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Electrodeposition and characterization of Ni–TiC composite using N-methylformamide bath

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ABSTRACT

Ni–TiC composite coatings containing a maximum of 14.62 wt.% TiC were obtained under optimum condition by the constant current electrodeposition of Ni and micrometer sized particles of TiC powder onto the surface of commercial grade copper substrates. A bath containing 200 g/l nickel acetate, 35 g/l boric acid and 40 g/l TiC in N-methylformamide at current density 2 A dm^{-2}, duration of electrolysis 30 min and bath temperature 60 °C was found to be optimum condition for electrodeposition. The composition, microstructure, hydrogen content and microhardness were investigated by AAS, EDAX, SEM, XRD and microhardness tester. The single line broadening analysis of peak shows that crystallite size decreases with increase in current density. The hydrogen content in the deposits was found to be minimal. The effect of annealing temperature on microstructure and microhardness was also examined.

1. Introduction

Composites can be fabricated by many techniques such as thermal, plasma spraying and combination of physical and chemical vapor deposition and have attracted extensive attention in science and technology [1]. Among these methods, electrodeposition has been recognized as the most technologically feasible and economically superior technique for the production of composite coatings with low residual porosity. Compared to other methods, the advantages of electrodeposition are uniform deposition on complex shaped substrate, low cost, good reproducibility, easy control, versatility, high production rate and reduction of waste [2].

In general, metal matrix composites and nickel based [3,4] composites in particular are very useful and find wide applications. These composites have been developed as hard facing for steel mill rolls and as coating for injection moulds [5]. It is important to note that the presence of ceramic particles in electrolysis solution used for the purpose of electrodeposition of metal matrix composites offers electrocatalytic properties [6] and significantly influences the hydrogen evolution and its adsorption [7,8]. The extent of hydrogen evolution and its incorporation in metal largely depend on the nature of ceramic particles. The consequences of hydrogen evolution and its adsorption/occlusion in electrodeposits are well known [9]. In the past, certain nano sized particles [10–13] have been incorporated in the Ni matrix to form nanocomposites. An exhaustive survey of literature has been done and it has been found that very little work has been done on the electrodeposition of Ni–TiC [14–16] composite and most of the reports are patented [17] and the operating details are not available. The development of composite plating with nano-sized particles is however hampered by the following two problems. In aqueous plating electrolytes, particles easily agglomerate due to the compression of the diffuse double layer [18] surrounding the particles by the high ionic strength. This effect is more pronounced for particles of submicrometer size (i.e. <1.0 μm) as the shearing forces on the agglomerates, created by the agitation of the plating bath, decrease with particle size. Secondly, the codeposition of particles decreases with particle size [19]. The volume percent of codeposited particles in aqueous electrolytes drops from 5 to 15 vol.% for micrometer sized particles to 0.1 vol.% or less for submicrometer sized particles.

Available literature reveals that mostly, the research on Ni–TiC composite involved either laser fabrication or electrodeposition from aqueous solutions. Considering the consequences of hydrogen evolution in aqueous solution and the potential advantages offered by organic liquids, the present investigation aims to systematically explore the electrodeposition of Ni–TiC composites using organic solvent and thus an attempt to reduce the hydrogen content in the deposit to a maximum possible extent. The electrodeposited coatings thus obtained are expected to possess interesting physical/structural characteristics.

In general organic liquids are favored compared to water, because they eliminate the electrode reaction and gas evolution

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Table 1
Bath composition and electrolysis condition for the electrodeposition of Ni–TiC composite in N-methylformamide.

Parameters	Value
Nickel acetate (g/l)	200
Boric acid (g/l)	35
TiC (g/l)	5–40
Duration of electrolysis (min)	10–120
Current density (A dm^{-2})	1–5
Temperature (°C)	20–80
Agitation (rpm)	200–1200

(H_2, O_2) commonly encountered in the latter case due to electrolysis of water on application of electric field. Generally the higher dielectric constant in organic liquids enhances its dissociating power as a result large quantity of electrolyte can be dissolved. The organic liquids are also preferred due to their high density and good chemical stability. So a proper selection of suitable solvent and optimization of the operating parameters are necessary for obtaining depositions of desired thickness and microstructure by electrodeposition.

Keeping all above in view, in the present investigation N-methylformamide (NMF), an organic solvent with high dielectric constant (182) and high boiling point (200 °C) having high stability and a common cheap metal salt (nickel acetate) have been used. Moreover, there are no reports on the electrodeposition of Ni–TiC using N-methylformamide as organic solvent.

