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Aluminum Work Function: Effect of Oxidation, Mechanical Scraping, and Ion Bombardment

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SUMMARY

Surface studies have been performed on aluminum polycrystalline surfaces which have been mechanically scraped. Such studies were initiated in order to understand surface effects occurring in tribological processes which involve rubbing surfaces and the effects of adsorption of oxygen.

To characterize the surfaces, the following three different experimental approaches have been used:

1. X.P.S. (x-ray photoelectron spectroscopy), in order to check the cleanliness of the surfaces and follow the adsorption and oxidation kinetics

2. Analysis of the work function changes by following the energy spectra of secondary electrons emitted under low energy electron bombardment

3. Analysis of photoemission intensities under U.V. excitation

The reference state being chosen to be the surface cleaned by ion bombardment, exposures to oxygen atmospheres have been shown to lower the work function of clean polycrystalline aluminum by 1.2 eV. The oxygen pressure is found to affect only the kinetics of these experiments.

Mechanical scraping has been shown to induce a decrease (>0.3 eV) in the work function, which could sharply modify the kinetics of adsorption on the surface.

INTRODUCTION

During dynamic experiments of wear or friction, surfaces in contact suffer many changes in their physical and chemical states which cannot be represented by static models. Since the formation of the interfacial film is of primary interest, the study of the reactivity of the surfaces within a contact could be an interesting contribution to a better understanding of these tribological phenomena.

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The friction process modifies the thermodynamical equilibrium of surfaces by causing new chemical reactions, especially with the lubricant or lubricant additive, or by creating fresh surfaces which can enhance adsorption and oxidation mechanisms (refs. 1 and 2).

Among the parameters representing the state of a surface during wear experiments is the work function which can give useful information by describing some aspects of the phenomena occurring in the contact: electric fields, electron affinity, or chemical reactivity (refs. 3 to 5). It must be also possible to follow some of the chemical, physical, or mechanical changes occurring on the surfaces by recording the evolution of the work function (refs. 6 to 8).

The literature contains many reports of experiments related to the effect of various treatments on metallic surfaces, either from work function changes or from surface composition measurements (surface analysis with X.P.S. or Auger spectroscopy) (refs. 6 to 8). Many theoretical calculations of work function are also available, especially those using the Jellium model (ref. 9).

Another related phenomenon is the so-called "exoelectron emission," which in many cases is only the experimental expression of a change in the work function allowing an enhanced photoelectronic or thermoelectronic effect (see, e.g., the review of Postnikov (ref. 6)). "Exoemission" has been observed in many experiments of adsorption and oxidation (refs. 10 to 13), or of mechanical transformations (stress, abrasion, etc.) (refs. 14 to 16) on metallic surfaces.

All these studies can lead to the conclusion that adsorbed species and mechanical treatments (elastic or plastic deformation) cause important changes in the work function.

In this study, powerful surface analysis techniques have been combined to follow, in the same experiment, the work function of a metallic sample, its surface composition, or even its "exoemission." Attention has been especially given to the effect of the method used to clean the surfaces in an ultra-high vacuum (ion bombardment or mechanical scraping).

EXPERIMENTAL METHOD

General Aspects

To achieve the goals proposed, the experimental method must offer three types of measurements as follows:

(1) A measurement of the work function of a metallic sample in the following configurations: clean, in a gaseous atmosphere under different pressures, or during mechanical scraping to simulate wear and friction

(2) A measurement of the energy spectra of the electrons emitted from the samples during the various experiments

(3) A measurement of the composition of the surfaces during the same experiments
The experimental tool used to perform these measurements is essentially an X.P.S. spectrometer which allows chemical analysis of the surface and both energy and intensity analysis of the extracted electrons. In addition (fig. 1), a low-energy electron gun allows the measurement of the work function of the sample as discussed later. The surfaces are cleaned by sputtering with an Ar⁺ ion beam, and photoemission is produced by an U.V. lamp.

