An investigation of fretting wear behaviour of nickel coatings for electrical contacts application in dry and lubricated conditions

S. Noël, D. Alamarguy, A. Brézard-Oudot, P. Gendre

A R T I C L E   I N F O

Article history:
Received 14 September 2012
Received in revised form 11 January 2013
Accepted 22 January 2013
Available online 8 February 2013

Keywords:
Fretting
Wear
Electrical contact
Nickel
Lubrication
Grafting

A B S T R A C T

Fretting remains a major cause of connector failure and can impair reliability of complex systems. Much work is devoted to minimise the effects of cyclic displacements in the contact interface. One of the options is to choose proper materials for the final layer and eventually select an underlayer. Another option is to apply a lubricant compatible with the electrical function of the connecting device. Its effect must be the reduction of friction with the preservation of conduction. In this work we have investigated the properties of nickel electrodeposited on cuprous coupons submitted to an imposed sine displacement fretting test (1 Hz, 25 μm, 2.5 N). The contacts are of the sphere on plane type. The plating conditions are shown to have a large effect on the microstructure, roughness and composition of the nickel coatings. Consequently the fretting behaviours of the compared coating are different. Fretting degradation is evaluated for our application as the number of cycles for which the build-up of oxidised debris gives a value of electrical resistance superior to a threshold. During the fretting test the rough nickel with large grains is observed to be prone to very high friction and partial slip. Fretting of the smoother coating with small grains is characterised by gross slip. Contacts were lubricated with solutions of perfluorinated polyether (PFPE). It is shown that a strong friction reduction takes place and that the fretting degradation is postponed. Surface analysis shows that fluorine is grafted in the interface and protects the interface. The electrodeposition process and the properties of the nickel coating are shown to have an effect on the lubricant behaviour in the contact interface. These results show the strong potential of lubricated nickel for applications in the field of electrical devices.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Fretting of electrical contacts has been identified to cause the failure of devices controlling major functions [1] and is still a problem. The approach we have been working on for several years is to optimise the materials and the coatings used for connector terminals.

Various types of electrical contacts involve electrodeposited nickel coatings either as an underlayer or as a finish. Nickel has interesting properties. Much work has been devoted to nickel electroplatings since the patent on nickel sulfamate bath [2]. Efforts were devoted to develop processes and also to study the microstructure of nickel coatings [3–5]. Reddy [6] has shown that a preferred orientation could develop in nickel electro-deposits and proposed a mechanism for the development of texture in Ni coatings [7]. More recently, with the development of the Lithographie, Galvaniformung, Abformung (LIGA) technique, much work has been undertaken on nickel electro-deposition processes in relation to the properties of the coatings. Kelly and Goods have related the properties and the structure of Ni electrodeposited films [8,9]. Recently nanocrystalline nickel coatings have shown interesting properties [10,11]. It is well known that Ni coatings show a good behaviour in certain corrosive atmospheres, mainly because of their propensity to form a thin passivating film [12,13], due to its particular surface chemistry. It has been reported by some authors that the properties of nickel electrodeposits could be tailored [3]. The first goal of this study was to correlate the structural, electrical and mechanical properties of the nickel coatings under investigation in order to find a layer delaying fretting degradation. In a second step we wanted to investigate the particular behaviour of lubricated nickel contacts submitted to the same fretting test. Lubrication, particularly with perfluorinated polyethers (PFPE), has been shown to reduce fretting degradation of tinned electrical contacts [14–16], but little work involves nickel contacts. It has been reported that some metals such as Al and Fe could, in some temperature or friction conditions, react with PFPE and decompose [17–19]. Very little work has been done on the behaviour of PFPE on nickel [20]. In this paper we show the effect of PFPE lubrication on
were of the sphere on plane type. The planes were 20 mm/C2 coupons; a spherical shape (radius of curvature \( R \)). Lubricant was a branched perfluorinated polyether (PFPE) of about 1854 cSt. PFPE are known for their inertness, stability and manufactured by Solvay Solexis S.p.A.. It has a kinematic viscosity/C0/C2/C0/C0.

following paragraphs.

