Available online at www.sciencedirect.com
ScienceDirect
Surface & Coatings Technology 201 (2007) 8552–8556
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Formation of nanostructures in metals by low-energy ion irradiation

I.V. Tereshko [a], V.V. Abidzina [a,*], I.E. Elkin [b], A.M. Tereshko [a], V.V. Glushchenko [a], Semfira Stoye [c]

[a] *Belarusian - Russian University, Prospect Mira 43, 212005 Mogilev, Belarus*
[b] *KAMA VT Plc. Research and Production Enterprise, Karl Libknecht Str. 3a, 212000 Mogilev, Belarus*
[c] *Noble Products, Clara Zetkin-Str. 34, 06862 Roslau, Germany*

Available online 12 March 2007

Abstract

The purpose of this paper is the study of nanostructure formation in metals by low-energy ion irradiation and computer simulation of nonlinear effects in crystal lattices on an atomic scale. Polycrystalline armco-iron and instrumental steel samples were irradiated by low-energy ions of residual gas in discharge plasma. The fine structure of the samples was studied by transmission electron microscopy. Computer simulations of the self-organizing processes induced by interaction of the low-energy ions with the crystal lattice surface were performed by means of a molecular dynamics method. We show that the process of low-energy irradiation results in the formation of complex multilayer structures in the near-surface region. There are layers with amorphous, microcrystalline and nanocrystalline structures. The formation of atomic clusters with nanometrical dimensions, running autosolitons, long-lived undamped oscillations in local areas were observed. Such modifications in materials can be understood by the concept of active self-organizing processes in crystal lattices, where the energy transition from a vibrational mode to a translational mode takes place. Low-energy ion irradiation results in a change in the physical and mechanical properties of the irradiated materials.

Keywords: Nanostructures; Nonlinear effects; Computer simulation; Self-organizing processes

1. Introduction

Nanostructures have typical sizes of less than one hundred nanometers and more than 1 nm. There are 0-D (zero-dimensional), 1-D (one-dimensional) and 2-D (two-dimensional) nanostructures. These are nanoparticles, nanowires and ultra thin films, accordingly. It is very important to focus on the synthesis and fabrication of nanostructures and nanomaterials. In particular, the interaction of energetic beams with matter forms the basis of a wide range of the processes that are used to form nanostructures for electronics and optoelectronics. Electron beam lithography, plasma etching and deposition, ion implantation are striking examples of such interaction [1–3].

There are very many books and detailed reviews concerning the interaction of charged particles with the surface of solids [4,5]. It is very important to understand the mechanism of interaction between solids and their surroundings through their surface to improve the technologies for making nanostructures, in particular, thin films. One should know structural, chemical and electronic properties of solid surfaces and interfaces for that. Also, it is necessary to take into account nonlinear effects that take place in ion or electron beams interaction with the irradiated surface of materials.

Nonlinear effects have been observed in low-energy ions interaction with the surface of solids [6,7]. In these papers we have shown that a decrease in ion energy to 1 keV leads to an increase in the depth of the modified layers. This is actually a bulk modification, which is referred to as a "long-range effect". This effect could be understood with the concept of active self-organizing processes in crystal lattices. Low-energy ion bombardment of a crystal lattice leads to nonlinear oscillations of atomic oscillators, which can result in the formation of new structures of the lattice.

The purpose of this paper is to show that nanocrystalline structures in samples of armco-iron are formed by low-energy ion irradiation and to study nonlinear effects induced by this interaction by a computer simulation method.

2. Experimental and model calculation

Polycrystalline samples of armco-iron with average grain size of 20 μm were placed in a specially constructed plasma generator and exposed to gas discharge plasma. The samples

* Corresponding author. Tel.: +375 296 466821; fax: +375 222 225518.
E-mail address: obidina@tut.by (V.V. Abidzina).

