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An experimental study of hydrogen solubility in liquid aluminium

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Hydrogen solubility in molten aluminium at different temperatures from 973–1123 K, has been measured using Sieverts' method. Inert gas (helium or argon) was used as a reference gas to calibrate the measurement system of the Sieverts' apparatus. The measured hydrogen solubility was found to vary with the reference gases. Helium was detected to be soluble in liquid aluminium. When helium is used as the reference gas, its solubility resulted in lower measured hydrogen solubility than that when argon was used to calibrate the measurement system of the apparatus. Argon gas was therefore considered as an appropriate reference gas when Sieverts' method is used to measure the hydrogen solubility in liquid aluminium. The hydrogen solubility, S, in liquid aluminium as a function of melt temperature, T, determined in the present investigation is expressed as $\log S = (-2980/T) + 3.07$.

1. Introduction

The study of hydrogen activity in molten aluminium can be traced back to the beginning of this century [1–15]. The low solubility of hydrogen gas in liquid aluminium causes experimental difficulties in determining its true values. Among the many techniques available for the determination of hydrogen solubility in molten aluminium, Sieverts' method [2] has been considered the most reliable and has been most frequently used.

Sieverts' method determines hydrogen solubility in molten aluminium using a Sieverts' apparatus, as schematically depicted in Fig. 1, which directly measures the volume of hydrogen gas absorbed by a known weight of liquid aluminium sample contained in an absorption bulb at a controlled temperature. The volume of the space occupied by hydrogen in Sieverts' apparatus needs to be calibrated by a reference gas which must be insoluble in liquid aluminium so that the volume change of hydrogen due to its dissolution can be calculated. The measurement accuracy and precision by this method depend upon several factors, such as the volume of the dead space of the absorption bulb, the weight of the sample, and the choice of the reference gas. The values of the hydrogen solubility in liquid aluminium determined by this method varied to a certain degree from one investigator to another, as listed in Table I, no doubt because of the experimental difficulties. Among the data reported, those in [8, 9, 12] have been well referred to so far, and in some of these investigations [9, 12] helium gas was used as the reference gas to calibrate the measurement system of the Sieverts' apparatus.

It is easy to understand that by Sieverts' method any solubility of a reference gas will result in biased readings of hydrogen solubility from their true values. For this reason, an inert gas such as neon, argon or helium, is usually chosen as the reference gas, because they do not react with liquid aluminium. However, "chemically inert" is not a synonym of "insoluble"; the insolubility of these inert gases in liquid aluminium needs to be verified before they are employed as the reference gas.

In the present work, a comparison was made of hydrogen solubilities measured by Sieverts' method with argon and helium as the reference gas, respectively, to investigate the influence of the reference gas on the accuracy of measurement. The solubility of helium in liquid aluminium was semi-quantitatively detected in the present investigation and the hydrogen solubility was therefore evaluated using argon as the reference gas. The measurements were carried out at melt temperatures of 973, 1023, 1073, and 1123 K and under different hydrogen partial pressures below 760 mm Hg.

2. Experimental procedure

2.1. Apparatus and materials

An apparatus working on Sieverts' principle was constructed to measure the gas content in liquid aluminium (Fig. 1). This apparatus is mainly constituted of two parts: an absorption bulb, and a mercury barometer which also works as a gas burette. A reference gas of helium or argon was used to calibrate the volume of the measurement system. The soluble gas to be measured, hydrogen or helium, in the same quantity as that of the reference gas, was admitted into the absorption bulb and its respective solubility in liquid aluminium was determined by comparing the volume occupied by the reference gas and that by the soluble gas after absorption equilibrium has been reached.

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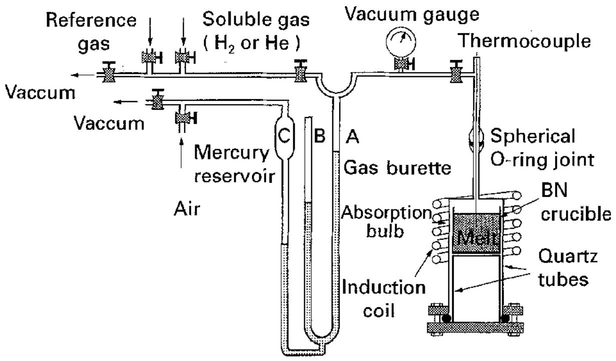

Figure 1 Schematic diagram of Sieverts' apparatus.

