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Optical properties of surface layers of amorphous and polycrystalline metallic materials modified by laser and ion implantation treatment

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The optical properties of the surface layers of amorphous Fe-Cr-B and polycrystalline Al-Si alloys modified by laser irradiation have been studied by spectroellipsometry. The laser irradiation changed optical conductivity of the surface layers of Fe-Cr-B and Al-Si samples significantly due to modification of their structure. Work deals with also effects of Ti^+ and C^+ ion-plasma mixed beam treatment onto optical properties of Mo and Ti surfaces in the infrared. The ion implantation of Ti sample changed the spectral dependence of its optical conductivity from the Drude-like to the Kaveh-Mott like one. It points to a stronger disordering of Ti compared to Mo sample.

1. Introduction

Binary polycrystalline alloys Al-Si among many other iron-less (i.e. light) alloys are widely used in a formation of components for various mechanical devices (including reactive engines) [1] which are resistant from one side to high load and from another to cryogenic temperature. In this connection it is interesting to know how change physical, in particularly structural and mechanical, properties in dependence on the condition of their preparation and external action in their processing. In contrary such iron-based amorphous alloys as Fe-Cr-B also must be in the attention because their disordered structure, namely their amorphous state after sample preparation [2] as a material which is resistant to the corrosion. Hence thermal treatment due to heating after laser subject both types of the studied alloys must be considered in relation with their thermostability which is necessity for saving and improving their physical properties [3, 4].

Often various treatments of such alloys improve their exploitation characteristics. In this connection it is important to determine how power laser subject changes inner structure in which the smallest variations may be registered by ellipsometry [5, 6] because skin-layer at thickness of several hundred nanometers is tested.

From another side pure polycrystalline metal Mo, Ti samples irradiated by Ti^+ and C^+ ion-plasma mixed beams in order to maintaining and hardening of the mechanical properties of the surface layer to improve abrasion resistance in accordance with ion implantation effect within the surface layer which may be reliably investigated by ellipsometry. Frequently in implantation process for metal surface the ions of those elements which weakly dissolve in these metals are used [7]. This fact was taken into account in the selection of Ti^+ and C^+ ion-plasma for irradiation of such metal as Mo and Ti samples.

Moreover, the optical properties of the above-mentioned metal materials and in particular their surface layer is a consequence of the specificity of their atomic and electronic structure, that may be probed by spectroscopic ellipsometry, and especially due to the fact that such materials may be used as a mirror under the action of the plasma where stability of their optical characteristics is important too [8].

That's why the aim of this work is to investigate the influence of laser irradiation on the optical properties of surface layers of the polycrystalline Al-Si alloys and rapidly quenched Fe-Cr-B alloys when the investigated ribbons are not completely amorphous in initial state but contain some amount of a crystalline phase. The optical properties and their interconnection with electronic structure of Mo and Ti surfaces under Ti^+ and C^+ ion-plasma mixed beam treatment have been studied in the infrared (IR) too.

2. Experimental

The optical properties of the surface layers of amorphous Fe-Cr-B and polycrystalline Al-Si alloys samples modified by laser irradiation have been studied by spectroellipsometry. The investigated $(Fe_{0.9}Cr_{0.1})_{85}B_{15}$ ribbons (12 mm in width and 30-35 μm in thickness) were prepared by rapidly quenched method. The laser treatment of the Fe-Cr-B sample surfaces was performed using a YAG pulse laser (λ = 1.06 μm, τ = 4 ms) with variation of pulse energy density E from 1 to 25 kJ/m^2 and number of pulses N (dose) from 20 to 2200 respectively. The hypoeutectic (9% Si) and eutectic (12% Si) Al-Si alloys were irradiated by pulse ruby laser (λ = 0.6739 nm, τ = 4 ms) with power density J below (300-400 mW/m^2) and above (900 mW/m^2) the melting threshold.

The method of multiple-angle-of-incidence single-wavelength ellipsometry (λ = 632.8 nm, photon energy E = 2 eV) [5] was applied to study the optical properties of the surface layers of Fe-Cr-B and Al-Si samples. The angular dependences of the ellipsometric parameters such as a phase shift Δ (or cosΔ) between the orthogonal components of the polarization vector and azimuth Ψ (or tgΨ) of the restored linear polarization were obtained using a laser ellipsometer LEF-3M-1. From these dependences the principal angle of incidence φ_0 (cosΔ = 90°) and minimal value of the azimuth Ψ_{min} were obtained.

