BRIEF COMMUNICATIONS

EFFECT OF CRYSTALLOGRAPHIC ORIENTATION ON THE ANODIC OXIDATION OF NICKEL SINGLE CRYSTALS

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UDC 620.195

It is well known that many properties of metals, including electrochemical, catalytic, and adsorption characteristics, are anisotropic. The present work is an investigation of the effect of crystallographic orientation on the process of anodic polarization of nickel in an acidic medium. This investigation is a continuation of an earlier work on the properties of high-purity nickel [1].

Nickel single crystals were obtained by electron beam vacuum remelting of NO grade nickel. Samples were mechanically cut from the ingot and subjected to careful chemical polishing. The orientation of the faces was determined by x-ray diffraction. The single crystal was cut by electroerosion, after which the cold-worked layer was removed by chemical polishing.* Samples used in electrochemical investigations were in the form of prisms with a square cross section (3 × 3 mm), with the end surfaces having the required orientation. The lateral surfaces of the samples were insulated by BF glue and polystyrene. Samples with end surfaces of (111), (100), and (110) plane configuration were studied. The medium used was 1 N H_2SO_4 at 25, 45, 55, and 65°C. The technique used for electrochemical measurements was the same as in the earlier work [1]. The experiments were carried out in a special electrolytic cell, in which all electrode spaces, and the glass cocks connecting them, were at the investigation temperature. The sample surfaces, after anodic oxidation, were studied metallographically.

Polarization curves obtained at 25°, for nickel single crystals with (111), (100), and (110) faces, show that anodic processes depend on crystallographic orientation (Fig. 1). A bend appears in the region of active state of the surface for the (111) face. This bend becomes more marked for the (100) face, while in the case of the (110) face the curve shows two maxima, with $i_{max\ I}$ greater than $i_{max\ II}$. The (111) face is the most difficult to oxidize, as evidenced by the large values of the currents of active solution. The (110) face is the most easily oxidized among all the investigated surfaces. The stable passivation potential ($\varphi_{pass}^{(110)}$) for this face equals 0.23 V. There is no difference between the stable passivation potentials for the (111) and (100) faces, both being equal to 0.26 V. These values are considerably more negative than φ_{pass} for polycrystalline nickel [1].

Figure 2 shows the anodic curves for the (110) and (100) faces at 25, 45, 55, and 65°. Polarization curves for the (111) face at 45, 55, and 65° are practically identical with the curves for the (100) face. These data indicate that raising the temperature up to 65° has no effect on the stable passivation potential. However, the nature of the anodic processes on each face undergoes a change on heating the electrolyte. In the case of the (111) and (100) faces there occurs another maximum in the region of active state of the surface at 55 and 65°. The high rates of solution of nickel single crystals at 65° bring about a situation in which, even as the first maximum is attained, the surface loses its crystallographic characteristics and acquires the indices of the fastest dissolving face. The anodic curves at 65° are therefore identical for all the three investigated surfaces. The polarization curves in the regions of total passivation and overpassivation do not show any special features, and do not differ from the curves for polycrystalline nickel.

It was also possible to establish (by calculation, using the method of least squares) from the experimental data that, in the range of potentials from 0.17 to 0.23 V, there exists a linear relation between the

* The polishing was carried out in such a way that the crystallographic orientation of the sample surface was not disturbed. This was verified by observing the shape of etch pits.

E. O. Paton Institute of Electric Welding, Academy of Sciences of the Ukrainian SSR. Translated from Zashchita Metallov, Vol. 6, No. 6, pp. 674-678, November-December, 1970. Original article submitted March 3, 1969.

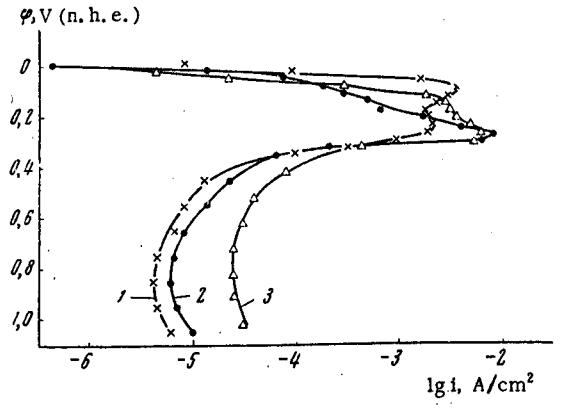

Fig. 1. Polarization curves of nickel single crystal in 1 N H_2SO_4. 1) (110) face; 2) (111) face; 3) (100) face.

logarithm of anode current density and 1/T. The values obtained for the apparent activation energy (ε_φ) are, for instance, 12.8, 14.3, and 18.0 kcal/mole for the (111), (100), and (110) faces respectively, at $\varphi = 0.20$ V. The fact that the highest value of ε_φ is obtained for the (110) face is in conformity with the tendency of this face to become passive. At potentials that are more negative than 0.17 V, there is no linear relation between log i and 1/T, which is indicative of the complex nature of the processes that occur.

