Isotope-periodic multilayer method for short self-diffusion paths – a comparative neutron and synchrotron Mössbauer reflectometric study of FePd alloys

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Abstract. FePt, FePd, CoPt, and CoPd in equilibrium exhibit the $L1_0$ structure with high perpendicular magnetic anisotropy making them attractive candidates for high-density magnetic recording. Magnetic properties of these films depend on the distribution and orientation of the $L1_0$ fraction controlled by diffusion on atomic scale. Epitaxial isotope-periodic ^{nat}FePd/^{57}FePd alloy films were prepared by molecular beam epitaxy and heat treated at 500°C for various retention times. Isotope-sensitive non-destructive methods, neutron reflectometry and synchrotron Mössbauer reflectometry were applied to follow very short diffusion paths normal to the film plane. Squared diffusion lengths and diffusion profiles were obtained from the fitting of experimental reflectivity curves for each annealing treatment steps. The somewhat different diffusion lengths obtained for the neutron and synchrotronMössbauer reflectograms of the same samples are explained by the larger footprint of the sample in the neutron experiment for which interface inhomogeneities are to be averaged. Diffusion in the microscopically different local environments were modelled by piecewise constant diffusion coefficients in the regions identified as different species by conversion electron Mössbauer spectroscopy.

1. Introduction

Due to their high perpendicular magnetic anisotropy [1,2,3], CoPt, CoPd, FePt as well as FePd are candidate materials for future ultra-high density magnetic recording [4,5,6]. In the composition range between $0.5 < x < 0.6$, in equilibrium $Fe_{1-x}Pd_x$ exhibits $L1_0$ (CuAu(I)-type) order with alternating Fe and Pd planes along the crystallographic [001] direction. In this ordered structure the face centred cubic (fcc) unit cell with random Fe and Pd occupation is distorted to tetragonal, the lattice parameter

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ratio (c/a) varying between 0.96 and 0.97 [7]. The changes of magnetic and structural properties in this alloy are associated with the atomic-scale diffusion processes governing the local structure.

There are several methods to study chemical diffusion processes but the spatial resolution of most of them is far above the atomic scale. By sectioning and profiling techniques [8,9,10] it is possible to measure very low diffusion paths but they are not suitable to follow self-diffusion processes in chemically homogeneous materials since the solely electronic interaction with the x-ray photons produces no contrast between the adjacent chemically identical layers.

In order to study self diffusion, an isotope-sensitive technique is needed. Due to the difference in the nuclear cross section of different isotopes of the same element, neutron reflectometry (NR) is a suitable non-destructive method to study self diffusion in a chemically homogeneous isotope multilayer with a diffusion length in the range of a few angstroms [11,12,13]. Another isotope-sensitive non-destructive method is Synchrotron Mössbauer Reflectometry (SMR) [14,15,16] due to the nuclear hyperfine (hf) interaction between the atomic nuclei and the highly monochromatized synchrotron radiation.

In this paper we present a comparative study of Fe self diffusion in FePd by NR and SMR using an isotope-periodic ^{nat}FePd/^{57}FePd multilayer film.

2. Experimental procedure

Partially ordered (52% L1$_0$) isotope-periodic [^{nat}Fe$_{47}$Pd$_{53}$(3 nm)/^{57}Fe$_{47}$Pd$_{53}$(2 nm)]$_{10}$ multilayers were evaporated onto MgO(001) substrates by molecular beam epitaxy (MBE). To improve epitaxial growing, Cr seed and Pd buffer layers (of 3 and 15 nm, resp.) were applied. To prevent oxidation, a 1 nm Pd capping layer was grown on top of the periodic multilayer. During evaporation the substrate temperature was held at 350°C.

For NR experiments, the originally 20×20×2 mm^3 size sample was cut to four equal (10×10×2 mm^3) pieces. One of them was left in the as-deposited state, the others were annealed at 500°C for 90, 360, and 1800 minutes. The heat treatments were carried out under UHV condition. The NR experiments were performed using a 2D ^{3}He detector and the non-polarized monochromatic beam (λ=5 Å) at the NREX$^+$ reflectometer (operated by MPI-MF Stuttgart at FRM II, Garching) [17]. A supermirror filter was used to suppress higher harmonics.

The SMR experiments were performed at the ID18 beam line [18] of the European Synchrotron Radiation Facility (ESRF, Grenoble) in 16-bunch mode. The samples previously measured by NR were then cut into half (5×10×2 mm^3). The beam was sequentially monochromatized by a Si(111), then a Si(4.2.2)/Si(12.2.2) double channel cut monochromator, respectively, to the vicinity of the 14.4 keV Mössbauer transition (λ=0.86025 Å) of ^{57}Fe. The lateral beam size was restricted to 0.2 mm. Nuclear resonant (delayed) time-integrated and electronic (prompt) reflectograms were simultaneously recorded by avalanche photo diode (APD) detectors.

Conversion electron Mössbauer spectroscopy (CEMS) was performed using a ^{57}Co(Rh) source and a home-made gas-flow single-wire proportional counter operating with ^{4}He and additional 4.7% CH$_4$ extinction gas at a bias voltage of 830(±10) V.

