

## Research Article

# Process Heating and Postannealing Effects on Microstructure and Hardness of the Sputtered Ni-P-Al Coatings

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Ternary Ni-P-Al alloy coating was fabricated by magnetron sputtering technique with a Ni-P/Al composite target source. The effects of thermal treatments, including deposition process heating and postannealing, on phase transformation phenomenon and related mechanical properties were investigated. The as-deposited coatings produced under process temperature below 475°C showed an amorphous/nanocrystalline microstructure. Significant crystallization of Ni matrix and precipitation of  $\text{Ni}_x\text{P}_y$  and  $\text{Ni}_p\text{Al}_q$  compounds were observed for the coatings manufactured under high sputtering temperatures above 500°C. The amorphous Ni-P-Al coatings were postannealed from 500 to 600°C in vacuum environment for comparison. The amorphous feature of the Ni-P-Al coating remained unchanged under a high annealing temperature of 550°C, showing a superior thermal stability as compared to those fabricated under high process temperatures. Superior hardness was obtained for the post-annealed Ni-P-Al coatings due to volumetric constraint of crystallization and precipitation. On the other hand, the overaging phenomenon and subsequent degradation in hardness were found for the Ni-P-Al coatings fabricated under high-temperature deposition processes. The phase transformation mechanisms of the coatings through different thermal treatments were intensively discussed.

## 1. Introduction

Nickel-Phosphorus (Ni-P) coating is frequently adopted as a hard alloy coating due to its various merits, such as corrosion resistance, high hardness and toughness, and wear resistance [1–4]. Under adequate heat treatment, the binary Ni-P can be strengthened by precipitation of intermetallic compounds, including  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_5\text{P}_2$ ,  $\text{Ni}_{12}\text{P}_5$ , and NiP hard phases [5]. In order to further enhance its mechanical and thermal properties, the introduction of the third elements, including Al [6], Cr [7], Cu [8, 9], and so forth, has been proposed. Especially for Ni-P-Al coatings, it has been pointed out that not only the crystallization temperature is increased but also the related mechanical properties are enhanced owing to the addition of Al [6]. Ni-P-based coatings are usually fabricated through wet chemical methods, including electroless and electroplating techniques [4, 10]. The codeposition of third element into Ni-P alloy through wet chemical procedures is sometimes complicated and not easy to control. Recently, the sputtering technique

is successfully adopted to produce multicomponent Ni-P-based alloy coatings with good composition control [6, 9, 11, 12]. Since the Ni-P-based material is sensitive to thermal history, the process temperature during sputtering and postannealing are, thus, critical to the phase evolution and related mechanical property variation. In the present, study we focus on the temperature dependency of microstructure and correlated mechanical behaviors of the sputtering Ni-P-Al coatings. Thermal histories, including continuous heat treatment, process heating, and postannealing, are applied for comparison. The evolution in phase, microstructure, surface characteristics, and hardness with respect to the designed thermal procedures is intensively discussed.

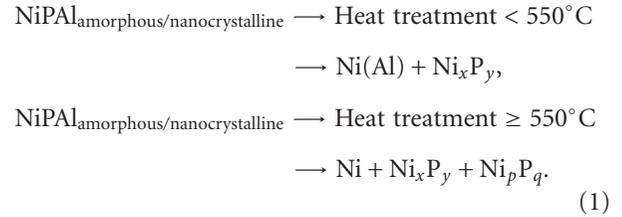
## 2. Experimental Procedures

The ternary Ni-P-Al coatings were fabricated by radio frequency (r.f.) magnetron sputtering technique with a Ni-P/Al composite alloy target. The composite target was produced by an electrodeposited Ni-P thick film of approximately

