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Grain growth in nanocrystalline Fe–Ag thin film

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Abstract

Isothermal grain growth kinetics of nanocrystalline Fe–Ag single-phase thin film, prepared by pulsed laser deposition, was investigated by X-ray diffraction (XRD). Using an empirical relation assuming that σ_b reduces with solute segregation, grain growth stops with saturated grain boundaries, corresponding to a metastable equilibrium system. It was found that higher Ag concentration gives smaller grain size at the metastable equilibrium, but favours phase separation upon annealing.

Keywords: Nanocrystalline materials; Grain growth; Kinetics; X-ray diffraction (XRD)

1. Introduction

Taking advantage of the novel properties of nanocrystalline materials generally necessitates stabilizing the microstructure against grain growth. Two strategies have until now been devised for improving its thermal stability: a kinetic one, in which the grain boundary (GB) mobility is reduced [1–3], or a thermodynamic one, in which the driving force, i.e. GB energy, σ_b, is suppressed [4–6]. Potentially more effective would be a reduction in σ_b, which manifests only weak temperature dependence [7]. According to the Gibbs adsorption theorem [8,9], σ_b reduces with segregation of solute species to the GBs [4,6].

$$\sigma_b = \sigma_0 - \Gamma_{b0}[RT\ln X_0 + \Delta H_{seg}] \quad (1)$$

where σ_0 is the GB energy for pure solvent, X_0 the bulk solute concentration, Γ_{b0} the solute excess of GB monolayer available for segregation at saturation, and ΔH_{seg} the enthalpy change of segregation per mole of solute. Whenever σ_b is positive, grain growth will decrease the free energy of the system. Therefore the only case where grain growth can be suppressed is σ_b=0 [6]. Experiment has shown that the effect of solute segregation on σ_b can be substantial, and theoretical considerations predict that driving σ_b to zero is possible in alloy system with a high enthalpy of segregation [5,6].

As compared to an unchanged grain size and solute segregation, precipitation of solute or stable phase at GBs and grain growth leads to a more stable equilibrium [6]. So stopping nano-scale grain growth corresponds to the saturated GB with zero GB energy, a metastable nanocrystalline system. The grain diameter, D^*, at the metastable equilibrium is given as [6,10],

$$D^* = \frac{3\Gamma_{b0}V_M}{X_{total} - \exp\left(\frac{\sigma_0 - \Gamma_{b0}\Delta H_{seg}}{\Gamma_{b0}RT}\right)} \quad (2)$$

where X_{total} is the summation of the bulk and GB concentration, and V_M the molar mass of the alloy. Hence Eq. (2) demonstrates there exists a state for which the polycrystal is stable with respect to variation of GB area, i.e. grain size.

Pulsed laser deposition (PLD) was used to grow thin films particularly of Fe–Ag alloys onto substrates cooled to 150 K, leading to the formation of nanocrystalline single-phase bcc films with up to 40 at.% Ag [11]. The most striking feature of PLD in the preparation of alloys is the formation of solid states far away from thermodynamic equilibrium. The high particle energy and the high

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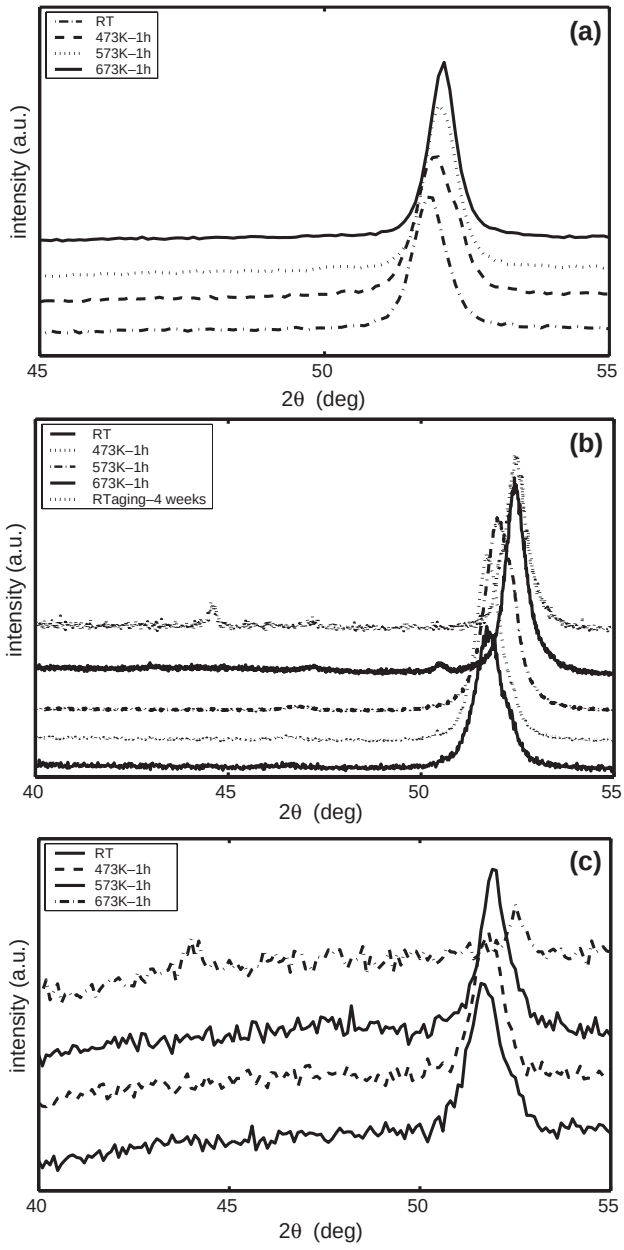

