



## Grafting and characterization of dodecylphosphonic acid on copper: Macro-tribological behavior and surface properties

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### ABSTRACT

Thin film of n-dodecylphosphonic acid (DDPA) was prepared on a copper oxide substrate via a molecular self-assembly process. The composition, structure, organization, surface energy, morphology, and electrochemical behavior of the DDPA film were characterized by means of X-ray photoelectron spectroscopic analysis (XPS), polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), contact angle measurement (CAM), microscopic observations, and electrochemistry. The friction behavior of the DDPA film adsorbed on copper oxide substrate sliding against a Si<sub>3</sub>N<sub>4</sub> ball was examined on a linear reciprocating tribological tester. Worn surfaces of the DDPA film were observed with a scanning electron microscope. All properties of the DDPA film were compared and discussed in terms of sonication effects just after surface functionalization. The presence and organization of alkyl phosphonate molecule on Cu were confirmed by XPS, PM-IRRAS and CAM analyses. PM-IRRAS data gave some indication of tridentate bonding between phosphonic groups and oxidized Cu surface. Electrochemical studies showed strong anti-corrosion behavior. Excellent tribological behavior was observed for DDPA film before sonication (DDPA/Cu BS) under contact pressure of 133 MPa and low sliding speed of 1 mm·s<sup>-1</sup> conditions. In the case of DDPA/Cu BS surface, very low friction coefficient value ( $\mu \approx 0.12$ ) and increase in antiwear life (100 times higher) were observed, compared to a DDPA film after sonication (DDPA/Cu AS) and a bare Cu substrate.

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### 1. Introduction

Metal forming processes of sheet components such as rolling, cutting, stamping, embossing, are widely used for various applications employed in important industrial sectors (automotive, aircraft, energy production, building and electronic devices). During metal elaboration, mechanical stresses are transmitted from the tool to the shaped metal sheet, and sliding between these two parts should be facilitated. In order to perfect processes in terms of energy consumption and cost limitation, one obvious objective is to minimize friction and wear of tool/sheet contacts. This point is particularly important in order to assure tool integrity, as far as used metal sheets are generally oxidized in a way that fine and very hard metal oxide particles could be trapped at the tool/metal sheet interface, tending to promote abrasion wear mechanisms. In this way, one common technique to protect surfaces and to limit friction forces is to employ oil-based lubricants, which should be selected depending on forming process parameters such as tools, sheet materials' nature and composition, sliding speed, temperature, and normal load. Nevertheless, classical lubricants have two main

drawbacks resulting in additional expenses. First, optimization of the lubricant amount is difficult to reach, because of both tool and sheet roughness on one side and lubricant's high viscosity on the other side. These difficulties lead to over-consumption of the later to assure contact lubrication. Second, in most cases the lubricant has to be removed from the metal sheet after forming; thus subsequent cleaning operations have to be performed, leading to additional and undesirable costs.

Consequently, an eventual replacement of metal sheet and tool lubrication method could be of great interest in order to limit forming process costs. Thus, one idea is to functionalize metal sheet surfaces with Self-Assembled Molecules acting as an eventual lubricant. Self-Assembled Monolayers (SAMs) allow the production of functionalized surfaces based on grafting of organic molecule film by means of a chemical reaction, leading to chemisorption of molecules on the substrate. This physicochemical surface modification method offers several advantages, since it is easier to implement than other existing coating techniques. Indeed, spontaneous film is formed on the surface by simply immersing the substrate in a weakly concentrated solution of reactive molecules dispersed in a solvent without any external energy supply. Note that the solvent used in this study (high purity ethanol) is a limiting factor in terms of industrial applications, but classical 95% ethanol solution could be used as well, leading to cheaper experiments.

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Moreover, the sharpness of SAMs produced (nanometer scale thickness) avoids subsequent cleaning operation.

