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On the dependence of true hydrogen equilibrium pressure on the granular size distribution of the $Zr(Fe_{0.5}Mn_{0.5})_2$ getter alloy

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Abstract

The influence of grain size distribution on the achievement of the chemical equilibrium between the solid solution region and the hydrogen gas phase for the St909 alloy isotherms has been investigated for two different grain size distributions to test the possibility of using this alloy without a previous cycling treatment. The small grain size distribution gave $\Delta\overline{H} = -33.54 \pm 1.03$ kJ/mol$_H$, $\Delta\overline{S} = -18.31 \pm 3.43$ J/K mol$_H$ in a H_2 concentration range $0.05 \leq x \leq 0.09$, and $\Delta\overline{H} = -42.30 \pm 1.06$ kJ/mol$_D$, $\Delta\overline{S} = -21.78 \pm 4.49$ J/K mol$_D$ in a D_2 concentration range $0.02 \leq x \leq 0.09$. A comparison with $\Delta\overline{H}$ and $\Delta\overline{S}$ values in the infinite dilution range for H_2 and T_2 obtained for the conditioned St737 alloy suggested that the small grain distribution gave H_2 pressure values close to but not yet at equilibrium. A qualitative inquiry on the possible factors limiting the achievement of equilibrium is also presented and suggests surface dissociation phenomena as the most probable cause. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: St909 alloy; Hydrogen equilibrium pressure

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1. Introduction

St909 alloy showed potential as a candidate material for tritiated water purification [1]. The production of tritiated water is an inherent process that arises during impurity processing of the exhaust stream in a deuterium–tritium plasma fusion device [2]. However, an experiment [1] on these alloys for such applications showed some drawbacks that could compromise the process.

- In order to maximize the active surface area of the alloy, it needs ‘cycling’ of the alloy off-line with protium [3]. A residual protium inventory, can recombine with the tritium atoms during exposure to tritium giving HT molecules. To obtain pure tritium, the outcoming HT flow should be sent to an Isotope Separation System.
- Accidental air ingress on a bed conditioned and activated with protium off-line would require a successive activation on-line with consumption of a fraction of the alloy.

A viable alternative to avoid these problems is the knowledge ‘a priori’ of the optimum average size of the grains resulting as a compromise of two competing processes: the increase in the active surface and the oxygen coverage at the end of the grinding. However, at the end of the cycling, the alloys usually show a grain size distribution rather than a single size.

In this work, we report and discuss measurements of hydrogen pressures for St909[1] intermetallic compounds carried out at different hydrogen concentrations and temperatures, in the solubility range, for two different typical grain size distributions. For a better understanding of the onset of equilibrium, we carried out an analysis of $\Delta\overline{H}$ and $\Delta\overline{S}$ at infinite dilution. For comparison, measurements and analysis were repeated with deuterium for the alloy with the finest grains.

2. Experimental set-up

An ultra-high vacuum (UHV) system was built to carry out PCT measurements on getter alloys (isopleth mode [4]). Details were reported in Ref. [5].

In this work, the hydrogen concentration spanned from $x = 0.01$ to 0.2 in steps of 0.01, the pressure spanned from

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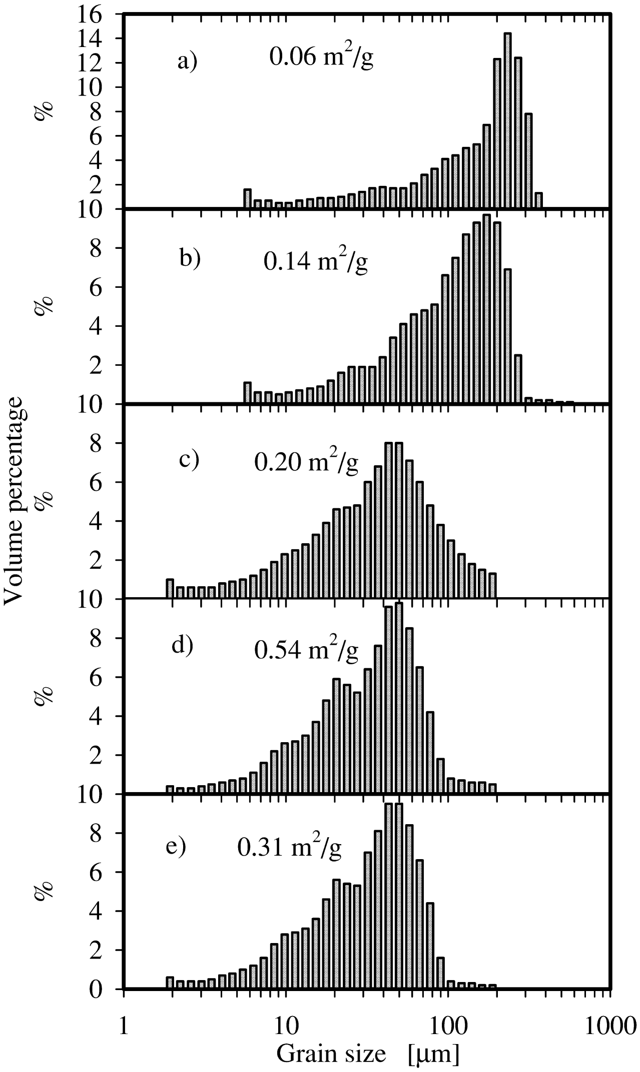

