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FRACTAL STRUCTURE OF SURFACE LAYERS AND FLUCTUATION OF ELECTRON OUTPUT FROM METALS

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The paper shows that the surface layer of a metal is a nanostructure. This surface layer possesses nonlinear properties that depend on its size and all physical properties. The phenomenon of electron emission from a metal under the action of an external electric field is considered. Taking into account the dimensional dependence of the conductivity of the surface layer leads to the Mandelbrot equation. This result shows that the surface layer has a fractal structure. The study of fluctuations of the contact potential difference on samples made of structural metal alloys is carried out. It has been experimentally established that the magnitude of the fluctuation of the contact potential difference at one point of the sample does not depend on the surface roughness. Several mechanisms that lead to fluctuations in the contact potential difference are considered. The first mechanism is associated with the thermal motion of the atoms inside the sample. The second mechanism is related to the processes occurring on the surface of the sample. The third mechanism is related to the processes in the measuring instrument.

Keywords: the surface layer, a metal, a nanostructure, contact potential difference, the Mandelbrot equation.

Introduction

Classical thermodynamics describes heterogeneous phenomena, ignoring the existence of a interface between phases. The thermodynamics of surface phenomena can consider both the surface itself and the surface as part of a hetero-phase system. In this case, there are two approaches: the Gibbs approach [1], in which the surface layer is conditionally regarded as a geometric, non-thick surface; The Van der Waals approach, Guggenheim, Rusanov, in which the surface layer is considered as a layer of finite thickness [2].

According to modern concepts [3, 4], the surface phase is a hyperfine film that is in an equilibrium state with a crystalline base, properties whose structure and composition are different from the bulk properties.

In the technique, alloys based on iron, aluminum, titanium, copper, magnesium and other metals were widely used. The most important characteristic of metals is the work function of electrons (RVE). According to the RVE, many physico-chemical characteristics of metal parts are judged. A simple and affordable method for determining the RVE values from metal parts under atmospheric conditions is the method of measuring the contact potential difference (CPD). The contact potential difference is the difference between the RVE of the monitored object (KO) and the measuring electrode (IE) of the device sensor according to the formula [5]:

$$U \cdot e = \phi_{ie} - \phi_{co}, \quad (1)$$

where U is the IF, V;

$E \approx 1.6022 \cdot 10^{-19}$ C is the electron charge;

ϕ_{ie} - RVE of the IE of the instrument for measuring the CPD, J;

ϕ_{co} - RVE KO, J;

From the formula (1) it is possible to deduce RVE ϕ_{co} :

$$\phi_{co} = \phi_{ie} - U \cdot e. \quad (2)$$

The work function of the electrons in the formula (2) is known in advance - usually the IE of the CPD measuring device is made of metals with stable RVE - gold, nickel, etc. And we measure the PIM U with a measuring instrument. The accuracy of determining the RVE by the CPD method is influenced by the fluctuation of the CPD - stochastic changes in its magnitude with time. Fluctuation is a manifestation of the thermal motion of matter and the discreteness of its structure [6].

1. The thickness of the surface layer of atomically pure metals

In [7] and a number of others we obtained a formula that describes the dependence of the physical property of a solid on its size:

$$A(h) = A_0 \cdot \left(1 - \frac{d}{h}\right). \quad (3)$$

Here A_0 is the physical property of a massive sample; $A(h)$ is the physical property of a small particle or a thin film; d is a dimensional parameter. For the size parameter d we obtained the formula [7]:

$$d = \frac{2\sigma v}{RT}. \quad (4)$$

Here σ is the surface tension of a massive sample; v is the molar volume; R is the gas constant; T is the temperature.

For $h < d$, the formula (3) loses its physical meaning ($A(h) \rightarrow \infty$), so we extend the function $A(h)$ in this region so that the function $A(h)$ vanishes at the point $h = 0$ (Figure 1).

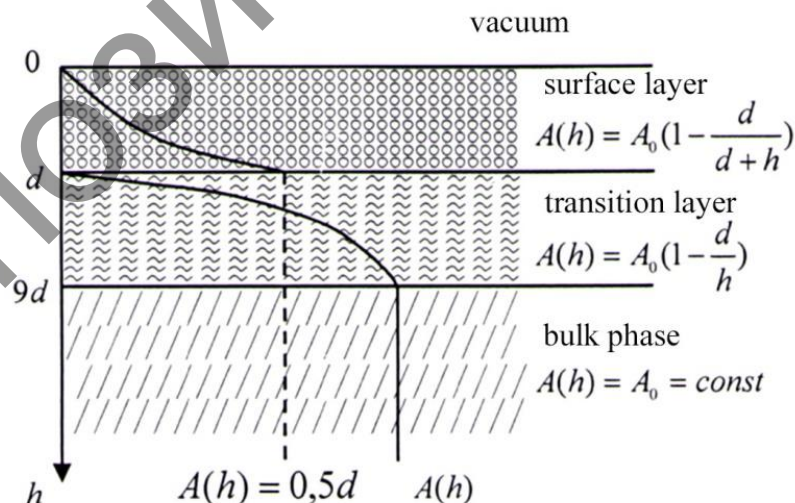


Fig. 1. Schematic representation of the surface layer

This condition is satisfied when the function (3) is rewritten as:

$$A(r) = A_0 \cdot \left(1 - \frac{d}{d+h}\right). \quad (5)$$

It is natural to call the quantity d the thickness of the surface layer.

It follows from formulas (3) and (5) that, by investigating the dependence of some physical property A (h) on the particle size or film thickness, in coordinates A (h) $\sim 1/h$, we obtain a straight line whose tangent of angle determines the value of d .

From formula (4) we obtain a linear dependence of surface tension on temperature:

$$\sigma = \alpha T. \quad (6)$$

Using the data of our work [7], it is not difficult to calculate the coefficient α . If we take into account the measurement error, then the value of the coefficient is $\alpha = 0.7 \cdot 10^{-3} \text{ J} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ for all metals. Thus, the surface tension σ of a metal can be determined from its melting point T_0 :

$$\sigma = 0,7 \cdot 10^{-3} T_0. \quad (7)$$

Using (5) and the known values of the quantities T_0 , ν , R , we determine by formula (4) d . For 55 pure metals, the values of d are shown in the table 1.

Table 1. Thickness of the surface layer of pure metals (M)

| M | d, nm | M | d, nm | M | d, nm | M | d, nm | M | d, nm | M | d, nm |
|----|-------|----|-------|----|-------|----|-------|----|-------|----|-------|
| Li | 0.98 | Sr | 5.81 | Sn | 1.40 | Cd | 1.33 | Fe | 2.17 | Gd | 5.32 |
| Na | 1.47 | Ba | 6.23 | Pb | 1.82 | Hg | 0.56 | Co | 1.96 | Tb | 5.25 |
| K | 2.59 | Al | 1.54 | Se | 1.33 | Cr | 2.66 | Ni | 1.89 | Dy | 5.32 |
| Rb | 2.94 | Ga | 0.63 | Te | 2.45 | Mo | 4.55 | Ce | 3.78 | Ho | 5.46 |
| Cs | 3.64 | In | 1.12 | Cu | 1.61 | W | 5.88 | Pr | 4.20 | Er | 5.46 |
| Be | 1.26 | Tl | 1.68 | Ag | 2.17 | Mn | 1.96 | Nd | 4.48 | Tm | 5.18 |
| Mg | 2.17 | Si | 3.43 | Au | 2.31 | Tc | 3.57 | Sm | 4.41 | Yb | 4.55 |
| Ca | 4.90 | Ge | 2.80 | Zn | 1.05 | Re | 4.97 | Eu | 5.81 | Lu | 5.74 |

Table 1 shows that the thickness of the surface layer of pure metals does not exceed 10 nm. This means that the surface layer of pure metal is a nanostructure. In [8], it was proposed to determine the surface tension by determining the work function of an electron of a controlled object by measuring the contact potential difference and then calculating the original technique developed by the authors, taking into account the electronic structure and elastic characteristics of the controlled parts.

2. Cold electron emission from metals

Let us consider the well-known phenomenon of cold emission of electrons from a metal under the action of an external electric field, due mainly to the quantum tunneling effect.

As is known, the cold emission current is described by the expression [9]:

$$j = j_0 \exp(E/E_0), \quad (8)$$

Where E is the strength of the external field, E_0 is the effective electric field of the metal surface:

$$E_0 = \frac{4\sqrt{2m}}{3e\hbar} (A - T_e)^{3/2}. \quad (9)$$

A is the work function of the electron, T_e is its kinetic energy.

In [10], for the dependence of the electrical conductivity of a film on its thickness h , we obtained the following expression:

$$\mu = \mu_0 \left(1 - \frac{d}{h}\right), \quad (10)$$

Where d is the thickness of the surface layer.

