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Determination of hydrogen diffusivity by subscale microhardness profiling

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Abstract

A novel method of determining hydrogen diffusivity in ductile metallic materials by microhardness profiling the cross-section after cathodic hydrogen charging is addressed. Hydrogen in solid solution strains the metallic lattice which results in higher hardness. Therefore, the increase in the concentration of hydrogen at a certain depth below the surface can be related to the microhardness increase at this location compared to the bulk value. The procedures to obtain the diffusion coefficient of hydrogen from the microhardness profiles are discussed. The application of the technique to determine hydrogen diffusivity in stoichiometric Fe_3Al is illustrated. The estimated hydrogen diffusivity is comparable with published data. The main advantage of the microhardness profiling technique is the relatively simple experimentation tools required. The disadvantages of the technique are also discussed.

Keywords: Hydrogen diffusivity, Microhardness profiling, Iron aluminide

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1. Introduction

Estimating the diffusivity of hydrogen in metallic materials is an important area of research. There are several techniques (like electrochemical permeation, Gorsky relaxation, gas permeation, internal friction measurements, etc.) proposed in the literature for determining hydrogen diffusivities in materials. The aim of the present communication is to outline a new and simple method to determine hydrogen diffusivity in metallic materials, which requires relatively simple experimentation. This is the method of subscale microhardness profiling after charging hydrogen into the material. Bückle showed in 1942 that microhardness profiling could be used to understand diffusivities in solid solution systems [1]. Our group has shown its usefulness in determining hydrogen diffusivities in several materials like Al–Li alloys [2], austenitic stainless steels [3] and several iron aluminides [4]. We also applied this method to determine oxygen and nitrogen diffusivities in titanium aluminides [5]. Hosada et al. have applied a modified version of the technique to determine hydrogen diffusivities in two iron aluminides [6].

2. Experimental procedure

The first step in the experiment is to suitably load hydrogen into the material. The use of thick, flat specimens aids data analysis. The most convenient method of loading hydrogen into metallic materials is by electrochemical hydrogen charging. During the charging procedure, care should be taken to maintain reproducible surface conditions and also to eliminate any surface contamination effects. Relatively long charging times lead to distinct microhardness profiles. The 74.4Fe–25.6Al (±0.25) intermetallic was electrochemically charged with hydrogen at 25°C for 12 h in a 0.05 mol/l sulphuric acid solution at a constant current density of 10 mA/cm^2. In order to maintain a constant surface hydrogen concentration throughout the sample surface, it is ideal if the specimen is surrounded on all the sides by the counter electrode (preferably in the form of a wire gauze) during the charging procedure. Otherwise, the sample side that faces away from the counter electrode would have a relatively lower surface hydrogen concentration due to solution resistivity. It would not be possible to completely eliminate the surface layer that forms during cathodic hydrogen charging; however, by choosing an appropriate electrolyte, the thickness of the layer can be kept to a minimum and hydrogen diffusivity through the layer can be conveniently neglected, as a first approximation. Once the material is charged with hydrogen, it has to be immediately cold mounted and the cross-section surface finished (by grind-

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ing and polishing) to a condition that is suitable for performing microhardness measurements. The next step is the determination of microhardness profiles across the polished cross-section. The variables in the hardness measurement are the indentation load that is to be used and the distance between successive indentations. Higher indentation loads produce larger indentations and, therefore, the area that is being sampled is also large in this case [6]. However, larger indentations would result in successive indentations being further apart and, therefore, would not help in gathering more data points. Therefore, lower indentation loads are preferred. A Leitz Wetzlar Miniload microhardness tester with an indentation load of 50 g was used in the study.

3. Analysis of data

Several microhardness profiles should be generated for each surface of the sample. Averaging over the profiles minimizes the measurement errors. Once the microhardness profiles are obtained, it is possible to estimate the diffusivity of hydrogen by making use of the following assumptions. The variation of microhardness (MHv) from surface to bulk is due to the diffusing species (hydrogen). This is reasonable as generally the variation in microhardness with depth for the uncharged specimens is constant. Assuming $(C - C_b)$ to be proportional to increase in MHv over the bulk value, i.e. $(\mathrm{MH}v - \mathrm{MH}v_b)$, we obtain

$$\frac{C - C_b}{C_s - C_b} = \frac{\mathrm{MHv} - \mathrm{MHv}_b}{\mathrm{MHv}_s - \mathrm{MHv}_b} \tag{1}$$

where C_s is the surface concentration, C_b the bulk concentration, and C the concentration of diffusing species at any point. Subscripts b and s denote bulk and surface, respectively.

As the specimen surfaces are flat and the depths of diffusion field are small compared to thickness of samples, the problem may be treated as unsteady diffusion through a semi-infinite flat specimen. Further assumptions that have to be applied to determine the diffusivity is that diffusion occurs through a single phase, there is no internal phase formation in the diffusion field, the diffusion coefficient is constant in the entire diffusion zone, and the surface concentration is not a function of time. It is evident, therefore, that this method is not applicable to determine diffusivities in materials that hydride. However, in such a case, the microhardness profiling technique can be used to monitor the progress of the internal hydriding front, if hydrogen diffusivity is low [7]. Eq. (1) can then be combined with the standard diffusion equation to give

$$\frac{\mathrm{MHv} - \mathrm{MHv}_b}{\mathrm{MHv}_s - \mathrm{MHv}_b} = \frac{C - C_b}{C_s - C_b} = 1 - \mathrm{erf}\left(\frac{z}{\sqrt{4Dt}}\right) = \mathrm{erfc}\left(\frac{z}{\sqrt{4Dt}}\right) \tag{2}$$