TABLE I Values of hydrogen solubility measured at 973 K and under 1 atm hydrogen partial pressure by different authors

Reference	Solubility (ml/100 g)
Röntgen and Braun [3]	0.08
Baukloh and Oesterlen [5]	0.95
Baukloh and Redjali [6]	0.45
Ransley and Neufeld [8]	0.91
Opie and Grant [9]	1.00
Eichenauer *et al.* [10]	0.62
Talbot and Anyalebechi [12]	0.88

The measurement accuracy and precision in this experiment are dependent upon (i) the volume of the dead space of the absorption bulb, (ii) the weight of the aluminium sample, and (iii) the properties of the reference gas. A small dead space of the absorption bulb is favourable to measurement precision. In order to make the dead space as small as possible, two cylindrical quartz tubes were used to construct the absorption bulb so that its dead space could be limited to about 50 cm^3. It is apparent that a weighty sample was preferred to absorb more soluble gas in order to reduce relative error. In the present work, a sample of about 300 g was used, which was about three times that used by previous investigators. Inert gases which have been used as the reference gas include neon [8] and helium [9, 12, 13]. The solubility of these inert gases in liquid aluminium and their thermal properties are the important criteria for the selection of the reference gas. In the present investigation, helium or argon gas was used as the reference gas, for comparison. All the gases used in the present investigation have a purity of over 99.99%.

A boron nitride crucible with a dimension of 64 mm diameter × 64 mm was installed inside the absorption bulb. The selection of crucible material was based on the following criteria: (i) chemical stability, (ii) thermostability, and (iii) cost. Several candidates, such as graphite, silicon carbide, alumina, and boron nitride, were tried in the present experiment, and boron nitride was finally chosen because it satisfied the above-mentioned conditions the best. An induction heating system was employed to melt the sample because it has certain advantages over resistance heating system, such as more precise temperature control ($\pm 1\,^{\circ}C$ in the present experiment) and the accelerated absorption effect due to the induction stirring. Aluminium of 99.99% purity was used to prepare the ingots. The ingots were then machined to the dimensions which just fitted the crucible with sufficient tolerance for thermal expansion during heating.

2.2. Measurement procedure

Before heating, the absorption bulb and the manifold were evacuated up to $\sim 10^{-3}$ Pa to avoid surface oxidation of the aluminium sample during heating. The heating rate was controlled such that all the volatile materials which vaporized during heating could be removed without significantly worsening the vacuum. The sample was then melted and its temperature was controlled at a prescribed value, normally 1073 K, for about 30 min for degassing. It is imperative to achieve a vacuum degree of at least 10^{-3} Pa before measurement, because the vacuum degree is a critical factor in the accuracy of measurement.

The melt temperature was adjusted to a predetermined value after degassing and was maintained at that level for about 5 min in order to stabilize it. Reference gas was admitted into the gas burette and the manifold between the absorption bulb and the mercury column A (Fig. 1) at a prescribed pressure, and then it was introduced into the absorption bulb. The volume of the dead space was thus calibrated from the pressure drop and the volume change of the space occupied by the calibration gas. The melt temperature would drop to certain degree due to the heat exchange between the introduced gas and the hot melt, it was therefore accordingly adjusted to the predetermined temperature and was held at that temperature for at least 10 min, this being approximately equal to the maximum absorption time of the soluble gas in molten aluminium. The system was then evacuated up to the same level as that before the reference gas was admitted, and the whole procedure was repeated using the soluble gas to be measured. The solubility of the soluble gas could be calculated from the difference between the volume of the reference gas and that of the soluble gas left in the absorption bulb under the same pressure.

Three sets of experiments with different reference/soluble gas combinations, as listed in Table II, were carried out. These experiments were designed such as to detect the helium solubility in liquid aluminium and to evaluate its influence on the accuracy of hydrogen solubility measurement when helium was used as the reference gas, while obtaining true values of the hydrogen solubility in liquid aluminium was the ultimate target of this investigation. This experimental design was based on the assumptions that argon was insoluble in liquid aluminium and did not significantly differ in thermal behaviour from that of hydrogen. The measurements were carried out at given melt temperatures from 973–1123 K and under different levels of partial pressure of the soluble gas, below 760 mm Hg.

