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Structural Transformations in Ni at the Implantation C+ Ions

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Structural transformations in nickel films exposed to C+ ions were investigated through the use of electron diffraction and electron microscopy.

With an increasing exposure dose, there occurred a smooth transition of the FCC structure of Ni with lattice parameter a = 0.352 to the HCP structure of carbide Ni_3C with the lattice parameters a = 0.266 nm and c = 0.433 nm. The completion of the transition was observed once the implanted carbon concentration corresponding to the stoichiometry ratio of Ni_3C was attained, this giving evidence for the chemical nature of the structural change observed. However, recognising that atoms of the composite do not form chemical compounds, it is possible to draw a conclusion that atoms of carbon form hexagonal structure and promote reorganisation of atoms of nickel in structure HCP. Thus of introduction atoms carry out a prevailing role in formation of the composite structure.

Keywords: Nickel, Carbon, Electron diffraction, Structural transformations, Ion implantation.

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1. INTRODUCTION

The phases of interstitial formed as a result of interaction of atoms of transitive metals with atoms of smaller sizes, certainly, are the main product of ferrous metallurgy: their formation provides possibility of carrying out of training of a steel and reception of carbides. Besides, they present at a steel in the form of the harmful impurity which quantity is necessary for reducing therefore to a minimum.

As Jacobson and Westgren [1] have shown direct introduction of carbon in the fused nickel does not lead to carbide formation. As a result of this, for reception of connections of carbon with nickel [2] carried out annealing of a small powder of nickel in gas CO at temperature 550–600 K. The structure of the samples of nickel processed this way was hexagonal with lattice parameters a = 0.263 nm, c = 0.431 nm, c_h/a_h = 1.636 [2]. This structure of carbide of nickel Ni_3C was included into hand-books [3-7].

It is important to notice, that on diffraction pattern, received by X-ray spectrometry [1], are observed diffraction reflexes of hexagonal phases with lattice parameters a = 0.26 nm, c = 0.43 nm, and on diffraction pattern, received with electron diffraction investigation [2] besides diffraction reflexes of the HCP structure with lattice parameters a = 0.26 nm, c = 0.43 nm are presented additional diffraction reflexes, some of them authors attribute to a superlattice of atoms of carbon, and others carry to forbidden, i.e. not found an explanation. Nagacura [2] emphasizes that disseminating ability of atoms of carbon concerning atoms of nickel for electrons more effectively more than twice in comparison with X-rays and, because of it, electronic diffraction is more preferable to studying of structure of carbides.

It is not enough just only data about structure of arising phases for judgment about the nature of phase transitions. For the well-founded conclusion about the

nature of observable phases it is necessary to have the data about stoichiometry of a component at the moment of end of structural transformation. Besides, considerable scientific interest represents the studying kinetics of formation and disintegration of carbides of metals (including, nickel carbide). From experience of the previous works [8-9] is following that studying of phase conditions most correctly at complex use of the methods providing high extent of cleanliness of samples, the dosed out introduction of impurity of introduction and electron diffraction investigation in a wide range of temperatures.

In the given work it is realized of experiments on studying of phase transformations in system Ni-C, investigated kinetics formation phases in nickel by ion implantation of carbon.

2. EXPERIMENTAL PROCEDURES

For experiments, thin polycrystalline Ni films (δ = 100 ±10 nm) were produced by electron bombardment evaporation of a Ni single crystal in vacuum (3×10^{-6} Pa) onto KCl crystal substrates. The films were taken off the substrates in distilled water and were picked out onto $\varnothing$ 3 mm nickel discs with a $\varnothing$ 1.2 mm hole at the canter. For recrystallization and removal of impurities from the surface, the films were annealed in vacuum 3×10^{-6} Pa at T~700 K for 10 min. The purity of such prepared films was no different from the purity of the standard Ni single crystal [9-10] as revealed from the Auger analysis. The average size of grain was 30–40 nm.

