

Structure Features of Metals Obtained by Electrochemical Deposition and by Solidification from Liquid State in Saturated Hydrogen Environment

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Abstract The aim of the work was the experimental verification of the validity of the phenomenon of phase formation through a stage of liquid state in metals being electrodeposited. It is found that saturation of metal by hydrogen during electrodeposition is one of the major factors determining its porosity. Growth of porosity of metal with the increase of its saturation by hydrogen during electrodeposition is discovered. It is found that polymorphous metal being electrodeposited crystallizes in the form of intermediate modification, which is identical to the one of polymorphous metal solidified from liquid state in saturated hydrogen environment. Formation of porous structure in metal being electrodeposited, which possesses all typical features of porous structure of metal solidified from liquid state in saturated hydrogen environment, is discovered. The obtained results prove the validity of the phenomenon of phase formation through a stage of liquid state in metals being electrodeposited.

Keywords Structure, Electrodeposition, Metal, Solidification, Liquid State, Hydrogen

1. Introduction

There are many works describing the phenomenon of phase formation through a stage of liquid state in metals being electrodeposited [1-6]. The essence of this phenomenon is that during the electrochemical deposition of a metal onto a solid cathode in a water solution an undercooled metallic liquid is being formed and superfast solidified at the deposition temperature in the form of a crystalline or/and an amorphous phase.

The validity of the discovered phenomenon is confirmed by the formation of intermetallides, carbides and eutectics in metal alloys being electrodeposited in water solutions of their salts at low temperatures [7]. The reliability of this phenomenon is proved by the increase of density of metals

being electrodeposited under the influence of centrifugal force directed perpendicular to the crystallization front and by the change of the form of deposits of metals being electrodeposited and wave-like flow of their surface layers under the influence of centrifugal force directed parallel to the crystallization front [8].

The aim of this work was the further experimental verification of the validity of the phenomenon of phase formation through a stage of liquid state in metals being electrodeposited. General idea of the completed research was as follows. As metals being electrodeposited crystallize in the environment of evolving hydrogen, their structure features must be similar to those of metals solidified from liquid state in saturated hydrogen environment. The presence of structure features of metals solidified in saturated hydrogen environment in metals being electrodeposited will be a proof of the validity of the discovered phenomenon.

2. Experimental Proof of Validity of the Phenomenon

2.1. Idea One and Its Realization

It is known that formation of pores during casting of metal solidified in saturated hydrogen environment occurs as a result of evolving of hydrogen dissolved in liquid phase of metal [9,10]. At that, pores volume in solidified metal is proportional to the volume of hydrogen dissolved in the melt [11]. On the other hand, phase formation of metal being electrodeposited also occurs in saturated hydrogen environment [12].

Therefore, in case of validity of the discussed phenomenon the porosity of electrodeposited metal must depend on the degree of its saturation by hydrogen during electrodeposition. The interdependence between saturation of metal by hydrogen during electrodeposition and its porosity will be a confirmation of the reliability of the discussed phenomenon.

2.1.1. Materials and Methods

The realization of the idea mentioned above was done using copper deposits 10 μm thick electrodeposited at the temperature of 25 $^{\circ}\text{C}$ in the sulphate electrolyte containing (g/l): $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – 200, H_2SO_4 – 50. Stainless steel was used as the substrate to provide a possibility of separating the deposits from the substrate. The choice of copper deposits as model samples was caused by the possibility to change their degree of saturation by hydrogen in a wide range of values.

In the work [13] the method for estimation of the degree of metal saturation by hydrogen during its electrodeposition was suggested. According to this method the ratio of volumes of hydrogen being formed on the cathode V_2 and of the metal being electrodeposited V_1 was calculated by the formula:

$$V_2/V_1 = (k_2 \cdot \eta_2 \cdot \gamma_1) / (k_1 \cdot \eta_1 \cdot \gamma_2) \quad (1)$$

where k_2 is the electrochemical equivalent of hydrogen, η_2 is the current yield of hydrogen, γ_1 is the metal density, k_1 is the electrochemical equivalent of metal, η_1 is the current yield of metal, γ_2 is the hydrogen density.

