

Hydrogen diffusion coefficient in liquid metals evaluated by solid–gas eutectic unidirectional solidification

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Abstract: Based on the solid–gas eutectic unidirectional solidification technique and the principle of unidirectional solidification of single-phase alloy, a new method for evaluating the diffusion coefficient of hydrogen in liquid metals was proposed. Taking Cu–H₂ system for example, the influences of argon partial pressure and superheat degree of melt on the diffusion coefficient of hydrogen in liquid metal were studied and the predicted values were similar to each other. The obtained temperature-dependent equation for diffusion coefficient of hydrogen in liquid copper is comparable with experimental data in literature, which validates the effectiveness of this method. The temperature-dependent equations for diffusion coefficient of hydrogen in liquid Mg, Si and Cu–34.6%Mn alloy were also evaluated by this method, along with the values at the melting point of each metal and alloy.

Key words: hydrogen; diffusion coefficient; liquid metal; solid–gas eutectic; unidirectional solidification

1 Introduction

Investigation of the diffusion process in liquid metals is vital for gaining an effective understanding of nucleation, crystal growth, and liquid dynamics. The diffusion coefficient in particular is essential to the study of microstructural evolution, and has been the subject of interest for a number of materials and metallurgical researchers over recent years [1–4]. What is more, the similarity in physical properties between liquid metals and semiconductors means that such research can potentially have broader implications.

Up to now, a number of different experimental methods have been developed to measure the diffusion coefficient of solute atoms in liquid metals [5,6], i.e., capillary-reservoir, diffusion couple, shear-cell, plane source, electrochemical concentration-cell, slow neutron scattering, nuclear magnetic resonance and electrochemical methods. Furthermore, a number of theoretical models have also been developed over the past several decades, such as the Einstein relation model [6], rigid sphere model [7], density fluctuation model [8],

and a modified “hole” theory model based on the Arrhenius relation [9]. However, despite this progress, it is still more difficult to obtain the diffusion coefficient of solute atoms in liquid metals than in solid ones because of the high sensitivity to external convection effects [10]. Experimental data regarding the diffusion coefficient for a small number of liquid metals are quite scarce and the results obtained tend to be quite diverse due to variation in the experimental method [11, 12]. In addition, many theoretical models cannot be applied widely, due to the absence of data for some important physical parameters. For example, CAHOON [9] presented the diffusion coefficient for solute impurity in liquid metals:

$$\begin{cases} D = D_0 \exp[-(\Delta Q^L + Q_0^L)/(RT)] \\ \Delta Q^L = -\frac{0.17Z_2V_0e^2\alpha}{(11a/16)} \exp(-11qa/16) \end{cases} \quad (1)$$

where Z_2 is the effective relative valence calculated by the Engel–Brewer ground state valence and α is the screening potential factor which is related to both the solvent properties and Z_2 . CHHABRA and ROY [13] regarded that the ratio of diameters between the solute

impurity and solvent atoms (d_A and d_B) exerted a tremendous influence on the diffusion coefficient of solute impurity. The corresponding equation is

$$D = 0.2 \frac{CRd_B^3}{d_A} \left[\frac{T}{V} \left(\frac{V - V_0}{V_0} \right) \right] \quad (2)$$

where V_0 is the atomic volume of liquid metal with the infinite viscosity and C is the characteristic constant of liquid metal. The complicity and difficulty in acquiring those above parameters is a hindrance to the development of those theoretical models.

Compared with other atoms, the small atomic radius of hydrogen allows it to penetrate far more readily into metals and react with almost all other elements of the periodic table. The reaction exerts an impact on the microstructure and performance. Taking steel for example, the diffusion of hydrogen can accelerate the crack propagation which could result in the occurrence of hydrogen embrittlement (HE, a phenomenon which is notorious for significantly reducing the strength of steel) [14]. In other words, the appearance of HE is affected by the diffusion rate of hydrogen. Meanwhile, as for the technology of liquid state hydrogenation, the redistribution of alloy elements and the ascension of nucleation rate owing to the different diffusion coefficients of hydrogen in α and β phases could improve the microstructure of TC21 alloy [15]. In addition, the diffusion coefficient of hydrogen in liquid metal is the key parameter which influences the pore size in lotus-type porous structure [16]. Therefore, the study of hydrogen diffusion is quite important, particularly in the liquid metals within the casting industry. However, the high flammability of hydrogen and risks associated with high temperatures make it far more difficult to apply conventional means of measuring the diffusion coefficient of hydrogen.

