Features of the physicochemical processes in a metal–polymer system

A.A. Ryskulov, V.A. Liopo, S.V. Avdeichik, and L.V. Mikhailova
Yanka Kupala State University of Grodno, Grodno, Belarus

Summary
An examination is made of the mechanism of charge mosaiz formation on the surface of a polycrystalline metal particle. It is shown that two particles in contact with each other, owing to the presence of a potential barrier between them, acquire electric charges of different sign. This effect must be taken into account when assessing the adhesion, adsorption, tribotechnical, and other service characteristics of metal-polymer systems.

Introduction
According to modern ideas based on complex multifactorial analysis, metal-polymer systems comprise a combination of components interacting in the process of static or dynamic contact under certain temperature-time and load-speed regimes, the service parameters of which are determined by the kinetics and type of physicochemical processes governing the formation of products of certain composition and structure [1, 2]. Both static (adhesion) and dynamic (friction) metal-polymer contacts are characterised by a predominant type of contact process determining the nature of combined boundary-layer transformation of the composition and structure of components of the metal-polymer system. In a static system, this process determines the parameters of adhesion interaction and the life of the system under prescribed service conditions [1]. In a dynamic system (a tribosystem), the most characteristic physicochemical process determines the kinetic laws governing wear [2, 3]. Establishing the predominant physicochemical contact process and mechanisms of its control makes it possible to create substances with the properties of wear inhibitors at the contact in tribosystems [2-5] and modifying (reinforcing, antioxidative, etc.) phases leading to increase in the life of functional coatings and glue lines [6].

A characteristic feature of the physicochemical processes in different metal-polymer systems (static and dynamic) is the presence of common kinetic laws [1, 7]. At the same time, the tribochemical factor in a number of cases makes a key contribution to the combined transformation of the structure and composition of the boundary layers, promoting activation both of the metal and of the polymer component [2-5].

Analysis of literature sources examining different aspects of the interaction of the components in metal-polymer systems [1-7] indicates the predominant use, in examining the mechanism of physicochemical reactions, of an approach based on the theory of the occurrence of thermooxidative and thermodegradative transformations of the surface layers of the polymer and metal elements, which result in the formation of thermal degradation products, low-molecular-weight products of oxidation and condensation, and metal-containing compounds of different composition [1-6]. The main role of the metal component of the system with this approach consists in its influence on the kinetics of thermooxidative and thermodegradative transformations of the polymer component [2, 6].

At the same time, a number of studies have shown the considerable contribution of charge transfer between the individual components of the system to the kinetics and mechanism of contact processes [4]. For example, control of the electrochemical parameters in adhesive joints or metal-polymer pairs makes it possible to change...
the adhesion and tribotechnical characteristics of static and dynamic systems of different types [8, 9]. Here it is assumed that the metal component (as a rule, an industrial alloy of certain composition and structure) is fairly homogeneous and exerts an influence on the polymer component by initiation of a characteristic physicochemical process (for example, catalysis or inhibition of thermooxidative and thermodegradative transformations of the polymer specimen layer) [8].

Meanwhile, modern ideas of the materials science of metal alloys indicate the heterogeneous structure of industrial semiproducts, governed by the presence of impurities, alloying elements, and features of the occurrence of processes of crystallisation and heat treatment and machining [10]. The heterogeneous structure of metal articles manufactured using standard technologies is considered to be clearly established [11]. This structural aspect creates the prerequisites for the occurrence of contact processes with charge and mass transfer, differing in kinetics and mechanism and therefore in the composition of the products formed on local sections of interaction of the components of the metal-polymer system. Charge mosaic formation on the surface of metal conductors with similarly charged sections of global sections of interaction of the components of the metal-polymer system arises, on the basis of features of the electronic structure of metals and metal-containing compounds.

Let us consider the mechanism by which a charge mosaic arises, on the basis of features of the electronic structure of metals and metal-containing compounds.

In a model of a free independent electron (adiabatic approximation), the Hamiltonian in the Schrödinger equation has the form:

$$\hat{H} = -\frac{\hbar^2}{2m} \Delta + u(\vec{r})$$

(1)

where $\hbar$ is Planck’s constant, $m$ is the mass of an electron, and $u(\vec{r})$ is the potential function.

