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Electrocodeposition and characterization of Ni-WC composite coating from non – aqueous bath

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Abstract: Composite coating of tungsten carbide (WC) in the matrix of nickel has been achieved by direct current (DC) electrodeposition technique using a non aqueous bath. The deposition parameters such as current density, bath temperature, and stirring rate were maintained at constant levels for all the coating configurations. The composition of the coating and its microstructure were studied using energy dispersive x-ray spectroscopy, uv-vis spectrophotometry and x-ray diffraction, respectively. Surface morphology of the coatings was studied by scanning electron microscopy (SEM and TEM). Effect of heat treatment on the deposits microstructures and microhardness was also investigated. The Ni–WC composites, prepared at optimum conditions, exhibited improved mechanical properties in comparison to pure nickel electrodeposits.

Keywords: Electrodeposition, Ni-WC composite, Microhardness, Microstructure

1. Introduction

The production of composite coatings by electrocodeposition of inert ceramic particles with metal from plating baths has attracted the attention from numerous researches [1] and is also being recognized as an effective technique for the fabrication of metal matrix composites. The interest shown in these composite deposits was due to simultaneous deposition of the non-metal inclusions and metal phases to form composite layers which bring a significant improvement on several physical and mechanical properties of the coating leading to their various engineering applications. Among the processes deployed in order to produce metal matrix composites, electrodeposition technique has proved itself to be a convenient method by producing smoother and harder surfaces, better bonding between particles and metal, easy control of the coating thickness, the ability to deposit metallic and composite coatings and suitability for automation. In the recent past [2,3] electrodeposition of composites attracted renewed attention, due its adoption by major companies for the processing of advanced microelectronic components.

Nickel, being an engineering material and most commonly used matrix [4] plays a major role in our everyday lives – food preparation equipment, mobile phones, medical equipment, transport, buildings, power generation etc.

Apart from these, nickel has long been utilized as coating [5-7] on various metallic and non metallic surfaces and ornaments seem to be the most favoured matrix material for electrocomposites because it combines strength and hardness with good corrosion resistance [8,9]. However, the scopes of such coatings are limited by the life span, mechanical strength, and wear and corrosion resistance to the aggressive environment. Similarly, Tungsten carbide (WC) attracts much attention owing to its unique physical and chemical properties such as extreme hardness, high melting point, chemical inertness, interesting catalytic behaviour etc, and belongs to the most promising engineering materials with a wide range of industrial applications [10-12]. Nickel based WC composites, in particular, finds their main uses as hard faces for anti wear [13-15], anticorrosive [13] and as electrocatalytic cathode for hydrogen evolution reaction [16].

Electrodeposition of nickel matrix based composites containing reinforced ceramic particulates whose use is reported in literature [17–26] includes Al_2O_3, SiC, Cr_2O_3, TiO_2, MoS_2, WC etc. However, very scanty work has been reported on the electrocodeposition of WC [27,28] with nickel from aqueous bath. Literature survey reveals very little research on the electrodedeposition of metal matrix composites using non aqueous solvent except the work of Saji and Kulshrestha [29] and Fransaer et. al. [30]. There

has been no published information in the literature concerning the electrodeposition of Ni-WC from non aqueous solvent. Advantages of use of organic solvent have already been highlighted in our earlier publications [31,32].

In the present study, it is aimed to investigate the co-electrodeposition of Ni and WC, the latter of which is selected as a reinforcing material due to its high hardness and superior wear resistance. The paper focuses on the production of nickel-tungsten carbide (Ni–WC) composites from a very cheap and economical metal salt i.e. nickel acetate using N-methylformamide as a non aqueous solvent and their characterization. The influence of current density, bath composition, particle concentration in the bath, bath temperature and rate of stirring on the incorporated particle weight fraction and on the characteristics of the coatings was analyzed. The properties of the composite coatings were compared with those of pure nickel deposits.

