

LOCAL MAGNETIC PROPERTIES OF NANOCRYSTALLINE Ni AND Pd-Fe

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Abstract -- Ferromagnetic nanocrystalline materials, consisting of Ni and Pd-Fe, are investigated on an atomic scale by perturbed γ -angular correlation spectroscopy, complemented by X-ray diffraction and energy dispersive X-ray spectroscopy. Nanocrystalline Ni was produced by pulsed electrodeposition and simultaneously doped with ¹¹¹In probe atoms. Besides the local magnetic field known from polycrystalline Ni, a second component is detected, which is attributed to a magnetic perturbation due to grain boundaries. During ball-milling of Pd, a Pd_{0.70}Fe_{0.30} solid solution caused by Fe impurities is obtained, which is ferromagnetic at room temperature. Annealing between 600 K and 1000 K transforms this solid solution into the compound γ_2 -Pd₃Fe.

INTRODUCTION

The magnetic properties of nanocrystalline materials are of interest because of their hard-magnetic (1) and soft-magnetic (2) applications. The investigation of macroscopic magnetisation reveals the dependence of the saturation magnetisation and the coercitive field on the grain size (3, 4). The domain structure is analysed e.g. by magneto-optic Kerr-microscopy (3) or small angle neutron scattering (5). In addition, the application of hyperfine techniques, like Mößbauer spectroscopy, muon spin rotation or perturbed γ -angular correlation spectroscopy (PAC), detects the local magnetic field at the site of probe atoms or muons. In this paper, nanocrystalline Ni prepared by pulsed electrodeposition (PED) and ferromagnetic Pd-Fe alloys obtained by ball-milling of Pd powder are investigated by PAC experiments.

EXPERIMENTAL DETAILS

The PAC investigations were performed using radioactive ¹¹¹In, which emits a γ - γ cascade following its decay to the isotope ¹¹¹Cd. The hyperfine interaction of the ¹¹¹Cd nucleus with a magnetic field or an electric field gradient (efg) becomes observable by recording the second γ -quantum of the cascade with respect to the first one as a function of the elapsed time t. Due to hyperfine interaction, the PAC time spectrum R(t) is modulated by characteristic frequencies ω_n . In case of pure magnetic dipole interaction, two frequencies $\omega_1 = \omega_L$ (Larmor frequency) and $\omega_2 = 2 \omega_L$ are observed. Using the relation $\omega_L = (\mu/I) \cdot B_{loc}$ ($\mu = -0.7656 \mu_N$, $I = 5/2 \hbar$), the local

magnetic field B_{loc} at the site of the probe nucleus is determined. In case of pure electrical quadrupole interaction and $I = 5/2$, the three frequencies ω_1 , ω_2 , and $\omega_3 = \omega_1 + \omega_2$ are measured, which allow the characterisation of the traceless efg by the coupling constant $v_Q = e \cdot Q \cdot V_{zz} / h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy}) / V_{zz}$. Slightly different magnetic fields (or efg) at the site of the probe atoms lead to a frequency distribution centred at $\bar{\omega}_L$ (or $\bar{\nu}_Q$) with a width of $\Delta\omega_L$ ($\Delta\nu_Q$).

A detailed description of PAC can be found elsewhere (6).

Nanocrystalline Ni was prepared by pulsed electrodeposition (7). Short current pulses with a length of $t_{on} = 2$ ms and a current density of 1 A/cm^2 were applied followed by an off-time of 48 ms. The used electrolyte consisted of Ni(II)sulfate (40 g/l), K,Na-tartrate (120 g/l), and ammonium chloride (40 g/l). The doping of Ni with ^{111}In was achieved during the electrodeposition by adding $^{111}\text{InCl}_3$ to the electrolyte. As reference, polycrystalline Ni was doped with ^{111}In by diffusion at 1330 K under vacuum.

Polycrystalline Pd powder was diffused with ^{111}In at 1550 K and was subsequently milled for 40 h in a SPEX 8000 ball-mill. Milling was performed in an Ar atmosphere using non-standard vials. The incorporation of Fe impurities originating from the vials resulted in the formation of an $\text{Pd}_{0.70}\text{Fe}_{0.30}$ alloy. Its composition was determined by energy dispersive X-ray spectroscopy (EDX).