Fig. 1. Grain size distribution for the St909 alloy in different conditions. (a) Virgin large grain size alloy; (b) large grain alloy after protium PCT measurements; (c) virgin small grain size alloy; (d) small grain alloy after deuterium PCT; (e) small grain alloy after protium PCT.

10^{-5} up to 1.4×10^{4} Pa while the getter temperature was from room temperature up to 400°C.

Fig. 1 shows the two different distributions of the grain size, along with their active surface areas (BET), for the St909 alloy used in the experiment[2]. For comparison, the grain size distribution of the virgin alloy is also reported.

3. Results and discussion

PCT curves, for large and small grain alloys, are shown in Fig. 2. This figure shows that:

- the pressures measured with protium for the large grain size alloy are always higher than for the small grain size alloy;
- for the small grain size alloy, the pressure measured at the alloy temperature of 400°C with protium is lower than that measured with deuterium; conversely, at 25°C, the pressure with protium is higher than that with deuterium; and at the temperature of 200°C, the protium pressure is lower than the deuterium pressure for some concentrations and higher for others.

Replotting these isotherms in a log–log diagram, it became clear that some of the isotherms did not follow Sievert's law [6]. In particular, from the slopes of the fitting, given in Table 1, one can notice that the isotherms at 200°C and above follow Sievert's law quite nicely, while for lower temperatures the rule is obeyed only at relatively large concentrations.

At low concentrations and low temperatures, several factors like slow interstitial diffusion, surface limiting phenomena, and high outgassing rate of the apparatus can obstruct the achievement of equilibrium. To seek out the possible limiting factor, we carried out an analysis of the solubility in a concentration range where the Sieverts' law holds. In a $\sqrt{P}$ versus x diagram, the inverse of the slope gives the Sievert's constants K (Table 1).

At equal concentrations, it holds the relation:

$$\left(\frac{P_{D_2}}{P_{H_2}}\right) = \left(\frac{K_{H_2}}{K_{D_2}}\right)^2 \tag{1}$$

using the values of K from Table 1

$$\left.\frac{P_{D_2}}{P_{H_2}}\right|_{T=200,400°C} > 1 \tag{2}$$

the deuterium pressure is always higher than the protium pressure. This result at 200°C does not completely agree with the experimental data. Although, one can argue that it could be an artifact of the fitting, we still believe Eq. (2) because the temperature at 200°C is the last isotherm that follows Sievert's law for the x-values considered. At lower temperatures, the above mentioned limiting factor keeps the pressures higher than the expected equilibrium value, ruling out Sievert's law. Due to the fact that the hydrogen pressures measured for the alloy with the large grain size are always higher than the other values, it was useless to obtain the K values for that case.

In order to understand if the value of pressures measured for protium and deuterium for the small grain size alloy do represent equilibrium, we obtained the values of $\Delta\overline{H}$ and $\Delta\overline{S}$ for solution at infinite dilution. The details of this study are explained in Ref. [6]. The results are:

$$\Delta\overline{H}_{H}^{\infty} = -33.54 \pm 1.03\ \mathrm{kJ/mol_H},$$

$$\Delta\overline{S}_{H}^{nc\infty} = -55.39 \pm 1.99\ \mathrm{J/K\,mol_H}\ \text{and}$$

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[2] Measurements made at SAES Getters SpA, Viale Italia 77, Lainate, Milan, Italy.