TABLE II List of experiments with different reference/soluble gas combinations

Experiment	Reference gas	Soluble gas	Melt temperature (°C)
A	Argon	Hydrogen	700–850
B	Helium	Hydrogen	700, 800
C	Argon	Helium	700, 800

3. Results and discussion

3.1. Hydrogen solubility measured in experiment A (reference gas: argon)

Plots for the relationship between the measured hydrogen solubility and the square root of the hydrogen partial pressure are shown in Fig. 2. It is easily seen that at each melt temperature the hydrogen solubility has a linear relationship with the square root of hydrogen partial pressure. Such a relationship is the so-called Sieverts' law and can be theoretically obtained from the equilibrium for the absorption process of hydrogen in molten aluminium

$$\frac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{H(in\ Al)} \tag{1}$$

for which the equilibrium constant is

$$K_{\mathrm{H_2}}^{\mathrm{Ar}} = \frac{[\mathrm{H}]_{\mathrm{in\,Al}}^{\mathrm{Ar}}}{(P_{\mathrm{H_2}})^{\frac{1}{2}}} \tag{2}$$

where $P_{\mathrm{H_2}}$ is the hydrogen partial pressure in equilibrium with the dissolved hydrogen in liquid aluminium, $[H]_{\mathrm{in\,Al}}^{\mathrm{Ar}}$ and $K_{\mathrm{H_2}}^{\mathrm{Ar}}$ are hydrogen content in liquid aluminium and the equilibrium constant, with the superscripts denoting that measurement was performed with argon being used as the reference gas.

In Equation 2 instead of activity the hydrogen content is directly used because the Al–H solution is a typical dilute solution and hence Henry's activity coefficient is 1. Also, Henry's standard state for hydrogen content in Equation 2 is chosen as 1 ml volume hydrogen gas at the standard state (SPT, i.e. 1 atm pressure and 273 K) dissolved in 100 g aluminium (ml/100 g) which corresponds to 8.93×10^{-4} mol kg^{-1} in molality units. The linear relationship displayed in Fig. 2 indicates that Sieverts' law was well obeyed which, in turn, proved the reliability of the measurements in the present experiment.

The value of hydrogen solubility under 1 atm hydrogen partial pressure for each melt temperature can be simply evaluated by extrapolation of each straight line in Fig. 2. The temperature dependence of the hydrogen solubility under 1 atm hydrogen partial pressure can then be obtained by application of a van't Hoff isobar [16]

$$\frac{\mathrm{d}(\log K_{\mathrm{H_2}}^{\mathrm{Ar}})}{\mathrm{d}(1/T)} = -\frac{\Delta H^\circ}{R} \tag{3}$$

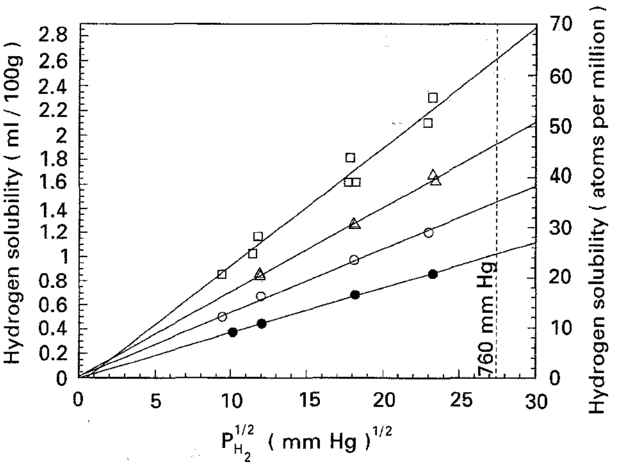

Figure 2 Plots of the relationship between the measured hydrogen solubility and the square root of the hydrogen partial pressure at different melt temperatures from 973–1123 K with argon being used as the reference gas: (●) 973 K, (○) 1023 K, (△) 1073 K, (□) 1123 K.

where ΔH° is the standard heat of solution of hydrogen in molten aluminium and T is the Kelvin temperature. For convenience, let S represent the hydrogen solubility $[H]_{\mathrm{in\,Al}}^{\mathrm{Ar}}$, then from Equation 2 we obtain

$$\frac{K_{\mathrm{H_2}}^{\mathrm{Ar}}}{K_{\mathrm{H_2}}^{0,\mathrm{Ar}}} = \frac{S}{S^0} \tag{4}$$

where $K_{\mathrm{H_2}}^{0,\mathrm{Ar}}$ and S^0 denote the equilibrium constant and the hydrogen solubility under 1 atm hydrogen partial pressure and at the melt temperature of 973 K. Integrating Equation 3 and introducing Equation 4 into the consequent equation yields

$$\log S = -\frac{\Delta H^\circ}{RT} + C \tag{5}$$

where C is the integration constant, and ΔH° is considered to be temperature-independent. The values of C and ΔH° can be obtained by plotting the values of $\log S$ versus the reciprocal of the melt temperature, T, which yields a straight line and is displayed in Fig. 3, accompanied by those obtained from previous investigations.

