PHYSICAL CHEMISTRY

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1961

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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INVESTIGATION OF THE STRUCTURE OF PASSIVE OXIDE FILMS ON THE SURFACE OF TITANIUM

(Presented by Academician V. I. Spitsyn, July 5, 1961)

The literature contains certain information on the composition and structure of oxide films formed on the surface of titanium under conditions of high-temperature oxidation in air, oxidation in boiling solutions of oxidizing agents, and anodic oxidation at high positive potentials ([1–3]). The data of various authors, together with the results of the present work, are given in Table 1. There is no information in the literature on the structure of passive films formed on the surface of titanium during self-passivation in solutions at room temperature, or during anodic passivation in solutions at not very high positive potentials.

Table 1

Structures of oxide films formed on titanium under various oxidation conditions

Oxidation conditions and time	Temp., °C	Composition of the oxide film	Literature source
Oxidation in air for up to 10 days	18–20	TiO with a small amount of Ti_3O_5	(8)
Corrosion in 92% H_2SO_4 for 100 h	18–20	Ti_3O_5	(15)
Self-passivation in solutions: 5% HCl, 5% H_2SO_4, 6% HNO_3, 1N NaCl, 1N NaOH for up to 10 days	18–20	$Ti_2O_3 \cdot 3 \div 4TiO_2$	Author' s data

Oxidation conditions and time	Temp., °C	Composition of the oxide film	Literature source
Anodic oxidation in 40% H_2SO_4. At a potential of −0.05 and +1.0 V, 5 h	18–20	$Ti_2O_3 \cdot 3 \div 4TiO_2$	Same
Oxidation in air	875–1050	Layered scale TiO, Ti_2O_3, TiO_2, rutile	(1)
Oxidation in 10% CrO_3 for 10 h	Boiling	TiO_2, anatase and rutile	(2)
Oxidation in aqua regia, 0.5 h	»	TiO_2, anatase	(2)
Oxidation in 50% HNO_3 for 2 h	»	Same	(2)
Anodic oxidation in 0.1N H_2SO_4. At a potential of +8.0 V, 5 h	18–20	» »	(3)
Oxidation in 65% HNO_3 for 5 h	Boiling	TiO_2, anatase with a small amount of rutile	Author' s data
Anodic oxidation in 40% H_2SO_4. At a potential of +8.0 V, 15 min	18–20	Same	Same

In a number of our previous works ([4,5]) it was shown that titanium can spontaneously restore a protective oxide film after its mechanical removal under dilute (up to 5%) solutions of sulfuric and hydrochloric acids. It was subsequently also established that titanium self-passivates after its surface has been cleaned in solutions of sodium chloride and sodium hydroxide, as well as in solutions of nitric acid. In sulfuric and hydrochloric acids of concentration 10% and higher, titanium can passivate only under anodic polarization ([5–7]). The passive state occurs when the potential of titanium becomes more positive than the potential of complete passivation.

in the given acid solution. For example, in a 40% solution of H_2SO_4 at room temperature the potential of complete passivation of titanium is about $\pm 0.0 V*, and therefore the anodic passivity of titanium under these conditions becomes possible if its potential ha
To explain the passive properties of titanium, it is of great interest to determine the composition and structure of the passivating films formed during self-passivation in various solutions, and also during anodic passivity.

Table 2

Interplanar spacings d and qualitative characterization of the intensity of diffraction lines I of electron diffraction patterns of oxide films obtained on titanium in H_2SO_4 and HNO_3

	Self-passivation in 5% H_2SO_4 transmission: exposure in solution 1 day		Self-passivation in 5% H_2SO_4 transmission: exposure in solution 10 days		Anodic oxidation in 40% H_2SO_4 reflection: exposure 5 h, −0.05 V		Anodic oxidation in 40% H_2SO_4 reflection: exposure 5 h, +1.0 V		Anodic oxidation in 40% H_2SO_4 reflection: exposure 15 min at potential +8.0 V		Anodic oxidation in 40% H_2SO_4 reflection: exposure 15 min at potential +8.0 V		Oxidation in boiling 65% HNO_3, transmission		Oxidation in boiling 65% HNO_3, reflection	
No.	d	I^*	d	I^*	d	I^*	d	I^*	d	I	d	I	d	I	d	I
1	2	3.49	3	3.50					7	3.52	7	3.51	6	3.52		
2	2	3.4 — 2.8							2 diffuse	3.24	2 diffuse	3.21				
3	6	2.46	5	2.46	5	2.42	4	2.43	3	2.44	4	2.44	1	2.46		
4									4	2.34	5	2.35	3	2.34		
5	5	2.10	4	2.09	3	2.03	2	2.03	3	2.13	2	2.04				
6	2	1.90	2	1.89					5	1.88	6	1.89	4	1.88		
7	2	1.69	3	1.67					7 broad	1.66	7 broad	1.67	5	1.68		