The solid–gas eutectic unidirectional solidification technique [17–19] (or Gasar process) is a new method for fabricating porous materials with long cylindrical pores aligned in one direction. In this process, a melt saturated with hydrogen is solidified unidirectionally in a closed high-pressure chamber, which subsequently induces the formation of bubbles due to the difference in hydrogen solubility between the liquid and solid phases. By adjusting processing parameters such as the partial pressures of hydrogen and argon, or the superheat degree of melt, the initial hydrogen concentration and the required one for bubble nucleation of the melt will be changed. If the initial hydrogen concentration is smaller than the later one, the bubble-free layer will be formed. The diffusion coefficient of hydrogen in the liquid metal has an essential impact on the accumulation rate of hydrogen at the solid–liquid interface and finally determines the thickness of the initial bubble-free layer

at the bottom of the ingot.

By measuring the thickness of the initial bubble-free layer and combining the principle of unidirectional solidification of single-phase alloy, a new method of evaluating the diffusion coefficient of hydrogen in liquid metals was proposed. The predicted result for Cu–H₂ system is comparable with literature values, which verifies the viability of this method. The values at the melting point and temperature-dependent equations for diffusion coefficients of hydrogen in liquid Mg, Si and Cu–34.6%Mn alloy were also predicted by this method. This method is easy to be carried out and solves the difficult problem of getting the diffusion coefficient of hydrogen in high-melting metals. Meanwhile, the obtained values through this method are much valuable for investigating the structure evolution of casting process, especially for the solid–gas eutectic unidirectional solidification.

2 Experiment and calculation

A simple mold casting technique was utilized for unidirectional solidification. The apparatus used is depicted in Fig. 1(a), and consists of a vacuum system that incorporated both the melting part and solidification part. To fabricate the ingot, high-purity (99.99%) material was first melted under vacuum. A gas mixture of hydrogen and argon was then introduced into the chamber, and the melt was held at a constant superheat degree until the hydrogen was uniformly dissolved in the melt (usually 10–90 min which was decided by melting method). Finally, the melt was poured into an insulated mold with a copper chiller, and then unidirectionally solidified upwards. This resulted in the formation of unique regular porous structure, which was known as a lotus-type porous structure owing to its resemblance to the roots of the lotus plant. This processing technique is a variation on the so-called solid–gas eutectic reaction, in which the melt is solidified into a solid solution and entrapped gas phase ($L \leftrightarrow S + H_2$) [19]. Lotus-type porous Cu, Mg, Si and Cu–34.6%Mn alloy were fabricated by this method, respectively.

The ingot produced was sectioned along its central axis into two parts using a spark-erosion wire-cutting machine. The height (H) was determined as the average distance between the initial nucleation bubbles and the bottom of the ingot, as shown in Figs. 1(b) and (c).

According to the Sievert's law, the original hydrogen concentration (C_0) in liquid metal can be expressed as

$$C_0 = \exp \left(-\frac{A}{T_m + \Delta T} + B \right) \cdot \sqrt{p_{H_2}} = \xi(T) \cdot \sqrt{p_{H_2}} \quad (3)$$

