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ULTRA FINE TiO₂ DISPERSED METALLIC COATING ON STEEL

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Abstract: In the present study, an attempt has been made to develop nano scale TiO₂ disperse nickel coating on steel substrate by direct current deposition from Watt's solution to improve the mechanical property of conventional nickel coating. To resist agglomeration of ultra fine particles in plating bath due to high surface free energy and to get homogeneous coating, magnetic stirring and ultrasonic agitations have been used. The coating microstructures were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) method. Ultra fine dispersion of TiO₂ of below 100 nm size was observed in the faceted nickel matrix and the coating thickness was approximately 33 µm. Homogeneous and sharp increase in surface microhardness was observed after incorporation of TiO₂ powder.

Key Words: Electrodeposition, Nickel, TiO₂, Nanoparticles

1.0 INTRODUCTION

Electrodeposition of nickel is widely used to provide surface properties like corrosion resistance and physical appearance. The nickel-plated surface shows low surface mechanical properties such as hardness and wear resistance and to improve this electro-co-deposition of Ni with non-metal was investigated regularly [1-12]. Ceramic dispersed metal matrix composite coating has been widely used in industry where the particle reinforcements include alumina (Al₂O₃) and titania (TiO₂). Due to its noble properties, reinforcement in nano size is being investigated recently [1, 4, 7] with same or similar ceramic materials. The electro co-deposition of Ni with second phase nano-particles such as aluminum oxide, titanium nitride, carbon nanotube (CNTs), diamond, silicon carbide, silicon nitride and zirconium oxide have been studied extensively over the past two decades. Some such investigations with Ni-Al₂O₃ [1,4,8], Ni-CNTs[2,3], Ni-Si₃N₄[4,6], Ni-diamond [4], Ni-SiC [5,9,14], Ni-ZrO₂ [7], Ni-TiO₂ [10,12] have been reported recently. These have the large projected applications for automotive parts, aerospace, printed circuitry and electrical contacts,

gold-silver wares and jewelry, musical instruments and trophies, soft metal gaskets, decorative door, light & bathroom fittings [16].

As the grain / particle size is of major concern, this type of composite coating should ideally be developed at lower temperature range / room temperature by the process of electrodeposition. Again, electrodeposition is a process which also incurs low cost and is simple in operation. Watt's solution is widely used for Ni deposition; but Watt's bath produces stresses to the plated material which leads to lower fatigue properties. Ultrasonic agitation during deposition is required to lower the stress limit of the plating material along with increased current efficiency and current density of the plating bath which in turn decreases the coating time [11].

For co-deposition of ceramic particles, ceramic particle dispersed [8] plating bath is being used; but, problems like sedimentation of large particles and agglomeration of fine particle are of major concern. Ultrasonic agitation helps to avoid agglomeration of ultra fine particles in plating bath and thus in coating

which is a common problem due to high surface free energy of the fine particles. Addition of organic surfactant in an electrolytic bath also improves the homogeneity of the composite coating [16, 17] by changing the contact angle between the particle and the electrolyte. It was reported that it can also reduce the grain size of the deposited nickel [11]. The composition, structure and properties of the composite are affected by several parameters, such as composition of particles, concentration of the plating bath, particle characteristics, temperature, pH, agitation, type of applied current and current density [15, 16, 17].

The present work aims to improve mechanical and electrochemical properties by electro-co-deposition of Ni with dispersed second phase ultrafine titanium oxide particles. The Ni/TiO₂ metal matrix composite coatings were prepared on steel substrate by using Watt's solution dispersed with TiO₂ powder (by double layer theory). In the first phase of this work, our objective is to optimize the plating parameters to obtain dispersed coating. Next step is aimed at optimization of mechanical properties in terms of microhardness and wear resistance and electrochemical properties. For determination of optimum condition of solution pH, amount of particle and surfactant amount were taken as variables, whereas current density and temperature of the bath were maintained constant in presence of magnetic stirring and ultrasonic agitation.

2.0 EXPERIMENTAL

Small specimens with approximate dimensions of 10 mm x 15 mm x 6 mm were cut from hot rolled SAE 1020 grade mild steel bar with nominal composition of % C: 0.18-0.22; % Si: 0.1-0.35; % Mn: 0.6-0.7; % Al: 0.01(max); %S: 0.02(max); % P: 0.03; and balance Fe (in wt.%). This steel was selected for the present study as model plain carbon steel used for structural applications. The steel samples were metallographically polished before electroplating.

