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Electrodeposition of Ni composites and nanocomposites from aqueous organic solution

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Abstract: *Electrodeposition of composites and nano composites composed of metal matrix (nickel) and inert particles (TiO_2) has been carried out successfully in a mixed aqueous-organic solvent under different current densities. The ceramic particles are uniformly dispersed and embedded in nickel matrix. Titania content varied with its concentration in bath and with current density. SEM and XRD, EDAX studies have been performed to characterise the composites and nano composites. The particle size 60 - 1500 nm were obtained. In some cases preferred orientation of nickel has been observed. The TiO_2 content ranged between 3.02 to 11.92 wt% in the composites.*

Key words : Ni-TiO_2 composites, nanocomposites, electrodeposition, diethanolamine-water bath.

1. INTRODUCTION

The electrolytic codeposition of particles with metals has been the object of investigation for some decades [1-8]. Composite electrodeposition consists of the electrolysis of plating solutions in which micron or submicron-size particles are suspended. Variable amounts of these particles become dispersed and embedded in the metal matrix to which they impart special properties. The application of such composites and nanocomposites have been highlighted in publications [1-4]. Codeposition of particles induces dramatic changes in the texture of the metals and alloys [7,9].

In recent past, there has been great interest in studying nanocrystalline alloys and nanocomposites, since these open up a new possibility in controlling material properties [9,10]. The codeposition of particles during electrochemical deposition of a metallic film depends on the rate of metal deposition and on the flux of particles to the film surface. The growth rate of the metal film is determined by the deposition current density, where as the flux of particles to the electrode surface is dependent on the particle size, particle concentration in the bath, the agitation rate, particle diffusion coefficient and the electrode geometry. In corporation of particles into growing film can be thought of to be influenced by convective diffusion of particles to the surface. The gravitional force can have significant role on the kinetics of particle codeposition which may be dependent on the particle size.

Keeping all above factors in mind for codeposition of particles with metal; mixed aqueous-organic solution bath was thought to be worthwhile for the deposition purpose. Since the aqueous organic mixture solutions offer a wide scope of complexation with metal favouring ultrafine grained deposits and also provide much variation of physical properties of the solutions i.e. viscosity, conductivity, etc. In turn these may largely influence the diffusion process and convective flow under gravitational force. Electrodeposition of nanocomposites has been rarely reported. The nanoparticles are difficult to disperse in metal matrix being very light and the factors like viscosity, conductivity, diffusion and gravitational forces may much significantly influence the codeposition of particles in metal matrix. In organic solvents the suspension of the particles is easy and also remains stable for a quite long time which is an additional advantage of the organic solution bath.

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Therefore an attempt has been made to codeposit composites and nanocomposites of nickel with TiO_2 particles (using known size nanoparticles) from aqueous organic solution bath. For this purpose an organic solvent of high viscosity (diethanolamine) with water as mixture solution containing nickel sulphamate, boric acid and different concentrations of TiO_2 particles of known size has been used for electrolysis.

2. EXPERIMENTAL

The aqueous organic solution mixture of diethanolamine 50vol% + 50vol% water was prepared that contained nickel sulphamate, boric acid and different concentrations of suspension particles (TiO_2). The experimental setup and working procedure have been described elsewhere [11-13]. Highly polished copper cathode plate (2.0 × 1.0 × 0.01 cm) was placed between two parallel rectangular pure nickel anodes. The suspension of the TiO_2 particles in solution mixture was made after vigorous shaking for several hours and electrolysis was carried out under highly agitated condition using a small panel fan fitted in electrolytic cell assembly; at 35°C, at varying current densities.

The composition of the Ni/TiO_2 films was determined from EDAX (Jeol 840A) and the XRD (DW 1710) studied were also performed. The morphology of the film was examined using SEM (Philips XL-20).

3. RESULTS AND DISCUSSION

The optimum bath composition and conditions of electrolytic deposition of nickel-TiO_2 composites have been given in Table 1. Effect of concentration of titania particles of different particle size and current density on the content of incorporation of the particles in the film has been studied and the results are shown in Figs. 1, 2. Satisfactory shining and adherent grey film was obtained at medium current densities in each case. The quality of the deposits began to deteriorate at higher current densities beyond 2 A/dm^2 and at current density > 3 A/dm^2 the film was of unacceptable quality.

Table 1: Bath composition and electrolysis conditions for electrodeposition of nickel composites and nanocomposites in mixed 50 vol% diethanolamine + 50 vol% water at 35°C.

