AFM- and XPS-Investigations of Surface Layers of Nanocrystalline Fe-Cu-Nb-Si-B

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Atomic force microscopy and X-ray photoelectron spectroscopy were used to study the surface layers of a nanocrystalline Fe-Cu-Nb-Si-B alloy. The grain size has been shown to increase when passing from bulk layers to the surface from 20 to 200 nm, which is associated with the processes of the surface segregation of Si and B. Furthermore, during annealing and ion treatment the processes of recrystallization occur on the surface.

1. Introduction

Remarkable attention has been focussed on nanocrystalline (NC) materials for the last decade [1]. To study the surface microstructure of NC materials the atomic force microscopy technique (AFM) has widely been used. However, the AFM-stated grain size is often much larger than the values obtained by other techniques, namely X-ray diffraction analysis [2–5]. The discrepancy is sometimes explained by the inadequate AFM resolution determined by the tip quality. We assume that since the NC-state is a metastable one the processes providing a more equilibrium state with lower surface energy, such as adsorption, oxidation, surface segregations, intergrain boundary relaxation, recrystallization, etc., are possible at the boundary between air and NC material surface. As a result, the surface microstructure may change and become strongly different from the bulk structure. Thus, it was shown in Ref. [5] that an order of magnitude larger grains compared to the bulk were observed if adsorption of organic surfactants onto the newly-formed surface of NC iron had taken place.

In the paper presented the AFM and XPS were used to investigate the microstructure and surface layer composition of the $Fe_{76.1}Cu_1Nb_3Si_{13.8}B_{6.1}$ alloy in its initial state as well as after etching in acid solutions and annealing. The choice of the alloy was determined by the grain size of 10–15 nm in its NC state as determined by X-ray diffraction [6]. Structural inhomogeneities of this size

are readily identified by means of AFM, hence it is possible to correctly compare the AFM- and X-ray diffraction data.

2. Experimental

The amorphous foil 10 mm wide and 20–25 μm thick was prepared by the spinning technique. The heat treatment was performed for 1 h in vacuum under the pressure of 10^{-4} Torr at $T = 550°C$ and 600°C. The volume fraction of NC phase made up 90% and represented $Fe_3(Si,B)$ [6]. An aqueous mixture of hydrofluoric and nitrous acids (1:1:1) was taken for the etching process. Surface layers 1 and 3 μm thick have been dissolved.

The scanning probe microscope P4-SPM-MDT (NT-MDT) was used to measure the surface topography. Silicon cantilevers with a tip curvature radius < 10 nm and an apex angle of cone $< 20°$ were provided by the "Silicon" company. The measurements were performed in air in contact mode of imaging the topography and lateral forces.

The XP-spectra were measured on the ES-2401 spectrometer with a MgK_α source of excitation under the pressure of 10^{-10} Torr. The C1s, O1s, Fe2p, Cu2p, Si2p, Nb3d, B1s spectra were recorded. The analyzed layer depth was of the order of 3 nm.

3. Results and discussion

Both sides of the initial tape surface are crystallized. An average grain size was 80 nm from the contact side and 20 nm from the outer side. The data on the quantitative analysis of the surface layers are summarized in Table 1. The Si content is 3 times higher than its bulk content. The content of B is doubled compared to the bulk. The X-ray diffraction data indicate the thickness of the crystallized layer approximately equal to 3 μm. After the removal of 1 μm surface layer, the grain size has decreased to 40 nm; the Si-content was also reduced.

Fig.1 illustrates the image of the contact (a) and the outer (b) surfaces after annealing at 550°C. Two grain types are observed, with average sizes of 120 and 220 nm on the contact surface and 100 and 120 nm on the outer surface. The increase in annealing temperature to 600°C results in only the growth of the quantity of the second type grains and increase of their size to 270 nm on the contact surface and to 220 nm on the outer surface. Correspondingly, the surface content of Si also increases. The formation and growth of new grains indicate a recrystallization process. The AFM-measured sizes of surface grains exceed the X-ray diffraction determined values by a factor of 100–200. After the

