

Marking of titanium passive film breakdowns as a function of their appearance time and to increase the contrast of SEM images

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The problem of determining the breakdown location of a passive titanium film is very difficult for SEM microscopy. The reason is that there are no significant differences in the interaction of the electron in SEM with both titanium dioxide in the passive film and with metatitanic acid, which fills new places of breakdowns. It has been shown that metatitanic acid can be marked more contrast with heavy metal ions due to the formation of insoluble metatitanates. The breakdowns of the titanium passive film are marked in such a way that the contrast chemical composition of the breakdown places depends on breakdowns appearance time due to the consistent change of the marker-ions composition in the experimental solution over time.

1. Introduction

Investigation of the properties of passive oxide layers on the surface of metals and alloys often involves the obtaining SEM images. One of the goals of obtaining such images is to study the size and location of breakdowns of the passive oxide film. At the same time, the use of SEM is associated with some difficulties, which are related to the features of its physical principles and using methods.

The main difficulty is the continuous preparation of SEM for investigations with a limited area of samples that SEM investigates at a time. At the same time, the higher the maximum possible increase in the image, the longer it takes to create an appropriate vacuum in the microscope. Consequently, the study of a large amount of metal samples can take an unacceptably long time because of the relatively long preparation of SEM for the study of each new batch of samples (or each single sample, the size of which is large).

The second difficulty is characteristic for pure titanium samples and is associated with the absence of any contrast in SEM images between the passive film of titanium dioxide and the breakdown places, which are almost immediately delayed by metatitanic acid. The interaction with the electron flux is practically identical for metatitanic acid and for titanium dioxide because their chemical composition is identical for the SEM and even the condition of the electron shells of the corresponding atoms does not differ significantly. Consequently, the presence, location, and form of breakdowns can sometimes be guessed only by the contrast of the areas irradiated by the electron areas of the protrusions and valleys in comparison with the "shadow" behind them.

This work is aimed at to solving the problem of increasing the contrast of the breakdown places of the passive titanium film, when the breakdowns are investigated using SEM. At the same time, it is also necessary to solve the problem of contrast marking of breakdowns, which are obtained on one sample at different times. Including breakdowns, which are obtained with a consistent change in the electrochemical surface treatment of a titanium sample. Solving these problems will help increase the amount of information that can be obtained from one sample. It will also be possible to reduce significantly the number of SEM experiments, which is especially important for extensive studies of the breakdown processes development or pitting of a passive film over time.

2. Theoretical justification

The ability of heavy metal ions to emit intensively secondary electrons at SEM in comparison with the ions of light metals and other lighter elements is well known. If the determined surface area, which is covered with titanium dioxide, is attached with heavy metal ions, then such places in SEM images will look bright and contrast. Based on the known properties of titanium, it can be assumed that this metal in the places of passive film breakdowns should react actively with the water-oxygen medium. It is generally known that the pores in the oxide film on aluminum are first filled with gel-like aluminum hydroxide. Therefore, it is known that the first product of the interaction of titanium with water should be metatitanic acid, which is slightly

soluble and exists as a gel. Solid polymeric acids are capable of ion exchange with heavy metal salts [1] and often form insoluble compounds. The tendency of metatitanic acid to form insoluble salts with lead ions is known.

It is generally known that, other equal conditions, ions of heavy metals with a large charge (+3) are inclined to form less soluble compounds with solid polymeric acids than ions with a smaller charge. Though it is possible that after the interaction of Fe^{3+} ions with metatitanic acid, this acid will be incapable to interact with Pb^{2+} ions. And only newly formed metatitanic acid will be able to exchange hydrogen ions for Pb^{2+} ions from the solution.

Thus, it is possible to mark gelled metatitanic acid with various heavy metal ions if these ions are introduced in order to increase the solubility equilibrium of their salts. It is possible that the kinetics of ion exchange in this case will allow to ignore the differences in solubility of salts. However, each subsequent ion will be unable to displace the precursor from the metatitanate due to the slowing down of the corresponding stages of the replacement reaction.

In principle, this can be prevented by the unexpectedly large ion-exchange capacity of the titanium dioxide surface outside the breakdown places. This ability exists in some non-stoichiometric oxides [1].

