Synthesis and characterization of nickel/barium hexa-aluminate composite coatings

DINESH KUMAR*, SAMPADA GURAV, VIKRAM JAYARAM and SANJAY KUMAR BISWAS†

Department of Materials Engineering, †Department of Mechanical Engineering, Indian Institute of Science, Bangalore 560 012, India

MS received 4 October 2011; revised 18 February 2012

Abstract. Electrodeposition of nickel/barium hexa-aluminate (Ni/BHA) composite coatings has been carried out from a Watt's bath on mild steel substrate. BHA powders with plate habit were synthesized by solution combustion synthesis followed by heat treatment to ensure complete conversion to the hexa-aluminate phase. Heat treated material was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) combined with X-ray analysis. The dispersion behaviour and stability of BHA suspensions with cationic and anionic surfactants at room temperature were studied by dynamic light scattering under different pH. The influence of BHA concentration in the electrolytic bath, deposition temperature, pH, current density and duty cycle on particle incorporation in the coatings were studied and conditions for maximum particle incorporation were established. Coatings with a roughness of about 0.4 μm were produced by using this technique. Effect of BHA content on microhardness was also investigated. A reasonably good thickness of the coatings was achieved in a given set of conditions.

Keywords. Volume fraction; composite coatings; microstructure; scanning electron microscope; X-ray diffraction.

1. Introduction

Electrodeposition is gaining much attention during the past few decades for preparing metal matrix composites (MMCs). Many deposition methods have been utilized, including thermal spray, physical vapour deposition, chemical vapour deposition, and electro co-deposition. Out of these and other available techniques, electro co-deposition is the most sought after method for producing MMCs with several merits, such as low cost, low operating temperature, ease of fabrication and high quality deposits, free from porosity and uncontrolled oxide inclusion. The most important advantage of this process is good adhesion which would play a key role for subsequent studies. This process involves the suspension of inert particles in a conventional plating electrolyte and which are captured in the growing metal layer to form a composite coating. Nickel matrix composites (NMCs) are materials in which the properties of a metallic host material are modified by dispersing different types of refractory oxides, nitrides and carbides including several materials that are used as solid lubricants (SLs) (Allam 1991; Ramesh *et al* 1991a, b; Surender *et al* 2004). Out of these materials, SLs are important for the reduction of friction and wear between contacting surfaces in extreme environments such as those encountered in aerospace, tooling, materials-forming, automotive and nuclear-power industries (Corte and Sliney

1990; Donnet and Erdemir 2004; Voevodin and Zabinski 2005; Baker *et al* 2007; Gupta *et al* 2007; Miyoshi 2007). In such applications, conventional lubricants, such as oils or greases, exhibit volatility or undergo chemical degradation. The low shear strength characteristic of nearly all the SLs occurs only in a very limited range of ambient conditions. For example, graphite and molybdenum disulfide (MoS_2) are the most widely used SLs at room temperature. Graphite cannot provide lubrication in vacuum or dry environments as it needs condensable vapours (e.g. water) to terminate dangling bonds that are otherwise adhesive in nature. MoS_2 oxidizes rather quickly in moist air and acts as an abrasive at room temperature. Both of these mechanically soft materials do not impart lubrication property at high temperatures and are not optimized to resist wear in any environment. These limitations lead to the need for new solid lubricants that possess low wear rates and low coefficients of friction over a wide range of working environment (Corte and Sliney 1990; Gupta *et al* 2007). Of these, MMCs coatings in which ceramic layered oxides can be co-deposited with any metal are potential candidates for providing lubrication at ambient as well as high temperatures in oxidizing environments. Since these MMC coatings possess excellent tribological and wear resistance properties (Ramesh *et al* 1991a, b, c, d; Pompei *et al* 2009), high temperature applicability of these layered oxides could be investigated by incorporating them into the metal matrix composite. Among various metals, nickel which possesses high tensile strength, good toughness and corrosion resistances, is a popular choice as the matrix to disperse both hard and soft reinforcements to improve its wear and

