The Formation of Nanoclusters in Metals by the Low-Energy Ion Irradiation in Glow Discharge Plasma

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Abstract – The goal of this paper is to show the results of the experimental studies of the formation of nanoclusters in metals by the low-energy ion irradiation and computer simulation of nonlinear effects on an atomic scale.

The subjects of the investigation were polycrystalline armco-iron and instrumental steels. All samples were irradiated by low-energy ions of residual gases in discharge plasma. The fine dislocation structure of the samples was being studied using the transmission electron microscopic method. We showed that the process of low-energy influence led to the formation of a complex multilayer structure in the near-surface area. There were the layers with the amorphous structure, a microcrystalline and nanocrystalline structure. The low-energy ion irradiation led to a change of physical and mechanical properties of the irradiated materials. It is necessary to emphasize that samples behavior depends on the time elapsed after stopping the irradiation.

These modifications in materials could be understood within the conception of active self-organizing processes in crystal lattices. We showed by a computer simulation that nonlinear oscillations were excited in the system of coupled atomic oscillators in crystal lattices, which resulted in the formation of nanoclusters.

1. Introduction

Investigations of nanodimensional systems are most dynamically developing field in the modern physics. Effective increase in operating characteristics and functional complexity of constructional materials is possible on the basis of the formation of nanodimensional complexes and clusters in materials as well as nanosurface layers. Developing nanotechnologyes, especially in the field of new materials designing, it is important to take into consideration that many problems may be solved on the basis of well studied and widly used metods of modification of solid structures by charged accelerated beams [1–3].

In papers [4–7] it was shown that nonlinear effects take place during interaction between charged particles and irradiated surface of crystal materials. These effects become one of underlying reasons for self-organization of irradiated materials that results in their deep modification, often unexplained in the course of classic solid-state physics. This modification is strongly observed after low-energy ion irradiation in glow-discharge plasma. A decrease in ion energy up to 1 keV leads to a great increase in the depth of modified layer of the irradiated materials. In fact, related to long-range effect bulk modification occurs. Bombardment of solid surfaces by low-energy ions leads to nonlinear fluctuations of atom oscillators of crystal latties. As a result new metastable and long-lived structures form and nanodimensional structures deserve more attention among of them.

The main aims of this paper are the following:

– to show using computer simulation how nanocrystal structures may be formed in solids by low-energy ion irradiation in glow-discharge plasma;
– to show how structure of materials with already formed nanodimentional clusters may be modified by low-energy ion irradiation in glow-discharge plasma.

2. Experimental and model calculation

Polycrystalline samples of armco-iron with the average grain size of 20 μm were placed into a specially constructed plasma generator and were exposed to glow discharge plasma. The samples had the form of cylinders with 10 mm in diameter and 12 mm in height. They were exposed to irradiation by ions of residual gases of vacuum (nitrogen, oxygen, hydrogen, etc.). The ion energy depended on the voltage in the plasmatron and did not exceed 0.8–2.5 keV. The current in the plasmagenerator was 40–50 mA. Barometric pressure of residual gases in the plasmagenerator chamber was 5.3 Pa. Irradiated dose was $2 \cdot 10^{17}$ ion$\cdot$cm^{-2}. The temperature of the specimens was controlled during the irradiation process and did not exceed 343 K.

The fine structures of materials were studied layer-by-layer using the transmission electron microscopy method.

The calculation experiment was made by a molecular dynamics method.

We chose Morse potential for armco-Fe as the potential of atomic interaction

$$U(r) = J\left\langle \exp[-2\alpha(r-r_0)] - 2\exp[-\alpha(r-r_0)]\right\rangle, \quad (1)$$

where J and α are parameters of the dissociation energy of a couple of atoms and the degree of the potential unharmonicity, respectively; $\Delta r=(r-r_0)$ is displacement from the equilibrium position. Expanding the potential (1) in a Taylor series and taking advantage of the well-known relationship we obtain:

$$F = -\frac{dU(r)}{dr} = -K\Delta r + A\Delta r^2 - B\Delta r^3 + C\Delta r^4 - D\Delta r^5, \quad (2)$$

$$K = 2\alpha^2 J, \quad A = 3\alpha^3 J, \quad B = 2.3\alpha^4 J,$$
$$C = 1.25\alpha^5 J, \quad D = 1.1\alpha^6 J,$$

where K, A, B, C, D are coefficients of elasticity, quadratic and cubic nonlinearity and coefficients of nonlinearity of the fourth and fifth orders, respectively.

