Nanodiamonds in magnetic recording system technologies

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The features of codeposition process of Ni, Ni–Fe, Co–P, Co–Fe–P, Ni–P, Ni, and Cu matrixes with ultra dispersed diamond particles from sulphate, chloride, acetate, glycine, citrate, sulphamate bath were investigated in view of magnetic recording systems application. The cation and anion surfactants were used to study the liophobic colloid systems and the behavior of ultra fine particles, to prevent agglomeration and sedimentation and to control the particle incorporation into metal matrix. Mechanical properties of composite films were described from the point of view of applications in high-tech devices. It was determined that wear resistance increased 2–2.5 times, microhardness increased 2 times, coefficient of friction and corrosion current were reduced by factor 1.5 and 1.6 respectively.

Application of nanodiamond particles in technology of composite functional layers of hard disks, magnetic heads, micromotors, and micromechanical components allows increasing reliability of storage information systems considerably.

1. Introduction

The problems of static and dynamic friction, as well as wear of functional layers are fundamental for high-tech devices and magnetic recording systems, in particular for magnetic hard disks, heads, micromotors, and micromechanical systems of positioning. It is connected with the rising requirements of the record density (longitudinal and track), the decrease of the bit dimensions and minimization of displacements and errors [1].

One of the approaches to solve the problem of friction and wear of mechanically moving elements of micron dimensions for high-tech devices is the use of the composite materials, in particular, codeposited metal and alloy with inert hard particles by electroless or electrochemical processes [2–5]. The methods of electrochemical synthesis of magnetic films for magnetic recording systems are well known since sixties [6]. From the period, this method was considered to be a competitive with vacuum methods of film deposition. The same situation took place in the mentioned period related to hybrid and silicon ICs. However finally, it became obvious for both cases that the every method should be considered in viewpoint of concrete application field. At present, the electrochemical methods due to their obvious advantages allow for fabrication of magnetic films not only in the traditional fields of application (magnetic tapes, disks, heads). One of the most exciting applications of the electrodeposition methods is the MicroElectroMechanical system that has a tremendous potential in future. Now, the micromotors are already created and used in storage devices for precise positioning magnetic heads. Indeed, the peculiarities of the electrodeposition process make possible fabrication of high-quality 3D structures (LIGA Process) [7].

The aim of the present work is to carry out integrated researches on technology and application of composite soft and hard magnetic films, as well as composite conducting films with inclusion of nanodiamond particles.

2. Experimental details

The electrodeposition of composite coatings containing ultra-fine diamond particles was performed from sulfate, glycine, acetic, and Watts bathes. Soft magnetic (NiFe, CoFeP, CoP) and hard magnetic (CoNiP, CoW, CoP) alloys as well as conductive matrix of Cu and Ni were investigated. The influence of the ampholyte (pyridine carboxylic acid, aminoacetic acid), cation-active (monoethanol amide), anion-active (CTAC, SLS) was estimated. Concentration of ultra-fine diamond particles was varied from 0 to $20\,\text{g} \cdot \text{dm}^{-3}$ (dry substance). Nanodiamond particles were obtaines by a detonation process [8].