Parameter	Value
Nickel sulphamate $Ni(SO_3NH_2)_2.2H_2O$, (M)	0.4
Boric acid, (M)	0.2
TiO_2, (g/L)	5 - 20
Current density, (A dm^{-2})	1 - 3
pH	10.7
Duration of electrolysis, (min)	30
Agitation	Yes

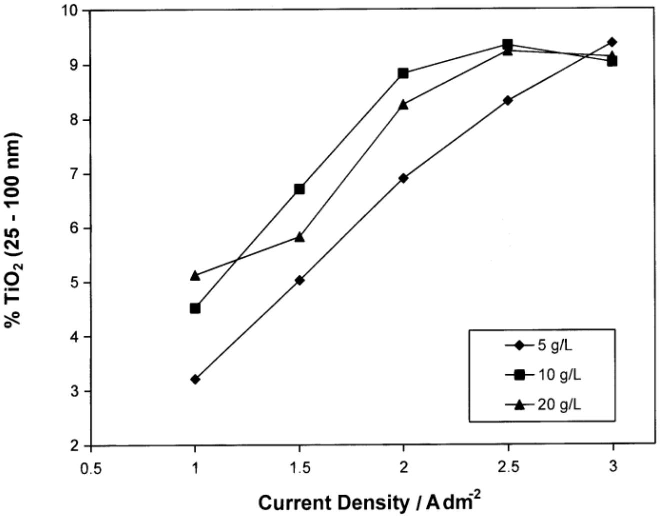


Figure 1: Effect of current density on TiO_2 content in film. Concentration of TiO_2 (25 - 100 nm) in bath ◇ 5 g/L* 10 g/L* 20 g/L TiO_2

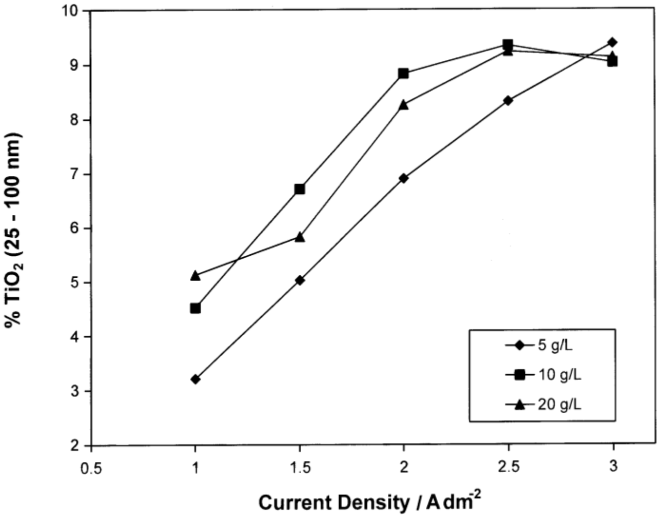


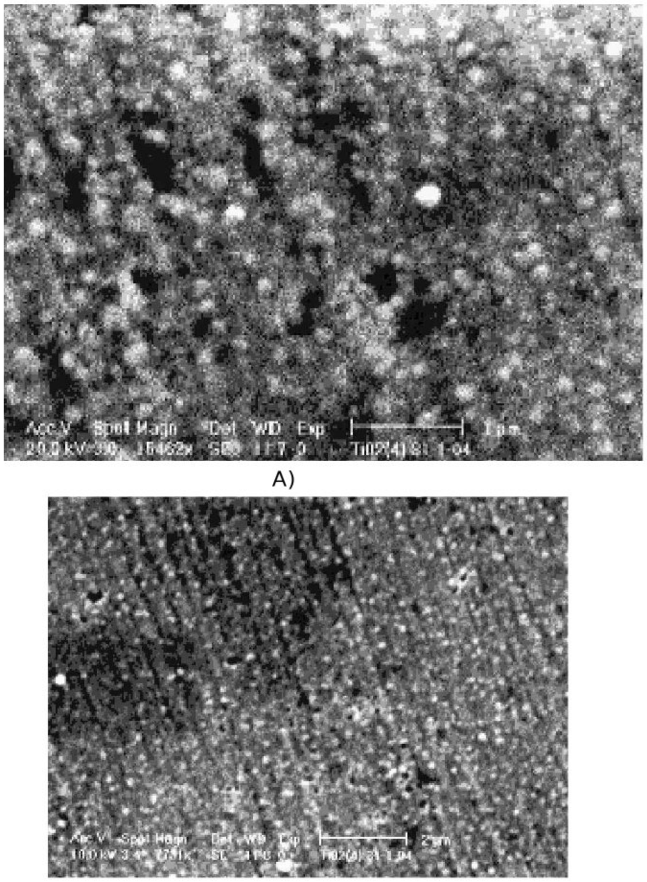
Figure 2: Effect of current density on TiO_2 content in film. Concentration of TiO_2 (100 - 500 nm) in bath ◇ 5 g/L* 10 g/L* 20 g/L

It is observed that the content of the titania particle in the deposit increases with increase in concentration of the particles suspended in the solution (Figs. 1, 2). The increase is relatively more in lower current density range in comparison with that of at higher current densities. However, at 20 g/L of particle concentration appreciable change in content in the film is not recorded.

