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Steps and kinks on {2 1 1} iron surfaces and the kinetics of the iron electrode

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The quantitative analysis of the morphology of dislocation-free {2 1 1} iron surfaces during electrochemical dissolution and measurements of distances and directions of monatomic steps provide information about the rates and potential dependences of three different elementary processes involving iron atoms bound to the lattice in three geometrically and energetically different states. The interaction of the three elementary processes explains the well-known anomalies of the kinetics of the iron electrode. A statistical analysis of the step distances is given.

1. Introduction

The catalytic mechanism of the iron electrode emphasizes the importance of the crystallographic structure of the metal surface [1, 2]. The mechanism postulates that the surface concentration of kinks is an exponential function of the overvoltage. In agreement with the classical theory of electrocrystallization, growth or dissolution of the crystal occurs at kinks which are formed at atomic steps on low-index crystal planes. These steps may originate from two-dimensional nucleation or from defects in the crystal lattice, e.g. screw dislocations. A new mechanism for the generation of steps and kinks was found to be predominant during the anodic dissolution of iron from surfaces vicinal to {2 1 1} [3, 4]. On iron electrodes, only {2 1 1} and {1 1 0} surfaces are stable in a wide range of potentials and current densities [4, 5]. The observed steady-state non-equilibrium morphologies are only compatible with mechanisms in which the rate-determining charge transfer occurs directly at kinks. It is shown below that the postulated steps can be detected experimentally. Preliminary results are presented concerning the densities of steps and kinks on {2 1 1} surfaces of iron resulting from the anodic dissolution in sulphuric acid at different current densities and electrode potentials.

2. Theoretical

According to the catalytic mechanism, charge transfer occurs at kinks. Neglecting the pH-dependence of the rate, the rate-determining step may be written

$$\mathrm{Fe'Fe_k} \rightleftharpoons \mathrm{Fe'_k} + \mathrm{Fe^{2+}} + 2\mathrm{e^-} \qquad (1)$$

$\mathrm{Fe_k}$ is an atom in a kink which upon dissolving leaves its neighbouring atom Fe′ in the position of a kink, $\mathrm{Fe'_k}$. Mechanism 1 is in agreement with transient polarization curves exhibiting a slope of about 60 mV/decade for both the dissolution and deposition of iron. When measuring transient polarization curves starting from a given steady-state, one can suppose that the surface concentration of kinks remains constant. From a comparison of transient polarization curves and steady-state polarization curves with Tafel slopes close to 30 mV/decade for both the anodic and cathodic directions of the reaction, it was concluded that the surface concentration of kinks increases with overvoltage by about 60 mV/decade.

In order to obtain information about the generation and the concentration of the kinks, it was first necessary to have a quantitative analysis of the morphology of iron surfaces [3–5]. During the dissolution of surfaces vicinal to {2 1 1} a relatively simple steady-state morphology was found experimentally; triangular pyramids are

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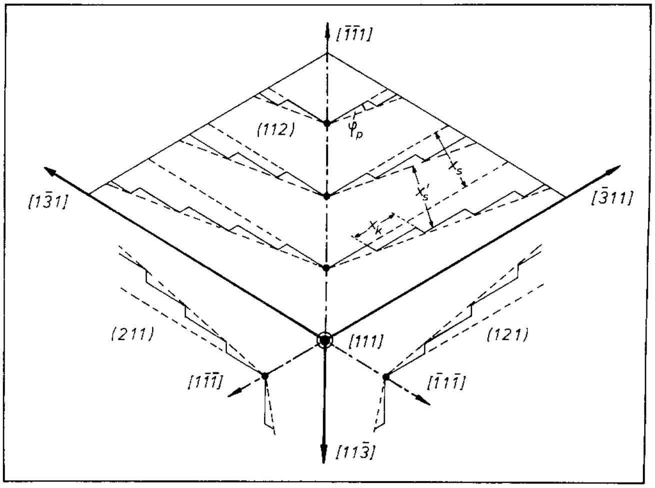

Fig. 1. Schematic model of steps and kinks on crystallographic (2 1 1), (1 1 2) and (1 2 1) planes projected into a (1 1 1) plane.

