
The impact of current reversal in the presence of inhibitory additives on the thermomechanical stability of galvanic copper coatings

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Abstract

The impact of current reversal on the morphology, physical and mechanical properties and thermomechanical stability of galvanic copper coatings in through holes of printed circuit boards is studied in this work. Copper was electrodeposited from a sulfate electrolyte with a complex additive based on polyalkylene glycols, nitrogen-containing heterocyclic compounds, and organic sulfur-containing compounds. At a constant current in the presence of the inhibitory additive, the surface microrelief is formed by an accumulation of smooth hemispherical micro protrusions. The observed "micro-waviness" of the surface may be associated with the adsorption of the additive components on the surface of the growing deposit and their inhibitory impact on the course of copper electrodeposition. The low plasticity of such coatings may be caused by internal stresses, including those due to inclusion of components of the complex additive into the deposit on the electrode. Current reversal during electrodeposition significantly changes the copper morphology in comparison with that in the DC mode by favoring a decrease in the adsorption of components of the inhibitory additive. However, at the reversal frequency of ~100 Hz, rough, hard and brittle copper coatings that are unstable to thermomechanical loads are obtained. Annealing in order to relieve internal stresses did not improve the plastic properties of copper. Thus, the fragility of coatings in reversal mode at a frequency of ~100 Hz can be associated with a high density of microstructure defects. The use of current reversal with a frequency of ~50 Hz makes it possible to significantly reduce the roughness of the copper layer. The plasticity of electrodeposited copper is improved significantly, which ensures the thermomechanical stability of copper coatings in through holes with various diameters. Both in direct current mode and in current reversal modes, the sizes of coherent scattering regions *D* are approximately the same. Apparently, the plasticity in the case of current reversal with a frequency of ~50 Hz and the fragility of samples obtained under direct current conditions and with current reversal at ~100 Hz are associated not so much with the size of crystallites as with differences in the stress state of electrodeposited copper due to changes in the adsorption of organic components of the additive.

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Introduction

The electrodeposition of copper from sulfuric acid electrolytes is widely used, in particular, for the formation of copper conductors in printed circuit boards [1–7]. In this case, uniform micro- and macro-distribution of copper both on the surface and in through holes has to be ensured [1, 8–10]. The requirements for uniformity and physical and mechanical properties of galvanic copper coatings in through holes of printed circuit boards are determined according to their purpose and scope of application, depending on the required probability level of trouble-free operation [11]. The uniformity of copper distribution on the surface and inside through holes can be provided by means of electrolyte stirring, including that by reciprocating motion of the cathode in the plane perpendicular to that of the anodes [12], the use of electrolytes with special inhibitory additives [3–5], and by electrodeposition in reversal modes [3, 6, 7]. Many publications [13–17] consider the prospects of using current reversal to improve the metal distribution. It is indicated [18] that increasing the frequency of current reversal with rectangular current pulses in the range from 1 to 50 Hz makes it possible to increase the Haring-Blum electrolyte throwing power and reduce the roughness of copper. It is reported that high-frequency current reversal modes in the range of ~50–100 Hz favor an improvement of the uniformity of electrodeposited copper interlayer electrical contacts in through holes of printed circuit boards compared to the DC mode, all other things being equal [3, 6, 7], and as the frequency increases to ~100 Hz, the grain size decreases [10].

The electrodeposition in reversal mode makes it possible to reduce the inclusion of inhibitory additives and products of their conversion into the electrode deposit, thereby reducing the consumption of additives and improving the plasticity of the resulting electroplating coatings [14–16]. Meanwhile, the uninterrupted operation of electronic devices based thereon largely depends on the plasticity of electrodeposited copper and, accordingly, on the stability of electrical contacts between the layers of printed circuit boards to thermomechanical loads [2, 19]. The occurrence of thermomechanical loads is caused by the dimensional instability of the board dielectric base in heating-cooling cycles as electronic components are soldered [2, 20] and in the course of subsequent operation [19]. Plastic uniform copper coatings make it possible to avoid cracks and annular breaks of metallization in holes under thermomechanical loads. The plasticity of coatings is significantly affected by the stressed state and grain structure of the resulting coatings [21].

