Crystallization behaviors and microhardness of sputtered Ni–P, Ni–P–Cr and Ni–P–W deposits on tool steel

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Abstract

The Ni–P-based coatings, including binary Ni–P, ternary Ni–P–Cr and Ni–P–W, were fabricated by the RF magnetron sputtering technique with dual target of electroless Ni–P alloy and a third metal element. To evaluate the influence of the doping element in Ni–P deposit, differential scanning calorimeter (DSC) analysis was employed to characterize the temperature of phase transformation. The phase transition during thermal evolution under heat-treatment was analyzed by X-ray diffractometry (XRD). Crystallization behavior in binary and ternary Ni–P-based coatings was quite distinct due to the addition of Cr and W. Microhardness tests indicated that the sputtered Ni–P–Cr and Ni–P–W coatings exhibited superior hardness and excellent thermal stability than the Ni–P coating. In addition, chromium exhibited compatible thermal characteristics with the tungsten for the ternary Ni–P-based system. The strengthening mechanism in the sputtered Ni–P–Cr and Ni–P–W deposits is also discussed.

Keywords: RF sputter; Ni–P-based deposit; Thermal stability; Strengthening mechanism; Differential thermal analysis; Microhardness

1. Introduction

Electroless Ni–P plating is well known for its good performance as a surface coating and as a low cost process for a wide range or industrial applications. However, the inferiority of Ni–P coatings often occurs due to the over grain growth of Ni and Ni–P crystallites with excessive annealing [1,2]. Therefore, it is critical to promote the crystallization temperature of the binary Ni–P system. To solve the problem and to extend its range of application, the co-deposition of third element to form ternary electroless nickel alloy, such as Ni–P–Cu [3,4], Ni–P–Mo [5], Ni–P–Zn [6] and Ni–P–W [7,8] has been proposed. The doping with a third element would change the crystallization behavior and enhance the performance of binary Ni–P deposit. Ternary electroless Ni–P–X coatings thus have been developed for their good thermal stability, excellent mechanical properties and corrosion resistance as compared to the conventional electroless binary Ni–P deposits [9,10]. Nevertheless, it is difficult to control the composition among Ni, P and the third element during electroless plating due to the complicated relationship of chemical potential [11]. Chang et al. [12] employed an alternative deposition method, i.e. physical vapor deposition (PVD) [13], to fabricate the ternary Ni–P-based deposit instead of chemical solution process. Sputter deposition has been used to produce alloy coatings with a wide range of alloy composition. In addition, the structure and deposition rate of sputtered deposit can be well controlled through the working pressure, target input power and the distance between substrate and target [14].

The performance and crystallization behavior of Ni–P-based coatings are usually affected by the doping element. In the present study, Cr and W were introduced as the third element based on their high melting point and superior hardness. The binary Ni–P and ternary Ni–P–X doped with either Cr or W were investigated by the RF sputtering technique. To obtain more knowledge for the crystallization of sputtered Ni–P-based coatings, the evaluation of DSC and XRD analysis were introduced. Transitions of phase transformation temperatures and crystallization behavior in sputtered Ni–P, Ni–P–Cr and Ni–P–W coatings after various heat-
3. Results and discussion

3.1. Composition of NiP based deposit

The compositions of sputtered Ni–P based coatings are listed in Table 1. The process of sputtered ternary Ni–P–Cr and Ni–P–W coatings has been well developed by the multi-gun sputtering system and a controlled elemental content of Cr and W in the alloy could be achieved by adjusting the input power of the target [15,16]. The thickness of all coatings was approximately 2 μm. To evaluate the influence of various dopants into sputtered Ni–P coatings, the P content was controlled in the medium phosphorus (9–14 at.%) range [17], and the content of third element for Cr and W were 10.0 and 5.0 at.%, respectively. The content of third element was deliberately selected to avoid crystallization of the third element and thus, the same amount of solid solution can be retained in ternary system. It was assumed that all the phosphorus atoms precipitate with nickel and form Ni₃P in the final state in Ni–P–Cr and Ni–P–W deposits. The Ni/P ratio in ternary Ni–P–Cr and Ni–P–W deposits is 5.4 and 7.6, respectively, which are larger than the stoichiometry ratio of 3:1 for Ni₃P. Therefore, the excess nickel will co-precipitate with Cr and W to form either Ni–Cr or Ni–W solid solution in the ternary coating. Table 1 indicates that the atomic ratios of Cr and W to excess nickel are 0.29 and 0.10, respectively. The Ni–Cr and Ni–W alloy would be formed with calculated solute solubility of 21 and 23 mass%, respectively, which was smaller than the upper limit, 36 and 31 mass%, estimated from the binary phase diagrams of Ni–Cr and Ni–W, respectively [18]. The detailed evaluation approach of the excess nickel was recently reported by Wu et al. [19]. It appears that the evaluated Ni-21 mass% Cr and Ni-23 mass% W are feasible states in the ternary alloy coatings.

