AN AUTOMATIC EQUIPMENT FOR DETERMINATION OF THE FeO ACTIVITY

-Laboratory and In-Plant Applications

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ABSTRACT

By employing an electrochemical technique incorporating stabilized zirconia as solid electrolyte and mixture of Mo + MoO_2 as reference electrode, an automatic facility for "on-floor" determinations of the activities of FeO in steelmaking slags has been developed. With this equipment, one datum is obtainable within 5 minutes. In this paper an over view on the application of this facility is given. In addition to laboratory application, discussions are also made on in-plant applications of this system in steelmaking processes. A particular emphasis is given to (i) slag reduction practice for minimizing reoxidation of molten steel by slag, (ii) partition of manganese and sulfur in BOF, and (iii) control of chromium levels in slags for stainless steelmaking.

1. INTRODUCTION

The study of chemical reactions of liquid steel and molten slag involves complex slags containing at least eight important components, i.e., CaO, MgO, MnO, FeO, SiO_2, Al_2O_3, P_2O_5, CaF_2, and often a number of others such as TiO_2, Cr_2O_3, CaS and so on. The application of physico-chemical principles to the elucidation of slag-metal and slag-gas reactions can often be handicapped by the lack of knowledge of the activities of reacting species. Since iron oxide in slag participates in numerous reactions between metal, slag and gas, the evaluation of the activities of ferrous oxide should be first considered.

Since 1940's, a number of experimental determinations of the activities of ferrous oxide have been conducted$^{(1)}$. Because of such concerted efforts of many laboratories during the five decades, approximately two thousand data were obtained for the FeO activities, although there are many duplicate measurements. Our knowledge of the activities of FeO is, nevertheless, still far from satisfactory. For example, consider a slag of 40 wt% CaO, 10 wt% MgO, 5 wt% MnO, 15 wt% SiO_2, 10 wt % Al_2O_3, 3 wt% P_2O_5, 5 wt% CaF_2 and 12 wt% FeO. The literature data obtained during a half century do not allow us to evaluate the a_{FeO} value of this slag. From this example it is evident that experimental determinations of the FeO activities are still required. However, if one intends to know the activities of FeO in eight-component slags at a reasonable interval of mole fractions of the constituent components, activity measurements must be conducted until millions of data are obtained. Even if the activity determinations were focused on slags of high basicity, e.g. $X_{CaO} / X_{SiO_2} > 2$, following the authors' estimation, hundred thousand data for a_{FeO} would be required. When do we have enough data to know the FeO activities of multi-component slags at any given compositions? As is well known, high temperature experiments are time consuming and involve a variety of difficulties.

Recently, by employing an electrochemical technique, an automatic facility for the measurements of the FeO activities has been developed by the present author and his coworkers$^{(2)}$. A schematic illustration of the automatic activity determinator is given in **figure 1**. The electrochemical cell consists of zirconia tube **D** of 3.6 mm o.d., 2.2 mm i.d. and 32 mm in length, a Mo + MoO_2 mixture **C**, and a molybdenum rod **A** of 1 mm diameter and 200 mm length. For operating this system, firstly, the electrochemical cell is attached to the elevator mechanism **E**. Second, an iron crucible **K** of 19 mm o.d., 16 mm i.d. and 37.5 mm in length, is placed on a steel pedestal **O**. The

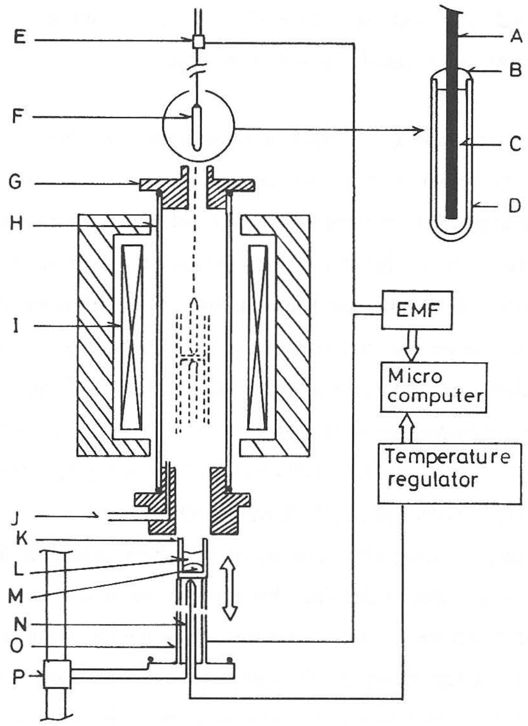

Figure 1 A schematic illustration of the equipment
A, Molybdenum rod; B, Refractory cement; C, Mo + MoO_2 reference electrode; D, Zirconia tube; E, Elevator mechanism; F, Electrochemical cell; G, Water-cooled brass cap; H, Transparent silica tube; I, Tungsten filament; J, Argon inlet; K, Iron crucible; L, Slag; M, Silver; N, Pt-PtRh13 thermocouple; O, Steel pedestal; P, Elevator mechanism.

