

ANALYSIS OF SUBSTRATES OBTAINED IN ELECTRO CRYSTALLIZATION PROCESSES USING POTENTIALS AND GERM FORMATION WORK

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Abstract: In this present paper are analyzed the substrates obtained in the electro crystallization processes by using chemical potentials and germs formations work.

Key words: electrodeposition, electrochemistry, potentials atoms, intermolecular potentials, and work formation

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1. INTRODUCTION

Electrochemical deposition of metals and alloys are widely employed in different areas of materials processing from the purification of metals to electronic microfabrication. In its first applications, electrodeposition developed largely along empirical lines, and this approach is still largely employed in practice. Due to its increasing importance in advanced technologies however, a purely approach to the development and optimization of electrochemical deposition.

Nano dimensional permanent magnet and magneto-optical materials can be fabricated by electrodeposition of Co, Ni and Fe –rare earth thin films alloys. [1-3]

In this paper is presented the electrocrystallization theory and some potential and germ work formation calculations and its influence through adsorption and discharging ions concentration.

2. ELECTROCRYSTALLIZATION THEORY

Volmer and Erdey-Gruz introduced the theory of metallic electro crystallization on a smooth surface in 1931. [4] This theory is based on the new phase turn up mechanism from a supersaturated phase. The work done here for the obtaining of unit crystal germs is smaller.

Volmer presumed that electro crystallization germ is the elementary particle, which is in equilibrium with the supersaturated system. If the supersaturation is higher the crystalline germ grow up further. For this reason the elementary crystal need to have a “Critical Size”.

By using the conditions from the chemical crystallization we can obtain the 3D work for the crystalline germ:

$$L_g = \frac{4 \cdot \chi \cdot \sigma^3}{3} \cdot \frac{V^2}{(G_r - G_\infty)^2} \quad (1)$$

where: χ is a geometrical coefficient, σ is the interface stress, V is the molar volume and G_r is the free enthalpy of the crystalline germs G_∞ is the free enthalpy of the free plane surface of the crystal.

Volmer introduced the term " frequency of germs appearance " J: the number of germs which appears in the time unit and the volume unit:

$$J = c \cdot e^{-\frac{L_g}{KT}} \quad (2)$$

where c is a constant which depend on σ , on the density and Avogadro number, and K is Boltzman constant.

If we replace the form of L_g from the relation (1) to (2) we can observe the influence of the supersaturation degree on the frequency of the germs appearance.

The frequency of germs appearance is strongly influenced by the interface stress σ as we can see from relation (1).

Interface stress can be influenced. The activity of different particles, which decrease the interface stress by increasing the frequency of germs appearance. Electrical charges can influence in a good way the germs formation by increasing the J value.

When the crystalline radius of the germs is smaller, by different situations, the frequency of germs appearance has to increase. If they are formed crystalline germs on a foreign crystals surface their growth depends on the substrate structure.

When the forces from the substrate structure of the crystal are different from those in the new phase, tri dimensional germs have to be formed and they are completely different from on the basic crystal supposed to be a support. If the forces from the substrate structure and from the new phase have the same character the tri dimensional germs will be formed [4-6], which can be forced to grow in a preferable direction to the substrate structure.

Increasing the radius of the germs depend on crystal structure substrates if the crystalline germs formed on the surface of different crystals. When the forces which acts in the substrates of the crystal texture are different from those of the new phase it have to form a 3D crystalline germs which grows entire independent from the support. If the forces which acts in the structure and in those from the new phase are the same [4-6], it will grows a crystalline germ with a preferable orientation.

Metals can be homeopolare especially when are formed neutral atoms (like in vapor deposition). When the first surface is already formed the germs of the next surface have to be formed in the plane where the deposition energy is maximum. The new crystalline germs will grow in the middle of the homeopolare structure. This is possible because the deposition energy which is consider to be free is bigger then the deposition energy, which can be consider to be free during the particle deposition on the boundary or in the corner of the structure.

We can use the following notations: $A_{ad} = 1/4$, $A_{boundary} = 1/3/2$, $A_{corner} = 1/2/1$ as in figure 1.

