JOURNAL OF APPLIED ELECTROCHEMISTRY **15** (1985) 879–886

Recovery and recrystallization of electrodeposited bright copper coatings at room temperature. I. Microhardness in relation to coating structure

D. S. STOYCHEV, I. V. TOMOV, I. B. VITANOVA

Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

Received 5 March 1984; revised 3 October 1984

The electrolyte composition effect on the microhardness of bright copper coatings electrodeposited from sulphuric acid electrolytes was established. It is shown that the sulphuric acid content and the type of brightener agent strongly influence the rate of decrease of microhardness of deposited coatings with time. The systematic quantitative and qualitative investigations performed *in situ* determined the microhardness changes on the one hand, and the change in microdeformations, dislocation defects, crystallites size and texture of copper coatings on the other hand, thus demonstrating unambiguously the correlation betweeen them. The decrease in copper coating microhardness is explained by the occurrence of recovery and recrystallization processes at room temperature.

1. Introduction

It is known that the physicomechanical properties of metals are a function of their crystal structure. This also holds for the interconnection between microhardness and structure of galvanic coatings. A number of studies have shown the influence of the preparation conditions of such coatings on their physicomechanical properties. Thus it has been unambiguously established [1–8] that copper coatings which are fine-grained, have large numbers of microdeformations and a more definitely oriented texture have higher microhardness.

It has also been shown that many of the properties of galvanic copper coatings [9], including microhardness [10, 11], undergo substantial changes within a relatively long period of time (from several days to several months) after preparation. This process of 'ageing' has been explained by the partial decrease of packing defects and crystal lattice deformations (generated by high deposition overpotential, adsorption and incorporation of different surfactants) and the increase in lattice perfection. In fact, for all the investigations cited, indirect arguments have been forwarded to explain the change in galvanic coating properties (including microhardness) during the period following electrolysis.

Since microhardness and its decrease after obtaining copper coatings with enhanced microhardness are especially important for some specific areas of application, it is the aim of the present study to perform a systematic analysis, with the help of suitable X-ray structural methods, of the structure defining parameters, i.e. size of coherent diffraction regions (D_{111}), density of dislocations (ϱ), probability of the appearance of twin defects ($\bar{\beta}$), microdeformations ($\Delta d/d_{111}$) and texture, as well as their connection with the change of microhardness with time.

2. Sample preparation

The samples to be studied were cut from a foil deposited on a cylindrical, copper-plated steel cathode (with a diameter of 50 mm and cylinder length 120 mm) in a 1.3-litre bath with horizontally placed anodes (a commercial bath of a scale 1:1000 was reproduced). The cylinder was rotated at a rate of 60 rpm. Before each plating of the bright copper coating with enhanced microhardness, the cathode surface was polished

0021–891X/85 $03.00 + .12

mechanically, degreased and passivated so that the plated coating could be removed easily. The cathode current density was $12\,\mathrm{A\,dm^{-2}}$ and the plated copper coating thickness was $140 \pm 2\,\mu\mathrm{m}$. The temperature was varied between 23 and 28° C. The coatings were obtained from the electrolyte proposed in [12] which contained: $CuSO_4 \cdot 5H_2O$, $220\,\mathrm{g\,l^{-1}}$; H_2SO_4, $30\,\mathrm{g\,l^{-1}}$; NaCl, $50\,\mathrm{mg\,l^{-1}}$; and THB-I and THB-II, $3\,\mathrm{ml\,l^{-1}}$.*

3. Determination of D_{111}, ϱ, $\bar{\beta}$ and $\Delta d/d_{111}$

For X-ray determination of crystallite size and microdeformation by the approximation method of Hall [13], it is necessary to use different reflection orders hkl from a family of crystallographic planes $\{hkl\}$. Thus the influence of anisotropy of the elasticity module E_{hkl} and packing defects can be eliminated.

