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Alternative system to measure hydrogen content in molten aluminium using an electrochemical sensor

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The most reliable techniques for the direct measurement of hydrogen content in liquid aluminium are based on Sievert's law or use electrochemical probes introduced directly in liquid aluminium. The main drawback of these methods is the high cost of the equipment. An alternative apparatus has been developed and tested. This equipment combines a widely used and much cheaper hydrogen electrochemical sensor with the procedure already patented and commonly used by gas recirculation techniques. The device has been constructed and calibrated using gaseous mixtures of known hydrogen content. For validation, the results obtained with this apparatus have been compared with hydrogen content measurements in liquid aluminium using the commercial Alscan equipment in an industrial facility. Experimental results suggest that the apparatus proposed in this work is capable of detecting hydrogen content in liquid aluminium obtaining measurements that are in a good agreement with those obtained using the commercial Alscan equipment. On the other hand, results also suggest that it is important to take into account the operating atmospheric pressure to correct the readings obtained from Alscan when operating at atmospheric pressure levels far from 1 atm.

Keywords: Degassing, Aluminium alloys, Hydrogen content, Electrochemical gas sensor, Physical pores, Solidification

1 Introduction

Control of hydrogen content in aluminium alloys is of paramount importance in the aluminium casting industry because high residual hydrogen contents in molten aluminum cause significant porosity in the solid aluminium after casting. This increases the possibility of mechanical failure and renders useless the engineering aluminium components[1]. Molten aluminum has a high affinity to moisture giving, as a result of this chemical interaction, aluminum oxide and dissolved atomic hydrogen. Liquid aluminum has a high solubility for hydrogen, and so large amounts of hydrogen remain in the melt. This problem can be eliminated by a proper degassing process which usually comprises the introduction of an inert gas into the molten body or stream of metal in the form of a dispersion of fine bubbles. Different techniques to achieve degassing are commonly applied such as the rotary impeller[2,3] and recently Jet cleaner by a high velocity gas injection[4,5]. Efficient degassing processes operation requires an accurate knowledge of hydrogen content in liquid aluminium.

Over the years a number of techniques have evolved for the analysis of hydrogen in aluminium alloys and these can be broadly split into three categories. First category includes all semi-quantitative cast shop techniques, such as the so called bubble methods[6]. The second type of tests are quantitative laboratory analysis of solidified samples like the Hot Vacuum Subfusion Extraction and the Nitrogen Carrier Fusion techniques[7] and finally, there are in situ quantitative determination of hydrogen concentration in molten metal, like in the case of the Telegas method[8]. Detailed surveys of the commonly employed techniques for the determination of hydrogen in aluminum are given in References [6-10].

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From these techniques, only the third category is suitable for on-line quality control of the degassing process. For the direct determination of hydrogen content in liquid aluminium there are two main types of techniques: those based in Sievert's law and named gas recirculation techniques like the Telegas and Alscan[11,12] methods and those using electrochemical probes introduced directly into liquid aluminium like the Notorp[13] and more recently the ALSPEK H[14] system.

Gas recirculation techniques have become the standard method and are widely used and accepted in industry. These methods typically employ a measurement porous tube immersed into the molten metal and an analyzer for providing readout of the hydrogen concentration. In this test, a stream of nitrogen is continuously circulated through the porous tube immersed in the melt and equilibrates with the dissolved hydrogen. The nitrogen stream coming from the porous tube is analyzed for hydrogen by means of a thermal conductivity measurement device. The main drawback of these methods is the high cost of the equipment.

Electrochemical probes are supposed to have the potential to overcome the disadvantages associated with the conventional gas techniques. Measurements could be done in-situ and a fast response time may be expected. The sensor commonly used includes a proton conductive high temperature ceramic, which compares the hydrogen activity in the melt with the fixed hydrogen activity in a reference gas or a solid reference electrode. Indeed, two electrochemical systems are currently available in the market[10,15,16], they are less expensive than the gas recirculation equipment, but their cost remains still high for educational purposes in low budget foundries and metallurgy schools.

Although these techniques for measuring hydrogen can be the most reliable, the problem of using very expensive commercial equipment is eliminated here by the development of an alternative apparatus which combines a widely used and much cheaper hydrogen electrochemical sensor with the procedure already patented[2,8] and commonly used by the gas recirculation techniques.

The purpose of this work was to develop an apparatus of the gas recirculation type, capable of detecting the hydrogen content in liquid aluminium using a commercially available electrochemical hydrogen sensor. Accordingly, the apparatus was constructed and calibrated using gaseous mixtures of known hydrogen content.

