4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

AUTOMATIC DETERMINATOR FOR THE FeO ACTIVITIES IN METALLURGICAL SLAGS BASED ON AN ELECTROCHEMICAL TECHNIQUE

T. Ogura*, R. Fujiwara*, R. Mochizuki*, Y. Kawamoto*, T. Oishi** and M. Iwase**

* Research Institute, Yamari Electronite Co. Ltd., Minami-Befu, Settsu-shi, Osaka 566, JAPAN,
** Department of Metallurgy, Kyoto University, Kyoto 606, JAPAN.

Synopisis: An automatic system for rapid determinations of the activities of FeO in metallurgical slags has been developed. With this facility, one datum is obtainable within 5 minutes. The equipment can be applied for control of FeO activities in secondary refining processes as well as thermodynamic studies of slags and fluxes.
Key words: Activity, Slag, Steelmaking, Ferrous oxide, Zirconia, Electrochemical technique

1. Introduction

Traditionally, many of the large objectionable oxide inclusions in steel have been attributed to deoxidation practices. A significant amount of thought and effort has been concentrated on deoxidation practices specifically designed to control the type and distribution of nonmetallic inclusions. At the present, with argon rinsing, the oxide inclusions remaining dispersed in the metal at the time of teeming are less than about 5 microns in diameter; the total concentration of oxygen in Al-killed steel should be about 20 ppm or less, corresponding to about 0.01 volume per cent alumina inclusions[1]. In continuous casting or ingot making practice, inclusions of 50 to 100 microns and 0.1 to 0.3 volume per cent are not unusual. Farrell, Belek and Hilty[2], in 1970, have shown that such large inclusions are caused by reoxidation of molten steel rather than deoxidation. Large inclusions counts and sizes frequently observed in practice are primarily due to reoxidation of the metal during teeming or poor practice of mold additions. It is to be mentioned that in steelmaking processes molten steel is inevitably brought into direct and/or indirect contact with air. A bare bath, a molten stream, or a mold cavity, all provide ample opportunities for liquid steel to react with air, which is an unlimited supplier of oxygen. An obvious solution to the problem of reoxidation is to eliminate open stream pouring during transfer from ladle to tundish, and tundish to mold by the use of submerged entry nozzles.

Even with such shrouding technologies, however, reoxidation can still take place when molten steel is contained in ladle. One may consider the reoxidation of aluminum in liquid steel by ferrous oxide in molten slag:

$$2\ \mathrm{Al(in\ Fe)} + 3\ \mathrm{FeO(in\ slag)} = \mathrm{Al_2O_3(in\ slag)} + 3\ \mathrm{Fe} \quad \text{.................}(1)$$

Reaction(1) will proceed to the right-hand side with an increase in FeO activities in molten slag. Much attention, hence, has been focused to develop an appropriate practice that can lower the FeO activities in molten slag. Currently, control strategies for lowering the FeO activities are based upon samples taken from molten slag during ladle treatment. Based on practical experiences, ladle shop operators pay attention to the concentrations of total Fe plus MnO, (%T.Fe) + (%MnO). Manganese oxide can also re-oxidize aluminum, although (%MnO) << (%T.Fe). Chemical analysis for FeO and MnO in slags, however, requires at least 40 minutes, while the ladle treatment must be completed within 15 to 30 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 operations.

From the forgoing comments, it would be evident that the key to better control of FeO levels in molten slag would be an electrochemical sensor which rapidly measures the FeO activities. In case of slag phases, however, an obvious draw back of solid state sensor arises from the fact that the refractory components of such sensors would readily be attacked by the molten slag. In addition, due to less slag volume of about 10 kg/ton for the ladle treatment, it is extremely difficult to immerse a sensor within the slag phase only. For these reasons it was decided to develop an 'on floor' activity determinator for FeO[2]. This equipment is based on samples taken from slag phase. However, activity measurement can be completed within 5 minutes in order to meet the requirements of the ladle shop operators.

