Magnetic properties of grain boundaries of nanocrystalline Ni and of Ni precipitates in nanocrystalline NiCu alloys

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Perturbed $\gamma\gamma$-angular correlation spectroscopy (PAC) was used to investigate nanocrystalline Ni and NiCu alloys, which are prepared by pulsed electrodeposition (PED). Using diffusion for doping nanocrystalline Ni with ^{111}In four different ordered grain boundary structures are observed, which are characterized by unique electric field gradients. The incorporation of ^{111}In on substitutional bulk sites of Ni is caused by moving grain boundaries below 1000 K and by volume diffusion above 1000 K. The nanocrystalline NiCu alloys prepared by PED are microscopically inhomogeneous as observed by PAC. In contrast, this inhomogeneity can not be detected by X-ray diffraction. The influence of the temperature of the electrolyte, the current density during deposition, and the optional addition of saccharin to the electrolyte on the homogeneity of nanocrystalline NiCu alloys was investigated.

1. Introduction

Nanocrystalline materials are of interest for many technological applications. Their properties are mainly determined by the microscopic properties of the grain boundaries [1]. The properties of nanocrystalline alloys additionally depend on the presence of precipitates. However, there are only few experimental techniques being sensitive to the microscopic properties of grain boundaries and small precipitates in nanocrystals. By detecting the hyperfine interaction at the site of suitable probe atoms e.g. by perturbed $\gamma\gamma$-angular correlation spectroscopy (PAC) using the probe ^{111}In, information about the local structure of grain boundaries can be obtained if the probe atoms are placed in the grain boundaries. In polycrystalline materials, however, it is difficult to place an essential fraction of the probe atoms into grain boundaries, but some attempts have been made [2]. The signals of grain boundaries in most cases are too weak to be detected since the fraction of probe atoms in grain boundaries in general is very small (typically 10^{-5}) [3]. After diffusing ^{111}In atoms at low temperatures into nanocrystalline samples, however, the ^{111}In probe atoms might be incorporated predominantly in the grain boundaries and a detectable fraction of probe atoms might be located at unique grain boundaries sites. The homogeneity of nanocrystalline alloys is generally difficult to detect for many experimental techniques. In case of nanocrystalline alloys containing one magnetic component, precipitates of the magnetic component can be easily detected by PAC.

2. Experimental details

The PAC investigations on nanocrystalline Ni and NiCu alloys were performed using the probe ^{111}In/[111]Cd. The PAC time spectrum is modulated by two frequencies (ω_L and $2\omega_L$) in case of an interaction with one magnetic field and by three frequencies (ω_1, ω_2, and $\omega_3 = \omega_1 + \omega_2$) in case of an interaction with one electric field gradient (efg). The frequencies are proportional the local magnetic field or the local efg, respectively. The efg tensor is characterized by $\nu_Q = eQV_{zz}/h$ and $\eta = (V_{xx}-V_{yy})/V_{zz}$ using the nuclear quadrupole moment Q of the 5/2 state of [111]Cd. If the probe atoms are distributed over many non-equivalent lattice sites a frequency distribution is observed, which still may have some characteristic features. A detailed description of PAC can be found elsewhere [4].

Nanocrystalline samples of Ni and NiCu were prepared by pulsed electrodeposition (PED) [5]. The corresponding preparation parameters are given in table 1. The Ni samples

Table 1

Composition of the electrolyte, temperature, current density, on-and off-times of the current pulses, used for the deposition of nanocrystalline Ni and $Ni_{0.5}Cu_{0.5}$ alloys. The grain size was determined by X-ray diffraction in case of Ni and by atomic force microscopy in case of NiCu.

samples	grain size	electrolyte	preparation parameters		
			T (°C)	j (A/cm^2)	t_{on}(ms) / t_{off}(ms)
n-Ni	19nm	$NiSO_4$ (40g/l), K,Na-tartrate (120g/l), NH_4Cl (40g/l)	36.5	0.13	1 / 49
n-$Ni_{0.5}Cu_{0.5}$	30nm	$CuSO_4$(6g/l), $NiSO_4$ (80g/l) Na-citrate (100g/l), Saccharin(2g/l) (optional)	15 ... 70	0.1 ... 0.3	1 ... 2 / 48 ... 49

were doped *ex-situ* with ^{111}In by diffusion at 623K (30 min). The incorporation of the ^{111}In atoms on substitutional Ni sites was investigated as a function of the temperature of a pre-annealing step (60 min), i.e. annealing before ^{111}In diffusion, and subsequent annealing (30 min) after ^{111}In diffusion. The annealing steps were performed under vacuum and the PAC spectra were taken at 295 K after each annealing step. The NiCu alloys were doped *in-situ* with ^{111}In by adding [111]$InCl_3$ to the electrolyte. The formation of Ni precipitates was investigated as a function of the temperature of the electrolyte, the current density during deposition, and the optional addition of saccharin.