The variation in particle content in the film is influenced by variation in current density. The ceramic particle content increased with increase in current density but at higher current densities beyond 2A/dm^2 it reaches saturation and increase is not much appreciable rather it showed the tendency to decline at highest applied current density. The saturation of incorporation of particles in the film at higher current densities and at higher concentration may be due to the repulsive interaction between particles that imposes an upper limit on the particle volume fraction in the film. The content of the bigger size (100 - 500 nm) particles in the film under similar experimental conditions, is found to be slightly higher in comparison with smaller ones (25 - 100 nm). Though it has been reported [10] that gravitational force plays much significant role on bigger particles in comparison to the small ones and results in decrease of the particle surface concentration compared to the bulk concentration. Similarly diffusion coefficients of the particles in solution is also found to influence the incorporation of the particles in the film. Bigger particles deposition is under diffusion control while smaller particles (50 nm) were found to not under diffusion control; and its content in film is favoured [10].

The results of the present investigation show that neither gravitational nor diffusion related effects significantly influences the particle incorporation in the film. It seems likely that in organic solution mixture the gravitational force and diffusion coefficient influence the deposition process to the nearly same extent for both types of particles and therefore no appreciable change in the content of the particles was observed under similar set of experimental conditions. This may be due to the present size of the particles for those the above mentioned effects may not be pronounced and applicable being in upper limit of the size.

SEM studies of the deposited composite film (Fig. 3a, b) clearly shows uniform dispersion and incorporation of titania particles (100-500 nm) in the nickel matrix. It forms a regular array of the particles dispersed in the metal matrix in columnar form. The measured size of the particles by SEM ranged between 100 - 220 nm. In case of the particles 25-100 nm dispersion was not very uniform and measured particle size ranged mostly between 60 - 110 nm and some of them are of 290 nm size (Figs. 4a, b). In the case of suspensions of powder of the largest size particles (>1200 nm), much dispersion of the particle is observed and the measured size ranged 130 - 1500 nm (Fig. 5a, b) in deposited film. Tendency of agglomeration of the particles in the deposits is also frequently observed.



A)

B)

Figure 3: SEM micrograph of composite film. CD 2.0 A/dm^2, 10 g/L TiO_2 (100 - 500 nm) in bath.

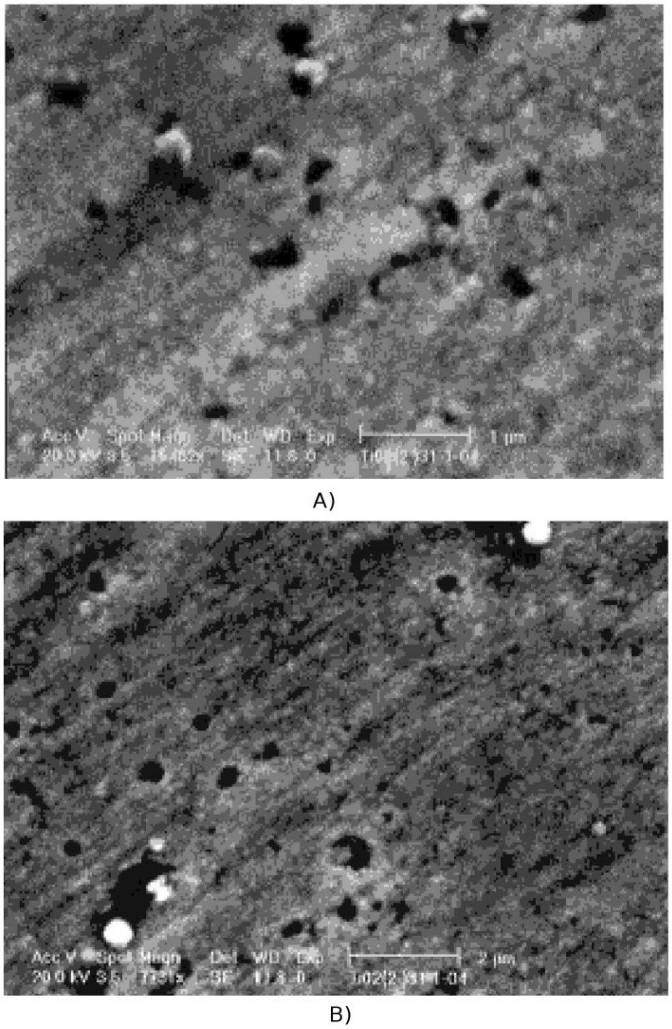


Figure 4: SEM micrograph of composite film. CD 2.0 A/dm^2, 10 g/L TiO_2 (25 - 100 nm) in bath.

