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Local hydrogen environments in $\text{Gd}_{1-x}\text{Fe}_x$ thin films amorphous alloys from effusion experiments

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Thin films of hydrogenated $\text{Gd}_{1-x}\text{Fe}_x$ ($0.25 \leq x \leq 0.90$) amorphous alloys were prepared by reactive evaporation. Effusion experiments, showing several hydrogen release peaks, allowed us to describe the site distribution of hydrogen in these alloys. The different local environments correspond to tetrahedral sites and the stability of these sites increases with the number of rare-earth neighbors.

This letter reports on the site distribution of hydrogen in $\text{Gd}_{1-x}\text{Fe}_x$ thin films amorphous alloys. We show that the effusion of hydrogen occurs in several stages corresponding to the release of hydrogen from different atomic sites. Such experiments have already been performed on amorphous metallic alloys,¹⁻³ but the effusion curves never showed several separate peaks. As the $\text{Gd}_{1-x}\text{Fe}_x$ alloys are constituted of elements having a very large hydrogen affinity difference, we have distinguished the local hydrogen environments, which correspond to tetrahedral sites, and we have followed the evolution of these effusion peaks with composition.

Hydrogenated $\text{Gd}_{1-x}\text{Fe}_x$ ($0.25 \leq x \leq 0.90$) amorphous alloys were prepared by reactive evaporation. Gadolinium and iron were evaporated from a thermal cell and from an electron beam gun, respectively, in a molecular hydrogen atmosphere on substrates maintained at 77 K. The deposition rate was 3 Å/s. The hydrogen flow was regulated by maintaining the total pressure in the evaporation chamber at 10^{-4} Torr. This procedure allowed us to obtain hydrogenated films, which do not fracture or disintegrate as in the case of the post-hydrogenation method.

Transmission electron microscopy was performed on 200-Å-thick samples annealed at temperatures ranging between 100 and 800 °C. The as-deposited alloys were amorphous in the composition range $0.25 \leq x \leq 0.90$ and two steps were observed in the crystallization process, a primary crystallization of α iron (or gadolinium for the $\text{Gd}_{0.75}\text{Fe}_{0.25}$ alloy) in the amorphous matrix, and next the crystallization of this matrix with the apparition of other phases. The different crystallization temperatures T_{cr} are shown in Fig. 1. The $\text{Gd}_{1-x}\text{Fe}_x$ alloys are rather stable since, except the $\text{Gd}_{0.10}\text{Fe}_{0.90}$ sample which crystallizes at 100 °C, the other samples have a crystallization temperature greater than 500 °C.

The stability of hydrogen was monitored by effusion experiments performed on 1000-Å-thick samples deposited on float glass substrates, with a heating rate of 15 °C/min. In fact, deuterated films were used to suppress background effects due to adsorbed water, but the generic term hydrogen will be used in subsequent discussions. The hydrogen concentration in the samples was obtained from the area of these spectra after calibration of the quadrupole mass spectrometer.

Three typical effusion spectra are shown in Figs. 2–4. The $\text{Gd}_{0.10}\text{Fe}_{0.90}$ alloy presents a single peak of 200 °C (Fig.

2). The hydrogen concentration is weak, it corresponds to a ratio (H/M) (M is the number of Gd and Fe metallic atoms) equal to 0.01. The temperature of the peak is higher than the crystallization temperature of α iron in the film. In fact, it can be supposed that a part of the iron atoms is in excess in the amorphous matrix and this excess precipitates as soon as 100 °C. The hydrogen atoms remain in the amorphous phase. At 200 °C, hydrogen effuses from this phase which crystallizes after 600 °C. For the $\text{Gd}_{0.25}\text{Fe}_{0.75}$ alloy, the intensity of this peak increases and a well separated second peak, very less intense, appears at higher temperature, 260 °C. The hydrogen concentration increases with a ratio H/M equal to 0.15. Contrary to the preceding sample, the amorphous phase is much more stable since T_{cr} is greater than 500 °C. Therefore, the effusion process appears in a perfectly amorphous phase and this occurs well before the crystallization. The presence of the two peaks can be explained by assuming that hydrogen is trapped at specific sites of different energy in the network. The $\text{Gd}_{0.33}\text{Fe}_{0.67}$ alloy presents a more complex spectrum (Fig. 3), with a ratio H/M of 0.55. The second peak has increased and a third peak has appeared at higher temperature, 370 °C. With the increasing gadolinium concentration, the high-temperature peaks take more and more im-

