

MODIFICATION OF METAL SURFACE BY ELECTROPLATING AND VACUUM ARC DEPOSITION

O. Sheveiko (1), A. Kazakevich (1), B. Straumal (2), N. Vershinin (2,3), D. Startsev (1)

(1) Moscow Institute of Steel and Alloys (Technical University), Moscow, Leninsky Prospekt 4, 119991 Russia

(2) Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow district, 142432 Russia

(3) SONG Ltd., P.O. Box 98, Chernogolovka, Moscow district, 142432 Russia

ABSTRACT

The decorative finishing by metal plating allows one to improve the aesthetic appearance and corrosion resistance. The new compositions of the additives for copper and nickel electroplating were developed allowing to deposit coatings with given brilliance, roughness and surface patterns. These characteristics of a deposited coating vary depending on the composition of an additive and the electrolysis mode. For example, the change of velocity and flow direction of agitated electrolyte during electrolysis considerably influences a degree of the electrodeposit roughness. The new technique permits to deposit the novel protective and decorative copper and nickel coatings with the "Velvet", "Sateen" and "Velour" surface patterns. An electrodeposition of thin Ni and Cr layers or vacuum arc deposition of TiN or TiO₂ on the "Velvet", "Sateen" and "Velour" patterned coatings strengthens the decorative effect and essentially increases the corrosion resistance of coated parts.

KEYWORDS: Copper, electrodeposition, structure, surface, morphology.

INTRODUCTION

The final surface treatment is one of the main parts of any technological process. At present various modern methods of the metal finishing exist permitting semi-manufactures to produce the parts with different properties, appearance, surface configurations and requirements. The electroplating of protective and decorative coatings is the traditional method for finishing. The copper underlayer is deposited often before the main metal coating. Copper coatings allow us to get more stable and adhesive sublayers between substrates and the final decorative layer. This attitude permits to reduce the thickness of the top metal layer (nickel for example) and to form up the new unexpected appearance of the coating in general. It is concerned with the surface morphology of the copper underlayer being either brilliant or matt and microrough [1–4]. It is rather traditional for metallurgists to deal with brilliant coatings, however it is more promising to plate items with matt and microrough layers concentrating the observer's glance at their attractive appearance and hiding some defects [4–6]. Nowadays various technological electroplating schemes are known in metal treatment. They are applied for getting matt, microrough and textured surface, one of them is used for obtaining "Sateen" and "Pearl" coatings which belong to composite type layers [5–7].

Other direction is the development of decorative mat deposits such as "velour" and "velvet" with application solutions containing not a solid heterogeneous phase but a stabilized emulsion. Thus formation of microdimples on the deposit gives the mat surface by dispersion of a luminous flux [4, 6–9]. The surface roughness magnitude can vary not only from a nature of a disperse phase, but also from its concentration. For maintenance of emulsions in a stable state in an electrolyte an emulsifier can be added. The emulsifier is a substance capable to reduce sharp transition from one not immixing fluid to another. Electrodeposition of metals is accompanied by some processes, which affect the coatings structures and

properties. Nucleation and crystal growth are among them, they form up the different samples structures and are influenced by electrochemical and thermodynamical conditions of metal plating. The real types of microstructures depend on the grain size and shape. According to our data, the final surface morphology of the coatings correlates with grain orientation and crystal defects (such as twins, dislocations, etc.) [1, 2].

This paper is devoted to investigation of the influence of "Velour"-forming additive VDG on the structure copper microrough coatings in accordance with electroplating conditions. The finishing of designed deposits does not hide and even strengthens the decorative effect of a velvety surface. Both the electrodeposition of laminas (1-3 μm) of chrome and vacuum arc deposition of titanium oxide or nitride by PVD method a top of deposits such as "velvet", "sateen" and "velour" also intensifies decorative effect and essentially (by 15-70%) raises corrosion resistance of parts. Parts with a velvety surface after colouring them for imitation "gold" and "old bronze" looked most attractive [4, 6, 10-11].

