ON THE CONTACT POTENTIAL DIFFERENCE AND THE METHODS FOR ITS MEASUREMENT FOR THE PURPOSES OF SPACE TRIBOLOGY

Medy Astrukova

Space Research Institute, Bulgarian Academy of Sciences,1113 Sofia

Introduction

In this work, a review is made of some of the existing scientific theories for the contact potential difference and the methods for its measurement. Grounds are also provided explaining why one of these methods is most widely used in practice, for the purposes of space tribology including.

The theory of the contact potential difference has numerous applications in many scientific fields like biophysics, biochemistry, electrochemistry etc. In engineering, it is accounted for in electrovacuum units, highvacuum units in particular, as well as in solid rectifiers, crystal detectors ,etc.

In modern space research, space materials, and space tribology, the measurement and reading of the contact potential difference, respectively the work function, is of great importance. For example:

1. In probe methods, the measurement of electron and ion temperature and electrostatic field by the "double probe" method is related accordingly with the use of flat and spherical probes (sensors), and probes with carbonglass cover. The material, geometry, and surface state of these probes, respectively the change and reading of the work function, is of crucial importance for the precision of space measurements.

2. In space tribology, the choice of material for instrumentation operating in bare space (scanner driving mechanisms, probe supporting mechanisms, antennae, solar batteries etc.) is related with the specific tribological processes in high vacuum [1]. The state of the material's surface at contact (friction, wearing rate, structural modifications, etc.) is judged by the magnitude of the contact potential difference, respectively the work function of the given material.

In this aspect, the reading of the magnitude of the contact potential difference, respectively the work function, appears to be, on the one hand, an

indicator of the precision of measurement in space experiments, and on the other hand, an indicator of the magnitude and direction of surface change, and of the best couple of heterogeneous metals from the viewpoint of space tribology, i.e. one that would be characterized by low wearing intensity, high reliability, and operational longevity.

Theory

The theory of the contact potential difference is based on the phenomenon "electrization" [2] discovered by *Al. Volta*, according to which, when two heterogeneous conductors (metals) come in touch, contact potential difference appears. Later, the scientists *Kelvin*, *Lodge, de la Riva*, and others developed the theory further, until two arguing theories appeared, the physical theory supported mainly by *Kelvin*, and the chemical theory supported mainly by *de la Riva*, and modified later by *Lodge*. The argue was focused on the problem where exactly appears the contact potential difference. While *Volta, Kelvin*, and the supporters of the physical theory argued that it appeared at the very place of contact, *de la Riva, Lodge*, and other supporters of the chemical theory argued that the contact potential difference is the result of the chemical reactions taking place on the metal surface.

The further studies aimed at proving the existence of the contact potential difference, and particularly the experiments for production of chemically very pure metals by the high vacuum technique dealt a severe blow at the chemical theory. Nowadays, the modern electronic theory of metals and semiconductors proves definitely that at the place of contact of heterogeneous metals, contact potential difference appears, and that the phenomenon is of purely physical, to put it still more precisely, of purely electrodynamical nature. Authors [5], by using the *Fermi - Dirak* statistics, show that the energy (ε) distribution of the electrons within the metal is expressed by the formula:

(1)
$$f_{(\varepsilon)} = \frac{1}{\exp(\dfrac{\varepsilon - W_i}{kT}) + 1},$$

where W_i is the ultimate energy value or *Fermi*'s ultimate energy value, and k is *Boltzman* constant.

Al. Volta was the first to order the metals in sequence [2], to be later supplemented and expanded [3, 4]:

+ *Zn, Pb, Sn, Fe, Cu, Ag, Au, graphite, MnO₂* –

+ *Cs, Rb, K, Na, Li, Al, Zn, Cd, Pb, Bi, Fe, Cu, Ag, Au, Pt, C* –

Each metal from the above sequence is characterized by a quantity G, called "galvanic value" [2], which is constant for the given metal and determines its position in the sequence. This quantity increases starting from the noble metals and proceeding in the direction of the metals that are readily oxidized. At contact, the metals in the left hand side of the sequence are more positively electrified.

