Non-Arrhenius behavior of the diffusion coefficient of hydrogen in amorphous metals

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Abstract

A new model that explains the deviation from Arrhenius law of the diffusion coefficient of hydrogen in amorphous metals is suggested. This model relates the deviation to the temperature dependence of the short-range order. The suggested model is applied to simulate the diffusion behavior of hydrogen in dilute amorphous Fe–H alloy. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The interaction of hydrogen with amorphous metals and alloys has been studied extensively during the last two decades (e.g., Refs. [1–23]). These studies were motivated by either scientific or technological interest. Hydrogen in amorphous metals may be used as a probe to study the structure of the amorphous state. In addition, the study of hydrogen transport processes in the amorphous structure may enable to better understand the diffusion of hydrogen through grain boundaries and its interaction with structural defects (trapping) in crystalline metals. Various potential applications of amorphous metals are concerned with exposure to hydrogen (e.g., alloy-ing with hydrogen of components for the micro-electronic industry in order to improve the electrical properties, materials for hydrogen storage, devices for fusion reactors, etc.). Therefore, the study of hydrogen embrittlement, hydrogen diffusion, characteristics of hydrogen absorption and desorption and hydrogen effects on the electrical and magnetic properties is of great importance.

Many structural models [1–9] have been suggested in order to explain hydrogen diffusion and absorption in amorphous alloys. Kirchheim et al. [1–4] suggests that hydrogen atoms might occupy a wide variety of interstitial sites, resulting from both chemical and geometrical configurations in the amorphous structure. Hence, a broad continuous distribution of interstitial site energies is used to explain the concentration dependence of the chemical potential of hydrogen and its diffusivity in amorphous metals. Due to theoretical considerations [10], the

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shape of this energy distribution can be related to the shape of the first peak of the radial distribution function (RDF), which is usually assumed to be of a Gaussian form for amorphous metals.

The idea that hydrogen might occupy in amorphous alloys interstitial sites, which are similar to the octahedral and tetrahedral interstitial sites in crystalline alloys, was suggested in various papers (see, for example, Refs. [3,11]). This idea is based on measurements of similar values of hydrogen solubility [11], frequency factor (D_0) and activation energy for diffusion (Q) [3] in amorphous and in fcc structures.

Techniques that can monitor motion over wide temperature ranges (above 100 degrees) often exhibit very anomalous temperature dependencies of the diffusion coefficient of hydrogen in amorphous metals, which simple Arrhenius models cannot describe [19]. NMR measurements, for example, have revealed non-Arrhenius character for amorphous $TiCuH_{1.41}$ and Zr_2PdH_x hydrides [19–22].

Numerous theoretical concepts and computer modeling, mainly based on Monte-Carlo simulations, have been used to forecast the diffusion of hydrogen in amorphous metals. Ahmadzadeh and Cantor [12] were probably the first ones to use the concept of varying site and saddle-point energies for light interstitial atoms diffusion and to run Monte-Carlo calculations for amorphous metals. Kirchheim and Stolz [13] used similar simulations to study the effect of presence/absence of distributions of site and saddle-point energies on the characteristics of hydrogen diffusion in amorphous metals. Assuming no distribution of site energies, either with or without distribution of saddle-point energies, the linear behavior of the Arrhenius plots for the diffusion coefficient was obtained. Allowing for a distribution of site energies, however, resulted in a pronounced negative curvature that was related to trapping. It should be noted, however, that many inconsistencies arise from Gaussian distribution models, trying to explain the deviation from the Arrhenius behavior [19,22].

The non-Arrhenius behavior may be also explained by assuming that the microscopic diffusion processes consist of two basic kinds of jump: (1) relatively rapid motion within localized regions of the lattice; and (2) jumps that permit movement of hydrogen between these regions, which will determine the long distance diffusion properties. Examples of this descriptive scheme are presented in Refs. [19,23].