Matte Ni coatings and bright Ni coatings are compared in the specially deposited thicker layers (10/C2/C2/C2/C2/C2/m) with a 50 gf load; this gives a good estimation of the values for the two types of samples. Matte Ni coatings and bright Ni coatings are compared in the following paragraphs.

The Ni coatings were deposited at 60 °C with a current density of 10 A dm\(^{-2}\). The coatings for the study were 2 \( \mu \)m thick. Contacts were of the sphere on plane type. The planes were 20 mm \( \times \) 20 mm coupons; a spherical shape (radius of curvature \( R = 1.3 \) mm) was stamped on dedicated 10 mm \( \times \) 50 mm coupons of the same substrate. Lubricant was a branched perfluorinated polyether (PFPE) manufactured by Solvay Solexis S.p.A.. It has a kinematic viscosity of about 1854 cSt. PFPE are known for their inertness, stability and good temperature pressure curve.

\[
\text{CF}_2\left\{(\text{O-CF-CF}_2)_m(\text{O-CF})_n\right\}\text{O-CF}_3
\]

with \( m/n = 30 \)

 Coupons were dipped in solutions (5% vol) of lubricant in Galden\(^\circ\) SV90 and dried in air.

2. Samples and experimental set-up

2.1. Samples

Substrates were brass (CuZn30) coupons; they were coated with two types of nickel layers from the sulphate baths described in Table 1. The mechanical properties of the substrate are given in Table 2. The hardness of the nickel coatings were measured on specially deposited thicker layers (10 \( \mu \)m) with a 50 gf load; this gives a good estimation of the values for the two types of samples. Matte Ni coatings and bright Ni coatings are compared in the following paragraphs.

The Ni coatings were deposited at 60 °C with a current density of 10 A dm\(^{-2}\). The coatings for the study were 2 \( \mu \)m thick. Contacts were of the sphere on plane type. The planes were 20 mm \( \times \) 20 mm coupons; a spherical shape (radius of curvature \( R = 1.3 \) mm) was stamped on dedicated 10 mm \( \times \) 50 mm coupons of the same substrate. Lubricant was a branched perfluorinated polyether (PFPE) manufactured by Solvay Solexis S.p.A.. It has a kinematic viscosity of about 1854 cSt. PFPE are known for their inertness, stability and

2.2. Experimental set-up

The composition of the coatings, their oxidation state, their topography and microstructure were analysed with the appropriate techniques.

2.2.1. Characterisations

3D images were made with a Wyko optical profiler allowing the calculation of topography parameters. AFM topographic images were performed with a Veeco multimode Nanoscope IIIa system.

XPS surface analyses were obtained with a PHI Versaprobe multitechnique XPS microprobe comprising an Al K\(_\alpha\) monochromated source. The pressure in the analyser chamber was around 10\(^{-7}\) Pa; for all the experiments the power was set at 50 W and the analysed zone was 420 \( \mu \)m \( \times \) 420 \( \mu \)m. Survey spectra (0–1400 eV) were acquired with a pass energy of 187.85 eV, an energy step of 0.4 eV and a dwell time of 20 ms. High resolution spectra for chosen energy ranges were taken with energy pass of 23.5 eV, an energy step of 0.1 eV and a dwell time of 20 ms. A system of charge neutralisation involving a low energy ion source and a low energy electron source avoided charging of the surfaces. The system was calibrated by setting Cu 2p\(_{3/2}\) and Cu LMM of clean copper at 932.7 eV and 918.7 eV respectively. The take off angle was 45° unless specified. All the spectra were fitted using the PHI Multipak software; the background was removed by the Shirley method. Gaussian, Lorentzian and asymmetric peaks could be chosen for the fits. The stoichiometries of the samples were determined using the appropriate sensitivity factors. (see http://www.lasurface.com/xps/index.php for basics). Linear Least Squares (LLS) fitting was used to obtain maps of different chemical states for a given element [23].

2.2.2. Fretting test

A dedicated device, already described [24], comprising an electro-dynamic shaker applied controlled cyclic movements (50 \( \mu \)m peak to peak, 1 Hz) to the contact under a 2.5 N constant normal load. A feedback loop imposed the sine displacement; the maximum displacement value remained rigorously constant during the test. The compliance of the fretting device was measured from the slope of friction cycles. This slope was constant for all the samples investigated and gave a value of \( Cm = 1.8 \mu \)m/N. This parameter has been shown to be very important [25,26].

