

Mechanical Preparation of TiO₂ Nanoparticles and their Incorporation in Electroless Ni-P Coatings

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Abstract -The present study focuses on the mechanical preparation of the TiO₂ nanoparticles by milling using high energy planetary ball mill at 250 rpm for 40h. The milled TiO₂ nanoparticles are then used as the reinforcement to develop electroless (EL) Ni-P-TiO₂ nanocomposite coatings on mild steel substrate. The hypophosphite reduced alkaline bath was used with a suspension of 4g/l TiO₂ nanoparticles for the synthesis of Ni-P-TiO₂ nanocomposite coating. The morphology, particle size and phase analysis of as prepared TiO₂ nanoparticles were analysed using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and properties in terms of hardness and wear resistance were investigated for Ni-P-TiO₂ nanocomposite coating and compared with Ni-P coating. The results shows that as prepared TiO₂ particles exhibit irregular shape and particle size ranges from 35-45nm. The microhardness and wear resistance of the coatings is found to be significantly improved after heat treatment at 400°C for 1h in argon atmosphere. The EL Ni-P-TiO₂ nanocomposite coatings exhibit higher wear resistance over Ni-P coating.

Keywords: Electroless (EL); Ni-P-TiO₂; Nanocomposite; Milling; Microhardness; Wear resistance

1. Introduction

Electroless (EL) nickel coating due to its uniform deposition and excellent wear and corrosion resistance is one of the reliable and efficient method of surface engineering (Krishnan et al. (2006). It is well known by literature that embedding several hard particles into Ni-P matrix and by suitable heat treatment, one can further enhance the coating properties (Agarwala et al., 2006); (Makkar et al., 2013); (Sahoo et al., 2011). Titania (TiO₂) due to its high hardness and thus wear resistance is most commonly used as the second phase particles for producing electroless Ni-P composite coatings (Novakovic et al., 2004,2009); (Momenzadeh et al., 2012); (Khalifa et al., 2011). Most of the TiO₂ reinforced Ni-P nanocomposites prepared by electroless method concentrates upon the inclusion of micron sized particles (Novakovic et al., 2009); (Novakovic et al., 2004) or chemically prepared nanoparticles (Momenzadeh et al., 2012); (Khalifa et al., 2011) into the Ni-P matrix to yield better coating properties. However, the studies on reinforcement of TiO₂ nanoparticles prepared by mechanical milling into Ni-P matrix are not reported till date. In the present study, TiO₂ nanoparticles were first prepared using mechanical milling method and then codeposited on Ni-P to develop EL Ni-P-TiO₂ nanocomposite coatings on mild steel substrate. The morphology, phase changes and the nanocomposite coating properties such as hardness and wear with respect to Ni-P alloy was studied.

2. Experimental

2.1. Preparation of Nanosized Titania powder/ Ni-P/ Ni-P-TiO₂ Nanocomposite Coatings

The nanosized titania powder was prepared by mechanical milling using high energy planetary ball mill at 250 rpm with ball to powder ratio 10:1. Micron-sized titania powder (the particle size: ~43µm, 99.5% purity) provided by Merck was used as the starting precursor for mechanical milling. Hardened steel jars and balls were used as the media for mechanical milling while toluene was used for avoiding oxidation of the powders. The milling of TiO₂ powders were carried out upto 40h, with milling time of 2h. An half an hour was introduced to avoid the overheating of the milling media. Mild steel (2.5mm×2.5mm×2mm) were used as substrate for plating EL Ni-P and Ni-P-TiO₂ nanocomposite coatings. Substrates were polished upto 1000 grit size paper and then sensitized by 0.1% stannous chloride and 0.01% palladium chloride solution with intermediate rinse with distilled water. The activated substrates were immersed into the plating solution and as prepared milled TiO₂ powder was then added into the prepared EL bath under continuously stirring. The EL bath contains nickel sulphate as metal source ions (30 g/l), sodium hypophosphite as reducing agent (20 g/l), sodium tri-citrate (100 g/l), ammonium sulphate (50 g/l), ammonium chloride (50 g/l) as complexing agent and stabilizers respectively and milled titania nanopowder (4 g/l) as the reinforcement (Agarwala et al., 2006). The EL bath maintains at pH 9.0, temperature 90°C and plating time was 30 min. The samples were oven dried after plating at 45°C for 15min.

