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DEVELOPMENT OF A PHOSPHORUS SENSOR IN HIGH TEMPERATURE SLAG-METAL SYSTEMS

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Synopsis: A high temperature solid state galvanic cell based upon MgO-doped calcium aluminate ($CaO \cdot 6Al_2O_3$) solid electrolyte with calcium orthophosphate ($3CaO \cdot P_2O_5$) auxiliary electrode was developed to use as a phosphorus sensor in high temperature melts. The electrolyte was synthesized by a solid state reaction at 1873 K from a mixture of high purity γ-Al_2O_3, $CaCO_3$ and MgO and small tubes were isostatically pressed and then sintered at 1973 K. The galvanic cell was tested in the Fe-C-P melt and it has been found that there is a correlationship between the EMF of the cell and the phosphorus content in the melt.

Key words: solid state galvanic cell, calcium aluminate, phosphorus sensor, Nernst equation, thermodynamic equilibrium.

1. Introduction

It is well known that phosphorus is a detrimental element for the mechanical properties of steel, except enhancing the fluidity of cast irons and for producing free machining steels. Any phosphorus present in iron ores is readily reduced to metallic phosphorus and the recovery of phosphorus in a blast furnace is almost 100% since it is soluble in iron. From this reason, dephosphorization of hot metal is inevitable in the steel making processes. Although dephosphorization is possible in modern oxygen converters, external dephosphorization of hot metal in the hot metal torpedo cars or transfer ladle is preferred and the flux normally used consists of lime, iron oxide and spar. Therefore, an electrochemical phosphorus sensor would be highly useful for monitoring of phosphorus levels in hot metals.

On the other hand, phosphorus is an important deoxidizer for molten copper, for it reacts with the dissolved oxygen to produce a copper phosphate slag. However, high phosphorus content in oxygen free copper is harmful since it increases electrical resistivity of oxygen-free copper. It is, therefore, very important to use minimum amount of deoxidizer, usually copper phosphide, to keep the phosphorus levels within the specification limits and again a phosphorus probe would be an effective tool.

Although modern analytical instruments for determination of phosphorus contents in metal samples are relatively accurate and reproducible, valuable time may be spent in sampling and transportation as well as in actual analysis. During this time lapse, huge amount of heat may have to be supplied to prevent undesirable temperature drop of melt, and often the analytical information obtained may only be of retrospective use. Therefore, it is highly desirable to have a in-situ chemical sensor for quick on-line measurement of phosphorus content in molten metals at high temperatures.

2. Principles

As no solid electrolyte in which phosphorus ion is mobile is known at present, it is not

possible to take the simple galvanic cell design, such as the well-known oxygen sensor using partially stabilized zirconia electrolyte, for a phosphorus sensor. Fortunately, a novel idea based upon the use of an auxiliary electrode[1-3] in order to have a chemical coupling between the species being measured and the species ionically moblie in the electrolyte can be utilized for the development of an electrochemical phosphorus sensor. For example, a galvanic cell using CaO-stabilized zirconia as an oxygen ion conductor and Cr_2O_3 as an auxiliary electrode was used by Heinz and Janke[4] to measure chromium content in Fe-O-Cr melt. The local equilibrium oxygen partial pressure at the interface between the melt and auxiliary electrode is determined according to the reaction:

$$\langle Cr_2O_3 \rangle = 2\,[Cr] + 3\,[O] \qquad (1)$$

Since the activity of solid Cr_2O_3 is fixed at a given temperature, and the activity of oxygen at the interface is governed by that of chromium, it is possible to measure the chromium activity in the melt by simply using an oxygen sensor.

In the case of a phosphorus sensor based upon a cation conductor, phosphides are natural candidates for the auxiliary electrode materials, but it seems not practical to use phosphides because they are easily hydrolyzed in the atmosphere and oxidized at elevated temperatures. However, phosphates are generally quite stable compounds even at high temperatures and can be used as promising auxiliary electrode materials. In the present study, MgO-doped calcium hexa-aluminate ($CaO \cdot 6Al_2O_3$) electrolyte which is known as a Ca^{2+} ion conductor at high temperatures and calcium orthophosphate($3CaO \cdot P_2O_5$) auxiliary electrode were used to develop a solid state galvanic cell for the measurement of phosphorus content in Fe-C-P melt. The galvanic cell can be represented as follows:

$$Ca(ref) \;\|\; Ca^{2+} \text{ ion conductor} \;\|\; Ca_3(PO_4)_2/Fe\text{-}\underline{O}\text{-}\underline{P} \qquad (2)$$