where $\xi(T)$ is the solubility coefficient; T , T_m and ΔT are

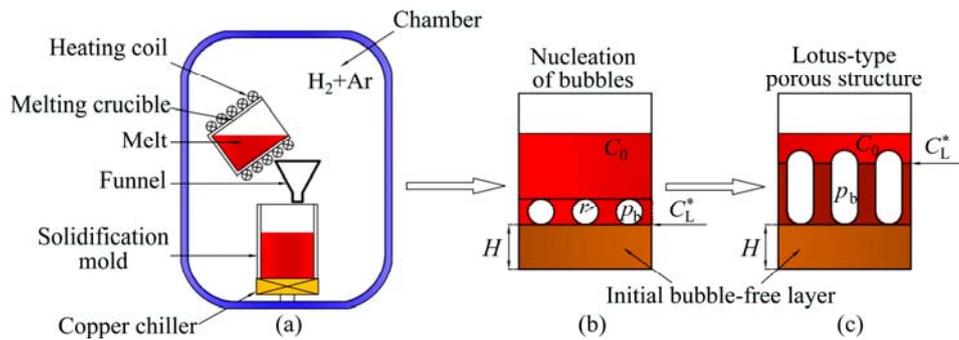


Fig. 1 Schematic of solid–gas eutectic unidirectional solidification apparatus (a), formation of initial bubble-free layer (b) and evolution of lotus-type porous structure (c)

the initial temperature, melting point and the superheat degree of the melt, respectively; A and B are the solubility constants of the corresponding metal; p_{H_2} is the hydrogen partial pressure in the chamber.

At the beginning of unidirectional solidification, the value of C_0 is less than the hydrogen concentration required for bubble nucleation. A single solid phase is therefore formed, and the excess hydrogen is expelled into the liquid phase. This leads to a continuous increase in the hydrogen concentration of the liquid phase ahead of the solid–liquid interface ($C_L(x')$), as shown in Fig. 2. When C_L^* is sufficiently increased, an abundant number of bubbles are nucleated and eventually grow into the elongated pores depicted in Fig. 1(c).

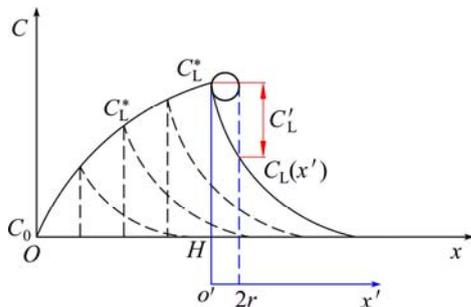


Fig. 2 Distribution of hydrogen in liquid ahead of solid–liquid interface during solidification of initial bubble-free layer (C_L^* —Hydrogen concentration of liquid phase in solid–liquid interface)

According to the principle of unidirectional solidification of single-phase alloy, the formation of the initial bubble-free layer corresponds to the initial growth stage. As the diffusion coefficient of hydrogen in liquid phase is generally three orders of that in solid [14], only the diffusion of hydrogen in the liquid phase needs to be considered. Therefore, regardless of the convection in the melt, C_L^* can be expressed as [14]

$$C_L^* = \frac{C_0}{k_0} \left[1 - (1 - k_0) \exp\left(-\frac{k_0 \cdot v}{D_L} x\right) \right] \quad (4)$$

where k_0 is the distribution coefficient of hydrogen; v is the solidification velocity; D_L is the diffusion coefficient of hydrogen in the liquid phase; x is the height of the solid phase. This demonstrates that there is a positive correlation between v and C_L^* ; while a negative correlation exists between D_L and C_L^* .

The investigation of bubble nucleation in Gasar solidification [20,21] revealed that heterogeneous nucleation of impurities (such as alumina, silicon oxide) in the pits and cracks was the most likely mechanism when C_L^* satisfied the following conditions:

$$\begin{cases} C_L^* \geq C_n = \exp(-A/T_m + B) \sqrt{p_b} \\ p_b = p_{H_2} + \Delta p = p_{H_2} + p_{Ar} + 0.1\rho_L gh + 0.2\sigma_{LG}/r \end{cases} \quad (5)$$

where p_b is the gas pressure inside the bubble, from which the concentration of hydrogen for bubble nucleation (C_n) is determined; Δp is the additional pressure provided by the argon partial pressure (p_{Ar}) in the chamber, the hydrostatic pressure (p_s) of the melt above the bubble and the capillary pressure (p_c); ρ_L is the density; σ_{LG} is the surface tension of the melt; g is the gravitational acceleration; h is the height of the melt above the bubble; r is the average radius of the initial nucleation bubbles.

