Influence of the inert and active ion bombardment on structure of the transition metal thin films

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Abstract

The results of the experimental research of the inert (He, Ne, Ar, Kr, Xe) and active (O, N) ion impact on the transition metal structure are presented. Thin high-purity (99.999 at.%) films of nickel, chrome and iron were used in the experiment. The bombardment was realized under room temperature at high vacuum ($P < 1 \times 10^{-7}$ Pa) by a separated ion beam of $10–10^3$ keV. As a main result of the experiment, the full absence of crystal matrix changes was ascertained for all the transition metals irradiated by inert gas ions. The chemical nature of the crystal structure changes observed in transition metals being under active ion bombardment was found out too.

Keywords: Ion bombardment; Metal film structure

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1. Introduction

The metal microstructure research includes the study of grain pattern, availability of the preferred crystallographic orientation (texture), structure of grain boundaries, presence and distribution of second phases and so on.

The results of the experimental research of interrelation between electron diffraction reflex tailing (blurring) and microstructure changes in the metal films are presented in this work. The main attention was drawn to such parameters of the metal microstructure, as grain sizes in polycrystalline films and block sizes in single crystals. There are many data for the ion bombardment influence on microstructure of thin metal films [1,2] including nickel films [3] in contemporary publications, but these data do not agree and they are often conflicting. Even the question whether the grain size increases or decreases under ion irradiation has no unambiguous answer in these works. The mentioned data disagreement can be explained by the presence in these works significant divergences of such experimental conditions as ion energy, ion beam current density, temperature of the sample under irradiation and so on.

Here, our experiment results being free from the above pointed defects are presented. The experiments are carried out on setups of National Science Center "Kharkov Institute of Physics and Technology".

Polycrystalline and single Ni crystal films have been used in the present work. The most homogeneous films without defects or imperfections were

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selected for the experiment. The irradiation was realized by the used well separated He^+ ions with energies of 20 and 100 keV. Film packs (six films in one pack) were used for irradiation with 100 keV ions. The films were irradiated up to doze of 5×10^{17} and 1×10^{18} ion/cm^2 accordingly under either value of the ion energy. Single crystal films were irradiated to the same dozes. Both the bright-field and dark-field methods of the transmission microscopy were used in the experiment for studying the microstructure of the films.

To be convinced that the results obtained for nickel are representative for other transition metals it is necessary to spread the investigation over pure films of other metals. With the goal to do it in present work we have carried the investigation with pure films of Fe and Cr, which have typical characteristic of transition metals and already was studied earlier [4,5]. The main results of these investigations are given in the last part of this article.

2. Microstructure changes in thin nickel films being under the He^+ ion of middle energies bombardment

The investigations of the microstructure was carried out on polycrystalline Ni films with thickness of 100 nm by good separated 20 keV He^+ ion

