Phase Formation through a Stage of Liquid State in Metallic Materials Being Electrodeposited: Recent Experimental Proofs

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Abstract

The effect of increase of density of metals being electrodeposited under the influence of a centrifugal force acting perpendicular to the crystallization front is found. Wave-like flow of surface layers of metals being electrodeposited under the influence of a centrifugal force acting parallel to the crystallization front, as well as bending of waves by mechanical hindrances and formation of foam on the crests of waves are discovered. Change of form of the deposits of metals being electrodeposited under the influence of a centrifugal force including the growth of length and thickness of the deposits at the direction of force action with a modification of their configuration depending on overload values is discovered. Predominant development of deposits of metals being electrodeposited beyond the edge of the cathode in the direction of the action of a centrifugal force parallel to the crystallization front is found. The obtained results prove the validity of the discovered phenomenon of phase formation through a stage of liquid state in metallic materials being electrodeposited.

Keywords

Phase Formation; Electrodeposited Metal; Liquid State; Centrifugal Force; Density; Surface Morphology

Introduction

The phenomenon of phase formation through a stage of liquid state in metallic materials being electrodeposited was theoretically predicted in 1986 [1] and in 1988 it was experimentally found [2]. The essence of the discovered phenomenon is that during the electrochemical deposition of a metallic material onto a solid cathode in an aqueous medium a supercooled metallic liquid is being formed and solidified at the deposition temperature in the form of a crystalline or/and an amorphous phase.

In the work [3] it is shown that liquid state of a metallic material being electrodeposited is caused by very quick (explosive) character of its formation as a result of chain reaction of electrochemical formation of atoms. At that during one act of explosive growth 40-60 atoms are being formed on average. With regard to very quick passage of the act of explosive growth (about 10^{-7} sec), the atoms have no time to form a structure with long-distance order of their arrangement. Multitude of such clusters of atoms are being formed in avalanche-like manner in various places on the surface of the cathode or the growing deposit and then being combined into larger formations constitute liquid phase of a metallic material being electrodeposited.

The two aspects should be mentioned. First, a liquid being formed during electrodeposition of a metallic material is always supercooled. Second, a liquid of a metallic material being electrodeposited is consequence of its high-energy but not a high-temperature state as in conventional melts.

During recent years many experimental results proving the validity of this phenomenon were obtained [4-9]. The goal of this work was the further experimental proof of the validity of the discovered phenomenon.

Experimental Proof of Validity of the Phenomenon

Idea One and Its Realization

It is known that during the centrifuging of a liquid metallic material due to the action of a centrifugal force it presses itself to the walls of a rotating mould, becomes denser and crystallizes in a more compact ingot (so called centrifugal casting). Therefore, if during electrocrystallization a metallic material really passes through a stage of liquid state, then as a result of a centrifugal force acting perpendicular to the crystallization front it should be expected the formation of an electrodeposit, which is denser in comparison with an electrodeposit obtained under ordinary conditions.

For the obtaining of metals being electrodeposited in the field of a centrifugal force, the unit was developed and constructed [10]. The unit provided the action of a centrifugal force proportional to the normal acceleration *kg* (where *k* – overload coefficient) ranging from 1 *g* to 1256 *g*. The values of a centrifugal force was changed stepwise by varying the number of rotations of the centrifuge rotor from 0 to 3000 rotations per minute with the step of 500, which resulted in the normal acceleration of 1 *g*, 35 *g*, 140 *g*, 314 *g*, 558 *g*, 872 *g* and 1256 *g*. The unit allowed influencing by a centrifugal force on a metal being electrodeposited both perpendicular and parallel to the crystallization front depending on the electrodes positions in the electrochemical cell.

Construction features of the centrifuge and the electrochemical cells completely eliminated a possibility of electrolyte flow relatively to the cathode during electrodeposition of metals [10]. During the operation of centrifuge the cells rotated horizontally jointly with the rotor. The cathode was mounted on the bottom of the cell perpendicular to its axis, thus during rotation of the cell the cathode was perpendicular to the rotor radius. As a centrifugal force during rotation is always directed along with the rotor radius from its center, such position of the cathode provided force influence on a metal is electrodeposited perpendicular to the crystallization front.

In order to eliminate the influence of hydrogen on the density of deposits being formed in the field of a centrifugal force, the investigations were performed on samples of copper and nickel being electrodeposited with the current yield values of 99.5-100 % (Table 1).

The duration of obtaining of each sample was 60 min. In order to avoid the reduction of concentration of metal ions in the electrolytes during electrodeposition, the soluble anodes were used. Density of copper and nickel electrodeposits was determined by the method of hydrostatic weighing.

As a result of the completed investigations, it was found that the influence of a centrifugal force on metals was electrodeposited perpendicular to the crystallization front causes increase of their density (Fig. 1).

TABLE I ELECTROLYTES COMPOSITION AND PARAMETERS OF DEPOSITION OF METALS IN THE FIELD OF CENTRIFUGAL FORCE

Metal	Electrolytes Composition, g L^{-1}	Electrolyte Temperature, °C	Current Density, A dm^{-2}	Current Yield, %
Cu	$CuSO_4{\cdot}5H_2O$ – 250 H_2SO_4 – 50	25	1	100
Ni	$NiSO_4{\cdot}7H_2O$ – 330 $NiCl_2{\cdot}6H_2O$ – 50 H_3BO_3 – 35 $C_{11}H_{23}COONa$ – 0.1	25	1	99.5

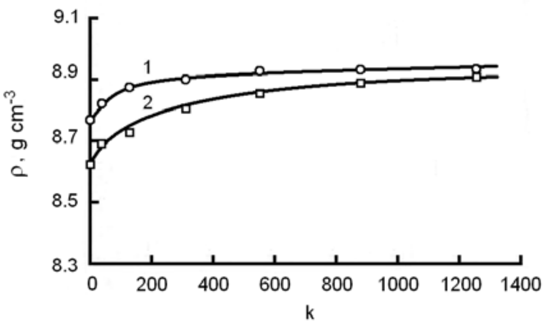


FIG. 1 CHANGE OF DENSITY OF COPPER (1) AND NICKEL (2) BEING ELECTRODEPOSITED DEPENDING ON THE OVERLOAD COEFFICIENT

Character of the influence of the overload on the density of the investigated metals is the same: growth of *k* value up to 314 cause's significant increase of density and subsequent growth of *k* value up to 1256 results in minor increase of density of metals. The most abrupt increase of metals density (from 8.76 to 8.88 g cm^{-3} for copper and from 8.62 to 8.72 g cm^{-3} for nickel) was found during low overloads (under k = 139).

