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THE IMPACT OF THE ENVIRONMENT ON THE CONTACT POTENTIAL DIFFERENCE OF METAL MACHINE PARTS

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In this paper we consider the influence of environmental parameters on the electrons work function and the contact potential difference of metal parts of machines. Experimental studies have been carried out, including measurements of the contact potential difference on samples from Al, Ti and Ni by the Kelvin-Zisman method at different temperatures, pressures and relative humidity, as well as in non-equilibrium and equilibrium environmental conditions. Measurements of the contact potential difference were carried out by the device "Surface-11". Atmospheric parameters were measured by the digital meteorological station HAMA EWS-800. The results of measurements of the contact potential difference of metals were processed by methods of mathematical statistics. The results of experimental studies have shown a direct effect of changes in ambient temperature on the contact potential difference and the electrons work function of metal samples, which has an average correlation. It is found that atmospheric pressure and relative humidity have a weak effect on the contact potential difference and the electrons work function of the metals under study, their influence can be neglected. The effect of equilibrium and non-equilibrium environmental parameters on the contact potential difference and electrons work function of metal samples is studied. The results confirming the reduction of the contact potential difference (increase in the electrons work function) of metals, as well as an increase in the mean square deviation of the measurement results under non-equilibrium environmental conditions are obtained. On the basis of the research it is recommended to measure the contact potential difference of metals in the laboratory.

Keywords: electrons work function, contact potential difference, metal, surface, temperature, pressure, humidity.

Introduction

The method of contact potential difference, which consists in the comparison of the electrons work function of metals, is promising method of nondestructive testing of metal machine parts [1]. The actual task is to ensure the reliability of nondestructive testing of metal parts of machines. Not fully studied is the effect on the method of contact potential difference parameters of the ambient air. Consider the effect on the electrons work function and the contact potential difference of metals such parameters of the atmosphere as temperature, pressure and humidity. Let's start with the analysis of literary sources devoted to this problem.

Temperature dependence of the electrons work function and the contact potential difference of metals. The temperature dependence of the contact potential difference was discovered and studied by A. Volta, his First law States: "On the contact of two different metals, a potential difference arises, which depends on the chemical nature and the temperature of the junctions." A.F. Vladimirov points out [2] that the electrons work function depends on the temperature, which is one of the main thermodynamic parameters of a solid. This dependence is reflected in the concept of temperature coefficients of the electrons work function. However, the experimental data on the temperature coefficients of the electrons work function are contradictory; their sign can be both positive and negative, depending on the experimental conditions [2].

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Meanwhile, in [3] it is indicated that at present there is no quantitative theory of temperature dependence of the electrons work function. An example of the temperature dependence of the contact potential difference is the capacitor sensors of temperature measuring devices [4]. The sensor of the device for measuring the contact potential difference of the design scheme Kelvin-Zisman has in its composition a vibrating measuring electrode for comparing the workings of the electrons work function, which when measuring the contact potential difference is applied to the controlled object and forms a dynamic capacitor, one of the plates of which fluctuates. The temperature dependence of the dynamic capacitor is based on the change in its capacitance C due to changes in the relative permittivity between the surface of the metal part and the measuring electrode according to the following formula:

$$C = \frac{\varepsilon_0 \cdot \varepsilon \cdot S}{d},$$ (1)

where $\varepsilon_0 \approx 8.8542 \cdot 10^{-12}$ F/m is the electric constant (vacuum permittivity);

ε is the relative dielectric constant, for dry air $\varepsilon \approx 1.00059$;

S is measuring electrode area, m^2;

d is the gap between the measuring electrode and the metal surface, m.

In [4] it is shown that significant changes in the ambient temperature can affect the capacitance of the dynamic capacitor due to changes in the area of the measuring electrode S according to the formula (1) due to the thermal expansion of the metal of the measuring electrode.

In [5] calculations of electrons work function Cu with Ni, Co and Fe coatings at different temperatures are presented. It is shown that with increasing ambient temperature the electrons work function of these systems decreases.

