Foundry experiences with a new electrochemical sensor for determining hydrogen concentrations in aluminium alloys

As the use of aluminium castings has grown to encompass more and more critical applications, so has the need for higher quality requirements in the finished casting.

Introduction

The fundamental prerequisite for a quality casting is to establish the optimum quality of the molten alloy before the casting process. Much effort has recently gone into the development of improved metal treatments practices to improve metal quality.

However, with the demands of today's end user of castings, particularly the automotive industry, having good metal treatment practices alone is no longer sufficient. The control and consistent application of these treatments is also very important in order that the foundry is able to supply his customer with castings of a consistently high quality.

There are two main impurities in molten aluminium, non-metallic inclusions and dissolved hydrogen. Dissolved hydrogen is arguably the most difficult impurity to manage in the production of aluminium castings. The initial levels in the molten alloy can vary due to the type of furnace charge and atmospheric conditions, excess hydrogen can cause porosity and insufficient hydrogen can cause shrinkage in the finished casting. Often the optimum level of hydrogen in the molten alloy is specific to particular castings and production processes and is not necessarily the lowest level possible.

Many different methods of assessing or measuring hydrogen levels have been developed but to date none has been able to give the foundryman true control over the hydrogen content. A new device has now been developed that offers the possibility of measuring hydrogen concentrations in such a way that allows real process control thus improving quality and consistency of the finished casting.

The Sensor

The function of this novel sensor has been described in detail elsewhere (1). This paper will concentrate on the potential applications of this new technology in the foundry industry; however, a brief description of the main features of the sensor will be helpful.

The sensor is an electrochemical device based upon a calcium zirconate solid electrolyte. Under certain conditions calcium zirconate becomes a proton conductor allowing it's use as a sensor for hydrogen. To function as a sensor the calcium zirconate needs to encapsulate a reference material with a known partial pressure of hydrogen. When the outer surface of the sensor is then exposed to an unknown hydrogen partial pressure, a voltage is generated that when measured allows the unknown hydrogen partial pressure to be calculated.

A particular feature of this novel sensor is that it includes a solid-state reference making this sensor a very practical and self contained device that does not require an external source of hydrogen to provide the reference.

The Probe

A probe has been constructed around the sensor to carry it into the melt thus enabling the hydrogen concentration of the melt to be measured. The sensor is located in a cavity at the end of the probe; this cavity has a porous window that allows the diffusion of dissolved hydrogen but not the ingress of aluminium. A schematic of the probe section containing the sensor is given in Figure 1.

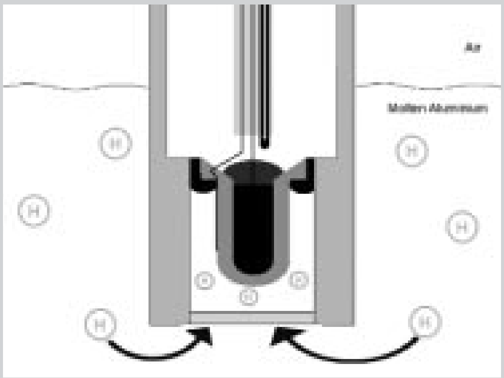

Figure 1 Schematic of the Probe Section Containing the Sensor

The partial pressure measured by the sensor in this way is the level of hydrogen in equilibrium with the melt. This equilibrium level then needs to be related to the level of dissolved hydrogen in the melt by using an equation based on Sievert's Law.

The Analyser

The third element required to enable the novel sensor to be used as a practical device is an analyser to convert the electrical output of the sensor to a read out of hydrogen concentration. The analyser processes the signal and displays the dissolved hydrogen concentration in terms of either ppm or $cm^3/100g$. The output from a thermocouple positioned adjacent to the sensor is also displayed giving a continuous read out of metal temperature.

The analyser has a built in data logger that allows both hydrogen and temperature readings to be recorded and subsequently downloaded. These data logs can be plotted to produce real time curves of hydrogen concentration with time.

Figure 2 shows the complete ALSPEK* H unit consisting of the probe, housing the sensor, and the analyser.

