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Solid-State Electrochemical Sensor For Monitoring Mg In Al Refining Process

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Novel solid-state electrochemical sensors have been designed using the Mg^{2+} cation conductors incorporating novel solid-state reference electrodes for in-line monitoring of Mg in molten Al during the refining process and also for in-line monitoring of Mg content in molten Al in the alloying process. In this paper we report the preparation of Mg^{2+} ion conductors, $MgAl_2O_4$ and $MgZr_4(PO_4)_6$, by the solid state ceramic synthesis route, measurement of their electrical properties using ac-impedance spectroscopy and application of the above cation conductors for designing novel electrochemical sensors for monitoring Mg dissolved in molten Al. The activation energy for Mg^{2+} ion conduction in $MgAl_2O_4$ is 2.08 eV and in $MgZr_4(PO_4)_6$ is 1.7 eV, respectively. The sensors have been found to respond rapidly to change in Mg content in molten aluminium around 1000 K.

Introduction

High purity secondary aluminium production requires removal of impurity metals such as lithium (Li) and magnesium (Mg) from aluminium (Al) scrap by chlorination process whereas alloying operations require controlled addition of the light metals such as Li and Mg in molten Al. In either case the process needs to be monitored continuously in order to improve the process efficiency and minimise environmental pollution due to fugitive gases and excessive dross. Therefore, availability of reliable and robust solid-state sensors for in-line monitoring of lithium and magnesium in molten aluminium at elevated temperatures between 950 – 1000 K is important for the aluminium industry. It is clear that if the sensors are developed for continuous in situ measurement of the concentration of dissolved elements then the metallurgical industries would benefit as a result of increased through-put, lower dross production, lower refractory consumption, lower energy losses, lower environmental pollution, greater automation, better product quality, lower consumption of refining agents and many more. In view of the high temperatures involved in aluminium refining and alloying processes, ion-conducting ceramics having high fracture toughness and greater thermodynamic stability in reducing conditions will become increasingly important.

Several attempts have been made in recent past for the development of electrochemical sensors for sensing Mg in molten Al. Tiwari and Howie (1), Belton and Rao (2), Tsyplakove and Strelets (3) used molten $MgCl_2$, a Mg^{2+} ion conductor, as an electrolyte for sensing Mg in molten aluminium and to deduce the thermodynamic properties of dilute Al-Mg liquid alloys containing less than 0.15 atomic fraction Mg. Larose et al (4) used 1 to 2 wt.% MgO stabilised Na-β"-Al_2O_3, a Na^+ ion conductor, as a solid electrolyte to sense Mg in molten Al. Fergus and coworkers (5,6) used MgF_2, a F^- ion conductor, as a solid electrolyte for sensing Mg in molten Al. More recently, Zhang and Fray (7) used immobilised $MgCl_2$ in porous MgO thimble as an electrolyte for sensing Mg in molten Al. In all the above investigations, the principle of sensing Mg in molten Al is based on indirect measurement when solid electrolyte is used for designing the Mg-sensor (4-7). Sensing mechanisms for different types of electrolytes are discussed in details elsewhere (8). It is clear that none of the above measurements involve the application of a solid Mg^{2+} ion conductor as an electrolyte in the Mg-sensor.

Therefore in this paper we report the design of novel Mg sensors using $MgAl_2O_4$ and $MgZr_4(PO_4)_6$ as Mg^{2+} ion conducting electrolytes and testing them in molten Al. Novel solid-state reference electrodes used for Mg sensor are a biphasic mixture consisting of $MgFe_2O_4 + Fe_2O_3$ and $MgCr_2O_4 + Cr_2O_3$.

Theory

There are three important components of a solid-state electrochemical sensor that is operated in a potentiometric mode. The heart of the system is the solid electrolyte, which should be carefully selected in order to sense selectively the desired species in molten metal. The choice of solid electrolytes is wider for applications at low temperatures however, the choice becomes progressively limited as the temperature of application increases, particularly in molten metals. This is mainly because of the corrosive nature of most of the molten metals, low oxygen potentials prevailing in the molten metals and rapid kinetics of undesired chemical reactions between the solid electrolyte and either the reference electrode material or the working electrode material such as molten metal that deteriorate the mechanical, chemical and electrical properties of the solid electrolyte.