The auxiliary electrode provides a local chemical equilibrium at the metal/auxiliary electrode/ electrolyte interface according to the reaction:

$$\langle Ca_3(PO_4)_2 \rangle = 3[Ca] + 2[P] + 8[O] \qquad K = \frac{a_{Ca}{}^3 \cdot a_P{}^2 \cdot a_O{}^8}{a_{Ca_3(PO_4)_2}} \qquad (3)$$

At a given temperature, the activity of calcium phosphate is constant and that of oxygen is also fixed when the iron melt is saturated by carbon. Consequently the activity of phosphorus in the melt can be ditermined by measuring the activity of calcium at the metal/auxiliary electrode/ electrolyte interface.

One of the most important factors which influences the performance of a solid electrolyte cell is the selection of the reference material as this needs to come to equilibrium quickly at a given temperature and ideally should be a mixed conductor. In the case of sensors for oxygen determination it is relatively easy to find a suitable reference which can either be atmospheric air or metal/metal oxide mixtures. However, the selection of a reference for the systems involving calcium is not so easy as the presence of liquid calcium is undesirable. In the present study, a mixture of $CaO \cdot Cr_2O_3$, Cr_2O_3 and Cr was used as a Ca reference. If one considers the region closest to the Cr_2O_3 end of the $CaO\text{-}Cr_2O_3$ phase diagram[5], there is a region where $CaO \cdot Cr_2O_3$ and Cr_2O_3 are equilibrium phases. When the temperature is fixed, both the activities of CaO and Cr_2O_3 are fixed according to the Gibbs pahse rule. If the oxygen partial pressure of the system is fixed by keeping the sensor open to the atmosphere or by the use of metal/metal oxide mixtures, Cr/Cr_2O_3 in the present case, the calcium activity is also fixed.

3. Experimental

3.1 Synthesis of electrolyte and reference material

$CaCO_3$(99.99%), MgO prepared by calcining basic magnesium carbonate at 1273 K, and γ-Al_2O_3(99.99%) dried at 473 K overnight in an oven were used as starting materials. The powders were weighed in appropriate proportions and ball-milled in ethanol for 3 days with high purity alumina balls. The slurrys were then dried and subsequently calcined at 1373 K for 12 hours in a high purity alumina crucible. The calcined powders were ground by an alumina mortar and pestle, reacted at 1873 K for 5 hours, and ball-milled again for 3 days. For the measurement of relative density and analysis of crystalline phases by a X-ray diffraction(XRD), the powders were uni-axially pressed into 15 mmφ x 2~4 mm thick discs and sintered at 1973 K for 5 hours followed by annealing

at 1723 K for 5 hours.

One-end closed tubes of 85%CaO·$6Al_2O_3$·0.4MgO-15%$Ca_3(PO_4)_2$ were isostatically pressed using a mandrel made of tool steel and a PVC mold, and then sintered using the same heating procedure as decsribed above. The dimension of the sintered tubes was approximately 5 mm OD, 3 mm ID, and 30 mm L. These electrolyte/auxiliary electrode composite tubes were used to fabricate the phosphorus sensors used in the present study.

β-CaO·Cr_2O_3 + Cr_2O_3 two phase mixture was synthesized by calcining a mixture of $CaCO_3$ and Cr_2O_3(99%) at 1373 K for 12 hours followed by reaction at 1673 K for 10 hours. The crystalline phases of the reaction product were confirmed by XRD. The powder mixture was then thoroughly mixed with Cr(99%) powder and used as the reference material.

3.2 Galvanic cell assembly

A schematic diagram of the galvanic cell assembly used in the present study is shown in Figure 1. About 0.3 gram of the reference powder was filled into the electrolyte tube which was attached to an alumina tube of 9 mm OD, 7 mm ID, 50 mm L using alumina cement. This was then cemented to an alumina extention tube of 7 mm OD, 5mm ID, 500 mm L. Molybdenum rods of 3 mm dia. were used as leads for both the reference and counter electrodes.