2.2. Characterization

The phase analysis of milled TiO₂, Ni-P and Ni-P-TiO₂ coatings were carried out by X-ray diffraction (XRD) with Cu target (D8 Bruker AXS diffractometer). The morphology and particle size of the milled titania nanopowder and the coatings are characterized by field emission scanning electron microscope, FESEM (Quanta FEI-200) and transmission electron microscope, TEM (TECNAI G2-20). For desired mechanical properties of Ni-P and Ni-P-TiO₂ coatings, heat treatment was carried out in argon atmosphere for 1 h at 400°C. The microhardness (VHN) of Ni-P and Ni-P-TiO₂ nanocomposite coatings were determined (Wilson Instruments) on as coated and heat-treated specimens under a 10 gf load for 15 sec. Hardness value as an average of three measurements was reported. Ball-on-Disc tests were carried out to determine the wear resistance of the coatings. The 3mm thickness and 42mm diameter mild steel discs were used against chromium steel ball of hardness 65 HRC. The wear test of the coatings were carried out at sliding speed of 0.1 m/s, temperature of 32°C, 40% moisture, under 1N load and 800m sliding distance.

3. Results and Discussion

Figure 1(a),(b) shows the morphological characteristics of the as received and milled TiO₂ powder respectively. The fractured surfaces of the particles display the effect of external energy provide by milling to the system. Brittleness of the TiO₂ ceramic particles with irregular shapes [Fig 1(b)] facilitate the lowering of the particle sizes to a range of 35-45 nm as confirmed by TEM studies [Fig 1(c)]. The milling results convince fracturing over the cold welding procedure. Ni-P coating reveals the globular structure [Fig 1(d)] with the evidences of lateral growth followed by vertical way. The presence of nodules transforms the surface topography of the Ni-P-TiO₂ [Fig. 1(e)] from smooth state to non smooth state. In some regions, TiO₂ particles are clearly seen on the Ni-P globules (region 1) while in certain areas, the particles are observed to be coated with Ni-P alloy (region 2). Figure 1(f) shows the FESEM micrograph of worn surface of the Ni-P-TiO₂ nanocomposite coating. The wide longitudinal grooves and partial irregular pits along the sliding direction are seen on the worn surface of EL Ni-P-TiO₂ nanocomposite coating. The grooves imply the micro-cutting and micro-ploughing effect of the counterface, while pits reveal the ductile fracture. The mild adhesive wear mechanism is observed as the predominant phenomena over here.

The diffraction pattern of as received and 40h milled TiO₂ were shown in Fig 2(a). The figure confirms the presence of anatase phase of titania after 40 h milling (JCPDS: 01-073-1764). The crystallite

size was determined by using Scherrer's formula ($d = 0.9\lambda/\beta \cos\theta$) where d is the crystallite size, λ is the wavelength of X-ray, β is line broadening at half the maximum intensity (FWHM) in radians, θ is the Bragg angle, which is found to be 33 nm and is further confirmed by TEM studies. XRD studies of the Ni-P coating display single broadened peak [Fig.2(b)] which can be attributed towards the microcrystalline nickel Ni (JCPDS: 00-045-1027) in 'as coated' condition. Microcrystalline nickel and Ni_xP_y are converted to crystalline structures and Ni_3P phase when heat treated (JCPDS: 01-074-1384) [2]. Apart from single broadened peak of Ni, peaks of TiO_2 (JCPDS Ref No.: 01-073-1764) are also present [Fig.2(c)]. It is being noticed that the Ni and Ni_3P structures peaks remain the same, which confirms the undistorted structure of the phases on reinforcement of TiO_2 nanoparticles. Fe peak (JCPDS: 00-006-0696) arises from the substrate used.