200  $\mu\text{m}$  on a pure Al disc of 50.8 mm in diameter. Part of the Ni-P thick film was drilled off to expose the Al disc underneath, and, thus, a composite target providing Ni, P, and Al was ready for cosputtering. The silicon wafer and polished 420 stainless steel with  $20 \times 20 \text{ mm}^2$  in surface area were employed as substrate materials. After loading the substrate on sample holder, the chamber was evacuated down to  $8 \times 10^{-4} \text{ Pa}$  followed by the inlet of Ar as the plasma source gas. The input power and target-to-substrate distance for all coatings were fixed at 100 W and 120 mm, respectively. Substrate temperatures from room temperature to  $600^\circ\text{C}$  were carefully controlled. The coating thickness was approximately  $1.0 \mu\text{m}$ , as shown in Figure 1(a). The cross-sectional and plane-view images of the Ni-P-Al coatings were carried out with a field-emission scanning electron microscope (FE-SEM, JXA-6700, JEOL, Japan). The composition of the Ni-P-Al coating was evaluated to be  $\text{Ni}_{74}\text{P}_{14}\text{Al}_{12}$  by the electron probe microanalysis, EPMA, system equipped on the FE-SEM. An X-ray diffractometer (XRD-6000, Shimadzu, Japan) was adopted to inspect the phase and microstructure of the Ni-P-Al coatings. In order to investigate the phase transformation phenomenon with respect to temperature, the continuous heating program was applied during in-situ X-ray diffraction. The temperature was raised from room temperature to  $600^\circ\text{C}$  with a fixed heating rate of  $25^\circ\text{C}/\text{min}$ . Conventional X-ray diffraction analysis was also carried out for phase identification for the coatings deposited under process heating and postannealing at 500, 550, and  $600^\circ\text{C}$  for comparison. Detailed surface morphology and roughness data were analyzed through an atomic force microscope (AFM, Solver P47H, NT-MDT, the Netherlands). The hardness of the Ni-P-Al coatings was evaluated with a nanoindentation tester (CSM, Nano Hardness Tester, Switzerland).

### 3. Results and Discussion

**3.1. Phase Transformation.** With the aid of the in-situ X-ray diffraction program, the instantaneous phase transformation phenomenon of the room temperature deposited Ni-P-Al coating was carried out. Figure 2 shows the diffraction patterns of the Ni-P-Al coatings heat-treated continuously at various temperature setpoints. Below  $350^\circ\text{C}$ , a broadened peak with its highest intensity around  $44.5^\circ$  was obtained and was recognized as a phase of amorphous Ni(111) matrix codeposited with P and Al [6]. When the temperature was increased between 400 and  $450^\circ\text{C}$ , another broadened peak comprised of transient phases of  $\text{Ni}_5\text{P}_2(600)$  and  $\text{Ni}_{12}\text{P}_5(240)$  were observed. From  $475$  to  $525^\circ\text{C}$ , the Ni(111) crystallized significantly with the development of various  $\text{Ni}_x\text{P}_y$  compounds, such as  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_5\text{P}_2$ , and  $\text{Ni}_{12}\text{P}_5$ . For example, the peaks around  $36^\circ$  at  $500$ – $525^\circ\text{C}$  in the XRD pattern in Figure 2, which referred to  $\text{Ni}_3\text{Al}(110)$  and  $\text{Ni}_3\text{P}(301)$ , were not clearly resolved, implying a very early stage forming of the metastable  $\text{Ni}_p\text{Al}_q$  and  $\text{Ni}_x\text{P}_y$  phases. With further heating above  $550^\circ\text{C}$ , the phases including Ni,  $\text{Ni}_3\text{Al}$ ,  $\text{Ni}_3\text{Al}_4$ ,  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_5\text{P}_2$ , and  $\text{Ni}_{12}\text{P}_5$  developed significantly. The transformation of Ni-P-Al coating with respect to temperature could be summarized as follows:



Consequently, it was believed that the Ni-P-Al exhibited a thermal stability and transformed into final stage up to  $550^\circ\text{C}$  under continuous heating.