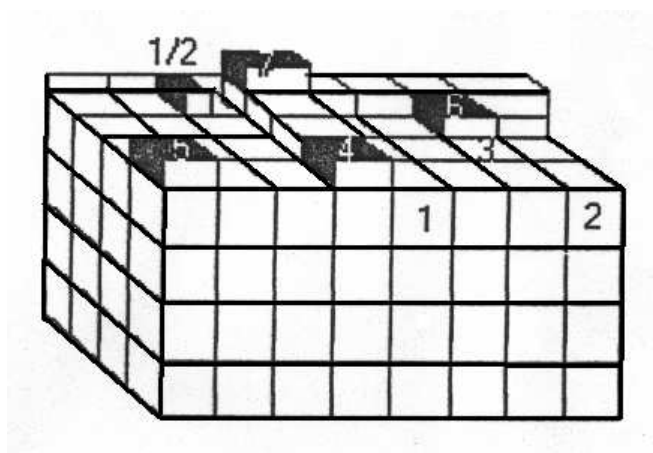


Fig. 1 - Knacke and Stranski crystal

The energy, which is set free during the deposition of the atoms at the boundary of the growing surface is more than A_{ad} . Immediately appears an intermediate phase of crystallization with a bigger energy. This state is possible because for the first time after some atoms chains formation, start a new atom chains: the position with $\frac{1}{2}$ notation in figure 1.

Because the maximum of the energy is set free, the structure will be continuing. This process will be repeated during the crystal growth process. Kossel named this process “repeatable step” [4]. A new surface from the crystalline structure start to growth with a relatively small gain of energy. Once the new surface is formed these will grow faster with a “repeatable step”. The growth velocity of a surface will be obtained in the slowest stage of the growth process: the crystalline germs formation in the middle of the surface stage.

The growing process of a surface depends on two components: the vertical substance deposition (a perpendicular growing related to the basis and a parallel growing related to the basis respectively). Deposition on the vertical is slow because A_{ad} is small. The tangential deposition which starts after the germ formation (seed formation) is much faster.

From the figure 1 we can find the next characteristic positions of the particles: (1) on the border, (2) and (5) in the corner, (3), (4) and (7) on the surface and (6) on the step.

Except these can appear voids on the surface.

The most important position is $(\frac{1}{2})$ [4].

In the case of a small value of super saturation only the “repeatable step” with a higher energy will exist. The crystal can grow infinitely and will have the equilibrium form in conditions of no perturbation from outside. At a higher super saturation the surface already formed will grow further and it will form new surfaces. So the crystal will grow step by step.

During electro crystallization the atoms from the metal lattice (structure) are formed from the simple or complex metal ions solvated or not discharging process.

Because of the applied electric field, metallic ions are attracted to the electrode, neutralized and included in the metal lattice.

The general electro crystallization process takes place in different way:

Model I

- Ions discharging leads to adsorbed ions formation process (formation of “ad- atoms”)
- Diffusion of “ad- atoms“ on the electrode surface to the inclusions from the lattice
- Obtaining the lattice

Model II

- Ions diffusion which have to be discharged
- Discharging of ions in the place where is formed the crystalline structure (the lattice)
- Obtaining the lattice

Every step can have different phase as breaking the complex of ions before discharging. The stage with a smaller velocity will influence the electro crystallization process.

In electro crystallization case is better to use potential electrode instead of free enthalpy, which appear at the interface of the metallic crystal phase, and the electrolyte, which contains metallic ions phase. This potential electrode can be measured by using a reference electrode. We can use the chemical potential of metallic ions in the germs of a radius r ($\mu_{Me\ g}^+$) and for the crystal with infinite dimensions ($\mu_{Me\ \infty}^+$) to establish the relationship between free enthalpy and electrode potential ϵ_e on the metallic infinite crystal during the electric flow passing through the germs of radius r .

Equilibrium potential electrode is:

$$\epsilon_e = \frac{\mu_{Me^+(2)}^0 - \mu_{Me^+\infty}}{zF} + \frac{RT}{zF} \ln a_{Me^+} \quad (3)$$

and the potential established during the current passing through ε_i will be :

$$\varepsilon_e = \frac{\mu_{\text{Me}^+(2)}^0 - \mu_{\text{Me}^+g}}{zF} + \frac{RT}{zF} \ln a_{\text{Me}^+}^I \quad (4)$$

where: a_{Me^+} is the metallic ions activity from the electrode vicinity of the infinite crystal (with no electric flow); $a_{\text{Me}^+}^I$ is the metallic ions activity when the electric flow pass through the crystalline germ during the growth process: $a_{\text{Me}^+} < a_{\text{Me}^+}^I$; $\mu_{\text{Me}^+(2)}^0$ is the standard chemical potential of the ionic metals from the solution.

Relationship between free enthalpy and chemical potentials is:

$$G = n_i \cdot \mu_{\text{Me}^+} \quad (5)$$

where n_i is the number of moles during the process.

