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Nickel electrodeposition from acidicchloride bath containing SDS additive

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Abstract

The electrodeposition of nickel on to steel substrates from acidic chloride electrolyte containing sodium dodecyl sulphate (SDS) has been investigated using the potentiodynamic polarization technique. The optimum bath composition and operating conditions necessary to produce a highly adherent nickel deposit have been found to be: 150 g/L $NiCl_2.6H_2O$, 115 g/L HCl and 1.94×10^{-3} g/L SDSat pH1.5, i =0.33 A dm^{-2}, t=10 min and at 20ºC. The results indicate that the addition of SDS greatly increase the cathodic polarization curves as a result of its adsorption on the steel surface. Moreover, the cathodic polarization decreases with increasing either the nickel content in the bath or the bath temperature.XRD analysis showed that the nickel deposit exhibit face centered–cubic (fcc) structure with the preferential orientation (111).

Keywords: Nickel deposition; Polarization; Sodium dodecyl sulphate; Cathodicefficiency; XRD analysis

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1. Introduction

Nickel electrodeposition is one of the oldest protective and decorative metallic coating for steel, brass and other basis metals. Therefore, intensive studies were carried out to obtain nickel electroplates suitable for different purposes from, for example chloride, sulphamate, fluoborate, chloride-sulphate, acetate, citrate, glycine and glutamate baths, in addition to the well-known Watts bath, with or without additives [1-15]. Surfactants represent an important category of organic compounds, which are used widely in industry especially inelectrodeposition of metals [16-19] and as corrosion inhibitors for metals in differentacidic solutions [20-23]. In this work, the electrodeposition of nickel from acidic chloride electrolyte containing sodium dodecyl sulfate (SDS) as an anionic surfactantwas investigated. In addition the study aims to throw light on the mechanism of nickel electrodeposition.

2. Experimental

All the plating baths and reagents were prepared from Analar chemicals without further purification, and doubly distilled water. The compositions of the baths examined for nickel electrodeposition are given in Table 1. However,the optimum bath composition for Nielectrodeposition comprised of: 150 g/L $NiCl_2.6H_2O$, 115 g/L HCl and 1.94 x 10^{-3} g/L SDS, pH 1.5 and at 20°C. For electrodeposition, a steel cathode and platinum sheet anode, both of dimensions 2.5 cmx3.0 cm, were used. The plating cell used was a rectangular Perspex trough (10 cmx3 cm) with vertical grooves on each of the side walls, with which to fix the electrodes. Before each run, the steel cathode was mechanically polished with different grade emery papers (600, 800, 1000 and 1500) and then washed with distilled water, rinsed with ethanol and weighed. Direct current was supplied by a D.C. power supply unit (GPS-3030D). The cathodic current efficiency, f (%), was determined with the help of a Cu-coulometer ($f = w_{exp}/w_{th}$) where w_{exp} is the weight of the deposit obtained experimentally and w_{th} is the weight of the deposit calculated theoretically according to Faraday’s law.

Table 1. Concentration of the Ni-electrodeposition baths used (pH of each of these baths ~ 1.5).

Bath No.	Concentration g/L		Concentration g/L
	$NiCl_2.6H_2O$	HCl	SDS
Ni-1	150	115	-
Ni-2	150	115	1.94 x 10^{-3}
Ni-3	150	115	3.88 x 10^{-3}
Ni-4	50	115	1.94 x 10^{-3}
Ni-5	100	115	1.94 x 10^{-3}
Ni-6	75	115	1.94 x 10^{-3}

Deposition was carried out for 10 min in each case at 20°C.A potentiostat/galvanostat (EG & G model 273) controlled by a computer wasused for the electrochemical measurements.All potentials were measured relative to a saturated calomel electrode (SCE). To avoid contamination, the reference electrode was connected to the working cathode *via* a bridge provided with a Luggin-Haber tip and filled with the solution under test. Potentiodynamiccathodicpolarization curves were recorded using steel substrates by sweeping the potentialfrom the rest potential in the negative direction with a scan rate of 10 mV s^{-1}.The crystalline structure ofthe nickel thin film deposited on to the steelsurface from the optimum bath was examinedby X-ray diffraction analysis usinga Philips PW 1390 diffractometer (40 kV, 20 mA) with Ni filter and Cu Ka radiation.