Belyakova et al. [14] combined computer modeling (Molecular-Dynamics) and experiments in order to study the effect of hydrogen on the structural and thermodynamic properties of iron and its alloys in amorphous, liquid and solid states.

The main objective of this paper is to describe the deviation from Arrhenius law of hydrogen diffusivity in amorphous metals, based on the short-range order of the structure and its temperature dependence. To illustrate the applicability of our model, the results on hydrogen diffusion in amorphous iron are presented. We show that accounting for the temperature dependence of the structure of amorphous metals leads to pronounced temperature dependence of the activation energy for diffusion processes. This effect reflects itself in the non-Arrhenius behavior of the diffusivity of small-atomic-volume impurities in amorphous metals.

The metal that was chosen to illustrate our model is iron. The reason for this is the comprehensive data that exists in the literature on the local structure of iron in its solid, amorphous and liquid states (e.g., Refs. [24–28]), as well as on hydrogen diffusion in crystalline iron and in amorphous Fe-base alloys (e.g., Refs. [15–18]).

2. Modeling procedure

Experimental measurements of the RDF are often used to characterize the local atomic arrangement in materials, including amorphous metals and alloys. Amorphous metals may be assumed as 'frozen' liquids, with a RDF similar to that of liquid metals, though showing a characteristic splitting of the second peak [24].

Making use of the experimental RDF of amorphous iron and its temperature dependence, one can calculate the coordination number as a function of temperature. However, since this information was unavailable for us, we referred to the similarity between the first peak of the RDF of amorphous and liquid metals and used the experimental density function of liquid iron from Ref. [27]. We assume that

atom distribution varies with temperature according to a Boltzmann relation:

$$g(r) = \exp\left[-\phi(r)/k_B T\right] \tag{1}$$

where $g(r)$ is the density function, $\phi(r)$ is the average potential between a certain origin atom and all neighbor atoms located at a distance r from it (see, for example, Ref. [29]), k_B is Boltzmann constant $(1.38 \times 10^{-23}$ J K$^{-1})$ and T is the absolute temperature. Eq. (1) may be treated also as the main contribution to the Percus–Yevick or Born–Green equations, which define the fine structure of liquid metals.

From the experimental data for $g(r)$ at fixed temperature we can extract $\phi(r)$ and use it to model $g(r)$ at different temperatures. The radial distribution function of the mono-atomic amorphous solid can now be expressed by the following equation:

$$\text{RDF}(r) = 4\pi r^2 \rho(r), \tag{2}$$

where $\rho(r) = g(r)/\Omega$ is the local atomic density and Ω is the mean volume per atom. We neglect the small changes in the value of Ω at varying temperatures and use the value of 13.44 Å^3 (90.79 a.u.^{3}) [27].

The coordination number (CN) can now be calculated by the routine integration procedure:

$$\text{CN} = 4\pi\rho_0 \int_{r_1}^{r_2} g(r) r^2 \, dr, \tag{3}$$

where r_1 and r_2 are the limits of the relevant peak of the RDF and $\rho_0 = 1/\Omega$ is the mean atomic density. Practically, one can either integrate directly the first peak of the RDF or run a Gaussian fitting for $g(r)$ in order to calculate the first-shell coordination number (CN$_1$). Using the first option and $g(r)$ at different temperatures, we receive the temperature dependence of the first-shell coordination number that is displayed in Fig. 1.

The observed decrease of the coordination number with temperature can be explained by substantial decrease and small broadening of the intensity of the density function at increased temperatures. It should be mentioned that the values of coordination number presented herein are in accordance with the experimental results of Ruppersberg and Seemann [28], who used X-ray testing of liquid iron to estimate the first-shell coordination number.
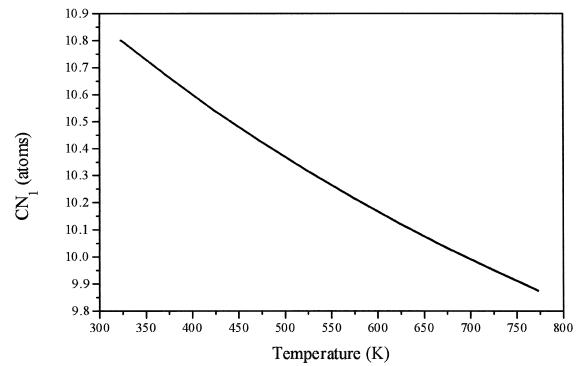

Fig. 1. The dependence of the first-shell coordination number of amorphous iron on temperature, calculated from Eq. (3).

