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Short Communication

The Influence of Magnetohydrodynamic Power on the Deposition of Silver Dendrites on the Titanium the Surface of Titanium after Anodic Oxidation

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The publication presents the influence of an external magnetic field of 1.2T on the process of silver deposition. The external magnetic field interacted perpendicularly to the sample surface during the deposition process. The surface of the titanium sample was pre-modified by anodic oxidation. Such a surface modification causes the deposited silver to take the form of dendrites. As a result of the influence of the magnetic field, the silver dendrites were shortened and the size of their crystallites was reduced. Changes have also been reported at the nucleation stage during the deposition process. The negative magnetic field accelerated the process, causing the deposited silver particles to become thinner. The positive magnetic field slowed down the process, causing the deposited silver particles to become thicker. By modifying the magnetic field, the morphology of the deposited silver particles can be changed.

Keywords: Magnetohydrodynamic deposition, silver nanoparticles, titanium, anodic oxidation

1. INTRODUCTION

The influence of the external magnetic field on the metal deposition process was predicted already in the 1970s. Preliminary studies on the effect of these processes on the efficiency and transport of mass were conducted. However, the magnetohydrodynamic deposition (MHD) effect was not sufficiently tested and confirmed [1,2].

Today, it is well known that the magnetic field increases the electrochemical galvanic current of the metal and has an impact on the corrosion rate. Usually, the plating current in concentrated acidified electrolyte can be doubled in 1 T. The field effect is similar to gentle mixing and the effect can be suppressed by increasing the viscosity of the electrolytes [3,4]. The influence of the magnetic field on the galvanic current depends on the Lorentz force.

$$F_l = j \times B \qquad (1)$$

F_l is the Lorentz force, j is the current density and B is the applied magnetic field.

The Lorentz force acts on the moving ions in the solution and affects the flow of electrolyte. It is referred to as the magnetohydrodynamic force [4].

A unified magnetic field acts on the magnetic susceptibility of ions to form local energy density. This force causes the diamagnetic and paramagnetic ions to be displaced in opposite directions in the applied magnetic field [5].

$$F_p = X_m \frac{B^2}{2\mu_0} \vec{\nabla} c \qquad (2)$$

X_m is the molar susceptibility of the ions, B is the applied magnetic field, μ_0 is the permeability of free space and c is the concentration in mol.

This affects the deposition rate that depends on the magnetic properties of the ions. The force on the diamagnetic ions is approximately one order of magnitude smaller and is set in the opposite direction.

The third magnetic field effect associated with the magnetochydrodynamic force works only in the dispersed double layer near the electrode. The magnetic field perpendicular to the current, induces the Lorentz's force with excess charge density. This produces a nonelectrostatic field parallel to the working electrode trigerring a motion of the solution near the interface. It is referred to as electrokinetic magnetohydrodynamic effect[6].

$$F_{EK} = \frac{\sigma_d E}{\delta_0} \qquad (3)$$

σ_d is the charge density of the diffuse layer, E is the induced nonelectrostatic field, δ_0 is the boundary layer thickness.

The above formulas allow calculating the influence of the external magnetic field on the deposition of metals in the electrolytes. In order to fully model the reaction, it is necessary to consider the mass transport effects, the kinetic effects, the cathodic deposit morphology effects and the anodic effects. Interactions of the magnetic fields on the metal crystallization behavior lead to practically applicable results. Studies of electron transfer and, particularly, corrosion in magnetic fields have generated new and, sometimes, controversial, insights. The broad area of magnetoelectrolytic research is still expanding [7, 8].

The influence of the magnetic field effects on the transient response of a cathodic current to a voltage step has been confirmed. Electrodeposition of four different metals: Ag, Cu, Bi and Zn (different valence ions and magnetic properties) has shown significant differences after chronoamperometry investigations [9]. It has also been observed that the mass transport was increased by diamagnetic (Ag^+, Zn^{2+}, Bi^{3+}) and paramagnetic (Cu^{2+}, Ni^{2+}) elements. Theoretical models of hydrodynamics of the influence of magnetic field on the electrochemical processes have been developed [10]. Microscopic investigations have confirmed the magnetohydrodynamic flow in the electrolyte and that it is more intense when the direction of vector (B) is parallel to the working surface of the electrode compared to its perpendicular orientation to its working surface [11]. The effect of MHD is also dependent on the strength of the magnetic field [12].