As shown previously [22], the main cause that internal stresses are formed lies in point defects, namely, vacancies and interstitial atoms. In turn, the microhardness and plasticity of galvanic copper coatings correlates with the magnitudes of internal stress. Thus, the increase in the hardness of galvanic copper coatings was explained [23] by the grain atomization and high density of the defective microstructure resulting from the use of additives. It was found [24] that varying the parameters of current pulses leads to a significant change in the elasticity modulus and in the hardness of galvanic copper determined by the nanoindentation method, as well as a change in the predominant crystallographic orientation of grains. However, the regularities of the effect of current reversal during electrodeposition on the structure, internal stresses, and physical and mechanical properties of the resulting coatings remain insufficiently clear.

The impact of current reversal on the morphology, physico-mechanical properties and thermomechanical stability of galvanic copper coatings obtained from sulfuric acid electrolytes in the presence of inhibitory additives is studied in this paper.

Experimental

The coatings were obtained from an electrolyte containing 60 g/l $CuSO_4 \cdot 5H_2O$ (“pure” grade), 230 g/l H_2SO_4 (“chemically pure” grade), 0.12 g/l NaCl (“chemically pure” grade), and 0.5 g/l $FeSO_4 \cdot 7H_2O$ (“chemically pure” grade). In order to improve the uniformity of coatings, 22 g/l of a complex additive containing leveling agents based on polyalkylene glycols and heterocyclic nitrogen-containing compounds with 5–6 carbon atoms in the ring, as well as gloss-forming organic sulfur-containing compounds (thiols, disulfides, sulfonic acids), were added to the electrolyte. According to our data [8, 25], a sufficiently uniform macro- and microdistribution in through holes is provided in the electrolyte with this composition.

Copper electrodeposition was carried out using an IPC-Pro MF potentiostat (Research and Production Company “Volta”, Russia) at a solution temperature of 23±1°C. The coatings were obtained at a cathodic current density of 1 A/dm^2 and in two reversal modes with frequencies of ~50 and ~100 Hz. The use of these current reversal modes in combination with the complex additive made it possible to obtain a copper coating with a thickness of at least 80% of the external thickness in the middle of through holes [25]. At the current reversal frequency of ~50 Hz, the forward and reverse pulse time ratio $t_c : t_a$ was 20 ms : 1 ms, at amplitudes of $i_c = 1$ and $i_a = 3$ A/dm^2, respectively. In reversal mode with a frequency of ~100 Hz, the $t_c : t_a$ ratio was 9 ms : 1 ms at $i_c = 1$ and $i_a = 1.3$ A/dm^2. The nature and parameters of the current pulses were monitored using a C1-112M oscilloscope (CJSC ProfKip, Russian Federation).

To study the morphology and physico-mechanical properties of copper coatings, samples of copper foil on the surface of a pre-anodized titanium plate were taken. The estimated foil thickness and that of coatings in the through holes was 38–40 μm. This value was chosen in view of the fact that in the diffusion-inaccessible areas in the depth of the hole, the copper layer thickness should be at least ~30 μm (~80% of the estimated 38–40 μm). Titanium was anodized in 10% H_2SO_4 solution, and a plate of M1 copper was used as the cathode. The cathode was degreased with Viennese lime before electrolysis and activated in 30% HNO_3. The electrical contact between the titanium surface and the current supply line was achieved by applying a chemical nickel coating ~10 μm thick and then a galvanic copper layer ~25–30 μm thick on the upper part of the plate, to which the current supply line was then soldered. Chemical nickel plating was carried out according to a reported procedure [26]. After degreasing, the titanium plate polished to a roughness of R_a~1.8 μm was activated for 10 min in a solution containing 250 g/l of sulfuric acid and 5 g/l of potassium hydrogen difluoride. Then the sample was rinsed with running water and the chemical nickel coating was applied at T=70°C for 1 hour according to [26]. A galvanic copper coating providing electrical contact between the titanium surface and the current supply line was applied from the copper plating electrolyte used in this work, at a current density of 1 A/dm^2.

The morphology of the surface copper foil samples taken from the titanium plate surface was studied using a JEOL 1610 (JEOL, Japan) scanning electron microscope and a LEXT OLS4100 (Olympus Europa Holding GmbH, Japan) confocal laser microscope. The roughness parameters were calculated in the ROUGHNESS software module of the LEXT OLS4100 microscope in compliance with GOST R ISO 4287-2014. The roughness parameters of the titanium substrate R_a and R_z were 0.13 and 1.31 μm, respectively. The Vickers microhardness of copper coatings was measured using a PMT-3M (JSC LOMO, Russian Federation) microhardness meter in compliance with GOST R ISO 6507-1-2007.

