J Mater Sci (2008) 43:1716–1722
DOI 10.1007/s10853-007-2352-9

Formation of composite Cu–graphite and Cu–PTFE coatings and their tribological characterization

Hamid Omidvar · Guy Stremsdoerfer · Yunny Meas

Received: 2 September 2007 / Accepted: 27 November 2007 / Published online: 12 January 2008

Abstract The Dynamic Chemical Plating (DCP) technique allows production of 2-μm copper films containing particles of graphite or PTFE in 18 and 15 min, respectively, at ambient temperature. DCP yields composites with particle-incorporation fractions of 12% for graphite microparticles and 22% for PTFE nano-particles. The composite films show excellent tribological properties, acting as self-lubricating coatings with friction coefficients as low as 0.18.

Introduction

Electroless copper deposition is used for many applications in the electronics and electrical engineering industries (electronic circuits, shielding, etc.). Electroless copper films are frequently used as underlayers to be thickened chemically or electrochemically afterwards [1]. Copper-based composite films have been studied much less than nickel-based composite films [2]. Nonetheless, composite films of Cu–graphite have been developed for various applications [3, 4]. This composite offers at the same time the thermal and electrical properties of copper as well as the useful physical properties of graphite (lubrication and low coefficient of thermal expansion). Copper films containing graphite particles are used in mechanical systems requiring both good electric conduction and lubrication [3, 5, 6]. The friction coefficient and mechanical erosion of electroless composite Cu–PTFE deposits are found to be lower than those of electroless composite NiP–PTFE deposits. In the case of oil-lubricated friction, the wear of the copper–PTFE films is 57% lower, in mass loss, than that of a lubricated NiP–PTFE coating. Since copper is more lipophilic than nickel, oil is apparently spread more easily over the surface of a Cu–PTFE composite film than on NiP–PTFE [7].

Formaldehyde is commonly used as the reducing agent to make composite copper films by electroless deposition. The toxicity of this reducing agent has a negative impact, however, on industrial implementation and the effluent-treatment requirements. One of the advantages that arise from the present study of the dynamic chemical plating (DCP) technique is the elimination of formaldehyde.

In this article we describe the application of DCP, in which particles of graphite or PTFE are incorporated in the metal-salt solution in order to form composite metal-particle films. The tribological properties of the resulting films are reported.

Experimental

The composite Cu–graphite and Cu–PTFE deposits were prepared by the DCP technique. It can be described as a

H. Omidvar (✉)
Department of Mining and Metallurgical Engineering,
Amirkabir University of Technology, 424 Hafez Ave.,
Tehran 15914, Iran
e-mail: hamid_omidvar@yahoo.com

G. Stremsdoerfer
Tribological & Dynamical Systems Laboratory, Ecole Centrale
of Lyon, 36 Guy de Collongue Ave., P.O. Box 163,
Ecully 69134, France

Y. Meas
Centro de Investigación y Desarrollo Tecnológico en
Electroquímica (CIDETEQ), Parque Tecnológico Querétaro,
Sanfandila, Pedro Escobedo, A.P. 064, Querétaro C.P. 76700,
México

metal plating process using intermittent spraying of two or several solutions simultaneously. Using compressed air and a double nozzle spraying gun, the oxidizing solutions, containing copper sulfate which were mixed with graphite solution or PTFE emulsion, and reducing solutions such as potassium borohydride are sprayed at the same time but separately onto a steel substrate. The operating conditions are identical to those described previously [8].

The advantages to use two containers containing the solution of metal salt and reduction agent separately are to eliminate the instability problem as existed in electroless bath and to operate at room temperature instead of 40–50 °C used in a copper electroless deposition.

The graphite powder and the PTFE suspension were all Sigma Aldrich standard-grade reagents used without further purification. The graphite suspension was prepared from standard synthetic graphite powder (grain sized 1–2 microns). The dispersion was stabilized effectively with 0.5 g/L of standard anionic MT sodium lauryl sulfonate ($C_{12}H_{25}NaSO_4$). The graphite dispersion was mixed with the copper-salt solution in order to obtain a carbon concentration between 15 and 60 g/L.

