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Tribological properties of surface-modified Pd nanoparticles for electrical contacts

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ABSTRACT

A fully comprehensive study of the tribological behavior of palladium nanoparticles (Pd NPs) capped by tetrabutylammonium chains using a ball-on-disk tribometer under different conditions of applied load, concentration, tribometer motion, linear speed and nature of the counterface is revised. A low concentration of NPs (2 wt%) in tetrabutylammonium acetate was found sufficient to improve the tribological properties due to the formation of a protective transfer film (TF) comprised of metallic Pd. The increase of the applied load (up to 20 N, 1.82 GPa of contact pressure) confirmed the excellent extreme-pressure behavior avoiding the counterfaces from severe wear. After a running-in period whose duration depends on the operating conditions, the TF build-up allows to maintain a low contact electrical resistance through the contact (<0.1 kΩ) during the entire test. When the Pd NPs are used with ceramic counterfaces, the nanoparticles increase the load-bearing capabilities and performance of the base without forming TF, likely by mixed or boundary lubrication and healing effects. Finally, the Pd NPs are demonstrated to be useful as a thin solid lubricant film in reciprocating motion yielding a comparable tribological behavior. Hence, the presented surface Pd NPs can be very helpful to extend life of sliding components due to their high strength resistance providing a gateway to electrical conduction as well.

1. Introduction

The addition of nanoparticles into lubricating oil significantly reduces the friction coefficient and increases the load-bearing capacity of the friction parts in mechanical systems [1–6]. A variety of mechanisms have been proposed to explain the lubrication enhancement of the nanoparticle-suspended lubricating oil, including colloidal effect [7], rolling effect [8], protective film [9–11], healing or mending effect and polishing effect [12]. The friction-reduction and anti-wear behaviors are dependent on the characteristics of the nanoparticles, such as size, shape, composition and concentration. Intensive studies have been carried out in the last few years to tune their properties by appropriate selection of the synthesis conditions including surface modification for its dispersion in lubricant oils to become more feasible (see for instance, metals: Cu [13–18], Ag [19,20], Au [21]; Mo [22], Ni [23,24], Pb [25]; oxides: TiO_2 [26], SiO_2 [27], ZrO_2 [28,29], ZnO [30], Al_2O_3 [31]; chalcogenides: WS_2 [32], MoS_2 [33,34], CuS [35]; Sb_2S_3 [36]; FeS [37]; and carbon-based compounds (fullerene-like [38,39], nano-diamond [40], CNTs [41])).

Focusing on the use of noble metals, like gold, silver and even palladium, they have been currently employed to reinforce polymer or composite coatings with the aim of improving mechanical, tribological and thermal stability properties [42–44]. The noble character of these metals makes them very suitable for preventing corrosion or reaction of the surfaces in contact [45]. This property qualifies its employment as a good candidate for lubrication of electrical contacts where a sharp increase of the contact resistance results in a fault of the electronic device [46]. This protection mechanism lasts as long as the substrate is not reached. The refilling with noble nanoparticles can be an interesting approach to supplement or substitute this protective action.

In a previous paper [9] we have demonstrated the remarkable capabilities of Pd nanoparticles as a lubricant additive in rotary motion allowing a simultaneous decrease of the electrical resistance of the contact in comparison with the initial value measured for the base oil alone. Likewise, a comparison carried out with Au nanoparticles similar in size demonstrated comparable or improved anti-wear effect in certain conditions [10]. The investigation of the wear mechanisms allowed to discover the benefits of the nanoparticles helping to accommodate the sliding motion, increasing the load capacity, and decreasing the wear rate. Furthermore, in the case of Pd nanoparticles, a decrease of the electrical resistance of the contact was obtained making their application suitable for small connectors and microelectronics

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devices [10,47]. The origin of such behavior was attributed to the formation of a homogeneous metal-like layer rich in Pd on the counterfaces when the particles are trapped in their transit through the contact. In this work, the potentialities of these metallic NPs for practical uses are profusely evaluated under many different experimental parameters (load, counterface, tribo-motion) including optimization of the NP concentration in the solution. Moreover, the current paper introduces for the first time the usage of Pd nanoparticles directly dropped onto the contact (without dispersion in base lubricant) using linear reciprocating motion. The present study is of interest both for fundamental understanding as well as for prospective technological applications. Moreover, the improved knowledge of the tribological behavior of these nanoparticles may be useful for designing new applications.