The tensile testing of copper foil samples ~40 mm long, ~35–40 μm thick and ~10 mm wide taken from the titanium surface was carried out in compliance with GOST 9.317-2010 using a SHIMADZU AGS-X tensile-testing machine under 500 N load at a strain rate of 0.5 mm/min.

Diffractograms of copper foil samples in reflected beam were obtained using an ARL EQUINOX 100 (Thermo Scientific, USA) X-ray diffractometer. The wavelength of characteristic Cu copper radiation, Cu K_α, was 0.154 nm. The JCPDS database was used to identify the phase composition [27]. The calculation of the average effective size in the coherent scattering regions (D) was carried out according to Ref. [28].

The thermomechanical stability of galvanic copper coatings was studied on film-clad dielectric samples 1.56 mm thick with through holes 0.2, 0.4, 0.8, and 1.0 mm in diameter. Before electrodeposition, a copper layer ~1–2 μm thick was chemically applied (Perfecto 670, JKem) to the surface of the samples. The solution was stirred by swinging the cathode rod in horizontal direction with a frequency of 30 min^{-1} and an amplitude of 2.5 cm.

Thermomechanical stability tests of printed circuit board samples with through holes were carried out by immersing them in molten POS-61 solder in compliance with GOST IEK 61189-3-2013 at 260°C. Defects in galvanic copper coatings inside the through holes after reliability tests in compliance with GOST R 55693-2013 were determined from micrographs of transverse sections obtained using a LEXT OLS4100 confocal laser microscope.

Results and Discussion

To study the impact of current reversal on the morphology and physico-mechanical properties of electrodeposited copper, copper foil samples were taken from the titanium plate surface. Upon electrodeposition under DC conditions, the copper surface looks like a combination of smooth and shiny rounded irregularities, as seen in the micrograph

(Figure 1a). In contrast, when the current is reversed, rough samples of copper foil are obtained (Figure 1b,c). Three-dimensional images confirm the 3D nature of the "micro-waviness" of hemispherical micro protrusions 20–30 μm wide and up to 20 μm high in DC mode (Figure 2a). In the case of current reversal, the foil surface microrelief in Figure 2b,c shows signs of the so-called crystal roughness with an irregularity width in the range of micrometers, according to Ref. [22], formed due to different growth rates of facets with different indices on the polycrystalline surface of the growing deposit.

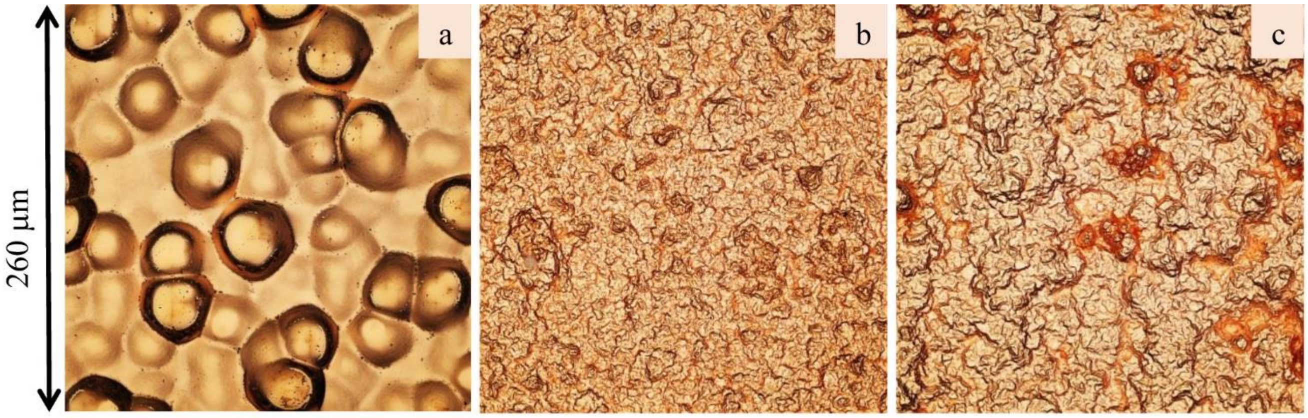

Figure 1. Micrographs of copper foil obtained in DC mode (a), and those obtained in current reversal modes with a frequency of ~50 Hz (b) and ~100 Hz (c). The microphotograph size is 260×260 μm.