The obtained result can be explained by tightening of a liquid phase being formed during electrochemical deposition of metals. A possibility of obtaining of more dense metals by their electrodeposition in the field of a centrifugal force in comparison with metals obtained under ordinary conditions indicates that metals during electrochemical deposition really pass through a stage of liquid state.

Thus, the found effect of increase of density of metals being electrodeposited under the influence of a centrifugal force directed perpendicular to the crystallization front confirms the validity of the discussed phenomenon.

Idea Two and Its Realization

It is known that a liquid metallic material in contrast to a solid one is able to flow i.e. to move its mass in the direction of action of the applied force. Therefore if a metallic material during electrochemical deposition really passes through a stage of liquid state, then under the influence of a centrifugal force parallel to the crystallization front it should be expected the movement of its mass by the wave-like flow of continuously replenishing liquid surface layers. Indeed, the force influence on the continuously forming liquid surface layers of a material being electrodeposited will cause oscillating motion of liquid surface which in turn will result in formation of waves.

The investigations were performed on samples of nickel and copper electrodeposited in the field of a centrifugal force. The cathode was mounted in the cell parallel to its axis, therefore during the rotation of the cell, the cathode was parallel to the rotor radius which provided force influence on a metal being electrodeposited parallel to the crystallization front. Due to the metal current yield values 99.5-100% and impossibility of electrolyte motion relative to the cathode in the cell during electrodeposition [10], the influence of hydrogen and electrolyte motion on surface morphology were completely eliminated.

As a result of the completed investigations, the effect of wave-like flow of surface layers of metals being electrodeposited in the direction of action of a centrifugal force was found. The most obviously solidified waves were fixed on the surface of nickel electrodeposits obtained at the force influence proportional to 1256 *g* (Fig. 2).

Thus at the absence of a centrifugal force the surface of nickel deposits is smooth and does not contain wave-like forms (Fig. 2 a), but as a result of significant overload the surface of deposits of nickel being electrodeposited contains solidified waves (Figs. 2 b-d). Such surface morphology is a result of solidification of surface layers of nickel being electrodeposited which are in liquid state and participate in wave-like motion under the influence of a centrifugal force parallel to the crystallization front.

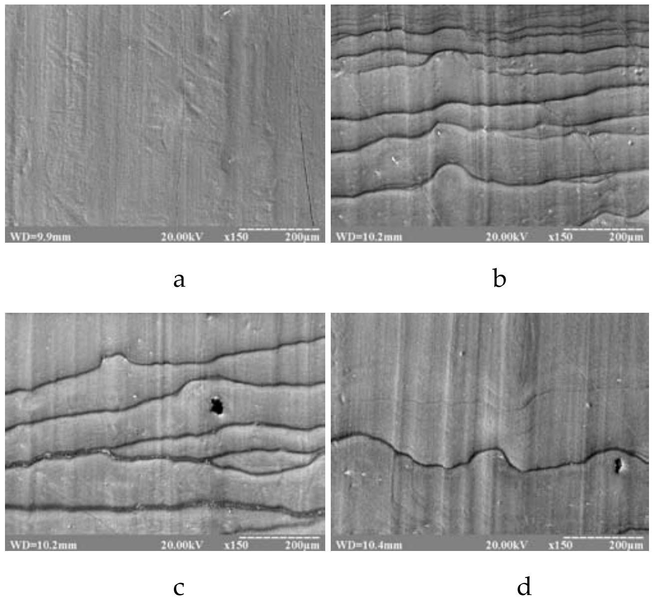


FIG. 2 SCANNING ELECTRON MICROSCOPY IMAGES OF NICKEL ELECTRODEPOSITS DEMONSTRATING WAVE-LIKE FLOW OF SURFACE LAYERS OF NICKEL BEING ELECTRODEPOSITED UNDER THE INFLUENCE OF A CENTRIFUGAL FORCE PROPORTIONAL TO ACCELERATION OF 1 *G* (A – INITIAL CONDITION) AND 1256 *G* (B-D) THE FORCE IS DIRECTED FROM TOP TO BOTTOM

There are two main features of wave-like flow of surface layers of metals being electrodeposited. First, metallic waves are bent by macroscopic defects such as solid inclusions (Fig. 2 b) or through pores (Figs. 2 c, d). Such bending of waves by mechanical hindrances is typical for a liquid material with high viscosity. Assume that a material being electrodeposited is in solid state only (e.g. as fine solid particles), then in that case pores would be filled with particles and there would be cavities around solid inclusions caused by curl-like motion of particles.

In Fig. 3, typical images of metallic waves bent by a through pore and by a solid inclusion as well as structure of waves nearby the mentioned hindrances are presented. As it is seen in Fig. 3, wave-like areas of material have a form of semicircular terraces and contain particles of a globular form which are seemingly solidified clusters or groups of clusters of a material.

Another typical feature proving the origin of wave-like forms from solidification of metallic liquid moving under the influence of a centrifugal force is the formation of foam on the crests of waves. Thus in Figs. 3 a, b the areas of solidified foam formed on the crests of waves as a result of mechanical dispersion of metallic liquid under force influence are seen.

