MAGNETIC AND STRUCTURAL BEHAVIOUR OF ALNICO THIN FILMS

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Lucrarea prezintă un studiu al evoluției proprietăților structurale în strânsă conexiune cu cele magnetice a filmelor cu compoziția chimică de tipul Alnico, obținute prin tehnica depunerii cu laser pulsat (PLD), în urma succesiunii de tratamente termice aplicate. Scopul acestui studiu este acela al punerii în evidență a unei noi abordări privind obținerea unor noi tipuri de filme subțiri cu proprietăți magnetic dure şi, prin folosirea unor tehnici de caracterizare avansate, magnetometrie cu gradient de forță alternativ (AGFM), microscopie de forță magnetică (MFM), difractometrie de raze X (XRD), microscopie electronică de baleiaj (SEM), punerea în evidență a acestor proprietăți în strânsă corelație cu proprietățile structurale.

The paper present a study of the evolution of the structural properties well connected to the magnetic properties of some thin films having the chemical composition close to those of the Alnico's, obtained by pulsed laser deposition technique (PLD), after an applied sequence of thermal annealing treatments. The aim of this study is to put in evidence a new approach regarding the obtaining of new types of thin films having hard magnetic properties and to put in evidence these properties using some advanced characterization techniques, like alternating gradient force magnetometry (AGFM), magnetic force microscopy (MFM), X-ray diffractometry (XRD),scanning electron microscopy (SEM).

Keywords: Alnico, thin films, pulsed laser deposition

1. Introduction

One of the main challenges in solid state physics and materials science is the discovery and integration of new materials in devices with such a large area of applications as in biophysics, optoelectronic and nanotechnology. In all of these fields, the novel thin films deposition techniques are very important for production, while the demand on the control of size and properties of the materials is increasing. In the development of magnetically hard materials, one guiding

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principle is to obtain, by alloying and heat treatment, a matrix containing finely divided particles of a second phase. These fine precipitates, usually differing in lattice parameter from the matrix, set up coherency strains in the lattice which affect the domain wall movement. An important advance in this field was to make the particle size of the alloy so small, less than a hundred nanometres diameter, that each grain contains only a single domain. Then the magnetization reversal can occur only by the rotation of the direction of magnetization "en bloc". Alnico alloys depend on this feature and for a long period they have been included among the most commercially important permanent magnetic materials.

Although rare-earth based alloys are now the reference for the production of permanent magnets and taking into account the difficulties of obtaining rare earth based thin films and preventing them of the oxidization, knowing the costs of obtaining Fe-Co and Fe-Pt thin films, some efforts have been devised to prepare different typologies of thin films based on the Alnico compositions. The aim of this work is trying to understand both mechanisms, structural and magnetic, in the development of such films, starting from a bulk Alnico 5. There have been a few literature studies on this subject: Ganzha and co. [1]. reported on the production of films of Fe-Ni-Al-Co by vacuum evaporation on quartz, NaCl or ceramic substrate. They concluded that the films have inferior high-coercivity characteristics than the bulk, but also they report a difference in film composition (in terms of aluminium), which can be responsible of a different mechanism of phase transformations with respect to the bulk material. More recently, Hadjipanayis et al.[2] tried to obtain such films on silicon substrates by sputtering starting from a commercial Alnico 5 magnet. They reported higher coercivity with respect to the bulk, but – as reported by the author himself – this result is of difficult to explain, because the source of such a high coercivity can not be related with the low anisotropy of the crystalline phases formed after the annealing treatments. Therefore, in order to appreciate any development occurring in the production of Alnico thin films, it is necessary to understand the mechanisms of both magnetization processes and phase formation starting from the knowledge already developed on the corresponding bulk material.

2. Experimental

The thin films were prepared by pulsed laser deposition [3] using a Nd:YAG laser working at a repetition rate of 10 Hz; 266 nm wavelength (5–7 ns per pulse) and an incident fluence (i.e. the radiative flux integrated over time) of 1,6 J/cm^2. As substrates, we used 0.5 cm^2 and 1 cm^2 plates of double-polished ceramic plates. The substrates were placed at a distance of 4 cm from the target and held at room temperature during deposition. The number of applied pulses was in the range of 6.000-100.000. In order to have a uniform ablation, the target was rotated and the laser beam was scanned on the target surface, during all the experiments. The depositions took place in vacuum at low pressures, namely at $6.9x10^{-6}$ mbar and $9x10^{-6}$ mbar. The target was made by conventional casting method starting from raw elements in order to obtain the desired thin films. The target composition was calculated to obtain a little imbalance in Fe-Co-Al elements with respect to the commercial Alnico5 as a mean in order to optimize appropriately the composition of the produced films.