According to Ref. [9], smoothing of submicron irregularities in DC mode in the electrolyte with the complex additive used in this work is accompanied by an increase in cathodic polarization by more than 100 mV and may be associated with the inhibitory effect of the additive on the copper electrodeposition process. According to [29], the formation of three-dimensional "microwaves" similar to those observed in Figure 2a depends on the differences in the local intensity of the additive supply to the surface and is largely determined by the leveling power of the electrolyte. Indeed, the positive value of the leveling power in the presence of the complex additive used was confirmed in [8].

The differences in the morphology of various foil samples, depending on the electrodeposition mode, were revealed more distinctly using a scanning electron microscope. It can be seen in Figure 3 that under DC conditions, the deposit surface is a set of rounded smooth partially overlapping segments. According to [22], this morphological type of deposit corresponds to the so-called "somatoid structure" and is formed upon electrodeposition under conditions of strong inhibition at overvoltages of hundreds of mV. At larger magnification, it is difficult to identify any details of the crystal structure on the surface (Figure 3b). However, it may be noted that the size of individual crystallites is apparently clearly less than 1 μm. For samples obtained under current reversal, the crystalline type of deposit growth is observed (Figure 3c–f). Copper electrodeposited from sulfuric acid electrolytes without surfactants is characterized by a pyramidal morphological type of deposit growth [22]. The main role in the emergence of pyramidal structures belongs to groups of spiral dislocations, although twinning processes may not be ruled out [22].