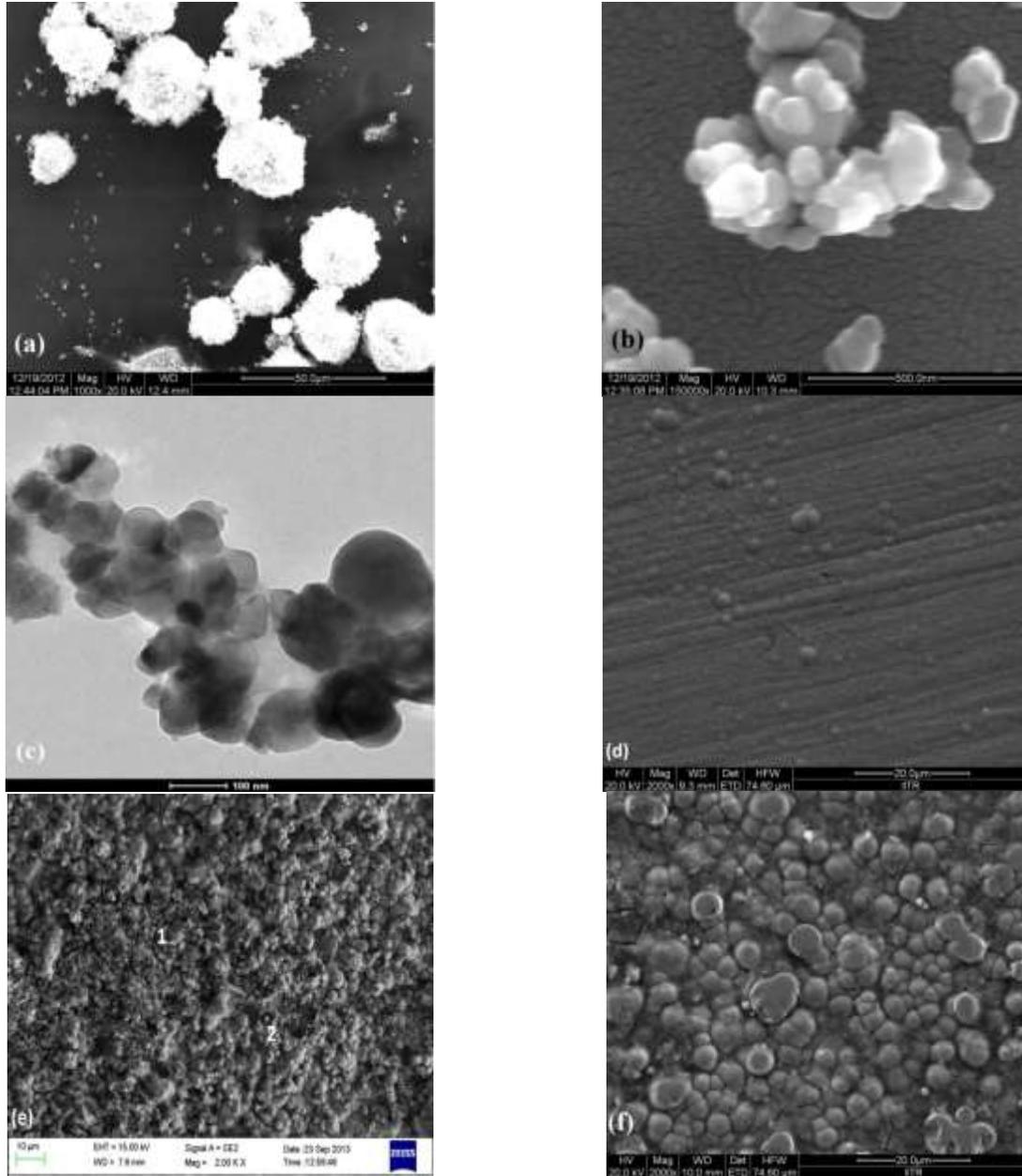


Fig. 1. FESEM micrographs of TiO_2 powder (a) As received (b) 40 h milled; (c) TEM micrograph of TiO_2 powder; FESEM micrographs of electroless coatings (d) Ni-P (e) Ni-P- TiO_2 (f) Worn surface of EL Ni-P- TiO_2 nanocomposite coating.