After the transformations, we get:

$$\begin{aligned} j &= \mu E, \quad j_0 = \mu_0 E_0, \\ \mu E &= \mu_0 E_0 \exp(E/E_0) \approx \mu_0 E_0 (1 - E_0/E), \\ \mu_0 \left(1 - \frac{d}{h}\right) E &= \mu_0 E_0 (1 - E_0/E), \\ \left(1 - \frac{d}{h}\right) E &= \frac{E_0 E - E_0^2}{E}. \quad \left(1 - \frac{d}{h}\right) = \frac{E_0 E - E_0^2}{E^2} = \frac{E_0}{E} - \frac{E_0^2}{E^2}. \end{aligned} \quad (11)$$

Denoting $E_0/E = z$, $1-d/h = k$, where z are complex numbers, and k is real, we obtain the famous iterative Mandelbrot equation:

$$z = z^2 + k. \quad (12)$$

The decision algorithm is quite simple. Iterations are performed for each starting point from a rectangular or square area - a subset of the complex plane. The iteration process continues until z extends beyond the circumference of radius 2, whose center lies at (0,0), (which means that the attractor of the dynamic system is at infinity), or after a sufficiently large number of iterations (for example, 200-500) z converges to some point of the circle. Depending on the number of iterations, during which z remained inside the circle, you can set the color of the point C (if z remains inside the circle for a sufficiently large number of iterations, the iterative process stops and this dot is painted black).

For us, the following is important: this example shows the fractal structure of the metal surface. Similar regularities are also manifested in thermoemission, exoemission of electrons from metals and semiconductors. All this indicates that the fractal structure of the surface of many solids is their fundamental property.

3. The study of fluctuations of the contact potential difference

We have carried out an investigation of the magnitude of the CPD fluctuations when it is determined by the "Surface-3I" method, which realizes the ionization method. At the same points of samples made of structural metal alloys, in the laboratory conditions, PSC measurements were made every minute for 1 hour. The surface of the samples was previously purified by petroleum ether and dried for 20 minutes. After each CPD measurement, the sensor of the device was removed from the sample. The results of the studies are shown in Figure 2.

Figure 2 shows the fluctuation of the CPD around the mean value. There is also a general trend towards an increase of the CPD (for samples from ZhS6K-VI, 30HGSA, VT8 and VT3-1) or to reduce it (for a steel-3 sample) for 1 hour allocated for measurements.

The results of statistical processing of the obtained results of the CPD measurement characterizing the parameters of its fluctuations are presented in the table and in Fig. 3. Figure 3 shows the results of grouping the values of the measured CPD.

The estimation of the mathematical expectation \bar{U} of the measured values of the CPD presented in the Table 2 was calculated by the formula [11]:

$$\bar{U} = \frac{1}{n} \sum_{i=1}^n U_i,$$

Where U_i is the current value of the measured CPD, mV; $n = 60$ - number of CPD measurements.

The dispersion of the D values of the measured CPD was determined by the formula, mV^2 :