The samples were exposed to different doses of 65 keV C+ ions at a current density of 3 $\mu A/cm^2$ using a "Skif" device [11].The ion energy was chosen so that the peak of the implanted nitrogen concentration profile should fall on approximately the half-thickness of the film. The crystal structure of initial and irradiated

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films was examined by electron diffraction method with an operating voltage of 100 kV. The samples implanted by various doses of ions C^+, subjected to annealing with constant speed ~2 К×s^{-1} from room temperature to 1100 K in a column of an electron microscope. The photographing of electron diffraction pattern was simultaneously carried out at various temperatures that gave the chance to get the data about the structure of observable phases and temperature ranges of their existence.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Nickel films were bombardment with ions of carbon to doses of 1×10^{16}, 3.7×10^{16}, 5×10^{16}, 1×10^{17}, 2×10^{17}, 3×10^{17}, 4×10^{17} and 6×10^{17} C/cm^2. The electron diffraction data have demonstrated the dependence of the Ni films structure on the implantation dose. When annealing the films the kinetics of structural transformations was studied.

Electron diffraction pattern of initial polycrystalline film of nickel is presented on fig. 1. There is the system in electron diffraction pattern from six visible rings, corresponding FCC structure of pure nickel with lattice parameter a = 0.352 nm is observed. Decoding of this electron diffraction pattern is resulted in tabl. 1.
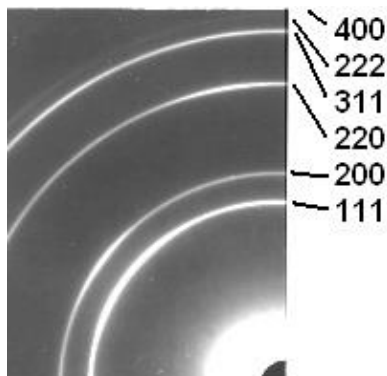

Fig. 1 – Electron diffraction pattern of film Ni

There are resulted electron diffraction pattern (EDP) of the nickel films of irradiated with various doses of ions C^+ on fig. 2. The studying of dependence of nickel films structure from a dose of the implanted

carbon allows tracking the kinetic of occurrences of diffraction reflexes of new phases which are formed in the course of increase of carbon concentration. For the dose 1×10^{16} C/sm^2 EDP of the irradiated sample is almost identical to electron diffraction pattern of not irradiated sample. The first signs of occurrence of a new phase are observed on EDP of the sample irradiated with dose 3.7×10^{16} C/sm^2 at which appear: the first additional ring (the first ring of a triplet (00.2) HCP-phases) and diffusive area in zones is closer than the first (111), the second (200) and the third (220) rings of an initial matrix of nickel which become more accurate at increase in a dose to value 5×10^{16} C/sm^2

Table 1 – Diffraction data for nickel

$d_{exp.}$, nm	Ni	
	hkl	d_{theo}, nm
0.203	111	0.2034
0.176	200	0.1760
0.125	220	0.1244
0.106	311	0.1061
0.102	222	0.1017
0.081	400	0.0808
a_{Ni}=0.352	a_{Ni}=0.3524	

There are observed additional diffraction HCP-phase reflexes on EDP of the samples of nickel irradiated with dose 1×10^{17} C/sm^2 are: the third ring of a triplet (10.1), a ring (11.0) and a weak ring on intensity (10.2). It is necessary to notice that there are two well visible close located diffraction rings of HCP-phase: (200) nickels and the third ring (10.1) on EDP. The further increase in a dose to value $(2–3)\times10^{17}$ C/sm^2, is accompanied by intensity growing of diffraction reflexes of the HCP-phase and intensity reduction of diffraction reflexes of the FCC-phase (nickel). Diffraction reflexes of nickel remain on electron diffraction pattern up to a dose 3×10^{17} C/sm^2 (fig. 2f, see), and at a dose 4×10^{17} C/sm^2 on EDP are visible diffraction reflexes only of a HCP-phases with lattice parameters a = 0.265 nm, c = 0.23 nm (fig. 2g, see).

