Electroless nickel ternary and quaternary alloy coatings

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Abstract: Autocatalytic/electroless nickel alloy coatings are most popular due to their unique properties such as coating uniformity, excellent adhesion, corrosion and wear resistance. These coatings are widely used for various strategic, electronics, aerospace and other industrial applications. It is well known that hard chromium coatings are widely used in metal finishing industries due to their excellent wear resistance properties. However, hexavalent chromium compounds are hazardous and carcinogenic and hence, their usage is restricted. One of the alternatives to replace hard chromium coatings is by incorporating one or two alloying elements Ni-P alloy matrix. Studies were carried out towards the development of electroless nickel polyalloys coatings by co-depositing ternary elements such as Cu, W, Sn, Mo, etc. It was found that co-deposition of these alloying elements reduced the phosphorus content from 11 wt.% to about 4 wt.%. XRD diffraction patterns showed the amorphous nature of as-plated binary Ni-P coatings and alloying elements co-deposition resulting in microcrystalline. Differential scanning calorimetry studies also indicated improved thermal stability of ternary and quaternary coatings. These coatings upon heat treatment also exhibited comparable mechanical properties to hard chromium coatings.

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Introduction

Electroless plating is a well-known metal finishing process in which a variety of alloys and composite coatings can be obtained by a simple chemical reduction (autocatalytic) process. The main advantage of this process is that even and more uniform coating thickness can be obtained on deep bores and recesses, and at corners and edges compared to the electroplating process. It is possible to deposit metals such as nickel, cobalt, silver, gold, platinum, etc., by electroless plating method on both ferrous and non-ferrous substrates apart from insulating materials. Among the metals deposited by this method, electroless nickel coatings are very much popular due to their unique properties such as uniform thickness, excellent wear, abrasion, corrosion resistance and solderability. In general, electroless nickel is not a pure nickel deposit instead it is an alloy. Electroless Ni-P and Ni-B alloys are most widely used for many strategic and industrial applications such as aerospace, electronics, automobile, etc. [1].
Stringent regulations in metal finishing industries demand the development of alternative coating processes specifically for toxic hard chrome coatings. In general, a variety of alloying elements such as W, Co, Cu, Sn, etc. are co-deposited with Ni-P/ Ni-B matrix to achieve improved hardness, wear and abrasion resistance. These properties can also be improved co-depositing second-phase particles such as oxides, nitrides, and carbides apart from solid lubricant particles like graphite, MoS_2, PTFE, etc. in nickel alloy matrix to obtain a composite coating [2].

In the present work, ternary and quaternary alloys and composite coatings were obtained by co-depositing alloying elements such as W, Mo, Cu, Sn and second-phase particles such as alumina and silicon carbide on a mild steel substrate. Obtained coatings were characterized for their composition, structure, phase transformation behavior, microhardness in as-deposited and heat-treated conditions and corrosion resistance.

2. Experimental

Mild steel specimens of size 1" X 1" were used as specimens for plating electroless nickel alloy deposits. These specimens were degreased, cathodically cleaned, deoxidized and after a thorough rinse with distilled water placed in an electroless nickel plating

bath for about 3 hours. The basic bath used for electroless nickel plating contained nickel sulphate, sodium hypophosphite, complexing and buffering agents. Sodium tungstate, sodium molybdate, sodium stannate and copper sulphate were used in the bath as ingredients to deposit ternary and quaternary alloy deposits. These baths were maintained at 85± 2°C using a constant temperature water bath. Plating was carried out about 2 hours to obtain a thickness of approx. 25 microns.

As-deposited and heat treated (at 200, 400 and 600°C for 1 hour) were characterized for their structure, morphology, phase transformation behaviour, microhardness and corrosion resistance using XRD, SEM, DSC, Vickers hardness tester and electrochemical workstation, respectively.

Results & discussions

Electroless ternary and quaternary alloy coatings were deposited on a mild steel substrate using alkaline citrate-based baths. It is possible to co-deposit Cu, W, Sn, Co, etc. in the Ni-P matrix by varying the bath compositions [3]. About 9 wt.% Cu co-deposition observed with the addition of copper sulphate (3 mM) in nickel sulphate and hypophosphite-based bath. Similarly, the addition of sodium tungsten resulted in a ternary NiWP deposit with 4.5 wt.% W. Co-deposition of Cu and W was achieved with the addition of both tungstate and copper sulphate chemicals in an alkaline electroless Ni bath. It was noticed that the incorporation of both W and Cu elements in the NiP matrix resulted in the reduction of P co-deposition from 11 to 4.5 wt.%. X-ray diffraction studies revealed that high P deposits exhibited amorphous or nanocrystalline and with the co-deposition of alloying elements resulted in the crystalline structure. Binary Ni-P deposits showed nodular morphology and upon co-deposition of both W and Cu resulted in smooth morphology [Fig.1].