Within the investigation a special model for calculating the atom displacement of the crystal lattice under the influence of external low-energy ion irradiation was developed. It was based on the conception of three-dimensional lattice as a nonlinear atom chain system. It is in this model calculations that in three-dimensional and planar (two dimensional) variants using classical dynamic equation were made. The accuracy of this model and the results of calculations were checked during extracting from three-dimentional lattice one atom chain which can be described by the equations given in this paper and in which errors in calculations were minimal.

Thus, for the chain of n – coupled oscillators the system of equations can be written:

$$\begin{cases} m\dfrac{d^2x_1}{dt^2} = -K'x_1 + Ax_1^2 - Bx_1^3 + Cx_1^4 - Dx_1^5 + \\ +K(x_2-x_1) - A(x_2-x_1)^2 + B(x_2-x_1)^3 - \\ -C(x_2-x_1)^4 + D(x_2-x_1)^5 - \beta'\dfrac{dx_1}{dt}, \\ m\dfrac{d^2x_i}{dt^2} = -K'(x_i-x_{i-1}) + A(x_i-x_{i-1})^2 - \\ -B(x_i-x_{i-1})^3 + C(x_i-x_{i-1})^4 - D(x_i-x_{i-1})^5 + \\ +K(x_{i+1}-x_i) - A(x_{i+1}-x_i)^2 + B(x_{i+1}-x_i)^3 - \\ -C(x_{i+1}-x_i)^4 + D(x_{i+1}-x_i)^5 - \beta\dfrac{dx_i}{dt}, \\ m\dfrac{d^2x_n}{dt^2} = -K(x_n-x_{n-1}) + A(x_n-x_{n-1})^2 - \\ -B(x_n-x_{n-1})^3 + C(x_n-x_{n-1})^4 - D(x_n-x_{n-1})^5 - \\ -K'x_n + Ax_n^2 - Bx_n^3 + Cx_n^4 - Dx_n^5 - \beta'\dfrac{dx_n}{dt}, \end{cases} \quad (3)$$

where x_i, i=1,...,n is displacement of i-th oscillator from the equilibrium position; K', K are coefficients of elasticity in boundary and internal areas, respectively; β', β are damping factors in boundary and internal areas. Coefficients K, A, B, C, D have been calculated using the parameters of Morse potential [5] for armco-Fe.

The equation system (3) was solved by means of the Runge-Kutta method.

A molecular dynamics method has been applied for calculating the evolution of atom ensembles in lattices of different dimensions using the equations of classical dynamics. The dependence of each atom displacement on time passed after stopping the ion bombardment was investigated.

The main task is to achieve the excitation of nonlinear oscillations in the system and to observe stabilization process of lattices after ceasing of external irradiation. The amount of the energy transferred from the impinging ion to the crystal atom is determined by classic equations given in [8]. Moreover, the initial energy must be less than the energy needed to form point defects in crystals. It is important that the atom chain should not be broken as a condition for excitation of nonlinear oscillations in the chain.

We studied Born-Mayer's, Tode's, Johnson's, Lindhard's potentials using this scheme. We showed that K, A, B, C, D coefficients varied with the variation of the potential but for strongly nonlinear medium (for real crystals) many valleys potentials are more appropriate. The quantity and the depth of additional valleys depend on the choise of the potential and its specific parameters.

3. Results and discussion

It had been shown earlier in [4–7, 9] that after low-energy ion irradiation modification of materials was observed up to the depth of 10 mm from the irradiated surface. That result was described as a "long-range effect". This is actually a bulk modification. It had been observed that the decrease in ion energy from 2.5 keV to 1 keV led to the increase in the depth of the modified layer [7]. During the irradiation, the samples did not experience either thermal or mechanical stresses, though they revealed a dislocation structure corresponding to the strained state even in a large depth from the irradiated surface [9]. There were formed cell, cell-net and even band dislocation structures, the macroscopic dimensions of irradiated materials remaining invariable.

In paper [4] using the transmission electron microscopic method, we observe that the complex multilayer heterogeneous nanometric structure of a "sandwich" type is formed at near-surface layers (0–1 μm) of irradiated armco-iron. Ultrathin layers that were formed during the irradiation as well as localized nanocrystals have nanodimensions.

