GALVANIC COATINGS ON TITANIUM ALLOYS
COMMUNICATION 1. THE ROLE OF HYDROGEN IN PROCESSES
OF PREPARATION OF THE BASE UNDER THE COATING

R. M. Sageeva and S. I. Berezina

UDC 621.235.76 + 546.3-19 + 546.821

Earlier investigations [1, 2] have established that the sorption of cathodic hydrogen and hydrogen absorbed by the base (platinum, iron) during its preliminary treatment exert a decisive influence upon the electro-deposition of coatings — their hydrogenation, fine structure, and physicomechanical properties. If the base contains sorbed hydrogen, which prevents the diffusion of hydrogen atoms liberated during the process of deposition of the metal, deep within the cathode, then a strongly hydrogenated layer of deposit is formed on the cathode. If, however, the hydrogen sorbed by the base is in an electrochemically active state (i.e., at a given potential it is capable of participating in electrochemical reactions), then the electrochemical desorption of hydrogen discharged at the cathode simultaneously with the metal can be thereby insured.

The state of the surface of the base is of exceptional importance in the application of galvanic coatings on titanium and its alloys. Titanium is one of the transition metals possessing free orbitals that can participate in the formation of molecular orbitals and thereby ensure stronger chemical bonds. This distinguishes titanium from the metals of the eighth group in their behavior toward hydrogen. Thus, titanium is capable of absorbing hydrogen in substantially greater amounts than nickel and iron, and of forming compounds of variable composition with different structures, properties, and stabilities, during this combination. These peculiarities of hydrogen compounds of titanium should evidently substantially influence the process of electrodeposition of metallic coatings. A hydride phase of definite composition and properties depending upon the nature of the deposited metal and conditions of electrolysis may be the most favorable for the application of the coating.

The purpose of this investigation was to study the sorption of hydrogen by titanium and its alloys during the process of preliminary preparation of the surface under galvanic coatings, and to determine the influence of the composition of the solution and conditions of treatment upon the nature of the compounds formed.

EXPERIMENTAL

Sheet titanium, brand VT-1, with the composition (in wt. %): Ti 99.25; O 0.1; N 0.02; H 2 0.15; Si 0.15; Fe 0.30 and titanium alloy OT-4, containing the following additives (in %): Al 2-3.5; Mn 0.8-2.0; Fe 0.4; Si 0.5; C 0.1 were investigated. According to the literature data [3], titanium possesses a hexagonal lattice with parameters a = 2.95 Å, c = 4.73 Å, ratio c/a = 1.60. In view of the absence of detailed information on the structure of the alloy OT-4 in the literature, its structure was determined by x-ray diffraction study. It was established that this alloy possesses a hexagonal lattice with parameters a = 2.903 Å, c = 4.62 Å, ratio c/a = 1.59.

The surface of the samples was subjected before the investigation to standard treatment with emery paper and degreased with a paste of trisubstituted sodium phosphate. The adsorption of hydrogen and change in the state of the surface during the treatment of the samples in various solutions were studied according to electron diffraction patterns, as well as by taking polarization curves and by oscillographic study of the anodic charging curves. A description of the procedure is not cited here, since it was already given in [1] and [4, 5].

A study of the behavior of titanium samples was conducted in a solution containing 5.15 M H₂SO₄ and 8.67 M HCl, as well as in conc. H₂SO₄ (sp.gr. 1.83) and in conc. HCl (sp.gr. 1.19). The solution containing

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR.
The stationary potentials were measured for samples OT-4 and VT-1 in conc. H_2SO_4 and HCl, as well as in mordant solution 1. Figure 1 presents the results of a measurement of the potentials with time for samples of VT-1. On all the curves there is a sharp potential jump in the region of negative values, which is evidently associated with the dissolution of oxides on the surface of titanium. Then titanium begins to dissolve, and its ions begin to be accumulated around the electrode. Approximately 30–40 min after the beginning of immersion of the sample in the corresponding solution, a constant potential is established, characterizing the process of dissolution of titanium and the formation of surface compounds. The values of the established potentials in HCl, in mordant solution 1, and in H_2SO_4 are equal to -0.370, -0.350, and -0.210 V, respectively. Visual observations of sample OT-4 and VT-1 after exposure in these solutions indicated that in the first and second cases, a dark gray dull film is formed on their surface, while in H_2SO_4 the surface remains light-colored and shining.

The nature of the compounds formed on the surface was investigated by electron diffraction studies. Figure 2 presents characteristic electron diffraction patterns. Interpretation of the electron diffraction patterns indicated that in mordant solution 1 at room temperature, titanium hydride with a cubic face-centered lattice, possessing a parameter of 4.41 Å (a), is formed on the surface of the titanium alloy OT-4. In the etching of titanium in conc. HCl according to our data and the data of [6], the lattice parameter of the hydride formed is equal to 4.46 Å. If a sample of the titanium alloy OT-4 is exposed for 20 min at room temperature to solution 1 with an addition of 0.03 M hydrofluoric acid, then titanium hydride with parameter 4.46 Å (b) is identified on an electron diffraction pattern from this sample.

In conc. H_2SO_4, there is no formation of titanium compounds with hydrogen, but a titanium oxide of mixed composition is formed [7]. If a sample treated in mordant solution 1 is exposed to conc. H_2SO_4 for 1 h, titanium hydride is still identified on the electron diffraction pattern. When the sample is exposed for 12 h, the picture changes entirely (c), which is evidently due to the oxidation of its surface. The exposure of titanium samples to mordant solution 1 and to conc. HCl is always accompanied by the accumulation of titanium ions. The divalent titanium ions formed during dissolution are very rapidly oxidized to the trivalent state, and more slowly to the tetravalent state.

To determine the influence of titanium ions on the process of etching, we measured the potentials of samples of VT-1 in a solution of conc. HCl, containing 10 g/liter Ti. Figure 3 presents curves of the change in the potentials with time in the indicated solution directly after the dissolution of metallic titanium in it (1) and after 24 h exposure of this solution to air (2). The nature of the curves obtained differs. A stable value of the stationary potential in a freshly prepared solution is established immediately after immersion of the sample in the solution. Such a value of the potential in a solution exposed to air for 24 h is reached only after the passage of 35–40 min, after the surface of the metal has reached a sufficient concentration of titanium ions of lower stages of oxidation, eliminating the oxidative function of tetravalent titanium.