REVIEW

Electrocrystallization—factors influencing structure

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Abstract The relation between layer properties and structure of the deposit is of permanent importance in the development of electrocrystallization. The continuous question is the influence of the experimental conditions on the structure and with this bridge on the properties of electrodeposits. A very important step in electrodeposition is nucleation. Some recent developments of nucleation will be discussed. An important factor to influence nucleation and growths are additives. Adsorption of additives is still described by the thermodynamic approach of adsorption isotherms. But a new impetus might provide the transfer of Pearson's hard–soft concept to adsorption on electrified interfaces. An important step is the correlation of hardness and softness with the chemical potential of electrons and the dependence of the chemical potential on the electrode potential. A further new step is the application of distributed field calculations to calculate chemical potentials of electrons. An outlook into further developments is given at the end of the article.

Introduction

Electrocrystallization marks the birth of modern electrochemistry. The first source for the continuous supply of electricity was Volta's invention of the pile [1]. An enormous development of applications of the new source of energy started in chemistry. Faraday worked on the reduction of metal ions into metals [2]. It was an application, which could be used for a quantitative correlation of electrical charge and chemical product generation. Faraday's law was derived. But the deposited metals soon found industrial applications; plating and galvanoforming was born [3]. Fundamental studies of the complex process of electrodeposition followed. A general description of the work up to the first half of the nineteenth century can be found in the books of Volmer or of Raub [4, 5]. Another summary is given in the presentation of Fleischmann and Thirsk [6]. Brenner summarized fundamental aspects of alloy deposition [7].

A special problem of electrocrystallization is the influence of additives; early concepts of the action of additives on electrochemical processes can be found in the book of Damaskin, Petrii and Batrakov [8]. With the development of scanning tunnelling microscopy, a new method was applied to study electrodeposition. A special step is underpotenital deposition; a summary of main

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results can be found in the book of Budevsky, Staikow and Lorenz [9].

In the following article, the history of electrodeposition will not be presented, but some of the present concepts of the correlation between layer properties, structure and the experimental conditions to modify structure will be described. Problems will be emphasized in a summarizing manner. Finally, an outlook will be given to most recent developments.

Nucleation and structures

The properties of a solid phase are connected with the crystallographic structure. Parameters influencing the structure will be treated in this paragraph. Most prominent parameters are electrode potential or current density, respectively, temperature, metal ion concentration, and electrolyte convection. Of special importance are additives usually used as a combination of two or more different compounds. The influence of the additives depends on the concentration of these compounds. Winand [10] described the combination of current density relative to the diffusion-limiting current density and the inhibition by additives in a diagram. This is shown in Fig. 1. To understand the phenomenological character of this diagram, one has to consider the different mechanisms determining the structure.
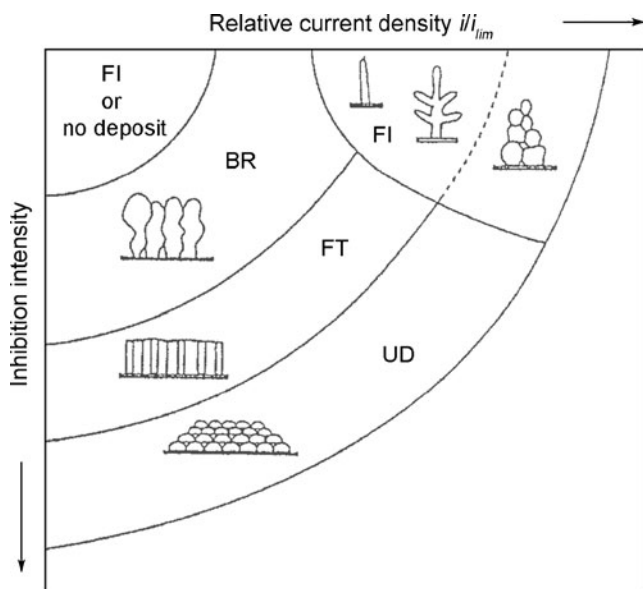

