Deposition of Ni-Fe/Si_3N_4 Nanocomposite Prepared by Electroplating

Yusrini Marita[1] and Iskandar Idris Yaacob[2]

***Abstract*—Ni-Fe/Si_3N_4 nanocomposite coatings with various ratio of Si_3N_4 to Na-saccharine were prepared by electrodeposition technique. The effect of Si_3N_4 nanoparticulates in the Ni-Fe nanocomposite coatings was investigated in relation to the ratio of Si_3N_4 to Na-saccharine in the plating bath. X-ray diffraction analysis showed that the Ni-Fe nanocomposite coating has face center cubic structure (FCC). However, a mixture of body center cubic (BCC) and face center cubic (FCC) phase was observed when the ratio of Si_3N_4 to Na-saccharine is 8.3. The crystallite size of Ni-Fe nanocomposite coating reduced when the ratio of Si_3N_4 to Na-saccharine was increased. From the elemental mapping procedure, inclusions of silicon were uniformly distributed in Ni-Fe composite coating and contributed in increasing the microhardness.**

***Index Terms*— Electroplating, Nanocomposite, Ni-Fe alloy coating, Si_3N_4 nano-particulates.**

I. Introduction

Composite electroplating is a method of codepositing fine particles of metallic, non-metallic or polymeric coumpounds in plated layer to improve the properties of material such as wear resistance, lubrication, or corrosion resistance [1]. During this process, these insoluble filler materials are suspended in the plating electrolyte and are then captured in the deposited metal film. Nanocomposites of a metallic matrix containing dispersion of second phase particles usually display a variety of novel properties. The second-phase material can be powder, fiber or encapsulated particles. In general, the presence of the second phase particles in a codeposited film offers a variety of benefits on physical and mechanical properties compared to the pure metal coatings, such as increased microhardness, yield strength, tensile strength and improved wear resistance [2]. The emergence of technology revives electrodeposition techniques for synthesizing a variety of new nanostuctured materials. These include nanocrytalline deposits, nanowires, nanotubes, nanomultilayers, and nanocomposites. For the purpose of increasing the hardness and wear resistance of various electrodeposited metal and metal alloy based coatings, various inorganic particles including SiC [3], ZrO_2 [4], Al_2O_3 [5], [6], and TiO_2 [7] are incorporated within the coating.

There are only a few reports on the incorporation of Si_3N_4 nanoparticulates in electrodeposited alloy coating, although it is known that Si_3N_4 nanoparticulates as fillers contribute to improvement on hardness of the film [8]. Improvement of the properties of the film can also be achieved by refining the grain size of deposited film. Therefore, electrodeposition processes are usually carried out with addition of brightener such as saccharine in the electrolyte solution because it makes the grain size of the films form smaller [9]. In this research, we report formation of Ni-Fe/Si_3N_4 nanosrtuctured thin film composite by electroplating technique. The properties of the film are also characterized.

II. Experimental Procedure

The Ni-Fe/Si_3N_4 nanostructured composite coatings were prepared by constant current electrodeposition process. Experiments were performed in a simple beaker cell. The Ni-Fe/Si_3N_4 was deposited on copper substrates. The copper substrate was mechanically polished using SiC abrasive paper up to 1200 grit, it was then degreased and dried. The substrate's surface was then chemically treated for a few seconds using dilute solution of H_2SO_4 for further removal of impurities. The anode material used was nickel. Each experiment was carried out using a plating bath that contains nickel sulphate hexahydrate as the source of nickel, ferrous sulphate heptahydrate as the source of iron, nickel chloride hexahydrate as complexing agent, boric acid as the buffer, and sodium saccharine as the grain refinement agent. Prior to plating, nanosized silicon nitride (mean diameter of 86 nm) were dispersed in the electrolyte bath and were stirred for about six hours. Ratios of silicon nitride to sodium saccharine were 0, 0.83, 1.67, and 8.3. Magnetic stirrer was used throughout the plating process to ensure uniform suspension of particles in the solution. Nickel chloride hexahydrate was chosen as the complexing agent because it was essential to minimize corrosion on anode material and to improve the conductivity of plating bath. The temperature of the electrolyte was maintained at 55°C (to maintain dissolution of boric acid). The pH of the bath is adjusted to 3.0 by dilute sulfuric acid. The experiments were conducted at current density of 11.5 A/dm^2. The thickness of the coating was fixed at approximately 50 µm by adjusting deposition duration. Each experiment was carried out with a freshly prepared solution. After completion, the specimens were taken out and then thoroughly rinsed with deionized water to remove any loose particles that were physically stuck to the surface.

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The structural characteristics of the NiFe-Si_3N_4 composite coatings were investigated by X-ray diffraction (XRD) with Cu-Kα radiation (λ = 1.542 Å) (Philips X-Pert MPD PW3040). The composition of the NiFe nanocomposite coating was determined by an energy dispersive X-ray spectroscopy. The presence of Si_3N_4 particles was assessed using an elemental mapping procedure. Microhardness of the composites coating was measured using a Vickers' microhardness instrument at an applied load of 50 g.

III. RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction patterns of Ni-Fe alloy films and Ni-Fe/Si_3N_4 composite coating obtained at the current density of 11.5 A/dm^2. The diffraction peaks of the Ni-Fe alloy films show considerable broadening. This is an indication of very fine grain size of the films. The broadening of (111) peak increase considerably when the ratio of Si_3N_4 to Na-saccharine is increased from 0 to 1.67. All the reflection patterns for these samples indicate that the films are face center cubic (FCC). No other phase is detected on these patterns. When the ratio of Si_3N_4 to Na-saccharine is increased to 8.3, the crystal structure of the nanocomposite changed from FCC to mixture of BCC and FCC. The change crystal structure to BBC + FCC is because of higher Fe content in the deposit. Mixed structure of BCC and FCC starts to form at 60 at. % Fe [10]. The presence of Si_3N_4 inhibits the growth of Ni-Fe film and therefore, decreases the crystallite size to 5 nm. The crystallite sizes of the Ni-Fe alloy film and Ni-Fe/Si_3N_4 nanocomposite coating was determined using Scherer's formula. The presence of Si_3N_4 could not be detected by XRD because Si_3N_4 content in the film is low.

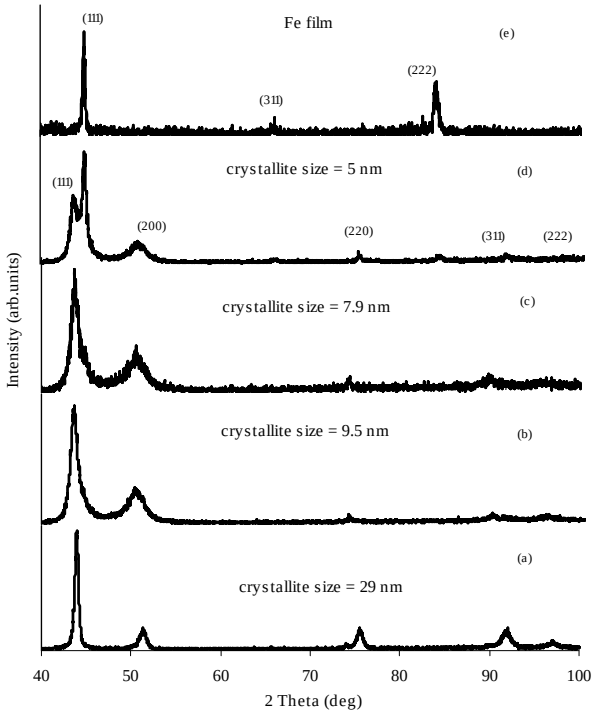

Fig. 1. XRD patterns of Ni-Fe nanocomposite coating obtained at various ratio of silicon nitride to sodium saccharine (a) Si_3N_4 / Na-Saccharine = 0; (b) Si_3N_4/Na-Saccharine = 0.83; (c) Si_3N_4/Na-Saccharine = 1.67; (d) Si_3N_4/Na-Saccharine = 8.3; and (e) Fe film

The addition of sodium saccharine into the electrolyte solution decreases the average crystallite size of Ni-Fe films. The crystallite size of film formed without sodium saccharine is 29 nm. The addition 6 g/l of sodium saccharine into the plating bath reduces the crystallite size of the film to 15 nm.

Ni-Fe film properties can be improved by addition of Si_3N_4 nanoparticles. XRD investigation on the samples with addition of Si_3N_4 shows that the crystallite size decreases with increasing ratio of Si_3N_4 to Na-Saccharine. A little addition of Si_3N_4 causes the crystallite size to decrease sharply. Further addition of Si_3N_4 causes only slight decrease of the crystallite size. The crystallite sizes of the samples are 29 nm, 9.5 nm, 7.9 nm, and 5 nm for Si_3N_4 to Na-Saccharine ratio of 0, 0.83, 1.67, and 8.3 respectively.

Fig. 2 shows SEM image of Ni-Fe film with and without addition of sodium saccharine. The surface morphology of the film prepared with sodium saccharine is smoother than the one without sodium saccharine. Sodium saccharine acts as an inhibitor limiting the surface mobility of the ions on the cathode surface resulting in nanosized grains [3]. Moreover, by visually observing the deposits, we can notice that addition of sodium saccharine causes the film of more optically reflective.