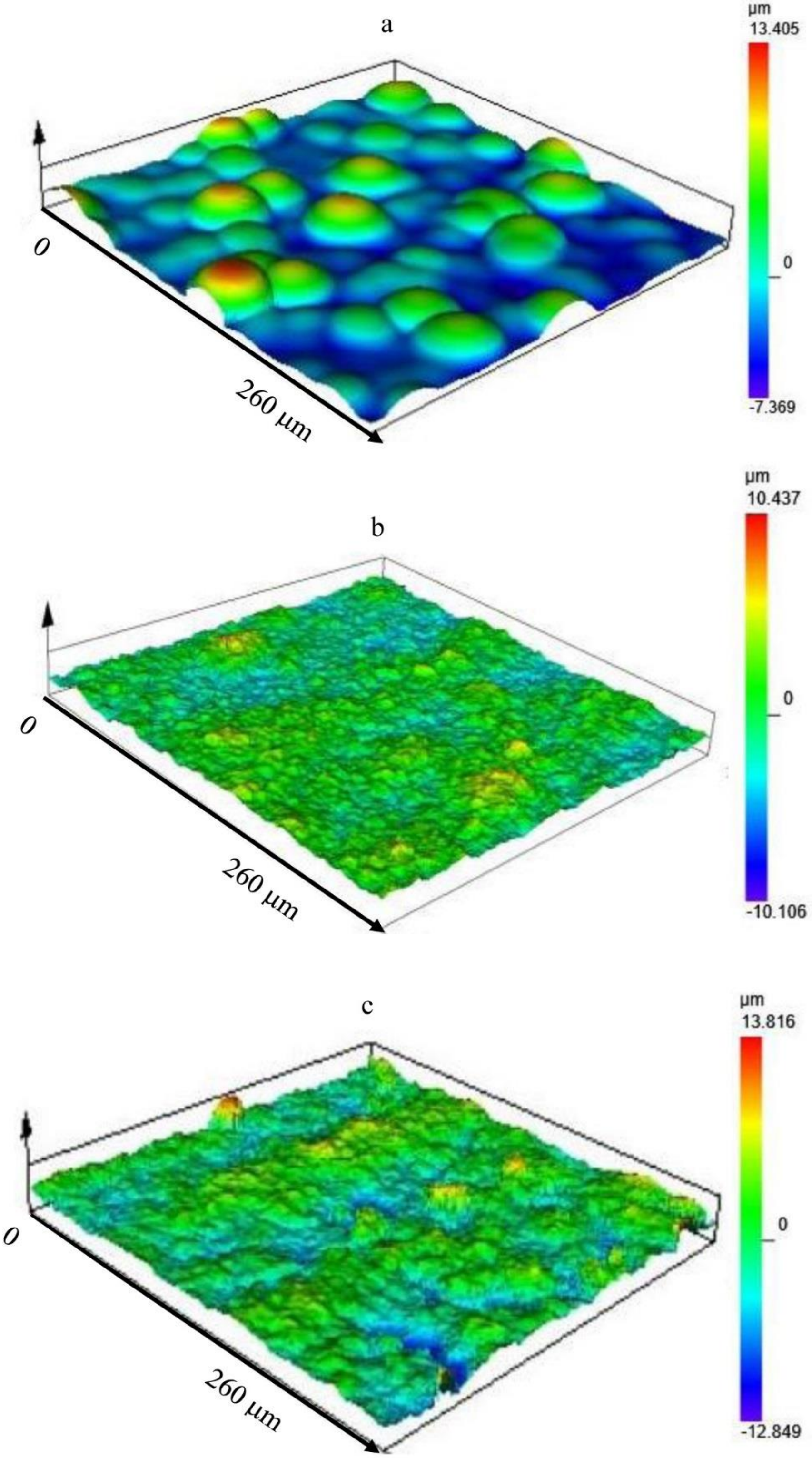

Figure 2. Microrelief of the foil surface obtained in DC mode (a) and in reversal modes at a frequency of ~50 Hz (b) and ~100 Hz (c).

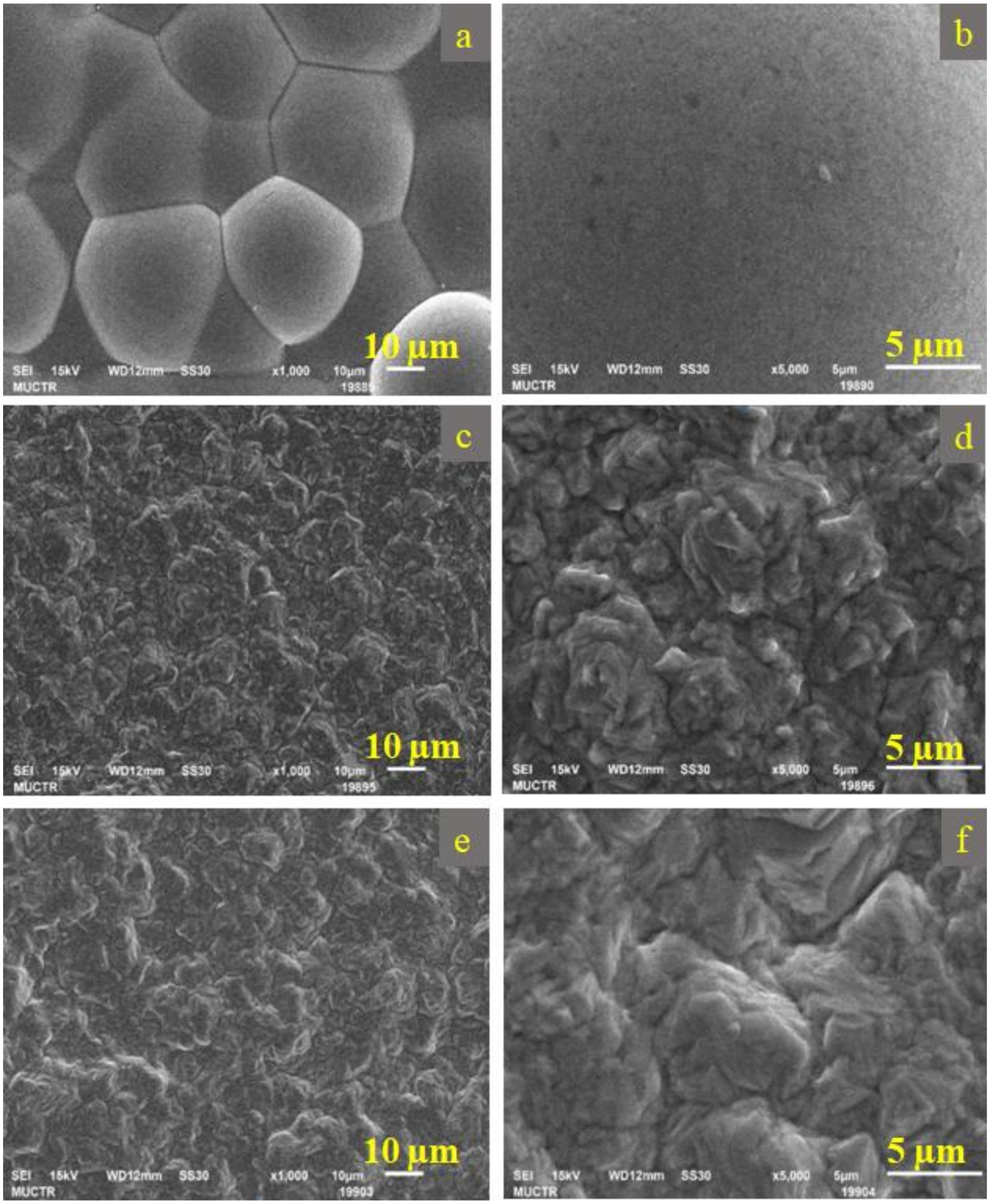

Figure 3. Electronic micrographs of copper foil obtained in DC mode (a and b) and in reversal modes at a frequency of ~50 Hz (c and d) and ~100 Hz (e and f).