* Author for correspondence (dkumar_2008@yahoo.co.in, dkumar@platinum.materials.iisc.ernet.in)

anti-friction resistance (Lele *et al* 1989; Ramesh *et al* 1991a, b, c; Hou *et al* 2002; Wang and Cheng 2003; Wang *et al* 2005; Pompei *et al* 2009). Burzynska *et al* (2008) reported electrodeposition and heat treatment of nickel/silicon carbide composites and their results suggested two phase transformations in the temperature range 20–700 °C. For annealed samples, Ni₂Si and Ni₃Si₂ phases were identified. Aoudi *et al* (2009) studied the tribological behaviour of Mo₂N/MoS₂/Ag coatings at room temperature, 350 °C and 600 °C against Si₃N₄ balls and found the lowest value of coefficient of friction (cof) at 600 °C. This cof value was attributed to the formation of lubricious silver molybdate phases including Ag₂Mo₄O₁₃, Ag₂Mo₂O₇ and Ag₂MoO₄ at the contact surfaces. They claim that the superior performance of all the three compounds is due to their layered structure in which weak bonds may shear or even break easily at high temperature and cause reduction in coefficient of friction. Several other groups (Rethinam *et al* 2004; Kirchhoff *et al* 2005; Sun and Li 2007; Xia *et al* 2007, 2008) are also involved in these types of investigations.

Oxide phases have a natural stability at high temperatures when compared to other reinforcements. Layered oxides in which low shear resistance may be expected include natural clay minerals and structures such as the hexa-aluminates and perovskites. It has been reported that magnetoplumbites containing alkaline-earth or rare-earth cations do not exhibit vaporization problem i.e. metal cation loss during heat treatment. The present work aims to develop a processing protocol for the synthesis of phase pure, plate-like barium hexa-aluminate (BaAl₁₂O₁₉) with appropriate layered orientation of the platelets and to incorporate it in a Ni matrix through electrodeposition. Objectives was the achievement of a significant volume fraction of oxide particles in films of the desired thicknesses.

2. Materials and methods

All chemicals were received from different commercial suppliers and used without any further purification. The purity of each chemical has been mentioned as: Ba(NO₃)₂ (99.9 %), Al(NO₃)₃·9H₂O (95 %), urea (99 %), Ni(SO₄)₂·6H₂O (98 %), NiCl₂·4H₂O (97 %), boric acid (99.5 %), SDS (94 %) and CTAB (96 %).

BHA was synthesized by combustion synthesis in which reactions were carried out using 1:12 molar ratios of barium to aluminum nitrates. The reactants, barium, aluminum nitrates and urea, were dissolved in a minimum quantity of deionized water in a round bottom glass container using a magnetic stirrer. This solution was placed into a preheated muffle furnace at 500 (±5) °C. At this temperature the solution becomes viscous as water goes out leading to spontaneous combustion of the viscous solution. Evolution of various gases such as oxides of nitrogen and ammonia takes place which lead to the formation of foamy material. XRD analysis of the as-prepared foamy material indicated the presence of BHA, barium mono-aluminate (BMA) and alumina.

In order to get single phase BHA this material was further subjected to heat treatment at 1550 °C. Morphological and micro chemical analysis (EDS) was performed on a high resolution scanning electron microscope (Sirion, FEI Instruments) equipped with a Schottky field emission source.

The dispersion behaviour and stability of BHA suspensions with water, sodium dodecyl sulfate (SDS) as anionic surfactant and cetyltrimethylammonium bromide (CTAB) as cationic surfactant were established by dynamic light scattering (Brookhaven Instruments Corporation, Holtsville, USA) under different pH. 1 mM dispersion of BHA in water was prepared with and without surfactants by adding calculated amount of CTAB (0.0182 g) and SDS (0.0144 g). Before particle size and zeta potential measurements, solutions were ultra-sonicated for 3 min and then subjected to the measurements. Data for particle size measurement was acquired for 25 min with water, CTAB and SDS. Each data point for zeta-potential measurements (calculated Zeta Potential Analyser Software-PALS Analyser software) is an average of five runs. In order to adjust the pH, 10 % HNO₃ (acidic medium) and 10 % KOH (basic medium) solutions were used.

In order to find the pH at which charge density on its surface is zero, the point of zero charge (pzc) value was measured. For this measurement, 20 mg of BHA powder was taken in different twelve vials each containing 10 ml of 1 M KNO₃ solution. pH of each vial was adjusted starting from 1 to 12 at an interval of 1, with the help of 0.1 M HNO₃ and 0.1 M KOH solution and then the vials were shaken well and kept for 24 h. After this the pH of each solution was measured and then initial pH was plotted against final pH. A line was drawn by joining the points which are almost linear i.e. the points which form a line with lowest slope, and the pzc was determined from the extrapolation of this line to the y-axis.

