compared to the conventional aqueous bath with respect to the quality, CCE and structure of the deposits.

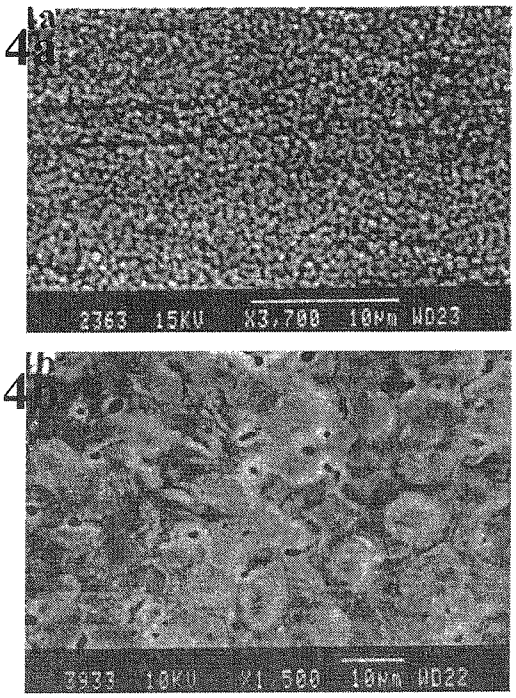

Fig. 4. SEM micrographs of deposited nickel (4a) under optimum conditions (4b) annealed at 700 °C

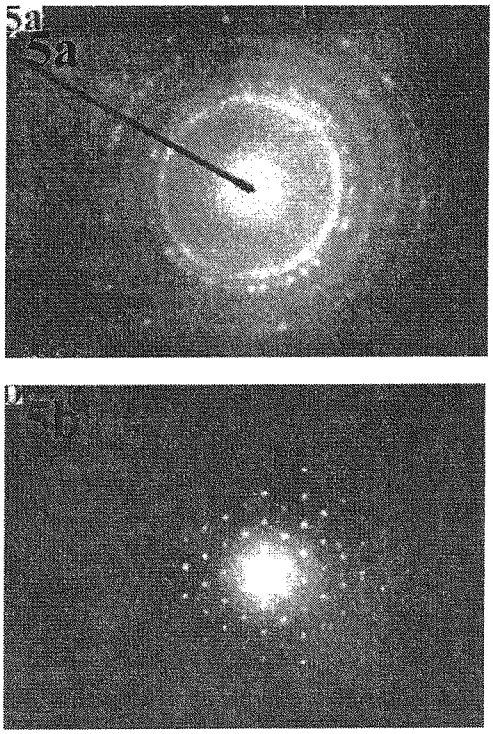

Fig. 5. TEM micro graphs of deposited nickel obtained under optimum conditions.

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The decrease in hardness with increase in temperature can be due to the increase in grain size; indeed the ions are more mobile at higher temperatures which favors the equilibrium deposition and the formation of larger grains with a low free- energy.

The effect of annealing temperature (200- 700 °C) on microhardness of the electrodeposited nickel, obtained under optimum conditions. (0.5 M nickel chloride, 2.2 Adm $^{-2}$. and 40 °C), was studied. There was considerable decrease in hardness, from 375 HV at 200 °C to 171 HV when annealing temperature was elevated up to 600°C and thereafter decreased only slightly. The decrease in the hardness may be due to relief in internal microstresses in the deposits which might have existed in the metal during deposition and also occurrence of recrystallization at relatively higher annealing temperature. Such observation of decrease in hardness with increasing annealing temperature for nickel deposits have also been reported elsewhere [10, 11].

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) studies

The SEM micrograph indicated that microcrack deposits have been produced at a CD of 2.2 Adm $^{-2}$. and 20 °C, but with increasing the bath temperature up to 40 °C, the fine- grained deposits with few mild micro cracks at cathode corners have been obtained (Fig. 4 a).

