Effect of steel composition and slag properties on NMI in clean steel production

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Abstract. The modern steel plants for clean steel production depend to large extent on the efficiency of the refining processes that applied for the production. Refining processes that applied for low alloy and alloyed steel production include degassing via vacuum or ladle and ladle furnace units. This technique could help in producing homogeneous steel with low gas content and minimum internal defects. In certain grades of steel for tools and penetration and impact resistance uses, non-metallic inclusions (NMI) and sulphur content are the key factors for the steel performance and applications. ESR, Electro-slag refining (or remelting), is the technique that can efficiently produce clean steel with minimum content of NMI and sulphur due to the special nature and mechanism of this technique. In this study, the effect of initial chemical composition of steel and slag properties on the efficiency of ESR process in removal of NMI and sulphur from steel are evaluated. Different grades of steels were refined using ESR process. The efficiency of ESR in modifying and enhancing NMI shape, size and counts as well as removal of sulphur in different steel grades was evaluated at different slag composition and physical properties. The effect of chemical composition of steel on the efficiency of ESR process was studied. It was found that ESR process has a great effect in producing clean steel where both viscosity and initial composition of steel have influence on the final NMI status and sulphur content in the produced steel.

1 Introduction

Among the different refining processes such as vacuum arc remelting, electron beam remelting, plasma arc remelting and electro-slag remelting, ESR process is considered as the most distinguished secondary refining process due to its reality, economical production and the competitive and high efficiency in refining different and complicated steel grades. ESR of alloyed steels has many advantages; that could be concluded in the improvement of quality structure, chemistry, processing, application and properties. It has been found that refining of steels by ESR process improves ductility, impact transition characteristics, transverse properties elevated temperature properties and corrosion resistance [1,2]. However, it was well proved that the composition and the physical properties of the slag used in such refining process has the main powerful effect on the yield of alloying elements, desulfurization, and removal of non metallic inclusions as well. The melting of the electrode in the ESR process is made by heat generated by current flow through fused slag, which gives an importance to the electrical properties of slag [3, 4]. Calcium fluoride based slag is the common slag used for ESR because of its desirable electric properties Kato [5]. The viscosity and surface tension of used slag should have been considered to obtain a desirable ESR process. It has been proved that a high-viscosity slag would increase the residence time of metal drops in the slag bath, thus providing greater time for chemical exchanges between the two media but it has the disadvantages of slowing down the diffusion of refining compounds and products. However a low-viscosity slag would facilitate the escape of gases from the solidifying metal and also due to formation of a thin slag skin over the surface of the refined ingot. On the other hand, interfacial properties of the liquid slag are important factors in the removal of impurities from the metal across the two-liquid interface. As decreasing the slag viscosity, the impurities removal is enhanced. CaF$_2$-Al$_2$O$_3$-CaO (70-15-15) slag system has been studied through detecting its viscosity and surface tensions at 1600°C, to identify its feasibility to be used in ESR process [6, 7]. In spite of the calcium rich slag has a great power in desulfurizing rate during the ESR process, but it has a negative effect on the physical properties of the slag, as well as its affinity for producing calcium hydroxide Ca(OH)$_2$, being a source of hydrogen through ESR process. At the mean time, it was well proved that the heavy oxides as TiO$_2$ has a desirable effect on the viscosity and the surface tension of the slag used in ESR [8, 9]. Moreover, Titanium is the most oxidizable alloying element in the steel, which reflects on its recovery during remelting process, and consequently on the economical aspect of the titanium containing steel. Thus, this research is aiming at studying the effect of replacing CaO by TiO$_2$ in CaF$_2$-Al$_2$O$_3$-CaO (70-15-15)
slag system on the ESR process of titanium containing high strength low carbon steel.

2 Experimental Method

Two heats of Ti-containing maraging steel have been carried out in high frequency induction furnace by melting low carbon scrap and other ferroalloys, the chemical compositions of the produced steels is listed in table 1. The molten metal has been poured in metal mold, then the produced ingots was forged at 1000°C to square cross section rod 25*25mm. Three slags with different TiO₂ have been melted in Submerged Arc Furnace. The physical properties of the slag are shown in table 2[10]. ESR unit has been used for remelting the steels under the three slag compositions. Samples have been collected before and after ESR and subjected for emission spectrophotometer to evaluate the recovery of alloying elements and desulfurizing efficiency Image analyzer has been used for detecting the morphology, and the size characters of non metallic inclusions under the three nominated slag compositions. Finally, the effect of ESR using different slag compositions on the mechanical properties of the steels has been determined.

