A novel electrochemical analyser for hydrogen determination in aluminium melts

Introduction and Background

Hydrogen is the main non-metallic impurity in molten aluminium and aluminium alloys. Its presence in the melt originates from the high affinity of molten aluminium to react with moisture in the air to form dross from the oxide and hydrogen in the melt. As liquid aluminium has a much larger solubility for hydrogen than solid aluminium, hydrogen is released from the melt on cooling, creating pores and holes in the solid. This deteriorates the quality of the cast aluminium. Degassing of aluminium melts prior to casting is often mandatory for the production of high quality cast aluminium. However, degassing is an energy intensive and costly process. Precise knowledge of the hydrogen content in the melt before and during degassing is therefore highly desirable in the processing of aluminium.

Most of the conventional techniques for the determination of hydrogen in molten aluminium and its alloys are fairly empirical. For instance, the reduced pressure (Straube-Pfeiffer) test or the initial bubble test are based on the visual analysis of gas bubbles. These methods do not require sophisticated equipment, but they are qualitative rather than quantitative and also retrospective in nature. Over the last decades, the Alscan test has become the standard technique for hydrogen determination in molten aluminium. In this method a stream of an inert gas is recirculated through the melt in order to equilibrate with the dissolved hydrogen. After passing through the melt, the gas is analysed for hydrogen by means of a thermal conductivity cell. This method is accepted to yield reliable quantitative results, but the equipment is expensive. Particular drawbacks are that the immersed ceramic probe is fragile and has a limited lifetime and, particularly in the presence of high vapour pressure elements like zinc, magnesium and lithium, tends to plug.

Analysis techniques for solid aluminium samples are more direct and accurate than those for molten samples. Most of these methods rely on hydrogen extraction. Depending on temperature and desorption technique applied, these are classified as the vacuum fusion technique, the nitrogen carrier fusion technique, and the vacuum subfusion (Ransley) technique. Refinement of the latter technique has led to high levels of accuracy, which makes it a recognised standard against which other methods are calibrated. Drawbacks of these techniques are the requirement to adhere to strict procedures for sample preparation and handling, the long analysis time, and the sophisticated equipment needed. This excludes these methods from being applied routinely on foundry shop floors.

Considering the particular disadvantages of the techniques mentioned above, it may be supposed that the utilisation of electrochemical sensors is a favourable and viable alternative for hydrogen determination in aluminium melts. Electrochemical sensors should have the potential to provide quantitative and rapid in-situ measurements at moderate costs. This article presents a novel electrochemical hydrogen analyser for use in molten aluminium and its alloys. The probe relies on a solid state hydrogen sensor with an internal hydrogen reference.

The Novel Hydrogen Analyser

The novel analyser for hydrogen determination in molten aluminium and aluminium alloys comprises two entities, the actual electrochemical sensor as well as an assembly to protect the sensor from the melt and allow for gas exchange with the melt.

The sensor consists of a gas tight cap-shaped proton conducting solid electrolyte, a measuring and a reference electrode. For the present application, calcium zirconate partially substituted with indium oxide $CaZr_{0.9}In_{0.1}O_{3-\delta}$ was selected as the solid electrolyte. Under reducing conditions, this material functions as a virtually pure proton conductor. It also provides good mechanical and thermal stability. The outer and the inner surface of the electrolyte body are covered with thin porous platinum layers that form the measuring electrode and the reference electrode, respectively. These are contacted with platinum

