A Study of the Optimal Conditions for the Development of Preferred Oriented Platinum Surfaces by Means of Fast Square Wave Potential Perturbations

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ABSTRACT

Changes in the voltammetric response of polycrystalline platinum in the direction expected for preferred oriented surface electrodes are achieved by using a fast repetitive square wave potential signal (RSWPS) within the potential range of H- and O-electroadsorption/electrodesorption in acid solution (1). Similar results were earlier obtained by applying a fast triangular potential signal to a platinum electrode in an acid electrolyte at room temperature (2, 3). After applying the fast potential perturbation the electrode surface modifications were voltammetrically followed at a low potential sweep rate in the H- and O-electroadsorption/electrodesorption potential range by using an acid electrolyte. These changes in the electrode surface can also be seen through SEM for a relatively low magnification factor (4). The changes from the initial polycrystalline platinum surface to the preferred oriented surface is independent of the shape of the periodic potential perturbation, but it is extremely sensitive to its frequency and potential limits (1, 2, 5). Thus, depending on the preset parameters of the potential perturbation either the platinum (100) preferred oriented surface or the platinum (111) preferred oriented surface are obtained (1-5).

In the present work the influence of the RSWPS characteristics on the voltammetric response at low potential sweep rate of the resulting platinum surfaces is systematically studied to establish the optimal conditions for obtaining surface structures with determined preferred orientation.

Experimental

Runs were made in 1M H₂SO₄ at 25°C with commercially available polycrystalline platinum wire shaped working electrodes of ca. 0.10 cm² geometric area. Previous to each experiment the working electrode was electropolished with ac (50 Hz; 10-15V) in a slightly acid (HCl) saturated CaCl₂ solution. Later, the electrode was repeatedly rinsed with triply distilled water and kept in water for 1h before use. The potential of the working electrode was measured against a RHE in the acid electrolyte. A large area platinum counterelectrode (ca. 50 cm²) concentrically surrounding the working electrode was used. The electrochemical cell and the instrumentation have been described elsewhere (1, 5). The distortion of the RSWPS, which was due to the proper risetime of the electrochemical setup, was less than 5% at frequencies lower than 6 kHz.

After the pretreatment, the working electrode was subjected to the RSWPS between lower (Eₘ) and upper (Eₚ) potential limits at a certain frequency (f) during a preset time (t). The duration of each potential step, τ, and τₛ, respectively, was adjusted at convenience. Most of the results reported in this paper correspond to τₛ = τ, except where otherwise stated. After the RSWPS treatment, voltammograms were run either in the 0.05-0.60V or in the 0.05-1.50V range at 0.1 V/s.

Results

Development of the (100) preferred crystal orientation.—When an electropolished polycrystalline platinum electrode in 1M H₂SO₄ at 25°C is subjected to a constant amplitude RSWPS at 4 kHz during 5 min, the voltammogram run afterwards at 0.1 V/s between 0.05 and 0.60V in the same electrolyte depends on the location of Eₘ and Eₚ (Fig. 1). In any case, clear differences are seen between the voltammograms run before and after the RSWPS treatment. Thus, for the particular set of perturbation conditions indicated in Fig. 1, the heights of the weakly adsorbed H-adatom current peaks decrease, those corresponding to the strongly adsorbed H-adatom current peaks simultaneously increase, and a pair of reversible conjugated current peaks located at ca. 0.34V is noticed. The greatest voltammetric difference between the treated platinum surface and the initial polycrystalline platinum surface corresponds to Eₘ = 0.25V and Eₚ = 1.25V (Fig. 1b), approaching the voltammetric response assigned to the platinum (100) single crystal surface (6-14). For a constant set of potential perturbation conditions, the influence of Eₘ on the development of the (100) preferred orientation is determined (Fig. 2). For this purpose, the ratio of the strongly adsorbed H-electroadsorption current peak height (hₙ) to the weakly adsorbed H-electrodesorption current peak height (hₙ) is taken as an arbitrary measure of the degree of development of the (100) preferred orientation. Thus, for 0.20V ≤ Eₘ ≤ 0.40V, f = 4 kHz and t = 5 min, Eₘ must be within the 1.10-1.40V range for producing a surface structure whose voltammogram at 0.1 V/s approaches that of the platinum (100) single crystal surface. At Eₘ values either lower than