3. Results and discussion

3.1 Cathodic current efficiency:

Preliminary experiments were carried out for the electrodeposition of nickel from the acidic chloride solutions without addition of SDS. It is found that in the absence of SDS, only strong hydrogen evolution was observed. It is probable that the strong hydrogen evolution in this acidic solution inhibits the diffusion of Ni^{2+} ions to the cathodic diffusion layer possibly to concurrent hydrogen adsorption and bubbles formation [24,25]. On the other hand, in the presence of SDS, both hydrogen evolution and nickel deposition occur simultaneously. The additive molecules are thought to adsorb on the active sites available for hydrogen evolution reaction. This phenomenon increases the overpotential for this reaction. Consequently, the presence of SDS in the solution inhibits the hydrogen evolution and therefore allows the deposition of nickel.

The effect of nickel content in acidic chloride solution containing HCl, SDS at 20°C and current density of 0.33 A dm^{-2} on cathodic current efficiency, f%, of nickel deposition is shown in Fig. 1. The results imply that the current efficiency is very low as expected from this acidic solution. The f% increases with increasing the nickel content of the bath up to 100 g/L $NiCl_2.6H_2O$ and then tends to attain a steady state value of 14.6%. The increase in f% with increasing the nickel content in the bath agrees well with the cathodic polarization curves (Fig.1).

Fig. 2 shows the effect of bath temperature on the cathodiccurrent efficiency of nickel electrodeposition from the acidic chloride bath containing 1.94 x 10^{-3} g/L SDS at current density of 0.33 Adm^{-2}. It is observed that, the f% for Ni deposition decreases sharply with rising temperature up to 45°C and then tends to reach a steady state value of 7.3%. The most likely explanation for decreasing the f% is related to the enhancement of the rate of hydrogen evolution at high temperature as expected from the polarization curves. These results indicate that the decrease in cathodic polarization with increasing temperature observed in Fig.2 is mainly due to the effect of temperature on the activation overpotential of hydrogen evolution reaction.

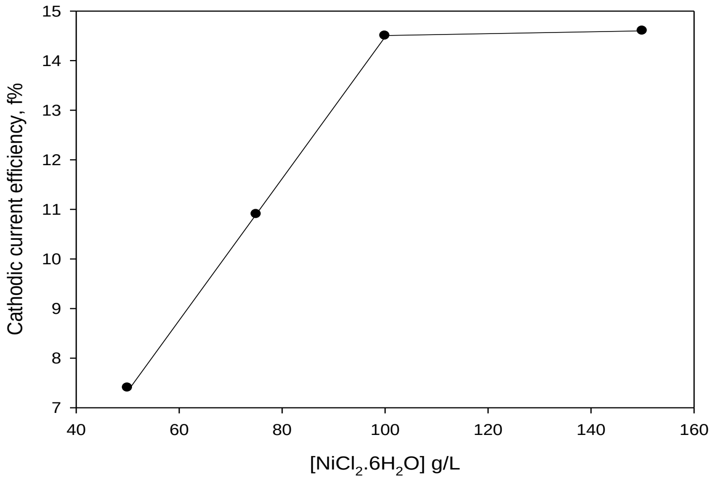

Fig. 1. Effect of $NiCl_2$ concentration on the cathodic current efficiency for Ni-electrodeposition at 20°C, i = 0.33A dm^{-2}, t = 10 min.

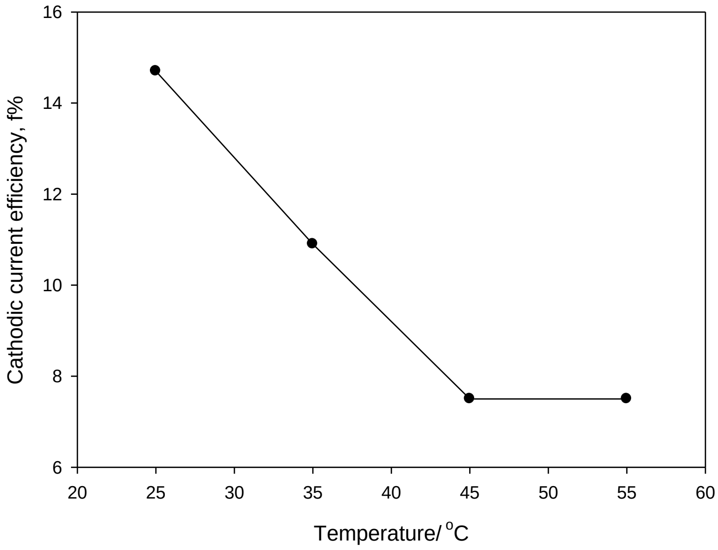

Fig.2. Effect of bath temperature on the cathodic current efficiency for Ni-electrodeposition from bath Ni-2, i = 0.33A dm^{-2}, t = 10 min.

