Communications

The Use of Secondary Ion Mass Spectrometry for Investigating Oxygen in Pyrometallurgical Reactions

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Oxygen has an important role in pyrometallurgical systems because many of the reactions involve the transfer and reaction of oxygen at an interface. In the case of reactions involving liquid metal, adsorption of oxygen also occurs, resulting in oxygen preferentially residing along the interface due to its surface active nature. In molten metals such as iron and copper, the presence of oxygen at the interface significantly lowers the interfacial tension and may create interfacial tension gradients along the interface. These interfacial tension gradients can enhance the overall kinetics of reactions in these systems.[1,2]

Despite the importance and complexity of the role of oxygen in many reactions, there is only limited knowledge of the distribution of oxygen in liquid metal during reactions. An analytical technique for investigating oxygen concentration gradients in metal is essential for better fundamental understanding. However, a major constraint of oxygen characterization in pyrometallurgical systems, for example, in ferrous systems reacting with slag, is that the concentration of oxygen is very low and may range from few ppb to a maximum of 2800 ppm, which is the maximum solubility of oxygen in liquid iron at 1923 K. To the authors' knowledge, secondary ion mass spectrometry (SIMS) is the only available technique at present that can be used for characterization of oxygen in this range of concentration.[3,4] This article discusses the use of dynamic SIMS for investigating oxygen distribution in samples generated from reactions between Fe-Al droplets and $CaO\text{-}SiO_2\text{-}Al_2O_3$ slag.

Secondary ion mass spectrometry is a characterization technique based on the mass analysis of either positive or negative ions ejected from the top few monolayers of a solid surface resulting from a sputtering process using a primary ion beam. One of the strengths of SIMS is its detection limits. The detection limit is down to the parts per billion range and applicable for light elements analysis such as oxygen. These capabilities are not possessed by other surface analytical techniques such as Auger electron spectrometry, X-ray photoelectron spectrometry, and Rutherford backscattering spectrometry.[3,4] A drawback of SIMS is the "matrix effect," which refers to a wide variation of sensitivity with different elements and with the same element in different matrices. Thus, an empirical approach must be used for accurate quantitative analysis of SIMS, for example, by calculating the relative sensitivity factor or developing calibration curves from standard samples of similar composition as the subject samples. An error of ±10 to ±20 pct is achievable with ion implantation calibration methods.[5]

Secondary ion mass spectrometry is widely used for trace element analysis in solid materials. Applications for the metallurgical system have increased; however, most of them concentrated on trace element analysis in steel or other metal systems.[6–10] The authors are not aware of any previously published work that used calibration standards for studying oxygen gradients in ferrous systems.

There have been several studies that used SIMS for analyzing oxygen in nonferrous systems. Evans[11] used ion microprobe mass spectrometry for investigating oxygen in a copper matrix. Positive ions, $^{16}O^+$ and $^{63}Cu^+$, from standard samples were analyzed and the ratios were plotted against their known oxygen concentrations to construct a calibration curve. The repeatability of the measurements was assessed by calculating the relative standard deviation (RSD), which is a ratio of standard deviation to the average value. Measurements of 20 to 25 pct RSD were obtained for samples with oxygen concentration higher than 100 ppm. Nishi *et al.*[12] also used dynamic SIMS to analyze sulfur and oxygen in copper. Plots of $^{16}O^-/^{63}Cu^-$ and $^{79}(CuO)^-/^{63}Cu^-$ *vs* oxygen concentration were developed and precisions comparable to Evans's were obtained. Takeshita *et al.*[13] conducted experiments to determine oxygen contents in titanium. Calibration curves for oxygen were developed by plotting $^{16}O^-/^{96}(Ti_2)^-$ and $^{64}(TiO)^-/^{96}(Ti_2)^-$ *vs* oxygen content. The calculated RSDs of $^{16}O^-$ and $^{64}(TiO)^-$ were 9.2 to 19 pct and 2.3 to 12 pct, respectively.