The increase in ambient temperature intensifies physical and chemical processes on the surface of metal parts of machines, for example, such as adsorption, corrosion tribological and others. As a result, the electrons work function of metal parts also changes [6].

In [7] provides details of the calculations of the temperature dependence of the electrons work function of the Al, which show the constancy of the electrons work function in the temperature range from 0 to 420 K. At ambient temperatures of more than 420 To the work function of the electrons begins to decrease.

In [8] it is indicated that the electrons work function of metals, as well as their other properties, depends on temperature, the formula of dependence electrons work function φ on temperature T Is given:

$$\varphi = \varphi_0 - \frac{3}{2} k \cdot T,$$ (2)

or

$$\varphi = \varphi_0 - \xi \cdot \frac{(k \cdot T)^2}{\varphi_0},$$ (3)

where φ_0 is the electrons work function at absolute zero;

k is Boltzmann constant;

ξ is the coefficient dependent on the crystal structure of the metal ($\xi_{Al}=583$, $\xi_{Fe}=438$, $\xi_{Ag}=478$, $\xi_{Ni}=318$, $\xi_{Cu}=307$).

As can be seen from the formulas (2) and (3) with increasing temperature T electrons work function φ decreases. The authors [8] associate this with the absorption of energy by electrons inside the metal. It is assumed that the increase in the energy of each electron with increasing temperature is 3/2 $k \cdot T$. The temperature dependence of electrons work function of 74 metals was analyzed in [9] and it was found that it is insignificant for most metals. In this paper, it is indicated that the determination of the temperature dependence of the electrons work function by measuring the contact potential difference is ineffective.

In [10] it is indicated that the electrons work function changes with temperature. The author of the work [10] connects this fact with the change in the concentration of gases destabilizing the electrons work function, the concentration of which depends heavily on the ambient temperature. In the same work it is noted that the determination of the electron yield according to thermionic emission gives reproducible results only for refractory metals such as W, Mo, Ta. For Fe, Cu, Ni, Ag reliable results of the temperature dependence of the electrons work function at electron thermal emission have not been obtained. In [4] it is shown that the capacitance of the capacitor changes with temperature due to changes in the relative permittivity ε (see formula (1)).

1. The effect on the electron work function of contact and difference potential of metal parts of machinery pressure and humidity of the atmosphere.

The operation of the electrons work function depends to a large extent on the conditions of interaction of surfaces with the surrounding atmosphere. Therefore, in order to exclude the atmospheric effect on the value of the measured electrons work function, its laboratory studies are trying to be carried out in a vacuum. However, when determining the electrons work function for technical purposes it is difficult to observe.

The results of experimental studies of the dependence of the contact potential difference between the measuring electrode from Pt and samples from different materials determined at different atmospheric pressures are shown in [11]. The authors point out that at different pressures the contact potential difference of metals varies slightly. Almost always, the contact potential difference at a pressure of $1 \cdot 10^5$ Pa is greater than in vacuum. This is explained by the authors of [11] the difference in the adsorption-desorption processes on the surface of the samples.

The authors of [12] were performed to measure the distribution of the electron work function at the surface of samples of alloy ЭП479 for several months with simultaneous fixation of the temperature, pressure and humidity. The correlation of the change in the values of the electrons work function with the change in air pressure and humidity is established. An increase in humidity by 5 % leads to a corresponding decrease in the electrons work function, by about 20 meV, and Vice versa. The authors of this work believe that the increase in the electrons work function with increasing humidity is associated with an increase in the number of water molecules adsorbed on the surface of metal parts of machines. In the absence of aggressive substances in the air, the electrons work function is stable enough for tens of minutes.

In [6] the results of experimental studies to determine the effect on the measurement of the electrons work function of atmospheric humidity are shown. The electrons work function of Sb, Zn, Cd and their alloys was measured by the contact potential difference method. Studies have shown that the electron yield of these metals and alloys in a humid air atmosphere is greater by a value of 30 to 50 meV than in a dry air atmosphere. The measurement of the electrons work function in the dehydrated air the authors the work was carried out in a special chamber, the entrance to which is set a trap for moisture from the liquid nitrogen, which allowed to reduce the concentration of H_2O in the chamber to a value of 0.005 g/m^3.