electrical contact to the outer electrode of the zirconia cell is made *via* this pedestal. Pure silver **M** of 8 g is pre-melted within the iron crucible. A sample of slag **L**, 1 to 3 g, is charged in the iron crucible. These procedures require manual operations. Subsequent steps, however, will occur automatically upon touching the LCD (Liquid crystal display) of a micro computer installed within the facility;

(1) The iron crucible is moved upward, *via* an elevator mechanism **P**, into a transparent silica reaction tube **H** of 48 mm o.d., 44 mm i.d., and 238 mm in length.
(2) The tube is sealed and flushed with a stream of argon.
(3) By means of infrared ray generated by four tungsten filaments **I**, the furnace is subsequently heated to desired temperature up to 1723 K within 2.5 minutes in conforming to the computer program.
(4) The furnace temperature is measured with a Pt-PtRh13 thermocouple **N** placed below the iron crucible and monitored on the LCD.
(5) Upon temperature reaching the pre-determined value, the electrochemical cell is lowered until it contacts both the molten silver and the slag.
(6) Open-circuit cell voltages generated between the molybdenum rod and the steel pedestal are monitored on the LCD of the micro computer. Normally stable cell potential were obtainable within 0.5 to 1 min.
(7) After stable emfs (± 0.8 mV) were obtained for at least 1 minute, the electrochemical cell is removed from the iron crucible, which is, in turn, lowered and abandoned in order to prepare for the subsequent activity determinations.
(8) 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 5 minutes.

The chemical potential of oxygen at the slag electrode is established by the reaction

$$Fe(s) + (1/2)\ O_2(g) = FeO(\text{in slag}) \quad \ldots\ldots\ldots\ldots[1]$$

The activities of FeO can be defined as

$$a_{FeO} = \{P_{O_2}(slag)\ /\ P_{O_2}{}^{o}(slag)\}^{1/2} \quad \ldots\ldots\ldots\ldots[2]$$

where $P_{O_2}{}^{o}(slag)$ is the equilibrium oxygen partial pressure of the mixture, 'pure' FeO(l) + Fe(s). The standard state for a_{FeO} is taken as 'pure' non-stoichiometric liquid FeO in equilibrium with pure solid iron.

2. LABORATORY APPLICATIONS

The automatic activity determinator can be applied for laboratory measurements of the FeO activity. **Figure 2** shows the iso-activity curves for FeO for the system CaO + SiO_2 + FeO at 1673 K obtained by the automatic equipment. It is worth noting that the a_{FeO} data, given in **figure 2** based on 140 emf measurements were obtainable within 35 hours. The detailed discussion on the a_{FeO} data obtained by this equipments revealed that the activities are in consistent with the phase diagram(2). The application of this facility to thermodynamic studies of metallurgical slags would be a fruitful area of research in the future.

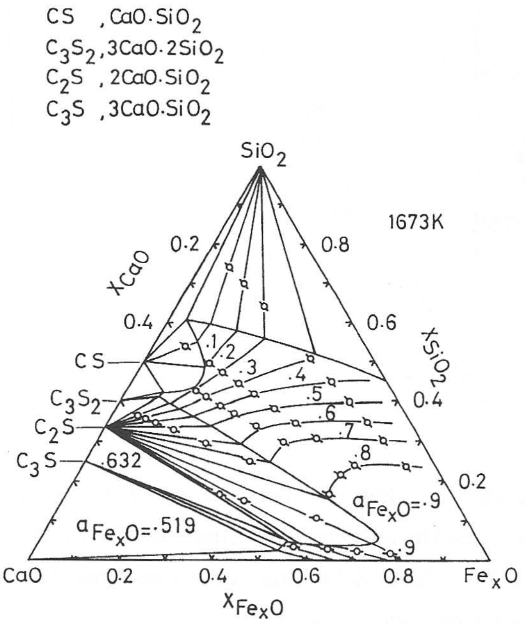

Figure 2 Iso-activity curves for FeO in the system CaO + SiO_2 + FeO at 1673 K as determined by the automatic activity determinator.