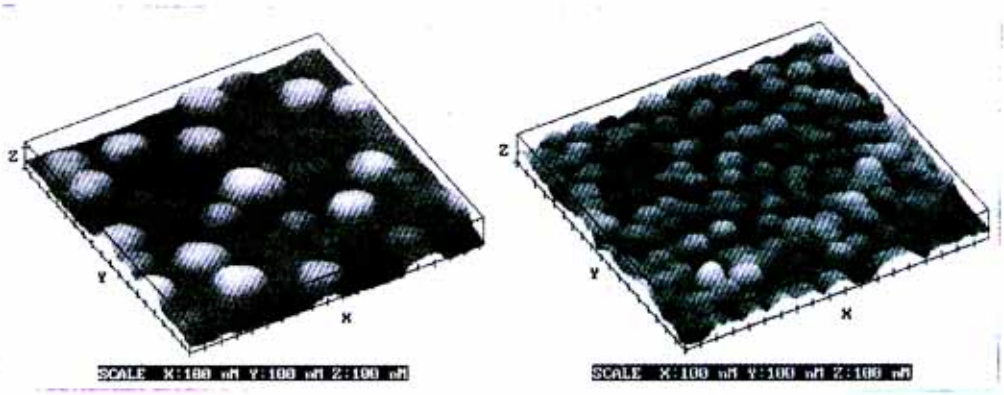

Figure 1. 3D-image of the contact (a) and outer (b) surfaces after annealing at 550°C.

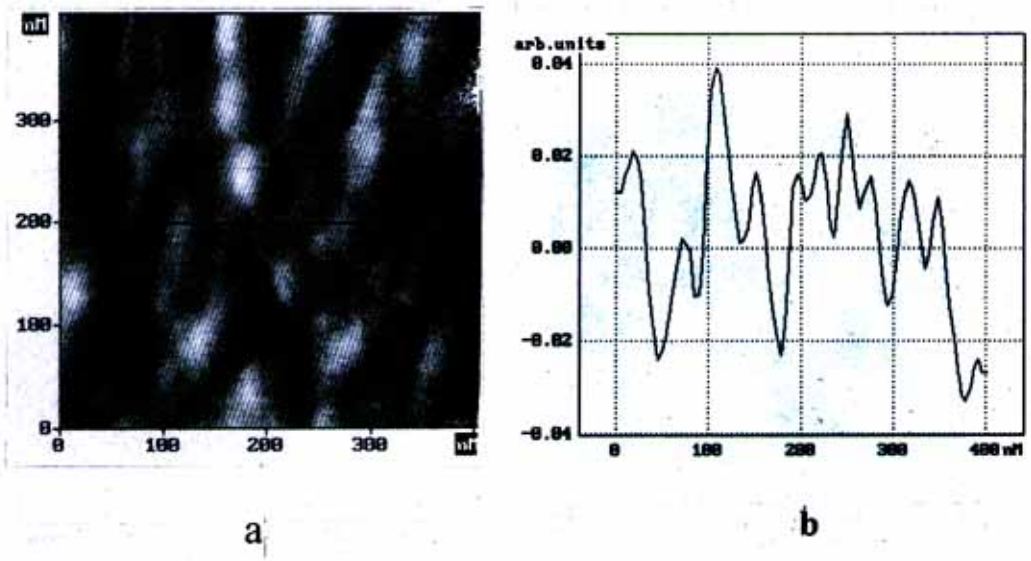

Figure 2. The lateral force image (a) of the surface (Fig.1a) and the respective profile (b) after 1 μm etching.

surface layers 1 μm and 3 μm thick have been removed the AFM-observed grain size decreased to 40 nm and 20 nm, respectively (Fig.2,3). This value is of the same order as the bulk value.