Fig. 1 Winand diagram. Depending on current density and inhibition activity, Fischer classified four structural types of preferential observation: a base-oriented reproduction type BR, a field-oriented texture type FT, an unoriented dispersion type UD, and the field-oriented isolation type FI, deposition or formation of isolated crystals

The first step of deposition of any new phase is nucleation. Nuclei must be formed before growth can start. Depending on the intensity of inhibition, one can distinguish different steps of nucleation. Native centres of nucleation are provided by the topography of the surface. Distortions on the surface like phase boundaries, dislocations, impurities, etc. are pre-steps of nucleus formation. Milchev described the kinetics of reactions of metal ions with these pre-steps [11]. The rate constant k_n and the number of pre-steps N_0 depend on the potential and on the concentration of inhibitors. Then, one can write for the nucleation rate, r_{nuc}:

$$r_{nuc} = k_n(E, c_{inh}) \cdot N_0(E, c_{inh}) \cdot c_{Me^{z+}} \tag{1}$$

This formula could be used to explain the Winand diagram at a lower concentration of inhibitors. Two types of structure are formed, the field-oriented isolation (FI) type and the base-oriented reproduction (BR) type, in the notation of Fischer.

Nuclei will also be formed on a statistical basis. Volmer and Weber suggested the principle mechanism based on a calculation of an energy profile as a function of the number of atoms in the nucleus [12]. The concept of this model was the introduction of a critical nucleus. The critical nucleus has a size, which enables constant growth. Smaller nuclei are not stable, and the probability of dissolution dominates. The Bulgarian school transformed this concept into an atomistic model [13]. Becker and Döring suggested another model considering the rate of addition of an atom to the nucleus in comparison to the rate of separation of an atom from the nucleus [14]. The statistical nucleation explains the Winand diagram at a higher inhibitor concentration.

In principal in all models of statistical nucleation rates of nucleation are described by very similar equations. One can formulate a general equation for the rate of nucleation, r_{nuc}:

$$r_{nuc} = A_n \exp\left(-\frac{B_n}{\eta^{a_n}}\right) \tag{2}$$

The constant A_n can be called crystallization constant and is a large number representing the possible maximum of nuclei formed on the surface. The constant B_n is the probability to form the critical nucleus. The exponent α_v describes the dependence on the overvoltage η.

The concept of statistical nucleation is the main requirement for the deposition of a structure no longer influenced by the substrate, and two types can be considered depending on the growth mode, the unoriented dispersion (UD) type or the field-oriented texture (Ft) type.

The mechanism of electrocrystallization from an inhibited surface cannot be described by a single step, but actually, it is a continuous chain of reaction steps. In a

continuous manner, nucleation takes place, followed by the growths of the nuclei (now active grains) to a maximum size, and then, the growth of the active grain stops. The active grain gets inactive; it dies. Such process chains take place parallel to each other; the situation is illustrated in Figs. 2 and 3. A statistical description of the principal parameters is possible. The details are described in the literature; in the following paragraph, a summary is given [15, 16].

An equation for the rate of nucleation in a general form is Eq. 2. From a statistical analysis of the growth process, one can determine the mean number of growing nuclei (active grains) N_n, which is the reciprocal value of the maximum statistical area of the active grain.

$$N_n = \frac{1}{F_{n,max}} \tag{3}$$

One can also describe the average growth rate, r_{gr}, which is the change of the volume of the nuclei with time. In this analysis, one has to distinguish two coordinates, the growth rate in the horizontal direction, which is the increase of the surface area of the active grain with time, and the growth rate in the vertical direction, which is the increase of the height of the active grain with time.

