

Alloying of the Be, Al, Ti, and Zr oxide films on a metal substrate by ion mixing and investigation of their properties by the methods of optical spectroscopy

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Abstract – Results of investigation by the methods of optical and infrared spectroscopy of the structure of oxide films obtained on an ion-alloyed surface under oxidation of Be, Al, Ti, and Zr samples in a water-steam environment at the temperature of 350°C and the pressure of 20 MPa are presented. The results show that the oxide films on the ion-alloyed surface of Be, Ti, and Zr samples have a higher optical density and homogeneity. At definite parameters of the ion alloying, the oxide films have a laminated fine-crystalline structure and higher electrophysical properties which are interesting for making insulating coatings, optical filters, and sensor devices.

1. Introduction

One of the main problems connected to the formation of oxide films with stable properties on a metal substrate is the development of non-destructive control methods of their properties directly in the process of their growth, among which optical and infrared spectroscopy can be proposed [1].

The aim of the given work was to study the optical properties of the surface of Be, Al, Ti, and Zr samples, as well as their oxides in the nonequilibrium state. To achieve the aim, the atoms of Be, Al, Fe, Mo, and Y in various combinations were implanted into the surface layer of metals; the samples were oxidized in a water-steam environment at the temperature of 350°C and the pressure of 20 MPa. The reflectance $R\%(\lambda)$ characterizing the optical properties of the "film-substrate" system was selected as the main parameter. It was determined for the optical and infrared range of wavelengths of 0.2–0.9 μm and 1–30 μm , respectively [2].

2. Experimental technique

The surface of Be, Al, Ti, and Zr samples was alloyed by implantation of the atoms of a film under irradiation by a polyenergetic Ar^+ ion beam [3,4]. Be, Al, Fe, Mo, and Y films 30 – 50 nm in thickness were obtained on the surface of samples by thermal evaporation in vacuum at the pressure of 3×10^{-4} Pa. Irradiation of the samples was made on an installation forming a polyenergetic Ar^+ ion beam with a mean energy of 10 keV. The beam had a Gauss-like energy spectrum in the 3 – 15 keV range; the current in the beam ranged from 20 to 30 $\mu\text{A}/\text{cm}^2$ [5]. The use of a polyenergetic

beam made it possible to obtain a more uniform implantation of the alloying atoms along the sample depth at a lower extent of radiation damages in the implanted layer [4,6], which positively influences the structural-phase state of the modified surface layers of metals.

The oxidation of the initial and alloyed surface in a water-steam environment was carried out in 12Cr18Ni10Ti steel ampoules at the temperature of 350°C, the pressure of 20 MPa, for 300, 600, 1200, and 3000 h.

To determine the state of oxide films on the surface of metals, the spectroscopy of reflected radiation from the "oxide-metal" system in optical (200–900 nm) and infrared (1–50 μm) ranges was used. Fig. 1 shows the scheme of measuring the reflected flux from the "oxide-metal" system, where: I_0 , the initial incident flux, $I(z=0)$, the flux reflected from the surface of an oxide at the angle α , $I(z_i)$, a part of the flux reflected at the angle α_1 which transmitted a z_i -thick oxide layer with the refractive index n_1 .

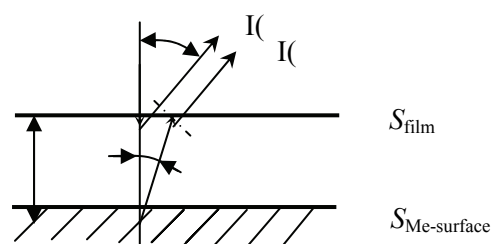


Fig. 1. The scheme of formation of the reflected stream of an electromagnetic wave from a homogeneous film on a metal surface: the path-length difference will be equal $\Delta = z_i(2n_1 - \alpha^2)$

The main ratio balance between the energy of an incident electromagnetic wave, reflected and transmitted ones, is the condition $R+T+X=1$, where: R , the reflectance (ratio of the reflected flux to the incident one, $I(R)/I_0$), X , the absorption coefficient of radiation, $I(X)/I_0$, and T , the transmission coefficient, $I(T)/I_0$.

In case of investigation of the oxide film state on a metal substrate, it should be assumed that the most appropriate parameter is the reflectance R , as the oxide films are transparent in optical and infrared ranges ($X \approx 0$).