As the assumption of constant surface concentration is not strictly valid because of slight variations in the specimen potential during cathodic hydrogen charging, C_s should be ideally eliminated from Eq. (2). C_s can be eliminated and the diffusion coefficient can be determined by the following method. A pair of points on the microhardness versus distance curve can be chosen and the following parameter Y_{12} obtained (for two given points 1 and 2) based on Eq. (2).

$$Y_{12} = \frac{(C_1 - C_b)/(C_s - C_b)}{(C_2 - C_b)/(C_s - C_b)} = \frac{C_1 - C_b}{C_2 - C_b} = \frac{\mathrm{erfc}(z_1/\sqrt{4Dt})}{\mathrm{erfc}(z_2/\sqrt{4Dt})} = \frac{\mathrm{MHv}_1 - \mathrm{MHv}_b}{\mathrm{MHv}_2 - \mathrm{MHv}_b} \tag{3}$$

where $(\mathrm{MH}v)_1$, $(\mathrm{MH}v)_2$ and $(\mathrm{MH}v)_b$ are the microhardness values and C_1, C_2 and C_b are the hydrogen concentrations at locations 1, 2 and in the bulk, respectively. D is the only unknown parameter in Eq. (3) for a given experiment. Eq. (3) can be solved by using error function tables and by trial and error.

The above method was applied for determining hydrogen diffusivity in the stoichiometric Fe_3Al. The microhardness profile (average of six profiles with the maximum scatter in the microhardness data of ±8 MHv) is shown in Fig. 1 [4]. The diffusivity of hydrogen obtained by using several pairs of points are 1.87, 1.67, 1.18, 1.30, 1.13, 1.26, 1.37, 2.07, 1.48 and 1.24×10^{-13} m^2/s and the average diffusivity is 1.45×10^{-13} m^2/s. The estimated value is compared with data in the literature. The diffusivity of hydrogen in pure BCC Fe is of the order of 10^{-9} m^2/s at room temperature [8]. Alloying Fe with Al further decreases hydrogen diffusivity due to the local trapping of hydrogen by Al (possibly by disturbing the periodicity in the local arrangements of atoms) [4]. The measured diffusivity of hydrogen in Fe_3Al is reasonable as it is lower than that in Fe–18Al [6] but higher than that in Fe–(35–40)Al [9,10]. Therefore, the measured hydrogen

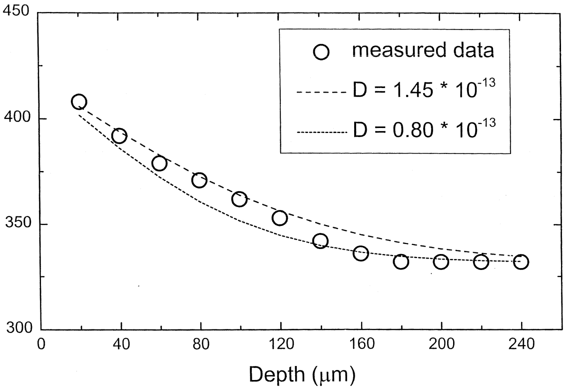

Fig. 1. Microhardness profile after cathodic hydrogen charging in 0.05 mol/l H_2SO_4 solution at 10 mA/cm^2 for 12 h. Theoretical diffusion profiles for assumed hydrogen diffusivities of 1.45 and 0.80×10^{-13} m^2/s are also presented.

diffusivity by subscale microhardness profiling is reasonable and according to expectation.

A graphical method can also be used to determine hydrogen diffusivity, In this case, a ‘theoretical’ surface hardness must be assumed for the profile by extending the straight line portion of the curve near the surface and using the intercept with the hardness axis as the ‘theoretical’ surface hardness. It is further assumed that the bulk hydrogen concentration is proportional to the bulk microhardness value. It is then possible to use Eq. (2) and draw theoretical microhardness curves (i.e. diffusion profiles). Such a procedure was also applied to the data presented in Fig. 1 (with a ‘theoretical’ surface hardness of 418 MHv and bulk microhardness of 332 MHv). The diffusion profiles for assumed hydrogen diffusivity of 1.45 and 0.80×10^{-13} m^2/s are also presented in Fig. 1. Notice that by using the former value, the fit of the calculated profile to the slope of the microhardness profile is reasonable, whereas by using the latter, the fit to the microhardness points in the bulk is better. These calculated profiles, nevertheless, indicate the appropriateness of the trial-and-error solution and the validity of using microhardness profiles to determine hydrogen diffusivity.

The advantage of the microhardness profiling technique is that hydrogen diffusivity can be measured by relatively simple experiments. Moreover, the estimated values are representative of bulk hydrogen diffusion. Of course. the problem with the technique is that it cannot be utilized for materials in which hydrogen diffusivity is relatively fast (for example, Pd) and also for materials that hydride or severely crack on introduction of hydrogen. Interestingly, materials that crack on introduction of hydrogen are also not suitable for experimentation in the permeation techniques. In this case, the microhardness profiling technique can be used for a rough determination of diffusivity as the microcracking can be taken into account in the microhardness measurements by choosing an area that is free from cracks for the measurement of microhardness. Another source of error arises if a thick surface layer develops during cathodic charging. This problem can be minimized by choosing a suitable electrolyte that does not produce a thick surface layer during charging.

4. Conclusions

The determination of hydrogen diffusivity by the method of microhardness profiling is outlined. The advantage of this method is that hydrogen diffusivities can be determined quite easily with relatively simple experimentation. Hydrogen can be conveniently charged into the metallic specimen by cathodic charging. The microhardness profiles obtained after cathodic charging can be analyzed either by trial-and-error or graphical method to determine hydrogen diffusivities. The application of this method has been illustrated by determining hydrogen diffusivity in stoichiometric Fe_3Al.

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