RAPID SENSORS FOR FERROALLOY PRODUCTION AND PROCESSING

M. Iwase[1], A. McLean[2], K. Katogi[3] and K. Wakimoto[4]

[1]Ferrous Metallurgy Research Group, Department of Energy Science and Technology, Kyoto University.
E-mail: iwase@namihei.mtl.kyoto-u.ac.jp
[2]Department of Materials Science and Engineering, University of Toronto, Toronto, Canada, and
Department of Energy Science and Technology, Kyoto University, Kyoto 606-8501, Japan.
[3]Heraeus Electro-Nite Japan, Ltd., Osaka Japan.
[4]Environmental Solution Center, JFE-Holdings, Tokyo, Japan.

ABSTRACT

For many decades control strategies have been based upon samples taken from liquid steel, molten slag and gas phase as well as from solid products. Because of recent developments in the areas of dynamic control models, artificial intelligence and expert systems, there is an increasing incentive to develop diagnostic sensors, which permit in-situ rapid determinations of concentrations of various elements in molten steel. In this paper, an overview is given on recent developments in the areas of sensors for use in ferroalloy and steel production. Particular emphasis will be given on (i) innovative application of sensors for on-line determinations of dissolved elements, Si, P, N, H and Cr in molten iron and ferroalloys, (ii) evaluation of inclusions in liquid metal and (iii) rapid determinations of slag compositions.

1. INTRODUCTION

As we move into this century, there is an increasing need for new process control strategies in order to achieve consistent quality products with maximum yield, optimum cost and minimum impact on the environment. Successful new strategies are most likely to evolve from a knowledge-based foundation of measurements, models and a solid understanding of the fundamental aspects of the manufacturing process.

In our efforts to characterize and improve the performance of an existing process, or in our quest to generate useful knowledge as a basis for the development of new manufacturing routes, measurements and models should be considered as two interdependent requirements. Without measurements, our models are incomplete and unsatisfactory. Without models, we fail to realize, or perhaps even comprehend, the potential significance of our measurements. Sometimes in our enthusiasm, we construct sophisticated, elegant models and forget the reality of the actual manufacturing process. In this computer age, we need to remember again the importance of observations and accurate measurements. In addition, as engineers and applied scientists we have an obligation and a responsibility to facilitate the transfer of new knowledge into the realm of operating practice. In this paper, an overview will be given on recent development of sensors that permit in-situ determinations of various elements in molten iron, which could have potential application for ferroalloy production.

2. ON-LINE DETERMINATIONS OF DISSOLVED ELEMENTS

2.1 Silicon Sensor

Ferrochromium is classified into grades by carbon contents, with some selling premium normally being associated with higher chromium/carbon ratio. The cheaper grades, charge chrome and high-carbon ferrochromium (collectively designated as HC-FeCr here), typically contain 4 to 9 wt% C, 50 to 70 wt% Cr and less than 6 wt% Si. More expensive medium-carbon ferrochromium (MC-FeCr) contains 1.0 to 2.0 wt% C, and less than 1 wt% Si.

Proceedings: Tenth International Ferroalloys Congress;
INFACON X: '*Transformation through Technology*'
ISBN: 0-9584663-5-1

1 – 4 February 2004
Cape Town, South Africa
Produced by: Document Transformation Technologies

The production of MC-FeCr can be either by the "Perrin type" silicothermic reduction/lime-ore melt refining or, more typically, *via* an oxygen refining. The latter involves distinct decarburisation and reduction/refining stages, Figure 1. HC-FeCr, tapped from a conventional submerged arc furnace, is first charged to a converter vessel containing Cr_2O_3-rich slag, produced during the previous decarburisation blow. This initiates the reduction/refining stage, with the slag Cr_2O_3 content, $(\%\ Cr_2O_3)_{slag}$, being reduced simultaneously with refining of the alloy silicon content, according to the basic reaction:

$$2\ Cr_2O_3(\text{in slag}) + 3\ Si(\text{in HC-FeCr}) = 4\ Cr(\text{in HC-FeCr}) + 3\ SiO_2\ (\text{in slag}) \qquad (1)$$

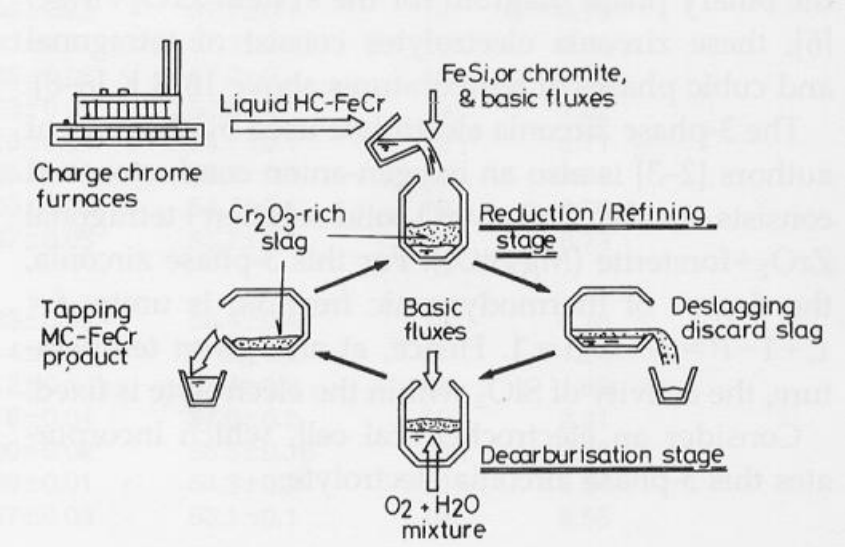

Figure 1. Schematic diagram showing the production route for medium carbon ferrochromium [1].

The resulting slag, stripped of Cr_2O_3, is then carefully tapped out of the converter. The "slag free" alloy remaining in the converter is then decarburised with a gas mixture of oxygen and steam (or other inert gas). Some oxidation of chromium is inevitable during this decarburisation stage, resulting in a Cr_2O_3-rich slag. The MC-FeCr alloys are tapped when the desired carbon endpoint is achieved, and fresh HC-FeCr is charged to the residual Cr_2O_3-rich slag to commence the next production cycle.

