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Solid state electrochemical hydrogen sensor for aluminium and aluminium alloy melts

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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 metal/hydrogen-based solid reference electrode. This article summarises the main steps of the underlying research and development programme, covering the actual gas sensor, test measurements in gas phases under laboratory conditions, the probe for molten metal application, and test measurements in aluminium melts under industrial conditions.

1. Introduction

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].

Electrochemical sensors based on solid electrolytes are of great promise for the analysis of dissolved species in metallurgical melts [4–8]. The most straightforward technique of analysing dissolved hydrogen in aluminium melts should be solid state electrochemical gas sensing, using a potentiometric sensor with a proton-conducting solid electrolyte that measures the unknown hydrogen pressure at the measuring side against a known hydrogen pressure at the reference side. One such sensor system has already been presented in the literature and developed to the stage of commercialisation [9,10], but its key disadvantage is that its reference electrode requires a flow of hydrogen gas to be fed into the system from an external supply unit, which renders its use in an industrial environment awkward. In an alternative design, the hydrogen gas reference electrode is generated in situ within the sensor arrangement [11,12], but no development of this system towards commercialisation has apparently been reported, possibly because its design is too sophisticated for routine use in industry.

A more convenient type of solid state electrochemical hydrogen sensor would be one relying on solid components only, and this may be achieved through the incorporation of a self-contained solid reference electrode. Various approaches have been published in the literature in which materials based on solid hydrates [13–15] or calcium hydride [16–18] were attempted, but eventually these sensor developments did not succeed. This is understandable since either the reference electrode did not fix the reference potential in a thermodynamically strict manner or the reference material and the solid electrolyte underwent a slow reaction with each other. In a more recent development, a solid reference electrode consisting of titanium, oxygen and hydrogen is used in conjunction with a proton-conducting solid electrolyte [19,20]. Initial results are promising, but verification under industrial conditions remains

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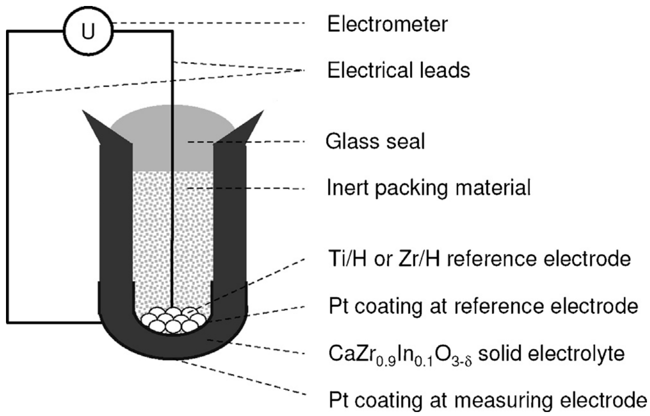

Fig. 1. Schematic design of the new solid state electrochemical hydrogen sensor.

yet to be reported. An earlier development rests on the work of the present author and uses a solid reference electrode of partially hydrided metal in combination with a proton-conducting solid electrolyte [21,22]. This work has been successful and did reach the stage of commercialisation [23–25].

The present article reports the main stages of the research and development work undertaken at the Department of Materials Science and Metallurgy of the University of Cambridge and at Environmental Monitoring & Control Ltd. as its industrial partner, with the aim of developing a completely novel solid state electrochemical hydrogen sensor for aluminium and aluminium alloy melts. The article summarises the entire programme all the way from fundamental studies in the laboratory to field trials in industry, and it also highlights the various materials challenges that had to be overcome in the design and construction of the hydrogen gas sensor and the refractory probe housing the sensor in molten metal applications.

2. Materials and methods

2.1. Hydrogen sensor

A new solid state electrochemical hydrogen gas 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 [26–29]. 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 [21,22].

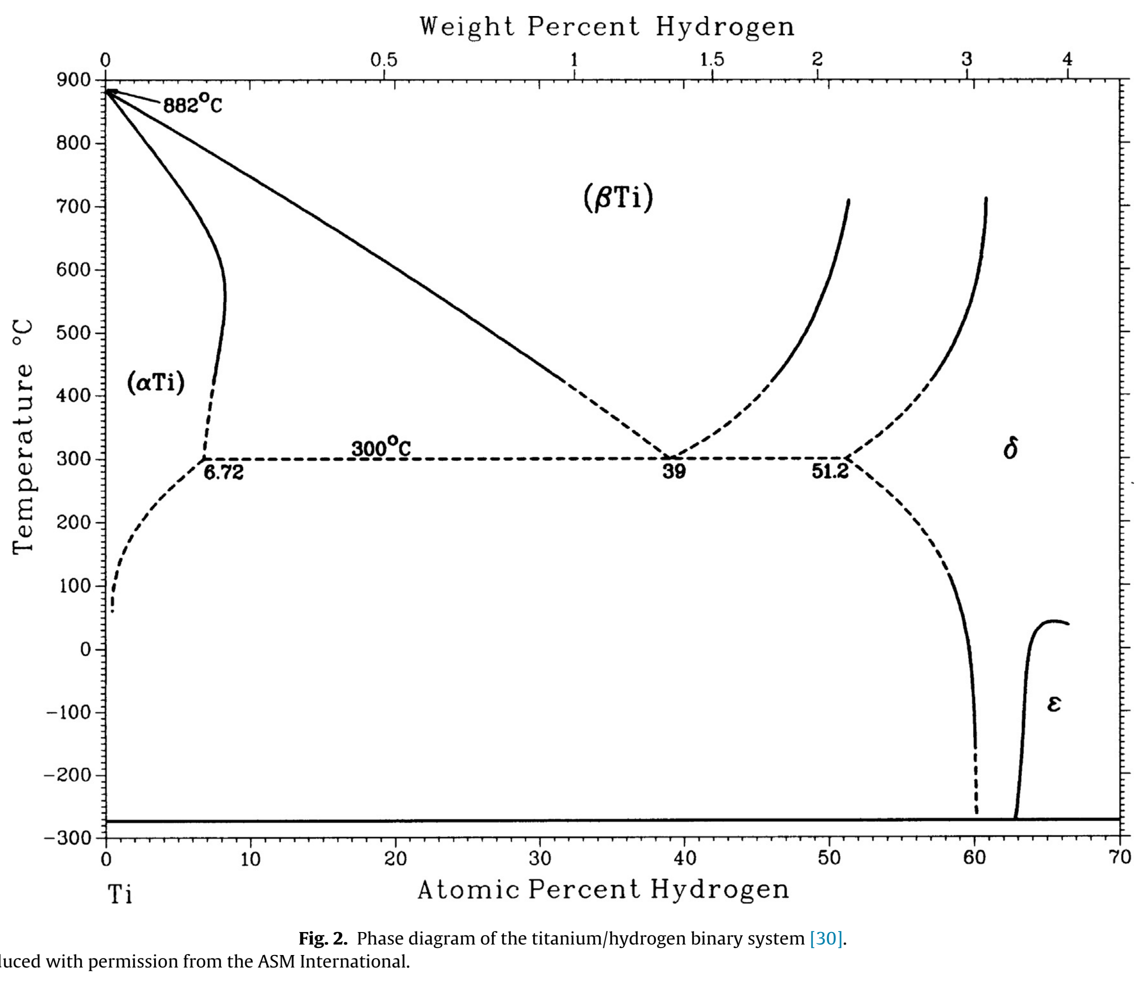

Fig. 2. Phase diagram of the titanium/hydrogen binary system [30].
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