Since the aim of the present work is to obtain in thin film a crystalline structure similar to the Alnico bulk (i.e. a soft magnetic matrix containing finely divided particles of a second phase- hard magnetic one), the deposited films were heat treated in vacuum following three successive steps at 600 ^{o}C, 800 ^{o}C, 900^{o}C, for 1 hour, in order to evaluate both structural and magnetic changes of the structurally confined system (see tables 1, 2, 3). The specific parameters of each annealing step are presented below:

Table 1

Step no1:

Ramp	5^{o}C/min	1.5^{o}C/min	Slow cooling to RT
Level Point	500 ^{o}C	600 ^{o}C	
Dwelling time	15’	60’	
Vacuum level		3.10^{-5}mbar	

Table 2

Step no2:

Ramp	20^{o}C/min	2^{o}C/min	Slow cooling to RT
Level Point	600 ^{o}C	800 ^{o}C	
Dwelling time	15’	60’	
Vacuum level		$2.5\ 10^{-5}$mbar	

Table 3

***Step no3*:**

Ramp	20^{o}C/min	2^{o}C/min	Slow cooling to RT
Level Point	800 ^{o}C	900 ^{o}C	
Dwelling time	15’	60’	
Vacuum level		2.10^{-5}mbar	

For structural characterization it was used XRD (X-ray diffraction) technique, Co K_α radiation in a parallel beam configuration, in order to minimize the substrate contribution to the observed diffracted intensities. The angle of incidence of the x-ray beam on the sample surface was fixed at 1°. Morphological and compositional observations were made at NanoFacility Piemonte, INRIM, a laboratory supported by the Italian “Compagnia San Paolo” using an Inspect

F SEM (scanning electron microscope). Magnetic characterization, was performed by AGFM (Alternating Gradient Force Magnetometry), MFM (Magnetic Force Microscopy) using an Ntegra Aura instrument.

3. Results and discussion

XRD analysis (see fig.1) on as made films reveals amorphous structure, with small and rare crystalline nuclei most probably of α-Fe, Co and Ni. This observation could confirm the existence of a preliminary α-phase, as previously mentioned in literature [4]. SEM images too evidenced an amorphous structure and no granular arrangements; additionally by means of quantitative microanalysis and BSE (back scattered electrons) images, it was possible to detect the presence of all the elements coming from the initial target composition (see fig.2). Both, XRD and SEM analysis showed a continuous evolution with temperature, from the amorphous structure to a crystalline one. On the films deposited on ceramic substrate after the first step of annealing treatment (at 600^{o}C) the XRD pattern indicates the presence of Fe oxides, the oxygen coming from the interface layer. Oxygen is released in the first step of annealing from the substrate into the film. After the successive annealing steps, one can observe the development of the Fe-Co phase as the temperature increases.

The films deposited on ceramic substrate, independently of their thickness, showed the same kind of structural evolution. The growth of the grains occurs by a superficial de-wetting and by creation of a sponge-like matrix; it has to be noticed that after the annealing treatment at 800 °C some of the grains seem to be structurally interconnected. This kind of structure was observed also by Hetherington et al. [4]. At the later stage of the annealing treatment (900^{o}C) SE and BSE images put in evidence core-shell grains with different elemental composition reminding of a similar structure in bulk materials (see fig.1). Regarding the microanalysis, it is difficult to make a clear difference between the phases formed and assess if they are richer in one or another element (in terms of Co or Ni in particular), because of the instrumental spatial resolution is comparable with the grain dimension. The presence of the formed phases could be resolved by an further TEM analysis, but this involves also choosing a convenient method to prepare the samples for TEM analysis, without changing the real structural and magnetic behaviour of the films.