Finally and for validation, the results obtained with this apparatus are compared with hydrogen content measurements in liquid aluminium obtained using the commercial Alscan equipment in an industrial facility during a period of four days. The Measurements were made in a 400 kg holding furnace using an aluminium silicon based alloy of the mean chemical composition shown in Table 1.

2 Working principles and development of the apparatus

In this work, the apparatus uses an electrochemical sensor to measure the hydrogen content in a recirculation gas that has been equilibrated with the dissolved hydrogen in liquid aluminium based alloys under the same principles of the so called gas recirculation techniques.

The reaction of interest is:

$$\tfrac{1}{2}[H_2]_{\text{in the atmosphere}} \rightarrow [\underline{H}]_{\text{in Al}} \quad \dots (1)$$

and the solubility of hydrogen $[H]_{\text{in Al}}$ in the liquid aluminium alloy is found with Sievert´s law given by:

$$[\underline{H}] = S_0 * \sqrt{p_{H_2}} * CF(A) * CF(T) \quad \dots (2)$$

Here, S_o is the solubility of hydrogen in pure aluminium at a temperature of 973K and equals 0.92 ml H_2/100g, and CF(A) and CF(T) are correction factors which take into account the chemical composition in aluminium alloys and operating temperature[17], respectively. CF(A) can be obtained from Eq. (3):

$$\log CF(A) = 0.017\ \%\ \text{Mg} - 0.0269\ \%\ \text{Cu} - 0.0119\ \%\ \text{Si} \quad \dots (3)$$

CF(T) is the correction factor for metal temperature, CF(T) = 1 at 973K and is given by:

$$CF(T) = 10^{\left(\frac{-2760}{T} + 2.837\right)} \quad \dots (4)$$

Electrochemical sensors are based on solid electrolytes and designed for hydrogen content determination in gaseous atmospheres, the electrical conductivity increases with temperature and hydrogen

Table 1 — Nominal alloy composition in wt %.

% Si	% Fe	% Cu	% Mn	% Mg	% Zn	% Ni	% Cr	% Ti	% Na	% P	% Sr	% Al
8.87	0.79	2.39	0.19	0.67	0.21	0.20	0.0303	0.05	0.0012	0.0006	0.0026	85.9

gas concentration. Ionic conduction in the sensor occurs through the transport of specific ionic point defects. The output of the electrochemical sensor is a resistance proportional to the hydrogen concentration[18].

3 Working principle demonstration

Different commercial electrochemical sensors, made with SnO_2, [19] for hydrogen content determination in gaseous atmospheres were tested in order to identify the best suited for hydrogen determination in terms of their velocity of response and reproducibility. For this purpose, controlled atmospheres of known hydrogen content were put in contact with the sensors and their velocity of response and their reproducibility were established and compared.

Thus, the TGS2611 sensor was selected, it has an operation range between 300 and 10000 ppm H_2 [19].

The apparatus was designed and dimensioned taking into account the limitation imposed by detection limits of commercial gas sensors and the usual hydrogen contents present in liquid aluminium before and after degassing. The apparatus included a vacuum system, a pure nitrogen supply (Fig. 1), a dilution chamber where temperature, pressure and gas content sensors were located, and a gas recirculation system connected to a hydrogen extraction plug forming which was called the extraction circuit. Here, the carrier gas N_2 conveyed the hydrogen gas in a stainless steel tube crossing through an alumina permeable assembly made with commercial alumina cement (Fig. 1a), intended to be immersed in liquid aluminium under study and equilibrate hydrogen