Our experiments consisted of oxygen analyses of standard reference samples and samples generated from reactions between Fe-Al droplets and $CaO\text{-}SiO_2\text{-}Al_2O_3$ slag. Metal droplets were prepared by melting iron and aluminum pieces (95.55 : 4.45 wt pct) in a small electric arc furnace in an argon atmosphere. The droplets were melted three times to ensure homogenization. The composition of the slag was chosen to be $CaO\text{-}SiO_2\text{-}Al_2O_3$ (40 pct : 40 pct : 20 pct, in weight). The correct amount of each component was weighed, mixed by ball mill, and then melted at 1500 °C in Pt crucible.

Approximately 140 g of the slag was put in a zirconia crucible. The crucible was then placed into a resistance furnace with molybdenum disilicide elements and heated to 1600 °C at a heating rate of 10 °C per minute. The crucible and the slag were held for 30 minutes after reaching 1600 °C to allow homogenization. A solid iron alloy droplet of 2.5 g containing 4.45 wt pct aluminum was then introduced into the crucible and allowed to react for certain periods of time, before the entire crucible containing the slag and the droplet was quenched. The crucibles containing the quenched slag and metal droplets were crushed and the metallic pieces were recovered. Details of the experiments, including microscopic examination, interfacial area measurements, and kinetics calculations, have been described elsewhere.[1,2]

Calibration curves were developed and then used for oxygen quantification of the reacted samples. Five standard reference samples were prepared by implanting $^{16}(O)^-$ ions onto the surface of Fe-Al-Si alloys, prepared using the same technique used for the reacting droplets. The fluences used were $8 \cdot 10^{14}$, $2 \cdot 10^{15}$, $6 \cdot 10^{15}$, $8 \cdot 10^{15}$, and $1.2 \cdot 10^{16}$ ions/cm^2, which correspond to oxygen concentrations of 16, 40, 120, 160, and 240 ppm, respectively. Ion implantations were carried out by using a General Ionex 1.7 MV tandem

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Table I. Instrument Parameters of Cameca IMS-3f for the Analysis

Primary Sputtering		Analysis	
Beam	Cs	polarity	negative
Polarity	positive	accelerating voltage	4500 V
Accelerating voltage	10 kV	transfer optics	25 μm (imaged field)
Primary beam raster	50×50 μm	contrast aperture	4 (largest)
Beam current	200 nA	field aperture	2 (10 μm diameter)
		energy window	130 eV
		offset voltage	200 V, 0 V on ^{72}FeO

accelerator (Amersfoorst, The Netherlands). Energy of 8.5 MeV was used for the ion implantation, which was enough to place the implants 2 μm below the surface. The error associated with oxygen content of the implantations was expected to be ±5 pct.

A Cameca (Paris, France) IMS-3f dynamic SIMS with a magnetic sector analyzer was used for investigating the standard reference samples and samples generated from reactions between Fe-Al droplets and $CaO-SiO_2-Al_2O_3$ slag. A cesium beam was used as the primary beam for the analysis. Sputtering of the sample was carried out in a 50×50 μm area and the analysis was carried out in a circle of 10-μm diameter. Details of the instrument parameters are shown in Table I. A Tencor P-10 surface profiler (San Jose, CA) was used to measure the depth of the craters created after the analyses. The error associated with the depth measurement was also expected to be ±5 pct.

Oxygen in the standard reference samples was investigated by analyzing the $^{16}(O)^-$, $^{72}(FeO)^-$, as well as the matrix $^{56}Fe^-$ ion spectra. The measured $^{16}(O)^-$ and $^{72}(FeO)^-$ intensities were then normalized to the matrix intensity. The variations of the normalized $^{16}(O)^-$ and $^{72}(FeO)^-$ intensities to the oxygen contents were developed and are shown in Figures 1(a) and (b). The normalized intensities of the ions of interest increased linearly as the oxygen content increases. The average RSD values were found to be 22 pct for $^{16}O^-/^{56}Fe^-$ and 25 pct for $^{72}(FeO)^-/^{56}Fe^-$. These values are in the range of typical values obtained by Evans,[11] as previously described. Other researchers[14] discovered that typical precision of measurements of impurities (other than oxygen) in NIST steel standards are 7.9 pct to 20.5 pct. Thus, in general, measurements with RSD up to 25 pct are satisfactory for oxygen quantification. It has been suggested[14] that large surface irregularity and complexity of the crater geometry after sputtering lowers measurement repeatability in steel samples.

