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Hydrogen diffusion in multi-phase LaNiFe alloys

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Abstract

The dependence of the hydrogen diffusion on the composition and microstructure of multi-phase LaNiFe alloys was investigated by magnetic after-effect and thermal desorption spectrometry measurements. Heterogeneous alloys of the composition $La_x(Ni_{0.7}Fe_{0.3})_{1-x}$ in the range of $x=0.08...\ 0.11$ were produced by eutectic solidification. The volume fractions of the phases were varied by changing the initial composition between hypoeutectic and eutectic. In addition, the characteristic eutectic microstructure, as grain size and lamellar spacing was varied by different cooling rates. By applying the melt-spin technique a nanocrystalline grain structure with lamellar spacings of about 10 nm was achieved. The amount of hydrogen absorbed in the initial charging depends strongly on the grain size of the eutectic microstructure. The activation enthalpy of short-range diffusion depends on microstructure and hydrogen concentration.

Keywords: Hydrogen diffusion; Heterogeneous alloys; Eutectic microstructure; La–Ni–Fe

1. Introduction

Multi-phase alloys open a vast new field for materials applied in hydrogen storage systems and hydride batteries. By choosing the appropriate composition and microstructure of these heterogeneous alloys new effective materials can be tailored with excellent absorption and desorption kinetics and desirable working temperatures [1–3]. However, owing to the many parameters involved, this extremely complicated task has to be approached by systematic experimental studies and theoretical calculations of heterogeneous model systems [4]. In the present experiments we systematically investigated the dependence of the hydrogen diffusion on the composition and microstructure of multi-phase LaNiFe alloys.

2. Experimental

2.1. Specimen preparation and characterization

The LaNiFe multi-phase alloys were prepared by induction melting in argon atmosphere using high purity metals (La 99.9 at.%, Ni 99.97 at.%, Fe 99.99 at.%). To obtain samples with different volume fractions of the two phases we prepared eutectic $La_{0.08}(Ni_{0.7}Fe_{0.3})_{0.92}$ and hypoeutectic $La_{0.11}(Ni_{0.7}Fe_{0.3})_{0.89}$ samples. All specimens show a lamellar eutectic microstructure consisting of two phases (Fig. 1), which were determined to $La(Ni_{0.7}Fe_{0.3})_5$ and $Ni_{0.7}Fe_{0.3}$ by EDX measurements. X-ray diffraction measurements showed the characteristic peaks of a hexagonal AB_5 phase and a fcc NiFe phase. The grain size was determined by the peak width of the X-ray diffraction peaks, SEM and TEM investigations (Fig. 1). By applying heat treatments with different cooling rates and melt-spinning technique all samples (eutectic and hypoeutectic) could be obtained with grain structures of lamellar spacings of 1000 nm, 100 nm and about 10 nm. The as-produced, i.e., inactivated, samples were charged with

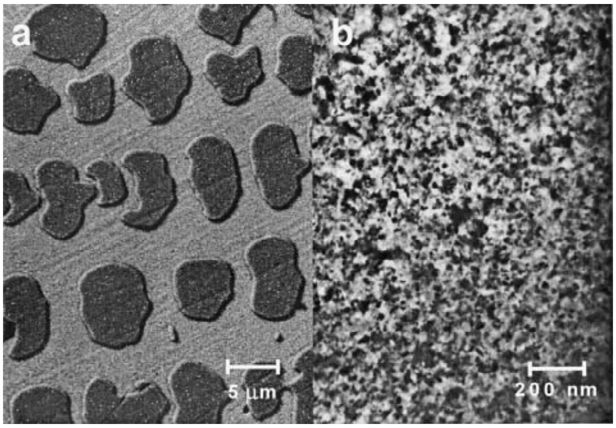

Fig. 1. (a) SEM micrograph of a heterogeneous multi-phase alloy after slowly cooling from the melt with eutectic composition. The bright area corresponds to the $La(Ni_{0.7}Fe_{0.3})_5$ phase and the dark to the $Ni_{0.7}Fe_{0.3}$ phase. (b)TEM bright-field image of a heterogeneous multi-phase alloy produced by melt spinning.

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hydrogen and deuterium by heating them up to 573 K, cooling them down to 290 K and keeping them for a day in a H_2 or D_2 atmosphere of 0.13 MPa. After this initial charging the alloy contained several atomic percent of hydrogen.

Additionally $La(Ni_{0.7}Fe_{0.3})_5$ single-phase compounds were produced and charged in a H_2 atmosphere of 10 MPa at 290 K.

