Abstract: - In this work we show some results about some correlations between microstructure and magnetic properties for the Ni-Zn thin films obtained use electrodeposition in ultrasounds field. We modified ultrasounds power start 1 to 10 kW/m$^2$ one by one. Ultrasounds were applied perpendicular to the direction of electrical field between electrodes. The thickness of studied samples was in the range of 100-120 nm. We studied microstructure used Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Selected Area Electron Diffraction (SAED) and X Ray Diffraction (XRD) respectively. Morphology of thin films were studied used Atomic Force Microscopy. The use of ultrasounds with different power on electrolytic bath leads to formation of polycrystalline thin films with greater uniformity of grain diameter.

Key-Words: - ultrasounds, electrodeposition, microstructure, magnetic properties, thin films, Ni-Zn

1 Introduction
Alloying of zinc by iron group elements (Ni, Fe or Co) has been the subject of extensive research mainly directed towards two different fields: the corrosion resistance and the catalytic activity. From the first viewpoint, many authors reported on the important role of the alloy composition, indicating that the optimal corrosion resistance is reached for the zinc alloys containing between 12 and 13 % Ni, for example [1, 2]. From the second viewpoint, Ni-Zn films can have a porous structure or-and a high surface roughness depending on electrodeposition parameters: pH, current density, bath concentration and temperature, deposit growth rate, nature of additive reagents [3-7]. The electrodeposition by pulse-plating technique is an interesting case for microstructure of Ni-Zn films and their physico-chemical properties [8].

The aim of this work was to investigate the ultrasounds influence on surface microstructure of the Ni-Zn thin films and changes in surface roughness of these kinds of films.

2 Experimental
The Ni-Zn thin films were obtained by DC electrodeposition from an aqueous bath. The electrolyte was a mixed aqueous solution containing NiSO$_4$·7H$_2$O = 250 g/l, ZnSO$_4$ = 50 g/l, H$_2$BO$_3$ = 20 g/l and natrium lauryl sulphate = 0.5 g/l. The pH value was fixed at 4.0 by a small addition of sulphuric acid. During deposition, the electrolytic cell was kept at a constant temperature of $T=298$K. The film substrate was copper. The electrolyte was irradiated with ultrasounds of 20 kHz and, respectively, 1MHz frequency applied perpendicular to the deposition direction. Ultrasound generator was applied to the cathode. For obtaining ultrasounds of 1 MHz frequency we used a piezoelectric transducer. The thicknesses of studied samples were 1.8 µm, 3.2 µm and 9.7 µm respectively. The surface microstructure was investigated using an atomic force microscope (AFM). In order to investigate microstructure of the thin films we used XRD (X Ray Diffraction) method, TEM (Transmission Electron Microscopy), HRTEM (Height Resolution

Magnetic and microstructure properties for the Ni-Zn thin films electrodeposited in ultrasounds field

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Transmission Microscopy), SAED (Selected Area of Electron Diffraction).

3 Results and Discussion
I studied influence of ultrasounds power on the surfaces roughness and microstructure for different thickness of the thin films (different time of deposition). I analysed Ni-Zn thin films with thicknesses 1.8 µm, 3.2 µm and 9.7 µm corresponding at 1 min., 3 min., and 5 min. respectively, time of deposition.

Fig. 1 (a) presents the dependence of grain average area (S_m) on deposition time (thin films thickness) and on ultrasounds power. I notice that the minimum of S_m was reached for thin films with 3.2 µm thickness (3 min. time of deposition) and for 5 kW/m² ultrasounds power.

Fig. 1 (b) show the dependence of coercitivity (H_c) on deposition time (thin films thickness) and on ultrasounds power.

One can see in Fig. 1 (a) and (b) that the minimum of S_m corresponds to the maximum of H_c. We can obtain thin films with S_m minim and H_c maxim respectively for 5 kW/m² power ultrasounds and for 3 min. time of deposition. When S_m is minim RMS (root mean square) roughness is maxim. This aspect can be notice in Fig. 2, where we can see that the minimum of RMS roughness correspond for 5 kW/m² power of ultrasounds and for 3 min. time of deposition.

Fig. 2 the dependence of RMS roughness on deposition time (thin films thickness) and on ultrasounds power.

RMS roughness dependence on ultrasound power can be observed from AFM images for thin films with 1.8 µm (1 min. time of deposition) (Fig. 3).
Fig. 3 AFM images of Ni-Zn thin films electrodeposited in ultrasounds fields: (a) without ultrasounds, $R_q=394.53$ Å; (b) for 5 kW/m$^2$ ultrasounds power, $R_q=128.38$ Å; (c) for 10 kW/m$^2$ ultrasounds power, $R_q=231.21$ Å.

Fig. 4 shows SEM images for Ni-Zn thin films electrodeposited in ultrasound field with 5 kW/m$^2$ powers. We can notice that for thin films with greater thickness, the number of Ni grain increases and their size decreases. The increased number and the decreased size of Ni grains are due to ultrasounds action on deposition supra-voltage (crystallization supra-voltage) [9,10,11].