To form the Cu–PTFE composite deposit, a PTFE emulsion from Aldrich contained 60% by weight of PTFE particles, in the size range of 0.05–0.5 micron range (0.23 micron average). The dispersion was stabilized by means of the non-ionic surfactant polyoxyethylene nonylphenyl ether and a cationic surfactant $C_{20}H_{20}F_{23}N_2O_4I$ to overcome the strongly hydrophobic nature of PTFE. Both the PTFE emulsion and the surfactants were diluted with deionized water. The suspension was maintained at various concentrations from 2.5 cm^3/L to 25 cm^3/L by magnetic stirring (200 rpm).

The average thickness of the deposits formed was determined gravimetrically by weighting the substrate before and after plating. The average thickness of the various copper films deposited was about 2 μm. Tribological tests were carried out on these composite films at ambient temperature and normal atmospheric conditions with a standard ball/plane tribometer. The surface studied was rotated at 100 rpm, and a 100C6-steel ball of 12.7 mm diameter was applied as a stylus at 5N load. Before a test, the steel ball was cleaned with ethanol. The ball/coating friction zone leaves a circular print of radius about 10 mm on the film. In order to compare the tribological performance among the deposited films, the evolution of the friction coefficient was measured as a function of the number of cycles and hence of the distance covered by the ball.

Elemental analysis (EDAX) was used to obtain the elemental composition of the deposits. The mass of PTFE in the matrix was measured by reflective infrared absorption spectroscopy (IRRAS) (Perkin–Elmer Spectrum One). The incidence angle used was 80°, and the polarization was TM (transverse magnetic field in relation to the plane of incidence). In order to obtain a reference spectrum that accounts for the dispersed state of the PTFE particles, the liquid suspension with 60% PTFE was filtered and dried. The spectrum presents two absorption lines, which are related to the vibrations of the C–F bonds of PTFE, one at 1,148 cm^{-1} and the other at 1,203 cm^{-1}. This infrared spectrum of the dried PTFE dispersion coating was then used as the reference for the composite deposits.

The volume percentage of particles (graphite or PTFE) in a film was calculated by means of the following formula:

$$\text{Volume percentage of particles} = \frac{V_2}{V_1 + V_2} \times 100\,\% \quad (1)$$

where V_1 = Cu mass / Cu density and V_2 = mass of carbon (or PTFE) / density of carbon (or PTFE). (The density of a single-phase Cu film (7% B), obtained by DCP with borohydride, is 8.5 g/cm^3 [8] and the density of carbon and PTFE are 2.26 g/$cm^3$and 2.2 g/cm^3, respectively.) A scanning electron microscope (SEM) (Philips Model XL 20), provided with an EDAX probe (10kV), was used to observe the morphology of the surfaces as well its evolution during the wear tests.

These qualitative and semi-quantitative analyses facilitate an understanding of the friction mechanism and the effects of the particles on the value of the friction coefficient and on the wear resistance, thus guiding the development and conditions of optimal use of such films at the industrial level.

Results and discussion

Development of the composite copper deposits

Cu-12%graphite and Cu-22%PTFE films were produced with suspensions of 45g/L graphite and of 10 cm^3/L PTFE, respectively. Figure 1 shows that the growth kinetic of composite deposits (8 μm/h and 6.8 μm/h for Cu-22%PTFE and Cu-12%graphite deposits) is lower than the one of copper deposit without particles (11 μm/h), which is the reference film.

Figure 2 shows the FTIR spectra of deposits containing various amounts of PTFE. These spectra exhibit the two absorption bands that are characteristic of C–F bonds in PTFE. The intensities of the absorption lines at 1,148 and 1,203 cm^{-1} increase as the PTFE concentration in the oxidizing solution is increased (evolving from line (a) to line (d)).

The variation of the PTFE incorporation percentage in the Cu film and the mass deposited as functions of the PTFE suspension concentration are shown in Fig. 3. The

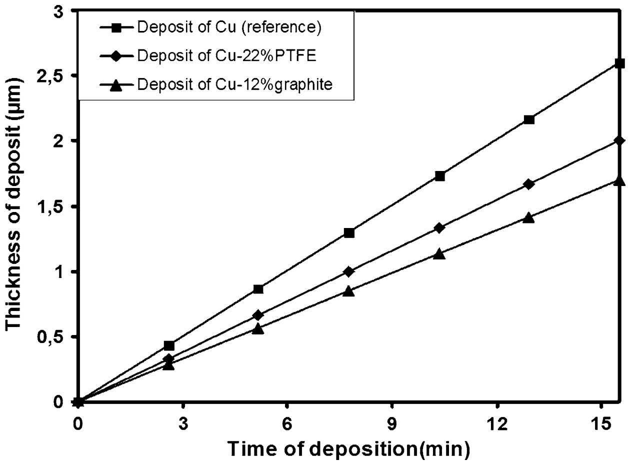


Fig. 1 Comparison of DCP growth curves for Cu, Cu–graphite, and Cu–PTFE deposits. Films produced at room temperature

