

Furnace Atmosphere and Dissolved Hydrogen in Aluminium

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Abstract

Hydrogen solubility is much higher in liquid than in solid aluminium. Therefore, if the hydrogen concentration in liquid aluminium is too high prior to solidification, there is high risk of gas porosity formation during the solidification.

In a gas or oil fired reverberatory furnace for aluminium, combustion produces large amounts of water vapour. The water vapour may react with aluminium forming aluminium oxide and hydrogen gas. This hydrogen gas is then the main source for hydrogen in molten aluminium.

Measurements of both water vapour in the furnace atmosphere (combustion off-gas) and dissolved hydrogen in the melt are presented. The measurements are compared to a model for hydrogen concentration in aluminium as function of the measured water vapour concentration. It is concluded that H₂O reacts with aluminium to H₂ and Al₂O₃. 49 % of this H₂ escapes from the interface to the bulk gas phase, and 51 % acts as a source for dissolved hydrogen in the melt.

Introduction

For many years it has been known that the gas which is in contact with liquid aluminium can have a large impact on the properties of the aluminium melt. For instance, both the oxidation rate [1, 2] and pickup of hydrogen from hydrogen gas been extensively studied [3, 4, 5, 6]. Previous studies often mention water vapour as the main source for hydrogen pick-up. However, no real measurements of water vapour and resulting hydrogen content have been found.

The work presented here includes measurements of water vapour in the atmosphere in contact with the melt, inside a gas fired melting furnace and measurements of hydrogen in the aluminium melt in the launder close to the furnace spout.

In the aluminium industry, liquid aluminium is commonly held in reverberatory furnaces for treatment and alloying before casting. The furnaces are heated by gas (or oil), which burns above the metal surface as shown in figure 1.

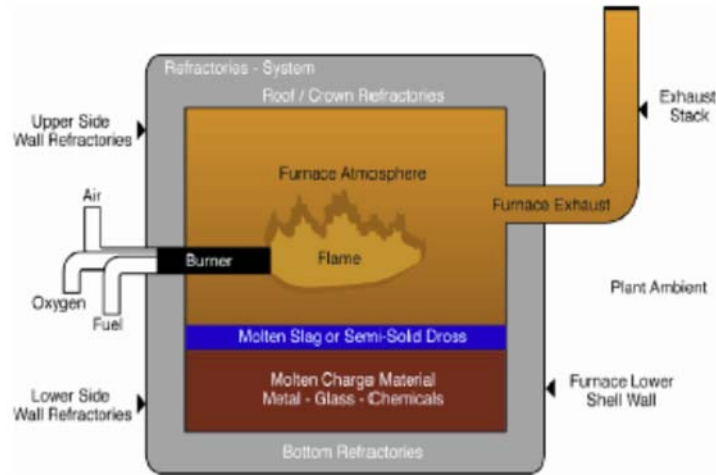
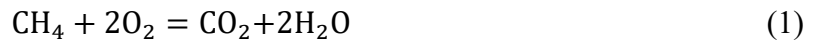
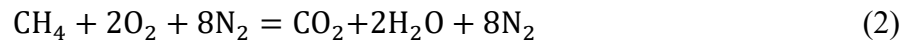


Figure 1: Schematic of a reverberatory furnace. Heat is supplied by gas-burners, by radiation from the flame and indirectly via the walls and ceiling. [7]

The fuel in a gas burner is often methane or propane. For methane, the combustion is given by

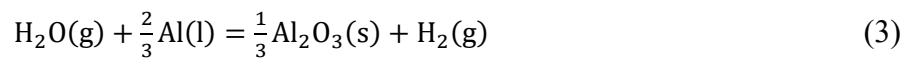


As seen from equation 1, two moles of water are produced for every mole of methane combusted. Often air, rather than pure oxygen, is used as source for oxygen. Then the combustion reaction can be written as



Which means that there will be "only" 18 % water in the atmosphere from an air-fuel burner compared to 67 % from an oxy-fuel burner. However, due to leakages industrial furnaces are never completely sealed. There are openings in tapping holes and around the main door where charging of solid material and dross removal etc. take place. If the furnace is not operated with an overpressure, these leakages will lead to suction of air into the chamber and reduce the water vapour concentration in the furnace atmosphere.

The water molecules may then in turn react with aluminium according to



With the possibility of hydrogen dissolution as



Then there is hydrogen gas present at the aluminium surface, which can enter the metal. The question becomes: What hydrogen concentration do we get in the melt from H_2O humidity in contact with Al?

Theory

The theory for hydrogen pick-up from water vapour is presented in *Principles of Metal Refining* by Thorvald Abel Engh [8]. In this paper, the model presented by Engh is extended by using the theory of

mass transfer between a gas phase and a solid surface presented by Davies [9]. This model is later compared to a model where all hydrogen from the reaction in equation (3) is available as a source for dissolution of hydrogen in the melt.