During the test, the voltage drop in the contact \( Uc \) was measured with an acquisition card (333 \( \times \) 10\(^3\) samples per second) with the
current value set at 20 mA and the voltage limit at 250 mV. During each cycle, 500 values of the position \( d \), of the friction force \( F \) and of the voltage drop \( U_c \) were acquired. The mean value of \( R_c \) for a cycle was calculated during the experiment from the 500 measurements of \( U_c \). The mean \( R_c \) values were plotted versus the number of fretting cycles every 10 cycles. A characteristic value \( F_t \) was also calculated every 10 cycles and plotted versus the number of cycles. \( F_t \) during a cycle was defined as the average between the maximum and minimum values of a cycle \( F_t = (F_{\text{max}} + F_{\text{min}})/2 \). We chose to plot this value because the parallelogram shape of the cycles evolves during the fretting test.

### 3. Results and discussion

#### 3.1. Characterisations

#### 3.1.1. Composition and identification of the oxide peaks

Survey XPS analyses were performed to determine the compositions of the two nickel surfaces. The results are gathered in Table 3. The sulphur and chlorine found on the bright Ni come from the brighteners specific to the bright nickel bath. Both samples have a large amount of carbon contamination on the upper surface.

High resolution analyses were then performed at lower pass energy in order to study chosen peaks: C 1s, O 1s, Ni 2p. The Ni 2p\(_{3/2}\) and O 1s peaks for matte Ni are shown in Fig. 1(a) and (b) together with the decompositions spectra corresponding to the different chemical forms. They can be compared to the Ni and O peaks for the bright nickel in Fig. 1(c) and (d).

The results are in good agreement with other authors [13]; the assignments of the different chemical forms of nickel and oxygen are summarised in Tables 4 and 5. In these tables, the components are listed in order of increasing binding energy; they appear from left to right on Fig. 1(a–d). Metallic nickel [component (1) and (5)], NiO [component (2), (4) and (6)] and Ni(OH)\(_2\) [component (3) and (6)] can be identified. Component (6) is unresolved and corresponds to satellites of NiO and Ni(OH)\(_2\). The oxygen peak at about 529.6 eV corresponds to NiO while the components at higher energy correspond to satellites of NiO and Ni(OH)\(_2\). This is confirmed here by the analyses performed at different take off angles from 15° to 75°. At low take off angle (15° here) the photo-electrons come from the uppermost surface, while for higher take off angles (75° here) the analysis involves a thicker layer. By varying the take off angle, a non destructive depth analysis can be performed. Calculating the amount of metallic Ni from the value of the peak surface and the amount

<table>
<thead>
<tr>
<th>S. No°el et al. / Wear 301 (2013) 551–561</th>
<th>553</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 3 Composition in at% of the matte and bright nickel coatings.</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Matte Ni</td>
<td>49.3</td>
</tr>
<tr>
<td>Bright Ni</td>
<td>56.7</td>
</tr>
</tbody>
</table>

<p>| Table 4 Peak assignment for Ni 2p(_{3/2}). |
|---|---|---|</p>
<table>
<thead>
<tr>
<th>No.</th>
<th>Component</th>
<th>Matte Ni (eV)</th>
<th>Bright Ni (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni metal</td>
<td>852.73</td>
<td>852.73</td>
</tr>
<tr>
<td>2</td>
<td>NiO</td>
<td>854.22</td>
<td>854.41</td>
</tr>
<tr>
<td>3</td>
<td>Ni(OH)(_2)</td>
<td>855.95</td>
<td>856.05</td>
</tr>
<tr>
<td>4</td>
<td>NiO</td>
<td>856.52</td>
<td>857.10</td>
</tr>
<tr>
<td>5</td>
<td>Shake up</td>
<td>858.34</td>
<td>858.35</td>
</tr>
<tr>
<td>6</td>
<td>Satellite</td>
<td>861.30</td>
<td>861.30</td>
</tr>
<tr>
<td>7</td>
<td>–</td>
<td>864.00</td>
<td>863.92</td>
</tr>
</tbody>
</table>