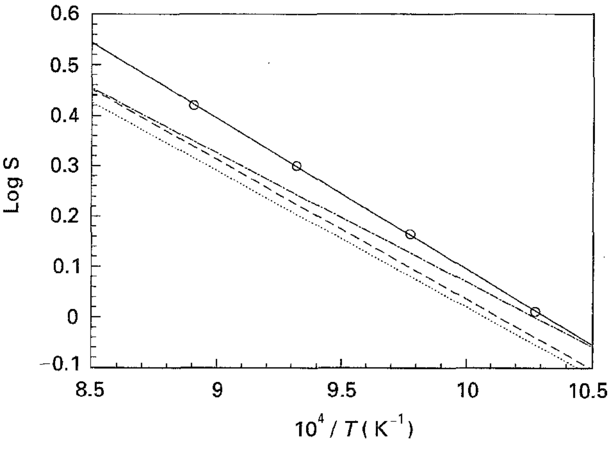

Figure 3 Plots of the relationship between the hydrogen solubility and the melt temperature determined by different authors: (○) present work, (- - -) [8], (· · ·) [12], (— - —) [9].

TABLE III Sample weight, heat of solution of hydrogen in liquid aluminium ΔH^0, integration constant, C, in Equation 5, and the determined hydrogen solubility at 973 K melt temperature and under 1 atm hydrogen partial pressure, S^0, by different authors

Reference	Reference gas	Weight of sample (g)	ΔH^0 (kcal mol^{-1})	C	S^0 (ml/100 g)
Talbot [12]	Helium	~ 100	5.365	2.72	0.881
Opie [9]	Helium	~ 100	5.067	2.62	0.998
Ransley [8]	Neon	30–40	5.484	2.80	0.911
Present authors	Argon	~ 300	5.921	3.07	1.026

It is seen that the present work gives relatively higher hydrogen solubility in molten aluminium over the whole investigated temperature range than those of the previous investigators using the same technique and similar experimental procedures except for the difference of the reference gases. Because the values were obtained by the same experimental principle, the difference between the hydrogen solubility values obtained by the present authors and those by the previous investigators must have been caused by the difference in the experimental conditions. In addition to the sample weight factor which determines the experimental relative error, the selection of the reference gas is believed to be the dominant factor in the experimental accuracy. In Table III these two factors, the determined values of hydrogen solubility, the heat of solution of hydrogen in liquid aluminium, and the integration constant, C, in Equation. 5, obtained by different investigators are listed. The temperature dependence of the hydrogen solubility in liquid aluminium was determined by the present investigation to be

$$\log S = -\frac{2980}{T} + 3.07 \tag{6}$$

where S is in the units of ml(SPT)/100 g. Equation. 6 is valid within the temperature range investigated in the present work.

3.2. Hydrogen solubility measured in experiment B (reference gas: helium)

Experiment B listed in Table II was carried out to determine the effects of different reference gases on the measured hydrogen solubility values. The plots of the measured hydrogen solubility versus the square root of the hydrogen partial pressure are shown in Fig. 4 in comparison with the results obtained from Experiment A where argon was used as the reference gas. Application of the least squares method to the measured hydrogen solubility in experiment B and the square root of the hydrogen partial pressure, showed that a quadratic model suited the experimental data better than a linear model.

It is believed that the quadratic feature of the relationship between the measured hydrogen solubility and the square root of the hydrogen partial pressure was due to the solubility of helium in liquid aluminium, to which a theoretical explanation will be given in the next section. However, different observations were obtained by Opie and Grant [9] and Talbot *et al.* [12, 13] where helium was used as the reference gas and linear relationships between the measured hydrogen solubility and the square root of hydrogen partial pressure were reported. The present authors are not surprised at their results, because the quadratic feature found in the present experiment, as shown in Fig. 4, was not very strong either.