![Fig. 1. Voltammograms (third cycle) run at 0.1 V/s in 1M H₂SO₄ at 25°C. (---): (a) After 5 min RSWPS at 4 kHz between 0.30 and 1.30V; (b) after 5 min RSWPS at 4 kHz between 0.25 and 1.25V; (c) after 5 min RSWPS at 4 kHz between 0.20 and 1.10V. (---) Untreated electropolished polycrystalline platinum electrode.](image-url)
1.10V or higher than 1.40V only small changes in the height ratio of the H-electroadsorption/electrodesorption current peaks are observed.

The efficiency for the development of the (100) preferred crystal orientation, \( H(100) \), can be arbitrarily expressed as follows

\[
H(100) = \frac{(h_2/h_1)_{\text{pos}} - (h_2/h_1)_{\text{pc}}}{(h_2/h_1)_{\text{pc}}} \tag{1}
\]

where \( \text{pos} \) and \( \text{pc} \) denote the preferred oriented surface and the polycrystalline electrode, respectively. For electropolished polycrystalline platinum electrodes an average \( h_2/h_1 \) ratio equal to 0.7 is taken as reference value.

On the other hand, for \( E_u = 1.20 \) or 1.40V, \( f = 4 \) kHz, and \( t = 5 \) min, the useful \( E_1 \) potential range for obtaining the (100) preferred orientation is comprised between 0 and 0.40V (Fig. 3). At \( E_1 \) values either higher than 0.40 or lower than 0 V, the development of the (100) preferred orientation is no longer observed.

Under constant \( E_1, E_u, \) and \( t (E_1 = 0.25V, E_u = 1.25V, t = 5 \) min) the influence of the frequency on the voltammetric response of the resulting surfaces is also studied (Fig. 4). The maximum efficiency for developing surfaces with a (100) preferred orientation is found at 2-6 kHz (Fig. 5). Furthermore, the preferred orientation occurs only beyond a threshold frequency close to ca. 0.5 kHz.

It is interesting to notice that the optimal \( E_1 \) and \( E_u \) values are practically independent of \( f \) for values less than 8 kHz. At \( f \) larger than 8 kHz, the decrease in the efficiency for developing the (100) preferred orientation is accompanied by the increase in the sharpness of the two main pairs of current peaks related to the H-electroadsorption/electrodesorption processes. This suggests that although no preferred orientation is practically achieved at values of \( f \) as large as 20 kHz (Fig. 4), the remarkable sharpness of the current peaks can be related to a decrease in the heterogeneity of the electrode surface, as recently reported for the case of platinized platinum electrodes in acid electrolytes (15). On the other hand, as \( f \) increases beyond 8 kHz the RSWPS approaches a periodic signal of trapezoidal shape. Hence, to optimize the development of the (100) preferred orientation, for instance, at \( f = 20 \) kHz, it seems more realistic to set \( E_1 \) and \( E_u \) approaching those corresponding to a fast triangular potential signal, namely, \( E_1 = 0.10V \) and \( E_u = 1.50V \) (3, 5).

The influence of the duration, \( t \), of the RSWPS treatment on the \( h_2/h_1 \) ratio, for the optimal conditions for developing the (100) preferred orientation, is depicted in Fig. 6. The \( h_2/h_1 \) ratio tends to a limiting value for \( t \) larger than 60 min. In this case, after 4h of RSWPS treatment, the voltammetric response at 0.1 V/s of the resulting surface (Fig. 7), is very close to that reported for platinum (100) single crystal surfaces in 0.5M H\(_2\)SO\(_4\) (12, 13). Furthermore, as has already been observed for the repetitive voltammetric response of platinum (100) single crystal surfaces, covering the O-electroadsorption potential range (12, 13, 16), the platinum (100) preferred oriented surface also shows during cycling between 0.05 and 1.50V the decrease in height of the main reversible current peaks of H-electroadsorption/electrodesorption and the disappearance of the reversibility of the minor redox peaks.
system at ca. 0.34V (Fig. 7). Values of $h_2/h_1$, including double layer charging correction, and $H$(100) derived from voltammograms run at low potential sweep rate for different treated platinum electrodes, including those derived for platinum (100) single crystals surfaces, are assembled in Table I.