Nickel/BHA coatings were deposited from a nickel Watts bath solution with a volume of 100 ml consisting of BHA, 300 g/l NiSO₄·6H₂O, 45 g/l NiCl₂·6H₂O, 45 g/l H₃BO₃ and SDS. The ratio of SDS and BHA was kept constant (which

Figure 1. XRD pattern of as synthesized powder containing BaAl₁₂O₁₉ (BHA), BaAl₂O₄ (BMA) and alpha alumina.

Figure 2. XRD pattern of heat treated oxide powders at 1550 °C showing single phase BHA.

Figure 3. (a) SEM images showing plate-like morphology of BHA and (b) EDS spectrum showing presence of Ba, Al and O in BHA powder.

was 1:100 by weight) in each and every experiment i.e. as the concentration of BHA increases the amount of SDS increases accordingly. Before adding the BHA into the solution, it was ultra-sonicated for 3 min and then added to the bath. pH of the bath was adjusted to 3.0 by adding H_2SO_4 and NH_4OH . A rounded double jacketed electrolytic cell with an internal

diameter of 5 cm containing inlet and outlets for flowing hot water from the water bath, was used as an electrodeposition assembly. The temperature of the bath was measured within an error of ± 0.5 °C throughout the experiments. Mild steel plates ($2 \times 1 \times 0.2$ cm) were used as cathode and pure nickel plates of purity, 99.9 % ($3 \times 3 \times 0.3$ cm) were used as

anode. Both the cathode and anode were hung vertically with the help of copper wires and separated by a distance of 3.5 (± 0.5) cm in each experiment. Prior to each experiment the mild steel plates were polished on 220, 400, 600, 800, 1000, 1200, 1500 and 2000 grit SiC papers and degreased with

Figure 4. Plot of particle size and time showing bimodal distribution of finer and coarser particles in suspensions.

Figure 5. Plot showing variation of zeta potential with pH for different suspensions.

Table 1. Bath composition and different operating conditions for a fixed deposition time.

NiSO ₄ ·6H ₂ O	300 g/l
NiCl ₂ ·6H ₂ O	45 g/l
H ₃ BO ₃	45 g/l
Surfactant	SDS
pH	3.0 (± 0.05)
Temperature (°C)	50 & 60 (± 0.5)
Current density (mA/cm ²)	50
T _{ON} (ms)	2
T _{OFF} (ms)	18
Duty cycle (%)	10
Deposition time (min)	60
Stirring (rpm)	50–100 (magnetic)

acetone in a sonicator for 5 min. Electrodeposition was carried out galvanostatically using square-wave pulsed current with current cut-off during the interval between the pulses (Digilog Instruments, Bangalore, India). Different plating parameters such as pH, temperature, current density and duty cycle were varied. The BHA concentration in the bath was varied from 1 to 420 g/l. During electrodeposition, the suspension was subjected to continuous stirring (50–100 rpm)

by a magnetic stirrer. All the plating parameters are summarized in tabular form. Deposition time, current densities and duty cycles were fixed in such a way so that a desired thickness of coating could be achieved. After 1 h plating the coatings were washed with running water and acetone and characterized by XRD (X-Pert PRO, PANalytical instrument) and SEM. The roughness of the as deposited coatings was measured by 3D Optical Profilometer (WYKO NT100) and average values of roughness were calculated by Vision32 software. Thickness was measured from cross-sectional view of the coatings by SEM measurements. One fourth of the sample was cut from the bottom and polished with 1200, 1500 and 2000 grit SiC papers and then finally with 1 μm diamond paste using diamond polishing lubricant on a cloth (supplied from Buehler). After polishing, the samples were

cleaned properly in acetone and desiccated before SEM imaging. SEM images were acquired for both microstructural characterizations as well as image analysis measurements and EDS analysis for micro chemical analysis of the phases present. In order to calculate the volume fraction (area fraction) of BHA in the coatings, image analysis measurements on the BSE images of different samples were performed by using Image j 1.42q software (Wayne Rasband, National Institute of Health, USA). Vickers hardness tester (Diamond Indenter, CSM Instrument) was employed to evaluate the microhardness of the coatings (top view) using a load of 1 N. Five measurements were conducted on each sample.