It is known that gel-like corrosion products are capable of dehydration and recrystallization. For example, for the corrosion of iron and steel, it was shown that the electrochemical activity of iron hydroxides is responsible for the significant discrepancy between the results of gravimetry and measurement of the polarization resistance [2]. Obviously, this discrepancy is due to the ability of these compounds to oxidation-reduction reactions. These reactions would not be possible if there was no ability to ion exchange with the solution. Since it has been found that the electrochemical activity of iron corrosion products decreases with time [3], similar behavior can be expected from metatitanic acid.

Thus, if metatitanic acid crystallizes into titanium dioxide too quickly, this can prevent marking. If the time of phase transformations is optimal, recrystallization of metatitanates of heavy metals can promote reliable fixation of marker ions. After this,

this metatitanate will not be able to interact with the following solutions. Therefore, the chemical analysis of specific heavy metals in metatitanates on the surface will determine the time of their appearance from the time of contact of the titanium sample with a solution of a certain salt. Only an experiment can give further refinement.

3. Method

Samples of pure titanium of grade VT1-00 in the form of a foil 0.1 mm thick were made in the size 40x4 mm. Electrochemical surface treatment was carried out in an aqueous solution of 6 M lithium chloride by an impulse potentiostat. A standard three-electrode polarization scheme with a platinum auxiliary electrode was used, which is separated from the working electrode by a porous glass partition and a silver chloride reference electrode. The electrolyte for the silver chloride electrode was a 6 M solution of lithium chloride, in which the potential of the reference electrode was 0.16 V. Before the polarization, the titanium electrodes were handled and degreased with a paste of crystalline soda and distilled water. The polarization mode of the electrodes consisted of alternating anode (up to +4.0 V) and cathode (-0.05 V) impulses duration $1 \cdot 10^{-5}$ s for 2 seconds.

After electrochemical treatment of titanium electrodes, they were removed from a glass three-electrode cell and washed with a solution of heavy metal salts in distilled water. The first was an aqueous solution of iron (III) chloride with a concentration of $1 \cdot 10^{-5}$ M, and the second one was an aqueous solution of lead (II) nitrate with a concentration of $1 \cdot 10^{-3}$ M in a complex with polyhexamethyleneguanidine (PGMG) concentration $1 \cdot 10^{-2}$ M. Complex with PGMG was used because of the assumption about the need to reduce the activity of lead ions in the exchange reactions.

Titanium samples were contacted with a solution of heavy metal salts not more than 15 seconds. After this, preparations were made for SEM or the following electrochemical treatment, followed by washing with a solution of lead salt. Preparation for SEM was carried out by washing titanium electrodes in 50-ml non-condensing distilled water for two days. In the first day, water was changed 20 times, and on the second day three times. Samples were dried in air without heating for 24

hours and sent to SEM.

4. Results

Metatitanic acid showed high ability to sorb ions of even one-one valence electrolyte like lithium chloride. After drying, the breakdowns can be identified by tree-like crystals of salts, which crystallize and contain chlorides shown at point 2 in Fig. 1. Washing with distilled water for half an hour does not eliminate the electrolyte from the breakdown places. The content of the elements at point 2 is averaged for Fig. 1(b) and Fig. 1(c) and confirms that this object is a chloride crystal (probably lithium). The base of the crystal at point 1 in Fig. 1(b) and the recess at point 1 in Fig. 1(c) contains few chlorides.