3.3 Procedure of EMF measurements

EMF measurements of the cell were performed in a SiC heated furnace and the experimental set-up is depicted in Figure 2. About 20 grams of cast iron sample saturated by carbon(4.4%C) and predetermined amount of iron phosphide (25%P) were placed in an alumina crucible of 20 mm ID and 20 mm H. Before raising the furnace temperature, the inside of the alumina working tube was purged with argon(99.99%) for more than 2 hours. The sensor tip was positioned about 10 mm above the surface of the melt and after the furnace temperature reached the preset value, the sensor was lowered to a depth of approximately 5 mm below the surface of the melt. An electrometer with an input impedance of greater than $5x10^{13}$ ohm and a chart recorder were used to measure and record the EMF of the cell. Both the furnace and sample temperatures were measured by a Pt-Pt13%Rh thermocouple.

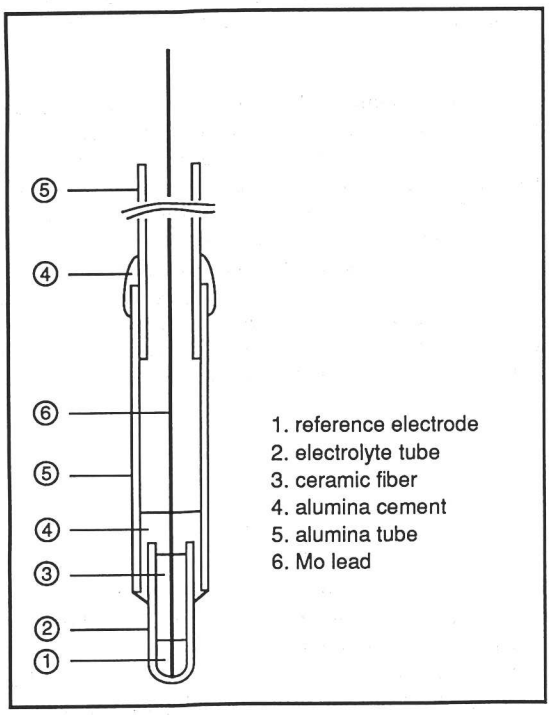

Figure 1 Schematic diagram of P sensor

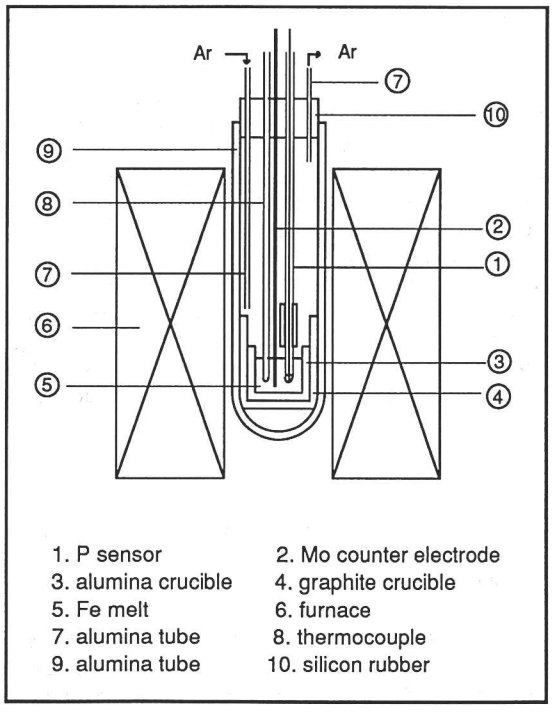

Figure 2 Schematic diagram of experimental set-up

4. Results and discussions

4.1 Evaluation of electrolyte

Calcium hexa-aluminate($CaO \cdot 6Al_2O_3$) has a magnetoplumbite structure and is rather poor ionic conductor while non-stoichiometric compound Caβ"-alumina($Ca_xMg_{2-x}Al_{12-2x}O_{17}$) is known to be a fast Ca^{2+} ion conductor[6]. Magnetoplumbite and some β-alumina of alcali -earth metals(Sr, Ba) may be prepared by direct high temperature synthesis[7], but β"-alumina phases are usually prepared by ion exchange from Naβ"-alumina precusor[6]. However, reports of a direct synthesis of Caβ" -alumina from consituent oxide powder mixtures have been appeared in the literature[8,9] but, according to recent publications[10,11], Caβ"-alumina seems not thermally stable above ~1273 K and only magnetoplumbite and spinel($MgO \cdot Al_2O_3$) phases were observed[11] when oxides or nitrates mixtures were reacted at high temperatures(1673 - 1923 K). This result agrees with the older publication[7].