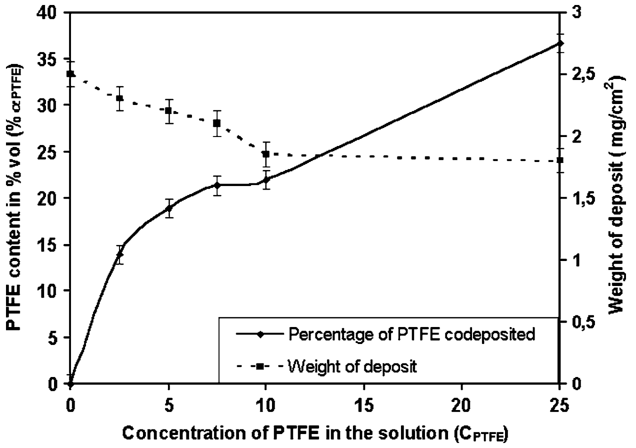


Fig. 3 Effect of PTFE suspension concentration: (a) on PTFE incorporation ratio in the Cu film, and (b) on the mass deposited (during 15 min)

fractional content of PTFE exhibits a progressive increase as a function of increasing PTFE suspension concentration in the oxidizing solution. The increase is rapid from 0 to 5 cm^3/L PTFE but slows up to 10 cm^3/L PTFE in suspension and then seems to increase again. The mass deposited in 15 min decreases with increasing PTFE suspension concentration. The shapes of these two curves indicate that there is an optimal condition for obtaining a Cu–PTFE film rich in particles. The range of PTFE suspension concentration between 7g/L and 10g/L offers at the same time a high incorporation ratio and rapid film growth. The PTFE incorporation ratio obtained here may be compared with that observed by Tang for an electroless Cu–PTFE, i.e., 25% PTFE by volume [7].