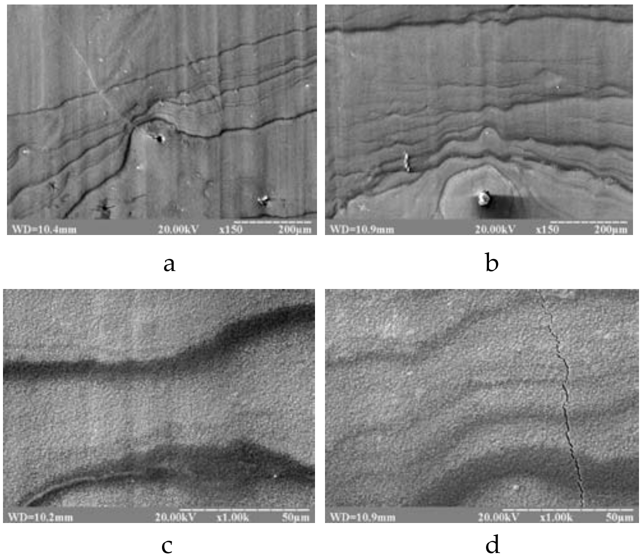


FIG. 3 SCANNING ELECTRON MICROSCOPY IMAGES OF NICKEL ELECTRODEPOSITS SHOWING WAVES BENT BY A PORE (A,C) AND BY AN INCLUSION (B,D) THE FORCE PROPORTIONAL TO ACCELERATION OF 1256*G* IS DIRECTED FROM TOP TO BOTTOM

As at minor values of a centrifugal force solidified waves have wide crests, the morphology of foam areas was investigated on the samples of nickel deposits obtained at minor force influence (proportional to 35 *g* and 140 *g*). As it is seen in Fig. 4 solidified foam is glassy formations of various configurations poorly adhered to the base. Thus in Figs. 4 a, b, the areas of the crests of waves of nickel deposits with partially peeled off fragments of solidified foam as a result of its cracking are clearly seen. The layer of glassy foam is thin enough for coating structure to be seen through it (Figs. 4 c, d).

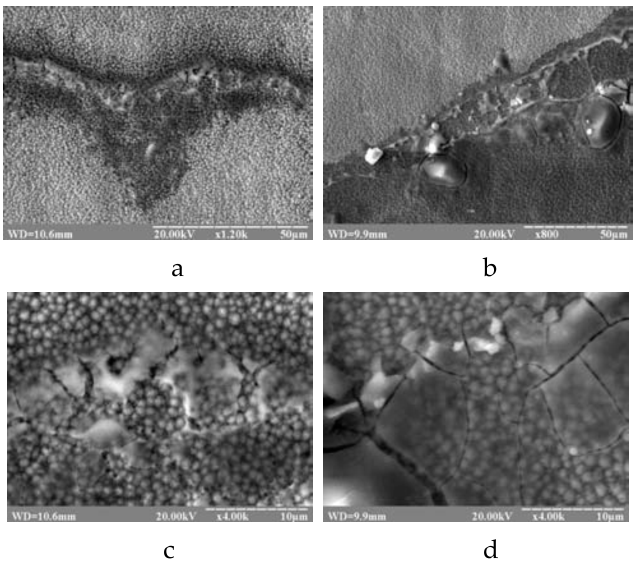


FIG. 4 SCANNING ELECTRON MICROSCOPY IMAGES OF NICKEL ELECTRODEPOSITS WITH FRAGMENTS OF SOLIDIFIED FOAM ON THE CRESTS OF WAVES THE FORCE PROPORTIONAL TO ACCELERATION OF 35*G* (A,C) AND 140*G* (B,D) IS DIRECTED FROM TOP TO BOTTOM

Fig. 4 clearly proves the existence of foam formed during wave-like flow of liquid surface layer of nickel being electrodeposited and frozen as a result of its very quick solidification. Indeed, assume that wave-like flow of surface layer of a metal being electrodeposited under the influence of a centrifugal force is caused by the movement of fine solid particles, then after the end of the process the foam should not exist and a metal should be not in a monolithic but in a powder form.

The differences in configurations of metallic waves of electrodeposited copper and nickel under the influence of a centrifugal force are caused by coarse structure of copper. At the same time, the main features of past liquid state retain. The first one is wave-like flow of its surface layers, the second one is bending of waves by mechanical hindrances (large globules and their groups) and the third one is the appearance of solidified foam on the crests of waves.

One of the results proving the validity of the discussed phenomenon is a wave-like area of solidified foam found on surface of a copper electrodeposit (Fig. 5 a). The various fragments of this foam wave area shown in Figs. 5 b-d clearly demonstrate the consequences of passing through a stage of liquid state by copper being electrodeposited.

Thus, wave-like flow of surface layers of metals being electrodeposited under the influence of a centrifugal

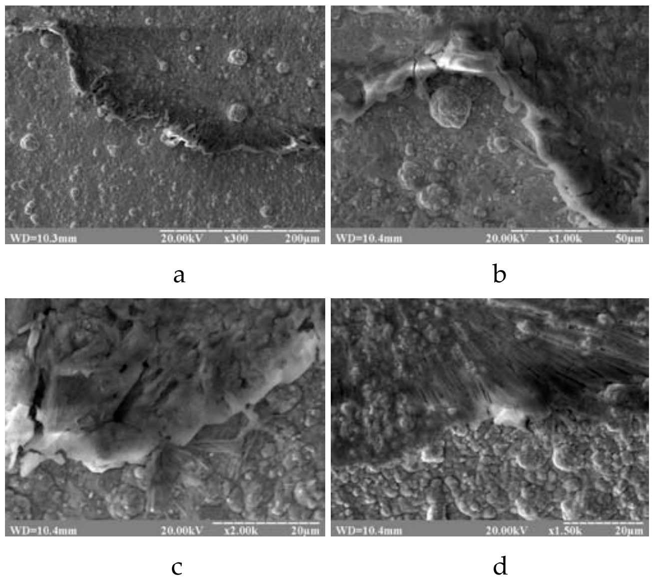


FIG. 5 SCANNING ELECTRON MICROSCOPY IMAGES OF COPPER ELECTRODEPOSIT DEMONSTRATING SOLIDIFIED WAVE-LIKE FOAM (A) AND FRAGMENTS OF ITS VARIOUS AREAS (B-D) THE FORCE PROPORTIONAL TO ACCELERATION OF 314*G* IS DIRECTED FROM TOP TO BOTTOM

force acting parallel to the crystallization front as well as bending of waves by mechanical hindrances and formation of foam on the crests of waves prove the validity of the discovered phenomenon.