3. Results and discussion

In former studies [16,19,20] SMR spectra were evaluated by normalizing the Bragg-peak height to the totalreflection peak height, but, as Andreeva showed, the peak height ratio is very sensitive to the value (and distribution) of the hf fields [21]. Furthermore, the actual peak heights may be modified by overlapping with the Kiessig beats, a condition that can hardly be avoided if, like in the present case, variable non-periodic (buffer and capping layer) contributions are present in the reflectivity. For the above reasons the hf fields (actually, the hf field distributions) were independently determined from CEMS spectra and fed into the robust full reflectivity curve fit [22] to extract the extent of the diffusion layer mixing. For the proper evaluation of the layer parameters, simultaneous fits were performed to the prompt (non-resonant) and delayed (nuclear resonant) reflectivity curves. Of course, in case of NR measurement, the latter is not possible. Substrate and interface roughness is always

present in a multilayer. Individual rms roughnesses were taken into account except for the multilayer stack, where a common roughness for all periods was fitted. With the above-described procedures and constraints both the NR and the SMR data were fitted by the FitSuite program [22]. The program accounts for the diffusive interface roughness in the form of a 1D diffusion profile characterized by $D{\cdot}t$ (squared diffusion length, D and t being the diffusion coefficient and the time of diffusion, respectively) and adjusts this profile through $D{\cdot}t$ to fit the measured reflectivity curves. Since the roughness and diffusion both have error-function profiles, the contributions are separated simply by assuming the non-diffusive interface roughness to be fully present in the as prepared sample and to remain constant during heat treatments.

Figure 1 shows the experimental and fitted SMR (a) and NR (b) curves of the Pd(3nm)/[^{nat}Fe$_{47}$Pd$_{53}$(3 nm)/^{57}Fe$_{47}$Pd$_{53}$(2 nm)]$_{10}$/Pd(15nm)/Cr(3nm)/MgO(001) alloy multilayer along with the corresponding isotope bilayer diffusion profiles adjusted in the fit.
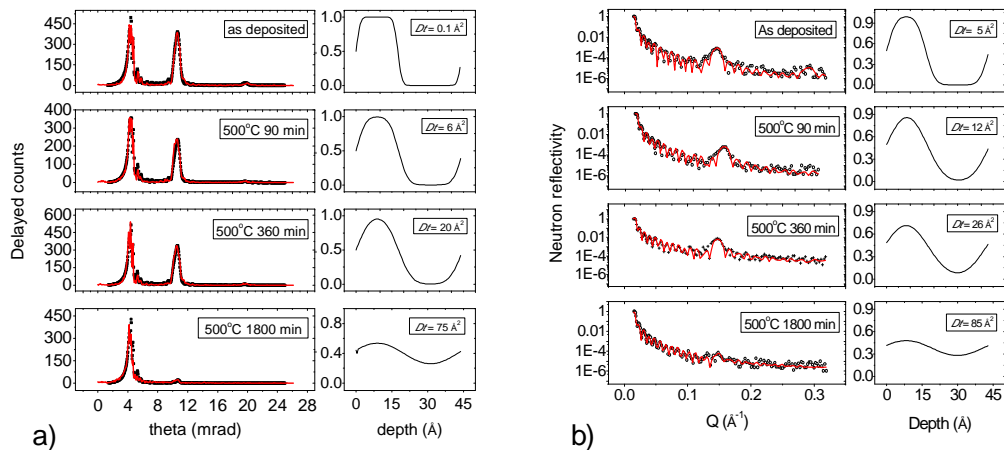

Figure 1 SMR (a) and NR (b) curves taken on the isotope-periodic FePd multilayer annealed at 500°C for 0, 90, 360 and 1800 minutes, resp. In the right columns the corresponding bi-layer diffusion profiles are shown.

It is clearly seen that, with increasing retention time, the diffusion profile flattens indicating the intermixing of the adjacent isotope layers. However, the extracted $D{\cdot}t$ values do not completely agree in the SMR and NR experiments (see Fig. 2a). The difference is already noticeable in the as deposited state. The diffusion profile in the SMR spectrum is more square-like than it is in the NR spectrum. The $D{\cdot}t$ values in the as deposited state extracted from SMR and NR are 0.1 and 5 Å^2, respectively.
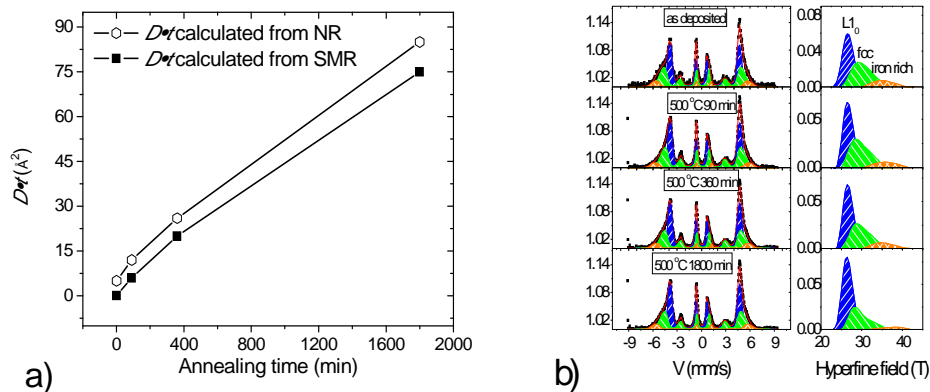
Figure 2 Variation of the squared diffusion length measured by NR and SMR. (panel *a)*, full lines for guiding the eye). Measured and fitted conversion electron Mössbauer spectra (taken after the annealing steps) along with the corresponding hyperfine field distributions (panel b).