FIG. 1. Crystallization temperatures T_{cr} of the $\text{Gd}_{1-x}\text{Fe}_x$ alloys vs annealing temperature. The symbol $\circ$ and $+$ correspond to the primary crystallization of α iron (or gadolinium) and to the apparition of the other crystallized phases respectively.

FIG. 2. Effusion rate R of the $\text{Gd}_{0.10}\text{Fe}_{0.90}$ amorphous alloy.

portance. In fact, hydrogen atoms with several gadolinium neighbors are more and more numerous and it may be assumed that these sites are deeper in energy, so that these hydrogen atoms can only escape at higher temperatures. The spectrum complexity still increases for the $\text{Gd}_{0.50}\text{Fe}_{0.50}$ alloy with the appearance of a fourth peak at 550 °C (Fig. 4). The ratio H/M is 0.6. Finally, the spectrum of the $\text{Gd}_{0.75}\text{Fe}_{0.25}$ alloy always contains four peaks, appearing at the same temperatures than for the preceding sample, but the first peak is very weak when the three following are very intense. The ratio H/M is 0.6. As expected, the hydrogen content increases with the gadolinium concentration since the rare earths can absorb a great deal of hydrogen. The measured values remain high since, except for the iron-rich alloys, one introduces as many hydrogen atoms as gadolinium by this reactive evaporation method.

The sites available for hydrogen storage in glass models are generally considered as basically (distorted) tetrahedral sites. Thus, in the $\text{Gd}_{1-x}\text{Fe}_x$ amorphous alloys, the interstitial sites can be divided into five tetrahedral groups, labeled by the types of atoms at its vertices (Gd_4 , Gd_3Fe , Gd_2Fe_2 , GdFe_3 , Fe_4 , or generally $\text{Gd}_{4-p}\text{Fe}_p$). The amount of hydro-

FIG. 4. Effusion rate R of the $\text{Gd}_{0.50}\text{Fe}_{0.50}$ amorphous alloy.

gen per metal atom which can be stored in each type of tetrahedral sites is proportional to the number of these tetrahedral sites in a chemically random glass, i.e., proportional, for a $\text{Gd}_{1-x}\text{Fe}_x$ alloy, to the different terms in the expansion of $[(1-x)+x]^4$. The energy level of a hydrogen atom at a particular site is determined by the nature of the four neighboring metal atoms. Because of the large exothermic heats of formation of rare earth hydrides relative to those of the transition metal hydrides, the site energy increases with the number p of iron neighbors. As the hydride formation enthalpy of iron is positive, the sites Fe_4 do not contain hydrogen atoms. Therefore, the four peaks observed in the experiments correspond to the GdFe_3 , Gd_2Fe_2 , Gd_3Fe , and Gd_4 sites.