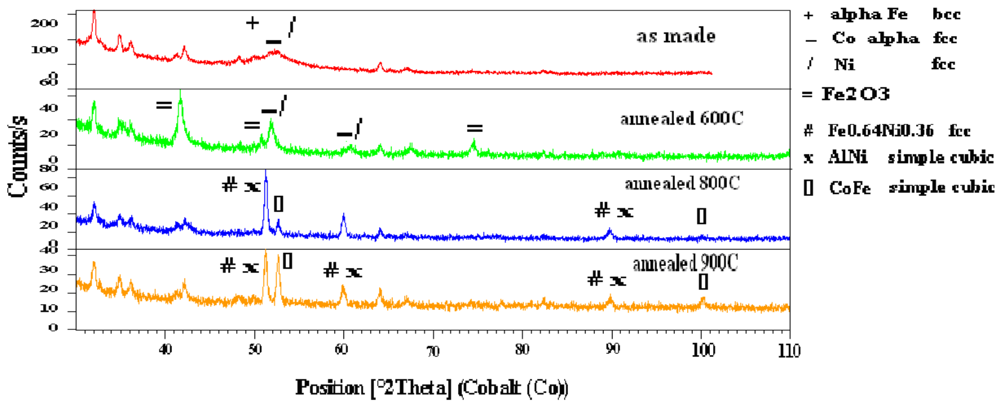


Fig. 1. XRD patterns (Intensity (counts/s) vs. angular position (2theta)) of a film on ceramic substrate (thickness = 130 nm) after each step of the annealing treatment (red pattern –as made film, green pattern – annealed at 600^0C, blue pattern – annealed at 800^0C, orange pattern – annealed at 900^0C).

Magnetic measurements put in evidence an increase of the coercive field with the temperature of annealing treatment up to 800^oC when the maximum value of coercivity is attained, close to the values reported by Ganzha et al. [1]. After last annealing treatment (i.e. 900^oC, 1 h.) not only the coercive field decreases, but also the magnetization per mass unit is reduced, probably due to the loss of material by evaporation phenomena during the annealing or more likely to further structural evolution into non-magnetic phases (see fig.4).

Low values of coercive field, saturation induction, and consequently of maximum energy product with respect to the Alnico bulk, could be related to the incomplete phase decomposition or the structural and magnetic interaction observed between the two ferromagnetic phases, Fe-Co and Fe-Ni. Since during the annealing treatments an external magnetic field was not applied, the random distribution of the formed Fe-Co phase could not lead to a coercive field as high as in the bulk, where FeCo crystal growth is strongly influenced by the external field. It has to be mentioned that we would not expect that the higher value of the coercive field could be reached trough the anisotropy of the system since the phases involved have a cubic structure. The anisotropy constant of the developed magnetic structure was estimated to be of the order of 10^5 J/m^3.

The following results are presented offering a general frame to appreciate the evolution of the magnetic properties with the structural changes taking place in the obtained films during different annealing treatments. Higher values of the coercive field were observed for out of plane measurements (that is when the magnetic field is applied perpendicular to the film surface), considering also the effect of the demagnetizing field, evaluated by applying the so-called μ^*

correction. In fig. 5, the hysteresis loop of the film annealed at 900°C is not reported due to the imprecise estimation of the volume magnetization related to a possible loss of material.

