Surface Modification and Wear Resistance of Electroless Ni-P Based Duplex Alloy Coating

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Abstract-
Ni-P-W multi-layered alloy coating was electrolessly deposited on 10 x 15 x 1.5 mm mild steel capons. The coated samples were heat treated between 200 – 800 °C and the resultant effect of the annealing on the small scale structure and mechanical properties of coating was studied by using X-ray diffraction, Scanning electron microscopy, nano-indenter, pin-on disc wear tester and interferometry Spectroscopy. The result shows that the as-deposited amorphous duplex coatings crystallise in steps as the annealing temperature increases and this gives raise to new phase formation in the mechanical properties of the coating. The study reveals the impact of high temperature annealing on the microstructure, morphology and microhardness of this duplex coating within certain temperature range; which was attributed to the formation of new Ni-P and Ni-W phases, its grain refinement and consequently, better linear microhardness and wear resistance relationship within given temperatures.

Keywords: Electroless Ni-P-W coating, annealing, microhardness and wear resistance

1. Introduction

The objective of this study is to evaluate the impact of heat treatment on the basic mechanical properties of electroless Ni-P-W alloy coating in order to extend its range of industrial application [1-2]. The failure of engineering materials in most cases is being initiated from its microstructure [3]. Therefore, the optimisation of the morphology to effectively enhance the performance of this metallic coating is very key in modern electroless plating [4-5]. One outstanding method to achieve this for metallic coatings is by appropriate annealing technique after successful deposition [6]. This approaches has several benefits which includes low cost and ready application on any complex metallic geometry with evolution of stable Ni based phases [7]. The structure, property and performance of Ni-P based coating depends on the phosphorus content and the post deposition heat treatment [7-8]. In this case, the duplex system comprises of a mixture of two overlays of Ni-P and Ni-P-W. Upon crystallization by annealing two major phases namely Ni-W and Ni3P precipitates are formed at a temperature slightly above 300 °C [9]. However, at a higher temperature, thickening of the particle of this intermetallic compound occurs [9-11]. Previous studies have indicated that; the microhardness of basic Ni-P coatings without any addition can attain up to 1100 HV0.1 after proper homogenisation for about an hour at 300 - 400°C temperature range [11-13]

2. Experimental Procedure
Mild steel coupons of 10 x 15 mm$^2$ and 1.1 mm thickness were used as substrate for the electroless deposition. The plating baths composition and deposition conditions are as described in Ref. [14-16]; with different concentration content for each deposit of Ni-P and Ni-W-P respectively. The plating procedures are as stated in Ref. [17]. SEM was used to characterize the surface and cross-section morphologies of the deposited layers as shown in Fig. 1. Energy dispersive X-ray spectroscopy (EDX) was used to identify the phase formation and to verify the chemical composition of the coatings respectively. The hardness of the coating was ascertained using a Leitz Wetzlar tester with a Vickers diamond indenter under a 100 g load for 15 s, with least average of five different measurements reported. The wear tracks and depths were measured after an experiments were performed under ambient laboratory conditions (22 °C, 45% relative humidity) and micrographs taken with interferometry machine and examined in a scanning electron microscope (SEM) for accuracy [18-19].

3. Results and Discussion

3.1 Microstructure and Phase formation of the deposits.

The uniformity of the deposition thickness and the resultant firm adhesiveness made electroless coating such a reliable technique for intricate multilayer alloy deposition. The base Ni-P layer acts as a catalyst for firm adhesion of Ni-W-P duplex layers, this phenomenon aids autocatalytic deposition. Fig. 1(a & b) shows the surface morphology as well as the cross-section of the as-deposited multilayer coating. Fig. 2 shows the XRD patterns of the as-plated and various crystallized heat treated (200-800 °C) samples. The EDX probe in form of elemental composition redistribution of the coating is as shown in Fig. 3; which follow the same pattern as intra-diffusion of major (grain refinement) constituents of the deposits [20].

![Figure 1: Morphologies (a) surface & (b) x-section of as-plated Ni-P/Ni-P-W duplex coating.](image)

This reveals the probe profile of constituent elements across the deposition, thereby providing information on the area of concentration of each element [21]. It is expected that more phosphorous will migrate to the top layer to form Ni$_3$P for better mechanical properties after sufficient heat treatment is best within the range of 300 – 400 °C.
Figure 2: Phase patterns of the samples at various annealing temperature after 1 hour.