A critical process control parameter is the knowledge of the $(\%\ Cr_2O_3)_{slag}$ to $[\%Si]_{alloy}$ ratio at the start of each reduction/refining cycle. It establishes the need for charging either chromite ore to refine excess silicon from the alloy, or ferrosilicon to reduce excess Cr_2O_3 in the slag. A condition of excess slag Cr_2O_3 content is undesirable in terms of loss of expensive chromium units. The alternative condition of excess alloy silicon content leads to unsatisfactory performance in the subsequent decarburisation stage, producing a highly acidic slag that is particularly aggressive to the basic converter lining.

The silicon content of the incoming HC-FeCr can vary considerably (especially if multiple furnaces are used for supply), and it strongly influences reliable calculation of $(\%Cr_2O_3)_{slag}$ following the decarburisation period. There is a strong incentive, therefore, to measure rapidly the silicon content of the incoming HC-FeCr, to determine appropriate reduction, or refining reagent requirements, and associated basic fluxing additions [1]. Additionally, a strong incentive also exists to measure rapidly the alloy silicon content following the reduction/refining stage, to ensure that the resulting alloy silicon content is sufficiently low to safely proceed to the decarburisation stage.

Electrochemical sensor incorporating three-phase zirconia electrolyte can be applied for rapid determinations of silicon levels in high-carbon ferrochromium [1,2]. The three-phase zirconia electrolyte is an oxygen-anion conductor, and consists of cubic ZrO_2-MgO solid solution + tetragonal ZrO_2 + forsterite (Mg_2SiO_4). For this three-phase zirconia, the degree of thermodynamic freedom, F, is unity; $F = C + 1\text{-}P = 3 + 1\text{-}3 = 1$, where C and P are the numbers of component and phases, respectively. Hence, at any given temperature, the activity of SiO_2 within the electrolyte is fixed.

Consider an electrochemical cell, which incorporates this three-phase zirconia electrolyte:

$$Mo + MoO_2 \text{ / three-phase zirconia electrolyte / Si (in ferrochromium)}$$

When the electrolyte is in contact with molten ferrochromium containing silicon, one can anticipate the following equilibrium at an interface between the electrolyte and the molten ferrochromium:

$$Si(\text{in ferrochromium}) + O_2 = SiO_2(\text{in electrolyte}) \quad (2)$$

$$\log K(2) = -\log h_{Si} - \log P_{O_2} + \log a_{SiO_2} \quad (3)$$

where h_{Si} is the Henrian activity of silicon in molten ferrochromium referred to 1 wt pct solution in pure iron, and a_{SiO_2} is the activity of SiO_2 in the three-phase zirconia electrolyte referred to pure solid SiO_2. Hence, from equation (3), it is evident that a measurement of oxygen partial pressure, P_{O_2} , permits the Henrian activity of silicon, h_{Si}, to be determined.

A schematic diagram of the electrochemical half-cell, Mo / Mo + MoO_2 / three-phase zirconia electrolyte, is given in Figure 2, while Figure 3 shows the relation between silicon content in ferrochromium as determined by emf sensors, $[\%Si]_{emf}$, and those by chemical analysis, $[\%Si]_{analysis}$.

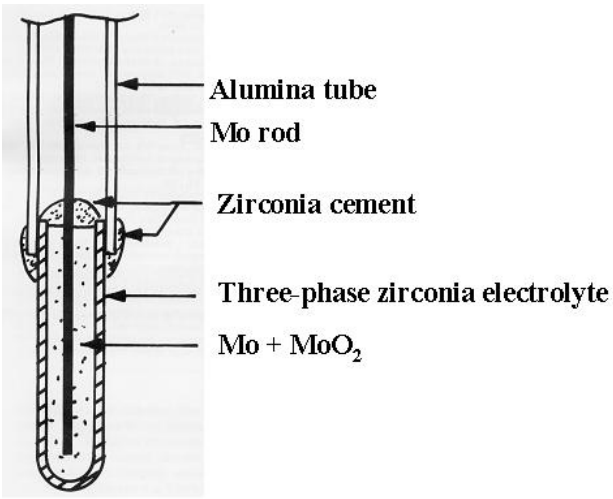

Figure 2. Electrochemical sensor incorporating a three-phase zirconia electrolyte for silicon determinations.

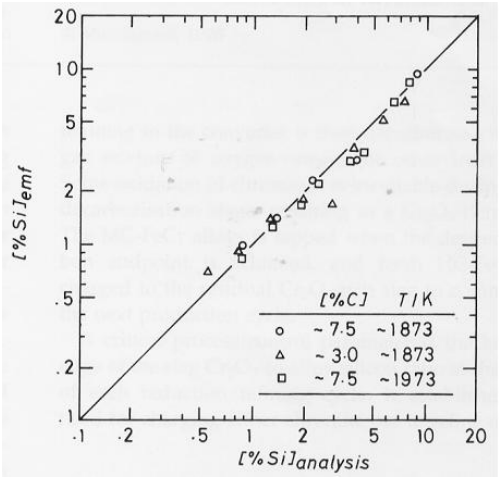

Figure 3. Relation between the silicon content of FeCr determined by an electrochemical sensor, $[\%Si]_{emf}$, and those by chemical analysis, $[\%Si]_{analysis}$ [2].

