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Electrodeposition of Nickel from its Sulphate Salt in a Ethylene Glycol–Water Mixture

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The effect of different factors, such as current density (CD) and annealing temperatures, on cathode current efficiency (CCE), microhardness and quality of electrodeposited nickel which obtained from a bath containing 0.2 M nickel sulphate and 0.2 M boric acid as electrolyte and buffer respectively in a glycol-water mixture, was investigated. Bright and adherent nickel deposits with high CCE were produced at a CD of 2.0 Adm^{-2} and 30°C. The microhardness of the deposits decreased with increasing annealing temperature. The structural features of the deposits were examined by SEM and TEM. The results have been explained by taking into account the hydrogen content in the deposits.

Key Words: Electrodeposition, Ni coatings, Ethylene glycol-Water mixture.

INTRODUCTION

Nickel possesses a combination of physical and chemical properties and is highly susceptible to passivation which makes it widely useful as a coating metal. Nickel electrodeposits are widely used industrially to improve corrosion and wear resistance or to prevent contamination of a chemical product. Earlier studies[1-4] indicated that there has been much interest in the electrodeposition of metals and alloys from organic solvents, because of the possibility of enhancing ion solvation owing to different dielectrical properties, the different natures of hydrogen bonding and alter ion size, *etc*.

The mixed solvents offer a variety of possibilities and an effective control of the diffusion and migration of metals ions due to the change in the solution properties. Moreover, the composition of the solvent can be accurately varied and the consequent change in the properties of the electrodeposit can be easily attributed to the effect of the content of co-solvent by way of change in the physico-chemical properties such as viscosity, conductance, solvation of the metal ion, checks in the concentration of hydrogen ions and formation of colloidal hydroxides in the catholyte.

Experiments carried out for electrodeposition of nickel from mixed baths[4,5] have shown interesting features and led to some promising results. The influence of heat treatment on the nickel deposits which produced particularly from binary mixtures has not been reported in the literature. This may reveal some interesting characteristics. Since the heat treatment affects the physico-mechanical properties and structure of deposits which are also related to the hydrogen or other inclusions to some extent.

Keeping in view the above and the importance of industrial and scientific values of nickel electrodeposits, it was planned to electrodeposit nickel from binary mixture and evaluate the effect of different plating variables on the cathode current efficiency, quality, microhardness and structure of the deposits.

EXPERIMENTAL

Typical bath composition and condition of electrolysis for ethylene glycol-water mixtures are shown in Table-1.

The 2, 5, 8 and 11 mol % (percent) ethylene glycol-water mixtures were prepared using double distilled water. Water was added to ethylene glycol (EG) and the mixture was allowed to stand for sometime before dissolving nickel sulphate and boric acid as electrolyte and buffer respectively in mixed solvents. Rectangular copper strips of dimensions 2.0 × 1.0 × 0.01 cm were chosen as cathodes and then mechanically polished, cleaned, electropolish and lightly pickled. The nickel sheets with high purity were used as anodes. The microhardness measurements of the surface of as-deposited nickel plates were performed with a Tukon Wilson hardness tester using a 136° vickers diamond pyramid indenter. The electrodeposited specimens were vacuum sealed in a glass tube and annealed at various temperatures (200-700°C) for 2 h.

TABLE-1

Parameters	Values
Nickel sulphate ($NiSO_4 \cdot 6H_2O$)	0.1-0.5 M
Boric acid (H_3BO_3)	0.2 M
Current density	0.4-2.8 Adm^{-2}
Bath temperature	20-50ºC
Annealing temperature	200-700ºC
Agitation	None

RESULTS AND DISCUSSION

The influence of change in ethylene glycol content (2, 5, 8 and 11 mol % ethylene glycol-water mixture) under otherwise indentical conditions on the characteristics of nickel electrodeposits, were studied first and 5 mol per cent ethylene glycol-water mixture with 0.2 M nickel sulphate and 0.2 M boric acid was found to be the appropriate composition (optimum) from which the satisfactory nickel deposits with respect to the quality, brightness and hardness can be obtained.

Taking into consideration the above, the influence of different plating variables on the quality, cathode current efficiency, microhardness, microstructure and hydrogen content of nickel deposits from a mixture of water and 5 mol % ethylene glycol, systematically investigated.