The second peak of the RDF of iron is not well defined. However, on the basis of experimental measurements it was concluded [28] that liquid iron has a fcc (γ) structure near its melting temperature (1809 K). Hence, we choose to calculate the second-shell coordination number (CN$_2$) in the amorphous state from the ratio between the first- and second-shell coordination numbers in the crystalline fcc structure.

The above mentioned considerations are used to model the diffusion process of small-volume-atoms in an amorphous metal. We assume these atoms to occupy the octahedral interstitial positions in a fcc structure because the volume of these positions is larger in comparison with tetrahedral ones. Now, the diffusion process of atoms of small atomic radius, for example hydrogen, can be described as the result of their jumps over the 'sublattice' of octahedral sites. Any tunneling, phonon assisted or otherwise, is neglected further in our work. The activation energy for this process may be calculated if the energies of hydrogen atom in the interstitial position, $\bar{u}_o$, and in the saddle-point, $\bar{u}_p$, are defined. Taking into account only the first- and second-nearest neighbors, we present these energies in the following form:

$$\bar{u}_o = -\left\{ \left(1 + \frac{4\text{CN}_1(T)}{12} + \frac{1\text{CN}_1(T)}{24}\right) V_{\text{FeH}}(a/2) \right.$$

$$\left. + \left(\frac{4\text{CN}_1(T)}{6} + \frac{4\text{CN}_1(T)}{12}\right) V_{\text{FeH}}(a\sqrt{3}/2) \right\} \tag{4}$$

$$\bar{u}_p = -\left\{ \left(1 + \frac{1CN_1(T)}{12}\right) V_{FeH}\left(a\sqrt{2}\,/4\right) \right.$$
$$\left. + \left(\frac{4CN_1(T)}{12}\right) V_{FeH}\left(a\sqrt{6}\,/4\right) \right\}, \tag{5}$$

where CN_1 is the first-shell coordination number, a is the quasi-fcc-lattice parameter and V_{FeH} is the interatomic interaction potential between a hydrogen atom and an iron atom at different distances between one another.

In Eqs. (4) and (5), we refer to the first- and second-nearest neighbors around an octahedral interstice and a saddle-point (6 first-nearest neighbors at $a/2[001]$ directions and 8 second-nearest neighbors at $a/2[111]$, 2 at $a/4[011]$ and 4 at $a/4[211]$, respectively) in terms of their position in the quasi-fcc-lattice of amorphous Fe. We take into account the ratio between the first- and second-shell coordination numbers in crystalline fcc structures, as previously explained.

Eqs. (4) and (5) reflect also the temperature dependence of the coordination numbers of a quasi-fcc amorphous metal in the vicinity of the 'interstitial' impurity. It is easy to see that the activation energy for the diffusion process, $\Delta u = |\bar{u}_p - \bar{u}_o|$, becomes temperature-dependent, describing thus the deviation from the Arrhenius law.