The experimental data obtained make it possible to place the crystallographic planes of nickel single crystal in the descending order (110) > (100) > (111), as far as the tendency towards anodic oxidation in 1 N H_2SO_4 is concerned. The same order is observed for the anodic oxidation of nickel single crystal in an alkaline solution as well [2].

In studying the electrochemical properties of different crystallographic planes of single crystals, three basic factors should be taken into account: 1) electronic and energetic properties of the plane surfaces; 2) geometric features of the spatial arrangement of atoms on different planes; 3) effect of imperfections in the crystal structure. Let us examine these factors in the light of the data obtained.

The differences in the atomic arrangements on different planes of single crystals lead to changes in the properties of these planes, including the atomic work function. Kashetov and Gorbatyi [3] determined the thermoelectronic characteristics of the planes of high-purity nickel single crystals. They established that the work function on the (111), (100), and (110) planes equals 5.22 ± 0.03, 4.89 ± 0.03, and 4.64 ± 0.03 eV respectively. If these data are considered in conjunction with the fact that adsorption of oxygen occurs primarily on those planes which have the lowest work function [4], and that planes with a large work function are more resistant to oxidation [5, 6], then it can be concluded that anodic oxidation of any plane is governed by its energy state. In nickel single crystals the passivating tendency of the different planes decreases with increasing work function values. This is borne out by the series (110) > (100) > (111), in which the planes with lower work function values are also less resistant to oxidation.

In a face-centered cubic crystal the (111) and (100) planes have the closest packing of atoms. The (110) plane is less closely packed and has a more complex structure, the atoms being arranged in rows. Germer, MacRae, and Hartman [7-9] studied the interaction of oxygen with nickel single crystals of different

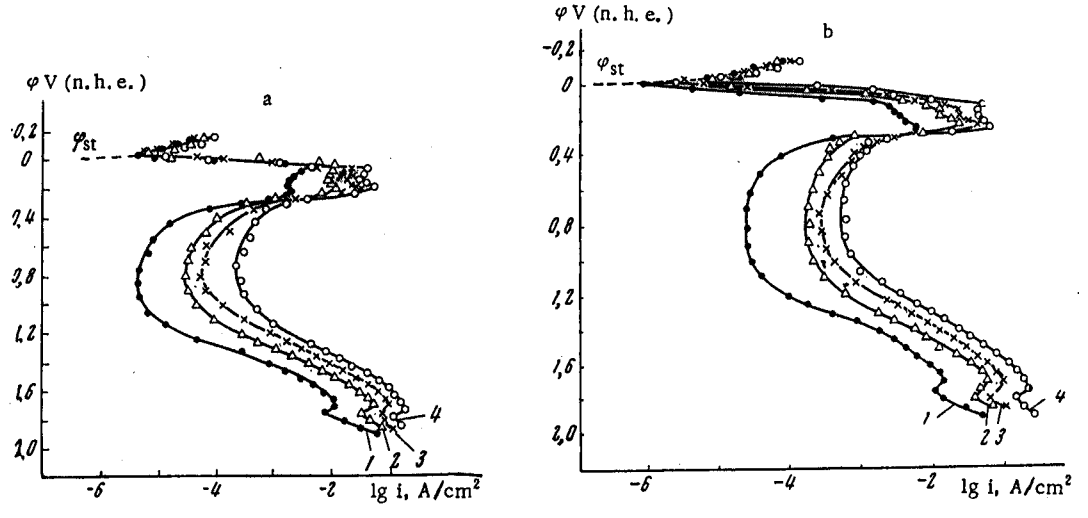

Fig. 2. Effect of temperature on the polarization characteristics of nickel single crystal with (110) (a) and (100) (b) faces. 1) 25; 2) 45; 3) 55; 4) 65°C. 1 N H_2SO_4.

