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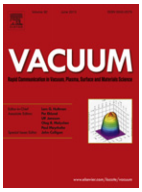

Enhancing Ni electroplated matrix through mixed boron nitride–carbide reinforcement

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ABSTRACT

Mixed Nitride–Carbide particles of boron as a reinforcement in Ni matrix has been used in an attempt to form three component composites of superior hardness. The colloidal form of the dispersed particles has pronounced effect on distribution of the particles and this can be traced back to their zeta potential which governs the agglomeration propensity of the particulates with direct bearing on hardness and resultant morphology. Specific steps must be taken for Ni–BN–B_4C formation and simultaneous deposition of two dissimilar compounds and thus getting the desired volume fraction of each in the coating. Copper as a well understood system when it comes to nickel plating was utilized as the substrate and Watts plating bath admixed with 1–10 g BN and 10–50 g B_4C powder at 30–60 mA/cm^2 was employed. To compare results without the possibility of elastic rebound effects from the substrate all experiments were performed on 50 micron thick composite layers. Microhardness and scanning electron microscope (SEM), X-ray diffraction (XRD), optical microscopy (OM) techniques were used to ascertain the role and advantages gained from co-deposition of mixed reinforcing powders and the overall conclusion was that superiority of such composites in strengthening hardness relies heavily on the regular and controlled distribution of the particulates.

1. Introduction

Metal-matrix composites (MMC) are materials in which the properties of a metallic host material are modified by the addition of a second phase (ceramic, polymer, etc.). Electrocodeposition of composite coatings, based on the second phase hard particles dispersed in a metallic matrix, is gaining importance for potential engineering applications [1–3]. Research on electrodeposition of nano-composite coatings has been directed toward determining the optimal production conditions i.e. stirring modality, current density, temperature, particle concentration and bath composition [4,5]. In the literature ceramic particles used for reinforcement is reported such as Al_2O_3, SiC, Cr_2O_3, TiO_2, BN, B_4C, WC, diamond, etc. however, the boride compounds seem to be more promising [6–8].

Ultrafine particles may agglomerate in the electrolyte bath due to high surface free energy, as well as high ionic strength of electrolyte together with inert particles in electroplating bath tend to encourage agglomeration. Such tied particles in coatings would cause poor mechanical properties in composite coatings. Thus, increasing the co-deposited content and improving the distribution of ultrafine particles in composite coatings is crucial to alleviate the adhesion, cohesion as well as mechanical properties of the surface layer. To this end, use of various physical and chemical methods has been reported by many researchers [9]. “Kuo et al.” [10] demonstrated enhanced homogeneity of the composite coating by decreasing electrolyte’s ionic concentration and the use of specific ultrasonic energy treatment. Among these methods, metal cationic accelerants and organic surfactants in an electrolytic bath markedly improved the amount and the distribution of co-deposited particles [11].

The development of an inert charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration ratio of opposite charged ions close to surface leading to the formation of an electrical double layer around each particle. The potential that exists at this boundary is known as the Zeta potential. The most important factor that affects Zeta potential is pH [12].

In this work, the electrocodeposition of nickel–BN–B_4C composites from a Watts bath is studied. The zeta-potential, microhardness and morphology of the coatings and the effects of codeposited particles on metal matrix structure are also investigated.

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Table 1
Bath compositions and electrodeposition conditions for BN and B_4C reinforced MMC composite layers.

Deposition parameters	Amount
Nickel sulfate ($NiSO_4.6H_2O$) (g/l)	300
Nickel chloride ($NiCl_2$) (g/l)	45
Boric acid (H_3BO_3) (g/l)	45
Surfactant ($NaC_{12}H_{25}SO_4$) (g/l)	0.5
Saccharine ($C_7H_5NO_3S$) (g/l)	2
BN (g/l)	50
B_4C (g/l)	10
pH	3–4
Temperature (°C)	30–60
Current density (mA/cm^2)	20–50
Speed of magnetic stirrer rotation (rpm)	500–700

2. Experimental procedure

The plating electrolyte for the electrodeposition of the particle reinforced composites MMCs is a Watt's-type bath whose composition and plating conditions are shown in Table 1. Polished nickel plated copper sheets (20 × 14 × 1 mm) were used as cathode and anode respectively. The substrates were degreased, activated in H_2PO_3 85 $^{v}/_{o}$, and then rinsed with distilled water before placing in the deposition bath. The concentration of BN and B_4C particles in the bath was 50 and 10 g/l respectively. The solution was preheated at process temperature and then boron nitride and boron carbide particles were added to the bath. The average size of hexagonal boron nitride and boron carbide particles, shown in Fig. 1, were 0.5 and 1 μm, respectively. Prior to the co-deposition, the BN and B_4C particles were ultrasonically dispersed in the bath for 30 min following that, the zeta potential of alumina particles was measured by the Zeta-sizer Series ZEN model instrument. The temperature of the electrolyte was maintained by an automatic controller; the pH of the bath is 3.5, adjusted by alkaline solution or dilute sulfuric acid. The bath was stirred by a magnetic stirrer in the electroplating process in order to maintain uniform particle concentration and prevent sedimentation in the solution. The plating time was 50 min in all the cases, and the thickness of the produced composite coatings was about 50 μm. The structure of the Ni–P–B_4C coating was analyzed by X-ray diffraction (XRD) and the spectra were measured by using Cu–K_α radiation. All the samples were cut, mounted in epoxy resin and polished using 1 μm Al_2O_3 abrasive slurry. The cross-section morphology and surface morphology of the deposits was examined with optical microscope (OM) and scanning electron microscope (SEM). Vickers micro-hardness measurements were carried out with a micro-hardness tester equipped with Vickers indenter under a load of 500 mN for 10 s. Each micro-hardness value was an average of five measurements.