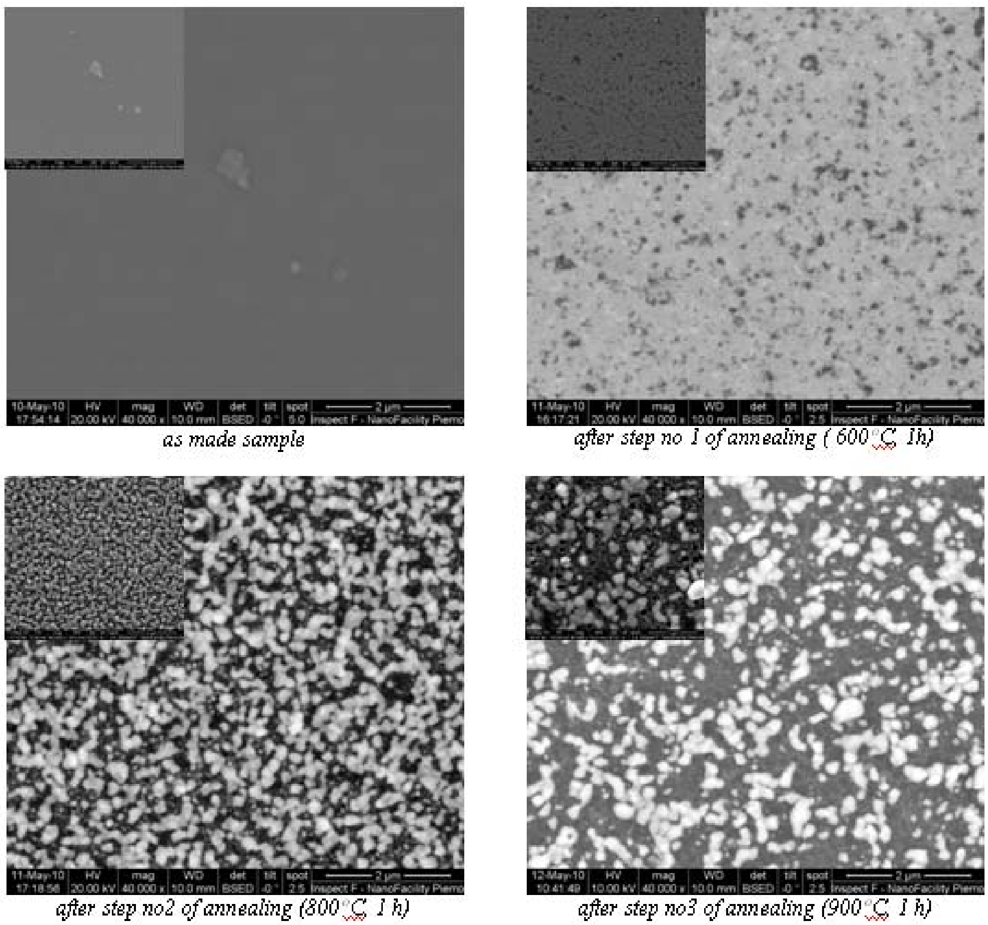


Fig. 2. SEM images (big image - BSE; left corner- SE) of a film on ceramic substrate (thickness =130nm) after each step of the annealing treatment.

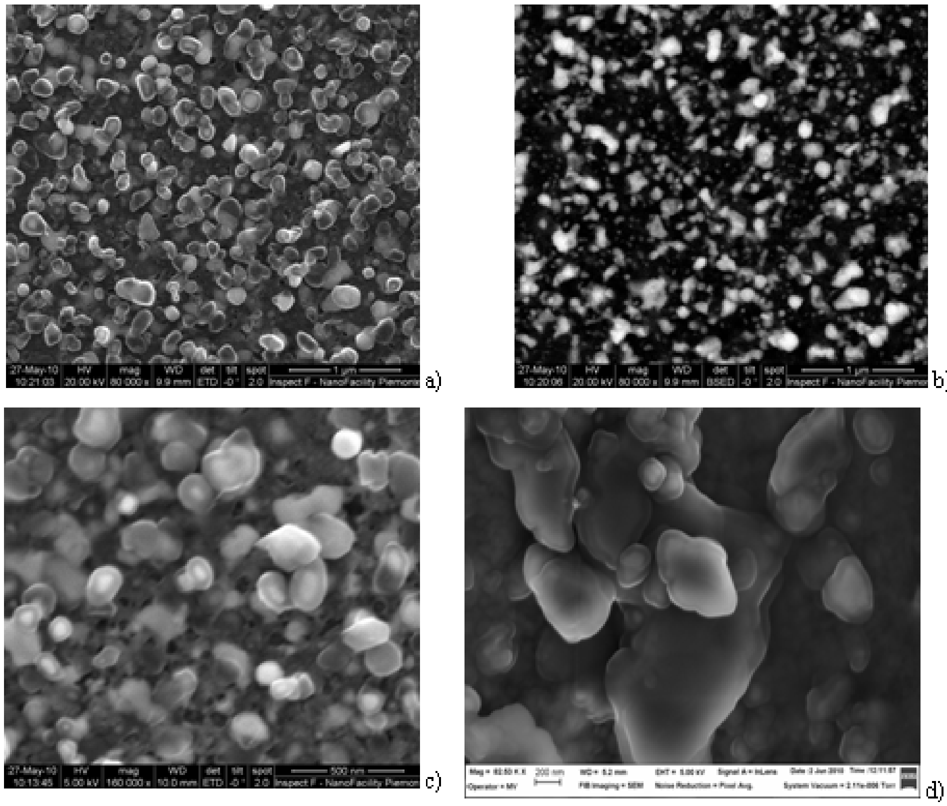


Fig. 3. SEM images [a),c)- SE, b)- BSE] of a film deposited on ceramic substrate (thickness =74nm) annealed at $900^{o}C$ d) bulk material (SE)

The shape of the out of plane hysteresis loop clearly observed after the second stage of the annealing treatment (at $800^{o}C$) may be related to the presence of two magnetization reversal processes, consisting of out-of -plane rotation coupled with out-of-plane switching from an easy direction to another one. (see fig.4d). We suppose the existence of two phases interacting when considering in plane magnetization reversal process and those behave independently out of plane. This kind of behaviour can be related also to the MFM images (see fig. 6) where is evidenced only the perpendicular contribution of the magnetization.