Since the Ni-P-Al coating was sensitive to thermal histories, it was essential to figure out the phase transformation phenomenon under various heat treatments. The phase identification of process heating and postannealing Ni-P-Al coatings under high temperatures from 500 to  $600^\circ\text{C}$  was carried out and illustrated in Figures 3 and 4, respectively. As deposited at  $500^\circ\text{C}$ , an early stage of Ni(111) matrix and intermetallic compounds, including  $\text{Ni}_3\text{P}(330)$ ,  $\text{Ni}_5\text{P}_2(600)$ , and  $\text{Ni}_{12}\text{P}_5(312)$ , were observed. With increased temperature of  $550^\circ\text{C}$ , the microstructure of the coating transformed into well-developed Ni crystalline matrix with  $\text{Ni}_3\text{P}$  precipitates [5]. These phases developed further accompanied with superior X-ray intensities when the Ni-P-Al coating was deposited at  $600^\circ\text{C}$ . The  $\text{Ni}_3\text{Al}$  high-temperature phase was also discovered. During sputtering, the nucleation and growth of thin films could be intensified through substrate heating. It was believed that the high-temperature heating during deposition enhanced the growth of Ni and Ni-P and Ni-Al intermetallic compounds as indicated in Figure 3. The trend in phase transition and development were thus comprehensible. On the other hand, the Ni-P-Al coating showed a higher phase transition temperature under postannealing. As illustrated in Figure 4, the coatings annealed at 500 to  $550^\circ\text{C}$  both showed a broadened peak around  $44.5^\circ$ , representing a Ni amorphous/nanocrystalline phase. Slightly developed  $\text{Ni}_x\text{P}_y$  phases were observed at  $550^\circ\text{C}$ . The  $\text{Ni}_x\text{P}_y$  developed further with  $\text{Ni}_3\text{Al}$  phase at  $600^\circ\text{C}$  annealing. Nevertheless, the coating was still not fully crystalline; for that, the diffraction peaks for various intermetallic compounds around  $40$  to  $45^\circ$  were not clearly recognized. It should be noted that considerable crystalline phases occurred for the Ni-P-Al coatings beyond  $500^\circ\text{C}$  in the previous study [6]. Since the addition amount of Al in Ni-P-Al in present study was much greater as compared to that in the previous work, a higher amorphous-to-crystalline transformation temperature for the coatings was expected.

**3.2. Surface Characteristics.** The phase transformation of Ni-P-Al coatings exhibited considerable dependency on surface characteristics. Table 1 indicates the roughness number, Ra, of the Ni-P-Al coatings under process heating and postannealing treatments. The 500, 550, and  $600^\circ\text{C}$  deposited Ni-P-Al films exhibited Ra numbers of 4.5, 6.5, and 22.5 nm, respectively. The Ra value of the room temperature as-deposited coating was evaluated as 0.4 nm for comparison. It should be noted that using process heating during sputtering deposition, the Ni-P-Al coatings tended to crystallize and