2. Automatic Activity Determinator

The technique adopted in the activity determinator consists of charging slags in an iron crucible together with pure silver to bring molten slag into equilibria with solid iron, and measuring the equilibrium oxygen partial pressures by means of a solid state zirconia cell.

A schematic illustration of the apparatus is given in **Figure 1**. The electrochemical cell, which consists of a 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.

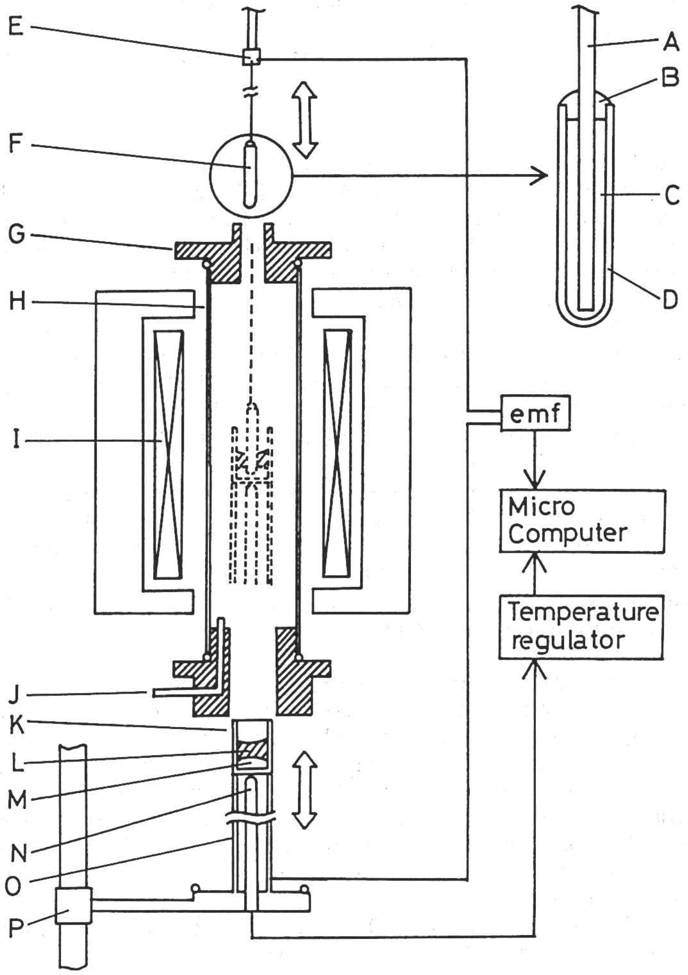
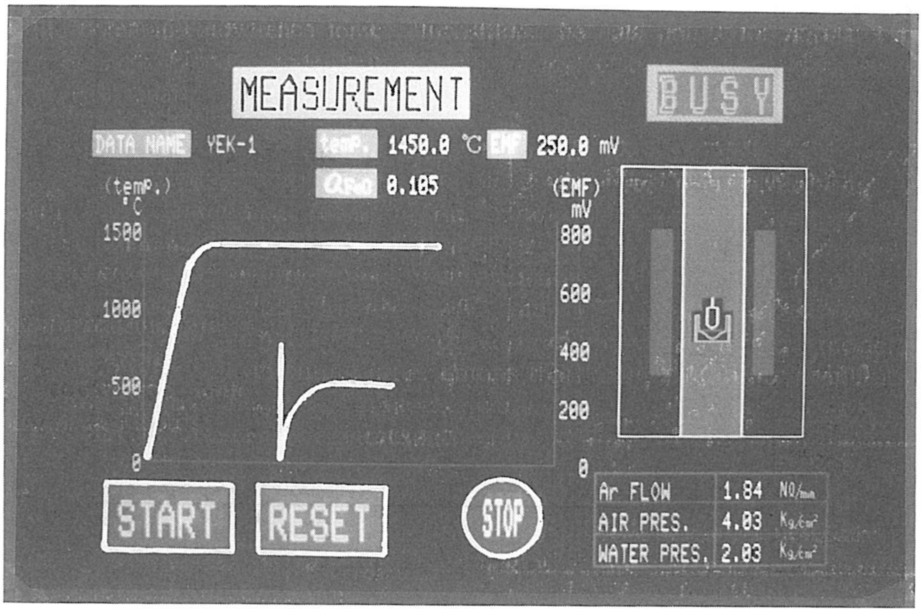


