The influence of thermal treatment on the microstructure and hardness in electroless Ni–P–W deposit

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Abstract

Ni–P–W alloy deposit on the mild steel substrate was obtained by the electroless process. Various thermal heat-treatment temperatures from 350 to 600 °C for 4 h were performed on the coating to evaluate the effect of crystallization behavior and grain size on the mechanical properties. The microstructure at as-deposited and heat-treatment states were investigated by the X-ray diffraction (XRD) and transmission electron microscope (TEM). The hardness at all depths of the coating on the substrate could be acquired by the nanoindentation. The Ni–P–W coating showed an amorphous structure in the as-deposited state and exhibited a relatively low hardness of approximately 6.8 GPa. As temperature was raised to 380 °C, the hardness was slightly increased to 8.7 GPa due to the partial precipitation of Ni and Ni$_3$P in the amorphous matrix. On heating to 500 °C for 4 h, the hardness reached the maximum value of 12.3 GPa with a grain size of 33.1 nm and followed by gradual degradation above 500 °C. The Young modulus of the amorphous Ni–P–W coating showed a relatively low value of 195 GPa. However, for increasing the heat-treatment temperature accompanied with the grain growth, the Young modulus was enhanced to the maximum of 233 GPa and then decreased gradually with temperature.

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1. Introduction

Electroless nickel–phosphorus alloy with excellent anti-corrosion, antiwear, thermal stability and mechanical properties has been applied in many kinds of industries as a surface modification coating [1–3]. The properties and structures of the Ni–P coatings, depending on its phosphorus content, were studied [4–7]. The Ni–P deposit with high phosphorus content was a phosphorus supersaturated solid solution, exhibiting amorphous structure. After suitable heat treatment, the Ni–P coating could be strengthened with the crystallization of nickel and nickel phosphide. However, the hardness of the coating was degraded with excessive heating at elevated temperature. The strengthening mechanism of either precipitation or grain size hardening owing to the crystallization of binary Ni–P coatings had been investigated by analyzing the microstructure with the use of transmission electron microscope (TEM) [8,9]. In fact, the thermal stability of the binary Ni–P coating is a critical issue when exceeding the crystallization temperature inasmuch as the coarsening of Ni and Ni$_3$P would lead to the hardness degradation. In order to improve the thermal stability, the incorporation of a third element into Ni–P based coating, for instance, Ni–P–W [10–15], Ni–P–Cu [16,17], Ni–P–Re [18] and Ni–P–Cr [19] was used to prolong the crystallization temperature of Ni–P compound. The ternary Ni–P–W coating exhibited higher mechanical properties than binary Ni–P [20,21]. Nevertheless, the strengthening mechanism for the ternary Ni–P–W coating had not been fully investigated. Consequently, the purpose of this study is to evaluate the strengthening mechanism of the Ni–P–W coating, including solution, precipitation and grain size hardening with high phosphorus content. Investigation of the effects on microstructure and Young modulus with respect to temperature was probed. The microstructure and
phase identification at as-deposited and heat-treatment states were analyzed by transmission electron microscope (TEM). The mechanical properties of ternary Ni–P–W coating, such as hardness and Young modulus, were evaluated by the nanoindentation technique.

2. Experimental procedure

Mild steel selected as substrate due to its low cost was firstly ground with silicon carbide sand paper and polished with diamond slurry up to 1 μm. The substrate was then degreased in the acetone with ultrasonic cleaning, rinsed in the running water, deoxidized in acid solution with H₂SO₄ and activated in the 15 vol.% HCl solution for 15 s. Finally, the sample with a load of 120 cm²/l was put into the electroless solution for plating. The chemicals in the plating bath contained (1) sodium hypophosphite, NaH₂PO₂·H₂O (0.1 M), (2) sodium citrate, Na₃C₆H₅O₇·2H₂O (0.35 M), (3) sodium sulfate, Ni₂SO₄·6H₂O (0.1 M) and (4) sodium tungstate, Na₂WO₄·2H₂O (0.1 M). The pH value of solution was fixed at 9, adjusted by NaOH, and the temperature was maintained at 90 ± 2 ℃. The thermal treatment of deposits was carried out from room temperature to 600 ℃, with a temperature interval of 50 ℃ for 4 h and cooled in the N₂ atmosphere. A nanoindentation tester (MTS Nano Innovation Center, Oak Ridge, TN) with a Berkovich-diamond indenter tip was used to determine the hardness and Young modulus of both film and substrate. The loading–unloading mode was chosen, and the continuous stiffness measurement (CSM) mode was used to analyze the relationship between indentation depth and hardness as well as Young modulus. The loading–unloading mode employed a load of 10 g and maintained 15 s at the maximum load. On the other hand, the continuous stiffness measurement test was operated with a constant strain rate of 0.05 s⁻¹, and penetration depth was fixed at 2000 nm. The composition of the Ni–P–W coating was determined with an electron probe microanalyzer (JXA-8800, JEOL, Japan). The microstructure and grain size at various states were observed by transmission electron microscopy (JSM-2010, JEOL, Japan). For the TEM analysis, the film was first ground and then transferred onto a Cu grid. A Gatan dual ion mill with incident angle of 10° to 15° and 5 keV was utilized for the electron transparency.