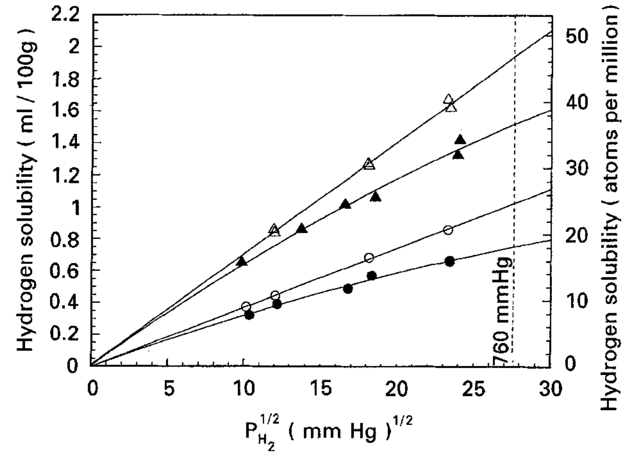

Figure 4 Comparison between the hydrogen solubility values determined with reference gases (△, ○) argon or (▲, ●) helium at different melt temperatures of (○, ●) 973 and (△, ▲) 1073 K.

3.3. Helium solubility measured in experiment C (reference: argon)

Helium, as an inert gas, had been supposed to have no solubility in liquid aluminium and hence was used as the reference gas to calibrate the volume of the measurement system of the Sieverts' apparatus by several investigators. The obtained results in experiments A and B (Fig. 4), however, suggested some solubility of helium gas in liquid aluminium. Because of this, experiment C listed in Table II was arranged to verify helium solubility with argon being used as the reference gas.

It was found that helium did dissolve in liquid aluminium. Its solubility values measured under different helium partial pressures and at melt temperatures of 973 and 1073 K are given in Fig. 5. The experimental results in Fig. 5 show that (i) the helium solubility has a linear relationship to helium partial pressure, and (ii) there exists a threshold of helium partial pressure for each melt temperature, above which the helium solubility increases at a higher rate with the helium partial pressure than it does on the lower helium partial pressure side.

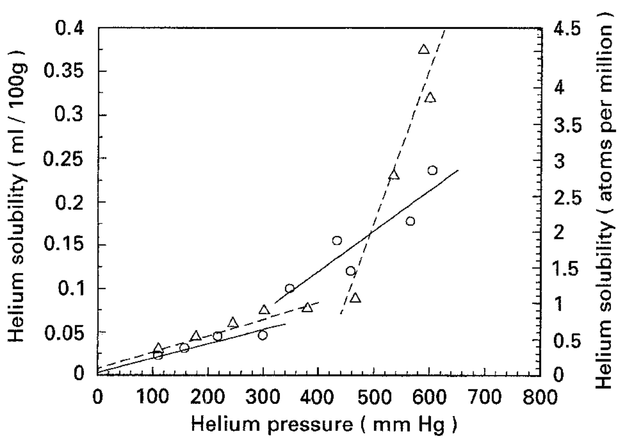

Figure 5 Plots of the relationship between the detected helium solubility and the helium partial pressure using argon as the reference gas: (○) 973 K, (△) 1073 K.

Our literature survey did not find any information concerning helium solubility in liquid aluminium except reference [17], in which the solubility of 350 atoms of helium per million aluminium atoms was reported. This solubility value seems to be unreasonably high, because it corresponds to about 29 ml/100 g which is even higher than that of hydrogen solubility in liquid aluminium. Unlike the absorption of hydrogen in liquid aluminium where hydrogen molecule dissociation is involved, the dissolution of helium, as a monatomic gas, in liquid aluminium does not obey Sieverts' law and can be expressed as:

$$\mathrm{He(gas)} \rightleftharpoons \mathrm{He(in\ Al)} \qquad (7)$$

and the corresponding equilibrium constant is

$$K_{\mathrm{He}}^{\mathrm{Ar}} = \frac{[\mathrm{He}]_{\mathrm{in\,Al}}^{\mathrm{Ar}}}{P_{\mathrm{He}}} \qquad (8)$$