Effect of current density

The influence of current density on cathode current efficiency (CCE), quality and microhardness of nickel electrodeposits was investigated between 0.4 to 2.8 A dm^{-2} at 30°C using optimum bath composition (5 mol % ethylene glycol-water, 0.2 M nickel sulphate and 0.2 M boric acid). The quality of deposits is seen to improve with increasing current density up to 2.0 A dm^{-2}, but all deposits were not much smooth and finally the bright, adherent and smooth nickel deposits have been produced at a current density of 2.0 A dm^{-2} and it is also observed that the cathode current efficiency increased with an increase in the current density (Fig. 1) and touched 99.80 % at optimum current density (2.0 A dm^{-2}). Moderately high current density leans to rise the rate of nucleation, resulting in high cathode current efficiency and fine-grained deposits.

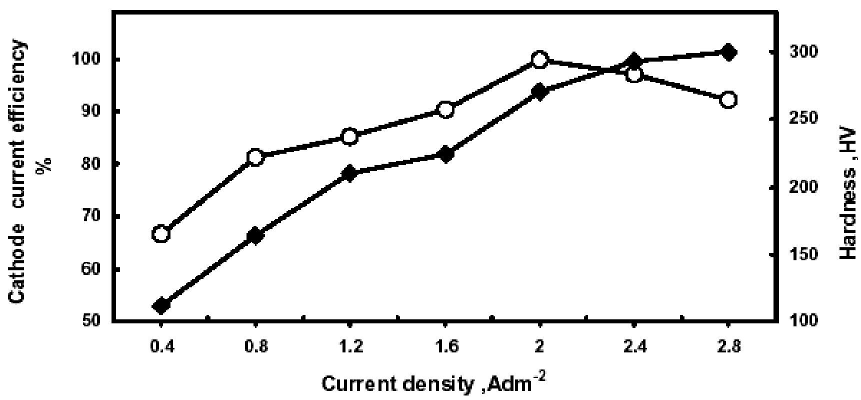

Fig. 1. Effect of current density on cathode current efficiency (–o–) and microhardness (–◆–): 5 mol % ethylene glycol-water, 0.2 M nickel sulphate, 30ºC (optimum condition)

A further increase in the current density (> 2.0 A dm^{-2}) was not advantageous, because of the deposits gradually diminishes to semi-bright with greyish streaks at central portions of plate at 2.4 A dm^{-2} and then dull greyish deposits with a marked tendency of peel off at the edges were found at current density of 2.8 A dm^{-2}. An increase in the current density beyond a certain value causes the plating solution near the cathode to be depleted of the metal ions required for discharge. These ions must diffuse from the bulk of the solution and the local change in concentration makes the deposits irregular, rough and non-adherent. The non-adherent deposits obtained at high current densities may also be attributed to the development of internal stress in the deposits. The cathode current efficiency showed reducing trend from 99.80 (at 2.0 A dm^{-2}) to 92.41 % (at 2.8 A dm^{-2}) with increasing current density.

Lowering of the CCE can be related to the evolution of gas bubbles (H_2) around the cathode surface during the electrodeposition and such gas evolution would also influence the physico–mechanical properties of the deposits. As it is observed (Fig. 1) the microhardness of nickel electrodeposits significantly improved from 112 to 300 HV with increase in current density. Initially the microhardness of the deposits considerably increased up to 2.0 A dm^{-2}, thereafter, there was gradual increment. This enhancement of hardness can be due to the reduction in the grain size of the deposits due to increase in the current density. Though, an increase in hardness is also caused by the inclusion of colloidal hydroxides[6].

Effect of bath and annealing temperatures

The effect of variation of bath temperature (20-50°C) on the cathode current efficiency, quality and hardness of nickel deposits was investigated at optimum current density (2.0 Adm^{-2}) using the optimum bath composition (0.2 M nickel sulphate, 0.2 M boric acid and 5 mol % ethylene glycol-water). It is found that the CCE increased when bath temperature was raised from 20 to 30°C and thereafter a declining trend was observed from 99.80 to 60.95 % by rising temperature up to 50°C (Fig. 2).

Hazy-bright deposit with some greyish lines was produced at 20°C, but bright and adherent deposits were obtained when bath temperature is increased to 30°C. Brightness of the deposits diminished when the temperature was raised above 30°C. The deposits tended to be semi-bright but milky on the edges (40°C) and dull with light grey streaks (50°C) retaining their adherence, respectively with increasing temperature of the bath.