While grafting quality is highly dependent on the nature of both molecules and substrate, SAM/substrate systems are claimed to form highly organized films on metal oxide surfaces including alkylphosphonic acids on steel, stainless steel, brass, aluminum, copper, passivated Ni–Ti and cobalt chromium (Co–Cr) alloy [1–6], arachidic acid on  $\text{Al}_2\text{O}_3$  thin film [7], n-alkanoic acids on natively oxidized Al, Cu and Ag [8,9], fatty acids on steel [10], octadecylsilane on  $\text{Al}_2\text{O}_3$  [11] and alkanethiol on Ni, Ag and Cu [12–15]. Due to their low toxicity, alkylphosphonic acids could be destined to replace former SAMs like organothiols or organoselenols derivatives. The grafting mechanism of alkylphosphonic acid molecules is generally described as an acid–base reaction between the SAM's phosphonic groups and the hydroxyl groups present on copper surface [3]. Although a large number of studies described the reaction mechanism as a covalent bond formation, the number of so-formed bonds is actually highly dependent not only on the substrate properties, but also on the molecular grafting mode which could be mono-, bi- or tridentate.

SAMs have been the topic of extensive research, both for their fundamental importance in understanding interfacial properties as well as their potential applications in corrosion resistance, catalysis, biological sensors, adhesion systems, protein films, electronic devices fabrication etc. [14–24]. Nevertheless, few papers have been suggested to assess the tribological behavior and efficiency of such SAMs [3,10,15]; moreover, tribological tests are usually carried out using a nanotribometer, which is also not representative of the real metal sheet/tool contact scale [3].

In the present work, n-dodecylphosphonic acid (DDPA) synthesized in our laboratory is used as a reactive group to form SAM films on copper oxide substrates in order to investigate the tribological efficiency of this surface modification route in the case of forming processes used in microelectronic industrial sector (cutting, stamping ...). Specimens employed in this study are CuA1 copper (99.9% Cu). In the first part, SAMs' composition, structure and organization are characterized by spectroscopic techniques. Results stemming from electrochemical techniques are presented, revealing oxidation blocking factor and anti-corrosion properties of SAMs. In the second part, the influence of surface modification on friction and wear behavior is studied by means of tribological experiments. The effects of sonication on DDPA films in terms of chemical and tribological properties are then investigated. Thereafter, functionalized copper substrates with DDPA film before and after ultrasonic cleaning will be called DDPA/Cu BS and DDPA/Cu AS, respectively.

## 2. Experimental section

### 2.1. Chemicals

De-ionized water (Milli-Q, resistivity  $18 \text{ M}\Omega \cdot \text{cm}$ ) was distilled twice before use. 1-Bromododecane (ALFA AESAR, 98 %, 143–15-7), triethylphosphite (ALFA AESAR, 98%, 122–52-1), perchloric acid (ACROS, 70%, 7601–90-3), sulfuric acid (ACROS, 96%, 7664–93-9), absolute ethanol (ACROS, pure, 64–17-5), sodium hydroxide (ACROS, 97+%, 1310–73-2) and sodium chloride (ACROS, extra pure, 7647–14-5) were used as received.  $^{31}\text{P}$  NMR spectrum was performed from a Bruker AC 300 apparatus, using a solution in  $\text{CD}_3\text{SOCD}_3$  with 1 M  $\text{H}_3\text{PO}_4$  as an external standard. Mass spectrum was obtained from a LTQ Orbitrap apparatus with a negative ESI source.

1-Bromododecane (50.0 g, 200 mmol) was heated to  $200^\circ\text{C}$  (oil bath). Triethylphosphite (45.0 g, 240 mmol) was added dropwise during 30 min., whereas bromoethane was continuously distilled-off (vapor temperature below  $40^\circ\text{C}$ ). The mixture was then brought to  $220\text{--}225^\circ\text{C}$  and maintained at this temperature until the distillate flow slowed down (30–40 min.) Excess triethylphosphite was eliminated at 50–100 mm Hg for 5–10 min and the resulting oil cooled to

room-temperature. Concentrated aqueous hydrochloric acid (12 M, 250 mL) was added and the heterogeneous mixture stirred and boiled ( $100^\circ\text{C}$ ) for 15 h. After cooling to room-temperature, the semi-oily mixture was extracted with dichloromethane ( $2 \times 100 \text{ mL}$ ). After drying (anhydrous sodium sulfate), the organic phase was concentrated ( $60^\circ\text{C}$ , 400 mm Hg) to an oil, which soon solidified. It was recrystallized from cyclohexane to afford off-white plates.