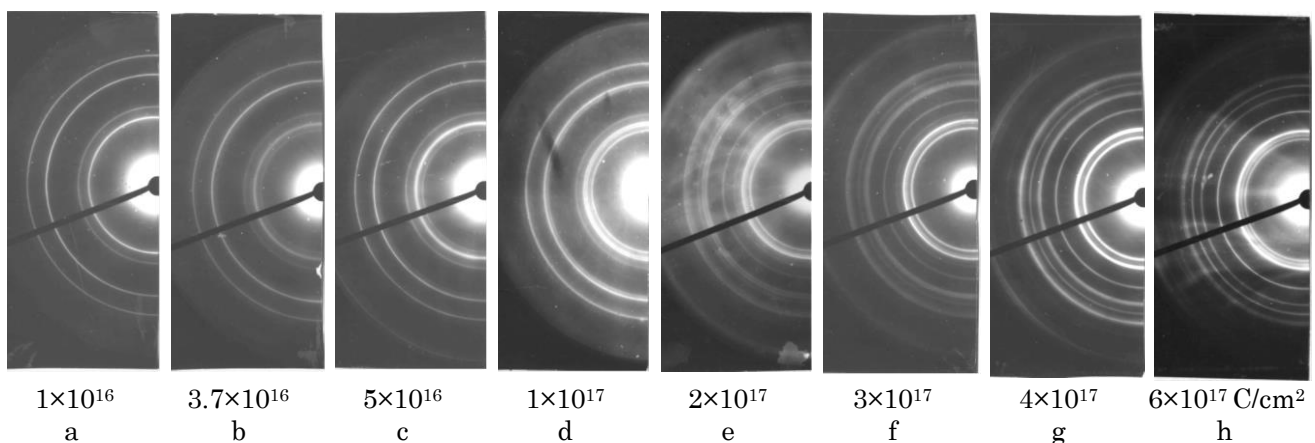| 1×10^{16} | 3.7×10^{16} | 5×10^{16} | 1×10^{17} | 2×10^{17} | 3×10^{17} | 4×10^{17} | 6×10^{17} C/cm^2 |
| a | b | c | d | e | f | g | h |

Fig. 2 – Electron diffraction patterns of films Ni irradiated with various doses of carbon ions

The estimations have shown that at this dose of the implanted carbon the nuclear relation of the components of the sample (nickel and carbon) almost precisely corresponds to parity C:Ni≈1:3. Thus concentration of the implanted carbon is ~33 at % and corresponds to stoichiometry of carbide of nickel Ni_3C. So, the full structural transformation into the HCP-phase occurs only at achievement of demanded for this purpose of stoichiometry parities of components. At doses lower than 4×10^{17} C/sm² when the concentration of the implanted carbon is insufficient for maintenance of stoichiometry of components 1:3, on electron diffraction pattern, along with HCP-phase reflexes (Ni_3C) are observed reflexes FCC of nickel structure (fig. 2f; see).

The analysis of electron diffraction pattern of the samples implanted by ions of carbon by doses 3×10^{17} sm² and 4×10^{17} C/sm² (look fig 2f and 2g, tabl. 2) and has shown absence of an average ring of a triplet of hexagonal structures (Ni_3C) at doses 3×10^{17} C/sm² and lower. It testifies that hexagonal structure of Ni_3C is formed in a kind of similar to graphen hexagonal planes with unsteady distance between them – parameter **c**. Only after achievement of stoichiometry Ni_3C the parameter **c** is accurately shown, i.e. the distance between hexagonal planes.
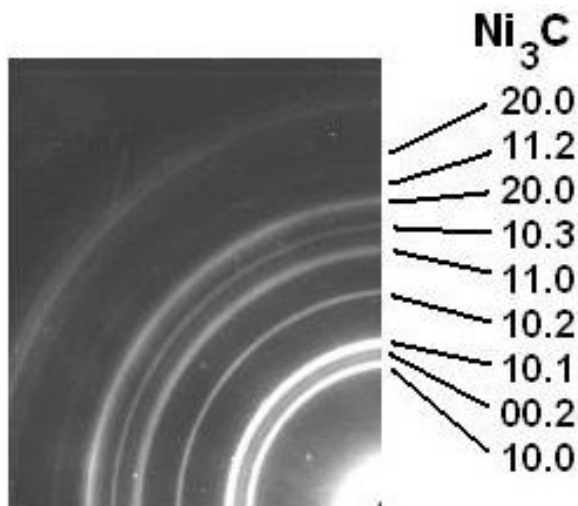