limited by nearly perfect {2 1 1} planes and ⟨3 1 1⟩ edges. The model in Fig. 1 shows a top view along [1 1 1]. The theoretical angle between two ⟨3 1 1⟩ directions is 117·04°. The dimensions of one pyramid are determined by the misorientation of the actual surface with respect to {2 1 1} and by the composition of the electrolyte, but within a certain range they are independent of the rate of dissolution. The pyramids are not formed at dislocations. The surface concentration of the pyramids is not related to the dislocation density. Etch pits generated at dislocations exhibit a distinctly different morphology.

The theoretical analysis [3, 4] of iron dissolution at the pyramids shows that the morphology is incompatible with the formation of steps by local statistical two-dimensional nucleation or with the formation of kinks by one-dimensional nucleation which would result in a statistical roughening of the surface and of the steps. Steps can only be produced when one atom dissolves at the apex of a pyramid, which contains three equivalent atoms in a (1 1 1) plane. The point of generation of new kinks is the intersection of two steps in one plane.

Therefore the dissolution can be described by three elementary processes $\dot{N}_s$, $\dot{N}_p$ and $\dot{N}_k$. $\dot{N}_s$ stands for the probability of generating a set of six monatomic steps in a given time interval on the three {2 1 1} planes intersecting at the apex of one pyramid. $\dot{N}_p$ is the probability of generating kinks at the intersection of two monatomic steps and $\dot{N}_k$ the probability of removing an atom from a kink.

These three elementary processes determine the structural parameters of the surface. The mean distance x_s of steps perpendicular to their ⟨3 1 1⟩ direction is given by $\dot{N}_p$ and $\dot{N}_s$

$$x_s = b^*\dot{N}_p/\dot{N}_s \qquad (2)$$

where b^* is the distance of the atoms perpendicular to a monatomic step. The mean distance x_k of kinks at a step is described by $\dot{N}_k$ and $\dot{N}_p$

$$x_k = b\dot{N}_k/\dot{N}_p \qquad (3)$$

where b is the distance of the atoms parallel to a monatomic step.

The kinks at the steps lead to a misorientation φ_p of the steps; then, the real mean distance of monatomic steps is

$$x_s' \doteq x_s(1 + \dot{N}_p/\dot{N}_k) \cos \arctan (\dot{N}_p/\dot{N}_k). \quad (4)$$

If kinks were generated by statistical roughening of the steps, the misorientation with respect to ⟨3 1 1⟩ would be $\varphi_p = 0$.

The steady-state current density j_s is determined only by $\dot{N}_s$

$$j_s = ze_0\dot{N}_s/bb^*. \qquad (5)$$

The current density j in terms of the surface concentration $(x_s x_k)^{-1}$ of kinks and the current $I_k = ze_0\dot{N}_k$ at one kink is given by

$$j = ze_0\dot{N}_k/x_s x_k. \qquad (6)$$

Equation 6 is valid for both stationary and transient states. In principle, this mechanism operates for both dissolution and crystal growth.

In order to prove these theoretical considerations it is necessary to detect the monatomic steps with a height of 1·17 Å and measure their morphological properties. The statistical analysis of step distances and their curvature permits conclusions about the statistics of the elementary processes at the three particular positions. By examining these elementary processes at various electrode potentials and pH values one can obtain detailed information about the mechanism of the iron electrode.

3. Experimental

Iron single crystals prepared by dynamic recrystallization from Johnson–Matthey zone-refined iron were used [4]. The absolute orientation of surfaces vicinal to {2 1 1} was determined by the Laue method. After mechanical and electrolytic polishing the crystals were placed in an electrolytic cell containing 0·05 M $Fe(ClO_4)_2$ + 0·95 M $Ba(ClO_4)_2$ with a pH-value 0·90 ± 0·04 at 20° C in a nitrogen atmosphere. During anodic polarization at various potentials the morphology of the iron surfaces was simultaneously observed through an optical window by means of an optical microscope.