The connection between the average effective crystallite size D_{hkl} and the microdeformations

$$\frac{\Delta d}{d_{111}} = \frac{\bar{\sigma}}{E_{hkl}} \tag{1}$$

in the same direction is given by the expression

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{D_{hkl}} + \left(\frac{2\bar{\sigma}}{E_{hkl}}\right)\left(\frac{\sin\theta_{hkl}}{\lambda}\right) \tag{2}$$

where $\bar{\sigma}$ is the Laue breadth of the stress distribution function, θ is the Bragg angle, λ is the wavelength, and β is the diffraction expansion arising from the small size of the crystallites and their microdeformations. The last term is calculated from the expansion (B) of the sample studied, which includes both the diffraction expansion and the expansion determined by the geometry of photographing (b):

$$\beta = [(\mathrm{B} - \mathrm{b})(\mathrm{B}^2 - \mathrm{b}^2)^{1/2}]^{1/2} \tag{3}$$

An estimation of the geometrical expansion, b, is obtained by a model sample of the same material annealed so that its crystallites have an average size of $1\,\mu\mathrm{m}$ and no microdeformations.

The diffraction lines 111 and 222 of the copper samples were measured. The investigation was performed with a Philips X-ray unit. $\mathrm{Co}K\beta$-radiation isolated by a curved crystal monochromator of LiF was used. The Laue width B was directly determined from the X-ray line profile.

The probability of packing twin defects was determined from the $\{111\}$ line profile asymmetry by the method of Cohen and Wagner [14]:

$$\Delta\mathrm{CG}(2\theta^0)_{111} = \bar{\beta}\,(11\,\mathrm{tg}\,\theta_{111}) \tag{4}$$

For this purpose the displacement of the centre of gravity, $\Delta\mathrm{CG}(2\theta^0)$ in relation to the line maximum, was calculated.

The dislocation density ϱ was determined by the method of Williamson and Smallman [15]

$$\varrho = \frac{3n}{D^2} \tag{5}$$

where $n = 1/3$.

4. Physicomechanical properties of plated copper coatings

The addition of brighter agents determined the plating of copper coatings with the following properties (average values are cited): brightness = 93% (measured in comparison to a silver mirror by a 'Dr Lange' unit); levelling = 88% (measured by a 'Perthen' profilograph-profilometer); microstresses = $+45\,\mathrm{kg\,cm^{-2}}$ (measured by a spiral contractometer type 'Brenner-Senderov'); microhardness (HV) = $240\,\mathrm{kg\ mm^{-2}}$ (measured by a Leitz microhardness meter at indentor loading of 100 g); wear resistance = $72\,\mathrm{mm^3}$ per 1000 cycles (the Taber factor of wearing was determined by a 'Taber' abraser, model 503 STANDARD by the losses in sample weight in mg per 1000 cycles of erasement).

It is interesting to note that the microhardness and wear resistance of matt copper coatings plated from the same electrolyte (without brightener agents) are correspondingly 90–100 kg $\mathrm{mm^{-2}}$ and $111\,\mathrm{mm^3}$ per 1000 cycles.

The fact that the copper coatings were obtained mirror smooth eliminated the need for any special preliminary treatment of the sample before measuring the microhardness. The latter was simultaneously measured on reference samples as well as on samples (35 × 35 mm) further investigated in a X-ray diffractometer and a texture goniometer.

---

* THB-I and THB-II are the trade names of industrial brightener agents. Bulgarian Patent No. 48537/18.07. 1980.