Figure 1 A schematic illustration of the equipment.
A, Molybdenum rod; B, Refractory cement; C, Mo + MoO_2 reference electrode; D, Zirconia tube; E, Elevator mechanism; F, Electrochemical cell; G, Water-cooled brass cap; H, Transparent silica tube; I, Tungsten filament; J, Argon inlet; K, Iron crucible;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

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 electrical contact to the outer electrode of the zirconia cell is made via this pedestal. Pure silver M of 8 g is contained within the iron crucible, and 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 1750 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 with 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.
(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 to prepare for the subsequent activity determinations.
(8) The cell potential is then converted to the FeO activity, and displayed on the LCD as shown in **Figure 2**.

In this way, a single activity measurement is completed within 5 minutes.



DATA NAME YEK-1
temp. 1450.0 ℃
EMF 250.0 mV
a_{FeO} 0.105

Ar FLOW	1.84	Nℓ/min
AIR PRES.	4.03	Kg/cm²
WATER PRES.	2.03	Kg/cm²

Figure 2 Computer display appeared during an activity measurement.

3. In-Plant Applications

Figure 3 shows the relation between a_{FeO} determined by the activity determinator and (%T.Fe) + (%MnO) obtained by chemical analysis for industrial slags taken from different ladle shops. As shown in this figure, the empirical parameter, (%T.Fe) + (%MnO), would be proportional to the FeO activities. The slope of a_{FeO} against (%T.Fe) + (%MnO) for slags taken at one ladle shop, however, differ from that of another, even although the values for the empirical parameter, (%T.Fe) + (%MnO), are the same. From thermochemical point of view this behavior is quite understandable, if difference in slag basicity was taken into account. It can be stated, in other words, that the empirical parameter would not be appropriate for close control of the activities of FeO.

4. Laboratory Applications

The activity determinator can also be applied to thermochemical studies of slags and fluxes. For example, the iso-activity curves for FeO determined by the automatic equipment for the system CaO + SiO_2 + FeO have been reported as shown in **Figure 4**. It is worthy of noting that the activity data, based on 140 emf measurements, were obtainable with 35 hours. The application of this facility to elucidate slag/metal reaction in steelmaking processes would be a fruitful area of research in the future.

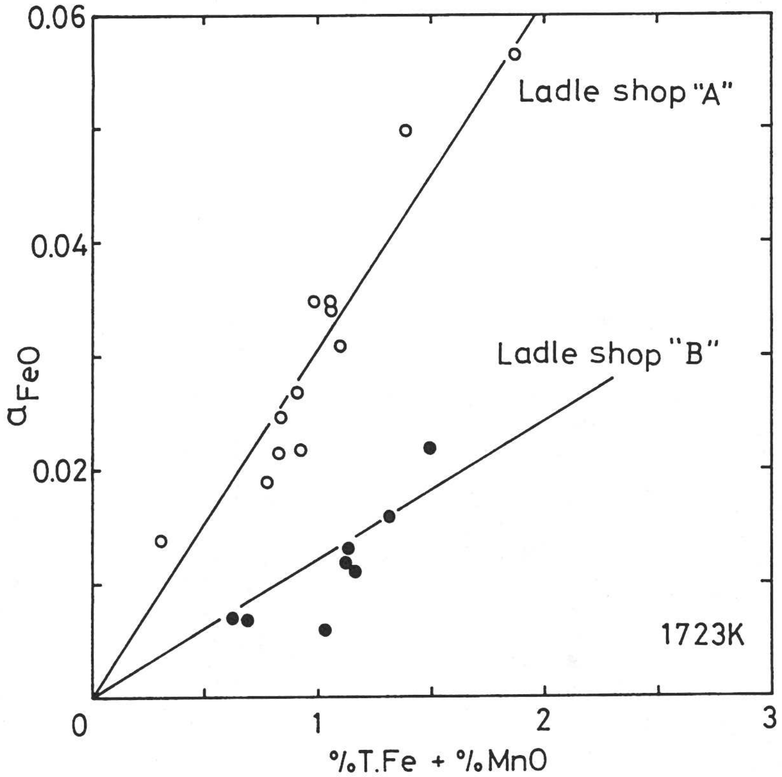


Figure 3 Activities of FeO as the function of the empirical parameter, (%T.Fe) + (%MnO), for slags taken at different ladle shops.