By using relation (3) and (4) in (5) we can get:

$$\begin{aligned} G_\infty &= n_i \mu_{\text{Me}^+_\infty} = n_i \left(\mu_{\text{Me}^+(2)}^0 - zF\varepsilon_e + RT \ln a_{\text{Me}^+} \right) \\ G_r &= n_i \mu_{\text{Me}^+_g} = n_i \left(\mu_{\text{Me}^+(2)}^0 - zF\varepsilon_i + RT \ln a_{\text{Me}^+}^I \right) \end{aligned} \quad (6)$$

The difference between those two relations is

$$G_r - G_\infty = n_i \left[zF(\varepsilon_e - \varepsilon_i) + RT \left(\ln a_{\text{Me}^+}^I - \ln a_{\text{Me}^+} \right) \right] \quad (7)$$

where $\eta_c = \varepsilon_e - \varepsilon_i$ is the cathodic overpotential

By replacing the relation (7) in (1) we can get the germ formation work as follows:

$$L_g = \frac{4 \cdot \chi \cdot \sigma^3}{3n_i^2} \cdot \frac{V^2}{\left[-zF\eta_c + RT \ln \frac{a_{\text{Me}^+}^I}{a_{\text{Me}^+}} \right]^2} \quad (8)$$

In conditions very close to equilibrium: at the very small values of the flow densities and in solutions not very diluted the second term in the denominator can be neglected. That term can be take into account only when the metallic ions activity from the vicinity of the cathode is smaller inside of the electrolyte solution.

We can see the relationship between all the values, which can influence the overpotential on the metallic deposition of the substrates in relation (8). From relation (8) we can conclude that the germs formation work is inverse proportion with the number of germs formed on the surface unit. So during the increasing of the overpotential, the germs number have to increase and their size have to decrease.

From the same formula (8) we can analyze the influence of the different factors on the germs formations.

3. ADSORPTION INFLUENCE

Taking into account that adsorption is the influence of a layer of foreign substance on an impermeable surface we will analyze the influence of adsorption on the germ formation work.

During adsorption of different substances, the growth of crystals at the cathode is slow down and is obtained a very big polarity of that one. These substances can be organics and colloids. By increasing of adsorption process, the interface stress (σ) will decrease and these will decrease the values of germ formation work L_g too.

By decreasing the germ formation work, the number of germs will increase and their diameter will decrease. Because of a height inhibition will take place this phenomena. When the values of the inhibition are very low the germ formations will decrease but the dimension of the particle will increase. That experimental result is not in agreement with relation (8).

Low inhibition will act on the germ formation for one-, bi-, and tri dimensional germs. The one dimensional germs formation work for a chain of atoms is:

$$L_g^1 = (\varphi_i - \varphi_a) \quad (9)$$

where: φ_i is the taking off work of a singular particle and φ_a is the average taking off work.

In conclusion the difference $(\varphi_i - \varphi_a)$ become higher and from relation (9) is obvious that one dimensional germ formation work L_g is higher and prevent the formation of a new germs, but influence by increasing the existing germs.

The tri dimensional germ formation work is:

$$L_g^3 = 2.a^2.\Psi + 8.a.\chi + 8.\varepsilon \quad (10)$$

where Ψ is the specific interface energy; χ is specific border energy; ε specific corner energy.

For a low inhibition, the specific corner energy ε will decrease because of the stacking of the corner atoms. So the face of the germ is increased (because of the decreasing) one dimensional germ formation frequency.

We can get an increasing of the tri dimensional germ formation work L_g^3 .

4. DISCHARGING IONS CONCENTRATION INFLUENCE

Metallic existing ions concentration from the substrates in the vicinity of the cathode influences the germs formation. By decreasing the metallic ions concentration we can obtain a polarity with height or low concentration.

Another effect of the reduced ions concentration in the cathodic film is the following: at small current densities we can get the limited current region.

In the most cases these lead to discharging of hydrogen and using this electro crystallization processes will be inhibit by hydrogen adsorption at the cathode.

5. CONCLUSION

We can conclude that a singular atomic chain is produced at low inhibition, so just the first atom from the chain will be stacked, the other atoms and the surface will not be cover with inhibitors. Inhibition will slow down the new one dimensional germs formation. By stacking the atoms from the corner, the taking off work φ_i is increasing and the average of the token off work for the big crystalline face is unchanged.

In conclusion we can say that is very hard to obtain tri dimensional and bi dimensional germs, but we can obtain only one dimensional germs and the crystals can grow further on the existing germs.

We can conclude the following: a height polarity encourages the appearance of the germs, which brake down the growing of them, which is in a good agreement with the experiments.

Discharging ions concentration can be decreased by electrolyte concentration reduction using another salt or another complexing agent.

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