2.2 Chromium Sensor

In the production of stainless steel, close control of chromium levels in molten steel is of critical importance from the standpoint of better chromium recovery, metal yields, alloy additions, deoxidation and final product quality. For better control of chromium levels, electrochemical chromium sensor would be of great help. An alternative design for an electrochemical sensor is to use a conventional zirconia electrolyte in conjunction with the appropriate auxiliary electrode. The electrochemical sensor (3), shown in Figure 4, can be expressed as: Mo / Mo + MoO_2 / ZrO_2(MgO) / Cr_2O_3 + CaO + SiO_2 / Cr(in Fe-Cr alloy)/Mo

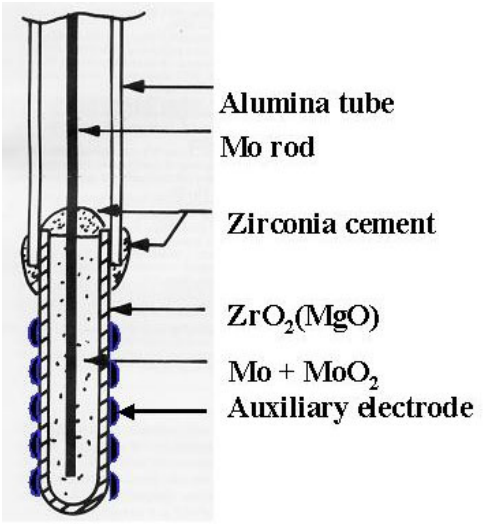

Figure 4. Electrochemical sensor incorporating an auxiliary electrode for rapid determinations of chromium and phosphorus.

The chromium sensor involves a mixture of Cr_2O_3 + CaO + SiO_2 as auxiliary electrode. Following the available phase diagram [3] for the system CaO + SiO_2 + Cr_2O_3, the composition of the mixture would lie in a two-phase region of solid <Cr_2O_3> + liquid {CaO + SiO_2 + Cr_2O_3} slag at 1873 K, corresponding to unit activity of Cr_2O_3 at the experimental temperature. Figure 5 shows the relation between emf and chromium concentration. Results of in-plant tests conducted at AOD vessels are given in Figure 6, which compares the chromium concentration as measured by the chromium sensor, $[\%Cr]_{emf}$, with those determined by chemical analysis, $[\%Cr]_{analysis}$.

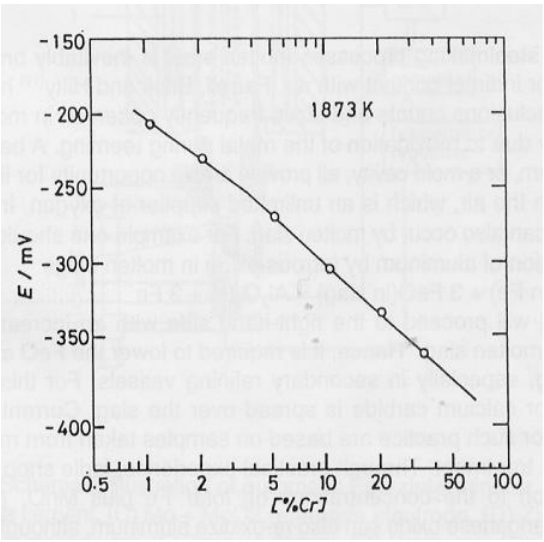

Figure 5. Measured cell potentials with a chromium sensor as the function of chromium content.

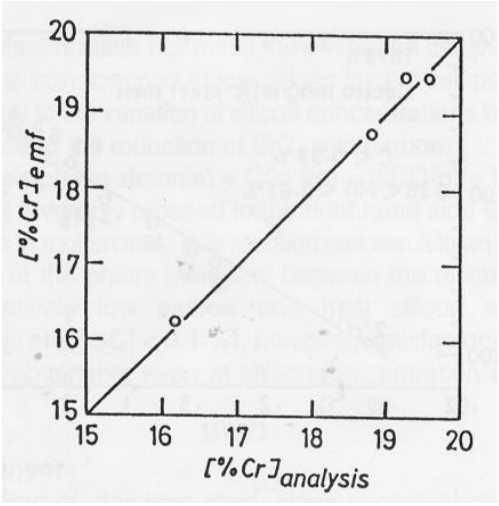

Figure 6. Relation between chromium content determined by sensor, $[\%Cr]_{emf}$ and those by chemical analysis, $[\%Cr]_{analysis}$. (Unpublished work of the authors)

2.3 Phosphorus Sensor

Many of the ores used for blast furnace ironmaking and ferroalloy production contain appreciable amounts of phosphorus. During reduction within the furnaces, substantially all the phosphorus is transferred from the slag phase to the liquid ferroalloy. For close control of phosphorus, an electrochemical sensor incorporating auxiliary electrode has been developed by the present authors [4].

$$Mo / Mo + MoO_2 / ZrO_2(MgO) / Al_2O_3 + AlPO_4 / P \text{ (in Fe- C- P alloy) / Fe}$$

Figure 7 shows the relation between cell potentials and phosphorus concentration in molten Fe-C-P alloys at 1673 K.

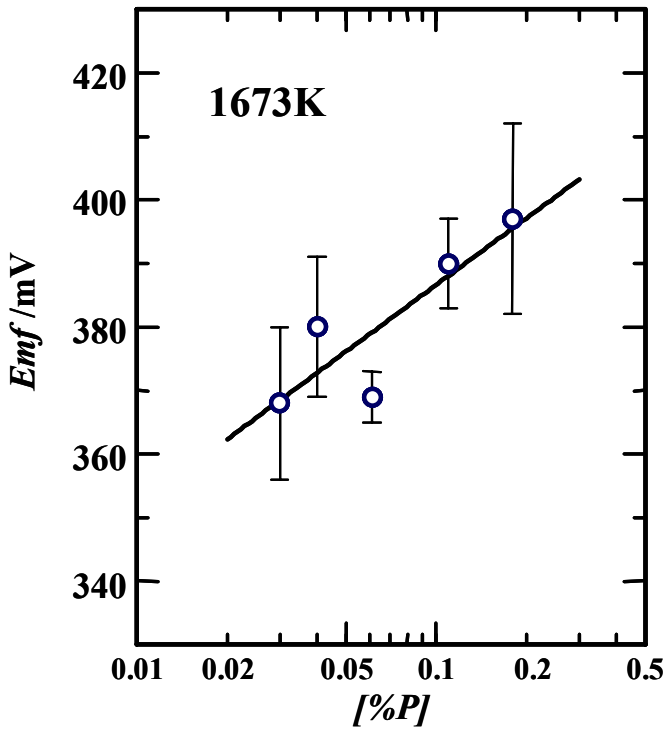

Figure 7. Measured cell potentials obtained with a phosphorus sensor, as a function of phosphorus content. (Unpublished work of the authors).