The anodic dissolution was stopped when the steady-state morphology was attained. After removing the electrodes from the cell and cleaning them with distilled water, they were then immediately dried in a vacuum. The subsequent decoration with gold was performed at a pressure of 10^{-6} torr. Afterwards thin carbon replicas were prepared for investigation in an electron microscope.

4. Results

In Fig. 2 most of the gold islands with a diameter of 10–30 nm exhibit a statistical distribution, but a distinct ordering of the islands along straight lines is also visible. In all the experiments two systems of lines are observed forming an angle very close to the theoretical angle of 117·04° between two ⟨3 1 1⟩ directions. The experimental angles are slightly larger than the theoretical angle. The misorientation grows with the anodic current density, but does not exceed about 1·5°.

Sometimes a step changes its direction for a short distance, creating a parallel displacement of the step continuation in the main direction. The mean angles, including the displacements, are always larger than the angles obtained without considering visible displacements. The frequency of displacements grows with current density. At high current densities steps frequently change direction and the displacements become larger. The pictures of replicas then convey the impression that steps are merging or disintegrating.

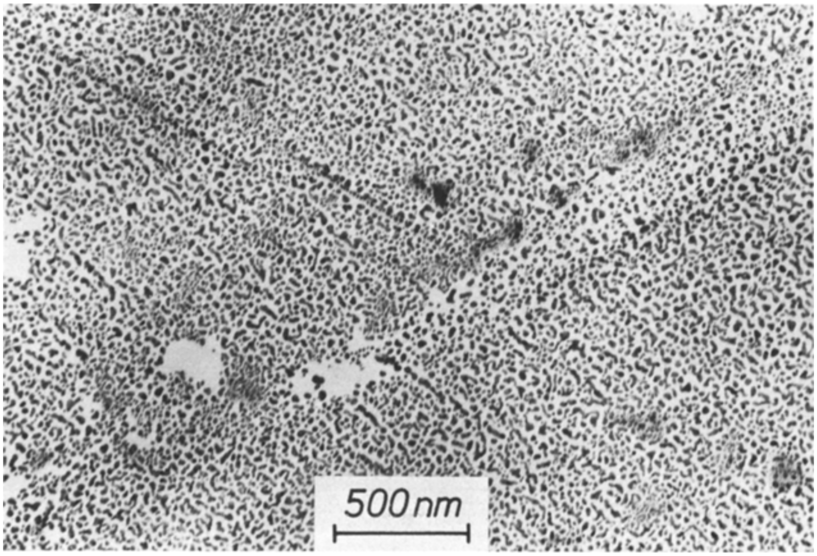

Fig. 2. Electron microscopic picture of a replica showing a gold-decorated {2 1 1} surface. The experimental conditions correspond to case A in Figs. 3 and 4, respectively.

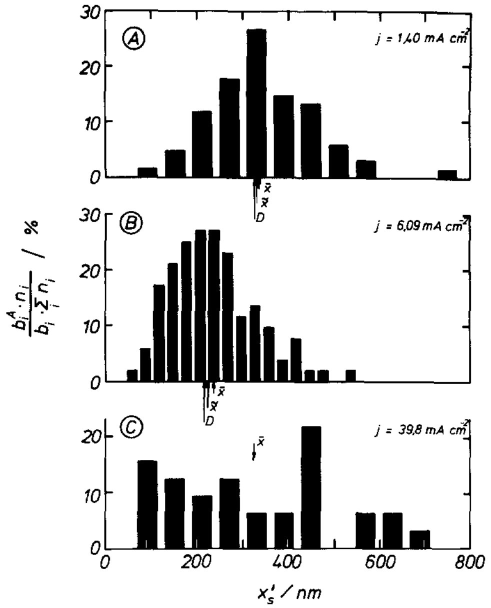

Fig. 3. Normalized histograms for the distribution of real step distances x_s' at different current densities. Number of measurements, Σn_i, in case A, 68; case B, 104; and case C, 32.

