Surfactant Assisted Electrodeposition of Nanostructured CoNiCu Alloys

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Abstract. In order to obtain a desirable deposition thickness, nanostructured ternary CoNiCu alloys have been electrodeposited from salt solutions containing Co²⁺, Ni²⁺ and Cu²⁺ in the presence of a neutral surfactant alkyl polyglucoside (APG). Electrodeposition of CoNiCu was carried out in a three-electrode cell with indium–tin oxide (ITO) on glass plate, platinum wire and saturated calomel electrode (SCE) as working electrode, counter electrode and reference electrode, respectively. The nanostructured alloys were characterized by means of atomic force microscopy (AFM) and supported by field emission scanning electron microscopy (FESEM). The nanostructured CoNiCu alloys prepared in sulphate solutions in the presence of APG produced a thinner layer of nanoparticles of the alloys compared with the one deposited in the absence of APG. For a fixed deposition time, 160s and at an applied potential of -875mV (SCE) the layer thickness was about 56 nm for electrodeposition in the presence of 3.25 wt.% APG and about 110 nm without APG. Only a small increase in thickness was observed when the potential was increased to more negative values i.e. -875 to -950 mV(SCE).

1. Introduction
Electrodeposited magnetic thin films iron- group metals (Fe, Co and Ni) have been developed because of potential applications in electronics, optics, catalyst and magnetic data storage. In recent years, research in magnetic materials has increased and being applied in energy converter devices, sensor, data storage and memory devices[1]. CoNiCu alloys have attractive magnetic properties, magnetoresistive characteristic and sufficient ductility required for forming them into complex shape[2].

For the preparation of the nanoparticles, electrodeposition has been identified as one of the most efficient techniques because of the particles growth parameters can be controlled through potential, current density and temperature [3]. It is considered as a practical technique and widely used for nanoparticles preparation due to its ability to directly attach the nanoparticles on the substrate [4, 5]. Due to its simple and easy process in terms of controlling the experimental parameters[6], economically cheap and wide range industrial applicability[7] put this method as a potential tool for future nanoparticles synthesis.

Controlling size and shape of the electrodeposited nanoparticles is an important issue in the nanomaterials synthesis due to the strong dependence of properties on shape and size. The addition of surfactant into the electrolyte is among a straight forward method in controlling the nanoparticles growth. As the result of the unique roles in modifying the deposition preference such as thinner deposited thickness and properties that in turn enable for obtaining controlled size particles[8, 9],

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According to Siddig et al. [11], the addition of surfactant into the electrolyte is believed to modify the morphology and structure of materials due to its nonionic characteristic and good psychochemical properties. Alkyl polyglucoside (APG) is a surfactant that possesses environmental friendly features [12-14] such as non-toxic and biodegradable in aqueous media [15, 16].

In this study, we report the results of the synthesis of nanostructured CoNiCu alloys via electrodeposition in the presence of APG surfactant. The effect of APG concentration in the electrolyte on thickness of nanostructured CoNiCu alloys deposited on the substrate was also quantified.

2. Experimental

Technical grade Glucopone 215 CSUP, commercial name of the alkyl polyglucoside (APG), was obtained from Fluka. Analytical grade boric acid (H$_3$BO$_3$) and all metal salts (technical grade CoSO$_4$·7H$_2$O, NiSO$_4$·6H$_2$O and CuSO$_4$·5H$_2$O) were purchased from Sigma-Aldrich. Indium-tin oxide (ITO) coated on glass plate with sheet resistance 10Ω/cm$^2$ was obtained from Praezisions Glas & Optik GmbH.

Electrodeposition of CoNiCu was carried out in a three-electrode cell with ITO on glass plate, platinum wire and saturated calomel electrode (SCE) as working electrode, counter electrode and reference electrode, respectively. The electrolyte containing 0.0018M CoSO$_4$, 0.18M NiSO$_4$, 0.002M CuSO$_4$ and 0.4M H$_3$BO$_3$ were prepared using pure water with resistivity of 18.2 MΩ cm. The electrodeposition process was carried out by using electrolyte without APG surfactant and electrolyte with up to 3.25 wt. % of APG surfactant under room temperature. Co-electrodeposition potentials werer from -875 to -975 mV (SCE) and the deposition time was 160 s.

The thickness of deposited CoNiCu alloys was determined using an atomic force microscope (AFM) Veeco Dimension V. A Zeiss field emission scanning electron microscope (FESEM) SUPRA 55VP supported by an energy dispersive X-ray analyzer (EDX) was used in morphological study and determination of elemental composition of nanostructured CoNiCu alloys deposited on ITO film.

3. Results and discussion

Effect of the presence of APG surfactant on condition of deposited CoNiCu alloy particles was studied at concentration below and above the critical micelle concentration (CMC) value which was 1.3x10$^{-2}$ wt.%. The concentrations studied were 2.6x10$^{-3}$ and 1.3 wt.% respectively. Figure 1 shows typical FESEM images of the CoNiCu alloys nanoparticles prepared in mentioned APG concentrations.