3. IN-PLANT APPLICATIONS

"Look after the slag, and metal looks after itself". The importance of slag control is most directly explained in this phrase. However, currently, the BOF operators pay less attention to slag than metal. Consider chemistry and temperature of slag. Although chemistry of molten steel are determined for every heats, for slags even temperature are not determined. It is noted here at this point that the automatic equipment can be used for "on floor" determinations of the FeO activities of steelmaking slags. In the present paper, discussions are made on the industrial applications of this facility to steelmaking processes.

3.1 Reoxidation of molten steel

In steelmaking processes, molten steel is inevitably brought into direct and/or indirect contact with air. Farrell, Bilek and Hilty(3) showed that large inclusions counts and sizes frequently observed in practice are primarily due to reoxidation of the metal. A bare bath, a molten stream, or a mold cavity, all provide ample opportunity for liquid steel to react with the air, which is an unlimited supplier of oxygen. In addition, reoxidation can also occur by molten slag. For example, one should consider the reoxidation of aluminum by ferrous oxide in molten slags.

$$2\ Al(\text{in metal}) + 3\ FeO(\text{in slag}) = Al_2O_3(s) + 3\ Fe \quad ....[3]$$

Reaction[3] will proceed to the right-hand side with an increase in the activities (or concentrations) of FeO. Normally, slags formed at secondary steelmaking processes contain 5 to 15 % FeO. Based on practical experience, ladle shop operators pay attention to the concentrations of *'total'* Fe plus MnO, *(%T.Fe) + (%MnO)* or *(%FeO) + (%MnO)*; manganese oxide can also re-oxidize aluminum, although *(%MnO) << (%T.Fe)*. For example, Hara et al(4) have reported such an anticipated effect of FeO in slag phase as shown in **figure 3**; the total oxygen concentrations in steel after RH degassing increased with an increase *(%FeO) + (%MnO)*. Much attention, hence, has been focused to develop an appropriate practice that can lower the FeO activities in molten slag, especially in secondary refining vessels. In general, metallic aluminum(5) or calcium carbide(6) is spread over molten slag to reduce FeO within slag phase. Currently, control strategies for lowering the FeO activities in such practices are based on samples taken from molten slag during ladle treatment. Chemical analysis for FeO and MnO in slags, however, requires at least 20 minutes, while ladle treatment must be completed within 15

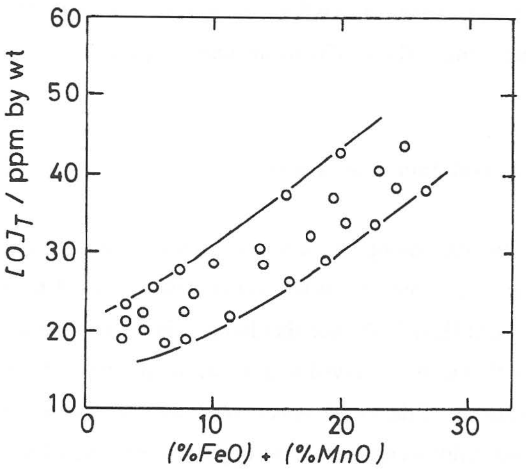

Figure 3 Relation between total oxygen concentration, *[O]$_T$*, attained at RH degassing and *(%FeO) + (%MnO)*, after Hara et al[(4)].

to 20 minutes. Hence, a knowledge of *(%T.Fe) + (%MnO)* based on chemical analysis does not assist the ladle shop operators to control the molten slag under operation. The automatic activity determinator can be used for slag control in secondary steelmaking.

Figure 4 shows the relation between a_{FeO} obtained by the automatic facility and *(%T.Fe) + (%MnO)* obtained by chemical analysis for industrial slags taken from different ladle shops[(7)]. As shown in this figure, the empirical parameter, *(%T.Fe) + (%MnO)*, would be fairly proportional to the FeO activities. However, FeO activities of slags at one ladle shop are different from those at another even although the empirical parameter, *(%T.Fe) + (MnO)*, was the same. Similar results are also reported by Hamm et al[(8)]. From thermochemical point of view, this behaviors is quite understandable if difference in slag basicity is taken into account. In other words, however, it is evident that the empirical parameter would not be appropriate for close control of the activities of FeO.

For practical application of the automatic activity determinator, slag samples would be taken before slag-reduction practice to know the a_{FeO} values. Through such activity measurements appropriate amounts of aluminum or calcium carbide for slag-reduction can be estimated. A recent article in the literature[(9)] has reported improved slag-reduction practice with the aids of the FeO activity determinator, and the resulting better steel cleanliness.