Idea Three and Its Realization

It is known that a metallic material in liquid state in contrast to a material in solid state possesses very low shear strength. Hence, a liquid metallic material is principally different from a solid one by its ability to change its form under the influence of an acting force. Therefore, if during electrochemical deposition a metallic material really passes through a stage of liquid state, then under the influence of a centrifugal force acting parallel to the crystallization front it should be expected a change of form of the deposit in the direction of the force action. Indeed, as a result of the solidification of the metallic liquid, shifted relative to the cathode, increase of length and thickness of the deposit as well as change of its configuration in the direction of an acting force are quite probable.

For the realization of this idea, a change of form of deposits of copper and nickel being electrodeposited under the influence of a centrifugal force acting parallel to the crystallization front was investigated. The cathode was mounted in the cell parallel to its axis, therefore during rotation of the cell the cathode was parallel to the rotor radius, which provided force influence on a metal being electrodeposited parallel to the crystallization front.

Thin plates of nickel (for copper deposition) and copper (for nickel deposition) were used as the cathode. Due to current yield of a metal of 99.5%～100 % and impossibility of electrolyte motion relative to the cathode in the cell during electrodeposition [10] the influence of hydrogen formation and electrolyte motion on a form of metal deposits was completely eliminated. A change of form of deposits of metals being electrodeposited was controlled by comparison of electron microscopy images of the far edge of deposits in the direction of action of a centrifugal force.

As a result of the completed investigations, it was found a change of form of the deposits of metals being electrodeposited under the influence of a centrifugal force acting parallel to the crystallization front (Fig. 6). Thus under usual electrodeposition conditions, i.e. when the rotor is at rest (k = 1), the far edge of copper electrodeposit was level and somewhat curved to the cathode surface (Fig. 6a). With an increase of overload to k = 35 the far edge of the deposit became thicker and this bulge had a form of spherical segment along the edge of the cathode (Fig. 6 b).

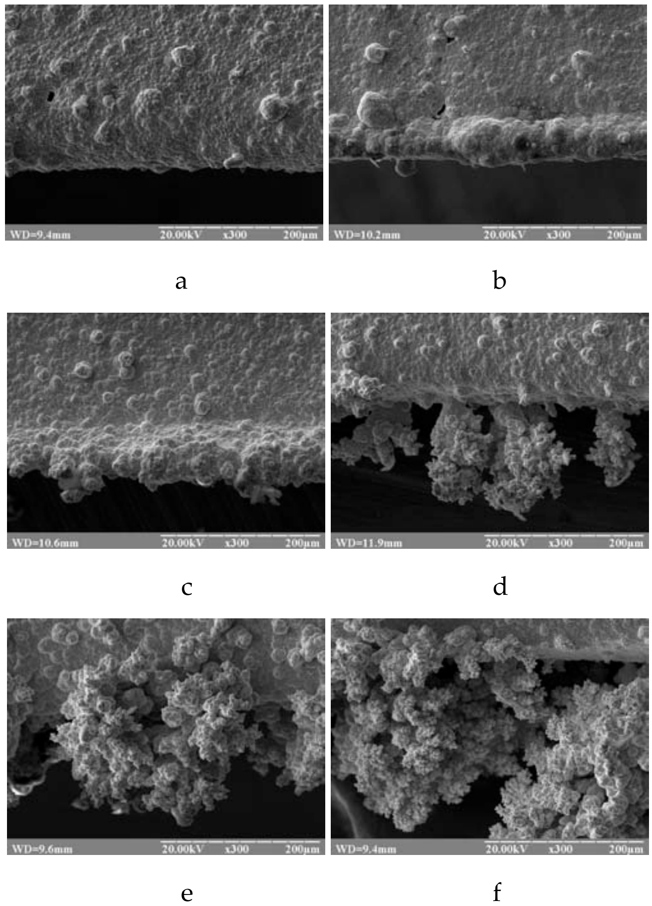


FIG. 6 SCANNING ELECTRON MICROSCOPY IMAGES OF THE FAR EDGE OF COPPER DEPOSITS ILLUSTRATING A CHANGE OF THEIR FORM DURING ELECTRODEPOSITION UNDER THE INFLUENCE OF A CENTRIFUGAL FORCE PROPORTIONAL TO ACCELERATION OF 1 *G* (A) – INITIAL CONDITION, 35 *G* (B), 140 *G* (C), 558 *G* (D), 872 *G* (E) AND 1256 *G* (F) THE FORCE IS DIRECTED FROM TOP TO BOTTOM

The observed change of form of copper deposit is explained by the fact that forming clusters of copper being electrodeposited and being in liquid state or their formations move toward the edge of the cathode under the influence of a centrifugal force. Adhesion force of copper clusters being solidified and the cathode (or an already solidified deposit area) seemingly is greater than the value of a centrifugal force. Therefore the influence of a minor centrifugal force, directed parallel to the crystallization front, on a metal being electrodeposited causes mainly thickening of a deposit edge.

The further increase of overload to k = 140 causes deformation of the bulge edge of a deposit in the direction of action of the force and formation of evident deposit areas going beyond the edge of the cathode (Fig. 6 c). Drastic change of form of the copper deposit occurs after the increase of overload to k = 558 (Fig. 6 d). At this overload botryoidal deposit areas appear beyond the edge of the cathode in the direction of the action of the force.

The obtained form of the deposit is explained by the fact that at k = 558 a centrifugal force is seemingly greater than adhesion force of copper clusters being solidified and the cathode (or already solidified area of the deposit). As a result of the influence on copper, during its electrodeposition by a centrifugal force of a significant value parallel to the crystallization front, the essential shift of continuously replenishing liquid copper clusters or their formations relative to the deposit surface occurs. Solidification of continuously forming liquid phase being under force influence causes both the development of already existing deposit areas beyond the edge of the cathode and the formation of new areas.