The amount of codeposited ultra–fine diamond particles was determined both by integral Couloumbmetric analysis with the express analyser AH-7529 (USSR) and by local Auger spectroscopy (PHI-660 Perkin Elmer Corp., USA). The Vickers microhardness of coating was measured at a load of 0.5N with MICROMET-II (Buehler-Met, CH). The structure of the deposits was examined by TEM (EM-125, USSR). The coefficient of friction and the wear were evaluated by a FRETTING II test machine (KU Leuven, BE) [9]. A ball-on-flat geometry was used for the low amplitude oscillating sliding wear tests. Corundum balls of 10 nm diameter (Ceratec, N1) were loaded on top of the vibrating surface of samples with constant normal force of 2N. Displacement strokes of 100 and $500\,\mu$m were used at frequencies of 8 and 2 Hz respectively. The tests were performed in ambient air at 20°C and a relative humidity of 50%. Wear volumes were estimated by the RM600 laser profilometry (Rodenstok, D) after 100 000 fretting cycles.
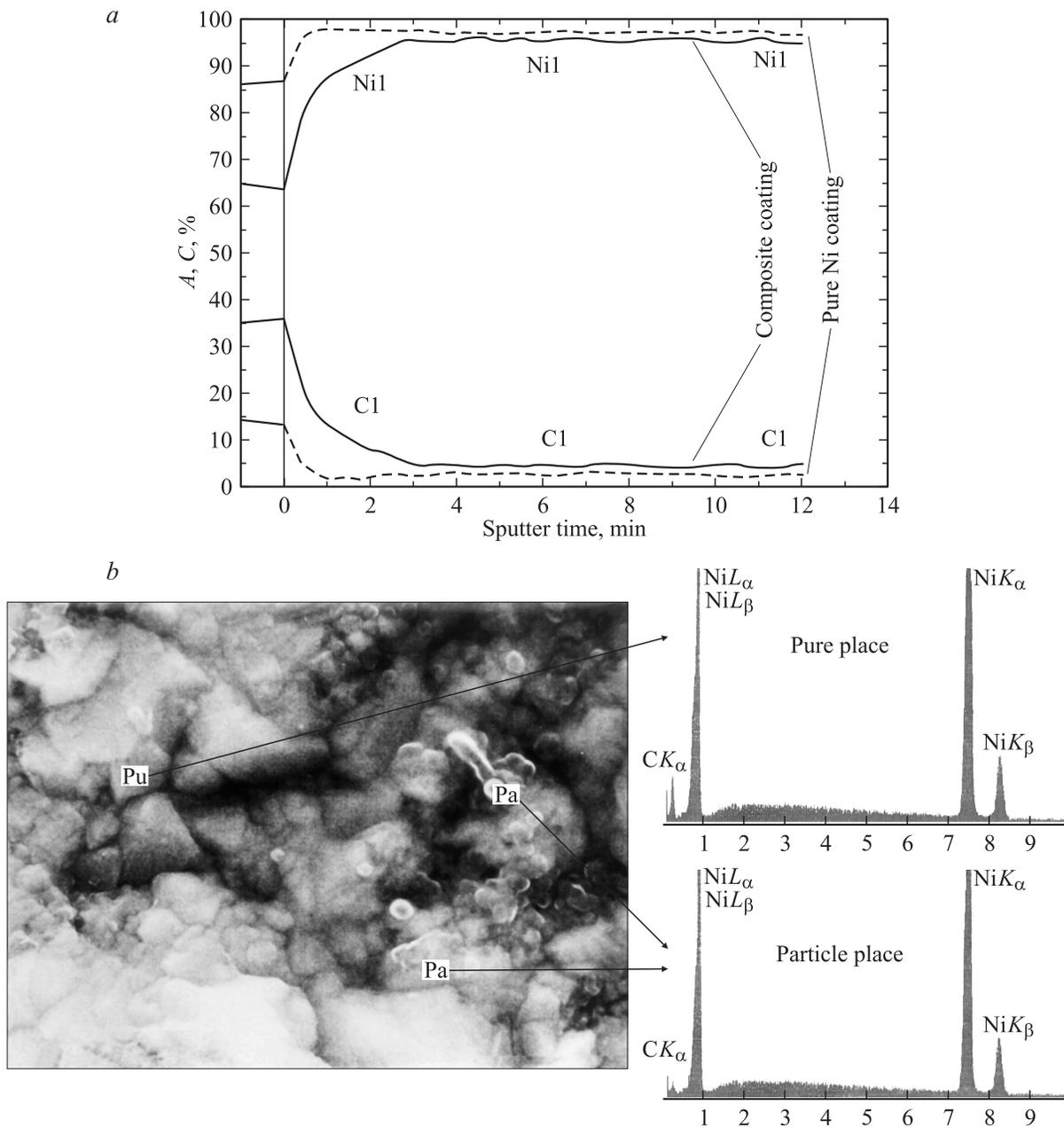
Figure 1. AES sputter-etch elemental profiles (*a*) and local *X*-ray analysis (*b*) of pure and composite Ni coatings containing nanodiamond particles.