The structure of the oxide films and their optical properties were studied in the optical range of wavelengths by the spectrophotometer Cary-300 (firm Varian) and in the infrared range by the device Nicollet Nexus (firm Thermo Electron Corporation) for two regimes transmission T and reflection R . At that, the initial beam was directed perpendicular to a surface under investigation. The reflection angles in relation to the perpendicular of the surface under investigation corresponded to the angle of 1.5 and 22.5 degrees. That made it possible to obtain additional information on the contribution value (R_d) of diffusion sputtering. The measured reflection- and transmission-spectra were processed by standard programs. To identify the resonance lines obtained, databases of the producer firms of devices and of a number of research laboratories were used. X-ray diffraction investigations, electron microscopy, secondary-ion-mass-spectrometry and other methods, as well as such devices as PHI-660 and OXFORD-LINK were also used to determine the modification depth and the structural-phase state of both the alloyed layers of metals and the oxide films.

3. Experimental results and their discussion

– Optical microscopy.

As shown by the results of investigation on the state of oxide films on a metal surface, the oxide films in their initial state grow epitaxially. Their various growth rate results in reveal of the boundaries of individual grains. In case of the growth of oxide films on an ion-alloyed surface, their growth rate equalizes on individual crystallites. Take an example, optical pictures of the surface of oxide films obtained on zirconium of a technical purity after oxidation for 100 h are shown in Fig.2.

It is seen from the figure that in the initial state, a polycrystalline oxide film with different thickness is formed on individual crystallites; the intercrystalline boundary of ZrO_2 is revealed with a higher contrast. As to the ion-alloyed surface, a pseudo-amorphous, as a rule, oxide film of equal thickness (as shown in Fig. 2,b; its intercrystalline boundary is more fuzzy) is formed on such a surface.

– Electron microscopy.

Investigation of the structure of oxide films on a metal substrate in its initial state (Fig. 3) reveals a typical rotting structure with a cross size of crystallites of 0.1 – 0.2 μm ; the oxidation front, i.e. the oxide-metal boundary, is unequal, there are micropores in the oxide bulk, as well as there are individual metal inclusions and metal oxides.

The oxide films obtained on an ion-alloyed surface usually have an even boundary of the oxidation front (oxide-metal). Depending on the conditions of alloying, there is a possibility that the rotting structure of an oxide (Fig. 4.) will not be revealed, as a fine-crystalline structure of the oxide can be formed in this case (Fig. 5). At that, multi-layer oxide films can be

formed under oxidation for more than 1000 h owing to a different diffusion mobility of implanted atoms and oxygen [7].

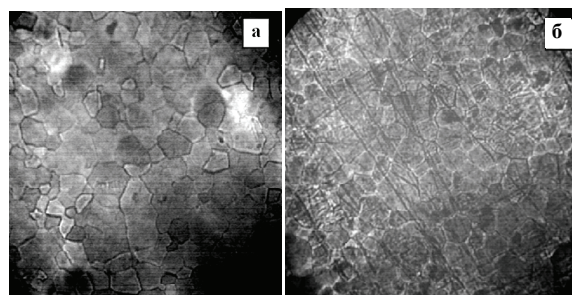


Fig. 2. Optical photo the oxide films on a zirconium surface: a, the surface in an initial state; b, the surface is simultaneously alloyed by Al, Y, Rh atoms, x350

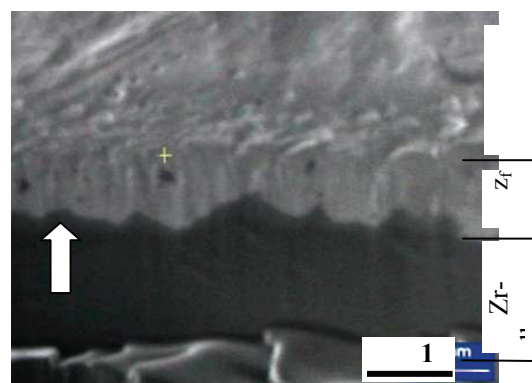


Fig. 3. Photo of cross-section "oxide film – Zr-substrate" (E110) in an initial state, time of oxidation 300 h: the arrow (pointer) specifies front of oxidation (border "oxide-metal")

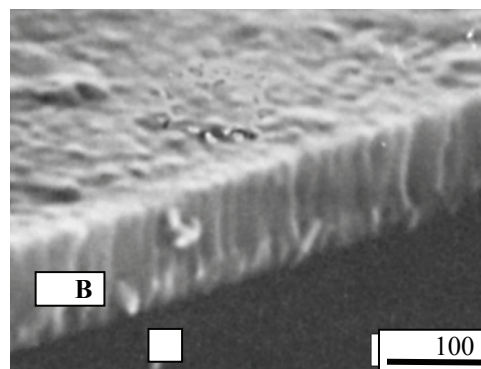


Fig. 4. Photo of cross-section of "oxide film on Be-substrate", alloyed by Al-atoms (the image in secondary ions)

The content distribution $C(z)$ of implanted Al, Fe, Y, and oxygen atoms in the "oxide film-metal substrate" system at the oxidation time of zirconium (alloy E110) samples of 600 and 1200 h is shown in Fig. 6 as an example.

