New Developments in Steelmaking Process Measurements

MONDAY AFTERNOON, APRIL 10, 1972

The session on New Developments in Steelmaking Process Measurements convened at 2:00 pm. The chairmen were J. H. Bucher, Staff Metallurgist, Quality Control Div., Jones & Laughlin Steel Corp., Pittsburgh, Pa., and J. H. Cox, Homer Research Laboratory, Bethlehem Steel Corp., Bethlehem, Pa.
DEOXIDATION CONTROL OF BASIC OXYGEN STEEL

USING OXYGEN SENSOR MEASUREMENTS

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Abstract

By using the U. S. Steel oxygen sensor to measure the oxygen content of the steel, deoxidation practices have been developed for silicon-killed fine-grain steel produced by the basic oxygen process. Measurements of oxygen content taken at final turndown are related to the amount of the aluminum addition to the ladle necessary to obtain the desired aluminum analysis for proper grain refinement. In comparison with heats deoxidized by the standard approach, which is based on carbon content, the heats deoxidized according to the oxygen-sensor-based schedule showed a 25 percent decrease in variability from the desired aluminum content. As more heats of a particular grade are made, it is expected that improved quality will result in decreased rejections and better analysis control. Sensor-based deoxidation schedules are also being developed for semikilled, rimmed, and capped steels.

Introduction

The control of oxygen content in liquid steel so that desired final chemical compositions and solidification structures can be realized is a prime objective in steelmaking. However, the parameters conventionally used to govern deoxidation are indirect measures of the dissolved oxygen content. Such parameters are carbon content, FeO content of the slag, slag basicity, temperature, and the total oxygen content of a solid sample.

In 1968, Turkdogan and Fruehan presented a paper describing a laboratory oxygen sensor that was able to rapidly measure the dissolved oxygen content of liquid steel (1). Continued developmental work on this sensor resulted in a rugged and dependable unit that could be used in a steelmaking shop (2). Therefore, for the first time an alternative to the indirect measurement of oxygen content was available, and studies began on the use of the U. S. Steel oxygen sensor in steelmaking.

The application of the oxygen sensor was first demonstrated in development of deoxidation schedules for various grades of open-hearth steel at Homestead Works (3). These grades included rimmed, capped, and semikilled steel. The results from Homestead Works showed that deoxidation schedules based on oxygen-sensor measurements produced improvements in meeting the ladle deoxidant aims and resulted in quality benefits. For example, in the case of semikilled steel, there was a 50 percent
decrease in rejections off the 100-inch plate mill in comparison with steel deoxidized on the basis of carbon content.

Upon completion of this phase of the program at the open hearth, which included operator training in the use of the oxygen sensor, efforts were concentrated on determining the usefulness of the oxygen sensor in the basic oxygen steelmaking process. The fact that meaningful measurements could be related to ladle deoxidation requirements in the open hearth was no guarantee that similar results would be obtainable from the basic oxygen process (BOF). The processes are certainly different in the degree of bath agitation, and this condition may produce a difference in endpoint stability with respect to oxygen content. There are other important differences; for example, from the time the oxygen is shut off in the basic oxygen furnace (BOF) the bath is cooling, whereas in the open hearth, fuel is kept on during tapping. In addition, the average tapping time for the BOF is about 6 minutes compared with about 12 minutes for the open hearth.

Therefore, to investigate the applicability of the oxygen sensor, a program was planned with National-Duquesne Works to measure the oxygen content of 220-ton BOP heats. The results of this program are the subject of the present paper.

Experimental Procedure

The basic components of the oxygen sensor used in the BOP trials are shown in Figure 1. Briefly, the expendable oxygen sensor contains two electrodes, one a Mo rod and the other a reference electrode of Cr + Cr₂O₃ powder encased in a quartz tube and separated from the liquid steel by a stabilized zirconia button. This zirconia button functions as a solid electrolyte at high temperature. Since the temperature value of the steel is required for determination of the oxygen content from the generated cell voltage, it is convenient to have a thermocouple in the oxygen sensor, which is contained in the U tube shown in Figure 1. The sensor tip is protected from slag by a steellCaB and the refractory is encased by a cardboard tube.

On turndown at National-Duquesne Works, a spoon sample was first taken for obtaining carbon pin samples, a solid slug for the spectrograph, and a thermal-arrest determination of carbon content. Then a standard immersion thermocouple was used to measure bath temperature. After these measurements were completed, usually 1 or 2 minutes after turndown, the oxygen sensor was immersed. Sometimes measurements were taken on more than one turndown, for example, before and after rebloows or coolings. Figure 2 is a photograph of an oxygen-sensor immersion. The technique is similar to that of taking a standard immersion thermocouple reading, and it is very important to keep the oxygen sensor from floating up into the slag phase. This is essential because slag contamination ruins the cell components and therefore produces an obviously incorrect trace. The tendency to float was minimized by changing to the heavier schedule 80 pipe rather than schedule 40 for use as the lance.