3. Results and discussion

In general, during the electrolytic codeposition, the suspended diamond particles interact with the surface of the growing film due to hydrodynamic, molecular and electrostatic forces [9]. This complex process results in the formation of composite coatings. Auger profiles and local *X*-ray analysis demonstrate that ultra-fine diamond particles are effectively incorporated into the meal matrix (Fig. 1).

Visually the composite coatings have grey apppearance. Pitting was not noticed on the surface. A structural investigation shows (Fig. 2) that pure Ni coatings contain twins, dislocation aggregates inside the grains, and a concentration of solitary dislocations and dislocation walls of 20 nm thick along the grain boundaries. The average grain size is about 500 nm. As for composite coatings the grain size reduces up to 30−100 nm. An accumulation of ball-type dislocations along the grain boundaries takes place. Thus, for the first time it was determined that during codeposition of matrix and nanodiamond particles, nanocrystalline Ni electrodeposites were formed. The electron diffraction patterns of the coating confirm the presence of cubic carbon according to ASTM 6-675, indicative of the incorporation of diamond particles into the nickel matrix.

Pure Ni coating Ni–diamond (type III, 75% : 25%) composite coating
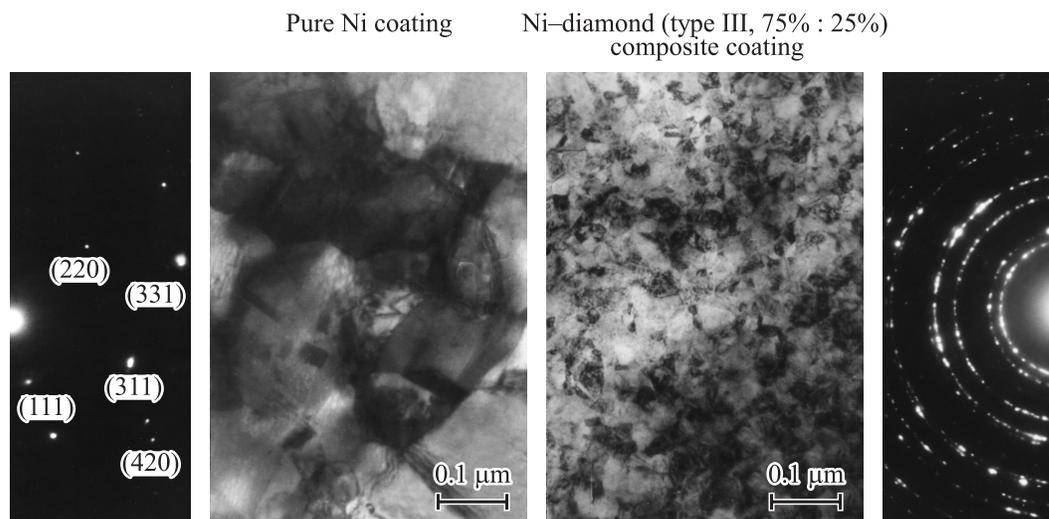
Figure 2. TEM micrographs of pure and nanocrystalline composite Ni coatings [5].

Based on the experimental data [5], the qualitative codeposition model of the composite coatings with the ultra-fine particles is proposed. The peculiarities of the ultra-fine particles behaviour are considered in the model. The model worked out is based on the assumption the codeposition of ultra-fine particles proceeds through the following stages (Fig. 3):

1) coagulation of ultra-fine particles in plating solution;

2) formation of quasi-stable aggregates and therefore change of system dispersion constitution;

3) transport of the aggregates to the cathode surface by convection, migration and diffusion;

4) disintegration of the aggregates in the near-cathode surface;

5) weak adsorption of ultra-fine particles and aggregate fragments onto the cathode surface;

6) strong adsorption of spersion fraction (embedment).

Hydrophobic colloidal systems are thermodynamically unstable due to the surplus of the surface energy. They exist owing to stabilization by protective ionic and molecular layers. In general, in the bulk of suspension the particles encounter one another due to the Brownian movement, gravity and convection. The forces between them determine whether the encounters result in sticking the particles or the particles remain free.