3. Results and discussion

3.1 Synthesis and characterization of BHA

The powder obtained at 500 °C by solution combustion synthesis (Das and Patil 1994) (as synthesized powder) contains BHA, BMA and alumina (Al_2O_3). The following reaction is expected to take place during combustion of the aqueous reaction mixture:

From the above reaction we can conclude that its incompleteness leads to free BaAl_2O_4 ($\text{BaO} \cdot \text{Al}_2\text{O}_3$) and Al_2O_3 which is obvious from the XRD pattern of as-synthesized powder (figure 1). From XRD pattern we can clearly see two maximum intensity peaks, one at $2\theta = 35.6$ corresponding to (114) which is the maximum intensity peak for BHA and $2\theta = 28.3$ which is the maximum intensity peak for BMA corresponding to (202) peak. The peaks for alumina

Figure 6. Plot between volume (area) fraction of BHA in coatings and BHA concentration (g/l) in plating bath.

Table 2. Thickness, volume fraction of BHA in coatings and roughness of coatings at pH 3.0 (± 0.05) for 1 h deposition and 50 mA/cm² current density.

Sl. no.	BHA conc. in bath(g/l)	Volume fraction of BHA in coating	Thickness (μm)	Surface roughness of as deposited sample(nm)
Electrodeposition at 60 $\pm$ 0.5 °C				
1	10	1.5	80	600
2	50	2.0	70	380
3	100	5.6	50	335
4	200	17	60	375
5	350	9.3	85	495
Electrodeposition at 50 $\pm$ 0.5 °C				
6	50	7.1	–	545
7	100	11	8	190
8	200	14	8	175
9	300	14.3	8	200
10	350	20.7	11	120
11	420	15.5	5	235

are at $2\theta = 42.3$, 66.9 and 82.4 which correspond to (202), (330) and (402) peaks, respectively. Single phase BHA was obtained when this powder was subjected to heat treatment at 1550°C (heating rate, $10^\circ\text{C}/\text{min}$) for 6 h (figure 2) which could be inferred by the disappearance in the intensity of peak at 28.3 . It has been reported that for powder mixtures, BHA is formed through solid state reaction between $\text{BaO} \cdot \text{Al}_2\text{O}_3$ and alumina by diffusion (Machida *et al* 1988). Davies *et al* (1998) also mentioned that BMA is formed as an intermediate phase, with little densification and converts to BHA with densification from mixture of alumina and barium carbonate powders.

(a)

(b)

Figure 7. Cross-sectional view (SEM) of composite coating deposited at 50 and 60°C .

SEM examination of BHA powders (figure 3(a)) reveals its layered structure and plate-like morphology in which each plate is located above the other and so on. Since the lattice is hexagonal, the 001 basal planes correspond to the plate habit (Debsikdar 1989). Microanalysis of all the elements present was confirmed by EDS analysis (figure 3(b)). This layered structure of the mixed oxide has magnetoplumbite ($\text{Pb}^{2+}\text{Fe}_{12}\text{O}_{19}$) structure which in the present case consists of layered spinel blocks of $(\text{Al}_{11}\text{O}_{16})^+$ with Ba^{2+} cation (Utsonomiya *et al* 1988).

3.2 Dispersion behaviour and stability of different suspensions

Particle size analysis of different suspensions with water, SDS and CTAB by DLS shows a bimodal distribution curve (figure 4) indicating that the suspensions contain both fine as well as coarse particles. On the basis of these observations, it could be inferred that the dispersion of BHA particles in SDS at pH 3 is reasonably homogeneous. The magnitude of zeta potential of the particle is a measure of this particle interaction, which provides an indication of the long term stability of a suspension. If the particles in a suspension have a large negative or positive zeta potential then they will tend to repel each other and check aggregate formation. On the other hand, if they have low or close to 0 zeta potential values then particles are free to attract through van der Waals forces and aggregate. Conventionally, the border line of zeta potential for any suspension to be stable is ± 30 mV (Malvern Instruments 2005). Figure 5 shows the zeta potential values of different suspensions at various pH. It can be concluded that zeta potential values are higher with CTAB at all pH than with water or SDS. Point of zero charge for BHA was determined to be 6.6 above which the surface is positively charged and below which it is negatively charged. Thus, codeposition of BHA in acidic media will require anionic surfactants and for basic condition cationic surfactants in order to carry particles towards cathode.