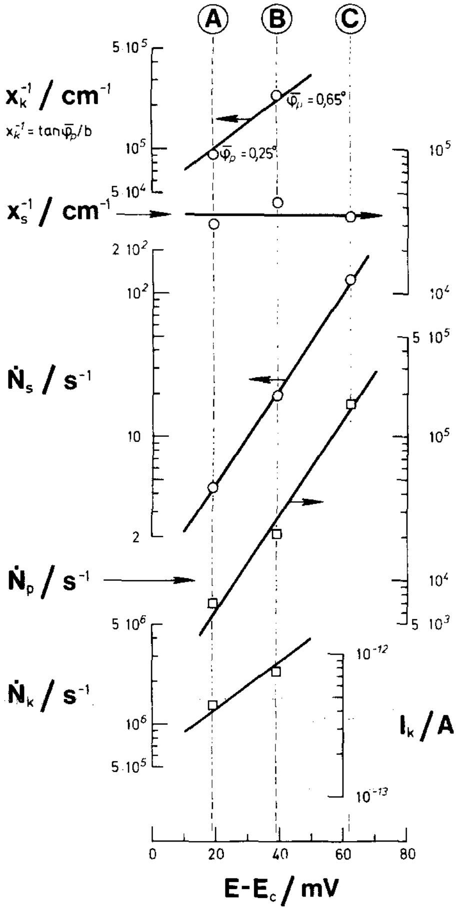

Fig. 4. Potential dependences of structural parameters and mean rates of elementary processes for cases A, B, C indicated in Fig. 3. The straight lines correspond to the description given by Equations 8–10.

Thus it is difficult to define mean angles between two systems of step at very high current densities.

Fig. 3 shows three histograms for the distribution of step distances x_s' taken perpendicular to the step directions, not considering visible displacements. The frequency as a percentage is normalized to the total number Σn_i of individual measurements and to the histogram cells b_i. The mean step distances, $\bar{x}$, the median values, $\tilde{x}$, and the points of maximum density, D, are indicated. At low current densities, in cases A and B, one obtains distributions with one peak and a slightly positive skewness. The excess is close to normal. Thus, the distribution is almost Gaussian. At high current densities, case C, there is no simple description of the distribution. A significant change of the mean step distance $\bar{x}$ with current density is not observed.

5. Discussion

The mean distances between steps are in agreement with an earlier estimate [3, 4] from morphological data obtained by conventional microscopy. The estimate was based on the fact that triangular pyramids bounded by stepped {2 1 1} faces could be observed, even if the misorientation of the actual surface with respect to {2 1 1} was of the order of 0·1°. Thus, with the mean step distances of Fig. 4 the height of the steps can only be monatomic or diatomic. According to the theory developed earlier it is impossible to envisage the formation of sets of diatomic steps at the top of the triangular pyramids. Only sets of monatomic steps can be generated.

Knowing the steady-state current density j_s, the mean distance of steps, x_s, and the mean distance of kinks, x_k, the rates $\dot{N}_s$, $\dot{N}_p$, and $\dot{N}_k$ of the three elementary processes at the apices of the pyramids, at the intersections of steps, and at the kinks, respectively, are obtained. The mean distance of kinks is calculated from the misorientation of the steps with respect to ⟨3 1 1⟩. Typically, in case B of

Fig. 4 it is $x_k = 42$ nm corresponding to a misorientation $\varphi_p = 0{\cdot}65°$. The mean distance of kinks is thus large compared to the distance between neighbouring atoms in the iron lattice. The steps cannot be atomically rough with a large number of positive and negative kinks close together. If this were true, there would be no misorientation of the steps: a step from which the metal is dissolving can only stay rough if the processes of formation of kinks are fast compared to the removal of metal atoms from kink sites, or if the probabilities for removal of atoms from kink sites and from complete steps are essentially equal.