The degree of saturation of copper deposits by hydrogen during electrodeposition was changed by varying of the current density from 1 to 8 A/dm^2 , which caused significant change of current yield of copper and hydrogen. At that, the ratio between the hydrogen volume evolving at the cathode V_H and the volume of copper being electrodeposited V_{Cu} was determined. The ratio V_H/V_{Cu} was a measure of saturation of copper being electrodeposited by hydrogen [14]. The values of V_H/V_{Cu} for the used electrolyte composition are presented in Table 1.

Table 1. Change of the degree of saturation of copper being electrodeposited by hydrogen with the increase of current density

Current density (A/dm^2)	Current yield of hydrogen (%)	Degree of saturation by hydrogen (V_H/V_{Cu})
1	5.86	198
2	10.19	361
3	13.09	479
5	16.01	606
6	17.08	655
8	19.07	749

As it is seen at Table 1, phase formation of copper being electrodeposited occurs in saturated hydrogen environment even at its relatively high current yield. Therefore, it is supposed that the deposits being formed on the cathode do not consist of pure copper but of solid solution of hydrogen in copper. Besides, all obtained deposits contain pores, the area and quantity of which depend on the degree of copper saturation by hydrogen.

As quantitative characteristics of porosity of investigated material the relative pores area at the sample surface (S), the quantity of pores per 1 mm^2 of sample surface (n) and the average diameter of pores (d) were used. Porous structure of

samples was investigated with the use of the structural analyzer EPIQUANT.

2.1.2. Results and Discussion

As a result of completed investigations it was found that saturation of metal being electrodeposited by hydrogen is one of the major factors that determine its porosity. In fact, as it is seen at Fig. 1, at the degree of saturation of hydrogen $V_H/V_{Cu} = 198$ structure of copper deposit possesses relatively low porosity ($S = 0.53\%$ and $n = 0.56\text{ mm}^{-2}$). With the increase of the degree of saturation by hydrogen porosity of metal being electrodeposited grows (Fig. 1) and at the increase of V_H/V_{Cu} value to 749 the relative pores area increases 8 times ($S = 4.38\%$), and the quantity of pores per 1 mm^2 grows 15 times ($n = 8.55\text{ mm}^{-2}$).

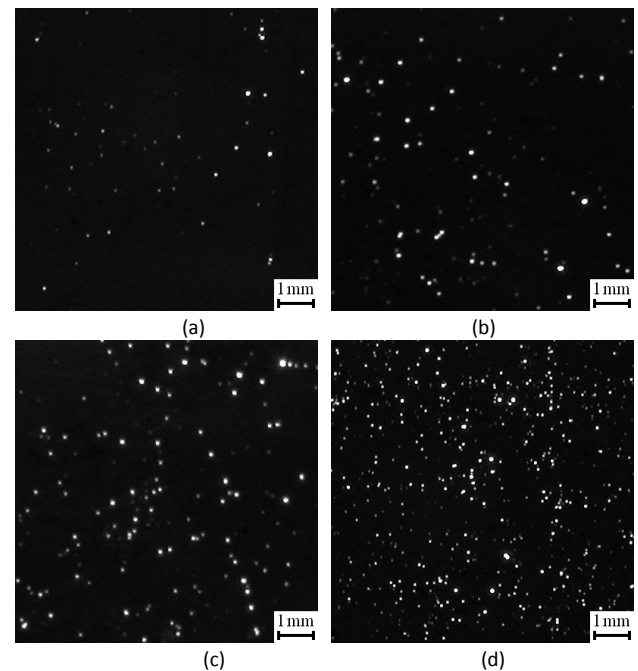


Figure 1. Porous structure of copper deposits obtained in saturated hydrogen environment, at the volume of hydrogen evolving during copper electrodeposition being 198 (a), 479 (b), 606 (c) and 749 (d) times higher than the volume of the metal being deposited

The change of quantitative characteristics of porosity of copper deposits depending on the degree of their saturation by hydrogen (Fig. 2) indicates the validity of the made conclusion. Thus, at Fig. 2 it is seen that the increase of the degree of saturation of copper being electrodeposited by hydrogen causes both the increase of the relative pores area (curve 1) and the growth of their quantity per 1 mm^2 (curve 2).