2.4 Hydrogen and Nitrogen Sensors

It is known that the concentrations of gaseous elements, such as oxygen, nitrogen, hydrogen and sulfur, are related to partial pressures of diatomic gases through Sievert's law. Chemical analysis of hydrogen in molten steel requires special precautions because of the high capability of atomic hydrogen to escape from even solidified steel. Upon being taken from molten bath, hence, the sample has to be immediately quenched in water and transferred to dry ice storage for transporting to an analytical lab. A hydrogen sensor based upon Sievert's law in combination with thermal conductivity measurements has been developed by Plessers et al [5]. Figure 8 illustrates schematically such a sensor for hydrogen. The system consists of a porous bell to be immersed within steel bath, pneumatic cable and thermal conductivity measuring unit. Upon immersing the probe into molten steel, nitrogen is first introduced to the system to be injected into molten steel, and collected in the porous ceramic bell. Hydrogen in molten steel diffuses into the carrier gas and is collected in the bell. The 4-way valve then directs the nitrogen gas to closed gas circuit to be recycled, until equilibrium is attained between diatomic and monatomic hydrogen in the gas phase and molten steel, respectively. The partial pressures of hydrogen within the closed circuit are determined *via* thermal conductivity measurements, and converted to concentrations of hydrogen in molten steel by Sievert's law.

$$(1/2)\ H_2(g) = H(\%, \text{in Fe}) \tag{4}$$

$$K(4) = [\%H] / P_{H_2}^{1/2} \tag{5}$$

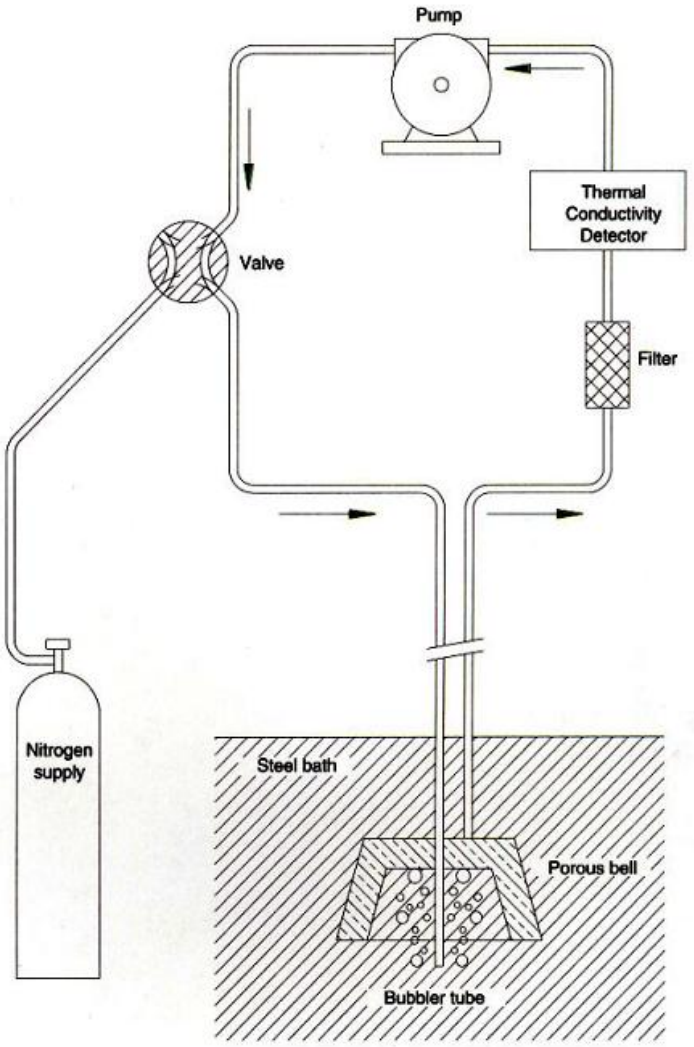

Figure 8. Gas circulation system for the hydrogen sensor.

The measuring system for the hydrogen sensor can also be applied to direct measurement of nitrogen and carbon with slight modifications [6,7]. Figure 9 shows such a modified system for nitrogen, while Figure 10 illustrates the relation between nitrogen content (ppm) as determined by the sensor and those by chemical analysis.

