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THE INFLUENCE OF PROCESS PARAMETERS ON PROPERTIES OF CONVERSION COATINGS DEPOSITED ON TITANIUM ALLOY

The effect of process parameters of conversion coatings on the corrosion resistance was investigated. To produce anodic coatings, the solutions of H_2SO_4 of 0.5 and 1 M concentrations and current densities of 0.5 and 1 A/dm² were applied. The coatings were deposited by galvanostatic technique on titanium Grade 1. The result of the study was comparison of the corrosion resistance of coatings produced under varying parameters such as: the anodic current density, the electrolyte concentration, and the speed of reaching the preset voltage. Corrosion tests performed by potentiodynamic polarization test have shown that even nanometric anodic films of amorphous structure improve the corrosion resistance of titanium alloy. The lowest corrosion current and the corrosion potential of the most cathodic nature were observed in the sample with anodic coating produced at $J = 1$ A/dm² in a 0.5 M H_2SO_4 electrolyte concentration.

Keywords: Titanium alloys, anodising, corrosion resistance, polarisation curves, conversion coatings

1. Introduction

Titanium with a good ratio of density to strength, high corrosion resistance and high mechanical properties becomes a competitive construction material. It has already found application in various sectors of the industry, like aerospace, automotive, chemical, and medical. Titanium oxide which forms on the surface of products is compact and morphologically homogeneous [1], and protects the material from the effect of corrosive environment. One of the methods of producing oxide films is a galvanostatic method where the oxidation takes place at a constant current density. The thickness of the oxide film which can be obtained by this method ranges from several to several hundred nanometres [2] and depends on the voltage applied during its process [3].

The voltage used in the process of oxide film growth affects on the structure of the film. There are two voltage ranges which give different types of structure: up to 20 V gives an amorphous structure, and above 45 V nanocrystalline anatase and rutile are formed [4]. Anatase, brookite and rutile are different crystallographic forms of titanium dioxide. Rutile is the most stable and has the highest corrosion resistance [2]. Titanium dioxide is characterised by transparency, but as a result of the interference of reflected rays, a colour effect is obtained with tint depending on the thickness of the oxide film [8]. Studies of the chemical composition of oxide films showed the presence of not only the basic elements such as titanium and oxygen, but also of additional elements which were transferred from the electrolyte [5]. Another parameter affecting the quality of films, in addition to the structure and chemical composition of the electrolyte, is the chemical composition of titanium alloy on the film is formed. The studies of the Ti6Al4V alloys confirm the presence of Al_2O_3

[6] and V_2O_5 phases [7] in oxide films formed on the surface.

The corrosion resistance of titanium alloys depends on the quality of oxide coating. This, in turn, depends on the coating structure, voltage applied, electrolyte type, and chemical composition of the substrate on which the protective coating is formed.

2. Test methods and materials

Titanium alloy from the Grade 1 series is characterised by optimum ductility, high impact strength, good weldability, and the ability for deep drawing [9]. This alloy was used in aircraft fuselages, and in the chemical and marine industry [10]. Table 1 shows the chemical composition of the titanium alloy Grade 1 on which the oxide films were produced. To determine the chemical composition, the following devices were used: GDS 850A (LECO) glow discharge emission spectrometer, CS600 (LECO) carbon and sulphur analyser, analyser of oxygen, nitrogen and hydrogen TCH 600 (LECO) and AAS Solaar M6 (Thermo).

TABLE 1
Chemical composition of Ti Grade 1 alloy [%]

Element	N	C	H	Fe	O
Content	0,012	0,016	0,0062	0,03	0,100

Samples with dimensions of 30 x 25 x 1.2 mm were polished with abrasive papers, starting with 180 grit and passing to 320, 1000 and 4000. The washed samples were dried, and prior to the formation of protective film, were degreased with acetone and etched in a Kroll's solution

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containing HF, HNO₃ and H₂O. On thus prepared samples, oxide films were produced by galvanostatic method in two solutions. The solutions which were used in the tests were 0.5 M H₂SO₄ and 1 M H₂SO₄. Current densities amounted to 0.5 A/dm² and 1 A/dm². The time of the film formation amounted to a few dozen seconds until the required tension was obtained. The study continued until the voltage of ~ 20 V was achieved.

Electrochemical studies were performed using an AUTOLAB PGSTAT 302 set for electrochemical analysis using a GPES ver. 4.9 software. Samples were tested by potentiodynamic method in the range of potential values from -1.0 to 0.5, with the potential scan rate of 0.005 V/s. The electrodes were titanium samples with and without protective film. A platinum electrode was used as counter electrode and the reference electrode was Ag/AgCl 3M KCl electrode. Measurements were carried out in a 1 M NaCl solution at 25°C. Samples were polarised after 10 minutes of stabilisation of open circuit potential.

3. Results and discussion

During the process of creation the oxide films, constant current density of 0.5 A/dm² and 1 A/dm² was maintained in two concentrations of the H₂SO₄ solution (0.5 M and 1 M). Once the value of 20 V was reached, the experiment was stopped. At higher current densities, the speed of reaching the desired voltage was higher. According to literature indicates that thus obtained coating has an amorphous structure [4]. From the diffraction pattern it follows that the X-ray diffraction from the coating produced on titanium alloy is characterised by the background level enlarged by 50% in a low-angle range. This indicates the presence of an amorphous material on the surface of the examined sample. Absence of the crystallised titanium oxide variations results in corrosion resistance inferior to that which the presence of TiO₂ in the form of e.g. rutile would confer to the coating [2]. Studies have shown that even a thin amorphous oxide film on the material increases its resistance to corrosion. The diagrams compare the polarisation curves of titanium Grade 1 and titanium Grade 1 with oxide films produced in H₂SO₄ at different process parameters: electrolyte concentration and current densities are shown on Figs. 1 and 2. The coating had a deep blue colour indicating the thickness of about 40 - 50 nm [11].