The dependence of porosity of metal being electrodeposited on the degree of its saturation by hydrogen can be explained by the following. As phase formation of metal being electrodeposited occurs through a stage of liquid state [1-8], that because of large difference of hydrogen solubility in liquid and solid phases its evolving during solidification of metal results in the porosity formation. At that, the porosity of metal grows with the increase of

intensity of hydrogen saturation during electrodeposition, which was experimentally observed.

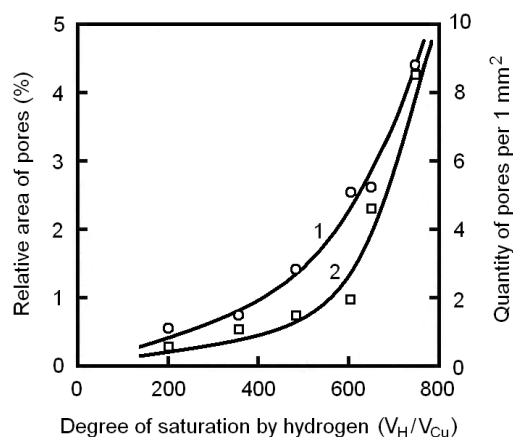


Figure 2. Influence of saturation degree of copper by hydrogen during its electrodeposition on relative area of pores (curve 1) and their quantity per 1 mm² (curve 2)

The proposed conception is also proved by the following feature of change of quantitative characteristics of porosity of copper samples with the increase of the degree of saturation by hydrogen during their electrodeposition. As it is seen at Fig. 2, at the increase of V_H/V_{Cu} value from 606 to 655 the relative pores area grows by only 3%, but the quantity of pores increases almost 2.5 times. In this case, if the discussed phenomenon is valid that pores size must decrease. In fact, the data of Table 2 indicates that in this interval of change of V_H/V_{Cu} values the significant decrease of the average pores diameter is observed. The decrease of pores size with the increase of the V_H/V_{Cu} value above 606 also can be noticed at the comparison of Fig. 1(c) and 1(d).

Table 2. Dependence of average diameter of pores in copper deposits on the degree of its saturation by hydrogen during electrodeposition

Degree of saturation by hydrogen (V_H/V_{Cu})	198	361	479	606	655	749
Average diameter of pores (μm)	94	112	116	127	84	81

This fact indicates that there is the critical degree of hydrogen saturation during electrodeposition for each metal, at which metallic liquid is saturated by hydrogen to the maximum and its subsequent solidification is accompanied by intense hydrogen removal. Intensification of the process of hydrogen removal from the deposit being solidified causes both the increase of the quantity of pores and the decrease of their average size.

Assuming that phase formation of metal being electrodeposited occurs as a result of embedding of atoms (ad-atoms or ions) into the crystal lattice of growing deposit (which has been universally recognized so far), the interdependence between metal's porosity and its saturation by hydrogen during electrodeposition should not be observed. The absence of such connection in this case is caused by the fact, that the solubility of hydrogen in solid

phase of metal at its maximum value is a constant.

Thus, the found interdependence between saturation of metal by hydrogen during electrodeposition and its porosity proves the validity of the phenomenon of phase formation through a stage of liquid state in metals being electrodeposited.

2.2. Idea Two and Its Realization

It is known that melted polymorphous metals solidify in saturated hydrogen environment forming the crystal structure with the type of intermediate modification [15]. On the other hand, it is known that structure formation of metals being electrodeposited also occurs in saturated hydrogen environment [16].

If polymorphous metals being electrodeposited really pass through a stage of liquid state, that they will crystallize forming structure with the type of intermediate modification. The similarity of structure type of polymorphous metals obtained by electrodeposition in water solution and by solidification of melt in saturated hydrogen environment will indicate the reliability of the discussed phenomenon.