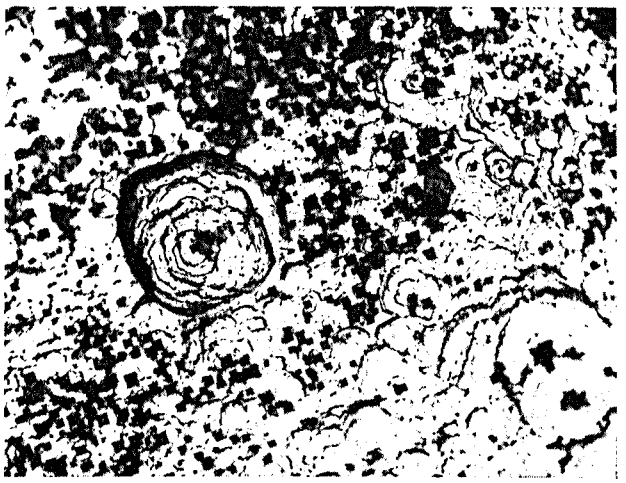

Fig. 3. Microstructure of anodically oxidized (100) plane in nickel single crystals. 1 N H_2SO_4, 55°, change in φ from −0.13 to +0.23 V (× 340).

orientations. They established that oxygen atoms are arranged in a two-dimensional structure in the first monolayer on the (111) and (100) planes, and that this layer consists only of oxygen atoms. Adsorption of oxygen on the (110) planes gives rise to a layer that consists of nickel and oxygen atoms. This difference is explained by the formation of a stronger bond between nickel and oxygen atoms on the (110) plane. Germer, MacRae, and Hartman also studied the structure of these layers by diffraction of slow electrons. These studies established the formation of different compounds of nickel with oxygen, depending on the orientation of the surface.

Kornilov [10, 11] has recently developed a suboxidic theory for the oxidation of transition metals. Using the basic concepts of Kornilov's theory, and the data of Germer, MacRae, and Hartman [7-9], one can visualize the following stagewise process of oxidation of nickel crystal:

plane (111) $Ni + O \rightarrow Ni(O) \rightarrow Ni_3O \rightarrow Ni_2O \rightarrow NiO.$

plane (100) $Ni + O \rightarrow Ni(O) \rightarrow Ni_4O \rightarrow Ni_2O \rightarrow NiO$

plane (110) $Ni + O \rightarrow Ni(O) \rightarrow Ni_5O \rightarrow Ni_3O \rightarrow Ni_{2,5}O \rightarrow Ni_2O \rightarrow NiO.$

The above ideas on the multistage nature of the process may now be considered in relation to the anodic oxidation of nickel single crystals. However, at present there is insufficient data to establish that one or another suboxide appears at a definite potential. It can be proposed that, in the region of active state of the surface, transfer of metal to the solution is accompanied by complex multistage processes of suboxide formation, right up to the formation of NiO. These processes result in the appearence of a bend, a maximum, or two maxima on the polarization curve. Their shape, and the conditions under which they appear, depend on the properties of the compounds formed. Obviously, it is the composition and properties of these compounds that determine the anodic behavior of the (111), (100), and (110) planes of nickel single crystals.

Our earlier work [12], in which we had studied the formation of NiO during anodic processes by electron diffraction, showed that defects in crystal structure are centers of formation of NiO. Nickel single crystals used in the present work have a defect density of the order of 10^8 cm^{-1}. No literature data are available on the distribution of dislocations on various planes of single crystals. Apparently, other things being equal, the closest packed planes will have a lesser number of dislocation outlets than planes that are not so closely packed. An increase in the number of structural defects facilitates the process of anodic passivation, which is what is observed on the (110) plane. Metallographic investigation of anodically oxidized surfaces in single crystals showed that the formation of compounds of nickel with oxygen occurs primarily at the sites where dislocations emerge. These regions acquire geometric forms which are characteristic for each plane: triangles on the (111) plane, squares on the (100) plane, and rectangles on the (110) plane. Figure 3, for instance, shows the formation of oxides on the (100) plane at those sites where screw and edge dislocations have emerged.

In conclusion it can be stated that the anodic oxidation of nickel single crystals depends on the crystallographic orientation of the surface, the governing factors being surface energy and geometry. Structural defects are centers of formation of nickel oxides.

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