Samples and X.P.S. System

These studies were performed on aluminum which has been one of the most studied metals in the literature and thus provides many comparisons with previous experiments. The samples used were thin polycrystalline aluminum foils (99.99 percent Al).

The atmospheres used were either the residual vacuum allowed by the system (5.10⁻¹⁰ Torr) or obtained by introducing pure oxygen into the system. The X.P.S. spectrometer used in Ecole Centrale de Lyon is a Vacuum Generator C.L.A.M. with hemispherical analyser and an Al (Ka) source. In these experiments, this apparatus allowed an examination of the cleanliness of the samples and a record of the chemical evolution of the surfaces during adsorption and oxidation experiments.

Experimental Measurements of the Work Function

The addition of an electron gun into the system allows work function measurements of a metallic sample by use of low kinetic energy and low flux electrons.

The schematic energy distribution of the electrons emitted from a surface excited by a low-energy (<100 eV) electron flux as analyzed by the spectrometer used during the present studies, is given in figure 2, according to classical interpretations (refs. 17 to 20).

The secondary electrons emitted with the lowest kinetic energy (close to 0 eV) indicate the vacuum level on the energy scale and then allow the measurement of the work function once the Fermi level energy of the sample is known. Figure 3 shows the energy levels related to the sample and the analyser. One electron, going through the spectrometer, experiences a slowing potential \( V_R \) and the difference between the work functions \( \phi_{\text{sample}} \) and \( \phi_{\text{analyser}} \).

If \( E_0 \) is the analysis energy, the following relationship holds:

\[
E_k/\text{vacuum} = E_0 + eV_R + (\phi_{\text{analyser}} - \phi_{\text{sample}})
\]

If the reference in energy is taken at the Fermi level of the sample, equation (1) becomes

\[
E_k/\text{Fermi} = E_0 + eV_R + \phi_{\text{analyser}}
\]

A first calibration of the spectrometer (\( \phi_{\text{analyser}} \) is unknown) is done with a gold sample (\( E(\text{Au 4f}7/2) = 84.0 \text{ eV} \)) as it is usually done in X.P.S. experiments.
It is then possible to calibrate the system with several samples whose work functions are well determined in the literature. This work has been done with pure and clean samples of gold and copper. (All sample purities are 99.99 percent.) The cleanliness was obtained by Ar\textsuperscript+ion bombardment until the X.P.S. analysis did not detect any carbon and oxygen contamination. This second calibration does not give a significant improvement but allows a test of the first calibration made in a different range of energy. However, it is very important to notice that the reference state for clean surfaces was taken to be an ion bombarded surface and not a mechanically cleaned surface or a cleaved surface.

The energy scale of the analyser is then calibrated to an accuracy of within 0.1 eV. That error level is mainly due to the following two factors:

(1) Inaccuracies of the calibration are due to disagreements between different authors in the literature (ref. 8). An average value of the work function has been chosen for each of the metals used for the calibration and some error may remain. It has to be also noticed that the work function of a polycrystalline sample is an average of the work functions of the different crystalline orientations present on the surface. Finally, the reference state chosen for the clean surfaces is also very important; most of the values found in the literature represent cleaved surfaces whose work function may be slightly different from ion bombarded surfaces.

(2) Experimental inaccuracies in the measurement of the work function are indicated in figure 4 (choice of a tangent to the experimental curve). However, within this accuracy, the reproducibility of the results was excellent for many measurements done with different samples.

For the experiment, it must be assumed that the work function of the analyzer does not change and thus does not interfere with the accuracy of the measured values of the energy of the electrons. The presence of an oxygen atmosphere in the vacuum chamber may lead to such undesirable variations. To avoid these problems, the chamber was not "baked out" in order to guarantee a permanent chemisorbed layer in the analyser, and therefore prevent any variation of the energy scale after calibration.