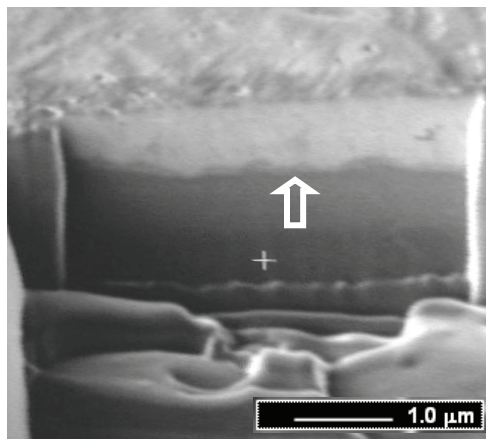


Fig. 5. Photo of cross-section "oxide film on Zr substrate" (E110) alloyed by Al-Fe-Mo-Y atoms after oxidation within 600 hours: the arrow (pointer) specifies front of oxidation (border "oxide-metal")

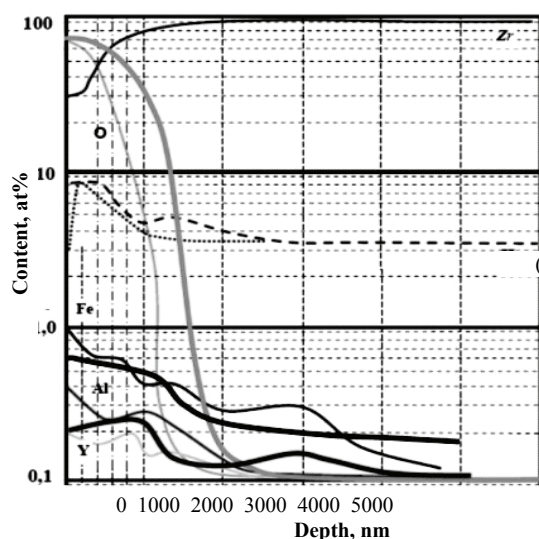


Fig. 6. Distribution of the Al, Fe, Y introduced atoms and oxygen on depth in system "oxide film – zirconium", time of oxidation 600 and 1200 h

The distributions obtained illustrate that at depths more 500 nm (for the oxidation time of 1200 h), an increased content of the implanted atoms is observed: (Al – 0.3 ± 0.05 at.%; Fe – 0.7 ± 0.1 at.%; Y < 0.2 ± 0.03 at.%). Secondary concentration maximums of Al and Fe atoms are also observed: – $z = 800 - 1200$ nm, Y – $z \approx 800$ and 1500 nm. Appearance of the second maximum $C(z)$ for Y seems to be due to a change of the oxygen concentration ratio at the "metal-oxide" boundary; for Fe and Mo that may be due to both diffusion processes and physicochemical interaction between the implanted atoms, oxygen, and the atoms of the matrix (Zr), what demands additional investigations.

Optical spectroscopy of oxide films.

Typical spectral characteristics of reflection from the surface of the zirconium oxides of ion-alloyed

samples are shown in Fig.7 as an example: 1, alloyed by Fe, Mo; 2, by Al, Fe; 3, by Al, Fe, Mo; 4, by Al, Fe, Mo, Y after oxidation for 600 h. It is seen from the figure that reflection maximums are observed within the 200–300 nm wavelength range. They become the most intensive for the samples simultaneously alloyed by the atoms of Al, Fe, Mo, Y.

According to the Lambert law [6,7], formation of maxima of reflection occurs because of absorbing ability of a material which is determined by its chemical nature, by a condition of the optical environment and in the wave-length of light. For the indicated wave-length range, it may be connected with decreasing the quantity and the size of scattering centers, or with formation in the reflecting layer of the atoms of chemical compounds having higher valent states.