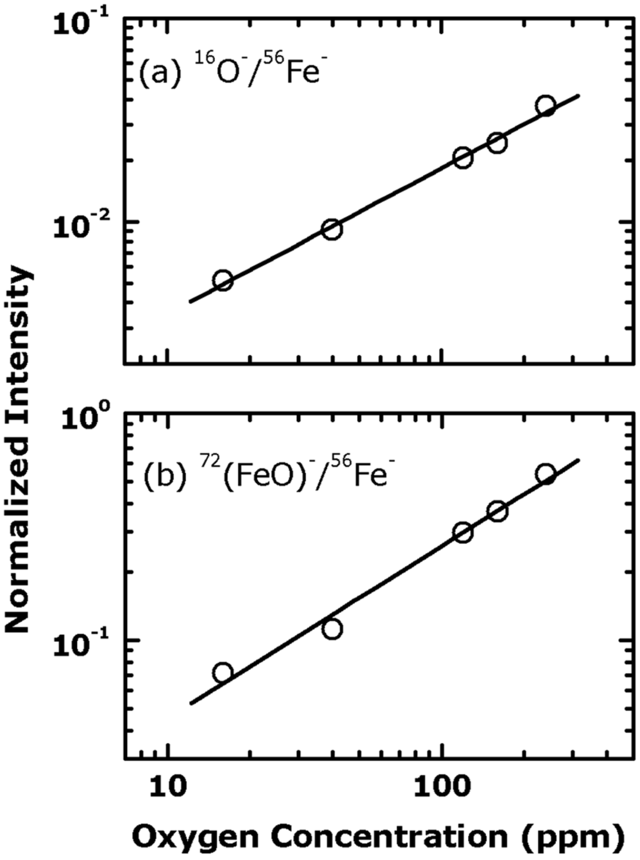

Fig. 1—Relationship between normalized ion intensity and oxygen concentration of standard reference samples prepared by oxygen ion implantation: (*a*) $^{16}O^-/^{56}Fe^-$ and (*b*) $^{72}(FeO)^-/^{56}Fe^-$.

To investigate oxygen distribution in metal-slag reactions, characterization was carried out on several samples that represent the sequence of reaction time of Fe-Al droplets with $CaO-SiO_2-Al_2O_3$ slag. The SIMS quantification for the system was conducted by calculating the relative sensitivity factor from the standard reference samples. Depth profile analyses were performed on several points on each sample, *i.e.,* along the top and bottom edges as well as on the center of the droplet cross section. "Top" and "bottom" in this context refer to the side of the sample that was in direct contact with the slag during reaction and the side that was originally in contact with the base wall of the crucible.

Oxygen concentration variations across the sample were observed on all the samples. The oxygen concentration gradients observed in the first few microns were consistent with the formation of oxide on the cross section and its diffusion toward the bulk. There were more variations of oxygen compared to the other elements, *i.e.,* Al and Si. The variations of the oxygen profile of the sample at the beginning of the reaction, *i.e.,* 5 minutes, after the reaction commenced are shown in Figure 2. The numbers next to the profile refer to the point at which the analysis was carried out. Differences in oxygen concentration were observed along the edge of the sample, *i.e.,* points 1 and 2 along the bottom and points 4 and 5 along the top. The concentration of oxygen at the center was higher than those at the edges. This was surprising because one would expect the opposite profile with high concentration near the interface and low in the center. However, this may indicate movement of pockets of oxygen-rich fluid from the interface toward the bulk induced by surface tension driven flow (Marangoni effect). For instance, if there was nonuniform mass transfer of oxygen

