Foamy slag in EAF stainless steel production

The benefits of foamy slag practice in EAF carbon steel production is well known and widely applied. However, until now, no suitable practice was available for stainless steel production due to the adverse effect of chromium oxidation and inadequate slag properties. A new process now allows production of controlled high foaming slag for stainless steels which covers the electric arcs so power input can be increased, arc noise reduced and yields of consumables increased.

The economics of electric arc furnace (EAF) technology are strongly dependent on the efficiency with which electrical energy is introduced into the metal bath. For many years the use of a foaming slag practice has been well established for low alloy steel production. It improves thermal efficiency of melting, lowers refractory and electrode consumptions and provides stable arcing at a reduced noise level. A good foaming effect is produced by having slag with a suitable viscosity and iron oxide content and by creating iron oxidation and iron oxide reduction reactions by injecting oxygen and carbon into the metal bath and slag, respectively. However, until now, no suitable practice was available for stainless steel production due to the effect of chromium oxidation and poor slag properties.

In the case of high chromium steels the preconditions for slag foaming effect are completely different:

- Oxygen injected into the steel produces mainly chromium oxide with totally different properties compared to iron oxide, and it significantly changes the slag viscosity.
- The solubility of chromium oxide in the slag is considerably lower compared to iron oxide at the same thermal and basicity conditions.
- The reduction of chromium oxide by carbon is not as efficient as the reduction of iron oxide.
- Gas generation is worse.
- The oxygen/carbon injection technique in high chromium alloyed steel production creates chemical and physical conditions which are hazardous and difficult for operation.
- The risk of uncontrolled oxidation of chromium is substantial, resulting in high chromium losses and poor foaming.

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SMS Siemag, AMIB (Acesita SA) and University of Science and Technology, Krakow

SMS Siemag, Germany, AcelorMittal Inox, Brazil (AMIB; formally Acesita SA) and the AGH-University of Science and Technology in Krakow, Poland have jointly developed a new sophisticated foaming slag technology that has been successfully tested both in laboratory and industrial environments. The most recent application of this technology is in the EAF of SMS II Jindal Stainless Ltd, Hisar, India.

Unlike conventional foaming technology which uses injection of oxygen and carbon via manipulator lances, the new technique is based on the reduction of iron and chromium oxide by carbon and thermal dissociation of limestone. Both carbon and limestone are added within small briquettes or pellets. The density of these briquettes is chosen to have a value between that of the slag and the metal such that when introduced into the melt, they float at the slag/metal boundary – the optimal place for the required gas-generating reaction.

SLAG FOAM FORMATION

Two factors define foamy slag formation: the foaming material – with the corresponding reacting components, which produce gaseous products, and a liquid slag with appropriate slag viscosity – which is dependent on chemistry and temperature. The principal reactions that create gas bubbles in the slag are the reduction of iron and chromium oxides:

\[
(FeO) + C_{\text{particle-or-dissolved}} \rightarrow [Fe] + \{CO\}
\]

(1)

\[
(Cr_2O_3) + 3C_{\text{particle-or-dissolved}} \rightarrow 2[Cr] + 3\{CO\}
\]

(2)

Reaction (1) is the principle one in carbon steelmaking because iron oxide is the major component in the slag. When the slag viscosity is suitable for sustaining foam, then simple carbon injection into the slag causes the foaming effect. With stainless steel slag, however, the major components are CaO, SiO₂, and Cr₂O₃, where SiO₂ is a fluxing component and Cr₂O₃ stiffens the slag. Due to
the higher chromium affinity for oxygen Cr$_2$O$_3$ formation is preferred over FeO formation, therefore it is important to control the chromium oxide content to avoid Cr losses. Slag basicity – which controls viscosity and hence affects gas bubble entrainment – must also be controlled.

The additional gas source in the briquettes is limestone. Thermal dissociation of this material provides CO$_2$ as per equation (3):

$$\text{(CaCO}_3\text{)} = \text{(CaO)} + \text{(CO}_2\text{)}$$  \hspace{1cm} (3)

The bubble forming phenomenon is a process that uses the mechanical force from reacting gases to produce new surface area in the slag. In the presented technology this gas is a product of the reduction of metal oxides by carbon and thermal dissociation of limestone taking place in briquettes or pellets introduced into the metal bath. Buoyancy forces on the bubbles break the slag surface, temporarily saturating the top layer to create the foam. With a sustained gas flow coming from the reacting briquettes bubble density increases and foaming occurs.

The optimum placing of the briquettes at the boundary between the slag layer and liquid metal to get the maximum foaming effectiveness is important for such a mechanism. By controlling the briquette density so that it is between that of slag and metal (3-7 g/cm$^3$) ideal placement is achieved. The foam height increases with an increase in gas flow rate and is directly proportional.