The microhardness of the deposits regularly decreases (from 279 to 246 HV) with raising the bath temperature from 20 to 50°C (Fig. 2), because, usually coarse deposits with a larger grain size are produced at higher temperatures and generally are softer which have also been reported earlier[3,7]. Keeping in the view, the microhardness value of nickel deposits which obtained under optimum conditions (2.0 A dm^{-2} and 30°C) is found to be 271 HV.

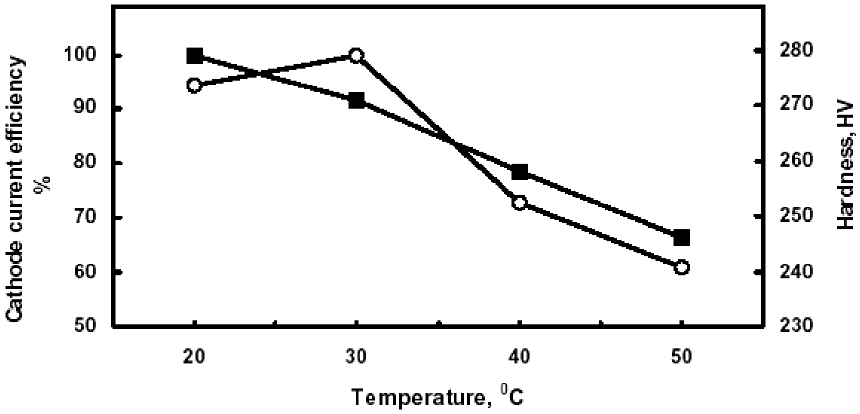

Fig. 2. Effect of temperature on CCE (–o–) and microhardness (–■–): 5 mol % ethylene glycol-water, 0.2 M nickel sulphate, current density 2.0 A dm^{-2}

The nickel deposits, produced under optimum conditions (2.0 A dm^{-2} and 30°C), were submitted to annealing at various temperatures (200-700°C) and hardness of thus annealed deposits is depicted in Fig. 3. It is observed that there is a declining tendency in the microhardness (263-138 HV) of the deposits with respect to the elevating of temperature (Fig. 3).

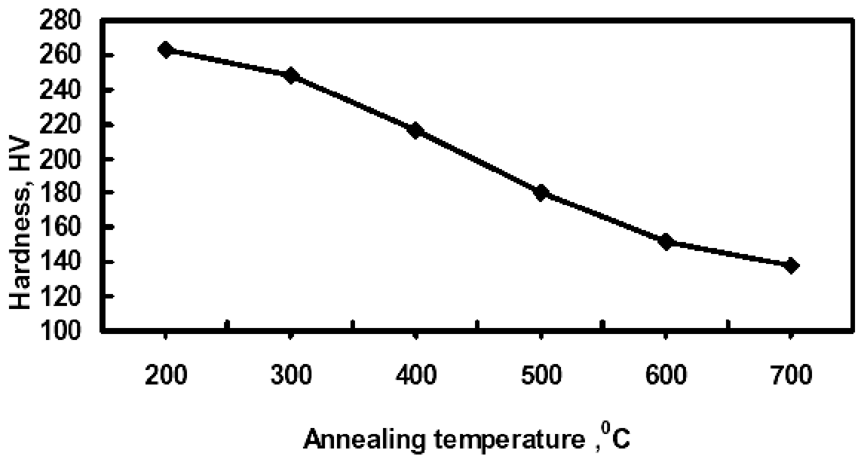

Fig. 3. Effect of annealing temperature on microharndess nickel deposits obtained under optimum conditions

The decrease in hardness in the range of 200-600°C is more significant than in higher range. Such trends can be considered as indications of the occurrence of different physical phenomena in these ranges. The lowering of hardness is probably related to the relief in internal microstresses.

The changes in the crystallites in the deposits that existed in the metal as a result of both cold working and the recrystallization process in the deposits and may be due to the removal of occluded hydrogen from the deposited nickel film as a result of the heating in vacuum which was confirmed subsequently by SEM studies. Such a decrease in hardness with increasing annealing temperature for nickel deposits has also been previously reported[4,8].

Conclusion

The satisfactory deposits (bright, adherent and smooth) with high CCE (99.80 %) and desirable hardness (271 HV) were produced at a current density of 2.0 A dm^{-2} and 30°C. The hardness decreased with increasing annealing temperature. Mixed bath (present work) seems to be advantageous as compared to the conventional aqueous bath with respect to the quality and CCE of the deposits.

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