Table 1. The chemical composition of steel.

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>Chemical Composition, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>ST1</td>
<td>0.04</td>
</tr>
<tr>
<td>ST2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

3 Results & Discussions

3.1. The effect of Flux compositions on the recovery of alloying elements

Certainly, the physical properties of the flux used in ESR process has the powerful effect on the recovery of alloying element, in particular a low free energy oxide forming elements like Ti, Al, Si. It is well known that raising up of slag viscosity inhibit the oxygen penetration through the refining process, while the low viscosity slag promote the oxygen activity in the slag–metal interface which leads to oxidize the alloying element like Ti, Cr, and Ni. Figure 1, 2, and 3 depicts the change of alloying elements of the investigated steels after electro slag remelting technique with different slag compositions. Strong relationship between the flux composition and the alloying elements recovery has been observed, that should have interpreted by the disparity in the physical properties of used flux as discussed in the next section. However, titanium increment has been observed at high TiO₂ containing slag (F3), which can be explained by the reducing condition of the used slag has a significant effect on inducing Aluminum to reduce the titanium from its oxide. Then, the increment of titanium is occurred at the expense of aluminum content, in particular in low Ti containing steel, and this fact is thoroughly observed in Table 3, and Fig.3.

Table 2. The chemical, and physical characterization of the fluxes used in ESR

<table>
<thead>
<tr>
<th>Flux No.</th>
<th>Chemical Composition, wt. %</th>
<th>Physical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaF₂</td>
<td>CaO</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>F1</td>
<td>70</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>F2</td>
<td>52.5</td>
<td>-</td>
<td>22.5</td>
</tr>
<tr>
<td>F3</td>
<td>70</td>
<td>-</td>
<td>30</td>
</tr>
</tbody>
</table>

3.2 The effect of the physical properties of flux on the recovery of alloying elements

It is expected that the recovery of alloying elements will depend on the viscosity of the flux used, which is completely assured in Fig.4, 5, 6. As mentioned before, the enlargement of viscosity value of the flux through the refining process lead to reduce the interaction time between the molten droplet and the surround atmosphere. Thus, the recovery of alloying elements is increasing linearly with the viscosity value of the flux. At the mean time, the interfacial tension of the slag has a similar effect on the recovery of alloying elements. Referring to Eq.1, the activity of oxygen in the Slag/metal interface layer is completely dependent on the interfacial tension of slag [11]. Thereby, any growth in the interfacial tension value of slag is stimulus to reduce the oxygen activity, and consequently lead to enhance the recovery of alloying elements.

\[
\Gamma = \frac{1}{kT} \cdot \frac{dy}{d\ln KO_2^{-2}} \quad \text{Eq.1}
\]

Where \(\Gamma\) is the saturation coverage, \(R\) is the gas constant, \(T\) is the absolute temperature, \(x\) is the interfacial tension, and \(XO_2\) is the mole fraction in the slag system at the interface.
3.3 The effect of physical properties of the flux on Desulfurizing and Dephosphorizing efficiency

Certainly, the electro-slag refining is considered as the most effective refining process in terms of desulphurization and dephosphorization processes. It was well proved that the activity of sulfur in the molten metal is completely depending on the activity of oxygen. Increasing the oxygen activity in the molten steel leads to reduction of the sulfur activity and consequently obstructs the desulphurization process [12]. On the contrary, the dephosphorization process is being performed at the high activity of oxygen in the slag/metal interface [13]. Undoubtedly, the physical character of molten slag has a significant effect on the activity of oxygen through the slag/metal interface. The desulfurizing rate of the two steels after ESR has been determined by Eq.2.

\[
\text{Desulfurizing rate} = \frac{Si}{S_s} \times 100 \quad \text{Eq.2}
\]

Figure 7 and 8 assure the significant role of the characteristic properties of the slag in terms of desulphurization and dephosphorization processes. The desulfurizing rate has been reduced as a result of viscosity. This fact can be interpreted by the growth in slag viscosity causes the increment of oxygen activity in the metal/slag interface, which consequently leads to reduce the activity of sulfur as in Eq.3. Thereby, the desulphurization process is mainly impeded by the increase in slag viscosity.

\[
\log L_s = \frac{\log [S]%}{[S]} = \frac{935}{t} + 1.375 + \log Cs + \log f_s - \log a_o \quad \text{Eq.3}
\]

$L_s$ sulphur partition coefficient, (S%) sulphur in slag, [S]% sulphur in metal, Cs sulphide capacity, $f_s$ activity of sulphur, $a_o$ activity of Oxygen.