The effect of applied current density on cathodic current efficiency of nickel deposition from the acidic chloride solution containing SDS at 20°C is shown in Fig. 3. Increasing the applied current density from 0.2 to 1.0 Adm^{-2} decreases markedly the f% of nickel deposition. At high current densities a sharp increase of hydrogen evolution occurs. As a result it enhances the rate of hydrogen evolution and retards the deposition rate of nickel. From the above results, it is found that bright, smooth and adhere deposits of nickel were electrodeposited from bath containing: 150 g/L $NiCl_2.6H_2O$, 115 g/L HCl and 1.94×10^{-3} g/L SDS at 20°C and current density of 0.33 A dm^{-2}.

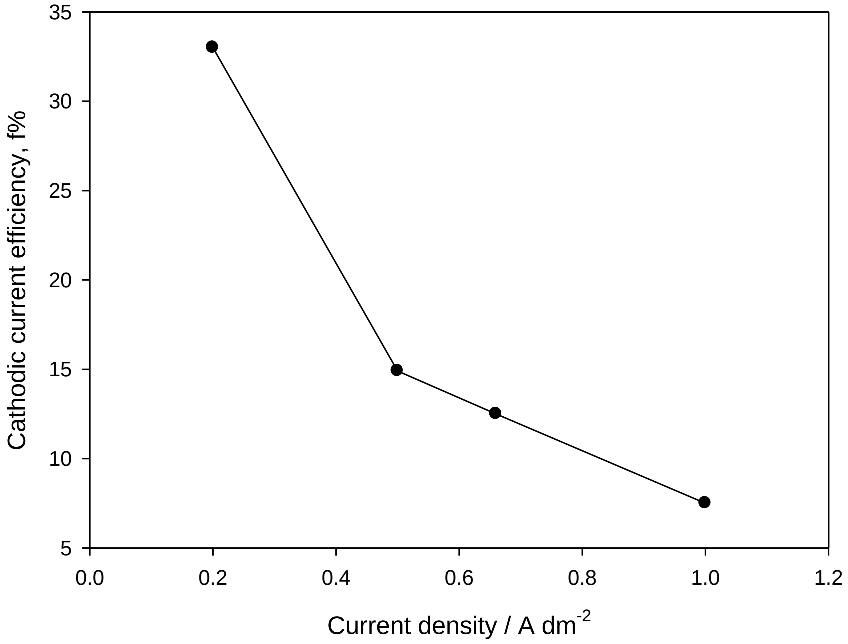

Fig.3. Effect of current density on the cathodic current efficiency for Ni-electrodeposition from bath Ni-2 at 20^{o}C , t = 10 min.

3.2 Potentiodynamiccathodic polarization curves

Figs. 4-6 represent the potentiodynamiccathodic polarization curves during electrodeposition of nickel from acidic chloride bath under different experimental conditions onto mild steel substrates. The curves were swept from the rest (the zero current) potentials to more negative potential values with scan rate of 10 mVs^{-1}. Inspections of the data reveal that the deposition of nickel occurs simultaneously with evolution of hydrogen gas. Therefore, these curves represent the simultaneous discharge of both H^+ and Ni^{2+} ions. The following discharge reactions are possible on the cathode surface:

$2H^+ + 2e \leftrightarrow H_2$

$Ni^{2+} + e \leftrightarrow Ni^+_{ads}$

$Ni^+_{ads} + e \leftrightarrow Ni$

$Ni^{2+} + Ni^+_{ads} + 2e \leftrightarrow Ni^+_{ads} + Ni$

$H^+ + Ni^+_{ads} + e \leftrightarrow Ni^+_{ads} + H_{ads}$

$Ni^+_{ads} + H_{ads} + e \leftrightarrow Ni + H_{include}$

This mechanism was proposed by Epelboin et al [26], to describe and propose all possible reactions for Ni deposition from acidic solutions.

Fig. 4 shows that theaddition of SDS into the chloride bath resulted in marked increase in cathodic polarization. Such effect of SDS could be a result of its adsorption on the cathode surface blocking the active sitesavailable for the cathodic reactions. It is assumed that SDS molecules are preferentially adsorbed on the active sites available for hydrogen evolution reaction. As a result, SDS retards the hydrogen evolution reaction and consequently enhances the deposition rate of nickel. As the concentration of SDS increases, the adsorption density of SDS on the cathode surface becomes sufficiently high and consequently the inhibitory effect of SDS for H_2 evolution increases.