EXPERIMENTAL

A standard electrolyte for acidic copper plating (180–250 g/l of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 50–70 g/l of H_2SO_4) was used at the relation $S_a:S_k = 1:1$. The electrolyte was prepared from reagent-grade chemicals and distilled water. The current efficiency makes 98-100 %. Phosphorous-containing copper was used as an anode material. The anodes put in covers from acid proof fabric. The new composition of the "Velour"-forming additive VDG was developed based on high-molecular compounds and polyols for precipitation of "sateen" and "velour" deposits with a different degree of a roughness. The addition of 0,1-40 ml/l VDG to standard copper electrolyte allows received a deposition with a required roughness, which varies depending on a condition of electrolysis. It is necessary to dump a bath about 5 to 7 hours after addition of VDG.

Electrodeposition was carried out at following conditions: temperature 25 and 50 $^{\circ}\text{C}$, with and without agitating, current density 0.04 A/m^2 , additive concentration was changed from 0,1 to 40 ml/l. Samples were degreased before the electrodeposition in the humid mixture of MgO and K_2CO_3 and washed out with water. The pH value of electrolyte was controlled by a pH-meter "pH -121". The electrochemical measurements were performed in three-electrode cell with separated volumes in air at the temperature 25 and 50 $^{\circ}\text{C}$, with and without agitating. The counterelectrode was made of platinum, working electrode was made of copper. The polarization behaviour was measured potentiodynamically with the aid of potentiostatic apparatus PI-50-1/PR8. All the potentials were measured an Ag/AgCl reference electrode filled with saturated KCl solution ($E_{\text{Ag}/\text{AgCl}} = 0$ corresponds to -200 mV in hydrogen electrode scale). The scanning rate was 1 mVs^{-1} . The polarization was changed from +400 mV to -500 mV. Microphotographs of copper deposits were taken using a JEOL 280 scanning electron microscope.

RESULTS AND DISCUSSION

In the standard electrolyte for copper deposition containing CuSO_4 and H_2SO_4 copper is mainly in a form of Cu^{2+} ions. However, due to the disproportionation in the presence of metallic copper, the Cu^+ ions together with Cu^{2+} ones can be present in the solution. With increasing temperature and decreasing acidity the equilibrium of the disproportionation reaction is shifted towards the formation of Cu^+ ions, and as a result their concentration in the solution increases [2]. The main electrode processes in the sulfate electrolyte for the copper deposition are the discharge of the Cu^{2+} ions on the cathode and copper ionization on the anode. The obtained polarization curves (Fig. 1) permit to suppose that the Cu^{2+} ions in the sulfate electrolyte discharge in two steps $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$, and the most slow step is the recombination with the first electron $\text{Cu}^{2+} + e^- = \text{Cu}^+$.

One can suppose that the additions influence on the deposition of the microrough copper coatings preventing the transport of the ions to the electrode surface, hindering their discharge and modifying the

process of the association of neutral atoms with crystal lattice. The prevention of the transport of the ions to the solution/substrate boundary can be due to the formation of the colloid-like layer at the electrode. These are also such layers which prevent the ion discharge and the association of neutral atoms with crystal lattice. The slow ion discharge is mainly due to the complex formation between the ions and addition molecules or due to the slow adsorption at the electrode. And at the last stage of the association of the discharged atoms with the crystal lattice, the influence of the addition can be due to the hindering of the surface diffusion or the modification of kinetics of nucleus formation [12].

Structure forming additive VDG forms the stable emulsion with the sulfate electrolyte for copper deposition. Therefore, one can suppose that formation of copper deposit will be controlled by the diffusion kinetics and will be accompanied by the selective adsorption of copper complexes on the cathode. Really, on the polarization curves one can see both areas of the diffusion and electrochemical reaction control. The copper layers in such electrolytes can be deposited in the broad interval of the current density. In this interval the deposition depends both on adsorption and diffusion. The increase of stirring and temperature facilitates the diffusion and increases the adsorption. The slope of the polarization curves demonstrates that the increase of the adsorption is more pronounced than the diffusion facilitation (Fig. 1).