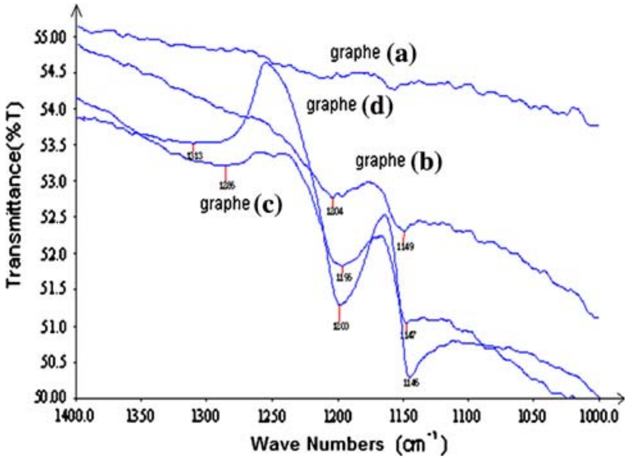


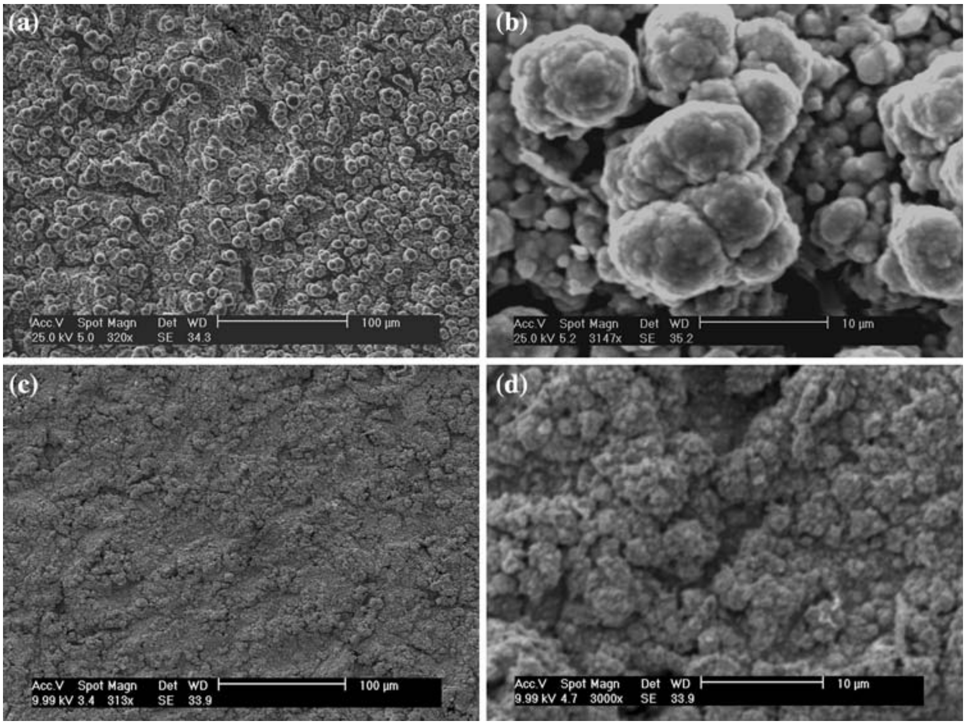
Fig. 2 IR spectra of composite Cu–PTFE deposits made with PTFE concentrations in suspension equal to: (a) 0 cm^3/L, (b) 2.5 cm^3/L, (c) 7.5 cm^3/L, (d) 25 cm^3/L

Surface morphology

The color of composite Cu–graphite films is matte brown. Composite coatings are rougher in comparison to a reference Cu film, as seen in Fig. 4. The surface is uniformly coated with metal clusters of, approximately, 5–10 µm in size. The composite's morphology suggests that graphite particles (micrometric size) are agglomerated and covered with copper. This assumption was confirmed by SEM analysis (by retro-diffused electrons). The comparison with a copper film without particles (reference) indicates greater irregularity in the morphology, with lumpy metal clusters in the shape of cauliflowers. Graphite particles being conductors, reduction of Cu^{2+} cations by KBH_4 is possible on the surface of the particles. Nevertheless, the steel surface energy being higher than that of graphite, the reaction develops preferentially on the surface of the substrate. Then, adsorption of the partly coppered carbon particles is favored and contributes to growing homogeneity of the film. It should be noted that Stankovic [9] has observed the same type of morphology in the case of electrodeposited composite Cu–graphite films.

Scanning electron microscope micrographs of composite Cu–PTFE films with different levels of particle incorporation are shown in Fig. 5. For a film low in PTFE content, the surface morphology is rather homogeneous with clusters of size of about 5 µm. The nanometric PTFE particles (50–500 nm) are trapped in copper's crystalline matrix. The 21% PTFE-film morphology shows metal clusters of size 10–20 µm. When the film is very rich in PTFE, the deposit is powdery, and irregularities appear with deposit outgrowths that seem to detach from the film.

Fig. 4 SEM Photos (**a**, **b**) of a Copper −12% graphite film. SEM Photographs (**c**, **d**) of a reference copper film. (**a**, **c**): 320×, (**b**, **d**): 3,000×