No.	Self-passivation in 5% H_2SO_4, transmission: exposure in solution 1 day d	Self-passivation in 5% H_2SO_4, transmission: exposure in solution 1 day I^*	Self-passivation in 5% H_2SO_4, transmission: exposure in solution 10 days d	Self-passivation in 5% H_2SO_4, transmission: exposure in solution 10 days I^*	Anodic oxidation in 40% H_2SO_4, reflection: exposure 5 h, −0.05 V d	Anodic oxidation in 40% H_2SO_4, reflection: exposure 5 h, −0.05 V I^*	Anodic oxidation in 40% H_2SO_4, reflection: exposure 5 h, +1.0 V d	Anodic oxidation in 40% H_2SO_4, reflection: exposure 5 h, +1.0 V I^*	Anodic oxidation in 40% H_2SO_4, reflection: exposure 15 min at potential +8.0 V d	Anodic oxidation in 40% H_2SO_4, reflection: exposure 15 min at potential +8.0 V I	Oxidation in boiling 65% HNO_3, transmission d	Oxidation in boiling 65% HNO_3, transmission I	Oxidation in boiling 65% HNO_3, reflection d	Oxidation in boiling 65% HNO_3, reflection I
8	6	1.43	6	1.43	4	1.47	3	1.49	4	1.46	5	1.47	4	1.46
9			2	1.34					4	1.32	4	1.33	2	1.32
10			2	1.24	3	1.29	2	1.29	4 broad	1.25	4 broad	1.24	3	1.25
11					2	1.22								
12	2	1.17	2	1.18					3	1.16	3	1.15	2	1.14
13									1	1.03	2	1.03	1	1.03
14			2 diffuse	1.03										
15											1	0.95		
16			2 diffuse	0.90							1	0.91		
17											1	0.88		
18											1	0.83		

* The qualitative assessment of line intensities was carried out on a ten-point scale: extremely strong–10, very strong–9, strong–8, medium-strong–7, medium–6, medium-weak–5, weak–4, very weak–3, very, very weak–2, very, very, very weak–1.

In our previous investigation, the composition and structure of the oxide film formed on titanium and some of its alloys (VT5, VT3, and VT3-1) during oxidation in air at room temperature were determined. It was shown that the oxide film consists of titanium oxide TiO ([8]). To study the structure of the film, it was separated from the metal surface in an anhydrous 5% solution of bromine in methyl alcohol and investigated by electron-diffraction analysis "in transmission" ([8]).

In the present work, the separation of oxide films for investigation of their structure by the transmission method was carried out using the same procedure. In some cases electron diffraction patterns were obtained by the method

* Potentials in the present article are everywhere given relative to the normal hydrogen electrode.

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Fig. 1. Electron diffraction patterns of oxide films obtained on the surface of titanium under various oxidation conditions.
a –5% H_2SO_4, exposure 1 day; **b** –5% H_2SO_4, exposure 10 days; **c** –65% boiling HNO_3, exposure 5 hours; **d** –65% boiling HNO_3, exposure 5 hours (reflection recording); **e** –40% H_2SO_4, anodic oxidation at a potential of 8 V, exposure 15 min.

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Fig. 1. a –anaphase with a bridge and a fragment (human breast cancer); **b** –anaphase with two bridges (human breast cancer); **c** –anaphase with 3 bridges (rat bone marrow); **d** –anaphase with 4 bridges (rat bone marrow); **e** –anaphase with one fragment (human breast cancer); **f** –multipolar mitosis (rat bone marrow).

Fig. 2. a –metaphase of a giant cell with numerous chromosomes (rat sarcoma); **b** –unequal division in the tripolar anaphase of a giant cell (rat sarcoma); **c** –chromosomes at the poles of metaphase (human uterine cancer); **d** –telophase –metaphase (human uterine cancer); **e** –somatic synapsis (rat sarcoma).

reflection. The photography was carried out on an EM-4 electron-diffraction apparatus with camera constants of 39.8 for transmission photography and 38.9 for reflection photography. The voltage in all cases was 40 kV.

The composition and structure of oxide films formed on titanium were investigated: 1) during self-passivation in solutions of 5% HCl, 5% H_2SO_4, 6% HNO_3, 1 N NaCl, and 1 N NaOH at room temperature; 2) during anodic oxidation in 40% H_2SO_4 at potentials of −0.05, +1.0, and +8.0 V; 3) during oxidation in a boiling solution of 65% HNO_3.