Behaviour of dispersed systems is described by the DLVO theory. Stability or coagulation rate of suspensions depends on sign and magnitude of the overall potential energy of interaction between the particles. Positive electrostatic repulsion energy $U_r(h)$ decreases by exponential law, whereas negative molecular attraction energy $U_a(h)$ is in inverse proportion to squared distance. As a result, at small distances ($h \to 0$, $U_r(h) \to \mathrm{const}$, $U_a(h) \to -\infty$) and large distances (exponent diminishes much rapidly than power function), the attraction energy between the particles prevails. The electrostatic repulsion energy pre-

vails at intermediate distences. The primary minimum 1 corresponds to direct sticking of particle. In the case, the particles are irreversibly stuck (coalescence). The secondary minimum 2 corresponds to attraction through interlayer of invironment. It this case, the aggregates may be counteracted relatively easily. The maximum corresponding to intermediate distances characterizes the potential barrier, which prevents sticking the particles. Forces of interaction are extended for hundreds of nanometers.

In the consideration of interaction between the particles, the following conclusions from the DLVO theory should be mentioned as well. The height of the energy maximum and the depth of the primary and secondary maxima depend on the parameters of the systems, namely the zeta potential,
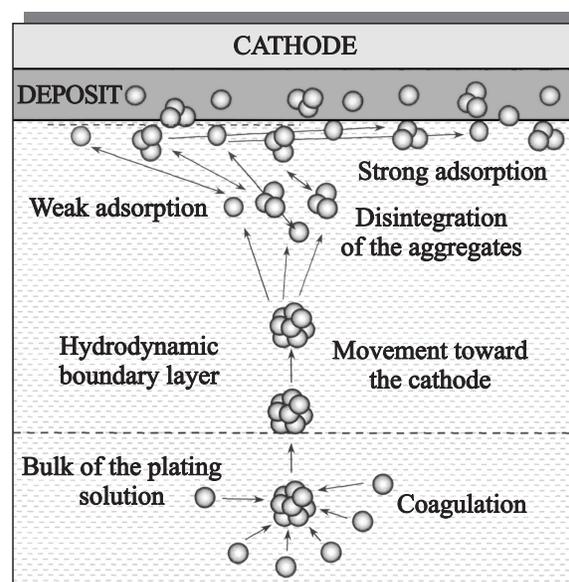
Figure 3. Mechanism of coodeposion of metal matrix and nanodiamond particles.

particle size, electrolyte concentration (and valence) and the Hamaker constant. At low electrolyte concentrations, the energy maximum may reach high values and this prevents the particle aggregation. At increase of the electrolyte concentration, the height of the energy maximum decreases and disappeares at a critical concentration (which depends on valence of electrolyte). The coagulation becomes more rapid. Thus, to enhance the suspension stability, one needs to reduce the electrolyte concentration and increase the zeta potential.

The transport of the particles toward the cathode surface occurs by convection, migration, diffusion, and the Brownian movement.

Migration is the movement of cations, anions or charged particles through the solution under influence of the applied potential between the electrodes in the solution. Diffusion is the second process. Electrode reaction deplete the concentration of oxidant or reluctant at en electrode surface and produces a concentration gradient there. This gives the rise to the movement species from the higher to the lower concentration. Unlike migration, which only occurs for charged particles, diffusion occurs for both charged and uncharged particles. Convection includes thermal and stirring effects, which can arise extraneously through vibration, shock and other types of stirring and temperature gradients. At last, the Brownian movement, as known, is affected strongly by the particle size, and may be neglected in the case of the particles size is above 1μm.

The stirring mode is required to be the transition mode between the turbulent flow and the laminar flow in the bulk of plating bath. Such a mode is of most practical significance. It is because the laminar flow does not provide the sufficient stirring of the electrolyte suspension. Alternatively, at the stirring rate corresponding to the turbulent mode, the conditions preventing totally the particles embedment appear.