This kind of deviation can be observed in all samples. The squared diffusion lengths increased from 0.1 and 5, 6 and 12, 20 and 26, 75 and 85 Å^2 in the 90, 360 and 1800 min heat treated samples obtained from SMR and NR spectra, respectively (Figure 2a). Since the measured samples were the same in the NR and SMR experiments, the difference cannot originate from different structural properties. Ageing of the samples between SMR and NR beam sessions can also be excluded since we re-measured several samples by CEMS at later dates and found no difference in the spectra. Moreover, in a later SMR session several re-measured samples gave unchanged fitted $D{\cdot}t$ values. However, such deviation may well originate from the difference of the footprint of the beams in the two experiments. In the case of NR, the reflected beam comes from a much wider area and therefore averaging the lateral thickness and interface roughness variation in the sample are reflected in the spectrum as an initial diffusive roughness causing an overall decrease of the Bragg peak intensity and a corresponding artificially higher $D{\cdot}t$. This effect is much smaller and will be neglected in case of SMR because the x-ray beam was 0.2 mm as compared to the 10 mm width of the neutron beam. (Further lateral restriction of the neutron beam was not possible for reasons of intensity and beam time constraints.) One can also see that the difference of the squared diffusion length reaches 10 Å^2 for the longest annealing time (1800 min) as compared to ~6 Å^2 for shorter annealing times. A possible explanation of this fact may be that, when the adjacent layers are almost completely inter-diffused, the error of the fitting can be as high as a few Å^2. Another possible explanation may be that new sources of roughness emerge at very long annealing times. It is also observable that the tendency of $D{\cdot}t$ as a function of annealing time is not linear as it should be for a structurally homogeneous material [23]. This deviation from the linear tendency indicates that the diffusion coefficient varies during the heat treatments. Therefore, one may suspect that the structure of the layers in the sample, changes. Indeed, from CEMS experiments three distinct environments, namely a low-hf field, a large-hf-field, and an intermediate-hf-field species were identified with wide distribution and average hf fields of ~27, ~35 and ~30 T and assigned to ordered $L1_0$, disordered fcc and a (here non-specified) iron-rich structural unit, respectively. These are visualized by the hf field distributions in Figure 2b. For details of the assignment see ref. [24]. The CEMS spectral fraction of the ordered $L1_0$ phase raises from 52% to 66% while the fraction of the disordered fcc unit decreases from 24% to 22% and the fraction of the iron-rich unit decreases from 24% to 12% with increasing annealing time from 0 to 1800 min. The significant increase of the $L1_0$ fraction and decrease of iron-rich regions indicate that the deviation from linear tendency in the $D{\cdot}t$ originates from the different diffusion properties of these environments, namely, the iron self diffusion in the crystallographic *c*-direction is considerably slower in the $L1_0$ phase than that in the iron-rich phase. With the plausible assumption that the diffusion constant takes an arbitrary positive value in volumes of distinct environments like in a random alloy;

the total $D{\cdot}t$ of the system can be described as a weighed sums of the individual squared diffusion lengths [25]. Since these annealing experiments were performed so far only at one temperature, the determination of the activation energies and pre-exponential factors of the distinct species is not yet possible. Further experiments on FePd films of different initial structures annealed at various temperatures are in progress.

4. Summary
In order to follow short-range diffusion processes in an isotope-periodic multilayer, a comparative neutron and synchrotron Mössbauer reflectometric study was performed on isotope-periodic, partially ordered FePd samples. Three distinct local structural units were identified and quantified by conversion-electron Mössbauer spectroscopy. The diffusion profiles and hence the squared diffusion lengths ($D{\cdot}t$) extracted from full-curve fits of neutron reflectivities show a positive and somewhat increasing difference of about 6 to 10 Å^2 for diffusion lengths 0 to 70 Å^2 for SMR. This deviation is attributed to the difference in the footprints of the beams and the correspondingly different lateral averages of the layer thickness and/or interface roughness variations in the NR and SMR experiments, resulting in an artificial extra flattening of the diffusion profile in the NR curve. The observed slight deviation from linear dependence in the $D{\cdot}t$ *vs t* curve is attributed to the variation of the fractions of the different structural units with different diffusion coefficients.

Acknowledgements

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