For electro co-deposition of Ni/TiO₂, Watt's solution was used as the plating bath. Ultra fine TiO₂ which was dispersed in the bath was procured from Inframet Advanced Materials, Formington, USA. Purity was claimed as 99.99% and particle size as ~ 30 nm. The particle size was checked by Malvern Zetasizer nano series Nano-ZS model instrument. The composition of the bath along with variable plating parameters are shown in the Table 1.

Ultrasonic agitation was used for the dispersion of particle for 1 h just before initiation of the plating process and magnetic stirring was done during plating. The temperature was maintained by the use of a hot plate and the electro-deposition was controlled by a DC source (APLAB 7103). A

stainless steel plate was used as anode where as the prepared specimens were used as cathode.

Table 1: The bath composition and deposition conditions

Electrolyte (Watt's bath)	Nickel sulphate (NiSO ₄ .6H ₂ O): 350 gm/lit
	Nickel chloride (NiCl ₂ .6H ₂ O): 45 gm/lit
	Boric acid (H ₃ BO ₄): 37 gm/lit
Wetting agent	Sodium dodecyl sulphate: 0.2 gm/lit
Surfactant	Hexa decylpyridinium bromide: 0, 0.1, 0.3 gm/lit
Dispersion	Titania (TiO ₂): 5, 10, 15 gm/lit
pH	~ 4
Temperature (°C)	~ 55-65
Current density	5 A/dm ²
Plating time	30 minutes

The pH of the plating solution was maintained by NH₄OH (for increasing pH) and CH₃COOH (for decreasing the pH). As the isoelectric point (IEP) of TiO₂ is about pH 5.7 [18], the pH was maintained below this value in acidic bath to get co-deposition on the cathode. Moreover, as, at pH ~ 4 the Nickel deposition gives optimal mechanical properties [19] the pH was tried to be maintained at value 4. The different surfactant concentrations (as mentioned in the Table 1) were used to improve the coating property.

After deposition, the phases obtained were analyzed by Bragg-Brentano (theta-2theta) x-ray diffraction (XRD) using Cu K_α ($\lambda = 0.15406$ nm) radiation in a Philips X-ray diffractometer.

Microscopic studies to examine the morphology, particle size and micro structure were done by a JEOL 6480 LV scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) detector of Oxford data reference system. The secondary electron imaging was used with suitable accelerating voltages for the best possible resolution. Cross sectional plane was also observed under SEM. For higher resolution, some samples were observed under a field emission gun assisted scanning electron microscope (FESEM) (ZEISS: SUPRA 40).

Microhardness measurements were carried out on the surface using a Vickers hardness indenter with 50 g load (Buhler microhardness tester). Each hardness value reported here is an average of 4-5 measurements on the same sample at equivalent locations.

3.0 RESULTS AND DISCUSSION

3.1 Particle size

As raw material characterization, the particle size of the TiO₂ powder procured was analyzed by Malvern

Zetasizer. Figure 1, which shows the particle size distribution of the powder, consists of two peaks, one below 100 nm (peak value at \sim 30 nm) and the other smaller one above 1 μm . The particle size distribution is bi-modal kind of distribution and particle size distribution is wide in nature. But after studying the cumulative value it can be observed that more than 50% particles are sized below 100 nm.

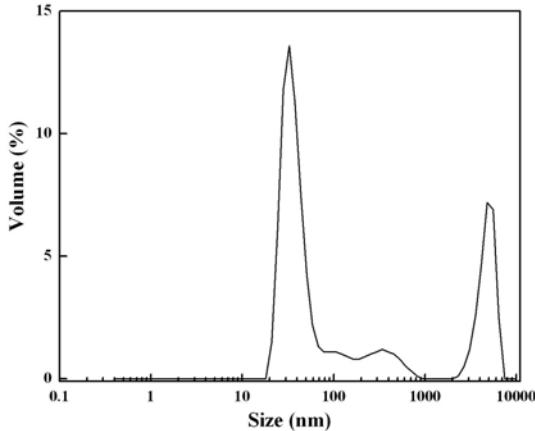


Figure 1: Particle size analysis of the TiO_2 powder.

3.2 XRD analysis

Figure 2 shows the x-ray diffraction patterns of procured TiO_2 powder. Peaks confirming tetragonal structure do not show appreciable broadening though the particles are nanometric in size. The powder source was confirmed to be synthesized by a chemical route which does not introduce strain in the material. So, the broadening observed was only due to the fine crystallite size, not due to the strain. Thus the XRD peaks do not show huge broadening though the crystallite size is ultrafine.

