# POTENTIOSTATIC METHOD OF INVESTIGATION IN PHYSICAL METALLURGY (REVIEW)

Ya. M. Kolotyrkin, L. M. Nerodenko, and L. N. Yagupol'skaya

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Electrolytic methods for the surface treatment of metallic materials find wide application in physical metallurgy. The structural peculiarities of metals and alloys have been studied using special sections, the preparation of which involves electropolishing and etching in addition to mechanical grinding and polishing. Thin foils for electron microscope investigations have also been prepared by the electrolytic method. These processes are based on the anodic dissolution of the metal. The operating conditions for the electrolytic treatment are generally selected according to the nature of the investigation, but, as a rule, this selection is empirical [1-3] and, while it allows for the regulation of the composition of the solution and for temperature changes, there is no allowance for the electrochemical parameters of the system. The current density and the potential on the bath do not determine the process of anodic dissolution to the proper degree.

The magnitude of the electrode potential is the basic parameter which determines the anodic behavior of metals and, depending on the value of this potential, the metal may find itself in a state of active dissolution, passivity, or repassivation [4-7]. During these processes the rate of ionization of metallic atoms is independent of whether the potential is maintained by anodic polarization, by the addition of oxidants, or by other means [8].

The potentiostatic method [9] is widely used at the present time for the investigation of the kinetics and mechanism of electrochemical reactions. The method consists of applying and maintaining constant values of the potential on a sample using an electronic potentiostat and measuring the current density which is established. The dependence between potential and current density is represented in the form of polarization curves.

A potentiostatic polarization curve is shown schematically in Fig. 1. The point b on the curve corresponds to the equilibrium value of the potential of the metal in the absence of polarization, that is, when no external current flows in the system. At potentials more negative than $\varphi_b$, cathodic processes (ab) take place, while, at more positive values of the potential, anodic processes occur. The region of active dissolution corresponds to the part of the curve bc and, furthermore, for metals such as nickel, for example, a more complex dependence with two maxima bb'b"c is observed in several media. At potentials which are more positive than $\varphi_c$, the electrode goes into a passive state (de) and subsequently into a region of superpassivation where the band corresponds to the point where oxygen begins to be evolved. In several cases the passive state of the metal is not observed. This is the case, for example, with electropolishing [10] when the dependence between the anodic current density and the potential is depicted by the curve bcg'h'.

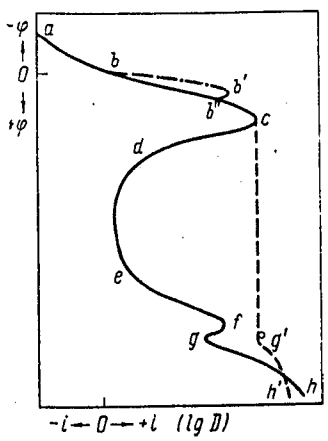


Fig. 1. Schematic diagram of a potentiostatic polarization curve.

The surface of the electrode can also acquire potentials which are close to the potentials indicated for the various different regions of the polarization curve by adding various types of compounds, for example, oxidants to the solution. The rate of dissolution of the metal under these conditions is also determined by the value of $\varphi$. It can be concluded from this that electrolytic and chemical methods for the surface treatment of metals are identical and the magnitude of the potential is the determining factor.

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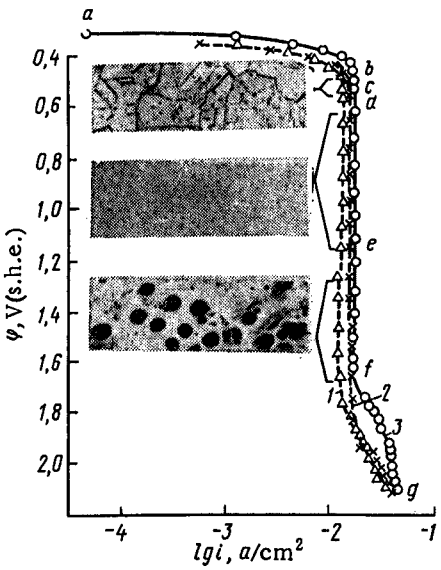


Fig. 2. Anodic polarization curves for the MO grade copper in $H_3PO_4$. (1) Cast; (2) deformed; (3) recrystallized metal.