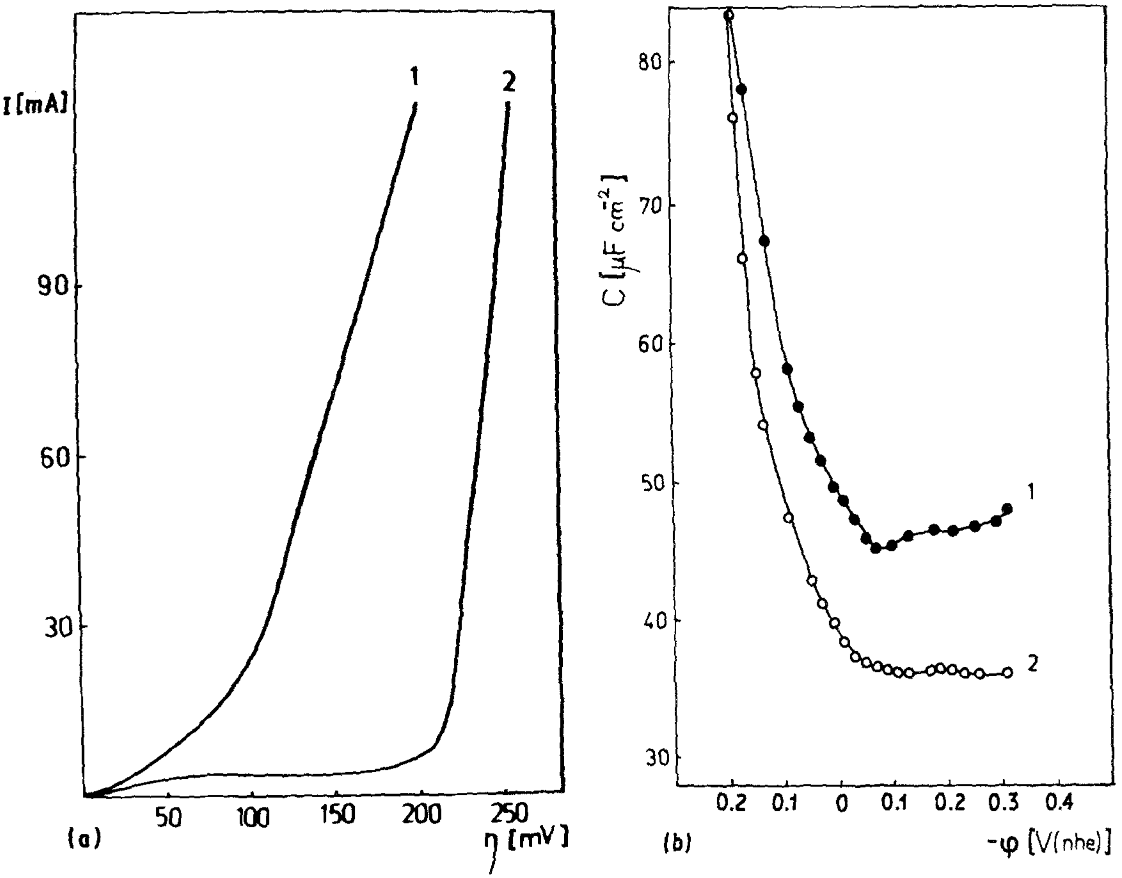

Fig. 1. (a) Potentiodynamic (current, I — overpotential, η) curves of the process of electrodeposition of copper coatings from: 1, basic electrolyte (220 g l^{-1} $CuSO_4 \cdot 5H_2O$ + 30 g l^{-1} H_2SO_4 + 50 mg l^{-1} NaCl); 2, basic electrolyte + 3 ml l^{-1} THB-I + 3 ml l^{-1} THB-II. (b) Double layer capacity, C, versus potential, φ, curves obtained on a copper electrode in: 1, supporting electrolyte of InH_2SO_4; 2, InH_2SO_4 + 3 ml l^{-1} THB-I + 3 ml l^{-1} THB-II.

5. Results and discussion

The increase by a factor of 2.5 in the microhardness of the copper coatings in the presence of brightener agents, as well as the abrupt improvement of the physicomechanical properties enumerated above, coincide with the results presented in Fig. 1. As can be seen in Fig. 1a, the addition of brightener agents strongly inhibits the electrode process as a consequence of the high adsorption of the agents (confirmed also by the substantially decreased capacity of the electric double layer found upon adding brightener agents, Fig. 1b) efficiently blocking [16, 17] a considerable part of the electrode surface (degree of filling $\bar{\theta}$ = 70%). The adsorption of these agents determines the decrease in size of the coherent diffraction area by more than one order of magnitude, as well as the increase in number of copper crystallite lattice defects (Tables 1 and 2).

The different rate of decrease in the bright copper coating microhardness after electrodeposition for the material investigated by us was of particular interest. Depending on the sulphuric acid content in the basic electrolyte as well as on the component ratio of the brightener agents, different rates of decrease in coating microhardness were observed. Fig. 2 illustrates this dependence as a function of copper-plating electrolyte sulphuric acid content. Fig. 3 shows the results for a constant sulphuric acid content, 30 g l^{-1}, and varying composition of THB-II.[†]

[†] (The composite agents of THB-II, i.e. THB_1-II and THB_6-II, differ only by the hydrocarbon chain length.)

Table 1. Change of the structure characteristics and microhardness of bright copper coatings plated from an electrolyte (containing THB$_1$-II) determining the rapid decrease of the microhardness with time. (The data given are obtained with Sample 162.)