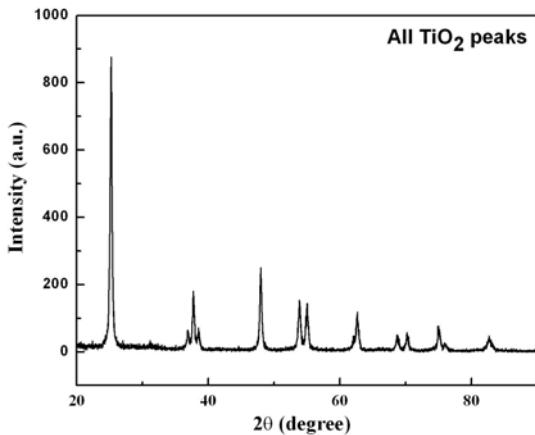


Figure 2: XRD pattern of TiO_2 powder.

XRD study was carried out on all the coated samples as well as the substrate to identify the phases present on the surfaces. Some of those data are presented here in Figure 3. Figure 3(a) shows XRD pattern of substrate, nickel coating without addition of ceramic

particles and XRD pattern of co-deposited samples (TiO_2 bath composition: 5, 10 and 15 gm/lit.) without addition of surfactant.

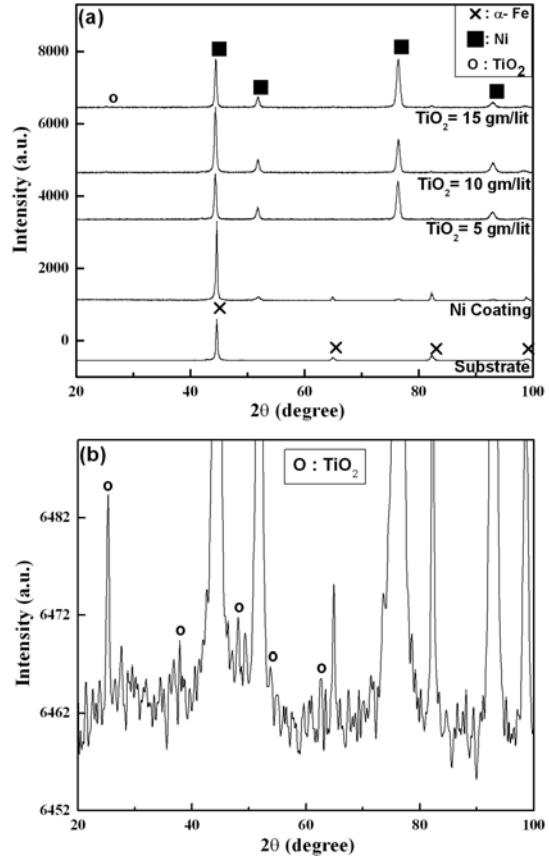


Figure 3: XRD pattern of (a) substrate, Nickel coating without ceramic particles, co-deposited samples without addition of surfactant and (b) enlargement of TiO_2 = 15 gm/lit sample data.

Substrate XRD shows only α -Fe peaks, whereas after nickel coating mainly peaks of nickel were observed as predicted. In the three co-deposited samples there was no significant intensity of TiO_2 peaks. To judge it properly one XRD profile (TiO_2 = 15 gm/lit, no surfactant) was enlarged to see the low intensity peaks (Figure 3(b)). Figure 3(b) shows the various peaks which confirm the presence of TiO_2 . With such technique TiO_2 peaks were observed in only 4 samples in the present study. Those are: all the samples with different amount of TiO_2 powder in the bath without surfactant and sample with bath concentration: TiO_2 15 gm/lit and surfactant 0.3 gm/lit. These may happen either due to the absence of TiO_2 in the deposit or due to the presence in very low amount [20]. From Figure 3(a) and their enlarged view it can be concluded that during co-deposition trial, TiO_2 deposition was successful with some specific deposition parameters.

3.3 Microstructure and composition

Microstructural analysis on the coated surface as well as on the cross section was carried out and Figure 4(a) & 4(b) show SEM & FESEM micrographs of sample co-deposited with 10 gm/lit TiO₂ concentration Watt's bath without surfactant respectively. The structure consists of facets of nickel with maximum size below 2 μm along with TiO₂ particles. To judge to particle size, figure 4(b) was analyzed and it was observed that particles are below 100 nm in size.