Yield: 74%. F:  $99^\circ\text{C}$ .  $^{31}\text{P}$  NMR (121.45 MHz, 300 K):  $\delta = 27.4 \text{ ppm}$ . MS (C =  $10^{-5} \text{ M}$  in methanol): exact mass ( $\text{g} \cdot \text{mol}^{-1}$ ): 249.1641; Found: 249.1666.

### 2.2. Pretreatment of the working electrode

Copper substrates were cut into  $20 \text{ mm} \times 20 \text{ mm}$  pieces, without additional polishing. The copper surfaces were sonicated in absolute ethanol and ultra-pure water for 5 min and then electrochemically reduced in 0.5 M aqueous perchloric acid under a current of  $-800 \mu\text{A}/\text{cm}^2$  for about 120 s, until metallic copper potential was attained ( $< -720 \text{ mV}/\text{SCE}$ ). The samples were cleaned again in aqueous nitric acid solution ( $\text{pH} = 1.8$ ) for 7 min and oxidized by exposure to a 5% aqueous hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution for 10 min at room temperature.

### 2.3. Monolayer preparation

The SAMs were grafted by dipping the oxidized copper surface in a  $10^{-3} \text{ M}$  solution of dodecylphosphonic acid (DDPA) in absolute ethanol for 16 h under argon flow. The surface was then rinsed with absolute ethanol. Subsequently, a first class of samples (called DDPA/Cu AS) was cleaned in a sonication bath for 5 min to remove physisorbed species, while a second group of samples (called DDPA/Cu BS) had no other post-treatment. Samples were kept in inert atmosphere until characterizations were completed. The sample preparation procedure used for this study was identical to that used for previous studies [3,4].

### 2.4. Surface characterization

#### 2.4.1. XPS

In this study, XPS is used to measure elemental composition in order to determine oxidation state of elements. Two different XPS equipments were used in this study. The first one was used for depth profiling of oxidized copper surface and the second one was used to analyze the SAM surface after functionalization tests, just in order to focus the grafting quality. All spectra for depth profiling were acquired using monochromatized Al K $\alpha$  radiation (1486.6 eV). X-ray radiation source operated in ultrahigh vacuum (UHV) (base pressure below  $10^{-11} \text{ mbar}$ ). The load lock chamber was pumped down to  $10^{-6} \text{ mbar}$  with a primary rotative pump and a secondary turbo molecular one. The main chamber was pumped down to  $10^{-11} \text{ mbar}$  with titanium sublimation pump and an ionic one. The binding energies of the cores levels were calibrated in function of the C 1 s binding energy set at 285.5 eV, a characteristic energy of alkyl moieties, and deconvolutions were made using mixed Gaussian–Lorentzian curves (80% of Gaussian character).

The surface chemical state of Cu samples just before functionalization after chemical tests was analyzed by an X-ray photoelectron spectroscopy (XPS). All binding energies were corrected to a carbon C 1 s binding energy of 285.5 eV to reduce the charging effects. All the oxidized samples were first pumped down to  $10^{-6} \text{ mbar}$  in a load lock vacuum chamber in order to degas the surface. Then the entire samples were introduced into the main chamber for analyses. The analyses were realized in several alternative levels of X-ray measurements and etching time in order to detect elements of the surface from the top layer to the bulk of the oxidized copper substrate. The etching step was realized using an ion argon gun with a tungsten filament and differential vacuum system in order to sputter pure argon ion in the chamber, through

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