Grain size gradually increases when passing from the bulk layers to the surface ones. The grain size of the surface NC alloy is an order of magnitude larger

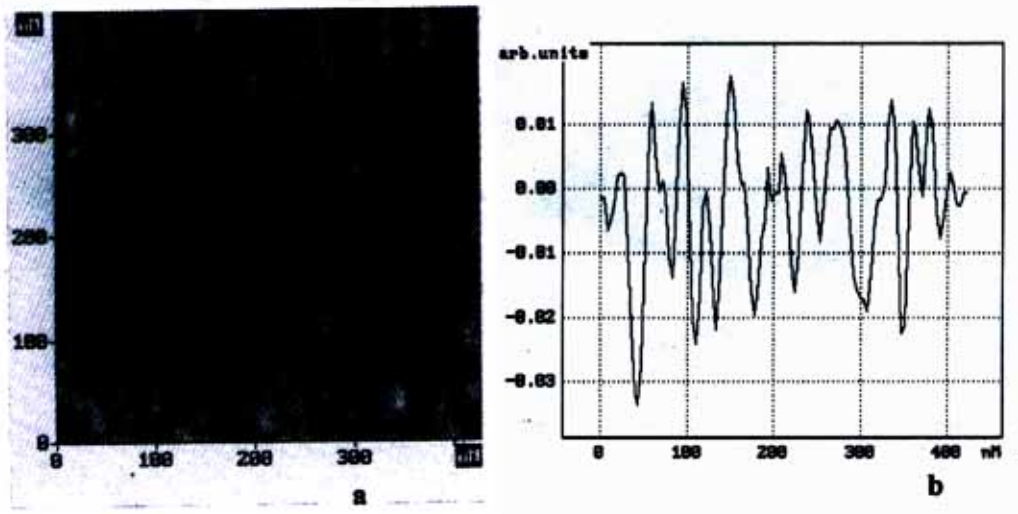

Figure 3. The lateral force image (a) of the surface (Fig.1a) and the respective profile (b) after 3 μm etching.

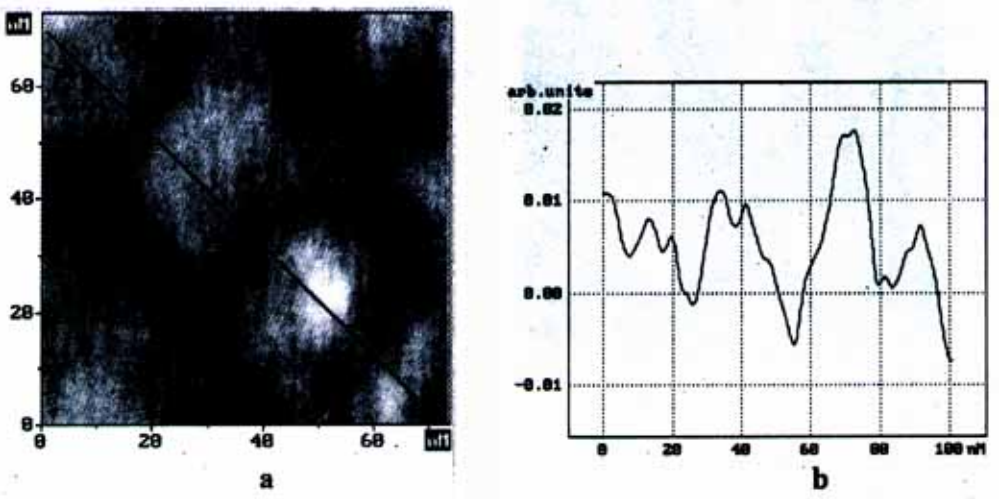

Figure 4. The lateral force image (a) of the initial tape outer surface and the respective profile (b).

than in the bulk. This phenomenon may be associated with surface segregation and oxidation of Si and B. As a result, an amorphous shell is formed around the NC phase consisting of Si- and B-oxides, with the thickness determined by the amount of Si and B in surface layers. Unfortunately, the ion profiling technique