In the present paper using computer simulation the possibility of the formation of nanocrystal structures in metals exposed by low-energy ion irradiation

in glow discharge plasma is shown and nonlinear effects caused by this interaction have been studied.

Fig. 1 shows the diagrams of local external disturbances of a section of an ultra-thin crystal film. Fig. 1a shows the diagram of external disturbances as the result of interaction between accidental "ions rain" (plasma) and the surface of the thin film (target atoms were given random impulses from falling ions and they displaced along *X*, *Y*, *Z* axes). Fig. 1, *b* illustrates the initial condition when an arbitrary atom on the surface (N 341) was given $m\frac{dx}{dt}$ impulse from a falling low-energy ion. For the convenience we shall refer to the ions in crystal lattices as "atoms" or "atomic oscillators".

It is supposed that the external influence energy is the energy for which the initial displacementt of lattice atoms is very small and the atoms which had been given impulses did not leave the chain.

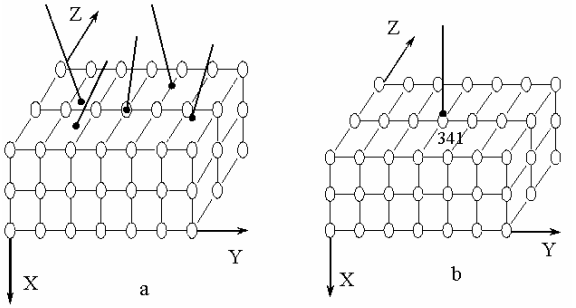


Fig. 1. Scheme of interaction between a falling ion and crystal thin films a) random "ions rain", b) single ion impact

We showed that in the system of coupled oscillators nonlinear oscillations are excited. The process of the propagation of nonlinear oscillations embraces the overall volume of the crystal. The time of stabilization is almost by 3–4 orders higher than that of ordinary atom relaxation.

Fig. 2 illustrates the dependence of atom displacement along the X-axis on the time elapsed after stopping the external influence. It is seen that atom N 341 of the lattice which initially received a small displacement by the external low-energy influence, as a result of collective nonlinear oscillations of all atom oscillators of the crystal lattice displaces very far from the initial equilibrium position at the time moment considerably exceeding the time of standard atom relaxations of metastabe long-living structures in the former target ordered structure.

Fig. 2 underscores that the time elapsed after stopping the irradiation of crystal is by three orders higher than that of ordinary relaxation but the lattiece has not been stabilized yet. Our calculation experience allows us to conclude that it will never return to its initial state and it is an element of new structures in crystal (probably with nanodimentions).

Fig. 3 illustrates the results of a numerical experiment in the investigation of a relaxation process in one-dimensional nonlinear atomic chain in the case that its first atom receives an impulse from an external ion impact.

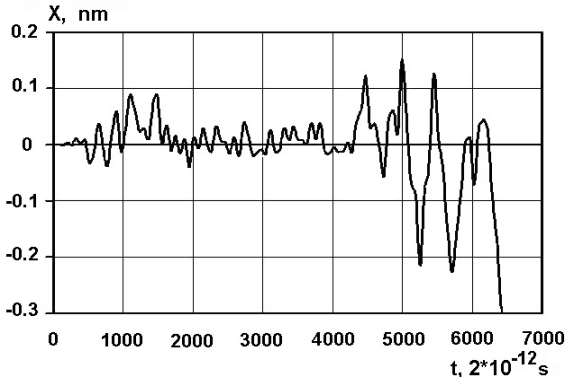


Fig. 2. Dependence of atom displacement (atom No 341) along the X-axis on the time elapsed after stopping the external influence for quite a long time

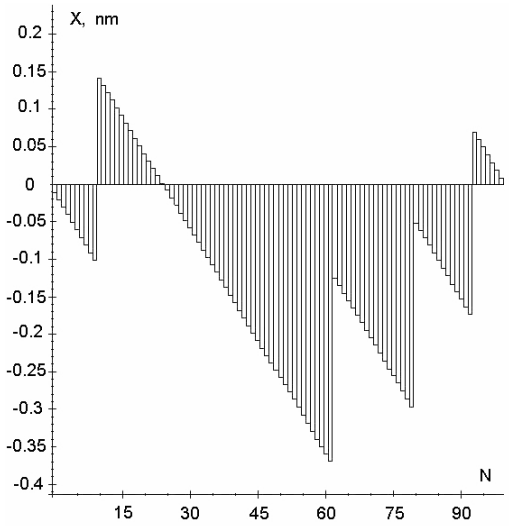


Fig. 3. Displacement of 100 atoms of the excited nonlinear atomic chain along the X axis at the time of stabilization. Y-axis represents atom displacement, X-axis shows atom number in the nonlinear chain

