Advances in the determination of hydrogen concentrations in aluminium alloys

Introduction

Dissolved hydrogen and the resultant porosity is a great problem in aluminium and aluminium alloys. The reason for this behaviour is the tendency of liquid aluminium to react with moisture as follows;

$$2\,Al + 3\,H_2O \quad Al_2O_3 + 3\,H_2$$

As liquid aluminium has a much higher solubility of hydrogen than solid aluminium, the hydrogen releases from the melt during the cooling and solidification process resulting in porosity.

As the end users of castings (e.g. the automotive industry) demand increasingly higher quality castings for their applications it becomes more and more important for every foundry to improve their melt quality and to be able to determine it as accurately as possible.

In practice, most commercial aluminium foundries use some sort of degassing process to reduce the hydrogen level of the melt to an acceptable level. Usually there is an optimum hydrogen level suitable for any particular casting or production process, therefore it is extremely important to check the melt gas level continuously to maintain quality.

Many different methods of measuring hydrogen have been developed but to date none has been able to give true control over the hydrogen level before, during and after the degassing process. In fact, there are several reliable methods to detect the hydrogen content but either the response time is too long for continuous use in foundries or the handling of the units is too complicated.

ALSPEK* H

The new device comprises of three basic components; an electrochemical sensor that can measure hydrogen concentration in the gaseous phase, a probe that carries the sensor into the molten metal and an analyser that processes the signal from the sensor and calculates the concentration of dissolved hydrogen in the melt.

The Sensor

The function of the 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 of benefit and are described as follows:

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 sensor that differentiates it from similar devices is that it includes a solid-state reference meaning that it does not require an external source of hydrogen to provide the reference. This makes the sensor a self contained device and thus ideal for a practical piece of foundry equipment.

The Probe

The sensor cannot operate in direct contact with molten aluminium therefore a probe is required to protect and carry the sensor into the melt. The specially designed probe has a cavity in which the sensor is located and 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.

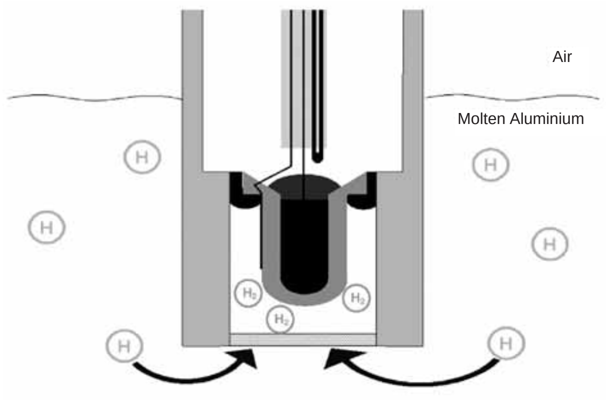

Figure 1 Schematic of the Probe section containing the sensor

The sensor thus sits in a gaseous environment where it measures the partial pressure of hydrogen in the probe cavity that is in equilibrium with dissolved hydrogen in the melt. The level of hydrogen measured in the cavity then needs to be related to the level of dissolved hydrogen in the melt, which is the value of real interest. This is done by the analyser using an equation based on Sieverts Law.

The Analyser

The third requirement to enable the sensor to be used as a practical device is an analyser to convert the electrical output of the sensor to a measure of the hydrogen concentration in the melt. The analyser first processes the voltage output from the sensor and calculates the partial pressure of hydrogen in the cavity. Using data on the hydrogen solubility of the alloy being measured the analyser then calculates the level of dissolved hydrogen in the melt and displays this value in ml/100g. Both of the calculations the analyser performs are temperature dependent therefore a thermocouple is positioned adjacent to the sensor to provide accurate temperature data.

In addition to calculating the dissolved hydrogen concentration, the analyser also has a built in data logger that allows both hydrogen and temperature readings to be recorded and subsequently downloaded onto a PC. These data logs can be plotted to produce real time curves of hydrogen concentration with time (figure 2).

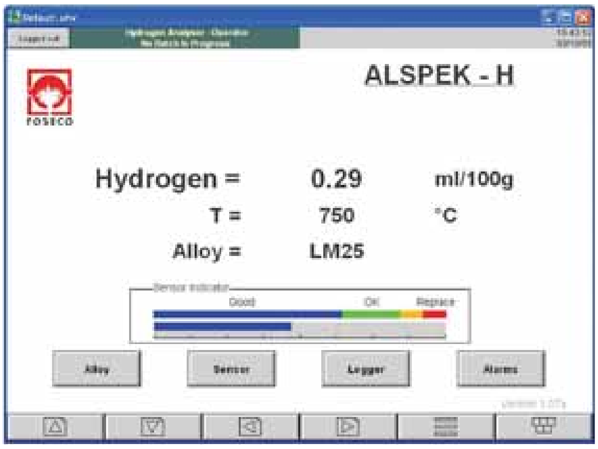

Figure 2 Home screen of the ALSPEK H analyser box

Figure 3 shows the complete ALSPEK H unit consisting of the probe, housing the sensor, and the analyser.