2.2. Magnetic after-effect and thermal desorption spectroscopy

The microscopic mechanism of the magnetic after-effect is based on the dependence of the magnetic interaction energy between the directions of spontaneous magnetization within a domain wall and the symmetry axis of anisotropic H interstitial configurations [5]. Owing to thermally activated jumps, the reorientation of H atoms lowers this interaction energy, leading to a decrease in the initial susceptibility $\chi(t)$, or increase in the reluctivity $r(t)=1/\chi(t)$, after demagnetization. The experimental results are represented as isochronal relaxation curves of the reluctivity amplitude between the times t_1 and t_2 defined as

$$\frac{\Delta r(t_1, t_2, T)}{r(t_1, T)} = \frac{r(t_2, T) - r(t_1, T)}{r(t_1, T)} \tag{1}$$

In the measurements presented, $t_1=0.5$ s and t_2 varies from 1.5 s to 179.5 s. The H reorientations were characterized by spectra of relaxation times, where each relaxation time was assumed to obey an Arrhenius law.

The hydrogen concentration of the samples was measured by thermal desorption of H and D in high vacuum using a differential method. The specimens were heated at a constant heating rate. The H and D partial pressure was continuously measured with a mass spectrometer, while a turbo-molecular pump, which had a constant pumping rate over a very large pressure range, was continuously evacuating the vessel.

3. Experimental results

The $La(Ni_{0.7}Fe_{0.3})_5$ phase is ferromagnetic below a Curie temperature of about 250 K and thus allows to investigate the short-range hydrogen diffusion by the highly sensitive technique of magnetic after-effect measurements in both phases of the multi-phase alloys.

After H charging, multi-phase LaNiFe alloys show a maximum at 120 K. Fig. 2 shows a relaxation spectrum of H charged eutectic $La(Ni_{0.7}Fe_{0.3})_5$–$Ni_{0.7}Fe_{0.3}$ with a lamellar spacing of about 10 nm. The H concentration is 12.2 at.%. A numerical evaluation using a spectrum of activation enthalpies yielded for this concentration a mean activation enthalpy of $Q=0.28\pm0.01$ eV and a pre-exponential factor $\tau_0=4\cdot10^{-11\pm0.5}$ s. Deuterium charged samples showed an isotopic effect, as their activation enthalpy was generally about 0.05 eV higher. In order to measure the activation enthalpy for different H/D concentrations on the same sample a stepwise desorption was performed. In the first step the sample was heated to a final temperature of 330 K with a rate of 100 K/h and in the consecutive steps the final temperatures were increased by 10 K each time. After about 10 such steps the sample was completely degassed. During each annealing step the amount of desorbed hydrogen and after each step the magnetic after-effect was measured. The relaxation maximum shifted with decreasing H/D concentration to higher temperatures, e.g., from 120 K (12.2 at.%) to 180 K (0.8 at.%) in the case of H in an eutectic sample with a lamellar spacing of about 10 nm. Combined with the shift of the maximum temperature was an increase of the activation enthalpy with lower H concentration. Fig. 3 shows the concentration dependence of the activation enthalpies for samples with different microstructures. Note that the H content in Fig. 3 refers to the fraction of metal atoms in the $La(Ni_{0.7}Fe_{0.3})_5$ phase only. The pre-exponential factor is always of the order of 10^{-11} s to 10^{-13} s and decreases slightly with decreasing hydrogen content. As one can see in Fig. 3 there is a pronounced difference between samples of grain size of about 10 nm and those of a grain size of 100 nm or 1000 nm. During initial charging, nanocrystalline heterogeneous alloys absorbed more than 2 times the amount of hydrogen of those with a lamellar spacing of 100 nm and about 6 times the amount of microcrystalline alloys. Compared to the influence of the microstructure the

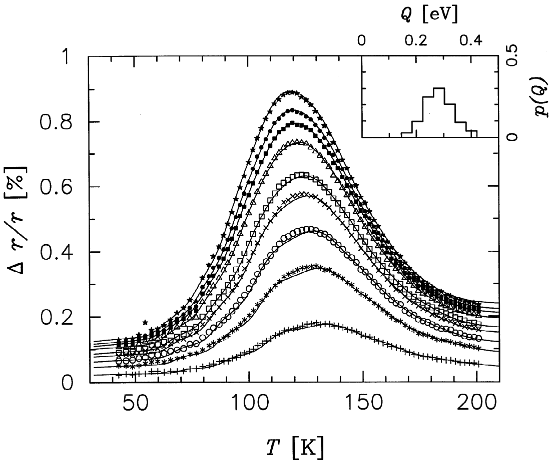

Fig. 2. H-induced MAE spectrum of eutectic $La(Ni_{0.7}Fe_{0.3})_5$–$Ni_{0.7}Fe_{0.3}$ with a lamellar spacing of about 10 nm and a hydrogen concentration in the AB_5 phase of 12.2 at.%. Experimental data are represented by symbols ($t_1=0.5$ s, $t_2=1.5$, 4.5, 9.5, 19.5, 29.5, 89.5, 119.5, 179.5 s) and the solid lines correspond to the numerical fit. The insert shows the distribution of activation enthalpies.