3.3 Electrodeposition with different operating conditions

The key parameters for the pulsed electrodeposition of any metal/metal ceramic composites are temperature, pH, current, and particle/ceramic concentration in the bath (table 1). There are other parameters such as the duty cycle (on and off times) which play a vital role in the quality and adherence of these composite coatings. In addition, bath composition, deposition time and agitation speed also play important roles.

The first key deposition parameter is temperature. The electrodeposition of nickel composites has been extensively performed at temperatures of 30 – 60°C (Rethinam *et al* 2004), 40°C (Wang *et al* 2005), 50°C (Hou *et al* 2002; Qu *et al* 2003; Lee *et al* 2007; Pompei *et al* 2009), 60°C (El-Sherik *et al* 1996; Webb and Roberstson 1994; Parida

et al 2011) and 65 °C (Chaparro *et al* 2007). In the present work, we have confined our attention to 2 temperatures of 50 and 60 °C. It has been found that the volume fraction (VF) of BHA in the coatings deposited at 50 °C was maximum for lower BHA concentration as compared to 60 °C for a given same set of parameters such as bath composition, current density, duty cycle and pH (figure 6). Another interesting result is that only 10 °C difference in temperature leads to a considerable effect on the thickness of the coating (i.e. the deposition rate) as shown in table 2. The thickness of the coatings deposited at 60 °C was about 60 μm , which is much higher than 8 μm formed at 50 °C, with other parameters constant as shown in figures 7(a) and (b). This is possibly due to the decrease in the rate of diffusion of the nickel ions with temperature (Hamid and Ghayad 2002). While deposition at 50 °C leads to the maximum incorporation of BHA,

60 °C is also suitable if a higher rate of deposition is required. While the thickness at 50 °C could also be increased by increasing deposition time, pH of the Watts bath tends to drift to higher values and requires constant adjustment if times much longer than an hour are involved.

The second key parameter to be considered is pH. It may be noted that while the electrolyte composition is different from that of the bath used for zeta potential measurements, there appears to be some consistency in the 2 sets of results. From figure 5, we see that the zeta potential value for BHA+SDS suspension at pH 3 was -44.7 mV which assures a degree of colloidal stability. Thus, electrodeposition at pH 3, as was actually performed, appears to be an acceptable compromise. In the present work, our contention is that, in order to facilitate greater incorporation of BHA in the coating, the rate of nickel deposition should be comparatively

Figure 8. (a) XRD pattern of Ni/BHA composite coating with 200 g/l BHA (full scan) and (b) XRD pattern between $2\theta = 30\text{--}42^\circ$ (marked in red region in figure 8a) and theoretical maximum intensity peak is 114.

(a)

(b)

(c)

Figure 9. SEM images of composite coating deposited at 60 °C with BHA suspension concentrations of (a) 10 g/l and (b) 200 g/l. (c) EDS spectra from dark (BHA) phase of as-deposited coating.

lower. So here we have worked with 50 mA/cm² peak current density in all the cases (table 1).

3.4 X-ray characterization and surface morphologies of as deposited coatings

From the XRD pattern of the coatings (figure 8(a)), we can see the characteristics peak for crystalline nickel only. Peaks for BHA are not clear in this XRD pattern. In order to trace the BHA peaks, XRD measurements have been carried out between different intervals of 2θ values. Only three peaks for BHA at $2\theta = 32.0$, 33.1 and 35.6 have been observed (figure 8(b)). These peaks correspond to (110), (107) and (114) plane, out of which (114) peak is the maximum intensity peak. Since Ni is the majority phase and has a higher scattering factor, its peak intensities are much higher than those of BHA. Hence, only BHA peaks with high relative intensities are detected in the XRD pattern. It has also been observed that for the coatings in which volume fraction of BHA was less than ~ 5 , these peaks could not be detected. However, surface morphologies of as-deposited composite coatings shown in figures 9(a) and (b), clearly show that these particles are embedded in the nickel matrix. EDS spectrum shown in figure 9(c) confirms the presence of BHA particles in the coatings. It is also obvious that the Ni grain size is almost homogeneous in the coatings (about 2–4 μm). The roughness of these coatings (table 2) is 300 (± 150) nm; indicative of the fact that deposition of Ni is homogeneous and that the particles are not agglomerated.