The millivoltage outputs of the oxygen cell and of the thermocouple were traced on a 2-pen recorder. Figure 3 is a drawing of the oxygen sensor and auxiliary equipment used to make the measurements in the basic oxygen furnace. The recorder was mounted on a dolly so that the system was portable and measurements could be made at either of the two operating furnaces. The 3/4-inch lance containing the electrical leads was protected by a 1-7/8-inch-OD cardboard tube with a 3/8-inch wall. Figure 4 shows traces from two heats. The chart speed was about 1 inch in 5 seconds for these traces. The temperature and oxygen-sensor curves are read after leveling off, which usually occurs after about 10 seconds of immersion.
Results and Discussion

During the initial testing of the oxygen sensor in the BOP, sensor measurements were made on a variety of grades over a range of carbon contents. The objective was to determine the response of the oxygen sensor to various situations present at the endpoint in basic oxygen steelmaking and to relate oxygen sensor measurements to ladle deoxidation requirements and develop deoxidation schedules for particular types of steel.

Preliminary Testing

In Figure 5 the results of over 90 oxygen sensor measurements are shown with the corresponding carbon contents. The carbon contents range from 0.48 to 0.020 percent and the oxygen contents from 50 to 875 ppm. As expected, the oxygen-carbon plot follows the general curvature of the equilibrium curve, which was determined from equations derived by Nilles (4), and takes into account the partial pressure of CO2 at carbon contents less than 0.10 percent. The measured oxygen values form a band displaced above the equilibrium line for a given carbon content. This scatter widens at lower carbon contents and indicates that the oxygen sensor should provide a more accurate tool for control of deoxidation.

In addition to carbon content, the total iron oxide (FeO) content of slag is often used as an aid in determining ladle deoxidation requirements. Figure 6 is a plot of the FeO content of the slag and the dissolved oxygen content of the steel as measured by the oxygen sensor. It is seen that although there is a trend, that is, higher FeO content corresponds to higher dissolved oxygen content, the variability is quite large. For example, at 20 percent FeO there could be 50 to 500 ppm oxygen in the steel.

The oxygen content may change at the end of a heat because of corrective actions taken to realize the specified temperature and composition requirements. Several heats that show a changing oxygen content are listed in Table I. In heat A21621, lime was added and the heat was rebloown for carbon and sulfur with essentially no change in temperature. The oxygen content increased from 113 to 210 ppm. Heat B33458 was rebloown because of a mold delay and then cooled because of excessive temperature. The oxygen content increased from 220 to 650 ppm, then, when the heat was cooled, decreased to 444 ppm. On heats for which the carbon content remains constant, for example during cooling of a hot heat, the oxygen content can change. In heat A22024 the carbon content remained constant at 0.062 percent, but the oxygen value decreased about 20 percent, from 365 to 302 ppm. In heat B33324, the carbon content only decreased from 0.34 to 0.30 percent, but the oxygen content increased about 75 percent.

Table I

<table>
<thead>
<tr>
<th>Heat Number</th>
<th>Carbon, percent</th>
<th>Temp., F</th>
<th>FeO, percent</th>
<th>Oxygen, ppm</th>
<th>Endpoint Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>A21621</td>
<td>0.196</td>
<td>2885</td>
<td>18.5</td>
<td>113</td>
<td>Added lime, rebloown for carbon and sulfur.</td>
</tr>
<tr>
<td></td>
<td>0.122</td>
<td>2880</td>
<td>19.8</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>B33458</td>
<td>0.143</td>
<td>2925</td>
<td>23.4</td>
<td>220</td>
<td>Mold delay, rebloown.</td>
</tr>
<tr>
<td></td>
<td>0.056</td>
<td>3010</td>
<td>25.5</td>
<td>650</td>
<td>Too hot, added coolant.</td>
</tr>
<tr>
<td></td>
<td>0.056</td>
<td>2870</td>
<td></td>
<td>444</td>
<td></td>
</tr>
<tr>
<td>A22024</td>
<td>0.062</td>
<td>2965</td>
<td>16.1</td>
<td>365</td>
<td>Too hot, added coolant.</td>
</tr>
<tr>
<td></td>
<td>0.062</td>
<td>2930</td>
<td></td>
<td>302</td>
<td></td>
</tr>
<tr>
<td>B33324</td>
<td>0.337</td>
<td>2955</td>
<td>13.8</td>
<td>73</td>
<td>Added spar, rebloown for phosphorus.</td>
</tr>
<tr>
<td></td>
<td>0.295</td>
<td>2915</td>
<td>17.7</td>
<td>128</td>
<td></td>
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</table>
Development of a Deoxidation Schedule

