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Hydrogen loading behaviour of multi-component amorphous alloys: model and experiment

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Abstract

In this paper a model is presented which predicts chemical potential versus hydrogen concentration isotherms for multi-component amorphous alloys. The main assumption of this model is that hydrogen occupies tetrahedral sites within the amorphous alloy. Depending on the concentrations of the constituents and the heats of solution of hydrogen in the pure elements, one obtains a 'density of energy-sites' of the material as seen by the hydrogen atoms. Considerations on the effect of blocking of neighbouring sites due to a hydrogen atom located in a certain site will be made. The isotherm resulting from the model after numerical calculation for a ZrCuNiAl alloy is compared with a measured isotherm showing a reasonable consistence.

Keywords: Hydrogen; Isotherm; Amorphous; Density of sites; Zr

1. Introduction

Some amorphous alloys absorb large amounts of hydrogen making them interesting for a potential use as storage materials. Therefore, a lot of work has been done to describe the hydrogen loading behavior of this class of materials [1–3]. A model which describes the hydrogen loading behaviour of binary amorphous alloys with great accuracy is given by Kirchheim et al. [4,5]. The aim of this work is to show that on bases of this simple model also the hydrogen loading behaviour of amorphous alloys with more than two constituents can be predicted. In this section the model for a binary alloy [4,5] will be briefly described. Section 2 gives the theoretical background to apply this model to a multi-component material. Also blocking effects resulting from electrostatic interaction of an occupied tetrahedron on the neighbouring sites will be taken into account. A measured isotherm on a ZrNiCuAl alloy is compared and discussed with the calculated one in Section 4.

Hydrogen atoms solved in a binary amorphous alloy are mainly located on tetrahedral sites [6]. Assuming an alloy of two distinct elements A and B, the heat of solution G_i for one hydrogen atom on a tetrahedral site of type i is estimated by [6]:

$$G_i = (a \cdot \Delta H_A + b \cdot \Delta H_B)/(a + b) \quad (1)$$

where the values a and b are indices for the number of A and B atoms of the tetrahedron and $\Delta H_{A(B)}$ the heats of solution for hydrogen in the pure elements A and B. Since a tetrahedron is formed by four atoms, the sum of a and b has to be four. In total, one can find five different types of tetrahedra A_4, A_3B_1, A_2B_2, A_1B_3 and B_4. The number of tetrahedra of a certain type i depends only on the concentration of the constituents assuming a homogeneous distribution of all the atoms. As the tetrahedra are located within an amorphous matrix, their individual size is not fixed, but distributed around a mean value leading to distributed heats of solution for each type of tetrahedron i around a mean value as calculated by Eq. (1). This distribution can be regarded to be a gaussian distribution with a width σ_i for a tetrahedra of type i [4]. Summation over all these distributions leads to a 'density of sites' $Z(G)$ for hydrogen, giving the fraction of tetrahedra with an energy G.

$$Z(G) = \sum_{i=1}^{5} N_i \frac{1}{\sigma_i \sqrt{\pi}} \exp\left[-\left(\frac{G - G_i}{\sigma_i} \right)^2 \right] \Big/ \sum_{i=1}^{5} N_i \quad (2)$$

Disregarding entropy (temperature) effects, one hydrogen

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atom entering an amorphous matrix will occupy the site with the lowest energy. Because of the repulsive interaction between two hydrogen atoms only one hydrogen atom can be located inside a tetrahedron. This principle allows to describe the behaviour of hydrogen in amorphous materials, analogue to electrons in solids, by Fermi–Dirac statistics. The density of sites is therefore filled from the lowest energies up to the chemical potential μ related to the amount of hydrogen in the sample. The concentration of hydrogen can then be written as:

$$c_H(\mu) = f \cdot \int_{-\infty}^{+\infty} \frac{Z(G)}{1 + \exp((G-\mu)/RT)}\,\mathrm{d}G \tag{3}$$

As the hydrogen pressure (or the electromotive force (emf) in case of electrochemical loading) is related to the chemical potential, Eq. (3) yields the experimental isotherm. To obtain c_H in the units $H/Metal\ atom$ (H/M) the factor f is used.

2. Theory for the multi-component amorphous alloy

For simplicity, we describe every possible tetrahedron i in an alloy that consists of m elements by a vector $\underline{T}_i = (n_{i1}, n_{i2}, \ldots, n_{im})$, where n_{ij} is the number of atoms of type j forming the tetrahedron i, the sum of all n_{ij} has to be 4. The number Z of tetrahedra that can be formed by m constituents is obtained by [7]:

$$Z = \binom{m+4-1}{4} \tag{4}$$

As an illustration this number is calculated and listed in Table 1.