Day after deposition	$D_{111\mathrm{ef}}$ (Å)	$\bar{\beta}$	$D_{111\,\mathrm{actual}}$ (Å)	$\Delta d/d_{111}$ ($\times 10^3$)	ϱ ($\times 10^{-11}$ cm^{-2})	*HV* ($kg\,mm^{-2}$)
1	2000	0.003	7000	3.79	6.26	234
2	2000	0.002	3500	3.62	5.78	230
3	2000	–	–	3.55	5.40	228
4	2000	–	–	2.37	4.95	210
5	1180	0.001	1400	2.09	1.94	191
6	–	–	–	–	1.94	180
7	1280	0.001	1500	0.77	0.26	176
8	–	–	–	–	–	158
9	–	–	–	–	–	145
10	–	–	–	–	–	134

The weight concentrations of THB$_1$-II and THB$_6$-II were identical. In both cases the concentration of copper sulphate was 220 g l^{-1} and the concentration of sodium chloride 50 mg l^{-1}.

The technological requirements of deposited copper platings do not allow microhardness under 170–180 kg mm^{-2} – the zone marked by a dotted line on Fig. 2. It is evident from the same figure that when THB$_6$-II is employed (sulphuric acid content 60–80 g l^{-1}, curves 3 and 4), the time interval in which the microhardness drops under the dotted line is 72 and 48 h respectively. At a sulphuric acid concentration of 40 g l^{-1} this period increases to about 140 h (curve 2), while at a concentration of 30 g l^{-1} this period is of the order of more than 500 h (curve 1).

When depositing coatings from a basic electrolyte containing 30 g l^{-1} sulphuric acid, the period of transition to under-optimal microhardness (Fig. 3) is about 160 h for variant THB$_1$-II and about 500 h for THB$_6$-II, depending on the

Table 2. Change of the structure characteristics and microhardness of bright copper coatings plated from an electrolyte (containing THB$_6$-II) determining the slow decrease of the microhardness with time. (The date given are obtained with Sample 163.)

Day after deposition	$D_{111\mathrm{ef}}$ (Å)	$\bar{\beta}$	$D_{111\,\mathrm{actual}}$ (Å)	$\Delta d/d_{111}$ ($\times 10^3$)	ϱ ($\times 10^{-11}$ cm^{-2})	*HV* ($kg\,mm^{-2}$)
5	2000	0.001	2600	3.26	2.98	226
6	2000	0.001	2600	3.18	2.83	234
7	2000	0.001	2600	3.04	2.59	230
8	1600	0.001	2000	2.53	1.75	227
9	1400	0.001	1680	2.40	1.61	224
13	950	0.001	970	1.69	0.801	223
14	1100	0.001	1180	1.58	0.699	221
15	1500	0.001	1830	1.52	0.648	210
16	1100	0.001	1180	1.15	0.370	202
17	1400	0.001	1680	1.08	0.326	193
19	1280	0.001	1500	0.87	0.212	177
20	1650	0.001	2050	0.70	–	168
25	–	–	–	–	–	146
26	–	–	–	–	–	140
27	–	–	–	–	–	137
28	–	–	–	–	–	137
29	–	–	–	–	–	137