RESULTS AND DISCUSSION

Nanocrystalline Ni

After deposition of nanocrystalline Ni, analysis by X-ray diffraction (XRD) indicates a mean grain size of 40 nm. The modulation in the PAC spectrum (Fig. 1a) is due to the magnetic dipole interaction of ferromagnetic Ni. The PAC spectrum consists of two components. The Larmor frequency $\omega_L^0 = 97.6 \text{ Mrad/s}$ (8) known from polycrystalline Ni (Fig. 1b) without measurable line broadening ($\Delta\omega_L^0 = 0 \text{ Mrad/s}$), and a second, new component, which is shifted to a lower frequency $\omega_L^1 = 95.8 \text{ Mrad/s}$ and is significantly broadened ($\Delta\omega_L^1 = 6 \text{ Mrad/s}$). About $f_0 = 49\%$ of the probe

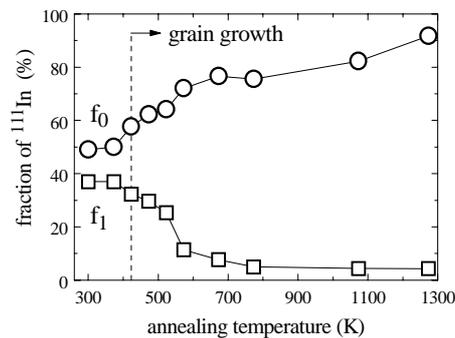


Fig. 2: Fractions of ^{111}In atoms f_0 and f_1 exposed to the two magnetic components.

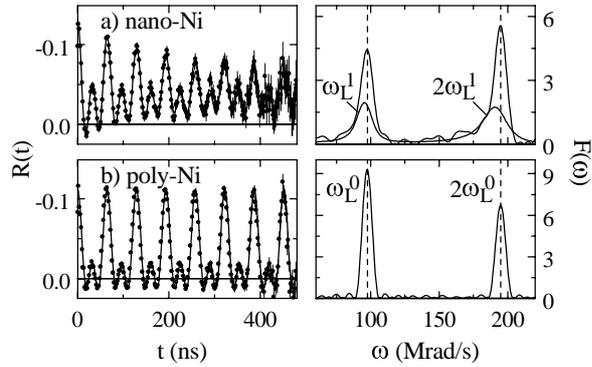


Fig. 1: PAC spectra of nanocrystalline (a) in comparison to polycrystalline Ni (b).

atoms measure ω_L^0 and $f_1 = 37\%$ the shifted frequency ω_L^1 . The observed shifted and broadened frequency component is similar to the results of PAC experiments, at which the ^{111}In atoms were incorporated one or two monolayers beneath a $\langle 111 \rangle$ -surface of Ni (9), or at which the ^{111}In atoms were surrounded by non-magnetic impurities in polycrystalline Ni (10).

The local structure of probe atoms corresponding to f_1 converts to that of f_0 , if the sample is annealed for 1 h at temperatures above 423 K (Fig. 2); the fraction f_1 completely disappears at an annealing temperature of 770 K. The temperature of 423 K is in agreement with the temperature, at which grain growth starts as observed by H. Natter and co-workers (7). The component ω_L^1 , therefore, is obviously characteristic for nanocrystalline Ni and not for impurities, because it is not expected that impurities start to disappear after annealing of the sample at 423 K. It is proposed that the component ω_L^1 belongs to lattice sites in the outer part of a crystallite, which is magnetically perturbed by the grain boundaries. The component ω_L^0 is measured by the probe atoms in the centre of the crystallites. From the fraction $f_1 = 37\%$, the width of the magnetically perturbed region is estimated to 3 - 4 nm, using the measured grain size of 40 nm and assuming a statistical distribution of the ^{111}In atoms over the whole sample.

