THE NATURE OF THE CURRENT MAXIMA ON THE POLARIZATION CURVE OF NICKEL IN 1 N H_2SO_4

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In spite of numerous investigations, the nature of the maxima on the anode polarization curve of nickel in 1 N H_2SO_4 remains unclear. In accordance with [1-4], the first current maximum corresponds to the formation of NiO; the critical passivation potential is connected with the transition from NiO to Ni_3O_4 [2, 5], or with the appearance of Ni_2O_3 [6, 7]. The presence of these compounds was not confirmed in [1-7] by any kind of physical methods, but was based on thermodynamic calculations of the formation potentials. The most probable is the formation of NiO [8-10], which has been confirmed by x-ray means and by x-ray photos in an electron microscope [11-14]. It has been confirmed by these same methods that NiO is the sole oxide formed with the oxidation of nickel, both at high temperatures [15-18] and in a solution with an oxidizer [19]. The compounds NiO, Ni_2O_3, and NiO_2 give different x-ray photos [20].

Taking account of the suboxide theory of oxidation of I. I. Kornilov [21-23], with application to the various faces of monocrystalline nickel, the present author advanced the postulation [24] that, with anode polarization, in the active region, along with dissolution, there are complex multi-state processes of the formation of suboxides, right up to the formation of NiO [12], leading to points of inflection on the polarization curve. This postulation can be extended also to a polycrystalline metal, where all the suboxides indicated in [24] should be formed.

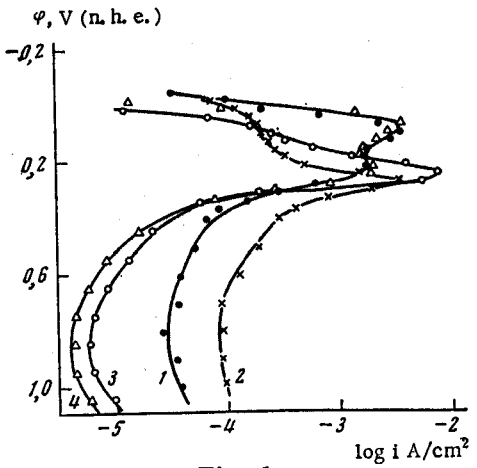

Fig. 1

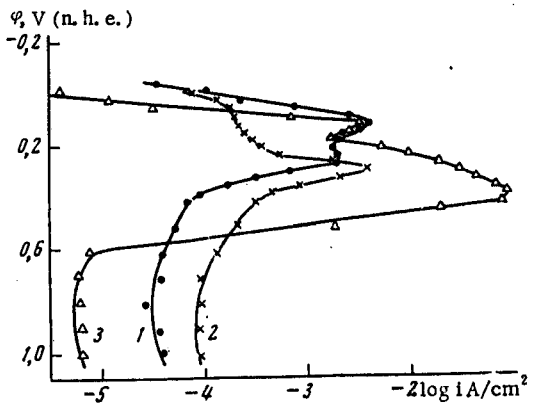

Fig. 2

Fig. 1. Anode polarization curves in 1 N H_2SO_4: 1) compounds Ni_9O—Ni_3O; 2) compounds $Ni_{2.5}O-Ni_{1.8}O$; 3) face of Ni (111); 4) face of Ni(110).

Fig. 2. Anode polarization curves in 1 N H_2SO_4: 1) compounds Ni_9O—Ni_3O; 2) compounds $Ni_{2.5}O$—$Ni_{1.8}O$; 3) Ni annealed at 750°C.

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TABLE 1

Nickel				Ni–O compounds			
monocryst. [24]		polycryst. [28]					
(110) face	(111) face	def 70%	anneal. at 750°C	$Ni_9O - Ni_3O$	$Ni_{2.5}O$	Ni_2O	Ni_2O, $Ni_{1.8}O$
0,26	0,23	0,29	0,38	0.23	0,29	0,32	0,35

For purposes of experimental verification, alloys of nickel with oxygen were prepared, and their properties were studied in 1 N H_2SO_4. Alloys of 12 compositions with an oxygen content from 10 to 35 at.% were obtained by melting NO nickel, refined by the electron-beam method, and "pure" NiO, in a controlled atmosphere. In accordance with an analysis for oxygen, and in accordance with [25-27], the following formulas can be assigned to the materials obtained:

$$Ni_9O,\ Ni_6O,\ Ni_5O,\ Ni_{4.5}O,\ Ni_4O,\ Ni_{3.5}O,\ Ni_{3.2}O,$$
$$Ni_3O,\ Ni_{2.5}O,\ Ni_{2.3}O,\ Ni_2O,\ Ni_{1.8}O.$$

Anode polarization curves were recorded using a P-5827 potentiostat, in 1 N H_2SO_4, in accordance with a previously described method [28].