Fig. 1. Nickel and oxygen core levels for various Ni coatings showing the experimental curve (– – –) and the different components (–) obtained by fitting: (a) Ni 2p\(_{3/2}\) matte coating; (b) O 1s matte Ni; (c) Ni 2p\(_{3/2}\) bright coating and (d) O 1s bright coating.
of oxidised Ni from the corresponding surfaces, a ratio \( r \) can be estimated. Table 6 summarises the values of \( r \) for the matte and the bright nickel versus the take off angle. It shows that in the uppermost layer, the quantity of oxidised nickel in the analysed volume is twice that of metallic nickel for both types of coating. Deeper in the layer, the bright Ni coating is composed of about as much metallic Ni as oxidised Ni.

The initial composition of the nickel surface was important to establish as a reference. Investigating the evolution of the composition can give a good insight into tribological transformation of the surface.

### 3.1.2. Roughness and microstructure

The average roughness \( \text{Ra} \) was measured by optical 3D profilometer on 200 \( \mu \)m \( \times \) 200 \( \mu \)m areas: the values are rather similar for the two coatings. For matte nickel \( \text{Ra}=199 \) nm and for bright nickel \( \text{Ra}=140 \) nm. A corrugated pattern due to the rolling process of the brass substrate is observed and affects the measurement for both coatings. Thus the topography was also measured by AFM with different scanning amplitudes varying from \( 1 \mu \text{m} \times 1 \mu \text{m} \) to \( 10 \mu \text{m} \times 10 \mu \text{m} \). Fig. 2(a) and (b) depicts AFM images (10 \( \mu \text{m} \times 10 \mu \text{m} \) of the matte and bright Ni coatings and show very different aspects of the two coatings. Large and medium size bumps revealing columnar grain terminations are observed for the matte Ni and very small bumps for bright Ni. The arithmetic roughness \( \text{Ra} \) values calculated from these images give \( \text{Ra}=151.5 \) nm for matte Ni and \( \text{Ra}=34.7 \) nm for bright Ni.

The bright surface is observed to be very smooth; thus the \( \text{Ra} \) values measured with the profilometer were taking into account the large amplitude grooves of the substrate. In AFM measurements both the load applied to the cantilever tip and the scanning amplitude might affect the results. Thus the topography is analysed in various conditions. The results of the different values of \( \text{Ra} \) obtained in these various conditions are gathered in Fig. 3. It shows that the \( \text{Ra} \) values are rather constant when increasing the normal load on the cantilever tip. The values for the matte coating are always higher than for the bright ones. Values corresponding to scans of 10 \( \mu \text{m} \) amplitude are higher than the 1 \( \mu \text{m} \) ones. Some scattering is observed for different spots. The micro-hardness measurements performed on special samples showed as expected higher values of hardness for the bright nickel samples, as expected.

### 3.2. Fretting results

#### 3.2.1. Dry nickel

Fretting experiments (normal load 2.5 N, amplitude 25 \( \mu \text{m} \) and frequency 1 Hz) were performed on the matte and bright nickel samples. Fig. 4(a) and (b) shows the mean \( R_c \) values per cycle and the maximum tangential force \( F_t \) per cycle for the two coatings. The behaviours are very different. For matte Ni \( R_c \) is almost constant and only shows a very slow increase; the threshold value of \( R_c \geq 10 \) m\( \Omega \) is reached after more than 700 cycles. Simultaneously the tangential force \( F_t \) increases very quickly to a high value of 2.5 N. For the bright nickel \( R_c \) increases very quickly to values around 500 m\( \Omega \) (\( R_c \geq 10 \) m\( \Omega \) after 80 cycles); at the same time the tangential force \( F_t \) reaches a value of 1.5 N and then stay almost constant at a value of 1.2 N. After about 2000 cycles a sudden decrease of \( R_c \) is observed as well as a slow increase of \( F_t \).

These results were duplicated several times and all the runs were superimposable; thus, Fig. 4(a) and (b) shows only one run per type of Ni. The initial values of the \( R_c \) (summarised in Fig. 14) are 3 m\( \Omega \) and 9 m\( \Omega \). The contact resistance value is the sum of the constriction resistance \( R_{co} \) and the surface film resistances \( R_f \). The matte coating does not have a continuous contamination film and the value of \( R_c \) is about equal to the value \( R_{co} \).