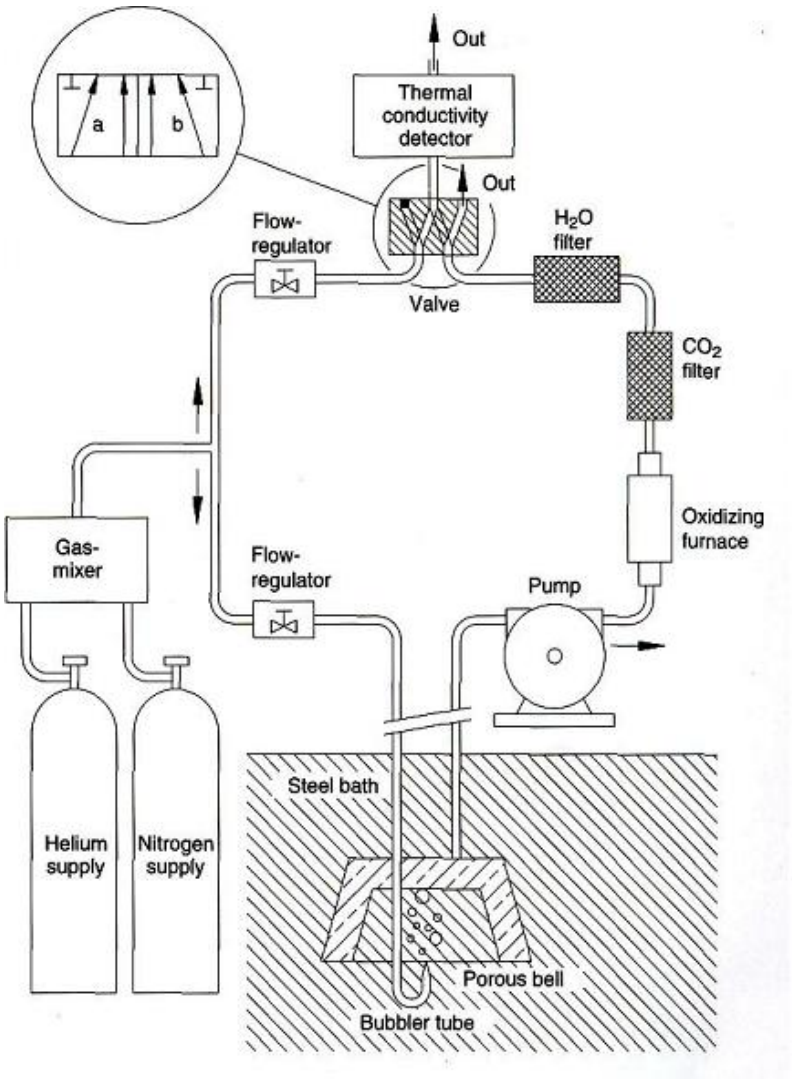

Figure 9. Gas circulation system for the nitrogen sensor.

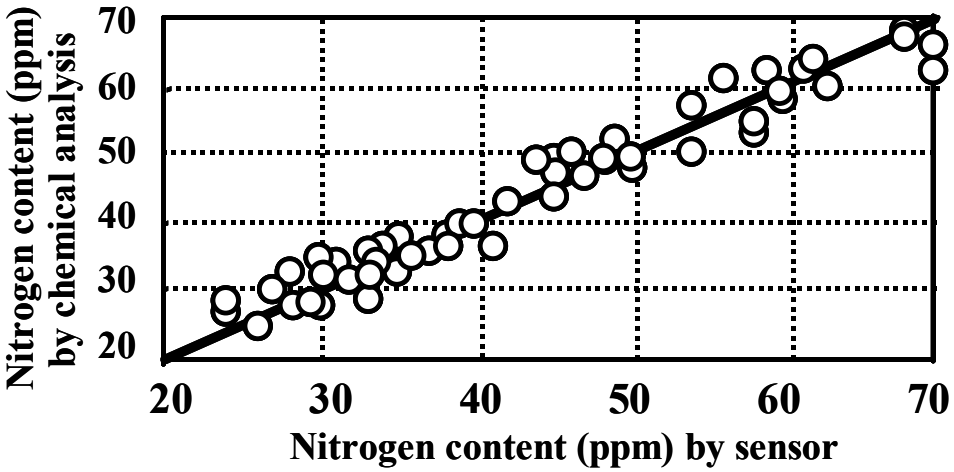

Figure 10. Relation between the nitrogen content determined by sensor and those by chemical analysis, $[\%Ni]_{analysis}$.

3 INCLUSION SENSOR

Inclusion sensor employs the electric sensing zone technique to provide a direct measure of the density of non-conductive particles in suspension in liquid metal, and performs real-time analysis of the volumetric distribution of these inclusions. A closed tube made of non-conductive material, such as glass or ceramic, and having a small orifice through its surface is immersed in the melt. The liquid metal is sucked through this orifice, where it is carried by incoming liquid metal, since this is the only electrically conducting path between the electrode. The voltage drop across the orifice is monitored, and when metal of constant electrical conductivity is passing, it remains constant. When a dielectric particle such as a non-metallic inclusion passes through the orifice, the conductivity is momentarily reduced, resulting in a sight increase in the voltage drop, the amplitude of the perturbation being a function of the particle size. This is illustrated in Figure 11. The instrument is equipped with signal and data processing electronics that can infer the density of particles in the melt from the frequency of the voltage fluctuations and the volumetric distribution of these particles from the distribution of the amplitudes of the same fluctuations.

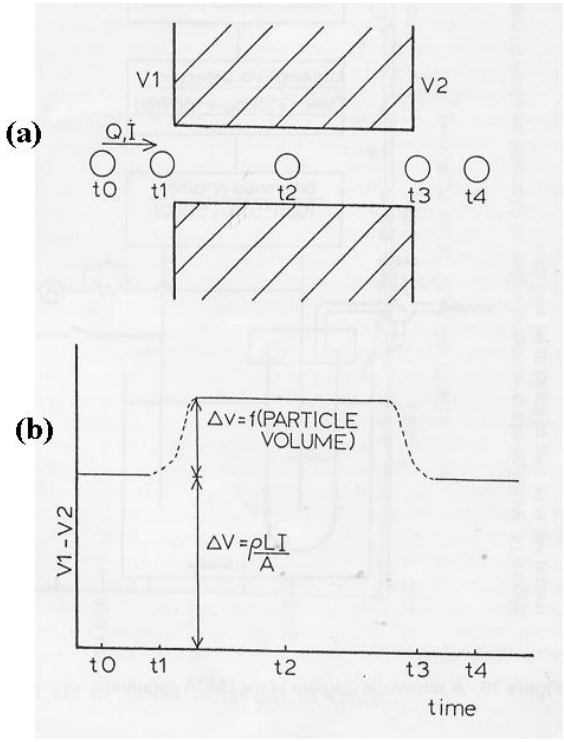

Figure 11. The resistive pulse principle of particle size measurements. During its passage, the particle changes the resistance of the orifice. In the presence of an applied current, a voltage change is produced which can be related to the volume of the particle.

This sensor gives an index of cleanliness, expressed in thousands of particles per kilogram melt. Once the tube is partly filed with metal, a positive pressure is applied inside the tube to expel the melt, so that the cycle can be repeated to provide continuous direct monitoring of the melt cleanliness throughout a cast, with a cycle time of about one minute.

This technique has been widely applied to the monitoring of liquid aluminum. Its ability to provide quantitative on-line measurements at frequent intervals is illustrated in Figure 12, which shows the effect of sudden increases in metal flow rate through a filter caused by two deliberate increases in the metallostatic head at cast length of 1900 and 3300 mm respectively. Normally, such measurements are made in the launder at some point between the holding furnace and the casting pit or machine. The technique has also been applied to molten alloys of magnesium [8] in copper-based metals [9] and in liquid steel [10]. A new generation inclusion sensor based on Digital Signal Processing technology has now been developed, which provides a more flexible environment for the analysis of the different type of signals monitored and hence opens up the possibility of inclusion type discriminations. Figure 13 shows the distribution of non-metallic inclusions in liquid steel thus determined.