The concept of metals being electrodeposited passing through a stage of liquid state is clearly proved by the further change of form of deposits of copper being electrodeposited with the increase of a centrifugal force. As it is seen in Fig. 6 e, the increase of force influence to the overload of k = 872 on copper being electrodeposited results in growth and branching of the deposit areas going beyond the edge of the cathode.

The results of an experiment on the influence of a centrifugal force proportional to acceleration of 1256 g on copper being electrodeposited are especially impressive. Fig. 6 f indicates that the far edge of copper deposit in the direction of such force influence changed its form fundamentally relative to the initial one (Fig. 6 a). Thus the edge of copper deposit contains grown dendrite areas going far beyond the edge of the cathode both in the direction of the action of the force and in the other directions (Fig. 6 f).

The analysis of morphology of deposit areas going beyond the edge of the cathode in the direction of the action of the force (Fig. 7) shows that under minor overload (k = 35) these areas consist of solidified half-round drops formed by many fine globular clusters formations (Fig. 7, a).

With the increase of overload to k = 140 globular form of the deposit surface retains but the areas going beyond the edge of the cathode obtain elongated form. The further increase of overload to k = 314 causes formation of more branched and relief areas of copper being electrodeposited beyond the edge of the cathode (Fig. 7 b). At overloads of k = 558 and 872 the size of particles of the areas decreases, they become flattened and gain more differentiated structure (Fig. 7 c).

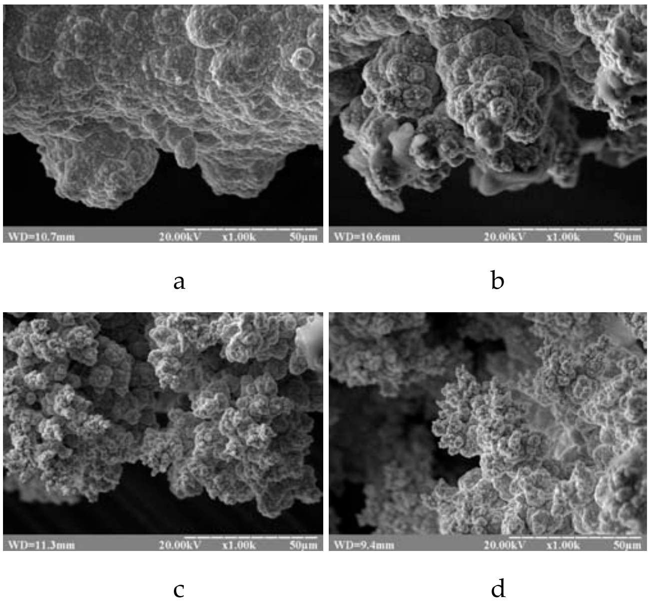
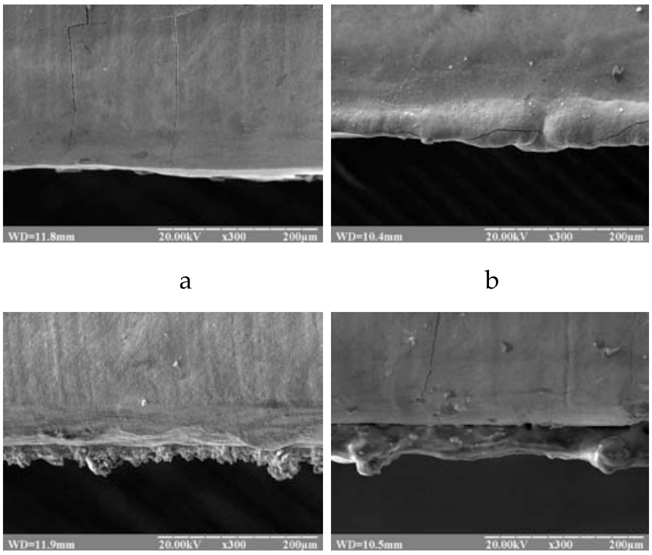


FIG. 7 SCANNING ELECTRON MICROSCOPY IMAGES OF THE FAR EDGE OF COPPER DEPOSITS SHOWING MORPHOLOGY OF THE AREAS GOING BEYOND THE EDGE OF THE CATHODE DEPOSITS WERE OBTAINED BY ELECTRODEPOSITION UNDER FORCE INFLUENCE PROPORTIONAL TO ACCELERATION OF 35 G (A), 314 G (B), 872 G (C) AND 1256 G (D). THE FORCE IS DIRECTED FROM TOP TO BOTTOM.

Electrodeposition of copper at great force overloads (k = 1256) results in fundamental change of morphology of deposit areas going beyond the edge of the cathode. The size of particles of these areas decreases significantly, they gain disk-like and spindle-like forms, their growth occurs in various directions. Thus in the center of Fig. 7 d, it is shown a deposit area beyond the edge of the cathode developing towards force influence.

The found effect of form change of deposits of copper being electrodeposited under the influence of a centrifugal force is completely proved by the analysis of the far edge of nickel deposits obtained under various force influences during their electrodeposition (Fig. 8). According to the obtained results, force influence on nickel being electrodeposited causes the growth of length and thickness of the deposits at the direction of force action with a modification of their configuration depending on overload values.

Thus under minor overload (k = 35) the discussed change of form is seen as thickening of the edge of a nickel deposit (Fig. 8 b). Such spherical segment bulge is more clear-cut than similar one of a copper deposit (Fig. 6 b). Seemingly it can be explained by finer crystal structure of nickel being electrodeposited in comparison with copper structure.