As the distribution of the constituting atoms within a tetrahedron is arbitrary, the number of permutations for each tetrahedron of type i is given by:

$$P_i = 4! \Big/ \prod_{j=1}^{m} n_{ij}! \tag{5}$$

The relative occurrence W_i of site i in an alloy of m elements with concentrations $x_1, x_2, \ldots, x_m$ equals:

$$W_i = \prod_{j=1}^{m} x_j^{n_{ij}} \tag{6}$$

The probability to find a tetrahedron i is $N_i = P_i \cdot W_i$. Table 2 demonstrates this principle with an example for an alloy of A and B ($m=2$) with concentrations $x_A = 0.75$ and $x_B = 0.25$.

Table 1
Number Z of possible tetrahedra depending on m, the number of constituents

m	1	2	3	4	5	6
Z	1	5	15	35	70	126

Table 2
Values following from Eqs. (4)–(6) applied on the example alloy $A_{0.75}B_{0.25}$

Tetrahedron	i	$\underline{T}_i$	P_i	W_i	N_i
A_4	1	(4, 0)	1	0.3164	0.3164
A_3B_1	2	(3, 1)	4	0.1055	0.4220
A_2B_2	3	(2, 2)	6	0.0352	0.2112
A_1B_3	4	(1, 3)	4	0.0117	0.0468
B_4	5	(0, 4)	1	0.0039	0.0039

The energy G_i of one hydrogen atom sitting on a tetrahedral site i will be estimated by taking the mean value of the heats of solution for hydrogen in the pure constituents $\Delta H_1, \Delta H_2, \ldots, \Delta H_m$ [8]. The site energy of a tetrahedron with four identical constituents is distributed as a gaussian function around this value G_i [4,5]. Fig. 1 demonstrates this for the binary alloy calculated in Table 2 for two different widths of the gaussians.

If a hydrogen atom is located at a tetrahedral site, neighbouring sites can be blocked due to a repulsive short range electrostatic hydrogen–hydrogen interaction. That is usually the case if the distance between two hydrogen atoms is less than 0.21 nm [9]. Generally, two neighbouring sites are at a smaller distance if they share three corner-atoms (e.g. one side of the tetrahedron). Therefore, if a hydrogen atom is located in a binary amorphous alloy at a tetrahedron of type A_3B_1, three other tetrahedra will be blocked (being in this case tetrahedra from the types A_4, A_3B_1 and A_2B_2).

3. Experimental

For the hydrogen loading experiment a 150 nm thin $Zr_{66.6}Al_{17.4}Ni_{7.2}Cu_{8.8}$ film was prepared on a glass substrate by sputter deposition. To prevent the sample from oxidation and to enhance the hydrogen uptake, a 30 nm thin Pd layer was deposited on top of the film. The

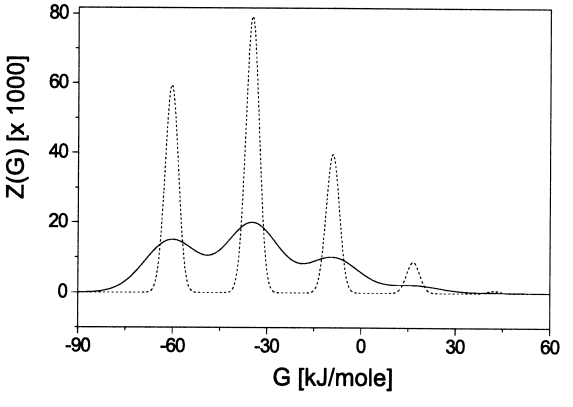

Fig. 1. Density of sites resulting for an $A_{0.75}B_{0.25}$ alloy with $\Delta H_A = -60$ kJ/mol and $\Delta H_B = +40$ kJ/mol. The narrow peaks ($\sigma = 2$ kJ/mol) demonstrate the five participating tetrahedra. For the wide peaks (dense line) a width of $\sigma = 12$ kJ/mol was chosen.

amorphous structure is confirmed by X-ray diffraction measurements. The concentrations of the constituents are determined by energy dispersive X-ray analysis. Hydrogen loading is performed electrochemically at room temperature, using a mixture of 50% glycerine and 50% phosphoric acid (85%) as electrolyte.

4. Discussion

The pure elements values ΔH_i used for the Zr–Al–Ni–Cu alloy in this work were taken from reference [10]. The calculated density of sites for the alloy is plotted in Fig. 2. A width of $\sigma = 12$ kJ/mol for every tetrahedron was taken as an average value obtained for hydrogen in other amorphous binary alloys [7]. This distribution is represented in the figure by the dense line. To demonstrate the large number of different tetrahedra also the density of sites for a small width of 2 kJ/mol is plotted with a dotted line.

Taking blocking effects into account the 'effective' density of sites is determined numerically: First the lowest energy site is filled, then the neighbouring sites are determined and the probability N_i to find them in the alloy is decreased. The procedure is now repeated by filling the lowest energy site in the remaining density of sites until all sites are blocked or filled. Kirchheim [5] suggested that as a result of blocking only 50% of the sites would finally be occupied. From Fig. 3 it can be seen, that this assumption holds. However, for the effective density of sites, a different shape arises, with a higher relative occupancy of lower energy sites compared to the unloaded site distribution.

