

Nano-grain and shape induced anisotropy dependence of magnetic properties in Ni electrodeposited films

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The parameters concerning Ni films electrodeposition are defined in this paper. Magnetic measurements in these films may be correlated with structure and film shape. They may also inform about defects and microstructure of the electrodeposited films. Magnetic properties and related microstructure may also be important for engineering applications of these films. The reasons of using this type of films in fluxgate applications are illustrated.

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1. Introduction

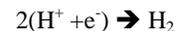
Correlation of structure and magnetic properties in magnetic films may enhance their properties and consequent engineering applications [1]. Their microstructure in terms of dislocation density and dislocation generated sub-grains, grain size and shape as well as anisotropy orientation determine the minor magnetic hysteresis loops, from the linear magnetization region till the major loop, in static or quasi-static conditions [2]. Therefore, microstructure may determine the properties of the under development films.

Tailoring the microstructure of the magnetic films may result in optimization of the magnetic properties of the films and thus, the optimization of devices based on these films may be obtained. Hence, provided that the dependence of at least one of the various characteristics of the minor loops on the sub-grain density, the shape and size of grains and the anisotropy orientation is monotonic, the testing and evaluation of the given magnetic substance can be realized in a fast, inexpensive and accurate way. It is clear that the above-mentioned correlation of the minor hysteresis loops with the measured sub-grain density, shape and size of grains and orientation of anisotropy has to be obtained for each type of magnetic substance separately.

Nickel and iron – nickel alloys play a significant role in engineering applications like sensors. Apart from the rather classical permalloy films, other compositions are also important for sensing and other applications. Therefore, it is interesting to study the properties of these films and therefore comment on their microstructure. The current paper refers to the development of pure Ni films and the study of their structure and magnetic properties. It is clear that magnetic properties are influenced not only by the crystalline anisotropy but also by the shape induced anisotropy of the films; but nevertheless the final magnetization response of the films is of importance, including defects and grain shape-size as well as crystalline and shape induced anisotropy.

2. Sample preparation

Peculiar magnetic measurements in Ni electrodeposited films have been observed concerning minor magnetization loops, showing modified magnetic parameters of Ni films. Ni films were electrodeposited on brass substrates, using simple bath of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, with $\text{pH}=3$, current density $25-55 \text{ mAcm}^{-2}$ and ambient temperature 52°C , as described in [3]. The preferred orientation of the deposits was the $\{100\}$ family of levels. TEM studies of the electrodeposited films illustrated presence of Ni nanograins inside large Ni grains. These nanograins were caused due to the H^+ presence, causing NiH or NiH_2 hydrides [4]. These hydrides developed the crystallization nucleus, causing nanograins exceeding a size of several nm, as shown in Fig. 1. The pH value is of great importance during electrodeposition because: i) it affects the discharge voltage of the cations (in our case the discharge voltage of Ni^{2+} is quite decreased at $\text{pH}=3$), ii) it affects the formation and the organization of axis texture and consequently the properties of the deposits because it influences and determinates the nature and distribution of the inclusion in the deposits. At low pH values during the chemical reaction:



the following takes place: H_2O discharge and H or H_2 inclusion or absorption and/or H_2 evolution and/or formation of hydride $\text{Ni}(\text{NiH})_n$. The latter is due to the fact that if atoms are small and mobile, so they can be found in voids and in interstitial positions. The formation of H^- is possible (H electronegativity). Ni electronegativity and so Ni hydride is easily formed, that is why a strong decrease of conductivity of Ni deposit is observed. When $[100]$ starts to be formed, hydrogen is abundantly present but as the process goes on it is eliminated (by agitation and by the chemical reactions mechanism / process), and so the formation and organization of $[100]$ is favored. The $[100]$ Ni deposits are compact materials although micropores may appear. The deposits showed a columnar structure:

between columns pyramidal / spherical, densely packed agglomerates are linearly arranged.