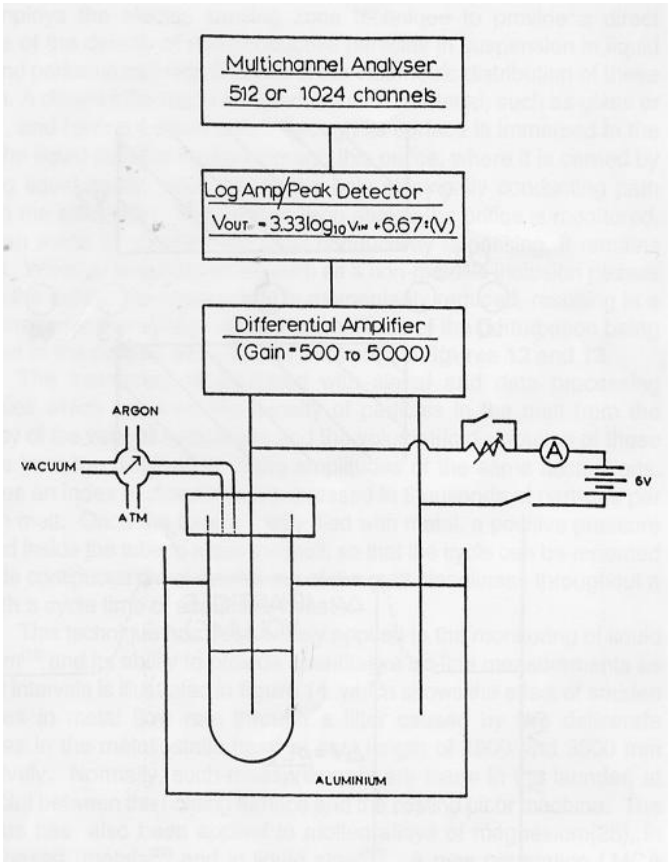

Figure 12. A schematic diagram of the inclusion sensor.

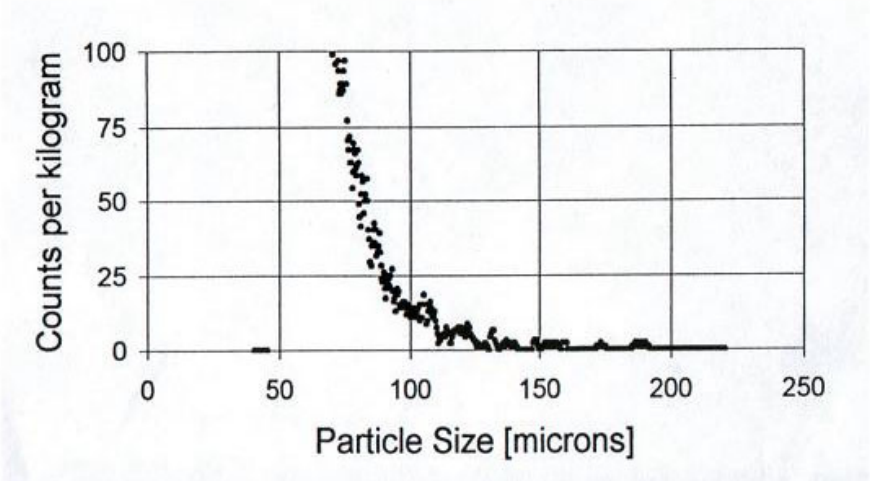

Figure 13. Particle size distributions as determined by the inclusion sensor [7].

4. SENSORS FOR SLAG CONTROL

To a large extent, oxygen control in ferroalloy production and steelmaking is affected by the composition and properties of the slag phase. Without oxygen control, the behavior of the other elements cannot be managed. Steelmaking slag systems involve at least eight important components: CaO, MgO, MnO, FeO, SiO_2, Al_2O_3, P_2O_5, CaF_2, and often a number of others such as Na_2O, TiO_2 and Cr_2O_3. One of the greatest obstacles to the application of physical chemistry principles to the elucidation of slag-metal and slag-gas reactions is a lack of knowledge of activities of the reacting species. Since iron oxide in slag participates in numerous reactions between metal, slag and gas phases, and important steelmaking reactions such as desulfurization and dephosphorization are related to the ferrous oxide activity, the evaluation of the activity of this component is particularly important.

In view of the industrial significance of ferrous oxide activity, numerous experimental determinations have been conducted by many laboratories during the past five decades. Nevertheless our knowledge of the activity of FeO in multi-component industrial slags is still far from satisfactory. The conventional experimental technique for determination of ferrous oxide activity consists of equilibrating molten slags with liquid iron. Chemical analysis for oxygen made on samples taken from liquid iron yields values of ferrous oxide activities. Alternatively, molten slags contained in an iron crucible are brought into equilibrium under a stream of CO-CO_2 or H_2-H_2O. These techniques however, require a relatively complex experimental setup and long duration.

Ogura et al. have developed a “shop floor” activity determinator for ferrous oxide based on the principles of zirconia sensors [11]. This equipment makes use of samples taken from the slag phase. However, knowledge of the sample weight is not required, and activity measurements can be completed within five minutes. This electrochemical technique based on magnesia-stabilized zirconia permits rapid determination of ferrous oxide activity within homogeneous and heterogeneous slag systems.

This research led to the manufacture of an analytical instrument for the determination of FeO activities. A schematic diagram of the automatic activity determinator is shown in Figure 14. For operating this system, a solid state sensor F is attached to the elevator mechanism E and an iron crucible K is placed on the steel pedestal O. The electrical contact to the outer electrode of the zirconia cell is made via this pedestal. Pure silver M is pre-melted within the iron crucible. A sample of slag L, 1 to 3 g, is placed in the iron crucible. The iron crucible is moved upward, via an elevator mechanism P, into a transparent silica reaction tube H. The furnace is subsequently heated to a temperature of 1750 K under a stream of argon within 2.5 minutes in accordance with a computer program. The electrochemical cell is lowered until it contacts both the molten silver and the slag. Open-circuit cell voltages generated are monitored on the LCD of the micro-computer. The cell potential is then converted to the FeO activity and displayed on the LCD. In this way, a single activity measurement is completed within five minutes. This determinator, which is now used by several steel companies in different parts of the world, has permitted new control strategies.