Analysis of the solution in contact with the platinum electrode subjected to the RSWPS under the optimal conditions referred to above (17) shows that the net amount of dissolved ionic platinum per cycle per unit electrode area is about three orders of magnitude lower than that reported in the literature for polycrystalline platinum electrodes cycled at 0.04 V/s between 0.40 and 1.50V (18).

At constant $E_i$, $E_u$, $f$, and $t$, the development of the (100) preferred orientation depends on the symmetry of the RSWPS, i.e., on both $\tau_0$ and $\tau_1$. Thus, for $E_i = 0.25V$, $E_u = 1.25V$, $f = 4$ kHz, and $t = 5$ min, the maximum efficiency of the RSWPS treatment is reached at $0.3 < \tau_1/\tau_0 < 3$ (Fig. 8).

Table I. Values of $h_2/h_1$ and $H$(100) for different platinum electrodes

| Electrode | Electrolyte (H$_2$SO$_4$) | Potential perturbation | $h_2/h_1$ | $H$(100) | Reference |
|-----------|---------------------------|------------------------|-----------|-----------|-----------|
| Pt(100) pos (1) | 1.0M | 3rd cycle in the H-adatom region at 0.1 V/s | 2.2 | 2.1 | This work |
| Pt(100) pos (2) | 1.0M | 3rd cycle in the H-adatom and dl charging region at 0.1 V/s | 2.7 | 2.9 | This work |
| Pt(100) pos (3) | 1.0M | 10th cycle in the H-adatom and dl charging region at 0.1 V/s | 4.7 | 4.2 | (5) |
| Pt(100) scs | 0.05M | One cycle in the H-adatom region at 0.05 V/s | 4.0 | - | (7) |
| Pt(100) scs | 0.05M | 3rd cycle in the H-adatom and dl charging region at 0.05 V/s | 3.4 | - | (9) |
| Pt(100) scs | 0.5M | A few cycles in the O-adatom region at 0.05 V/s | 1.9 | - | (9) |
| Pt(100) scs | 0.5M | One cycle in the O-adatom region at 0.05 V/s | 2.4 | - | (11) |
| Pt(100) scs | 1.0M | More than 5 cycles in the O-adatom region at 0.01 V/s | 3.1 | - | (8) |
| Pt(100) scs | 0.5M | One cycle in the H-adatom and dl charging region at 0.05 V/s | 6.9 | - | (12) |
| Pt(100) scs | 0.5M | One cycle in the O-adatom region at 0.05 V/s | 5.1 | - | (12) |
| Pt(100) scs | 0.5M | 6 cycles in the O-adatom region at 0.05 V/s | 3.6 | - | (12) |
| Pt(100) scs | 0.5M | Cycle in the H-adatom and dl charging region at 0.05 V/s | 5.4 | - | (13) |
| Pt(100) scs | 0.005M | Less than 15 cycles in the O-adatom region, then second or third cycle in H-adatom and dl charging region at 0.05 V/s | 2.7 | - | (14) |

pos: preferred oriented surface, scs: single crystal surface. (1) RSWPS ($E_i = 0.25V; E_u = 1.25V; f = 4$ kHz; $t = 5$ min). (2) RSWPS ($E_i = 0.25V; E_u = 1.25V; f = 4$ kHz; $t = 4h$). (3) Repetitive triangular potential scanning ($E_i = 0.002V; E_u = 1.50V; f = 4.7$ kHz; $t = 12h$).
line platinum electrode. The comparison of the different platinum surfaces shows that the RSWPS treatment develops a net faceting at each surface grain.

