ABSTRACT

The processing-structure-property relationships of Ni-W based nanocrystalline alloy and nanocomposite coatings have been studied by considering Ni-W/graphene oxide (GO) nanocomposites, annealed Ni-W alloys, and Ni-W-Cu ternary alloys. An aqueous sulphate-citrate electrolytic bath with a suspension of GO particles has been used for the pulse electrodeposition of Ni-W/GO composite coatings, whereas copper sulphate ($CuSO_4$) salt has been used additionally for the deposition of Ni-W-Cu ternary alloy coatings. Both GO particle content of the nanocomposite coatings and the Cu concentration in the Ni-W-Cu alloys have been found to scale with their respective amounts in the electrolytic baths. Co-deposition of Cu is facilitated by its greater electropositivity compared to that of Ni or W according to the EMF series. Measurements using the grazing incidence X-ray diffraction (GIXRD), as well as transmission electron microscopy (TEM) have indicated that the grain size of the alloy matrix in Ni-W/GO nanocomposite coatings decreases with the increase in amount of GO in the coating, but increases with the rise in Cu concentration of the Ni-W-Cu alloy coating, as well as increase in the duration of annealing. However, the matrix micro-strain in the aforementioned coatings has exhibited a trend opposite to that of the grain size. Furthermore, GIXRD analysis has shown preferred orientation of <111> for the fcc Ni_{ss} (Ni-rich solid solution) grains in both GO-added nanocomposite and Ni-W-Cu alloy coatings, causing reduction of surface energy. The annealed Ni-W alloy coatings are found to contain NiW and Ni_4W as additional phases besides the Ni_{ss}.

Nanoindentation studies have demonstrated that hardness of the Ni-W/GO nanocomposite coatings increases linearly with increase in GO content, because of dispersion strengthening and grain refinement of the alloy matrix. This observation is confirmed by the Hall-Petch relationship being followed. In contrast, coarsening of the grain size with increase in the concentration of Cu in Ni-W-Cu alloy has led to a proportionate decrease in hardness. The Young′s moduli of Ni-W/GO nanocomposite coatings and Ni-W-Cu ternary alloys are affected significantly by the Young’s modulus values of GO and Cu, respectively. However, both nanoindentation hardness and Young’s modulus of the Ni-W alloys reach their peak on annealing for 2 h owing to the formation of NiW and Ni_4W intermetallic phases. Annealing durations of ≥ 4 h have lowered the hardness and Young's modulus due to excessive grain growth and alloying with Cu by diffusion from the substrate, respectively. The increase in wt% of GO in the Ni-W alloy matrix assists in improving the scratch resistance and reducing the coefficient of friction by lowering the surface roughness, and lubrication by the GO particles. Studies using potentiodynamic polarization experiments in 3.5 wt% NaCl solution have depicted a significant increase in the corrosion resistance with the incorporation of GO particles as well as ternary alloying addition of Cu in the Ni-W alloy. The corrosion tested Ni-W/GO and Ni-W-Cu coatings have shown remarkable reduction in pit density of the corroded surfaces, as compared to the Ni-W alloy coating. Furthermore, the outcome of electrochemical impedance measurements for Ni-W-Cu ternary alloys is consistent with their potentiodynamic polarization behaviour. X-ray photoelectron spectroscopy analysis has confirmed the formation of a protective Cu_2O-rich barrier film, which is responsible for restricting corrosion of the Ni-W-Cu alloy coating. However, the corrosion resistance of the Ni-W alloy coating is found to deteriorate on annealing.

Keywords: Pulse electrodeposition; Ni-W/GO nanocomposite; Ni-W-Cu nanocrystalline alloy; annealing; microstructure; nanoindentation hardness; Young's modulus; scratch resistance; corrosion resistance, potentiodynamic polarization; electrochemical impedance spectroscopy.