A significant point is that on both sides of an interface between a gas and a liquid there is a laminar boundary layer (giving a diffusion boundary layer) where the gas and melt move parallel to the interface. In these boundary layers, a specie which has a concentration gradient will inevitably cause a flux of this specie according to Fick's first law:

$$\dot{n} = -D \frac{dc}{dx} \quad (5)$$

where D is the diffusion coefficient, and c (local) concentration of the specie.

Since H_2O and Al are separated by a boundary layer in the gas, we cannot obtain p_{H_2} at the interface simply from thermodynamic or stoichiometric considerations. It is useful to look at the various steps involved. These are listed below where some are indicated in Figure 2.

1. Water vapour diffuses through the gas boundary layer to the metal surface.
2. The water molecules are adsorbed at the surface.
3. The adsorbed molecules react with Al according to equation 3.
4. Hydrogen molecules are desorbed from the surface to the atmosphere.
5. Hydrogen molecules diffuse back out of the gas boundary layer.
6. Hydrogen goes through the oxide layer.
7. Hydrogen molecules dissociate and form atomic hydrogen on the surface.
8. Hydrogen atoms diffuse through the metal boundary layer.

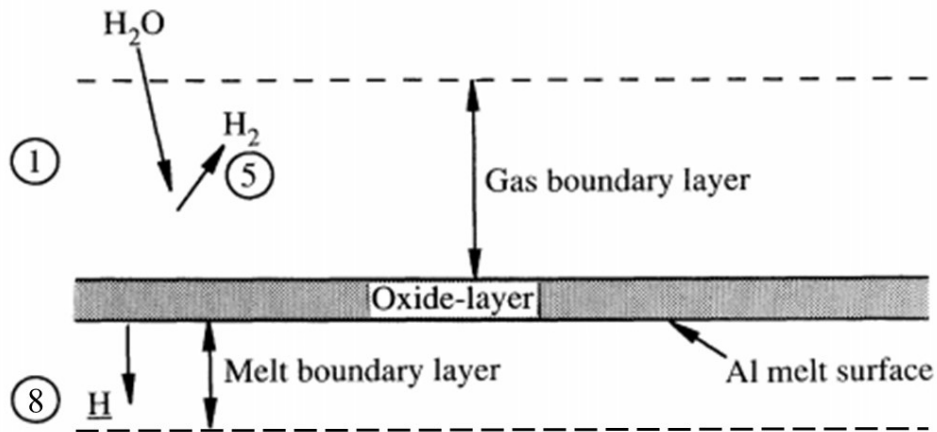


Figure 2: Some of the steps involved in the transfer of H to an Al melt [8]. The numbers inside the circles refer to the numbers in the list above.

We assume that chemical reactions, dissociation, absorption, desorption, and transfer through the oxide layer are rapid, and that diffusion through the gas and melt boundary layers are slow (steps 1, 5, and 8). As described in the textbook by Engh [8] this gives a ratio between the partial pressures of hydrogen at the interface and water vapour in bulk gas phase:

$$\frac{p_{H_2}}{p_{H_2O}} = \frac{k_{H_2O}}{k_{H_2}} \quad (6)$$

where k_{H_2O} and k_{H_2} are the mass transfer coefficients for step number 1 and 5 above.

The mass transfer coefficient is introduced since a detailed knowledge of the concentration profiles of H₂O and H₂ through the gas boundary layer is not known.

Often in refining metallurgy, when impurities are removed, the interesting boundary layer is in the melt. In the situation studied here, also the gas boundary layer, which the H₂O and H₂ molecules must diffuse through must be taken into account. This gas boundary layer is where H₂O molecules is transported inwards and H₂ molecules outwards. According to Davies [9] it can be deduced that for sufficiently large Sc (= ν/D) numbers:

$$k \propto D^{\frac{2}{3}} \quad (7)$$

Then the mass transfer coefficient ratio becomes

$$\frac{k_{\text{H}_2\text{O}}}{k_{\text{H}_2}} = \left(\frac{D_{\text{H}_2\text{O}}}{D_{\text{H}_2}} \right)^{\frac{2}{3}} \quad (8)$$

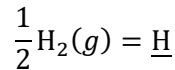
With the use of tabulated values for the diffusion coefficients [10], and the assumption that the ratio between them is not dependent on the temperature:

$$D_{\text{H}_2\text{O}}/D_{\text{H}_2} = 0.36$$

Then, with the assumption that the transport through the boundary layers are rate controlling, the flux of hydrogen into the melt is given by the expression for diffusion of hydrogen through the melt boundary layer

$$\dot{n} = k_{\text{H,tot}} \left(\frac{K_{\text{H}} \sqrt{p_{\text{H}_2}}}{f_{\text{H}}} - c_{\text{H}} \right) \quad (9)$$

where $k_{\text{H,tot}}$ is the mass transfer coefficient for the total transport from gas phase to the melt. K_{H} and f_{H} are the equilibrium constant and activity coefficient for the reaction