2. Experimental

Palladium nanoparticles have been prepared by the redox-controlled size-selective method proposed by Reetz and Maase [48] using tetrabutylammonium acetate (TBA) as surfactant in tetrahydrofurane (THF) (0.1 g in 2.5 ml of THF) and $Pd(NO_3)_2$ from Aldrich (99%) (0.02 g in 25 ml of THF) as palladium precursor. After mixing, nitrate is displaced by the more effective acetate ligand, which is followed by the reduction of the Pd^{2+} by electron-transfer, giving rise to Pd^0-stabilized clusters. The reaction is developed under nitrogen atmosphere to prevent oxidation. This method of preparation of the palladium is not expensive as the noble metal is prepared by chemical reduction of a commercially available worldwide salt precursor. The content of metallic palladium was estimated by plasma-inductive coupled plasma spectroscopy (ICP) in 10 wt% and the elemental chemical composition was found to be C (58.8%), H (11.0%) and N (5.47%), all expressed in wt%. The particle size distribution appears rather homogeneous with a mean particle size of around 2 nm. The palladium nanoparticles can be used as prepared in solid state or mixed with pure surfactant (TBA) using THF as solvent forming different lubricant formulations with variable palladium concentration. The resulting colloidal dispersion was poured onto a steel disk for measuring the tribological properties. More information about the synthesis and morphology of the nanoparticles can be found in [9,10]. Here, we further complete the structural characterization by measuring the X-ray diffractogram (XRD) of the Pd NPs using a Siemens D5000 apparatus with Cu Kα radiation in Bragg–Brentano configuration. Fig. 1 depicts the XRD pattern showing very broad peaks, indicative of the nanocrystalline character, at 40°, 46°, 66° and 80° coincident with the diffraction peaks (111), (200), (220) and (311) of metallic palladium respectively.

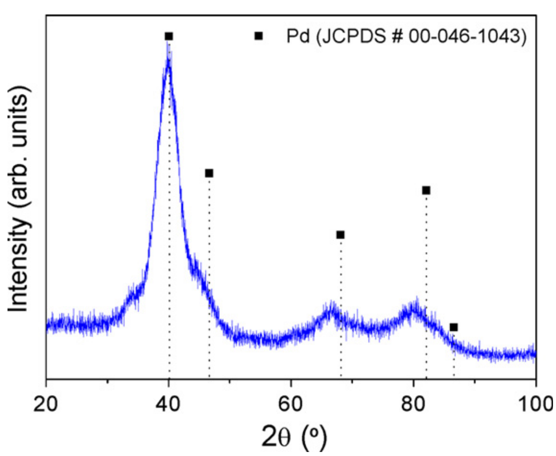

Fig. 1. XRD diffractogram of the Pd nanoparticles as-synthesized by electrochemical reduction.

The tribological properties were measured in a CSM ball-on-disk tribometer working under two different configurations, rotative and reciprocating. The test conditions varied depending on the parameter under study but ball diameter (6 mm), ambient conditions (relative humidity 30–50%) and steel disk counterface (mirror-polished AISI M2; $H=16$ GPa) were kept similar. The summary of the remaining parameters of the friction tests for the different cases are listed in Table 1. The electrical resistance (R_c) of the contact was monitored simultaneously in order to understand the tribological phenomena appearing at the contact. Normalized ball wear rates, K_{ball} (mm^3/Nm), were evaluated after examination of the balls and calculation of the worn volume using the spherical cap equation. Normalized disk wear rates, K_{disk} (mm^3/Nm), were evaluated from cross-sectional profiles taken across the disk-track using stylus profilometry.

3. Results

3.1. Influence of the load

The load applied in the tribological test was varied between 1 and 20 N (see Table 1). Under these conditions the maximum contact Hertzian pressure values are estimated to vary between 0.66 and 1.88 GPa, for the lowest and the highest load, respectively. In Fig. 2 the ball and disk wear rates and the friction coefficient measured for each test are shown. Friction coefficient does not seem to be very influenced by the load and it gets steadied at around 0.07–0.08. The ball wear rates are found in the range of $2–9\times10^{-10}$ mm^3/Nm although a marked trend to decrease as the applied load increases is observed. The disk wear rates also manifest a similar trend although their values are always one order of magnitude higher (between 2 and 9×10^{-9} mm^3/Nm). It is worth mentioning that the ball wear rate for a TBA dispersion without NPs under 7 and 15 N is measured to be 6×10^{-9} and 7×10^{-9} mm^3/Nm, respectively. All these results are in good agreement with the potentialities as anti-wear (AW) and extreme-pressure (EP) additives of these Pd NPs.

Fig. 3 shows the transfer films (TFs) formed at 1, 3, 10 and 20 N of normal loads. These results point to a protection of the ball counterface by the formation of a TF. At 1 N the TF is not yet well formed, indicating that a minimum load is necessary to form the TF. When the shearing is strong, the nanoparticles' core/shell

Table 1
Main parameters used in the tribological tests performed in this work.

Study	Mode	Ball-counterface	Sliding distance (m)	Linear speed (cm/s)	Load (N)	P_{max} (GPa)	[NPs] (wt%)
Load influence	Rotative	52100 steel	5000	10	1–20	0.66–1.88	5
NP concentration	Rotative	52100 steel	5000	10	15	1.62	1–10
Counterface	Rotative	52100 steel, Al_2O_3, Si_3N_4, WC–Co	5000	10	15	1.40–2.00	5
Configuration movement	Reciprocating	52100 steel	18	0.1,0.4	5,15	1.12,1.62	5