2.2.1. Materials and Methods

As a model metal for the verification of the idea described above cobalt was chosen, because it solidifies from liquid state in saturated hydrogen environment forming intermediate f.c.c. structure of β -Co [15]. It was expected that the increase of hydrogen concentration during cobalt electrodeposition will cause the growth of intermediate f.c.c. β -phase fraction in its phase composition and respective decrease of stable h.c.p. α -phase fraction.

Electrodeposited cobalt samples were obtained at room temperature in the sulphate electrolyte of the following composition (g/l): $\text{CoSO}_4 - 300$, $\text{NaCl} - 20$, $\text{H}_3\text{BO}_3 - 40$. The saturation of cobalt by hydrogen during electrodeposition was achieved by the increase of hydrogen concentration both by the decrease of the electrolyte pH value and by the increase of current density.

Table 3. Process parameters for obtaining of samples of electrodeposited cobalt and their degree of saturation by hydrogen

Electrolyte acidity (pH)	Degree of saturation by hydrogen (V_H/V_{Co})	Current density (A/dm^2)	Degree of saturation by hydrogen (V_H/V_{Co})
6	260	4	291
5	336	8	404
4	404	12	548
3	588	16	875
2	846	20	1287

Estimation of the ratio of volumes of hydrogen and cobalt (V_H/V_{Co}) being formed at different parameters of samples obtaining shows that with the decrease of electrolyte pH from 6 to 2 the value of V_H/V_{Co} increases more than 3 times

(Table 3). And the growth of current density from 4 to 20 A/dm² results in the increase of the V_H/V_{Co} value almost 4.5 times. Structure and phase composition of cobalt samples were investigated by the use automated X-ray diffractometer DRON-3 in Mo-K α radiation.

2.2.2. Results and Discussion

As a result of the completed investigations it was found that saturation of cobalt being electrodeposited by hydrogen causes its crystallization with the formation of f.c.c. structure of intermediate modification of β -Co (Fig. 3).

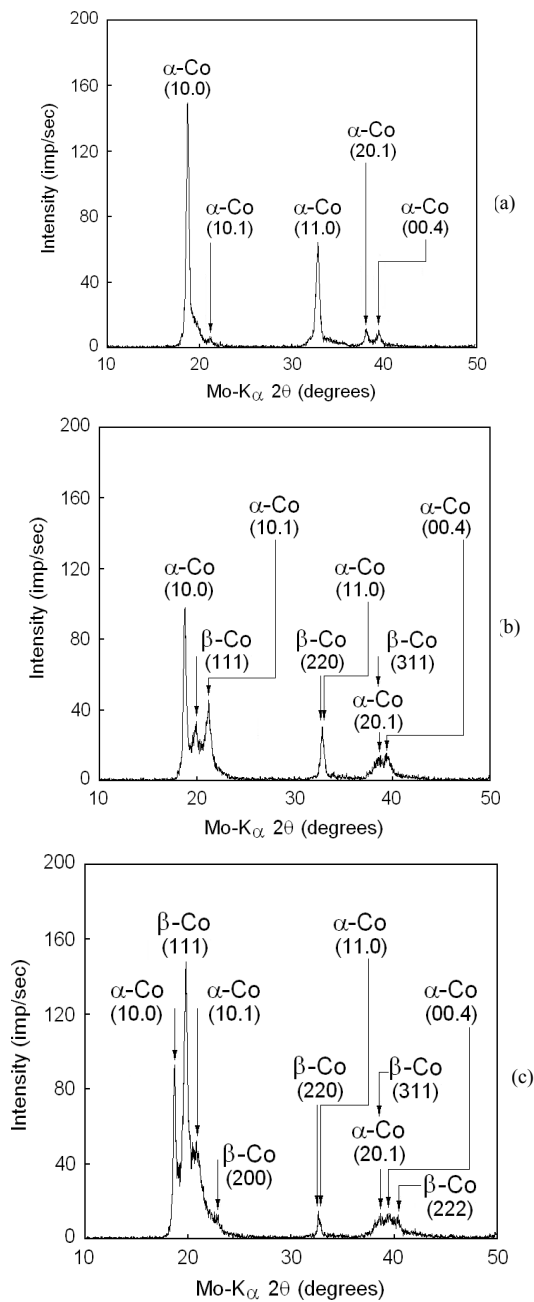


Figure 3. Diffractograms illustrating the transition from h.c.p. to f.c.c. structure of cobalt due to increase of the degree of saturation by hydrogen by the means of decrease of the electrolyte pH: (a) – pH 6; (b) – pH 4; (c) – pH 2