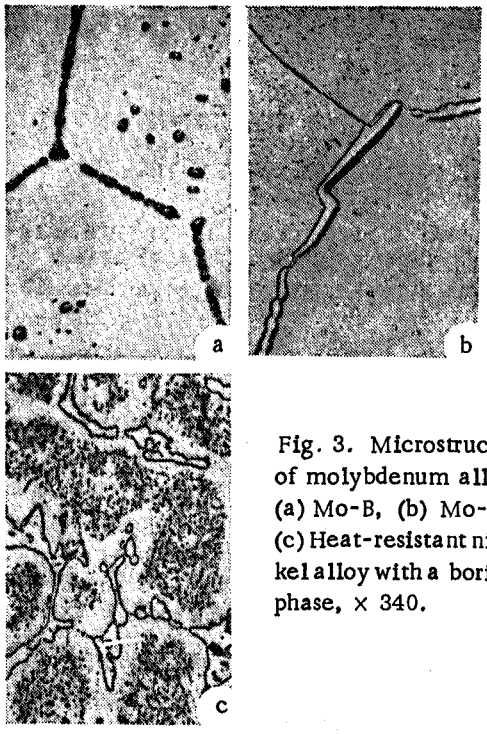


Fig. 3. Microstructure of molybdenum alloys (a) Mo-B, (b) Mo-C, (c) Heat-resistant nickel alloy with a boride phase, × 340.

In chemical processes the potential can only be regulated by empirical selection of the composition of the solution, which can only be realized with difficulty. In electrolytic processes it is possible and necessary to regulate the magnitude of the potential. For a given set of conditions, the potential is set at a definite level during the course of the process which may involve a long or short span of time. The latter requirement can only be attained by the use of potentiostatic techniques.

Results of the application of potentiostatic methods to several processes used in physical metallurgy are considered below.

Electrolytic Polishing. The process of electrolytic polishing is extensively used both in scientific investigations and in practice [10-14]. Electrolytic polishing has mainly been studied using the galvanostatic method, although the potentiostatic method was used in [13]. The process is conventionally controlled by adjusting the potential applied to the terminals of the bath and the current density.

We have studied the electropolishing of copper [15], molybdenum, and molybdenum base alloys under potentiostatic conditions. The anodic polarization curves in $H_3PO_4$ (specific gravity 1.55, room temperature) for samples of MO grade copper in the cast, deformed, and recrystallized states are shown in Fig. 2. These curves show the typical $\varphi - \lg i$ dependence for electropolishing processes. Etching occurs on the part of the curve marked bc while at more positive potentials electropolishing of the surface is observed (de) with practically the same current flowing. Oxygen begins to be evolved when the potential is increased still further and hemispherical pits appear on the surface of the copper. At values of $\varphi$ which are significantly more positive ($f_g$ and further), polishing is also observed but it is accompanied by the copious evolution of oxygen. Practical electropolishing is usually carried out under these latter conditions.

The following conclusions can be drawn on the basis of the results which have been obtained.

1. If electropolishing is carried out under conditions where only the current strength is controlled, then it is not possible to obtain a good quality surface since it is difficult to ensure that the process takes place in the required region of the part of the curve from b to f. According to the origin of the process, etching, polishing, or pit formation can occur at the one and the same current strength. By controlling the value of the potential, it is possible to carry out the process in the desired direction under strictly specified conditions.

2. The process of electropolishing copper in the cast, deformed, and recrystallized states has the same character which makes it possible to potentiostatically polish both the metal and its welding compound.