In [13] it is shown that the determination of electrons work function the samples of Al, Zn and W by the method of contact potential difference in a humid atmosphere leads to a decrease in the contact potential difference. The authors of [13] suggest that the reason for this is water vapor in the air, bringing a negative charge, which partially passes into the metal, and then remains on the surface of the metal in the water layer. When measuring the contact potential difference, the water then evaporates in the dry air and the contact potential difference increases (the electrons work function decreases).

With a joint change in the temperature and humidity of the ambient air according to the formula (1) capacitance of the capacitor formed by the metal part and the measuring electrode, the relative permittivity of ε_a changes according to the semi-empirical dependence derived by A.R. Volpert [14]:

$$\varepsilon_{\text{в}} = 1 + \frac{p}{T}\left(28 + \frac{\chi \cdot p_H}{p} \cdot \left(\frac{135}{T} - 0.0039\right)\right), \tag{4}$$

where p is the air pressure, Pa;

T is thermodynamic temperature, K;

p_H is elasticity of saturated water vapor at a given temperature;

$$\lg p_H = 23.19 + \frac{38.16}{T - 46.13} + 2.78;$$

χ is relative humidity, %.

Relative permittivity of air ε can be determined according to the formula [14]:

$$\varepsilon = 1 + \frac{n \cdot \alpha_e}{\varepsilon_0}, \tag{5}$$

where n is the number of gas atoms in 1 m^3 of air;

$\varepsilon_0 \approx 8.8542 \cdot 10^{-12}$ f/m is electric constant (permittivity of vacuum);

α_e is electron polarizability of the molecule, F·m^2.

With

$$n = \frac{p}{k \cdot T}, \tag{6}$$

where p is the air pressure, Pa;

k is Boltzmann constant;

T is the temperature, K.

The relative permittivity of air is very close to the square of refraction of sunlight and increases with the radius of atoms of gases contained in the air [14]. An example of the dependence of the contact potential difference on the atmospheric humidity is the condenser sensors of moisture meters [4]. Recall that the sensor developed by us meter contact potential difference is a dynamic capacitor. The dependence of the dynamic capacitor on humidity is based on the change in capacitance C due to changes in the relative permittivity ε between the surface of the metal part and the measuring electrode according to the formula (1). The dielectric constant generally increases with increasing ambient humidity [4]. Thus, the analysis of literature sources shows the dependence of the electrons work function and the contact potential difference on the environmental parameters.

2. Experimental procedure

The authors conducted experimental studies of the dependence of the contact potential difference of metal samples of pure Al, Ti and Ni on the temperature, pressure and relative humidity of the air atmosphere. The studies were conducted in laboratory conditions.

Parameters of the surrounding atmosphere — pressure, temperature and relative humidity were estimated by the digital weather station HAMA EWS-800 with the declared accuracy of 2 %.

The range of measured environmental parameters in the course of observations was:

- temperatures from 14 to 29 °C with an average temperature of 23 °C;
- atmospheric pressure from 963 to 1022 hPa, with the average value of pressure of 997 hPa;
- relative humidity from 19 to 59 % with an average value of 34 %.

The studied samples of Al, Ti and Ni were previously thoroughly cleaned and dried.

With the help of the device "Surface-11" [15] for several months, more than 300 sessions of measurements of the contact potential difference on the samples were performed. Each measurement session of the contact potential difference consisted of several measurements of the contact potential difference. Statistical methods were used to process the results of measurements of the contact potential difference, the results of calculations are presented in the Table 1. As can be

seen from the table, the greatest stability of the results of measurements of the contact potential difference has Ni, so it is used as a material of measuring electrodes of sensors for measuring the contact potential difference.