Theoretically, bubbles will start to nucleate once C_L^* is equal to C_n and the corresponding value of x in Eq. (4) is exactly the height of the initial bubble-free layer (H). However, the solid–liquid interface is not simple as the gas bubbles grow into the melt with a convex shape, which is assumed to be spherical (radius of r) in this study. Consequently, the hydrogen concentration for bubble nucleation should be satisfied by C_L' , which is an average value for the hydrogen concentration in the liquid bordered by a distance of $2r$ from the solid–liquid interface, as shown in Fig. 2.

The unidirectional solidification of single-phase alloy has previously been investigated by LI and LIU [22], who obtained a theoretical expression for the solute distribution in the liquid phase ahead of the solid–liquid interface during the initial growth stage:

$$C_L(x') = C_0 \cdot \left\{ \frac{1-k_0}{k_0} \left[1 - \exp\left(-\frac{k_0 v}{D_L} \cdot x\right) \right] \cdot \exp\left(-\frac{v}{D_L} \cdot x'\right) + 1 \right\} \quad (6)$$

where x' is the distance from the solid–liquid interface in the liquid phase. By substituting the height of the initial bubble-free layer (H) for x into Eq. (6), and integrating x' in the range of 0 to $2r$, C_L' can be obtained as follows:

$$C_L' = \frac{1}{2r} \int_0^{2r} C_L(x') dx' = \frac{1}{2r} \int_0^{2r} C_0 \cdot \left\{ \frac{1-k_0}{k_0} \left[1 - \exp\left(-\frac{k_0 v}{D_L} \cdot H\right) \right] \cdot \exp\left(-\frac{v}{D_L} \cdot x'\right) + 1 \right\} dx' \quad (7)$$

When C_L' is equal to C_n , the diffusion coefficient of hydrogen (D_L) in the liquid phase can be calculated by solving Eqs. (3), (5), and (7). As the hydrogen concentration in the liquid phase attenuates exponentially with increasing distance from the interface, diffusion only needs to be considered within a short distance ($x' \approx D_L/v$, which is called the characteristic distance). As the temperature of liquid phase changes slightly in this range, D_L can be regarded as being equal to the value at the melting point of the metal in the liquid phase (i.e., $D_{Lm} = D_L$).

According to the Arrhenius relation [9], both the self-diffusion and diffusion of solute impurities in the liquid metals can be given as

$$D = D_0 \exp\left(-\frac{H_D}{R_g T}\right) \quad (8)$$

where H_D is the apparent activation energy or diffusion activation energy; R_g is the gas constant; and D_0 is the pre-exponential factor, which can be calculated by substituting D_{Lm} into Eq. (8):

$$D_0 = D_{Lm} / \exp\left(-\frac{H_D}{R_g T_m}\right) \quad (9)$$

LARSSON et al [23] have provided an empirical formula for calculating the value of H_D for the self-diffusion of liquid metals and semiconductors:

$$H_D = \begin{cases} 2.50T_m^{1.15}, & \text{for metals} \\ 2.00T_m^{1.15}, & \text{for semiconductors} \end{cases} \quad (10)$$

In the rigid sphere model, CHHABRA and ROY [13] believed that the diffusion coefficient of solute impurity in liquid metals was proportional to the self-diffusion coefficient of liquid metal itself and the proportionality coefficient was the ratio of atom diameters of metal and solute impurity. This means that H_D only depends on the metal but nothing on the solute

impurity with regards to both self-diffusion and the diffusion of solute impurity in liquid metals.

Thus, the temperature-dependent equations for the diffusion coefficient of hydrogen in liquid metals and semiconductors can be obtained by incorporating Eqs. (9) and (10) into Eq. (8):

$$D_L = \begin{cases} D_{Lm} \cdot \exp\left[\frac{2.50T_m^{1.15}}{R_g} \left(\frac{1}{T_m} - \frac{1}{T}\right)\right], & \text{for metals} \\ D_{Lm} \cdot \exp\left[\frac{2.00T_m^{1.15}}{R_g} \left(\frac{1}{T_m} - \frac{1}{T}\right)\right], & \text{for semiconductors} \end{cases} \quad (11)$$

3 Results and discussion

In this section, a Cu–H₂ system was chosen as the basis for a theoretical model, as lotus-type porous Cu had previously been fabricated by the solid–gas eutectic unidirectional solidification technique [17]. What’s more, several temperature-dependent equations for diffusion coefficient of hydrogen had already been reported which allowed for verification of the predicted result.