$$r_{gr} = h_n \frac{dF_n}{dt} + F_n \frac{dh_n}{dt} \tag{4}$$

This separation is the reason for the anisotropic growth of the grains. The vertical growth is larger than the horizontal growth, and the result resembles a columnar structure of the layer similar to the FT type.
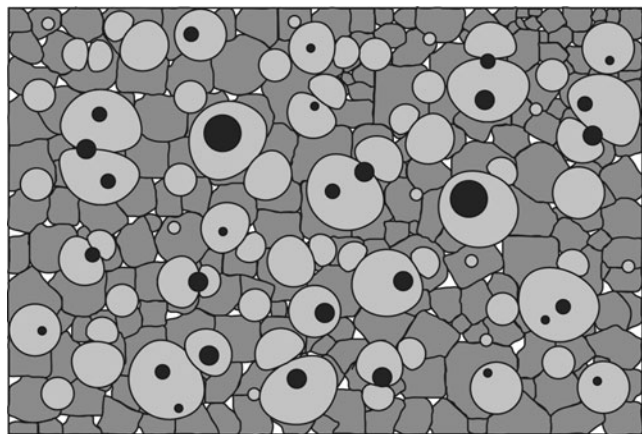

Fig. 2 Schematic representation of three generations of growing nuclei, top view: Dark grey (background): horizontal growth has mostly stopped, the image is nearly the grain structure of the final layer surface. Light grey: the active layer, the growing nuclei are represented as circles, deformed, if they have collided with other growing nuclei. Black: the young generation of nuclei, on top of the second generation
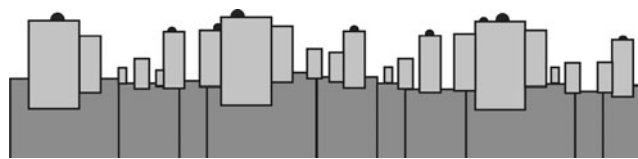

Fig. 3 Schematic representation of three generations of growing nuclei, side view: Dark grey: horizontal growth has mostly stopped, light grey: the active layer, the growing nuclei are represented as columns, black: the young generation of nuclei on top of the second generation, represented in this schematic description as semicircles

The average growth rate is proportional to the current density.

$$r_{gr} = \frac{M}{zF\rho} |i| F_{n,max} \tag{5}$$

M is the atomic weight, z is the charge of the metal ion, F is the Faraday constant, and ρ the specific density of the deposited metal.

One can determine the mean lifetime, τ_n of the active grains, the maximum volume divided by the average growth rate.

$$\tau_n = \frac{V_{n,max}}{r_{gr}} \tag{6}$$

From the mean lifetime, one can determine the average number of grains transforming from the active status into an inactive status, which can be called death rate.

$$r_{dth} = \frac{N_n}{\tau_n} = \frac{M}{zF\rho} \frac{|i|}{F_{n,max} h_{n,max}} \tag{7}$$

Under stable conditions, the death rate must be equal to the rate of formation of new nuclei. The result is an equation describing the average grain size $V_{n,max} = F_{n,max} h_{n,max}$ of the growing film and its dependence of the experimental parameters, current density and nucleation rate.

$$V_{n,max} = \frac{M}{zF\rho} \frac{|i|}{r_{nuc}} \tag{8}$$

It depends on the rate-controlling process, which equation one has to set in for the current density. Examples were calculated for charge transfer controlled processes, taking into account the diffusion limitation. The current density is then substituted by the equation

$$i = \frac{i_0 \exp\left(-\frac{\alpha_c zF}{RT}\eta\right)}{1 + \frac{i_0}{i_{lim}} \exp\left(-\frac{\alpha_c zF}{RT}\eta\right)} \tag{9}$$

where i_0 is the exchange current density, α_c is the cathodic charge transfer factor $(1-\alpha_a)$, and i_{lim} is the diffusion-limiting current.

The rate-controlling step can also be a rate-controlled formation of an intermediate with a rate-controlled limiting current.

$$i_r = zF \cdot v \tag{10a}$$

$$i_{r,\text{lim}} = zF \cdot v_{\text{max}} \tag{10b}$$

The reaction rates are v and v_{max}. Such a situation is often observed for electrolytes used in commercial plating processes.