Thus, at the pH 6 the electrodeposited cobalt is of stable h.c.p. structure (Fig. 3(a)), but with the decrease of pH value to 4 cobalt deposits possesses two-phase structure – besides stable h.c.p. structure intermediate f.c.c. structure also appears (Fig. 3(b)). At the further increase of hydrogen concentration to pH 2 the fraction of f.c.c. β -Co structure grows and the fraction of the h.c.p. α -Co structure decreases (Fig. 3(c)).

The similar result was obtained at saturation of cobalt being electrodeposited by hydrogen by the increase of current density (Fig. 4).

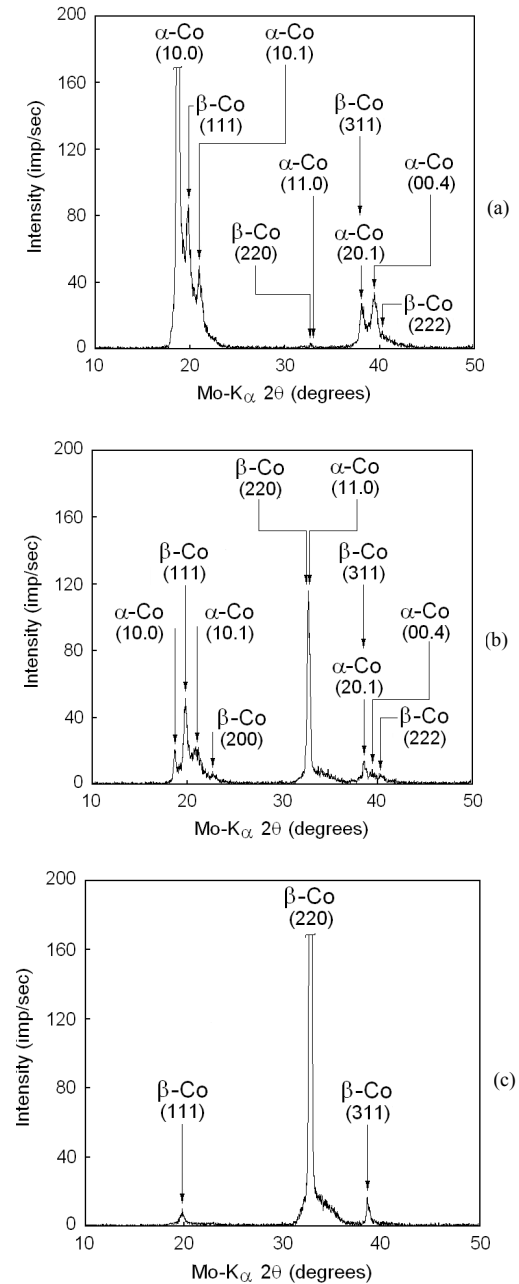
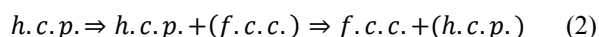
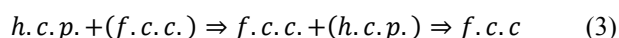


Figure 4. Diffractograms demonstrating the transition from h.c.p. to f.c.c. structure of cobalt due to increase of the degree of saturation by hydrogen by the means of increase of current density: (a) – 4 A/dm²; (b) – 12 A/dm²; (c) – 20 A/dm²

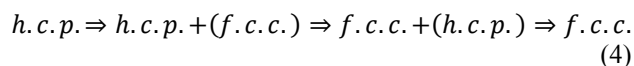
Schematically change of structure of cobalt being electrodeposited with the increase of the degree of its saturation by hydrogen by the decrease of electrolyte pH can be shown as follows:



And in case of saturation of cobalt by hydrogen by the increase of current density its structure changes according to the schema:



Therefore, as a result of the completed investigations it was found that saturation of cobalt being electrodeposited by hydrogen causes regular change of its structure – with the increase of hydrogen concentration the structure of cobalt deposits changes from stable h.c.p. to intermediate f.c.c. structure. Summarizing the obtained data, the change of structure of cobalt being electrodeposited with the increase of the degree of its saturation by hydrogen can be described by the following scheme:



The obtained result is confirmed by the data of the works [17,18], where it was found that at the electrolyte acidity less than pH 2 [17] cobalt being electrodeposited mainly crystallizes as f.c.c. β -phase and the increase of current density during electrochemical cobalt-plating causes the growth of β -phase fraction in phase composition of the deposit [18].

The similarity of crystal structure type (f.c.c.) of polymorphous metal obtained by electrodeposition in water solution and by solidification of melt in saturated hydrogen environment indicates that metals during electrochemical deposition really pass through a stage of liquid state.

To ensure the validity of this conclusion the investigations of structure of cobalt saturated by hydrogen, which was obtained by casting in liquid state, were performed. For crystallization of cobalt melt in saturated hydrogen environment the unit, that allows obtaining of materials saturated by hydrogen at increased temperature and pressure, was developed and constructed [19].

Cobalt was obtained by solidification of melt saturated by hydrogen at the pressure of 5.0 MPa and the temperature of 1600 °C. X-ray structure analysis of ingots shows that cobalt crystallized in saturated hydrogen environment possesses f.c.c. structure of β -Co intermediate modification (Fig. 5), which confirms the made conclusion.

Thus, crystallization of polymorphous metal being electrodeposited in the form of intermediate modification, which is identical to the one of polymorphous metal solidified from liquid state in saturated hydrogen environment, confirms the validity of the phenomenon of phase formation through a stage of liquid state in metals being electrodeposited.

2.3. Idea Three and Its Realization

It is known that as a result of crystallization of cast melt in saturated hydrogen environment pores appear in an ingot being solidified due to evolving of hydrogen dissolved in metal liquid phase [20]. These pores are of elongated form in the direction perpendicular to the crystallization front and they can coagulate during whole period of ingot crystallization [21].

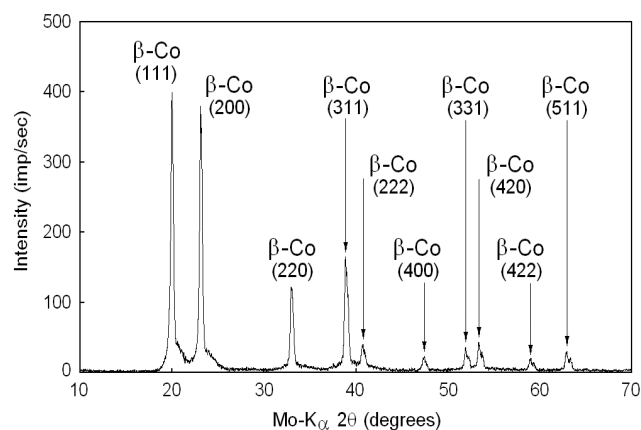


Figure 5. Diffractogram of cobalt with f.c.c. structure obtained by crystallization of melt in saturated hydrogen environment

On the other hand, phase formation of metal being electrodeposited also occurs in saturated hydrogen environment [22]. Therefore, in case of validity of the discussed phenomenon porous structure of electrodeposited metal must have typical features of porous structure of cast metal solidified from liquid state in saturated hydrogen environment.

2.3.1. Materials and Methods

To verify the idea described above chromium obtained in the universal electrolyte at the current density of 60 A/dm² and the temperature of 45 and 50 °C was used as a model electrodeposited metal. The choice of chromium was caused by the fact that this metal is electrodeposited at very low current yield (13-18 %), i.e. approximately 85% of electricity is used for the hydrogen evolving. At that, current yield of chromium decreases with the decrease of temperature of electrochemical chromium-plating.