However, in our case, since surfactants are present in the electrolyte as part of the complex additive, the deposit microrelief in the case of both reversal modes is represented by grain agglomerates with a distorted crystal structure. The manifestation of the crystal structure under reversal may indicate a weaker adsorption of the organic components of the electrolyte compared to the DC mode [22]. It proved difficult to identify the size of individual crystallites in agglomerates from the micrographs.

The morphological features in the formation of the copper crystal structure in the presence of inhibitory additives under DC conditions and in reversal modes are largely consistent with the physico-mechanical properties of copper foil samples. The samples obtained in DC mode and in reversal modes show low plasticity: the relative elongation δ does not exceed 4% (Table 1).

Table 1. Physical and mechanical properties of galvanic copper coatings.

Sample No.	Deposition mode	Annealing	R_a, μm	R_z, μm	δ, %	σ_u, MPa	*HV*, hPa
1	Direct current	–	0.9	16	3	230.5	0.72
		+			3	354.9	–
2	~50 Hz	–	1.0	8.8	4	293.8	0.83
		+			10	213.8	–
3	~100 Hz	–	2.8	23.3	3	153.9	1.22
		+			4	171.6	–

The value of δ no less than 6% was taken as a criterion of plasticity, since, according to the reported data [19], at a lower relative elongation of the copper coating ~30–35 μm thick in a through hole, fatigue failures of interlayer joints in multilayer printed circuit boards occur during operation under temperature variation conditions. The low plasticity of samples 1–3 may be associated with generation of internal stresses during the formation of the galvanic copper coating. Indeed, copper precipitates from sulfate electrolytes can have internal stress up to 200 MPa [30]. For this reason, the tensile tests were repeated after low-temperature annealing at 100°C for 1 hour to relieve internal stresses. However, the relative elongation value increases after annealing only in the case of the reversal mode at a frequency of ~50 Hz: from ~4% to ~10%. An increase in the plasticity of the copper coating is accompanied by a decrease in ultimate strength σ_u from ~290 to ~210 MPa. The small δ value of electrodeposited copper obtained with current reversal at a frequency of ~100 Hz and in DC mode may be associated with a significant height difference in the microrelief. In fact, in the case of current reversal at a frequency of ~100 Hz, the parameter of the mean unevenness height R_a assumes the largest value. The greatest irregularity height R_z of samples 1 and 3 according to Table 1 is about 20 μm, which correlates with their 3D images (Figure 2a,b). At the average thickness of the studied coatings being ~35–40 μm, the height difference up to 20 μm does not favor an improvement of plastic characteristics, since copper films 20 μm thick or thinner fail to withstand tensile loads [2]. For this reason, sections of galvanic copper coatings in the through holes of printed circuit boards less than 20 μm thick are qualified as "voids", and their number is regulated by GOST 55693-2013. At the same time, the samples with the smallest roughness obtained under reversal at a frequency of ~50 Hz are characterized by the highest δ values.

Based on the data obtained, it can be assumed that the formation of "micro-waviness" under DC conditions may be associated with the adsorption of components of the additive on the surface of the growing deposit and their inhibitory effect on the copper electrodeposition. The low plasticity of such coatings may be due to internal stresses, including those due to the inclusion of components of a complex additive in the electrode deposit. The adverse effect of a significant height difference in the microrelief on the relative elongation value may not be ruled out, either. The appearance of crystalline roughness upon current reversal apparently occurs due to a decrease in the adsorption of organic compounds contained in the additive. However, in the case of reversal with a frequency of ~100 Hz, brittle coatings are formed, moreover, the destruction of these samples occurs before the plastic deformations zone is reached. This may be due to the high concentration of defects in electrodeposited copper upon high-frequency current reversal, which is indirectly confirmed by the highest Vickers microhardness up to ~1.2 HPa (Table 1). The plasticity of copper obtained upon reversal with the frequency of ~50 Hz may be due to the removal of internal stresses as a result of annealing, as well as to the formation of a finer-grained structure during electrodeposition. Since the size of crystallites was difficult to determine by scanning electron microscopy, the X-ray diffraction method was used for this purpose later. According to the diffractograms of copper foil samples, one can see that current reversal does not significantly affect the predominant crystallographic orientation of the polycrystalline surface (Figure 4). The average size of coherent scattering regions D, which is less than 1 μm (~40 nm), practically does not change either, which correlates with the data of scanning electron microscopy. Apparently, the plasticity in the case of current reversal with a frequency of ~50 Hz and the fragility of samples obtained under direct current conditions and reversal at ~100 Hz are associated not so much with the size of the crystallites as with differences in the stressed state of electrodeposited copper due to changes in the adsorption of organic components of the additive.

