

# Effect of heat surface treatment on photoelectric work function of silver-metal alloys

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## Abstract

Contact materials used for electrical breakers are often made with silver alloys. Mechanical and thermodynamical properties as well as electron emission of such complicated alloys present a lack of reliable and accurate experimental data. At present, new types of contactors with longer duration are marketed, but manufacturers do not understand well why this improvement.

This paper deals mainly with electron work function (EWF) measurements in UHV conditions. Also, the photoelectric emission from silver-metal (Ag-Me) electrical contacts (Ag-Ni (60/40), Ag-Ni (70/30) and Ag-W (50/50)) has been investigated in the spectral range of 196-256 nm. The effects of thermal surface treatment on EWF of the abovementioned contacts were studied at room temperature and residual gas pressure of  $1.4 \times 10^{-7}$  mbar. The EWF of the contact pastille made with silver alloys Ag-Ni and Ag-W varies with surface treatments: cleaning by vacuum outgassing and annealing (long heating time in UHV). By heating alloy contact in ultra high vacuum large variations of EWF have been observed, which result from material component vaporization by sheets.

In addition, the influence of arcing on EWF of binary alloys has been investigated. Also, EWF varies with the number of applied arcs. Therefore, after 500 arcs in air, the observed EWF increasing is probably due to progressive inclusion of oxide on alloy surface. Microscopic examination is necessary to get better understandings on EWF of silver alloys, for both virgin and eroded electric contacts. So, surface analysis by SEM and EDS have been performed to produce proofs of these various phenomena.

## Keywords

Vacuum heat treatment, electron work function, fowler methods, contact materials, arcing effects.

## 1 Introduction

Materials used to provide both electrical current flow and creation of electric arc in low voltage switchgear devices such as contactors, relays, circuit breakers and switches, are made of silver based alloys namely Ag-CdO (88/12), Ag-ZnO (92/8), Ag-SnO<sub>2</sub> (88/12), Ag-Ni (70/30), Ag-Ni (60/40) and Ag-W (50/50) [Pandey 2008, Wingert 1989]. These alloys have been extensively used as electrical contact materials in current switching devices because of their high conductivity and good resistance to corrosion, fusion and wear [Holm 1967, Schröder 1987]. They are also characterized by reduced erosion rates due to the rheological properties of molten composite which stabilize the arc feet and limit the ejection of molten metal particles.

Nickel is a well known refractory material (melting point 1455°C) which increases both hardness and resistance to erosion for low power arcs when added to silver with 30% or 40% of mass fraction. Therefore, silver-nickel materials exhibit good contact and switching properties such as, high arc erosion resistance, resistance against welding, good arc moving properties, good arc extinguishing properties and good or sufficient ductility depending on the

Ni content. Moreover, the improved mechanical properties are maintained even after undergoing arcing. Silver-nickel system contacts, well known as materials with high workability and low contact resistance, are used as medium to weak current contacts [Schröder 1987] in power switch and breaker apparatus because of its excellent thermal and electrical conductivities, low and steady contact resistance and good arc-ablation resistance. Among other applications, the Ag-Ni electrical contacts are used as relay for vehicles, thermostats, power relays, current-limiting breakers and electromagnetic switches.

The Electron Work Function (EWF) is an important characteristic of the surface state of metals and alloys, which determines their emission properties [Holm 1967, Akbi 1998, Lefort 1994]. The EWF, denoted by  $\Phi$  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 [Lang 1971]. The EWF has two terms: a bulk term due to the fact that the environment of the electron is different in the solid and the vacuum, and a surface term which arises from the existence in the surface area of a dipole moment. The surface term depends on arrangement of atoms on the surface contact and also the potential distribution of foreign atoms adsorbed or attached by chemical bonds. The EWF of a metal 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 [Fain 1974].

Despite intense research over the past few decades, it must be recognized that little has been known on EWF of alloyed electrical contacts and their surface composition dependence. One of the main difficulties in studying EWF changes is the surface segregation which occurs during thermal treatment in vacuum, and thus modifies the chemical composition of the contact surface. On the other hand, surface contamination of the electrical contact increases its EWF. The most common contaminant species are oxides formed during thermal diffusion and vacuum outgassing processes [Koller 2001]. For most metals, experimental and theoretical values of the EWF values have been reliably determined [Michaelson 1977, Eastman 1970]. Unfortunately, up to the present time, EWF data for silver-metal alloys (Ag-Me) and pseudo-alloys such as silver-metal oxide (Ag-MeO) are still unavailable.