The microcracks observed at certain typical portion of the cathode corners may arise because a higher current density always exists at edges and corners of the plates and also it may be related to the development of internal stress as a consequence of the formation of fine-grained and dense deposits. When as- deposited nickel which produced under optimum conditions (0.5 M nickel chloride, 2.2 Adm^{-2}. and 40°C) subjected to annealing temperature, there was a remarkable alteration in the microstructure of the deposits, SEM micrographs revealed almost insignificant structural changes and a slow recovery at low annealing temperatures. But a new set of grains (recrystallization process) replaced the original cold-worked set of grain at a relatively higher temperature, i e, 500°C and well-defined grain growth has been observed at 700 °C (Fig- 4b). It is clearly marked with distinct grain boundaries. Fig. 4b clearly shows the presence of pores along the grain boundaries. These pores may have developed as a result of escaping hydrogen gas or inclusions in the deposits.

The transmission electron microscopic (TEM) studies were carried out for as- deposited nickel which obtained under optimum conditions. The ring diffraction patterns of the deposits (Fig. 5a) indicate that the deposits are fine- grained and polycrystalline in nature. The patterns do not indicate clearly the development of any preferred orientation in the deposits, rather random orientation is witnessed. Such absence of texture may be due to the fact that a critical grain size, above which preferred orientation can develop has not been attained in the present case. Figure 5b shows the selected area diffraction pattern obtained from one of the grains (Fig. 5a) which confirms the single-crystal nature of the grains.

Analysis of the diffraction pattern shows uniform classic ring pattern of the face centered cubic (fcc) lattice for the deposited nickel.

Conclusion

Bright, adherent and smooth nickel deposits with high CCE (99.3%) and moderately high hardness (390 HV) can be obtained at a CD of 2.2 Adm^{-2} and 40°C from a bath containing 5 mol.% EG-water, 0.5 M nickel chloride and 0.2 M boric acid (optimum conditions). The hardness decreased with increasing annealing temperature.

SEM studies revealed that the deposit produced at optimum conditions is fine-grained and re crystallization and also grain growth has been observed due to the annealing. TEM investigations indicated that the deposits are polycrystalline and randomly oriented wi[+] almost no structural defects. Mixed bath (present work) seems to be advantage

Effect of bath and annealing temperatures

The influence of different bath temperature on the cathode current efficiency, microhardness (Fig.2) and the quality of the deposits revealed that 40 °C can be considered as best operating temperature (optimum temperature) which led to the highest CCE (99.3%), suitable quality (bright, adherent and smooth) with moderately high hardness (390 HV) at the 2.2 Adm^{-2}. It was observed that CCE increased and the quality of the deposit improved on raising temperature up to 40 °C and deteriorated at higher temperature (50 °C).

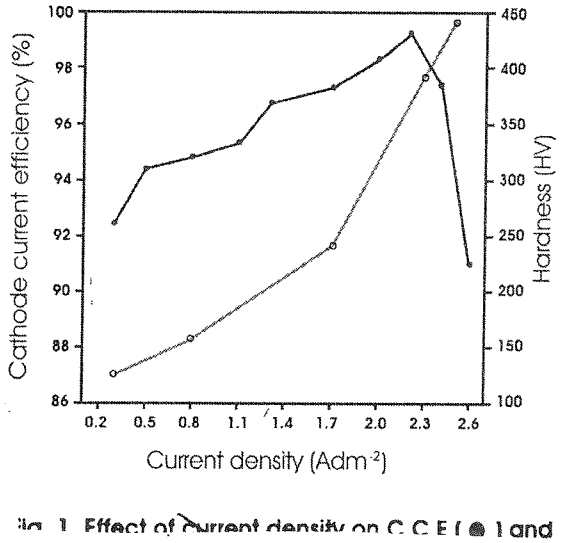

Figure (1) Effect of current density on C C E ( ) and microhardness (O): 5 mol-% EG – water, 0.5 M nicel chloride, 40 C (optimum composition).