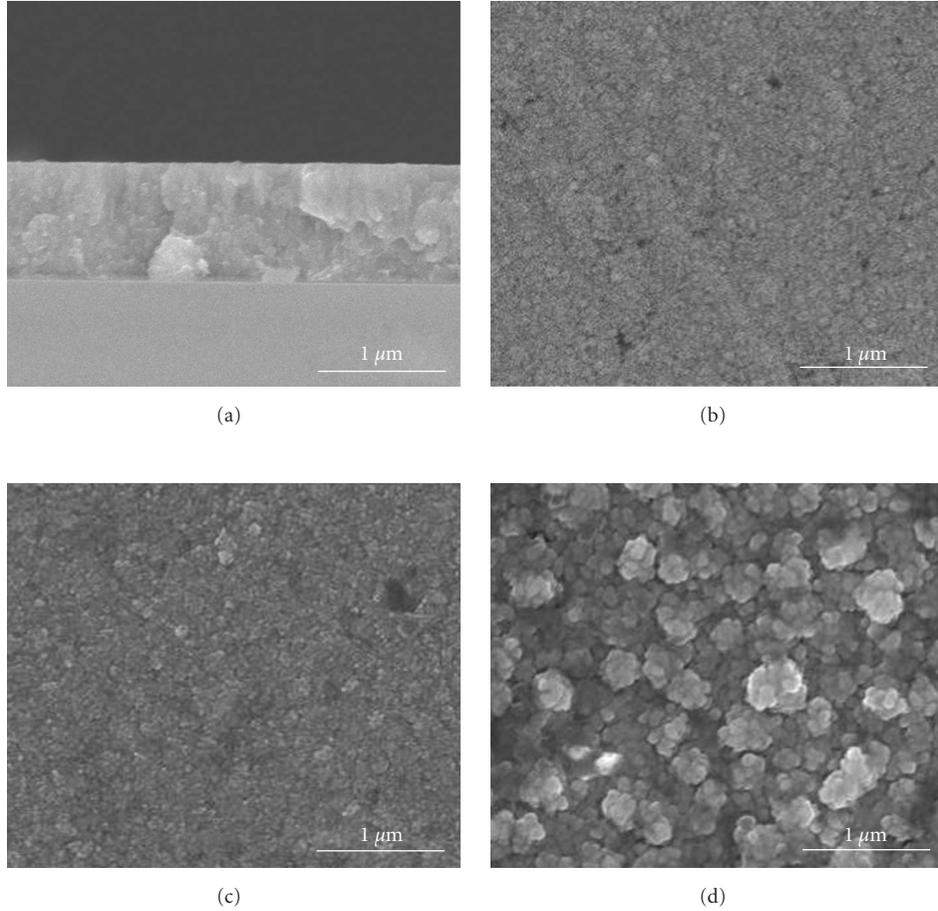


FIGURE 1: Scanning electron micrographs of (a) cross-sectional 475°C deposited, (b) plane-view as-deposited, (c) plane-view 475°C deposited, and (d) plane-view 550°C deposited Ni-P-Al coatings.

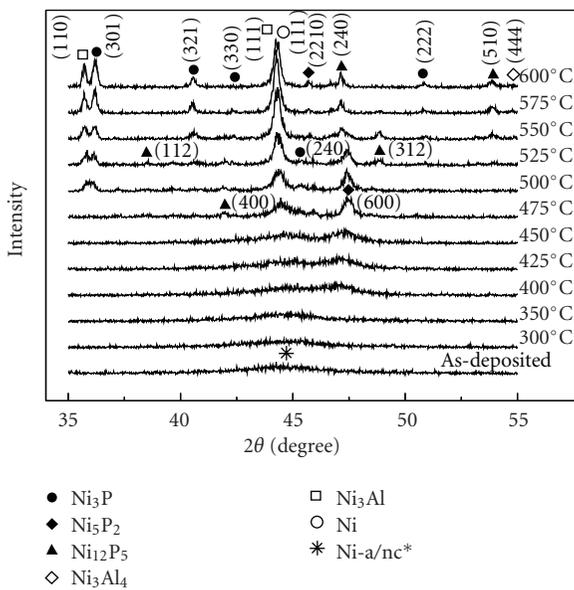


FIGURE 2: In-situ X-Ray diffraction patterns of the Ni-P-Al coating under continuous heating process. (\*a/nc: amorphous/nanocrystalline).

precipitate on the instantaneous coating surface. Under such circumstances, Ni and related compounds nucleated and grew freely on the surface and caused a loose structure. It could be seen in Figures 1(b), 1(c), and 1(d) that the surface morphology changed significantly with respect to deposition temperature. The coating surface morphology was quite smooth as deposited below 475°C, while large grains of several hundred nm in diameter were observed for the 550°C deposited Ni-P-Al coating. On the contrary, the postannealed coatings had a relatively lower Ra ranged from 0.5 to 3.2 nm. This was because the Ni and related compounds formed under the confinement of coating thickness. There was no free space for nucleation and growth inside the coating volume. The difference could also be recognized from detailed surface morphology observation through atomic force microscopy in Figures 5 and 6. Significant granular morphology and larger Z-axis scale up to 200 nm were found for the coatings with process heating at 600°C. Relatively smooth surface condition and reduced Z range were discovered for the postannealed samples in comparison. Consequently, granular and rougher surface was found for the Ni-P-Al coating with high deposited temperatures. Due to volumetric constraint, the postannealed coatings showed

