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A semi-empirical methodology to predict hydrogen permeability in amorphous alloy membranes

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ABSTRACT

A semi-empirical methodology for prediction of hydrogen permeability in metallic amorphous alloys is proposed by combining a thermodynamic calculation and a molecular dynamics simulation. A CALPHAD-type thermodynamic calculation technique is used to calculate hydrogen solubility and thermodynamic factor for hydrogen diffusivity, and a molecular dynamics simulation based on a second nearest-neighbor modified embedded-atom method (2NN MEAM) interatomic potential is used to predict concentration-independent (tracer) diffusivity. The approach is applied to a prediction of hydrogen permeability in amorphous $Cu_{50}Zr_{50}$ and $Cu_{65}Zr_{35}$ alloys for which experimental data is available. The predicted permeability is in good agreement with experimental data, successfully reproducing the overall trend for the effect of alloy composition, which enables an alloy design of amorphous or crystalline metal hydrogen purification membranes.

1. Introduction

For a practical use of hydrogen, an attractive clean energy carrier, technology of various fields from production to power generation is required [1]. As one of such technology, hydrogen purification methods using membranes manufactured from Pd and its crystalline alloys are being intensively studied [2]. Palladium has high hydrogen permeability but also has a drawback of high cost that comes from fabrication as well as materials [3]. Therefore, a large amount of research efforts are being made to enhance the cost effectiveness, by replacing Pd with low-cost elements [4,5]. In recent years, amorphous alloys composed of Zr, Ni, Cu and Al are focused as one of the replacements [6] as some experiments show that hydrogen permeability in amorphous alloys is comparable to that in pure Pd [7–10]. The high hydrogen permeability in amorphous alloys is thought to come from high solubility of hydrogen due to their low packing density [11]. Actually, it has been reported that hydrogen solubility of amorphous alloys is higher than that of their crystalline analogs [12–14]. On the other hand, hydrogen diffusivity of amorphous alloys, the other part of the permeability, is found to be lower than that in open structured crystals such as bcc (body-centered cubic) but higher than that in close-packed crystals such as fcc (face-centered cubic) or hcp (hexagonal close-packed) [15].

To adopt amorphous alloys for manufacturing hydrogen purification membranes, it is essential to figure out which alloy composition would present high permeability of hydrogen. However, only a few specific alloys are known to have high permeability until now [6–10], and it is required to investigate the hydrogen permeability in a wider range of amorphous alloys. The permeability is determined as the product of hydrogen solubility by diffusivity, both of which can be predicted by using computational approaches. Therefore, the use of computational approaches for the prediction of hydrogen permeability can accelerate the discovery toward better amorphous alloys. First-principle calculations in conjunction with Monte Carlo simulations can be an ideal way to predict the permeability [16–18]. However, the complexity of amorphous alloy structures requires a large number of cases to be considered for calculations. A lot of computational resources and time are necessary. Alternatively, semi-empirical methods such as traditional thermodynamic calculations [19] and molecular dynamics (MD) simulations based on semi-empirical interatomic potentials [20], which consume relatively low resources and time, can be an effective way to predict hydrogen permeability. In fact, recently, a semi-empirical methodology that combines CALPHAD (CALculation of PHAse Diagram)-type thermodynamic calculations [21] and MD simulations based on the second nearest-neighbor modified embedded-atom method (2NN MEAM) interatomic potential [22–25] had been proposed by Shim et al. [26] who

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successfully reproduced the overall trend of the alloying effect for the hydrogen permeability in V-based crystalline alloys. The solubility and diffusivity of hydrogen were estimated by the thermodynamic calculation and the MD simulation, respectively.

In the present work, we apply the above-mentioned semi-empirical methodology used for crystalline alloys [26] to the prediction of hydrogen permeability in amorphous alloys and evaluate its usefulness in search of adequate amorphous alloy compositions for hydrogen purification membranes. The hydrogen permeability in Cu–Zr amorphous alloys, one of alloy systems with superior glass forming ability, is predicted and compared with recent experimental data [27]. The hydrogen solubility is estimated from the CALPHAD-type thermodynamic calculation, for which a thermodynamic description for the amorphous phase of the ternary Cu–Zr–H system is newly constructed. The hydrogen diffusivity is obtained using an MD simulation based on a previously developed 2NN MEAM interatomic potential for the ternary Cu–Zr–H system [15,24,28,29]. In following sections, the computational procedure of each step (hydrogen solubility and diffusivity) is described, and then the applicability of the methodology to the investigation of amorphous alloys for hydrogen purification membranes is demonstrated.

2. Calculation of hydrogen solubility in Cu–Zr amorphous alloys

To estimate the hydrogen solubility in Cu–Zr amorphous alloys employing the CALPHAD-type thermodynamic calculation, the Gibbs energy of the amorphous phase should be described using a thermodynamic model. An ordinary substitutional solution model is applied to the ternary Cu–Zr–H amorphous phase as follows:

$$G_m^{amorphous} = x_{Cu}\,{}^{\circ}G_{Cu}^{amorphous} + x_{Zr}\,{}^{\circ}G_{Zr}^{amorphous} + x_{H}\,{}^{\circ}G_{H}^{amorphous} + RT(x_{Cu}\ln x_{Cu} + x_{Zr}\ln x_{Zr} + x_{H}\ln x_{H}) + \Delta^{ex}G_m^{amorphous} \tag{1}$$