Schematically, the solid-state sensor for measuring Mg in molten Al tested in this investigation can be written as:

$$M, \mu_{Mg}^{II} \| SolidElectrolyte[Mg] \| \mu_{Mg}^{I}, M \qquad [1]$$

The operating principle of a potentiometric sensor is relatively simple. In a potentiometric sensor, an open circuit voltage generated across the solid electrolyte is given by the Nernst expression,

$$E = -\frac{1}{nF} \int_{\mu_{ion}^{I}}^{\mu_{ion}^{II}} t_{ion} \, d\mu_{ion} \qquad [2]$$

which is a measure of the chemical potential gradient of the conducting species across the solid electrolyte.

In Eq. [2], E is the measured open circuit voltage in V, R is the universal gas constant in J mol^{-1} K^{-1}, T is the measured temperature in K, n is the number of electrons participating in the electrode reaction, F is the Faraday constant in Coulombs mol^{-1}, t_{ion} is the transport number of the conducting species, usually close to unity, and μ_{ion} is the chemical potential of the conducting species defined as $RTlna_{ion}$, where a_{ion} is the thermodynamic activity of the conducting species. A schematic diagram of the sensor assembly capable of measuring Mg dissolved in molten aluminium at elevated temperature and the configuration of the measuring and recording equipment is shown in Fig. 1. A potentiometric sensor relies on the Nernst equation that relates the measured open circuit voltage or the electromotive force (emf) logarithmically to the concentration of the dissolved impurity or alloying element in molten metal at a fixed temperature. As a result of this logarithmic relationship, a potentiometric sensor is more likely to be accurate and faster analytical tool in the dilute concentration region compared to most of the other analytical tools currently used in the metallurgical industry worldwide.

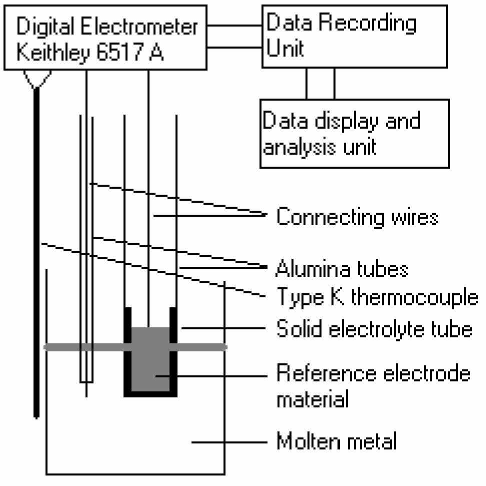

Fig. 1. Schematic diagram of the experimental set-up

The skill in designing a solid-state sensor, for monitoring either metallic or non-metallic impurities dissolved in molten metal, lies in making an appropriate choice of a solid electrolyte and reference electrode system from the already known ceramic electrolytes or synthesising a new solid electrolyte.

Experimental Procedure

Materials Synthesis

High purity (≥ 99.99%) fine powder of binary metal oxides, anhydrous metal carbonates and anhydrous ammonium di-hydrogen phosphate was obtained from Aldrich (Gillingham, UK). The solid electrolyte materials such as $MgAl_2O_4$ and $MgZr_4(PO_4)_6$ have been synthesised by the solid-state ceramic route at elevated temperatures from the precursor powders that were mixed in appropriate molar ratios. The precursor powders were mixed under acetone using a high-energy ball mill for a period of 30 minutes. The powders were contained inside a high-density alumina ball mill. High-density alumina balls were used as the milling media for mixing the precursor powders. The mixed powders were calcined prior to firing at high temperatures for the formation of single phase. Complete formation of single phase solid electrolyte materials was confirmed by the powder X-ray diffraction using Ni-filtered Cu-Kα radiation. Compounds such as $MgFe_2O_4$ and $MgCr_2O_4$ used in the reference electrode phase assemblages for Mg sensor were synthesised from the precursor powders following an identical procedure that has been described above. Formation of each of the single-phase compound was confirmed by powder X-ray diffraction analysis.