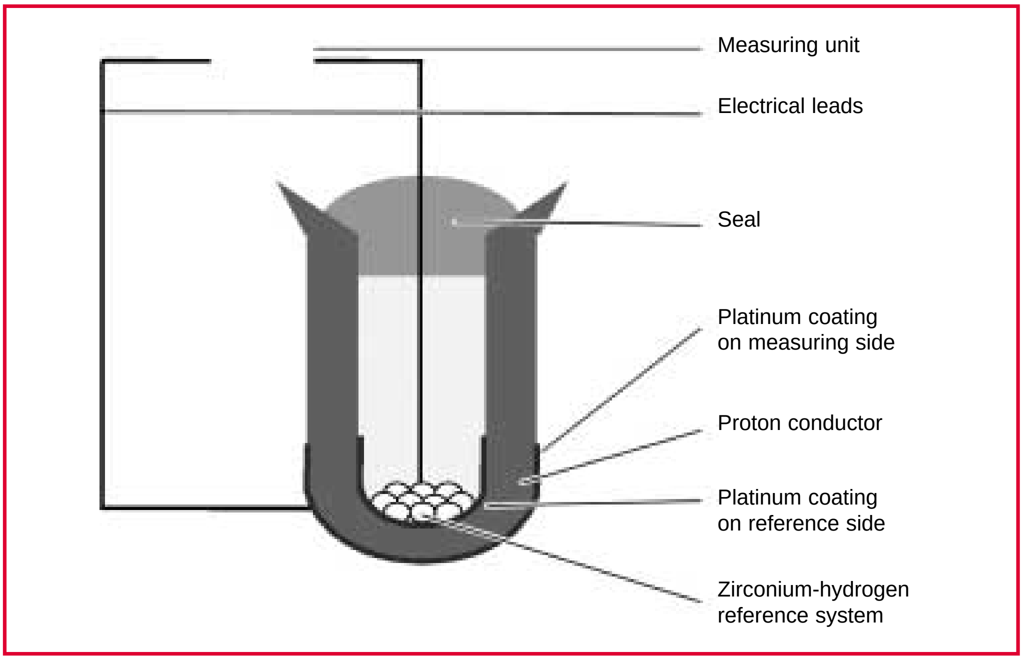

Figure 1: Schematic of the solid state electrochemical hydrogen sensor

wires leading to the terminals of an electronic unit. The measuring electrode is exposed to the medium to be analysed, and the reference electrode is in contact with an encapsulated solid zirconium/hydrogen mixture providing a known hydrogen partial pressure. A schematic drawing of the sensor is presented in Figure 1.

A number of engineering issues must be considered when designing an accurate and durable probe for application in molten aluminium. Materials exposed directly to the melt must not react with molten aluminium, and materials exposed to the measuring gas must be stable under high hydrogen partial pressures. Good contact is required between the probe and molten aluminium in order to prevent formation of a dross layer which will interfere with the hydrogen transfer between the melt and the probe. In order to meet these requirements, the following probe assembly was developed.

The hydrogen sensor is mounted onto an alumina support lance which is placed inside a specially designed graphite sheath. Graphite is a commonly used and accepted material in the aluminium industry. It does not react with molten aluminium, has excellent thermal shock resistance and is a good electronic conductor, screening the sensor from electrical noise when earthed. Measurements are recorded using a customised electronic unit that displays a continuous reading of the dissolved hydrogen content and temperature.

The approximate dimensions of the probe are 50 cm in length and 2.5 cm in diameter. Due to the materials involved, the maximum application temperature of the probe is limited to around 750°C, a photograph of the probe and the electronic unit is shown in Figure 2.

Figure 2: Photograph of the probe and electronic unit

Laboratory measurements

The development and investigation of the solid state electrochemical hydrogen sensor including a solid state hydrogen reference has been the subject of an extensive research study. This ensures good reproducibility and a fair degree of maturity regarding sensor preparation and application. Laboratory tests, involving measurements in hydrogen containing gases, revealed that the deviations between different sensors are minor and not critical for the application envisaged.

The sensors were assembled into probes for use in molten aluminium. Measurements were done in aluminium melts under laboratory conditions between 670 to 750°C. Immediately after the probe was immersed in the melt, unrealistically low dissolved hydrogen contents in the melt were displayed. However, by agitating the probe for several minutes, realistic readings were obtained. Measurements of dissolved hydrogen ranged from 0.23 to 0.34 ml/100g over a period of several hours. Since no further analysis technique was applied, no statement concerning accuracy may be made, but the readings taken were well inside the expected range, indicating that the probes were working successfully.

Field trials

Prototypes of the newly developed analyser were then investigated in two field trials.

Field trial 1

The trial was carried out at a commercial aluminium foundry. Figure 3 shows a comparison of the results obtained with the novel analyser and an Alscan analyser. There is good agreement between the results obtained by both analysers for different hydrogen levels in the melt, with the new analyser reading on average 10% lower than the Alscan unit.

To investigate the response behaviour of the novel analyser, hydrogen levels were increased by adding DYCASTAL tablets and reduced by an MDU rotary degassing unit. The probe was found to respond almost instantaneously. Moreover, reasonable readings could be obtained from the probe whilst the degassing process was being carried out, which is not possible with the fragile Alscan probe. Figure 4 shows how the analyser recorded the degassing process. After 6 min the dissolved hydrogen reading reached a minimum value of approximately 0.07 ml/100g.