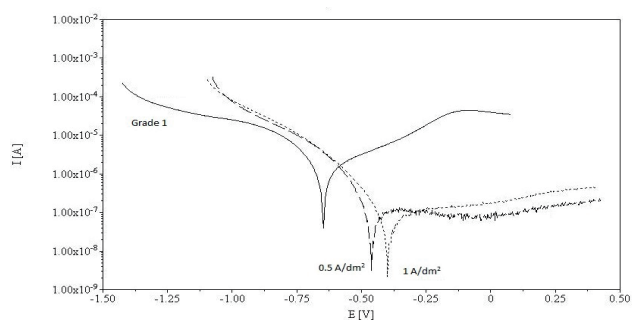


Fig. 1. Corrosion resistance of titanium Grade 1 and of the samples with oxide film produced in a 0.5 M H₂SO₄ solution at 0.5 A/dm² and 1 A/dm²

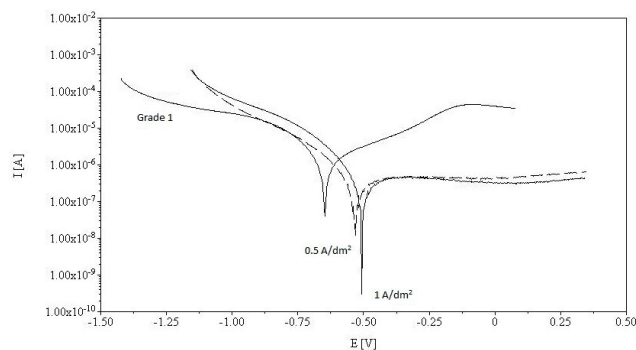


Fig. 2. Corrosion resistance of titanium Grade 1 and of the samples with oxide film produced in a 1 M H₂SO₄ solution at 0.5 A/dm² and 1 A/dm²

The numerical values of the electrochemical test results are compared in Table 2.

TABLE 2
Electrochemical test results for oxide films on titanium produced in a 0.5 M H₂SO₄ acid

	Grade 1	Concentration of solution: 0.5M H ₂ SO ₄		Concentration of solution: 1M H ₂ SO ₄	
		0.5 A/dm ²	1 A/dm ²	0.5 A/dm ²	1 A/dm ²
i_{corr} [μA/cm ²]	0.7076	0.03284	0.02986	0.1157	0.0563
$E_{\text{corr, calc}}$ [mV]	-641	-459	-387	-525	-505

For a less concentrated solution it can be observed that with increasing current density, the corrosion potential assumes a more cathodic character. The corrosion current densities were similar in both samples. The oxide film produced in a 1M sulphuric acid at 0.5 A/dm² shows, the corrosion current two times higher at a density of 1 A/dm². This may indicate that the slower is the process of reaching the specified voltage (in this case 20 V), the better is the quality of the oxide film, and consequently the more effective is the protection of titanium surface from corrosion. The higher speed of anodising causes in amorphous films higher rate of defects of a donor-acceptor type [12]. More defects result in a lower corrosion resistance of the protective oxide films.

The corrosion potential of the sample with oxide film produced in a 1M sulphuric acid at 1 A/dm² is slightly shifted towards more cathodic side. It can be stated that in these two cases, for an electrolyte less and more concentrated, the corrosion resistance of the oxide film produced at a higher current density assumes higher values. The polarisation diagrams are shifted towards more cathodic side and the value of corrosion current is lower which indicates better corrosion resistance.

The polarisation curves of oxide films produced at the same current density, but in two electrolytes with different concentrations of sulphuric acid was comparison. In the course of the studies it was found that when the oxide film was produced by galvanostatic method at a preset current value,

but without completing the test earlier, the sample voltage was increasing to a certain point, and then kept stable at a proper level. With parameters $J = 0.5 \text{ A/dm}^2$ and the electrolyte concentration of $0.5 \text{ M H}_2\text{SO}_4$, the maximum value of the voltage was 25.2 V , while for $J = 0.5 \text{ A/dm}^2$ and the electrolyte concentration of $1 \text{ M H}_2\text{SO}_4$, the voltage assumed a lower value of 21.7 V . E Krysicka – Cydzik [12] explains this phenomenon by describing changes in the anodic potential as a result of two processes. The first process is the film formation, and the second one is its dissolution in the electrolyte. If there is a plateau on the chart, it means that the system has reached the state of equilibrium between the film formation and its digestion in the electrolyte. This effect occurs when the oxide film has reached an adequate thickness.

In both cases it has been shown that the film produced at a higher current density, in an electrolyte less or more concentrated, has a lower corrosion potential than the film produced at a lower current density. The corrosion current is higher and the resistance is much lower.

4. Conclusions

The oxide films obtained in the conducted studies on a titanium alloy perform well their protective function. Based on the results of the experiments it can be concluded that with the increasing anodization current density, the corrosion resistance of titanium alloy increases, too. Another type of relationship exists between the electrolyte type and the corrosion potential. The more concentrated is the electrolyte, the more anodic corrosion potential is (at the two different current densities used in this study). These results have been used to determine optimal parameters of the anodic oxidation of a titanium alloy

from the Grade 1 series in H_2SO_4 . The lowest corrosion current and the most cathodic corrosion potential were observed in a sample with the oxide film produced at $J = 1 \text{ A/dm}^2$ and in the electrolyte concentration of $0.5 \text{ H}_2\text{SO}_4$

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