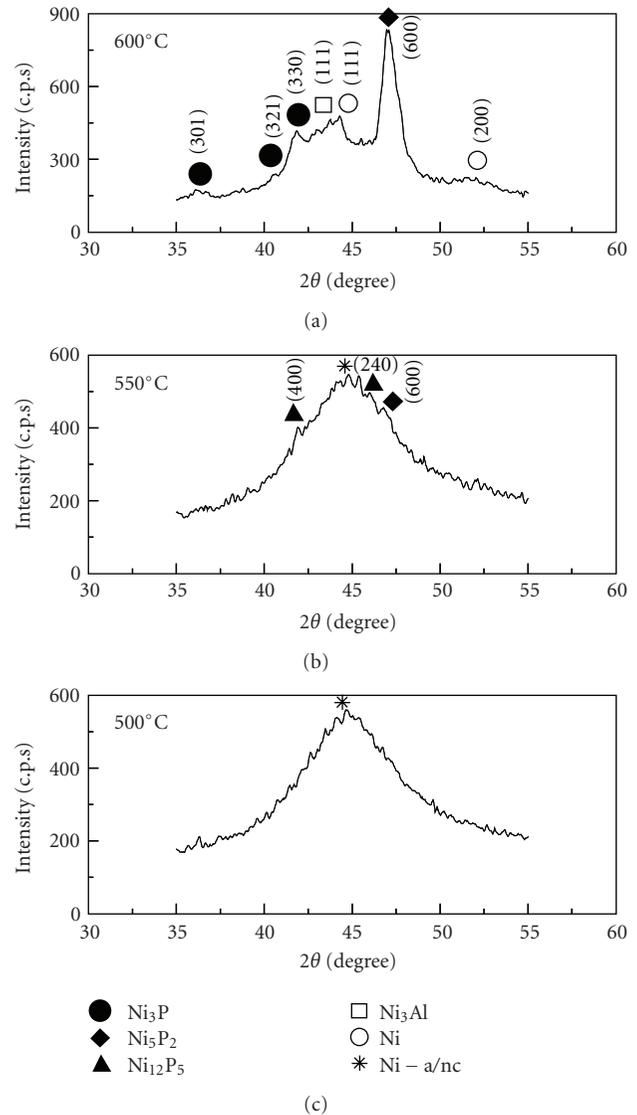
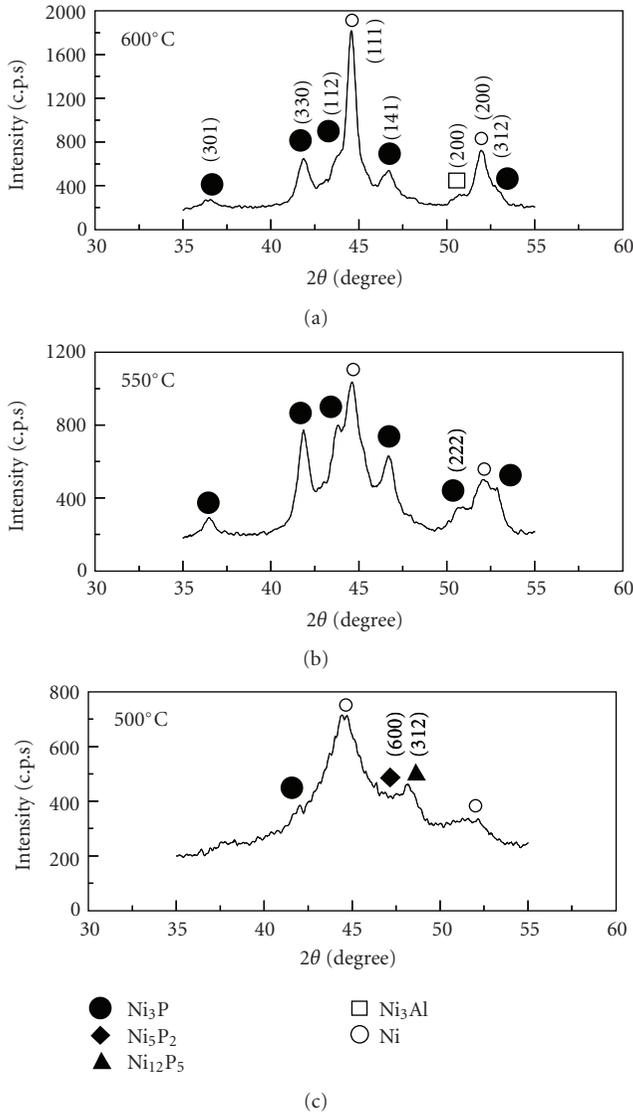