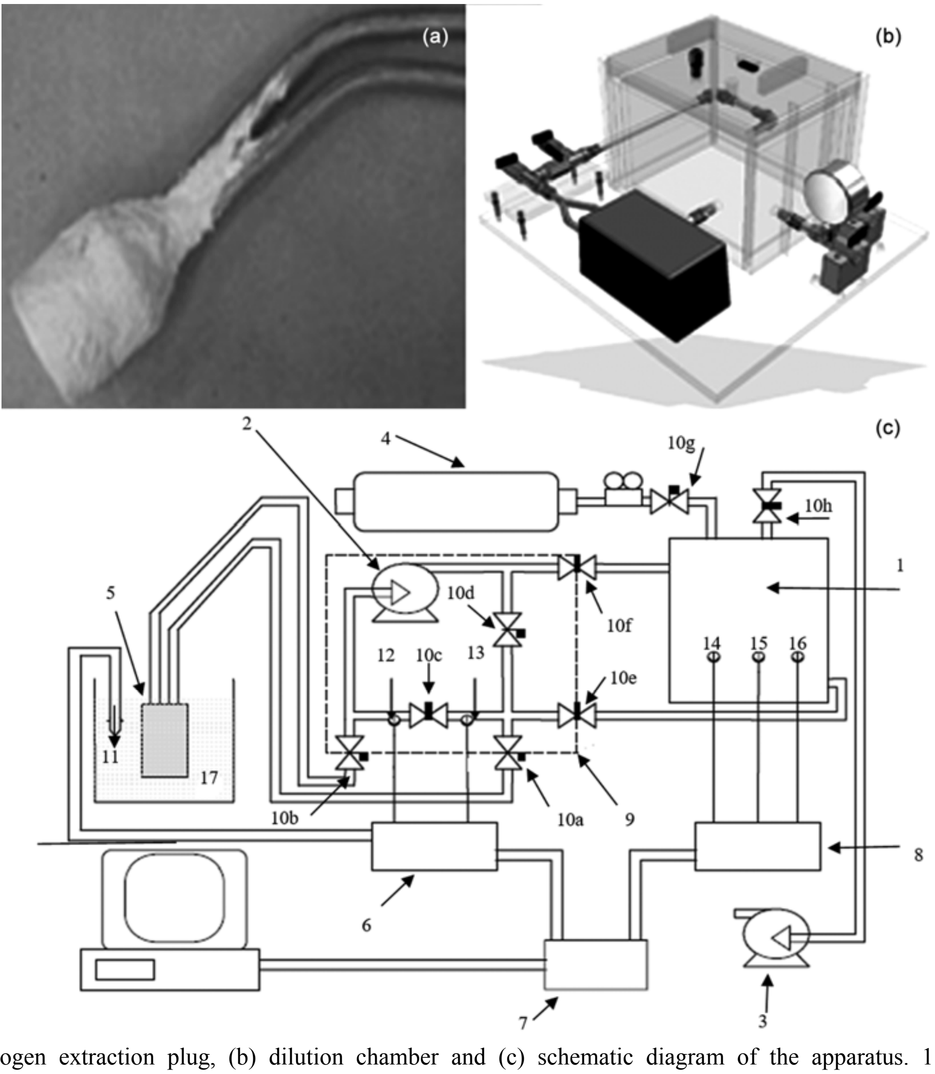

Fig. 1 — (a) Hydrogen extraction plug, (b) dilution chamber and (c) schematic diagram of the apparatus. 1 Dilution chamber, 2 Recirculation pump, 3 Vacuum pump, 4 Pure nitrogen, 5 Hydrogen extraction plug, 6 Acquisitions signal sensors, 7 Microcontroller, 8 Processing signal sensors, 9 Extraction circuit, 10 a to 10h Valves, 11 Temperature sensor, 12 Pressure sensor, 13 Temperature sensor, 14 Temperature sensor, 15 Pressure sensor, 16 Hydrogen gas sensor, 17 Liquid aluminum.

content of recirculation gas mixture with hydrogen dissolved in the melt.

The methodology used to calibrate the apparatus and to evaluate hydrogen content in liquid aluminium was the same. The measurement started having the system fill with air at room pressure and temperature, then applying a vacuum of 6 kPa absolute pressure in both the dilution chamber and the hydrogen extraction circuit (Fig. 1), with the extraction circuit having a volume of 40 cm^3 and the dilution chamber with a volume of 2340 cm^3. After three evacuations using the vacuum pump, the atmosphere present in the apparatus was replaced three times with pure nitrogen N_2 (99.998%). The final molar gas composition, obtained from a mass balance, was N_2 (99.99%) and O_2 (0.01%). In the case of sensor selection and calibration, known volumes of pure H_2 were introduced in the dilution chamber and measurements were performed with different gas sensors to test the velocity of response, reproducibility in electrical output and, in the case of the chosen gas sensor, obtaining a calibration curve.