The conditions of deposition of microrough copper coatings influence the surface morphology. Important feature of the deposition of microrough copper coatings at ambient temperature in the broad interval of concentration of VDG additive is the formation of multiply twinned spherulites. Such spherulites are the polycrystalline aggregates of spherical shape and radial structure. Each spherulite has the nucleus peripheric part. The number of active centers at the passivated surfaces is restricted. Therefore, the local current density at the beginning of electrocrystallization is so high, that the nucleation of new crystals prevails on the growth. As a result, conglomerates of fine disorientated crystals develop on separate sites of the substrate forming a nucleus being a central part of the spherulite. During the growth of the nuclei, the local current density decreases and the radial peripheric part of the spherulite grows. The development of radial periphery of spherulite is accompanied by the formation of twins (Fig. 2). Further growth of spherulite results in the formation of a continuous stratum of coatings.

An increase in the concentration of "Velour"-forming additive VDG in an electrolyte during electrodeposition of copper microrough coating at a room temperature and without stirring results in the increase of degree of dormancy of the process (Fig. 3), however an increase in the size of the crystals is observed (Fig. 4). We can explain this fact by forming of a gel-like layer close to the electrode. This layer consists mainly of copper complexes formed in the electrolyte solution. At the low concentration of the additive, the amount of the copper complexes is also low. Therefore, they consequently block only a small part of the surface of the sample and leave free numerous active nucleation centres on the cathode surface. This means, that at low concentrations of the additive VDG, the surface energy is mostly used for nucleation, and consequently the fine crystalline structure is formed.

Further with an increase of the concentration of the additive, the number of copper complexes increases. Those complexes when adsorbed on the surface of a sample, will block a majority of active nuclei. Consequently, the major part of the energy is spent for the growth of crystallites and only a minor is spent for the nucleation. Therefore, an increase of the VDG concentration leads to an increase of grain size (Fig. 4). The stirring of an electrolyte at room temperature results in some changes of the surface morphology. For example, at small concentrations of the VDG additive the grain size increases, whereas an increase of the additive concentration up to 10 ml/l and above leads to a decrease of the grain size (Fig. 4). During the growth process, we also observed the drastic dependence of the process degree of dormancy, whereas the minimum is obtained at small concentrations of the VDG additive (Fig. 3).

In our opinion, such influence of stirring is caused by the possibility of formation of copper complexes of a different structure. At small quantities of the additive, apparently, the relatively large composite complexes are formed. When they are adsorbed on the surface of a sample, they will screen off the nucleus, and will cause energy to be used for the growth of crystals, instead of the nucleation. This reason

explains the coarsening of the structure. An increase in the concentration of VDG results in the redistribution of copper ions in the electrolyte, and in the formation of simpler and smaller complexes. In other words, the release of a part of the cathode surface with new active nuclei will take place. As a result, the refinement of the structure will happen.

Changes in the temperature schedule of electrolysis (increase in the temperature of the solution up to 50°C) results in the change of surface morphology, i.e. there is a transformation from spherical to imperfect faceted structure, formed due to the mechanism of layered growth (Figs. 7 and 8). The perfection of structure of crystals growing on the mechanism of layered growth is determined primarily by the two-dimensional nucleation during formation of a new stratum. The formation of each consequent stratum starts by the formation of a two dimensional nucleus on a previous surface. The appearance of a nucleus in a normal position should result to coherent accretion of layers and absence of any boundaries between them. However, in the reality the surface of a growing crystal is covered to some extent with adsorbed impurity particles. Therefore, the nuclei originating on this surface can appear disoriented relative to the underlying stratum. As a result, during the growth of the stratum towards each other, the crystallographic misorientation of their lattices appears. This misorientation is compensated by the occurrence of grids of dislocation.