When evaluating the plastic properties of electrodeposited copper, it should be taken into account that the thermal coefficient of linear expansion of copper does not exceed $\sim 18 \cdot 10^{-6}\ \mathrm{K}^{-1}$ and practically does not change on heating, while it reaches $\sim 260 \cdot 10^{-6}\ \mathrm{K}^{-1}$ in the case of uncured dielectric FR-4, and for the FR-4/copper coating system, even after thermal setting, it is $\sim 120 \cdot 10^{-6}\ \mathrm{K}^{-1}$ [2, 20]. As a result, in the course of soldering of electronic components, a significant increase in the thickness of FR-4 fiberglass occurs in the direction of through holes of a printed circuit board, and thus thermomechanical loads occur that lead to cracks in the copper coating, and accordingly, to failures of interlayer electrical contacts [2, 19]. Therefore, in this work we evaluated the effect of current reversal on the thermomechanical stability of galvanic copper coatings in through holes by thermal shock in molten solder, which simulates the soldering of electronic components.

In the absence of an annealing stage, the samples obtained in all electrodeposition modes failed to pass thermomechanical stability tests. In the through holes with all diameters, in the case of DC mode, numerous cracks were found in the microphotographs of transverse sections. They are present both inside the holes and at the entrance edge, where, in addition to tensile deformations, copper coatings experience bending deformations [2]. Upon electrodeposition in the current reversal mode at a frequency of ~50 Hz, cracks were also observed in holes with the studied diameters from 0.2 to 1.0 mm. In the samples obtained with current reversal at a frequency of ~100 Hz, rough breaks of copper coatings at the mouth of the holes were observed. The results obtained correlate with the unsatisfactory plasticity of the non-annealed galvanic copper and may be related to the stress state of the coatings.