Measurement and Testing

It is important to not only characterise the solid electrolyte for the formation of single phase but also equally important to determine it's ionic conductivity and ionic transport properties in order to confirm it's suitability as a solid electrolyte for developing a solid state sensor. Therefore, two types of measurements have been performed during the course of the present investigation. The first one being the measurement of the cationic conductivity as a function of temperature of the solid electrolyte materials that will be used in designing the Mg sensors and the second one being the testing of the response of Mg sensor to change in concentration of Mg in molten aluminium around 1000 K.

Pellets of 10 mm diameter and 5 mm thickness, and one end closed tubes of 25 mm length, 1.5 mm wall thickness and 3 mm internal diameter were prepared by pressing the fine powder of $MgAl_2O_4$ and $MgZr_4(PO_4)_6$ at 200 MPa in a cold iso-static press. The pellets and one end closed tubes of different materials were then sintered separately at appropriate temperatures to form high density impervious compacts. The two flat surfaces of the high density pellet of different materials were polished and coated by a thin conducting layer of platinum paint (Englehardt type A4731). Pellets coated with platinum paint were then treated at 1073 K to burn out the polymeric binder and platinise the surfaces of the pellets. The ionic conductivity of each solid electrolyte pellet was measured as a function of temperature and frequency by a two-probe technique employing a computer controlled Solartron SI 1260 impedance/gain-phase analyser. During the conductivity measurement, each pellet was spring loaded using a quartz apparatus similar to that described elsewhere (9).

The general assembly for testing Mg sensor is shown in Fig. 1. Firstly, an appropriate reference electrode mixture was compacted inside the sintered high density solid electrolyte tube conducting Mg cation with Pt-lead embedded in the mixture for electrical contact. The reference electrode material used in the Mg sensor constituted of an intimate two-phase mixture of either $MgCr_2O_4+Cr_2O_3$ or $MgFe_2O_4+Fe_2O_3$. The solid electrolyte tube containing the reference electrode mixture and the connecting lead was attached to a 50 cm long recrystallised alumina tube using refractory cement as shown in Fig. 1. The counter electrode lead was sheathed inside a tightly fitting recrystallised alumina sleeve that was sealed with the refractory cement at the bottom end. Magnesium sensors were tested in approximately 1000 g of molten aluminium containing varying amounts of either magnesium. The concentration of Mg in Al varied between 0.04 wt% to 6.31 wt% during the testing of Mg sensors in the laboratory environment. The alloys were melted in a high-density alumina crucible using a non-inductive top loading Lenton furnace. During the experiment, high purity argon was flown over the molten metal to prevent oxidation and the temperature of the melt was recorded by a K-type thermocouple placed adjacent to the crucible containing the melt. The emf of the sensor and the thermocouple was continuously recorded by computer controlled multi-channel high impedance ($\geq 10^{13}$ Ω) Keithley 6517A digital electrometer. At the time when a stable emf of the sensor was recorded, a sample from the melt was drawn in a silica tube having an internal diameter of 2 mm. The Mg concentration at each time in the melt was determined by an Atomic Absorption Analysis of the samples using a computer controlled Varian Spectra AA10 spectrometer following a standard procedure (10).

Results

The variation of the ionic conductivity because of the migration of Mg^{2+} cations in $MgAl_2O_4$ spinel between 800 to 1333 K is shown in Fig. 2. The conductivity of $MgAl_2O_4$ was calculated by plotting the frequency dependence of impedance in a complex plane with real part of the impedance as abscissa and imaginary part of the impedance as ordinate. Similarly, the Mg^{2+} cation conductivity of $MgZr_4(PO_4)_6$ has been measured between 900 to 1175 K. The temperature dependence of the ionic conductivity of $MgZr_4(PO_4)_6$ is shown in Fig. 3.