If the Hamiltonian (1) is used to describe the state of an electron in a crystal, i.e. in the field of a periodic potential, then:

$$u(\vec{r}) = u(\vec{r} + \vec{R})$$

(2)

where $\vec{R}$ is the vector of translation, equal to:

$$\vec{R} = m\vec{a} + n\vec{b} + p\vec{c}$$

(3)

where $\vec{a}, \vec{b}, \vec{c}$ are Bravais points of reference, and $m, n, p$ are integers.

The solution to the Schrödinger equation for adiabatic approximation in the presence of a periodic potential is the wave function $\psi_{ik}$, defined by Bloch’s theorem:

$$\psi_{ik}(\vec{r}) = \phi_{ik}(\vec{r}) \cdot \exp(ik\vec{R})$$

(4)

where the wave vector $k = 2\pi\vec{s}$, $\vec{s}$ being the vector of the inverse lattice.

The function $\phi_{ik}(\vec{r})$ possesses the property of periodicity:

$$\phi_{ik}(\vec{r} + \vec{R}) = \phi_{ik}(\vec{r})$$

(5)

From formulae (1) to (5) it follows that:

$$\psi_{ik}(\vec{r} + \vec{R}) = \phi_{ik}(\vec{r} + \vec{R}) \exp(ik\vec{R}) = \phi_{ik}(\vec{r}) \exp(ik\vec{R}) \cdot \exp(ik\vec{R}) = \psi_{ik}(\vec{r})$$

(6)

The obtained equation:

$$\psi_{ik}(\vec{r} + \vec{R}) = \exp(ik\vec{R}) \cdot \psi_{ik}(\vec{r})$$

(7)

is another way of writing Bloch’s theorem [13].

From condition (7) it can be seen that the wave function of an electron in the field of a periodic potential $[u(\vec{r})]$ corresponds to the solution of Schrödinger’s equation for a free electron $[\psi(\vec{r})]$:

$$[\psi_k(\vec{r})] = \psi_0 \exp(ik\vec{r})$$

(8)

but, instead of the constant amplitude factor $\psi_0$, the solution of (7) contains a wave function with period $\vec{R}$. The wave number $|k|$ is termed the zone number. With a fixed $k$ there are many independent eigenstates of certain energy values that are distributed between zones, divided by energy values, and that are not eigenvalues of the Hamiltonian, i.e. are forbidden for electronic states.

In an attempt to describe the state of an electron close to the surface of a crystal, account must be taken of the fact that in these areas of the substance the periodicity of the potential is lost, and on the surface of the crystal a so-called surface barrier is created, the shape of which depends on very many factors, beginning with defects of different nature (incidentally, the surface itself is a two-dimensional defect), and also on the morphology of the surface layers. The function of the surface potential $[u_s]$ changes its shape on transition from one surface point to another, i.e.

$$u_s = u(\vec{Q})$$

(9)
where $\vec{Q}$ is the radius vector of points of the surface.

Avdeichik et al. [13] showed that, when periodicity of the potential close to the surface is lost, the wave function acquires a form that is different from those given by conditions (4) and (8). An example of the surface wave function is given in Figure 1.

Note that the function $\psi$ falls in exponent in the surface layer of the metal and has an exponentially decreasing envelope within it. In this case, along with the real wave vectors $k$ (see conditions (4) and (8)) within the crystal, there are other solutions with complex wave vectors that correspond to the states of the electrons localised close to the surface of the crystal, differing from the bulk. These surface states with certain energy levels were first examined by I.E. Tamm and are known as Tamm surface states. In discussion of the bulk properties of crystals, the influence of these surface levels is ignored, as the ratio of the number of surface levels to the number of Bloch levels does not exceed the ratio of the number of surface atoms to the total number of atoms in the crystal, which for a macroscopic specimen does not exceed $10^{-8}$.

As a result, the surface levels make a negligibly small contribution to the characteristics of the bulk properties; the only exceptions are nanosubstances, the surface and size factors in which play a large and often decisive role [14]. However, in monocrystals, the Tamm levels are also fairly important in determining the structure of the crystal surface. For example, they must be taken into account in any authentically microscopic calculation of the structure of the surface layer [13].