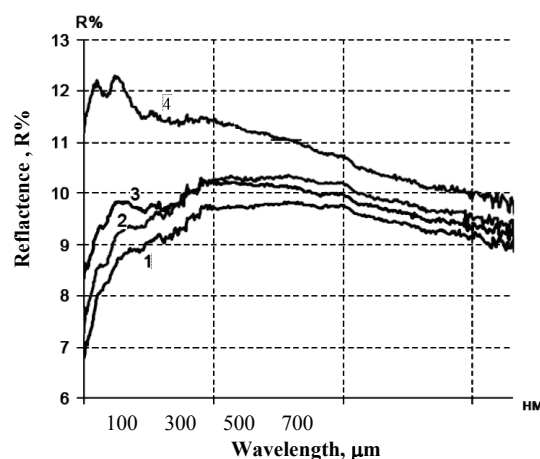


Fig. 7. Spectral characteristics of reflection from "oxide film-substrate" from Zr-samples (E110): 1 – it is alloyed Fe, Mo atoms; 2 – it is alloyed Al, Fe atoms; 3 – it is alloyed Al, Fe, Mo atoms; 4 – it is alloyed Al, Fe, Mo, Y atoms

The reflection spectra from the "oxide-metal" system obtained for the infrared area have a number of features. The dependence $R\%(\lambda)$ from the surface of zirconium samples alloyed by the atoms of Mo, Fe, Al are presented in Fig.8 for various oxidation times; the oxide film thickness was changed from 0.5 to 3 μm . The figure shows that the spectra shift to the are of smaller values of $R\%$ with increasing the time of oxidation. Interference peaks are located in the 1–10 μm wavelength range. Their location is determined by the superposition conditions of reflected electromagnetic waves from the oxide surface and underlying layers, including that of the metal. When the wavelength is more than 10 μm , formation of reflection peaks (12.5; 16, 21, ... μm) is mainly determined by the oxide film structure, the size of crystallites, and special additional investigations are demanded for their interpretation.

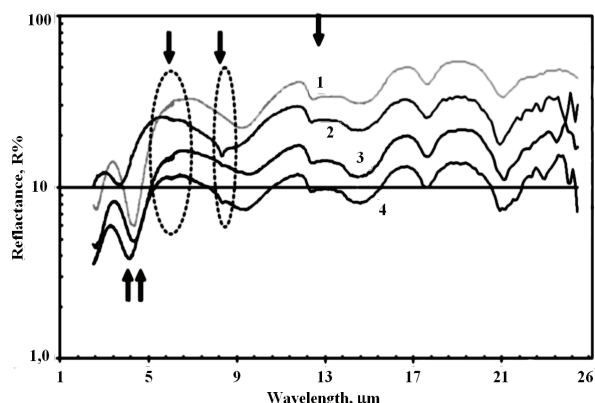


Fig. 8. A spectrum of reflection $R\%(\lambda)$ from system "oxide film-metal" on the ion-alloyed surfaces of Zr-samples (E110): times of oxidation 300 (1), 600 (2), 1200 (3) and 3000 (4) h: arrows(pointers) mark areas of change of spectra of reflection

An analysis of the fine structure of infrared spectra makes it possible to reveal the presence of structural features of oxides that are due to the presence of foreign atoms, for example implanted atoms. Resonance lines are observed for the wavelength interval from 8 μm to 20–30 μm . They are typical for the hydrogenous structures. For example in zirconium, its oxides and alloys the type Zr-H, Zr-OH, H-O, H_2O and other compounds are possible with the wavelength of 5.56 μm (1833 cm^{-2}); $\text{Fe}(\text{CO})_x$ (1830 cm^{-1}); line 6.40 ± 0.10 – CH_2 (the molecule is in a deformed state); line 7.7 ± 0.5 – OH (1200 cm^{-1}). Other reflection lines seem to be connected to the state of oxygen atoms, i.e. Zr – O, Zr – C – OH and others.

4. Conclusion

Therefore, alloying the surface layers of metals by ion mixing under irradiation by a polyenergetic ion beam results in a change in the growth kinetics of oxide films, it homogenizes their structure, gives them a number of positive properties, such as homogeneity, transparency, which can be used in various devices and units; for example, as insulating and corrosion-

resistant coatings, optical filters, and sensor units. The method of optical spectroscopy on reflection can be used as a method that will allow to control the state of oxide films during their growth on a metal surface. This method reveals an increased reflectance of the "polycrystalline oxide film – metal substrate" system in the 200–300 nm wavelength range. Using the method of infrared spectroscopy, a possibility has been shown to measure the thickness of oxide films on metal polycrystalline samples by shifting the interference maximums on reflection spectra. An increase of the optical density has been determined in comparison with the films growing on the surface of samples in the initial state. An analysis of the reflection spectra fine structure has shown that in the 1–10 μm wavelength range, the reflection spectrum is predominantly formed at the expense of reflection from the "oxide-metal" boundary, and for greater wavelengths the reflection spectrum structure is determined by the absorbing capacity of the oxide film itself.

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