Finally the calculation is compared with the experiment. Fig. 4 shows the measured and the calculated isotherm for comparison.

The calculated isotherm is obtained by integrating of the effective density of sites in Fig. 3. To fit the model to the experiment a value of 2.1 for the prefactor f in Eq. (3) was taken. The value f depends strongly on the structure of the amorphous material and is difficult to predict. For an amorphous structure one expects values larger than in the close packed f.c.c. lattice which is 3. The discrepancy can be related either to more blocked tetrahedra than assumed or to short range ordering leading to a non random distribution of the metal atoms. As can be seen in Fig. 4, experiment and theory agree reasonably well, despite the very simple assumptions of the model for such a complicated structure. Only at low hydrogen concentrations experiment and theory differ. We explain this basically on experimental uncertainties as the chemical potential at low hydrogen activities is more and more effected by other chemical reactions. Also this effect can be related to short-range ordering, as mentioned above.

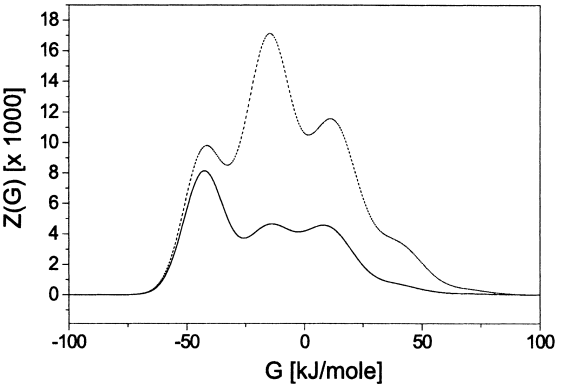

Fig. 3. Density of sites of $Zr_{66.6}Al_{17.4}Ni_{7.2}Cu_{8.8}$ before and after considering the blocking effects. Taking blocking effects into account one gets the 'effective' density of sites (dense line).

5. Conclusions

To our knowledge this is the first time that theoretical predictions are published about the isotherm of an amor-

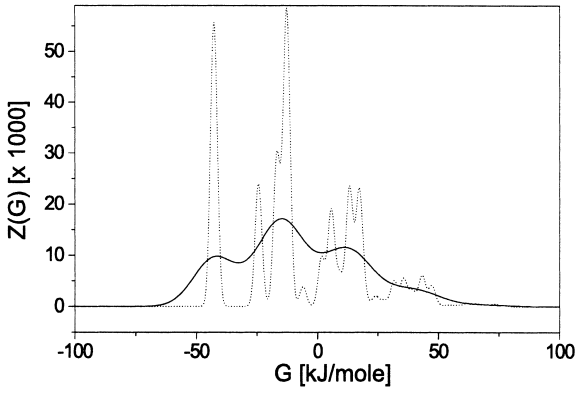

Fig. 2. Density of sites for an amorphous $Zr_{66.6}Al_{17.4}Ni_{7.2}Cu_{8.8}$ alloy. The 35 participating tetrahedra are visible in the dotted line, where a width for every single gaussian of $\sigma = 2$ kJ/mol was chosen. If $\sigma = 12$ kJ/mol a realistic energy distribution of sites (dense line) is obtained.

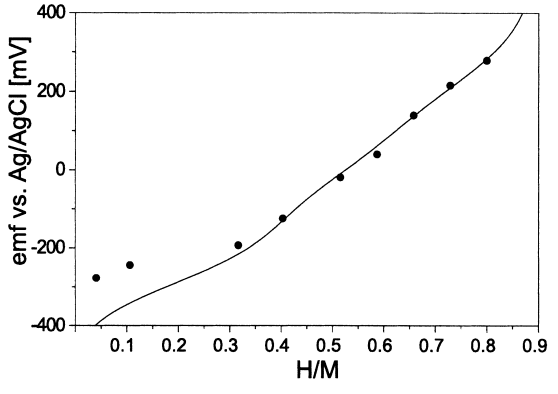

Fig. 4. Electrochemically measured isotherm ($T = 295$ K) for a 150 nm thin $Zr_{66.6}Al_{17.4}Ni_{7.2}Cu_{8.8}$ film (●). The dense line is the isotherm resulting from integration of the blocked density of sites. To fit the data with the model, the factor in Eq. (3) is chosen to $f = 2.1$.

phous structure containing more than two constituents. With the model the heats of solution for all possible tetrahedra can be calculated by taking the average of the pure element values for the constituents forming the tetrahedron. The amorphous structure leads to a gaussian distribution around this average value. The isotherm obtained by this model is compared with experimental results on $Zr_{66.6}Al_{17.4}Ni_{7.2}Cu_{8.8}$ films and the agreement is good. At low concentrations some deviations between theory and experiment occur which can be ascribed either to experimental conditions or to a non random distribution of the metal atoms.

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