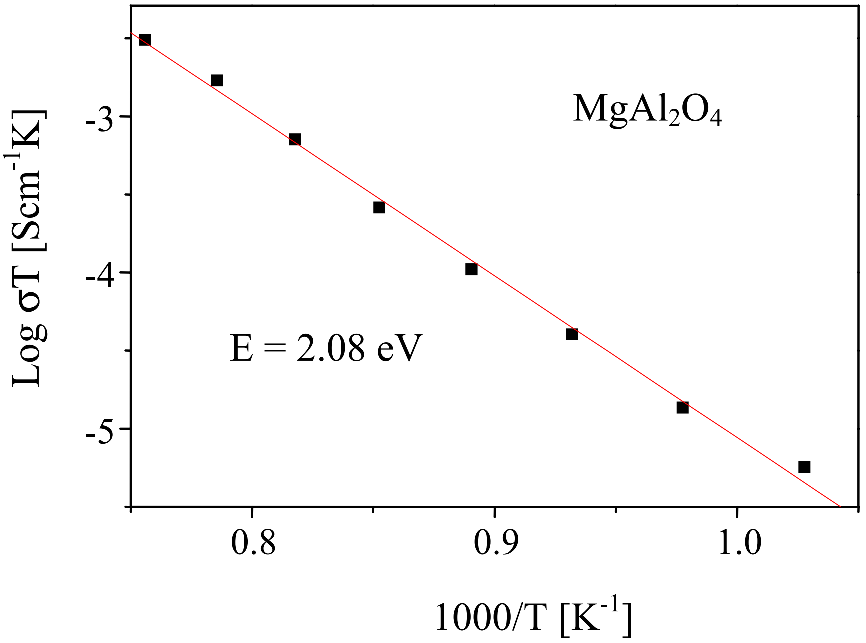

Figure 2. Temperature dependence of ionic conductivity of $MgAl_2O_4$

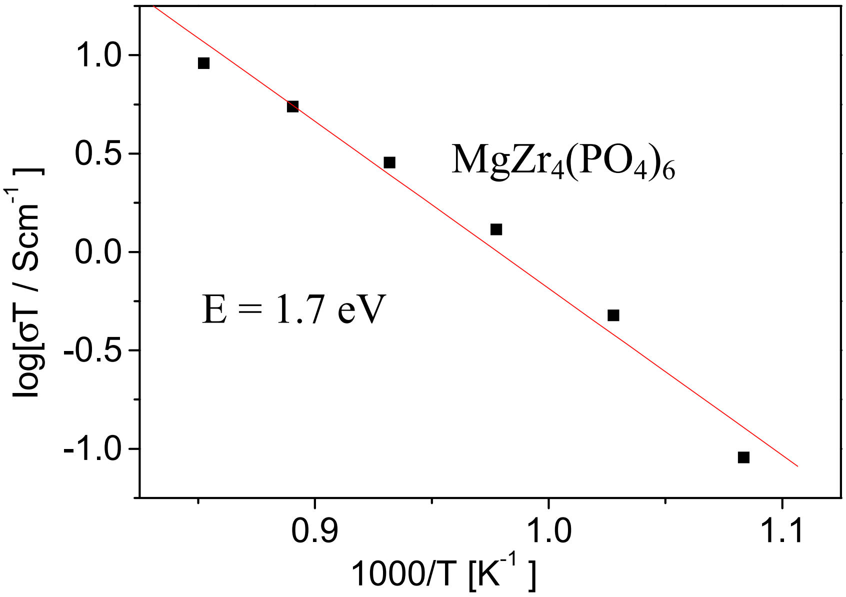

Figure 3. Variation of ionic conductivity of $MgZr_4(PO_4)_6$ with temperature

Solid-state sensors for measuring Mg in molten aluminium were fabricated as described in the earlier section and tested in the laboratory in 1000 g of molten metal at around 1000 K. The sensors for measuring Mg dissolved in molten aluminium were fabricated using $MgAl_2O_4$ or $MgZr_4(PO_4)_6$ as the solid electrolyte and $MgCr_2O_4$+Cr_2O_3 or $MgFe_2O_4$+Fe_2O_3 as the reference electrode. The response of the two Mg-sensors to change in the concentration of magnesium in molten aluminium is shown in Fig. 4. The two different traces are due to the two Mg-sensors, each incorporating $MgFe_2O_4$+Fe_2O_3 (series 1) and $MgCr_2O_4$+Cr_2O_3 (series 2) as the reference electrode, tested simultaneously in the same melt at 963 K using $MgZr_4(PO_4)_6$ as a Mg^{2+} cation conducting solid electrolyte. An identical test of Mg-sensor was conducted at 963 K using $MgAl_2O_4$ as a Mg^{2+} ion conducting solid electrolyte and the results of this test are shown in Fig. 5. In this measurement, series 1 corresponds to $MgFe_2O_4$+Fe_2O_3 as the reference electrode and series 2 corresponds to $MgCr_2O_4$+Cr_2O_3 as a reference electrode.

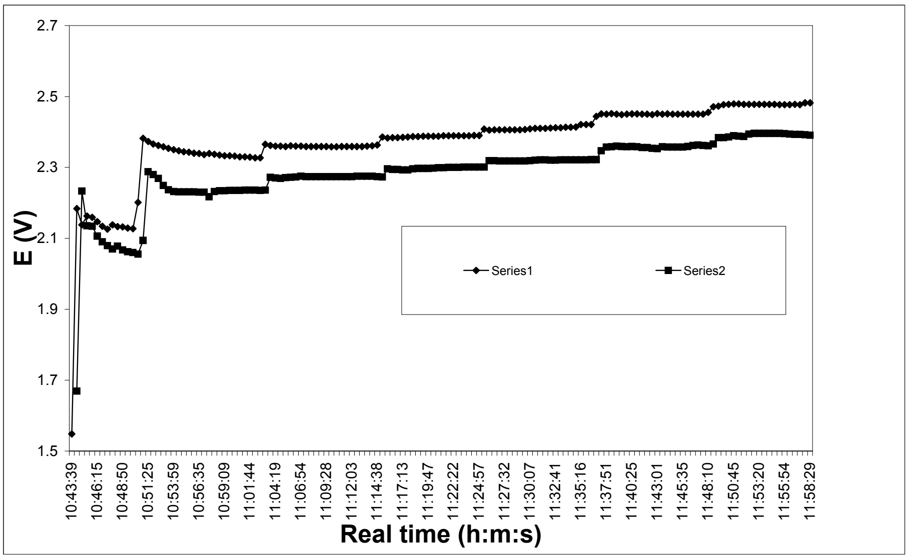

Figure 4. Response of Mg-sensor in Al(l) at 963 K using $MgZr_4(PO_4)_6$ solid electrolyte

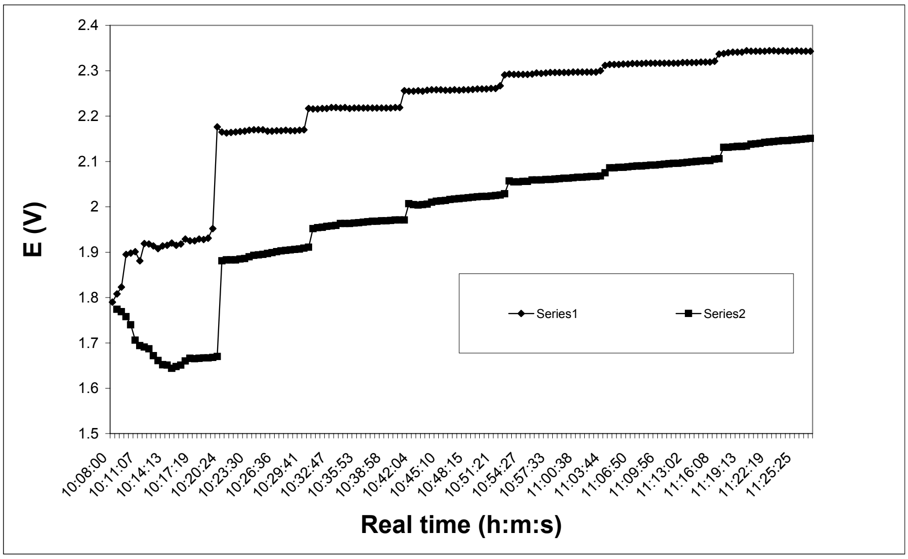

Figure 5. Response of Mg-sensor in Al(l) at 963 K using $MgAl_2O_4$ solid electrolyte