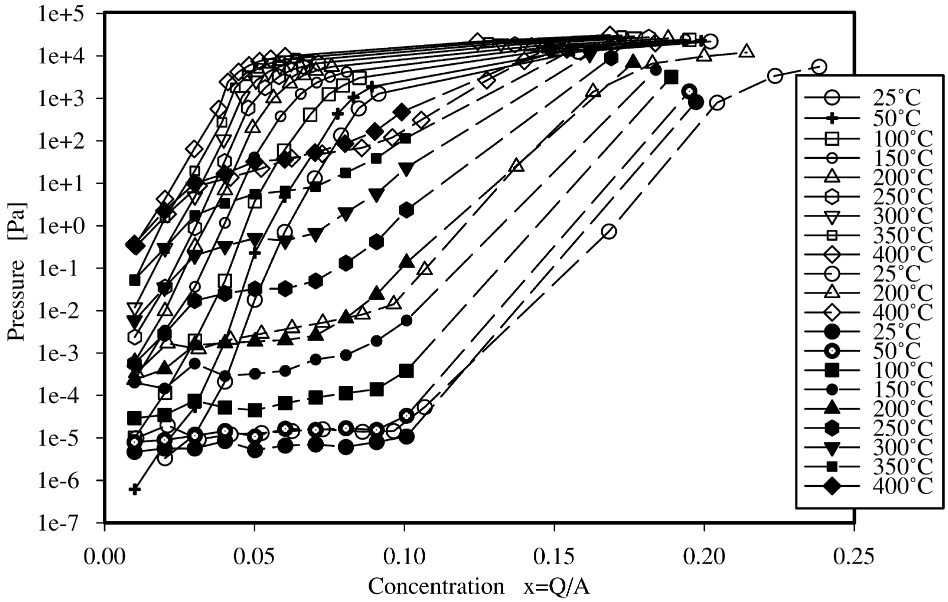

Fig. 2. PCT characteristic curves for large and small grain size alloy. Open symbols, protium; filled symbols, deuterium; solid lines, large grain size alloy; dashed lines, small grain size alloy. The hydrogen concentration x is expressed as: mol hydrogen/mol alloy.

Table 1
Slopes of the ln (P) versus ln (x) diagram (Sieverts' law) and Sieverts' constants K for protium and deuterium for the St909 small grain size alloy

Gas type Q	Alloy temperature (°C)	Slope (Sieverts' law)	Absorption coefficient, K	Concentration interval $x_{\mathrm{min}}-x_{\mathrm{max}}$
D	400	2.10	8.70×10^{-3}	0.03–0.08
	350	2.11	1.98×10^{-2}	0.03–0.08
	300	1.93	6.30×10^{-2}	0.03–0.08
	250	2.24	2.49×10^{-1}	0.02–0.08
	200	1.99	7.20×10^{-1}	0.02–0.09
	150	2.24	–	0.04–0.09
	100	1.93	–	0.05–0.09
	50	0.42	–	0.02–0.07
	25	0.13	–	0.02–0.07
H	400	2.13	9.88×10^{-3}	0.03–0.08
	200	2.02	8.45×10^{-1}	0.03–0.09
	25	0.86	–	0.03–0.1

$$\Delta\overline{H}^{\infty}_{\mathrm{D}} = -42.30\pm1.06\ \mathrm{kJ/mol_D},$$

$$\Delta\overline{S}^{\mathrm{nc}\infty}_{\mathrm{D}} = -61.59\pm1.65\ \mathrm{J/K\ mol_D}$$

where $\Delta\overline{H}^{\infty}$ is the molar enthalpy change at infinite dilution, and $\Delta\overline{S}^{\mathrm{nc}\infty}$ is the nonconfigurational molar entropy change, comprising vibrational, electronic and magnetic contributions.

The enthalpy for deuterium at infinite dilution is higher than that for protium. The reason for this can be ascribed to the isotope dependence of the form of the potential well [7].

The entropy term $\Delta\overline{S}^{\mathrm{nc}\infty}$ is essentially governed by the loss of gas entropy upon dissolution in the lattice, therefore it is fairly insensitive to the concentration. This feature can be observed by looking at Table 2, which summarizes the thermodynamic data. The value of $\Delta\overline{S}^{\mathrm{nc}\infty}/R$ is found to be

Table 2
Thermodynamic data for St909 at infinite dilution

Gas type Q	Concentration x	$-\Delta\overline{H}^{\infty}_{\mathrm{Q}}$ (kJ/mol$_{\mathrm{Q}}$)	$-\Delta\overline{S}^{\infty}_{\mathrm{Q}}$ (J/K mol$_{\mathrm{Q}}$)	$-\Delta\overline{S}^{\mathrm{nc}\infty}_{\mathrm{Q}}/R$
D	0.02	42.10	11.61	7.097
	0.03	41.19	18.35	7.500
	0.04	42.83	21.41	7.579
	0.05	39.39	17.82	6.922
	0.06	43.91	24.97	7.599
	0.07	43.56	25.80	7.543
	0.08	42.87	26.19	7.454
	0.09	42.55	28.11	7.566
H	0.05	31.90	12.42	6.273
	0.06	32.90	16.22	6.546
	0.07	33.23	17.72	6.571
	0.08	34.24	20.55	6.776
	0.09	35.42	24.64	7.149