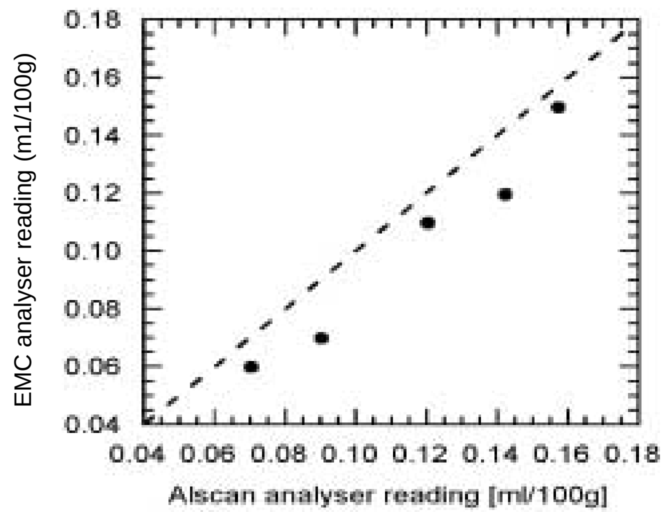

Figure 3: Comparison of hydrogen measurements in molten aluminium using the novel analyser and an Alscan analyser

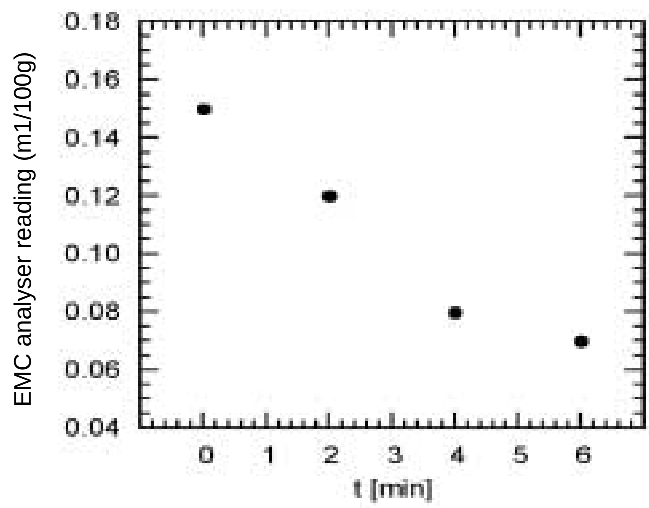

Figure 4: Degassing process of molten aluminium as recorded by the novel analyser

Field trial 2

A further trial was carried out at Birmingham University, using LM6 in a 400 kg electrically heated furnace. The tests involved increasing gas levels by plunging DYCASTAL tablets and lance degassing, similar to field trial 1, but with better control over conditions. An Alscan unit was available as a comparison, and two LECO samples were taken as references each time. Results obtained with the three different hydrogen measurement techniques are compiled in Table 1.

Sample	Comment	Alscan probe (ppm)	FOSECO probe (ppm)	LECO (ppm)	LECO (mean ppm)
1	First comparitive reading	0.216	0.17	0.163...0.208	0.186
2	Comparative reading after several hours	0.181	0.17	0.186...0.176	0.181
3	Melt gassed up using gassing tablets	0.318	0.32	0.300...0.294	0.297
4	Degassing lance inserted - Hydrogen content rose to high levels	0.570	0.28	0.542...0.484	0.513
5	3 h after degassing commenced	0.139	0.15	0.194...0.104	0.149
6	-10 min after taking sample 5 - Agitation of the melt around the FOSECO probe at this point produced a reading of 0.28 ppm	0.124	0.16	0.196...0.279	0.238
7	The Foseco probe used here used a different material for the porous plug	0.140	0.28	0.281...0.216	0.249

Table 1: Comparison of hydrogen measurements in molten LM6 obtained with three different techniques.

In general, agreement of the results is satisfactory. However, there are obvious disparities in a few cases, i.e., 1, 4, and 7, where two of the methods are in agreement and the third is not. There is also a surprising amount of variation in some of the LECO tests. Whilst the results are encouraging, it is thought that the experiment should be repeated, taking more LECO samples to give a better comparison. Also at that time, alternative materials for the probe sheath will be tested, which should allow faster attainment of equilibrium and increased reliability.

Discussion

The results achieved during the field trials show that the novel electrochemical hydrogen analyser is capable of performing quantitative in-situ measurements of hydrogen in aluminium melts under industrial conditions. Readings were reproducible and could be taken a few minutes after immersing the probe. It would appear that the analyser might have read slightly too low, the reasons for this are currently being investigated. The most extensively tested probe survived numerous dips and an overall dwell time in the melt of around 20 h.

Particular advantages of the new analyser are ease of fabrication and simple application, as well as on-line use and fast response. Successful field trials demonstrated the potential of the device for industrial application.

Addendum

This article is an abridged and modified version of a conference paper, presented at the 6th International Conference on Molten Aluminium Processing, November 11-13, 2001, Orlando, Florida, USA.