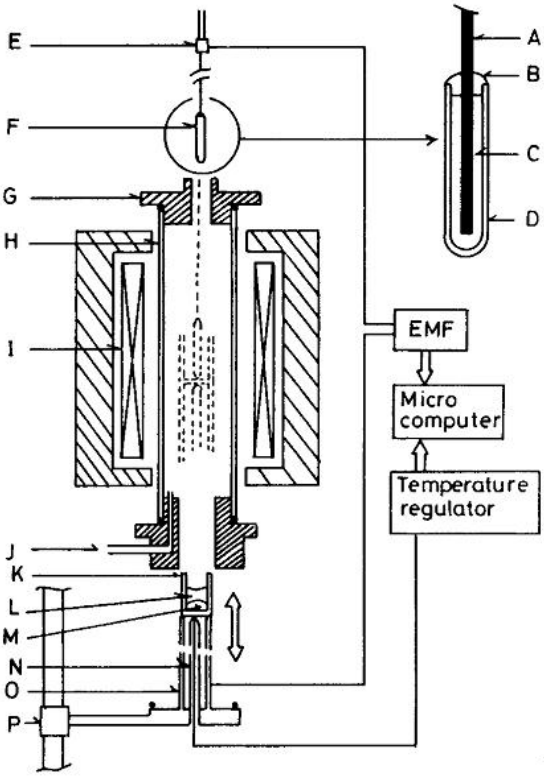

Figure 14. Schematic illustration of automatic activity determinator.

A, Mo rod; B, Zirconia cement; C, Mo + MoO_2 reference electrode; D, Zirconia tube; E, Elevator mechanism; F, Zirconia cell; G, Water-cooled bass flange; H, Transparent silica tube; I, Tungsten filament; J, Ar inlet; K, Iron crucible; L, Slag sample; M, Silver; N, Pt-PtRh13 Thermocouple; O, Stainless steel pedestal; P, Elevator mechanism.

In the production of stainless steel, removal of carbon from Fe + Cr alloys has to be made *via* selective oxidation of carbon:

$$C(\text{in metal}) + (1/2)\ O_2(g) = CO(g) \tag{6}$$

During such decarburisation reactions, oxidation of chromium would inevitably take place:

$$2\ Cr(\text{in metal}) + (3/2)O_2(g) = Cr_2O_3(\text{in slag}) \tag{7}$$

It is necessary, hence, to recover chromium through slag-reduction practice. Ferrosilicon or ferrochromium-silicon is commonly used for this purpose. Reduction of chromium oxide can be expressed as:

$$Cr_2O_3(\text{in slag}) = 2Cr(\text{in metal}) + (3/2)O_2(g) \tag{8}$$

The oxygen potential prevailing in reaction (6) can often be expressed as,

$$Fe + (1/2)O_2(g) = FeO(\text{in slag}) \tag{9}$$

By combining equations (8) and (9), it follows that:

$$Cr_2O_3(\text{in slag}) + 3\ Fe = 2\ Cr(\text{in metal}) + 3\ FeO(\text{in slag}) \tag{10}$$

In conforming to reaction (10), in laboratory studies by Pathy and Ward [12], a linear relation was found between the ratio of chromium in slag, *(%Cr)*, to that in metal, *[%Cr]*, and the concentration of FeO in the slags, *(%FeO)*. The proportionality constant varied between 0.5 at 1900 K and 0.3 at 1960 K. By averaging data from BOP and electric furnace heats, Aukurst et al. [13] obtained a value of 0.25, while Aukurst and Bishop [14] suggested the following equation for commercial heats:

$$(\%Cr) / [\%Cr] = 0.3\ (\%FeO) \tag{11}$$

A precise expression for the partition of chromium, however, should arise from the equilibrium constant of reaction (10);

$$K(11) = a_{FeO}^3\ a_{Cr}^2 / a_{Fe}^3\ f_{Cr_2O_3}\ (\%Cr_2O_3) \tag{12}$$

where a_{FeO}, a_{Cr} and a_{Fe} are the activities of FeO in slag, Cr in metal and Fe, respectively, and $f_{Cr_2O_3}$ and $(\%Cr_2O_3)$ are the activity coefficient and concentration of Cr_2O_3 in slag, respectively. It follows that

$$\log (\%Cr_2O_3) = 3 \log a_{FeO} + 1\log [a_{Cr}^2 / a_{Fe}^3\ f_{Cr_2O_3}\ K(11)] \tag{13}$$

Let us consider a series of production heats for a fixed stainless steel specification (fixed chromium contents); the activities of Cr and Fe, a_{Cr} and a_{Fe}, respectively, would be fairly constant. In addition, the activity coefficient of Cr_2O_3, $f_{Cr_2O_3}$, would not differ from one heat to another. With respect to this, reference should be made to a paper by McCoy and Langenberg [15]. These authors showed that the solubilities of Cr_2O_3 in stainless steelmaking slags are fairly insensitive to the variation of slag basicity, $\{(\%CaO) + (\%MgO)\}/(\%SiO_2)$. In summary, it can be anticipated that the second term of the right-hand side of equation (13) would be kept constant, so far as production heats of a fixed stainless steel specification are concerned. It follows, hence, that

$$\log (\%Cr_2O_3) = 3\ 1\log a_{FeO} + \text{constant} \tag{14}$$

In order to test the validity of equation (14), slag samples were taken from VOD vessels at various stages of slag-reduction practice, and submitted to activity determinations for FeO and chemical analysis for Cr_2O_3. The Cr concentrations in metal through the commercial heats were approximately l6 %. Figure 15 shows the logarithmic plot of a_{FeO} as determined by the automatic activity determinator against $(\%Cr_2O_3)$.