close to -7 for a large number of getter materials [8]. For hcp metals like the St909 alloy, values ranging from -6.2 to -7.08 for hydrogen are reported [9]. Therefore, the values

$$\frac{\Delta\bar{S}_{\mathrm{H}}^{\mathrm{nc}\infty}}{R}=-6.66\pm0.24 \text{ and } \frac{\Delta\bar{S}_{\mathrm{D}}^{\mathrm{nc}\infty}}{R}=-7.41\pm0.2$$

are reasonable, and the assumption made of $x_{\mathrm{s}}=6$, where x_{s} is the maximum number of protium (deuterium) atoms per unit formula of alloy is acceptable.

For the St909, $\Delta\bar{S}_{\mathrm{D}}^{\mathrm{nc}\infty}/R$ is constant over a concentration range $0.02\leq x\leq0.09$, and the corresponding value of $\Delta\bar{H}_{\mathrm{D}}^{\infty}=-42.30\pm1.06$ kJ/mol$_{\mathrm{D}}$ is constant as expected for an infinite dilution case. Similarly $\Delta\bar{S}_{\mathrm{H}}^{\mathrm{nc}\infty}/R$ and $\Delta\bar{H}_{\mathrm{H}}^{\infty}=-33.54\pm1.03$ kJ/mol$_{\mathrm{H}}$ are constant for $0.05\leq x\leq0.09$. Concentrations lower than $x=0.05$ for protium gave $\Delta\bar{H}_{\mathrm{H}}^{\infty}$ and $\Delta\bar{S}_{\mathrm{H}}^{\mathrm{nc}\infty}$ values very different and too scattered to be considered. These concentrations suggested a state far away from equilibrium, and therefore have been neglected.

Recalling that:

$$\Delta\bar{S}_{\mathrm{Q}}^{\mathrm{nc}}=\bar{S}_{\mathrm{Q}}^{\mathrm{nc}}-\frac{1}{2}\bar{S}_{\mathrm{Q}_{2(\mathrm{g})}}^{0} \tag{3}$$

using the values listed in Ref. [10] for the entropy in the gas phase, the following nonconfigurational entropy terms are calculated:

$$\bar{S}_{\mathrm{H}}^{\mathrm{nc}}=9.98\ \mathrm{J/K\,mol_{H}},\quad \bar{S}_{\mathrm{D}}^{\mathrm{nc}}=10.94\ \mathrm{J/K\,mol_{D}}$$

3.1. Factors limiting the achievement of the equilibrium

To study the different phases in the alloys, X-ray diffraction analyses, not reported for brevity, have been carried out on all the powder samples [6]. The small differences noticeable among the spectra cannot explain such large deviations in the equilibrium pressures.

In order to exclude alloy contamination, measurements of O_2 and N_2 content in the alloy showed that the maximum differences among the samples are less than 0.5 and 0.03% for O_2 and N_2, respectively.

Comparing the $\Delta\bar{H}^{\infty}$ and $\Delta\bar{S}^{\mathrm{nc}\infty}$ values found for the small grain alloys with those found for the St737 alloy for H, T [11], one can note that $\Delta\bar{S}^{\mathrm{nc}\infty}/R$ for D_2 is close to $\Delta\bar{S}^{\mathrm{nc}\infty}/R$ for T_2 for the St737 alloy.

With regards to $\Delta\bar{H}_{\mathrm{H}}^{\infty}$, the values found for St909 are much higher than those for St737 ($\Delta\bar{H}_{\mathrm{H}}^{\infty}=-27.36\pm0.59$ kJ/mol$_{\mathrm{H}}$).

On this basis, it is the opinion of the authors that the small grain alloy is close to but not yet at equilibrium. In fact the two alloys belong to the same space group C14, p63/*mmc* and have similar lattice constants: St909: $a=5.006$ Å, $c=8.178$ Å, and St737: $a=5.092$ Å, $c=8.314$ Å.

As explained, the decrease of the average size of the grain increases the active surface area, conversely, the diffusion properties do not change. This means that the equilibrium is obstructed by the slow rate of the surface dissociation phenomena or by the gas arrival rate. Because we carried out measurement of pressures at steady state, we disregard the gas arrival rate case and argue about the interstitial diffusion to claim the surface phenomena as the limiting factor.