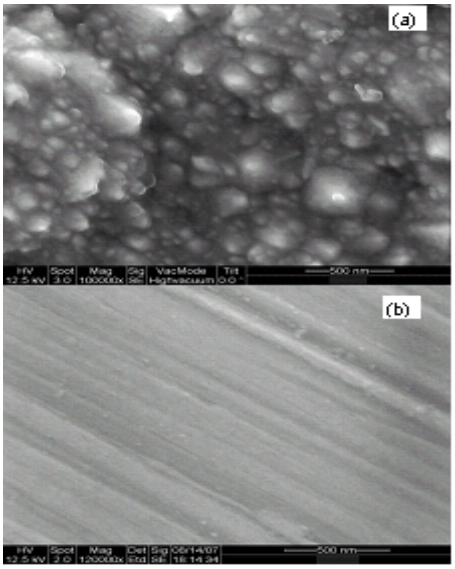

Fig. 2. SEM micrographs of Ni-Fe alloy electrodeposited (a) without sodium saccharine and (b) with sodium saccharine

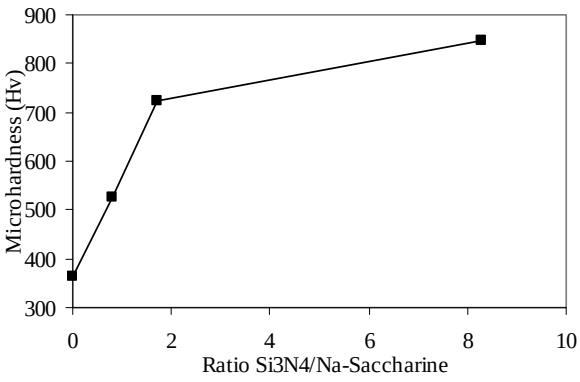

Fig 3. Variations of microhardness of Ni-Fe nanocomposite coating

The microhardness of the films is plotted as a function of the ratio of Si_3N_4 to Na-Saccharine (Fig. 3). The microhardness of the film increases with increasing ratio of Si_3N_4 to Na-saccharine. The microhardness of pure Ni-Fe coating is around 365 Hv. It increases significantly with addition of Si_3N_4.

The crystallite sizes of the Ni-Fe nanocomposite coating decrease from 29 to 5 nm with increasing ratio of Si_3N_4 to Na.-saccharine. Therefore the average microhardness of the composite coating is higher for the material with smaller crystallite size. It is well known that grain size in polycrystalline material influences its mechanical properties [11]. The relation between the crystallite size and microhardness can be expressed by Hall-Petch relation, $H = H_o + k/(d)^{1/2}$ where H is microhardness of the material, d is crystallite size, H_o and k are experimental constants and are different for each material [12]. Smaller crystallite size implies a greater number of grain boundaries that impede dislocation motion. This creates harder materials.

Fig. 4 shows SEM and elemental mapping images of Si in Ni-Fe composite coating using electrolyte solutions with ratio of Si_3N_4 to Na-saccharine of 1.67 and 8.3. Fig. 4 (a) is an SEM image of Ni-Fe nanocomposite coating prepared with Si_3N_4 to Na-saccharine of 1.67. The image shows existence of black spots. Using elemental mapping procedure the black spots are identified as Si_3N_4 nanoparticles (Fig. 4 (b)). Increasing the ratio of Si_3N_4 to Na-saccharine to 8.3 produces nanocomposite coating that appear to contain protruding particulates (Fig 4 (c)). Elemental mapping of the Ni-Fe nanocomposite coating shows quite uniform distribution of Si, indicating a good dispersion of Si_3N_4 on the film (Fig.4 (d)).

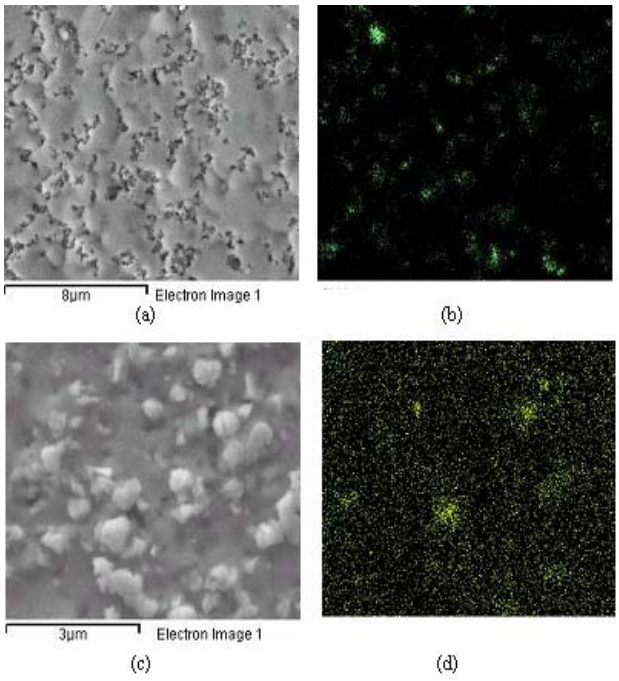

Fig 4. SEM and elemental mapping of Si image (a) SEM image of Ni-Fe nanocomposite coating with ratio of Si_3N_4 to Na-saccharine of 1.67; (b) Elemental mapping image of Si of (a); (c) SEM image of Ni-Fe nanocomposite coating with ratio of Si_3N_4 to Na-saccharine of 8.3; (d) Elemental mapping image of Si of (c).

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