Table 2 gives the results of the electron-diffraction analysis. The results of the analysis of oxide films formed during self-passivation are given only for 5% H_2SO_4, since similar electron-diffraction patterns were obtained in all the solutions studied. On the diffraction lines, texture maxima were present in

almost all cases (Fig. 1). This indicates the presence of an orientation of the crystals in the oxide film, apparently caused by the orientation in the surface layers of the metal that arose during grinding of its surface.

Comparison of the experimental interplanar spacings and line intensities with tabulated values for various titanium oxides and other titanium compounds showed that the diffraction patterns obtained from oxide films formed during self-passivation of titanium in all the above-mentioned solutions (item 1), as well as during anodic passivation in 40% H_2SO_4 at potentials of −0.05 and +1.0 V, agree best with the pattern obtained from titanium oxide of composition $Ti_2O_3 \cdot 3 \div 4TiO_2$. The observed scatter of line intensities for oxide films obtained in different solutions should apparently be explained by distortion of the crystal lattice of this intermediate oxide as a result of deviation from stoichiometric composition, and also by the presence of texture. The oxide of composition $Ti_2O_3 \cdot 3 \div 4TiO_2$ is an intermediate oxide between Ti_2O_3 and TiO_2. This oxide was first found in work ([9]), where the results of its X-ray structural analysis are also presented. Later the results of this work were confirmed in work ([10]), and also in works ([11], [12]). In the last cited works, the oxide of composition $Ti_2O_3 \cdot 3 \div 4TiO_2$ corresponds to two oxides, Ti_5O_9 and Ti_6O_{11}.

It is interesting to note that the oxide film formed on the surface of titanium in 40% H_2SO_4 in the passive state maintained by external anodic polarization, at a potential (+1.0 V) considerably more positive than the potential of complete passivation of titanium in 40% H_2SO_4, equal to 0.0 V, and also at a potential somewhat more negative (−0.05 V), consists of one and the same oxide, $Ti_2O_3 \cdot 3 \div 4TiO_2$. Therefore the transition of titanium into the passive state at the potential of complete passivation may be interpreted as a transition from a state of incomplete coverage of the surface by an oxide film (at potentials more negative than the potential of complete passivation) to a state of complete coverage of the surface by an oxide film (at potentials more positive than the potential of complete passivation); the composition and structure of the oxide layer remain the same.

It should also be pointed out that during anodic passivation of titanium (at potentials not higher than +1÷+2 V) and during its self-passivation in solutions, an oxide film of one and the same composition is likewise formed. This result emphasizes the validity of the conclusion previously drawn in the literature concerning the absence of any fundamental difference between chemical and anodic passivation of metals ([13], [14]).

Analysis of the electron-diffraction patterns of oxide films obtained during oxidation of titanium in 40% H_2SO_4 at more positive potentials, for example +8.0 V, and also during oxidation in boiling 65% HNO_3, shows that in these cases the film consists of the higher titanium oxide TiO_2 with the anatase structure, with a small amount of rutile. These results of ours agree with the results obtained in works ([2], [3]). In Table 2, lines Nos. 1, 4, 6-10, 13-18 are assigned to the anatase structure; to the rutile structure—

lines Nos. 2, 3, 5. The somewhat overestimated intensity of line No. 7 relative to the other lines in the anatase structure, as well as its broadening, is probably explained by the superposition of reflection from this oxide and from rutile, in whose pattern this line is the strongest in intensity. It is also evident from Table 2 that electron-diffraction analysis by reflection and by transmission gives one and the same structure for the oxide film formed during the oxidation of titanium in boiling 65% HNO_3. This indicates that, in the process of separating oxide films from the surface of titanium in a solution of bromine in methyl alcohol, the structure of the film is preserved.

Analyzing the data of Table 1, which presents information on the structures of oxide films obtained in the present work, as well as data available in the literature, one may conclude that the oxide of the highest degree of oxidation of titanium—TiO_2—appears on the surface of titanium under the most severe oxidation conditions. Such conditions are: oxidation in air at high temperature, oxidation in solution at boiling temperatures, and anodic oxidation at high positive potentials. Under less severe oxidation conditions—self-passivation in solutions at room temperature or anodic oxidation in solutions at not very high positive potentials—an oxide of a lower degree of oxidation than TiO_2 is formed on the surface of titanium, namely an oxide of composition $Ti_2O_3 \cdot 3 \div 4TiO_2$. Under still milder oxidation conditions, the formation of still lower oxides of titanium is possible. For example, during the self-dissolution of titanium in H_2SO_4 we detected on its surface the oxide Ti_3O_5 ([15]), while during oxidation in air at room temperature, as already indicated above, TiO is formed ([8]).

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Received
4 VII 1961

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Note: Figure translations are in progress. See original paper for figures.