To date, we do not have hydrogen diffusion data for these alloys. Besides, using the diffusion coefficient (D) for C14 alloys published [12,13] could bring to erroneous conclusions because it needs to know the D_0 values at low concentration [14] that are much higher than those available obtained with experiments that imply the fully hydride phase (NMR, QNS, etc.).

Furthermore, the diffusion experiments carried out in a classical way cover a temperature range much higher than our range.

A conservative estimate of the diffusion coefficient can be done using the results obtained by Kappesser et al. [15] by vibrational spectroscopy at low concentrations and low temperatures, and by Anderson et al. [16] by QNS at higher temperatures and concentrations for the hcp YH_x system.

The two methods cited above gave results that can be fitted nicely in a unique Arrhenius' plot, so that the diffusion coefficient for the St909 alloy can be estimated using the data at high temperature and for the concentration range of interest given by Anderson [16].

Since the slow diffusion process occurs along the basal plane [16,17] and using the attempt frequency ν_0 found by Anderson, the D_0 value for interstitial diffusion along the basal plane for St909 is 1.19×10^{-2} cm^2/s [18].

The larger approximation resides in the choice of the energy of activation for diffusion, E_{a}. There are no E_{a} data for St737 or for St909. The best guess was to use the value of E_{a} of 0.4337 eV found for St707 alloy [19] which gave a value of 6.13×10^{-10} cm^2/s for D(300 K).

To compare hydrogen diffusion through grains of different size we introduce the approximation of the equivalent sphere

$$\tau=\frac{R^2}{\pi^2 D}\ [20]$$

where τ is the characteristic diffusion time constant. The interstitial diffusion is not the limiting factor because it was always $3\tau\ll T$, where T is the period of time elapsed before reading a new value of pressure.

For the alloy with the small grain size, the average diameter is $d=36$ μm so that at 300 K we obtain $\tau\cong536$ s. A typical value of T for 300 K is about 1 day while, at higher temperature, T decreased to about 4 h so that the previous relation was always satisfied.

Another limiting factor could be the grain boundary diffusion. In fact, St909 has a polycrystalline grain with different orientation so that the diffusion along the grain boundary can also set on when

$$\frac{D(\mathrm{b})}{D(\mathrm{l})}\gg\frac{d}{s}\ [21]$$

where D(b) and D(l) are the grain boundary and lattice diffusion values, d is the average grain diameter, and s is the average grain boundary width. Taking for example $s=0.5$ nm and $d=36$ μm as reasonable values, the above ratio must become much greater than 7.2×10^4, so that it is improbable that grain boundary diffusion takes places.

By exclusion, the limiting factor is the surface dissociation phenomena.

If the dissociation at the surface occurs with a 'dual site mechanism' [22], the reaction rate is given by:

$$r=k\left(\theta_{H_2}\theta_v-\frac{\theta_H^2}{K_s}\right) \tag{4}$$

where k = rate constant, K_s = equilibrium constant, θ_{H_2} = factor of surface sites occupied by H_2, θ_v = factor of surface vacant available for reaction, and θ_H = factor of surface sites occupied by H.

If some of the sites are blocked by oxygen, θ_v decreases most probably with the θ_o^2 since also oxygen surface dissociation occurs; where θ_o is the factor of surface sites occupied by oxygen.

Decreasing the grain's diameter increases the active surface, that means, if the oxygen diffusion is fast, θ_v increases rapidly, and finally the reaction rate.

4. Conclusions

The protium PCT curves for St909 have been measured for two different grain size distributions in addition to the deuterium PCT curves for the smaller size distribution. These isotherms related to the solubility region only. In order to understand the influence of the grain size on the attainment of equilibrium, the above mentioned curves have been obtained without the cycling of the two alloys. A study of $\Delta\overline{H}$ and $\Delta\overline{S}$ in the 'infinite dilution' concentration range revealed that the large grain alloy presented a steady pressure not representative of equilibrium while the small grain alloy gave $\Delta\overline{H}$ and $\Delta\overline{S}$ values that could be interpreted as of real chemical equilibrium. However, by a comparison with the $\Delta\overline{H}$ and $\Delta\overline{S}$ value for H and T obtained for the conditioned St737 alloy in the infinite dilution region, the authors believe that the small grain alloy gave pressures close to, but not yet at equilibrium.

A qualitative inquiry on the possible limiting factors for the achievement of the equilibrium suggested surface dissociation phenomena as the most probable.

Even though the possibility of using a small grain alloy without 'cycling' appears to be a viable method of application we should, at the same time, warn the reader that this is likely only for those alloys that show enhanced diffusion for hydrogen and active gases like O_2, C_2, etc. (i.e. have low activation temperatures), but not true for others like St107, St198, etc. which require higher activation temperatures.

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