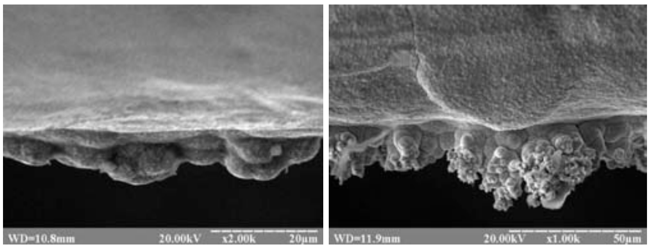
a b

c d

FIG. 8 SCANNING ELECTRON MICROSCOPY IMAGES OF THE FAR EDGE OF NICKEL DEPOSITS DEMONSTRATING A CHANGE OF THEIR FORM DURING ELECTRODEPOSITION UNDER THE INFLUENCE OF A CENTRIFUGAL FORCE PROPORTIONAL TO ACCELERATION OF 1*G* (A) – INITIAL CONDITION, 35*G* (B), 314*G* (C) AND 872*G* (D) THE FORCE IS DIRECTED FROM TOP TO BOTTOM

The further change of form of a deposit of nickel being electrodeposited with the increase of overload is seen as gradual growth of its length in the direction of the action of a centrifugal force (Fig. 8 c). Fig. 8 d illustrates new form of a nickel deposit obtained as a result of significant force influence (k = 872) parallel to its crystallization front during electrodeposition. There is a layer of solidified liquid phase of nickel 40-50 m thick beyond the copper cathode along its edge. Multi-layer formations in the direction of the action of the force, smooth relief and globular bulges of this grown layer prove the fact of its formation by solidification of metallic liquid wave-like layers.

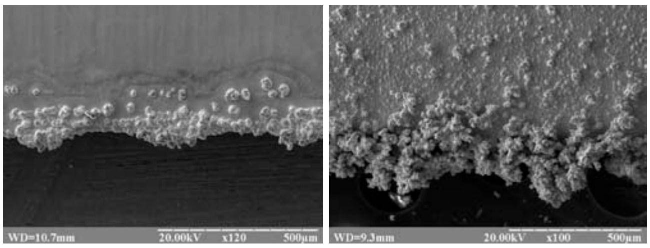
As a result of solidification of metallic liquid phase, the areas of a nickel deposits going beyond the edge of the cathode in the direction of the force influence can be considered (Fig. 9). It should be mentioned that morphologies of the areas of deposits of metals (nickel and copper) being electrodeposited under minor force influence differ insignificantly (Fig. 9 a and Fig. 7 a). With the increase of overload, the differences of morphologies of the areas of nickel and copper become more essential, but the general tendency of differentiation of structure of the areas going beyond the edge of the cathode remains (Fig. 9 b and Fig. 7 b).



a b

FIG. 9 SCANNING ELECTRON MICROSCOPY IMAGES OF THE FAR EDGE OF NICKEL DEPOSITS SHOWING MORPHOLOGY OF THE AREAS GOING BEYOND THE EDGE OF THE CATHODE DEPOSITS WERE OBTAINED BY ELECTRODEPOSITION UNDER FORCE INFLUENCE PROPORTIONAL TO ACCELERATION OF 140*G* (A) AND 314*G* (B). THE FORCE IS DIRECTED FROM TOP TO BOTTOM

A feature of configuration of nickel deposits under force influence parallel to their crystallization front is wave-like form of the far edge of the deposit at the direction of a centrifugal force action (Fig. 10 a). This form of the edge of the deposit is similar to wave-like form of the edge of copper deposit (Fig. 10 b). However, it is formed not as a result of growth of dendrite areas but due to the gathering of globular particles at the edge of the deposit. In Fig. 10 a, it is clearly seen that some globular particles are ingrown in nickel matrix which is an indication of its solidification from liquid state. This ingrowing effect intensifies at high overloads.



a b

FIG. 10 SCANNING ELECTRON MICROSCOPY IMAGES OF THE FAR EDGE OF NICKEL (A) AND COPPER (B) DEPOSITS ILLUSTRATING FEATURES OF THEIR CONFIGURATION UNDER FORCE INFLUENCE PROPORTIONAL TO ACCELERATION OF 140*G* (A) AND 1256*G* (B) THE FORCE IS DIRECTED FROM TOP TO BOTTOM

It should be mentioned that with the increase of overload during metals electrodeposition, the quantity of glassy fragments of solidified foam ingrown in the edges of the areas beyond the cathode increases (Fig. 6, c-f; 7, b-d; 8, c, d; 9, b and 10, b). Nickel deposits in contrast to copper ones contain such inclusions not only in the edges but also on the surface of the areas near the edges. For example the glassy inclusions partially ingrown in nickel matrix are shown at Fig. 11.

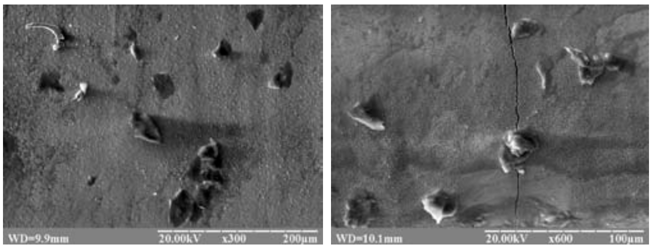


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FIG. 11 SCANNING ELECTRON MICROSCOPY IMAGES OF GLASSY INCLUSIONS ON THE SURFACE OF NICKEL ELECTRODEPOSITS CENTRIFUGAL FORCE IS PROPORTIONAL TO ACCELERATION OF 314*G* (A) AND 872*G* (D) AND DIRECTED FROM TOP TO BOTTOM.

Thus, a change of form of metals electrodeposits during their electrochemical deposition under force influence parallel to the crystallization front proves that metallic materials being electrodeposited pass through a stage of liquid state.

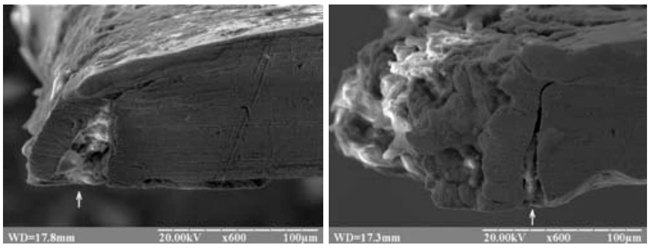
Idea Four and Its Realization

Assume that a metallic material during electrochemical deposition really passes through a stage of liquid state, then under the influence of a centrifugal force parallel to the crystallization front on the clusters of atoms, which have not yet formed a three-dimensional lattice typical for crystal state, it should be expected their movement at some distance at the direction of the force action. As a result of such movement, the combination of the clusters of atoms into larger formations (so called micro-droplets) will be easier. Such micro-droplets will form layers of liquid phase continuously replenishing during electrodeposition. At the increase of mass and size of liquid layers their shift in the direction of action of a centrifugal force will increase.