where

$$\Delta^{ex}G_m^{amorphous} = x_{Cu}x_{Zr}\sum_{n=0}^{m}(x_{Cu}-x_{Zr})^n L_{Cu,Zr}^{n} + x_{Cu}x_{H}\sum_{n=0}^{m}(x_{Cu}-x_{H})^n L_{Cu,H}^{n} + x_{Zr}x_{H}\sum_{n=0}^{m}(x_{Zr}-x_{H})^n L_{Zr,H}^{n}. \tag{2}$$

x_i denotes the mole fraction of element i. The parameter ${}^{\circ}G_i^{amorphous}$ in Eq. (1) is the Gibbs energy of pure element i in the amorphous phase and the parameters $L_{i,j}^{n}$ in Eq. (2) represent the interaction between elements i and j. The amorphous phase is regarded as an undercooled liquid. The L parameter values can be taken from those for liquid, while an approximation proposed by Gong and Hentzell [30] is adopted for ${}^{\circ}G_i^{amorphous}$. Here, the Gibbs energy difference between the undercooled liquid and crystalline state of an element i is expressed as follows:

$$\Delta^{\circ}G_i^{crystal\rightarrow liquid} = \Delta^{\circ}H_f - \int_T^{T_m}\left(C_p^l - C_p^c\right)dT - T\left(\Delta^{\circ}S_f - \int_T^{T_m}\frac{\left(C_p^l - C_p^c\right)}{T}dT\right). \tag{3}$$

$\Delta^{\circ}H_f$ and $\Delta^{\circ}S_f$ are the enthalpy and entropy of fusion, C_p^l and C_p^c are the heat capacity of liquid and crystalline state, respectively, and T_m is the melting temperature. While experimental information on the enthalpy and entropy of fusion and the heat capacity of crystal are usually available, information on the heat capacity of undercooled liquid is rare. Gong and Hentzell assumed that $(C_p^l - C_p^c)$ in Eq. (3) is constant between melting temperature and glass transition temperature which is approximated as $T_m/2$ and is negligible (zero) below that temperature ($T_m/2$). Eventually, below the temperature of $T_m/2$, the Gibbs energy of pure element in the amorphous phase is given by [30]

$${}^{\circ}G_i^{amorphous} = {}^{\circ}G_i^{crystal} + \left[(\ln 2 - 1)T + \frac{T_m}{2}\right]\frac{\Delta H_f}{T_m}. \tag{4}$$

Numeric values for the model parameters are necessary to estimate the Gibbs energy of the ternary Cu–Zr–H amorphous phase based on the above-mentioned thermodynamic model. The ${}^{\circ}G$ parameters for pure Cu and pure Zr could be determined straightly using Eq. (4) and thermodynamic descriptions in the SGTE database [31]. However, the model could not be applied to pure hydrogen since no thermodynamic information was available for crystalline hydrogen. Therefore, it had to be further assumed that the Gibbs energy of amorphous H is similar to that of liquid H, and a thermodynamic description for the liquid H [32] was directly adopted for amorphous H. The L parameters could be directly obtained from CALPHAD-type thermodynamic assessments, which were performed for all the binary systems, Cu–Zr [33], Cu–H [19] and Zr–H [34,35]. As mentioned already, the interaction parameters (L) for the liquid phase were directly used for the amorphous phase. However, the assessment works [34,35] for the Zr–H system did not include the liquid phase. Actually, liquid phase was not included in any phase diagram of the Zr–H system available in the literature [36] and it was not possible to get any thermodynamic information for the liquid Zr–H phase. On the other hand, recently, experimental data for hydrogen solubility in molten Ti [37] was published, from which the L parameter could be determined. Based on the fact that both of Ti and Zr belong to the same group on the periodic table and on the close resemblance between the Ti–H and Zr–H phase diagrams [35,36] in the solid state temperature range, it could be assumed that both elements may interact with hydrogen similarly. As a final approximation to estimate the thermodynamic property of the liquid Zr–H phase, the following two different approaches were attempted: First (method 1), the interaction parameter (L parameter) for the liquid Ti–H phase was optimized using the experimental hydrogen solubility data in molten Ti [37], and was used as the parameter for the liquid (amorphous) Zr–H phase. Second (method 2), the solubility of hydrogen in molten Zr was assumed to be the same as that in molten Ti at the same homologous temperatures. The temperature of each experimental data point in molten Ti [37] was adjusted so that the homologous temperature (normalized by the molting point of Ti) becomes the same when normalized by the melting point of Zr. Then, the data points were used to optimize the interaction parameter of the liquid (amorphous) Zr–H phase. The optimization of model parameters was carried out using the Parrot module [38] in the Thermo-Calc software [39]. The finally optimized model parameters for the Cu–Zr–H amorphous phase are listed in Table 1. Here, two different expressions are presented for the L parameter of the Zr–H binary amorphous phase, obtained using the above-mentioned two different approaches.

The hydrogen solubility in Cu–Zr amorphous alloys was calculated using the two different Gibbs energy descriptions of the Cu–Zr–H amorphous phase presented in Table 1 and the H_2 gas in the literature [31]. The calculation of phase equilibrium between the amorphous phase and H_2 gas was carried out also using the Thermo-Calc [39]. Fig. 1a (thick curves) shows the hydrogen solubility in amorphous Cu_xZr_{1-x} alloys calculated using the L parameter of the Ti–H binary system (method 1). Here x means the atomic fraction. It is noticeable that the amount of dissolved hydrogen is reduced rapidly with increasing Cu content. This could be expected from the fact that the heat of solution for hydrogen in Cu is positive while the opposite occurs in Zr. Further calculations were carried out over two experimental compositions, $Cu_{50}Zr_{50}$