**Lecture 6.**

**Surface properties of nanoparticles.** **Adhesion of nanoparticles. Adhesion and wetting of nanodroplets.**

Adhesion (cohesion) is the interaction between heterogeneous condensed phases at their molecular contact.

 An *adhesive* is a substance that sticks to surface or a *substrat*e. There is an adhesion of particles, liquids, films and structured (elastically viscous plastic) bodies. In the case of nanosystems, an adhesion of nanoparticles and films based on them will be considered.

The schemes of components and assemblies of radio engineering devices (conductors, insulators, capacitors, transistors, connecting elements) are formed as a result of adhesion of nanoparticles which provides miniaturization of these devices. Adhesion in some cases contributes to the stabilization of nanoparticles. Due to the high surface activity, the nanoparticles cannot exist separately; adhesion maintains the nanoparticles on the surface.

Adhesion of nanoparticles, in contrast to the adhesion of macroparticles, mainly depends on the method of formation of adhesion interaction, namely:

– application of nanoparticles with subsequent pressing of their layers (Fig. 1, a,b);

– formation of layers on the surface and inside the solid during the formation of the nanoparticles (Fig. 1, c, d);

In the first case the adhesion is formed by the applying of nanoparticles or their formation due to condensation, and in the second case by the molecular build-up inside of substrate, when nanoparticles arise as a result of external action (pressure, friction, etc.).



Figure 1 – The location of nanoparticles at adhesion

Under formation of a film from nanoparticles, the nucleation begins initially by condensation of steam or crystallization from the solution. Then, the growth of nucleus without their number increasing until the formation of nanoparticles. Subsequently, they can aggregate by coagulation of particles, or coalescence leading to the fusion of droplets and by crystallization.

Moreover, there is an autohesion of particles, that is, the interaction between particles that occurs spontaneously due to excess surface energy, diffusion and other processes, as well as under the influence of external factors (pressure, electromagnetic field, etc.)

It is possible the using of nanoparticles on the surface of larger particles, the adherent layer shields their surface and gives them the specific properties. So, nanoparticles of polystyrene screens the surface of the mica. Because of pressing, and under influence of high temperature, particles are sintered, when the phase boundary between the nanoparticles disappears, and the adhered film turns into a monolith. The disappearance of phase contacts can occur due to a chemical reaction, in particular, by the reduction of oxide films (Ni, Cu Al). For NiO2, this process proceeds as follows:

2NiO2= 2NiO + O2

A strong fixing of the nanoparticles and the formation of film on the surface due to adhesion causes the stabilization of the adhesive-substrate system.

Thus, particles of crystalline iron settled by means of low-temperature plasma of heptane were fixed at a pressure of 50 MPa. The height of the adhered film was 50 nm. The structure formed inside the body due to the tribo-effect and mechanic activation of nanoparticles has the form of flakes of irregular shape.

When polishing the surface of a film of silicon oxide from nanoparticles they are pressed into a rough surface.

Adhesion of nanoparticles depends on the conditions of their contact with the surface and further interaction.

The metals introduced into the polymeric nanoparticles contribute to the formation of a chemical bond between metal atoms and the individual functional groups of polymers and enhance the adhesive strength. The adherent layer of nanoparticles (Al2O3, TiO2) increases strength of the products by four times. Nanoparticles of metals as an adhesives change the electrical properties from the dielectric to the conductors, consequently, the electrical resistance decreases from 1011-1014 to 10-5-10-4 Ohm·m. This decreasing causes a change of the electrostatic interaction between the substrate and the adhesive.

At the formation of composites based on copper nanoparticles (20-30 nm) and formaldehyde and epoxy resines the systems with properties close to metallic have been obtained. The composites have electrical conductivity as well as composites based on polyesters filled with nickel nanoparticles. They can be used as electrodes for carrying out an electrochemical reaction, including reactions in alkaline media.

The above examples indicate a change not only the surface properties of the adhered films, but also their bulk characteristics.

The features of the adhesion of nanoscale particles also are characterized by size effect and by excess of surface energy.

The value of adhesion is determined by the adhesion force characterizing the bonding between the particle (adhesive) and the surface (substrate). The size effect can be expressed by the relative force of adhesion Frel ad  – a ratio of the adhesion force of one nanoparticle Fad per unit of volume V:

*Frel ad =* $\frac{F\_{ad} }{V}$(1)

The adhesion force Fad of nanoparticles is negligible and is estimated by tens of nanonewtons, that is, 10-9 N.

The force of adhesion of nanoparticle with diameter of 10 nm and macroparticle with diameter of 10 µm or 10·103 nm is presented in Table 10.