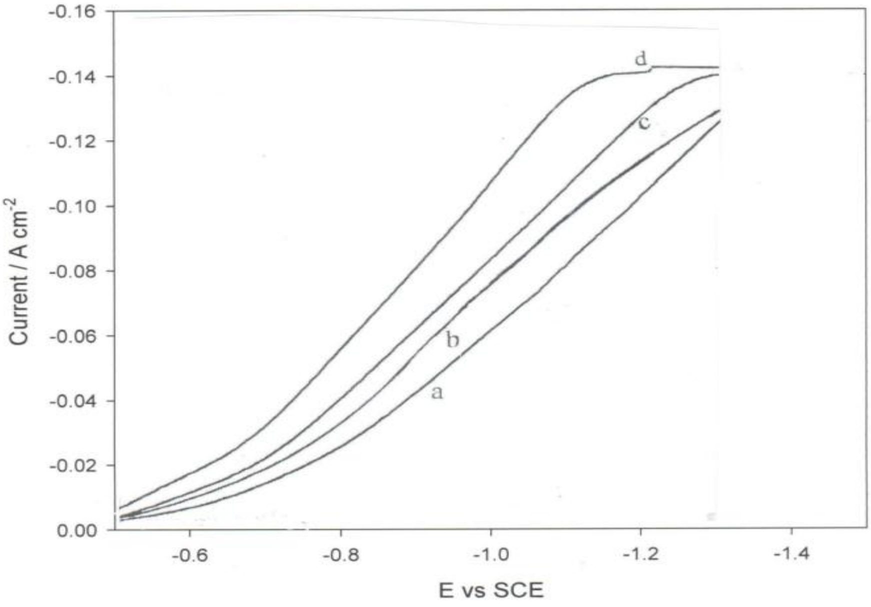

Fig.4. Effect of SDS concentration on the potentiodynamiccathodic polarization curves for Ni-electrodeposition for baths; Ni-3 curve a; Ni-2 curve b; Ni-1 curve c, at T = 20°C, scan rate 10 mVs^{-1}.

Fig. 5 illustrates the effect of $NiCl_2$concentration (50-150 g/L) in the bath on the cathodic polarization. It is observed that the cathodic polarization curves were shifted towards less negative potentials with increasing the nickel content in the bath. This trend in cathodic polarization is related to the decrease in concentration type of polarization associated with the deposition of nickel as a result of increasing the Ni^{2+} ion concentration in the diffusion layer. Similar behavior of decreasing the polarization curves with increasing metal ion concentration in the bath during the metal deposition was recorded previously [27,28].

Fig. 6 displays the influence of bath temperature on the cathodic polarization curves. It is found that the cathodic polarization shifts towards the less negative potentials. This behavior may be due to the depolarization effect of temperature on the activation type of polarization associated with the discharge of both H^+ and Ni^{2+} ions on the cathode surface. Moreover, a rise in temperature enhances the concentration of the two ions in the diffusion layer as a result of increasing their diffusion rates [16]. An increase in temperature also increases the deposition of SDS on the cathode surface. It seems that the effect of temperature is more pronounced on the discharge of hydrogen rather than on the deposition of nickel.

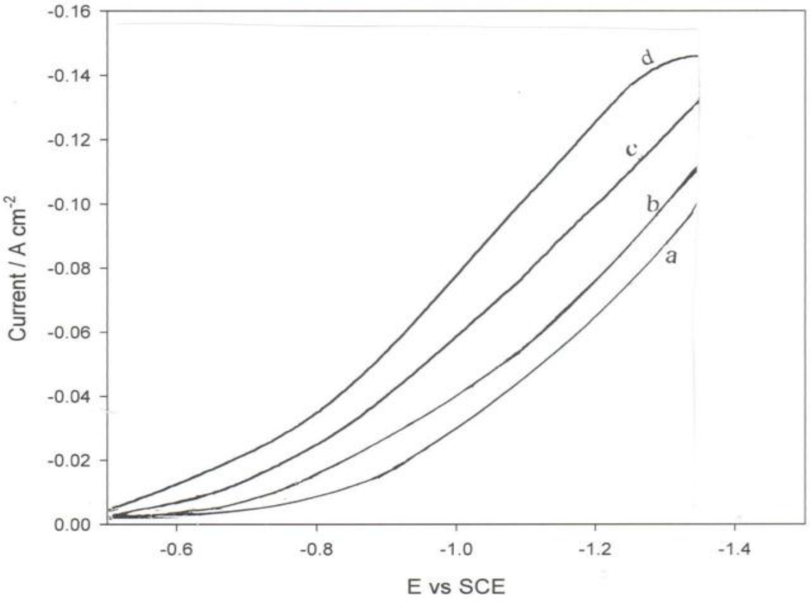

Fig. 5 Effect of $NiCl_2$ concentration on the potentiodynamiccathodic polarization curves for Ni-electrodeposition for baths; Ni-4 curve a; Ni-5 curve b; Ni-2 curve c; Ni-1 curve d at T = 20°C, scan rate 10 mVs^{-1}.

