On the Temperature Dependence of the Photoelectric Work Function of Contact Materials

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Abstract

The nature of the contact material plays a key role to determine the characteristics of the electric arcs and particularly those of the electronic emission. Mechanical and thermodynamic properties as well as electron emission of such complicated alloys present a lack of reliable and accurate experimental data.
The purpose of this paper is to present the development of a method for measuring photoelectric work function of pure contact materials that are actually used in relays. Also reported in this manuscript are the results of experimental work whose purpose has been the buildup of a reliable photoelectric system and associated monochromatic ultra-violet radiations source, and the photoelectric measurement of the electron work functions (EWF) of contact materials. In order to study the influence of temperature on the EWF, a vacuum furnace was used for heating the metallic samples up to 700 K.
The Fowler's method of isothermal curves was used for the photoelectric measurement of the EWF. As a first test of the experimental UHV set-up, the EWF of the silver contact materials, namely pure polycrystalline metals (Ag, Cu, Ni, Sn and Zn) were investigated to study the influence of surface cathode temperature on the EWF. In the present study, the photoelectric measurements about silver contacts have shown a linear decrease of the EWF with increasing temperature, i.e. the temperature coefficient $\alpha = \frac{d\phi}{dt}$ is constant and negative: $\alpha = -4.58 \cdot 10^{-4} eV/K$ in the experiment temperature range [300 K – 780 K].

1. Introduction

One of the main concerns of manufacturers of switching devices (contactors, circuit breakers) is to find a better compromise between cost and performance of the contact materials. Several authors [1, 2] have shown that surface state and its composition from initial ones have an effect on cathodic spot duration, on their dimensions and cathode erosion; this is due to electron crossing from electrode metallic state to plasma state of ionizing region. In this case, presence of materials different from basic one or existence of micro tips yields electric fields which extract electrons.

On the other hand, understanding of the phenomena of electron emission at the electrodes must pass through the knowledge of an important physical parameter: the electron work function. The evolution of this physical constant due to changes of the contact surface is a measurable physical reality. However, the problem is complex because many other phenomena, such as roughness, adsorption and contamination, can intervene and influence the electronic emissivity of the contact surface.

Furthermore, in the composition of the contact materials, often involved various metallic additives whose nature and proportions required by the industrial manufacturing are not known. If the melting temperature of the contact material cannot be modified by the addition of a few hundred ppm of sodium, for example, it is not the case for the work function of the composite material [3, 4]. It has been found that the latter physical parameter is a linear function of the atomic proportion of the metal additive [5]; and because the decrease in the work function implies increased electron emission, therefore, it is necessary to know this physical constant with good accuracy.

Electron Work Function (EWF) is crucially important for the characteristics of electron emission from solid surfaces. EWF, denoted by Φ and measured in electron volts, is equal to the minimum work that must be done to remove an electron from the surface of metal at 0 K, so it is a main decisive factor to the surface properties of materials. The EWF of a metal is a major physical quantity that is extremely sensitive to the chemical and physical conditions at its surface. Small amounts of contaminants present at a surface can invalidate EWF measurements. Furthermore, EWF measurements on alloys are subject to the complication that the alloy surface composition can be appreciably different from the bulk composition.

The electron work function of contact materials has not yet been studied in sufficient detail. Very little

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is known about the changes of the EWF of silver materials when subjected to heating procedures and arcing phenomena. Moreover, theoretical calculations made in the laboratory (LAEPT, Clermont-Ferrand - France) [2] showed how important is to know EWF value of the cathode material. In this arc root model, a variation of 0.1 eV gives rise to 100 K variation on temperature of cathodic spot (which temperature is about 3000 K to 5000 K). So, it is imperative to know this physical constant with a good accuracy. Thus, the need of reliable experimental data on electronic behavior obtained under controlled conditions for silver electrodes of known physical properties is emphasized.