For specific shapes of the surface potentials, it is necessary to seek a specific solution to the Schrödinger equation. Here it is necessary to analyse not only real but also complex wave vectors (see conditions (4) and (8)), and then to investigate the question as to how the wave functions of the surface layer will be ‘linked’ with internal Bloch functions and with the wave function, external to the crystal, exponentially decreasing in amplitude. The most important thing, in our view, is that, firstly, it is very difficult, if not impossible, to determine the shape of the potential barrier experimentally, as the process of measuring the barrier itself introduces great distortions into the shape of the barrier, and secondly the functional of the surface potential depends on many factors and is different for different points of the surface.

At the same time, the existence of a surface potential as a consequence of the appearance of a defect such as the surface itself, whatever its shape, leads to the appearance of surface (Tamm) levels that are absent in the bulk zonal structure.

Let us consider the one-dimensional case. Suppose that the state of the electrons is characterised by a discrete spectrum of eigenvalues of the Hamiltonian, and that the x-axis is perpendicular to the surface of the crystal. The wave functions in the bulk $\psi_0(x)$ and on the surface $\psi_s(x)$ are solutions of the corresponding Schrödinger equations:

\[
\hat{H}_0 \psi_n^{(0)}(x) = E_n^{(0)} \psi_n^{(0)}(x) \\
\hat{H}_s \psi_n^{(s)}(x) = E_n^{(s)} \psi_n^{(s)}(x)
\]

Let us assume that equation (10) has the same system of functions as regards the number of solutions, i.e. $n, k = 1, 2, 3, \ldots, N$. Then, the concept of the scalar product is applicable to them:

\[
\langle \psi_n, \psi_m \rangle = \delta_{nm}
\]

Hence:

\[
\langle \hat{H}_s \psi_n^{(s)}(x), \psi_m^{(s)}(x) \rangle = \langle \psi_n^{(s)}(x), \hat{H}_s^{(s)} \psi_m^{(s)}(x) \rangle = (E_n^{(s)} - E_m^{(s)}) \delta_{nm}
\]

As the expressions:

\[
\hat{H} = -\frac{\hbar^2}{2m} \Delta + U \\
\hat{H}_s^{(s)} = -\frac{\hbar^2}{2m} \Delta + V
\]

contain independent functions of the surface $U$ and volume $V$ potentials, the left-hand part of equation (12) is different from zero. Consequently:

\[
\langle \psi_n^{(s)}, \psi_m^{(s)} \rangle = 0
\]

This means that $\psi_n$ and $\psi_m^{(s)}$ form independent systems of functions, and here the number of eigenvalues for these two states in the general case are not related to each

![Figure 1. An example of the wave function of a single-electron surface level, depicted in direction x perpendicular to the surface [12]](image)
other. Equations (10), with account taken of system (13), will be written in the form:

\[
\frac{\partial^2 \psi_k(x)}{\partial x^2} + q_k^2 \psi_k(x) = 0
\]

\[
\frac{\partial^2 \psi_n(0)}{\partial x^2} + p_n^2 \psi_n(0) = 0
\]

(15)

where,

\[
q_k^2 = \frac{2m}{\hbar^2} \left( U - E_k \right), \quad p_n^2 = \frac{2m}{\hbar^2} \left( V - E_n \right)
\]

The solutions of equations (15) will be sought in the form:

\[
\psi_k(x) = A \exp \left( iq_k x \right)
\]

\[
\psi_n(0) = B \exp \left( ip_n x \right)
\]

(16)

and hence:

\[
\ln \frac{\psi_k}{\psi_n} = \ln C + ix \left( q_k - q_n \right)
\]

(17)

where \( C = A/B \).

As \( q \neq q_n \) and these quantities are independent, it follows that:

\[
\ln \frac{\psi_k}{\psi_n} = \text{const}
\]

(18)

That is, the functions \( \psi_n(0) \) or their linear combinations cannot be eigenfunctions of the Hamiltonian \( \hat{H} \), while \( \psi_k(x) \) are eigenfunctions of Hamiltonian \( \hat{H} \).