0257-8972/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2006.03.056

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 plasma generator was 40–50 mA. Barometric pressure of residual gases in the plasma generator chamber was 5.3 Pa. Irradiated dose was 2×10^{17} ion 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. For that, the irradiated samples were cut into thin plates (0.2 mm) by an electrosparking machine at a given distance from the irradiated surface. Then, foils were prepared from the obtained specimens by the electrolytical method using the standard technique. The investigation was made using EM-125 and TESLA BS-540 electron microscopes.

The calculation experiment was made by a molecular dynamics method. We chose a Morse potential for armco-Fe as the potential of atomic interaction

$$U(r) = J\langle \exp[-2\alpha(r-r_0)] - 2\exp[-\alpha(r-r_0)]\rangle \qquad (1)$$

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:

$$F = -\frac{\mathrm{d}U(r)}{\mathrm{d}r} = -K\Delta r + A\Delta r^2 - B\Delta r^3 + C\Delta r^4 - D\Delta r^5 \qquad (2)$$

$$K = 2\alpha^2 J,\ A = 3\alpha^3 J,\ B = 2.3\alpha^4 J,$$

$$C = 1.25\alpha^5 J,\ D = 1.1\alpha^6 J$$

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 these 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-dimensional 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:

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

where X_i, $i=1,\ldots,n$ 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.

Dimensions of the model 'crystal' vary within a wide range in the number of atoms in some chains of crystal branches (from $1\times1\times1$ to $1000\times1000\times1000$). However, the choice of big volumes does not give any new information except time consumption. 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. Time interval also varies from 10^{-15} to 10^{-12} s. The amount of the energy transferred from the impinging ion to the crystal atom is determined by classic equations given in [5]. 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. The impact frequency in the case of 'ion rain' corresponds to 10^{12} Hz.

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.

As to Morse potential, its multivalleys are achieved by expansion of the Morse potential into a Taylor series and due to this fact, as you can see in Fig. 1, there appear additional valleys (valleys 2 and 3). The quantity and the depth of additional

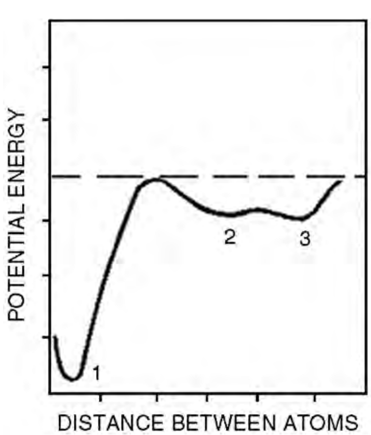

Fig. 1. Multipit potential of atomic interaction in crystal lattices.

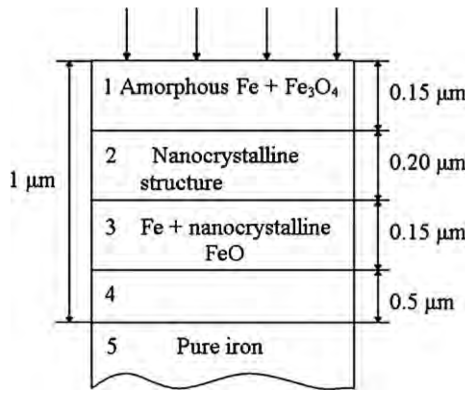

Fig. 2. Schematic of the "Sandwich" structure in near surface layers of after the low-energy ion irradiation in glow-discharge plasma.

valleys depend on the choice of the potential and its specific parameters.

3. Results and discussion

It has been shown earlier in [6,7] that 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 [8]. 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.