Based on this Cu–H₂ system, it was determined that in order to obtain an initial bubble-free layer in a lotus-type structure, the hydrogen concentration for bubble nucleation (C_n) must be greater than C_0 . This means that a certain amount of argon (p_{Ar}) is indispensable for the formation of bubble-free layer. However, a lotus-type structure cannot form if the amount of argon introduced is too great. The value of C_n must also satisfy the following expression [24]:

$$C_0 < C_n < C_0 / k_0 \quad (12)$$

According to Eqs. (3) and (5), Eq. (12) can be expressed by ignoring p_s and p_c , as both values are much smaller than p_{H_2} and p_{Ar} :

$$\exp\left[2A \left(\frac{1}{T_m} - \frac{1}{T_m + \Delta T}\right)\right] - 1 < \frac{p_{Ar}}{p_{H_2}} \leq \frac{1}{k_0^2} \exp\left[2A \left(\frac{1}{T_m} - \frac{1}{T_m + \Delta T}\right)\right] - 1 \quad (13)$$

The pressure conditions required for the formation of the lotus-type structure and bubble-free layer are indicated by the shaded area shown in Fig. 3(a). With an increase in the superheat degree of the melt, both the maximum and minimum values for argon pressure are increased for a given hydrogen pressure. Three sets of parameters for the shaded area were therefore selected, as shown in Fig. 3. Longitudinal section views of the three ingots are shown in Fig. 4. The heights of the initial bubble-free layer (H) and the average radius of the