For quantitative estimations, the model of interatomic interaction has to be chosen. The Fe–H interaction may be modeled by one of several flexible schemes, including the familiar Lennard–Jones and
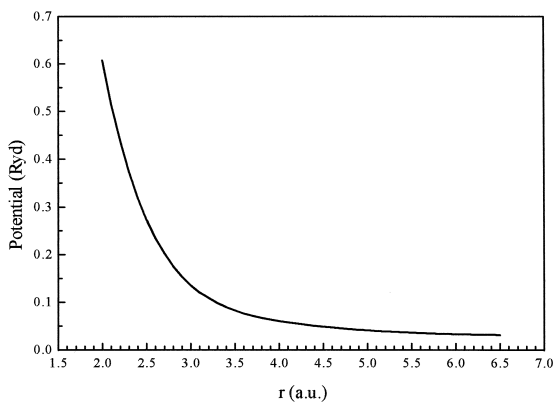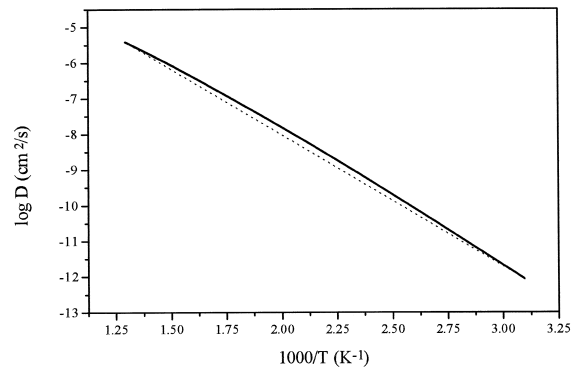
Fig. 3. Arrhenius plot of the diffusivity of hydrogen in amorphous Fe. Solid line was calculated using the temperature-dependent activation energy. Dotted line allows to see the deviation from the linear dependence.

Harmonic (Hook's law) potentials as well as generalized tabular functions. As follows from simple pseudopotential calculations (see, for example, Ref. [30] and references therein), the A–B type interaction is repulsive in systems with extremely limited solubility and with no tendencies to intermetallic phase formation. It reflects the tendency to the decomposition of the alloy. To treat the interatomic interactions one may use the perturbation series on potentials in reciprocal space (PSP RS-method). It is evident that this approximation will only roughly describe the basic peculiarities of the electronic spectra of solutions. This is especially true for the solutions with transition metals. But as thermodynamic quantities are always obtained as a result of averaging over the spectra, they are less sensitive to its particularities than, for instance, optical characteristics [31]. This is why the PSP RS-method can be applied to materials science problems that determine the quantities, which are not too sensitive to details of electron energy spectra of metals and alloys. Making use of the PSP RS-method we calculate the Fe–H interatomic interaction potential with soft-core pseudopotentials. The results of these calculations are presented in Fig. 2. It should be noted that we consider only very low concentrations of hydrogen (less than 0.1 at.%) in order to ensure conditions of dilute solid solution and to avoid interactions between hydrogen atoms.

Exploring this effective potential and Eqs. (4) and (5) we calculate the activation energy Δu as a function of temperature.

Fig. 2. The effective interatomic interaction potential Fe–H, calculated for extremely dilute Fe–H solid solution.

Fig. 3 presents the Arrhenius plot of the diffusion coefficient of hydrogen diffusion in amorphous Fe. It clearly demonstrates the non-Arrhenius behavior that is characterized by a negative curvature of the plot. This can be explained by temperature dependence of the activation energy for diffusion, which results from taking into account the temperature dependence of the local short-range order of the amorphous metal. This behavior is similar to the one reported by Kirchheim and Stolz [13] for small concentrations and/or high temperatures, when assuming a Gaussian distribution of site energies.

In conclusion, we showed that the deviation from Arrhenius law for the diffusion in amorphous metals may be related to the temperature dependence of the short-range order. The latter enters the activation energy in a natural way by means of coordination numbers, which appear to vary with temperature. This simple model may be used to study the tendencies in the diffusion behavior in amorphous metals under alloying, instead of using complicated and time-consuming Molecular-Dynamics or Monte-Carlo simulations. The temperature dependence of activation energy may influence also the other mechanisms of mass transfer in amorphous metals, for example the tunneling or phonon-assisted transport of light (hydrogen) atoms.