2. Experimental

The Ni-WC composite electrodeposition experiment was conducted in a non aqueous bath. N-methylforamide (Sigma-Aldrich) was used as solvent with boiling point (198-200 ^{0}C), density (1.003) and dielectric constant of (182), that allows high tolerance of electrolyte. The electrolytic bath was composed of 200 g/L of nickel acetate (Thomas Baker & Co.), 35 g/L of boric acid (Qualigens), varying amount (10, 20, 30 g/L) of WC (Sigma-Aldrich, particle size <10 μm) in N-methylformamide. Commercial grade copper plates (Cu 99.28 %, Ni 0.72 %) of dimension (2x1x0.01 cm) were prepared for deposition as reported [31] earlier. 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 used as cathodes and placed between two parallel rectangular pure nickel anodes. For obtaining homogeneous distribution of WC particles in the bath, the required amount of WC 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 four hours. Before deposition, the solution was sonicated for 30 minutes. The suspension of WC particles was maintained in the bath by continuous agitation using two small panel fans stirred at varying 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 WC in the bath. A glass cell (400 mL capacity) having 250 mL of plating solution was used as the electrolysis cell for Ni-WC electrodeposition. The experimental set–up has been described elsewhere [31-33]. The electrolysis was carried out at 20–80 ^{o}C in constant temperature thermostat (HAAKE DC 30) and at constant current density in the range (0.5-7.0 Adm^{-2}) for varying duration (10-120 minutes) depending on the current density applied. The extent of WC 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 minutes. A Thermoelectron (ARL$_{XTRA}$) X-Ray diffractometer was used for XRD to examine the orientation of electrodeposited Ni-WC 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 and strain determination. In this case the constituent Cauchy and Gaussian 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 ` and strain 'e ` can be related to Cauchy ($β_c$) and Gaussian ($β_G$) widths of the diffraction peak at the Bragg angle θ;

$$D = \lambda / \beta_c \cos \theta \qquad (1)$$

and

$$e = \beta_G / 4 \tan \theta \qquad (2)$$

The values of Cauchy and Gaussian constant have been taken from the table of Langford [34, 35]. From these, the crystallite size 'D' and the lattice strain 'e' for the composite were calculated. Scanning electron microscope (SUPRA^{TM} 40UP ZEISS) equipped with EDX (OXFORD 7426) analyzer was used to study the morphology and chemical composition of deposit. 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 uv-vis spectrophotometer. 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. WC content of composite could thus be deduced from the difference between the mass of each composite and Ni there in. 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 two hours at various temperatures (200-800 ^{o}C) and then allowed to cool slowly down to the room temperature. A "Shimadzu HMV-2" microhardness apparatus equipped with a Vickers diamond indenter of square pyramidal shape having a 136° apex angle was used to measure microhardness of the composites. A load of 10 gf has been applied for 15 sec.on the indenter. All indentations were made by applying the load perpendicular to the 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 =1854.4 F/d^2, where HV is expressed in kgf/mm^2, F in grams and the diagonal d of the indentation in micrometers [36].

3. Results and Discussion

3.1. Codeposition of WC Particles with Nickel

Electrodeposition of nickel –tungsten carbide (Ni-WC) composite coating was conducted with cathode current density of 1 – 5 Adm^{-2} and a plating time of 10 - 120 min. was given depending on the strength of current density. Electrodeposition was performed for shorter duration (~30 min) at higher current density (> 3 Adm^{-2}) and vice-versa. Electrodeposition for long duration (at all current density) leads to "dendrite like" branched outgrowth. Similar "dendrite like" growth has been reported earlier by Pavlatou et.al [37]. Fig. 1 shows the variation of particle contents in the coatings with respect to the current density. An increasing trend of incorporation of WC content in the composites was noticed with increasing current density however, this increase was more pronounced between 4-5 A dm^{-2}. Two of the main factors governing the particle content in the deposits are the current density and particle concentration in the suspension. The main parameter that influences the amount of deposited nickel is the current density. The amount of deposited particles is governed by the particle flux to the cathode surface. The present increasing trend of WC incorporation in the deposits with current density is reasonable because the enhancement of the flux of metal ions may increase the probability to be entrapped in the growing metal film. It appears that the deposition of matrix metal with increasing current density is fast enough to entrap and occlude some of the particles and incorporate them into deposits.
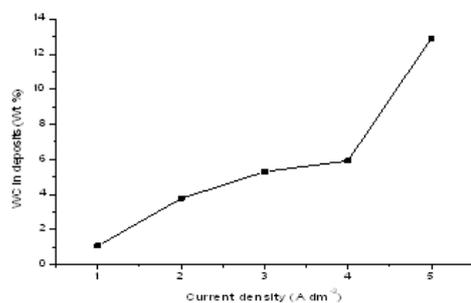
Figure 1. *Effect of current density on weight % incorporation of WC in the deposits at bath load of 30 g/L. (Condition of deposition 200 g/L nickel acetate, 35 g/L boric acid at stirring rate of 750 rpm and at 60 ^{0}C).*