Then, the partial pressure of hydrogen at the melt interface is

$$p_{\text{H}_2} = \frac{k_{\text{H}_2\text{O}}}{k_{\text{H}_2}} p_{\text{H}_2\text{O}} = \left(\frac{D_{\text{H}_2\text{O}}}{D_{\text{H}_2}} \right)^{\frac{2}{3}} p_{\text{H}_2\text{O}} = 0.36^2 \cdot p_{\text{H}_2\text{O}} = 0.51 \cdot p_{\text{H}_2\text{O}} \quad (10)$$

In equilibrium $\dot{n} = 0$. Then finally, the (equilibrium) hydrogen concentration in the metal is given by

$$c_{\text{H}} = \frac{K_{\text{H}} \sqrt{0.51 \times p_{\text{H}_2}}}{f_{\text{H}}} \quad (11)$$

Measurements

Hydro Aluminium's reference centre in Sunndal, Norway has a melting furnace with a 20 ton capacity, equipped with a launder loop and a metal pump. When running the metal in the loop, it is possible to adjust melt flow and melt temperature freely without considering a DC casting process where a constant melt temperature is crucial.

Furnace atmosphere

By inserting a probe into the furnace exhaust channel, gas samples can be extracted from the atmosphere by gas analyser equipment. One such system is a ProtIR 204M from Protea [11]. This system is capable of measuring several gas species in addition to H₂O. However, only the water vapour is shown. The water vapour concentration was measured for two days. Part of the measurements is shown in Figure 4. It has been assumed that the total pressure in the furnace is 1 atm with a variation of less than $\pm 1\%$. This assumption is used for converting between concentration and partial pressure.

During the measured periods, it was attempted to hold the burner at constant power. The reason for this was that it was expected that the dissolution of hydrogen from water vapour is a slow process, and a constant water vapour concentration would give more reliable calculations.

It can be seen from the figure that the average water vapour concentration was higher the first day than the second day. One reason for the low water vapour concentration the second day is that we did run the burner with more excess air than during the first day, so that the combustion gas became diluted. At about 13:00 the first day, the burner was shut off for about 20 minutes. On the second day at about 13:40 the power had to be increased in order to avoid the metal from cooling down too in the launder loop.