Current understanding of the effects of magnetic fields on the nucleation of metals from the solution is insufficient. In order to understand the dynamic boundary condition at the electrode surface, hydrodynamic modeling will have to be supplemented by molecular dynamics. It is necessary for a better understanding of the influence of the magnetic field on the structure and morphology of the deposited metals. [13,14].

MHD has an impact on the deposited metals, changes their structure, texture, chirality, affects the control of the hydrogen bubble release, microfluidic flow and influences the nucleation. Much of this impact depends on the micro-magnetohydrodynamic flow in a nano-scale and results from the the strength of the magnetic field [13,15-18].

The electrodeposition of silver without an additional magnetic field on the surface of titanium after anodic oxidation is characterized by a dendritic shape. The shape of the electrodeposits is closely related to the surface morphology of the sample, which defines the deposition process of this metal [19].

The initial stages of Cu, Ag and Zn electrodeposition processes were investigated in a magnetic field superimposed perpendicularly to an Au (1 1 1) electrode. Cyclic voltammetry shows no B field effects on the monolayer formation at underpotentials. On the other hand, the nucleation in the overpotential region is clearly inhibited [20].

The influence of the pulse magnetic field on the crystallization and growth of dendritic Co-Cu particles was also investigated. The theories of thermodynamics and kinetics explain the growth process of the dendritic nanostructures [21].

This work presents the influence of the magnetic field on the shape of the silver particles deposited on the anodized titanium surface. The shape, size and morphology of such particles are important for example in medical applications. Silver exhibits surface bactericidal properties, therefore it is important to increase the specific surface area of the particles and to control their deposition, which is possible using the magnetic field.

2. EXPERIMENTAL STUDIES

Studies have been conducted on the basis of a previous work treating on silver deposition on anodically oxidized titanium [19].

The samples were made of titanium foil (0.25mm, 99.7%). The samples were placed in the grips providing 25mm^2 of active surface. The sample along with the counter electrode (platinum grid, Wieland) and Ag/AgCl reference electrode were placed in the chamber (Fig.1). The chamber was filled with 2M H_3PO_4 + 1% HF electrolyte and connected to 210V for 30 minutes (Delta Elektronika SM 300-5) for anodically oxidized titanium surface. The process was carried out with additional stirring of the electrolyte 100 rpm. After the process, the samples were rinsed and dried.

For the silver deposition, a sample along with a counter electrode (silver foil 0.25 mm, 99.9%) and an Ag/AgCl reference electrode were placed in the chamber (Fig.1). The chamber was filled with electrolyte containing silver and nitrogen ions with the concentration of 0.01M. The use of a counter electrode in the form of a silver foil ensured constant concentration of the silver ions during the process. During silver deposition (60s) the DC voltage was set at -1V, according to the OCP (low voltage potentiostat SOLARTRON 1285). The deposition process was carried out under different magnetic conditions with the magnetic field acting perpendicularly to the sample surface (0/-1,.2T/1,.2T) with additional stirring of the electrolyte at 100 rpm. After the process, the samples were rinsed and dried.