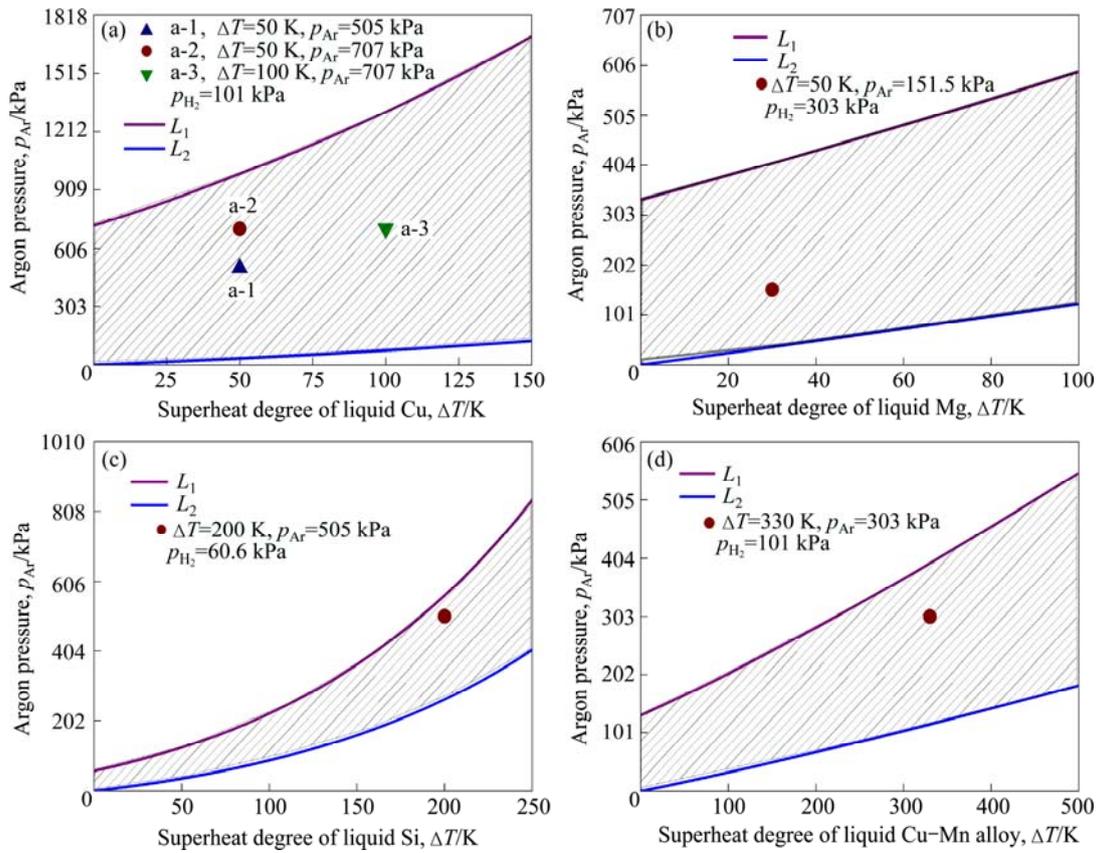


Fig. 3 Pressure conditions for formation of lotus-type porous structure and bubble-free layer with various superheat degrees of melt (L_1 —Critical (maximum) argon pressure for formation of lotus-type porous structure; L_2 —Critical (minimum) argon pressure for formation of initial bubble-free layer): (a) Cu-H₂ system; (b) Mg-H₂ system; (c) Si-H₂ system; (d) Cu-34.6%Mn-H₂ system

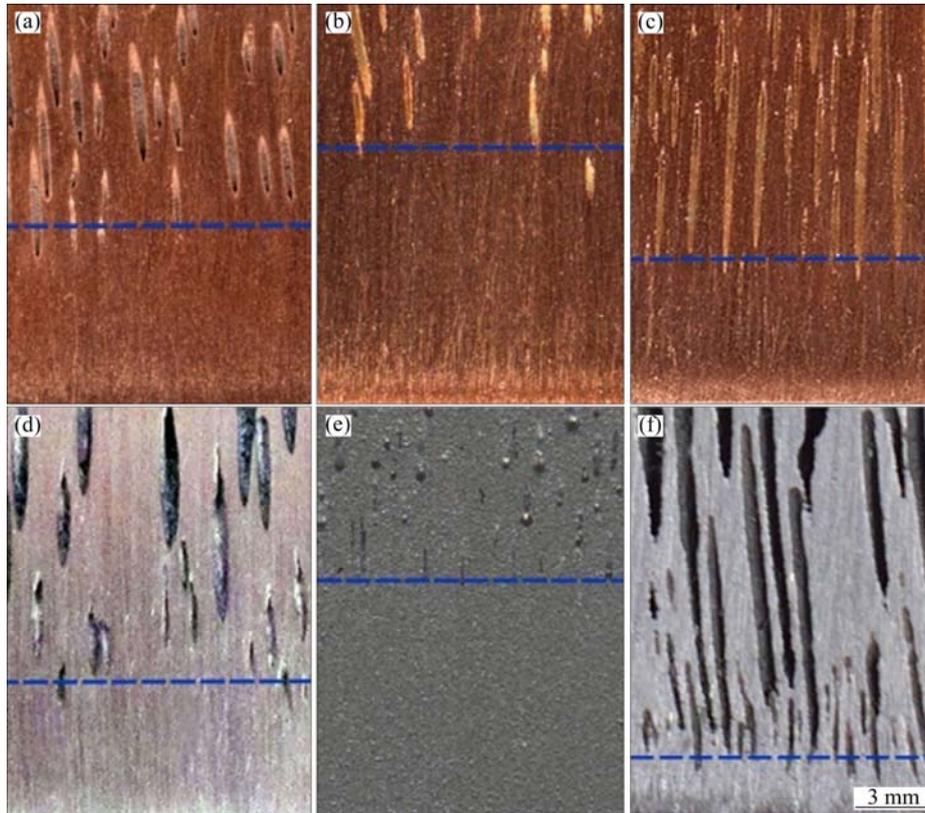


Fig. 4 Longitudinal section views of porous Cu (a–c) for (a1–a3) respectively, Mg (d), Si (e) and Cu-34.6%Mn alloy (f)

initial nucleation bubbles (r) were obtained and listed in Table 1 for each sample.