Figure 3 ALSPEK H unit

Commercial equipment

To be suitable for foundry applications, a device for measuring the hydrogen content in liquid aluminium has to meet a number of particular requirements:

- ❑ short response time
- ❑ reliable values
- ❑ reproducible results
- ❑ longevity in foundry environment
- ❑ simple handling

The ALSPEK H hydrogen analyser fulfils all these requirements and enables foundrymen to control the hydrogen content before, during and after the degassing process.

Probe accuracy

The quality and usefullness of each measurement process is determined by it's accuracy. To verify the accuracy of ALSPEK H, a particular melt was brought into equilibrium with a known hydrogen partial pressure by gassing up the melt with Formiergas (30 % H_2, 70 % N_2). The hydrogen content was calculated from known alloy solubility data. Figure 4 shows a typical sensor response.

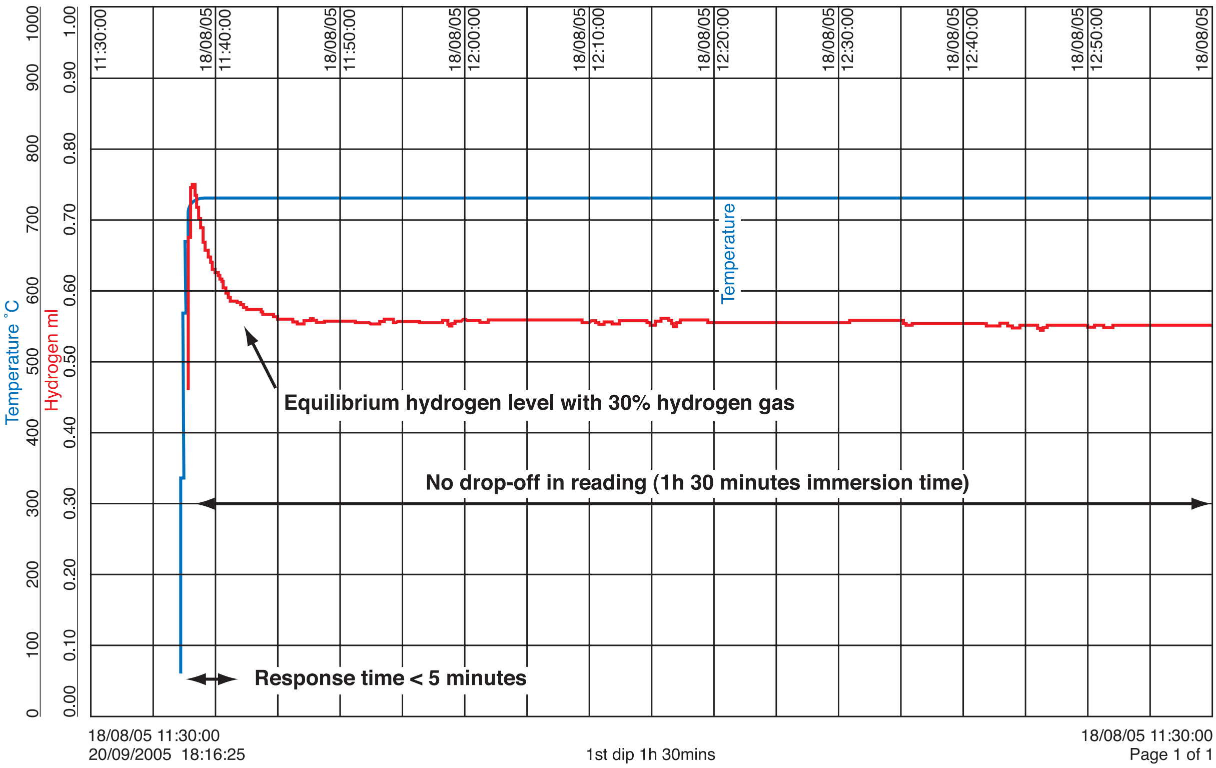

Figure 4 Measurement accuracy: Typical response

Measurement reproducibility

In the foundry it is important that results are reproducible with a number of insertions and removals of the probe. Figure 5 demonstrates the degassing process with probe removal and subsequent re-immersion and the result obtained.