Table 1.

|  |  |  |  |
| --- | --- | --- | --- |
| Diameter of particles, nm |  | 10 | 10·103 |
| Force of adhesion, nN |  | 10-9 | 107 |
| Relative adhesion force, Frel ad |  | 1015 | 102 |

The adhesion force of nanosize particles by 16 orders smaller than the non-nanosized particles with diameter of 10 μm. However, the relative force of adhesion, taking into account the volume for nanoparticles, by 13 orders higher than for non-nanosized particles. The area of contact of nanoparticle with the surface is calculated in fractions of nm.

Thus, due to the size effect the relative force of nanoparticle adhesion is significant and is determined by an additional excess of surface energy. There are difficulties of experimental measurements of nanoparticle adhesion, especially autohesion, that is, interactions between nanoparticles. There is the influence of micro-roughness on the atomic level on the adhesion. For this reason, the adhesion of nanoparticles is determined by calculation, modeling, and indirectly in comparison with friction force. The force of adhesion Fa can be calculated from the theory of JKR (Johnson-Kendall-Roberts) according to the equation:

*Fa =*$\frac{A\_{surf}·r}{6h^{2}},$ (2)

where A is the Hamaker constant, *r* is the radius of nanoparticles, and *h* is the distance between nanoparticles and the surface (under the conditions of intermolecular interaction due to van der Waals forces, this distance can be equal to 0.165 nm).

The Hamaker constant is obtained by calculation, for example, its value for nanoparticles with a diameter of about 100 nm varies within the range (40-70) 1021 J. In addition, the Hamaker constant is defined experimentally. According to formula (16), the adhesion force can be approximately estimated and for a nanoparticle with a radius of 10 nm; it equals to 3.10-9 N, i.е. it is insignificant.

The theory of JKR does not take into account the deformation in the area of contact of particles with the surface. The theory of Derjaguin-Muller-Toporov (DMT) taking into account the deformation of the contact area of particles with the surface and the adhesion force is:

*Fad = k·π·r·W, (3)*

where W – the equilibrium work of the adhesion, *W = σ + σs – σint = 2(σs\*σint)0.5*where, *σ, σs* is the surface tension of the substrate and the nanoparticles respectively, *σint*– the interfacial tension of the substrate-nanoparticle; *k* - coefficient of proportionality, *k* – according to theory of JKR equals to 3/2, and according to the theory of DMT – 2, *r* is the radius of nanoparticle.

The adhesion force of nanoparticles can be calculated from the value of the frictional force. If the adhesion force (Fadh) prevents the detachment of particles and is directed perpendicularly to the surface of the substrate, then the friction force acts in parallel and counteracts the mutual movement of the particles along the surface. The relationship between the frictional force and the adhesion force of individual particles can be represented by the following formula:

*Ffr = µ·Fadh,*(4),

where µ –is the coefficient of external friction.

By analogy with friction of powders, the value of the coefficient of external friction can be obtained by measuring the breakaway force Fbr that goes to overcome friction. The friction force is equal and opposite to the Fbr force causing the motion of nanoparticle tangentially to the surface. Considering the equality of the breakaway force and the frictional force, instead of equation (18), we can write:

*Fbr = µ·Fadh* (5)

Thus, it is not possible to determine experimentally the adhesion of nanoscale particles. But the force of adhesion can be defined according to (19) through the force and the coefficient of external friction which can be experimentally measured.

The coefficient of external friction with respect to the nanosized particles on the surface of ceramic products varies between 0.15-0.25. The breakaway force Fbr is measured using an indexer model with probe tip radius corresponds to the size of the nanoparticles (Fig. 2). The indexer can move along a plane, concave or convex surface. To determine the relief of nanoparticle layer and nanofilm, it is possible to move the index on a surface of different shapes, then, on it, the friction force is defined as follows:

*Fconcfr  ˃ Fplfr ˃ Fconvfr* ,

where *Fconcfr , Fplfr, Fconxfr* is the frictional force on a concave, plane and convex surface, in other words, under identical conditions, the frictional force on a concave surface is maximal, but on the convex surface is minimum, but the majority of studies have been carried out with reference to a plane surface.



Figure 2 – Scheme of the indexer: 1-probe with a rounding 2 radius r; 3-adhesion on surfaces; a - plane, b - concave, c - convex.

In addition, adhesion was determined for the ratio of not a single probe of the indexer, but their sets.