Table 1. Statistical characteristics of the investigated contact potential difference

Metal	Estimation of mathematical expectation, mV	Mean square deviation, mV
Al	874	75
Ti	284	70
Ni	208	65

3. Results of the experiment and their discussion.

3.1 Temperature influence.

Figure 1 shows the dependence of the contact potential difference U of the samples from Al, Ti, Ni on temperature t, ceteris paribus: at a pressure of 997±10 hPa and a relative humidity of 34±2 %. The graphs presented in figure 1 are constructed by the least squares method by 14 values of the contact potential difference measured at an air temperature of 14 to 29 °C.
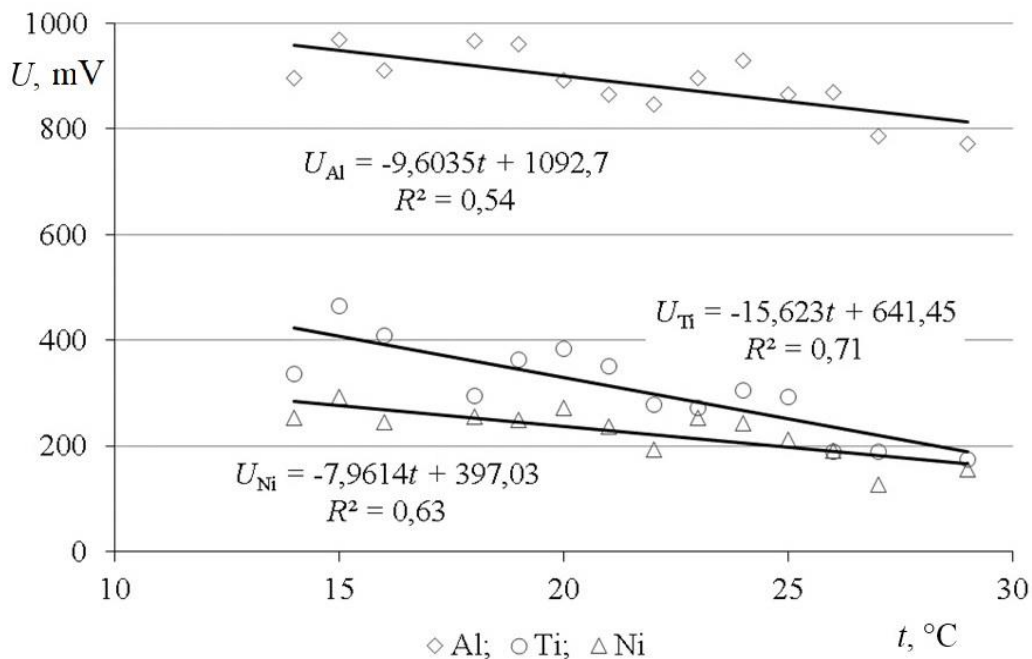

$$U_{Al} = -9{,}6035t + 1092{,}7$$
$$R^2 = 0{,}54$$

$$U_{Ti} = -15{,}623t + 641{,}45$$
$$R^2 = 0{,}71$$

$$U_{Ni} = -7{,}9614t + 397{,}03$$
$$R^2 = 0{,}63$$

◇ Al; ○ Ti; △ Ni

Fig.1. Dependence of the contact potential difference U on the ambient temperature t

Figure 1 also shows the formulas describing this dependence $U(t)$ for Al, Ti and Ni, as well as the value of the determination coefficient R^2. The reduction of the potential difference U with increasing ambient temperature t can be explained by an increase in the dielectric constant ε with increasing temperature according to the formula (1).

As can be seen from figure 1, there is a correlation between the contact potential difference U and ambient temperature t — high for Ni and Ti, and average for Al. The dielectric constant of the air ε increases due to the fact that with increasing temperature the air becomes more sparse and

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there is a smaller number of n air atoms in 1 m^3, transmitting an electric current between the measuring electrode and the metal part according to the dependencies (5) and (6).