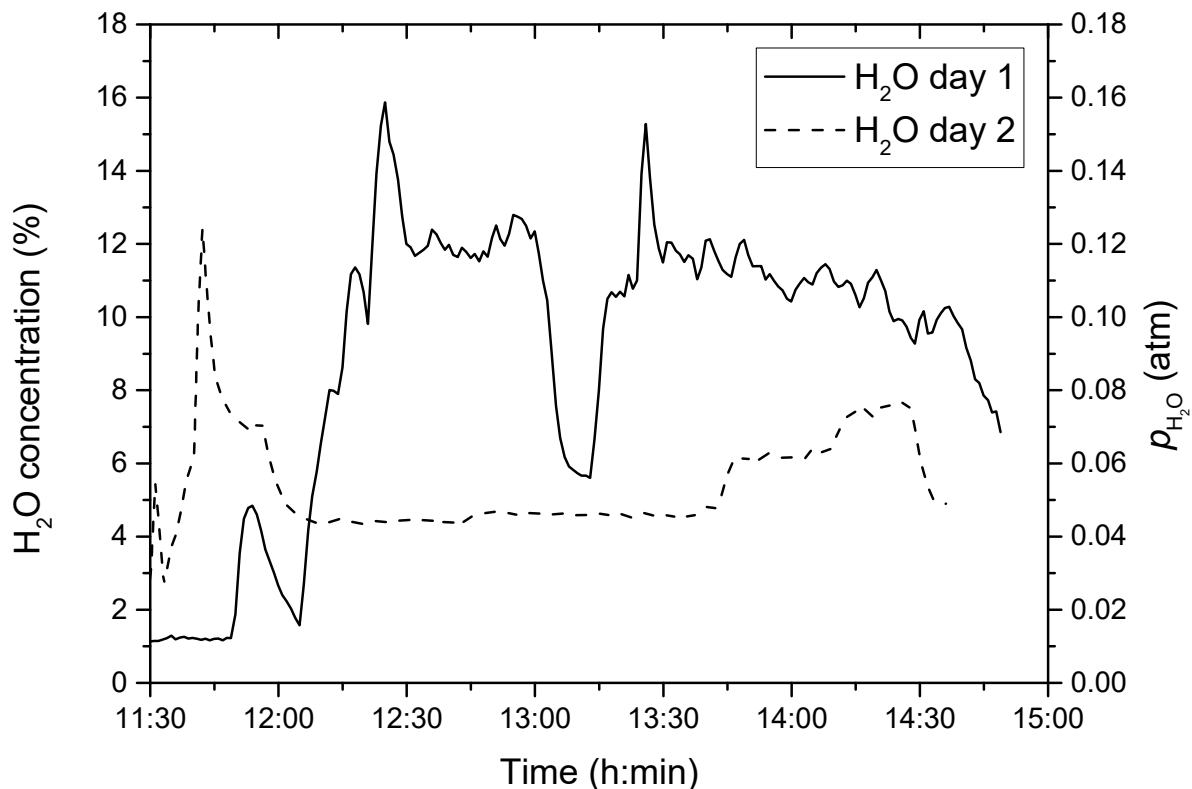


Figure 3: Measured water vapour concentration in the off-gas channel as function of time from an air-fuel burner. Left hand vertical axis is the measured water vapour concentration and right hand vertical axis the corresponding partial pressure of H₂O. For a total pressure of 1 atm, a H₂O concentration of 100 % corresponds to 1 atm partial pressure.

Hydrogen measurements

With an AISCAN instrument, the concentration of dissolved hydrogen in molten aluminium was measured right after the furnace spout. The instrument operates by putting a porous probe into the melt and running pure N₂-gas in a loop, from the instrument, down into the probe in the melt and up again into

the instrument. During this circulation of the N₂-gas, hydrogen atoms diffuse from the melt into the gas until the H₂ partial pressure in the gas is in equilibrium with the hydrogen concentration in the melt. This partial pressure of the gas mixture is then determined and together with a measured temperature and given alloy composition, the concentration of dissolved hydrogen in the melt is obtained.

According to the AISCAN user manual [12], the hydrogen concentration, S , in the melt is calculated according to

$$S = S_0 \times \sqrt{p_{H_2}} \times CF(A) \times CF(T) \quad (12)$$

Where $S_0 = 0.92$ ml/100g is the solubility of hydrogen in pure aluminium in equilibrium with 1 atm partial pressure of hydrogen at 700 °C, $CF(T)$ the temperature (given in °C) correction factor given by

$$CF(T) = \exp\left(6.531 \frac{T-700}{T+273}\right) \quad (13)$$

And an alloy correction factor $CF(A)$ defined by

$$CF(A) = 10^{0.0170 \times \%Mg - 0.0269 \times \%Cu - 0.0119 \times \%Si} \quad (14)$$

For the alloy used, which was a Hydro 300333 alloy containing 0.23 % Mg, 0.09 % Si, and 0.86% Cu, the alloy correction factor was

$$CF = 0.95$$

Equations 12 and 13 are basically Sieverts' law and a rewritten version of the model published by Ransley and Neufeld in 1948 [4].

The AISCAN unit was positioned by the launder, right after the furnace spout. Figure 4 shows the measured hydrogen concentration and melt temperature during test period for the two days.