where P_{He} is the partial pressure of helium gas, $[\mathrm{He}]_{\mathrm{in\,Al}}^{\mathrm{Ar}}$ is the helium content dissolved in liquid aluminium with argon being the reference gas, and $K_{\mathrm{He}}^{\mathrm{Ar}}$ is the equilibrium constant. Evidently, a linear relationship between the helium solubility in liquid aluminium and the helium partial pressure is correlated by the equilibrium constant $K_{\mathrm{He}}^{\mathrm{Ar}}$. Theoretically, when the helium partial pressure approaches zero, the measured helium solubility should also approach zero. However, the two straight lines on the lower helium partial pressure side in Fig. 5 do not pass through the origin. This is believed to be due to the fact that the helium solubility under low helium partial pressure is too low to be measured accurately by the present apparatus. The measurement principle using the present apparatus decides that the measurement accuracy and precision become worse with decreasing partial pressure. Although quantitative determination of helium solubility in liquid aluminium is beyond the competence of the apparatus used in the present investigation, this measurement leads the present investigators to the correct choice of calibration gas for measurement of hydrogen solubility by Sieverts' method.

From Equation 8 it is known that the equilibrium constant, $K_{\mathrm{He}}^{\mathrm{Ar}}$, is the gradient of the $[\mathrm{He}]_{\mathrm{in\,Al}}^{\mathrm{Ar}}$ versus P_{He} lines. Owing to the lack of information concerning the absorption of helium gas in liquid aluminium, the existence of the pressure threshold (the sudden change of equilibrium constant $K_{\mathrm{He}}^{\mathrm{Ar}}$) shown in Fig. 5 is not well understood. The present authors can suggest the following explanations for reference only. For this purpose a quasi-crystalline lattice model of a liquid [18, 19] will be employed here.

In the so-called quasi-crystalline lattice model of a liquid, liquid aluminium atoms are assumed to layer themselves by the most closed packed fashion in fcc structure, as in the case in its solid state. In such a structure there exist two kinds of interstices: octahedral and tetrahedral, as depicted in Fig. 6a and b [20]. The radii of these interstices are 0.059 and 0.032 nm, respectively. The positions at which the dissolved gas atoms possibly stay are in fact, the two above-mentioned interstices, as proposed by Ohnishi [20]. Two different activation energy levels are needed for soluble gas atoms to penetrate into these two different kinds of interstices. The activation energies are supplied by the kinetic energies of the soluble gas, with an average value per mole gas at a given temperature, T of

$$\langle \varepsilon \rangle = \frac{3}{2} kT \qquad (9)$$

where k is Boltzmann's constant [21]. Introducing the relationship $Tk = PV/N$, where N is Avogadro's constant, P and V are the pressure and the mole volume of the helium gas, respectively, we obtain

$$\langle \varepsilon \rangle = \frac{3V}{2N} P \qquad (10)$$

It is seen that different levels of kinetic energy (being equal to the respective level of the above mentioned activation energy) correspond to different levels of pressure of the soluble gas.

In the case of the absorption of hydrogen in liquid aluminium, according to Eichenauer [22] and Kato [23], only octahedral interstices can be occupied.

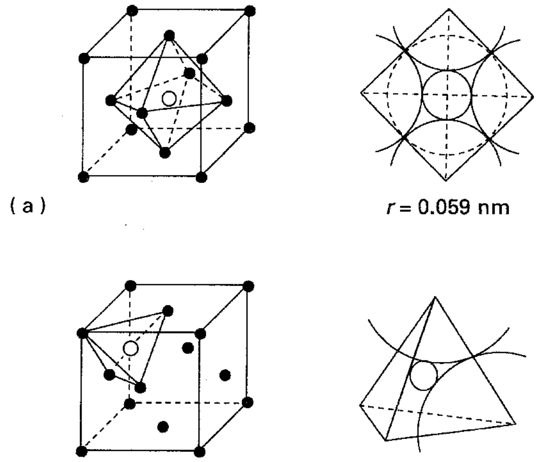

Figure 6 Schematic diagram showing the two kinds of interstices existing in the assumed crystal-like liquid model: (a) octahedral interstice; (b) tetrahedral interstice.

TABLE IV Atomic radii of hydrogen, helium and argon (quantum mechanical values for free atoms)

Atom	Atomic radius (nm)
Hydrogen	0.079
Helium	0.049
Argon	0.088

Therefore, no pressure threshold could be observed in the absorption process of hydrogen in liquid aluminium. However, in the case of helium absorption/penetration in liquid aluminium, both the octahedral and the tetrahedral interstices are believed to be occupied. Such a consideration is reasonable if the atomic radii of helium and hydrogen are compared, as listed in Table IV, where helium is shown to have a smaller atomic radius than hydrogen. Two different levels of pressure are therefore needed for helium to penetrate into these two different interstices. The critical pressure which corresponds to the activation energy of the tetrahedral interstices (being the higher activity energy level due to the smaller interstice radius) is considered to be the threshold of the helium partial pressure for each melt temperature shown in Fig. 5.