Adsorption of additives

Formation of the structure depends on surface inhibition by additives adsorbed on the electrode surface. Adsorption of additives can influence the structure of the growing phase in many ways. The influence on nucleation was already mentioned in the previous paragraphs. Adsorption can change the equilibrium shape of grains. Additives might influence the electronic structure of the growing surface. The link between the electronic structure and the growing morphology probably is complicated and will not be discussed in more detail.

In the classical literature, adsorption of additives is described by adsorption isotherms. Starting with the Langmuir isotherm, the equations describing adsorption can be developed and adapted to even sophisticated experimental conditions.

In praxis, several additives are used. This is a further complication because the models must be applied to two or more adsorption processes.

In the past, this concept was intensively invested. Damaskin, Petrii and Batrakov [8] gave a summary of the influence of additives on electrochemical processes.

For the future, one needs concepts for a faster prediction of the influence of additives and for a simulation of the action of the additives. One direction will be discussed in the following paragraph.

The hard–soft concept

The problem with the classical description of adsorption is the complex manner to determine the appropriate data and to compare different substances. Pearson presented in 1963 a new approach classifying the interaction of molecules with metal atoms in complexes by properties called hardness and softness [17]. A stable complex or a stable compound is formed when two hard species react with each other or by the combination of two soft species. An example for the reaction of two hard species is the reaction of protons with hydroxyl ions.

$$H^+ + : OH^- \longleftrightarrow H : OH \tag{11}$$

An example for the reaction of two soft species is the reaction of silver ions with iodide ions.

$$Ag^+ + J^- \longleftrightarrow AgJ \tag{12}$$

In a very phenomenological definition, the property hard–soft was connected with the number of electrons around the atom, ion or molecule. For a more general definition, soft was set proportional to the polarizability, and hard, to the electronegativity (Fig. 4). In the following paragraphs, this will be discussed in a more quantitative form.

Polarizability

An electrical field acts on a free mobile molecule in the following manner. If the molecule has a permanent dipole moment, the molecule will be oriented in the field. The electrons in the molecule will be reoriented, inducing an additional dipole moment depending linearly on the local electrical field.

$$\mu_{\text{ind}} = \alpha \cdot E_{\text{loc}} \tag{13}$$

The proportionality factor is called polarizability, α. In the SI system, E is measured in V/m, and μ_{ind} in C m. Then, the dimension of α is C^2m/J. In the cgs system, the dimension of α is cm^3. For a better comparability, a volume is also defined in the SI system

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0} \tag{14}$$

with ε_0 as the permittivity of the vacuum ($\varepsilon_0 = 8,854 \times 10^{-12}$ C^2/Jm).

The polarizability is proportional to the softness, but only for free atoms, ions or molecules is a correlation possible. The application of this definition to a compact metal is difficult.

Electronegativity

Electronegativity, χ corresponds with the negative value of the chemical potential of electrons (Mulliken [18]).

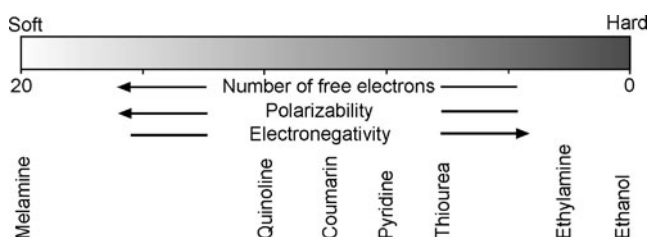$$\mu = -\chi \tag{15}$$

Fig. 4 Explanation concepts for hardness and softness of atoms, ions, and molecules by Pearson

Therefore, the electronegativity can be calculated if the chemical potential of electrons can be calculated.