As before carrying out the ellipsometric researches the surface of samples of the Fe-Cr-B and Al-Si alloys mirrors was polished mechanically with diamond paste with minimal grain size to remove surface layers with appropriate roughness, values of optical constants, namely, the refraction and the absorption indices weren't defined. The main attention was focused only to a valuation of the ellipsometric parameters changes which could result from structural transformations in subsurface layers of the studied samples after laser processings. It is caused by oxide film which is quickly formed enough on the aluminum surface as well as Al alloys one [1], the subsurface layer broken by mechanical polishing and the roughness of the surface influence the values of the measured ellipsometric parameters and they essentially differ from values of the same parameters for the surface of this material which is ideally smooth and free from oxides.

The Mo and Ti surfaces were treated by Ti^+ and C^+ ion-plasma mixed beam. The energy of implanting Ti^+ and C^+ ions was of 80 keV, the ion implantation dose was estimated to be $5x10^{17}$ cm^{-2}. Optical properties of the polycrystalline Mo and Ti in the IR before and after the ion implantation were studied using spectroscopic ellipsometry [9] within $\lambda = 2 - 25$ μm.

3. Results and Discussion

In Fig. 1 it shows the dependences of the principal angle of incidence φ_0 of the Fe-Cr-B ribbons on the number N of laser pulses with fixed values of energy density E = 7 and 25 kJ/m^2 (Fig. 1, a and b, respectively) and on E at fixed values N = 50 and 200 (Fig. 1, c and d, respectively).

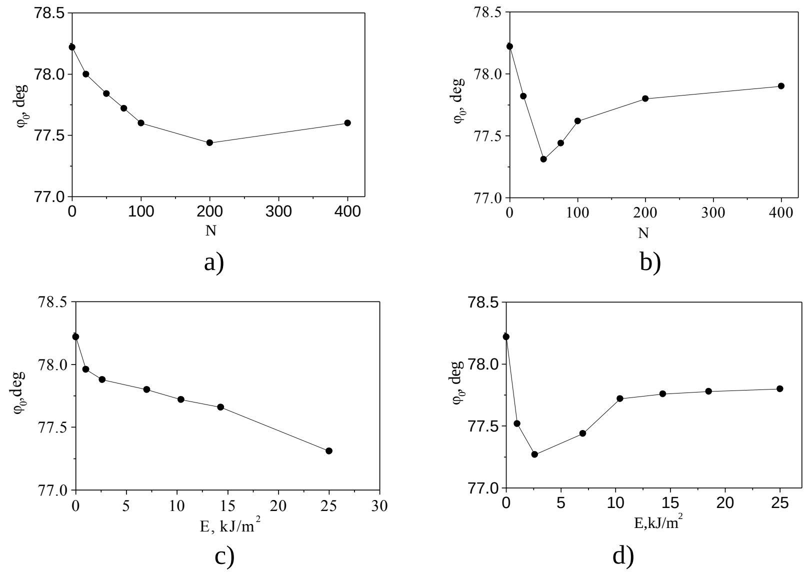

Fig. 1. The principal angle of incidence φ_0 of the Fe-Cr-B ribbons as a function of the number N of laser pulses (E = 7 (a) and 25 kJ/m^2 (b)) and laser pulse energy E (N = 50 (c) and 200 (d)).

One can see that the principal angle of incidence φ_0 at the fixed energy E nonmonotonously depends on the number of laser pulses N, reaching a minimum at certain N, which depends on E, and shifts to lower values with increasing E. It was obtained that the principal angle of incidence φ_0 depends similarly on E at the fixed value N. At the same time another ellipsometric parameter tg$\Psi_{\min}$ doesn't show the regularities at its variation after laser processing. The parameter tg$\Psi_{\min}$ is very dependent on the value of the roughness of a surface of metals and metal alloys sample while another ellipsometric parameter φ_0 is more sensitive to the changes in the behavior of a charge carriers within the subsurface layer of metallic systems. It is known [5] that optical conductivity σ may be defined through ellipsometric parameter Δ and Ψ and the angle of light incidence. At the principal angle φ_0 the formula for σ an is following

$$\sigma = \frac{\omega}{4\pi} \sin^2 \varphi_0 \, \mathrm{tg}^2 \varphi_0 \sin 4\Psi_0 \qquad (1)$$

where ω is a light frequency, Ψ_0 is an azimuth of the restored linear polarization at the principal angle of light incidence.