If the discussed phenomenon is valid, then at significant value of a centrifugal force acting parallel to the crystallization front it should be expected the movement of liquid layers toward the edge of the cathode and then beyond the edge of the cathode and next beyond the edge of previous solidified layers of metals being electrodeposited. This will cause predominant development of a deposit of a metal being electrodeposited beyond the edge of the cathode in the direction of the force action.

For the investigation of features of formation of the deposits of copper and nickel their cross-sections along the direction of a centrifugal force action were prepared. The deposits, obtained in the centrifuge under similar conditions but when the rotor was at rest (i.e. at $k = 1$), were used as reference samples.

As a result of completed investigations, the effect of predominant development of deposits of metals being electrodeposited beyond the edge of the cathode at the direction of the force action parallel to the crystallization front was found. Thus, in Fig. 12 a, it is seen that the edge of copper deposit, obtained under usual conditions on thin nickel cathode has almost the same thickness on all its areas. At that the edge of copper deposit peeled off the end of the cathode due to low adhesion (peeling spot is shown by an arrow).



a b

FIG. 12 SCANNING ELECTRON MICROSCOPY IMAGES OF THE CROSS-SECTION OF THE FAR EDGE OF COPPER DEPOSITS ALONG THE ACTION OF A CENTRIFUGAL FORCE PROPORTIONAL TO ACCELERATION OF 1*G* (A) – INITIAL CONDITION AND 872*G* (B), DEMONSTRATING THE EFFECT OF DEVELOPMENT OF THE DEPOSITS OF METALS BEING ELECTRODEPOSITED BEYOND THE EDGE OF THE CATHODE UNDER THE FORCE INFLUENCE THE FORCE IS DIRECTED FROM THE RIGHT TO THE LEFT

The image of cross-section of the edge of copper deposit formed under the influence of a centrifugal force of a significant value (Fig. 12 b) also indicates peeling off the edge of the deposit at the end of the cathode (peeling spot is shown by an arrow). But a form of the edge of this deposit is significantly different from the edge of usual deposit. The difference is the growth of its length by more than 100 μm along the force action (Fig. 12 b). Such result indicates that copper deposit during its electrodeposition was developing under the influence of a centrifugal force beyond the edge of the cathode.

If to compare thickness of the deposits electrodeposited in the field of a centrifugal force at various distances from the far edge of the cathode, significant thickening of the deposits in the direction of the force action is obvious. Thus under usual conditions of electrodeposition thickness of copper deposit at various distances from the far edge of the cathode is almost the same and equal to 10 μm (line 1 at Fig. 13).

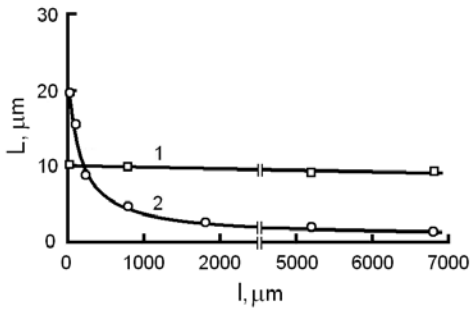
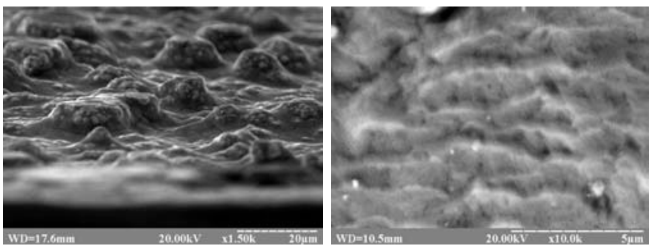


FIG. 13 CHANGE OF THICKNESS OF ELECTRODEPOSITED COPPER DEPOSITS (*L*) WITH AN INCREASE OF THE DISTANCE FROM THE FAR EDGE OF THE CATHODE (*L*) DEPOSITS WERE OBTAINED UNDER THE ACTION OF A CENTRIFUGAL FORCE PROPORTIONAL TO ACCELERATION OF 1*G* (1) – INITIAL CONDITION AND 1256*G* (2)

Under the action of a centrifugal force the deposits being electrodeposited thicken significantly toward the edge of the cathode at the direction of the force action (curve 2 at Fig. 13). Thus at the distance of 6800～1840 μm from far edge the thickness of the deposit obtained at overload of k = 1256 is just 1.58～2.55 μm, and with a decrease of l values to 800 and 230 μm the deposit thickens up to 4.88 and 9.09 μm respectively. And at the minimum distance from the far edge of the cathode (20 μm) the value of thickness of this deposit is two times as large as respective value of the deposit obtained under usual conditions (Fig. 13).

Such significant thickening of the deposits at the direction of the action of a centrifugal force can be explained by the combination of the clusters of atoms, which are in liquid state, in micro-droplets forming layers which move a metal being electrodeposited toward the edge of the cathode in a wave-like manner. Thus as an example in Fig. 14, metallic waves formed on the surface of the deposit of copper being electrodeposited at overload of k = 1256 are shown.



a b

FIG. 14 SOLIDIFIED WAVES OF LIQUID PHASE OF COPPER DEPOSIT BEING ELECTRODEPOSITED UNDER THE INFLUENCE OF A CENTRIFUGAL FORCE ACTING PARALLEL TO THE CRYSTALLIZATION FRONT WITH ACCELERATION PROPORTIONAL TO 1256*G*: A – SIDE VIEW (THE FORCE IS DIRECTED FROM THE RIGHT TO THE LEFT), B – TOP VIEW (THE FORCE IS DIRECTED FROM TOP TO BOTTOM)

It should be mentioned that wave-like flow of surface layers of metals being electrodeposited is the main motion of their liquid phase under the influence of a centrifugal force. Though, besides wave-like flow of layers of metals being electrodeposited (Fig. 15 a) overflow of layers (Fig. 15 b), their foaming (Fig. 15 c) and ripples on their surface (Fig. 15 d) occur depending on values of overload.