The electrochemical potential of an electron (calculations usually refer to 1 mol of electrons=6.023×10^{23} electrons) on a place with the electrical potential ϕ is the sum of the chemical potential minus the electrical energy of the electron.

$$\widetilde{\mu} = \mu - F\phi \qquad (16)$$

Parr and Young calculated the chemical potential, μ, of an electron in the density functional theory as the derivation of the electron energy E_e with the change of the number of electrons, N, keeping constant the potential energy, V [19].

$$\mu = \left(\frac{\partial E_e}{\partial N}\right)_V \qquad (17)$$

There is also an experimental way to determine the chemical potential of electrons. Mulliken gave an equation connecting electronegativity with ionization potential, I, and electron affinity, A.

$$\chi = \frac{I+A}{2} \qquad (18)$$

Ionization potential and electron affinity can be determined by experiments. Some values of ionization potential and electron affinity from the literature are given in Table 1.

The concept of electronegativity or chemical potential, respectively, can also be applied for solids and metals. According to Eq. 18 is the electronegativity of a solid the Fermi energy of the energy level between the highest occupied and lowest unoccupied electron energy levels. For metals, this is the work function, Φ.

$$\chi_{Me} = \Phi \qquad (19)$$

Data of work functions can also be found in the literature. Some examples for most relevant metals are contained in Table 2.

The work function is determined for an uncharged surface, but it is influenced by the surface potential. The surface potential depends on the surface dipole. The origin of the surface dipole for a (110)-surface is shown in Fig. 5. The surface dipole is different for different faces. Therefore, the work function differs for different faces as shown for some metals in Table 2.

With values for the chemical potential or the electronegativity, one can formulate for the stability of adsorption:

$$\chi_{Ads} = \chi_{Me} \qquad (20)$$

$$|\mu|_{Ads} = |\mu|_{Me} \qquad (21)$$

This condition has a very convincing physical explanation. Stable adsorption can be expected if the energetic conditions for electrons in both phases are similar. This can be considered as a general role for covalent bonding.

Electrified interfaces

Pearson tried to transfer the model to metal surfaces and to adsorption on electrified interfaces, but in this case, the

Table 1 Electronegativity calculated with Eq. 18 [24]

Substance	Formula	I [eV]	A [eV]	$\chi=(I+A)/2$ [eV]
Anthracene	$C_{14}H_{10}$	7.44	−0.53	3.46
Azulene	$C_{10}H_8$	7.38	−0.79	3.30
Benzophenone	$C_{13}H_{10}O$	9.08	−0.62	4.23
Carbon disulfide	CS_2	10.07	−0.58	4.75
Nitrobenzene	$C_6H_5NO_2$	9.86	−1.00	4.43
Perylene	$C_{20}H_{12}$	6.96	−0.97	3.00
Pyrene	$C_{16}H_{10}$	7.43	−0.41	3.51
Sulphur dioxide	SO_2	12.35	−1.11	5.62
Hydrogen (atomic)	H	13.60	−0.75	6.43

Values for ionization potential and electron affinity from CRC Handbook of Chemistry and Physics [24]

Table 2 Work function for a selection of metals

Element	Φ (eV)	Element	Φ (eV)
Ag (111)	4.74	In	4.09
Ag (100)	4.64	Li	2.93
Ag (110)	4.52	Mn	4.1
Al (111)	4.26	Ni (111)	5.35
Al (100)	4.20	Ni (100)	5.22
Al (110)	4.06	Ni (110)	5.04
Au (111)	5.31	Pb	4.25
Au (100)	5.47	Pd	5.22
Au (110)	5.37	Pt	5.64
Cd	4.08	Rh	4.98
Cu (111)	4.94	Ru	4.71
Cu (100)	5.10	Sn	4.42
Cu (110)	4.48	Ti	4.33
Fe	4.74	Zn	3.63

Values from CRC Handbook of Chemistry and Physics [24]. For some metals, values for different faces are given; the value for the (111) face should be larger than for the (100) face and larger then for the (110) face
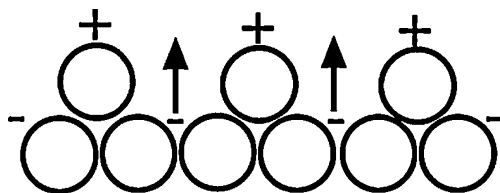
Fig. 5 Surface dipole of a (110)-surface. The surface dipole is built-up by a rearrangement of the free electrons of the metal lattice. At the highest points the electron density will be reduced, in the "valleys" it gets higher. This is indicated in the figure as well as the local dipole moments

predictions of the model were not convincing. The reason is Pearson's wrong model of the potential influence on the hard–soft property [20].