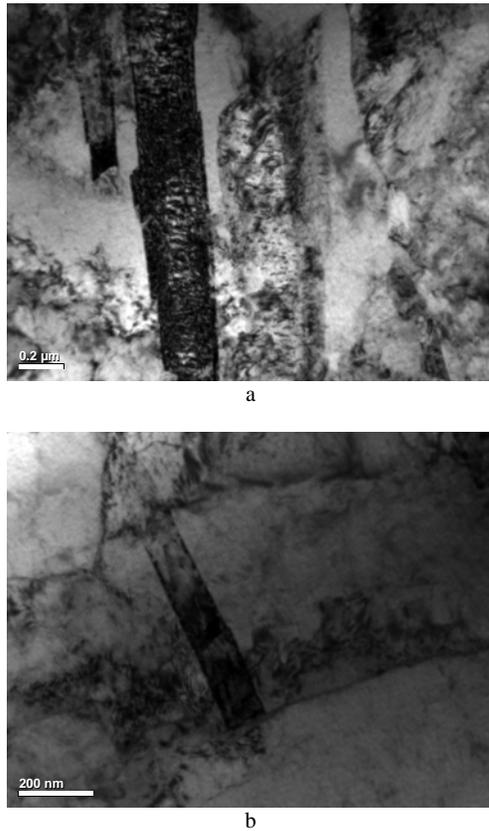


Fig. 1. Typical micrographs of the developed films.

3. Structural characterization

Structural and micro-structural characterization has been realized by means of Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD). Typical micrographs of the developed films are illustrated in Fig. 1. Fig. 1a illustrates an arrangement of plane developed long grains, while Fig. 1b illustrates the characteristic rectangular shaped type of grains introduced in the on-plane developed grains.

Although a typical bright field observation of the microstructure of the Ni films shows the expected sub-micron sized grains (micrograph in Fig. 2a), a more careful observation using dark field micrograph of the same sample (Fig. 2b) illustrates the presence of nano-grains introduced in the main Ni grain. In given areas of the film, such nano-grains are more obvious even in the bright field micrographs (Fig. 3a), while an ordered arrangement of such nano-grains is visible in the dark field micrograph of the same sample (Fig. 3b). In many grains it has been observed that such nano-grains have been arranged in arrays. The typical size of these nano-grains is of the order of 10-20 nm, being a little bit larger than the typical size of a Ni domain wall [5].

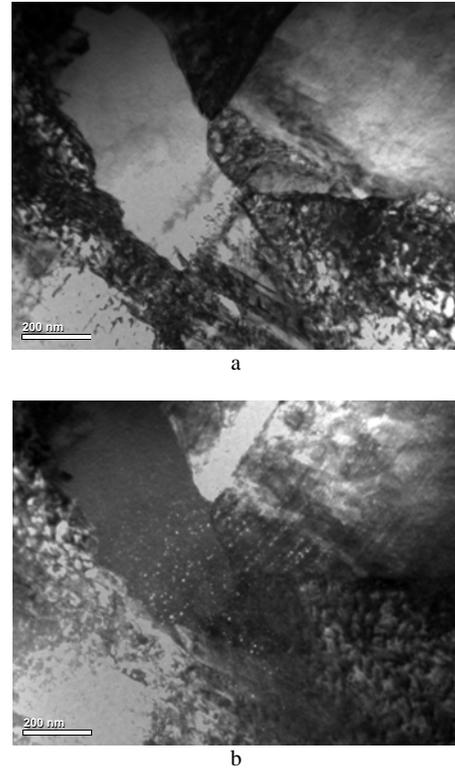


Fig. 2. Bright (a) and dark (b) field micrographs of Ni films illustrating the presence of nano-grains in the normal Ni grains.