3.2. Crystallization behavior of sputtered Ni–P, Ni–P–Cr and Ni–P–W deposits

3.2.1. DSC profile

The DSC curves of the sputtered Ni–P-based coatings at the heating rate of 10 °C/min are shown in Fig. 2. The thermal profile exhibits the exothermic peaks at 380, 420 and 420 °C for Ni–P, Ni–P–Cr and Ni–P–W, respectively, which correspond to the long-range atomic movements resulting in the precipitation of stable phase, such as fcc Ni and Ni₃P. The co-deposition of third element (Cr and W) retarded the formation of Ni₃P phase and the crystallization temperature was raised from 380 to 420 °C. The crystallization temperature of electroless and sputtered ternary Ni–P–Cu deposits was reported at approximately 400 °C [4] and 370 °C [12], respectively. Therefore, Cr and W are superior to Cu...
with regard to the restraint of phase transformation in the ternary Ni–P-based coatings.

3.2.2. XRD pattern

Phases of Ni–P-based coating with various annealing temperature were identified through X-ray diffraction technique and are shown in Figs. 3–5. All the deposits exhibited a broadened peak, and the peak of Fe(110) contributed from the substrate was also revealed in the as-deposited state. In binary sputtered Ni–P system, the original amorphous structure was transformed into a mixture of Ni and Ni–P crystallites after annealing at 400 °C for 4 h, as indicated in Fig. 3. The stable phase of Ni₃P was completely formed after heat-treatment, in which the result could be related to the temperature of phase transformation measured by DSC.

Table 1
The composition of the sputtered Ni–P-based coatings and the solute solubility of third element into Ni matrix

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Composition (at.%)</th>
<th>Solute solubility of X into Ni (wt.%)</th>
</tr>
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<tbody>
<tr>
<td>NiP</td>
<td>86.5 ± 0.2</td>
<td>13.5 ± 0.2</td>
</tr>
<tr>
<td>Ni–P–Cr</td>
<td>76.0 ± 0.4</td>
<td>14.0 ± 0.4</td>
</tr>
<tr>
<td>Ni–P–W</td>
<td>84.0 ± 0.3</td>
<td>11.0 ± 0.4</td>
</tr>
</tbody>
</table>

* The third element of Cr and W.

b Excess nickel to third element in ternary Ni–P–X coating.

However, the crystallization behavior of ternary Ni–P based coatings was altered by the doping of the third element of Cr and W. For the Ni–P–Cr deposit, the peaks of crystalline Ni₃P phase occurred at 500 °C as

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![Diagram](image_url) Fig. 1. (a) Schematic diagram of the deposition apparatus and (b) top view of the arrangement of samples and sputter guns.
shown in Fig. 4. The phase transformation of Ni–P crystalline was detected initially at 500 °C annealing for 4 h. In Fig. 3b, the diffraction pattern was similar to that in as-deposited state except the small fluctuation of the broadened peak. Therefore, the structure was still a mixture of amorphous and nano-crystalline below 500 °C. The introduction of Cr element cast a strong effect in retarding the Ni₃P precipitation and Ni crystallization.
After heating to 600 °C, diffraction peaks became sharper, indicating the grain growth. Besides the difference of phase transformation, it was reported that Cr also dissolved in the fcc Ni crystalline phase to form a solid solution for a Ni$_{x}$P$_{19}$Cr$_{16}$ alloy system [20]. However, in this study the diffraction peak of Ni–Cr(111) was shifted to the higher angle side due to the smaller atom size of Cr and possibly overlapped with the diffraction peak of Fe(110) substrate at 44.7°. Hence, at 2θ=44.5° it is difficult to distinguish the XRD analysis.

Fig. 5 shows the X-ray diffraction patterns of Ni–P–W deposit heat-treated at various temperatures. In a preliminary study, the solid solution of Ni–W in ternary
Ni–P–W deposit was reported after suitable heat-treatment [19]. However, the broadened peak contributed by Ni(111) matrix shifted slightly to a lower 2θ angle of 44.2° in the as-deposited state, as shown in Fig. 5a. The solid solution of Ni–W phase in the sputtered Ni–P–W coatings may be stressed in the plasma environment during sputtering. The intensity of major peak Ni–W(111) increased with the annealing temperature, and the minor peak of Ni–W(200) showed up at 2θ = 51.3° at 600 °C. The diffraction peak of Ni₃P occurred at 500 °C, as shown in Fig. 5c. In Fig. 5e, the formation of Ni₃P was restricted in limited orientation as compared to the Ni–P and Ni–P–Cr system in Fig. 3b and Fig. 4e, respectively. The distinction in the crystallization behavior may be attributed to the addition of tungsten, which is larger in size than both Cr and Ni. It is concluded that the introduction of a third element (Cr and W) can delay the crystallization behavior to the higher annealing temperature and also improve the thermal stability in Ni–P–W system.