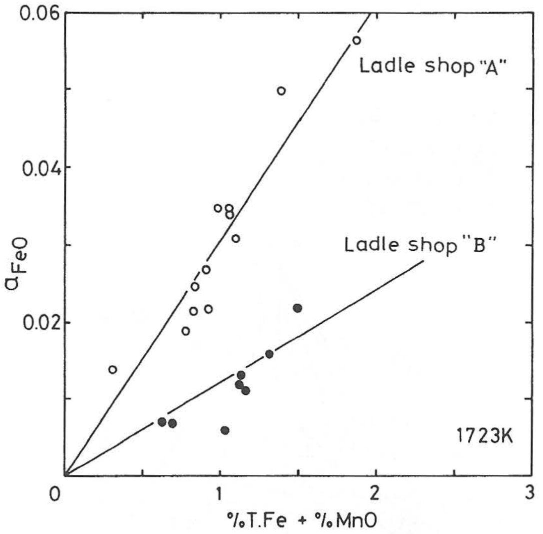

Figure 4 Relation between the FeO activities determined by the automatic activity determinator and *(%T.Fe) + (%MnO)* for slags taken from different ladle shops after Ogura et al[(7)].

3.2 Control of Manganese, Sulfur ad Phosphorous in BOF Steelmaking

Consider the equilibrium partition of manganese between slag and metal:

$$[\mathrm{Mn}] + (\mathrm{FeO}) = (\mathrm{MnO}) + \mathrm{Fe} \qquad [4]$$

where (i) and [i] indicate component, i, in slag and molten steel, respectively. The partition ratio would be formulated as

$$\log\{(\%Mn)/[\%Mn]\} = \log a_{FeO} + (\text{constant}) \qquad [5]$$

where *(%Mn)* and *[%Mn]* are the concentrations (pct by weight) of manganese in slag and metal. Following equation[5] a logarithmic plot between (%Mn)/[%Mn] should be a straight line with a slope of unity. Hamm et al(9) reported such anticipated relation between log *(%Mn)/[%Mn]* and log a_{FeO} was indeed obtained via practical BOF steelmaking processes, **figure 5**. They also mentioned measurement of a_{FeO} can be used to calculate alloying efficiency with a higher degree of precision resulting in significant cost reduction and accurate heat chemistries.

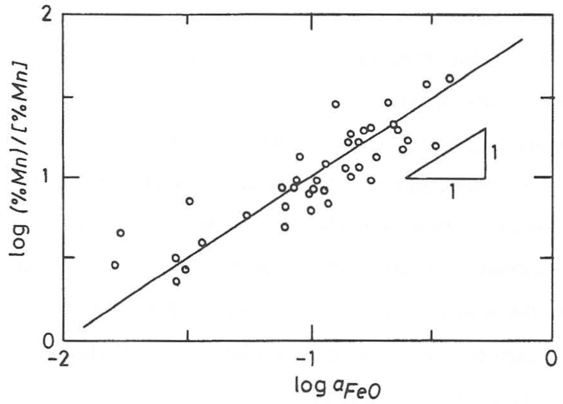

Figure 5 Manganese partition *(%Mn)/[%Mn]* as the function of a_{FeO} as determined by the automatic activity determinator after Hamm et al(8).

Next, consider desulfurization:

$$(CaO) + [S] + Fe = (CaS) + (FeO) \quad \ldots\ldots\ldots\ldots [6]$$

The partition ratio for sulfur can be given as

$$\log\{(\%S)/[\%S]\} = -\log a_{FeO} + \log a_{CaO} \quad \ldots\ldots\ldots\ldots [7]$$

Equation [7] suggest that so far as the activities of CaO (or the basicities of slag) are kept constant, a logarithmic plot of *(%S)/[%S]* against a_{FeO} should be a straight line with a slope of - 1. The relation between log{*(%S)/[%S]*} and log a_{FeO} as obtained by Hamm et al(9) are given in **figure 6**. As can be see in this figure although the slope was different from the ideal (-1) , there is a good correlation. This indicates that the sulfur partition ratio can be determined through FeO activity measurements.

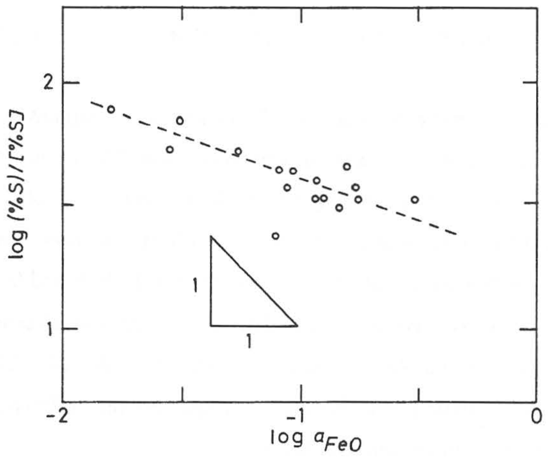

Figure 6 Sulfur partition *(%S)/[%S]* as the function of a_{FeO} as determined by the automatic activity determinator after Hamm et al(8).