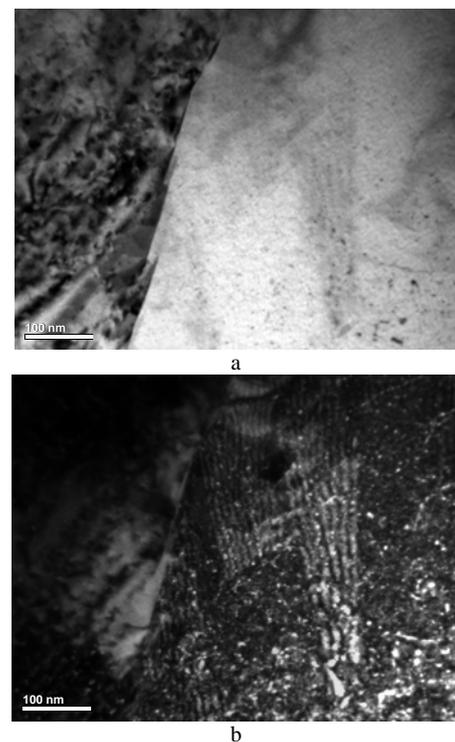


Fig. 3. Bright (a) and dark (b) field micrographs of Ni films illustrating the presence of arrays of nano-grains in the normal Ni grains.

From the reciprocal space study of the Ni films (SAED pictures as illustrated in Fig. 4) in the areas where nano-grains were present do not show other structure than the typically expected fcc structure of magnetic nickel. The same observation is obtained by using X-ray diffraction, as illustrated in Fig. 5.

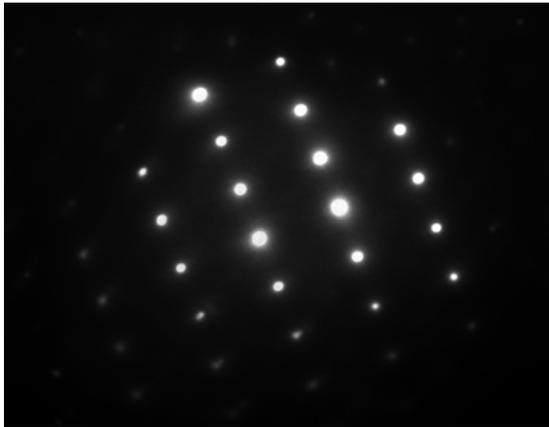


Fig. 4. SAED reciprocal response of the Ni grains with induced Ni nano-grains.

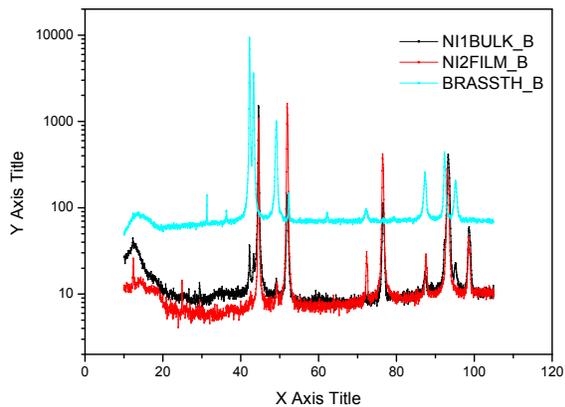


Fig. 5. X-ray response of the Ni films.

Therefore, structural characterization suggests that in given sub-micron Ni grains, several Ni nano-grains have been developed, their size being slightly larger than the width of a typical domain wall in nickel films. Therefore it has been expected that such nano-grain may influence the magnetic properties of the under test samples, together with the film shape induced anisotropy.

4. Magnetic measurements

Ni films were undergone magnetic characterization by using the VSM technique, using stress and dislocation relieved Ni sphere as reference standard. The response of such a reference Ni sphere is illustrated in Fig. 6, showing the linear magnetization dependence of nickel.