The constriction resistance can be written as \( R_{co} = \rho/2a \) where \( a \) is the radius of the contact disc and \( \rho \) is the resistivity. In a rough approximation the contact radius can be obtained from the Hertz equation \( a = \sqrt{(3/4)(F_aR/E)} \) where \( E = E/2(1\text{--}\nu^2) \).

Since the constriction is a bulk phenomenon the parameters used should be those of the brass substrate. This gives a value of \( a=33.7 \) \( \mu \text{m} \) and thus a value of \( R_{co} \) of about 1 m\( \Omega \) which is the...
The observation of these scars, as well as the $R_c$ and $F_t$ values of Fig. 4(a) and (b), indicate that the matte and bright nickel fretting regimes are very different. Additional information is obtained from the plot of the friction cycles constantly measured during the tests. Fig. 7 shows some of the friction cycles corresponding to Fig. 4 for matte and bright Ni.

For matte Ni a few cycles of gross slip (characterised by almost constant $F_t$ for a cycle) are followed by a period of partial slip (characterised by deformed cycles). During this period part of the contact area is blocked and the contact resistance remains almost at its initial value. This has been observed by several authors [29,30] who define a transition displacement value under which no degradation should occur. After 700 cycles, gross slip occurs and $R_c$ starts to increase. During the test, the sliding conditions have changed from gross slip to partial slip and then back to gross slip after enough modifications of the interface have occurred. This could be related to the formation of a tribologically transformed structure [31] several μm deep. For bright nickel gross slip occurs during the whole test as shown by the constant shape of the friction cycles Fig. 7(b).

After 5000 cycles the scar of the matte nickel coupon, Fig. 5(b), showed very large amounts of wear, material removal and debris. The scar of the bright Ni coatings submitted to the same amount of cycles showed little degradation. Fig. 8, shows scanning electron images of these scars. Because of the small amount of degradation of the bright Ni, these scars could be analysed by XPS in order to gain insight into the fretting mechanisms involved.

Having identified the initial composition of the as-deposited surface of the coatings, it was possible to acquire maps by elements on 250 μm × 250 μm areas. It is possible with this procedure to localise the different elements (O, Cu, Ni, F) and their chemical forms on the fretting tracks. An element is selected (interval of energy corresponding to the peak under investigation) and a map is built (Fig. 9(a)). It is then possible to select a subarea on the map, extract the corresponding spectra (Fig. 9(d)) and plot maps for a chemical form (Fig. 9(b) and (c)).

Fig. 9 corresponds to the 500 cycles fretting track of the bright nickel coating. It shows the presence of Ni mainly in the wear track: by applying a LLS procedure available in the Multipack PHI software [23], it was further possible to distinguish maps of different chemical forms of nickel. It is clearly seen in Fig. 9(d) that the chemical state of nickel in the fretting track (spectrum 1) is not the same as its state...
outside the track (spectrum 2). Spectrum 1 corresponding to inside the wear track is assigned to nickel in NiO. Fig. 10 represents the oxygen map for the same scar. The presence of NiO in the fretting track is even clearer. Because of the large difference in binding energy of oxygen in NiO (529.6 eV) and in Ni(OH)₂ and/or other hydrated components (531.7 eV) it can be deduced that the fretting track is evenly composed of NiO. NiO is known for being very insulating and hard; this is very well correlated to the very high values of $R_c$ in Fig. 4(a) and the stable values of $F_t$ in Fig. 4(b).

Such analysis was not possible for the matte scars because of the tormented topography of the scars after fretting. The same type of analysis was performed on the fretting track of the bright nickel after 5000 cycles. Fig. 11 represents the map of nickel and shows a very different pattern (compared to Fig. 10): the wear scar is composed of an outer ring of NiO. The centre of the wear scar is composed of copper, nickel, oxygen and carbonaceous species. At this stage of the fretting test, the tangential force has increased and some wear occurs; copper is detected as is shown in the map of Fig. 12.