By heating of the electrolyte up to the temperature of 50°C a part of the copper complexes breaks up and transforms into ethers and hydrated copper ions. This process, in turn, leads to a fractional release of a part of active centres on the surface of the cathode and results in an increase in the number of nuclei and refinement of the structure (Figs. 7 and 8). At high temperatures stirring practically does not change the surface morphology (Figs. 7 and 8), and the degree of a dormancy of the process is slightly increased. (Fig. 6). However, it is necessary to indicate the unexpected fact that large faceted chips (approximately in 4-5 times larger than expected) are formed at the maximal studied concentrations of the VDG additive of 40 ml/l (Fig. 9).

Basing on our results we can conclude that changing the process parameters like the additive concentration, solution temperature and the hydrodynamic conditions, it is possible to obtain coatings with the necessary decorative performances, in our case - to obtain coatings with a given surface morphology.

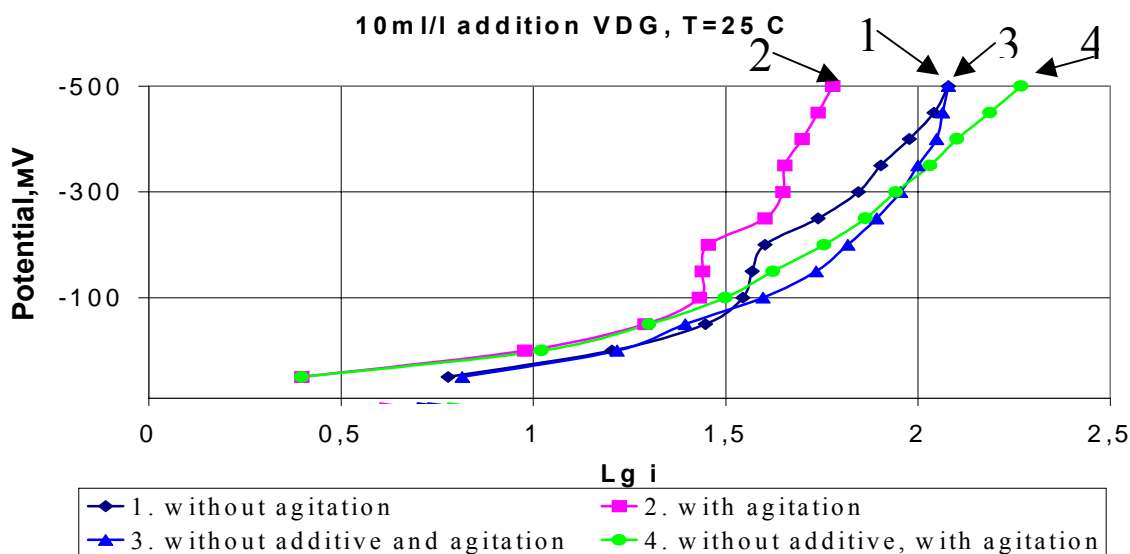


Fig. 1. The Influence of additive and stirring on the polarization curve of copper reduction at $T=25^{\circ}\text{C}$

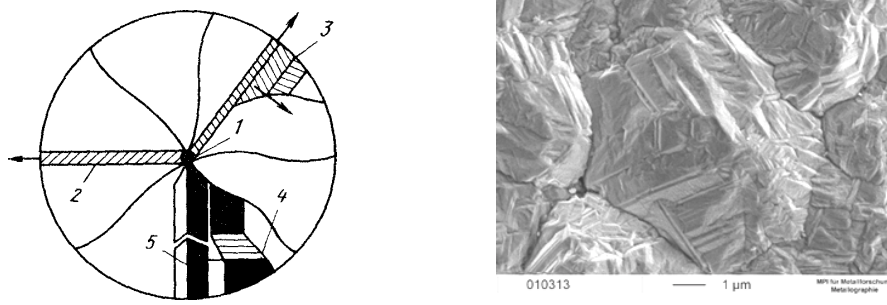


Fig. 2 Spherulite formation scheme with characteristic types of twins: 1 – Spherolyte nucleus; 2 – radial twins; 3 – secondary type of twins; 4 – fragments of multiple twins; 5 – group of multiple twins. The front of crystal growth is shown by arrows.

