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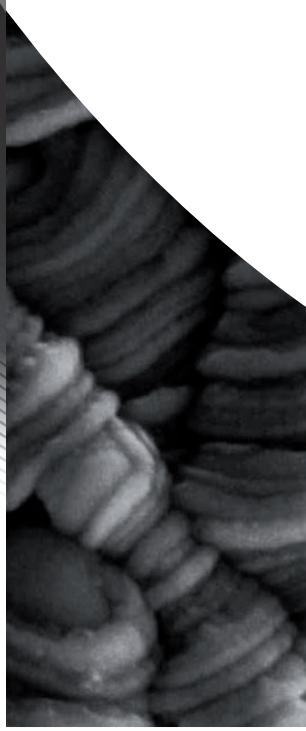

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Effect of magnetic field on current efficiency and crystal orientation of NiCo alloy using pulse electrodeposition technique

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The electrodeposition of NiCo alloy has been investigated in presence of various magnetic fields. The influence of superimposed magnetic field (0-0.5T) parallel to the electrode surface on current efficiency, surface morphology, preferred crystal orientation and electrochemical activity of Ni-Co alloy were studied. The maximum current efficiency was obtained by direct current at 100mA/cm^2 *with 0.4T. The optimized current density (100mA/*cm^2*) was pulsed at four different frequencies (10, 25, 50 and 100Hz) with the same magnetic field (0.4T). However, the superimposition of magnetic field significantly favors the preferred crystal orientation of (220) phase. Pulsed current deposits exhibit single orientation of (220) at lower magnetic field (0.4T) whereas direct current deposition require higher magnetic field (0.5T). Tafel plot shows that electro-catalytic activity and corrosion resistance property has improved when the deposit is having a preferred orientation of (220).*

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1. Introduction

The superimposition of magnetic field on the electrochemical process offers a powerful scientific tool in the research field and may open large potential applications. A number of studies have been done about the effect of magnetic field on electrodeposition of metals, alloys and composites [1-11]. They focused on the morphology [8] and crystallographic orientations of electrodeposits [1-7], and kinetics of electrodeposition process [11]. The most established impact on the electrochemical processes is the magnetohydrodynamic (MHD) effect [12]. The main driving force of the MHD effect is the Lorentz force, which occurs due to cross aligned components of the current and magnetic field lines. The effective MHD effect depends on the angle of cross alignment of current and magnetic field lines. When the magnetic field is applied perpendicular to the electric field (i.e. parallel to the electrode surface), the Lorentz force is maximal. This is a macroscopic effect, which induces additional convection to the electrolyte at the bulk as a result mass transport is increased [13-19]. It was found that convection could be also introduced on a microscopic level, when a magnetic field is applied parallel to the electric field. This is due to fluctuations in the current distribution at the electrode surface, which is called as micro- MHD effect [20]. The application of Permanent Parallel Magnetic Field (PPMF) to the electrode surface during the electrodeposi-

tion process alters chemical composition of the NiCo alloy [21] and reduces the limiting current densities and hence the electrodeposition rates are increased [22-23].

Many investigations have dealt with ways of increasing electro-catalytic activity of cathodes for the hydrogen evolution reaction (HER) in alkaline solutions. Research has been mostly focused on several areas of interest such as electrode composition and surface morphology to enhance activity and durability of electrode. Ni-based alloys exhibit a good electro-catalytic activity for hydrogen evolution in alkaline media [24-26], even though the high efficiency and durability of the electrode still required.

In the present work, the effect of magnetic field on current efficiency, morphology and crystal orientation of NiCo alloys when using direct or pulsed current is extensively studied. The investigation of electrocatalytic activity for HER of NiCo alloys were also carried out in alkaline solutions.