The use of ultrasounds leads to uniformity of grain size. Thin films with smaller grain size and greater uniformity are obtained by increasing the time of depositions, as we can see in TEM images (Fig. 5).
Fig. 5 TEM images of Ni-Zn thin films electrodeposited in ultrasound field with 5 kW/m$^2$ power; thickness for thin films: (a) 1.8 µm; (b) 3.2 µm; (c) 9.7 µm

Grain diameter distribution was approximated by a “Log Normal” function. Grain average diameter was of approximately 30 nm for 1.8 µm Ni-Zn thin films, of 6 nm for 3.2 µm thin films, and of 10 nm for 9.7 µm thin films (Fig. 6).

Ultrasound actions conducted to formation of new phases according to the power of ultrasounds applied. This behaviour can be observed in XRD pattern presented in Fig. 7. In this figure one may observe Ni$_5$Zn$_{21}$ and NiZn$_3$ phase formation.

Fig. 6 Grain diameter distribution function for Ni-Zn thin films electrodeposited in ultrasound field with 5 kW/m$^2$ power; thickness for thin films: (a) 1.8 µm; (b) 3.2 µm; (c) 9.7 µm
Coercitivity depends on the thin films microstructure because it is related to the grain size, RMS roughness and intern tensions of thin films respectively [12, 13]. Thus, for Ni-Zn thin films we can notice that the maximum of coercitivity occurs when the average surface of the grain is minimum (Fig. 1). We observe that for these thin films the average surfaces of grain (performed by AFM) is minimum for thin films electrodeposited in ultrasounds field with a power of 5 kW/m² for 3 min. time of deposition (d=3,25 µm) (Fig. 1 (a)). This notice is confirmed by TEM perform which shows that the average diameters of grain are the same with grain size by AFM performed.

In Fig. 1 (b) we can see that the maximum value of the coercitivity is for thin films electrodeposited in ultrasounds field with a power of 5 kW/m² for 3 min. time of deposition that corresponds for a minimum of grain average surfaces $S$ by Fig. 1 (a).

Another morphological parameter that determines changes of coercitivity is the RMS roughness of the thin films. Decrease of RMS roughness leads to the decreasing of coercitivity and if RMS roughness increases it leads to an increasing of coercitivity. This correlation between coercitivity and RMS roughness can be notice in Fig. 1(a) and Fig. 2. One can see that Ni-Zn thin films electrodeposited in ultrasound field have the highest RMS roughness when the power of ultrasound is 5 kW/m².

Coercitivity changes could be due to the stress in the film. Increasing of thin film thickness determines decreasing stress in the film and this determines the decreasing of coercitivity [14 - 18]. But, when the time of deposition in ultrasounds field increases it leads to bedded deposition which change the magnetic anisotropy of films.

Also, we studied influence of ultrasounds frequencies at formation of thin films electrodeposited in ultrasounds field. In Fig. 8 we show the dependence of the thin films coercitivity function of deposition time (different thin films thickness) for different frequencies of ultrasounds field applied to the electrolytic bath.

One can see in Fig. 8 coercitivity is approximately constant when thin films were electrodeposited without ultrasounds and in ultrasounds with 20 kHz frequency respectively, but when we used ultrasounds with 20 kHz frequency coercitivity is smaller then coercitivity for thin films electrodeposited without ultrasounds.

When we apply ultrasound with 20 kHz frequency at the electrolytic bath, nucleation speed is smaller then growth speed of crystals that leads to the obtain grain with large dimension that determine this decrease of coercitivity of thin films electrodeposited in ultrasounds with 20 kHz frequency comparative with thin films electrodeposited without ultrasounds [12].
Using ultrasounds with 1 MHz frequency, coercivity which depend by time of deposition it has values between values corresponding of thin films electrodeposited without ultrasounds and values corresponding thin films electrodeposited in ultrasounds with 20 kHz frequency.

For 2 minute time of deposition, nucleation speed is approximately equal with growth speed of the grain that leads to formation the grain with small dimension and formation the thin films with high coercitivity respectively, comparative with thin films electrodeposited without ultrasounds. When time of deposition is 4 minute the growth speed is bigger then nucleation speed that leads to obtain thin films with large dimension of grain and coercitivity small respectively, comparative with thin films electrodeposited in ultrasounds field with 20 kHz frequency.

4 Conclusion

The use of ultrasounds with different power on electrolytic bath leads to formation of polycrystalline thin films with greater uniformity of grain diameter. The increase of ultrasounds power determines the formation of new phases and the change of RMS roughness, respectively. Ultrasounds influence depends on the action time. The most important influence of ultrasounds is at 3 min. deposition time. Microstructure changes of thin films obtained in different power ultrasounds fields leads to changes in physical properties (electrical and magnetic properties) of these thin films. As an example, the decrease of grain size due to ultrasounds increasing power determines a rise of thin films coercitivity. The most important changes of microstructure and magnetic properties of thin films electrodeposited there are determined by ultrasounds with 1 MHz frequency.

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