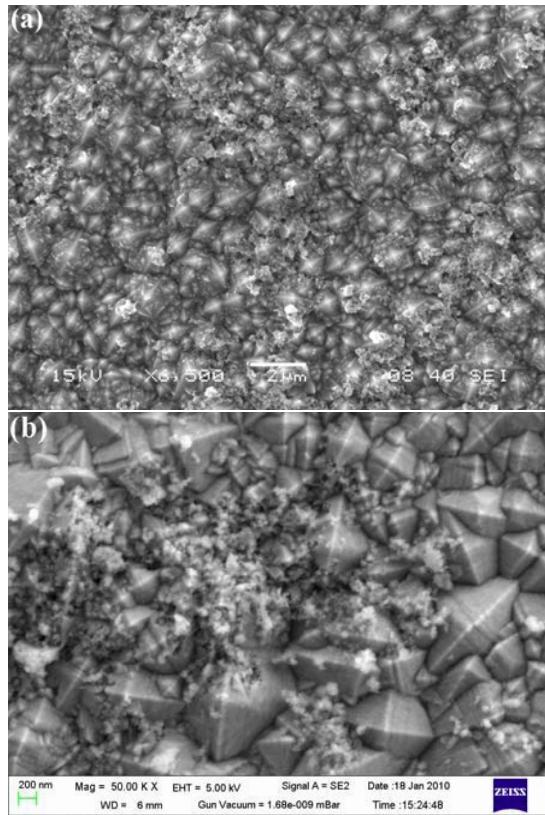


Figure 4: (a) SEM & (b) FESEM micrograph of sample co-deposited with 10 gm/lit TiO₂ bath concentration without surfactant.

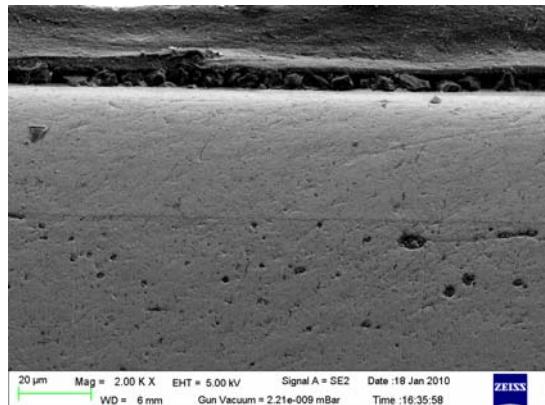


Figure 5: SEM micrograph of cross section of sample obtained from 15 gm/lit TiO₂ (without surfactant) bath.

Figure 5 shows the SEM micrograph of cross sectional plane perpendicular to the plane of deposition for the sample obtained from 15 gm/lit TiO₂ and without surfactant. The layer deposited was uniform in nature and the coating thickness observed was about $\sim 33\mu\text{m}$.

To establish the chemistry of the different phases observed in Figure 4, energy dispersive spectroscopy (EDS) study was done on different region on the coated surface. The overall spectrum of the sample which was viewed in Figure 4 is shown in Figure 6(a). The spectrum confirms the presence of Ti along with Ni and small amount of Fe. Quantitative analysis of the spectra was carried out for all the samples and such data are shown in Figure 6(b).

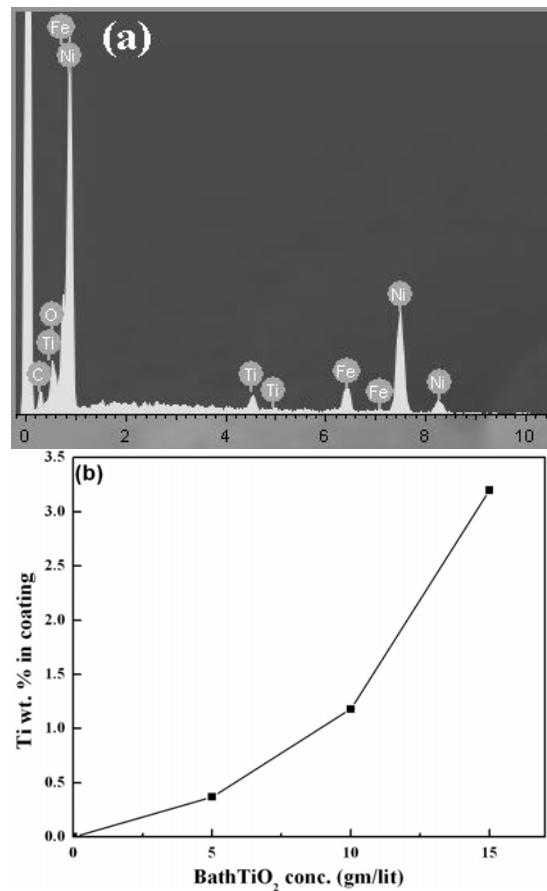


Figure 6: (a) EDS data from surface of the sample obtained from 10 gm/lit TiO₂ concentration bath without surfactant. (b) Elemental weight percentage of Ti on the surface of the co-deposited samples (without surfactant).