<table>
<thead>
<tr>
<th>Chemical composition, wt.%</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>Cr$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.3</td>
<td>30.2</td>
<td>2.3</td>
<td>2.0</td>
<td>7.8</td>
<td>5.5</td>
<td>11.9</td>
<td></td>
</tr>
</tbody>
</table>

*Table 1  Average chemical composition of the slags*
to the foaming material addition rate. Figure 1 illustrates the principle of slag foaming.

LABORATORY TESTS
The aim of the laboratory experiments was to establish adequate forms and chemical compositions of the materials for effective foaming of high chromium oxide slag and to define optimal slag conditions.

The materials used were produced as briquettes and pellets and contained iron oxide scales, carbon carriers, calcium carbonate or fluorite and binding agents. For density control, high carbon alloys typical of stainless steel production or scrap were used.

The study was carried out by making laboratory heats and sampling metal and slag phases for chemical analysis in order to optimise the foamability.

In the first stage of the work, the most promising materials for foaming were selected based on theoretical considerations. A model for computation of the densities of the foaming mixtures was applied.

In the second stage, the foaming mixtures were prepared as briquettes and pellets of different sizes. Forty heats were produced in a laboratory arc furnace to investigate the impact of various parameters on the height and stability of the generated foams.

In the third stage the results were analysed and the final conclusions and technological recommendations as to the optimal conditions for the slag foaming were established. Figure 2 illustrates the test stand, consisting of a single electrode EAF with a conductive bottom. The furnace was powered by a 75kVA transformer at a voltage of 380V. The total melt capacity was 5kg. The test metal was prepared from about 1.5kg of AISI 304 scrap then, after scrap melting, an industrial slag of defined composition and weight, ~3kg, was added and melted. Samples of metal and slag for analysis were taken. The average slag composition of the tests is shown in Table 1.

The temperature was controlled at approximately 1,600°C. The initial height of the slag was recorded and the foaming mixture was added to the furnace in small batches. The slag height was measured by immersion of a tungsten bar until it reached the crucible bottom from the initiation of foaming until the foam had ceased. After taking out the bar, the height of the solidified slag was obtained and taken as the foamed slag height.

The total duration time of the foaming process after slag
its industrial functionality and viability. The test was carried out in EAF No3 in the steel plant in Timoteo, Brazil. The EAF-AC, with a capacity of 25-35t and transformer rating of 32MVA, is designed for pre-metal production of austenitic and ferritic steel grades in conjunction with an 80t AOD-L and MRP-L (Metal Refining Process-Lance) converters.

The tests, integrated into the normal production programme, consisted of 45 austenitic and 15 ferritic heats. Forty heats were produced according to variant 1 (see Figure 4) where oxygen was blown until briquette additions started. The reason for such a procedure was to separate the oxygen effect on the carbon and metal oxidation and additional generation of CO bubbles as well as the impact effect of the gas stream. In the remaining 20 heats, melting was 7-14 minutes. When foaming was complete, the slag was re-sampled and the metal and slag were tapped into a mould. After solidification the metal and slag were weighed.

Two forms of foaming material were applied: briquettes and pellets. The briquettes were made by compression of a powder charge material by means of a specially designed press device. The briquettes were 30mm in diameter, 15-17mm in height and with a weight of 50-70g each. The pellets, either 2-5mm or 8-10mm diameter, were made in a drum by pelletising powdered materials with molasses as a binding agent.

The investigations were performed for the foaming additions as a mixture of stoichiometric amounts of Fe₂O₃ and C-graphite. The density of this foaming material was 3.80-4.2g/cm³. The composition was 7-18%C, 30-40% Fe₂O₃.

The results of the slag foaming trials are illustrated in Figure 3. MI 100g refers to a specific composition test. The results indicate that the pellets with 8-10mm diameter have the highest foamability, while those with a 2-5mm diameter have the lowest. The reason is that small pellets do not sink through the slag layer but float on the slag surface, thus the bubbles formed do not go into the slag layer but pass into the atmosphere. The phenomenon is caused by the interfacial tension forces at the pellet-slag boundary. The actual foaming time was lower for pellets than briquettes. This is explained by the difference in structure; briquettes are compressed materials, and thus have lower porosity and a decreased contact surface with liquid slag. This causes slower heat transfer and slower reduction of the iron oxides in the briquettes and, in consequence, a lower gas evolution rate. Only briquettes were selected for industrial examination.

INDUSTRIAL TESTS BY ACESITA SA

On the basis of the laboratory test results, AMIB (ACESITA SA) and SMS Siemag AG agreed on industrial tests of foamy slag with high Cr oxide content in an EAF to prove
heats oxygen was blown during the whole superheating period until tapping, as indicated by variant 2.

