

# THE 4TH INTERNATIONAL CONFERENCE ON ALUMINUM ALLOYS

## HYDROGEN SOLUBILITY IN Li CONTENT MOLTEN Al ALLOYS

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### Abstract

Several kinds of Al-Li-(Cu)-(Mg) alloys cast by means of DC casting, were studied of their hydrogen solubility. Hydrogen activity coefficients in these alloys were calculated by the measured equilibrium hydrogen gas partial pressure to the melt with CLR method, compared with the analyzed hydrogen content in the ingot by HVE method. Interaction coefficient of Li, -0.18, was presumed using the above calculated coefficients and published interaction coefficients of other elements, such as Cu, Mg etc. From these figures, hydrogen solubility in the molten metal is estimated of 1.5 times by 1 mass% Li addition.

### Introduction

The mechanical property of aluminium is spoiled by hydrogen in its strength and ductility<sup>1</sup>. In case of aluminium lithium alloy, although not explained clearly<sup>2</sup>, the existence of hydrogen at ingot casting stage is deemed to have similar affect, and its volume contents must be controlled. Partial pressure of hydrogen equilibrium to melt is measured by means of Closed Loop Recirculation method ( here in after called CLR), but the relationship between said partial pressure of hydrogen and hydrogen content in melt, in connection with lithium content, is not reported yet. This paper presents interaction coefficient to be applied for calculating hydrogen content from the results of CLR. This coefficient is introduced by comparing partial pressure of hydrogen measured by CLR and hydrogen content in DC ingot measured by Hot Vacuum Subfusion Extraction method.

### Calculating Procedure

The hydrogen content and partial pressure of hydrogen in pure aluminium are shown as follows. Relation between diatomic hydrogen in atmosphere and monatomic hydrogen in pure molten

aluminium are shown as the Equation (1).



Square root of activity  $a_{\text{H}_2}$  of hydrogen molecular and activity  $a_{\text{H}}$  of monatomic hydrogen in molten aluminium make constant proportion, and this equilibrium constant is placed K. Hydrogen activity in molten aluminium is given in the equation using  $\gamma$  (interaction coefficient of Henry's law) and S (hydrogen solved in molten aluminium). In case of ideal gas, activity of molecular hydrogen gives the same value with partial pressure of hydrogen. After all, hydrogen content in molten aluminium and square root of partial pressure in atmosphere result in constant ratio as shown in Equation (2). This is called "Henry's law".

$$K = \frac{a_{\text{H}}}{a_{\text{H}_2}^{1/2}} = \frac{\gamma S}{P_{\text{H}_2}^{1/2}} \quad (2)$$

Equilibrium constant is shown in Van't Hoff's law as a function of temperature. Equation (3) is derived from this law after integration.

$$\ln K = C + \frac{\Delta H^\circ}{RT} \quad (3)$$

where  $\Delta H^\circ$  is the enthalpy of dissociation and dissolution of diatomic hydrogen to molten metal. R is gas constant, T is absolute temperature, and C' is constant.

From Equation (2) and (3), Equation (4) is derived.

$$\ln\left(\frac{S}{S^\circ}\right) = \text{Constant} + \frac{\Delta H^\circ}{RT} + \frac{1}{2} \ln\left(\frac{P_{\text{H}_2}}{P^\circ}\right) \quad (4)$$

where  $S^\circ$  is a standard value of solubility equal to 1 cm<sup>3</sup> of diatomic hydrogen measured at 273K and 101325Pa per 100g of metal.  $P^\circ$  is a standard value of pressure equal to 101325Pa. This equation shows that solubility of hydrogen in molten pure aluminium is calculated using equilibrium partial pressure of molecular hydrogen and the temperature of the melt.

In case of aluminium alloys, Messrs. G.K.Sigworth and T.A.Engel calculated interaction coefficients of several components of aluminium alloys<sup>3</sup> under assumption, that the hydrogen activity was affected with respective component elements. The same way was applied in this study to determine the interaction coefficient of lithium in aluminium alloy. Hydrogen solved in molten aluminium (S) was affected, to the extent of interaction coefficient ( $f_{\text{H}}$ ) in Equation (5), and this  $f_{\text{H}}$  was calculated using Equation (6).

$$\ln\left(\frac{f_H S}{S^0}\right) = \text{Constant} + \frac{\Delta H^0}{RT} + \frac{1}{2} \ln\left(\frac{P_H}{P^0}\right) \quad (5)$$

$$\log(f_H) = \sum_{j=2}^n e_H^j [\text{wt}\% j] + \sum_{j=2}^n r_H^j [\text{wt}\% j]^2 \quad (6)$$

where j is element component metal,  $e_H^j$ ,  $r_H^j$  is effect of respective components to  $f_H$ .