$$D = \sum \frac{(U_i - \bar{U})^2}{n}.$$

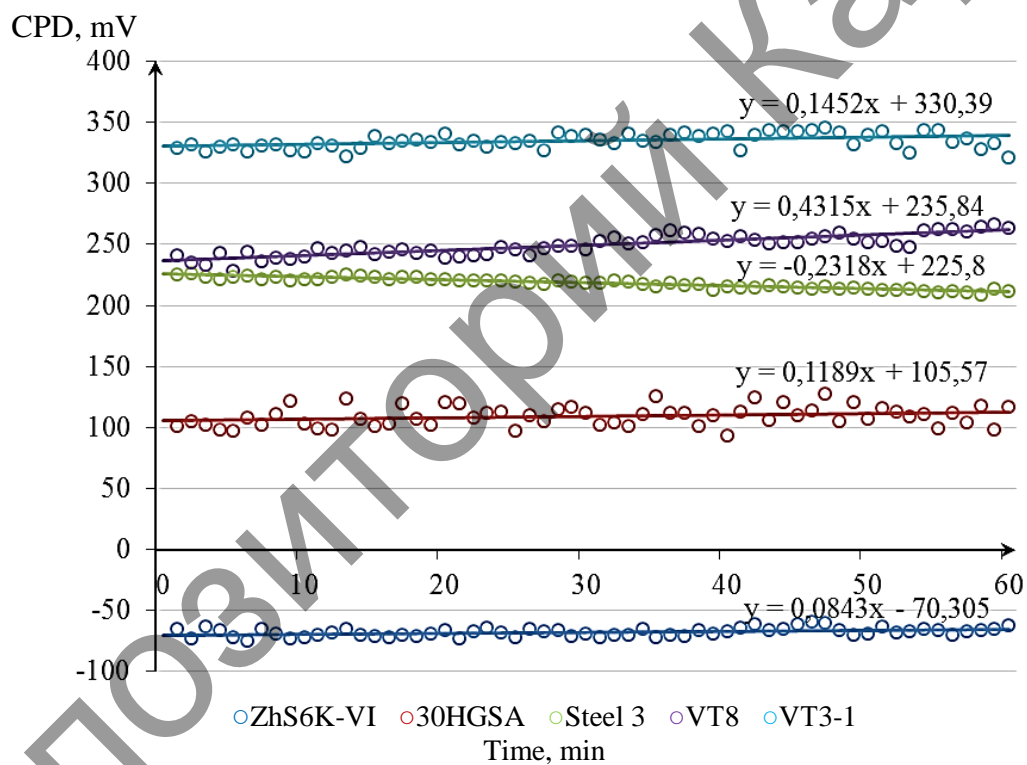


Fig. 2. Results of the study of fluctuations of the CPD in the determination of RVE from samples

The average quadratic deviation of the measured values of the IFR was calculated from the formula, mV:

$$\sigma = \sqrt{D}.$$

It can be seen from Fig. 2 that the law of distribution of the results of CPD measurements is close to normal.

Table 2. Statistical analysis of the results of CPD measurements

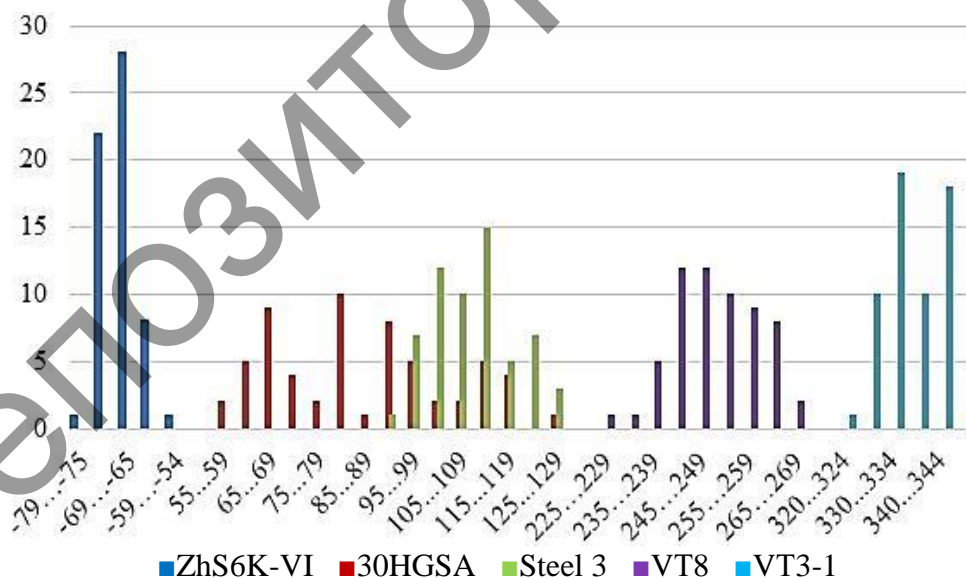
| Alloy | Surface roughness class | \bar{U} , mV | D , mV ² | σ , mV |
|----------|-------------------------|----------------|-----------------------|---------------|
| ZhS6K-VI | 8 | - 68 | 13.0092 | 3.6068 |
| 30HGSA | 6 | 109 | 69.1164 | 8.3136 |
| Steel 3 | 7 | 219 | 18.0167 | 4.2446 |
| VT8 | 11 | 249 | 75.5344 | 8.6911 |
| VT3-1 | 10 | 335 | 38.0989 | 6.1724 |

We tested the hypothesis that D and CPD measurements increase with an increase in the roughness of the KO surface. To this end, an assessment of the surface roughness class of the samples was carried out, which we carried out by comparison with the "Working samples of steel surface cleanliness" visually and using the MBS-2 microscope. However, as can be seen from the table, this hypothesis has not been confirmed in our studies. With an increase in the surface roughness, the so-called "energy relief" of the entire surface of the metal samples increases, i.e. The spread of the IF for the area of the KO [12]. The magnitude of the CPD fluctuations in measurements at one point of the QD surface may not depend on the roughness of its surface. This issue requires further research.

The analysis of published sources testifies to several components of the fluctuation of the CPD of metallic samples characterizing the RVE from them:

- due to the processes occurring inside the KO;
- due to the processes occurring on the surface of the KO;
- due to the processes occurring in the CPD measuring device;
- due to violation by the performer of the CPD measurement technology.

Fluctuation of the CPD as a result of processes occurring inside the QR.