If equations (10) have different numbers of solutions, then, in the case where the number of solutions is greater, it is possible to select linear combinations of wave functions, i.e. on the one hand all the solutions are taken into account and on the other hand a switch to an identical number of solutions will occur. Further analysis is conducted by the scheme examined above (see formulae (11) to (18)).

In crystals with cleavage, the structural defects on both sides of the plane of cleavage during the formation of a juvenile surface are different. This explains the presence of an electron mosaic on the surfaces of dielectrics, but does not make it possible, at first glance, to explain the appearance of electrically charged regions on the surface of the metals, and it is these charges that create, in the terminology of G.I. Distler, who studied this phenomenon in detail, a peculiar “electrical relief” of the surface of polycrystalline metals. This surface “relief” is formed by decoration of the surface by anthraquinone powder and even by the deposition on the surface of drops of water (Figure 2).

Let us examine (any) two particles (two crystallites in polycrystalline metal) with a common boundary (Figure 3). Each of the particles comprises a monocrystalline substance. On leaving the interphase boundary, on both sides of it, there are different crystallographic planes, i.e. along the normal to the boundary the periodicity of arrangement of the atoms is different, as the structures of the Bloch zones are different. The surface potentials are also different. Consequently, it can be assumed that the energy states of electrons in particles 1 and 2 close to the interzone boundary are also different. It must be pointed out that, for this reason alone, there will be a surface, and more precisely an intergranular, potential barrier. Here, the potentials on both sides of this barrier that belong to the contacting particles will be different. Consequently, the examined model corresponds to the physical situation observed in experiments by a number of authors.

This difference is allowed for if we consider that the distribution of defects in these particles is also dissimilar, while the interzone boundary is a potential barrier. Note that the crystal chemistry structure of this boundary may differ greatly from the structure of the particle itself. For example, it may comprise oxides, it may be rich in atoms of other elements (so-called paste), it may have a different phase composition, etc. In all these cases, the conductivity is different to that of the substance of the particles. Hence, for the given case, it follows that

\[
\text{Figure 2. Exposure of the electrical surface relief on steel: (a) deposition of anthraquinone; (b) adsorption of water. Magnification 100x [12]}
\]

\[
\text{Figure 3. An illustration of the use of a barrier model. 1, 2 – different particles in contact; IB – interzone boundary}
\]
it is possible to apply a barrier model. In Figure 4, regions I and III relate respectively to particles 1 and 2, the potentials for which are different. Let $E_1 < E_{III}$. It is evident that the inequality sign plays no role. Region II is a potential barrier corresponding to the interzone boundary. The $x$-axis is perpendicular to the interface, and, as can be seen in Figure 4, $W(x)$ has the form:

$$\begin{cases}
0, x \leq 0, & (I) \\
U, 0 < x < 1, & (II) \\
V, 1 \leq x, & (III)
\end{cases}$$

Let us examine the motion of a particle from left to right from region I to region III. The wave equations for the three examined regions have the form:

$$\psi_j'' + k_j^2 \psi_j = 0, \quad j = 1, 2, 3 \quad (20)$$

where,

$$k_j^2 = \frac{2mE_j}{\hbar^2}$$

We will seek the solution in the form:

$$\psi_j = A_j \exp(ik_jx) + B_j \exp(-ik_jx), \quad j = 1, 2, 3 \quad (21)$$

and here, without losing generality, it can be assumed that $A_1 = 1$ and $B_2 = 0$, as there is no wave moving from right to left in region III. From the condition of continuity of the wave function and its derivative $\psi'' = d\psi/dx$ it follows that:

$$\begin{align*}
\psi_1(0) &= \psi_2(0) \\
\psi_1'(0) &= \psi_2'(0) \\
\psi_2(0) &= \psi_3(a) \\
\psi_2'(a) &= \psi_3'(a)
\end{align*} \quad (22)$$

Conditions (22), with account taken of (20) and (21), lead to the system of equations:

$$\begin{align*}
1 + B_1 &= A_2 + B_2 \\
k_1(1 - B_1) &= k_2(A_2 - B_2) \\
A_2 \exp(ik_2a) + B_2 \exp(-ik_2a) &= A_3 \exp(ik_3a) \\
k_2A_2 \exp(ik_2a) - k_2B_2 \exp(-ik_2a) &= k_3A_3 \exp(ik_3a)
\end{align*} \quad (23)$$