In the near-cathode region, the aggregate is influenced by the forces of different nature and direction. Motion of the aggregate is determined by resultant force, and integrity of aggregate — by sum of forces values as well. For the investigated system, the following forces are considered:

1) mechanical forces, associated with interaction with the fluid flow and other particles, gravity and buoyancy;

2) electrical forces, connected with the electric field that presents in the plating solution during electrodeposition process;

3) molecular forces acting on the particle in the vicinity of the cathode surface.

Mechanical forces. At the laminar liquid flow in the boundary hydrodynamic layer the law of viscous friction is followed in this region, and the boundary conditions are following: $V = 0$ at $y = 0$ and $V = V_0$ at $y = \infty$.

If the particle moves in the flow having the transverse velocity gradient of liquid movement, the rotation motion can be imparted to the particle because the different velocities of flow past a particle from the top and from the bottom. The transverse particle migration appears as the result of the rotational motion. The transverse particle migration results from pressure drop on the side where the sum of the tangential velocity components of flowing past and rotating the particle reaches the maximum. The transverse particle migration is directed always toward this maximum. In the case being considered particle moves away from the cathode surface.

When the particle is trapped by cathode, the longitudinal force by flow the plating solution affects the particle. If this force exceeds the friction force keeping the particle onto the cathode surface, the particle is detached from the growing deposit.