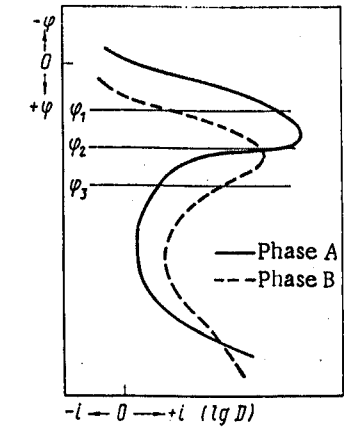


Fig. 4. Schematic anodic curves for two phases with different electrochemical properties.

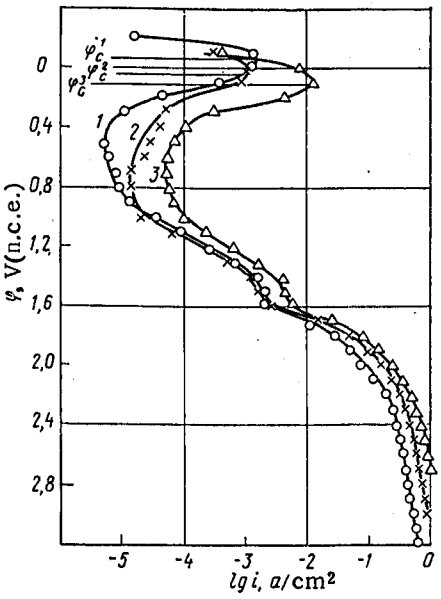


Fig. 5. Anodic potentiostatic curves of high purity nickel in $H_3PO_4$. (1) A single crystal of the metal (111 edge), (2) deformed, (3) heat treated at 750°C.

3. The best results were obtained for the polishing of copper in $H_3PO_4$ (sp. gr. 1.55) at $\varphi$ = 1.00 V and at a temperature of 20°C. Under these conditions no oxygen is evolved during the process.

The possibilities of the potentiostatic method can also be demonstrated using molybdenum alloys as an example. Sulfuric acid (sp. gr. 1.84) containing 10 vol. % of $CH_3OH$ was used as the electrolyte. At $\varphi$ = 1.5 V and a temperature of 40°C, good quality polishing of molybdenum was observed without the evolution of oxygen. The polishing of multiphase molybdenum alloys is of special significance. Thanks to the fact that the molybdenum matrix polishes well while a phase containing boron, for example, is not dissolved under these conditions, the structure of the alloy can be very clearly revealed (Fig. 3a) by polishing.

It has been established by special investigations using an interferometer that the boron-containing phase rises above the surface both inside of the grains as well as along the grain boundaries. These same experiments have shown that the phase with carbon, on the other hand, is dissolved under these conditions and hollows, the form of shapes which clearly indicates the phase distribution, remain on the surface of the section (Fig. 3b). When the conventional techniques for etching and polishing molybdenum alloys are used with no allowance being made for the value of the potential, it is difficult to obtain clear structures without pitting and also to obtain reproducible results.

Selective revelation of the second phase has been observed for a multiphase molybdenum alloy. However, for other purposes such as the preparation of their samples for investigation in a transmission electron microscope, it is necessary to carry out the process in such a manner that the matrix and the phases are polished practically identically [16-18]. As was shown in [19], the use of the potentiostatic method allow this aim to be realized. The authors of the above-cited work obtained good films from stainless steel and aluminum alloys under conditions where the samples were reduced in thickness at a specific potential which was held constant by means of a potentiostat.

Etching of Metals and Alloys. The etching of metals and alloys in electrolyte solutions in order to reveal their structures is based on the various different electrochemical properties of the individual structural components: grain boundaries, phase inclusions, boundaries phase inclusions, boundaries of blocks, etc. [3, 20]. The potential is also the parameter which defines this process. Hence if the dependence of $\varphi$ on lgi for a specific metal in a given electrolyte is known, then it is possible to select a value of the potential from the polarization curve at which the desired etching will take place. For instance, on passivated metals such as high purity nickel [21] strong dissolution of the blocks in the grains takes place in the region corresponding to anodic dissolution in the active state while the boundaries of the grains and blocks remain passive. However, at potentials in the region corresponding to superpassivation practically all the elements of the surface including the grain boundaries are dissolved.

