

INCREASE OF THE CORROSION-RESISTANCE AFTER LOW ENERGY ION TREATMENT

M.A. VASYLYEV, V.E. PANARIN, A.A. DEINA

Institute of Metal Physics NASU, 36 Vernadsky Str., UA-03142 Kiev, Ukraine

B.B. STRAUMAL

I.V.T. Ltd., Institute for Vacuum Technology, P.O. Box 47, RU-109180 Moscow, Russia

F.O. MUKTEPAVELA

Institute of Solid State Physics, University of Latvia, LV 1063, Riga, Latvia

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Considerable attention has been recently focussed on the ion beam bombardment of metal surfaces for improving both the adhesion behaviour and the corrosion-resistance of metals, specifically on the ion implantation, ion beam mixing, and ion beam assisted deposition including low energy physical or chemical plasma vapour deposition. The well known high energy (> 100 keV) ion implantation has some limitations, for example, it requires a beamline ion implantation system and complicated associated equipment; such techniques are too costly to be used industrially, specifically in continuous roll-to-roll coil coating; there is also a restriction on the size of the workpiece. On the other hand, it is well known that the metal surface properties can be altered by low energy (< 10 keV) ion bombardment as a result of the sputtering of surface atomic layers that occurs in a vacuum chamber. Such ion sputtering techniques are frequently used to clean solid surfaces, for improving adhesion properties on the metal substrates before coating as well as in sputter metalizing. It is important that the sputtering process can be applied to a variety of wide-width surfaces. As a rule in this cases, the inert gas ion bombardment is used, mainly Ar^+ ions.

It is generally believed that the enhanced adhesion phenomena of thin films on the metal surfaces by means of ion sputtering is related to removing from the substrate some natural oxides and various kinds of impurities. However, it has been known that the surface chemical activity can be also altered by inert gas low energy ion sputtering. For example, early experimental works [1, 2, 3] showed that for certain catalysts were almost one order of magnitude more efficient than unirradiated ones. Most naturally, these pioneering contributions were interpreted qualitatively in terms of a picture in which surface defects resulting from the ion bombardment were considered as structural descriptions of the rather elusive "active centres". It was first observed by the naked eye that after certain doses of bombardment by Ar^+ or He^+ ions (< 10 keV) the surface of U, Fe, Al and Cu become passivated with respect to oxidation under atmospheric conditions.

We have performed a closer examination of the influence of the inert gas ion bombardment with incident ion energies of the order of 1 keV on the surface chem-

ical activity by the examples of oxygen interaction with the surface of Fe using Secondary Ion Mass-Spectrometry (SIMS), and a corrosion test of low-carbon steel in the sea water by the “weight changes” method.

In the first experiment, the samples used in the present work consisted of pure polycrystalline iron (2×10^{-3} at. % of impurities). The surface studied was polished mechanically, diamond finished and rinsed in special solutions. After this treatment, the samples were kept in oxygen at atmospheric pressure in order to obtain an oxide layer of a definite thickness. Formation of the oxide layer ($\sim 80 \text{ \AA}$) was controlled by AES. Six samples were placed in the vacuum chamber of the SIMS apparatus and then bombarded with 1 keV Ar^+ ions beam (current density of $1.5 \times 10^{-3} \text{ A cm}^{-2}$). The time of bombardment was varied so that the doses of irradiation ranged from 10^{16} to $10^{19} \text{ ion cm}^{-2}$. The partial oxygen pressure during the bombardment was not higher than $2 \times 10^{-6} \text{ Pa}$. Immediately after the bombardment, oxygen at pressures of 10^{-5} , 10^{-4} and 10^{-3} Pa was led into the chamber. These pressures were maintained for a definite time to obtain oxygen doses of 3×10^2 , 3×10^3 and $3 \times 10^4 \text{ L}$, respectively. Then the chamber was pumped down again. The secondary ion currents of $^{56}\text{Fe}^+$ and $^{16}\text{O}^-$ were measured during bombardment with the argon ion beam having the above mentioned parameters. It was found that the exponential decrease of these secondary ion currents during sputtering by inert gas ions is due to the removal of the oxide layer from the surface. The final level of the secondary current may be considered as corresponding to a dynamic equilibrium between the rate of arrival of the primary ions (and hence sputtering rate of iron ions) and the rate of oxygen adsorption from the residual gas in the vacuum chamber.