The calculations shows that during chromium electrodeposition the volume of hydrogen evolving on the cathode is more than 60 thousand times higher than the volume of metal being electrodeposited [13]. It indicates that phase formation of chromium being electrodeposited really occurs in saturated hydrogen environment. Microstructure investigations of cross-section samples were performed with the use of the structural analyzer EPIQUANT.

For the correct comparison of porous structure of electrodeposited and cast metals formed in hydrogen environment almost similar conditions of their phase formation had to be provided. According to the discovered phenomenon [1-8] phase formation of metals being electrodeposited occurs as a result of superfast solidification of continuously renewed clusters of atoms which are in

liquid state in the plane crystallization front. Therefore, for the best approaching of the conditions of phase formation of metals during electrodeposition and casting the unit for obtaining of cast materials in saturated hydrogen environment was constructed and manufactured [23]. Solidification of metals in the unit was performed at high adjustable rate of movement of the plane crystallization front.

Cast metal was obtained by heating of a blank in the inductor and its melting in the electric arc. After melting of a certain quantity of the metal the process was stopped and the ingot was formed at the bottom water-cooled crystallizing dish [23]. The aluminum bronze (8.5 % Al) melted and solidified in hydrogen environment at the pressure of 0.6 MPa and the rate of plane crystallization front movement of 1.0 and 1.3 mm/sec was used as a model cast material. The microstructure of electrodeposited chromium was compared with the one of cast metals melted and solidified in saturated hydrogen environment at specially developed unit at the adjustable rates of movement of plane crystallization front being 1.0 and 1.3 mm/sec.

2.3.2. Results and Discussion

As a result of the completed investigations the presence of highly porous structure in samples of the electrodeposited metal was found (Fig. 6). In such structure there are anisotropic pores elongated in the direction perpendicular to the crystallization front. At that, the increase of the degree of hydrogen saturation causes the growth of porosity of electrodeposited metal. The features of porous structure of electrodeposited metal are the presence of through channels consisting of several united pores and the decrease of the average pore diameter with the increase of the degree of hydrogen saturation (Fig. 6).

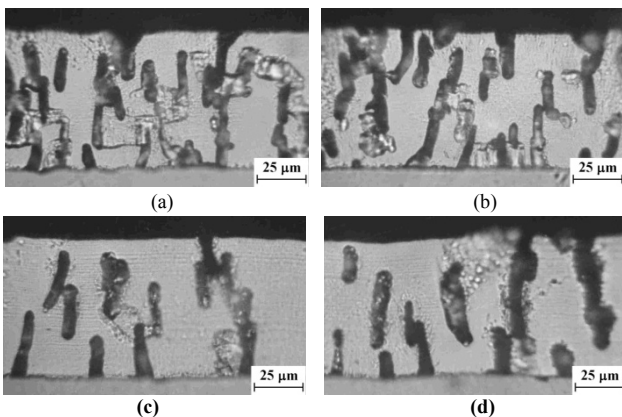


Figure 6. Cross-section microstructures of chromium samples electrodeposited in the universal electrolyte at the current density 60 A/dm² and temperature 45 (a),(b) and 50 °C (c),(d)

As it is seen at Fig. 7, pores of cast material solidified in saturated hydrogen environment at the high rate of movement of plane crystallization front (1.0-1.3 mm/sec) are also of anisotropic form and oriented in the direction perpendicular to the crystallization front. As a result of comparison Fig. 6 and 7 it is seen that in electrodeposited

metal porous structure is formed, which is similar by its form and orientation of pores to the structure appearing during solidification of melt in saturated hydrogen environment.

In the work [21] the classification of porous structure features of cast materials forming during crystallization of metal-hydrogen system alloys by simultaneous precipitation of crystals and evolving of hydrogen from metallic liquid is presented. Such features are: a) discontinuance of pores growth and initiation of new pores, b) coagulation (junction) of pores during the whole period of crystallization, and c) orientation of pores perpendicular to the crystallization front and form of pores being cylinder- and ellipse-like.