The coefficient of transparency (the coefficient of transmission) of the barrier $U$ for the examined case is equal to:

$$D = \left| A_3 \right| \quad (24)$$

As one of the roots of system (23), $A_3$ is described by the formula:

$$A_3 = \frac{4k_1k_2 \exp(-ik_3a)}{(k_1 + k_2)(k_1 + k_3)\exp(-ik_3a) + (k_1 - k_2)(k_2 - k_3)\exp(ik_3a)} \quad (25)$$

As a particle moves from region III through the barrier into region I, with the same function (see equation (19)), $A_1 = 0$ and $B_3 = 1$. In this case we will obtain the system of equations:

$$\begin{align*}
B_1 &= A_2 + B_2 \\
kB_1 &= k_2B_2 - A_2 \\
A_2 \exp(ik_2a) + B_2 \exp(-ik_2a) &= A_3 \exp(ik_3a) + \exp(-ik_3a) \\
k_2A_2 \exp(ik_2a) - k_2B_2 \exp(-ik_2a) &= k_3A_3 \exp(ik_3a) - k_3 \exp(-ik_3a)
\end{align*} \quad (26)$$

from which it follows that:

$$B_1 = \frac{4k_1k_2}{(k_1 + k_2)(k_1 + k_3)\exp(-ik_3a) + (k_1 - k_2)(k_2 - k_3)\exp(ik_3a)} \quad (27)$$

The coefficient of transparency of the barrier as the particle moves from region III to the left is equal to:

$$D = \left| B_1 \right| \quad (28)$$
and consequently the ratio of the coefficients of transparency:

\[ P = \frac{D}{D'} = k_2^2 = \frac{E}{E-V} \]

(29)

Thus, the different degrees of defectiveness on both sides of the juvenile surface also lead to the appearance on it of electrically charged areas with a size of many large atoms. Consequently, two particles (crystallite grains) in contact with each other acquire electric charges of different sign owing to the presence between them of a potential barrier.

The surface of the specimen of polycrystalline metal on the whole remains electrically neutral, but its adhesion properties depend not only on the crystal chemistry properties of the surface layers but also on the presence of a surface charge mosaic. Within the confines of an individual grain of a metal polycrystal, the electric charges diverge to maximum distances, i.e. are distributed on the periphery of the grains. It is this electrostatic structure (Distler's "electrical relief") that appeared during the decoration of metal surfaces by particles of anthaquinone or other components [12, 13].

It is evident that the presence of a charge mosaic on the surface of the metal component will result in a difference in the kinetics and nature of occurrence of different physicomechanical processes: the adsorption of low- and high-molecular-weight substances, transfer during frictional interaction with the formation of a strengthened boundary layer, redox transformations of the surface layers of the contacting components, the formation of metal-containing compounds (the "metal dissolution" effect) at the contact of the polymer melt and metal substrate, and so on. This is confirmed by the experimentally established effects of the reinforcing action of doping additives in polymer matrices [14], the influence of electrophysical processes on the kinetics of friction and wear [8, 9], and the formation of quasicrystalline structures in thin oligomer films by the action of the surface energy field [16].

It is to be expected that establishing the mechanism of formation and relaxation of the charge mosaic in the surface layers of metal components of different composition and production technology will make it possible to develop effective methods for controlling the tribotechnical and adhesion characteristics of metal-polymer systems.

CONCLUSIONS

Use of the quantum approach to describing features of the structure and energy state of the surface layers of metal specimens made it possible to establish the presence of prerequisites for the existence of regions with different energy potentials. With the application of a barrier model it has been shown that the different degrees of defectiveness on both sides of the boundary lead to the appearance of electrically charged areas with a greater relaxation time. With general electrical neutrality of the surface layer of the metal specimen, the presence of a charge mosaic has a considerable influence on the mechanism and kinetics of occurrence of the contact processes determining the adsorption, adhesion, and tribotechnical characteristics of metal-polymer systems of different composition and functional designation.

REFERENCES