Analysis of the kinetic curves I^+ for $^{56}\text{Fe}^+$ and $^{16}\text{O}^-$ ions showed that the initial ion treatment does not exclude oxidation of iron surface. However, variation of the initial bombardment and subsequent oxidation leads to an appreciable change in the height of the initial spike in the curves $I^+(t)$. The results of a quantitative estimate of the effects are shown in Fig. 1. Here, $\Delta I^+ = I_1^+ - I_0^+$ values are plotted as a function of bombardment doses D , where I^+ is the height of the initial current spike (corresponding to the initial oxide layer), I_0^+ is the current corresponding to the dynamic equilibrium (approximately, it corresponds to surface oxygen concentrations less than one monolayer). It should be mentioned that the value of I_0^+ does not depend on D . Hence, the initial bombardment does not influence the ion emission after the removal of the oxide layer of the surface. It follows from Fig. 1 that the quantity ΔI^+ depends on the exposure in oxygen and on the dose of ion bombardment. The minima in the $\Delta I^+(D)$ curves correspond to the doses of $(2 - 3) \times 10^{17} \text{ ion cm}^{-2}$. Bombardment with such doses makes the surface free of the primary oxide layer (formed under atmospheric conditions). Hence, the quoted minima refer to the secondary ion emission from the oxide formed on the metal exposed to oxygen.

The change in the oxidation rate caused by the ion treatment was explained as follows. When the irradiation dose is insufficient for a complete removal of the primary oxide, there remain oxide layers whose further growth is hindered by a possible formation of a barrier produced by argon atoms implanted into the oxide

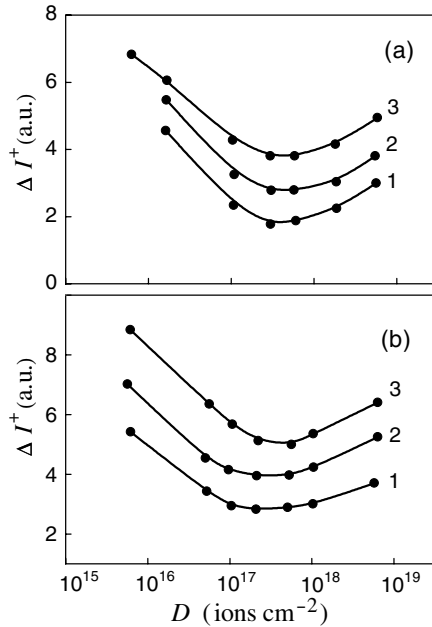


Fig. 1. $^{56}\text{Fe}^+$ (a) and $^{16}\text{O}^+$ (b) ion current from iron sample as a function of Ar^+ ion bombardment dose D (1 keV, 1.2 mA cm^{-2}): (1) 300 L, (2) 3000 L, (3) 30,000 L.

layer. This causes a decrease in the diffusion rate of the metal and oxygen atoms. Hence this effect is controlled by the optimum relation between the energy and the density of the primary ion current as well as by the sputtering rate of primary oxide and pure metal. The increase in the oxidation rate at high doses may be a result of a large number of defects and the relief created on the metal surfaces [4, 5].

The sea water was simulated by 3 % solution of NaCl in the distilled water. The samples of low carbon (< 0.1 %) steel have been subjected to Ar ion bombardment in the SIMS chamber in five different regimes: 1×10^{14} , 2×10^{15} , 3×10^{16} , 4×10^{17} , 4×10^{18} , 5×10^{19} ion cm^{-2} . In Fig. 2, the dependencies of the relative weight changes of the samples on the corrosion time for several regimes are shown. One can see that the corrosion behaviour is complicated. In the initial period of irradiation, the samples have higher rate of corrosion than an the initial sample. This, obviously, is connected with the increase of activation of the steel surface under the action of the ion bombardment. However, with the time the situation changes. Some regimes of irradiation lead to decreasing the corrosion in comparison with the initial sample.

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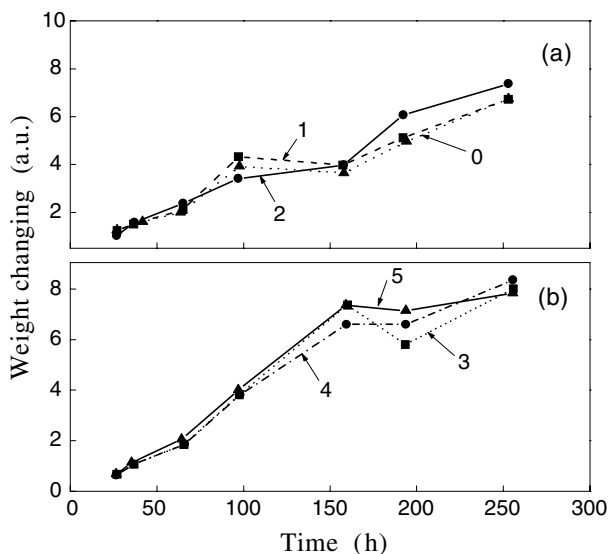


Fig. 2. Corrosion in the sea water of the steel after Ar^+ ion bombardment at several regimes 1-5. 0 is the initial state.

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