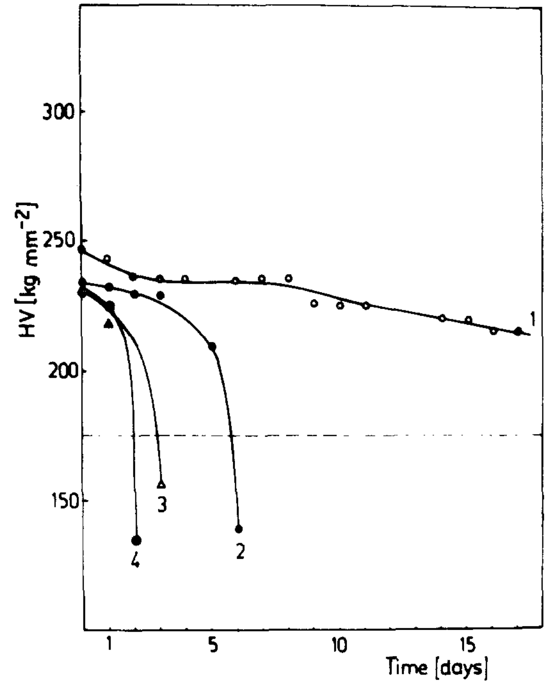

Fig. 2. Change of microhardness (HV) with time (days) of bright copper coatings obtained in the presence of $3\,\mathrm{ml\,l^{-1}}$ THB-I + $3\,\mathrm{ml\,l^{-1}}$ THB-II + $220\,\mathrm{g\,l^{-1}}$ $CuSO_4 \cdot 5H_2O$ + $50\,\mathrm{mg\,l^{-1}}$ NaCl and: 1, $30\,\mathrm{g\,l^{-1}}$ H_2SO_4; 2, $40\,\mathrm{g\,l^{-1}}$ H_2SO_4; 3, $60\,\mathrm{g\,l^{-1}}$ H_2SO_4; 4, $80\,\mathrm{g\,l^{-1}}$ H_2SO_4.

length of the polyether component hydrocarbon chain in the brightener composition. (Fig. 3 shows the curves of sample numbers 162 and 163 which are typical representatives of the samples exhibiting 'rapidly' with (THB_1-II) and 'slowly' (THB_6-II) dropping microhardness obtained by us.) The period of time necessary for obtaining constant, time unchanging microhardness of bright copper coatings ($\sim 135\,\mathrm{kg\,mm^{-2}}$) for both variants of THB-II is ~250 h for THB_1-II and ~650 h for THB_6-II.

According to literature data and concepts for materials similar to ours (electrodeposited copper and other metals) [6, 8–10, 18] the factors which determine this process are: high super-saturation, great energy excess of discharged particles during deposition of galvanic coatings as well as the presence of a great number of vacancies, dislocations and other lattice defects.

In our case (overpotential, $\eta \sim 250\,\mathrm{mV}$), the ratio between the rates of nucleation and growth changes substantially, giving preference to nucleation [19], which further favours strongly the formation of practically all kinds of growth defects. This assumption is confirmed by the results obtained by X-ray structural investigations (Tables 1 and 2). (According to our data and that in the literature, the crystallite size of copper coatings plated from basic electrolyte

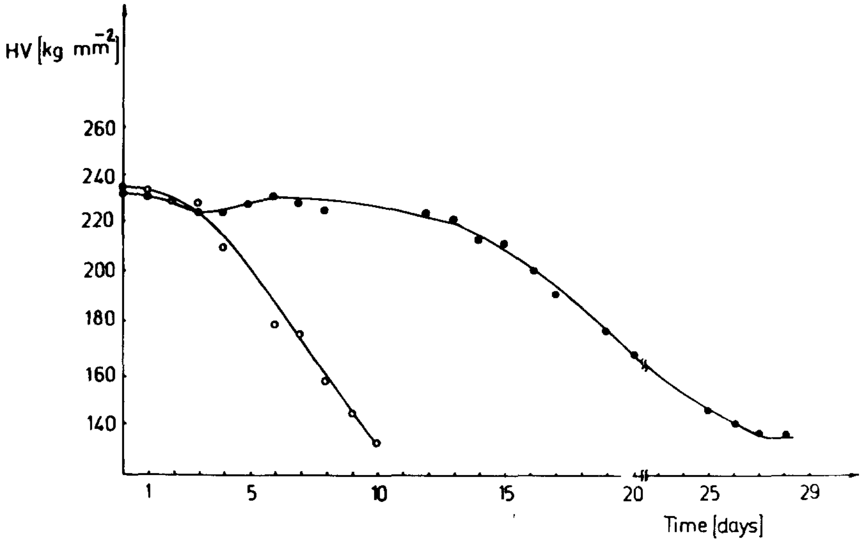

Fig. 3. Change of microhardness with time of bright copper coatings obtained from an electrolyte with composition $220\,\mathrm{g\,l^{-1}}$ $CuSO_4 \cdot 5H_2O$, $30\,\mathrm{g\,l^{-1}}$ H_2SO_4, $50\,\mathrm{mg\,l^{-1}}$ NaCl and: ○, $3\,\mathrm{ml\,l^{-1}}$ THB-I + $3\,\mathrm{ml\,l^{-1}}$ THB_1-II; ●, $3\,\mathrm{ml\,l^{-1}}$ THB-I + $3\,\mathrm{ml\,l^{-1}}$ THB_6-II.