To obtain a better understanding of electron emission occurring in a cathode alloy subject to vacuum outgassing and heat treatment, Fowler's method of isothermal curves is used [Fowler 1931] to determine accurately the EWF. In a previous paper [Akbi 2014-1], the effects of surface treatments by vacuum outgassing on EWF silver-nickel Ag-Ni (70/30) were described. The aim of this work is to measure and explain the phenomenon of electron emission occurring at the surface of two types of silver based cathode alloys namely Ag-Ni (60/40) and Ag-W (50/50). A scanning electron microscope (SEM) with energy dispersive X-ray spectrum was used for the microstructure measurements. Fowler's method of isothermal curves is used to study the effect of heat treatment in ultra-high vacuum (UHV) environment on surface morphology, microstructure, and the EWF of the Ag-Ni alloys. This paper also attempts to explain the correlation between EWF and surface morphology of the alloys when subject to vacuum heat treatment. Therefore, the role of the metal alloy nanoparticles (Ni, W) will be more clearly defined.

## 2 Experimental details

Because of a lack of theory of EWF nowadays, the EWF is usually determined experimentally. To bring our measurements to a successful conclusion, an adapted experimental set-up has been imagined and used. A detailed description of experimental device has been given elsewhere [Akbi 1998, Lefort 1994]. It consists of vacuum pumps, an ultraviolet radiation system, a photoelectric measurements apparatus, and an UHV heating

system of cathode. All the measurements were carried out with equipment of our own construction, in which a residual gas pressure of  $10^{-9}$  mbar could be obtained using a primary pump, a turbomolecular pump and an ionic pump [Akbi 1998, Lefort 1993]. Much experimental detail about UHV procedures, the electrical measurement principle, and the in-situ heating furnace have been given in [Akbi 1998, Akbi 2014-3].

The measurement principle of the experimental set-up is schematically shown in Fig. 1. A vacuum furnace 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 [Akbi 1998]. So the temperature of the cathode and heating element was measured by using two chromel-alumel thermocouples (Thermocoax).

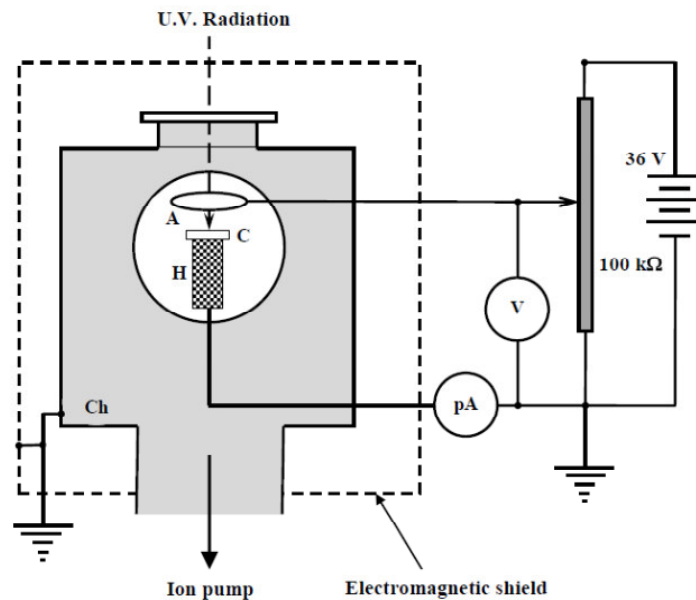


Figure 1: Principle of measurement

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. Temperature measurements were carried out when thermal equilibrium is reached within the vacuum chamber. Measurement accuracy is equal to  $\pm 2.5$  K up to 600 K and  $\pm 0.75\%$  beyond. A calibration curve gives cathode temperature versus furnace temperature [Akbi 1998]. 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.

Passage of ultraviolet radiation from the outside of high vacuum chamber towards inside was through a window made of sapphire having a spectral transmission factor greater than 80% in the wavelength range of work. The developed and used experimental method is based on measuring photoelectric currents, emitted by a small electrode exposed to ultraviolet radiations of different wavelengths and same intensity, in ultra high vacuum conditions. The monochromatic UV radiations with the following wavelengths: 196.0 nm, 206.1 nm, 213.1 nm, 223.4 nm, 229.1 nm, 247.8 nm, and 255.4 nm, are obtained with the use of a Hamamatsu

Deuterium Lamp and seven interferential filters with a passing band of 10 nm at the half of maximum transmission. A very complex electric circuit with an electromagnetic shielding has been set up; it allowed accurately photocurrent measurements whose values were of the order of  $10^{-13}$  A. Photocurrent measurements are carried out with a Keithley picoammeter (number 466). The electromagnetic shielding has been used to make stable the measurement of photoelectric current; it stops radiofrequency waves, external electrostatic field, etc.