It is known that the spectrum of the optical conductivity of polycrystalline iron belonging to the cubic crystalline system comprises a broad optical absorption band in the spectral range of 2-2.6 eV, while the energy of the probe photons in these experiments was about 2 eV. Thus, the obtained decrease in ellipsometric parameter φ_0 with small N and E may be caused by decomposition of α-Fe like crystalline grains in the surface layer of the Fe-Cr-B ribbons upon the additional laser-induced quenching of the surface. Upon reaching a sufficiently large dose of laser radiation the surface annealing may be observed with simultaneous formation of additional crystalline phases. This fact in turn leads to the increase of the principal angle of incidence φ_0 that observed for high values of N and E.

In Fig. 2 it demonstrates the dependences cos$\Delta(\varphi)$ of the hypoeutectic (a) and eutectic (b) Al-Si alloys mirrors before and after laser irradiation.

It was found that the values of φ_0 obtained from the dependences cos$\Delta(\varphi)$ of the Al-Si alloys mirrors decrease (~1-2 deg) after laser irradiation. At the same time another ellipsometric parameter tgΨ_{min} doesn't demonstrate the change after laser processing. From a formula (1) it follows that essential decrease of φ_0 corresponds to the decrease of optical conductivity σ. This means some increase of collision frequency of charge carriers with defects of aluminum crystal lattice and decrease of number of such charge carriers. It is known [10] that increase of speed of cooling from a liquid state leads to growth of solubility of silicon in aluminum. At dissolution atoms of Si which have the nuclear radius 10% less than Al atom replace atoms of Al in a crystal lattice.

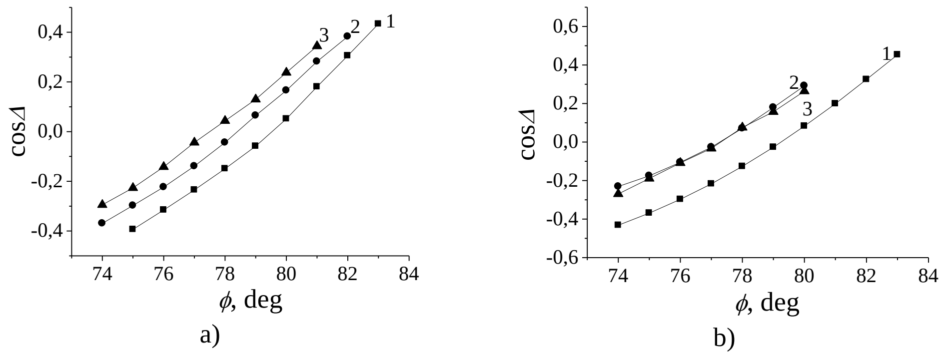

Fig. 2. The curves cos$\Delta(\varphi)$ of the hypoeutectic (a) and eutectic (b) Al-Si alloy samples as untreated (1), laser treated with J below (2) and above (3) the melting threshold.

Therefore such defects arise in Al-Si alloys as a result of partial replacement of Al atoms by ones of silicium which earlier are connected enough strongly with the same atoms in eutectic state after specimen preparation. But after high speed heating of surface layer by laser irradiation and its further self-cooling within bulk sample the interatomic bonds of the nearest pairs of Si atoms have become partially destroied.

The features of the process of implantation by Ti^+ and C^+ ion-plasma mixed beams of the metallic surfaces mirrors Mo and Ti were also studied. In Figs. 3 and 4 the curves demonstrate the spectral dependencies of the optical conductivity σ of Mo and Ti surface samples respectively. One can see that for nonirradiated Mo and Ti samples (Figs. 3 and 4, curve 1) the optical conductivity decreases monotonously while frequency increases. The behavior of these spectra is typical for metals in the infrared. Irradiation by Ti^+ and C^+ ion-plasma mixed beams is resulted in a significant increase for the values of the optical conductivity of Mo (Fig. 3, curve 2), excluding the spectral region of 400-645 cm^{-1} where the magnitude of this quantity decreased. It is important that the dispersion dependence of the optical conductivity of Mo after implantation is remained as decreasing, although it was smoother in the all spectral region. The difference of the optical conductivity spectra of the irradiated and unirradiated samples is presented in Fig. 3 (curve 3) to illustrate the change of the optical characteristics after ion treatment.