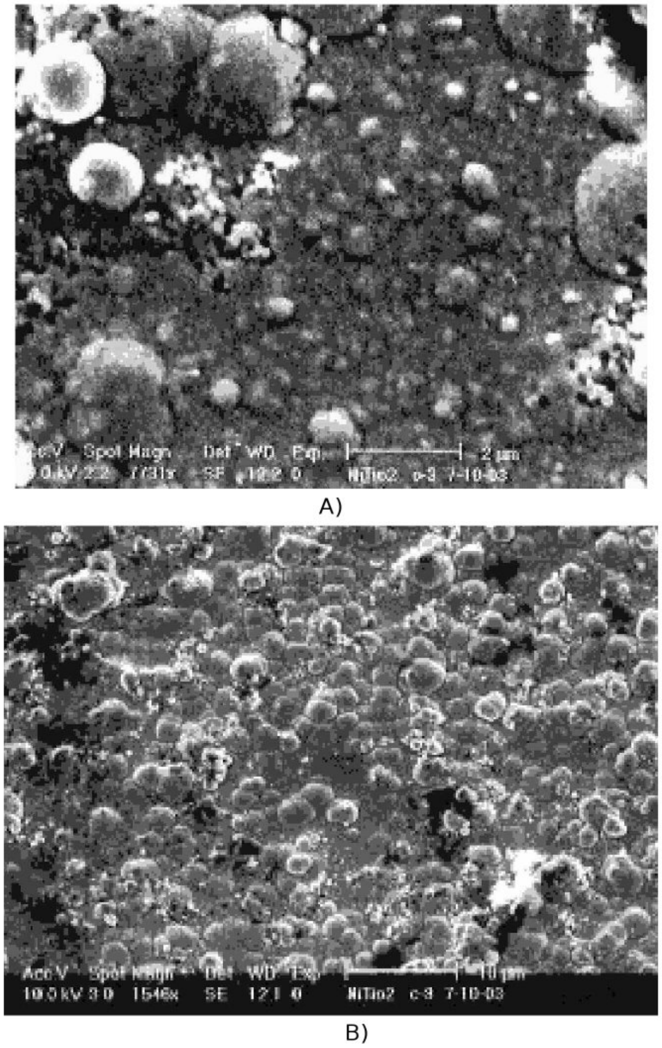


Figure 5: SEM micrograph of composite film. CD 2.0 A/dm^2, 10 g/L TiO_2 (>1200 nm) in bath.

XRD patterns of the deposited film containing different particles size of titania showed clear peaks of Ni(111) and Ni(200). There was no evidence of any peak of the ceramic particles. In few cases very weak intensity of Ti was observed. The intensity of the peak for Ni(111) is double in comparison to Ni(200). Thus preferred orientation is observed in each case along Ni (111) (Fig. 6). However, in case of big particles (> 1200 nm) such texture formation was not observed and both Ni(111) and Ni(200) showed almost equal peak intensity in the deposited film (Fig. 6c).

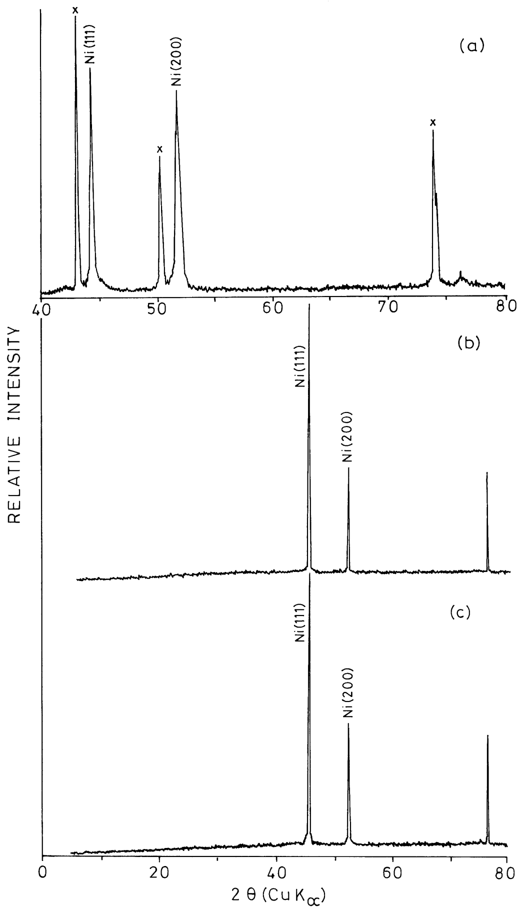


Figure 6: XRD pattern of the composite films of as mentioned in Figs. 3 to 5.

4. ACKNOWLEDGMENT

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