In the present study, mixtures having different $CaO:Al_2O_3:MgO$ ratio were reacted between 1873 and 1973K. The X-ray diffraction patterns of the reaction products are given in Figure 3 and Table 1 shows the phase compositions and relative densities data. When no MgO was present, only magnetoplumbite phase was observed. As MgO content increased, the spinel phase started to form, but too high MgO content resulted in the formation of both the spinel and $CaO \cdot 2Al_2O_3$ phases. No Caβ" -alumina phase was observed in the present experiment and this result is consistent with that of others[7,10,11]. However, observed relative intensities of strong peaks of the magnetoplumbite phase formed when MgO is present were not quite same as those of the single phase magnetoplumbite which agree well with the published data[12]. Some unknown peaks also observed when the MgO mix ratio is higher than 0.4 mole. Although it is not clear at present whether some MgO actually dissolved into the magnetoplumbite phase and distorted its crystal structure to form a "distorted magnetoplumbite" phase[7,13] or not, the phase formed from the $CaO:6Al_2O_3:0.4MgO$ mixture was indirectly proved to be useful Ca^{2+} ion conductor at high temperatures as indicated below. More detailed study on the ionic conductivity and transference number of this electrolyte at high temperatures is in progress and would be the subject of future publication.

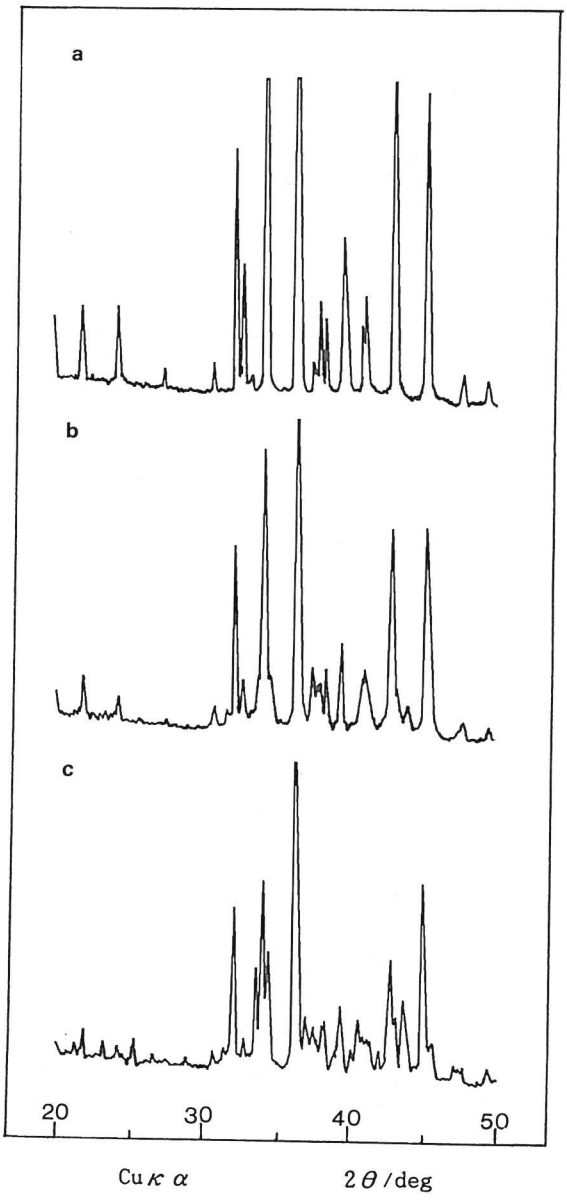

Figure 3 XRD patterns of $CaO \cdot 6Al_2O_3 \cdot xMgO$
a) $CaO \cdot 6Al_2O_3$, b)$CaO \cdot 6Al_2O_3 \cdot 0.4MgO$ and
c) $CaO \cdot 6Al_2O_3 \cdot 0.7MgO$

4.2 EMF of phosphorus sensor

Figure 4. represents a typical reading of the phosphorus sensor in the Fe-C-P melt at 1463 K. The average time for the sensors to reach a stable EMF value is about 2 minutes. The theoretical EMF of the phosphorus sensor is given as:

$$EMF = \frac{R \cdot T}{2 \cdot F} \ln \frac{a_{Ca(ref)}}{a_{Ca<Ca_3(PO_4)_2>}} \qquad (4)$$

where R is gas constant, T is absolute temperature and F is Faraday constant. As the activity of oxygen in the carbon saturated iron melt is almost fixed, the product of calcium and phosphorus