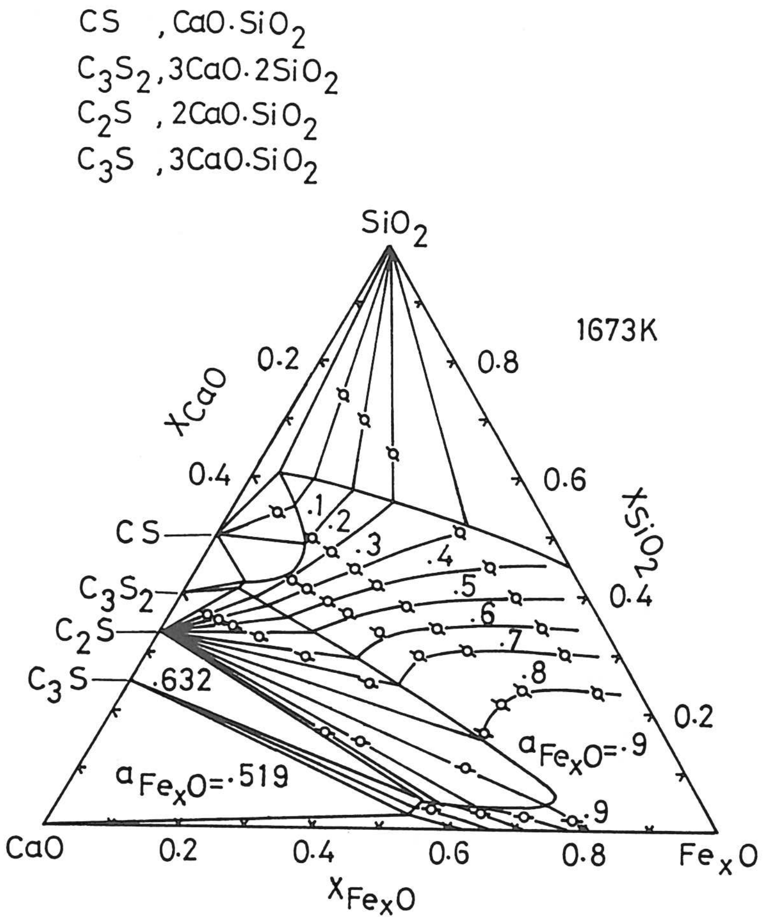


Figure 4 Iso-activity curves for FeO in the system CaO + SiO_2 + FeO at 1673 K.

Acknowledgments

Helpful comments, suggestions, discussions and encouragements were given by Professor Alex McLean, University of Toronto; and Mr. Masao Matsuoka, Executive Director, Yamari Electronite Co. Ltd., and Dr. Hisashi Matsunaga and Dr. Kazushige Umezawa, Nippon Steel Corporation, while financial supports were given by the Ministry of Education, Japanese Government, via Grant-in-Aid for Scientific Research (Shiken Kenkyu,1990). These are gratefully acknowledged.

References

1. E. T. Turkdogan, in "making, Shaping and treating of Steel", Chapter 13, association of Iron and Steel Engineer, eds, W. T. Lankford et al.1985.
2. J. W. Farrel, P. J. Belek and C. D. Hilty, Electric Furnace Proceedings/AIME, pp.64-86, 1970.
3. T. Ogura, R. Fujiwara, R. Mochizuki, R. Kawamoto, T. Oishi and M. Iwase, Met. Trans. 1992 in press.