Fe and N diffusion in nitrogen-rich FeN measured using neutron reflectometry

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Abstract. Grazing incidence neutron reflectometry provides an opportunity to measure the depth profile of a thin film sample with a resolution <1 nm, in a non-destructive way. In this way the diffusion across the interfaces can also be measured. In addition, neutrons have contrast among the isotopes, making it feasible to measure the self-diffusion. In the present work, the isotope multilayers of $[\text{FeN}/^{57}\text{FeN}]_{10}$ and $[\text{FeN}/\text{Fe}^{15}\text{N}]_{10}$ were prepared using magnetron sputtering and self-diffusion of Fe and N was investigated. It was found that N diffusion is slower compared to Fe and does not follow the atomic size dependence.

Keywords. FeN; iron nitride; reactive sputtering; self-diffusion; neutron reflectometry.

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1. Introduction

The structural stability of a system as well as its physical and chemical properties depend upon the atomic diffusion. Therefore understanding the diffusion behaviour is vital from both the application as well as the basic points of view. In the case of FeN, it is known that the nitrides of iron show a variety of structures and magnetic properties with a variation in the nitrogen content. Technologically, they are very important due to their application in several disciplines. The nitrogen-poor FeN phases are magnetic and are important magnetic functional materials [1]. The FeN phases with nitrogen content in the range of 18–33 at% (e.g. γ'-Fe4N) are used as hard coatings due to their excellent tribological and corrosion resistance properties [2,3]. Recently, some FeN phases containing more than 33% of nitrogen have been produced using sputtering [4] and pulsed laser deposition techniques [5]. A proper understanding of the stability and nitride formation requires in-depth knowledge of both Fe and N self-diffusion. Available experimental techniques for measuring self-diffusion e.g. secondary ion mass spectroscopy (SIMS), nuclear

reaction analysis (NRA), radioactive tracer etc. have depth resolution of several nm, which is sufficient to measure long-range diffusion. However, these techniques are not appropriate to measure the diffusion in nanoscale structure since measurements require diffusion lengths in the sub-nm regime. It is known that neutrons have different scattering cross-sections for the isotopes e.g. neutron scattering length for natural Fe and ^{57}Fe are 9.45 and 2.3 fm, and for natural N and ^{15}N 9.36 and 6.6 fm, respectively. Due to the distinct contrast between Fe and ^{57}Fe and N and ^{15}N, both Fe and N self-diffusion can be probed with a proper isotopic labelling. Grazing incidence neutron reflectivity offers a depth resolution in the sub-nm range [6] and could be used to probe self-diffusion of both Fe and N. In the present work, we measured Fe and N self-diffusion in FeN using neutron reflectivity technique.

2. Experimental

The multilayer structures of the type [FeN/^{57}FeN]$_{10}$ and [FeN/Fe^{15}N]$_{10}$ were prepared using N$_2$ as sputtering gas by DC magnetron sputtering operating at 50 W. A base pressure of 2×10^{-7} mbar was achieved prior to the deposition. The [FeN/^{57}FeN]$_{10}$ multilayer was deposited by alternatively sputtering natural Fe and ^{57}Fe enriched targets and the [FeN/Fe^{15}N]$_{10}$ multilayer was prepared using the same Fe target but using the natural and ^{15}N gas. The samples were characterized using X-ray diffraction (XRD) for the structure while thermal stability was examined using differential scanning calorimetry. Self-diffusion measurements were performed using neutron reflectometry in the time-of-fight mode at D17, ILL, Grenoble and AMOR at SINQ/PSI [7]. The samples were placed inside a specially designed vacuum furnace mounted on the sample stage of the reflectometer and the measurements were performed in the as-deposited state and at high temperatures.

3. Results and discussion

Figure 1 shows XRD pattern of the of [FeN/^{57}FeN]$_{10}$ samples in the as-prepared state and after annealing at different temperatures. The XRD pattern confirms γ-FeN-type structure [8]. As could be seen, the structure of the sample remains unchanged after annealing the samples at different temperatures. However, further annealing of a sample at higher temperatures resulted in nitrogen-poorer phases of FeN due to nitrogen out diffusion in this system [9].