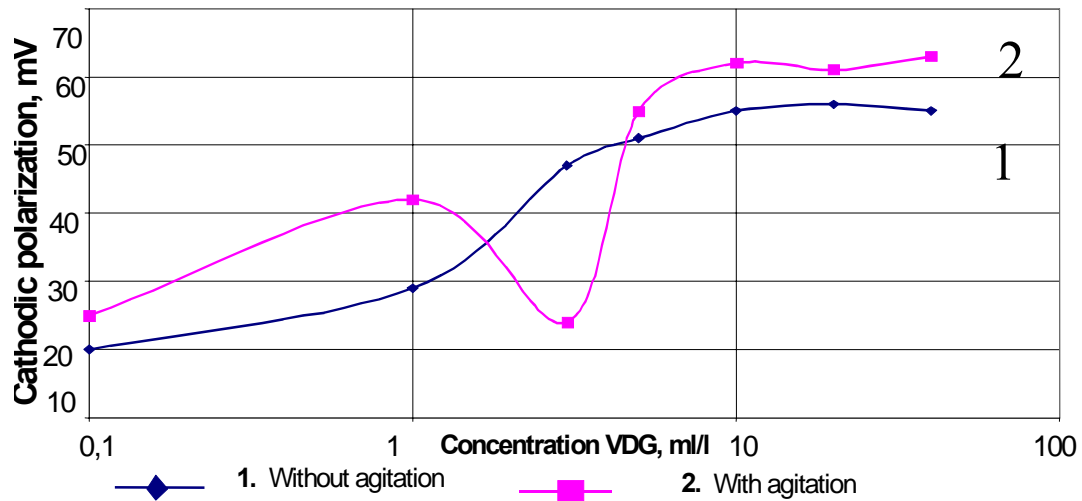


Fig. 3. The influence of additive concentration on the cathodic polarization of copper reduction at $T=25^{\circ}\text{C}$

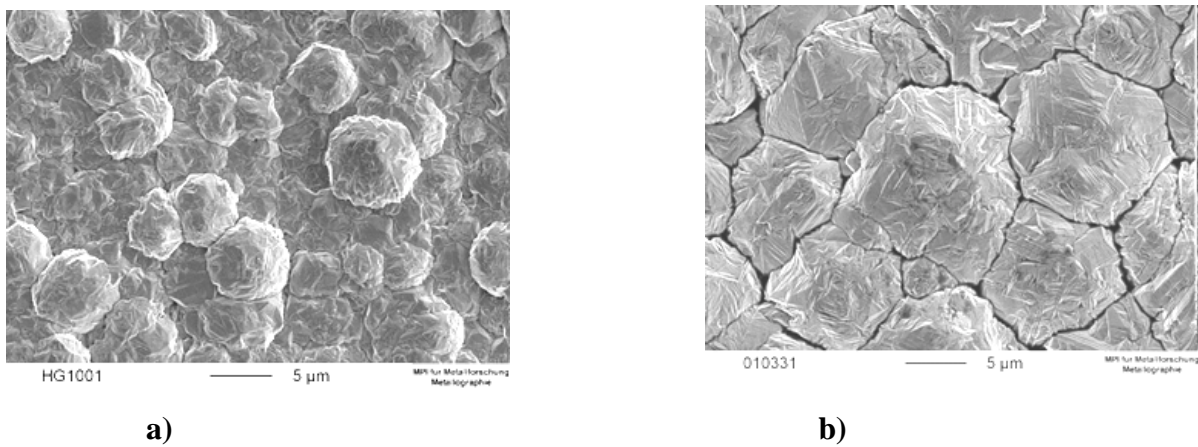
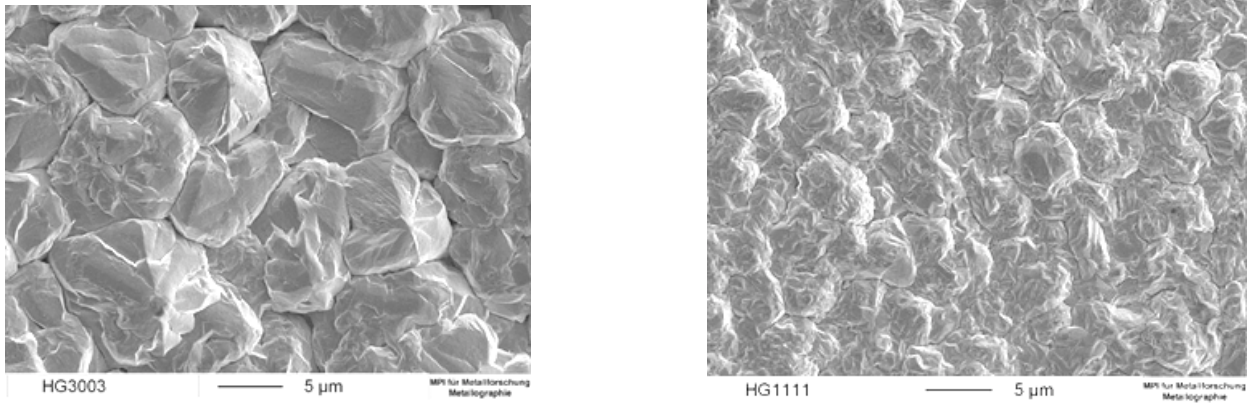