3. Results and discussion

3.1. Composition and microstructure analysis

The composition of the as-deposited ternary Ni–P–W coating evaluated by EPMA was Ni (77.7 at.%)–P (19.6 at.%)–W (2.7 at.%). Fig. 1(a) shows the differential scanning calorimetry plot with a heating rate of 10 ℃/min. A broad peak with onset and peak temperatures located at 380 and 390 ℃, respectively, is resulted from the crystallization of nickel, as analyzed by TEM in Fig. 1(b). The grain size around 10 nm appeared in the amorphous matrix, and the diffraction pattern exhibited a broad diffused ring and a narrow ring, indicating the precipitation of nickel.

Fig. 2 shows the micrographs and diffraction pattern of Ni–P–W coatings at the as-deposited and heat-treatment states. In Fig. 2(a), the diffraction pattern of the as-deposited Ni–P–W coating revealed only a broad Ni (111) ring, and no crystalline phase in the bright-field image was observed. From the results of TEM, the as-deposited coating exhibited an amorphous structure. When heated to 380 ℃ for 4 h, the crystalline phase in the bright-field image was observed. From the results of TEM, the as-deposited coating exhibited an amorphous structure. When heated to 380 ℃ for 4 h, the crystalline phase in the bright-field image was observed.
amorphous matrix, and the outer sharp ring was resulted from the precipitation of nickel. The bright spot encircling the sharp ring was attributed to the precipitation of Ni₃P. On heating the Ni–P–W coating to 450 °C, the diffraction pattern of the inner broad ring disappeared. Instead, the sharp ring of nickel (111) and nickel (200) showed up, as indicated in Fig. 2(c).

As observed in the bright field image of Ni–P–W coating at 450 °C from Fig. 2(c), the precipitated grain exhibits spherical shapes with a grain size of 13.6 nm. When temperature was increased to 500 °C, the grain size of the Ni and Ni₃P was enlarged up to 33.1 nm, and the grain still maintained the spherical shape. On heating up to 550 °C, the bright-field image in Fig. 2(e) shows two kinds of grain sizes, including the small one of 45 nm with spherical shape and the large one of 81.3 nm with polyhedron shape. Fig. 2(f) illustrates the microstructure of Ni–P–W coating after the heat treatment at 600 °C for 4 h. The average grain size exceeded 100 nm. The spot and the ring patterns are indexed as Ni₃P and nickel, respectively. As compared with the electroless binary Ni–P coating, the grain size of the Ni–P–W coating was relatively smaller than that of the binary Ni–P coating at the same heat treatment temperature [5]. As a result, the addition of tungsten would suppress the grain growth of the Ni–P-based coating.

### 3.2. Nanoindentation

Fig. 4 is the plot of hardness as a function of the temperature using the loading–unloading mode with a
load of 10 g. The as-deposited Ni–P–W coating, which has amorphous structure from the result of TEM analysis, showed a low hardness of 6.8 GPa. When heating at 380 °C for 4 h, the hardness was slightly enhanced to 8.7 GPa. The increase in hardness at 380 °C was attributed to the partial precipitation of Ni and Ni₃P, with a small grain size of 10.2 nm in the amorphous matrix. Amorphous matrix still existed in the bright-field image of 380 °C. After being heated at 400 °C, where the crystallization of Ni–P compound in the Ni–P–W coating started (406 °C), the hardness was substantially increased from 8.7 GPa at 380 °C to 11 GPa at 400 °C and reached the maximum value of 12.3 GPa at 500 °C with a grain size of 33.1 nm. Over the maximum hardness at 500 °C, the hardness of the coating was then gradually decreased and reached a lower value of 8.6 GPa at 600 °C as compared with the maximum hardness at 500 °C. From the results of TEM at 550 °C for 4 h, grains impinged with one another were transformed from spherical shapes to polyhedron ones, and two apparently different sizes of grains were revealed. The phenomenon was also observed by Hur et al. in the study of the crystallization in binary electroless Ni–P coating [5,8].