Development of the (111) preferred crystal orientation.—At constant \( f \) and \( t \), the useful ranges of \( E_t \) and \( E_u \) for producing surface structures with the (111) preferred orientation are narrower than those described in the section above, that is, \( 0.50V \leq E_t \leq 0.70V \) and \( 1.30V \leq E_u \leq 1.40V \). Thus, after applying the RSWPS with \( E_t = 0.70V, E_u = 1.40V, f = 2 \) kHz, and \( t = 5 \) min to a polycrystalline platinum electrode, the voltammogram of the resulting surface run at 0.1 V/s between 0.05 and 0.60V (Fig. 11) approaches that of a platinum (111) single crystal surface after it has been cycled a few times through the O-electroadsorption region at a relatively low potential sweep rate, e.g., 0.1 V/s (8-11, 13, 14, 16, 19, 20) and is also similar to that directly resulting from a platinum (111) single crystal surface cleaned in UHV (argon and oxygen ionic bombardment at 750 eV and 500°C) and characterized by LEED and AES (21). After one potential cycle in the O-electroadsorption potential range, the voltammogram of the platinum (111) preferred oriented surface remains unaltered, although after 10 min cycling a change in the height ratio of the smaller current peaks located between 0.20 and 0.30V is observed (Fig. 11).

The degree of voltammetric change associated with the (111) preferred orientation is arbitrarily given in terms of the \( h_i/h_2 \) ratio as derived from the voltammogram run at 0.1 V/s without entering the O-electroadsorption potential range. The average \( h_i/h_2 \) ratio for electropolished polycrystalline platinum is 1.4. Thus, the greatest \( h_i/h_2 \) ratio is found in the 2.0-3.5 kHz frequency range (Fig. 12). Likewise, the \( h_i/h_2 \) ratio decreases appreciably at \( f \) values lower than 0.5 kHz. Values of the \( h_i/h_2 \) ratio for different electrodes are given in Table II. In this case, the definition of the efficiency, \( H(111) \), in terms of an equation comparable to [1], is avoided because of the uncertainty in assigning a definite relationship between the relative current peak height and the (111) preferred orientation development.

The voltammetric response at 0.1 V/s of platinum (111) preferred oriented surfaces changes with the duration, \( t \), of the RSWPS under the optimal conditions. Thus, dif-

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Fig. 8. Dependence of \( h_i/h_2 \) on \( r \) at constant \( f \); \( E_t = 0.25V; E_u = 1.25V; f = 4 \) kHz, \( t = 5 \) min.

Fig. 9. Dependence of \( h_i/h_2 \) on \( t \). Sinusoidal potential signal (\( E_t = 0.20V; E_u = 1.40V; t = 5 \) min).

Fig. 10. SEM patterns (Scale 10 \( \mu m \)). (a) Initial electropolished polycrystalline platinum electrode; (b, c) platinum surfaces after 4h RSWPS (\( E_t = 0.25V; E_u = 1.25V, f = 4 \) kHz).
fierent $h_i/h_2$ vs. $t$ plots are obtained depending on whether the repetitive triangular potential sweep (RTPS) at 0.1 V/s is restricted to the 0.05-0.60V range, or is extended up to the O-electroadsorption potential range (Fig. 13). In the former case, the $h_i/h_2$ ratio increases initially with $t$, goes through a maximum at about 15s, and then decreases to a time independent value. The voltammetric sweep up to 1.50V decreases the $h_i/h_2$ ratio in the direction of the voltammetric response of the initial polycrystalline platinum electrode, according to the duration of the RTPS. In this case, the greatest influence of the RTPS at low potential sweep rate on the $h_i/h_2$ ratio is noticed for the resulting surfaces after RSWPS treatments of small duration. This suggests that the shorter the duration of the RSWPS, the greater the unstability of the modified platinum surface. On the other hand, those electrodes prepared with a RSWPS treatment lasting more than 5 min, still exhibit a relatively large $h_i/h_2$ ratio, and a good stability to the RTPS at 0.1 V/s covering the O-electroadsorption potential range. In this respect, the stability of the platinum (111) preferred oriented surface electrodes appears greater than that reported for platinum (111) single crystal electrodes (9-11, 13, 16, 20, 21).

The amount of soluble ionic platinum found after the RSWPS treatment for the optimal conditions for developing the (111) preferred orientation is slightly greater (ca. four times) than that reported in the section above (17).

The development of the (111) preferred orientation depends also on the symmetry of the RSWPS. Thus, for the optimal conditions, the maximum $h_i/h_2$ ratio is found for $r$ values between 0.5 and 2.0 (Fig. 14). Again, the greatest voltammetric change is associated with the symmetric RSWPS signal.

