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Electrochemical Hydrogen Sensor for Aluminium Melts

Carsten Schwandt
Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK
cs254@cam.ac.uk

Abstract:
The presence of dissolved hydrogen in molten aluminium and its alloys has a critical impact on the quality of cast aluminium components. The quantitative analysis of hydrogen in these melts is therefore of major importance in the aluminium industry. Research work conducted at the University of Cambridge and subsequent development work performed in conjunction with an industrial partner, have resulted in a novel, and now commercialised, electrochemical hydrogen sensor for aluminium melts. The sensor operates in the potentiostatic mode and relies on a proton-conducting solid electrolyte and a solid reference electrode. This contribution summarises the main steps of the underlying research and development programme, covering the actual gas sensor, test measurements in gas phases, the probe for molten metal application, and test measurements in aluminium melts.

Keywords: Aluminium, Hydrogen, Sensor, Solid electrolyte, Solid reference electrode.

Hydrogen in Aluminium

Molten aluminium typically contains significant quantities of hydrogen which arise from its reaction with ambient water vapour during processing. The products of this reaction are aluminium oxide forming a dross layer on the melt surface and elemental hydrogen dissolving into the melt bulk.

Hydrogen is many times more soluble in liquid aluminium than in solid aluminium. This creates a problem in the casting of high-quality aluminium components when substantial amounts of hydrogen gas are liberated during solidification. The hydrogen forms pores in the solid aluminium, and these deteriorate the quality of the cast workpiece [1-3].

Basic methods for analysing the dissolved hydrogen content in aluminium melts rely on the visual observation of bubble formation in melt samples. These tests are simple and fast but lack accuracy and reproducibility. More advanced methods are centred on thermal conductivity measurements of re-circulated inert gas after its equilibration with the aluminium melt. These tests are more accurate and widely used in industry but require costly equipment and have a delayed response [1-3].

The most straightforward technique of measuring hydrogen in aluminium melts should be solid state electrochemical gas sensing [4]. This consideration was the motivation of the research and development programme outlined in brief here.

Hydrogen Sensor and Experimental Results

A new solid state electrochemical hydrogen sensor has been developed in the Department of Materials Science and Metallurgy at the University of Cambridge over the recent years. The sensor is a hydrogen concentration cell with a proton-conducting solid electrolyte, which determines the unknown hydrogen pressure at the measuring electrode by comparing it against the known hydrogen pressure at the reference electrode.

The schematic design of the hydrogen sensor is displayed in Fig. 1. The solid electrolyte is a cap-shaped ceramic of perovskite type with approximate composition $CaZr_{0.9}In_{0.1}O_{3-\delta}$. This material exhibits proton conductivity over a wide range of conditions as it is able to dissolve and dissociate a quantity of water from suitable gas atmospheres at elevated temperatures [5-8]. The measuring electrode is on the outside of the ceramic cap and contains a porous film of platinum. This electrode is exposed to the gas to be analysed, equilibrates with it, and thereby senses its hydrogen pressure. The reference electrode is inside the glass-sealed cavity of the ceramic cap and contains a suitable two-phase mixture from either the titanium/hydrogen or the zirconium/hydrogen system. This electrode maintains a constant reference hydrogen pressure [9,10].

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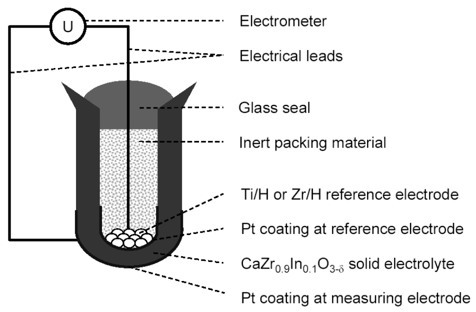

Fig. 1. Schematic design of the new solid state hydrogen sensor [9,10].

The sensor is operated in the potentiometric mode. The cell potential generated may be expressed, for a proton transference number of unity, through the Nernst equation,

$$U = -(RT/2F)\ln\left(p''_{H_2} / p'_{H_2}\right) \qquad (1)$$

wherein U, R, T, F, p''_{H2}, and p'_{H2} are cell potential, universal gas constant, absolute temperature, Faraday constant, hydrogen pressure at the measuring electrode, and hydrogen pressure at the reference electrode, respectively. Eq. (1) hence establishes a direct correlation between U as the measured quantity and p''_{H2} as the sought quantity.