This paper reports the results of experimental work whose purpose has been the buildup of a reliable photoelectric system and associated monochromatic ultra-violet radiations source and the photoelectric measurement of the EWF of pure silver contacts used in commercial breakers. As a first test of the experimental UHV set-up, experimental measurements of this parameter have been made versus vacuum heating cycles and temperature.

In order to improve understanding of the phenomena cited earlier, we have measured electron work function for different cases of basic material evolution. We present in this paper, the measurement of the photoemission electron work function for electrical contacts made with pure metal (Ag (99.99) versus temperature.

Experimental method developed and used is based on measuring, in ultrahigh vacuum conditions, photoelectric currents emitted by small electrode exposed to ultraviolet radiations of different wavelengths and same intensity. The electron work function (EWF) of silver alloyed contacts was measured using Fowler's method of isothermal curves [6]. We show in this paper how varies EWF of silver contact versus temperature.

2. Experiment

2.1 Experimental procedures

To bring our measurements to a successful conclusion, an adapted experimental set up has been imagined and built; it has been given in previous papers [7–11]. The measurement principle of the experimental set-up is schematically shown in Fig. 1.

A vacuum furnace, not shown in Figure 1, was used for heating the interchangeable cathode C. Molybdenum reflector screens, concentric to the furnace, reduce thermal losses. The furnace is heated by passing dc currents supplied by batteries, because ac current disturbs the measurement of the photoelectric current. The cathode is heated by thermal radiation between the furnace and the cathode, and then by the thermal conduction between the metallic holder H and the cathode C.

Within the vacuum chamber Ch the cathode was out of the line of sight, preventing measurements by contactless methods such as pyrometer and IR thermometer [7]. So the temperature of the cathode and heating element was measured by using two chromel-alumel thermocouples (Thermocoax). These measurements are made when there is no photoelectric current, because it is impossible to measure simultaneously both photoelectric current and cathode temperature. The thermocouple which is fixed on the cathode surface plays the role of an electromagnetic antenna which disturbs largely photoelectric current measurements. It must be removed when photoelectric current is measured.

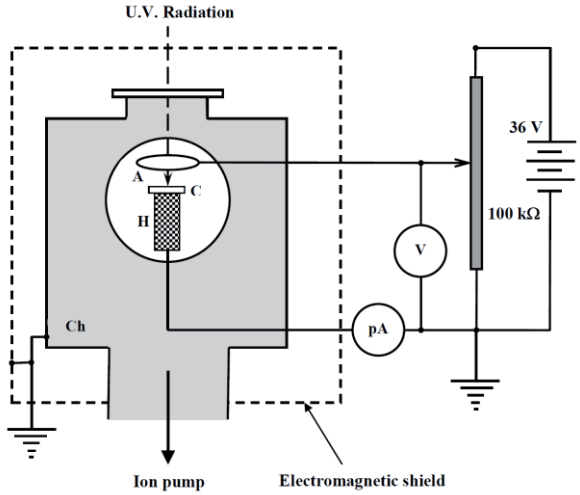

Figure 1 : Principle of measurement.

Temperature measurements were carried out when thermal equilibrium is reached within the vacuum chamber. Measurement accuracy is equal to ± 2.5 K up to 600 K and ±0.75% beyond. A calibration curve gives cathode temperature versus furnace temperature [7]. Thus, knowing the furnace temperature, the cathode temperature is determined by using the calibration curve. The calibration has been performed in the whole temperature range studied, thus avoiding extrapolation.