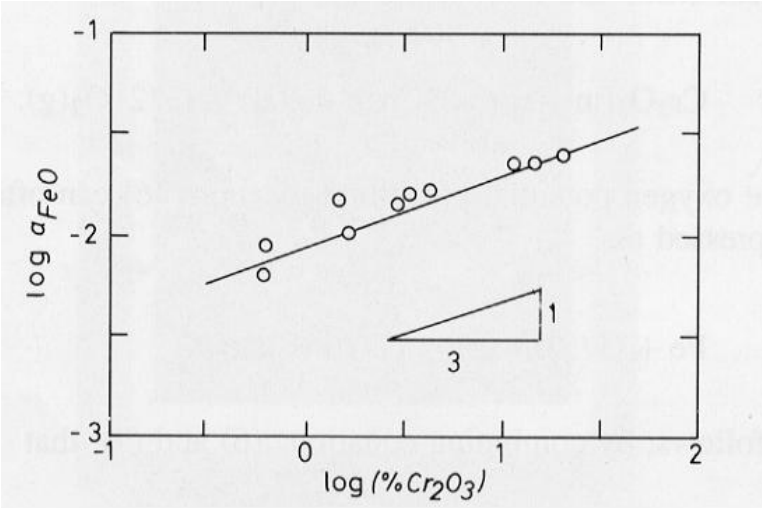

Figure 15. Relation between the chromium content in stainless steelmaking slag and the ferrous oxide activity as determined by the activity determinator.

Based upon ferrous oxide activity determinator, on-site rapid FeO sensor has been designed, while Figure 16 shows in-plant results of such on-site FeO sensors; the relation between measured emf and FeO concentrations, *(%FeO)*, as determined through chemical analysis.

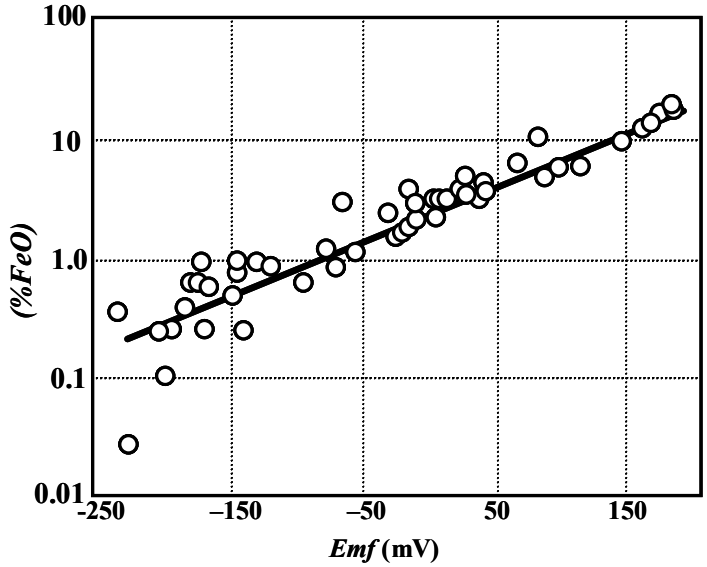

Figure 16. Relation between ferrous content in slag and measured cell potential by FeO sensor.

5. CONCLUSION

It must be emphasized that considerable research together with in-plant evaluation is required in order to transform a fundamental scientific concept into a reliable sensing device, which can be used as an integral component of a process control system. Three decades of combined efforts of researchers, instrument manufacturers and steel plant operators on several continents were required to bring electrochemical oxygen sensor from the laboratory to established technology within the steel plant. For truly effective technology transfer in the field of sensor development it is essential that basic studies be conducted in close cooperation with instrument manufacturers and the user community. With this three-partite interaction, there is excellent opportunity for linkages between people within the research, development and utilization communities. Successful implementation of a new Sensor can have a direct impact on conventional processes and also provide the essential knowledge required for the modelling and control of new processes for this century. Activities of this type are a critical link in the chain of quality and mandatory requirement for intelligent processing.

6. REFERENCES

[1] K. Gomyo, L. R. Nelson, Y. Shin-ya, A. McLean and M. Iwase, *Scandinavian Journal of Metallurgy*, Vol.25, 1996, pp.193-198.
[2] *Phase Equilibrium Diagram Data Base, Ver.2 for Windows 95*. American Ceramic Society
[3] T. Otoshige, H. Kosaka, K. Katogi, M. Hasegawa and M. Iwase, *Current Advances in Materials and Processing*, vol. 16, 2003, p. 195.
[4] J. Plessers, P. Wokkants, E. Vangelooven and J. R. Ross, *Stahl und Eisen*, Vol.10B, 1988, pp.451-459.
[5] J. Plessers, P. Wokkants, E. Vangelooven and J. R. Ross, *Proceedings of SCANINJECT, VI*, 1992, pp.327-348.
[6] K. Katogi, private communications.
[7] S. Kuyucak and R. L. Guthrie, *Proc. Light Metals Section, CIM Conference of Metallurgists*, Winnipeg, pp.1-10, 1987
[8] S. Kuyucak and R. L. Guthrie, C*an, Met. Quart.* Vol. 28, no.1, 1989, pp.412-448.
[9] R. L. Guthrie and H. C. Lee, *Steelmaking Conference Proceedings*, Vol.75, pp.799-805, ISS-AIME.
[10] T. Ogura, R. Fujiwara, R. Mochizuki, K. Kawamoto, T. Oishi and M. Iwase, *Metallurgical Transactions,* Vol. 23B,1992, pp.459-466. C. W. McCoy and F. C. Langenberg, J. Metals, Vol.16, 1964, May, pp.421/424. E.
[11] R. V. Pathy and R. G. Ward, *J. Iron. Steel. Inst*., Vol. 202, 1961, December, pp.995/1001.
[12] E. Aukurst, H. L. Bishop, Chapter 1, of "*BOH Steelmaking*", R. Pehlke, D. Porter, W. F. Urban, R. F. Gaines, Eds., ISS/AIME, 1977, New York, New York, U.S.A.
[13] E. Aukurst, P. J. Koros and H. W. Meyer, *J. Metals*, Vol.18, 1966, April, pp.433/439
[14] C. W. McCoy and F. C. Langenberg, *J. Metals*, Vol.16, 1964, May, pp.421/424