The ion treatment of the Ti surfaces by the same ion beam has caused the changes of the optical conductivity not only in value but also in the specificity of behavior of the dispersion (Fig. 4, curve 2). One can see that the spectrum of the optical conductivity $\sigma(\tilde{\nu})$ at first variation increases while wave number $\tilde{\nu}$ increases, reaching a peak near $\tilde{\nu} \approx 2970$ cm^{-1} and then decreases with increasing $\tilde{\nu}$. To find out the reasons for changes in the optical conductivity after ion treatment, the electronic parameters of the Mo and Ti samples were calculated, namely, plasma Ω and relaxation γ frequencies. Such calculations have shown that the ion implantation caused stronger change of Ti optical properties compared to those of Mo. The Mo optical conductivity may be described by the Drude-like dependence after the implantation, although the treatment has caused a decrease of the plasma frequency approximately of 22% and a significant increase of the relaxation frequency. This means the decrease in the number of charge carriers and change in the scattering mechanism of free electrons. These changes may be caused mainly by the accumulation of defects in the subsurface layer of samples due to ion implantation.

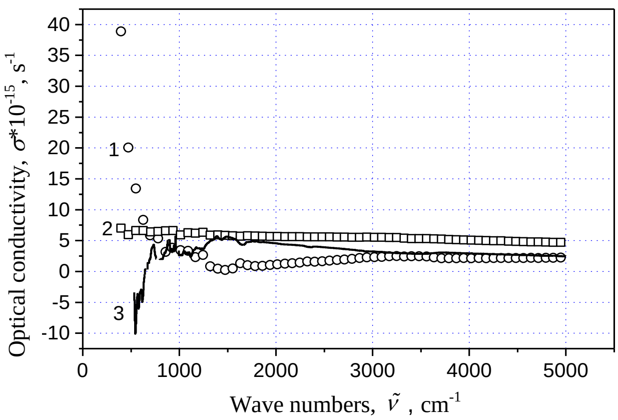

Fig. 3. The spectrum of optical conductivity of the surface of polycrystalline Mo before irradiation (curve 1), after irradiation by Ti^+ and C^+ ion-plasma mixed beam (curve 2), and the difference of previous graphs (curve 3) in the IR.

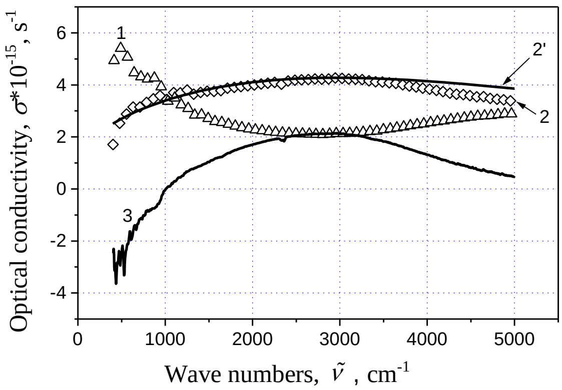

Fig. 4. The spectrum of optical conductivity of the surface of polycrystalline Ti before irradiation (curve 1), after irradiation by Ti^+ and C^+ ion-plasma mixed beam (curve 2), the difference of previous graphs (curve 3) in the IR. Curve 2′ is a result of the calculation of the optical conductivity in an approximation of Kaveh-Mott relationship (2).

The optical conductivity of Ti in the IR may not be described by the Drude-like dependence after ion implantation. The ion implantation of Ti has probably changed the spectral dependence of its optical conductivity from Drude-like to the Kaveh-Mott like one [11]:

$$\sigma(\omega) = \frac{\sigma(0)}{1+(\omega/\gamma)^2}\left\{1-\frac{3}{(k_F l)^2}\left[1-\sqrt{\omega/\gamma}\ \right]\right\}, \tag{2}$$

where $\sigma(0)$ is a static value of optical conductivity, γ is the relaxation frequency, k_F and l are the values of the electron wave vector at the Fermi level and the localization length of its wave function respectively, ω is the circular frequency of the incident light.

The calculations have showed a significant increase in both frequencies Ω and γ after ion treatment of Ti surface. Considering the deviation from the Drude-like behavior of the spectral dependence of the σ, it may indicate appearance of weak localization of electrons in strongly disordered subsurface layer after ion implantation. A stronger disordering of Ti surface compared to Mo sample by the same ion treatment may be explained by the prevalent diffusion of surface atoms having greater affinity both to the implanted atoms and to the atoms in the depth of a substrate.

3. Conclusion

Thus using laser and ion implantation treatment for the modification of atomic and electronic structure of the skin-layer of the amorphous and polycrystalline metallic materials one can find essential change of optical response (optical conductivity, dielectric function) reaching some tens percent in the visible and the IR. It may be practically used for a formation of stable reflecting layers in metallic mirrors at condition their functioning in air atmosphere or under action of plasma environment.

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