Figure 2 ALSPEK H Probe and Analyser

Foundry trials

To determine the operating characteristics of the new device, a FOSECO FDU* rotary degassing machine was modified to enable two different gases to be injected through the spinning rotor. A standard test cycle was then established whereby hydrogen was first introduced into the metal by injecting a commercially available hydrogen/nitrogen mixture containing 30% hydrogen. After 5 minutes gassing up the melt up with this mixture, the sparging gas was then switched to pure nitrogen and the melt degassed until the original level of hydrogen had been reached. A schematic of the experimental set up is given in Figure 3.

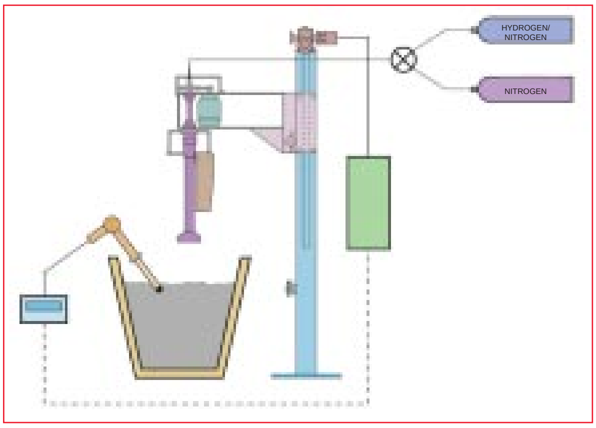

Figure 3 Schematic of Experimental Rig

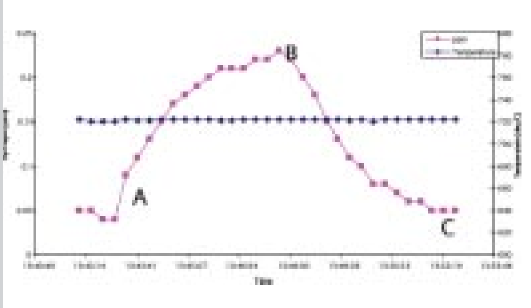

Figure 4 Typical Degassing Curve with Experimental Rig

A typical curve generated from the data points collected by the data logger is given in Figure 4. Prior to introducing the gas the probe was first placed in the melt and allowed to reach equilibrium with respect to both temperature and hydrogen concentration. At point A the FDU was introduced into the melt with the hydrogen/nitrogen gas mixture passing through the spinning rotor. Over the 5 minute gassing period the hydrogen concentration of the melt increased from 0.05 ppm to 0.23 ppm. At point B the sparging gas was switched to pure nitrogen and the degassing process begun until point C where the original hydrogen level was reached and the FDU removed from the melt.

The advantages of this system are that the hydrogen can be added at a consistent rate and to a consistent level thus allowing a standard gassing and degassing cycle to be established. With such a standardised test the comparison of probe response when varying other parameters was made much easier.

A series of experiments were then conducted to study the response of the probe over a range of metal temperatures. The results showed very similar response characteristics over the temperature range 705 to 740 °C (figures 5, 6 and 7).