EAF No3 works with power input divided into nine taps (20-28). Tap 28 with an arc length between 15.5cm and 21.5cm allows working with maximum power and is used generally in the first melting stage only. Because of the intensive energy radiation on the furnace walls during the superheating period, where the metal bath is flat, a protected operation is required, ie, short electric arcs and the lowest taps between 20 and 23 with an arc length of 10-16.6cm are applied. A high level of foaming slag above the electrode tips allows operations with higher taps so shortening the tap-to-tap time. The temperature rise between briquette start and end was significantly higher at an estimated 12-14°C/min with tap 28 against 6-7°C/min with taps 23 or 24 under normal operations.

The composition of briquettes was changed after the laboratory experiments. The ballast function of FeCrHC was substituted for finely shredded steel scrap due to non-availability of FeCrHC.

The briquettes (see Figure 5) were made from mixtures consisting of concast plant scale, coke, limestone, fine scrap and binder.

Briquettes were added into the furnace via the 5th hole in a controlled manner. Each test heat was recorded by video camera and metal and slag samples were taken for analysis before briquette additions and at tapping. The temperature was also measured during sampling. Noise measurements were recorded continuously on some heats by a portable audio device during the foaming period to compare with
standard operations. Other signals like voltage, current, energy consumption, power, $\cos \phi$ and the tap number were also recorded for each heat. Figure 6 illustrates the observation stand in the front of the EAF.

The trials indicated that the foaming of Cr$_2$O$_3$-rich EAF slag is difficult but possible under controlled slag conditions. The industrial tests have confirmed the correct recipe for the foaming material and the optimum reaction place of the briquettes at the slag-metal interface.

The tests also showed dependencies between the amount of initial slag and its foamability so as to be able to cover the arcs. The optimum initial slag quantity is 68-72kg/tls which is significantly lower than for carbon steels – typically 120-150kg/tls.

Figure 7 illustrates the slag compositions on a ternary diagram after briquette additions. It can be seen that most slags were well reduced, ie, low Cr$_2$O$_3$ and at an average residual Cr$_2$O$_3$ in the slag of 4.2%. The optimum basicity was found to be in the range 1.3-1.35. The viscosity in this area, however, is low, with partly undissolved lime and increasing viscosity as Cr$_2$O$_3$ content increases.

Figure 8 illustrates a typical slag height development of an AISI 304 heat. The slag heights were measured at the electrode position. As the curve shows, after approximately two minutes the slag reached the height suitable to cover the electric arc and which was maintained during the next four minutes, leaving the required range after 4.5 minutes. It should be mentioned, that after 3.5 minutes an overflow of the slag through the furnace door was observed, thus the weight of slag mass continuously reduced until a stable level was reached.

Figure 9 uses the secondary voltage to illustrate the electric arc behaviour in a standard operation and in the presence of foaming slag operation. Small signal fluctuations, low level of amplitudes, lower mechanical and thermal electrical tensions were observed. Consequently, the level of noise generation is also significantly lowered.

Figure 10 shows a comparison of the noise development in the case of a standard heat and foamy slag treated heat. It can be seen that the standard heat is operated in the super heating period with lower transformer taps 23 and 21 and generates a noise level between 100 and 95dB. Test heats show a correlation between foamy slag development that covers the electric and the noise levels. The impact of the foam damping can be seen in the final period where the noise level decreases from approximately 95 to 90dB at transformer tap 24.

Evaluations of metallurgical parameters show improvements in almost all aspects of production, for example, metal yield, chromium and manganese yields all improved by approximately 2%. The shortening of the super heating period by operation with higher transformer taps has the potential to increase plant production, but more heats are required to confirm this.

Long-term effects like electrode consumption, refractory life, electrical maintenance of switch transformer contacts and dust emission are also of high significance in the process economy.
SUMMARY

- Briquettes with density higher than 3.5g/cc assure correct positioning at the slag-metal interface. Use of FeCrHC or steel scrap as part of the mix provide the necessary density.
- Limestone improves gas formation.
- Good slag foaming is dependent on the slag viscosity as controlled by the temperature and basicity. Lower temperatures (1,500-1,550°C) are required for lower basicity (lime not completely dissolved). Higher temperatures (1,600-1,650°C) are required for higher basicity (lime completely dissolved).
- Good foaming also requires a sufficient quantity of original slag.
- High foaming slag stabilises the thermal and mechanical conditions on the operating electrodes tips, reduces noise and enables use of higher power input and heating rate.
- Metal, chromium and manganese yields are increased by ~2%.

CONCLUSIONS

Tests demonstrate that the new foaming slag technology for stainless steelmaking in the EAF by use of briquettes with specially developed composition, size and density produces good slag foaming such that power input can be increased, noise is reduced and yields of consumables are increased. 

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The original version of this article was presented at the XXXVIII International Steelmaking Seminar 20-23 May 2007, Belo Horizonte, Minas Gerais, Brazil and at the 9th European Electric Steelmaking Conference, 19-21 May 2008, Krakow, Poland.