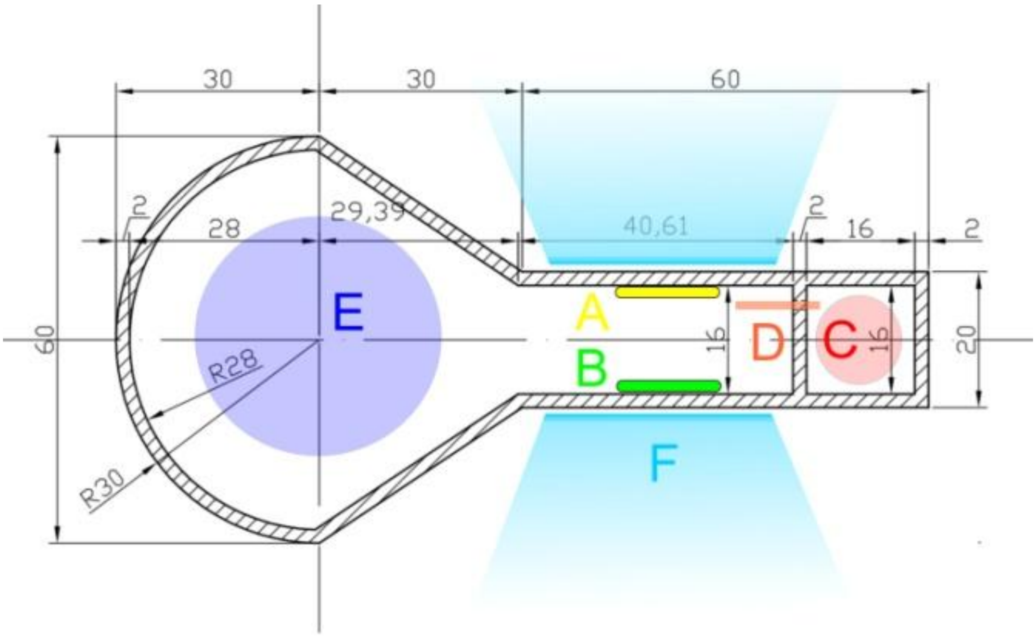

Figure 1. Homemade chamber made of PP for magnetohydrodynamic deposition, 120ml: sample A, counter electrode B, reference electrode C, luggin capillary D, mechanical stirrer E, electromagnet F

After the deposition process, the samples were characterized by SEM (Prism 200 Avalon, PGT) and XRD (EMPYREAN, PANalytical).

3. RESULTS AND DISCUSSION

The surface of the titanium foil after anodic oxidation was characterized by the characteristic gray color of the amorphous oxides. This is related to the process of high voltage oxidation. However, the characteristic structures associated with PEO (Plasma Electrolytic oxidation) have not been observed, which may result from the presence of the oxide layer on the pre-process samples [22].