The etching process becomes more complicated when one considers multiphase alloys. The potentiostatic technique of etching was first suggested for stainless steel and aluminum alloys [22-24]. Since each phase of the components of the alloys is characterized by a specific $\varphi$ – lgi dependence during anodic polarization, a value of the potential can be selected from a comparison of the polarization curves at which the differences between the rates of solution of the various separate phases will be minimal or maximal.

Schematic curves for two phases with different electrochemical properties are shown in Fig. 4. At $\varphi_1$ preferential solution of phase A occurs, at $\varphi_2$ the rate of solution of the two phases is identical while at $\varphi_3$ phase B is preferentially dissolved. Under these conditions the etching of specific components can be achieved if it is assumed [25] that during dissolution under potentiostatic conditions there are no synergistic effects in a multiphase material.

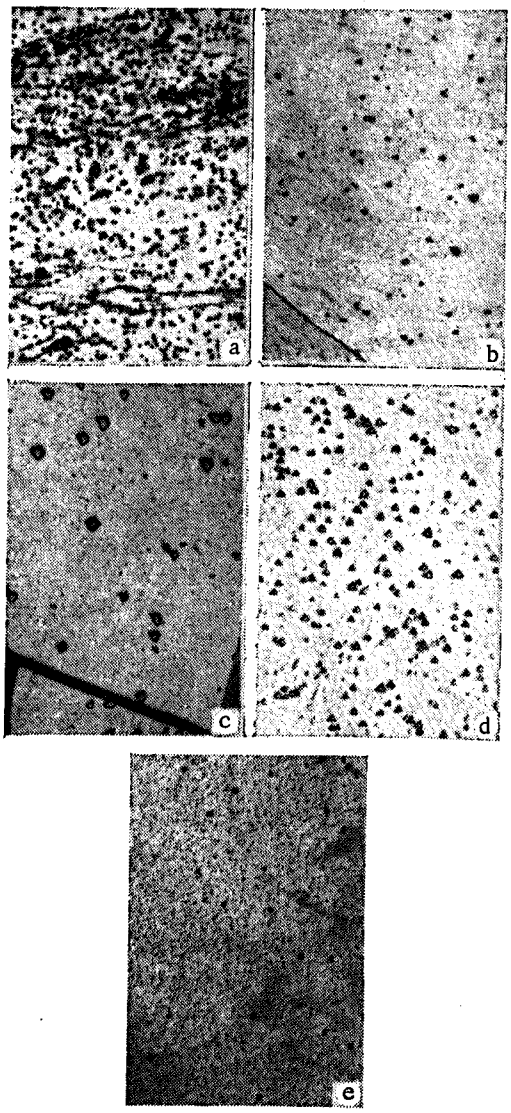


Fig. 6. Microstructure of high purity nickel, potentiostatic etching in $H_3PO_4$: a) deformed metal; b) annealed at 750°C, $\varphi$ of the transition region; c) the same, $\varphi$ of the superpassivation region; d) nickel single crystal, (III) edge, $\varphi$ of the transition region; e) the same, $\varphi$ of the superpassivation region. X 340.

Particularly good results are obtained with potentiostatic etching for the revelation of the structural and phase components of high alloy steels of the 18-8 type [26-31], and also cast iron [32], Ni - Al alloys [33] and V - Nb alloys [34]. For example, with Ni–Al alloys ranges of potentials have been established for the selective etching of the $\gamma$ and $\beta'$ phases in the presence of the $\gamma$ phase in 1-N $H_2SO_4$. The polarization characteristics of the individual phases have been studied on synthetic specimens as was done in [35] in order to establish the conditions for the separation and etching of the compounds formed between Fe and Cr, Mo, and Ti.