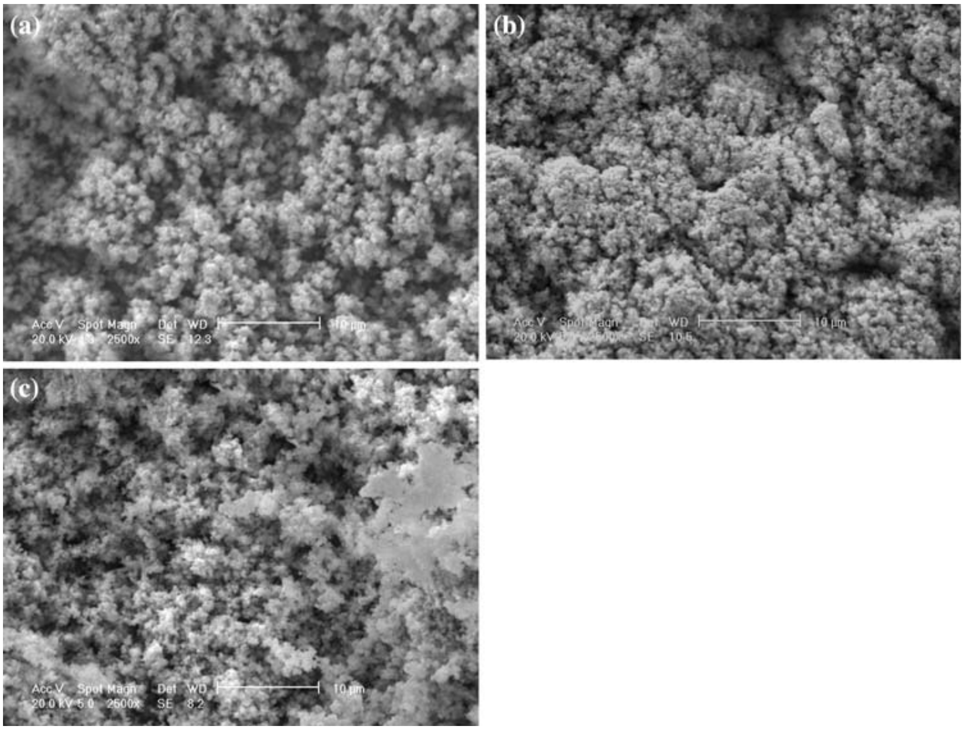


Tribological characterization of composite copper-particle films

In Fig. 6 the friction coefficient is shown as a function of the number of specimen-rotation cycles for a DCP copper deposit without particles and for a composite Cu–graphite deposit. The evolution of line (a) shows that a copper film without particles deteriorates quickly and leads after 80 revolutions to a value for the friction coefficient of 0.55, which may continue to rise. This rapid increase is due to adhesive wear and the accumulation of wear residue.

With an incorporation of 12% graphite in the copper film (line (c)), the friction coefficient is more stable and maintains an average value of 0.18. In the case of a film

Fig. 5 SEM images taken at 20 kV (2,500×) of composite Cu–PTFE deposits for (**a**) Cu-14%PTFE, (**b**) Cu-21%PTFE, (**c**) Cu-37%PTFE



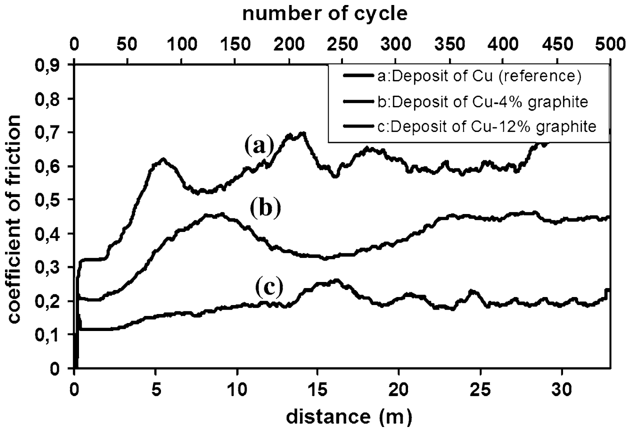


Fig. 6 Variation of the friction coefficient as a function of the number of tribometer cycles for a Cu deposit (reference) and two composite Cu–graphite deposits (load 5N)

low in graphite (4%) (line (b)), the particles are less effective since the friction coefficient reaches a higher value of 0.4. It is not surprising to find in the first part of the line (b) a shape similar to that found for the reference film (a). The coefficient passes quickly from 0.2 to 0.45 and then decreases to reach the constant value around 0.4. In the case of line (c) the curve does not exhibit the same shape, graphite being present in sufficient quantity to sustain dry lubrication.

Moustafa [3] found a friction coefficient of 0.2 for copper containing 15–20% graphite as a composite film formed from a metallurgical mixture of copper and graphite powders. Chen [4] reported a coefficient which varies from 0.09 to 0.19 for electroless composite Cu–CNT (carbon nano-tube) films with 12% of CNT under a load of 10N.