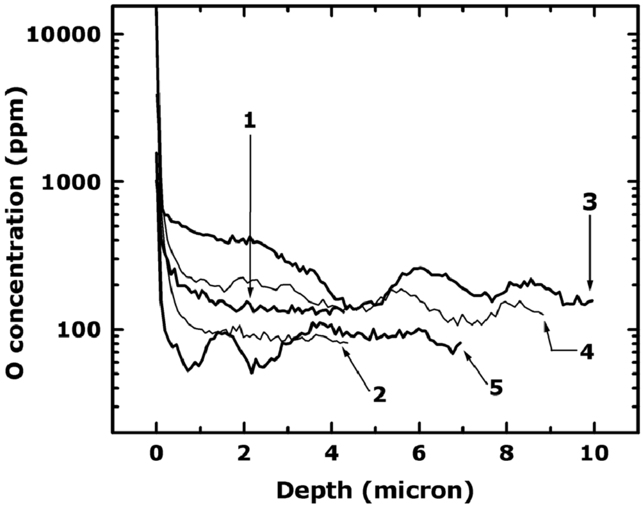

Fig. 2—Oxygen concentration profiles at 5 min of reaction: (1) and (2) bottom, (4) and (5) top, and (3) center of the sample.

from the slag to the metal due to either the wall effect[2] or a disturbance at the interface, an oxygen concentration difference would be created along the interface. A steep difference of oxygen concentration along the interface would result in a difference in interfacial tension, which would produce a flow along the interface. Further, this flow would bring pockets of fluid with less oxygen content from the bulk to the interface and *vice versa,* would bring pockets of fluid with high oxygen content from the interface to the bulk, and would alter the original oxygen profile. This is similar to the disordered interfacial convection model described by Sawitowski.[15] Therefore, the opposite trend of oxygen concentration that was observed is possible.

Variations of oxygen concentration with depth were also observed. The fluctuations with oxygen concentration difference up to 250 ppm were found at a scale of 1 to 2 μm. This may also suggest the presence of pockets of fluid of different oxygen concentrations in motion during the reaction. The profiles at the bottom of the sample were relatively flat compared to those at the top. This was consistent with the hypothesis that the reaction at the bottom part was delayed because at the very beginning it was not in direct contact with the slag.

Figure 3 shows the oxygen concentration profiles for the sample at 30 minutes of reaction. As the reaction nears completion and the transfer of oxygen slows, relatively flat profiles were obtained. However, increases of oxygen concentration of 50 and 150 ppm were observed at the top and the center of the sample, *i.e.,* depicted in spectra 1 and 2. It was also found that the Al and FeO spectra in these two areas followed the same trend as the oxygen at that depth. This strongly suggests that the increases were caused by an inclusion, for example, entrapped slag inside the metal droplet, as reported by other researchers.[16]

In general, the dynamic SIMS technique has been found to be useful for investigating oxygen concentration gradients in iron samples. The results presented are unique and suggest that oxygen behavior during reaction between metal and slag is more complex than that described by conventional mass transfer theory, such as the two-film model and the boundary diffusion layer model. The detection of "pockets" of oxygen-rich iron below the reaction interface is qualitatively consistent with the surface renewal model of mass transfer, and these observations are worthy of further research.

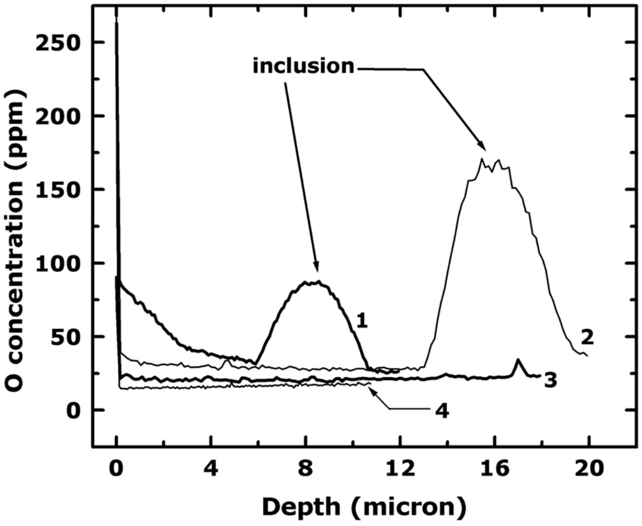

Fig. 3—Oxygen concentration profiles of the 30-min sample; the number next to the spectrum refers to the point at which the analysis was completed, *i.e.,* (1) top, (2) center, (3) bottom, and (4) right edge of the sample.

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