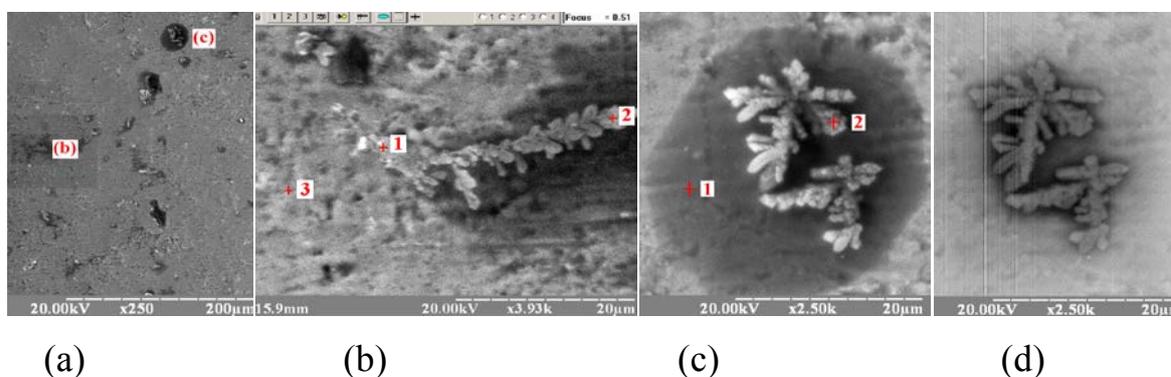


Fig. 1. The surface of titanium after electrochemical treatment in 6 M LiCl. SEM images in the secondary (a, b, c) and reflected (d) electrons with an analysis of the chemical composition at the points:

1. 99.88% Ti + 0.12% Cl;
2. 94% Ti + 6% Cl;
3. 100% Ti.

It is probably a metatitanic acid from which the ions of the electrolyte diffused into the crystallization zone. The remaining surface of the titanium is completely free of chlorides, as indicated by the chemical analysis at point 3 in Fig. 1. The result obtained suggested that it is possible to treat metatitanic acid with heavy metal salts after more thorough washing, as described in the method. The measured content of titanium in the surface oxide layers is 100% because SEM does not define light elements.

The points 1 and 2 in Fig. 2 contrasts stand out against the background of the rest of the titanium surface after treatment with salts of iron and lead.

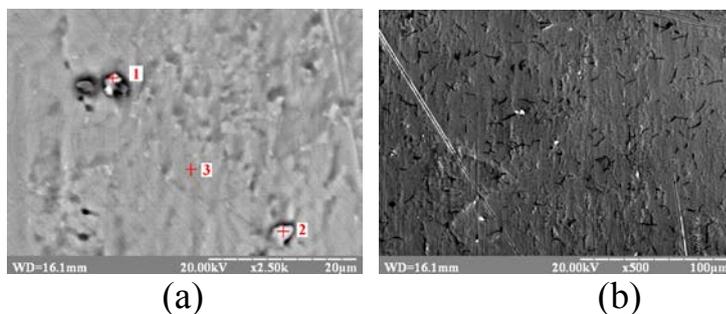


Fig. 2. The surface of titanium after electrochemical treatment and successive immersion in solutions of iron salts and lead (II) complex with PGMG. SEM images in the reflected (a) and secondary (b) electrons with the analysis of chemical composition at the points: 1. 49.90% Ti (IV) + 49.99% Fe (II) + 0.11% Pb (IV); 2. 70.29% Ti (IV) + 29.63% Fe (II) + 0.08% Pb (IV); 3. 100% Ti (IV).

Moreover, the content of lead in them does not exceed the measurement error precisely because metatitanic acid has already reacted with iron (III) salts. The chemical analysis at these points shows the product of the Fe^{2+} ions exchange with metatitanic acid. Probably Fe^{3+} ions were reduced by titanium to Fe^{2+} ions, in the same way as metallic iron is oxidized by corrosion products [2, 3]. The valence of lead (IV) in Fig. 2 can be considered wrong due to extremely low concentration. The rest of the titanium surface does not associate heavy metal ions, seen from the chemical analysis at point 3 (Fig. 2). The black strokes of a complex shape in Fig. 3(a) have a chemical composition of 100% Ti according to the SEM data. They are probably the remnants of polymer molecules PGMG, which are almost completely transparent in reflected electrons and almost do not form secondary electrons.

One should also pay attention to the smaller size of the degeneration zones of the passive film from titanium dioxide to metatitanic acid in Fig. 2 in comparison with Fig. 1. This is probably due to the presence of lithium chloride in the places of breakdowns in Fig. 1. This electrolyte is well known for its hygroscopicity. The presence of lithium chloride and moisture for a long time in the places of breakdowns caused more extensive damage to the surface of titanium during air drying in comparison with the experimental conditions for Fig. 2, where the electrolyte was eliminated by a longer and thorough rinsing.