2. Experimental

The electrodeposition of NiCo alloys was carried out on 6 mm dia copper disc electrode (area 0.28cm^2) using a two electrode cell with a modified Watt's solution and its composition and condition are given in table 1. The pH was adjusted by adding 10 % sulphuric acid. The electrodeposition was operated at different current densities (50, 100, 150, 200 mA /cm^2) in the presence and absence of electro-magnetic field. Pulse electrodepositions with four different frequencies (10, 25, 50, 100Hz at 40% duty cycle) were carried out at optimized condition of 100mA/cm^2 with 0.4T. A glass cell having 5 cm diameter and 50 ml volume is used for electrodeposition of NiCo alloy. The distance between the cathode and the graphite anode was 3 cm. The electro-magnetic poles were placed so that the magnetic field fall parallel to the electrode surface and the whole electrodeposition setup is shown in *Figure 1*. Before the electrodeposition process the copper plates were activated by treating in the following sequence; degreasing with acetone, electrochemical cleaning with alkaline solution and washing with distilled water. Duration of electrodeposition processes were optimized to get 10 µm thickness of alloy for all condition. The thicknesses of the deposits were calculated from weight gained by the cathode.

Tab. 1: Bath composition and deposition condition for Ni-Co alloy coatings.

Constituents and parameters	Quantity
$NiSO_4$. $6H_2O$	240 g/l
$NiCl_2$.$6H_2O$	35 g/l
$CoCl_2$. $6H_2O$	35 g/l
H_3BO_3	32 g/l
Current densities	50-200mA/cm^2
pH	3.5±0.1
Temperature	308 K

The surface morphology of the deposit were investigated by scanning electron microscopy (HITACHI Model S-3000H operated at 20 kV) and the content of Co and Ni in the alloy were measured by Energy- Dispersive X-ray Spectroscopy (EDX) attached with the SEM. A (PANalytical, model X' per PRO) X- ray diffractometer with a Cu Kα radiation (λ=1.5418 Å) was used to determine the preferred crystal orientation of deposited NiCo alloy by using standard θ-2θ geometry. Crystallites sizes were calculated from the peak broadening of XRD pattern according to the Scherrer equation.

Potentiodynamic polarization test for both catalytic activity for HER and corrosion test were car-

ried out in a 1M KOH solution using three-electrode cell with a platinum foil as counter electrode, a saturated calomel electrode (SCE) as

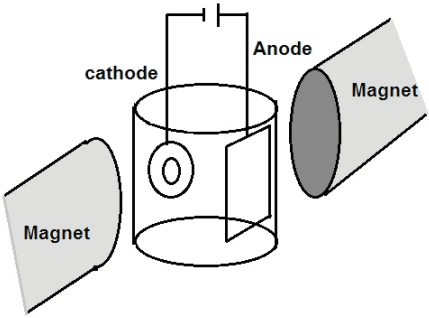

Fig. 1: Electrodeposition process setup

reference electrode and the deposited alloy on copper disc electrode as working electrode. Before the polarization studies, the samples were kept in 1M KOH solution for about 250 s to stabilize the open-circuit potential (OCP). Polarization curves were recorded by sweeping the electrode potential from -250mV to till reaching the breakdown potential with respect to OCP at a sweeping rate of 1 mV/s.

3. Results and discussions

3.1 Effect of magnetic field on current efficiency

The influences of superimposition of magnetic field (0 to 0.5T) parallel to the electrode surface on current efficiency of NiCo alloy were studied and it was shown in *Figure 2*. The current efficiency was calculated from the weight gained by the substrate after the electrodeposition.

Based on this investigation it is obvious that the rise on magnetic field would considerably increase the current efficiency. During the electrodeposition process in presence of magnetic field, the both nickel and cobalt ions experience Lorentz force which will enhance mass transport and thereby reduce the thickness of diffusion layer [22, 23]. Besides, water molecules do not experience Lorentz force and Paramagnetic force in the presence of a magnetic field. The highest current efficiency was obtained at 0.4T with 100mA/cm^2 whereas the current efficiency was