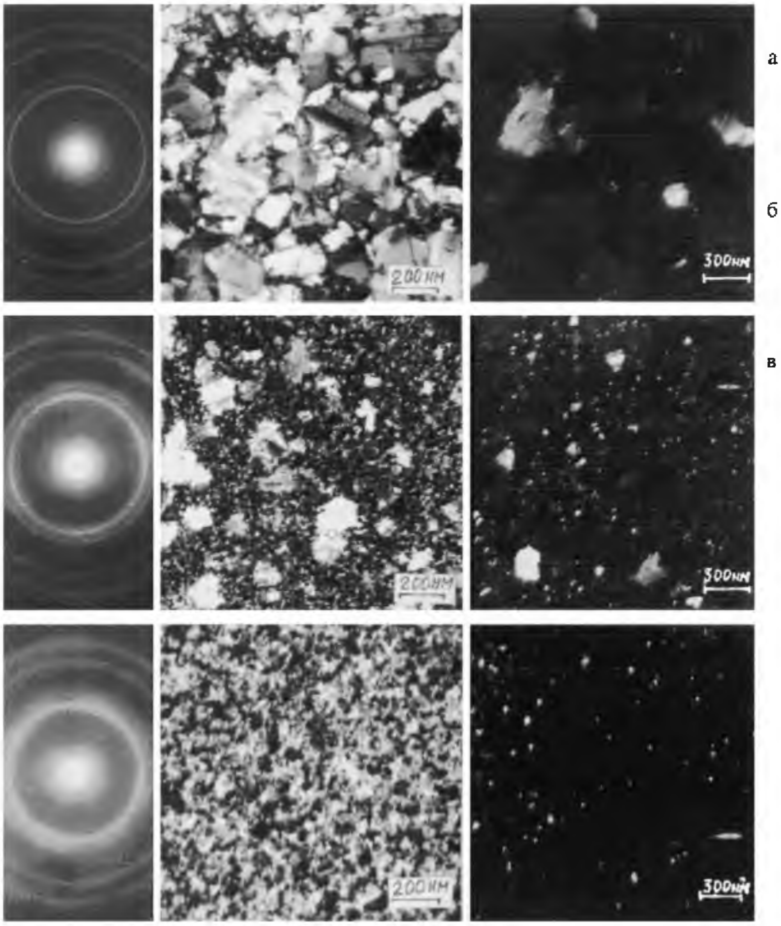

Fig. 1. Electron-diffraction pattern (on the left), the bright-field (in the middle) and dark-field (on the right) transmission electron micrographs obtained by the diffraction imagery on diffraction fringe (1 1 1) of initial Ni film (a) and films irradiated by 20 keV He^+ ions up to dose of 5×10^{17} (b) and up to 1×10^{18} ions/cm^2 (B).

beam with current density of (2–3) mkA/cm^2. Such a low current density was chosen to avoid appreciable warming of the film. The ion energy chosen is according to average projective path of the He ions into Ni $\overline{R}_p = 5944$ nm with profile half-width nm [6]. The bombardment pure polycrystalline Ni films by 20 keV He$^+$ separated ions do not change face-centered cubic latitude parameters, but significantly influence on its microstructure and surface morphology.

Electron transmission diffraction patterns and electron micrographs of the films obtained in bright-field and dark-field pictures is presented in Fig. 1. The dark-field pictures were got by the diffraction imagery on diffracting ring (1 1 1). In Fig. 2 the histograms of the microcrystalline size distribution for the above mentioned films are shown. The broad peak in polydisperse distribution with the maximum located in size value region 30–40 nm is observed for initial films. This distribution have a long "tail" aside big grain size values (up to 600 nm). As the result of irradiation by dose of 5×10^{17} ion/cm^2 the frame of grain size values was decreased from ~600 to 200 nm and maximum of size distribution was shifted to the region ~15–20 nm.

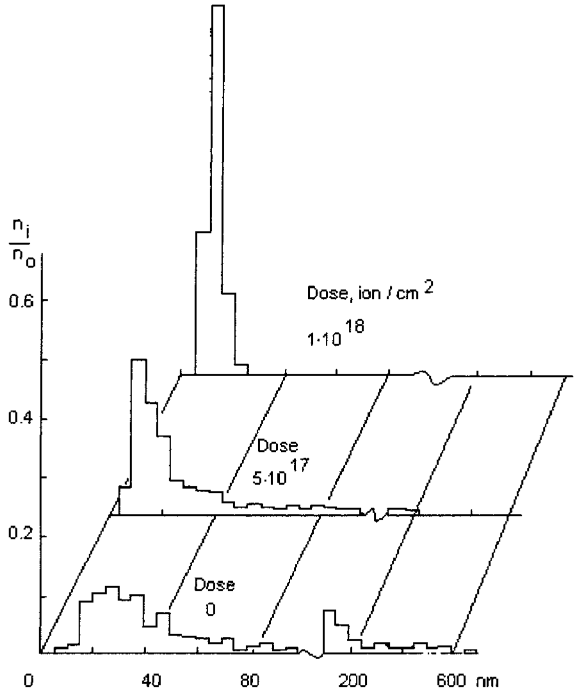

Fig. 2. Histogram of grain size distribution in polycrystalline Ni initial film (dose = 0) and after irradiation by 20 keV He$^+$ ions up to dose of 5×10^{17} and 1×10^{18} ions/cm^2.