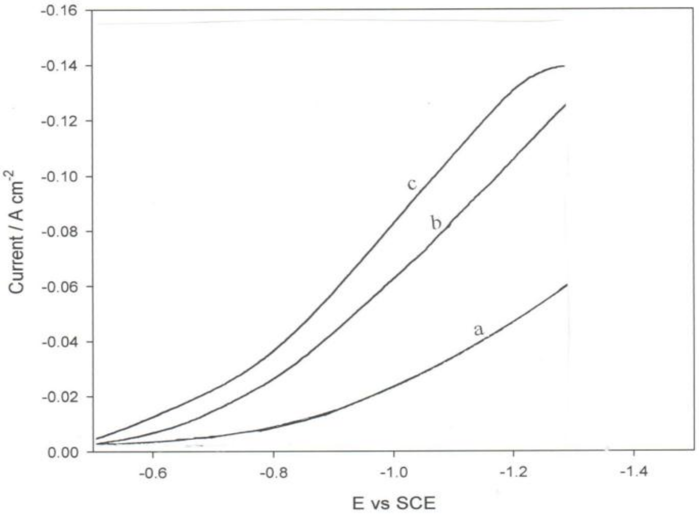

Fig.6 Effect of bath temperature on the potentiodynamiccathodic polarization curves for Ni-electrodeposition for bath Ni-2; T = 27°C curve a; T = 37°C curve b; T= 47°C curve c; T = 57°C curve d, scan rate 10 mVs^{-1}.

3.3 X-ray of nickel deposits:

X-ray diffraction (XRD) analysis of the as-deposited nickel obtained from bath containing:150 g/L $NiCl_2.6H_2O$, 115 g/L HCland 1.94 x 10^{-3} g/L SDS at 20°C and current density of 0.33 A dm^{-2} showed α-phase with face centered–cubic (fcc) structure. The preferential orientation of this structure is (111) with small intensity since the thickness of the deposit is small. The other peaks are related to the substrate as shown in Fig. 7.

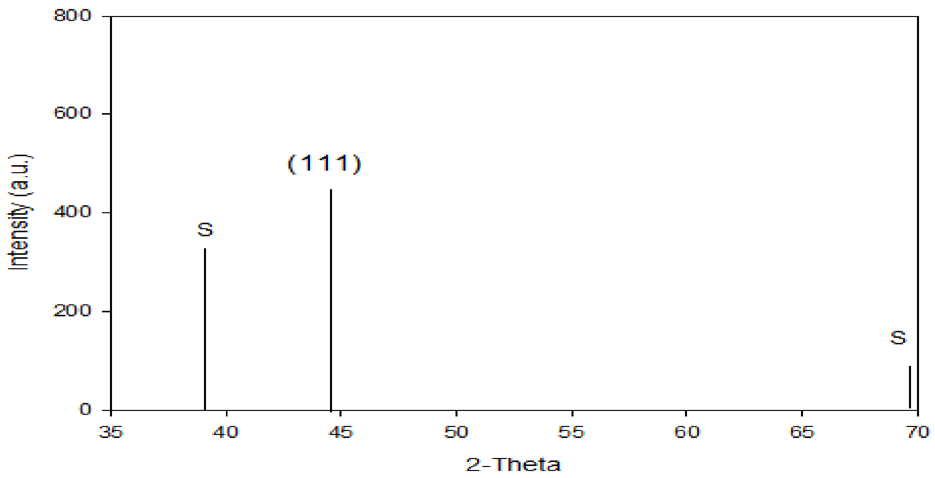

Fig. 7 X-ray diffraction patterns for Ni-electrodeposition for bath Ni-2 at i = 0.33A dm^{-2}, t = 10 min, T = 20ºC (S is the substrate).

Conclusions

Analysis of the results led to the following conclusions:

1. The presence of SDS in the solution inhibits the hydrogen evolution and therefore allows the deposition of nickel.
2. The f% of Ni deposition increases with increasing the nickel content in the bath but decreases with rising the bath temperature.
3. Increasing the applied current density from 0.2 to 1.0 Adm^{-2} decreases markedly the f% of nickel deposition.
4. Addition of SDS into the chloride bath resulted in marked increase in cathodic polarization as a result of its adsorption on the cathode surface.
5. The cathodic polarization decreases with increasing either the nickel content or the bath temperature.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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