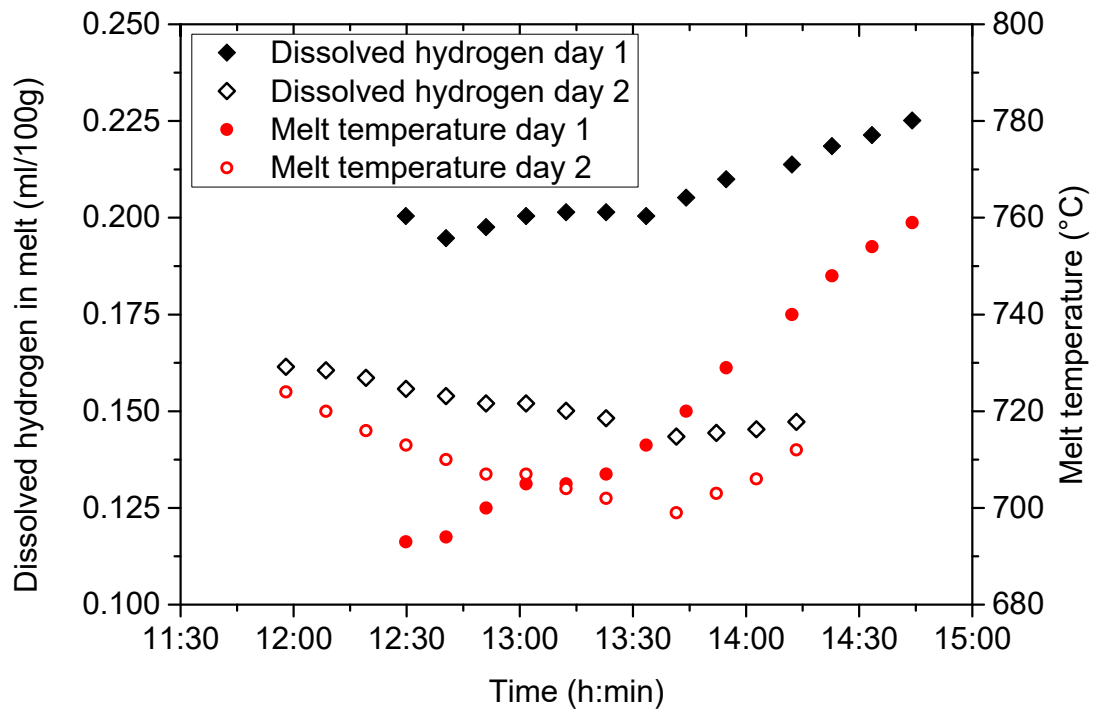


Figure 4: AISCAN measurements of melt temperature and hydrogen content during the two days. Diamonds show the hydrogen measurements and circles the melt temperature; filled symbols represent the first day and open symbols the second day.

The reason for the increased melt temperature the first day is that the power was kept at a relatively high level, basically too high to give constant temperature. The second day, when the burner power was relatively low, the melt temperature decreased until the power was increased somewhat (at about 13:40) and the melt temperature increased.

Discussion

Figure 5 shows both the water vapour measurements and the hydrogen measurements. This graph clearly shows that higher water vapour in the atmosphere gives higher hydrogen concentration in the melt. The figure also shows that the dissolution process of hydrogen from water vapour is slow. The gas measurements the first day show a drop in the water vapour at about 13:00 – 13:20. This water vapour drop does not give any significant drop in the measured hydrogen concentration in the melt.

The figure does not, however, give any information about how much of the water vapour acts as a hydrogen source.

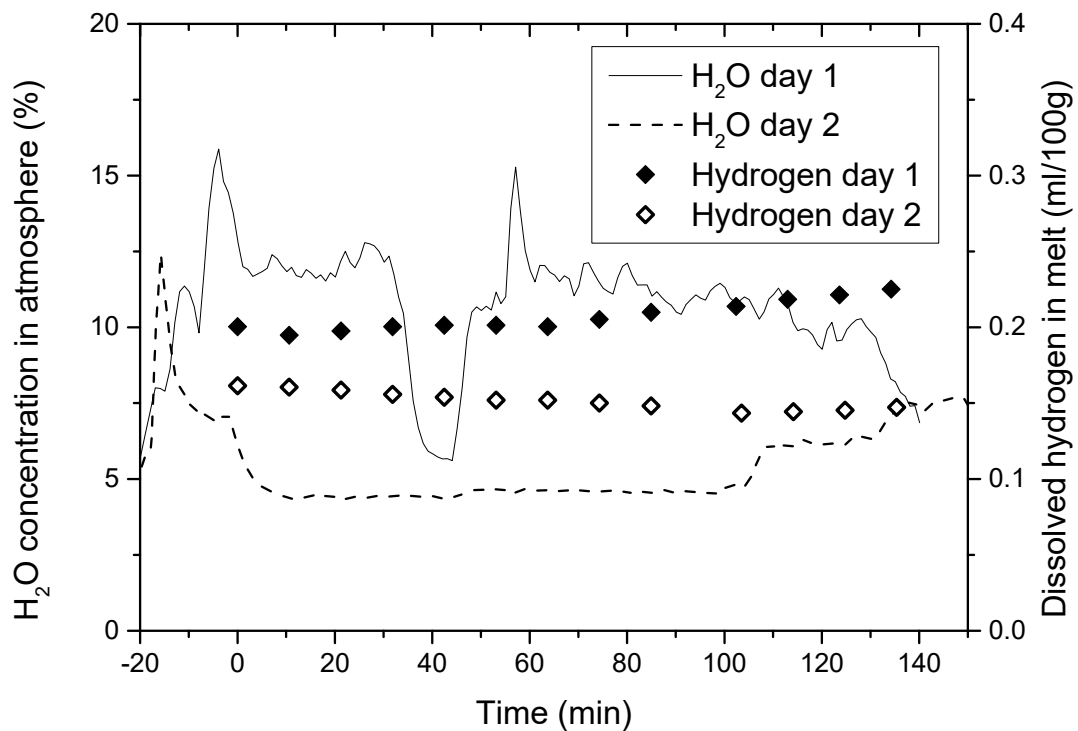


Figure 5: Water vapour concentration in furnace atmosphere and simultaneous hydrogen concentration in the melt for both days of measurements. The time scale is in minutes, starting from the first AISCAN measurement.