The *Fermi* levels of metals 1 and 2 at contact and individually are illustrated in Fig.1. The work function, respectively the electron's potential energy, is mathematically expressed by the equation:

(2)
$$W_P = -e\varphi$$

where W_P is the potential energy of the electron, e - the charge of the electron, and φ - the potential of the electron at a given point. At contact, a state of equilibrium is established, the condition for equilibrium between two heterogeneous contacting metals being expressed as follows:

(3)
$$\varphi_1 - G_1 = \varphi_2 - G_2 \, ,$$

(4)
$$\varphi_1 - \varphi_2 = G_1 - G_2 .$$

Fig.1

a
b
c

Fig.2
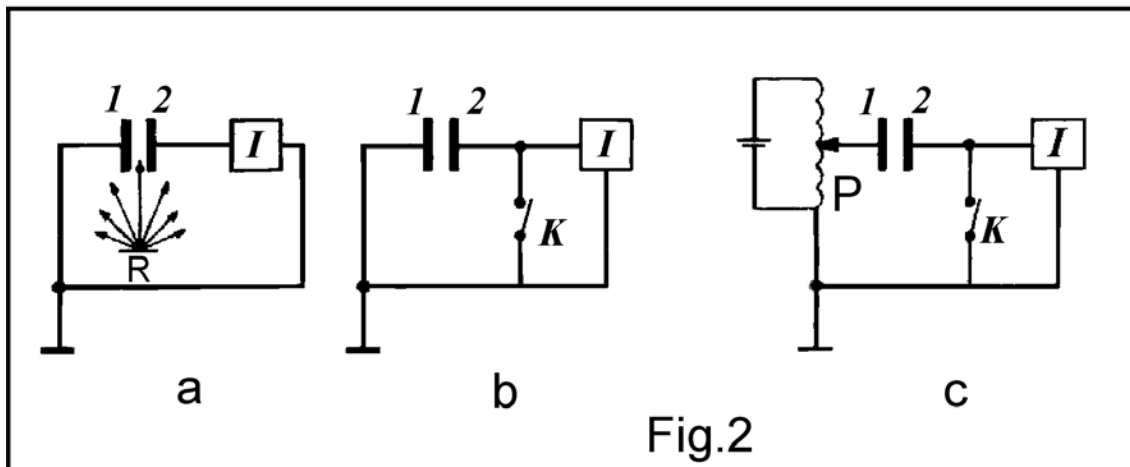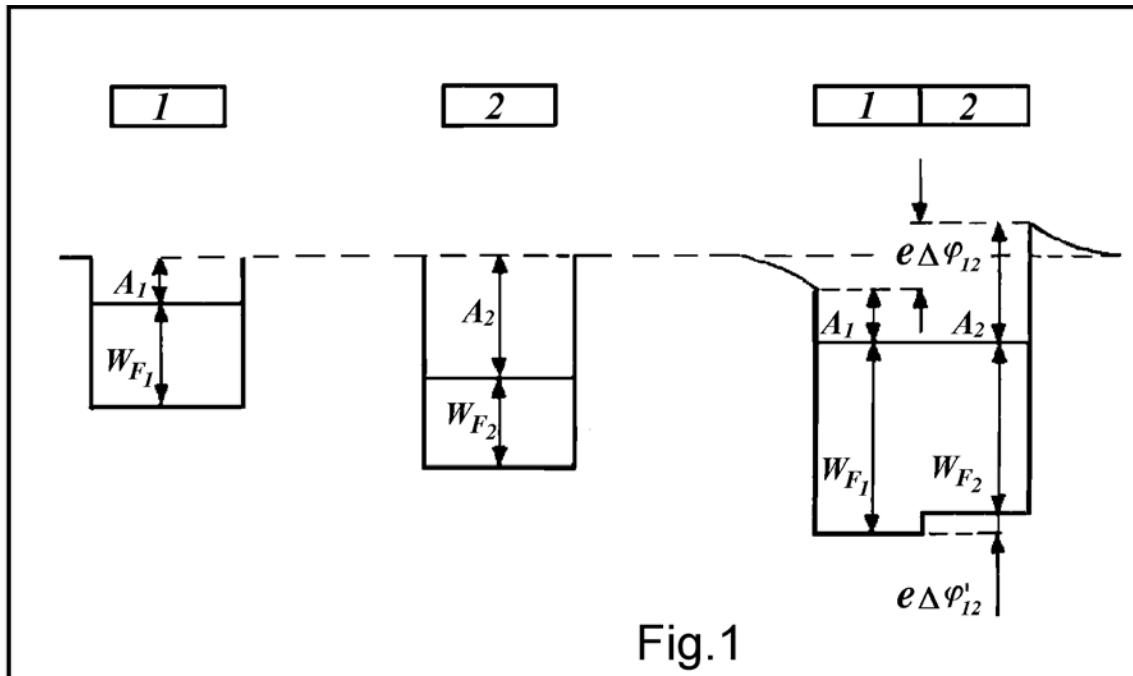
Equation (4) is in compliance with the modern interpretation of the phenomenon of the contact potential difference as difference of the metals work function:

(5)
$$\Delta\varphi_{12} = -\frac{A_1 - A_2}{e},$$

where $\Delta\varphi_{12}$ is also known as external contact potential difference. It has different values for different couples of metals. They vary from tenths of volts to several volts. The internal contact potential difference $\Delta\varphi'_{12}$ is not the subject of this work.