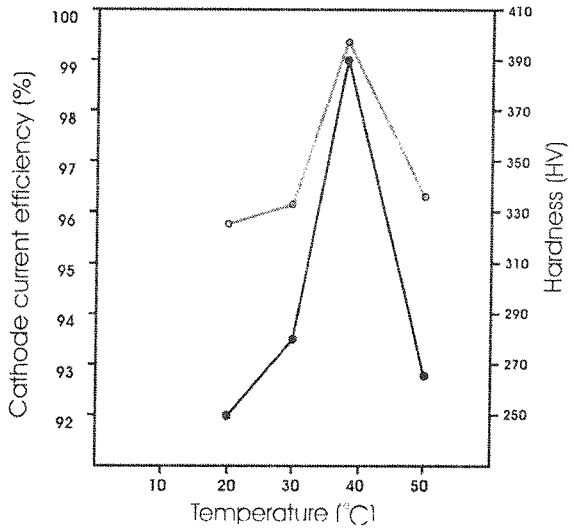

Figure (2) Effect of temperature on C C E ( ) and microhardness (O): 5 mol-% EG – water, 0.5 M nickel chloride, CD 2.2 Adm.

The increase in CCE with a rise in temperature could be due to increase in conductivity and decrease in viscosity resulting in the increased mobility of the ions. Slight decrease in CCE observed at 50 °C might be due to hydrogen evolution caused by lowering of it's over voltage around this temperature. It is cleared from figure 2 that with increasing bath temperature, the microhardness of the deposits increases up to 40 °C (from 326 to 390 HV) and then it declines sharply to attain a value of 265 HV at 50 °C.

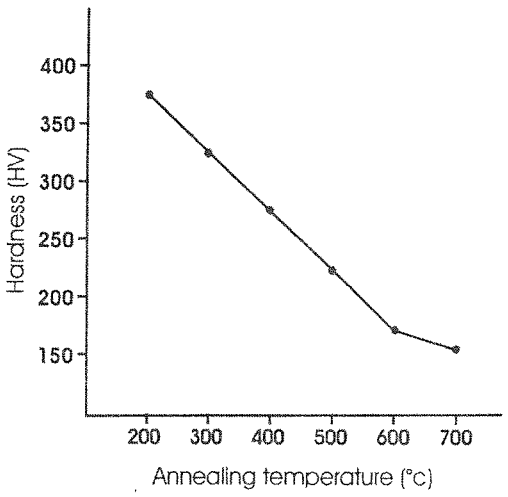

Figure (3) Effect of annealing temperature on microhardness of nickel deposits obtained under optimum conditions.

were vacuum sealed in a glass tube and annealed at various temperatures (200- 700 °C) for 2 hours and then allowed to cool slowly down to room temperature. Structural studies were conducted using scanning electron microscopy (SEM) model JEOL 84OA and transmission electron microscopy (TEM) model Philips CM 12 instruments operated at accelerating voltages of 10 - 15 KV and100KV,respectively.

Composition and operating conditions are given in table 1.

Table (1)

Parameters	Values
Nickel chloride ($NiCl_2$. $6H_2o$)	0.2- 0.6 M
Boric acid (H_3 BO_3)	0.2 M
Bath temperature	20- 50 °C
Current Density	0.2- 2.6 Adm^{-2}
Annealing temperature	200- 700 °C
Duration of electrolysis	30 min.

Results and Discussion:

Ethylene glycol - Water mixture of different composition (2, 5, 8 and 11 mol. % EG) were used as deposition media in the present investigations, and the characteristics of deposits obtained from such baths showed that the 5 mol. % EG- water mixture with 0.5 M nickel chloride as electrolyte and 0.2 M boric acid was found to be the optimum composition from which bright, smooth and hard deposits with high cathode current efficiency (CCE) were obtained. Hence, effect of different plating variables on the quality, CCE, microhardness and structure of the electrodeposits in optimum composition was examined.