The neutron reflectometry measurements on the samples with the structure [FeN/^{57}FeN]$_{10}$ and [FeN/Fe^{15}N]$_{10}$ were carried out and are shown in figures 2a and b. As could be seen in both the cases a well-resolved Bragg peak is due to isotope modulations. The patterns were fitted using PARRATT software [10] and the obtained structures for the ^{57}Fe and ^{15}N labelled samples are: Si(sub.)/[FeN (10.2 nm)/^{57}FeN (5.2 nm)]$_{10}$/FeN (11.1 nm) and Si(sub.)/[FeN (10.6 nm)/Fe^{15}N (5.2 nm)]$_{10}$/FeN (15 nm).

The roughnesses at the interfaces were in the range of 1–1.5 nm. The diffusion measurements in both the samples were carried out after annealing the samples at
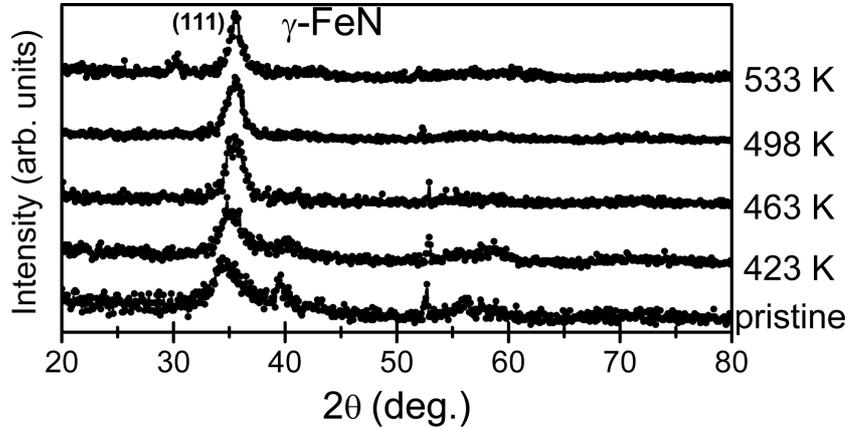
Figure 1. X-ray diffraction pattern of FeN samples in the pristine state and also after annealing at different temperatures.
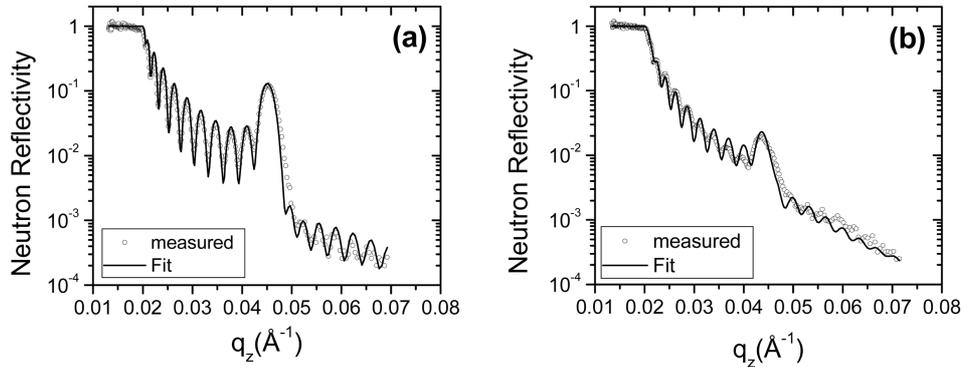

Figure 2. Neutron reflectivity pattern of [FeN/^{57}FeN] sample (**a**) and [FeN/Fe^{15}N] sample (**b**). Note that the contrast between Fe and ^{57}Fe is much larger when compared to N and ^{15}N, and this is the reason for higher intensity at the Bragg peak in the former case.

different temperatures. The annealing of the samples was performed *in situ*, i.e. during the neutron reflectivity measurements in dry nitrogen atmosphere.