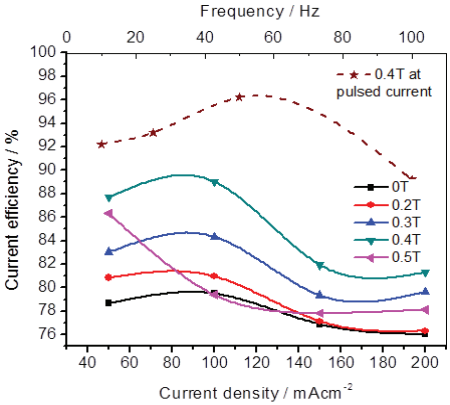

Fig. 2: Effect of magnetic field on current efficiency at four different current densities (50, 100, 150 and 200mA/cm^2 in solid line) and four different pulse frequencies (10, 25, 50 and 100Hz in dashed line)

decreased beyond 0.4T because the metal ions experiences very high Lorentz force. When pulsed at 100mA/cm^2 current density with four different frequencies (10, 25, 50 and 100Hz) at 0.4T, the current efficiency is increased significantly while the frequency increases up to 50Hz. The current efficiency gets decreased at 100Hz due to very short on- time [27].

3.2 XRD analysis

Figure 3 shows X-ray diffraction pattern of NiCo alloy electrodeposition at 100mA/cm^2 with dif-

ferent magnetic flux density as well as without magnetic field. The NiCo alloy forms solid solution with (111), (200), (220) and (311) crystal

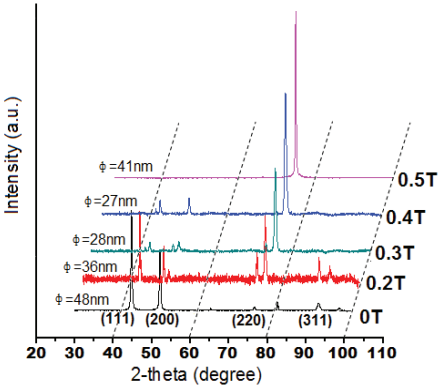

Fig. 3: XRD patterns of NiCo alloy on copper substrate obtained at 100mA/cm^2 with various magnetic field; 0T (without magnetic field), 0.2T, 0.3T, 0.4T and 0.5T

orientation. Generally the preferred orientation of (111) phase will be obtained at mechanically stirred condition [28, 29]. But, magnetic field has a little influence on (220) growth orientation at low magnetic field density. It is obvious that the intensity of the (220) orientation was enhanced with increasing MFD, while the other orientation was inhibited. Finally, the deposit seems to be a single orientation of (220) at 0.5T (100mA/cm^2). Preferential growth of the grains occurs in their easy magnetization axis when the magnetic field is induced [30]. However, the pulsed current deposits also exhibit single orientation of (220) phase at 0.4T (not shown) but direct current deposition requires more magnetic field (0.5T) to reach the single orientation of (220) phase. Because, hydrogen evolution is very low at pulsed current deposition it favors fresh nuclei as well as the preferred orientation in presence of magnetic field. The crystallite sizes of NiCo alloys were calculated from Debye-Scherrer equation; $D = 0.94\,\lambda / \beta \cos\theta$. Based on the above equation, the average crystallite sizes (ϕ) were calculated and the values vary from 27 - 48 nm for direct current and 18- 31 nm for pulsed current deposits.

3.3 Surface morphology and elemental composition of alloy

The surface morphologies and elemental composition of the deposited coatings were investigated by SEM and EDX attached with SEM, respectively. In order to compare the surface morphologies, the deposits were obtained from same electrolyte with and without magnetic field at 100mA/cm^2 and the results are shown in *Figure 4*. The surface of the NiCo alloy coating from the mechanically stirred condition is made up of pyramidal crystals surrounded by tiny particles. The size and the shape of the grains were significantly changed due to the application of magnetic field parallel to the electrode surface. Moreover, the Lorenz force leads to increase in the concentration gradient at the electrode surface and hence the grains become finer and more compact. In *Figure 4e* shows the more compact and uniform deposits by the application of pulse current because during the pulse current deposition the off-time favors the replenishment of metal ion in double layer and hence fresh nuclei is formed on cathode surface. But low frequency of 10 Hz is having more on-time, so that during the on-time metal ions deficiency takes place and thereby non uniform deposit (*Fig. 4c*) is obtained. At high frequency (100Hz) the grains are bigger in size (*Fig. 4f*) due to very short off- time and there is time-lack for replenishment of metal ion in double layer which reduces formation of fresh nuclei is reduced. However, the elemental composition of cobalt was enhanced in electrodeposited Ni-Co alloy. Because, magnetic moment of cobalt is greater