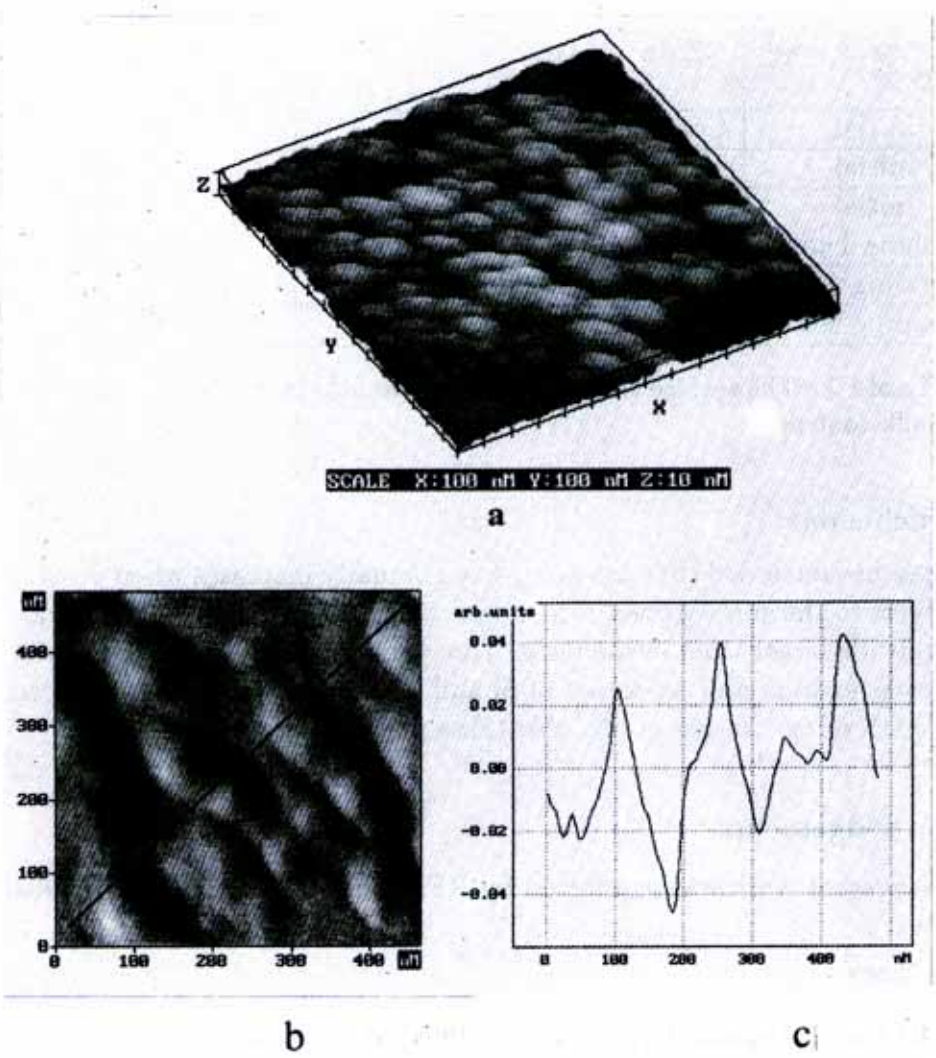

Figure 5. 3D-image (a) and the lateral force (b) image and the respective profile (c) of the initial tape outer surface after Ar-ion treatment.

cannot be used to correctly measure the resultant film thickness. Shown in Figs. 4 and 5 are the images of the initial sample outer surface before and after Ar-ion treatment (0.5 keV, 20 min). Recrystallization of the NC-alloy surface apparently takes place, as evidenced by the grain growth from 20 to 100 nm just as in the case of 550° C annealing.

Treatment type	Side	Grain size, nm	Fe (76.1)	Cu (1)	Nb (3)	Si (13.8)	B (6.1)
Initial	Contact	80	53	1	2	32	12
Initial	Outer	20	40	3	1	43	13
Initial Etching 1 μm	Contact	40	56	2	2	23	17
Annealing 550°C	Outer	100 and 120	22	1	4	64	10
Annealing 600°C	Outer	100 and 200	7	3	2	78	12

Table 1. The surface elemental content (at.%). In brackets given is the bulk content.

4. Conclusions

It can be concluded that the grain size gradually increases when passing from bulk layers to the surface ones. The grain size of the surface NC alloy is an order of magnitude larger than in the bulk. This phenomenon may be associated with surface segregation and oxidation of Si and B. Besides, the process of formation and growth of new larger grains also takes place on the surface.

Acknowledgements

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