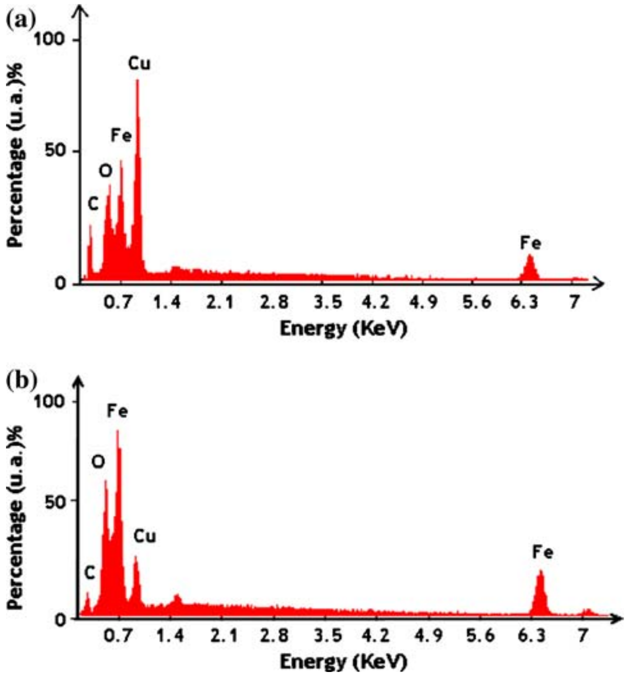


Fig. 7 EDAX spectra of the friction zone (after 500 cycles): (**a**) Cu-12%graphite deposit, (**b**) Cu-4%graphite deposit

In the case of a copper film without particles, the film is quickly abraded and degrades. On one hand there is transfer of copper onto the surface of the tribological ball, and on the other hand, a mixed layer of Cu and Fe is formed in the friction zone, Fe coming from the substrate. With the composite film rich in graphite, EDAX analysis of the friction zone (Fig. 7a) indicates a percentage of copper that is identical to that present before the friction test, which is not the case of the composite deposit with 4%-graphite (Fig. 7b). In both cases, iron from the substrate is detected. It is also necessary to point out the presence of the oxygen line on all the copper samples produced by DCP, with or without particles. Indeed, earlier studies showed that copper films made by DCP contain a small amount of copper oxide.

Retrodiffused-electron SEM observation of the friction-zone surface of a Cu-12% graphite film (Fig. 8) shows a

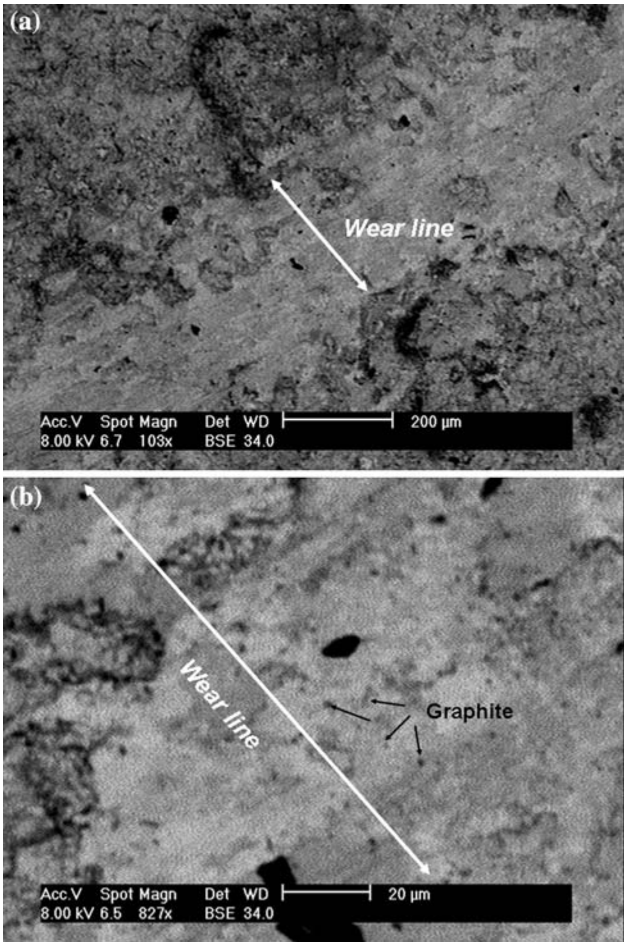


Fig. 8 Retro-diffused SEM micrograph of the friction zone of a Cu-12%graphite deposit (after 500 cycles): (**a**) 100×, (**b**) 800×