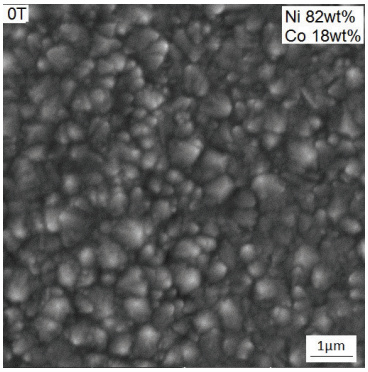

Fig. 4a

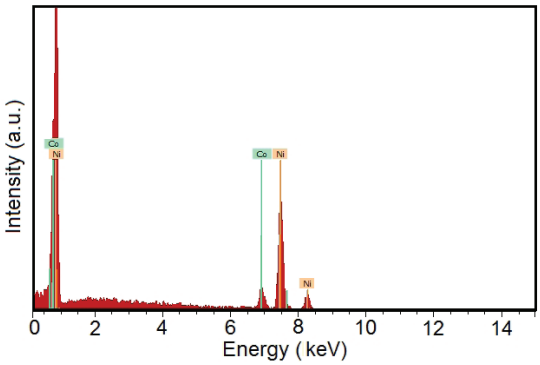

Fig. 4a$_1$

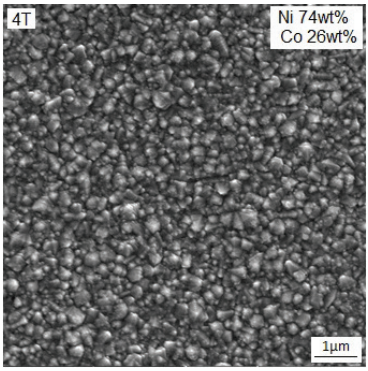

Fig. 4b

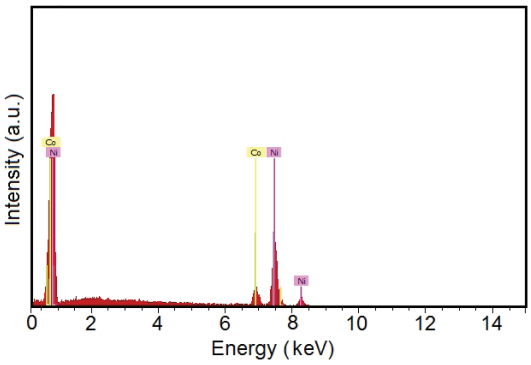

Fig. 4b$_1$

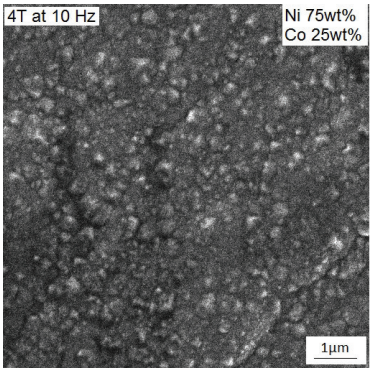

Fig. 4c

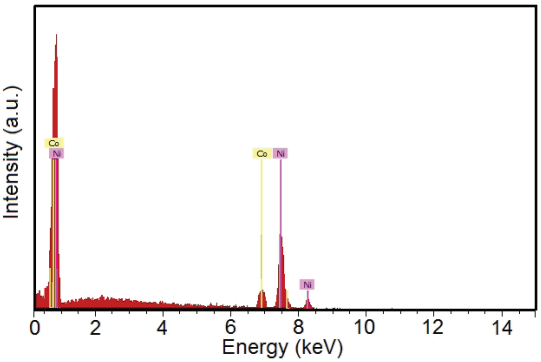

Fig. 4c$_1$

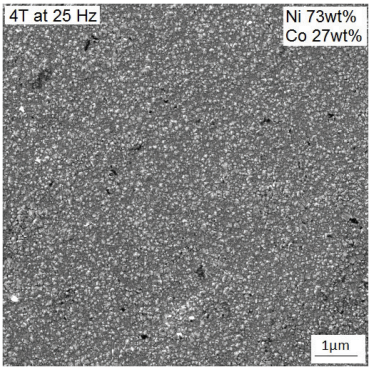

Fig. 4d

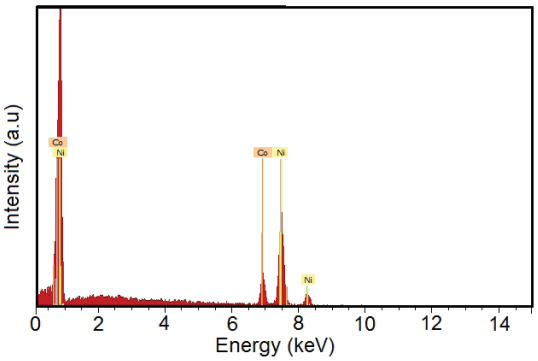

Fig. 4d$_1$

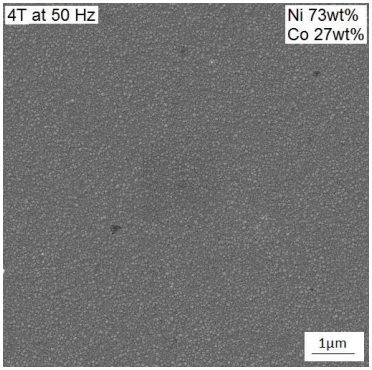

Fig. 4e

