 1 mass% over a refining period of 15 minutes. Electroslag refining of a plain carbon steel, using the same starting slag, saw similar decrease in the Cr<sub>2</sub>O<sub>3</sub> concentration in the slag. Fig. 2 illustrates the decrease in Cr<sub>2</sub>O<sub>3</sub> concentration in the slag, along with the corresponding transfer of chromium to the steel. The reduction of Cr<sub>2</sub>O<sub>3</sub> from the molten slag is evident, irrespective of Cr concentration in the metal. The aluminothermic reduction of Cr<sub>2</sub>O<sub>3</sub> appears feasible owing to the favourable Gibbs Free Energy change associated with it.



It is noteworthy that a recent work of Seetharaman *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 Cr<sub>2</sub>O<sub>3</sub> concentration in slag.

These observations led to the idea of chromium enrichment in the solidifying steel by deliberate reduction of excess Cr<sub>2</sub>O<sub>3</sub> 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 Cr<sub>2</sub>O<sub>3</sub> concentration in the slag. Once the initial melt-down occurred, excess Cr<sub>2</sub>O<sub>3</sub> 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 Cr<sub>2</sub>O<sub>3</sub> concentration reaching a local maximum of 9 – 10 mass% within 2 min of addition of Cr<sub>2</sub>O<sub>3</sub> powder. This delay might have resulted from the kinetics of dissolution of solid Cr<sub>2</sub>O<sub>3</sub> 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.

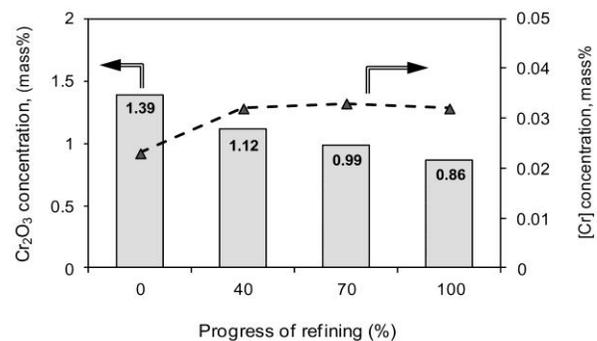


Fig. 2 Progressive decrease in Cr<sub>2</sub>O<sub>3</sub> concentration in the slag during electro-slag refining of a plain carbon steel

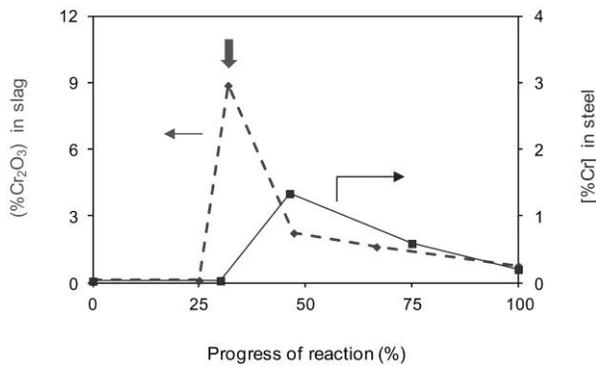


Fig. 3 Variation in Cr content in the steel upon  $\text{Cr}_2\text{O}_3$  addition to slag during electro-slag refining of a plain carbon steel

The nature of variations in the concentrations of Cr and  $\text{Cr}_2\text{O}_3$ , as illustrated in Fig. 3, indicated a gradual depletion of  $\text{Cr}_2\text{O}_3$  in the slag and a resulting slow-down in transfer of Cr to the solidifying metal. This led to the idea of multiple additions so that  $\text{Cr}_2\text{O}_3$  level in the slag is maintained. Fig. 4 shows the results when  $\text{Cr}_2\text{O}_3$  was added twice during the ESR process, 8 min and 14 min from the start. It can be seen clearly that addition of  $\text{Cr}_2\text{O}_3$ , on both occasions, is followed by a corresponding rise in the Cr concentration in steel. This confirms the hypothesis that reaction of  $\text{Cr}_2\text{O}_3$  with the added Al indeed leads to enrichment of Cr in the metal. It is evident that increase in Cr concentration by as much as 2 mass% can safely be attained by this method.

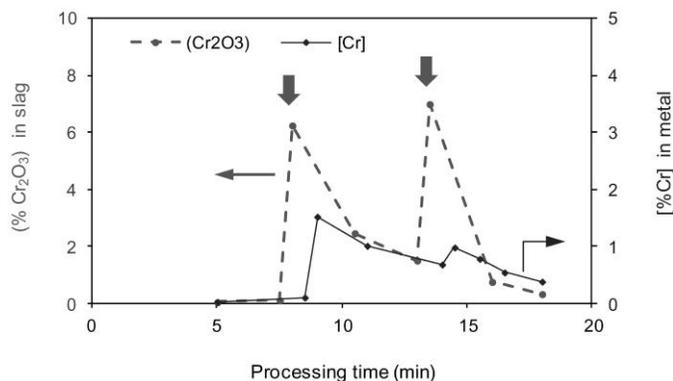


Fig. 4 Influence of  $\text{Cr}_2\text{O}_3$  addition to ESR slag upon Cr content in the steel, indicating transfer of chromium from slag to steel

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

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 ferroalloys. This promises to offer significant reduction in cost as well as energy consumption and emission of greenhouse gases since lesser amount of ferroalloys 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  $\text{Cr}_2\text{O}_3$  from the slag. Similar attempts were made to recover Ti from  $\text{TiO}_2$ , 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.

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