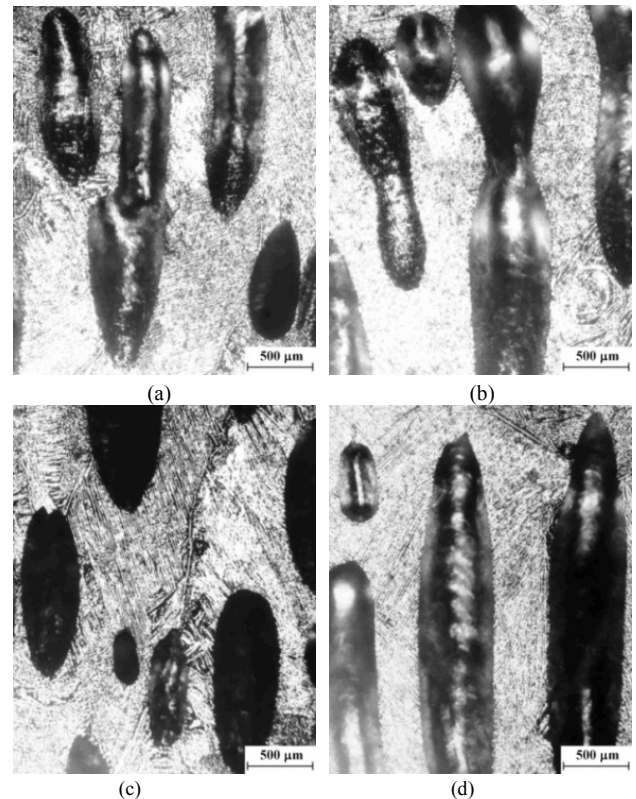


Figure 7. Cross-section microstructures of aluminum bronze samples melted and solidified in hydrogen environment at the pressure 0.6 MPa and the rate of movement of the plane crystallization front 1.0 (a),(b) and 1.3 mm/sec (c),(d)

At Fig.6 it is seen that all features of porous structure of cast metals saturated by hydrogen mentioned above are also typical for the porous structure of electrodeposited metals. Thus, with the movement of the crystallization front during electrodeposition both the discontinuance of pores growth and the initiation of new pores occur (Fig. 6).

The coagulation of adjacent pores during the whole period of solidification is clear demonstrated by through channels formed by coagulation of four or five pores (Fig. 6(a),(c)). As it is stated right in the work [21], as a result of such multiple coagulation coarse shapeless pores appear as it is seen at Fig. 6.

In porous structure of electrodeposited metal there are pores having cylindrical or ellipse-like form oriented in the direction perpendicular to the crystallization front (Fig. 6).

The author of the work [21] associates the deviation from parallelism in the pores growth of a cast sample with emerging of bulging and concave regions on the crystallization front, because the vector of growth rate of a pore is always directed perpendicular to the crystallization front in the place of its initiation. In fact, as it is seen at Fig. 6(d), deviation of a pore from the normal of the surface of the electrodeposit is caused by a bulging region on the crystallization front.

Thus, porous structure of electrodeposited metal possesses all typical features of porous structure of cast metal solidified from liquid state in saturated hydrogen environment. The similarity of orientation and form of pores in electrodeposited and cast metals, the effect of pores coagulation, the discontinuance of pores growth and initiation of new pores during the whole period of crystallization during electrodeposition confirm the reliability of the phenomenon of phase formation through a stage of liquid state in metals being electrodeposited.

3. Conclusions

It is found that saturation of metal by hydrogen during electrodeposition is one of the major factors determining its porosity. Growth of porosity of metal with the increase of its saturation by hydrogen during electrodeposition is discovered. It is found that polymorphous metal being electrodeposited crystallizes in the form of intermediate modification, which is identical to the one of polymorphous metal solidified from liquid state in saturated hydrogen environment. Formation of porous structure in metal being electrodeposited, which possesses all typical features of porous structure of metal solidified from liquid state in saturated hydrogen environment, is discovered. The obtained results prove the validity of the phenomenon of phase formation through a stage of liquid state in metals being electrodeposited.

Acknowledgements

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