**Fig. 3.** Results of grouping of CPD measurements

Inside the metals, thermal vibrations of atoms and chaotic motion of conduction electrons occur. Electrons moving inside the metal collide with the core of atoms located at the sites of the crystal lattice, with the scattering of atoms, including their exit to the metal surface, as a result of which fluctuations of the REE are observed, and, consequently, the fluctuation observed by us CPD when it is measured. Scattering of electrons in metals is of quantum-mechanical nature [6, 13].

Contribution to the scattering of electrons inside metals, and hence also to fluctuations of REE and CPD, also introduces the motion of submicroscopic defects-vacancies, dislocations, impurity atoms, etc. The work function of electrons from metals changes significantly when submicroscopic defects leave their surface.

The metal KO exchanges heat with the environment. In addition, there is an exchange of heat between parts of the KO. Since the thermal conductivity is a random process, this leads to fluctuations in the thermodynamic characteristics of the metal, and, consequently, the RVE from it and the measured CPD.

3.1 Fluctuation of the CPD due to processes occurring on the surface of the KO.

Adsorption, migration, and diffusion of impurity atoms are constantly occurring on the surface of metallic QDs, as a result of which, at each instant of time, the RVE of them changes and, consequently, according to formula (1), the measured PSC also changes. Especially this factor is manifested in the CPD measurements in non-stationary conditions outside the laboratory. Depending on the affinity of the metal or adsorbate, three types of interaction of the adsorbent metal with the atoms and molecules of the adsorbate are distinguished to the electron [14]:

1. The first type of interaction is characterized by a lower affinity for the electron surface of the adsorbent in comparison with the adsorbate. In these cases, the electrons of the adsorbent metal are partially or completely entrained in the electron orbit of the adsorbate-acceptor. In this case, the surface layer of the metal is charged negatively, which leads to an increase in RVE from it, and, consequently, to a decrease in the CPD. Adsorbates-acceptors include oxygen, carbon monoxide, nitrous oxide, etc.

2. The second type of interaction is characteristic for cases when the metal surface has a greater affinity for the electron than the adsorbate. In this case, the electrons of the donor adsorbate atoms or molecules partially or completely pass to the "electron gas" of the metal, the surface of which is positively charged, as a result of which the RVE decreases from it. To adsorbates-donors are such substances as hydrogen, water, ammonia, etc.

3. The third type of interaction is characteristic for substances that do not have an affinity for the electron, for example, inert gases, such as argon, but capable of being polarized under the influence of a metal. In this type of interaction, electronic transitions are absent, but some shift of the electron cloud towards the metal-adsorbent, which has a large affinity for the electron, is possible. Such metals are, for example, silver, platinum and gold. The surface of such a metal is charged positively and the RVE from it decreases.

Real adsorption processes are complex processes, characterized by a complex manifestation of various types of adsorption. The surface of the KO can be uneven, which leads to an increase in the gap between it and the sensor of the device. This is the reason for the increase in the variance of the CPD fluctuations. The increase in the spread of the measured CPD values is also caused by the "energy relief" mentioned by us earlier, formed by the uneven distribution along the surface of the RO of its roughness, the thickness of the oxide layer, the presence of contaminants, etc.

3.2 Fluctuation of the CPD as a result of processes occurring in the CPD measuring device.

The listed reasons for the CPD fluctuations due to the natural physicochemical processes occurring inside and on the surface of the metal KO are also characteristic for the CPD *measurement* devices. The difference is that the PSC measuring devices are orders of magnitude more complex systems compared to metal KO's.

In addition, the reasons for the fluctuations of the IF for reasons inherent in the instruments for measuring it can be: shot shot, flicker ($1/f$ noise), generation-recombination, and other types of electrical noise [15]. There is also a mutual negative influence of the constituent parts of the

electronic device, leading to noise and noise. Reduces the level of electrical noise in the device CPD measurement through screening, noise reduction, the use of rational electrical circuits.

Conclusion

The phenomenon of electron emission from a metal under the action of an external electric field is considered. Taking into account the dimensional dependence of the conductivity of the surface layer leads to the Mandelbrot equation. This result shows that the surface layer has a fractal structure. The parameters analyzed and the causes of the CPD fluctuations must be taken into account when determining the RVE from structural materials. To increase the accuracy of the CPD measurement, careful preparation of the KO surface is necessary. We used petroleum ether, which has a good cleansing ability and fast (no more than 15 minutes) volatility [15] to clean the surface of the KO before measuring the CPD. Measurements of the IF for the reduction of environmental effects are recommended in the laboratory. It should be carried out at least 10 CPD measurements, after which the statistical processing of the measurement results. And, of course, it is necessary to conduct further scientific research in this direction.

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