3.5 Microstructural studies

Figure 10 shows SEM micrographs of the top-view of Ni/BHA composite coatings after metallographic polishing. Comparison of figures 10(a) and (b) reveal the significant increase in BHA volume fraction when the dispersion loading in the bath is increased from 10 g/l to 200 g/l. However, the trend in particulate loading is nonlinear and displays a maximum with dispersion concentration (figure 6) which changes from 17 % at 200 g/l (at 60 °C) to ~ 21 % at 350 g/l (at 50 °C). Another pronounced difference observed between these two temperatures is the large difference in thickness (nearly an order of magnitude). Hence, from figure 6, three points emerge: (i) particulate loading in the film does not increase linearly with suspension concentration; indeed, a reversal takes place, i.e. volume fraction of BHA in the coating decreases beyond a critical bath concentration, (ii) the above nonlinearity and maximum value are different at the two temperatures and (iii) the volume fraction of BHA in the film is greater at 50 °C than at 60 °C.

Nonlinearity has been reported earlier (Muller *et al* 2002; Shi *et al* 2006) but without clear explanations. Here we have assumed that for a fixed area of the matrix, a limited number of particles can be accommodated. If we allow these particles to codeposit with the matrix then they will keep

Figure 10. Microstructures (planar view) of polished coatings with (a) 10, (b) 200 and (c) 350 g/l of BHA at 60 °C and (d) EDS spectrum from dark (BHA) region of coatings.

coming unless they have the space to sit on the matrix surface. After a certain concentration of these particles when the distances between these particles reaches the minimum i.e. inter-particle distance reaches minimum, they exhaust the available sites. In other words, we can say that inter-particle distance has reached at its minimum value. This is the event which appears to be taking place at higher BHA loadings where volume fraction was found to reach a maximum.

3.6 Extension of Guglielmi model

In order to understand second and third points we will explore the Guglielmi (1972) model according to which we can define adsorption coverage (σ) in the following way:

$$\sigma = S_T/S_P, \quad (1)$$

where S_T is the total electrode area and S_P the area overshadowed by the adsorbed particles, since, we have two

temperatures, 50 and 60 °C. At higher temperature, the particles will exert greater thermal agitation or Brownian movement while sitting at the electrode. During this period S_p would increase and cause a lowering of σ . Thus, the value of σ will be higher at 50 °C than at 60 °C. The other possible explanation lies in the increased movement of ions with temperature which causes increase in kinetic energy of BHA particulates. According to Langmuir theory, increase in temperature leads to the decrease in the absorbability of the particulates and hence to decrease in the overpotential and electric field. Thus it becomes harder for the BHA particulate to become embedded in the matrix and subsequently causes decrease in the area fraction of BHA particles (Chang and Lee 1988). The reason for decreases in thickness due to variation in temperature has already been mentioned in an earlier section.

Microhardness studies showed that the hardness of Ni/BHA composite coatings increases as the BHA content increases in coatings (figure 11). Hardness values are measured as 355 HV for coating having 1.5 % volume fraction of BHA and 410 HV for 17 % volume fraction of BHA. Hence it can be inferred that incorporation of BHA particulates has significant effect on hardness values of these coatings.

Interest has also been growing to see the effects of various plating parameters during electrodeposition of various composite coatings (Zoikis-Karathanasis *et al* 2010;

Figure 11. Plot showing variation of microhardness of different coatings with increase in volume fraction of BHA. Scatter in results is ~ 15 HV.

Table 3. Effect of pH on VF of BHA in coatings, at 200 g/l BHA loading, peak current density (i_p) 50 mA/cm², 60 °C and 10 % duty cycle.