3.2 Influence of atmospheric pressure.

Figure 2 shows the dependence of the contact potential difference U for samples from Al, Ti and Ni on the air pressure p, ceteris paribus: at an air temperature of 23±2 °C and its humidity of 34±2 %. The graphs presented in figure 2 are constructed by the least squares method using 39 values of the contact potential difference measured at atmospheric pressure from 963 to 1013 hPa. Also in figure 2 formulas describing the dependences $U(p)$ and the determination coefficients R^2 are presented.
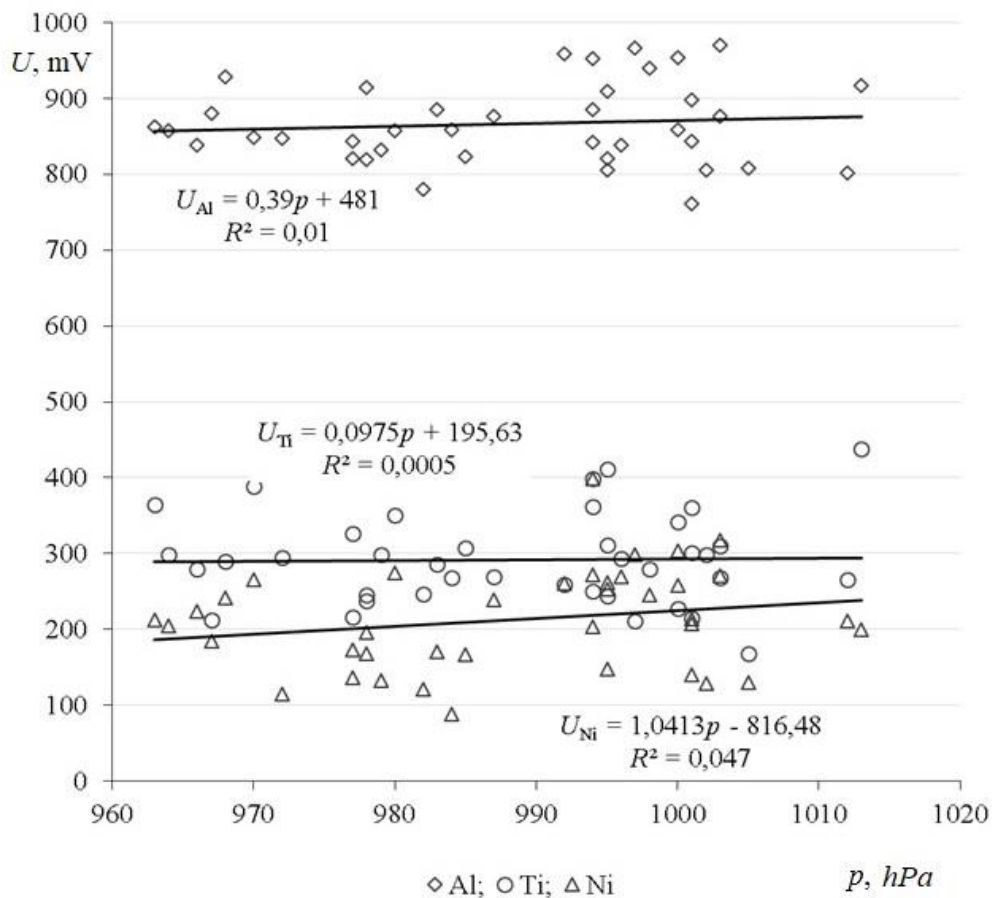

$$U_{Al} = 0.39p + 481$$
$$R^2 = 0.01$$

$$U_{Ti} = 0.0975p + 195.63$$
$$R^2 = 0.0005$$

$$U_{Ni} = 1.0413p - 816.48$$
$$R^2 = 0.047$$

◇ Al; ○ Ti; △ Ni p, hPa

Fig.2. Dependence of contact potential difference U on air pressure p

Figure 2 shows that there is a slight increase in the contact potential difference U with increasing atmospheric pressure p, due to the increase in the number of transmitting electric charges of atoms n according to the formulas (5) and (6), but the correlation between them is small. Under normal atmospheric conditions, the influence of atmospheric pressure on the contact potential difference and the work of the electron yield, apparently, can be neglected.