Hundreds of villi were used. Each villus has a radius of curvature corresponding to the radius of nanoparticle. The force of adhesion of the considerable number of villi was determined experimentally, that allowed modeling the adhesion of a multitude of nanoparticles. Then, the force of adhesion was calculated for a single villus. The idea of using of villi for modeling the measurement of adhesion of nanoparticles is borrowed from geckos, capable of moving along vertical walls and even over the ceiling. Studies using a scanning tunneling microscope showed that the surface of each of the fingers of the animal is covered with a midge of villi with a length of 30 to 130 microns. "Microvilli" have heads ("hats") with a diameter of tens of nm.

The force of adhesion per vortex is measured in nanonewton. It is not possible to measure directly this tiny force of adhesion. Modeling the adhesion of individual villi by measuring the adhesion force of the number of villi one can evaluate the adhesion force with respect to one villi, that is, essentially to separate nanoparicle. The adhesion force depends on the ability of the surface to be wetted, i.e. hydrophilicity or hydrophobicity.

The number of villi were pressed to the aluminum surface modified: hydrophilic (contact angle equals to 42.5°) and hydrophobic (contact angle equals to 145) °. The adhesion depending on the force of the pressure changes as shown in Table 11:

Table 2

|  |  |  |  |
| --- | --- | --- | --- |
| Clamping Force, µN (10-6N) | 1000 | 2000 | 4000 |
| The force of adhesion on the hydrophilic surface, nN | 20 | 35 | 47 |
| The force of adhesion on the hydrophobic surface, nN | 5 | 7 | 16 |

As one would expect, hydrophilization of the surface contributes to the enhancement of the adhesion of nanoparticles. As with nonnanosized particles, adhesion of nanoscale particles depends on the properties of the particle surface, the pressing force of particles and other factors (humidity, temperature, etc.).

So, the data obtained by various ways (calculation, modeling, as well as by measuring the adhesion interaction of a large number of nanoobjects) showed that the nanoparticle adhesion strength is negligible and amounts to tens of nN (nano-newtons, i.e 10-9 N). Nevertheless, a strong holding of nanoparticles on the surface favors the adhesion. Adhesion depends on the mass of the particles. For this reason, it is necessary to evaluate the adhesion interaction with respect to a unit volume of adherent particles. The relative adhesion force of the particle with a diameter of 10 μm taking into account its mass equals to 103 nN. The relative adhesion force of nanoparticle of 10 nm equals to 10-15 nN, that is, by thirteen orders of magnitude higher than the absolute adhesion force. For this reason, nanosized particles have significant adhesion and are firmly held on different surfaces.

*Nanodroplet adhesion and wetting.*Adhesion and wetting of nanodroplets on surfaces are specific and differ from similar processes for macroscopic drops. Wetting as a result of the adhesion of droplets is determined by the area of their contact with the surface, it is quantitatively characterized by the contact angle.

The line along which all three interfaces (L, G or L1 and S) intersect is referred to as the line of wetting; a closed line of wetting forms the perimeter of wetting. The angle between the liquid-gas and solid-liquid interfaces, θ, is referred to as the contact angle (Fig. 19). With respect to water droplets the surfaces are called as hydrophilic (when the contact angle of wetting varies from 0o to 90o) and hydrophobic (when the contact angle of wetting exceeds 90°). For other liquids the oleophilic (0° <0 <90 °) and oleophobic (θ > 90°) surfaces are distinguished (Fig. 3).



Figure 3 – Nonnanosized drop on a hydrophilic (a) and hydrophobic (b) surfaces; Ɵ-contact angle

The Young equation characterizes the equilibrium value of the contact angle of wetting of nonnanosized droplets as a function of the surface tensions

cos θ = (σsg – σsl) /σlg, (5)

 where σsg, σsl, σlg – surface tensions (specific free surface energy) at the interface of the corresponding phases: S-G, S-L, L-G.

Equation (14) is not appropriate for nanosized drops. This is due to the size effect and the dependence of the surface tension on the droplet size. The equation of Young for nanodroplets takes the following form:

cos θ = $\frac{σ\_{sg} - σ\_{sl} -r\frac{dσ\_{sg}}{dR}- \frac{r}{2}·\frac{dσ\_{sl}}{dR}}{σ\_{sg}+r·\frac{dσ\_{lg} }{dR}}$, (6)

where, r is the radius of the drop; R is the radius of the contact area of the droplet with a solid surface: $\frac{dσ\_{sg}}{dR}$*,* $\frac{dσ\_{sl}}{dR}$*,* $\frac{dσ\_{lg} }{dR}$ is the derivative of the surface tension by the radius of contact of a drop with a solid surface characterizing the size effect.

Equation (21) for nanodroplets differs from Young equation (20) for nonnanosized droplets by the size effect, the derivatives of surface tension by the size of the contact area of the drops $\frac{dσ}{dR}$.