The alloys can be separated into two groups with identical electrochemical properties (Fig. 1). The curves practically coincide for the compounds Ni_9O–Ni_3O (oxygen content 10-25 at.%) and $Ni_{2.5}O$–$Ni_{1.8}O$ (oxygen content 27-35 at.%). In the first case, curve 1 has two maxima; under these circumstances, the current corresponding to $\varphi_{max\,I}$ is considerably greater than with $\varphi_{max\,II}$. In the second case, curve 2 has one current maximum. The potential of this maximum depends on the oxygen content in the alloy (see Table 1). In the region of $\varphi_{max\,I}$, the curves for suboxides of the composition Ni_9O–Ni_3O practically coincide with the curve for the face (110) up to φ = 0.32 V, and differ considerably from the curve for the face (111) (Fig. 1). This constitutes evidence of the formation of different suboxides on the given faces with anode polarization; for (110), the formation of compounds with a lower oxygen content than for face (111) is obviously characteristic. Such suboxides have low passivation characteristics, which can be seen from a comparison of the currents, in the passive region for suboxides, of the faces (110) and (111) of single crystals, as well as of deformed and annealed polycrystalline nickel.

As can be seen from Fig. 2, the first current maximum of the curve for compounds with a low oxygen content coincides with the first maximum of the curve for the annealed polycrystalline metal. The appearance of the first maximum on the curve for nickel is obviously connected with the formation of suboxides with a low content of oxygen (up to 24 at.%). The polarization curves of these compounds are characterized by the absence of a developed active section ahead of the second current maximum (determined by the dissolution of polycrystalline nickel preferentially over the body of a grain). However, a similar section is observed on the polarization curve for $Ni_{2.5}O$–$Ni_{1.8}O$. These compounds are obviously formed, during the multi-stage process of the anode oxidation of nickel, from compounds with a lower oxygen content, mainly along the boundaries of the grains and blocks. The latter has been confirmed by metallographic data [28].

Taking account of what has been said, the data on the critical passivation potentials φ_{cr} (Table 1) can be explained in the following manner. If it is assumed that, at the moment when φ_{cr} is attained, there form on the surface of nickel compounds differing in their oxygen content, then, on face (110) which is most prone to passivation, they should contain less oxygen than on face (111). On deformed polycrystalline nickel, which is more prone to passivation than annealed nickel, compounds with a smaller oxygen content are also formed. The passivation potential is probably determined by the composition of the layer developed on the metal, which is different for different structural states.

Taking account of the results of [12, 24, 28] and of the present work, the process of the passivation of nickel in 1 N H_2SO_4 can be represented in the following manner. At potentials close to φ_{cor}, the oxygen of water is chemisorbed on nickel. With a shift of the potential into the region of higher positive values, the oxygen enters into the lattice of the metal, at first in a small amount. Then, the content of oxygen rises, most rapidly at the points of defects in the structure. This leads to distortion of the crystal lattice in the surface layer, which is evidenced by the washed-out character of the diffraction spots on electron-microscope photos.

In the region of the first maximum, NiO appears in small amounts, but mainly the compounds Ni_9O —Ni_3O (10-25 at.% oxygen), which also lead to a point of inflection on the polarization curve. With a further increase in the potential, the surface film becomes more complex; it already contains a considerable amount of NiO and suboxides with an increased oxygen content. With the attainment of the critical passivation potential, the process of dissolution of the metal with the participation of anions of the electrolyte is suppressed by the passivating layer which develops. The composition of this layer is complex, and depends on the structural state of the nickel, i.e., on the amount and distribution of the dislocations, the sizes of the grains and blocks, and the orientation of the surface.

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