One possible way of treating water vapour as a hydrogen source is to assume that the water vapour acts as hydrogen source in a one-to-one ratio. That is, the equivalent partial pressure of hydrogen in equilibrium with the melt is equal to the partial pressure of water vapour above the melt. This approach was mentioned by Talbot [13] in 1975. Also, the AISCAN manual [12] recommends using this as an estimation of the hydrogen level above the melt. By using equations 12 – 14 together with the measured hydrogen concentration in the melt, the actual partial pressure of hydrogen in the circulating gas in the AISCAN can be calculated. Even though there probably is a large temperature gradient in the melt inside the furnace, the metal flowing out of the furnace, into the launder, will have the same temperature as the upper melt layer inside the furnace.¹ And since the reaction for dissolution of hydrogen (equation 4) into aluminium goes both ways, the partial pressure of hydrogen measured by the AISCAN must be the same as the partial pressure of hydrogen at the interface from the water vapour inside the furnace.

In Figure 6 the measured water vapour concentration in the furnace atmosphere and the calculated partial pressure of hydrogen, p_{H_2} are shown. This shows that only part of the hydrogen produced by the reaction between water vapour and aluminium stays at the interface and acts as a hydrogen source for hydrogen dissolution.

¹ It is likely the upper melt layer which exist from a tilting melting or holding furnace. Similar to pouring water containing ice from a mug, into a glass, it is difficult to avoid the ice from leaving the mug.

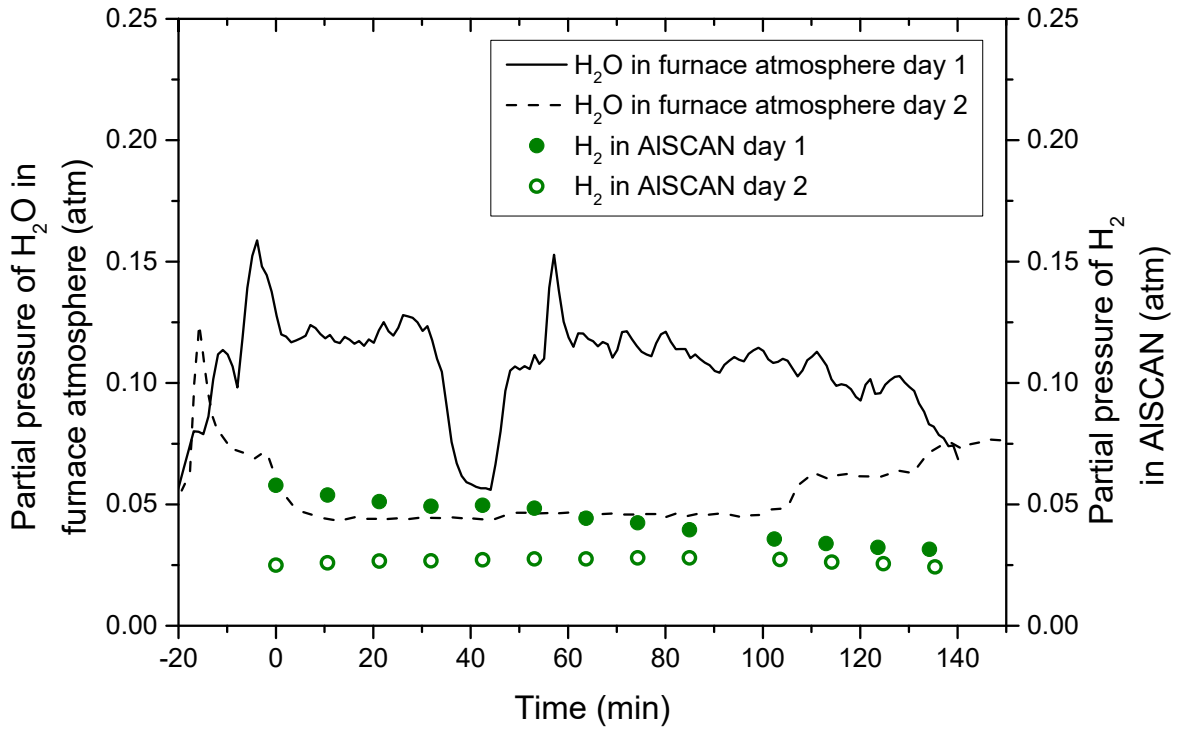


Figure 6: Calculated partial pressure of hydrogen in the AISCAN instrument (green dots) together with the partial pressure of water vapour during the two experiment periods are shown. Note that the units and scale of the two vertical axes are equal.