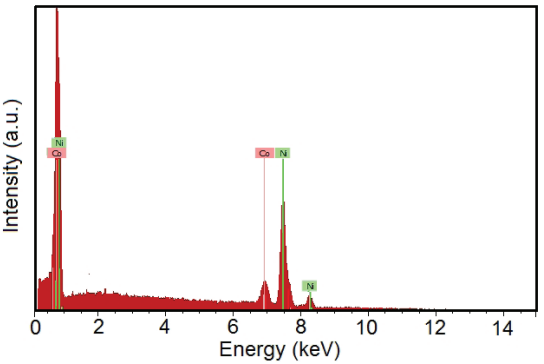

Fig. 4e$_1$

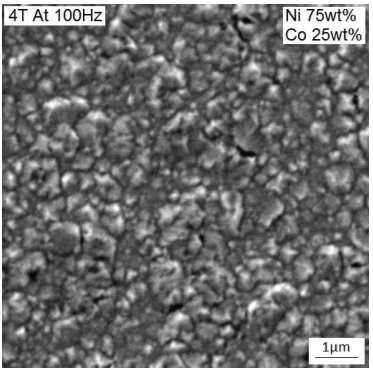

Fig. 4f

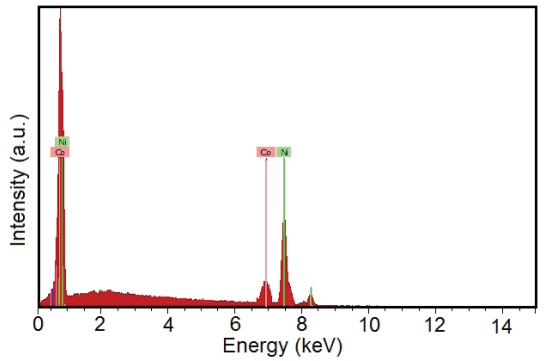

Fig. 4f$_1$

Fig. 4: SEM images of NiCo alloy on copper substrate obtained at 100mA/cm^2; a) 0T, b) 0.4T, c) 0.4T with 10Hz, d) 0.4T with 25Hz, e) 0.4T with 50Hz, f) 0.4T with 100Hz and their corresponding EDX spectrum are in right side of the SEM figures addressed by suffix '1'

Tab.2: Electrochemical parameters of alloys obtained from Tafel plot.