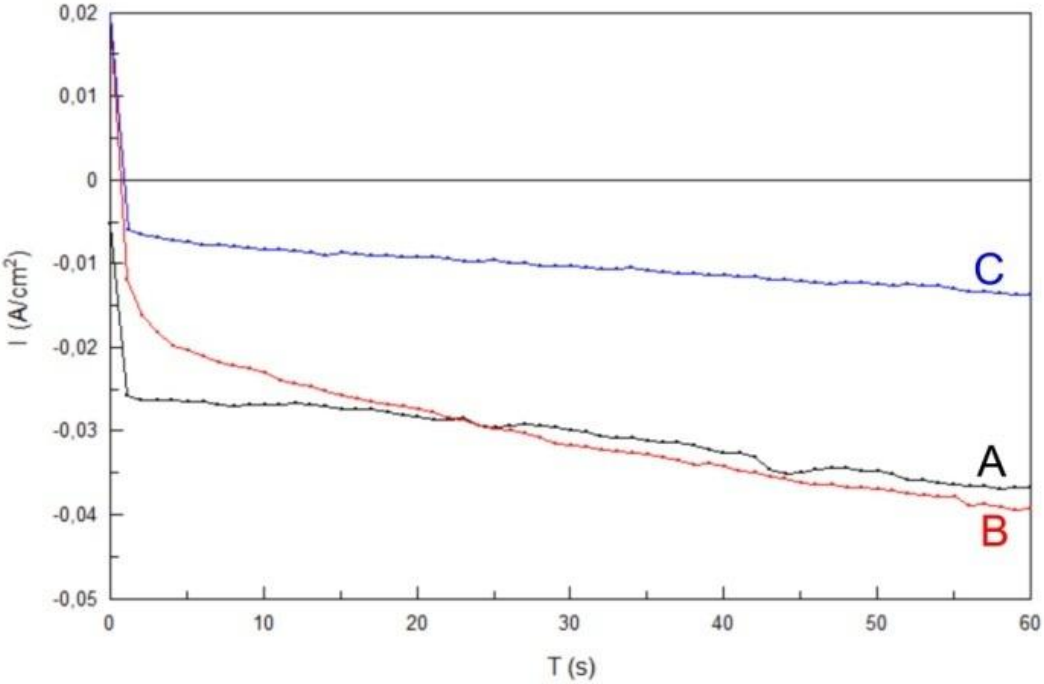

Figure 2. Curves of the current density in time of the silver particles depositing at -1V DC voltage (electrolyte containing 0.01M Ag^+ and 0.01M N^+) on the titanium surfaces after anodic oxidation process (2M H_3PO_4 + 1% HF, 210V, 30min) A) with negative magnetic field 1.2T B) with positive magnetic field 1.2T C)on the titanium surfaces A) with negative magnetic field 1,2T, B) with positive magnetic field 1,2T C)

During the process of silver particle deposition, the flow of electrical current was measured. The purpose of the measurement was to determine the actual influence of the external magnetic field on the flow of electrical charge through the electrolyte (Fig.2). Both positive and negative magnetic fields were impactful in the initial period of deposition, as seen in the measured current flow (the first 2 seconds). This could have a significant effect on the initial nucleation and crystallization of the silver crystals and the crystal growth in the form of dendritic structure. The negative magnetic field slightly increased the flow of current by accelerating the process. The positive magnetic field significantly reduced the flow of electricity, slowing down the process more than three times. The total electrical charge that flowed through the electrolyte during the deposition process (60s) has been shown in Table 1.

Table 1. Values of the electrical charge flowing through the samples during the process of silver deposition (0.01M Ag^+, 0.01M N^+, -1V, 60s) on the titanium surfaces after anodic oxidation process (2M H_3PO_4 + 1% HF, 210V, 30min) with additional magnetic field.

Magnetic fieldMagnetic field	- (0T)0	Negative (-1.2 T)Negative	Positive (1.2 T)Positive
Charge Q [C]Charge Q	-0.462	-0.457	-0.155