For the as made film it can be observed a similar strip domains structure, while for the film annealed at $800^{0}C$ the domain structure becomes a granular one.

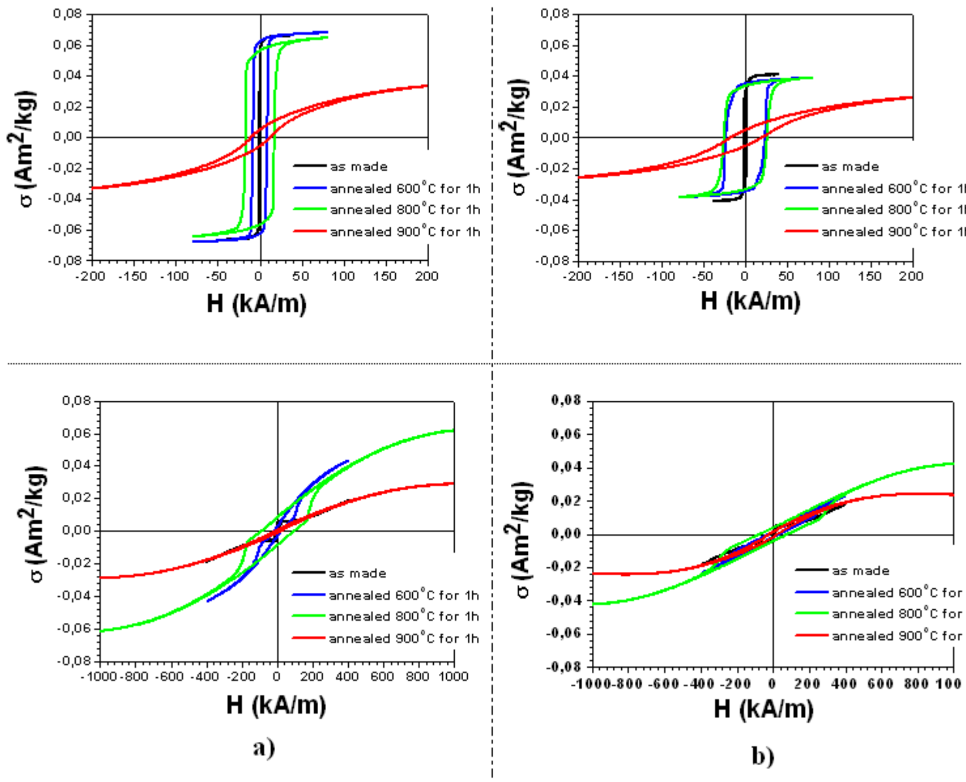
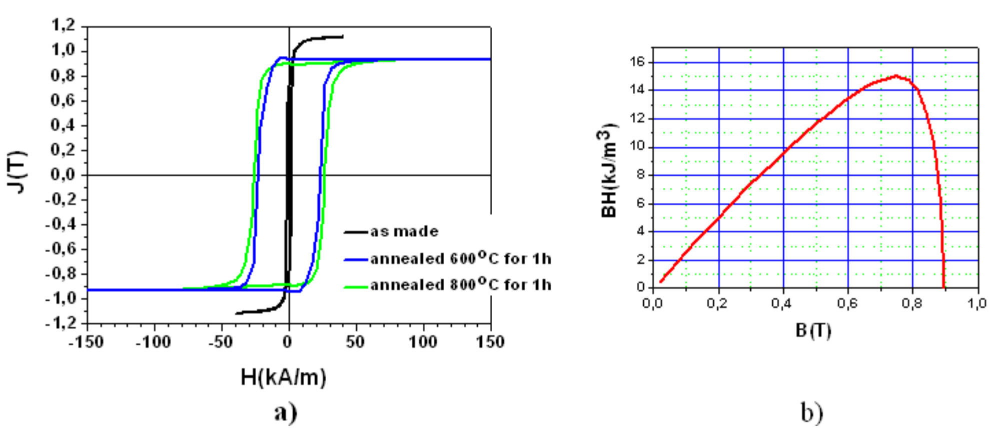
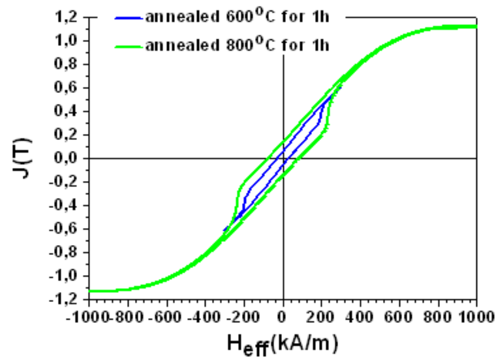
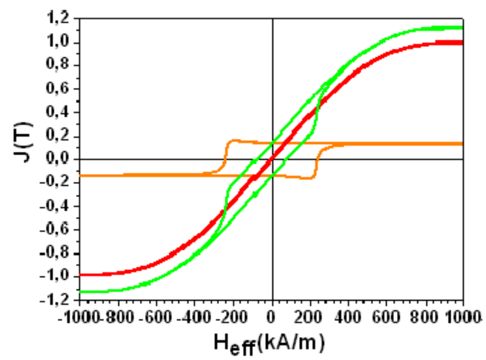