Figure 3: Electron probe for elemental distribution across the multilayer of the coating.
3.2 Hardness of the coating.

Hardness is a measure of a material’s resistance to localised plastic deformation by surface indentation. It is a major factor that contributes to the general mechanical performance of electroless coatings. Hence, the measured hardness of these samples at different annealing temperatures for 1 hour is as plotted in Fig. 4 (a) and (b). The maximum hardness value obtained for Ni-W-1.5% P coating was HV 1050 after annealing for 1 hour at 400 °C. This corresponds to the state of optimum distribution of Ni3P particles in the coating after heat treatment. Meanwhile, above 400 °C, the hardness of this medium phosphorus coating decreases slowly as a result of the recrystallization of Ni and thickening of Ni3P precipitates. However, the microhardness of Ni-W-10.5% P deposits reach maximum hardness of HV1100 after annealing at lower temperature of approximately 370 °C. At higher annealing temperature, the hardness of both decreases rapidly, even lower than the as-deposited sample. This can be explained by the grain growth behaviour of Ni-1.5% P deposit as recorded by Yuanet. al. [22]. The fast decline in hardness above 450 °C has a relation to the grain growth and coarsening of Ni3P. Hence, compared with Ni-W-1.5% P deposit, the Ni-W-10.5% P possesses higher hardness after annealing at a higher temperature and its decrease tendency in hardness after reaching maximum is somewhat gentle due to their difference in fraction of Ni3P phases within the coatings. After crystallization, the matrix for Ni-W-10.5% P deposit outer layer was about 70% by volume of Ni3P. This acts as the volume fraction of the coating shrinkage above which it become unstable.

3.3 Wear resistance of the coating.

Table 1 shows the variation in wear rate with time and the estimated microstrain for the entire coating deposits under same constant load at different annealing temperature. The wear rate varies with degree of heat treatment of the coating as stated by Li and Tandon [23]. Fig 5 and 6, show the scanning electron micrographs and interferometry surface morphologies of the coatings wear tracks after wear-test for the 400 °C and 600 °C heat treated samples.
At higher annealing temperature, say above 650 °C; the coatings’ hardness decreases somewhat considerably, but the coatings’ ductility can be enhanced as a result of the recrystallization of Ni and thickening of Ni$_3$P as mentioned above, which help in the interface bonding, that improves the coatings’ corrosion resistance but very poor mechanical properties. Finally, continuous annealing at a higher temperature will cause rapid increase in wear rate because of the abrupt decrease in hardness caused by grain growth, microstrain and agglomeration of Ni$_3$P. The lowest in the case of coating being subjected to heating at 400 °C can be seen to be Specific wear rate from Table 1 due to the maximum hardness of the coatings at this temperature. The specific wear rate was discovered to rise considerably when heated above 400 °C as a result of softening the coating by grain thickening and shrinkage [24].

Table 1: Wear rate & corresponding microstrain of the coating at various annealing.

| Wear rate [m$^3$N$^{-1}$m$^{-1}$] | As plated | 200°C | 300°C | 400°C | 500°C | 600°C |
|----------------------------------|-----------|-------|-------|-------|-------|-------|
| Microstrain [%]                 | 1.08      | 0.68  | 0.60  | 0.39  | 0.26  | 0.20  |

Figure 5: SEM morphologies of (a) 400 °C & (b) 600 °C samples after 1 hr. heat treatment.
Figure 6: Interferometry surface micrographs of (a) 400 and (b) 600 °C annealed samples.

4.0 Conclusions

With controlled annealing, desired hardness and wear resistance of this metallic coating can be enhanced and these obviously increases the longevity of the substrate due to the precipitation of Ni₃P phase within the coating outer-layer. For the as-deposited coatings, the Ni-W-10.5% P has relatively better hardness than the Ni-W-1.5% P coating. The optimum hardness of Ni-W-10.5% P deposit due to the existence of numerous hard phase Ni₃P, while the optimum hardness of Ni-W-1.5% P deposit corresponds to heat treatment at 375 °C for one hour respectively. As shown from this study, higher temperature annealing will cause rapid decrease in hardness due to recrystallization of Ni and severe coarsening of Ni₃P. In a like manner, the study shows that wear resistance is superior in the coating with higher phosphorus content, which can be further improved by controlled annealing around 400 °C.

Acknowledgements

The authors wish to acknowledge the support offered by College of Engineering, Afe Babalola University and Institute for Materials Research, University of Leeds in actualization of this research work for publication.

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