By using equations 12 – 14, the hydrogen concentration can be calculated from the measured water vapour measurements and (interpolated) melt temperature. Then two models for equilibrium between water vapour and dissolved hydrogen can be tested:

1. According to Talbot [3], setting the equilibrium hydrogen partial pressure in equation 12 equal to the partial pressure of water vapour in the bulk gas phase. That is $p_{H_2} = p_{H_2O}$. And
2. Taking into account that 49 % of hydrogen gas escapes from the melt-gas interface. That is, using equation 10: $p_{H_2} = 0.51 \cdot p_{H_2O}$

The results are presented in Figures 7 and 8 for day 1 and day 2, respectively. It can be concluded that for the two measurement series of water vapour concentrations and hydrogen concentration measurements in the melt, 49 % of the hydrogen produced at the melt interface escapes into bulk gas phase and 51 % acts as a source for hydrogen in aluminium. This supports the new model presented in this paper with the relation given in equation 10:

$$p_{H_2} = 0.51 \cdot p_{H_2O}$$

It can also be concluded that the process for obtaining equilibrium between atmospheric water vapour and dissolved hydrogen is slow. In Figure 8 where the temperature is relatively constant, the model presented fits the measured data well. However, in Figure 7, after about 13:00 – 13:30 where there is a drop in the measured water vapour concentration, the temperature is rising and the difference between the measured hydrogen concentration in the melt (black diamonds) and the models increases as the temperature increases (see Figure 4).

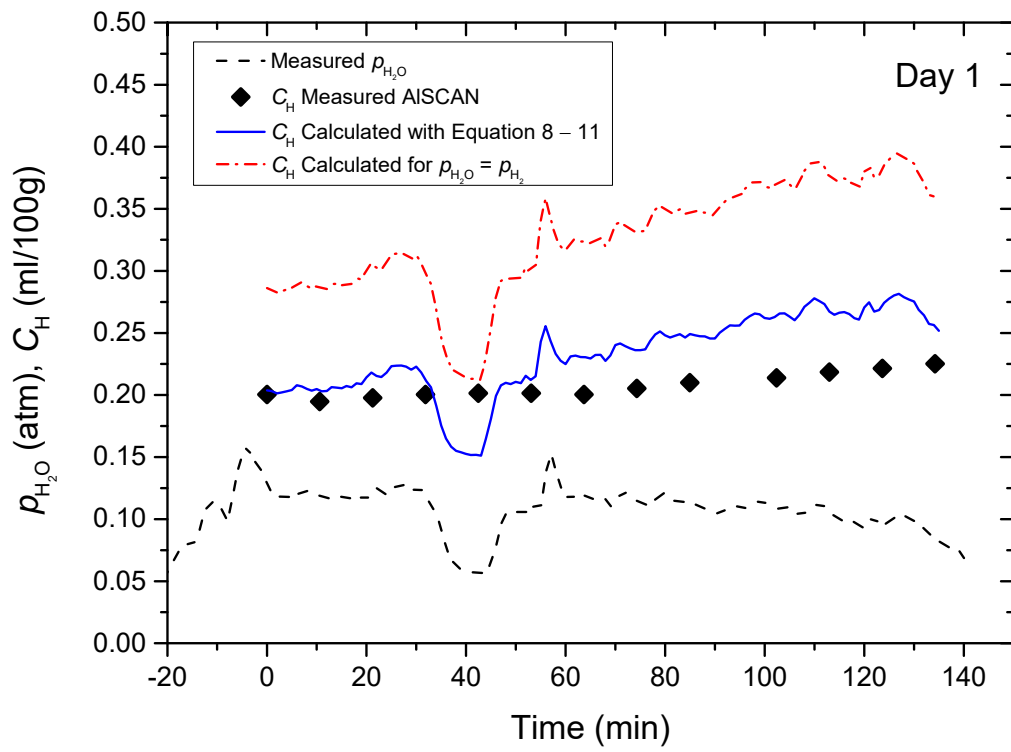


Figure 7: Measured hydrogen concentration in melt and water vapour partial pressure together with two different models for water vapour as source for hydrogen in melt for the first day with relatively high water vapour concentration. The temperature measurements (and interpolation between them) in Figure 4 is used to calculate the red and blue curves.