Besides the forces connected to interaction between the particle and hydrodynamic flow, the gravity and buoyancy contribute to the particle motion. The sum of forces by gravity and buoyancy results in the sedimentation force.
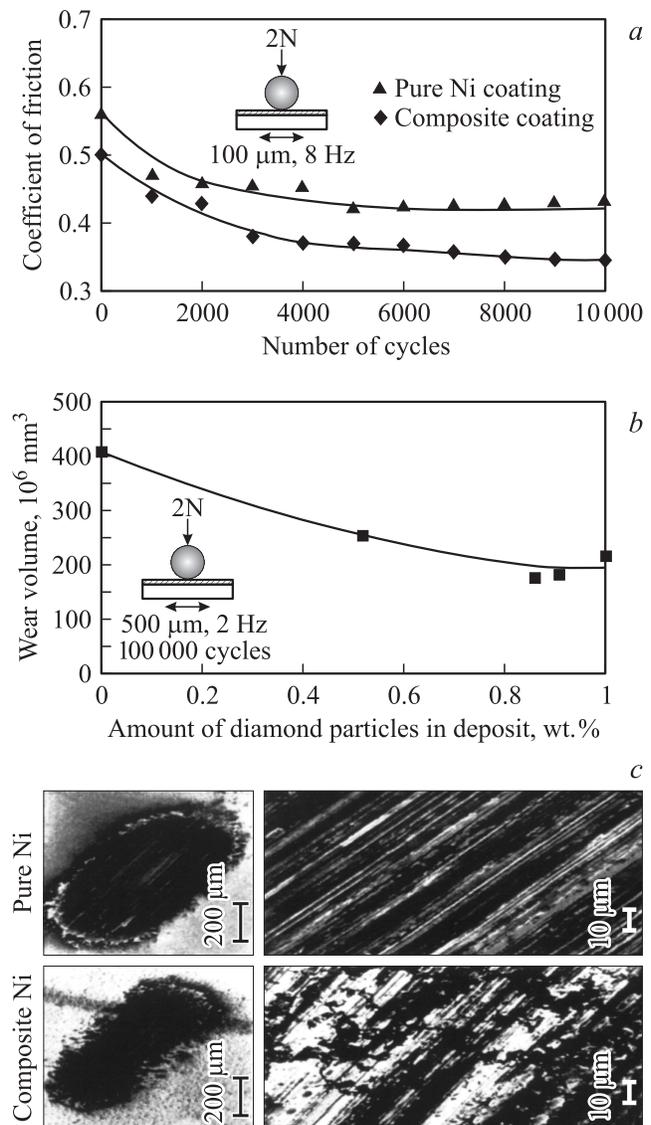
Figure 4. Physico-mechanical properties of the composite coatings: *a* — coefficient of friction, *b* — wear volume, *c* — SEM images of wear scars after $100\,000$ fretting cycles.
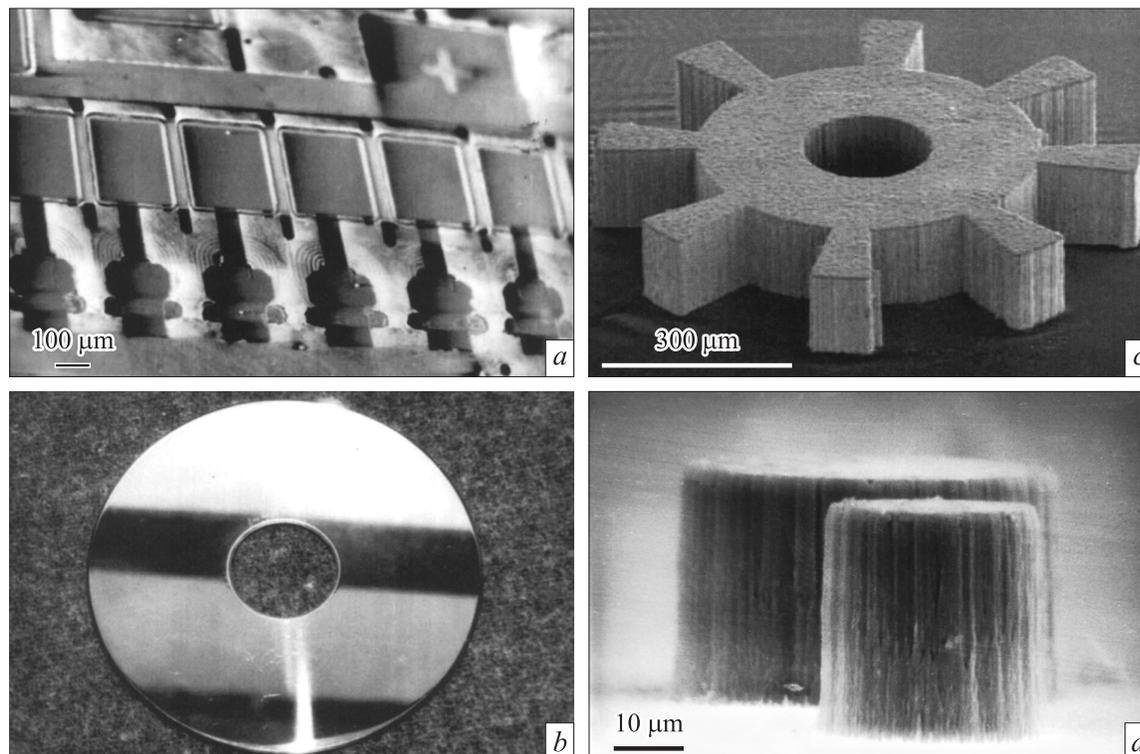
Figure 5. Some applications of nano-diamonds in magnetic recording systems: a — thin film magnetic heads; b — hard disk; c, d — MEMS elements [11].

Collisions between the particles in the near-cathode region may change the particle trajectory promoting or preventing the particle movement to the cathode. Moreover, the particle in the electrolyte may collide with the particle trapped by the cathode and prevent embedment.

Electric forces. The ions in the double layer around the particle interact with the electric field in the plating solution. This results in the particle motion along the lines of electric field. The motion is affected by the fluid permitivity, particle size, intensity of electric field in the particle place, and zeta potential. The sign and value of the zeta potential is determined by both the particle nature and the electrolyte constitution and can be changed by addition of surfactants into the plating solution. In the near-cathode region, the cathode itself affects ambiguosly the electrophoretic particle motion. On the one hand, modification of the electric field lines in the near-cathode region slows down the particle movement, and on the other hand, the cathode surface itself increases the intensity of the electrophoretic movement. It should be emphasized that it is not possible measurement of zeta potential in the near-cathode region because it depends on many factors and can change no only value but the sign as well. Therefore, it is difficult task to evaluate the contribution of electrophoretic particle motion into the codeposition process.

