Relaxation Kinetics of the Current of Hydrophilic Metal Dissolution Activated by Anodic Pulses

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Abstract—Relaxation kinetics of the metal dissolution current after pulsed anodic activation are analyzed using a model of spatial separation of the dissolution and passivation of hydrophilic metals. The current rise is contributed to mainly by the formation of new step sources resulting from the desorption of blocking oxygen atoms from vertexes of trihedral pyramids that are formed in excess quantities during the activation pulse.

Key words: anodic metal dissolution, metal passivation, iron, anodic activation of dissolution, electrode surface morphology

INTRODUCTION

Boris Nikolaevich Kabanov, to whose memory this issue of “Elektrokhimiya” is devoted, paid much attention to studies of the deposition, dissolution, and passivation of solid metals. One of the most important trends in his works was the revelation of the effects of the metal surface structure and adsorption state on the mechanism and kinetics of these processes. This trend of investigations is still topical nowadays. Moreover, it may be a factor in advancing theoretical basis for new technologies, due to the emergence of new experimental research methods, as well as new applications of electrochemical methods for machining and modifying metal surfaces.

Iron is one of the most topical objects for these studies. It was shown [1] that the model of spatial separation of dissolution and passivation (SSDP), as applied to hydrophilic metals [2, 3], allows one to explain qualitatively the phenomenon of anodic dissolution activation (ADA) of the iron subgroup metals [4–6]. With allowance for the steady-state ADA, we succeeded in a quantitative modeling [1, 7] of the shape of the steady-state dissolution and passivation (SSDP) requires an analysis of the non-steady-state kinetics of all conjugated processes involved in the model.

THE ROLE OF THE CHANGES IN THE SURFACE MORPHOLOGY IN THE NON-STEADY-STATE DISSOLUTION OF IRON

In our calculation of the anodic current relaxation after ADA, we will proceed from the results obtained in [1, 7]. According to the simplified model used in [1–3, 7], we will examine a square piece of surface with the area $s_{ss} = 1/N_{ss}$, where $N_{ss}$ is the concentration of SS (cm$^{-2}$), at one of the rectangular faces $xy$ of a trihedral pyramid located in the origin, carrying an SS at its vertex. The dissolution occurs only in the active part of this area, which comes to $s_{ac}(x_1, y_1) = (x_1 + y_1)N_{ss}^{1/2} - y_1 x_1$, where $x_1$ and $y_1$ are coordinates of the point $T_1(x_1, y_1)$ at which the adsorbed oxygen atom closest to the SS is located. This atom blocks the motion of kinks (positions of the semicrystal at steps) along the $x$ axis, as well as the motion of steps along the $y$ axis and thus prevents the dissolution in the area $s_{pas} = s_{ss} - s_{ac}(x_1, y_1)$ for the “residual” lifetime $\tau_r$ of $O_{ads}$. The time $\tau_2$ depends on the motion time of the step and the kink thereon from the SS to the point $T_2(x_1, y_1)$ and on the time $t_k$ of the collision motion of the left-side kink along the step at $y = y_1$ from the point $T_k(x_k > x_1, y_1)$, at
which a vacancy (that is, a couple of kinks) is born, to the point $T_1(x_1,y_1)$ at which the blocking atom of $O_{ads}$ is located:

$$I_k = 2e_0v_k/I_k b_k,$$

(1)

Here, $x_k$ is referred to the $O_{ads}$ locality, $e_0$ is the electron charge, $I_k$ is the current of iron dissolution in a unit kink, and $b_k$ is the distance along the $x$ axis between the neighboring iron atoms in the lattice. When the left-side kink encounters the $O_{ads}$ atom, the latter's bonding to the lattice is loosened [1], which leads to its premature "forced" desorption. As pointed out above, the desorption results in an additional SS formation at the point $T_1(x_1,y_1)$. Apart from the dissolution in the kinks, kink sources (KS) located at the step intersection points on stable faces [16–18] (in the discussed simplified model, at the $y$ axis), and SS, among other possible ways of creating structural defects at the iron surface during ADA, the vacancy formation at steps can be viewed as the most probable source of new active dissolution centers. According to calculations [1], the formation rate $I_{ss}$ (in A) of a single vacancy at a step at potentials $E$ approaching the steady-state corrosion potential $E_{cor}$ is negligibly small as compared with the iron dissolution rates in more active centers, namely, in the kinks ($I_k$), KS ($I_{ss}$), and SS ($I_{ss}$), as well as the desorption rate $I_{ss}$ of a single atom of $O_{ads}$. Only during the activating anodic pulse can $I_{ss}$ reach a value comparable with or exceeding $I_{ss}$. Therefore, after completion of the activating pulse at $E_a$ and relaxation to the initial value $E_i$, (related to the Tafel segment in the curves), the formation of vacancies at the steps and the slower processes (for example, the vacancy formation at the faces) cannot affect the current relaxation significantly. Thus, of all the processes interacting within the SSDP model, in analyzing the current relaxation after pulsed ADA, only processes of fast dissolution of iron in the kinks, KSs, and SSS should be allowed for, together with much slower processes of the formation and desorption of $O_{ads}$ atoms (the more so, the desorption of excess $O_{ads}$ at vertexes of blocked pyramids) and, depending on the $E_i$ value, the vacancy formation at the steps. The last process can be neglected when $E_i$ approaches $E_{cor}$ [1].