3.2.2. Lubricated nickel

Samples deposited as previously (matte and bright nickel) were coated with the PFPE film and submitted to the same fretting tests. The electrical and friction behaviours are shown in Fig. 13(a) and (b). For matte nickel the friction force values are very low ($F_t$ is about 0.5 N which gives a friction coefficient $\mu = 0.2$); gross slip occurs during the whole test. The contact resistance values increase to 10 mΩ quickly (in 50 cycles) but remain below 20 mΩ for more than 1500 cycles. Note that two single higher values of $F_t$ can be observed which could correspond to asperity shearing. For the bright coating, $R_c$ is very high (around 1 Ω) during the first cycles because of the additional resistance due to the lubricant film and the
low roughness of the surface; the value decreases to 20 \( \mu \)m after about 100 cycles. Simultaneously \( F_t \) increases from 0.3 N to 0.5 N.

Though the behaviours of the two coatings are not the same, lubrication has a strong friction reduction effect which lasts over the 5000 cycles for both layers.

The values of the contact resistance \( R_c \) for the two coatings under dry and lubricated conditions are summarised in Fig. 14. No error bars are displayed because the aim of the study is not to discuss accurately the various values of \( R_c \) but to analyse trends. Several experiments were performed and confirm the trends given here. The aim of the study was to compare the behaviours of the two types of coatings in view of an electrical application. They can be summarised as follows: for the lubricated matte Ni lower values of \( R_c \) are obtained after 5000 cycles as compared to dry conditions. For the bright Ni, after a short running in period during which \( R_c \) diminishes, the presence of the lubricant film avoids the very high values of \( R_c \) measured during the first thousand cycles.

The friction results for both lubricated nickel coatings submitted to fretting tests show a strong protection against degradations and rather stable contact resistance values. Previous work on the lubrication of tin coated contacts has shown that fluorinated lubricants

---

Fig. 8. Scanning electron microscopy (SEM) image of: (a) the 500 cycles and (b) the 5000 cycles fretting scars of bright nickel (3 kV, 10 nA); a 20 \( \mu \)m scale is shown on the image.

Fig. 9. XPS Ni map for the 500 cycles bright Ni: (a) global map; (b) inside of the track map; (c) outside the track map; (d) corresponding spectra: binding energy (BE) from 859 to 851 eV; 1 eV graduations.
could delay the onset of fretting degradation. The issue investigated here is how long does this lubricant last taking into account the particular chemical properties of nickel.

The action of lubricants on tin contacts was shown to strongly depend on the viscosity of the fluorinated lubricant [14,15]; tin being very soft and plastically deformed upon contact, the effect

---

**Fig. 10.** XPS O map for the 500 cycles bright Ni: (a) global map; (b) inside of the track map; (c) outside the track map; (d) corresponding spectra: binding energy (BE) from 534 to 527 eV, 1 eV graduations.

**Fig. 11.** XPS Ni map for the 5000 cycles bright Ni: (a) global map; (b) inside of the track spectra; (c) outside the track spectra; (d) corresponding spectra: BE from 858 to 850 eV, 1 eV graduations.
of the lubricant follows complex mechanisms. It was observed experimentally that the kinematic viscosity and the structure of the molecule had a strong effect on the efficiency of the lubrication.

In order to investigate if the particular chemical properties of nickel had consequences during the fretting test, the scars were analysed as previously for the dry contacts. The coupons were rinsed before they were put in the ultra high vacuum for spectroscopic analysis. Fig. 15 shows the wear scars after rinsing the samples in the PFPE solvent for PFPE, for both Ni coating after 500 and 5000 fretting cycles.

Before acquiring the element maps, survey spectra were measured in order to have the composition of the surface. These spectra were performed on areas including the wear scar of about 300 μm × 300 μm. The calculated compositions are listed in Tables 7 and 8. For the matte Ni fretting scars of 500 cycles and 5000 cycles, large amounts of fluorine are detected. After 5000 cycles, there is more oxygen and some copper is measured but the ratio of nickel and fluorine stays the same. For the bright Ni fretting scars, Table 8, there is also a large amount of fluorine. It can be seen though, that after 5000 cycles the fluorine concentration has decreased, the nickel and fluorine ratio is much higher.