The quadratic relationship between the measured hydrogen solubility and the square root of hydrogen partial pressure obtained in Experiment B where helium gas was used as the reference gas (Fig. 4) can be derived mathematically by subtracting Equation 8 from Equation 2

$$\begin{aligned}[\mathrm{H}]^{\mathrm{He}}_{\mathrm{in\,Al}} &= [\mathrm{H}]^{\mathrm{Ar}}_{\mathrm{in\,Al}} - [\mathrm{He}]^{\mathrm{Ar}}_{\mathrm{in\,Al}} \\ &= K^{\mathrm{Ar}}_{\mathrm{H_2}} P^{1/2}_{\mathrm{H_2}} - K^{\mathrm{Ar}}_{\mathrm{He}} P_{\mathrm{He}} \qquad (11)\end{aligned}$$

and by applying the condition $P_{\mathrm{H_2}} = P_{\mathrm{He}}$ to Equation 11

$$[\mathrm{H}]^{\mathrm{He}}_{\mathrm{in\,Al}} = K^{\mathrm{Ar}}_{\mathrm{H_2}} P^{1/2}_{\mathrm{H_2}} - K^{\mathrm{Ar}}_{\mathrm{He}} P_{\mathrm{H_2}} \qquad (12)$$

It can be seen from Equation 12 that when helium gas is used as reference gas, the measured hydrogen solubility has a quadratic dependence on the square root of hydrogen partial pressure; and that a linear relationship will exist between hydrogen solubility and the square root of hydrogen partial pressure assuming the insolubility of helium gas in molten aluminium. Because the value of $K^{\mathrm{Ar}}_{\mathrm{He}}$ is usually very small, it is easily ignored due to low experimental accuracy and precision and, consequently, a linear instead of a quadratic relationship between the measured hydrogen solubility and the square root of hydrogen partial pressure could be concluded.

3.4. Influence of helium solubility on the hydrogen solubility measurement

Results from the above three experiments are summarized in Table V in which hydrogen solubility values determined with helium being the reference gas, column 4, are seen to be evidently lower than those measured when argon was used as the reference gas, column 3, and the differences between these two groups of values generally match the corresponding helium solubility values listed in column 5. The influence of the solubility of helium as a reference gas on the measured hydrogen solubility in liquid aluminium can therefore be approximately evaluated because a relative error of up to 20% can be caused when helium gas is used as a reference gas to measure the hydrogen solubility in liquid aluminium by Sieverts' method.

4. Conclusions

Hydrogen solubility in liquid aluminium at different temperatures from 973–1123 K and the effect of helium as a reference gas to calibrate the measurement system of Sieverts' apparatus on the measured hydrogen solubility have been experimentally investigated employing Sieverts' method. The following conclusions can be drawn.

1. Helium has some solubility in molten pure aluminium. The absorption of helium as a monatomic gas in liquid aluminium does not obey Sieverts' law. Helium solubility is proportional to its equilibrium partial pressure, while a threshold of helium partial pressure exists for each melt temperature, over which the helium solubility increases at an elevated gradient with increasing helium partial pressure.

TABLE V Comparison of the hydrogen solubility values determined with different reference gases and the evaluated helium solubility values

Melt temperature (K)	Partial pressure (mm Hg)	Solubility of the soluble gases determined with different soluble gas/reference gas combinations (ml/100 g)		
		H_2/Ar	H_2/He	He/Ar
973	100	0.371	0.321	0.023
	300	0.632	0.514	0.049
	500	0.818	0.634	0.167
	650	0.930	0.700	0.237
	760	1.026	0.753	0.289
1073	100	0.709	0.644	0.030
	300	1.198	1.030	0.075
	500	1.548	1.275	0.177
	650	1.758	1.410	0.442
	760	1.937	1.518	0.636

2. Owing to the solubility of helium gas in liquid aluminium, a relative error of up to 20% could be caused when it is used as a reference gas in determining hydrogen solubility by Sieverts' method. Instead, the inert gas of argon is an appropriate candidate as a reference gas to calibrate the measurement system.

3. Hydrogen solubility over the temperature range 973–1123 K has a relationship to the melt temperature as follows

$$\log S = -\frac{2980}{T} + 3.07$$

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