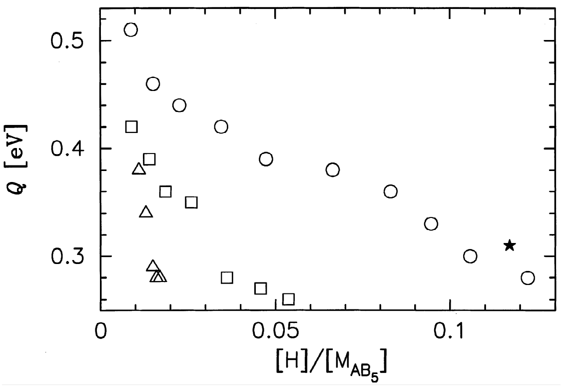

Fig. 3. Activation enthalpies of eutectic $La(Ni_{0.7}Fe_{0.3})_5$–$Ni_{0.7}Fe_{0.3}$ with different lamellar spacing d in dependence of the hydrogen concentration. ○ $d=10$ nm, □ $d=100$ nm, △ $d=1000$ nm, ★ single-phase $La(Ni_{0.7}Fe_{0.3})_5$.

influence of the composition is almost negligible between eutectic and hypoeutectic.

Additional MAE measurements on H-charged single-phase $La(Ni_{0.7}Fe_{0.3})_5$ show a relaxation maximum at 120 K (32.4 at.%) and 140 K (11.4 at.%).

4. Discussion

MAE measurements of H-charged multi-phase eutectic $La(Ni_{0.7}Fe_{0.3})_5$–$Ni_{0.7}Fe_{0.3}$ show a relaxation maximum similar to single-phase $La(Ni_{0.7}Fe_{0.3})_5$, which indicates that H is absorbed in the AB_5 storage phase. The solubility of the $Ni_{0.7}Fe_{0.3}$ phase is below 0.1 at.% [6].

For the heterogeneous alloys the main difference between nano- and microcrystalline samples is the amount of H uptake during the initial charging at identical H pressure and temperature. The much higher H content of the nanoscaled material indicates that the pressure–composition isotherm of nanocrystalline $La(Ni_{0.7}Fe_{0.3})_5$–$Ni_{0.7}Fe_{0.3}$ lies below the isotherm of microcrystalline $La(Ni_{0.7}Fe_{0.3})_5$–$Ni_{0.7}Fe_{0.3}$. Owing to the lattice expansion with increasing H uptake, the internal stresses will rise in the AB_5 grains and finally these stresses will limit the H solubility. According to the higher solubility in the nanocrystalline alloys, a better stress relaxation may occur in the nanostructured material. This relaxation may be due to the presence of the more ductile nanocrystalline NiFe phase surrounding the nanometer-sized AB_5 grains. A similar result was found by Seta and Uchida [7] who investigated the H solubility in dependence of the sample size in single-phase $LaNi_5$.

In the microcrystalline samples the activation enthalpy of H diffusion changes rapidly with the H content, whereas in the nanocrystalline samples values below $Q=0.3$ eV are only reached at 6 times higher H concentrations (Fig. 3). Since the MAE is sensitive to single jumps of H atoms, i.e., to short-range diffusion, the activation enthalpy for these jumps depends on the local environment and in the case here on the H concentration in this region. Therefore the similar activation enthalpies may be attributed to similar H concentrations in the regions where the H diffuses. Accordingly, in microcrystalline samples the rapid change of the activation enthalpy with H content, can only be explained by an inhomogeneous distribution of the H concentration. This indicates that in microcrystalline multi-phase alloys the micrometer-sized AB_5 grains can only be charged in the outer regions under a H pressure of 0.13 MPa at 573 K, due to the rising internal stresses. In contrast, the nanocrystalline multi-phase alloys can be charged homogeneously under these conditions, indicating lower stresses or a better stress relaxation in the nanostructured material.

An additional evidence for the homogeneous H distribution in the AB_5 grains of the nanocrystalline alloys is given by the activation enthalpy of H diffusion which is similar to the one of single-phase $La(Ni_{0.7}Fe_{0.3})_5$ with a comparable H content of 11.4 at.%. This single-phase AB_5 alloy was charged at 10 MPa and therefore is expected to have a uniform concentration profile. In turn the activation enthalpies in single-phase $La(Ni_{0.7}Fe_{0.3})_5$ for different H concentrations agree well with literature data on $LaNi_5$, considering that the diffusion coefficient increases with increasing hydrogen content. The present MAE measurements yield $Q=0.29\pm0.01$ eV in $La(Ni_{0.7}Fe_{0.3})_5H_2$ and $Q=0.32\pm0.01$ eV in $La(Ni_{0.7}Fe_{0.3})_5H_{0.7}$, which agree well with results of quasi-elastic neutron scattering $Q=0.275$ eV in single-phase $LaNi_5H_6$ [8] and electro-chemical measurements $Q=0.367$ eV and 0.395 eV in $LaNi_5H_{0.07}$ [9].

In conclusion, multi-phase alloys offer not only disintegration resistance [1], but by changing the microstructure to nano-scale material it may be possible to vary their ad- and desorption kinetics as well as their working temperature.

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