Pd-Fe alloy

The experiments at nanocrystalline Pd-Fe alloys start with polycrystalline Pd powder doped with ^{111}In . The PAC spectrum recorded at room temperature indicates no efg (Fig. 3a) showing that the ^{111}In atoms are incorporated on defect-free sites of the Pd lattice. After ball-milling for 40 h, spectrum (Fig. 3b) is recorded yielding that a fraction $f_c = 54\%$ of ^{111}In atoms is located still on defect-free lattice sites or is exposed to an efg distribution centred around $\bar{v}_Q = 0$ MHz, which is attributed to lattice defects induced by ball-milling. A second fraction $f_d = 39\%$ of ^{111}In atoms measures a distribution of Larmor frequencies centred at about $\bar{\omega}_L \approx 110$ Mrad/s, which indicates that the sample became ferromagnetic. The analysis of the composition of the sample by EDX shows an Fe-content of 30 at%. The lattice structure, determined by XRD, is an fcc solid solution having a grain size of about 15 nm. Since ferromagnetism is induced in Pd if the Fe-concentration exceeds 0.01 at% (11), the distribution of Larmor frequencies ($\bar{\omega}_L \approx 110$ Mrad/s) is attributed to the disordered $\text{Pd}_{0.70}\text{Fe}_{0.30}$ solid solution.

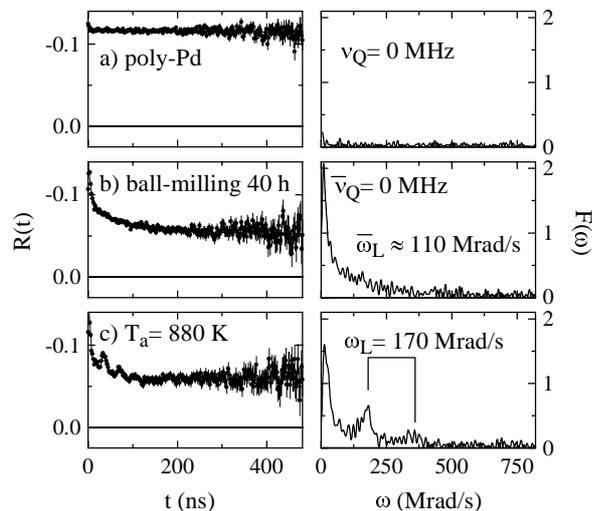


Fig. 3: The PAC spectra of polycrystalline Pd (a) and of the Pd-Fe alloy after ball-milling (b) and annealing (c).

Upon annealing the sample at 880 K, the fraction f_d disappears (Fig. 3c) and is replaced by a local structure characterized by a Larmor frequency of $\omega_L = 170$ Mrad/s ($f_{ord} = 30\%$). XRD analysis at the same time shows the formation of γ_2 -Pd₃Fe having an ordered L1₂-structure. In contrast to a disordered Pd_{0.70}Fe_{0.30} solid solution, the compound γ_2 -Pd₃Fe offers unique sites for the incorporation of ¹¹¹In resulting in the almost unique Larmor frequency ($\omega_L = 170$ Mrad/s). The conversion of f_d into f_{ord} as a function of annealing temperature is shown in Fig. 4. The fraction f_c of probes, which detect no magnetic interaction, remains almost constant indicating that only a part of the Pd-Fe alloy became ferromagnetic due to Fe impurities. The transformation from disordered Pd_{0.70}Fe_{0.30} to ordered γ_2 -Pd₃Fe begins at 600 K and is completed at about 1000 K.

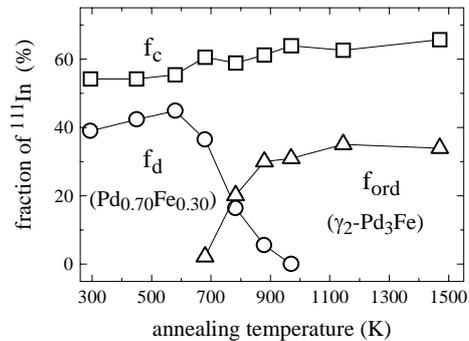


Fig. 4: Fractions of ¹¹¹In atoms in the Pd-Fe alloy.

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