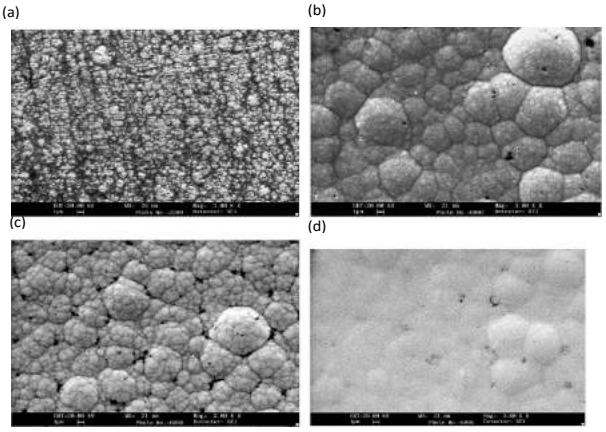


Fig. 1 SEM micrographs of the as plated electroless nickel coatings (x_3000) (a) Ni–P, (b) Ni–Cu–P, (c) Ni–W–P and (d) Ni–W–Cu–P. [after ref.3]

Studies have also been carried out towards the codeposition of W in Ni-P deposit by varying 5 to 80 g/L sodium tungstate in an alkaline electroless nickel bath to obtain ternary NiWP deposits. It has been observed that the addition of 20 g/L of sodium tungstate in an alkaline electroless nickel bath resulted in about 8 w.t.% W co-deposition in the Ni-P matrix. Beyond this addition, there is a gradual decrease in W content and could be due to the formation of a complex compound or suppression of the cathodic reaction of $H_2PO_2^-$ [4]. Hence, it is possible to obtain a ternary electroless Ni-W-P coating by varying W source in an alkaline bath in obtaining both either amorphous or crystalline deposits [5].

The conditions have been standardized to deposit ternary and quaternary alloys by co-depositing W and Mo in Ni-P matrix. It is well known that deposited nickel is catalytically active in the plating process. During the process, apart from phosphorus other elements such as W and Mo are also reduced which resulted in ternary Ni-W-P, Ni-Mo-P and Ni-W-Mo-P deposits [6]. It has also been reported that Ni and W form a mixed complex Ni^{2+}-WO_4^{2-}-Cit^{3-} in an alkaline solution which aids in the co-deposition of W in the Ni-P matrix through multi-step reduction. However, Mo (VI) species present as simple MoO_4^{2-} which will be subsequently reduced.

Similar to ternary NiCuP deposits, co-deposition of W and Mo and both of them in Ni-P matrix resulted

in more nodular deposits. The surface morphology of NiP deposit showed a cauliflower-like morphology. Co-deposition of both Mo and W resulted in a well-defined larger nodular structure resembling an orange peel shape [6].

Development of polyalloys such as NiWP, NiSnP and NiWSnP by autocatalytic method occurred due to the unique properties of W such as high melting point, hardness and solderability and corrosion resistance properties of Sn [7]. Cross-sections of the deposits reveal a lamellar/banded structure of all the deposits due to the variation in the composition of the deposit (Fig.2). Minor changes in pH during continuous electroless deposition resulted in compositional variation in the deposit.

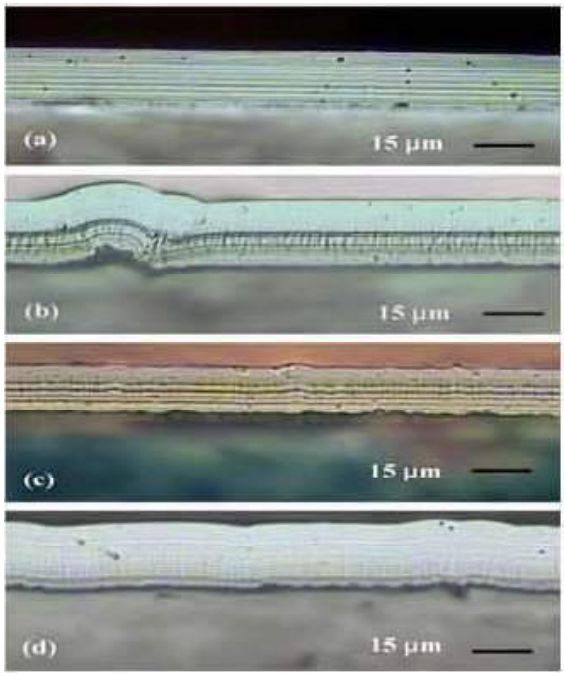


Fig. 2. Optical images of cross-sections of asdeposited electroless nickel

polyalloy coatings: (a) NiP; (b) NiSnP; (c) NiWP; (d) NiWSnP. [after ref.7]

Phase transformation behaviour studies carried out on these deposits at different scanning rates from 10, 20, 30 and 40°C/min. in the temperature range of 50 – 570°C. Exothermic peaks obtained for all these deposits is shown in figure 3. Higher exothermic peak temperatures were exhibited by ternary Ni-W-P and quaternary Ni-W-Sn-P deposits which indicates the improved thermal stability compared to other deposits.