Figure 6(b) shows elemental weight percentage of Ti on the top layer of the coating of the co-deposited samples (TiO₂ bath composition: 5, 10 and 15 gm/lit. without addition of surfactant). Increasing Ti wt. % in the coating is attributed to the increasing amount of embedded TiO₂ particles in the same. So, from this figure, idea about the variable amount of TiO₂ in the

coating can be obtained. In the present set of samples, except these three mentioned in Figure 6(b) and sample obtained from 0.3 gm/lit surfactant others show Ti wt. % below 0.1.

From the observation made from EDS it be concluded that bath concentration of TiO_2 has direct effect on the deposition amount. Surfactant addition only helps with certain values, details of which will be discussed in the next section.

3.4 Microhardness

Figure 7 shows variation of microhardness values measured on the coated surface as function of TiO_2 and surfactant concentration of the bath. Hardness values were measured with 50 gm load confirming that the values are not affected by the substrate (coating thickness $\sim 33 \mu\text{m}$). The base hardness of the steel substrate was measured 184 VHN and that of Nickel coating from Watt's solution was around 375 VHN.

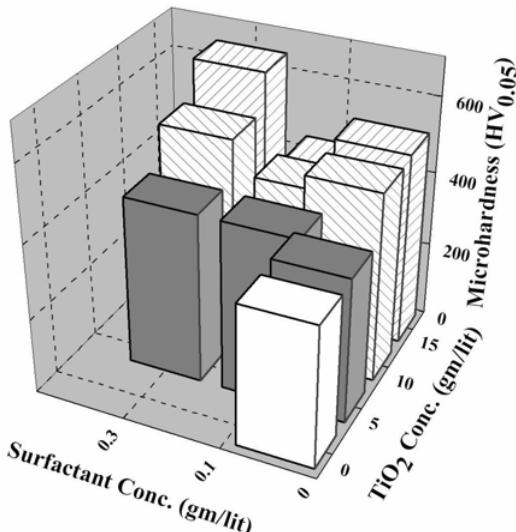


Figure 7: Variation of microhardness with TiO_2 bath concentration and surfactant concentration.

Microhardness values measured at different points on the surface shows that the microhardness readings are homogeneous. From the figure it is clear that with the addition of ceramic (TiO_2) powder in the bath the microhardness values increase even without addition of surfactant in the bath. This can only be attributed to the fact that more amount of ceramic particle got embedded with increase value of bath concentration. Thus dispersion strengthening helps in improving surface mechanical properties. Furthermore, as the particles are ultrafine in nature, the high temperature property of the coating should have gone up due to Zener pinning effect. Similar trend of increase in microhardness with bath TiO_2 is visible with the presence of surfactant also. Maximum hardness value was observed with 15 gm/lit TiO_2 powder and 0.3 gm/lit surfactant bath.

It can also be observed from Figure 7 that microhardness is increased after the addition of 0.3 gm/lit of surfactant in the deposition bath whereas with lower surfactant value there is even decrease also when compared with same TiO_2 bath concentration. Same trend was observed when quantitative EDS analysis was done for Ti. This may be due to the change in zeta potential value after addition of different amount of surfactant. In the present range of study 0.3 gm/lit surfactant shows the best result due to favorable bath condition for deposition of TiO_2 . Similar results were presented by Chen *et al.* [21].

4.0 CONCLUSIONS

In this study, an attempt was made to co-deposit Ni- TiO_2 from nano TiO_2 disperse Watt's bath. From the detailed investigation, the following conclusions can be drawn:

- (i) TiO_2 particles of $\sim 30 \text{ nm}$ size were successfully co-deposited with nickel on steel substrate.
- (ii) Nickel was present in the coating with faceted appearance along with TiO_2 dispersion and the thickness of the coating was about $33 \mu\text{m}$ after 30 minutes of deposition.
- (iii) Though TiO_2 particles could not be fully deagglomerated on the deposited layer, microhardness values were homogeneous and good increase in microhardness values were observed. With respect to the substrate, there was maximum 3.5 times increase in microhardness after addition of dispersion and with respect to pure nickel coating, that was 1.7 times; the bath condition was 0.3 gm/lit surfactant and 15 gm/lit TiO_2 .

5.0 ACKNOWLEDGEMENTS

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