It was observed that as the samples were annealed the intensity at the Bragg peak decreases both with temperature and time. A typical decay of the intensity for N diffusion is shown in figure 3a. Figure 3b shows the diffusion behaviour of Fe and N with annealing time.

As could be seen, the nitrogen diffusivity is smaller compared to iron for similar annealing times at a particular temperature. The decay of the Bragg peak intensity can be used to calculate initial diffusivity (D) using the expression [10]

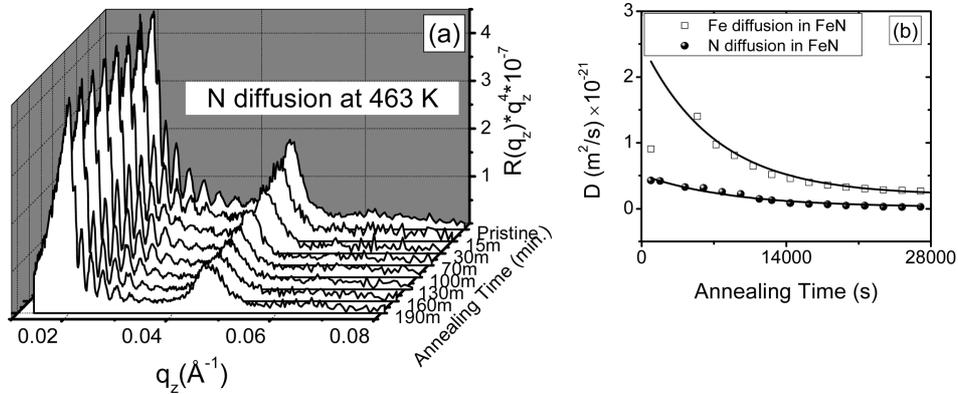$$I(t) = I(0) \exp\left(-\frac{8\pi^2 n^2 D}{\ell^2} t\right), \tag{1}$$

Figure 3. The decay of Bragg peak intensity in the neutron reflectivity pattern for the sample [FeN (10.6 nm)/Fe^{15}N (5.2 nm)]$_{10}$ (**a**) and a comparison of the diffusivity of Fe and N at 463 K with annealing time (**b**).

where $I_n(0)$ is the intensity of the nth order Bragg peak at time $t = 0$ (before annealing) and ℓ is the bilayer periodicity. The above equation is valid when the displacement of an atom during diffusion is given by $\langle x^2 \rangle = 2Dt$. In case structure tends to relax as diffusion takes place, D varies nonlinearly with time. The time-averaged diffusivity is defined by [11,12]

$$\bar{D} = \frac{1}{t} \int_0^t D(t')\mathrm{d}t'. \tag{2}$$

Assuming an exponential law for relaxation the instantaneous diffusion coefficient (for details, see ref. [6]) is

$$D(t) = A \exp(-t/\tau) + D_{\mathrm{SR}}, \tag{3}$$

where D_{SR} is the diffusivity in the relaxed state, A is a constant and τ is the relaxation time. The diffusivities in the structurally relaxed state were obtained by fitting the data of D vs. annealing time with eq. (3).

The observed self-diffusion behaviour of Fe and N is unexpected. Due to the small atomic size of N ($r_{\mathrm{Fe}}/r_{\mathrm{N}} \sim 1.6$), it was expected that N should be diffusing faster than Fe. In a number of studies performed in metal–metal type of alloys e.g. in $\mathrm{Zr}_{46.75}\mathrm{Ti}_{8.25}\mathrm{Cu}_{7.5}\mathrm{Ni}_{10}\mathrm{Be}_{27.5}$ alloy [13,14], Be being the atom with smallest size (atomic radius $r_{\mathrm{Be}} = 0.1128$ nm) has the fastest diffusivity followed by Ni ($r_{\mathrm{Ni}} = 0.1246$ nm) and Zr ($r_{\mathrm{Zr}} = 0.1602$ nm) [15]. Similar behaviour has been observed in other metal–metal alloys. The small diffusivity of N when compared to Fe in the present work could not be explained by the size dependence of self-diffusion in this compound. Further measurements as a function of structural state are required to understand this behaviour.

Acknowledgements

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