The hydrogen evolution in a hydrogenated sample, as a thermally activated process, can be considered to be controlled by the jumping process from one interstitial site to another. Assuming a constant saddle point energy, the activation energy for jump is directly related to the energy of the equilibrium position of the interstitial sites. Thus, when the sample is heated with a uniform warming rate, hydrogen atoms at high energy sites with a small activation energy preferentially evolve at low temperatures and hydrogen atoms at lower energy sites having a higher activation energy evolve at higher temperatures. In order to determine the energy associated with each site, the kinetics of the release of the dissolved hydrogen was analyzed. The classic calculation of the jump frequency from a site follows the same line as the calculation of a rate in chemical kinetics,⁴ the saddle point corresponding to the "activated state" of the Eyring theory of absolute reaction rates.⁵ This theory assumes that the hydrogen atom must overcome a Gibbs free energy barrier ΔG in order to be evolved and the frequency at which the barrier is confronted is approximated by the factor kT/h , where k and h are the Boltzmann and Planck constants respectively, and T is the absolute temperature. Therefore, the effusion rate R_p from each site follows:

$$R_p = \frac{d(c/c_p)}{dt} = \left(\frac{kT}{h}\right) \left(1 - \frac{c}{c_p}\right)^n \exp\left(\frac{\Delta S}{k}\right) \exp\left(-\frac{\Delta H}{kT}\right),$$

with c_p and c the original and evolved hydrogen concentrations and n the order of the reaction. The free energy ΔG is

FIG. 3. Effusion rate R of the $\text{Gd}_{0.33}\text{Fe}_{0.67}$ amorphous alloy.

equal to $\Delta H - T\Delta S$, where ΔH is the enthalpy and ΔS is the entropy of reaction. The total effusion rate is the summation of the effusion rates of each site. The best fit of the different experimental effusion spectra has been obtained with a second-order kinetics for the four peaks, as it can be expected since desorbed molecular hydrogen is formed with two hydrogen atoms. The dotted lines in Figs. 2–4 show the simulated individual peaks and the total effusion rate. The ΔG values are nearly equal for a given peak, whatever the composition of the alloy. Then, these simulations allow us to deduce the ΔG values of the different hydrogen sites, which are $\Delta G = 1.4, 1.6, 1.9$, and 2.5 ± 0.1 eV for the GdFe_3 , Gd_2Fe_2 , Gd_3Fe , and Gd_4 configurations, respectively. The relative contributions of the $\text{Gd}_{4-p}\text{Fe}_p$ sites, which can be theoretically written

$$\frac{C_4^p x p (1-x)^p}{\sum_{p=0}^3 C_4^p x p (1-x)^p}$$

are displayed in Table I, with the experimental values. A very good agreement is observed between the theoretical and experimental values, which confirms the existence of the tetrahedral sites.

In conclusion, coevaporation of gadolinium and iron under a pressure of molecular hydrogen allows us to obtain thin films of hydrogenated amorphous $\text{Gd}_{1-x}\text{Fe}_x$ alloys in the composition range $0.25 \leq x \leq 0.90$. Effusion experiments indicate hydrogen release at 200°C in $\text{Gd}_{0.10}\text{Fe}_{0.90}$ alloys. With increasing gadolinium concentration, three other peaks ap-

TABLE I. Values of the experimental and theoretical contributions of the $\text{Gd}_{4-p}\text{Fe}_p$ sites for different $\text{Gd}_{1-x}\text{Fe}_x$ alloys.

x	GdFe_3 site		Gd_2Fe_2 site		Gd_3Fe site		Gd_4 site	
	exp.	th.	exp.	th.	exp.	th.	exp.	th.
0.90	1	0.85	...	0.13	...	0.01	...	0
0.75	0.63	0.62	0.37	0.31	...	0.07	...	0.01
0.66	0.46	0.50	0.37	0.37	0.17	0.12	...	0.01
0.50	0.27	0.27	0.36	0.40	0.30	0.27	0.07	0.06
0.25	0.04	0.05	0.25	0.21	0.44	0.42	0.29	0.32

pear at higher temperatures with an increasing weight. The four peaks correspond to different hydrogen tetrahedral sites of $\text{Gd}_{4-p}\text{Fe}_p$ type with $0 \leq p \leq 3$. Moreover, the ΔG values of these sites can be obtained by computer modeling each peak of the effusion curves by the Eyring formula.

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