The increasing of implantation dose up to 1×10^{18} ion/cm^2 leads to the further grain fragmentation and as the result to decreasing the average grain size to 10–15 nm and maximal size to value <30 nm. The distinct expressed correlation between grain breaking in Ni films and electron diffraction fringes blurring in electron transmission diffraction pattern for films irradiated by He$^+$ ions of 20 and 100 keV is observed. The authors of [7,8] tried to explain the diffraction fringes blurring as amorphous state effect. Nevertheless no data on behalf of such a prediction was alleged.

One can expect an appreciable changing of metal lattice constant under amorphous state formation. The data presented on the last paragraph do not confirm this. However, the effect of extremely strong grain breakage allow to explain the diffraction fringes blurring on electron-diffraction patterns. The data obtained testify that the grains with size of several nm are vanished in irradiated metal and the average grain size reachs actually about several nm, namely became close to wave length of diffracted electron of 100 keV energy. This circumstance can be primarily responsible for the blurring of diffraction fringes observed in [9].

Notice that data obtained for Ni films irradiated by He$^+$ ions under conditions of ion transmission and implantation testify that electrical resistance of the films increase monotonously of 3% and 10% accordingly under irradiation dose ~1×10^{17} ion/cm^2 and current density 0.1–0.5 μA/cm^2 at room temperature [10].

3. Structure changes in polycrystalline films of Ni under irradiation by hard ions Ne$^+$, Ar$^+$, Kr$^+$, Xe$^+$ and ions N$^+$, O$^+$

In principle, the behavior of mono- and polycrystalline Ni films under irradiation can differ. We have studied either of this two cases. The main results of researches on influence irradiation of high grade polycrystalline Ni by ions of all inert

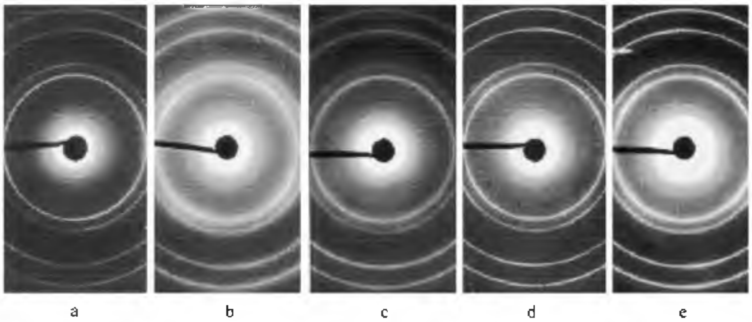

Fig. 3. Electron-diffraction pattern of Ni films source (a) and irradiated by inert gas ions: (b) 60 keV Ne^+, dose 2×10^{17} cm^{-2}; (c) 100 KeV Ar^+, dose 1.5×10^{17} cm^{-2}; (d) 50 KeV Kr^+, dose 1×10^{17} cm^{-2}; (e) 35 KeV Xe^+, dose 6×10^{16} cm^{-2}.

gases (excepting radon Rn) and by reactive gas ions N^+, O^+ are presented in this paragraph.

3.1. Irradiation of Ni films by ions of heave inert gases

The energy state estimations for various inert gas atoms in Ni lattice (matrix) was carried out theoretically in work [11] both for interstitial and substitutional atoms. These estimations predict the different behavior of the atoms of big (long) and small (short) radius. For example, a He atom generates a weak elastic strain field, being into either interstice or vacant lattice site. Whereas the Ar atom in interstice must generate such a strong elastic stress, that energy-optimal approach for Ar atom prove to force out the Ni atom in interstitial position to be as substituent. But the value of the elastic part of crystal latitude interaction energy turn out for this state much bigger than for the same state of He atom. The atoms of other inert gases, are close to Ar atoms by the latitude interaction characteristics, besides Ne, which is closer to He. Besides, the heave ion more effective generates the irradiation defects (damages) and the bound with they strain in metal lattice. Because of this we considered that absence of the phase transition under He^+ irradiation do not exclude its induction by heave inert gas ions. That is why we have carried out the experimental study of the Ni films irradiated by Ne^+, Ar^+, Kr^+, Xe^+ ions of different doses.