Table 1. The phase compositions of the reaction products at 1873 K and relative densities of sintered pellets: MP = magnetoplumbite, tr. = trace, CA_2 = $CaO \cdot 2Al_2O_3$

	phase composition	relative density
$CaO \cdot 6Al_2O_3$	MP	94%
$CaO \cdot 6Al_2O_3 \cdot 0.2MgO$	MP + tr. spinel	93%
$CaO \cdot 6Al_2O_3 \cdot 0.4MgO$	MP + tr. spinel	93%
$CaO \cdot 6Al_2O_3 \cdot 0.7MgO$	MP + Spinel + tr. CA_2	93%

activities is also fixed at a given temperature according to the equation (3). Therefore, there should be a linear relationship between the EMF and ln a_P. If the phosphorus content in the melt is low enough to apply Henry's law, the activity of phosphorus is proportional to the mole fraction of phosphorus and, therefore, there should again be a linear correlation between the EMF and the log [%P]. A plot of EMF vs log %[P] in the Fe-C-P melt is given in Figure 5, which shows a reasonably good linearity between the EMF and phosphorus content in the melt.

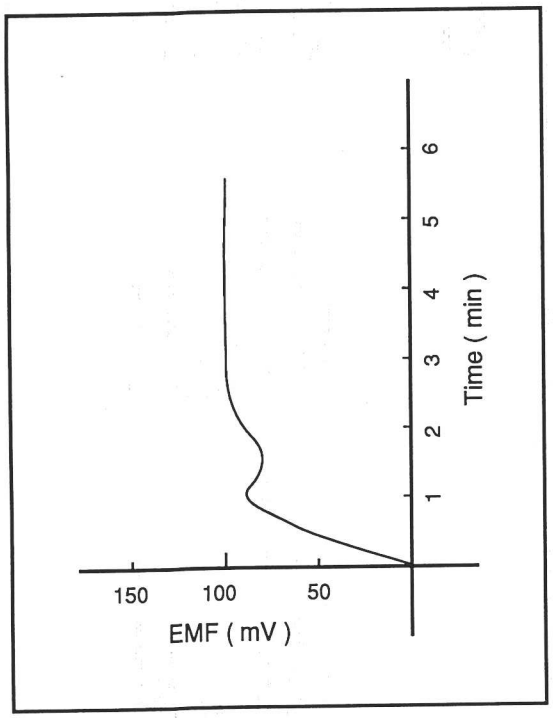

Figure 4. A typical EMF reading of the phosphorus sensor in Fe-C-P melt

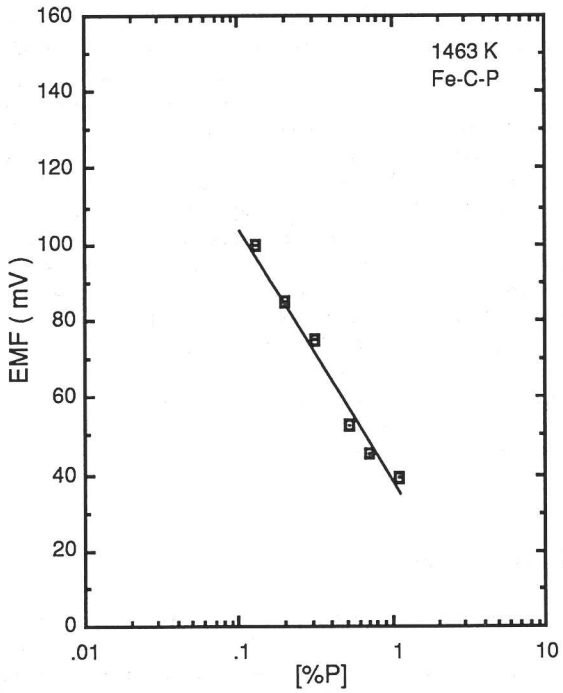

Figure 5. EMF-log[%P] relationship in Fe-C-P melt

5. Conclusion

A high temperature solid state galvanic cell utilizing MgO-doped calcium hexa-aluminate solid electrolyte with calcium orthophosphate as an auxiliary electrode was developed as a phosphorus sensor. This sensor was tested in the Fe-C-P melt having the phosphorus content between 0.1 and 1

wt.% phosphorus. A clear correlationship between EMF of the sensor and the phosphorus content of the melt was obtained. Further experimental work to prove the reproducibility of the phosphorus sensor is in progress.

6. References

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