Sl. no.	pH	VF of BHA in coatings
1	3.05	17.0
2	4.03	6.3

Sohrabia *et al* 2010; Choua *et al* 2005; Borkar and Harimkar 2011). Hence, in addition to these investigations we have also observed the effect of various factors such as pH (table 3), current density (table 4), and duty cycle (table 5) on volume fraction of BHA in the coatings. Electrodeposition for 200 g/l at pH 4 (at 60 °C) was also performed and results have shown that with the increase in pH from 3 to 4, there was a decrease in the volume fraction of BHA (table 3). Along with decrease in volume fraction, agglomeration of BHA particles in the coating was also observed (figure 12). Table 1 shows that the zeta potential value for SDS suspension at pH 4 was lower which may decrease the stability of the particles and cause agglomeration. After agglomerate formation the mobility of these particles will reduce and they will not reach to the cathode easily. Influence of peak current density was observed by decreasing current density from 50 to 20 mA/cm² (at 60 °C). From table 4, it is obvious that decrease in peak current density results in increase in area fraction. This may be due to the fact that by decreasing the peak current density, the rate of nickel deposition would be slower and during those periods more particles would be able to deposit. Another possible explanation for this observation may be related to the idea that electrochemical potential affects the adsorption of BHA particulates on substrate surface. Thereby, the higher the current density, the lower the cathodic deposition potential, the higher the negative charging of the double layer to repel BHA particulates, and lower the adsorption of BHA (Chang and Lee 1988).

From table 5 we can also see that for the same BHA loading, there was an increase in the volume fraction by decrease in duty cycle. Similar behaviour was also shown by the pulse electrodeposited composite coatings of Ni-P matrix (Zoikis-Karathanasis *et al* 2010). Decrease in duty cycle would naturally cause a decrease in the deposition rate of nickel. At the same time due to an increase in off time, the time experienced by double layer for discharging the negatively charged layer would be higher which would more readily enable the particle to approach the cathode.

Table 4. Effect of peak current density on VF of BHA in coatings at pH 3.0 (± 0.5), 350 g/l loading BHA, 60 °C and 10 % duty cycle.

Sl. no	i_p (mA/cm ²)	VF of BHA in coatings
1	50	9.3
2	20	20.8

Table 5. Effect of duty cycle on VF of BHA in coatings at pH 3.0 (± 0.5), 350 g/l BHA loading, 50 °C and 50 mA/cm² current density.

Sl. no.	Duty cycle (%)	VF of BHA in coatings
1	10	15.5
2	5	22.5

(a) At pH-3

(b) At pH-4

Figure 12. Microstructures showing effect of pH (3 and 4) on volume fraction of BHA measured on planar view of coatings.

4. Conclusions

Single phase BHA powder has been synthesized by combustion synthesis with sub-micron particle size and a plate-like morphology. The dispersion behaviour and stability of different suspensions with cationic and anionic surfactants have shown that BHA can be stabilized by addition of surfactants and control of pH and successfully incorporated into the nickel matrix by electrodeposition. The volume fraction of BHA incorporated in the coating displays a maximum with respect to increasing suspension concentration.

BHA was shown to be uniformly distributed in the film with a roughness of $\sim 0.4 \mu\text{m}$. A reduction of deposition temperature from 60 to 50 °C significantly lowers deposition rates as well as roughness. BHA content in the coatings has shown an increase in hardness values. Other plating parameters such as temperature, pH and current density have also been observed to have a significant effect on volume fraction of BHA in the film. By controlling the plating parameters a maximum of $\sim 20\%$ particulate could be incorporated in the Ni matrix at rates approaching $\sim 1 \mu\text{m}/\text{min}$.

Acknowledgements

Defence Research and Development Organization is acknowledged for financial assistance, Prof. Satish Kailash, Department of Mechanical Engineering, Indian Institute of Science, Bangalore, for providing Optical Profilometer facility and Mr Bhaskar Mukri, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, for helping in combustion synthesis experiments.