3.   Results and discussion

3.1. *Grain boundaries of nanocrystalline Ni*

After doping nanocrystalline Ni *in-situ* with ^{111}In during PED, essentially the magnetic hyperfine interaction known from ferromagnetic Ni is observed [6]. There are no additional signals observed resulting from probe atoms located directly in the grain boundaries. Since by *in-situ* doping the ^{111}In atoms are distributed homogeneously over the entire sample, the fraction of probe atoms on grain boundary sites is too small to be resolved in the PAC spectrum. In contrast, doping nanocrystalline Ni *ex-situ* with ^{111}In by diffusion at lower temperatures ($T_{diff} < 0.5 \, T_m$) the probe atoms are predominantly incorporated into the grain boundaries [3]. After doping with ^{111}In at 623K and subsequent annealing at different temperatures, a frequency distribution is observed in all of the Ni samples, which corresponds to disordered grain boundary structures. Additionally, four different frequency triplets corresponding to different efg can be observed (figure 1 and table 2). Etching of a sample after diffusion with ^{111}In effects no change of the measured PAC spectra, showing that lattice sites on the surface of the sample are not responsible for the detected efg. Furthermore, there are no defects known from polycrystalline Ni causing the efg measured here [7].

Since most of the probe atoms are placed in grain boundaries, it is concluded that the four observed unique efg arise from different ordered structures in the grain
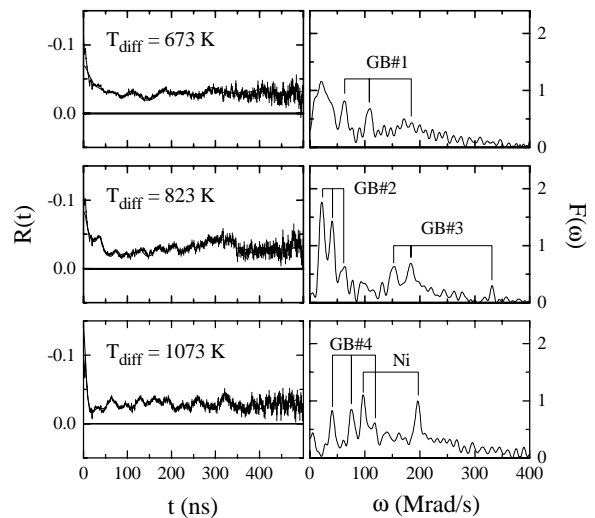

Figure 1:   PAC spectra showing via the occurrence of four unique efg the presence of ordered structures in grain boundaries of nanocrystalline Ni.

Table 2
The observed unique efg signals of grain boundaries in nanocrystalline Ni.

Signals	ν_Q (MHz)	η	$\Delta\nu_Q$ (MHz)	f (%)
GB#1	58(1)	0.38	0	3-5
GB#2	21(1)	0.33	0-6	10-15
GB#3	106(1)	0.77	0	3-5
GB#4	41(1)	0.21	0	3-7

boundaries. The existence of ordered structures in grain boundaries was predicted e.g. for Ag on the basis of theoretical studies [8] and could be observed experimentally by transmission electron microscopy e.g. in case of a NiO bi-crystal [9]. However, there are no reports about direct experimental evidences of ordered structures in grain boundaries in polycrystalline samples. Since the PAC data yield only pure efg, it is concluded that in the grain boundaries of ferromagnetic nanocrystalline Ni almost no or only a weak magnetic field (< 0.5 T) is present. The appearance of the ordered grain boundary structures, however, seems to be accidental since no systematic behaviour between the detected efg and the annealing temperature was observed. Nonetheless, a conversion between the ordered structures upon annealing was observed by PAC.

After diffusing ^{111}In into nanocrystalline Ni prepared by PED the incorporation on substitutional lattice sites is observed to start at about 623 K. Pre-annealing nanocrystalline Ni samples for 60 min before ^{111}In diffusion shows that the initial temperature of incorporation follows the pre-annealing temperature below 1000 K and depends no longer systematically on the pre-annealing temperature above 1000 K [10]. It is concluded that the incorporation of In on substitutional Ni sites below 1000 K is effected by the grain growth, which is closely related to the so-called diffusion induced grain boundary migration (DIGM) [11]. Above 1000 K, ^{111}In is incorporated on substitutional Ni sites by volume diffusion from the grain boundary into the crystallite [10].

Figure 2: The incorporation of ^{111}In on substitutional bulk sites of nancrstalline Ni as a function of the annealing temperature.