The component which has large " $e_H$ " (i.e. large  $f_H$ ) makes partial pressure of hydrogen higher. In other words, hydrogen solved in melt is reduced under same partial pressure.

In this report, effect of lithium to interaction coefficient was calculated and presented. Equation (7) was applied in the calculation.

$$e_H^{\text{Li}} = \frac{\log(f_H \text{ from measurement}) - \log(f_H \text{ other than Li})}{[\text{wt}\% \text{ Li}]} \quad (7)$$

Total interaction coefficient introduced from measurement by CLR was deducted respective interaction coefficients of components other than lithium, that were reported beforehand. Messrs. G.K.Sigworth and T.A.Engl's paper was introduced as interaction coefficients.

#### Experimental Procedure<sup>4</sup>

Experimental assembly is shown in Figure 1. Procedure is as follows;

- i) Aluminium and components, except lithium and Al-Ti-B, are melt in induction furnace covered by argon atmosphere.
- ii) Lithium is added.
- iii) Degassing by means of argon gas bubbling.
- iv) Al-Ti-B is added.
- v) DC casting in slab (150-350 mm) or billet ( $\phi 228\text{mm}$ ) form.

Following measurements were taken during this procedure.

- i) Equilibrium hydrogen concentration and temperature of melt at the fore end of trough in the course of DC casting.
- ii) Hydrogen and solute element concentration in ingot metal, sampled from stable portion.

Hydrogen solubility of metal by means of

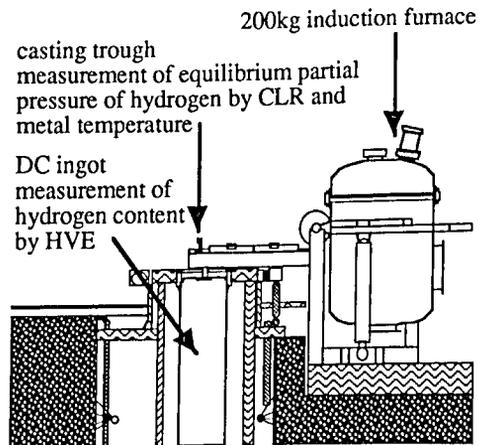


Figure 1. Experimental assembly.

HVE was carried out by Messrs. Sumitomo Light Metal Industries, LTD. Block diagram of hydrogen determinator using CLR method is shown in Figure 2<sup>5</sup>. Diaphragm pump, thermal conductivity detector, and probe made a circuit with high purity argon gas in it. Hydrogen in melt was absorbed in circulating argon gas, and equilibrium between gaseous hydrogen and hydrogen in the melt was established. Hydrogen solubility was measured by thermal conductivity detector. Temperature was taken simultaneously by K thermocouple. Hence; argon gas volume was about 6 cm<sup>3</sup> and pumping capacity was about 1.5 cm<sup>3</sup> per second.

### Results

Example of hydrogen measurement at casting trough is shown in Figure 3. Hydrogen gas solubility and temperature of melt were taken every 10 seconds after starting measurement. Mean of readings of 90% and higher was taken as equilibrium hydrogen concentration. Temperature of melt was taken corresponding to hydrogen concentration measurements. Equilibrium hydrogen partial pressure was calculated under assumption of total gas pressure was 101325Pa.

Several kinds with total 23 charges of aluminium alloys were provided in the experiment, such as 2090, 2091, 8090 standard alloys (10ch.), Al - 5 mass% Cu - 1 mass% Li (5ch.) and Al - 2.5 mass% Li - 2 mass% Mg (8ch). Measured partial pressure of hydrogen were in range of 0.01 and 0.1 Pa/Pa, temperature 943 and 993 K. Hydrogen solubility in DC ingot were around 0.2 to 0.5 (S/S<sup>o</sup>), that is similar Figure reported previously in other papers<sup>6</sup>.