From electrochemical experiments it was concluded [1] that the surface concentration $(x_s x_k)^{-1}$ of kinks is an exponential function of the overvoltage, or, for anodic dissolution

$$(x_s x_k)^{-1} \sim \exp\,(FE/RT). \qquad (7)$$

The results in Fig. 4 indicate that the mean distance x_k of kinks decreases exponentially with the potential,

$$x_k^{-1} \sim \exp\,(FE/RT) \qquad (8)$$

while the mean distance of steps x_s stays independent of the potential. Then, it follows from the steady-state Tafel slope that the probability, $\dot{N}_k$, of removing atoms from a kink site, or the current I_k at one kink depend on potential according to

$$\dot{N}_k \sim I_k \sim \exp\,(2\alpha FE/RT) \qquad (9)$$

with a transfer coefficient close to $\alpha = 0{\cdot}5$ for the transfer of a ferrous ion in one step. The potential dependence (Equation 9) describes the transient polarization curves [1], because the generation of steps and of kinks are both relatively slow processes compared to the removal of atoms from a kink site.

As a further consequence of the experiments one finds from Equations 2, 3, 8, and 9

$$\dot{N}_s \sim \dot{N}_p \sim \exp\,[(1 + 2\alpha) FE/RT]. \qquad (10)$$

The frequency, $\dot{N}_p$, of generating kinks at the intersection of two ⟨3 1 1⟩ steps is about 10^3 times higher than the probability, $\dot{N}_s$, of generating steps at the intersection of three {2 1 1} planes. However, it is almost certain that the ratio, $\dot{N}_p/\dot{N}_s$, decreases with the pH value of the solution. Further investigation of the step densities as a function of pH will clarify this question.

So far, it has been impossible to obtain useful values of x_k and hence of $\dot{N}_k$ at high current densities because of the frequent and large displacement of steps. Considering the distribution of step distances in case C of Fig. 3 one notes a relatively large frequency of occurrence of steps at small distances. This phenomenon, as well as the apparent merging of steps, is probably due to an interaction between monatomic steps and to the formation of multi-atomic steps. The interaction of steps can finally result in the formation of pyramids. At high current densities the transient appearance of new pyramids following an anodic potential step was observed [4, 5]. Consequently, the surface concentration of intersections of steps is transiently increased.

The interaction of steps is related to the sudden changes of step direction and the displacement of steps. Probably, the changes of the step direction are due to short steps close to the $[1\bar{3}1]$ direction denoting the main direction of the step close to $[\bar{3}11]$ as in Fig. 1. An experimental proof of this conjecture will be possible after an improvement of the decoration technique in order to enhance spatial resolution.

The sudden changes of the step direction can be explained by bunching of kinks. The probability distributions of $\dot{N}_p$ and $\dot{N}_k$ lead to local fluctuations of the kink density x_k^{-1} at steps. If the local kink density is high enough, a step in a new ⟨3 1 1⟩ direction will be stabilized. Since probability distributions seem to be Gaussian functions of potential-independent width, bunching of kinks becomes more probable as the kink density increases with the steady-state current density. It is not necessary to assume long-range energetic interactions or to invoke the participation of chemisorbed inhibitors in order to explain bunching of kinks. If two kinks coalesce into a double kink for statistical reasons, the probability of removing an atom from the apex of the double kink will be lower than that of removing it from a normal kink. Thus, the probability of capturing another kink at the double kink is high. Finally, the apex will behave like a normal intersection of long steps at which the probability, $\dot{N}_p$, of removing an atom is still smaller than the probability, $\dot{N}_k$, of removing it from a kink. The process transiently slows down the lateral movement of the step beyond the newly generated intersection. If the probability of bunching of kinks is high, the probability of bunching of steps is therefore high, too, for entirely statistical reasons.

Such a theory explains that the skewness of the distribution of steps grows with the anodic potential, that steps are displaced and merge, and that a transient formation of new pyramids is possible.

References

[1] K. E. Heusler, 'Elektrochemische Auftösung und Abscheidung von Metallen der Eisengruppe', Habilitationsschrift, Stuttgart (1966).

[2] *Idem, Z. Elektrochem., Ber. Bunsenges. physik. Chem.* **62** (1958) 582.

[3] W. Allgaier and K. E. Heusler, *Z. physik. Chem. N.F.* **98** (1975) 161.

[4] W. Allgaier, Dissertation, Clausthal (1975).

[5] W. Allgaier and K. E. Heusler, *Z. Metallkunde* **67** (1976) 766.