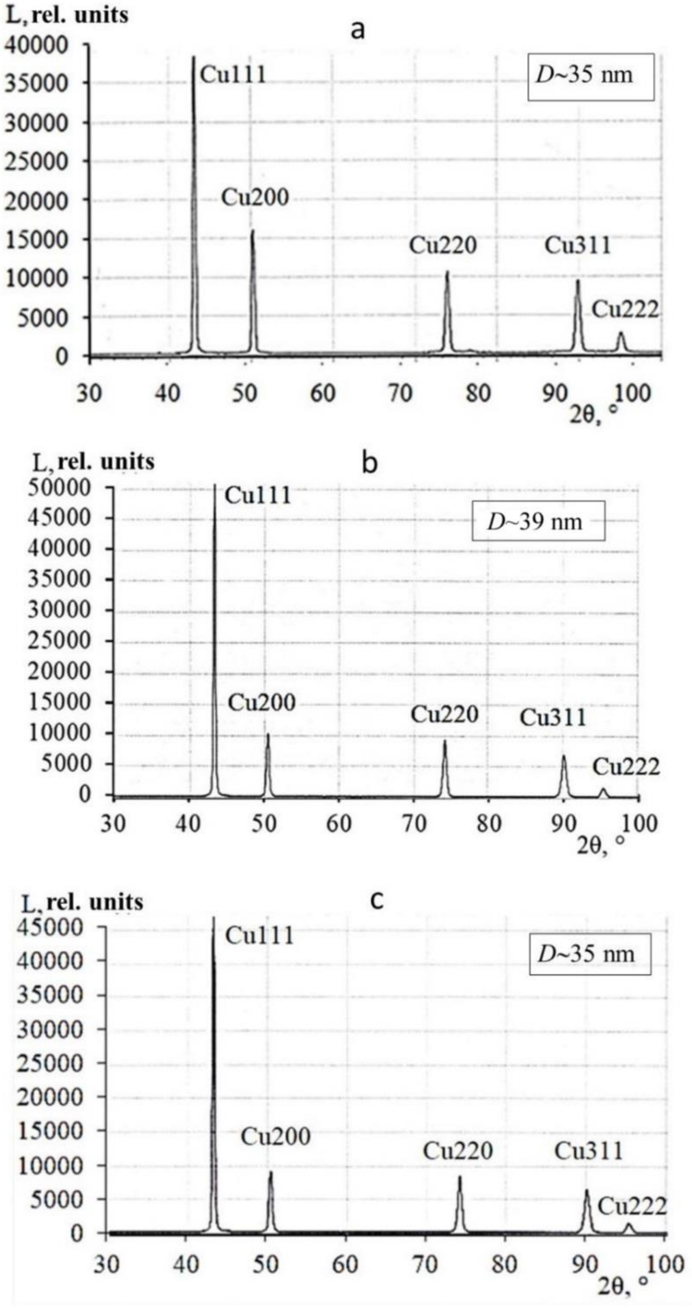

Figure 4. Diffractograms of copper foil samples obtained in DC mode (a) and in reversal modes at a frequency of ~50 Hz (b) and ~100 Hz (c). The *D* value corresponds to the coherent scattering region size.

Electrodeposition in reversal mode at a frequency of ~50 Hz makes it possible to obtain uniform coatings with low roughness resistant to thermomechanical load (Figure 5b), since there are no cracks after a thermal shock in holes of all diameters from 0.2 to 1.0 mm.

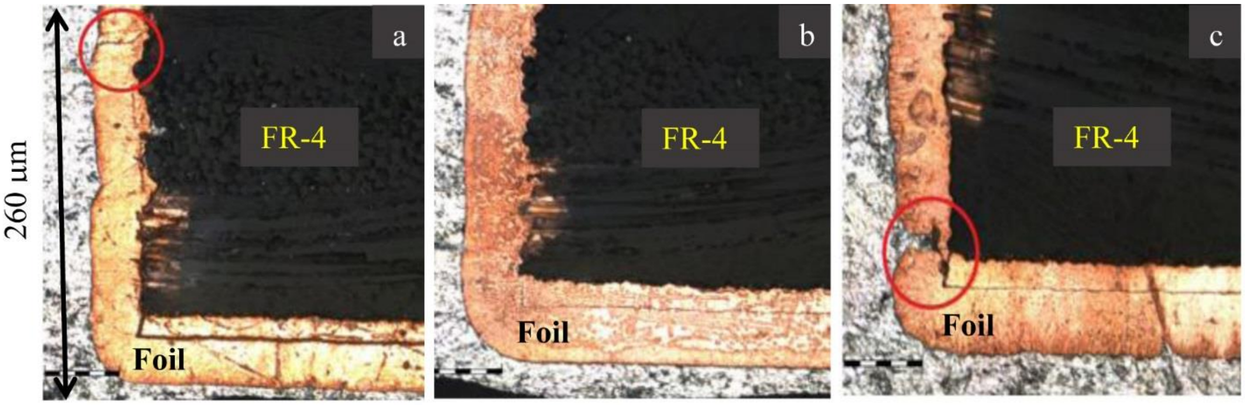

Figure 5. Micrographs of through holes in samples after thermal shock: a – in DC mode (diameter 0.8 mm); b – in reversal mode at a frequency of ~50 Hz (diameter 0.4 mm); c – in reversal mode at a frequency of ~100 Hz (diameter 0.4 mm). Annealing was carried out for 2 hours at 120°C.

Conclusion

In DC mode in the presence of a complex additive, conditions for electrical deposition of a copper coating under strong inhibition conditions, which is accompanied by a small relative elongation, are created. Current reversal during electrodeposition significantly changes the morphology of copper in comparison with the DC mode, favoring a decrease in the adsorption of inhibitory additive components. However, at a reversal frequency of ~100 Hz, rough, hard and brittle copper coatings are obtained that are unstable to thermomechanical loads. Annealing in order to relieve internal stresses fails to improve the plastic properties of copper. Thus, the fragility of coatings in reversal mode at a frequency of ~100 Hz may be associated with a high concentration of microstructure defects.

The use of current reversal at a frequency of ~50 Hz makes it possible to significantly reduce the copper layer roughness. The plasticity of electrodeposited copper is greatly improved, which provides thermomechanical stability of copper coatings in through holes with various diameters.

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