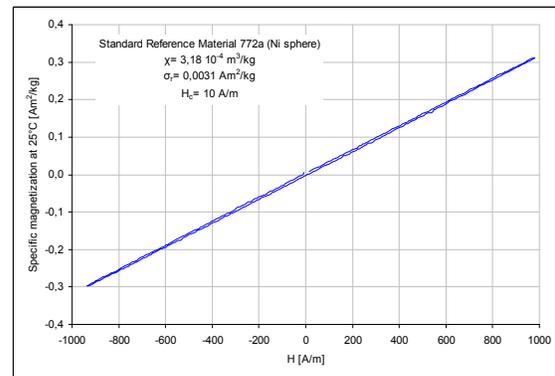


Fig. 6. M-H curve of the reference Ni sphere.

The magnetic hysteresis of the developed films is illustrated in Fig. 7, concerning measurement of two areas of the developed film. The magnetic response is very similar in both cases allowing for an assumption of repeatable results. Furthermore, magnetization measurements have been realized towards the long and short axes of the cut samples, also illustrating very similar response. This observation suggests an isotropic response on the film plane. This significant observation may allow for the use of the film in inductive field sensor applications [6]. The anisotropy field of the film H_k is $\sim 80 \text{ kA/m}$ while the permeability increases quite linearly up to H_k . This is another advantage of allowing for the use of the film in fluxgate type field sensors.

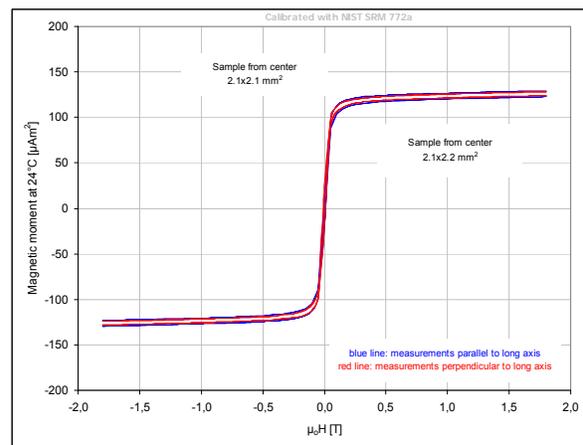


Fig. 7. Magnetization dependence of the Ni films.

Figs. 8 and 9 illustrate the dependence of the coercive force on the applied excitation field. Such a response follows a sigmoid response, which is attributed due to the presence of the nano-grains and the shape induced anisotropy of the film. Both of them cause a non-linear effect which can be used in non-linear magnetization based sensing devices such as inductive fluxgate magnetometers. Similarly, the remanent magnetization

dependence on the applied field (Fig. 10), may also be used for the realization of non-linear type of fluxgate magnetometers. Similar observation can be observed for the susceptibility dependence on the applied field, as illustrated in Fig. 11.

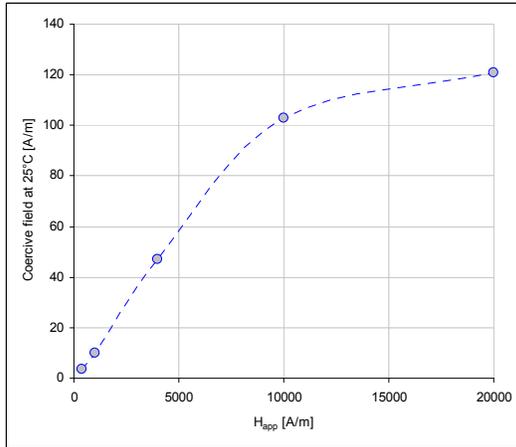


Fig. 8. Coercivity dependence field of the reference Ni film.