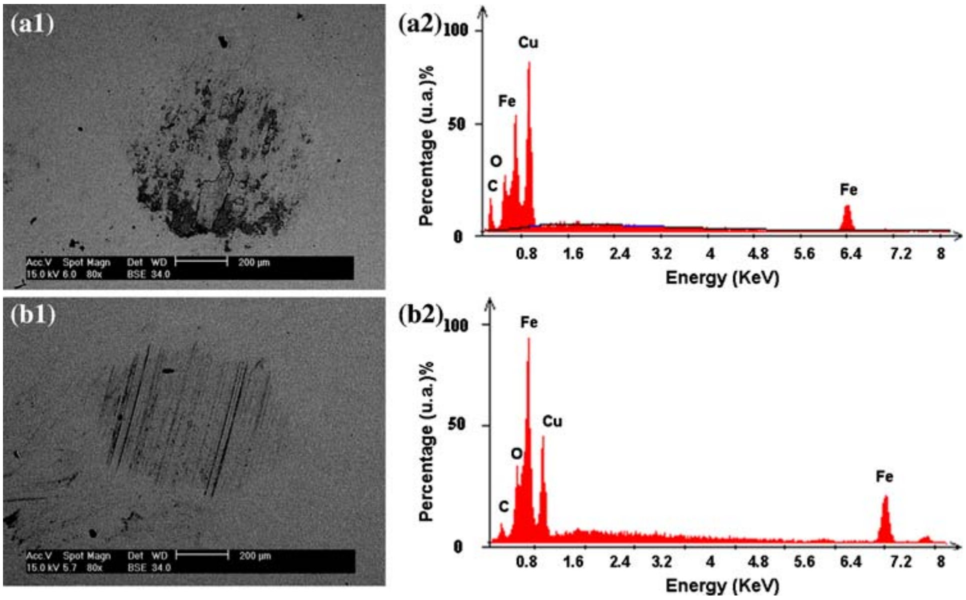


Fig. 9 Retro-diffused-electron SEM photos and EDAX analyses of the ball surface after the tribological test on: (**a**) Cu-12%graphite (80×), (**b**) Cu-4%graphite (80×)

worn surface presenting fine stripes. This image indicates that graphite (dark spots) is not completely torn off during friction. Its presence ensures a lubrication of the copper film, which thus avoids excessive abrasion of the film.

The lamellate properties of graphite as well as the formation of a mixed copper–graphite layer adhering on the surface of the ball, constituting a tribo-layer at the deposit/ball interface, allow one to achieve low attrition and a strong reduction in the friction coefficient in films that are rich in particles. Indeed, EDAX analysis and SEM observation of the tribological ball surface (Fig. 9) show that for composite films, either rich or low in graphite, copper and graphite were transferred onto the ball surface, and this in proportion to the initial amounts of copper and graphite in the film. In the case of the 4%-graphite film stripes indicating wear are seen more distinctly on the ball than in the case of 12%-graphite film.

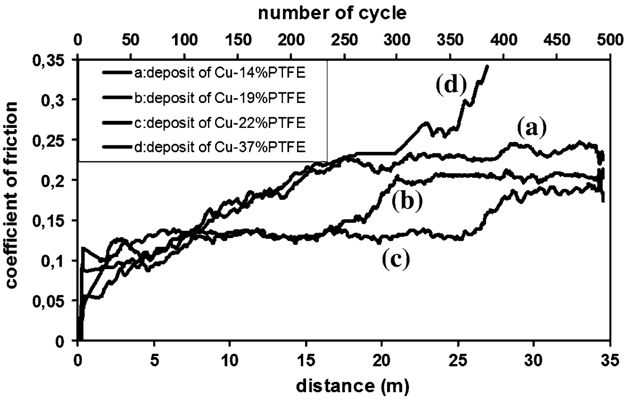


Fig. 10 Friction coefficient of composite Cu–PTFE deposits on mild steel (load 5N, tribological circle of radius 11 mm)

Figure 10 shows the friction coefficient as a function of the friction distance (or of the number of cycles) on composite Cu–PTFE deposits. A composite deposit rich in PTFE (22%) (curve c) confers lubricating properties to the film with a coefficient that decreased by 70% compared to the coefficient of a pure Cu film made by DCP (Fig. 6, curve a). The average value of this coefficient is 0.13 over 300 cycles. When the PTFE incorporation ratio is decreased to 19% (curve b), the value of the friction coefficient increases after 240 cycles passing from 0.13 to 0.2. With a PTFE content of 37%, the deposit is less compact and more fragile. It tends to detach from the substrate, with the failure appearing in curve (d).