### 3 Results and discussion

#### 3.1 Influence of vacuum heat treatment

After an initial heat-treating period of 24 h at 473 K, the EWF of the Ag-W (50/50) contact determined at room temperature was found to be equal to  $(4.37 \pm 0.03)$  eV. Further series of vacuum heat treatments changed the values considerably in a direction towards an increase of the work function for the Ag-W (50/50) electrical contact, measured at room temperature. After a first round of prolonged heating under vacuum conditions for a period of 16 hours, where the temperature of the cathode surface reached 573 K, we measured, at room temperature, a work function  $\Phi = (4.46 \pm 0.03)$  eV. After three rounds of additional heating for a total of 14 hours, where the temperature of the cathode surface reaches 1073 K for the first cycle period of 4 h, 773 K for the second cycle period of 4 h, and 573 K during the third cycle period of 6 h, the value of the EWF measured at room temperature is  $\Phi = (4.48 \pm 0.03)$  eV. Note that the EWF after this heating treatment takes a value close to that of tungsten (4.55 eV) [Fomenko 1966]. This suggests that during heating, an evaporation of silver atoms occurred from the surface layers towards the vacuum chamber, such as the surface of the cathode was found covered exclusively with a majority of tungsten atoms. This was confirmed by observations made at the cathode surface by scanning electron microscopy (Fig. 3) and analyzes of the contact surface by X-ray spectrometry with a selected energy spectrometer (EDS) [Zouache 1997].



Figure 3: Micrographs for (a) a virgin contact, Ag–W (50/50) and for (b) a vacuum heated contact, Ag–W(50/50). SEM magnification  $\times 1000$ .

The SEM observations made on a virgin and rough contact surface before heat treatment show clear areas scattered over a darker one (Figure 3(a)). The microanalyses by EDS spectra showed that the dark areas are composed of silver atoms (atomic number 47), whereas lighter ones correspond mainly to tungsten (atomic number 74) in different proportions [Akbi 2014-2]. The phase contrast image of a metal observed by SEM depends on the atomic number of the metal element. Areas of the specimen with high atomic number will be more whitish than those with a low atomic number. Areas of the specimen composed of higher atomic number

element, i.e. tungsten (W), emit more backscatter signal and thus appear brighter in the image. After three cycles of heating, it is clear through the electron microscope, that the contact surface of polished silver tungsten (Ag-W (50/50)) is mainly covered with bright areas. Darkest islands are much less extensive than before heating (Figure 3(b)), while brighter ones raised with increased temperature. The spectra of X-ray analyzes confirm that the pale zones are made up almost entirely of tungsten atoms, whereas darker are silver atoms [Akbi 2014-2].

### 3.2 Influence of arcing

In order to study the effects of arcing on the EWF, the silver-metal samples were subjected to electric arcs in air, at atmospheric pressure and room temperature, and after that introduced into the vacuum chamber of the experimental set-up for EWF measurements. The experiments described in this paragraph were performed with Ag-Ni contacts. The material composition of each pair of the tested contacts was the same. However, only cathodes were investigated.