Discussion

Most of the aluminium processing, refining, alloying and casting takes place at around 1000 K therefore the application of sensors in aluminium industry is likely to be around this temperature. Therefore, it is important that the cationic conductivity of the potential solid electrolyte materials used for the development of solid state sensors for aluminium industry should be at least greater than 10^{-4} S cm^{-1} at around 1000 K. The results shown in Fig. 2 suggests that the Mg^{2+} ion conductivity of $MgAl_2O_4$ is 10^{-4} S cm^{-1} whereas the results shown in Fig. 3 suggests that the Mg^{2+} ion conductivity of $MgZr_4(PO_4)_6$ is greater than 10^{-1} S cm^{-1} at 1000 K. Further, the activation energy for ionic migration, calculated from the Arrhenius plot of $\log_{10}(\sigma T)$ against $1000T^{-1}$, for $MgAl_2O_4$, and $MgZr_4(PO_4)_6$ has been found to be 2.08 eV and 1.7 eV, respectively. Therefore, based on only their ion conducting properties, the materials synthesised in this investigation have significant potential for using as a solid electrolyte for the development of solid state sensors for on-line monitoring of dissolved Mg in molten aluminium. The chemical potential of oxygen in molten aluminium and its alloys containing Mg could be as low as 10^{-43} Pa at 1000 K. Most of the oxides are not likely to be stable at such low oxygen potential and at elevated temperature. Therefore, it is important to know whether the solid electrolyte materials used in designing solid-state sensors will be stable enough to warrant their use as a solid electrolyte. There is no information in the literature on thermodynamics of formation of $MgZr_4(PO_4)_6$ and also the phase relations in the oxide systems consisting this compounds is not available. Gibbs energy of formation of $MgAl_2O_4$ measured recently by Jacob et al (11) suggests that the spinel compound will be stable at the extremely low oxygen potentials prevailing in molten aluminium and it's alloys at 1000 K. Therefore, instead of determining the thermodynamic stability of $MgAl_2O_4$ and $MgZr_4(PO_4)_6$ solid electrolyte materials, it was decided to fabricate the Mg sensors using the above electrolytes and observe the response of the sensors as a function of time and concentration of Mg in molten aluminium at around 1000 K. The signature of the chemical instability of the solid electrolyte material can be easily identified from the plot of emf versus time. The emf as a function of time of the Mg sensor incorporating $MgZr_4(PO_4)_6$ and $MgAl_2O_4$ as a solid electrolyte is shown in Fig. 4 and 5, respectively. It can be clearly seen that the change in emf of the sensors, because of change in concentration of Mg in molten aluminium, has been found to vary systematically as a function of time. Further, no drift in sensor emf was observed with time during the experiments and the emf attained stable values rapidly at each concentration of Mg. This suggests that both the solid electrolyte materials are chemically stable in molten Al-Mg alloys at around 1000 K. The variation of the emf of Mg sensors using two different electrolytes is shown in Fig. 6 and Fig. 7, respectively. It can be seen that the emf of Mg sensors vary linearly as a function of the concentration of Mg in molten aluminium, respectively. This is in accordance with Eq. [2].