On the other hand, there is never a prominent trend between the physical properties of slag and the dephosphorizing rate as shown in Fig.8. Although the boiling point of phosphorous is very low a considerable amount of it still dissolved in liquid iron because of its strong interaction parameter with iron. The steelmaking slag may contain up to 25% $P_2O_5$ but even then the activity of $P_2O_5$ in slag remains extremely low. In addition, in order to obtain effective removal of phosphorous, it must have been employed slags of high basicity. If the basicity falls, phosphorous may revert back to the metal phase. In acid steel making process since the slag is nearly saturated with silica, phosphorous cannot be eliminated at all. Then, the basicity of slag is complementary parameter in the dephosphorization process, and the basicity of slag is dependent on the alloying element recovery during ESR process. This means that the dephosphorization process is awkward process to control through ESR.

One of the many advantages claimed for consumable electrode remelting process (ESR) is that of reducing the nonmetallic inclusions (NMI) content. The separation of a droplet of steel from the electrode immersed in the slag is evidently only possible at fairly high liquidus temperatures, when the force of gravity affecting the droplet is greater than the forces of molecular cohesion and surface tension. Upon contact with the superheated slag, the temperature of the stream of steel droplets approximates to that of the slag. With the passage of the metal drops through the slag, a considerable proportion of solid and liquid particles in suspension are removed in the process. The improvement in cleanliness which occurs during the ESR process has been clearly established by
Martinez[14]. A number of authors, Baird[89], Duckworth, Gladman and Zabaluev have commented on the various mechanisms by which this reduction in nonmetallic inclusions is achieved[15-17]. But the role of ESR fluxes and its physical properties in the removal of nonmetallic inclusions was discussed in few articles. Mattar etal studied the effect of physical properties of ESR fluxes, i.e., viscosity and surface tension on the cleanliness of tool steels [18]. He concluded that slag with intermediate viscosity gives the optimum condition for these nonmetallic inclusions to be removed. Figure 9 depicts that the optimum physical character of the removal of NMI was established at mean value of viscosity and interfacial tension. This can be interpreted by the effect of low values of viscosity and interfacial tension in supplying the oxygen from the surrounding atmosphere, which leads to increase the no. of NMI. However, the high value of viscosity and interfacial tension allow the molten drop of metal to interact with slag for long time, which raise up the contamination possibility of the metal from the exogenous NMI in the slag.

Table 3. The chemical composition of the investigated steels before and after ESR

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>Process</th>
<th>ESR Flux</th>
<th>Chemical Composition, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>St1</td>
<td>IF</td>
<td></td>
<td>0.0433</td>
</tr>
<tr>
<td>St11</td>
<td>ESR1</td>
<td>F1</td>
<td>0.366</td>
</tr>
<tr>
<td>St12</td>
<td>ESR2</td>
<td>F2</td>
<td>0.0602</td>
</tr>
<tr>
<td>St13</td>
<td>ESR3</td>
<td>F3</td>
<td>0.0484</td>
</tr>
<tr>
<td>St2</td>
<td>IF</td>
<td></td>
<td>0.0535</td>
</tr>
<tr>
<td>St21</td>
<td>ESR1</td>
<td>F1</td>
<td>0.0572</td>
</tr>
<tr>
<td>St22</td>
<td>ESR2</td>
<td>F2</td>
<td>0.061</td>
</tr>
<tr>
<td>St23</td>
<td>ESR3</td>
<td>F3</td>
<td>0.0671</td>
</tr>
</tbody>
</table>

The first no after St refers to the steel no, while the second no declares the grade of the flux used in ESR process

Figure 5. The effect of interfacial tension and viscosity of slag on the recovery of Chromium

Figure 6. The effect of interfacial tension and viscosity of slag on the recovery of Titanium
The desulfurizing rate of the refined metal is hardly dependent on the viscosity of slag rather than its basicity.

The optimum removal of NMI can be obtained by intermediate value of viscosity and interfacial tension of slag, where low slag’s viscosity leads to further oxidation of alloying elements and increasing NMI and high viscosity slowdown the NMI removal and leads to further contamination of steel in the slag components.

References

11. Eun Jin Jung and Dong Joon Min, “Effect of Al2O3and MgO on Interfacial Tension Between Calcium Silicate-Based Melts and a Solid Steel Substrate”, steel research int. 83 (2012) No. 7.

4 Conclusions

- The recovery of alloying elements is sharply dependent on the physical character of the used slag in ESR process.
- TiO2 rich slag can be used to compensate the loss of Ti during ESR process.