However, it should be noted that when measuring the contact potential difference at extremely low atmospheric pressure, for example, at high altitude, the contact potential difference may decrease more intensively. Moreover, the factor of influence on the contact potential difference of air pressure should be taken into account when measuring the contact potential difference at artificially reduced (for example, in vacuum) or, on the contrary, at increased (for example, when pumping air) atmospheric pressure.

3.3 Influence of air humidity.

Figure 3 presents the results of analysis of 69 sessions of studies of the dependence of the contact potential difference U on the relative humidity χ all other things being equal: at an air temperature of 23±2 °C and an atmospheric pressure of 997±10 hPa. Also, figure 3 presents the formulas describing the dependence $U(\chi)$, and the coefficients of determination R^2, characterizing the relationship between the contact potential diversity and air humidity.
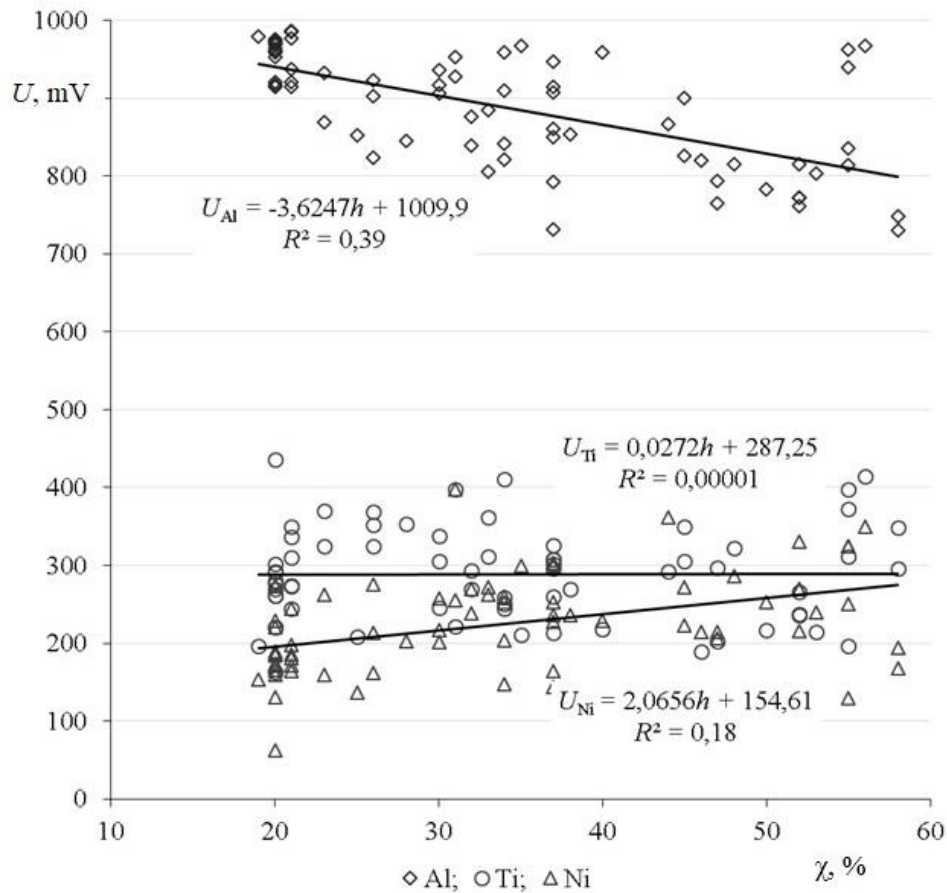

Fig.3. Dependence of the contact potential difference U on the relative humidity χ

Figure 3 shows an ambiguous dependence of the contact potential difference U of different metals on the relative humidity χ — direct for Al and inverse for Ni with low determination coefficients R^2. On the contact potential difference of the samples from Ti, the change in air humidity χ had virtually no effect ($R^2 \approx 0$).