3.3 Control of Chromium Levels in Slags Formed During Stainless Steelmaking

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

$$C(\text{in metal}) + (1/2)\ O_2(g) = CO(g) \quad \ldots\ldots\ldots\ldots [8]$$

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

$$2\ [Cr] + (3/2)\ O_2(g) = (Cr_2O_3) \quad \ldots\ldots\ldots\ldots [9]$$

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

$$(Cr_2O_3) = 2\ [Cr] + (3/2)\ O_2(g) \quad \ldots\ldots\ldots\ldots [10]$$

The oxygen potential prevailing reaction[6] can often be expressed as

$$Fe + (1/2)\ O_2(g) = (FeO) \quad .... [11]$$

It follows, by combining equations[9] and [11], that

$$(Cr_2O_3) + 3\ Fe = 2\ [Cr] + 3\ (FeO) \quad .... [12]$$

In conforming to reaction[12], in laboratory studies by Pathy and Ward(10), a linear relation was found between the ratio of chromium in slag, *(%Cr)*, to that in metal, *[%Cr]*, and the concentration of FeO, *(%FeO)*, in the slags. The proportionality constant varied from 0.5 at 1900 K and 0.3 at 1960 K. By averaging data from BOF and electric furnace heats, Aukurst et al(11) obtained a value of 0.25, while Aukurst and Bishop(12) suggested the following equation for commercial heats;

$$(\%Cr) / [\%Cr] = 0.3\ (\%FeO) \quad .... [13]$$

A precise expression for the partition of chromium, however, should arise from the equilibrium constant of reaction[12];

$$K(12) = a_{FeO}^3\ a_{Cr}^2 / f_{Cr_2O_3} (\%Cr_2O_3)\ a_{Fe}^3 \quad ......[14]$$

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

It follows that

$$\log (\%Cr_2O_3) = 3 \log a_{FeO} + \log \{a_{Cr}^2\ K(12) / f_{Cr_2O_3} a_{Fe}^3\} \quad ....[15]$$

Let us consider a series of production heats for a fixed stainless steel specification (fixed chromium contents); the activities of Cr and Fe, respectively, would be fairly constant. In addition, the activity coefficient of 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(13). 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[15] would be kept constant, so far as we concern production heats of a fixed stainless steel specification. It follows, hence, that

$$\log (\%Cr_2O_3) = 3 \log a_{FeO} + \text{constant} \quad ....[16]$$

In order to test the validity of equation[16], 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 16 %. **Figure** 7 shows the logarithmic plot of a_{FeO} as determined by the automatic activity determinator at 1723 K against $(\%Cr_2O_3)$ in slag obtained by chemical analysis(14). As shown in **figure** 7, in conforming to equation[16], the relation is essentially linear and the slope is very close to 3. These results indicate that a measure of a_{FeO} would give a knowledge of chromium concentrations in slag phase.

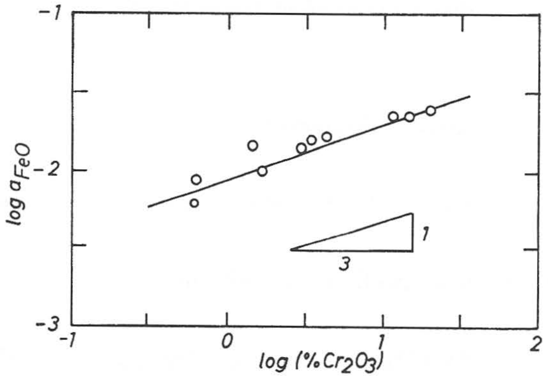

Figure 7 Relation between log a_{FeO} and log $(\%Cr_2O_3)$ for stainless steelmaking slags.

4. SUMMARY

By employing an electrochemical technique incorporating zirconia as electrolyte and Mo + MoO_2 as reference electrode, an automatic equipment for the rapid determinations of the activities of FeO in metallurgical slags has been developed. With this apparatus, "on-floor" activity determinations are possible, since one datum is obtainable within 5 minutes. This facility can be applied for better control of FeO concentrations in slags of secondary steelmaking and chromium control in stainless steelmaking. Further applications of this facility should be a subject of future publications, since desulfurization, manganese distribution and dephosphorization, all are related to the FeO activities.

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