Deposit obtained at	j_c /Acm^{-2}	b/Vdecade^{-1}	j_{corr} /Acm^{-2}	E_{corr}/V
0T	2.044 x 10^{-12}	-0.132	1.986 x 10^{-3}	-1.139
0.4T	5.165 x 10^{-7}	-0.121	0.371 x 10^{-3}	-0.381
0.4T at 50Hz	2.601 x 10^{-7}	-0.118	0.282 x 10^{-3}	-0.370

than nickel and hence larger magnetic susceptibility is induced on Co^{2+} than Ni^{2+}. The cobalt inclusion is enhanced in NiCo alloy while applying magnetic field. There is marginal effect on elemental composition of alloy by the application of pulsed current.

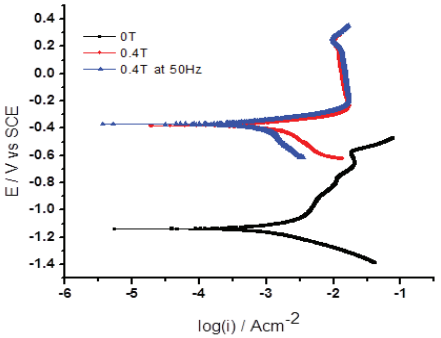

Fig. 5: Polarization curves of NiCo alloy obtained at 100mA/cm^2 with three different conditions (0T, 0.4T & 0.4T at 50Hz) in 1M KOH solution at room temperature; scan rate 1 mV/s

3.4 Potentiodynamic polarization tests

The potentiodynamic polarization technique is one of the methods to investigate electrochemical behavior of materials. Comparative investigations on electrochemical performance of NiCo alloys were carried out in 1M KOH solution. *Figure 5* shows polarization curves of NiCo alloys and the cathodic region corresponds to the hydrogen evolution whereas the anodic region corresponds to the corrosion resistance property of the alloys. In order to investigate electrocatalytic activity of as deposited alloys linear Tafel fit is performed on cathodic region of polarization curve. The kinetic parameters such as Tafel slope and exchange current density are derived from the Tafel relationship <1> which is given bellow

$$\log j = \log j_c + \eta/b \qquad <1>$$

Where, b is the Tafel slope; J_c the exchange current density and the values are summarized in table 2. The observed Tafel slopes are around 120mV/decade, which is in good agreement to the general model for the HER mechanism. The increased electrocatalytic activity is attributed to the grain refinement on surface morphology as well as an improvement in the intrinsic electrocatalytic properties of the material [31]. The E_{corr} and j_{corr} are obtained from Tafel extrapolation and the results are given in table 2. It is noticed in table 2 the NiCo alloy deposited by pulsed current at 50Hz with 0.4T has better corrosion resistance as well as electrocatalytic activity than the other alloys. However, the alloys having preferred orientation of (220) exhibits better electrocatalytic activity than the polycrystalline of NiCo alloy obtained from without magnetic field.

4. Conclusion

The electrodeposition of NiCo alloys were carried out by varying current density as well as magnetic field. The optimized condition for higher current

efficiency is 100mA/cm^2 at 0.4T. From the optimized condition pulsed current deposition were also carried out at four different frequencies. The superimposition of magnetic field on electrodeposition of NiCo alloys were investigated on current efficiency, surface morphology, crystal orientation and electrochemical property. The current efficiency and the surface morphology are significantly improved by applying pulsed current in the presence of magnetic field. Difference in magnetic susceptibility of metal ion alters the elemental composition of the alloy in presence of magnetic field. The preferential growth of (220) phase can be achieved by using pulsed current at lower magnetic field. The electrochemical properties of NiCo alloy in alkaline medium shows the enhancement of electro-catalytic activity and corrosion resistance property and this is due to the preferred orientation of (220) deposit.

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