3.2. Surface Morphological Studies

The morphology of the Ni-WC coatings produced at bath load of 30 g/l at various current densities (1-5 Adm^{-2}) is presented in fig. (2). The SEM image of coatings clearly shows the presence of particulates of WC with minimal agglomeration in the coating surrounded by nickel matrix. It should be noticed that the EDS spot analysis on the gray particles revealed a spectrum with high content of tungsten (Table 1). Figure 3 shows the TEM images of composites taken at different spots, shows particles of various diameters, ranging from tens to hundreds of nanometers (marked in Fig. 3c), are incorporated into the deposits.

Table 1.

Element	Weight %	Atomic %	Element	Weight %	Atomic %
Carbon	0.000	0.000	Carbon	0.000	0.000
Nickel	71.718	88.815	Nickel	96.462	98.842
Tungsten	28.282	11.185	Tungsten	3.538	1.158

Weight % composition obtained from EDAX of Ni-WC deposited at 5 Adm^{-2} (Condition of deposition 200 g/L nickel acetate, 35 g/L boric acid, 30 g/L WC particle at stirring rate of 750 rpm and at 60 ^{0}C).
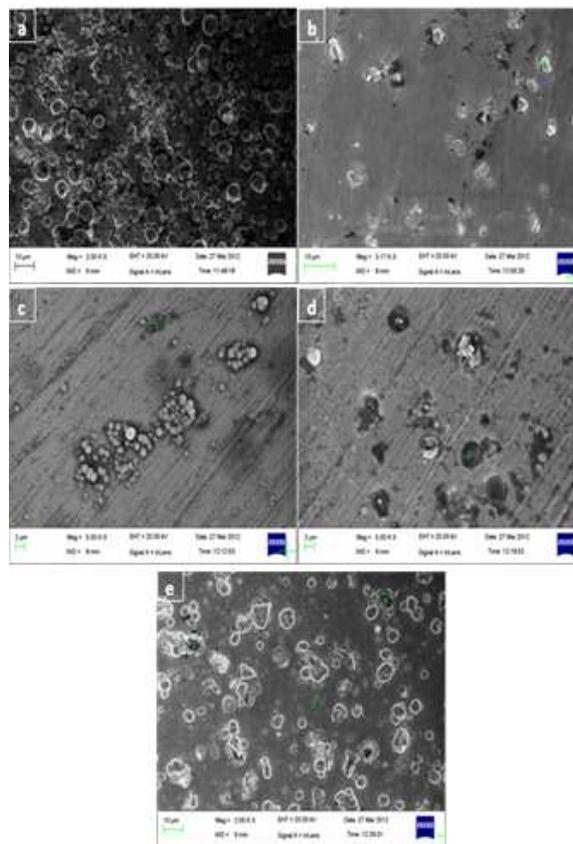
Figure 2. *SEM micrograph of Ni-WC composite at different current density (a) 1 Adm^{-2}, (b) 2 Adm^{-2}, (c) 3 Adm^{-2}, (d) 4 Adm^{-2} and (e) 5 Adm^{-2}. (Condition of deposition 200 g/L nickel acetate, 35 g/L boric acid, 30 g/L WC particle at stirring rate of 750 rpm and at 60 ^{0}C).*