Fig 4. Surface microstructure (x 3000) at $T=25^{\circ}\text{C}$ without stirring: (a) VDG 0.1 ml/l, (b) VDG 40 ml/l.



a)

b)

Fig 5. Surface microstructure (x 3000) at $T=25^{\circ}\text{C}$ with stirring: (a) VDG 0.1 ml/l, (b) VDG 10ml/l.

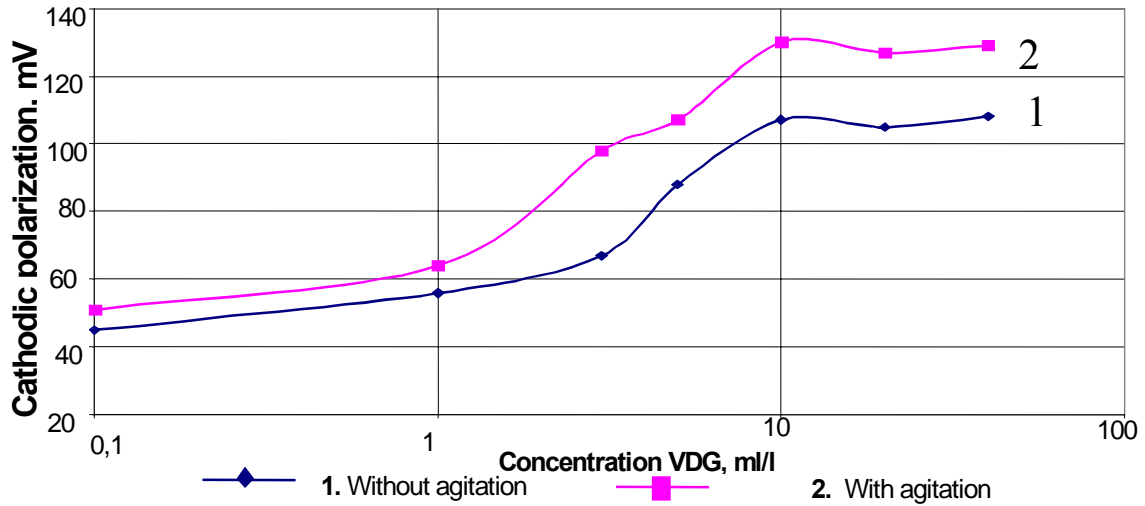
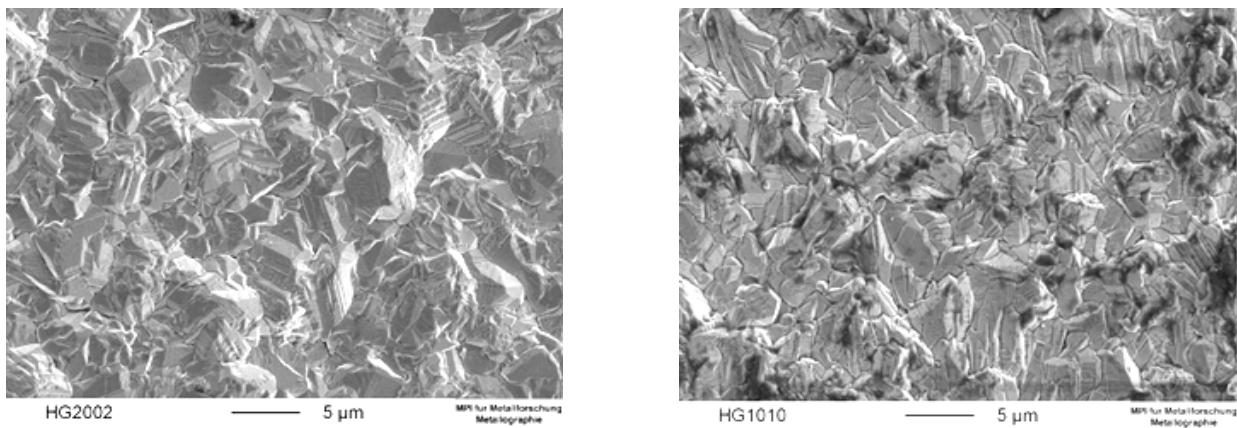