Interaction coefficient of lithium over activity coefficient ( $e_{II}$ ) were calculated for each charge

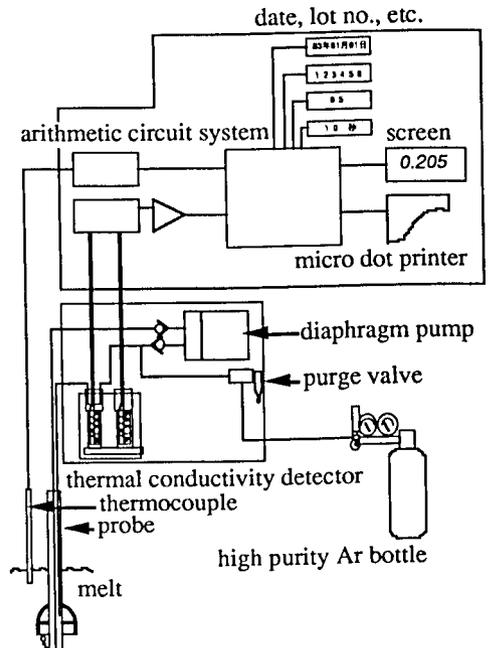


Figure 2. Block diagram of hydrogen determinator using CLR method.

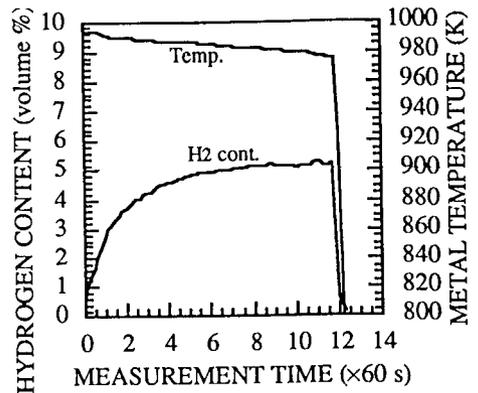


Figure 3. Example of hydrogen measurement.

of metals by each respective measurements. The result (i.e.  $e_H$  of lithium) had mean value of -0.18, with dispersion by about 3 times of maximum and minimum figures. This mean value of -0.18 is much larger figure compared with that of magnesium (-0.01) in absolute value. Figure 4 shows the plots of respective charges in measured hydrogen content (horizontal axis) against calculated value (vertical axis) using the  $e_H$  (-0.18) derived above. The diagonal chain line shows the result of proposed  $e_H$ ; which we believe applicable to estimate hydrogen content using measured value from melt by CLR.

### Discussions

#### Verification

Messrs. P.N.Anyalebechi, D.E.J.Talbot, and D.A.Granger measured hydrogen solubility in Al-Li binary melt<sup>7</sup>, and reported solubility was in the Equation (8).

$$\log\left(\frac{S}{S^0}\right) - \frac{1}{2} \log\left(\frac{P}{P^0}\right) = \frac{-A}{T} + B \quad (8)$$

where; A and B are constant.

Messrs. R.Y.Lin and M.Hoch proposed Equation (9) for hydrogen solubility<sup>8</sup>.

$$T \ln \gamma = \sum_{j=Al}^H X_j(A_j + A_j T) + \sum_{j=Cu}^H (B_j X_j X_{Al} (1 - X_j)^{n_0} + B_j T X_j X_{Al} X_j^{n_1}) \quad (9)$$

where;  $\gamma$  is Henry's constant. j is elements of melt; Al, Cu, Mg, Si and Li.

Figure 5. shows comparison of calculated value of hydrogen content in melt, versus metal temperature, under 101325Pa atmosphere, of Al - 2 mass% Li alloy. hence;

- i) All three values are much higher than that of pure aluminium, although these three lines are dispersed each other.
- ii) Line of this study is between the previous two.

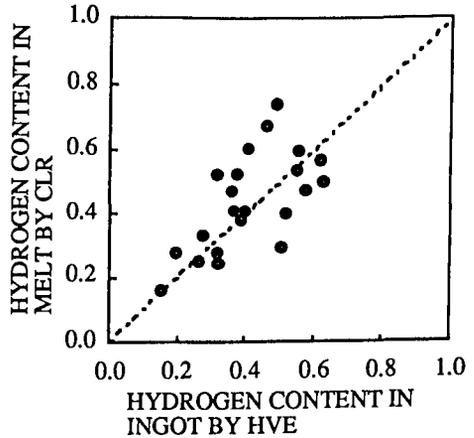


Figure 4. Comparison of hydrogen content in ingot with calculated value.