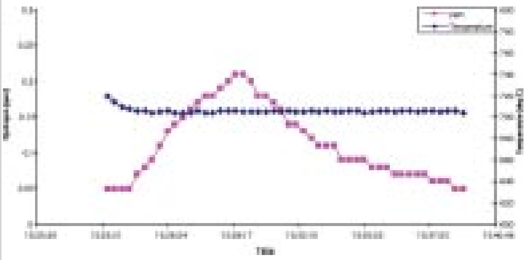

Figure 5 Probe Response at 705 °C

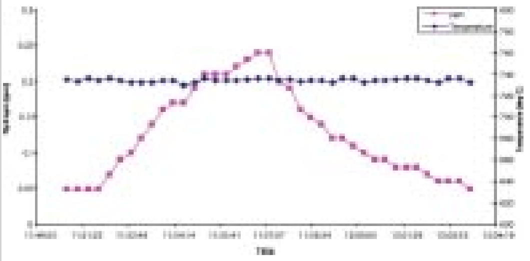

Figure 6 Probe Response at 730 °C

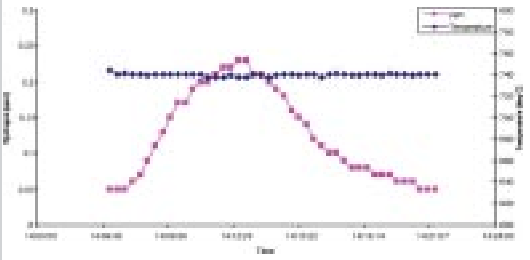

Figure 7 Probe Response at 740 °C

Trials with two different alloys, a 9% silicon and an 18% silicon alloy (figures 8 and 9) again showed very similar response characteristic for both alloy types.

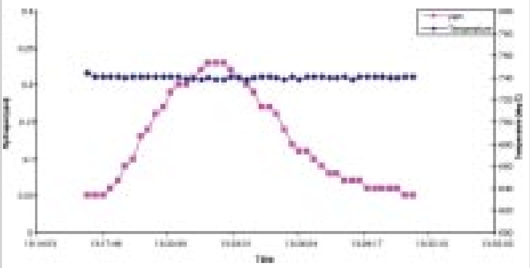

Figure 8 Probe Response with 9% silicon alloy

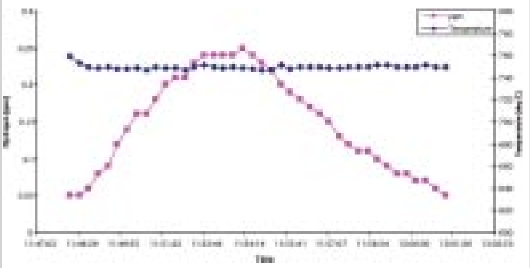

Figure 9 Probe Response with 18% silicon alloy

Both these studies on the effect of temperature and alloy are far from exhaustive and a more comprehensive series of trials is underway.

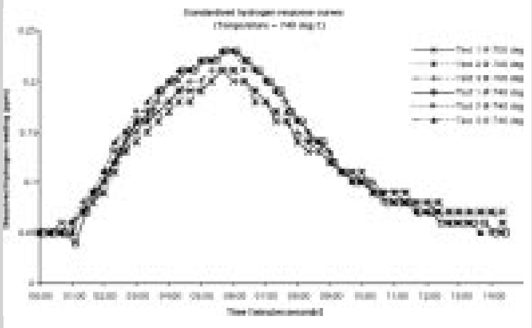

Figure 10 Consistency of Probe Response

The consistency of response was also determined by repeating several test runs under the same conditions. By superimposing the several curves carried out at the same temperature a good level of consistency can be observed (figure 10).

Accuracy of the sensor is obviously one of the most important characteristics of any method of hydrogen determination. Using the experimental degassing rig it was possible to obtain a measure of the accuracy of the new sensor. Assuming that the melt and the gas phase reach chemical equilibrium after a sufficiently long injection time of the hydrogen containing gas, the corresponding dissolved hydrogen level can be calculated as follows:

$$\log s[\text{ppmH by mass}] = C - \frac{D}{T} + \frac{1}{2}\log(pH_2)$$

In the equation above, based on Sievert's law, *s* is the amount of dissolved hydrogen, and *C* and *D* are constants dependent upon alloy composition. If the amount of hydrogen added to the melt, the alloy type and temperature are known, and then the theoretical equilibrium level can be calculated. The calculation was done for a certain set of conditions and then the experiment performed. The experimentally determined value of 0.42 ppm was in excellent agreement with the calculated value of 0.43 ppm (figure 11) and is a good indication of the level of accuracy possible with the new device.