Considering an specific resistance of the sensor measured in Ohms, at measured pressure and temperature in the dilution chamber, the hydrogen molar fraction χ_{H_2} was obtained from the known volume of hydrogen introduced into the recirculation current and converted to mole number using its measured temperature and pressure, and the known initial N_2 and O_2 mole numbers, denoted by the symbols n_{N_2} and n_{O_2}, respectively, by the Eq. (5):

$$\chi_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{N_2} + n_{O_2}} \quad \text{... (5)}$$

The calibration was done once pure nitrogen at measured room pressure and temperature was introduced during the purging process and a known volume of pure hydrogen was injected into the recirculation circuit, then the recirculation pump is switched on and at the same time the valves 10a, 10b, and 10d, (Fig .1), were kept opened and all the others closed, so that pure nitrogen started to convey the hydrogen gas from the point of hydrogen introduction. Gas recirculation was maintained in the circuit until the hydrogen was homogenously diluted, as indicated by the stabilization of the signal obtained from the gas sensor. At this point, pressure and temperature were measured by the sensors in the extraction circuit; afterwards a known volume from the recirculation circuit (40 cm^3) of the gaseous mixture was taken closing valves 10a, 10b, 10e and 10f to be diluted. Finally recirculation circuit and dilution chamber previously full with pure N_2 were connected in parallel (2380 cm^3) opening valves 10c, 10d, 10e and 10f, and temperature, pressure and hydrogen gas content were measured.

The measured hydrogen partial pressure denoted by P_{H_2} present in the recirculation circuit, pressure of hydrogen in equilibrium with the molten metal, it was obtained from hydrogen molar fraction χ_{H_2} from the measured electric resistance using the calibration curve, and applying the dilution factor using the ideal gas law:

$$P_{H_2} = P_{atm}\ \chi_{H_2} \frac{2380}{40} \quad \text{... (6)}$$

Where, P_{atm} is the atmospheric pressure measured in the dilution chamber. The hydrogen content was obtained from Equations (1-5) introducing the correction factors related to temperature and chemical composition present in the liquid alloy under study.

The selected sensor was carefully calibrated in order to obtain the characteristic equation of its conductivity as a function of hydrogen content. Finally, comparisons between measurements of the apparatus and determinations of the hydrogen content in liquid aluminium based alloy before and after industrial degassing treatment using the commercial equipment Alscan were performed.

4 Results and Discussion

Calibration experimental electrical resistance data under different hydrogen molar fractions χ_{H_2} from tests performed during ten days under a mean atmospheric pressure of 0.79 atm were numerically processed obtaining the following empirical relationship,.

$$\chi_{H_2} = 9.36 \times 10^{-10} r^2 - 1.14 \times 10^{-6} r + 0.0054 \quad R^2=0.98 \quad \text{... (7)}$$

where *r* is the sensor electrical resistance in ohms and R^2 the coefficient of determination.

The calibration curve is shown in Fig. 2 together with the data predicted from Eq. (6). When measuring the hydrogen content, the atmospheric pressure acting in the apparatus was considered as 0.79 atm (externally measured local atmospheric pressure). The *CF*(*A*) was found to be 0.7, according with the mean chemical composition present in the melts under study.

In the Alscan operation manual [20] is mentioned that a reference atmospheric pressure of 1 atm is considered for the readings directly obtained from screen. Taking into account the measured operating atmospheric pressure of 0.79 atm, in this work was suggested the introduction of a pressure correction factor CF(P) to the reading obtained from Alscan instrument using the gas law, given by:

$$CF(P) = \sqrt{\frac{1}{P}} \quad \text{... (8)}$$

Considering this atmospheric pressure correction factor *CF*(*P*), Eq. (2) becomes:

$$[H] = \frac{S_0 \cdot \sqrt{p_{H2}} \cdot CF(T) \cdot CF(A)}{CF(P)} \quad \text{... (9)}$$

At a pressure of 0.79 atm, the Alscan analyser results must be divided by the pressure correction factor *CF*(*P*)=1.125. It can be seen that this correction was not needed in the apparatus proposed in this work as measured atmospheric pressure, P_{atm}, was used for hydrogen determination, Eq. (6).

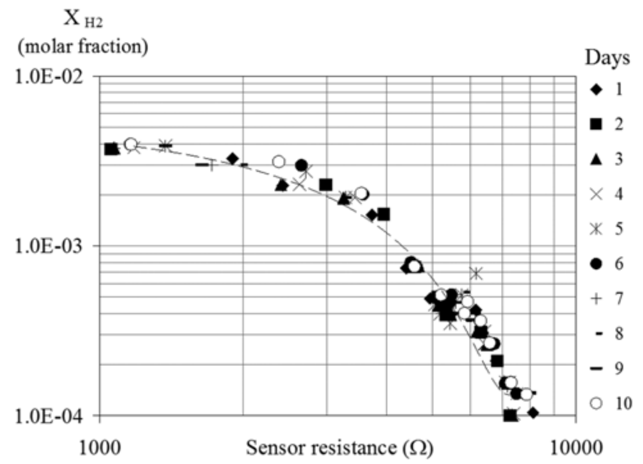

Fig. 2 — Calibration curve, Hydrogen molar fraction χ_{H_2} versus sensor resistance (Ω).