The energy of Ne^+ and Ar^+ ions was chosen so that the depth concentration profile have the maximum on depth near middle of film thickness and compose 60 and 100 keV, respectively. The choice of Kr^+ ion energy (50 keV) and of Xe^+ ion energy (35 keV) was defined by the possibilities characteristics of the used magnetic mass separator. The Ne^+, Ar^+, Kr^+, Xe^+ ion irradiation was carried out with doses from 5×10^{16} ion/cm^2 to dose of full film destruction by ions. In all these cases the same result was obtained: the full absence of phase change attributes. This facts are illustrated by electron transmission diffraction pattern of Ni films, irradiated by Ne^+, Ar^+, Kr^+, Xe^+ ions presented in Fig. 3. The irradiation lead only to tailing of the diffraction fringes in manner indicated in Fig. 3.

3.2. Irradiation of Ni films by reactive gas ions N^+ and O^+

The irradiation of polycrystalline Ni films as well as in case of monocrystalline films led to origination in the films new phases. At this rate the originating structure in each case are specified by chemical nature irradiating ion. The electron-diffraction patterns of Ni films irradiated by N^+ of 20 keV and by O^+ of the same energy are shown in Fig. 4. As may be seen from the diagram, in Ni films besides the reflexes of the Ni face-centered cubic latitude one can see also new phase reflexes.

The electron-diffraction patterns of Ni films undergo under N^+ irradiation absolutely other changes than under O^+ irradiation. Under N^+ irradiation in the electron-diffraction pattern the diffraction fringes system of hexagonal latitude

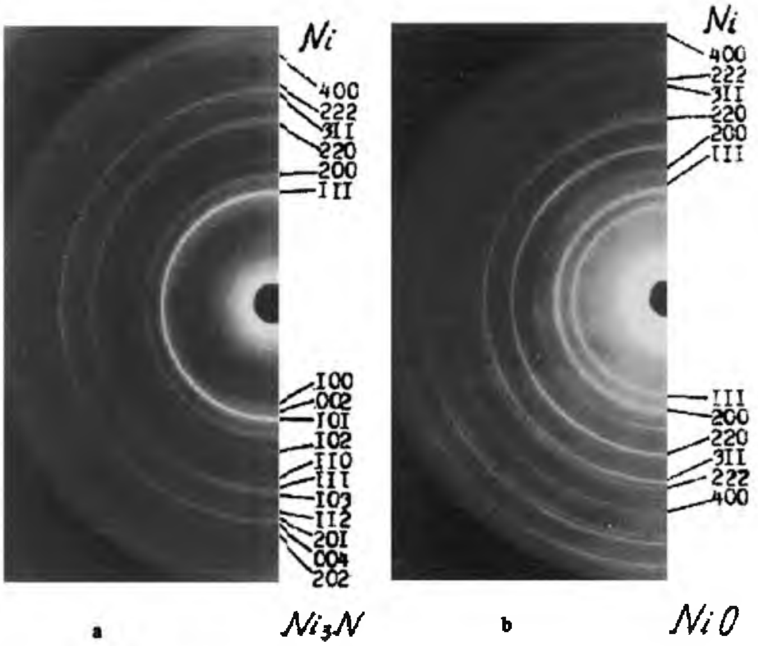

Fig. 4. Electron-diffraction patterns of Ni films irradiated by ions N^+ and O^+ of 20 keV: (a) dose 5×10^{17} cm^{-2}; (b) dose 3×10^{17} cm^{-2}.

appear in concert with source reflexes of the Ni face-centered cubic latitude. The result of this fringe system decryption presented in Table 1, point to initiation of hexagonal phase with parameters $a = 0.26 \times 10^{-7}$ cm and $c = 0.43 \times 10^{-7}$ cm, corresponding to hexagonal latitude of chemical $NiN_{0.33}$ [12,13].

Irradiation of (0 0 1)Ni single crystal film samples by O^+ ions of 20 keV upto dozes 1×10^{17}–3×10^{17} ion/cm^2 lead to initiation in electron-diffraction patterns a new system of reflexes, which are related to cubic latitude of NiO_x with lattice parameter $a = 0.414(1)$ nm (cubic latitude of Ni have a parameter $a = 0.3524(1)$ nm).

When the dose increase to 1×10^{18} cm^{-2}, the film crystal structure converse to the nickel oxide structure related to phase of NaCl tipe. The interfacial distances of Ni film irradiated by O^+ ions of 20 keV upto dose 3×10^{17} cm^{-2} are presented in Table 2.