SEM patterns of platinum (111) preferred oriented surfaces resulting after applying the RSWPS treatment under the optimal conditions are depicted in Fig. 15. In this case, a characteristic faceting is also developed, although the corresponding pictures at the largest magnifications are more diffuse than those shown for platinum (100) preferred oriented surfaces probably because of the different nature of the RTPS and RSWPS protocols.

**Table II. Values of $h_i/h_2$ for different platinum electrodes**

| Electrode | Electrolyte | Potential perturbation | $h_i/h_2$ | Reference |
|-----------|-------------|------------------------|-----------|-----------|
| Pt(111) pos (1) | 1.0M H$_2$SO$_4$ | 3rd cycle in the H-adatom and dl charging region at 0.1 V/s | 2.0 | This work |
| Pt(111) pos (2) | 1.0M H$_2$SO$_4$ | 3rd cycle in the H-adatom and dl charging region at 0.1 V/s | 1.8 | This work |
| Pt(111) pos (3) | 1.0M H$_2$SO$_4$ | 3rd cycle in the H-adatom and dl charging region at 0.1 V/s | 2.0 | (5) |
| Pt(111) scs (1) | 0.5M H$_2$SO$_4$ | One cycle in the O-adatom region at 0.05 V/s | 1.4 | (20) |
| Pt(111) scs (2) | 0.5M H$_2$SO$_4$ | One cycle between 0.05 and 1.55V at 0.1 V/s after Ar- and O-ionic bombardment | 1.4 | (21) |
| Pt(111) scs (3) | 0.5M H$_2$SO$_4$ | One cycle in the O-adatom region at 0.1 V/s | 3.0 | (21) |
| Pt(111) scs (4) | 0.1M HClO$_4$ | One cycle in the O-adatom region at 0.05 V/s | 3.0 | (11) |
| Pt(111) scs (5) | 0.1M HClO$_4$ | More than 5 cycles in the O-adatom region at 0.01 V/s | 2.8 | (8) |
| Pt(111) scs (6) | 0.1M HClO$_4$ | 10 cycles in the O-adatom region at 0.1 V/s | 2.9 | (10) |

pos: preferred oriented surface. scs: single crystal surface. (1) RSWPS ($E_i = 0.70V; E_u = 1.40V; f = 2.8$ kHz; $t = 40$ s). (2) RSWPS ($E_i = 0.70V; E_u = 1.40V; f = 2.8$ kHz; $t = 5$ min). (3) Repetitive triangular potential scanning ($E_i = 0.42V; E_u = 1.10V; f = 7.4$ kHz; $t = 12$ h). (4) "Initial state." (5) "Standard state."
shorter duration time of the RSWPS. The latter was usually selected in the region where the $h_1/h_2$ ratio attains a time independent value (Fig. 14).

Discussion

The preferred oriented platinum surfaces can be obtained by applying fast periodic potential perturbations to polycrystalline platinum electrodes between potential limits associated with the underpotential decomposition of water (1-5). Present results establish that for preset $E_1$ and $E_u$, the development of preferred orientations depends on the frequency of the potential perturbation independently of the actual shape of the periodic potential perturbation. This means that only the first harmonics are mainly responsible for promoting the preferred orientation (22). Despite this conclusion, data obtained with the RSWPS appears more reliable for defining the actual potential limits associated with the phenomenon. The overall process involves at least two consortial stages, one which promotes the atom rearrangement through the occurrence of surface processes, and another one which assists the penetration in depth of the atom rearrangement.