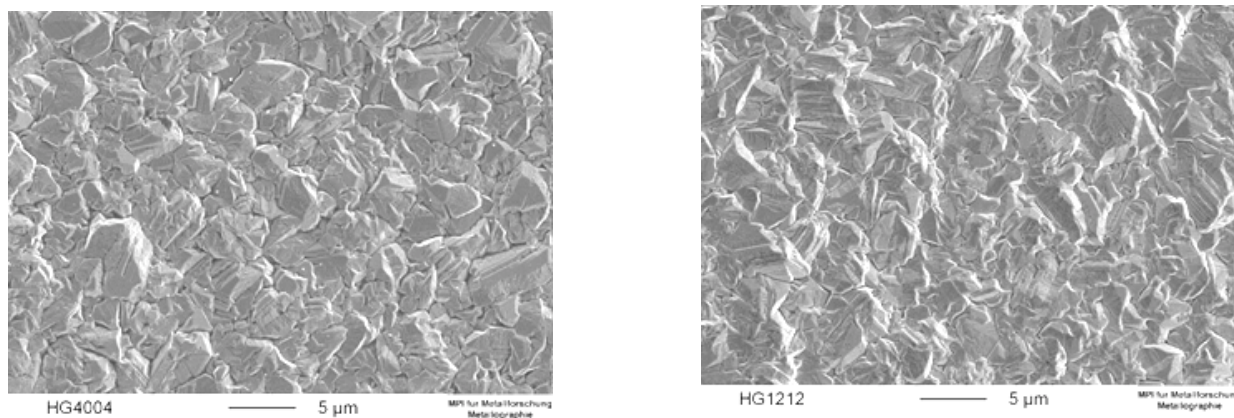
Fig. 6. The influence of additive concentration on the cathodic polarization of copper reduction at $T=50^{\circ}\text{C}$



a)

b)

Fig. 7. Surface microstructure (x3000) at $T=50^{\circ}\text{C}$ without stirring: (a) VDG 0.1 ml/l, (b) VDG 10ml/l.