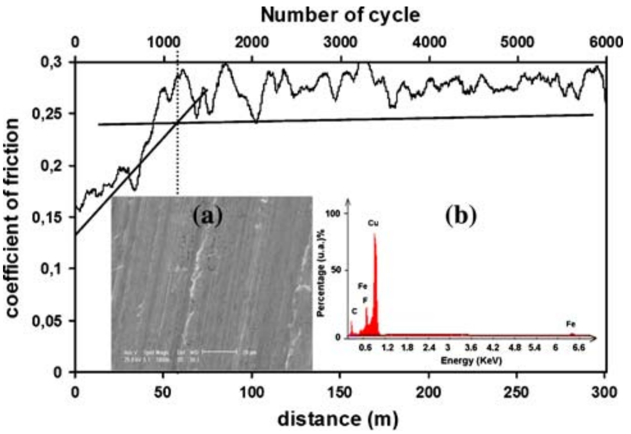


Fig. 11 Variation of the friction coefficient of a Cu-22%PTFE film over a long-duration test (6,000 cycles, load of 5N and tribological ring radius of 8 mm). Inserts: (**a**) SEM of ball-surface morphology after the friction test (1,000×); (**b**) EDAX analysis of the ball surface after the friction test

Figure 11 gives the friction coefficient evolution of a Cu-22%PTFE film for a long-time test (from 0 to 6,000 revolutions or from 0 to 300 m). The occurrence of two periods is noted in the tribological record. The first from 0 to 60 m (0–1,200 cycles) shows that the friction coefficient rises from 0.17 to 0.25. During this stage, part of the composite coating is transferred onto the steel-ball surface, transforming the tribological steel/Cu–PTFE system into a Cu–PTFE/Cu–PTFE system. Cartographic EDAX analysis confirms the presence of Cu and PTFE on the steel ball. The composite film undergoes adhesive wear and creates, by itself, products that are spread out on the steel-ball surface. The second period starts at about 1,200 cycles, and the friction coefficient subsequently fluctuates around 0.25. This effect is related to the formation of a PTFE-rich surface layer (Fig. 11a,b) that is renewed regularly under the action of friction and that provides a self-lubricating function. Under these conditions, the morphological observation (SEM) and EDAX show that, even after prolonged tribological testing (6,000 cycles), the friction zone is polished and homogeneous and comprises the elements of copper and PTFE.

Conclusions

It is possible to obtain composite copper/graphite or copper/PTFE films at room temperature with the DCP technique. A 2 µm-thick composite film is obtained in 18 min for Cu/graphite and in 15 min for Cu/PTFE. With these thin films, with 12% graphite or 22% PTFE, it is possible to lower the friction coefficient of a copper coating from 0.55 to values as low as 0.25 for Cu/PTFE and 0.18 for Cu/graphite. The composite Cu films with 22%PTFE content, or graphite content of 12%, provide the best lubricating characteristics during short-time tests. The lamellate properties of graphite as well as the formation of a mixed copper–graphite layer adhering to the surface of the ball, which constitutes a tribo-layer at the deposit/ball interface, allow one to obtain a low attrition rate and a significant reduction in the friction coefficient with films that are rich in carbon particles. The composite Cu film with PTFE content of 22% exhibits a stable coefficient of friction of 0.25 for a large number of cycles in the tribometric test. With lower PTFE content the friction coefficient increases, and with higher PTFE content the layer weakens.

Acknowledgement The authors thank T.W. Chapman and M. Vilallon of CIDETEQ for their helpful comments on the manuscript.

References

1. Kalantary MR, Holbrook KA, Wells PB (1993) Trans Inst Metal Finish 71(2):55
2. Balaraju JN, Sankara Narayanan TSN, Seshadri SK (2003) J Appl Electrochem 33:807
3. Moustafa SF, El-Badry SA, Sanad AM, Kieback B (2002) Wear 253:699
4. Chen WX, Tu JP, Wang LY, Gan HY, Xu ZD, Zhang XB (2003) Carbon 41(2):215
5. Rohatgi PK, Ray S, Liu Y (1992) Int Mater Rev 37(3):129
6. El-Badry SA (2003) Met Powder Rep 58(2):39
7. Tang JN, Yiao SB, Zhou SM, Xie YB (1995) Trans IMF 73(4):129
8. Stremsdoerfer G, Ghanem F, Saikali Y, Fares Karam A (2003) J Mater Sci 38(15):3285. doi:10.1023/A:1025190022069
9. Stankovic VD, Gojo M (1996) Surf Coat Technol 81(2–3):225