It follows from (21) that the contact angle depends on the size of the droplets and the contact area realized on the surface. The dependence of the wetting contact angle on the size of tin droplets on an amorphous carbon substrate (a lyophobic surface with a contact angle greater than 90°) is shown in Fig. 4.



Figure 4 – Dependence of the wetting contact angle on the radius of tin nanodroplets on an amorphous carbon surface

Similar changes were observed for bismuth nanodrops on the same surface. As follows from experimental data (Fig. 20), with an increase of the droplet radius from 2 to 25 nm, the contact angle increases sharply, and for droplets larger than 40 nm the contact angle remains constant.

In a certain range of sizes and drops, the contact angle decreases as their size decreases. The values of the contact angle obtained by various methods are in agreement with each other. The decreasing of the contact angle was also observed for lead nanodroplets on amorphous oleophobic carbon and silicon surfaces. Under these conditions the decreasing of the droplet radius from 30 to 4-5 nm leads to a decrease of the contact angle by 20-250.

The effect of the droplet volume on the wetting contact angle is taken into account by introducing into the Young equation an additional linear tension parameter that represents the excess of Helmholtz free energy per unit length of the contact line. For a drop on a horizontal substrate, the contact line is the circle of the base of the droplet of radius L.

The linear tension æ acts along a circle of radius L and gives for some finite values of L the horizontal component of the force equal to σlg·cos θ 1 (Figure 21), applied to the contact point of three phases:

*σlg·cos* θ *1 = σsg· σsl -* æ */L* (7)

For æ > 0, the linear tension decreases, and it increases for æ < 0. According to theoretical estimation, the equilibrium state of the drops is achieved at a relatively low value of the linear tension of 10-11-10-10N. The contact angles θn formed by drops of sufficiently small size should be calculated with the inclusion of linear tension in the Young equation:

*cos* θ *1 = cos* θ *o +* æ */R σlg* ,(8)

where, θ o is the equilibrium contact angle of nonnanosized droplets larger than 100 nm, æ -linear tension; σlg surface tension of the liquid at the boundary with the gas; r is the radius of the base of the drop. In accordance with the formula (23)

*cos* θn *˃ cos* θ0 (9)



Figure 5 – Structure of nanodroplets: 1 - equilibrium film; 2 - bulk, 3 - transition region

According to the condition (24), on the lyophilic (hydrophilic) surface, when *0 ≤ cos* θ***o ≤*** *1* increases, which means that on the hydrophilic surface the wetting with nanosized drops increases. On lyophobic (hydrophobic) surfaces, when -*1* ≤ *cos* θ *o < 1* and *cos* θ *1 ˃ cos* θ *o* wetting decreases for analogous conditions.

Thus, on lyophobic surfaces with a decrease of thedroplet size the wetting deteriorates (the contact angle increases, see Fig. 20), and on the lyophilic surfaces, on the contrary, decrease of droplet size improves the wetting (contact angle decreases).

In addition to contact wetting (by separate drops), nanoparticles are characterized by immersion wetting (over the surface of the solid body). The quantitative determination of immersion wetting is difficult. For this reason, the thermal effect of immersion wetting is measured. It is determined by the enthalpy (ΔH). The dependence of the contact angle value of the wetting of silica powder particles with a diameter of 12 nm on the enthalpy of immersion wetting is shown below in Table 3.

Table 3

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| cos θ | 141 | 118 | 94 | 72 |
| ( H), J/m2 | -0.09 | +0.04 | +0.02 | -0.03 |

With increasing of contact angle, i.e. with decreasing of the cosine of the contact angle, the wetting process transfer from exothermic to endothermic (the negative value is getting positive), and then again it becomes exothermic process.

So, like the adhesion of nanoparticles, wetting of nanodroplets of solid surfaces is significantly different from similar processes for macroobjects.

A certain regularity of wetting change is observed depending on the size of droplets, as well as the possibility of changing the properties (hydrophobization or hydrophilization) surfaces contacting with nanodroplets.

**Revision questions:**

1. What is the adhesion?
2. What is the autohesion? And describe the external factors that affect of this process.
3. What is the connection between adhesion and size effect?
4. How is the force of adhesion defined?
5. Describe the theory of Johnson-Kendall-Roberts.
6. Describe the equation of Derjaguin-Muller-Toporov.
7. What are hydrophilic and hydrophobic surfaces?
8. Describe the Young equation for nonnanosized droplets and for nanosized droplets.
9. What is the linear tension æ for nanodroplets?
10. What is the immersion wetting?