a)

b)

Fig. 8. Surface microstructure (x3000) at $T=50^{\circ}\text{C}$ with stirring: (a) VDG 0.1 ml/l, (b) VDG 10ml/l,

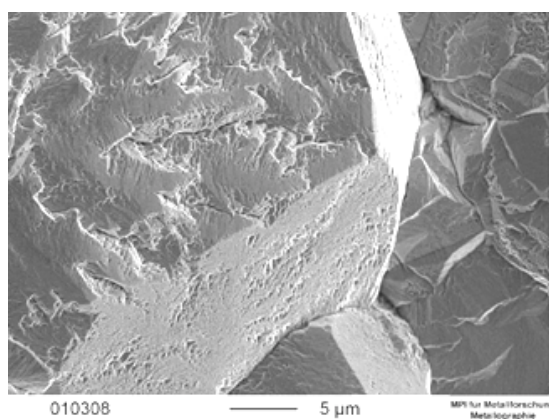


Fig. 9. Surface microstructure (x3000) at $T=50^{\circ}\text{C}$ with stirring: VDG 40ml/l.

CONCLUSIONS

1. It has been observed that the increase of the concentration of the "Velour"-forming additive VDG in a sulphate electrolyte for copper plating changes non-monotonously the grain size of the coatings.
2. The increase of the VDG concentration without stirring of the electrolyte increases the grain size. Such behaviour with stirring is observed only at small concentrations of glycerol.
3. Increase of the electrolyte temperature results in the change of the crystal shape (transformation from spherical to faceted structure due to the mechanism of layered growth).
4. Stirring of the electrolyte at high temperatures practically does not change the shape and size of crystallites.
5. Increase of the VDG additive concentration results in the inhibition process of electrocrystallization owing to interlock of active centres of the surface during adsorption of copper complexes.
6. In our opinion, non-monotonous influential character of the concentration of the additive VDG on the parameters of electrochemical process, is due to the formation of copper complexes of different structure.

7. The supplementary finishing (colouring and vacuum deposition) of designed coatings does not hide but even strengthens the decorative effect of a velvety surface. Articles with a velvety surface after colouring with "gold" and "old bronze" imitation looked most effective.
8. The degree of surface roughness varies according to electrolytic condition (current density and temperature). The designed compositions allow precipitates of decorative deposits with a given surface morphology: from velvet up to fractal-shaped.

REFERENCES

- [1] Kudriavtsev N.T., "Electroplating" (in Russian), Chemistry Publishers, (Moscow) 1979
- [2] Lainer V.I., "Electroplating of metals" (in Russian), Metallurgia Publishers, (Moscow) 1974
- [3] Valentelis L., Grinčevichene L., Protection of metals, 35 (1999) 255
- [4] Gribkova O., Kazakevich A., Straumal B. Protective and decorative copper and nickel coatings "velour", "velvet", "sateen". Eurocorr 2000, Sept. 10-14, London.
- [5] Klyuchkov B., Electroplat. Surf. Treat. 1 (1992) 18
- [6] Gribkova O.V., Kazakevich A.V., Kabankova M.L., Sidorova E.A., Startsev D.Y. Microrough copper and nickel coatings. Abstr. International conference Electrochemistry and surface technology, June 4-8, 2001, Moscow, Russia.
- [6] Metzger W., Newman D.R., Galvanotechnik 63 (1962) 297
- [7] Pat. USA 3152973
- [8] Pat. USA 3865702.
- [9] Hughes R., Rowe M. "The Colouring, Bronzing, and Patination of Metals: A Manual for the Fine Metalworker and Sculptor: Cast Bronze, Cast Brass, Copper and Copper-Plat", Wiley, (N. Y.) 1991
- [10] Vershinin N., Filonov K., Straumal B., Gust W., Surf. Coat. Technol. 125 (2000) 229
- [11] Vetter K.J. "Elektrochemische kinetik ", Springer-Verlag, (Berlin) 1961