Fig. 4. In plane (up) and out of plane (down) hysteresis loops (mass magnetization vs. applied field) of the films on ceramic substrate (a) thickness = 130nm and b) thickness =74nm) after each step of annealing treatment (black line –as made film, blue line –annealed at 600^0C for 1h, green line –annealed at 800^0C for 1h, red line – annealed at 900^0C for 1h)





c)



d)

Fig. 5. Hysteresis loops (polarization vs. applied field) of a film on ceramic substrate (thickness of 74nm) a) in plane magnetization, (black line – as made film, blue line-annealed at 600^{0}C for 1h, green line – annealed at 800^{0}C), b) energy product vs. induction after annealing at 800^{o}C, c) out of plane magnetization (blue line-annealed at 600^{0}C for 1h, green line – annealed at 800^{0}C), d) out of plane magnetization as obtained after annealing at 800^{o}C (green) and after subtraction (orange)of a reversible contribution (red)

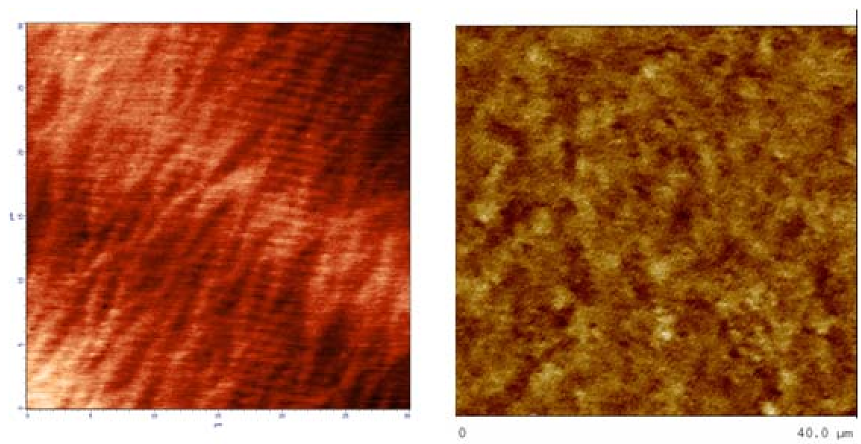


Fig. 6. MFM patterns for a) an as prepared film (scan surface 30x30um); b) annealed at 800^{o}C for 1h (scan surface 40x40um) deposited on ceramic substrate (74nm)

6. Conclusions

The present study offers just a general frame for a more striving purpose that is obtaining an Alnico-type structure- similar to the conventional permanent magnet alloy- confined into a thin film and understanding the structural evolution occurring upon the alloy after the thermal treatments, along with its connection with the magnetic properties evidenced in comparison with the conventional Alnico alloys.

Although Alnico alloys have been applied for a long period as permanent magnets before the venture of rare-earth alloys, their possible production as thin films has been so far only slightly investigated in the literature, probably because of the difficulty of reproducing a hard magnetic behaviour in thin structures associated with the complexity of controlling the material's composition and its structural evolution towards the high coercivity phases in such a confined structure.

Concerning our experimental results it is still not possible to affirm that a clear structural behaviour has been individuated, besides the inherent complex effects due to the multiple element composition of the alloys, this is due to some limitation of the investigation technique used (in particular BSE observations and microanalysis, associated with SEM). Therefore, for further investigations one has to consider the inclusion of other specific methods of investigations, like TEM and thermal analysis on thin films. Regarding the magnetic properties, the observed coercivity was of order of 30kA/m for in plane measurements and around 80kA/m for out of plane measurements. The out of plane behaviour remains still to be explained in strong relationship with the structural development.

Acknowledgments

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R E F E R E N C E S

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