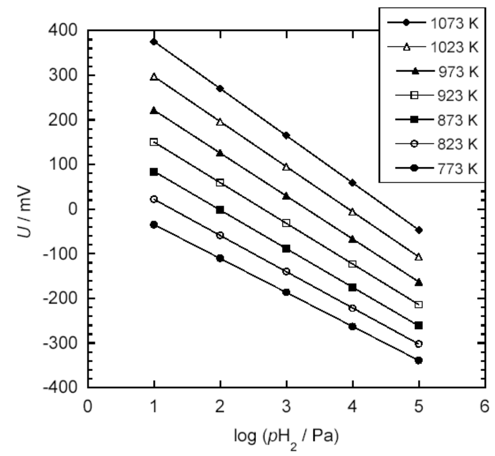

Fig. 2. Cell potential measurements with the new solid state hydrogen sensor in hydrogen/argon gas mixtures [10].

Hydrogen sensors of the above type were tested extensively in the laboratory, using gas mixtures of hydrogen and argon with different hydrogen pressures. In all cases, the sensors exhibited Nernstian cell potentials, responded quickly to hydrogen pressure changes with equilibration times on the order of seconds to minutes, and showed little or no signal drift over timescales of days to weeks. Fig. 2 presents the results obtained for a sensor with a Zr/ZrH_2 reference electrode for temperatures ranging from 500 to 800°C and hydrogen pressures ranging from 10^1 to 10^5 Pa.

Molten Metal Probe and Experimental Results

A probe has been engineered in cooperation with Environmental Monitoring and Control Ltd as the industrial partner in order to make the hydrogen sensor applicable in aluminium melts. The probe protects the sensor from the melt, permits gas exchange with it, and is connected to a customised data processing unit.

The schematic design of the probe is displayed in Fig. 3. The lance of the probe is made from a highly refractory material such as graphite or SiAlON that is chemically stable in molten aluminium. The gas-pervious porous plug at the lower end of the lance is made from carbon. The hydrogen sensor is positioned in a cavity inside the probe. The cavity is filled with hydrogen gas that has been released from the melt and diffused through the plug. The electrical leads from the sensor are fed via gastight leadthroughs to a customised data processing unit [11].

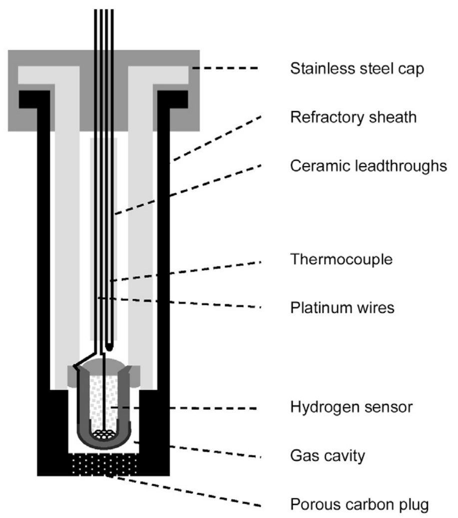

Fig. 3. Schematic design of the probe for sensor application in aluminium melts [11].

The sensor inside the probe senses the hydrogen gas in the cavity according to eq. (1). Consequently, the determination of the dissolved hydrogen content in the melt relies on the equilibration of the hydrogen between the melt phase and the gas phase above it. This equilibration may be expressed through the Sieverts equation,

$$S = k\sqrt{p''_{H_2}} \qquad (2)$$

wherein S, k and p''_{H2} are hydrogen content in the aluminium melt, Sieverts coefficient, and hydrogen pressure above the melt, respectively. The Sieverts coefficient depends on composition and temperature and is known for pure aluminium and many of its alloys.

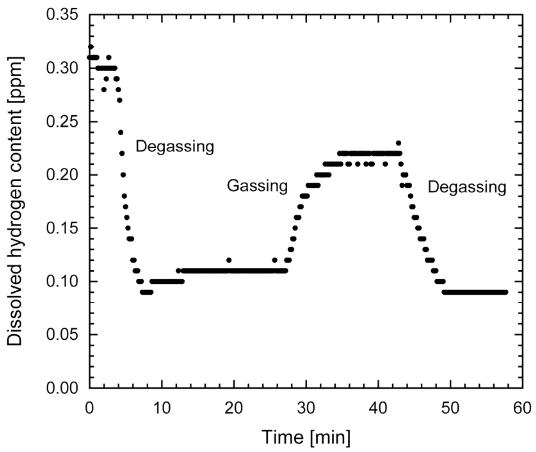

Fig. 4. Dissolved hydrogen content measurements with the new solid state hydrogen sensor in an aluminium alloy melt [11].

