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Wear and scratch behaviour of electroless Ni-P-nano-TiO_2: Effect of surfactants

T.R. Tamilarasan [a,1], R. Rajendran [a], M. Siva shankar [a], U. Sanjith [a], G. Rajagopal [b], J. Sudagar [c]

[a] *Department of Mechanical Engineering, School of Mechanical Sciences, B.S. Abdur Rahman University, Vandalur, Chennai 600048, Tamil Nadu, India*
[b] *CSIR-Central Electrochemical Research Institute, Karaikudi 630006, Tamil Nadu, India*
[c] *Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India*

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ABSTRACT

This paper investigates the effects of surfactants on microhardness, scratch, wear and friction behaviour of the Ni-P-nano-TiO_2 composite coatings. Nano TiO_2 particles were co-deposited with electroless Ni–P coating on low carbon steel substrates in the presence of anionic and cationic surfactants-sodium dodecyl sulphate (SDS) and dodecyl trimethyl ammonium bromide (DTAB) respectively. Results revealed that at an optimum concentration of the surfactants, the coatings obtained a smoother surface, low frictional coefficient, enhanced microhardness and high wear resistance. The findings of scratch test showed that the composite coatings with surfactants exhibited the ability to withstand higher critical load and lower penetration depth. This can be ascribed to the reinforcing action of co-deposited TiO_2 nanoparticles in the composite coatings. The cationic surfactant DTAB contributed to the increase in weight percentage of TiO_2 in the Ni–P matrix considerably. At critical micelle concentration (CMC) value of the DTAB surfactant, the coatings had the highest weight percent of incorporated TiO_2 and showed a better homogenous distribution.

1. Introduction

Modern industries expect to meet their ever growing demands with the development of technology in the area of materials engineering. The emphasis is now more on the use of reliable and novel materials with improved mechanical properties which will ensure the effective utilisation of appliances for a longer period even if they are subjected to an aggressive environment. The prospects of using composite materials with superior attributes also paved a way as one of the possible solutions. In this regard, the widely used groups of composite compounds are metallic coatings with secondary phase of solid particles co-deposited during the coating process which could greatly modify the physical and chemical properties of the composite coatings [1–3]. Electrochemical or electroless methods are the most commonly used techniques that involve composites in the coatings. Electroless Ni–P based composite coatings are currently used in various industrial applications as it greatly improves the time-testing properties like corrosion and wear resistance besides enhancing microhardness and helps in attaining uniform thickness [4–6]. Recent development in electroless Ni–P based composite coatings has been inclusion of secondary phase nano solid particles like TiO_2, ZrO_2, SiC, Al_2O_3, etc., into Ni–P matrix to augment the mechanical and tribological characteristics of the coating. It is important to consider the factors like type, size, concentration and properties of the embedded particles, as they play the primary role in determining the characteristics of the composite coatings [7–9].

There are two ways of performing electroless composite coating process with the prime focus on tribology. In the first instance, the lubricant composite coating involves embedded solid lubricants like PTFE, graphite, etc., that generally produces the coatings having lesser frictional coefficient when compared to the conventional Ni–P coatings. On the other hand, coating is wear resistant when aided by co-deposition of hard particles like SiC, Al_2O_3, and TiO_2, etc., which exhibit relatively increased hardness [10,11]. Among the several particles, nano TiO_2 has gained widespread interest among researchers because of its exceptional mechanical properties and enhanced surface behaviour. Studies have shown that introduction of nano TiO_2 particles resulted in increased wear resistance, anti-corrosion behaviour and electrocatalysis related properties [12,13]. At the same time, the high surface area of the nano-particles contributes to increased chemical reactivity and high surface energy of the particles, which tend to increase the chances of the particles to agglomerate during the coating process. Therefore, the amount of incorporation of nano TiO_2 into Ni–P matrix gets reduced in terms of weight or

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E-mail address: tamilarasan.tr@gmail.com (T.R. Tamilarasan).

[1] Corresponding author. Tel.: +91 44 22751347.

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volume percentage subsequently affecting the characteristics of composite coatings. Moreover, electroless Ni–P coatings are more vulnerable to intense adhesive wear under dry sliding interaction. Therefore, in order to achieve the desirable characteristics of coatings effectively, it is essential to make use of surfactants in the plating bath [14–17]. Surfactants are surface active agents that lower the surface tension of a fluid, allowing easier spreading and lower the interfacial tension between two fluids. Also, surfactants are responsible for enhancing the stability of suspension and has a strong influence on wetting, absorption and adhesion behaviour. Hence, surfactants are used to achieve uniform distribution of particles in the coatings so that it will enhance the tribological properties of the deposits. Surfactants are generally characterized in terms of critical micelle concentration (CMC) and if the concentration of the surfactant is varied with respect to its CMC range, the physical properties of the electrolytic solution will also be affected to a considerable extent. Hence, CMC is used as a means to distinguish and study the surface activity of every surfactant [18]. Here, the concentration of surfactants used in the electroless deposition of Ni-P-nano-TiO_2 is also varied in terms of CMC.