Fig. 5 is the result of continuous stiffness measurement in which the hardness is expressed as a function of indentation depth. The trend of hardness variation at different temperatures was consistent with the loading–unloading mode. In the plot of CSM mode, the relationship between hardness and indentation depth was easily obtained and could be separated into three regimes. Within the indentation depth of 350 nm, the sharp decrease of hardness with respect to the indentation depth was due to the indentation size effect and the surface morphology [24]. Therefore, the hardness obtained in this area could not be regarded as the true hardness of the Ni–P–W coating. An approximately horizontal line appeared in the range from 350 nm up to 1200 nm, where the hardness was independent of the indentation depth. As the indentation depth was beyond 1200 nm, the plastic deformation zone contained not only the Ni–P–W coating but also mild steel substrate. As a result, the low hardness associated with the substrate led to the substantial drop in hardness. Saha and Nix reported that, when the indentation depth exceeded about 10% of the film thickness in the hard film deposited onto the soft material substrate assembly, the hardness of the film would be affected by the substrate effect [24]. In this study, the indentation-depth-independent hardness appeared in the range between 350 nm and 1200 nm, with an average around 800 nm, which is one-tenth of the film thickness 8 μm. Thus, the hardness in the range 350–1200 nm can be considered as the intrinsic value of the coating in this material system.

3.3. Young modulus

Fig. 6 is the relationship between Young modulus and heat-treatment temperatures. The Young modulus of as-deposited coating exhibited a low value of 195 GPa. With increasing heat-treatment temperature, the modulus was slightly raised to the maximum value of 233 GPa at 500 °C and then gradually decreased at the elevated temperature higher than 500 °C. From the analysis of the electron diffraction pattern for each heat-treatment conditions shown in Fig. 2, the microstructure of the Ni–P–W coatings maintained the amorphous structure below 350 °C. The modulus values at as-deposited and heat-treatment state at 350 °C for 4 h were around 200 GPa, which was a little lower than that of the crystalline nickel (211 GPa) [25]. It is argued that the amorphous metallic materials formed by the incorporation of a suitable amount of metalloid in the metal matrix display a lower Young
modulus as compared to the crystalline state of the metal in the matrix [26].

After 380 °C for 4 h, Ni and Ni3P were precipitated from the amorphous coating. The Young modulus increased to 216 GPa which was close to that of crystalline nickel. With respect to the calculated average grain size at different temperatures by bright-field image and dark-field image, the Young modulus increased from 216 GPa at 380 °C with a grain size of 10 nm to 233 GPa at 500 °C with a grain size of 33 nm. Above 500 °C, the grain size increased with temperature, while Young modulus revealed the opposite trend. It is reported that both the grain size of the coating and the heat-treatment temperature would affect the Young modulus. Zhou et al. argued that the decrease in grain size, which accompanied the increase fraction of triple junctions, would lead to the degradation in Young modulus [27]. Besides, the Young modulus was observed to decrease with increasing temperature [26,28]. From the result of the relationship among Young modulus, grain size and temperature in this study, it appeared that the effect of grain size on the Young modulus was more dominant at temperature below 500 °C. When the temperature was above 500 °C, the effect of temperature on Young modulus exceeded that of grain size, and thus Young modulus decreased with increasing temperature.

4. Conclusions

From the results of DSC and TEM analyses, the crystallization behavior of Ni–P–W deposit was revealed. Nickel was first precipitated at 390 °C, and the Ni3P compound was then crystallized at 406 °C. The hardness and Young modulus of amorphous Ni–P–W coating at as-deposited state was relatively low. As heating to 380 °C for 4 h, nickel and Ni3P compound with grain size of 10.2 nm were precipitated coherently in the amorphous matrix, and the hardness slightly increased due to both precipitation hardening and solution hardening. With heat treatment above the crystallization temperature, the grain size with the spherical shape increased to 13.6 and 33.1 nm, respectively, at 450 and 500 °C. The hardness at both two treatment temperatures was much higher than that of as-deposited. The obvious raise in hardness may be attributed to the increased fraction of Ni and Ni3P precipitation from as-deposited amorphous Ni–P–W coating. After the heat treatment at 550 °C for 4 h, the grain size was increased to 66.7 nm. Moreover, the grain at 550 °C transformed from spherical shape to polyhedron one, indicating grain coarsening which caused the decrease in hardness. For excessive thermal treatment at 600 °C, the grain size over 100 nm led to the substantial drop in hardness. Young modulus of the Ni–P–W coating was controlled by grain size and temperature. Below 550 °C, the effect of grain size was dominated so the Young modulus increased from 380 to 500 °C due to grain growth. Above 500 °C, the influence of temperature predominated over that of grain size, and thus Young modulus decreased with increasing temperature.

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References


Fig. 6. Young modulus of Ni (77.7 at.%)–P (19.6 at.%)–W (2.7 at.%) coatings at different annealing temperatures for 4 h.