In the electron-diffraction patterns of polycrystalline Ni films irradiated by O^+ ions unto dose 3×10^{17} ion/cm^2 the supplementary system of the diffraction fringes corresponding to latitude with lattice constant $a = 0.414$ nm (Table 2) appear on the background of the source diffraction fringes.

Table 1
The interfacial distances of nickel irradiated N^+ ions $E = 20$ keV, dose $= 5 \times 10^{17}$ cm^{-2}

Measure data d (nm)	Calculated lengths			
	Ni		$NiN_{0.33}$ [13]	
	hkl	d (nm)	hkl	d (nm)
0.2304	–	–	100	0.2304
0.215	–	–	002	0.2152
0.203	111	0.2035	101	0.2031
0.180	002	0.1762	–	–
0.157	–	–	102	0.1573
0.133	–	–	110	0.1330
0.127	–	–	111	0.1271
0.122	022	0.1246	103	0.1218
0.1135	–	–	112	0.1131
0.111	–	–	201	0.1113
0.1075	113	0.1063	004	0.1076
0.1015	222	–	202	0.1015
0.0896	004	0.1017	–	–
$a_0 = 0.35$ nm; $a = 0.2656$ nm; $c = 0.4301$ nm	$a = 0.352$ nm		$a = 0.4607$ $\sqrt{3} = 0.266$ nm; $c = 0.4304$ nm	

Table 2
The interfacial distances of nickel irradiated O^+ ions $E = 20$ keV, dose $= 3 \times 10^{17}$ cm^{-2}

Measure data *d* (nm)	Calculated lengths			
	Ni		NiO [13]	
	hkl	*d* (nm)	hkl	*d* (nm)
1	2	3	4	5
0.239	–	–	111	0.245
0.207	–	–	002	0.210
0.203	111	0.2035	–	–
0.180	002	0.1762	–	–
0.146	–	–	–	0.148
0.127	–	–	022	0.127
0.125	022	0.1246	113	–
0.120	–	–	–	0.121
0.1075	113	0.1063	222	–
0.1015	222	0.1017	–	–
$a_1 = 0.35$ nm; $a_2 = 0.414$ nm	$a = 0.352$ nm	$a = 0.419$ nm		

This phase appearance good agree with the initiation of NiO_x oxide [12,13], which have a cubical latitude of NaCl tipe.

4. Conclusions

The researches, carried out in this work with mono- and polycrystalline Ni films have shown at the first time, that the irradiation by ion of different nature leads to absolutely different results in respect to structure-phase changes in irradiated film. Namely, bombardment by ions of any inert gas generate no changes in crystallographic structure of nickel films, while irradiation by ions of reaction gas (N, O) leads to origination in the films of new phases, which defined by chemical nature of the ions.

The result obtained demolish the traditional conception of independence crystallographic changes originated in the metal films on nature irradiated ions. This conception was based on the experimental facts demonstrating that new phase formed in metal films under irradiation not dependent on nature projectile ions. But, as all further experience shows, the mentioned facts are the result of such experimental conditions as not enough high vacuum in the target chamber, not enough clean material of films, bad separated ion beam and so on. Under condition of sharply separation ion beam and using the most pure metal films. Really all named reasons was practically the same in different experiments, resulting in standard condition of new phases formation.

Therefore, our results obtained with used of pure Ni films contradict the data, published early and do not coincide with the physical notation of nature of the ion-induced structure conversions.

The results of our research on the irradiation of mono- and polycrystalline Ni films show, that the irradiation effect on Ni crystallography structure do not depend on ion energy in range 20–100 keV.

The source microstructure mono- and polycrystalline Ni films change under irradiation by inert gas ions in direction to block disorientation and grain fragmentation accordingly.

The results of the investigations ion irradiation influence on thin Fe and Cr film allow to generalize the data obtained for Ni films on transition metals.

The data obtained for Fe films, which suffer the polymorphous conversion from body-centered cubic arrangement to body-centered cubic one at temperature T_c, point out that the polymorphism do not impact on behavior of transition metals under ion irradiation.

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