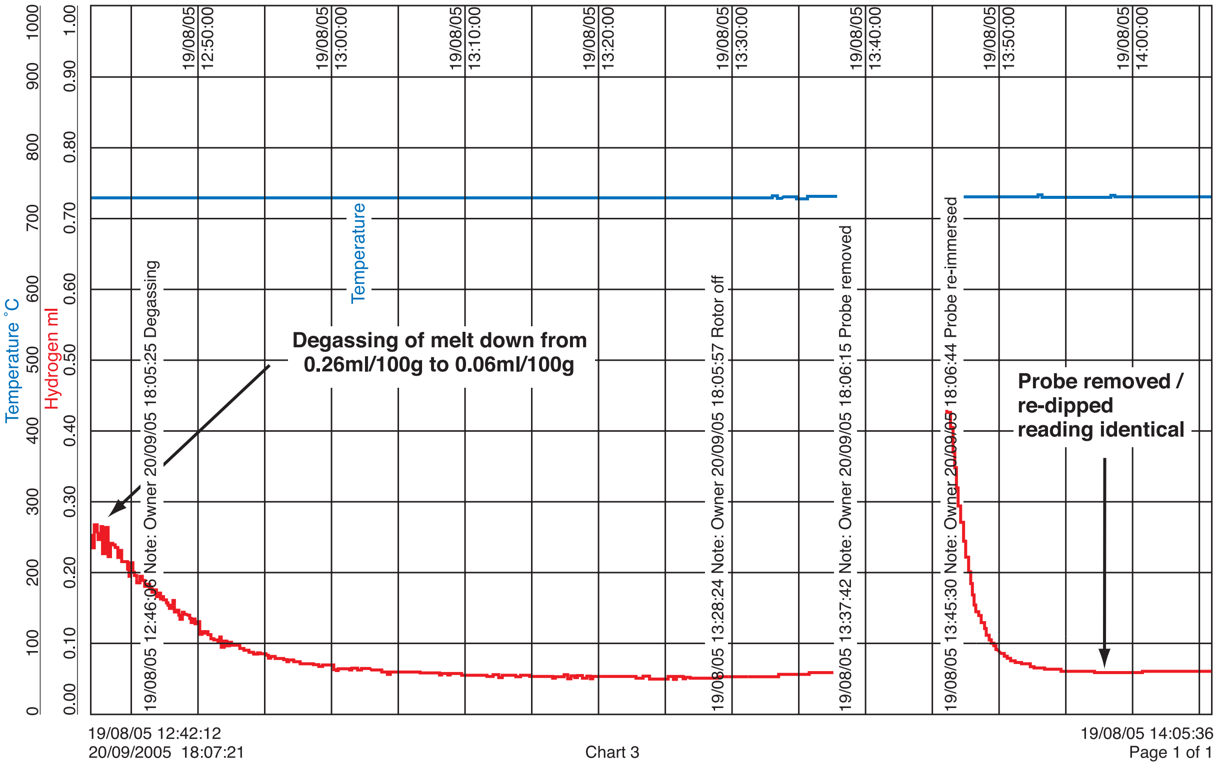

Figure 5 Degassing and accuracy at low hydrogen levels

Comparison with other methods

Many different methods of measuring hydrogen have been developed in the past therefore any new development such as ALSPEK H must stand comparison or better these methods.

The best-known devices to measure hydrogen in aluminium alloys directly include AlScan, Chapel and TYK Notorp. Table 1 shows comparitive values for these devices:

	ALSPEK H	Chapel	AlScan	TYK Notorp
Response time	< 5 min	10 - 15 min	10 - 15 min	10 min
Accuracy	0,01 ml/100g	0,015 ml/100g	0,01 ml/100g	0,01 ml/100g
Lifetime	100x/20h	10-15x	10x/3h	3-5x
Weight	10,2 kg	18,7 kg	17,2 kg	9,8 kg + Gas bottle
Spot measurement	yes	yes	yes	yes
Degassing	yes	no	no	no

Table 1 Hydrogen determination equipment

The table shows, because of time delay, that devices like Chapel, AlScan and TYK are often not suitable for the continuous use in foundries. The response time of any hydrogen analyser should be as short as possible to maintain productivity in the foundry. With a response time between 10 and 15 minutes, Chapel, AlScan and TYK are therefore not very practical for daily use.

Conclusion

With ALSPEK H, foundrymen are able for the very first time to determine the hydrogen content of the melt at a given moment of the degassing process and be able to adjust the hydrogen level to that required for a particular casting. This is an extremely valuable advantage of ALSPEK H, as none of the other devices can remain in the melt during the degassing process. The ALSPEK H hydrogen sensor is only influenced by hydrogen and not by other gasses like nitrogen or argon, which are mostly used for degassing.

The longevity of ALSPEK H consumables is between 10 and 20 times longer than competitive units. Again, this is an advantage for ALSPEK H, as it is often not possible in a foundry to change the consumables regularly without interruptions in the working process.

Another advantage of ALSPEK H is that it is relatively small and portable, it is light and easily manoeuvrable around the foundry. The length of cable from probe to analyser can be of such a length that the analyser can be positioned in a safe and convenient location, and possibly serve more than one furnace at any given time. Other devices quite often do not have this facility and are therefore limited in practicability.

The paper shows that ALSPEK H is a suitable device for measuring hydrogen in aluminium under demanding foundry conditions. The short response time, its

References

robustness and accuracy makes this a very attractive unit for most aluminium foundries.

1) C. Schwandt et al