In the near-cathode region, the osmotic pressure of the electrolyte affects the particle motion. The electroosmotic motion is the phenomenon of liquid movement through porous body under application of electric field. Assuming the particles in the near-cathode region as porous bodies, the ionic species move through this „body" due to the electric field in the plating solution. In its turn, the ion flow exerts the pressure upon the particles and assists the particle movement toward the cathode surface. It should be mentioned that the electroosmotic motion of particle is influenced by those parameters as for electrophoretic motion (see above).

Molecular forces. At the immediate vicinity of a cathode surface the van der Waals attraction force appears. It occurs with all types atoms or molecules. It arises from the charge fluctuations within an atom or molecule that is associated with the motion of its electrons.

A strong repulsive force appears at short distances, when the electrolyte concentration exceeds a certain value. This force is called the structural or hydration force. It originates from the fact that the thin solvent layer presents near the interfaces. This solvent layer is ordered by hydration of cations adsorbed onto surfaces as the interfaces approaches each other. The hydration force results from change in the structure of solvent between the interfaces and prevents interfaces from close approach.

As particles aggregate approaches the near-cathode region, the force field increases. If these forces exceed a certain certain critical value, which keeps the particles in the aggregated state, the aggregates are disintegrated. Further, the solitary particles and the aggregate chips interact

with the cathode and can be adsorbed weakly onto the cathode. The weak adsorption step assumes the interaction between the particle and cathode surface through adsorbed layers of ions and solvent molecules. Further, the electric field helps to uncover the particle. The thin interlayer between the cathode surface and particle disappears. It leads to the strong field-assisted adsorption and the particle is overgrown with deposit.

Related to functionality, the most important ptoperties are friction and wear resistance. For the composite systems, mechanical properties are determined by the phase composition of materials, i.e. the matrix / particle ratio. The dependence of the amount of codeposited diamond particles on particle concentration in the plating bath (Fig. 4) shows that the investigated system may be described by Guglielmi's model [10]. The evolution of the coefficient of friction is shown in Fig. 4. Among the coatings tested, composite nickel coatings containing ultra-fine diamond particles show the lower coefficient of friction. The wear volume for pure Ni and composite coatings is shown for fretting tests operated for 100 000 cycles. The amount of particles in the coatings affects the wear rate. The friction behaviour of multiphase materials has been described in the literature. The main problem with these approaches is that they are static ones and applied to ideal surfaces because during wear of a multiphase material the topography changes in practice continuously. Localised wear of the matrix takes place in the first phase. After that, the particles become more loaded. This dynamic process may lead to an increased wear resistance of composite materials. Of course, the fretting wear properties of coatings are also influenced by the size, shape and distribution of the reinforcing phase.

Some composite elements of the magnetic recording systems are shown in Fig. 5.

4. Conclusion

This investigation on composite coatings containing nano-diamond particles has led to the following scientific results and common conclusions.

1) The grain size of electrolytic nickel coatings is affected by the codeposition of ultra-fine diamond particles. Nanocrystalline Ni deposits may be formed by codeposition of ultra-fine diamond particles.

2) The microhardness of the composite coatings increases up to $420 \, \text{kg} \cdot \text{mm}^{-3}$ (250 for pure metal).

3) Embedment of ultra-fine diamond particles results in both decreasing the coefficient of friction from 0.43 to 0.33 and increasing the wear resistance by a factor of 2.

4) Composite films with nanodiamond particles obtained may be applied for components of magnetic recording devices and elements of the MicroElectroMechanical systems.

5) Tribology problem (friction, wear, lubrication) for high-tech devices, in general, and for magnetic recording systems, in particular, is the fundamental problem. In future the place of micro- and nano-tribology will be more important. The solution of the trybology problem for high-tech devices can be made by joint efforts of scientists working in the field of nanodiamond manufacture, design of the devices, technology of composite coatings.

6) Application of composite electrochemical coatings and layers, in general, and nanodiamonds, in particular, solves the tribology problem. As for MicroElectroMechanical systems application of composite coatings and layers is the only way.

7) Particle incorporation of the fine, compared with geometric limits, homogeneous sizes for mechanical high-tech devices — the key task to apply the composite coatings in the moveable micromechanical systems.

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