XPS maps of the wear tracks after the fretting tests are summarised in Fig. 16. The fluorine and copper maps are shown for matte and bright nickel fretting after 500 and 5000 cycles. Fig. 16(a) and (b) show the F 1s map for 500 and 5000 fretting cycles of matte Ni.
Fluorine is located only inside the wear track; there is no fluorine outside the wear scar; it has been reported that no chemical reaction occurs between nickel and/or its oxides and PFPE. This indicates that the measured fluorine has not been eliminated by the repeated rinsing operations because it is grafted on the nickel surface due to friction. Friction removes some of the carbon–oxygen contaminations and causes metallic nickel to be exposed and react with the PFPE molecules. The grafted layer reduces friction, the friction coefficient being low in Fig. 13(b). In the long run some copper is exposed but the map of Fig. 16(c) shows that is evenly distributed in the wear scar.

Fig. 16(d) and (e) show the F 1s maps for 500 and 5000 fretting cycles of bright Ni. Fluorine is also grafted in the fretting scar as for the matte coating, but less fluorine is detected and after 5000 cycles it can be observed to be localised at specific spots. Fig. 16(f) of Cu 2p3/2 shows small amounts of copper localised mainly on a specific area. This means that the lubricant efficiency has decreased and could suggest that failure of the lubricating effect is occurring. This can be analysed in terms of roughness of the lubricated surfaces. The rougher surface tends to retain the lubricant longer and the efficiency is extended.

It is interesting to note that the same kinds of analyses have been performed with fretting scars from tinned contacts and that no reaction of metallic tin with the lubricant was evidenced.

4. Conclusion

Nickel layers are largely used in the electrical contact industry either as a barrier or as a final coating because it has a fairly good behaviour under most corrosive atmospheres. Much work has been aimed at developing electroplating baths and showed the influence of various process parameters on the characteristics of the coatings.

The first results of this study compare the physico-chemical, electrical and mechanical properties of matte and bright nickel coatings. A fretting test simulating the micro-displacements caused by vibrations shows that different behaviours are observed for coatings with different properties such as composition, microstructure and roughness. The following conclusions can be made:

- With matte nickel a partial slip regime occurs during which the failure of the contact is postponed. This partial slip is followed by a gross slip one causing large degradations of the surface leading to high increase of the resistance.
- With bright nickel an initial drastic increase of the resistance is observed. Surface analyses show that with low roughness nickel coatings such as bright Ni, slow wear during fretting leads to the formation of an insulating NiO layer.

The effect of a fluorinated lubricant on these mechanisms is investigated. It is shown that a fluorinated compound is created in the nickel contact interface during fretting.

<table>
<thead>
<tr>
<th>Table 7</th>
<th>Composition (at% element) for the lubricated matte Ni after 500 and 5000 fretting cycles.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>500 cycles</td>
<td>28</td>
</tr>
<tr>
<td>5000 cycles</td>
<td>25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 8</th>
<th>Composition (at% element) for the lubricated bright Ni after 500 and 5000 fretting cycles fretting cycles.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>500 cycles</td>
<td>33</td>
</tr>
<tr>
<td>5000 cycles</td>
<td>45</td>
</tr>
</tbody>
</table>

*Fig. 16.* XPS maps for: (a) F 1s map for matte Ni 500 cycles; (b) F 1s map for matte Ni 5000 cycles; (c) Cu 2p map for matte Ni 5000 cycles; (d) F 1s map for bright Ni 500 cycles; (e) F 1s map for bright Ni 5000 cycles and (f) Cu 2p3/2 map for bright Ni 5000 cycles.
The results also indicate that the presence of the lubricant film can avoid the adhesion and sticking phenomena occurring in the case of matte coatings. This avoids the drastic increase of $R_c$ occurring after the transition from partial slip to gross slip.

Clear evidence is given that a thin PFPE lubricant film brings a protection from the atmosphere minimising the oxidation of the surface. In the case of bright nickel the lubricant film can increase the initial value of $R_c$ and a running period is needed before measuring low $R_c$.

The lubrication effect during the fretting test is observed to last longer in the case of rougher nickel surfaces such as the matte one because of a reservoir effect.

These observations and analyses can be helpful during the design of connector terminals by engineers who have to assess different solutions with pros and cons.

Acknowledgements

The Phi Versaprobe equipment was acquired thanks to fundings from CNRS, ANR and Conseil Regional Ile de France.

References