Experimental results are shown in Table 2, obtained from the apparatus, before (B) and after (A) degassing, over four different days of industrial tests where it is observed that the partial pressure P_{H_2} (atm) is proportional to hydrogen concentration, and as hydrogen concentration increases resistance R (Ohms) decreases and voltage V(volts) increases.

Figure 3 presents a comparison of hydrogen content for the apparatus and Alscan results with and without atmospheric pressure correction. Here, it is observed that apparatus developed in this work was capable to obtain hydrogen content readings quite acceptably close to results given by Alscan and it was apparent that there was a better concordance when atmospheric correction factor was applied to Alscan results. This suggest in turn that apparatus proposed in this work was capable to detect the hydrogen content in liquid aluminium and also suggest that it was very important to take into account the operating atmospheric pressure to correct the readings obtained from Alscan when operating atmospheric pressure is far from 1 atm.

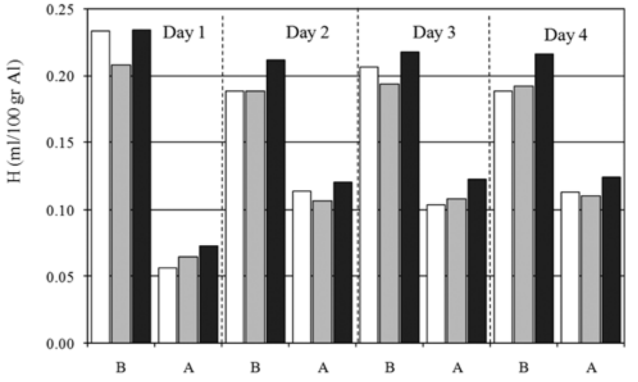

Fig. 3 — Comparison of results obtained before (B) and after (A) degassing in the apparatus (□), Alscan after correcting by pressure (■) and Alscan direct reading (■).

Table 2 — Experimental results for (A) after and (B) before degassing.

Day		*V* (volts)	*R* (Ohms)	χ_{H_2} (Eq. 4)	P_{H_2} (atm) (Eq. 5)	T_m (°C)	*CF*(*T*) (Eq. 2)
1	B	2.158	2861.1	0.002181	0.10	720	1.14
	A	1.154	7240.4	0.000129	0.01	720	1.14
2	B	1.963	3361.1	0.001768	0.08	702	1.01
	A	1.398	5597.5	0.000484	0.02	725	1.18
3	B	2.032	3173.2	0.001918	0.09	711	1.08
	A	1.379	5704.6	0.000446	0.02	717	1.12
4	B	1.988	3291.5	0.001823	0.09	701	1.01
	A	1.420	5477.1	0.000530	0.02	717	1.12

Experimental results are in good agreement between the apparatus and Alscan when the last were corrected by the atmospheric pressure correction factor, Eq. (9).

It must be mentioned that the main drawback of the apparatus developed in this work lies on the time needed to obtain a determination during measurement of hydrogen content in liquid aluminum. This delay was related to the dilution operation that was needed to perform before hydrogen determination in the dilution chamber due to the limitations of the sensor employed.

As a result, a complete reading took about 30 minutes, while Alscan determinations were obtained between 10-15 minutes. On the other hand, care should have been taken with the ceramic porous tubes introduced into the aluminum bath as they are sensible to thermal shock causing cracks resulting in metal infiltration or gas leaking. Finally, it is interesting to comment that apparatus proposed in this work is very economical in terms of construction when compared with commercial equipment and represents a good alternative for educational purposes.

5 Conclusions

Experimental results suggest that apparatus proposed in this work is capable to detect the hydrogen content in liquid aluminium obtaining measurements that are in a good agreement with those obtained using the commercial Alscan equipment.

Calibration curve and test results shows that good accuracy and reproducibility can be achieved when using electrochemical sensors for measuring hydrogen content in gaseous atmospheres.

Obtained results suggest that it is important to take into account the operating atmospheric pressure to correct the readings obtained from Alscan when operating at atmospheric pressure far from 1 atm.

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