The first stage is directly related to the characteristics of the fast periodic potential perturbation. Thus, for constant $E_1$, $f$, and $t$, there is a lower threshold $E_u$ value located at ca. 1.10V to develop a platinum (100) preferred oriented surface. This means that $E_u$ should attain the O-electroadsorption potential range for weakening the Pt-Pt bonds for further producing the platinum surface.
atom rearrangement. However, at $E_t$ values higher than 1.40-1.50V, that is, at potentials sufficiently positive to form irreversible O-surface species (23, 24), the efficiency for developing the preferred orientation declines significantly, indicating that the strong O-electroadsorption hinders the surface restructuring process. Likewise, development of the (111) preferred orientation is slow on the electrodes on which the $E_t$ value should also be located in the O-electroadsorption potential range, although, in this case, the useful $E_t$ range is restricted to 1.30-1.40V. Furthermore, for the development of either the (100) or the (111) preferred orientation the $E_t$ values should lie in the potential range where O-Pt bonds are broken. Therefore, very active electrosorbed oxygen containing species promoting the disruption and the rearrangement of the surface structure, play a fundamental role in the development of preferred orientations. This is consistent with the fact that there is a frequency threshold for producing preferred oriented platinum surfaces, which is ca. 0.5 kHz. The reciprocal of this figure was associated with the half-life time of adsorbed OH species on platinum produced in the early stages of underpotential electro-oxidation of water (25, 26). Thus, the anodic processes which initiate the surface rearrangement are

$$\text{H}_2\text{O} + \text{Pt} \rightarrow [\text{Pt(OH)}]^* + \text{H}^+ + e^- \quad [2a]$$
$$[\text{Pt(OH)}]^* = [\text{Pt(O)}]^* + \text{H}^+ + e^- \quad [2b]$$

Reactions [2a] and [2b] involve two successive reactions leading to the formation of adsorbed nonstabilized O-containing species. These reactions should occur preferentially at those sites which involve the smallest overvoltage, that is, at the most reactive sites of the polycrystalline surface (steps, kinks, etc.). The surface rearrangement occurring during the O-electroadsorption half-cycle is associated with reactions such as

$$[\text{Pt(O)}]^* + \text{H}^+ + e^- = [\text{Pt(OH)}]^* \quad [3a]$$
$$[\text{Pt(OH)}]^* + \text{H}^+ + e^- = \text{Pt}^* + \text{H}_2\text{O} \quad [3b]$$

where the freshly formed Pt* atom occupies, in principle, a new equilibrium position in the metal lattice, according to

$$\text{Pt}^* \rightarrow \text{Pt}($$ lattice$$) \quad [4]$$

The reaccommodation reaction [4] depends on the number of degrees of freedom of Pt* atoms on the metal surface. Hence, the first layers of metal atoms under the fast periodic potential perturbations behave as a dynamic surface structure where the metal atoms move on the electrode surface, from initial metastable positions at the polycrystalline metal towards a certain equilibrium configuration. Furthermore, the presence of H-adatoms interacting with the metal lattice promotes the formation of the lower dense metal surface structure. This is the case for developing the (100) preferred orientation which requires an $E_t$ value located in the H-adatom electroadsorption/electrodesorption potential range. Conversely, surface structures where the (111) preferred orientation prevails do not imply no-electroadsorption/electrodesorption during the RSWPS.

The dependence of the efficiency of preferred oriented surface development on both the frequency and the symmetry of the RSWPS indicates that either aging reactions yielding irreversible electrosorbed O-containing species or strong ion-metal and solvent-metal interactions, hinder the development of surface structures with a preferred orientation. Therefore, the optimal frequency and symmetry conditions of the RSWPS result from a compromise between the rates of reactions [2a] and [2b] coupled to the aging reaction of the O-electroadsorbed species and the rates of reactions [3a], [3b], and [4] coupled to the different adsorption processes on bare platinum.

The second stage of the preferred oriented surface development process, which occurs in parallel with the first one already discussed, concerns the penetration in depth of the rearrangement of metal atoms. The occurrence of this stage is consistent with recent results obtained with polycrystalline platinum electrodes subjected to fast potential perturbations (17) which show that the amount of dissolved platinum per cycle under the optimal conditions for developing preferred oriented surfaces is $10^{-10}$ times lower than that produced per cycle under potential cycling at 0.04 V/s between 0.40 and 1.50V (18). This suggests that a local electrodissolution and redeposition of platinum contribute to the penetration of the rearrangement effect. The mechanism of the second stage is similar, in principle, to that earlier proposed by other authors to explain the roughened type of platinum electrodes by cyclic potential perturbation (27, 28).