nickel deposited from the bath having same composition in absence of particles while fig. (4b) is of Ni-WC composite deposited under similar conditions. Along with nickel peaks, WC peaks (001, 100 and 101) are also present confirming the incorporation of WC in the composites. Fig. (4c) show the XRD patterns of annealed Ni-WC composite deposited at 3 Adm^{-2}. The absence of any additional peaks other than Ni and WC in annealed sample reveals the stability of deposits at high temperature (900°C). The nickel crystallite size as calculated from XRD line broadening for Ni-WC
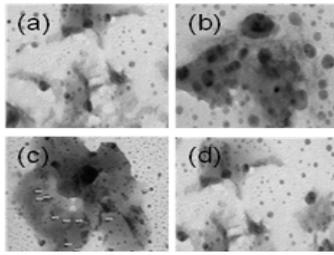
Figure 3. *TEM image of Ni-WC taken from different spots (a,b,c and d)deposited at 3 Adm^{-2}. (Condition of deposition 200 g/L nickel acetate, 35 g/L boric acid, 30 g/L WC particle at stirring rate of 750 rpm and at 60 ^{0}C).*

electrodeposited at 3 Adm^{-2} was 49.9 Å while that of as deposited pure Ni was 1340 Å. The lattice parameter calculation using d$_{(111)}$ plane for as deposited pure nickel, Ni-WC and vacuum annealed Ni-WC gives 3.5189, 3.5204 and 3.5399 Å respectively, which is very close to the reported value for electrodeposited nickel. The intensity of the diffraction peaks of the nickel in Ni-WC composite is observed to be lower and the peak width is broader than the nickel coating (Fig. 4a). This is attributed to the decrease in the crystallite size of the Ni-WC composite coating by the addition of WC particulates into the plating bath. Similar effect of particulates addition on crystallite size has been reported earlier also [31, 38]. However, in the case of non metallic carbide (i.e. WC) the codeposition of the particles modifies the adsorption–desorption phenomena occurring on the metallic surface that results in change of the catholyte composition [37]. This alteration exerts a much more intense inhibition to the Ni crystal growth, which leads to the grain refinement. Crystallite size in annealed deposit was found to be 274 Å and this increase in the crystallite size in comparison to as deposited composite may be due to recrystallization and grain growth caused by annealing. XRD also showed random orientation of nickel growth in both the cases i.e. with and without particles in the bath. An almost negligible value of strain (0.0150) in composite is expected since the probability of inclusion of impurities (hydrogen and metal hydroxide) in the deposits is greatly reduced due to use of N-methylformamide.
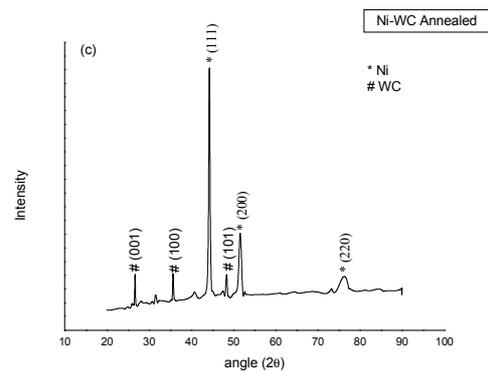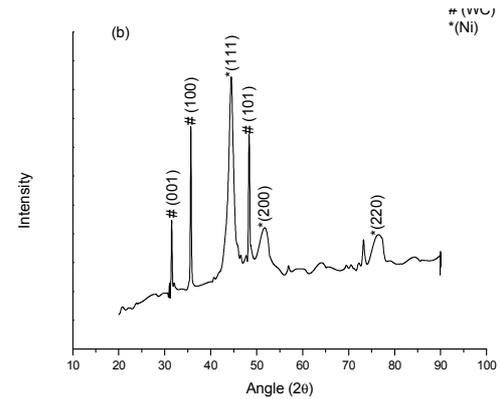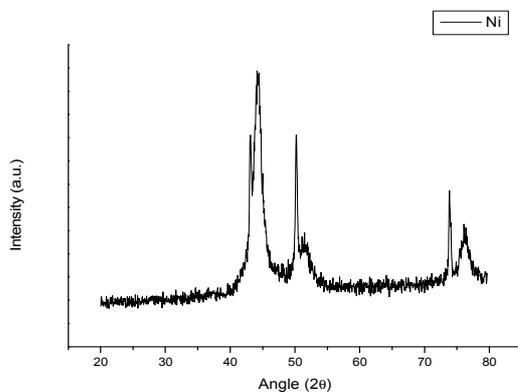