At Fig. 15 globular solid particles of copper deposit, moving under the influence of a centrifugal force toward the edge of the cathode, are seen. With an increase of overload the size of particles, moved relative to the deposit surface, increases significantly. Ingrowth of particles in the matrix (Fig. 15 a, b) and configuration of the vacant places, that were previously occupied by such particles (Fig. 15 b), indicates solidification of copper matrix from liquid state.

Similar results were also obtained during investigations of development features of nickel deposits being electrodeposited beyond the edge of the cathode in the direction of the force influence. Therefore, predominant development of deposits of metals being electrodeposited beyond the edge of the cathode in the direction of the action of a centrifugal force parallel to the crystallization front is a sufficient confirmation of the validity of the discussed phenomenon.

Thus, the obtained results prove the validity of the phenomenon of phase formation through a stage of liquid state in metallic materials being electrodeposited.

Conclusions

The found effect of increase of density of metals being electrodeposited under the influence of a centrifugal force directed perpendicular to the crystallization front confirms the validity of the phenomenon of phase formation through a stage of liquid state in metallic materials being electrodeposited. Wave-like flow of surface layers of metals being electrodeposited under the influence of a centrifugal force acting parallel to the crystallization front as well as bending of waves by mechanical hindrances and formation of foam on the crests of waves prove the validity of this phenomenon. Change of form of the deposits of metals being electrodeposited under the influence of a centrifugal force including the growth of length and thickness of the deposits at the direction of force action with a modification of their configuration depending on overload values prove the validity of the discovered phenomenon. Predominant development of deposits of metals being electrodeposited beyond the edge of the cathode in the direction of the action of a centrifugal force parallel to the crystallization front confirms the validity of the discussed phenomenon.

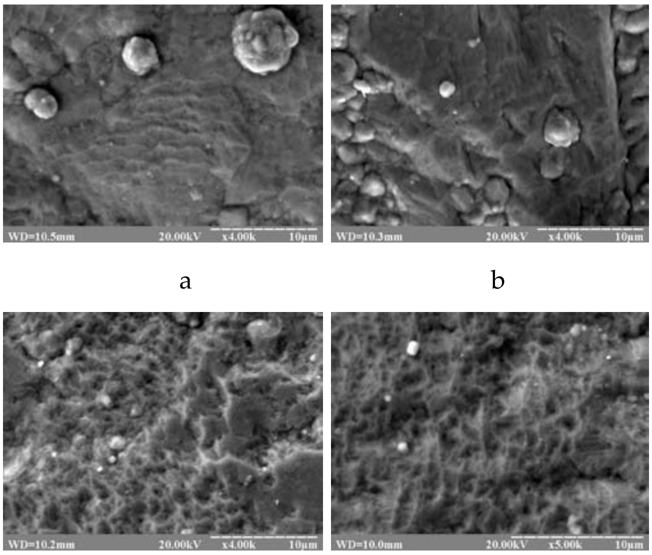


FIG. 15 SCANNING ELECTRON MICROSCOPY IMAGES OF THE SURFACE OF COPPER DEPOSITS BEING ELECTRODEPOSITED UNDER THE INFLUENCE OF A CENTRIFUGAL FORCE, ILLUSTRATING MORPHOLOGY OF SOLIDIFIED LIQUID PHASE DEPENDING ON OVERLOAD VALUE: A AND B – OVERLOAD IS 1256, C AND D – 558 THE FORCE IS DIRECTED FROM TOP TO BOTTOM

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Oleg B. Girin was born in Dnipropetrovsk region, Ukraine in 1952. In 1974 he graduated with honors from technological faculty of Dnipropetrovsk Metallurgical Institute and started his post-graduate course. In 1977 he completed the post-graduate course, and in 1990 ahead of the schedule – his doctorate course at this institution defending his doctorate's dissertation by specialty of "Physical Metallurgy and Heat Treatment of Metals". He has PhD (1981) and DSc (1991) degrees, certificates of Senior Research Fellow (1992) and Professor (2002).

During 1977-1998 he worked at Dnipropetrovsk Metallurgical Institute as junior (1977-1981), senior (1981-1991) and leading research fellow (1991-1998). Since 1998 he has been working at Ukrainian State University of Chemical Technology as the HEAD OF THE MATERIALS SCIENCE DEPARTMENT, that was established with his direct involvement, and since 2010 – as the VICE-RECTOR OF SCIENCE. Main directions of his scientific activity are the investigation of laws of structure formation of metallic materials and the development of advanced technologies for obtaining of coatings with enhanced properties. Under his scientific supervision the advanced technologies for producing new types of protective coatings on metal-roll were developed and the special-property composite film materials were created. He obtained priority results in investigations of influence of nanocrystal, amorphous and oriented structure on the properties of electrochemical coatings.

Prof. Girin has won a worldwide recognition as a scientist. Under scientific supervision of Prof. Girin and with his involvement three international competitions of R&D projects financed by the governments of the USA, Canada and the European Union have been won. He has been elected as an active member of the New-York Academy of Sciences (1997), TMS (1995), ASM (2004) and ECS (2005). For the outstanding contribution to electrochemical materials science and unique developments in the field of special materials science Prof. Girin was awarded with The International Einstein Award for Scientific Achievement (United Kingdom, 2011), the Order Badge "K.K. Rokossovsky" (Russian Federation, 2011), the medal "Great Minds of the 21st Century" (USA, 2011), the medal "2000 Outstanding Intellectuals of the 21st Century" (United Kingdom, 2010), the certificate "Decree of Merit" (United Kingdom, 2010), the Certificate of Honors of the Cabinet of Ministers of Ukraine (2005), the Badge of Honors "For Scientific Achievements" (Ukraine, 2005).