According to the study by LIU [25], there is a relationship between the solidification velocity and pore diameter, which can be expressed as

$$vr^2 = \frac{\sigma_{LS}T_E\varepsilon}{14.44F \cdot \Delta H_m(1-\sqrt{\varepsilon})\rho_S} \quad (14)$$

where σ_{LS} is the interfacial energy between liquid and solid phases; ε is the porosity of the obtained ingot; T_E ($\approx T_m$) is the eutectic temperature; ΔH_m and ρ_S are the fusion enthalpy and density of the solid phase, respectively; F is a constant determined by the solid–gas system, melt temperature, and gas pressure in the chamber. By submitting the average radius of r and ε into Eq. (14), values of v are obtained, as shown in Table 1.

Using the equations outlined in Section 2, values for the diffusion coefficient of hydrogen in liquid Cu at the melting point were obtained under three different conditions, i.e., 4.4×10^{-3} , 3.8×10^{-3} and 3.9×10^{-3} cm²/s.

Figure 4 shows that the largest value of H for the initial bubble-free layer exists when p_{Ar} is equal to 707 kPa and ΔT equals 50 K. Reducing the pressure of argon allows the bubbles to nucleate at a lower concentration, while increasing the superheat degree of melt increases the initial concentration of hydrogen in the liquid phase, making both easier for bubbles to nucleate and reducing the distance of hydrogen enrichment required during solidification. The similarity in the diffusion coefficients obtained with different experimental parameters means that the error produced by this method is relatively small and acceptable. By submitting the average value of 4.0×10^{-3} cm²/s into Eq. (11), a temperature-dependent equation for the diffusion coefficient of hydrogen in liquid Cu is obtained:

$$D_{L,Cu} = 0.01 \exp\left(-\frac{10001}{RT}\right) \quad (15)$$

Figure 5 shows a comparison between the predicted results of $D_{L,Cu}$ and the literature values. From this, the data obtained by the traditional method are dispersed over a wide range due to the inevitable influence of convection and the inherent limitations of some methods. It has in fact been reported that variation in the published values of diffusion coefficients is between 50% and

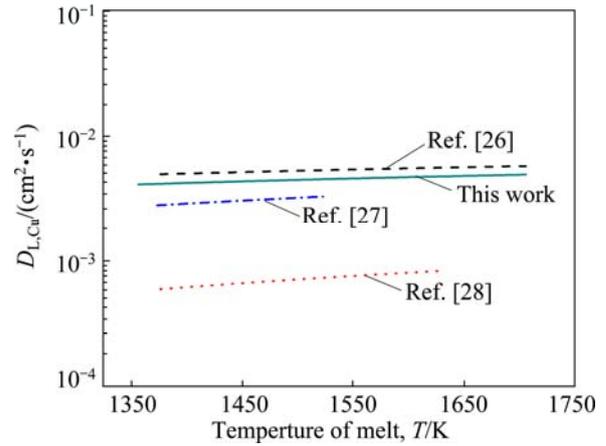


Fig. 5 Comparison between predicted results and literatures' values of diffusion coefficients of hydrogen in liquid Cu

100% for most metals [12]. Though the predicted results were somewhat greater than most of the literature values, it remained within an order of magnitude, and thus this method is considered reliable.

Lotus-type porous Mg, Si and Cu–34.6%Mn alloy were also fabricated under the conditions listed in Table 1. As with the Cu–H₂ system, Figs. 3(b)–(d) and 4(d)–(f) show the determination of the experimental parameters based on the theoretical calculations and longitudinal section views, respectively. Finally, temperature-dependent equations for the diffusion coefficient of hydrogen in liquid Mg, Si and Cu–34.6%Mn alloy were obtained as follows:

$$D_{L,Mg} = 0.04 \exp\left(-\frac{6426}{R_g T}\right) \quad (16)$$

$$D_{L,Si} = 0.009 \exp\left(-\frac{10271}{R_g T}\right) \quad (17)$$

$$D_{L,Cu-34.6\%Mn} = 0.012 \exp\left(-\frac{8241}{R_g T}\right) \quad (18)$$

From this, the respective diffusion coefficients of hydrogen at the melting point for each metal are determined as 1.75×10^{-2} , 4.4×10^{-3} and 4.9×10^{-3} cm²/s. The physical property parameters used in the fabrication and calculation of the Cu–H₂, Mg–H₂, Si–H₂ and Cu–34.6%Mn–H₂ systems are shown in Table 2.