In chemical thermodynamics, the problem for the contact potential difference is perceived as a change of the thermodynamic or electrochemical potential in transportation of charges from one point of the system to another [2]. It is not difficult to see the coincidence with the electrostatic definition of the contact potential difference in purely electrostatic phenomena, and that this definition fits and is appropiate for all cases from the theory of the contact potential difference, i.e. in the state of equilibrium, between a definite point from the surface of a given metal and another nearby point from the surface of another metal, a contact potential difference exists, respectively a difference in the metals work function .

Methods of measurement

There are several different methods of measurement of the contact potential difference.

The principle of measurement of the ionization method is illustrated in Fig.2a, where 1 and 2 are metal plates (e.g. copper and zinc) which are connected to the indicator I (electrometer). One of the plates is grounded. R is a small amount of radioactive substance, ionizing the air between the plates, where contact potential difference is created, equal to the work function of both studied metals which is directly measured by the indicator. The method is convenient, it does not require a complex structure but its use is quite limited, because of the measurement error due to ionizing of the surrounding gas, and the method's inapplicability in high vacuum which provides for the maximum cleanness of the studied surface.

The photoelectric method is based on the photoelectric effect. The magnitude of photoemission is different for the different metals; it is related with the magnitude of the contact potential difference between them, respectively the difference between their work functions. The method has been named after the latter circumstance. However, it is inapplicable, too, much like the ionization method, because it does not allow for the correct determination of the contact potential difference, being related with drawing of the $V - A$ characteristics, the saturation current characteristics ,etc.

The only difference between the thermoelectron and the photoelectric measurement method is the different electron source. Here again, $V - A$ characteristics are drawn to read the contact potential difference, the method of shifting the characteristics is used, and the saturation current is read. In some of the configurations, the shift of the characteristics is effected by the use of magnetic field which reduces the anode current to a magnitude corresponding to the saturation current. It is at this moment that the difference in anode tensions is read which is different for the different metals. This method is also inaccurate. The magnitude is read graphically, and not immediately. Moreover, movable parts are used to replace the anodes.

The most widely used method is the capacitor one. The principle of measurement is presented schematically in Fig.2b. Between metal plates 1 and 2, contact potential difference, respectively difference in the work function, is established. The plates are charged by:

(6) $$q = U_{12}C_1$$

where C_1 is the capacity between the plates. Since the plate 1 is grounded, the charge appears on plate 2. With increase of the distance between the plates, changing the capacity C_1 to C_2, charge q provokes potential difference U which is measured by the indicator I. Mathematically, this is expressed by the equation

(7) $$U' = \frac{q}{C_1 + C_n}$$

where C_n is the capacity of conductor and indicator. From here, it is easy to calculate the contact potential difference U_{12}:

(8) $$U_{12} = U' \frac{C_2 + C_n}{C_1}$$

In the above version, the method is inaccurate because it relies on the precise determination of the distance between the plates and the specific capacity of the system. *Kelvin* avoids this inconvenience (Fig. 2c), [2]. By the use of potentiometer P, such tension can be chosen that would

compensate for the contact potential difference between metal plates 1 and 2 until the indicator shows zero. And last, *Zisman* [6] introduces vibrating (mechanically or electronically) plates. Thus, the capacitor method with vibrating capacitor assumes its most effective and refined version. It becomes the basic method for development of modern techniques for measurement of contact potential difference.

Conclusions

1.While, with the ionization and thermoelectron method for measurement of the contact potential difference between two heterogeneous metals, the ultraviolet emission and the heating to high temperatures provides inaccurate data, resulting from the change of the chemical composition on the surface of the studied material, respectively to change in the work function, with the capacitor method with vibrating capacitor, the measurement can be done in any type of medium: air and vacuum. The surface of the metal plates can assume any form and size, as much as the size of a vacuum friction trace which is important to vacuum tribology and which substantially increases the potentials of the measurement method. The measurement accuracy is high   (up to one tenth volts on an area a little bit greater than two square millimeters). The values of the measured quantity can be read continuously.

2.Based on the theory of the contact potential difference, modern measurement techniques can be developed to be applied not only in electrochemistry and high vacuum instrumentation, but in modern space instrumentation vacuum tribology, space technologies and space materials. Determination and forecast of the compatibility of space-used materials becomes reality.

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A brief review is made of some of the major definitions, quantities, and ratios from the theory of the contact potential difference. Some methods for its measurement are described, greatest attention being paid to one of them which is most widely applied and having the greatest advantages in the field of space tribology.