2. Experimental

The Ni–TiC composite was electrolytically deposited from an additive free bath (see Table 1) using N-methylformamide (Sigma–Aldrich) that allows high tolerance of electrolyte. The experimental details have been described earlier [20–23]. The electrolytic bath was composed of 200 g/l of nickel acetate (Thomas Baker & Co.), 35 g/l of boric acid (Qualigens) and varying amount (5, 10, 20, 30, 40 g/l) of TiC (Sigma–Aldrich, particle size <4 μm). Commercial grade copper plates which were used as cathode of dimension (2 cm × 1 cm × 0.01 cm) were first mechanically polished for obtaining smooth surfaces, scratches being removed by polishing consecutively with different grades of emery polishing papers (1/0, 2/0, 3/0 and 4/0). Smooth reflective surfaces free of stains and pits were obtained subsequently by disc polishing using Geosyn Polishing Alumina Grade II (Geologists' Syndicate Pvt. Ltd., India) on fine quality sylbeth cloth. Copper strips thus prepared were washed with distilled water, methanol and then degreased in hot soap (Idipol) solution between 40 and 50 °C and were washed thoroughly under running water followed by repeated washing with distilled water. Solvent degreasing was done by dipping strips in acetone for a few minutes and then washed with distilled water. The strips were pickled in a light pickling solution (10% sulphuric acid) then finally cleaned ultrasonically before use. The highly polished copper strips thus obtained were placed between two parallel rectangular pure nickel anodes. For obtaining homogeneous distribution of TiC particles in the bath, the required amount of TiC along with other electrolytes was first blended in a mortar with a small quantity of the solvent to get slurry. The electrolytic solution was prepared by transferring the slurry to appropriate volume of N-methylformamide and was shaken thoroughly for 4 h. Before deposition, the solution was sonicated for 4 h. The suspension of TiC particles was maintained in the bath by continuous agitation using two small panel fans stirred at the rate of 200–1200 rpm which were fitted in electrolytic cell assembly during electrolysis. Agitation at a stirring rate of 750 rpm was found sufficient to maintain the suspension of TiC in the bath. A glass cell (400 mL capacity) having 250 mL of plating solution was used as the electrolysis cell for Ni–TiC electrodeposition. The electrolysis was carried out at 20–80 °C in constant temperature thermostat (HAAKE DC 30). The electrolysis was carried out at constant current density in the range (0.5–7.0 A dm^{-2}) for varying duration (10–120 min) depending on the current density applied. The extent of TiC incorporation in the Ni matrix was studied at varying current density and particle concentration. An optimum condition for electrodeposition was achieved by varying one parameter at a time and keeping others to a fixed value. After the deposition, the cathode was ultrasonically cleaned for 10 min. A Thermoelectron (ARL$_{\mathrm{XTRA}}$) X-ray diffractometer was used for XRD to examine the orientation of electrodeposited Ni–TiC composite. The use of the Voigt function for the analysis of the integral breadths of broadened X-ray diffraction line profiles forms the basis of a rapid and powerful single line method of crystallite-size determination. In this case the constituent Cauchy components can be obtained from the ratio of full width at half maximum intensity (2ω) and integral breadth (β). In a single line analysis, the apparent crystallite size '*D*' can be related to Cauchy (β_c) widths of the diffraction peak at the Bragg angle θ;

$$D = \frac{\lambda}{\beta_c \cos\theta} \qquad (1)$$

The constituent Cauchy and Gaussian components can be given as

$$\beta_c = (a_0 + a_1\psi + a_2\psi^2)\beta \qquad (2)$$

where a_0, a_1 and a_2 are Cauchy constants and $\psi = 2\omega/\beta$ where β is the integral breadth obtained from XRD peak.

$$a_0 = 2.0207, \quad a_1 = -0.4803, \quad a_2 = -1.7756$$

The values of Cauchy constant have been taken from the table of Langford [24,25]. From these, the crystallite size '*D*' for the composite was calculated. Scanning electron microscope (FEI) equipped with EDX (FEI) analyzer was used to study the morphology and chemical composition of deposits. All the chemical composition values of the deposits are quoted in the weight percent which is the average of at least five measurements. Nickel content of composite was also determined from atomic absorption spectrometry. For this measurement, the known weight of composite was digested in 100 mL hot solution of nitric acid (20%, v/v) to get the clear transparent solution of nickel. TiC content of composite could thus be deduced from the difference between the mass of each composite and Ni therein. The hydrogen incorporation analysis in the composite was measured using H_2, N_2 and O_2 analyzer (Model: LECO TC 436). As deposited composite was annealed in vacuum for 2 h at various temperatures (200–800 °C) and then allowed to cool slowly down to the room temperature. Because of the small thickness of the coatings that was in the range of a few tens of micrometers, the hardness was characterized by a microhardness indentation method. A "Shimadzu HMV-2" microhardness apparatus equipped with a Vickers diamond indenter of square pyramidal shape having a 136° apex angle was used. A load of 10 gf has been applied on the indenter. All indentations were made by applying the load perpendicular to the smooth free surface of the coating. Five indentations have been made on the same sample to obtain a statistical average value for the microhardness. The microhardness was calculated by means of relationship $HV = 1854.4F/d^2$, where HV is expressed in kgf/mm^2, F in grams and the diagonal d of the indentation in micrometers [26].

3. Results and discussion

3.1. Effect of concentration of particle in suspension and current density on electrodeposition of Ni–TiC composite

Fig. 1a shows the influence of TiC concentration in bath on the chemical composition of Ni–TiC composite. The effect of TiC