3.2. Ni precipitates in NiCu alloys

Nanocrystalline $Ni_{0.5}Cu_{0.5}$ alloys have been prepared by PED and were investigated by PAC and XRD [12]. It has turned out that PAC is highly sensitive to small Ni precipitates (figure 3a). In contrast, the Ni precipitates could not be detected by X-ray diffraction (XRD) (figure 3b). By monitoring the fraction of probe atoms measuring the Larmor frequency $\omega_L = 97.6$ Mrad/s as a function of the current density, the temperature
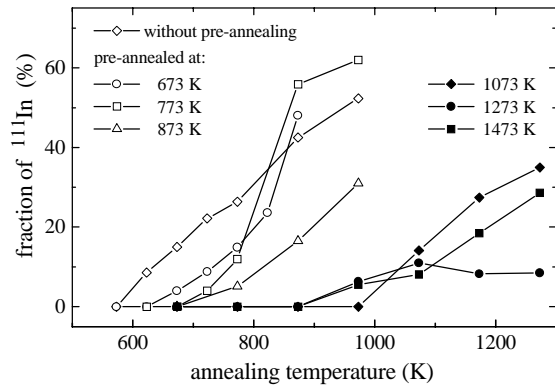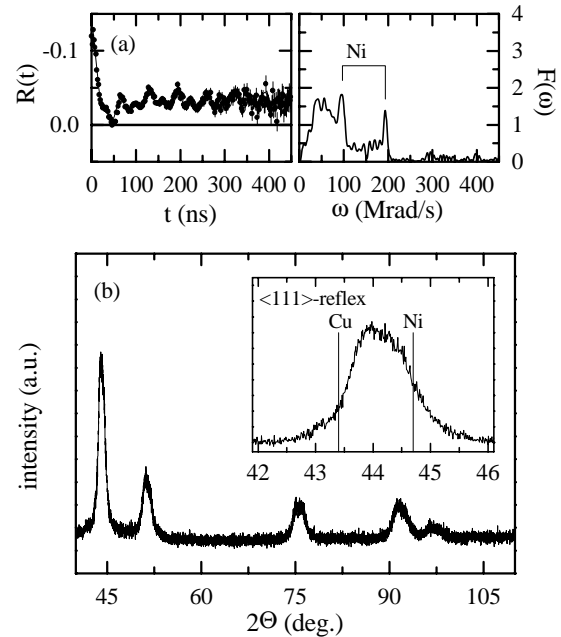

Figure 3: Investigation of a nanocrystalline NiCu sample by (a) PAC and (b) XRD

of the electrolyte, and the optional addition of saccharin to the electrolyte, it is shown that the homogeneity of the NiCu alloy is improved by a lower current density, a higher temperature, and the addition of saccharin, respectively (figure 4). At the same time the lower current density and the higher temperature leads to a larger grain size, whereas the grain size is reduced by adding saccharin to the electrolyte [12].
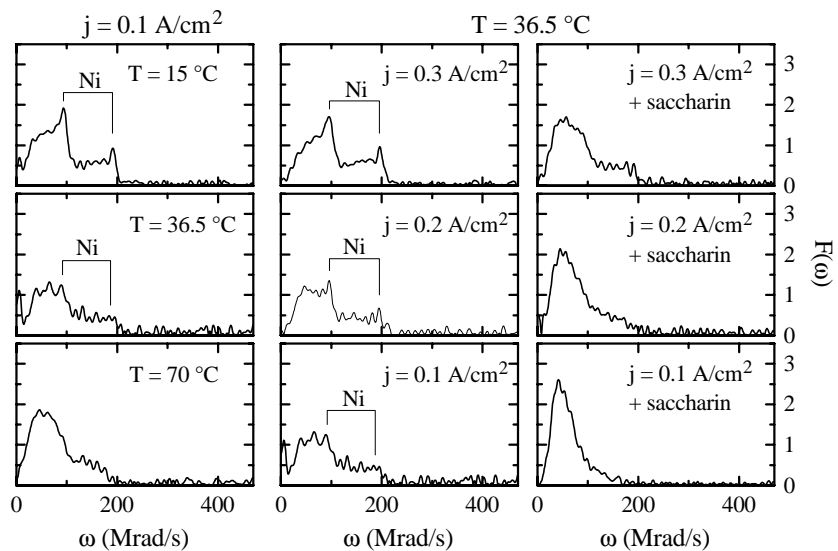

Figure 4: The formation of Ni precipitates in NiCu alloys for different conditions during the PED process

The formation of inhomogeneous NiCu nanoparticles is proposed to be caused by the following mechanism: Since for preparing a $Ni_{0.5}Cu_{0.5}$ alloy the electrolyte contains much more Ni than Cu, the ratio $Ni^{2+}:Cu^{2+}$ near the cathode, collecting the deposited material, has to increase with time during the current pulse. In case of a high deposition rate, i.e. a high current density, and a weak intermixing of the electrolyte, i.e. at low temperatures, the Cu^{2+} concentration near the cathode tends to zero at the end of the current pulse, and pure Ni will be deposited.

Acknowledgements

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