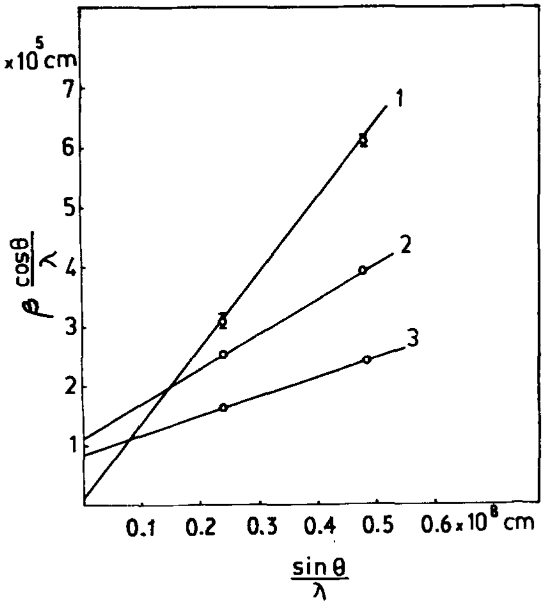

Fig. 4. Determination of the microdeformations $\Delta d/d_{111}$ and crystallite size D_{111} from the broadening of diffraction lines 111 and 222. The data refer to: 1, 6th day; 2, 13th day; 3, 19th day.

with no additives is $\simeq$ 1–30 μm; dislocation density $\varrho \simeq 10^8 - 10^9\,\text{cm}^{-2}$, and microdeformation $\Delta d/d_{111} \simeq 1/5 \times 10^{-2}$ [20]).

The separation of effective crystallite size $D_{111\text{ef}}$ and strain $\Delta d/d_{111}$ is made by plotting $\beta \cos \theta/\lambda$ against $\sin \theta/\lambda$ (Fig. 4). The slope of the graph is a measure of the strain, and the intercept on the $\beta \cos \theta/\lambda$ axis gives the reciprocal of the crystallite size. A tendency towards a decrease in the microdeformations and a change of crystallite size in copper coatings with time are evident.

The results obtained from the data treatment of the X-ray structural analysis (Tables 1 and 2) show that the crystallite size changes continuously during the period of considerable decrease in microhardness.

Wilson and Tomassen [21] have demonstrated that the microhardness of copper and other metals deteriorates to the same degree as their diffraction lines narrow. On the basis of this idea we measured the X-ray line 222 by employing Co$K\alpha$ radiation. The results are presented in Fig.