References

- Aoudi S M, Paudel Y, Simonson W J, Kohli Q G, Muratore C and Voevodin A A 2009 *Surf. Coat. Technol.* **203** 1304
- Allam I M 1991 *J. Mater. Sci.* **26** 3977
- Borkar T and Harimkar S P 2011 *Surf. Coat. Technol.* **205** 4124
- Burzynska L, Rudnik E, Koza J, Blaz L and Szymanski W 2008 *Surf. Coat. Technol.* **202** 2545
- Baker C C, Chromik R R, Wahl K J, Hu J J and Voevodin A A 2007 *Thin Solid Films* **515** 6737
- Chang Y and Lee L 1988 *Mater. Chem. Phys.* **20** 309
- Chaparro A, Arnulfo W and Vera L E 2007 *Revista Matéria* **12** 583
- Choua M, Ger M, Ke S, Huangc Y and Wu S 2005 *Mater. Chem. Phys.* **92** 146
- Corte C D and Sliney H E 1990 *Powder Metall. Compos.* (NASA-TM-102355)
- Das N A and Patil K C 1994 *Ceram. Int.* **20** 57
- Davies T J, Emblem H G, Biedermann M, Chen W and Douri W A 1998 *J. Mater. Sci. Lett.* **21** 1845
- Donnet C and Erdemir A 2004 *Surf. Coat. Technol.* **180–181** 76
- Debsikdar J C 1989 *J. Mater. Sci.* **24** 3565
- El-Sherik A M, Erb U and Page J 1996 *Surf. Coat. Technol.* **88** 70
- Gupta S, Filimonov D, Palanisamy T, El-Raghy T and Barsoum M W 2007 *Wear* **262** 1479
- Guglielmi N 1972 *J. Electrochem. Soc: Electrochem. Sci. Technol.* **119** 1009
- Hamid Z A and Ghayad I M 2002 *Mater. Lett.* **53** 238
- Hou K H, Ger M D, Wang L M and Ke S T 2002 *Wear* **253** 994
- Kirchhoff M, Specht U and Vesper G 2005 *Nanotechnology* **16** S401
- Lee H K, Lee H Y and Jeon J M 2007 *Surf. Coat. Technol.* **201** 4711
- Lele M B, Seshadri S K and Ramesh C S 1989 *Proceedings of the annual technical meeting* (Calcutta: Indian Institute of Metals) **50**
- Machida M, Eguchi K and Arai H 1988 *Bull. Chem. Soc. Jpn* **61** 3659
- Miyoshi K 2007 NASA-TM-214668
- Muller C, Sarret M and Benballa M 2002 *Surf. Coat. Technol.* **162** 49

- Parida G, Chaira D, Chopkar M and Basu A 2011 *Surf. Coat. Technol.* **205** 4871
- Pompei E, Magagnin L, Lecis N and Cavallotti P L 2009 *Electrochim. Acta* **54** 2571
- Qu N S, Zhu D, Chan K C and Lei W N 2003 *Surf. Coat. Technol.* **168** 123
- Ramesh C S, Seshadri S K and Iyer K J L 1991a *Indian J. Technol.* **29** 179
- Ramesh C S, Seshadri S K and Iyer K J L 1991b *Wear* **145** 189
- Ramesh C S, Seshadri S K and Iyer K J L 1991c *Wear* **156** 205
- Ramesh C S, Seshadri S K and Iyer K J L 1991d *Ceramic Trans. Adv. Compos. Mater.* **19** 885
- Rethinam A J, Ramesh Babu G N K and Krishnan R M 2004 *Mater. Chem. Phys.* **85** 251
- Sohrabia A, Dolatib A, Ghorbania M, Monfared A and Stroevec P 2010 *Mater. Chem. Phys.* **121** 497
- Sun X J and Li J G 2007 *Tribol. Lett.* **28** 223
- Shi L, Sun C, Gao P, Zhou F and Liu W 2006 *Appl. Surf. Sci.* **252** 3591
- Surender M, Balasubramaniam R and Basu B 2004 *Surf. Coat. Technol.* **187** 93
- The measurement of Zeta potential Using an Autotitrator: Effect of pH, Application Note by Malvern Instruments 2005
- Utsonomiya A, Tanaka K, Morikawa H, Marumo F and Kojima H 1988 *J. Solid State Chem.* **75** 197
- Voevodin A A and Zabinski J S 2005 *Compos. Sci. Technol.* **65** 741
- Wang S C and Cheng W C J 2003 *Mater. Chem. Phys.* **78** 574
- Wang W, Hou F Y, Wang H and Guo H T 2005 *Scr. Mater.* **53** 613
- Webb P R and Roberstson N L 1994 *J. Electrochem. Soc.* **141** 669
- Xia Y, Sasaki S, Murakami T, Nakano M, Sh Li and Wang H 2007 *Wear* **262** 765
- Xia Y, Wang L, Liu X and Qiao Y 2008 *Tribol. Lett.* **30** 151
- Zoikis-Karathanasis A, Pavlatou E A and Spyrellis N 2010 *J. Alloys Compd* **494** 396