Table 1 Processing and obtained parameters of Cu–H₂, Mg–H₂, Si–H₂ and Cu–34.6%Mn–H₂ systems

System		T/K	p_{H_2} /kPa	p_{Ar} /kPa	H/cm	r/cm	v /(cm·s ⁻¹)
Cu–H ₂	a-1	50	101	505	0.7	0.03	0.023
	a-2	50	101	707	1.2	0.025	0.025
	a-3	100	101	707	0.6	0.015	0.022
Mg–H ₂		30	30.3	15.15	0.6	0.025	0.020
Si–H ₂		200	60.6	50.5	1.1	0.1	0.013
Cu–34.6%Mn–H ₂		330	10.1	30.3	0.3	0.15	0.050

Table 2 Physical property parameters of Cu–H₂, Mg–H₂, Si–H₂ and Cu–34.6%Mn–H₂ systems

System	T_m/K	k_0	$\sigma_{LS}/(N\cdot cm^{-1})$	$\sigma_{LG}/(N\cdot cm^{-1})$	$H_m/((N\cdot cm\cdot mol^{-1})$	$\xi(T)/(g\cdot cm^{-3})$
Cu–H ₂ [24]	1356	0.35	2.56×10^{-3}	1.303×10^{-2}	1.326×10^6	$\exp(-5348/T-14.14)$
Mg–H ₂ [24]	923	0.69	1.06×10^{-3}	5.59×10^{-3}	8.95×10^5	$\exp(-1611.81/T-7.92)$
Si–H ₂	1685	0.72 [29]	1.67×10^{-3} [30]	8.65×10^{-3} [6]	5.06×10^6 [6]	$\exp(-13318/T-2.24)$ [31]
Cu–34.6%Mn–H ₂ [32]	1146	0.66	1.6×10^{-3}	1.331×10^{-2}	8.924×10^5	$\exp(-1952.17/T-8.50)$

4 Conclusions

1) A new method for evaluating the diffusion coefficient of hydrogen in liquid metals was proposed, by combining the solid–gas eutectic unidirectional solidification technique and the principle of unidirectional solidification of single-phase alloy.

2) For Cu–H₂ system, the influence of argon pressure and superheat degree of melt on the diffusion coefficient of hydrogen in liquid phase is relatively small and acceptable. The obtained temperature-dependent equation for diffusion coefficient of hydrogen in liquid copper is comparable with experimental data in literature, thus validating the effectiveness of this method.

3) The temperature-dependent equations for diffusion coefficient of hydrogen in liquid Mg, Si and Cu–34.6%Mn alloy were evaluated, along with the values at the melting point of each metal and alloy.

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固-气共晶定向凝固法测定氢在金属熔体中的扩散系数

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摘要: 基于固-气共晶定向凝固技术和单相合金的定向凝固原理, 提出一种测定氢在金属熔体中扩散系数的方法。以 Cu-H₂ 系为例, 研究氩气分压和熔体过热度对氢在金属熔体中熔点处扩散系数的影响。结果显示, 不同工艺参数条件下所获得的扩散系数差别很小, 且采用该方法获得的氢在金属 Cu 熔体中温度相关的扩散系数方程与文献中采用实验方法获得的结果吻合得较好, 并验证了该方法的可行性。除 Cu-H₂ 系外, 还计算了氢在金属 Mg、Si 以及 Cu-34.6%Mn 合金熔点温度熔体中的扩散系数值以及温度相关的扩散系数方程。

关键词: 氢; 扩散系数; 液态金属; 固-气共晶; 定向凝固

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