The influence of the electron flux has been neglected in the present study, although it could be an important parameter. The irradiation damages due to induced temperature variations have been discussed in an article by Le Gressus and Sopize (ref. 19). From their conclusions, it can be deduced that, in the present experiments, where flux and energy are small and where the samples have a good conductivity, the change in temperature occurring under the electron bombardment is small.

However, the effect of this bombardment on the chemical composition of the surfaces cannot be accurately described. Especially, desorption, dissociation of adsorbed species, or enhanced adsorption could occur but have been neglected.

To complete the experimental method, a U.V. lamp has been added to stimulate "exoemission" from the samples and, therefore, to reproduce the experimental conditions used by some other authors (refs. 10, 11, and 16). The lamp has a continuous background (310 nm < \lambda < 400 nm) with a maximum intensity at \lambda = 365 nm. (These values correspond to a background between 3.1 eV and 4 eV with a peak at 3.4 eV.)
EXPERIMENTAL RESULTS

Clean Samples: Effect of the Ion Bombardment

Structural disorders created by the ion bombardment on a metallic surface may increase the surface energy and therefore decrease the work function of a clean cleaved surface (ref. 18). However, in the case of aluminum, Grepstad et al. (ref. 21) have shown that this effect is limited to within 0.1 eV for the (100) faces and negligible for the (111) and (110) faces. They suppose that a kind of annealing occurs during the bombardment which eliminates the main part of the defects created by the ions.

Therefore, assuming the conclusions of Grepstad et al. hold for a polycrystalline surface, the effects of the ion bombardment have been neglected and an experimental work function for a clean polycrystalline aluminum surface of 4.3±0.1 eV has been found. This will be taken as reference in the discussion of the following experimental results.

Examination of the cleanliness of the surfaces has been achieved by using X.P.S. analysis. No oxygen contamination could be detected and the Al (2p) peak did not show any peak shift due to oxidation.

In addition, the energy loss spectra obtained with low-energy electron bombardment showed the characteristic energy loss peaks for clean aluminum of \( \Delta E_1 = 10.2 \) eV and \( \Delta E_2 = 15.4 \) eV, which compare well with values obtained in the literature (ref. 17). (See fig. 5.) It has to be noticed that the reproducibility of the work function measurement of the clean reference surface was excellent, the same result being always obtained after completion of the ion bombardment.

Oxygen Adsorption on a Clean Aluminum Surface

Change in work function. - Several experiments of adsorption under oxygen pressure have been carried out by using the experimental method which has been previously discussed. The following three different conditions were used:

1. Oxygen partial pressure of 5.10\(^{-8}\) Torr
2. Oxygen partial pressure of 3.10\(^{-9}\) Torr
3. Residual vacuum of the experimental chamber (5.10\(^{-10}\) Torr). In this case, the atmosphere is essentially composed of hydrogen (3.10\(^{-10}\) Torr) and of traces of gaseous oxygen, water, methane, carbon dioxide, and argon.

Since the pressure influences the kinetics of the phenomena, it has been useful to use those three different experimental conditions. The residual vacuum experiment can be a "reference." The 5.10\(^{-8}\) Torr experiment gives very fast changes, especially interesting in the study of the final stages of the oxidation. The 3.10\(^{-9}\) Torr experiment is a good compromise to study the complete kinetics.

The experimental changes in the work function are shown on figure 6. (Figure 7 also gives an example of the actual changes in the energy spectra giving the work function.) In each case, the final change in work function has
almost the same value \( \Delta \Phi = -1.2 \) eV. This result is larger than that obtained by Agarwala and Fort (refs. 22 and 23) with similar pressure conditions (\(|\Delta \Phi| < 0.6 \) eV for different temperatures) but is smaller than the result obtained by the same authors in the case of adsorption of water vapor (\( \Delta \Phi = -1.4 \) eV). However, a very important difference can be noticed between these studies. In their experiments, Agarwala and Fort clean their aluminum surfaces mechanically by using a cutting tool. It will be shown later that such a mechanical treatment can induce a decrease in the work function. Another difference is the use in this study of an electron beam to determine the work function, a method whose effects are not accurately described.