Numerous researchers have worked on co-deposition of nano TiO_2 in Ni–P matrix using electroless plating technique. However, there is no adequate information related to the effects of surfactant and concentration on tribological characteristics of Ni-P-nano-TiO_2 coatings. The present work aims to achieve Ni-P-nano-TiO_2 coating on low carbon steel substrate by means of electroless deposition method. Also it is intended to investigate the impact of cationic surfactant dodecyl trimethyl ammonium bromide (DTAB) and anionic surfactant sodium dodecyl sulphate (SDS) on the wear and friction behaviour of the composite coatings. This paper further reports the consequent effects of these surfactants on the surface morphology, scratch resistance, microhardness and composition of the composite coatings.

2. Experimental procedure

2.1. Specimen preparation

AISI 1018 low carbon steel samples (10 mm × 25 mm) were used as the substrate material for the coating process, with composition (in wt%) of 0.20% C, 0.60% Mn, 0.04% P, 0.05% S, and 99.11% Fe. The samples were grounded and then surface finished by disc polishing. A stylus instrument was used to determine the surface finish values and the finished samples had an average roughness value of 0.48 μm. The cleaning process of samples comprised of ultrasonic agitated cleaning of specimens using acetone for about 15 min, removing greasy particles using ethanol for around 10 min, intermediate washing with deionized water and then activated in 50 vol% HCl solution for 30 s. Finally, the samples were rinsed with deionized water and instantly shifted to the electroless plating bath.

2.2. Plating procedure

In the plating bath, nickel sulphate was chosen to be the source of nickel, sodium hypophosphite as the reducing agent, lactic and propionic acids as complexing agents. Stabiliser was used to evade bath decomposition. The composition of the plating bath and the conditions of functioning are given in Table 1. The experiment was carried out completely using analytical grade ingredients. The pH metre (Eco Tester) was used to measure the pH value of the plating bath and was regulated to 6 and maintained constant for the period of plating by introducing ammonia solution whenever required. The rate of stirring and plating bath temperature were kept at 400 rpm and 88 ± 2 °C respectively. The TiO_2 nano-particles with standard particle size of 25 nm were used and the concentration of nano TiO_2 in the bath was maintained constant at 2 g/l. The different surfactant concentrations were arrived based on CMC values of SDS and DTAB, wherein CMC equals to 2.39 g/l for SDS and 4.35 g/l for DTAB [19].

Table 1
Compositions and operating conditions of the plating bath.

Constituent	Quantity
Nickel sulphate	30 (g/l)
Sodium hypophosphite	40 (g/l)
Lactic acid	36 (ml/l)
Propionic acid	2.4 (ml/l)
Stabiliser	1 ppm
Nano TiO_2	0 and 2 (g/l)
SDS or DTAB surfactant	(0.25–2) × CMC
pH	6
Temperature	88 ± 2 °C

The TiO_2 nano-particles were ultrasonically agitated for 30 min prior to introducing them to the bath. Initially, Ni–P deposits were coated for 15 min and then nano-TiO_2 was introduced to the bath and then coating process was continued for 45 min. The overall duration of plating was 60 min. For the purpose of comparative analysis of the coating characteristics, basic Ni–P deposition and composite Ni-P-nano-TiO_2 deposition without any surfactants were also performed using similar procedure. After allowing the plating for the stipulated duration, the coatings were washed with deionized water and dried up at ambient conditions.

2.3. Characterisation of deposits

The surface morphology and wear tracks of the electroless Ni-P-nano-TiO_2 coatings were examined using high resolution scanning electron microscope (HR-SEM) furnished with energy dispersive spectroscopy (EDS), using which the elemental composition of the coatings were determined. The deposition rate was calculated by an analytical formula [20] and found to be in the range of 25–34 μm/h and it was also verified by cross sectional SEM image (see Fig. 1e).

Adhesion of the coatings on substrate was examined using scratch test. Acoustic signals were emitted when delamination or cracking took place at the scratch path. The adhesion strength of coating is normally characterized by Critical Load (L_c), described as the load at which failure happens and first acoustic signal is sensed [21–24]. The adhesive strength of the coating was measured with the help of linear scratch test equipment (Revtest, CSM, Switzerland). The coating adhesion strength was measured at the coating surface by progressive test load method, in which the load was gradually increased from 1 to 40 N at a loading rate of 3 N/min for a distance of 3 mm. Scratch test was conducted using Rockwell diamond indenter (200 μm). Scratches with progressive scar width were produced consequently with a gap of 5 mm in between scratches. Four different runs were conducted for each specimen and the two coinciding values are reported as the critical load for each specimen. The parameters like applied load range and scratch length were chosen based on the literature which also state that a critical load of 30 N with a Rockwell C diamond tip is sufficient for sliding contact applications [21,25]. Also, the scratch test was conducted as per standard ASTM C 1624-05. Parameters like applied normal load, frictional force, tangential force, penetration depth of the indenter and acoustic emission were recorded in the computer simultaneously during running of the tests.

The microhardness of the coating was measured with a Future-Tech Microhardness tester, Japan, with a Vickers diamond indenter.