Fig. 2g – Electron diffraction pattern of film Ni irradiated with ions C⁺ by a dose 4×10^{17} C/sm²

Smoothness of transition of FCC structure of nickel with growing of a dose of introduced carbon in the HCP-phase and end of transition in carbide of nickel Ni_3C only after achievement by demanded stoic-?iometry of carbon concentration testifies about *the chemical nature of observable structural change*. However, recognising that atoms of the composite do not form chemical compounds, it is possible to draw a conclusion that atoms of carbon form hexagonal structure (graphene planes in the environment of nickel atoms) and promote reorganisation of atoms of nickel in structure HCP. Thus of introduction atoms carry out a prevailing role in formation of the composite structure.

Let's notice that formation of layers graphene served at high-temperature implantation of carbon ions in nickel films in work [12].

At dose 6×10^{17} C/sm² when concentration of the implanted carbon exceeds the stochiometry of carbide of nickel Ni_3C, on electron diffraction patterns along with diffraction HCP-phase reflexes are observed diffraction reflexes of the carbon having hexagonal structure of graphite with parameter a = 0.3642 nm. It testifies to presence at the sample of allocations of the free carbon which has not formed a chemical compound with nickel. There are not revealed any other structures and superstructural reflexes on electron diffraction patterns.

Table 2 – The measured and settlement sizes d_{hkl} for nickel implanted with carbon ions with energy 65 keV and dose 4×10^{17} C/sm²

$d_{exp.}$. nm	Ni_3C	
	hkl	$d_{theo.}$ nm
0.228	10.0	0.2281
0.216	00.2	0.2156
0.202	10.1	0.2019
0.157	10.2	0.1573
0.133	11.0	0.1323
0.122	10.3	0.1221
0.114	20.0	0.1142
0.113	11.2	0.1128
0.111	20.1	0.1108
a_{Ni_3C}= 0.265 c_{Ni_3C}= 0.43	a_{Ni_3C}= 0.265 c_{Ni_3C}= 0.43	

On the basis of the data received the crystal structure hexagonal lattices with stoichiometry Ni_3C (fig. 3 see).
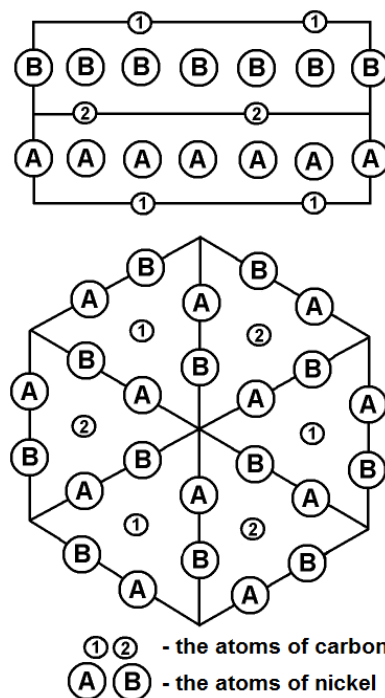

Fig. 3 – Crystal structure hexagonal structure with stoichiometry Ni_3C

4. CONCLUSIONS

1. With an increasing exposure dose, there occurred a smooth transition of the FCC structure of Ni with lattice parameter a = 0.352 to the HCP structure with the lattice parameters a = 0.266 nm and c = 0.433 nm.
2. The completion of the transition was observed once the implanted carbon concentration corresponding to the stoichiometry ratio of Ni_3C was attained, this giving evidence for the chemical nature of the structural change observed. However, recognising that atoms of the composite do not form chemical compounds, it is possible to draw a conclusion that atoms of carbon form hexagonal structure and promote reorganisation of atoms of nickel in structure HCP. Thus of introduction atoms carry out a prevailing role in formation of the composite structure.
3. Exceeding of stoichiometry Ni_3C is accompanied by occurrence of free carbon (not forming chemical compound with nickel) with graphite structure in nickel films.

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