Now we would like to focus on the modification of surface layers. Using the transmission electron microscopic method, we observe that the complex multilayer heterogeneous nanometric structure of a "sandwich" type (Fig. 2) is formed at near-surface layers (0–1 μm) of irradiated armco-iron. The first layer (0.15 μm thick) is a two-phase amorphous structure, i.e. a mixture of amorphous iron and Fe_3O_4 oxide. The next layer (layer 2, with 0.20 μm thick) is a nanocrystalline structure having nanocrystals with 0.1–0.15 μm size. Present in this layer are also Fe_2O_3, FeO, Fe_3O_4 oxides. Layer 3 (0.15 μm thick) consists of iron crystals with a small dislocation density (approximately equals 10^8 cm^2). There are iron oxides and nanocrystalline FeO phase inside the layer. Layer 4 (0.5 μm thick) includes crystals of pure iron with dislocation density 3.2×10^9 cm^2. Present in layer 4 are round Fe_3O_4 particles, the diameter of which is 0.12–0.15 μm. Layer 5 expands into the material volume and represents pure iron.

These experimental data raise two questions: (1) How is such a complex structure formed near the armco-iron surface after its low-energy irradiation in glow discharge plasma? (2) In what way is the structure of thin films with nanometrical dimensions modified by their low-energy ion irradiation?

These questions cannot be answered in terms of the well-known ideas about radiation defects in metals and alloys bombarded by ions. The authors suggest a hypothesis based on the idea of nonlinear oscillations excitation in crystals which lead to the active self-organizing processes in the ion subsystem of irradiated crystals.

Fig. 3 shows the diagrams of local external disturbances of a section of an ultra-thin crystal film. Fig. 3a 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. 3b illustrates the initial condition when an arbitrary atom on the surface (No 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 displacement of lattice atoms is very small and the atoms which had been given impulses did not leave the potential pit 1 (Fig. 1). We show that in the system of coupled oscillators nonlinear oscillations are excited. The process of the propagation of nonlinear oscillations embraces the overall volume

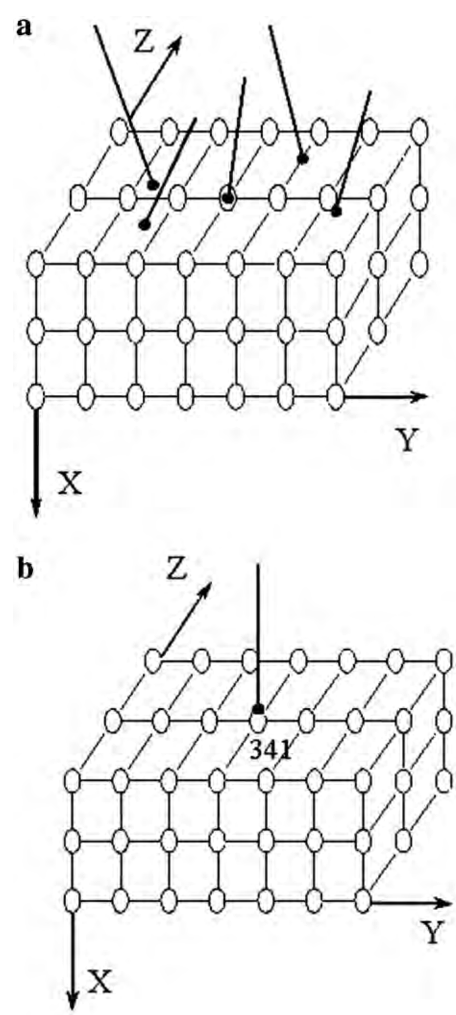

Fig. 3. Schematic of interaction between a falling ion and crystal thin films. (a) Random "ions rain", (b) single ion impact.

of the crystal. The time of stabilization is almost by 3–4 orders higher than that of ordinary atom relaxation.

Fig. 4 illustrates the dependence of atom displacement along the *X*-axis on the time elapsed after stopping the external influence. It is seen that atom N341 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 metastable long-living structures in the former target ordered structure.

The results of calculations also depend on the dimensionality of chosen objects and dimensions of the model object, particularly on the amount of energy and the dose of external influence needed to excite nonlinear oscillations in irradiated systems. However, after the excitation of such oscillations in the system and the development of collective self-organization processes in nonlinear systems, types of new structures formed after the lattice stabilization hardly depend on dimensionality, dimension of objects and even on a potential type. This dependence will look like this: one-dimensional cluster is formed in one-dimensional lattice, three-dimensional cluster is formed in three-dimensional lattice. Therefore, practically types of structures formed after low-energy irradiation may be presented in one-dimensional model of nonlinear chains cut from three-dimensional lattice.