FIGURE 3: X-ray diffraction patterns of the Ni-P-Al coatings under various deposition process heating temperatures.

FIGURE 4: X-ray diffraction patterns of the Ni-P-Al coatings after postannealing process at various temperatures for 4 hrs.

TABLE 1: Surface roughness of the Ni-P-Al coatings under various process and postheat treatments.

Treatments	Temperature (°C)		
	500	550	600
PostAnnealing	0.5	1.4	3.2
Process Heating	4.5	6.5	22.5

\* Ra unit: nm.

a smooth surface morphology and small Ra numbers as compared to those deposited under process heating.

3.3. *Hardness.* Figure 7 shows the hardness of the Ni-P-Al coatings after process heating and postannealing thermal histories. The hardness of the room temperature as-deposited Ni-P-Al coating was also evaluated to be  $478 \pm 16$  HV for

reference. Under process heating at 500°C, the Ni-P-Al coating exhibited a hardness of around 500 HV, which was comparable to Ni-P-based alloy coatings [7, 9, 13] and the room temperature deposited Ni-P-Al film in this study. The hardness slightly increased to approximately 590 HV as the deposition temperature was raised to 550°C and then decreased to 410 HV when 600°C substrate heating was applied. Such variation in hardness could be referred to the overaging phenomenon for most precipitation strengthening materials. It should be noted that in Figure 3, the Ni-P-Al coating approached to a fully crystalline state at 550°C and reached a well-defined final state of crystallization at 600°C. Moreover, the enlarged grain size and loose microstructure found for the 550°C deposited Ni-P-Al coating in Figures 1(d) and 5 were responsible for the degeneration in hardness. On the other hand, the hardness of the postannealed Ni-P-Al coatings varied with an ever-increasing surface hardness