After it was established that oxygen-sensor measurements could be taken in the BOF under a variety of conditions, work was directed toward obtaining data on a specific steel. The type chosen was silicon-killed fine-grain steel. This steel contains from 0.13 to 0.55 percent carbon, 0.40 to 1.50 percent manganese, and 0.15 to 0.35 percent silicon. The desired aluminum level is 0.03 percent. Depending upon the ladle carbon content, the grades are designated by the plant as A2, from 0.13 to 0.29 percent, and B2, from 0.30 to 0.55 percent. Alloying elements added to the ladle besides silicon, manganese, and aluminum include chromium and sulfur. When required, nickel, molybdenum, and copper are added to the furnace with the scrap charge. Heats with additions of boron or titanium to the ladle were not investigated. To provide more heats for the study and also to compare fine-grain product with coarse grain in the finishing mill, a number of normally coarse-grain heats were intentionally made fine grain. Data from these heats and from the regular A2 and B2 type heats were used in the mathematical derivation of a model describing total ladle aluminum content for silicon-killed fine-grain steel.

The model is such that at a given oxygen level the ladle aluminum content increases exponentially as the aluminum addition increases. Therefore, each bundle of aluminum added has an incremental effect on aluminum content which is slightly greater than the increase caused by the previous bundle. Conversely, at a given aluminum addition with increases in oxygen content, the expected ladle aluminum content decreases asymptotically. By using the model, deoxidation schedules specifying the ladle aluminum additions were prepared for various desired aluminum contents.

Results of On-Line Testing of Deoxidation Schedule

The results of on-line testing of the deoxidation schedule on 24 heats, for which the desired aluminum content was 0.030 percent, are shown in the frequency plot in Figure 7. For comparison, the ladle aluminum distribution of 157 A2 and B2 heats made according to conventional deoxidation procedures is also shown. As is evident, the heats made according to the oxygen-sensor-based deoxidation schedules show a narrower distribution. The reduction in variability is significant.

The quantitative improvement in accuracy in attaining the desired aluminum level is shown in Table II, which lists the 95 percent confidence intervals for ladle aluminum levels of 0.025, 0.030, and 0.035 percent. The limits for the oxygen-content-controlled deoxidation practice are based on the predicting error of the mathematical model. An estimate of the carbon-content-based deoxidation practice variability was obtained from actual production data. The oxygen-content-based practice shows about a 25 percent reduction in meeting the desired aluminum content.

Table II

<table>
<thead>
<tr>
<th>Ladle Aluminum - weight percent</th>
<th>Expected Results - 95% Confidence Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desired</td>
<td>Oxygen Practice</td>
</tr>
<tr>
<td>Level</td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>0.015 - 0.041</td>
</tr>
<tr>
<td>0.030</td>
<td>0.018 - 0.049</td>
</tr>
<tr>
<td>0.035</td>
<td>0.021 - 0.058</td>
</tr>
</tbody>
</table>
Grain-size determinations of the structure of the heats showed the desired fine grain size averaging No. 7, and etch tests, as expected, showed no problems with porosity. With the small number of heats available at this time, it is not possible to identify benefits such as decreased rejections for surface defects. However, with extended application of oxygen sensor deoxidation control on silicon-killed fine-grain steel, it is expected that this type of quality benefit would be forthcoming because of better control of ladle aluminum content. No doubt another benefit that will accrue from routine use of the oxygen sensor on silicon-killed fine-grain steel will be the saving of that occasional heat which is far out of line with respect to conventional deoxidation. The oxygen sensor would detect these large deviations in dissolved oxygen and the appropriate addition of aluminum could be made to the ladle.

In addition to the program on silicon-killed fine-grain steel, several heats of semikilled steel have been deoxidized with satisfactory results in meeting the aim silicon content. Developmental work is also proceeding toward applying the oxygen sensor to rimmed and capped grades.

We believe that the oxygen sensor has been shown to be a useful tool in basic oxygen steelmaking. As plant development work increases, the usefulness of the oxygen sensor in steelmaking should greatly increase.

Acknowledgments

The authors would like to acknowledge the aid received in this work from the National-Duquesne Works Steel Producing Division; in particular, W. F. Walter, H. B. Simpson, and W. C. Porr.

References


Fig. 1. Oxygen sensor.
Fig. 2. Oxygen sensor immersion in BOF at National-Duquesna Works.

Fig. 3. Auxiliary equipment used in oxygen sensor measurement.

Fig. 4. Recorder traces obtained at National-Duquesna shop shows oxygen sensor millivoltage and temperature measurements for two heats.

Fig. 5. Oxygen-carbon contents for National-Duquesne Works BOF heats.

Fig. 6. Bath oxygen-slag contents for National-Duquesne Works BOF heats.

Fig. 7. Distribution of ladle Al contents for oxygen based and carbon based deoxidation practices.