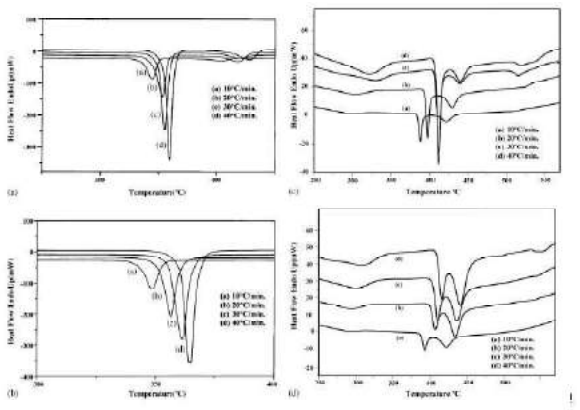


Fig. 3 DSC thermogram of electroless deposit at various scanning rates: a) Ni-P; b) Ni-Sn-P; c) Ni-W-P; d) Ni-W-Sn-P. [after ref.7]

Microhardness studies were carried out for these ternary and quaternary deposits at various heat treatment temperatures. It has been observed that as-plated electroless deposits exhibited improved hardness (400 to 500 HV50gf) due to the lamellar/ banded structure of the deposit which was evident from Fig. 2. By heat treating the as-plated coating to 400°C there is an increase in microhardness for all the deposits due to the formation of nickel phosphide apart from the solid solution strengthening of these alloying elements (500 to 970 HV_{50gf}). Quaternary Ni-W-Sn-P deposits exhibited improved hardness or retained its hardness even after heat treatment at 600°C (980 HV_{50gf}).

In addition, electroless nickel coatings exhibited improved corrosion resistance in the simulated seawater environment. Potentiodynamic polarization curves of as-deposited Ni-Cu-P, Ni-W-P and Ni-W-Cu-P deposits in 3.5% NaCl environment is shown in figure 4. From the figure, it is clearly seen that the corrosion current density obtained for all the deposits is around 0.8 $\mu A/cm^2$. The excellent corrosion resistance of these deposits could be due to the presence of phosphorus apart from the co-deposition of alloying elements which are in solid solution form [3].

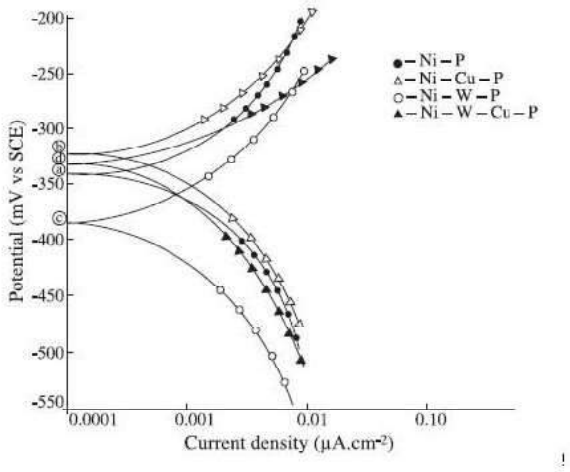


Fig. 4 Potentiodynamic polarization curves of as-plated electroless Ni-P, Ni-Cu-P, Ni-W-P and Ni-W-Cu-P coatings in 3.5% NaCl solution in non-deaerated condition. [after ref. 3]

Conclusions

Autocatalytic/electroless plating is a simple chemical reduction process and is possible to deposit on both metal and non-metallic surfaces. Hypophosite reduced electroless nickel plating baths are more popular for many industrial applications. Properties of these binary Ni-P deposits are further enhanced by codepositing various alloying elements. As-plated deposits exhibited amorphous to microcrystalline in nature. The composition of the deposits varies with the co-deposited alloying elements. Co-deposition of W and Cu in the Ni-P matrix resulted in a smooth morphology from the nodular. DSC thermograms obtained for these deposits indicated better thermal stability with the incorporation of one or two alloying elements. Excellent microhardness values were obtained for heat-treated ternary and quaternary deposits which are comparable with hard chrome deposits. Hence, these alloy coatings can be used as a replacement for carcinogenic hard chrome deposits.

References

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