Let the excess SSs, $O_{ads}$ atoms at the faces, $O_{ads}$- blocked pyramids, and vacancies at monatomic steps in non-steady-state quantities remain at the surface by the time of the completion of an anodic activating pulse (AAP) at $E = E_a$ that is, when passing from $E_a$ to $E = E_i$. The concentrations of the listed entities are $N_{ss}$, $N_{oa}$, $N_{pba}$ (in cm$^{-2}$), and $N_{ss}$ (cm$^{-1}$), respectively. Upon completing fast processes of charging the electrical double layer, the dissolution rates (corresponding to $E_d$) for the dissolution in a unit kink, in KSs, in SSs, and during the formation of vacancies at the steps are set in, as well as the rates of formation ($I_{ss}$) and desorption ($I_{ss}$) of a single atom of $O_{ads}$. Then the area $s_{ss}$ contains one (by definition) KS, $N_{op} s_{ss}$ of $O_{ads}$ atoms at the $xy$ face, and $N_{pba} s_{ss}$ of $O_{ads}$ atoms at vertexes of blocked pyramids at this face. We take this time instant as the reference point in the process of current relaxation after ADA ($t_0 = 0$). Further changes with time $t$ in the concentrations of the above entities participating in the iron surface morphology formation result from (a) the complete dissolution of a pyramid carrying an SS, i.e. the SS disappearance; (b) the formation and desorption of $O_{ads}$ at the dissolving face; (c) the formation of pyramids after steps encountered $O_{ads}$; and (d) the formation of SS after a “normal” (i.e. not “electromechanical” [12–15]) desorption of $O_{ads}$ from vertexes of pyramids (both excess $O_{ads}$ at time instant $t = 0$ and those formed later as a result of encounters between steps and $O_{ads}$). Unlike the steady-state cases discussed in [1–3, 7], a dominant part in the non-steady-state dissolution is played by the SSs and $O_{ads}$ atoms generated during AAP. In addition to the increasing SS concentration, the anodic activation gives birth to a large number of pyramids blocked by $O_{ads}$, which after the desorption of $O_{ads}$ convert into additional SSS, thus increasing the overall current (or slow down its relaxation). The residual lifetime (counted from $t_0 = 0$) of the blocking $O_{ads}$ atoms formed during AAP is on average shorter than that of $O_{ads}$ formed at the face in the steady-state mode. Therefore, the emergence of new SSS at the previously blocked pyramids, after completing the activation, dominates over the slower (now, at $E = E_i$) process of the SS formation in the full cycle (i.e. with the $O_{ads}$ formation and with its collision with a kink and subsequent desorption). During AAP, the dissolution in kinks, KSs, and SSs accelerates by a few orders of magnitude; hence, the time intervals it takes the steps to encounter $O_{ads}$ are extremely short, while the heights of the formed pyramids, because of the high dissolution rates, must on average be the same as during the steady-state dissolution. However, the number of blocked pyramids must be very high, i.e. $N_{pba}$ is presumably commensurate with $N_{oa}$.

The rate constants for the iron dissolution at all active centers are by orders of magnitude higher than those for the $O_{ads}$ formation and desorption [1–3, 7, 19]. Therefore, the dissolution processes in the area $s_{ss}$ proceed at a slow changing $O_{ads}$ concentration $N_{oa}$, practically in a steady-state mode described in [3]. As the passive (more precisely, blocked by $O_{ads}$) areas form in individual collisions of steps with the nearest $O_{ads}$ atoms, the slow changes in $N_{oa}$ practically do not disturb the steady-state character of dissolution and passivation processes over the area $s_{ss}$: The concentrations of blocked pyramids, on the other hand, upon switching AAP off, decay with time via a simple monomolecular kinetic law, as the SSDP model prohibits the $O_{ads}$ formation at vertexes of dissolving pyramids [1–3]:

$$N_{pba}(t) = N_{pba} \exp(-t/t_2/2e_0).$$

(2)

However, as $N_{pba}(t)$ decreases and the situation approaches a steady state, the number of $O_{ads}$ at non-deformed faces, where the SS formation occurs in the mode described in [3], increases and raises the probability of encounters between steps and these $O_{ads}$ and,