Effect of Current density

Figure 1. shows that in optimum bath composition (5 mol. % EG- water, 0.5 M nickel chloride and 0.2 M boric acid), the cathode current efficiency (CCE) increased with increasing in current density (CD) and reached a maximum (99.3%) at 2.2 Adm^{-2}. The quality of electrodeposits was improving along with rising CD and finally bright, adherent, smooth deposit obtained at 2.2 Adm^{-2}. Above this current density, CCE showed decreasing trend and touched 91 % at 2.6Adm^{-2} and the quality also is deteriorated to dull deposit with some bright streaks at central portions and showing burning effect at the edges of the cathode surface, these was probably due to the lower activity of nickel ions near the cathode. The evolution of gas bubbles (Hydrogen) was observed over the cathode surface during the electrode position and this intensified noticeably at higher current densities. Such development of gas bubbles may be related to the rapid depletion of metal ions in the cathode layer. Tobias [7] has elucidated that gas bubble evolution would affect the distribution of cathodic current density and thus CCE would vary.The microhardness of the electrodeposited nickel from optimum bath composition increases regularly with increasing current density (Fig. 1) but the increase in hardness is more noticeable between 1.70 and 2.2 Adm^{-2}. The microhardness of nickel deposits obtained under optimum current density (2.2 Adm^{-2}) was found to be 390 HV. Such an improvement in the microhardness with increasing CD can be explained by the progressive grain refinement of the deposits which occur to a significant extent at higher current densities. As the current density increases, the rate of formation of fresh nuclei will be greater than the rate of growth of crystals, and consequently the deposits become more and more fine- grained with successive increases in the current density. The high hardness of nickel deposits at such current densities may also be related to the presence of chloride ions in the solution which cause an adequate supply of nickel ions in the bath. A similar trend of the variation of the hardness with respect to the current density has been reported by other investigators [8, 9].

Study of Some Physical Properties and Structure of Nickel Electrodeposits from Ethylene Glycol - Water Bath

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Abstract

Electrodeposition of nickel from the bath containing nickel chloride and ethylene glycol- water mixture under different plating conditions has been carried out. The influence of current density (CD) concentration of electrolyte and bath temperature on cathode current efficiency (CCE) physical properties and structure of the deposits was investigated. The microhardness of the deposits declined with increasing annealing temperature. The microstructure and crystallographic structure were examined by SEM and TEM.

Keywords:

Nickel, Electrodeposits, Chloride – mixed Solvents, Microhardness

Introduction:

An aqueous chloride bath has good conductivity and throwing power. With these baths moderately high current densities are permissible [1], and chloride ion reduces anode polarization, thus permitting smooth dissolution of anode. The deposits obtained have a lower ductility and a higher tensile stress than those obtained from a Watts bath. Furthermore, electrodeposition from organic and mixed solvents seems to be very attractive from the viewpoint of the electrochemistry involved in the deposition process, particularly for nickel. Effect of organic molecules on the grain refinement and adsorption of these large molecules and their influence in checking the outgrowth of crystals by offering resistance have been studied by Vermilyea [2].

Takei extensively investigated [3] the electrodeposition of nickel and copper from trifluoroacetate - amide bath. Electrodeposition of nickel also has been studied by sadeghi sarabi and singh [4] from mixed solvents bath. Taking into consideration that suitable nickel deposits may be specified to improve corrosion and wear resistance, therefore, the present work was undertaken to electrodeposit nickel from ethylene glycol - water bath using nickel chloride as electrolyte under different plating conditions.

Experimental procedure

The experimental details were the same as those described earlier [5,6]. Rectangular copper strips of dimensions 2.0 × 1.0 × 0.01 cm were used as cathodes. These strips were subjected to the mechanical polishing followed by solvent degreasing using acetone and pickling with 10% sulphorice acid. High purity nickel strips were used as anodes. 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 the addition of nickel chloride and boric acid as electrolyte and buffer respectively in this mixture. The microhardness of nickel deposits were measured on a Tukon Wilson hardness tester using a 136° diamond pyramid indenter. The nickel plated specimens