Fig. 4 shows that the time elapsed after the irradiation of the crystal exceeds the time of normal atom relaxations of 3 orders but the lattice has not been stabilized yet.

We showed that for 'rain' case much lower energy was required to develop self-organization processes than for the case of a single ion impact. That is achieved by a fast transition: chaos of falling ions → the formation of new structures in the crystal (probably with nanodimension).

Fig. 5 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. 5 shows the displacement of 100 atoms of the excited chain along the *X*-axis at the moment when nonlinear oscillations have stopped and the atoms have stabilized in new positions, which results in the formation and development of new metastable atomic groups

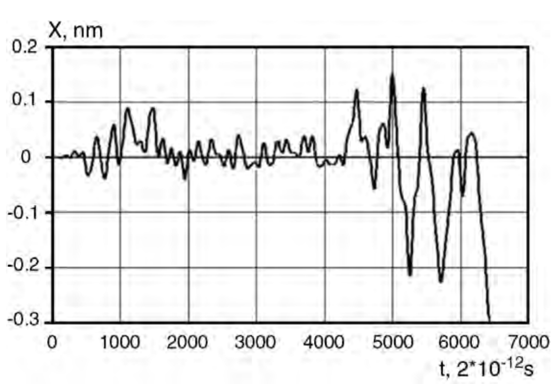

Fig. 4. Dependence of atom displacement (atom No 341) along the *X*-axis on the time elapsed after stopping the external influence for quite a long time.

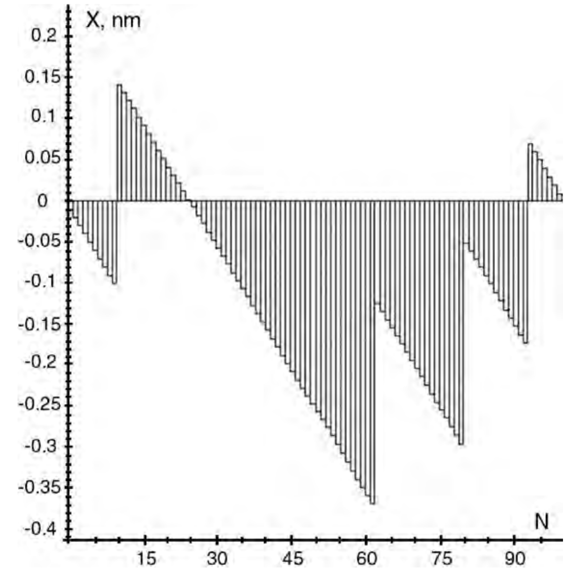

Fig. 5. Displacement of 100 atoms of the excited nonlinear atomic chain along the *X*-axis at the time of stabilization. *Y*-axis represents atom displacement, *X*-axis shows atom number in the nonlinear chain.

(nanoclusters). The period of the lattice inside the clusters does not correspond to the initial one, some clusters being separated with areas having a much larger size that the initial one (for example, N10 and N11, N93 and N94 atoms). It is the clusters that provide new complexes of physical and mechanical properties to lattices (irradiated materials). For absolute interpretation it is desirable 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.

Fig. 6 shows a phase diagram of randomly chosen atom N2 out of the chain. We see that its new final attractor (A point in the figure) is a highly displaced state out of the initial state. This