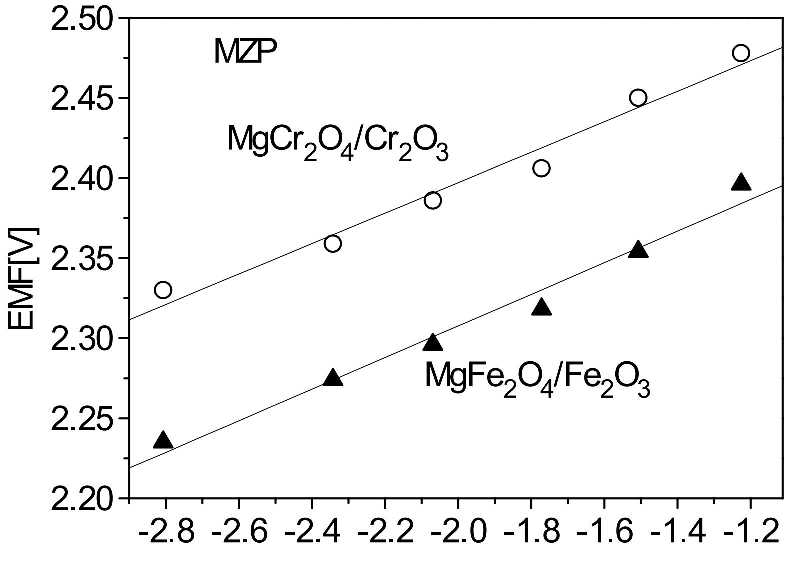

Figure 6. Variation of the emf of Mg sensor as a function of concentration of Mg in Al (l) at 963 K using $MgZr_4(PO_4)_6$ solid electrolyte and different reference electrodes

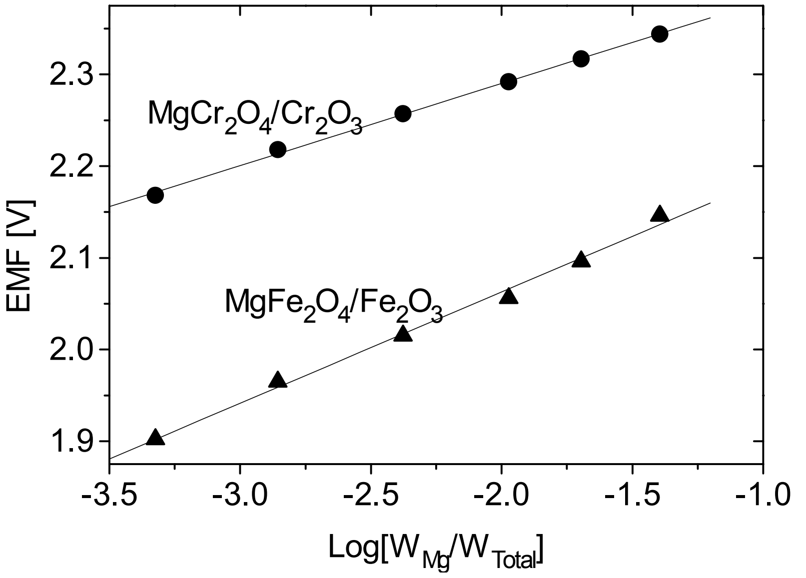

Figure 7. Dependence of the emf of Mg sensor as a function of concentration of Mg in molten Al at 963 K using $MgAl_2O_4$ solid electrolyte and different reference electrodes

Conclusions

Solid state sensors for continuous in-line monitoring of Mg in molten aluminium alloys at around 1000 K have been successfully tested in the laboratory. Novel solid electrolytes and novel reference electrodes for Mg sensors have been developed and have been shown to perform well in molten aluminium at around 1000 K. The duration of measurement in molten aluminium varied from 60 to 90 minutes. Results obtained in the present investigation strongly indicate that, with appropriate packaging of sensor components, the prototypes of Mg sensors can be easily manufactured to suit the industrial processes. Based on the laboratory tests of the electrochemical sensors for measuring magnesium in molten aluminium, it can be concluded that the sensors using chromium-based as well as iron-based reference electrodes exhibit rapid and stable response to change in concentration of Mg in the molten aluminium. A prototype industrial probe (12) has been designed and tested successfully during the plant trials in the Al refining and alloying plants in the United Kingdom.

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