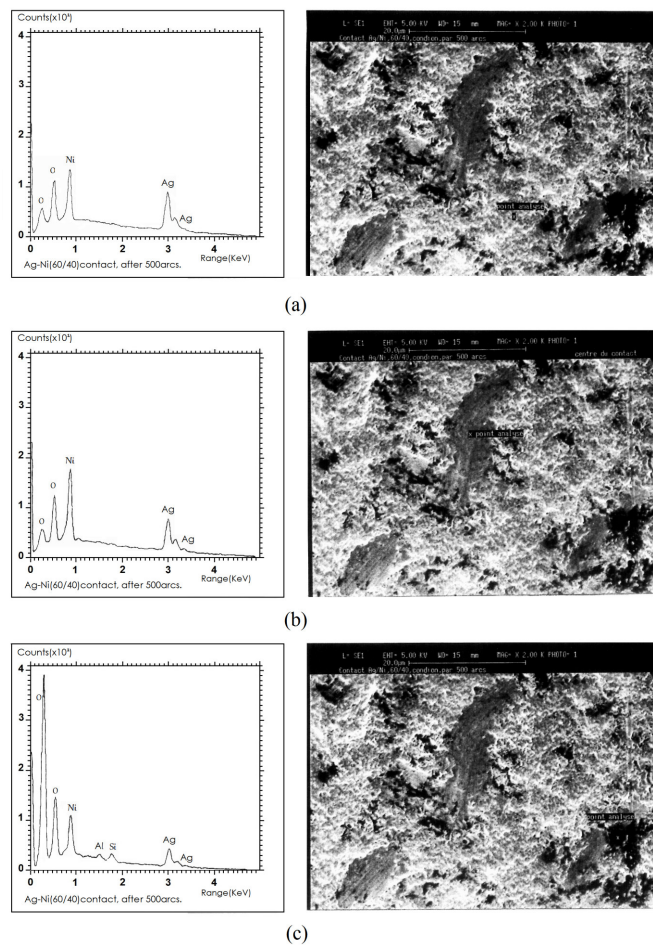
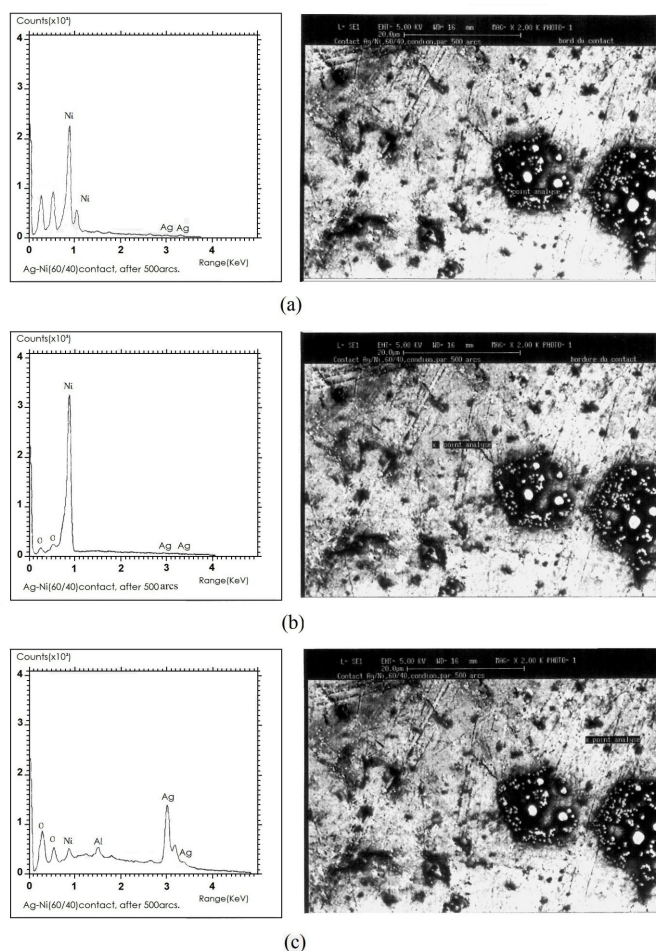


Figure 4: EDS line scans of silver and nickel oxides formed on the centre of Ag-Ni (60/40) cathode surface conditioned by 500 electric arcs in air. Three representative points ((a), (b) and (c)) situated at different locations were analyzed, SEM magnification x 2000.

Contacts were mounted in a contactor working repeatedly on air (laboratory atmosphere). When submitted to 100 electric arcs, Ag-Ni (60/40) contact EWF varies from  $(4.33 \pm 0.03)$  eV to  $(4.30 \pm 0.03)$  eV. To obtain a very good vacuum for work function measurements, we had to clean contact before measuring it. It is obvious that measurement value should not be the same if oxide created on surface remained on it. A same measurement made after 500 make-and-break operations gives  $(4.38 \pm 0.03)$  eV. In this case, the EWF increasing is due to progressive inclusion of oxide on alloy surface. Hence, we were dealing with a layer of both nickel oxide and silver oxide, because usually, the work function of a metal oxide is greater

than that of the corresponding metal because of the Fermi level change. As the metal is oxidized, it loses its electrons resulting in a decrease of Fermi level.

The scanning electron micrograph of damage on a silver-nickel Ag-Ni (60/40) after 500 make-and-break operations shows several small individual craters, especially in the central area of the surface electrode, and a large number of protuberances and submicron spheres at the cathode periphery. Examination of the contact centre in Ag-Ni (60/40) conditioned with 500 arcs (Fig. 4) shows a disturbed area where the ripples of molten metal are fixed, with surrounding dark hollow areas and relatively uniform areas. Spectra analyzes of three representative points corresponding to various regions (Fig. 4) indicate the presence of nickel, silver, carbon and oxygen in varying proportions.