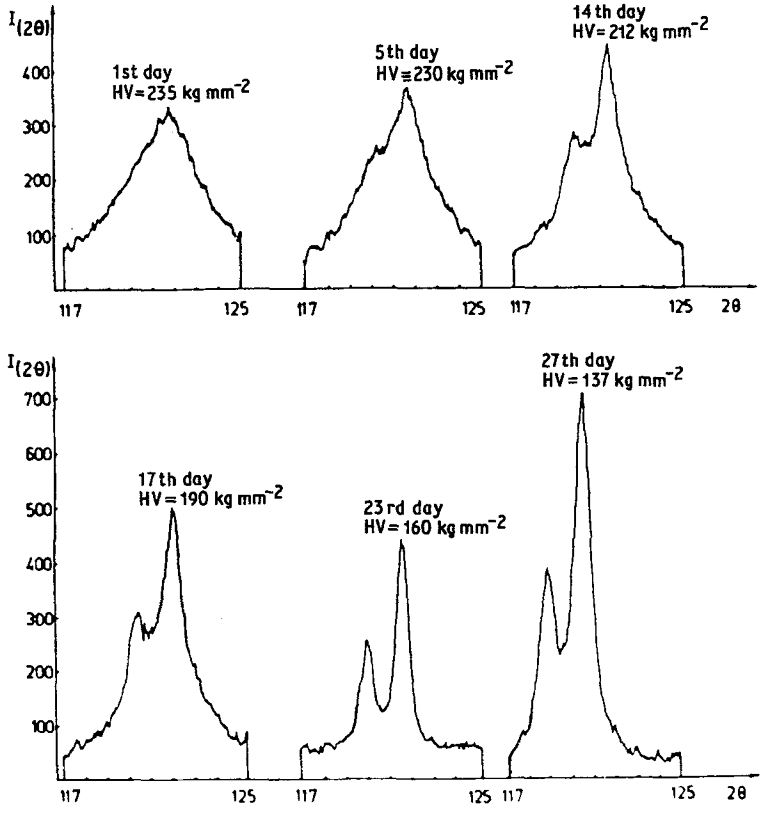

Fig. 5. Change in broadening of diffraction line 222 of a sample with slowly decreasing microhardness. The connection is shown between line broadening and the change in sample microhardness with time (after the 1st, 5th, 14th, 17th, 23rd and 27th day).

5 and show the relationship between microhardness and diffraction line broadening. A continuous change in the parameters discussed is evident.

Systematic studies of texture changes with time for the same samples are presented in the next paper [22]. In all cases a texture with main texture components ⟨311⟩, ⟨111⟩ and ⟨110⟩ was established immediately after plating. When their microhardness fell to ~ 140 kg mm^{-2} a texture with main components ⟨100⟩, ⟨110⟩ and ⟨111⟩ was found. A quantitative measure for the texture components ⟨*hkl*⟩ is their volume fractions M_{hkl}. Some indication of how M_{hkl} changes with time can be obtained from Fig. 6a, b. It is also evident from Fig. 6 that the change in microhardness with time is linked with a change in microdeformations (strain) and dislocation density.

6. Conclusion

It can be concluded on the basis of the above results that there exists a definite connection between the change in microhardness on the one hand, and the changes in crystallite size, texture, microdeformations and dislocations in copper coatings on the other hand. Moreover, it is established that these processes are exceptionally strongly influenced by plating conditions, particularly by the sulphuric acid content in the electrolyte and the organic compound structure of the brightener agents. The sulphuric acid concentration is probably of substantial importance for the form and quantity of the organic compounds encountered in the copper coating lattice to lead to considerable deformations there. This further determines the extent of the recovery and recrystallization processes, causing in turn a