Adsorption and Oxidation. - The oxygen partial pressure used in each experiment affects only the rate of change of the work function, which seems to be directly related to the adsorption rate. That conclusion agrees with some previous works, especially the study of Fort and Wells (ref. 24) in the case of water vapor adsorption.

An estimate of the adsorption rate can be obtained by examining the X.P.S. spectra taken during exposure. Figure 8 and 9 show the evolution of the O(1s) and Al(2p) peaks at two different oxygen pressures. Figure 8(b) \((p(O_2) = 5.10^{-8} \) Torr\) shows a high adsorption rate of oxygen on the surface as indicated by the quick decrease of the work function (fig. 6). However, the Al(2p) peak (fig. 8(a)) does not show fast growth at the characteristic energy of the aluminum oxide peak. A similar result can be observed with lower partial pressures of oxygen (fig. 9). Thus, the oxidation of aluminum under an oxygen atmosphere seems to follow the two steps of (1) adsorption of oxygen shown by the rapid growth of the O(1s) peak and (2) oxidation to Al2O3 shown by the slow growth of the Al(III)(2p) peak.

"Exoemission". - As discussed previously, a U.V. lamp has been added to the experimental apparatus in order to obtain stimulated "exoemission." Two sets of measurements, the exoemission intensity and the energy distribution of the emitted electrons, have been recorded under a partial pressure of oxygen of 10^{-8} Torr.

Figure 10 presents the evolution of the work function and of the energy for which the exoemission is maximum. The work function change during the experiment shows the same behavior as in the previous experiments. (It has to be noticed that, before the work function reaches 4 eV, which corresponds to the most energetic wavelength emitted by the lamp, no recording can be made.)

The final value of the energy corresponding to the maximum of exoemission appears also to be 3.4 eV which is the point where the lamp emission is maximum.

Figure 11 gives the change of exoemission intensity with time. No emission occurs for a work function below 4 eV which is the energy limit of the lamp. The emission grows as the work function decreases because more photons have sufficient energy to cause emission of electrons from the surface.

However, after 30 min under an oxygen pressure of 10^{-8} Torr, although the value of the work function remains constant at 3.1 eV, the exoemission still increases. The creation of trap sites during the adsorption, where the electrons are in a loosely bound energy state, could explain this phenomenon. The emission of these electrons can cause the increase of exoemission although the work function remains at the same value.
The final step of the exoemission is a slow decrease of the intensity. This step occurs after a time depending on the oxygen pressure in the chamber (e.g., 2 hr with p(O₂) = 10⁻⁸ Torr). This seems, following the explanation of Ramsey (ref. 10), to result from the slow growth of the oxide layer on the metallic surface which creates a screening effect and prevents the electron emission.

Mechanical Scraping of a Clean Aluminum Surface

As indicated earlier, mechanical scraping and its effects on adsorption, oxidation, and surface state are important in tribology, since these represent the conditions during wear and friction.

Many articles in the literature insist on the importance of the structural defects on the work function (refs. 2, and 25 to 27). The same experiments as in the case of adsorption have been carried out by using a small dentistry tool to achieve the scraping of the aluminum surface in the vacuum chamber.

Figure 12 shows the variations of the work function with scraping under the experimental residual vacuum (in this case, 5.10⁻⁹ Torr). It shows essentially a very fast decrease of the work function of ΔΦ = -0.3 eV, right after the mechanical treatment. One can also observe a small increase of the work function during the early stages of adsorption under residual vacuum (time <20 min). This result can be understood as an effect of the adsorbed species, which can screen the local changes in the electronic distribution on the surface around the defects created by the scraping mechanism. But, this result can also be simply due to an annealing effect occurring shortly after the abrasion.