**Figure 5:** EDS line scans of silver and nickel oxides formed on the periphery of Ag-Ni (60/40) cathode surface conditioned by 500 electric arcs in air. The additives have migrated towards the cathode periphery. Three representative points ((a), (b) and (c)) situated at different locations were analyzed, SEM magnification x 2000.

The melting point of silver (960.5 ° C) is lower than that of nickel (1455 ° C), thus it is likely that the most regions affected by the arc are the beaches of silver. As, it is also likely that the arc ignition could be done by one of these areas, given the value of the work function of silver ( $4.26 \pm 0.03$ ) eV, lower than the corresponding nickel ( $4.51 \pm 0.03$ ) eV. In addition to that, it can be noted that the spectrum analysis of three various points in the contact centre, as shown in Figures 4 (a), 4 (b) and 4 (c), show a predominance of silver, nickel, and sometimes oxygen atoms, and the almost complete absence of additives. The latter have migrated to the periphery of the contact and were evaporated; thus, we are witnessing a cleaning of the cathode by opening arcs. One starts with the centre of the contact and extending towards the periphery, in such a way that the number of opening arcs increases. The droplets deposited on the side of the contact suggest strong ejections of liquid metal when a sufficient melt is

formed on the surface of the electrode. However, because of polishing, Si and Al particles were observed on the whole contact surface. Examination of the contact periphery shows a scratched surface, unaffected by the electromechanical conditioning, on which are deposited droplets of molten metal radially ejected; it also shows macroscopic droplets of molten nickel (Fig. 5(a)) on which are clustered a multitude of grains of liquid sodium. The EDS lines analysis show sometimes a predominance of nickel (Fig. 5 (b)), and in some cases a significant presence of silver (Fig.5 (c)). It must be noted that even few hundreds of ppm of sodium may change the EWF of silver materials containing additives [Bentounes 1986].

The alkaline additive has been added to the contact material as a salt during the blending process ( $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{Li}_2\text{CO}_3$ ). According to these authors, in the absence of data, it is possible to use estimation, assuming that emission in a composite material follows the law of mixture [Lindermayer 1981]:

$$J_T = 1.2 \cdot 10^{-6} T^2 \left[ (1 - a_i) \exp\left(-\frac{e\Phi_A}{kT}\right) + a_i \exp\left(-\frac{e\Phi_i}{kT}\right) \right] \quad (4)$$

where  $\Phi_a$  is work function of basic metal,  $\Phi_i$  is work function of the additive,  $a_i$  is proportion of additive,  $k$  is Boltzmann constant,  $e$  is electron charge and  $T$  is temperature. Thus,

for	pure Ag	$J_T = 5.10^3 \text{ A.m}^{-2}$
for	Ag + 460 ppm Na	$J_T = 10^6 \text{ A.m}^{-2}$

## 4 Conclusion

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.

In addition, all the experiments carried out in this study demonstrate perfectly how the EWF of the binary alloys varies between the EWF values of each of the two components ( $4.26 \pm 0.03$ ) eV for Ag and ( $4.51 \pm 0.03$ ) eV for Ni. The observations made in the present investigation reveal the multiple layer structure of the silver-nickel alloys. Indeed, segregation of nickel interfaces of a solid solution Ni-Ag is important. A good interpretation of the results is thus obtained by a multilayer model for silver-metal alloys taking into account the strong intergranular and volume segregation of metal nanoparticles (Ni or W). The observations and analyses made with electron microscopy have illustrated the evolution of the surface composition for contact material after several heating treatments.

The observations through SEM and the analyses by EDS enabled us to show how the EWF of silver-nickel alloys increases after arcing. The relationships between material behaviors and its structures are extremely complicated, especially the correlation between electronic emission of metals and alloys, and their surface properties. Moreover, the effect of heat treatment on the electrical and physical properties of silver based materials has received insufficient attention. Hence, additional studies are worth to be carried out on the correlation between surface conditions and electron work function.

Finally, we are still lacking sufficient knowledge on the electronic properties of alloy surfaces to fully understand the behavior of EWF. The mechanism responsible for the effect of surface conditions on EWF is not yet clear or controversial. Therefore, further investigations are very

necessary and significant for a better understanding of the correlation between EWF and surface morphology of metals and alloys.

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