2.2 Experimental method

In determining the work function, the emitted electron current was measured as a function of photon energy. Typical curves of photoelectron spectral distributions for silver and silver-zinc oxide contacts, at room temperature and UHV conditions, are given in Fig. 2. The EWF data were obtained with the aid of Fowler's theory for the photoelectric current. R. H. Fowler has developed a theory of the energy distribution of electrons, based upon the assumption that the free electrons in a metal obey the Fermi-Dirac statistics. According to this theory the photocurrent is given by:

$$Log\left(\frac{I}{T^2}\right) = B + F(x); \qquad x = \frac{h(\nu - \nu_0)}{kT} \qquad (1)$$

where T is absolute temperature of the emitting surface, h is Planck's constant, k is Boltzmann's constant. F(x) is an increasing function of the variable x, it is a so-called Fowler universal curve, whose shape is the same for all metals and alloys. The constant B which is

independent of frequency ν and temperature T represents the photoelectric surface yield; it depends upon the optical absorption of the specimen and the photoelectric efficiency of the surface and the probability of escape of the photoelectrons. In order to obtain the work function $\Phi = h\nu_0$ the well known equation (1) has to be used. Theory of uncertainties applied in equation (1) gives:

$$\frac{u_\Phi^2}{\Phi^2} = \frac{u_T^2}{T^2} + \frac{1}{D^2}\left\{\left[4+\left(\frac{h\nu}{kT}\right)^2\right]\frac{u_T^2}{T^2} + \frac{u_I^2}{I^2} + \left(\frac{h\nu}{kT}\right)^2\frac{u_\nu^2}{\nu^2}\right\} \quad (2)$$

where :

- T is the absolute temperature, in Kelvin;
- I is the photocurrent intensity, in Ampere;
- ν is the photon frequency of UV radiation, in Hertz;
- $u_\nu = \frac{c}{\lambda^2}u_\lambda$, c being the light celerity;
- $D = \frac{\Phi}{kT} = \frac{h\nu_0}{kT}$, ν_0 being the threshold frequency.

We pass from the absolute uncertainty Δ to the standard deviation u by dividing the former by 3 (realistic convention – fact of experience). Thus the theory of uncertainties allows calculating the measurement accuracy by using equation (2). The procedures of cathode heating and temperature measurements have been given in much details in an earlier paper [7] where the Fowler's photoelectric method of isothermal curves was used for the following EWF investigations which are presented in this work.

3. Results

In order to investigate the influence of temperature on EWF for silver contacts, it was necessary to extend photocurrent measurements to higher temperatures. Work function measurements carried out at high temperature are rather difficult because the thermionic emission is superposed on the photocurrents.

Furthermore, the total current obtained fluctuates enormously, so exact photoelectric measurements are not possible. An averaging method was used where total current is measured every 10 s at a well defined high temperature. Twenty values were stored by the picoammeter for each wavelength of incident radiation. Photoemission was then interrupted by switching off the deuterium lamp supply, and similar measurements were made for the thermionic current alone. Photoelectric current is obtained by subtracting the thermionic current from the total current.

When attempts were made to obtain photocurrent readings at higher temperatures, severe power fluctuations of current started to appear at approximately 700 K and became more intense as temperature increased. Unfortunately, it was very difficult to undertake photocurrent measurements with such fluctuations.

Cycle	Cleaning Time, [day]	Heating Time, [hour]	Maximal Temperature, [K]	Temperature Measurement, [K]	Electron Work Function Φ, [eV]
1	1	–	297	297	3.70 ± 0.03
2	1	6	**533**	**533**	**3.96 ± 0.07**
3	2	–	299	299	4.03 ± 0.07
4	2	–	293	293	4.25 ± 0.03
5	5	24	530	297	4.30 ± 0.03
	5	–	297	297	4.24 ± 0.03
	5	–	297	297	4.26 ± 0.03
6	5	6	**533**	**533**	**4.15 ± 0.07**
	5	6	**533**	**533**	**4.17 ± 0.07**
7	6	2	**533**	**533**	**4.11 ± 0.07**
	6	2	**533**	**533**	**4.05 ± 0.07**
8	6	2	**773**	**773**	**3.73 ± 0.08**
	6	2	**773**	**773**	**4.04 ± 0.08**
9	8	–	296	296	4.25 ± 0.03
	8	–	296	296	4.24 ± 0.03

Table 1 : EWFs of the unpolished contact Ag (99.99%).