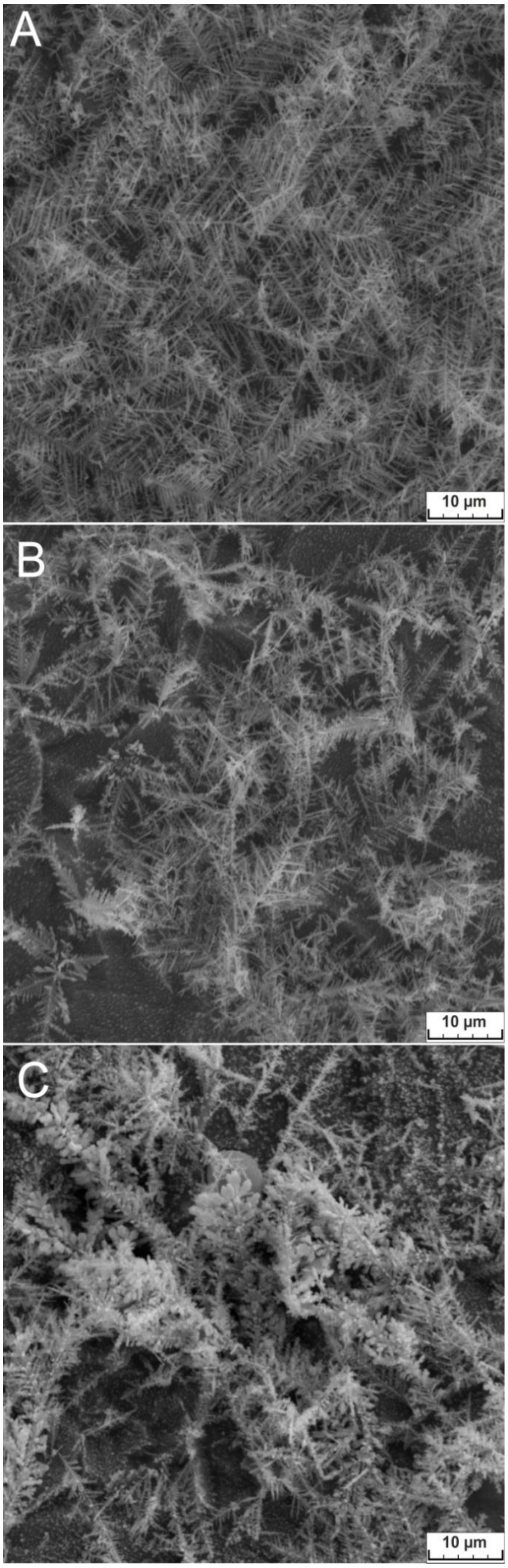

Figure 3. SEM image of the sample surface after anodic oxidation (2M H_3PO_4 + 1% HF, 210V, 30min) and silver deposition (0.01M Ag^+, 0.01M N^+, -1V, 60s) A) silver deposition in the negative magnetic field -1,.2T B) silver deposition in the positive magnetic field 1.2T C)

An additional mixing of the electrolyte was observed during the deposition in the positive and negative magnetic fields. This phenomenon was independent of the electrolyte external mechanical mixing and remains consistent with the current state of knowledge [13].

The microscopic examination (SEM) allowed an observation of the structure of the deposited silver particles on the titanium surface after anodic oxidation (Fig.3).

Silver particles formed during the deposition without additional magnetic field are characterized by a dendritic structure characteristic of this type of surface [19]. Silver dendrites have a length of up to 100 μm with distinct branches to level 3. The thickness of the dendrite branches exceeds 100 nm and decreases slightly with their level. This form of silver particles signifies their free growth during the deposition process. (Fig.3A). The negative magnetic field caused a significant reduction of the length of the dendrites to approx. 20 μm. In addition, with the negative magnetic field, there were less frequent third-level branches and their thickness dropped to less than 100nm. The presence of fine crystalline silver particles was observed on the surface of the sample between the dendrites. This form of deposits may signify a change during the nucleation and production of a greater proportion of nucleus. Since the process was slightly accelerated, the growth of the dendrites was not free, which reduced their thickness and length (Fig.3B). The positive magnetic field caused a significant reduction of the dendrites length to approx. 10 μm. In addition, with the positive magnetic field, third-level branches were not observed. There was a significant increase in the thickness of the dendrites to more than 100nm. The third level branches joined together to create the tiles, preventing further growth of the dendrites. The presence of the expanded silver crystals was observed on the surface of the sample between the dendrites. This form of deposits may signify a change during the nucleation and production of a greater proportion of nucleus. Because the process of deposition was significantly slowed down, a significant change in the morphology of the particles was observed (Fig.3C).

The presence of an external magnetic field during the deposition of silver particles also influenced its crystallization, which is consistent with the literature findings [20]. The X-ray studies showed significant changes in the surface pattern after the process (Fig.4). The diffraction pattern of the sample after depositing silver without additional magnetic field showed weak silver peaks. The size of the crystallites calculated with the Scherrer's Formula was 32.45 nm (Tab.2). This is the largest crystallite size among the samples presented. This may signify the most free crystal growth during the process. This is also consistent with earlier observations. The presence of an external magnetic field during the deposition process resulted in a decrease in the size of the silver crystals. This may result from the changes in the process at the nucleation stage. The crystallite size calculated with the Scherrer's Formula was 24.94 nm for the negative magnetic field and 22.60 nm for the positive magnetic field. The intensity of the peak on the samples produced in the positive magnetic field may result from the presence of the tiles in the form of plate at the ends of the dendrites, which could cause an intense X-ray diffraction.

The presented results show a significant influence of the presence of an external magnetic field on the deposition of silver particles on the surface of anodically oxidized titanium. The differences in the dendrite morphology affect their surface area relative to the surface of the sample. This parameter is important in situations where the surface properties of silver are important with their possibly small quantities on the surface. Examples of such applications are biomaterials where silver-bactericidal properties are important [23].