Acknowledgements

References

[1] R. Kirchheim, Acta Metall. 21 (1973) 1233.
[2] R. Kirchheim, Acta Metall. 30 (1982) 1069.
[3] R. Kirchheim, F. Sommer, G. Schluckebier, Acta Metall. 30 (1982) 1059.
[4] R. Kirchheim, T. Mütschele, W. Kieninger, Mater. Sci. Eng. 99 (1988) 457.
[5] J.H. Harris, W.A. Curtin, M.A. Tenhover, Phys. Rev. B 36 (1987) 5784.
[6] W.A. Curtin, J.H. Harris, Mater. Sci. Eng. 99 (1988) 463.
[7] J.H. Harris, W.A. Curtin, J. Phys. Chem. 163 (1989) 315.
[8] M. Kijek, M. Ahmadzadeh, B. Cantor, R.W. Cahn, Scripta Metall. 14 (1980) 1337.
[9] M. Ahmadzadeh, B. Cantor, J. Non-Cryst. Solids 43 (1981) 189.
[10] P.M. Richards, Phys. Rev. B 27 (1983) 2059.
[11] J.-J. Lin, T.-P. Perng, Scripta Metall. 25 (1991) 1179.
[12] M. Ahmadzadeh, B. Cantor, in: T. Masumoto, K. Suzuki (Eds.), Proc. 4th Int. Conf. on Rapidly Quenched Metals, Japan Institute of Metals, Sendai, 1982, p. 591.
[13] R. Kirchheim, U. Stolz, Acta Metall. 35 (1987) 281.
[14] R.M. Belyakova, V.A. Polukhin, N.A. Vatolin, E.A. Pastukhov, Melts 1 (1988) 212.
[15] Y. Fukai, The Metal–Hydrogen System, Springer, Berlin, 1993.
[16] J.-J. Lin, T.-P. Perng, Acta Metall. 39 (1991) 1101.
[17] J. Flis, S. Ashok, N.S. Stoloff, D.J. Duquette, Acta Metall. 35 (1987) 2071.
[18] R.M. Latanision, C.R. Compeau, M. Kurkela, in: R. Gibala, R.F. Hehemann (Eds.), Hydrogen Embrittlement and Stress Corrosion Cracking, ASM, Metals Park, OH, 1984, p. 297.
[19] R.C. Bowman Jr., Mater. Sci. Forum 31 (1988) 197.
[20] R.C. Bowman Jr., A.J. Maeland, W.-K. Rhim, Phys. Rev. B 26 (1982) 6362.
[21] R.C. Bowman Jr., A. Attalla, A.J. Maeland, W.L. Johnson, Solid State Commun. 47 (1983) 779.
[22] D. Richter, R. Hempelmann, R.C. Bowman Jr., in: L. Schlapbach (Ed.), Hydrogen in Intermetallic Compounds II, Springer, Berlin, 1992, p. 97.
[23] D. Richter, G. Driesen, R. Hempelmann, I.S. Anderson, Phys. Rev. Lett. 57 (1986) 731.
[24] M. Doyama, R. Yamamoto, in: V. Vitek (Ed.), Amorphous Materials—Modeling of Structure and Properties, AIME, 1983, p. 243.
[25] R. Yamamoto, H. Matsuoka, M. Doyama, Phys. Lett. 64A (1978) 457.
[26] T. Ichikawa, Phys. Stat. Sol. A 19 (1973) 707.
[27] Y. Waseda, K. Suzuki, The Science Reports of the Research Institutes, Tôhoku University, Series A, 24 (1973) 139.
[28] H. Ruppersberg, H.J. Seemann, Z. Naturforschg. 21A (1966) 820.
[29] M.F. Johnson, P. Hutchinson, N.H. March, Proc. R. Soc. London A 282 (1964) 283.
[30] S. Dorfman, D. Fuks, Composite Interfaces 3 (1996) 431.
[31] R.J. Elliott, J.A. Krumhansl, P.L. Leath, Rev. Mod. Phys. 46 (1978) 465.