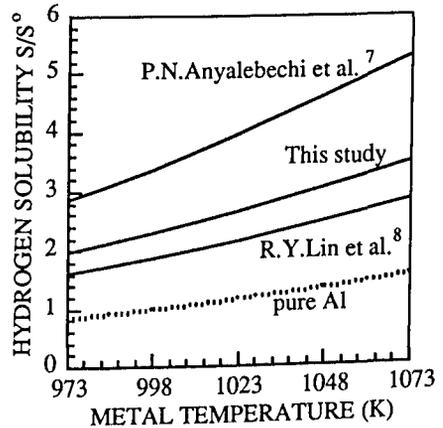
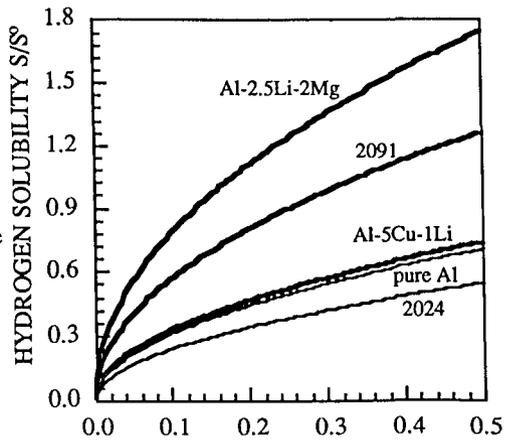


Figure 5. Comparison of calculated values in Al-2Li.

Hydrogen solubility difference in alloys

Calculations were carried out, using the interaction coefficient on several alloys, shown in Figure 6. Al-Li-Cu alloys containing small lithium element shows similar value of pure aluminium. Standard alloy 2091 has hydrogen solution about double of pure aluminium and Al-Li-Mg alloys, in which Li and Mg contents are larger than those of 2091, shows about 3 times of pure aluminium. On the other hands, non lithium content alloys, for example, standard 2024, gives smaller value of that of pure aluminium.



PARTIAL PRESSURE OF HYDROGEN P/P<sup>0</sup>  
 Figure 6. partial pressure of hydrogen vs hydrogen solubility at 973K in the several kinds of alloys.

Minimum attainable hydrogen solubility

Minimum hydrogen solubility attainable by means of rotary nozzle degassing system, against interaction coefficient was reported by Messrs. Otsuka et al., which was plotted around the curve shown in Figure 7<sup>9</sup>. Al-Li alloys with respective interaction coefficient are shown by vertical line on the figure, and the cross points with the curve give minimum attainable hydrogen solubility; standard Al-Li alloys, about 0.2; Al-Li-Mg system, about 0.25; and so on.

Atmosphere in degassing system might affect minimum attainable solubility<sup>10</sup>, minimum value possibly be reduced by improving this covering gas. On the other hand, the hydrogen porosity development in ingot is influenced by magnitude of solubilities in the solid metal and thickness of mushy zone, then high content of hydrogen in the liquid metal does not result in high porosity density in the ingot.

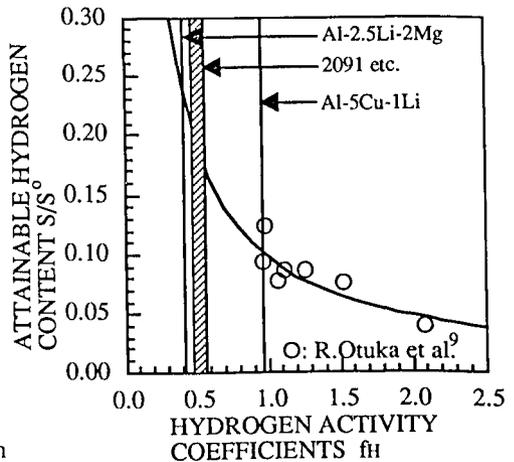


Figure 7. attainable hydrogen solubility by Ar gas bubbling vs hydrogen activity coefficient.

## Summary

As for Al-Li system alloys, the relation between the hydrogen solubility in melt and the equilibrium partial pressure of hydrogen was examined experimentally, in relation to the change in interaction coefficient as a function of elements. Effect of lithium upon interaction coefficient was numerically expressed (-0.18). Applying this value, CLR method became possible to evaluate hydrogen solubility in molten Al-Li alloys. Results of calculation using this value shows that, Al-Li alloys has solubility of hydrogen much larger, by several times, than other Al alloys.

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