Probes of the above type incorporating the hydrogen sensor were tested in many trials using pure and alloyed aluminium melts. In all these trials, sensor and probe demonstrated an adequate performance that compared well with that of alternative techniques. Fig. 4 shows the results obtained with the new system in a trial, in which the hydrogen content of an alloy melt composed of aluminium with additions of silicon and magnesium was decreased and increased through degassing and gassing treatments.

In the recent past, the performance of hydrogen sensor and probe has been assessed and verified in industrial environments by several industrial companies. Based thereupon, the device has been commercialised successfully, and it is now available under the tradename ALSPEK H [12,13].

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References

[1] D.V. Neff, Nonferrous molten metal processes, in: *ASM Handbook*, Edition 9, Volume 15: Casting, American Society for Metals, 1988, pp. 445-496; ISBN: 0871700212.

[2] P.N. Anyalebechi, Techniques for determination of the hydrogen content in aluminum and its alloys, in: *Light Metals 1991*, The Minerals, Metals & Materials Society, Warrendale, PA, 1991, pp. 1025-1046; ISBN: 0873391616.

[3] D.P. Lapham, C. Schwandt, M.P. Hills, R.V. Kumar, D.J. Fray, The detection of hydrogen in molten aluminium, *Ionics* 8, 391-401 (2002); doi: 10.1007/BF02376052.

[4] R.V. Kumar, C. Schwandt, Solid electrolytes and their applications in chemical sensors, in: *Chemical Sensors − Fundamentals of Sensing Materials*, Volume 3: Polymers and Other Materials, Momentum Press LCC, New York, 2010, pp. 291-349; ISBN-13: 978-1-60650-230-3.

[5] T. Yajima, H. Kazeoka, T. Yogo, H. Iwahara, Proton conduction in sintered oxides based on $CaZrO_3$, *Solid State Ionics* 47, 271-275 (1991); doi: 10.1016/0167-2738(91)90249-B.

[6] N. Kurita, N. Fukatsu, K. Ito, T. Ohashi, Proton conduction domains of indium-doped calcium zirconate, *J. Electrochem. Soc.* 142, 1552-1559 (1995); doi: 10.1016/0167-2738(91)90249-B.

[7] C. Schwandt, D.J. Fray, Hydrogen sensing in molten aluminium using a commercial electrochemical sensor, *Ionics* 6, 222-229 (2000); doi: 10.1007/BF02374070.

[8] M.P. Hills, C. Schwandt, R.V. Kumar, Oxide ion conduction in indium-oxide-substituted calcium zirconate, *J. Electrochem. Soc.* 153, H189-H194 (2006); doi: 10.1149/1.2229274.

[9] C. Schwandt, D.J. Fray, The titanium/hydrogen system as the solid-state reference in high-temperature proton conductor-based hydrogen sensors, *J. Appl. Electrochem.* 36, 557-565 (2006); doi: 10.1007/s10800-005-9108-5.

[10] M.P. Hills, C. Schwandt, R.V. Kumar, The zirconium/hydrogen system as the solid-state reference of a high-temperature proton conductor-based hydrogen sensor, *J. Appl. Electrochem.* 41, 499-506 (2011); doi: 10.1007/s10800-011-0260-9.

[11] C. Schwandt, M.P. Hills, M.A. Henson, D.J. Fray, R.M. Henson, A. Moores, Determination of hydrogen in molten aluminium and its alloys using an electrochemical sensor, in: *EPD Congress 2003*, The Minerals, Metals & Materials Society, Warrendale, PA, 2003, pp. 427-438; ISBN: 0873395328.

[12] M.P. Hills, C. Thompson, M.A. Henson, A. Moores, C. Schwandt, R.V. Kumar, Accurate measurement of hydrogen in molten aluminium using current reversal mode, in: *Light Metals 2009*, The Minerals, Metals & Materials Society, Warrendale, PA, 2009, pp. 707-712; ISBN: 978-0-87339-731-5.

[13] M.P. Hills, M.A. Henson, C. Thompson, B. Geddes, C. Schwandt, R.V. Kumar, D.J. Fray, In-situ measurement of dissolved hydrogen during low pressure die casting of aluminium, in: *Light Metals 2010*, The Minerals, Metals & Materials Society, Warrendale, PA, 2010, pp. 801-805; ISBN: 978-0-87339-747-6.