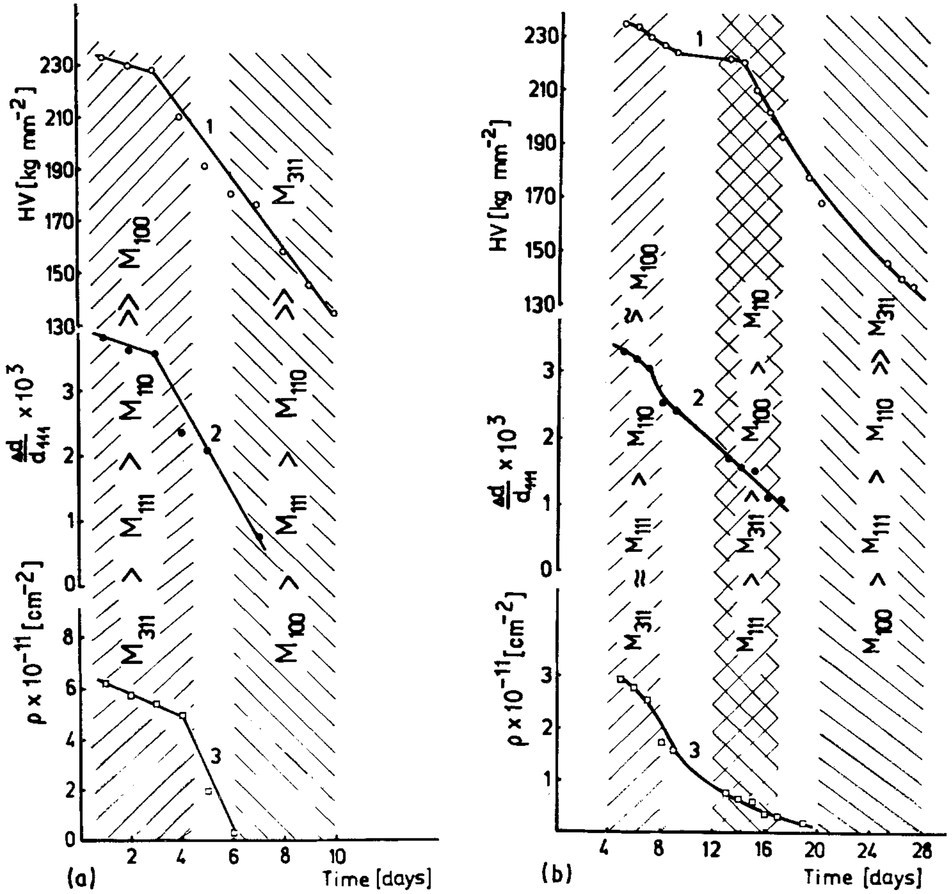

Fig. 6. The change in volume parts M_{hkl} of the texture components, microhardness (1), microdeformations (2), and dislocation density (3) vs time of copper coatings displaying a 'rapid' (a) and 'slow' (b) decrease in microhardness.

strong change in the microhardness of bright copper coatings within a definite period of time.

By comparing the quantitative and qualitative results registered *in situ* after studying the microdeformations, dislocation defects, crystallite sizes and the characteristic changes in the texture of copper coatings along with the change in microhardness, the correlation is unambiguously demonstrated. To further elucidate the connection between the physicomechanical properties and structure, in particular the link between microhardness and structure of bright copper coatings, it is necessary to investigate the processes occurring in copper coatings at room temperature, concentrating specifically on the processes of recrystallization.

References

[1] A. Sieverts and W. Wippelmann, *Z. anorg. Chem.* **91** (1915) 1.

[2] A. Butts and V. De Nora, *Trans. Electrochem. Soc.* **79** (1941) 22.

[3] N. P. Fedotiev and P. M. Viatcheslavov, *Trudi LTI im. Lensoveta,* **53** (1959) 9.

[4] N. P.Fedotiev, P. M. Viatchelslavov, V. I. Gribel and E. M. Zaleskaya, *J. Appl. Chem.* (*USSR*) **37** (1964) 691.

[5] K. Schmidt and K. I. Tihonov, *J. Appl. Chem.* (*USSR*) **44** (1971) 1896.

[6] V. M. Kozlov, *Fiz. Metal. i. Metalov.* **45** (1978) 1322.

[7] E. A. Mamontov, L. A. Kurbatova, J. N. Ojogina and T. A. Stepanova, *Electrochimia* **17** (1981) 1804.

[8] J. D. Gamburg, L. I. Lihosherstova, V. V. Trofimenko and L. I. Malikova, *ibid.* **17** (1981) 1491.

[9] J. M. Polukarov and V. A. Kuznetsov, *J. Phys. Chem.* (*USSR*) **36** (1962) 2382.

[10] V. I. Gribel, N. P. Fedotev and P. M. Viatchelslavov *Electrochimia* **1** (1965) 364.

[11] G. Michael, *Metalloberfläche* **32** (1978) 430.

[12] D. S. Stoychev, I. B. Vitanova, I. G. Pozarliev and S. Rashkov, *Polygraphia (USSR)* **9** (1984) 39.

[13] W. H. Hall, *Proc. Phys. Soc.* **A62** (1949) 741.

[14] J. B. Cohen and J. Wagner, *Appl. Phys.* **33** (1962) 2073.

[15] G. Wiliamson and R. Smallman, *Phil. Mag.* **1** (1956) 34.

[16] D. S. Stoychev, I. B. Vitanova, S. Rashkov and T. D. Vitanov, *Surf. Tech.* **7** (1978) 427.

[17] D. S. Stoychev, I. B. Vitanova, T. D. Vitanov and S. Rashkov, *Compt. rend. Acad. bulg. Sci.* **32** (1979) 1515.

[18] Ju. D. Gamburg, Dr thesis, NIFHI im. Karpova, Moscow (1981).

[19] A. Milchev and E. Vasileva, *Compt. rend. Acad. bulg. Sci.* **9** (1976) 496.

[20] L. Reimer, J. Ficket and T. Pieper, *Z. Metallkde.* **52** (1961) 753.

[21] J. E. Wilson and L. Tomassen, *Trans. Amer. Soc. Met.* **22** (1934) 769.

[22] I. Tomov, D. S. Stoychev and I. Vitanova, *J. Appl. Electrochem.* **15** (1985) 887.