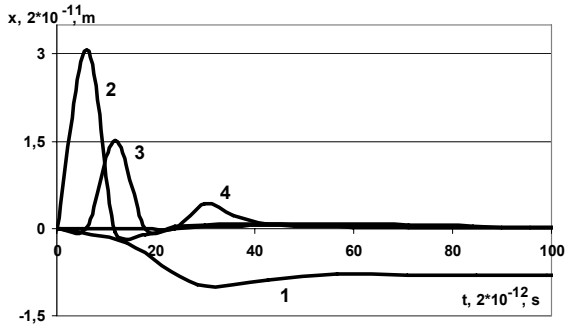
Nonlinear oscillations become excited in the chain along the X axis and as a result the atoms become stabilized in new positions, which results in the formation and development of new metastable atomic groups (nanoclusters). The time of stabilization is very long. It specifically depends on rigidity of atomic bondings in lattices (nonlinear coefficients are based on them) and on the value of ion energy of external irradiation.

The period of the lattice inside the clusters does not correspond to the initial one, some clusters are separated with areas having negative atom density (for example, N 10 and N 11, N 93 and N 94 atoms).

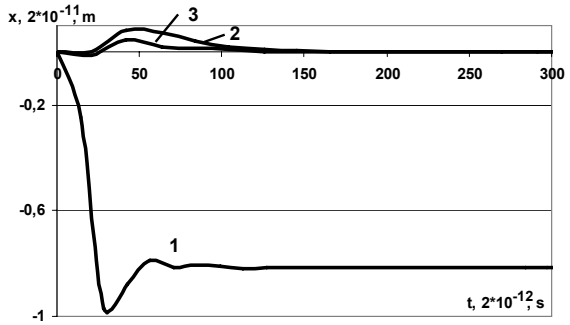
It is clusters that provide new complexes of physical and mechanical properties for lattices (irradiated materials). For absolute interpretation it is desireable to take into consideration that the initial potential of the lattice is also constantly 'deformable', i. e. new long-lived structures do not correspond to the 'old' potential, therefore new lattice 'periods' appear inside clusters.

Following the main aim of this paper that is to show how nanocrystal structures in solids may be formed by low-energy ion irradiation, we focused our attention on initial processes in nonlinear atom chains after the first atom gained impulse from ion impact. Either homogeneous chains with constant interatomic distance or chains with imbedded clusters were exposed to low-energy ion impact.

Fig. 4, *a* shows initial stages of atom displasment in crystal lattiece with cluster. For comparison the similar graph for homogeneous chain is presented in fig. 4, *b*.



a



b

Fig. 4. Dependence of atom displacement (1 – atom N 1, 2 – atom N 5, 3 – atom N 25, 4 – atom N 35) along the X-axis on the time elapsed after stopping the external influence: a – for the chain with imbedded cluster; b – for homogeneous nonlinear atom chain

It is necessary to notice the following peculiarities:

1) Atom displacement into cluster is much bigger than that in homogenious chain without clusters (compare curve N 2 in a and b).
2) Atom displacement outside of cluster in clustered chain is also much bigger than that in homogeneous chain without clusters (compare curve N 3 in a and b).
3) Nanoclusters are stable structural formations in nonlinear atom chains.
4) Nanodimensional clusters considerably change physical, chemical and mechanical properties of solids.

Conclusions

1) Low-energy ion irradiation of solids in glow discharge plasma leads to the formation of complex, multilayer nanocrystalline structures in near-surface layers and nanocluster structures in the irradiated volume. These changes can not be explained withing the framework of the classical physics of radiation damages of solids.
2) Computer simulation (using a molecular dynamics method) of nonlinear oscillations in atom oscillator systems of crystal lattieces after their low-energy ion irradiation showed the possibility of nanostructures formation and their stability.
3) Low-energy ion irradiation in glow-discharge plasma may be used to develop new hardening technologies of metals and alloys on the basis of the formation of nanoelements in them.

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