In this respect it is interesting to notice that working under a constant potential amplitude and time, there is a development of surface roughness together with the preferred orientation effect as has been reported earlier for fast repetitive triangular potential cycling (3). The development of roughness is particularly remarkable for (111) preferred oriented surfaces as, in this case, the $E_t$ value should be more positive than that required for developing the (100) preferred orientation. The relative contributions of roughening and preferred orientation effects depend on the frequency of the periodic potential perturbation. Thus, at $f$ lower than 2 kHz, the former occurs simultaneously with the latter, but when $f$ exceeds 2 kHz, then there is practically no increase in surface roughness. The optimal $f$ range for developing the platinum (111) preferred orientation is comprised between 2 and 3.5 kHz, but for $f$ greater than 3.5 kHz the preferred orientation effect decreases again. On the other hand, for the optimal $E_t$ and $E_u$ values to develop the (100) preferred orientation, an appreciable roughness is only produced at $f$ values lower than 0.05 kHz. The greatest efficiency for developing the (111) preferred orientation is exhibited in the 2.5-6 kHz range with a negligible increase in the electrode roughness. Nevertheless, at $f$ values larger than 8 kHz, as the RSWPS is appreciably distorted, the preferred orientation effect decreases. In this case, a decrease in the surface heterogeneity is observed as it is reflected through the sharpening of the main H-adatom electroadsorption/electrodesorption current peaks and the disappearance of the anodic intermediate current peak in the voltamogram at 0.1 V/s.

As was pointed out in previous work (5, 15), the effect of fast periodic potential perturbations on the surface modification resembles those induced in single crystals by either bombardment with high energy particles (31, 29) or thermal treatment (21, 30, 31) or O-adsorption from the gas-phase (30, 32) yielding restructuring and eventually faceting. In these cases, the stabilization process of the perturbed surface implies an energy dissipation effect involving short and large range atom rearrangements. The former is associated principally with filling of holes in the metal structure induced by the mobility of the metastable atoms produced by the perturbation and to mutual annihilation of dislocations. The energy dissipation effect is associated with the faceting of the surface and implies a transfer of momentum from the mobile atom to the metal atom network (15, 33). The metastable metal atoms stabilize in the metal lattice when its translation energy turns into the vibrational lattice energy corresponding to the equilibrium metal structure.

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The Effect of an Impinging Fluid Jet on Mass Transfer and Current Distribution in a Circular Through-Hole

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ABSTRACT

The effect of a single circular impinging fluid jet on hydrodynamic flow and mass transfer in a single through-hole centered at the stagnation point was investigated. Both submerged and unsubmerged jets were studied. Sectioned electrodes were used for direct experimental measurement of local rates of mass transfer and of hydrodynamic shear stress within individual through-holes. The ferricyanide system was used to obtain convective mass transfer rates upon controlled variation of jet Reynolds number, nozzle-to-workpiece distance, through-hole diameter, and aspect ratio. Data were used to establish mass-transfer correlations for both submerged and unsubmerged systems. It was found that the fluid flow in the through-hole corresponded to the hydrodynamic entrance region. A mathematical model of the current and potential distribution phenomena determine the cathodic limiting current density, or maximum deposition rate. Mathematical models based on mass transfer and potential field principles thus find use in predicting and scaling operating conditions to achieve both uniform and high speed performance. In the present study, the effect of impinging jet flow on the current and potential distribution in a single through-hole was investigated (1).

Kessler and Alkire (2, 3) investigated electrodeposition in through-holes and developed procedures for estimating flow velocity and pumping of electrolyte through nozzles directed at the board. Sonin (7) investigated the configuration corresponding to the hydrodynamic entrance region. A mathematical model of the current and potential distribution was used to identify dimensionless conditions for achieving uniform deposits and for insuring adequate convection rates.

In applications where electrodeposits of uniform thickness are required over a surface of complex geometry, there usually exists an upper limit of plating rate above which the desired uniformity is not obtained. Deposition uniformity depends upon the current and potential field distribution within the cell. For high speed plating, there is usually a minimum flow rate needed to avoid pourover of “burned” deposits. Convective mass transport phenomena determine the cathodic limiting current density, or maximum deposition rate. Mathematical models based on mass transfer and potential field principles thus find use in predicting and scaling operating conditions to achieve both uniform and high speed performance. In the present study, the effect of impinging jet flow on the current and potential distribution in a single through-hole was investigated (1).

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