Different adsorption processes can explain the difference between the dependence of the contact potential difference on the relative humidity of the air— direct for Al and reverse for Ni, on their surface when interacting with water. For samples from Al, this interaction is acceptor (leads to a decrease in the contact potential difference), and for samples from Ni — is donor in nature, resulting in a slight increase in the contact potential difference [6]. However, it should be noted that the measurements of the contact potential difference took place in a relatively dry air atmosphere and it can be assumed that higher humidity can have a greater impact on the contact potential difference.

Thus, the pressure and humidity under normal atmospheric conditions do not significantly affect the value of the contact potential difference, in contrast to the temperature, which slightly changes the relative permittivity ε of the gap between the metal part and the measuring electrode, and accordingly to the measured capacitance of the linamic capacitor C according to the formula

(1). However, in the source [4] there are indications of a joint effect of atmospheric parameters — an increase in air humidity further enhances the effect of temperature on the relative permittivity ε of air humidity, and, consequently, on the contact potential difference. Therefore, the measurement of the contact potential difference in a humid air atmosphere, in our opinion, is not acceptable.

We carried out measurements contact potential difference in an artificially humidified atmosphere. When measuring the contact potential difference device "Surface-11" at a relative humidity of more than 80 %, the mean square deviation σ of the contact potential difference increased sharply. Reliability of measurements of contact potential difference decreased. This should be taken into account when nondestructive testing of metal parts of machines. Therefore, nondestructive testing by the method of contact potential difference of metal parts of machines is recommended to be carried out in the laboratory with normal and stable air parameters.

3.4 Measurement of contact potential difference in non-equilibrium atmospheric conditions.

In [16] it is shown that in non-equilibrium environmental conditions the electrons work function increases in comparison with the electrons work function measured in equilibrium conditions. The authors carried out experimental measurements of the contact potential difference by the device "Surface-11" [15] on 10 flat samples from pure Al, Ti and Ni. The surface of the samples was pre-cleaned with petroleum ether and dried for 15 minutes. Measurements of the contact potential difference were first carried out in the laboratory under the following environmental parameters: atmospheric pressure 1007 hPa, temperature 24 °C and relative humidity 19 %. Then measurements of the contact potential difference on the same samples from Al, Ti and Ni were carried out in non-equilibrium conditions on the street for 10 minutes, where the atmospheric pressure increased to 1009 hPa, the air temperature decreased to 15 °C (the samples and the surface-11 device were cooled) and the relative humidity increased to 23 %. The parameters of the surrounding air atmosphere were estimated by the digital weather station HAMA EWS-800. At the same time, a decrease in the contact potential difference of the samples measured on the street under non-equilibrium conditions of the surrounding atmosphere was observed. With further stabilization of the new values of temperature and relative humidity (outside), the contact potential difference of the samples increased slightly, although it did not reach the laboratory level.

The arithmetic mean value (estimation of mathematical expectation), dispersion and the mean square deviation of the measured values of the contact potential difference were calculated. The results of measurements of the contact potential difference U and its mean square deviation σ in equilibrium conditions (indoors) and non-equilibrium conditions (outdoors) of 10 samples from Al, Ti and Ni are presented in figures 4 and 5, respectively.

Figures 4 and 5 show that in non-equilibrium atmospheric conditions the contact potential difference decreases and the mean square deviation of the contact potential difference increases. Moreover, this effect of reducing the contact potential difference of metal samples and increasing its mean square deviation is observed when cooling the samples on the street and when they are heated indoors. The values of the contact potential difference measured in equilibrium and non-equilibrium conditions, as seen in figure 4, differ: 80, 29 and 35 mV for Al, Ti and Ni, respectively. The decrease of the contact potential difference (increase of the electrons work function) of metal samples under non-equilibrium conditions is explained by the increase of temperature gradient on the surface and in the depth of the metal, increase of the electrons work function due to the decrease of internal energy of a solid with the stabilization of its energy state.