A number of further remarks can be made as follows:

(1) The effect of the scraping is immediate and within the time needed to record the first spectrum.

(2) An important difference in work function does exist between an ion bombarded surface and a mechanically scraped surface. Therefore, a part of the differences between the present adsorption results and those of Agarwala and Fort can be explained by the two distinct structural states taken as clean surfaces.

(3) The scraping seems to increase the kinetics of adsorption and oxidation under residual vacuum. The structural defects created during the scraping must act as preferential adsorption sites. To the authors' knowledge, this work is the first such study made with abrading a surface.

CONCLUSION

This study has associated the variations of the work function and of "exoemission" and the changes in the chemical or structural state of a polycrystalline aluminum surface during adsorption or abrasion.

It can be concluded that "exoemission" is related to a decrease in the work function, either on a macroscopic scale during adsorption and the creation
of a polar layer or on a more microstructural scale during the creation of defects and therefore of active energetic sites as a result of mechanical scraping.

In order to achieve a better comprehension of the fundamentals of friction and lubrication, it is interesting to characterize the energetic state of the surface as the result of mechanical abrasion. During friction, energetic changes occurring on a surface, as shown by the variations of the work function, could contribute to the formation of oxides or degradation products in a reaction film. The contribution of this study was to show that mechanical scraping affects the work function and therefore the energetic state of an aluminum surface.

REFERENCES


Analyser

X-ray (Al (Ka))

U. V. (310 nm < λ < 400 nm)

e⁻ (E < 100 eV)

Ar⁺ (4 keV)

Sample

Figure 1 - General experimental method.

Elastic peak

Secondary electrons

Collective excitations (plasmons, phonons)

Background

ϕ = Work function

E_K (Kinetic energy)

0 = E_k/vacuum

0 = E_k/Fermi

Figure 2 - Energy distribution of secondary electrons.
Figure 3. - Energy levels from the sample and the analyser.

Figure 4. - Measurement of the work function.
Figure 5. Energy loss spectrum of clean aluminum.

Figure 6. Work function changes of clean aluminum under oxygen pressure.
Figure 7. - Aluminum work function evolution under oxygen pressure (3.10^{-9} Torr).

Figure 8. - X.P.S. analysis of clean aluminum under oxygen pressure (p = 5.10^{-8} Torr).
Figure 9. - X.P.S. analysis of clean aluminum under oxygen pressure. (p(O₂) = 3.10⁻⁸ Torr).

Figure 10. - Exocmission evolution of clean aluminum under oxygen pressure (p(O₂) = 10⁻⁸ Torr).
Figure 11. - Exoemission intensity of clean aluminum under oxygen pressure \( p(O_2) = 10^{-8}\text{Torr} \).

Figure 12. - Work function of clean aluminum evolution after mechanical scraping under residual vacuum \( 5\times10^{-9}\text{Torr} \).
Surface studies have been performed on aluminum polycrystalline surfaces which have been mechanically scraped. Such studies were initiated in order to understand surface effects occurring in tribological processes which involve rubbing surfaces and the effects of adsorption of oxygen. To characterize the surfaces, the following three different experimental approaches have been used: (1) X.P.S. (X-ray photoelectron spectroscopy), in order to check the cleanliness of the surfaces and follow the adsorption and oxidation kinetics. (2) Analysis of the work function changes by following the energy spectra of secondary electrons emitted under low energy electron bombardment. (3) Analysis of photoemission intensities under U.V. excitation. The reference state being chosen to be the surface cleaned by ion bombardment, exposures to oxygen atmospheres have been shown to lower the work function of clean polycrystalline aluminum by 1.2 eV. The oxygen pressure is found to affect only the kinetics of these experiments. Mechanical scraping has been shown to induce a decrease (>0.3 eV) in the work function, which could sharply modify the kinetics of adsorption on the surface.