A new attempt of the application of the hard–soft concept to electrified interfaces was presented recently, and it was especially a new definition of the potential dependence of the hard–soft properties of metal surfaces, which provided new predictions [21, 22]. The hard–soft properties cannot be described by the electron density but must take into account the dependence of the hard–soft property on the electrode potential.

The reference point for this discussion is the potential of zero charge, the potential of the uncharged metal. The work function is determined at this potential. But, while the surface charge is zero at this potential there are still dipoles on the surface building up a surface potential (Fig. 5). One can separate the chemical potential into a bulk part and a surface part. The surface part is the surface energy (surface tension) times the surface area.

$$\mu = \mu_{bulk} + \sigma A \tag{22}$$

The surface energy depends on the potential, U.[1]

$$\sigma = \sigma_{pzc} - k_\sigma \left(U - U_{pzc}\right)^2 \tag{23}$$

The constant k_σ corresponds to the differential capacitance of the surface.

$$k_\sigma = \frac{1}{2} C_{dif} \tag{24}$$

It follows for the potential dependence of the chemical potential and the electronegativity, respectively:

$$\mu = \mu_{max} - k \left(U - U_{pzc}\right)^2 \tag{25}$$

$$\chi_{Me} = \chi_{min} + k\left(U - U_{pzc}\right)^2 \tag{26}$$

The metal is soft at the potential of zero charge and gets increasingly harder with increasing positive or negative potential. In Fig. 6, this is shown for silver. The softness has a minimum at the potential of zero charge. The differences of the potential of zero charge for different crystallographic faces are marked in Fig. 6.

The density functional theory also provides definitions of hardness and softness as a derivation of the chemical potential and the electronegativity, respectively, with the number of electrons.

$$h = \frac{1}{2}\left(\frac{\partial\mu}{\partial N}\right)_V = -\frac{1}{2}\left(\frac{\partial\chi}{\partial N}\right)_V \tag{22}$$

$$s = \frac{1}{\left(\frac{\partial\mu}{\partial N}\right)_V} = -\frac{1}{\left(\frac{\partial\chi}{\partial N}\right)_V} \tag{23}$$

Because the energy function in the density functional theory can even be calculated for special groups of atoms in a molecule, this new approach to the characterization of additives provides a new insight into the alchemistic treatment of these interactions in the past.

The previous treatment of adsorption described situations near the equilibrium. The deposition is often driven by far from equilibrium structure-inducing phenomena. Under these conditions, additional concepts might be needed, which will not be discussed in this article.

Future developments

There are programmes on the market, simulating current density and convection of galvanic cells. These programmes can be used to calculate the distribution of the layer thickness. Recently, programmes were developed simulating also the structural properties of the deposit [23]. These programmes are based on equations similar to Eqs. 9 or 10a and 10b. In a large number of experiments, the properties of the deposits were determined and tabulated as a function of the plating
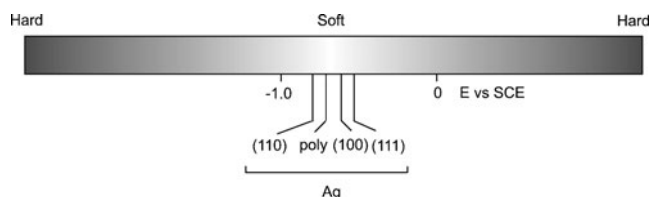

Fig. 6 Hardness and softness at electrified interfaces, Maximum softness is found at the potential of zero charge, slightly different for different crystallographic faces

conditions. The simulation used these data for the calculation of the film properties. The experiments were done for zinc plating. In the future, one can expect that such tables will be developed for other metals.

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