The EWFs of the unpolished contact Ag (99.99%), after 9 cleaning and/or heating cycles and 8 days of vacuum outgassing, in high vacuum 1.4x10^{-7} mbar at various temperatures, are listed in Table 1.

Typical curves of photoelectron spectral distribution for a virgin and unpolished contact made of silver (purity 99.99%) at T = 300 K, T = 530 K and T = 780 K, and UHV conditions, are given in Figure 2.

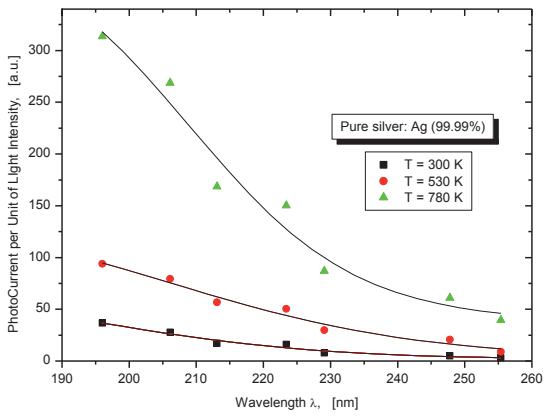

Figure 2 : Photoelectron spectral distribution curves.

In determining the EWF for polycrystalline silver (virgin commercial contact), at these temperatures, the

emitted current was measured as a function of photon energy. The EWFs were determined with a precision of less than one percent and compared with the results given by other authors.

Typical Fowler isothermal curves are plotted in Figure 3 for the virgin Ag contact subjected to heating in ultra-high vacuum. Solid line is the theoretical curve. Points are displaced experimental values. The EWFs obtained from this curve are 4.25 ± 0.03 eV at T = 297 K, 4.15 ± 0.07 eV at T = 530 K, and 4.04 ± 0.08 eV.

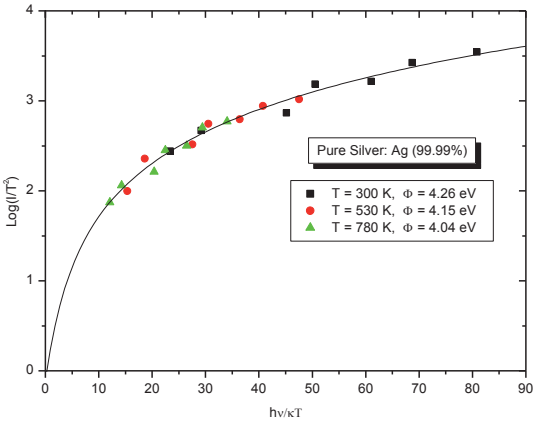

Figure 3 : Typical Fowler isothermal curves.

It is worth pointed out from photoelectric measurements that the EWF of silver contact decreases linearly with increasing temperature, i.e. the temperature coefficients $\alpha = \frac{d\phi}{dt}$ is constant and negative. According to Table 1, Fig. 4 shows the temperature dependent reduction of the EWF of polycrystalline silver contact. The temperature coefficient obtained for polycrystalline silver contact is $\alpha = -4.58 \cdot 10^{-4} eV/K$ in the experiment temperature range [300 K – 780 K].

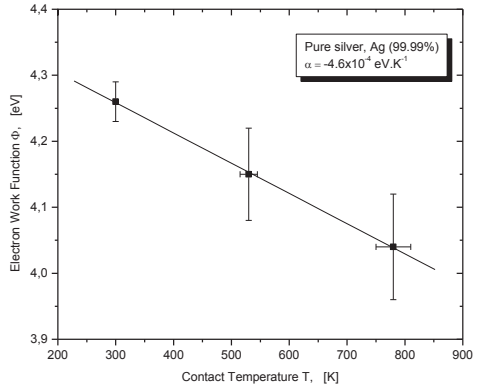

Figure 4 : Temperature dependence of EWF for silver.