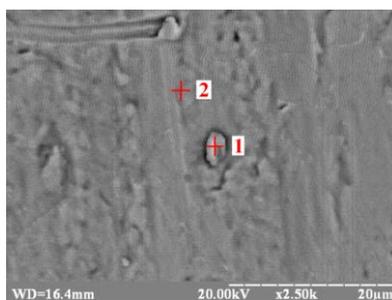


Fig. 3. The surface of titanium after electrochemical treatment and immersion in a solution of lead (II) complex with PGMG. SEM images with the analysis of the chemical composition at the points: 1. 94.12% Ti (IV) + 5.88% Pb (II); 2. 100% Ti (IV).

If the titanium electrode after electrochemical treatment was immersed in a solution of lead (II) salt with PGMG, then the passive film breakdown places were bound by lead ions. This is indicated by the chemical analysis at point 1 in Fig. 3.

If the titanium electrode after electrochemical treatment is rinsed for 5 hours in distilled water, the result of the interaction with iron and lead salts reveals a substantially lower concentration of heavy metal ions at the breakdown points (Fig. 4). This indicates the course of aging and dehydration of metatitanic acid, during which this acid gradually loses its ability to ion exchange. Such a phenomenon will contribute to an increase in the irreversibility of fixing heavy metal ions in the breakdown areas, if ion exchange is carried out immediately after the formation of the breakdown.

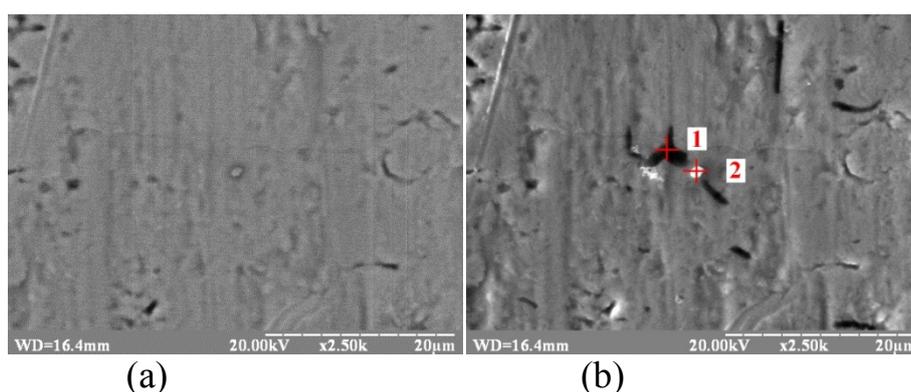


Fig. 4. The surface of titanium after electrochemical treatment, washing for 5 hours and immersion in a solution of an iron salt and lead (II) complex with PGMG. SEM images in the reflected (a) and secondary (b) electrons with an analysis of the chemical composition at the points:

1. 100% Ti (IV); 2. 89.18% Ti (IV) + 9.86% Fe (II) + 0.96% Pb (IV).

5. Discussion and Conclusion

This work shows the possibility of contrast (for SEM) marking of breakdowns of a passive titanium film in such a way that it is possible to determine the time interval for the appearance of specific breakdowns. In this case, the breakdowns can be caused either by the development of the current corrosion process over time, or caused by a change in the corrosion conditions over time. It is established that the places of breakdowns of the passive titanium film are tightened with metatitanic acid. This gelatinous acid loses its ability for ion exchange for several hours and therefore it is capable of fixing heavy metal ions irreversibly if interaction with them occurred immediately after the breakdown. Heavy metal ions contrast in SEM images in both reflected and secondary electrons against the background of titanium oxygen compounds. It is possible to carry out experiments in such a way so as to pump the solution through a three-electrode cell to conduct polarization of the electrodes. In this case, the background solution can be periodically replaced with a solution with a certain marker ion. Thus, it is possible to increase the informativity of a single titanium sample and to reduce the number of SEM preparations for work, which is especially important in the study of many samples with a strong increase in a deep vacuum.

6. Acknowledgment

The authors would like to thank the staff of the Physical Engineering Faculty of the National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute” for the opportunity to obtain SEM images.

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