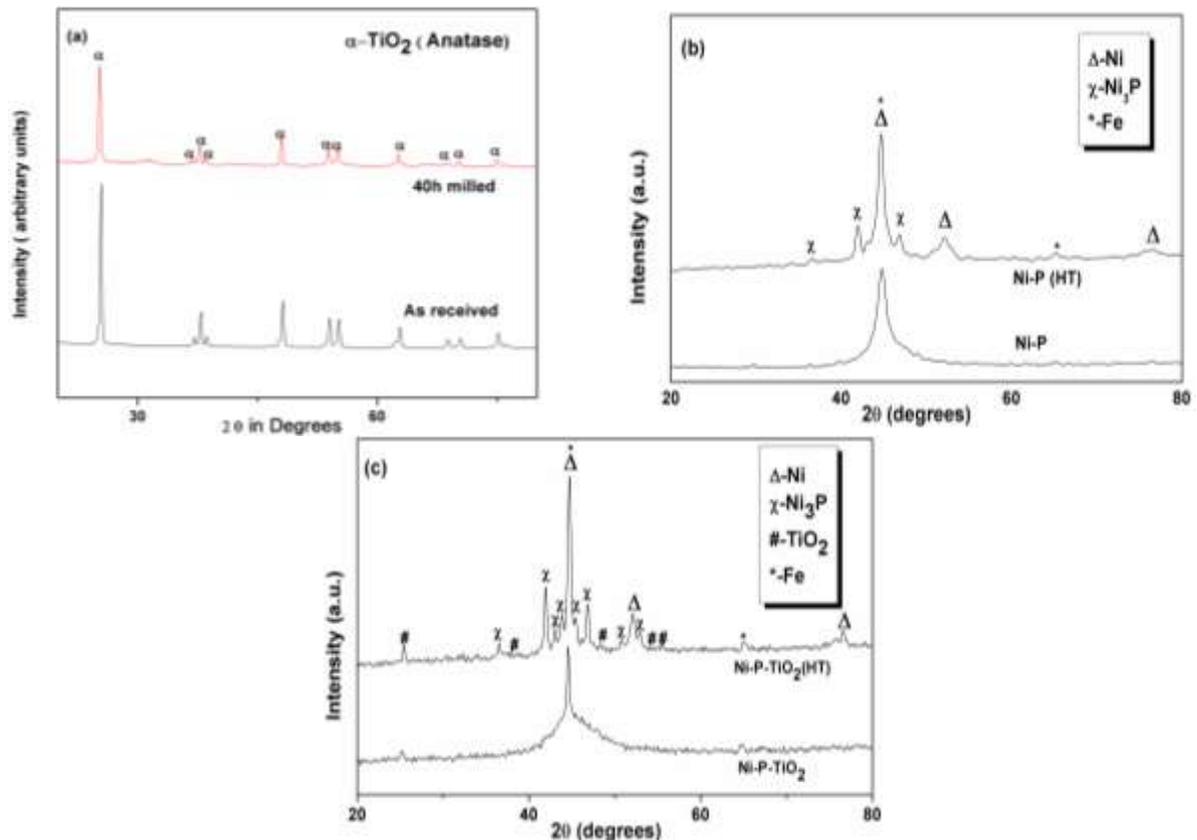


Fig. 2. XRD patterns of (a) as received & 40h milled TiO_2 powders; (b) Ni-P coating; (c) Ni-P- TiO_2 coating

The microhardness of the 'as coated' Ni-P is found to be 414 VHN and the hardness increased to 815 VHN during heat treatment at 400°C for 1h as phase transformation occur within the deposit, which leads to the precipitation of Ni_3P phase which inturn produce maximum hardness. When as prepared milled titania nanoparticles are embedded with Ni-P, the hardness increased to 570 VHN. It is due to the reinforcement of hard titania particle as second phase in Ni-P matrix. The heat treatment further enhances the hardness of EL Ni-P- TiO_2 nanocomposite coating to 1010 VHN.

4. Conclusion

- 1) TiO_2 nanoparticles with crystallite sizes $\sim 35\text{-}45$ nm are prepared by mechanical milling method.
- 2) Codeposition of as prepared TiO_2 nanoparticles into Ni-P matrix results in the modification of surface morphology of the coatings.
- 3) XRD of EL Ni-P- TiO_2 nanocomposite coating confirms the anatase phase of TiO_2 along with Ni phase.
- 4) Milling prepared Ni-P- TiO_2 nanocomposites exhibit high hardness, 1010 VHN after appropriate heat treatment (400°C , 1h).
- 5) The mild adhesive wear mechanism is observed by worn surface of the nanocomposite coatings.

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References

- Agarwala, R., Agarwala, V., Sharma, R. (2006). Electroless Ni-P based Nanocoating Technology—A review, *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry*. 36, 493-515.
- Krishnan, K., John, S., Srinivasan, K., Praveen, J., Ganesan, M. Kavimani, P. (2006), An overall aspect of electroless Ni-P depositions: a review article, *Metallurgical and Materials Transactions A* 37A, 1917–1926.
- Khalifa, O., Wahab, E., Tilp, A. (2011). The effect of Sn and TiO₂ Nano Particles added in Electroless Ni-P Plating Solution on the Properties of Composite Coatings, *Australian Journal of Basic Applied Science*. 5(6), 136-144.
- Makkar, P., Agarwala, R., Agarwala, V. (2013). Studies on Electroless Coatings at IIT Roorkee-A Brief Review. *Materials Science Forum*. 33, 275-288.
- Makkar, P., Agarwala, R., Agarwala, V. (2013). Development of Electroless Ni-P-ZrO₂ Nanocomposite Coatings by Codeposition of Mechanically Reduced ZrO₂ Nanoparticles. *Advanced Materials Research*. 740, 545-549.
- Momenzadeh, M., Sanjabi, S. (2012). The effect of TiO₂ nanoparticle codeposition on microstructure and corrosion resistance of electroless Ni P coating. *Materials & Corrosion*, 63, 614-619.
- Novakovic, J., Vassiliou, P. (2009). Vacuum thermal treated electroless Ni-P-TiO₂ composite coatings. *Electrochimica Acta*, 54, 2499–2503.
- Novakovic, J., Vassiliou, P., Samara, Kl., Argyropoulos, Th. (2004). Electroless Ni-P-TiO₂ composite coatings: Their production and properties. *Surface Coating Technology*, 201, 895–901.
- Sahoo, P., Das, S. (2011). Tribology of electroless nickel coatings – A review. *Materials and Design*, 32, 1760–1775