It may be deduced from our measurements that α for pure silver (99.99%) is equal to −5.315 k, where k = 8.617 x 10^{-5} eV.K^{-1}, in good agreement with the general rule that α for pure metals is generally less than ± a few Boltzmann constants [12].

It is emphasized from this investigation that the EWF of polycrystalline Ag contact have increased from 3.70 eV at room temperature, without any annealing, to 4.30 eV, and finally have stabilized at the vicinity of 4.26 eV after several vacuum heat treatments at 533 K and 773 K. These results tell us that the clean surface is essential to obtain reliable EWF. Further, they indicate that the EWF of a contact material when its surface is the cleanest is greater than when it is virgin (as commercially available) in agreement with the data obtained by many authors as discussed below.

Studies of the photoelectric properties of silver have been made by many authors and various other values have been reported [12]. Forty years before the present study, Haque and Fritz [13] investigated the work function changes on contact materials. These authors found Φ_{Ag} = 3.94 eV and noted the increase in this value to 4.33 eV when the Ag surface consists of silver oxide and silver sulfide after heating at about 873 K.

The EWF for the virgin silver contact subjected to various vacuum heating cycles, determined here as 4.26 ± 0.03 eV at room temperature, is in agreement with the result of Dweydari and Mee [14]. The results presented in this work show the temperature dependence of the work function of the silver contact. The latter is very sensitive to conditions on sample surface. Indeed, this one can be covered with atomic or molecular layers of impurities such as CO, H_2, H_2O, O_2, N_2 and CO_2 [1, 2].

4. Discussion

The results for pure silver metal show an evolution of the work function with temperature; a decrease of this parameter of about 0.2 – 0.3 eV is observed when the cathode temperature reaches 700 K, independently of the nature of the material. The obtained results are rather approximate. This method is not very accurate at higher temperature, because above 700 K the thermionic current dominates and the measurements of the photoelectric current are falsified by large fluctuations.

The temperature variation of the EWF of metals with increasing temperature may be caused by a series of different combined factors like thermal expansion, the internal effect of atomic vibrations, the variation of the chemical potential, spontaneous volume magnetostriction (for ferromagnetic metals Ni, Fe, …) etc [7].

It is important to note that EWF variation of order of 0.2 eV has a significant effect on physical properties of the new-born spot; underlying material does not reach immediately working temperature. It would be interesting to measure EWF of material reaching its melting point.

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Furthermore, measuring the EWF of silver alloys electrodes during operation would be strongly helpful for a better understanding of the physical behavior of the cathodic spot. The temperature in the cathode spot is greater than 2000 K, and there is an enormous pressure of metal vapor. Question arises as to how we can apply the obtained results to a temperature lower than 1000 K and under vacuum. There is still a lack of understanding of the physics of this phenomenon.

5. Conclusions

In the present study, the influence of temperature on the EWF of Ag-Me electrical contacts has been revealed. This electronic parameter is very sensitive to surface state which drastically changes after vaporization and diffusion due to long heating time in vacuum. Generally speaking, one can keep in mind from this investigation that, EWF of pure metals decreases with the increase of temperature; but how is the case for Ag-Me and Ag-MeO alloys.

The measurement method used in this investigation is well adapted to pure metals, but it would be necessary to be careful for Ag-Me and Ag-MeO electrical contacts, particularly when emitting surfaces are covered with oxide layer due to action of numerous electrical arcs. Further experimental investigation would be extremely helpful for a better knowledge of the electron emission for the new contact materials (Ag-Me and Ag-MeO) during operation under industrial use. At the time of establishment of the arc, the temperature at the cathode, near 3500 K will increase the diffusion and evaporation of the various components of the metal alloy, altering the structure of the contact surface. Moreover, additional studies are worth to be carried out on the correlation between surface roughness and electron work function.

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