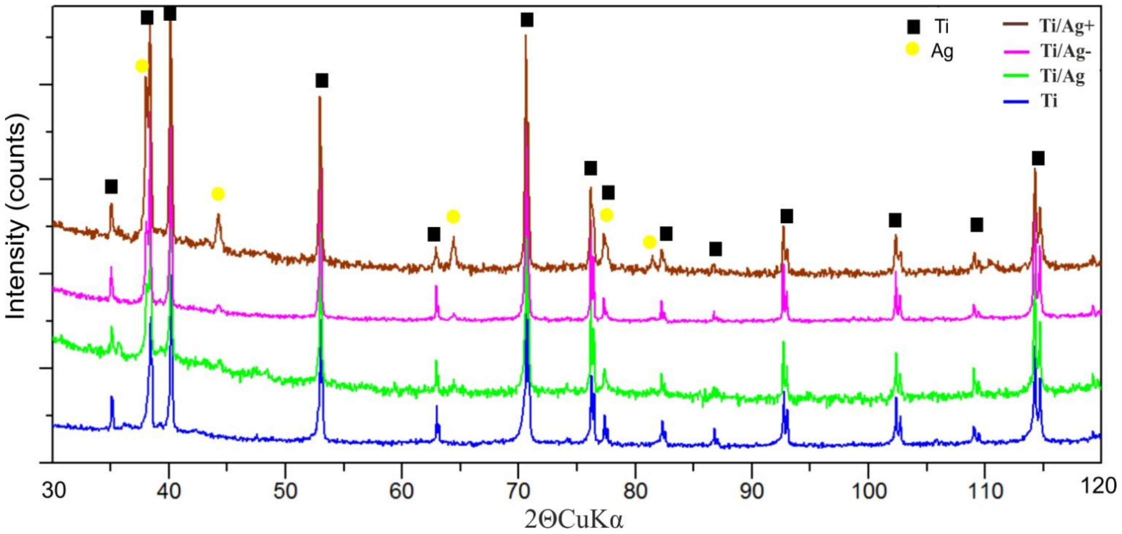

Figure 4. XRD spectra of titanium (Ti) and samples after anodic oxidation (2M H_3PO_4 + 1% HF, 210V, 30min) with silver deposition (0.01M Ag^+, 0.01M N^+, -1V, 60s) (Ti/Ag), silver deposition in the negative magnetic field -1.2T (Ti/Ag-) and silver deposition in the positive magnetic field 1.2T (TTi/Ag+)

Table 2. Values of the crystal size deposition (0.01M Ag^+, 0.01M N^+, -1V, 60s) on the titanium surface after anodic oxidation (2M H_3PO_4 + 1% HF, 210V, 30min) calculated with the calculated with the Scherrer's Formula*

Magnetic field (T)Magnetic field	Peak position 2θ (°)	FWHM size (°)	τ (nm)	τ Average (nm)
00	44.4	0.307	29.21	32.45
00	64.6	0.275	35.69	
- 1.2Negative	44.4	0.402	22.31	24.94
- 1.2Negative	64.6	0.356	27.57	
1.2Positive	44.4	0.424	21.15	22.60
1.2Positive	64.6	0.408	24.05	

*Scherrer's Formula

$$\tau = \frac{K\lambda}{\beta \cos\theta} \qquad (4)$$

τ is the size of the ordered (crystalline) domains, K is the dimensionless shape factor = 0.94, β is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle (in degrees).

4. CONCLUSIONS

The presence of an external magnetic field of 1.2T during deposition of silver particles on the anodically oxidized titanium surface influences the morphology of the deposited particles. The external magnetic field affects the nucleation step by increasing the number of nuclei. Silver dendrites deposited in an external magnetic field are shorter and are characterized by smaller crystallites. Negative magnetic field causes a slight acceleration of the process and the deposited silver dendrites are slightly thinner. Positive magnetic field causes a significant slow-down of the process and the deposited silver dendrites are slightly thicker with the tiles in the form of plates at the ends of the dendrites.

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