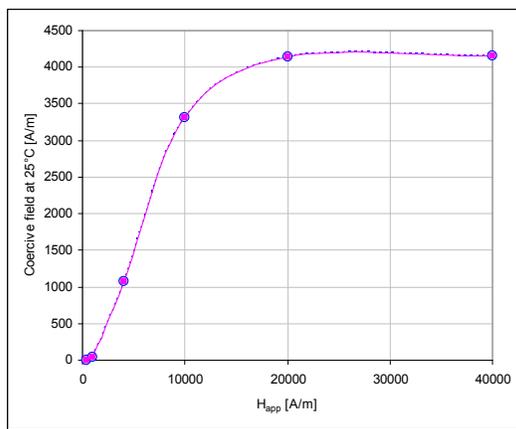


Fig. 9. Remanence dependence on maximum applied field.

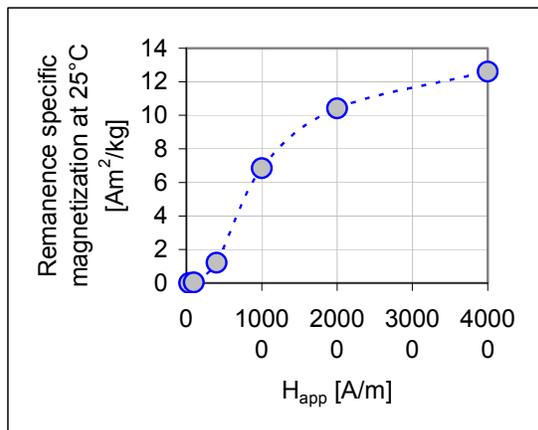


Fig. 10. Susceptibility dependence on maximum field.

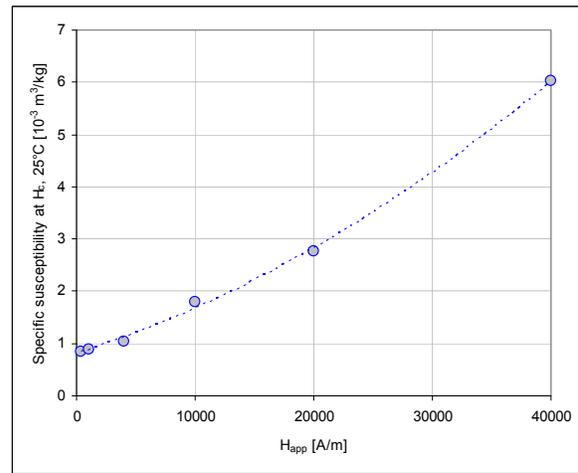


Fig. 11. Coercivity dependence on maximum applied field.

5. Discussion and conclusions

Taking into account that TEM analysis and SAED diffraction illustrated absence of inhomogeneities in the Ni structure, allowed the assumption that the Ni nanograins, have been developed after H ion depletion.

These nanograins were acting as pinning centers causing anomalies and delays in domain wall nucleation and propagation during magnetization process. The magnetization process was studied and the presence of nanograins and was manipulated as a minor crystal imperfection indicating a field dependent coefficient of the dislocation theory of Takahashi [7]. The nano-grain induced crystalline anisotropy aided by the shaped induced anisotropy due to the film structure allowed for the sigmoid magnetization response, which is quite suitable for sensor applications.

The advantage of these nano-grained Ni films is that they may maintain their properties when scaled down. This will have a result in the possibility of maintaining the magnetic characteristics in miniaturized device. This in turn may allow for the stability of the sensitivity of the magnetic field sensors of fluxgate type.

These observations have re-direct our research towards the development of Ni-rich films targeting the tailoring of films with sigmoid, linear up to H_k and unhyseretic response with significantly lower anisotropy field H_k . This way the Ni films may be considered as precursors for a new family of fluxgate sensing cores. The

Although the shape of the magnetization may allow for the use of these Ni films for sensor applications, their magnetic moment is not sufficiently high to allow for energy based applications such as motors and magnetic actuators.

As a conclusion, it can be said that such films and Ni-rich alloys with nano-grained structure may allow the miniaturization of fluxgate type of field sensors, due to the ability of keeping the magnetic sensitivity and therefore the sensor sensitivity in miniaturized scale.

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