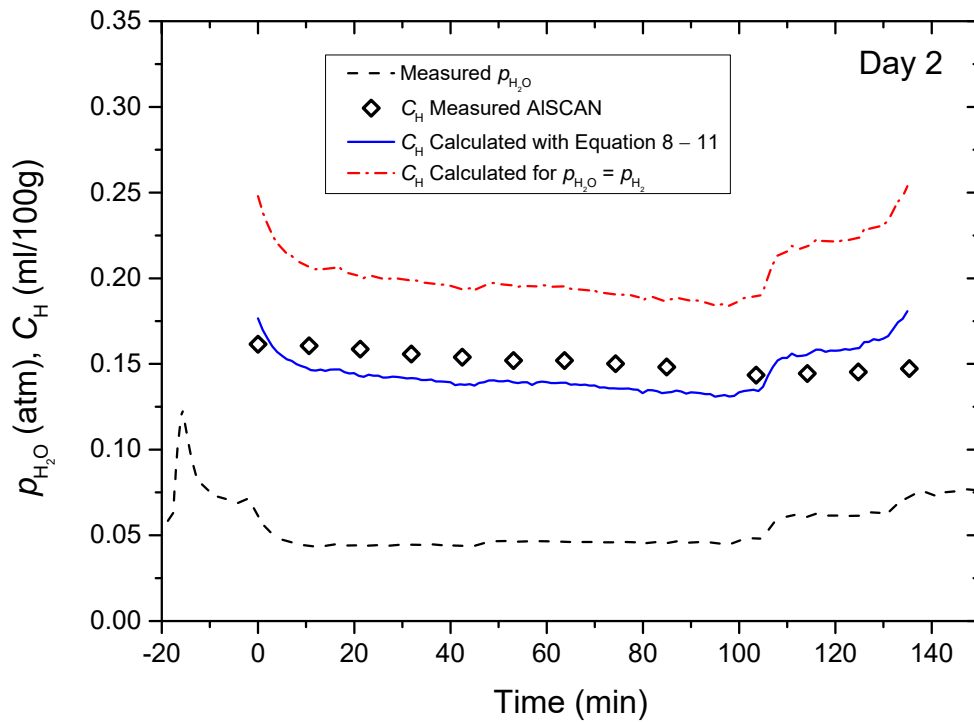


Figure 8: Measured hydrogen concentration in melt and water vapour partial pressure together with two different models for water vapour as source for hydrogen in melt for the second day with relatively low water vapour concentration. The temperature measurements (and interpolation between them) in Figure 4 is used to calculate the red and blue curves.

Conclusion

Concentration of water vapour in the off gas from a gas fired reverberatory furnace has been compared to AISCAN measurements of hydrogen in the liquid metal from the same furnace. Two measurement series were done with one relatively low and one relatively high water vapour concentration in the off gas. The measurements confirm that:

- There is a direct relation between water vapour concentration in the furnace atmosphere and the dissolved hydrogen in the melt.
- The transport of hydrogen from water vapour into the liquid metal is a slow process.
- By setting $p_{H_2} = 0.51 \cdot p_{H_2O}$, the measured water vapour concentration can be used directly as a source for hydrogen in the equations for dissolution.

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References

1. W. Thiele: *Die Oxydation von Aluminium-und Aluminium-legierungs-schmelzen*, **Aluminium** **38**, **1962**, pp. 780 – 786
2. C.N. Cochran, D.L. Belitskus, and D.L. Kinosz: *Oxidation of Aluminum-Manganese Melts in Air, Oxygen, Flue Gas, and Carbon Dioxide*, **Metallurgical Transactions B**, Vol 8B 1977, pp. 323 – 332
3. D.E.J. Talbot and P.N. Anyalebechi: *Solubility of hydrogen in liquid aluminium*. **Materials Science and Technology**, Vol. 4, January 1988, pp. 1 – 5
4. C.E. Ransley and H. Neufeld: *The solubility of hydrogen in liquid and solid aluminium*, **The Journal of the Institute of Metals**, Vol. 74, 1947-48 pp. 599 – 620
5. W.R. Opie and N.J. Grant: *Hydrogen Solubility In Aluminum and Some Aluminum Alloys*, **Transaction AIME Journal of Metals**, Vol. 188, October 1950, pp. 1237 – 1241
6. H. Liu, M. Bouchard, and L. Zhang: *An experimental study of hydrogen solubility in liquid aluminium*, **Journal of Materials Science**, Vol. 30 1995, pp. 4309 – 4315
7. J. Furu: *An Experimental and Numerical Study of Heat Transfer in Aluminium Melting and Remelting Furnaces*, **Doctoral thesis NTNU 2013:30**
8. T.A. Engh: *Principles of Metal Refining*, **Oxford University Press**, 1992, Chapter 7
9. J.T. Davies: *Turbulence Phenomena*, **Academic Press**, 1972, Chapter 3
10. D.R. Lide: *CRC Handbook of Chemistry and Physics*, 85th Edition 2004 – 2005, p. 6-220
11. <https://www.protea.ltd.uk/protir-204m.html>
12. ABB: *AISCAN Manual – Analyser for hydrogen in liquid aluminium*, IMZ9165, Rev. J Sep. 2015
13. D.E.J. Talbot: *Effect of Hydrogen in Aluminium, Magnesium, Copper, and Their alloys*, **International Metallurgical Reviews**, Vol. 20 1975, pp. 166 – 183