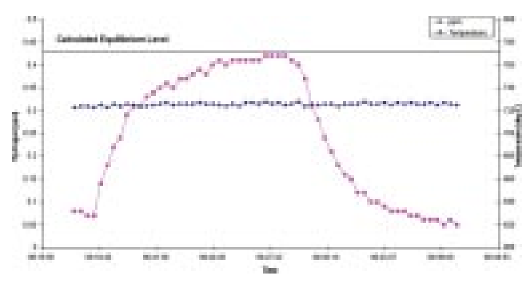

Figure 11 Accuracy of Probe Response

Comparison with other methods

Most of the commonly used techniques for the determination of hydrogen in molten aluminium in foundries tend to be qualitative rather than quantitative. The Reduced Pressure Test (RPT) is the most simple and involves solidifying a small sample of liquid metal under a vacuum. The resulting sample is then sectioned and examined for gas porosity, generally against a set of visual standards

The RPT concept has been used as the basis for improved methods such as Density Index. This method compares the density of a sample solidified in air with one solidified under vacuum. Both these methods are semi quantitative in that a number is generated that is related to hydrogen concentration but that can also be influenced for example by the level of non-metallic inclusions present.

The equipment needed for both these tests is relatively simple and the costs of performing the test relatively low. These methods are therefore used widely in the foundry industry to perform regular quality control tests. However, the results are only an indication of hydrogen concentration and can be operator sensitive.

The most sophisticated device found in foundries today is probably the Alscan hydrogen analyser. This test is based on stream of an inert gas that is continuously circulated through a porous probe immersed in the melt. Over time the level of hydrogen in the inert gas equilibrates with the dissolved hydrogen in the melt. The thermal conductivity of the inert gas is then measured and used to calculate back to the level of dissolved hydrogen in the melt.

This method is recognised as giving reliable and accurate quantitative results but the equipment is relatively complex and the costs of running the test relatively high. For this reason Alscan tends to be used as process development or trouble shooting tool rather than for day to day process control or quality control device.

All the current methods commonly used today are only really capable of making spot checks on hydrogen levels and can take several minutes to give a result. None of the methods is capable of being used during a degassing treatment therefore the limit of their capability is to take measurements before and after such a treatment.

In comparison with current methods, the new analyser is a quantitative device that is capable of giving similarly reliable and accurate results as the more sophisticated methods but with the ease of use of the simpler qualitative and semi qualitative tests. Indications are that the cost of running the ALSPEK H unit are low enough for the foundry to be able to consider using it on a day-to-day basis. The ALSPEK H probe is also capable of being constantly immersed in aluminium, for example in a holding furnace, over a period of days and giving a direct and continuous read out of changes in hydrogen levels.

A comprehensive review of hydrogen measurement techniques has been prepared by Anyalebechi (2)

Potential applications of ALSPEK H

The new device can be used to make simple spot measurements in both furnaces and ladles and the operating characteristics give the foundryman the possibility of performing accurate quantitative measurements with the ease of today’s qualitative tests. The data logging capability of the analyser allows improved gathering and recording of measurements and their subsequent presentation for quality control purposes.

However, ALSPEK H also offers new possibilities that would allow the foundry to work as never before. Continuous measurement in furnaces where access allows gives the potential for the direct measurement and instantaneous read out of changes in hydrogen concentration over days rather than periodic spot checks.

Arguably the major potential advance for the foundry industry is the possibility of combining an ALSPEK H unit with a degassing machine such that the alarm outputs from the analyser can be used to send a signal to the degassing machine to stop operating when a preset level of hydrogen has been reached. This would allow the foundryman to establish and then consistently reach the optimum hydrogen level for a particular casting thus establishing real control of the degassing process for the first time.

In addition to the quality control and process control possibilities offered by ALSPEK H there is the potential for an improved understanding of hydrogen dissolution in aluminium alloys. The ability to measure continuously and during the degassing process allows the behaviour of hydrogen in different alloys and the effect of temperature to be studied in detail thus offering the possibility of further improvements in casting quality.

Conclusion

A new device for measuring hydrogen in aluminium alloys has been developed that significantly improves the foundryman's ability to manage dissolved hydrogen and the problems it generates. It offers the possibility of performing accurate quantitative measurements with the ease of today's qualitative tests and the potential to establish for the first time real control over the degassing process.

References

1) C Schwandt et al, Determination of hydrogen in molten aluminium alloys using an electrochemical sensor. TMS Annual Conference, March 2-6th, 2003

2) P.N Anyalebechi, Techniques for Determination of the Hydrogen Content in Aluminium and its Alloys. Light Metals 1991, The Minerals, Metals, and Materials Society, 1991, pp.1026