Fig. 1. XRD patterns after successive 1 h isothermal anneals of $Fe_{98.2}Ag_{1.8}$ (a), $Fe_{96.8}Ag_{3.2}$ (b) and $Fe_{95}Ag_5$ (c) alloys at different temperatures.

deposition rate [13] result in the formation of metastable nanocrystalline solid solutions.

Here, we conducted isothermal annealing of Fe–Ag thin films (by PLD) at temperatures between 473 K and 673 K. The gain growth behaviour was analysed using the above thermodynamical model to verify that nano-scale grain growth is inhibited by reducing GB energy through solute segregation, and that the grain size can be attributed to the combined effect of solute concentration and GB excess, Γ_{b0}.

2. Experimental procedure

Fe(Ag) alloys with a thickness of 100–300 nm were laser deposited at room temperature (RT) onto Si substrates in an ultrahigh vacuum system (with a base pressure of about 5×10^{-9} mbar). At a laser fluency of 8 J/cm^2 and with a target-to-substrate distance of 3 cm, thin films with different concentrations were prepared by alternating illumination of Fe and Ag foils with a focused KrF excimer laser beam as described earlier [11]. The overall composition of the films was determined using X-ray fluorescence (XRF).

Structural characterization was performed by X-ray diffraction (XRD) with monochromatic Co Kα radiation. Diffraction patterns of selected samples were taken in situ during successive isothermal 1 h anneals at various temperatures in a vacuum better than 10^{-6} Torr; the duration of each scan was 10 min. The corresponding XRD-patterns at RT were also taken. From the Bragg angles (2θ) of the RT reflections of the phases the lattice parameters, a, of the phases can be determined.

3. Results

Fig. 1 (a–c) displays enlarged parts of XRD-patterns of the as-prepared $Fe_{100-x}Ag_x$ (initial concentration, x=1.8, 3.2, 5.0 at.%) thin films after isothermal 1 h anneals between 473 K and 673 K (for different times). The as-prepared state and corresponding XRD-patterns at RT for $Fe_{98.2}Ag_{1.8}$ and $Fe_{96.8}Ag_{3.2}$ are shown in Fig. 1 (a and b), respectively. Unfortunately, RT XRD-patterns were not recorded for $Fe_{95}Ag_5$ and in situ XRD patterns were provided instead. Although the resolution of Fig. 1c is not as good as that of Fig. 1 (a and b), the influence on the experimental results is negligible. The grain sizes of the Fe–Ag films were determined with the aid of the Scherrer formula [12] and were gathered in Table 1. The change of the lattice parameter of Fe(Ag) solid solutions upon annealing is shown in Fig. 2a. The lattice parameter can be reasonably expected according to Vegard's law [11,13,14], thus giving Ag concentration as a function of

Table 1
Evolution of grain size and peak position (2θ) of the XRD patterns upon annealing Fe(Ag) supersaturated solid solutions

Ag content	RT		473 K		523 K		573 K		623 K		673 K	
	2θ/°	D, nm	2θ/°	D, nm	2θ/°	D, nm	2θ/°	D, nm	2θ/°	D, nm	2θ/°	D, nm
1.8 at.%	51.94	12.1	51.96	12.8	51.98	13.2	51.99	15.5	52.02	16.9	52.09	19.2
3.2 at.%	51.70	11.5	51.77	12.2	51.84	12.9	51.90	14.3	51.99	15.2	52.41	17.2
5.0 at.%	51.45	10.4	51.50	11.7	51.59	12.2	51.72	12.8	51.85	13.4	51.98(0.5 h)	14.7
											52.41(1 h)	16.4