For ternary Ni–P–Cr and Ni–P–W coating, the crystallization reaction with Ni and Ni₃P as final products is similar to hypoeutectic Ni–P alloy due to the low content of P at high temperature [21]. However, the single exothermic peak observed in DSC curve implies that the structure in as-deposited state is transformed directly into the final stable structure of Ni and Ni₃P phase without the formation of other intermediate phases.

3.3. Thermal stability evaluated by microhardness

Fig. 6 shows the Knoop hardness of Ni–P, Ni–P–Cr and Ni–P–W alloys in both as-plated and heat-treated states with an indentation load of 0.098 N. The measured microhardness is sensitive to the penetration depth, which increases with the applied load. Under the applied load of 0.098 N, the penetration depth is in the range of 0.3–0.4 μm for this sputtered Ni–P-based coating system with the Knoop indenter. The film thickness of Ni–P, Ni–P–Cr and Ni–P–W deposits were approximately 2 μm that is much larger than the indentation depth. Therefore, the substrate effect is eliminated, as indicated in Fig. 6. In the as-deposited state, a hardness value of 1040 HK in Ni–P–Cr and 1030 HK in Ni–P–W coatings were higher than that of 840 HK in binary Ni–P deposits due to the co-deposition of harder element (Cr and W). After heat-treatment, the hardness of Ni–P deposit increased to 1250 HK at 400 °C. The temperature of hardness peak was located between 350 and 400 °C, owing to the formation of Ni₃P phase on the basis of DSC and XRD data. The maximum heat-treated hardness of sputtered Ni–P deposit is approximately 1250 HK, which is the same as that for electroless Ni–P reported by Tsai and coworker [19].  Appreciable decrease of hardness occurred after the heat treatment at 550 °C due to grain coarsening. For the Ni–P–Cr deposit, the hardness increased from 1040 HK in the as-deposited state, and reached the maximum hardness at 1400 HK after heat treatment at 500–550 °C. However, the microhardness decreased to 1200 HK at 600 °C. For sputtered Ni–(13.1 at.%P)–(12.7 at.%Cu) coating, Chang et al. reported a hardness of 1500 HK at 375 °C [12]. In comparison, the introduction of chromium successfully delays the precipitation of Ni₃P and exhibits a maximum hardness at elevated temperature of 500–550 °C, which is much higher than the Ni–P–Cu system. The hardness of Ni–P–W coating increased slightly from as-deposited to 500 °C and reached a maximum value of 1450 HK at 500 °C. As to strengthen the mechanism, all deposits are hardened after heat-treatment and achieve a maximum hardness at a critical temperature. It is believed that the increase of hardness with an increasing heating temperature is attributed to the crystallization of initial state leading to the formation of nano-crystallization. Nano-scale size grains, solid solution and the presence of hard compound are all attributed to the maximum microhardness of heat-treated Ni–P–Cr and Ni–P–W coatings. However, decrease in microhardness after annealing at higher temperature is due to the increase in the grain size, i.e. the so-called Hall–Petch effect [22,23]. As a result, the addition of a third element affects the thermal property of Ni–P-based deposited in two ways. Firstly, the increase of maximum heat-treated hardness of sputtered Ni–P-based system was contributed by the solid solution of Ni–Cr and Ni–W as revealed in XRD analysis. Secondly, the location of hardness peak temperature is raised to approximately 500 °C. In fact, the Ni–P–Cr deposit exhibits an even better performance.
than Ni–P–W, with regard to identical range of P content and solid solution amount. In addition, Cr is more beneficial for the sputtered Ni–P-based coating due to its lower cost and higher sputtering efficiency.

4. Conclusions

Either Cr or W was a beneficial addition for the Ni–P-based coatings fabricated by RF sputter process on 420 ss tool steel. The phase transformation temperatures of Ni–P–Cr and Ni–P–W were raised to 420 °C as analyzed by DSC, which was higher than the binary Ni–P and ternary Ni–P–Cu system analysis. DSC and XRD analysis also indicated that the crystallization of sputtered Ni–P-based coating occurred with a single reaction and exhibited final products of Ni and Ni₃P. The solid solution effect, due to the introduction of Cr and W in ternary Ni–P-based coatings was also evidenced in the XRD analysis. Besides the precipitation of Ni₃P phase, the surface hardness of the binary Ni–P sputtered coating was enhanced by the additional strengthening mechanism of solid solution. After suitable heat-treatment, the sputtered Ni–P, Ni–P–Cr and Ni–P–W deposits exhibited relatively high hardness of 1250, 1400 and 1450 HK, respectively. By the addition of Cr and W, the temperature of hardness peak in the ternary coatings was raised by 150 °C more than sputtered Ni–P deposits.

Acknowledgments

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References