Figure 4. XRD pattern of coatings obtained at 3 Adm^{-2} Ni (a), Ni-WC composite (b) and vacuum annealed Ni-WC (c). (Condition of deposition 200 g/L nickel acetate, 35 g/L boric acid, 30 g/L WC particle at stirring rate of 750 rpm and at 60 ^{0}C).

3.4. Microhardness Measurement

Fig. 5 shows the variation of microhardness with respect to the current density. All the deposited composites show a moderate improvement in the microhardness value compared to the pure as deposited nickel. Ni-WC composites show a gradual increase in hardness value upto 3 Adm^{-2} followed by comparatively rapid increase between 3-4 Adm^{-2} and then again a gradual increase between 4-5 A dm^{-2}. On correlating the hardness value of composites from amount of WC incorporated in the deposits at various current densities, it is observed that hardness value increases with the WC in the deposits. A proportionately large increment beyond 3 Adm^{-2} could be the result of increased hydrogen adsorption due to presence of WC [39] in deposits and measured hydrogen in composite (17.74 ppm) strongly supports the trend. Microhardness values were also measured at 10 and 20 gL^{-1} of WC in the bath at constant current density of 3 A dm^{-2}. The hardness value increases with increase in WC in the bath and it is probable that increased concentration of WC in bath lead to more incorporation of WC in the deposits resulting into higher microhaerdness. Effect of annealing on microhardness value at various temperatures (200-800 ˚C) has also been investigated. Annealing upto 400 ˚C has no any effect on composites microhardness value and it remains more or less the same as that of as deposited sample. However, beyond 400 ˚C Ni-WC

shows a decrease in hardness from 420 to 93 HV at 800 ˚C.
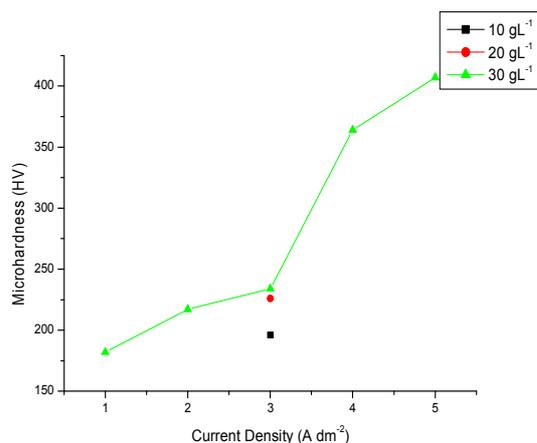
Figure 5. *Effect of current density on microhardness value of Ni-WC composite. (Condition of deposition 200 g/L nickel acetate, 35 g/L boric acid at stirring rate of 750 rpm and at 60 ^{0}C).*

4. Conclusion

Ni-WC nanocrystalline composite coating with improved microhardness has been successfully electrolytically code-posited under direct current condition from a bath using N-methylformamide. The use of N–methylformamide shows minimal agglomeration of WC in the bath as well as in the composite deposits. Evolution of hydrogen and its incorporation in the deposits are significantly reduced. A maximum of 13 weight % WC was found to be uniformly distributed and incorporated in the deposits under the investigated current density range (1-5 A dm^{-2}).

Acknowledgement

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