For the concentration of APG below the CMC (figure 1b), it was found that high-density nanoparticles with irregular shape grew on the surface ITO substrate which was almost similar to that formed in electrolyte without APG (figure 1a). The size of the particles was less than 100 nm. However, it can be seen that the nanoparticles seemed to agglomerate and formed a dense surface. This might be due to the limited number of surfactant molecules presence were unable to act as a template in deposition of Co, Ni and Cu ions thus the CoNiCu particles were freely formed on the surface of ITO. A significant change was observed when the APG concentration was increased above the CMC value (figure 1c) where spherical shape nanoparticles were formed on the surface of the substrate. The size of the nanoparticles was found to be in the range of 25-70 nm. In this case a sufficient number of APG molecules are available to serve as templates for Co, Ni and Cu deposition on the ITO substrate. The hydrophobic part of APG molecules may also attach to the metal ions consequently control the size and shape of deposited particles. This phenomenon was also observed by Gomes and da Silva Pereira [17] who reported that the addition of surfactant into the electrolyte has affected deposition orientation and morphology.
Figure 1. FESEM images of CoNiCu nanoparticles electrodeposited on ITO glass substrate from different concentrations of APG at co-deposition potential -925 mV vs SCE (a) 0 wt.%; (b) 2.6x10^-3 wt.%; (c) 1.3 wt.%

Figure 2 shows a typical EDX spectrum of the electrodeposited nanoparticles prepared in the presence of 1.3 wt.% of the APG surfactant with deposition time of 160 s. It can be seen that the peaks related to the Co, Ni and Cu were present confirming the CoNiCu alloy nanoparticles were successfully formed on the ITO surface. Other elements such as In, Sn, Si, O and Ca were also observed which were related to the components of ITO substrate coated on glass. Typical elemental composition of the alloy prepared at this condition was 16.01, 31.45 and 52.54 at.% for Co, Ni and Cu, respectively.

Figure 2. An EDX spectrum of CoNiCu alloy nanoparticles electrodeposited on ITO substrate coated on a glass plate from the electrolyte containing 1.3 wt.% of APG with deposition time of 160 s

Thin layers of nanoparticles of CoNiCu alloy which were electrodeposited on ITO substrate were also observed using FESEM as shown in figure 3 and their thicknesses were determined by AFM. Figure 4 shows the step mode technique based on AFM image used in determination of thickness of an electrodeposited layer of CoNiCu alloy nanoparticles.
Figure 3. A typical FESEM image of a cross sectional thin layer of CoNiCu nanoparticles electrodeposited on ITO substrate. Scale bar is 200 nm.

Figure 4. Thickness measurement using AFM for the electrodeposited CoNiCu nanoparticles layer on ITO substrate.

The presence of APG in the electrolyte produced a thinner layer of nanoparticles of the alloys compared with the one deposited in the absence of APG. However, for APG concentration of less than the CMC value, insignificant thickness difference was observed compared with the layer of CoNiCu alloy produced in the absence of APG surfactant. According to Budi et al. [18] the presence of limited number of surfactant molecules or in the absence surfactant concentration, Co, Ni and Cu can be freely deposited on the surface of substrate followed by agglomeration of deposited CoNiCu alloy particles. This has resulted in a thicker layer of deposit compared to those deposited with APG concentrations above the CMC value. As mentioned earlier concentration above CMC value has provided sufficient number of surfactant molecules to act as template in electrodeposition effectively. For example, at electrodeposition potential of -925 mV (SCE), the nanoparticles of CoNiCu alloy layers in the absence of surfactant and in the presence of 3.25 wt% surfactant have thickness of 160 and 65 nm, respectively (figure 5).
Figure 5. Samples deposition thickness prepared by varying the concentration of APG surfactant at deposition potential -925 mV vs SCE.

Figure 6 shows thickness variation of layers of the electrodeposited CoNiCu alloys nanoparticles prepared using electrolytes without surfactant and with 3.25 wt.% surfactant and electropotential from -975 to -875 mV(SCE). For a fixed deposition time, 160s and potential of -875mV(SCE) the layer thickness was about 56 nm for electrodeposition with the presence of 3.25 wt.% APG whereas for without APG the thickness obtained was about 110 nm. The thinner deposited layer of nanoparticles obtained in the presence APG was due to lack of electrons transfer for deposition process. This phenomenon was the effect of APG molecules adsorption onto the working electrode surface i.e. ITO substrate whereby hydrophobic part of APG molecules absorbed onto ITO which is hydrophobic. The electrodeposition potentials seem to have little influence on thickness of deposited nanostructured CoNiCu alloys for the electrolyte containing APG especially for potentials from -950 to -875(SCE) except at -975 mV(SCE) whereas in the electrolyte without APG the influence of electrodeposition potentials was significant (figure 6). This is in good agreement with the work of Zhou et al. [19] who report that the electrodeposition current has increased when electrodeposition potential was more negative thus increases reaction rate for deposition consequently increases the thickness of deposit.

Figure 6. Thickness of deposited nanostructured CoNiCu alloys at different electrodeposition potentials.
4. Conclusion
The effect of alkyl polyglucoside (APG) concentration on the electrodeposition of nanostructured CoNiCu alloys particularly the deposited thickness has been studied. At higher APG concentrations compared with the critical micelle concentration (CMC) value, spherical shape nanoparticles of CoNiCu alloys can be produced. A thin layer of CoNiCu alloy nanoparticles with thickness of about 65 nm can be obtained from the electrolyte containing 3.25 wt.% APG by using electrodeposition potentials from -950 to -875 (SCE). The thinner deposited layer of nanoparticles obtained in the presence of APG is resulted by less electrons transfer during deposition process due to adsorption of APG molecules onto the ITO surface.

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