3. Results and discussion

3.1. Effect of pH on deposition

In an attempt to clarify the effects of pH on the deposition of BN and B_4C particles, the effect of pH on zeta potential of BN and B_4C particles were studied and the result is shown in Fig. 2. The zeta potential of the BN and B_4C particle mix in the electrolyte solution initially increases in step with pH up to a maximum pH of 3.5 where it reaches close to 0 mV (zero point of charge). While the positive zeta potential offers an extra adhesion force between inert particles and cathode, enhancing the inclusion of embedded BN and B_4C particles in Ni matrix and preventing agglomeration during the electrodeposition process, however, the BN and B_4C particles continue to exhibit negative zeta potentials at pH's lower or higher than 3.5. Accordingly, pH = 3.5 resulted in increasing co-deposition of BN and B_4C particles in nickel metal matrix as well as preventing agglomeration of particles due to forced migration during the electrodeposition.

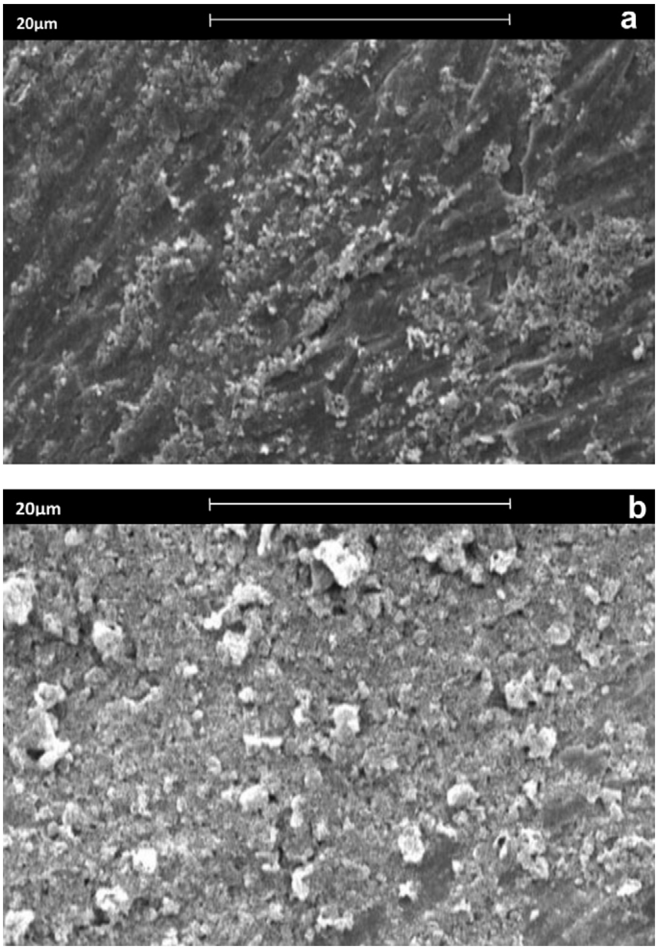

Fig. 1. (a) and (b): SEM image of agglomerated hexagonal boron nitride and boron carbide particles.

3.2. Coating morphology and structure

The surface morphology of the composite coatings obtained from pure Ni, Ni–BN, Ni–B_4C and Ni–BN–B_4C coatings by applying a current density of 40 mA/cm^2 for 50 min are shown in Fig. 3. Addition of BN micro particles to the pure Ni coating with regular

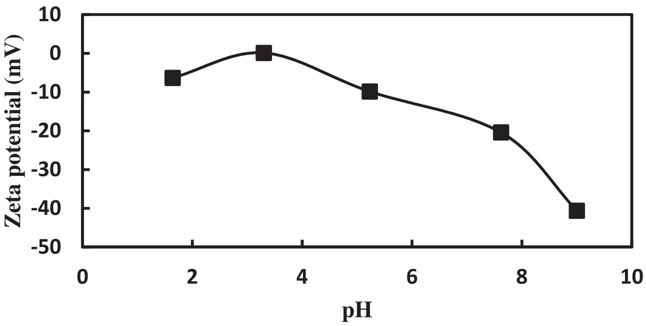

Fig. 2. pH – zeta potential relationship for Watts plating solution.