In several cases it has not been possible in general to reveal complex phases using conventional methods. For instance, the boron phase in a heat-resistant nickel base alloy was only revealed by us using potentiostatic etching in 10% oxalic acid at $\varphi$ = 1.2 V (Fig. 3b).

Dislocation Pit Etching. Selective etching is one of the methods for observing dislocations on the surface of a solid body. It is supposed that there is a link between the etching pits and the places where the dislocations emerge onto this surface [4].* Dislocations, on account of their nature, promote both the chemisorption of particles from solution and an increased mobility of the metal atoms which jointly determine the selective dissolution. According to Cabrer [37], the effectiveness of dislocations as the places of formation of the nuclei of elementary pits depends on the nature of the dislocation and the impurity content. The rate of formation of pit nuclei is greater on boundary dislocations, since their energy is greater, and less on dislocations with precipitated impurities which lower the energy of the dislocations. At the same time an atmosphere of impurities can locally increase the solubility due to electrochemical heterogeneity. Some one of these factors will determine the process, depending on the etching conditions.

The etching is usually carried out by the chemical or electrolytic method. As was the case of the other processes, its efficacity is determined by the value of the potential. It therefore follows that the etching should also be carried out under potentiostatic conditions and this is even more necessary since the process of revealing the pits is very sensitive to the solution composition and to the operating conditions under which the etching is done. Small deviations in composition and operating conditions can lead to changes in the external form of the pits, their orientation, and even to the complete absence of pits. The potentiostatic method of selective etching has been successfully applied to single crystals of copper [41] and tungsten [42].

We have investigated the etching of high purity nickel prepared by electron beam refining. Specimens of a single crystal of the metal with a (111) orientation, the polycrystalline metal subjected to a 70% deformation, and the polycrystalline metal heated in vacuum at 750°C were anodically polarized in 35% $H_3PO_4$ (the electrolyte used to reveal the etch pits on Ni according to [43]) using a potentiostat.

*There is a very large amount of data available in the literature concerning etching pits. For example, the review [36] and also the bibliography in [37-40].

The resulting curves are shown in Fig. 5, from where it can be seen that nickel in 35% $H_3PO_4$ is a typical passivated metal. The nickel single crystal was the most inclined to passivation followed by the deformed metal and then the heat-treated metal which exhibited significantly less inclination to passivation. Values of the potentials were taken from these curves which correspond to the region of dissolution in the active state and to the transition region. Sections which had been carefully chemically polished after mechanical preparations were maintained at these potentials for 10 to 15 minutes. The sections were subsequently investigated metallographically.

Etch pits were formed at potentials more negative than $\varphi_c$, and at $\varphi$ values corresponding to the transition region. During this process the sample was covered by a film. The etch pits were also formed at potentials more positive than the potential at which oxygen begins to be evolved.

The etch pits formed on the deformed metal at a potential $\varphi$ in the transition region are shown in Fig. 6a. At potentials lying in the superpassivation region, the number of pits did not increase but they became larger. At potentials close to $\varphi_c^3$ etch pits were produced on the surface of the metal which had been heat treated at 750°C which were very clear and sharply defined. Their form corresponded to the crystallographic orientation of the grains (Fig. 6b). Upon selective etching in the superpassivation region, the pits lost their shapes to some extent while increasing in dimension (Fig. 6c). The etch pits on the (111) plane of a single crystal sample obtained at potentials in the transition region and in the superpassivation region are shown in Fig. 6 (d, e).

The pits are quite different both in size, in the clarity of their boundaries, and especially in quantity. The latter is possibly associated with the fact that etch pits can only form on a given crystallographic plane at definite potentials. Hence reagents which differ in comparison and create different potentials on the surface of the metal cause the appearance of etch pits only on specific crystallographic planes.

The data obtained indicate that selective etching under potentiostatic conditions yields significant information concerning dislocations than etching carried out under uncontrolled conditions. The etch pits are usually revealed in the superpassivation region. It is very difficult to carry out the process under conditions where the surface is in the active state without maintaining the potential at a constant value, although the best results are obtained under the latter condition.

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