The increase in the mean square deviation of the contact potential difference for Al in figure 5 was 48 mV, for Ti 43 mV and for Ni 22 mV. The increase in the mean square deviation of the measurement results of the contact potential difference is explained by the intensification of adsorption-desorption processes on the metal surface, as a result of which the electron yield and the surface potential of the metal change.
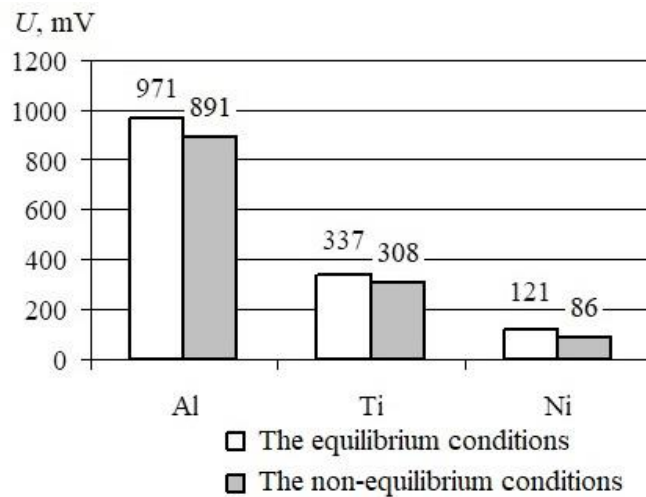
Fig.4. Average values of contact potential difference *U* of samples from Al, Ti and Ni measured in equilibrium and non-equilibrium atmospheric conditions
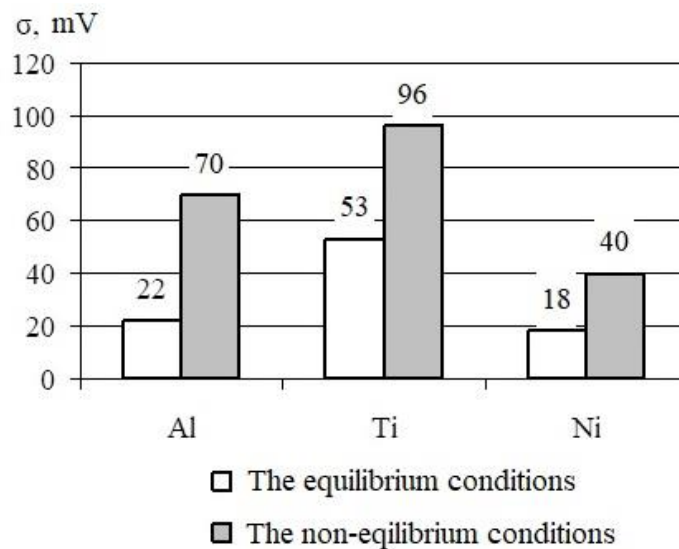

Fig.5. Values of the mean square deviation σ of the contact potential difference of samples from Al, Ti and Ni measured in equilibrium and non-equilibrium atmospheric conditions

Reducing the contact potential difference U and increasing its mean square deviation σ when measured under non-equilibrium conditions according to figures 4 and 5 is a reversible process. In subsequent measurements in the laboratory, the contact potential difference of the samples came to the initial state. In addition, figures 4 and 5 show that the decrease in the contact potential difference U is commensurate with the magnitude of the change in the mean square deviation σ. This indicates a slight influence of non-equilibrium environmental conditions on the reduction of the contact potential difference (increase in the electrons work function).

It should also be noted that the reduction of the electrons work function under non-equilibrium environmental conditions is not strictly. Figure 4 shows the arithmetic mean values of the contact potential difference calculated from 10 samples from each metal. On the surface of metals, new energy States can be formed and with less electrons work function (greater contact potential difference) than under equilibrium conditions [16].

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Conclusion

Thus, the determination of the electrons work function of metal parts of machines by the method of contact potential difference, in order to increase the reliability, it is recommended to carry out in the laboratory with constant environmental parameters. This recommendation will make it possible to more accurately obtain the values of the contact potential difference and, accordingly, the electrons work function of structural metal materials, adequately assess the energy state of the surface of metal parts of machines, reduce the economic costs in their manufacture, operation and repair.

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