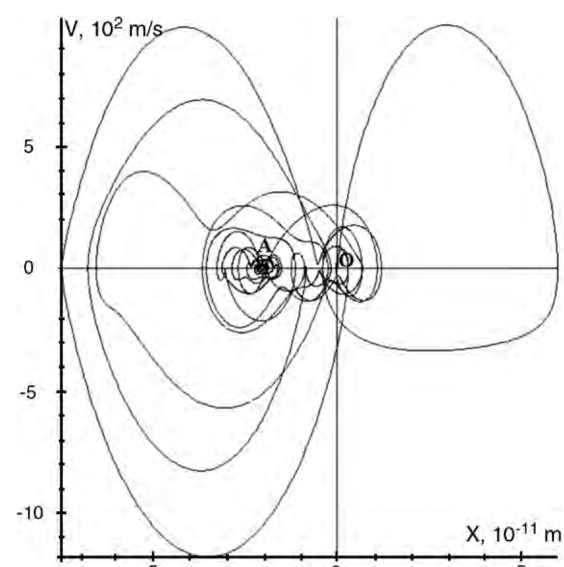

Fig. 6. Phase diagram for N2 atom from the atomic chain after stopping the low-energy irradiation, O point is initial state of the atom, A point is a new final attractor.

state is achieved by numerous nonlinear oscillations. Consequently, the energy transition from the vibration mode to the translational one takes place.

In fact, the finite state of the atomic lattice irradiated by low-energy ions is a highly fragmented distorted structure having nanometrical dimensions.

In the irradiated materials the formation of a wide spectrum of new long-lived metastabilities occurs, in particular, nanostructural complexes with different dimensions. Thus, after the low-energy ion irradiation in glow-discharge plasma in armco-iron samples it is possible to form nanostuctures in four-layer surface area (and clusters with nanodimension even at a pretty great depth from the irradiated surface). The formation of this kind of layers and structures may be explained by the excitation of nonlinear oscillations in ion subsystem of irradiated lattices and their synergetic effect. In the result high fragmentation structures with nanodimensions are formed. The dimension (average size) of fragmentation areas must increase with the distance from the irradiated surface. Then transitions amorphous layer → nanocrystal layer → small-grained layer become logical.

4. Conclusions

(1) We showed experimentally by the electron microscopy method that in the near-surface of armco-iron complex, multilayer nanocrystalline structures are formed as a result of low-energy ions irradiation.

(2) We showed by a computer simulation that the low-energy influence on a crystal lattice leads to nonlinear oscillations of atomic oscillators, which can result in the formation of structures with nanometrical dimensions near the irradiated surface.

(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.

References

[1] E. Sligte, B. Smeets, R.C.M. Bosch, K.M.R. van der Stam, L.P. Maguire, R.E. Scholten, H.C.W. Beijerinck, K.A.H. van Leeuwen, Microelectron. Eng. 67–68 (2003) 664.

[2] Isao Yamada, Jiro Matsuo, Zinetulla Insepov, Takaaki Aoki, Toshio Seki, Noriaki Toyoda, NIMB 164–165 (2000) 944.

[3] S.I. Matuchin, Izvestia of Oryol State Technical University, vol. 1–2, 2003, p. 59.

[4] J.F. Ziegler, J.P Biersack, U. Littmark, The Stopping and Range of Ions in Solids, vol. 1, Pergamon, New York, 1985.

[5] W. Eckstein, Computer Simulation of Ion-Solids Interaction, Springer, Berlin, 1991.

[6] I.V. Tereshko, V.I. Khodyrev, V.M. Tereshko, E.A. Lipsky, I.V. Romanenko, Application of Particle and Laser Beams in Materials Technology, in: Misaelides (Ed.), NATO ASI Series, Kluwer Academic Publishers, Dordrecht, Boston, 1995, p. 595, London.

[7] I.V. Tereshko, V.I. Khodyrev, V.M. Tereshko, E.A. Lipsky, A.V. Goncharenya, S. Ofori-sey, NIMB 80–81 (1993) 115.

[8] I.V. Tereshko, V.I. Khodyrev, E.A. Lipsky, A.V. Goncharenya, A.M. Tereshko, NIMB 127–128 (1997) 861.

[9] E.V. Kozlov, I.V. Tereshko, V.I. Khodyrev, E.A. Lipsky, N.A. Popova, Izvestia Vyzov Phisica, vol. 1, 1992, p. 14.