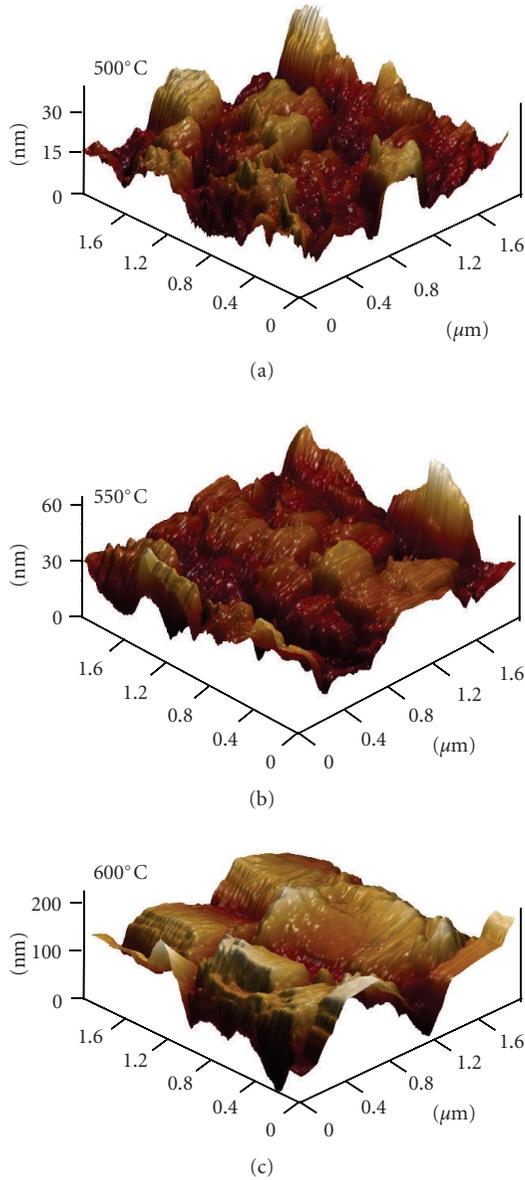


FIGURE 5: Surface morphology of the Ni-P-Al coatings under various deposition process heating temperatures.

from 500 to 600°C. The hardness was firstly raised from 478 to 670 HV at 500°C. A further promotion to approximately 730 HV was discovered as the annealing temperature went up to 550°C. Unlike the trend for process heating specimens, the hardness was enhanced over 920 HV under 600°C annealing. According to the phase transformation identification in Figure 4, early stage of transient  $Ni_xP_y$  precipitations occurred at 550°C and led to a slight increase in hardness as compared to the room temperature and 500°C annealed Ni-P-Al coatings. As annealed at 600°C, the further development in precipitates took place and the increase of hardness as a function of annealing temperature from 500 to 600°C was thus expected. Such phenomenon of annealing temperature effect on hardness of the Ni-P-Al sputtered

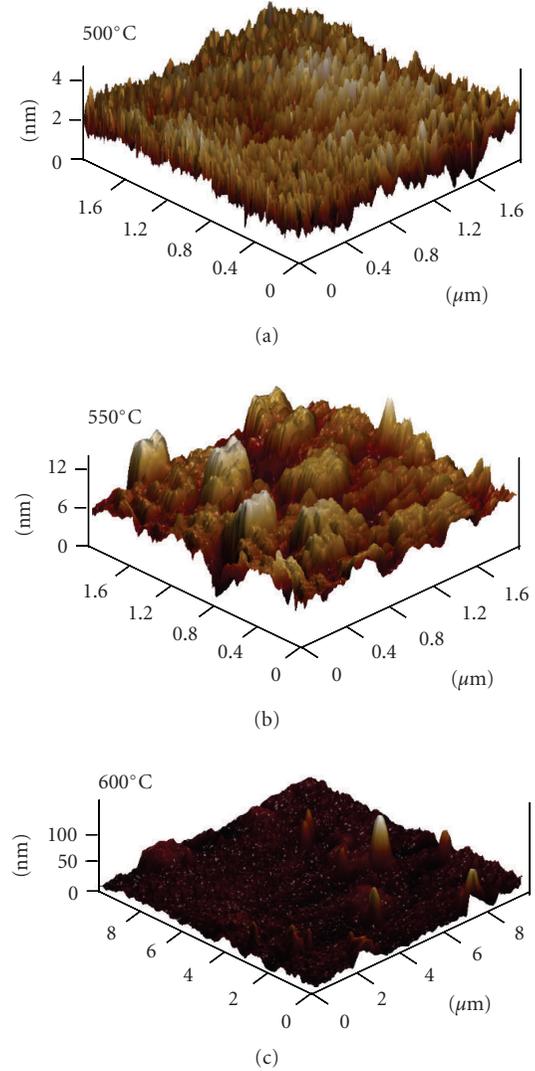


FIGURE 6: Surface morphology of the Ni-P-Al coatings after postannealing process at various temperatures for 4 hrs.

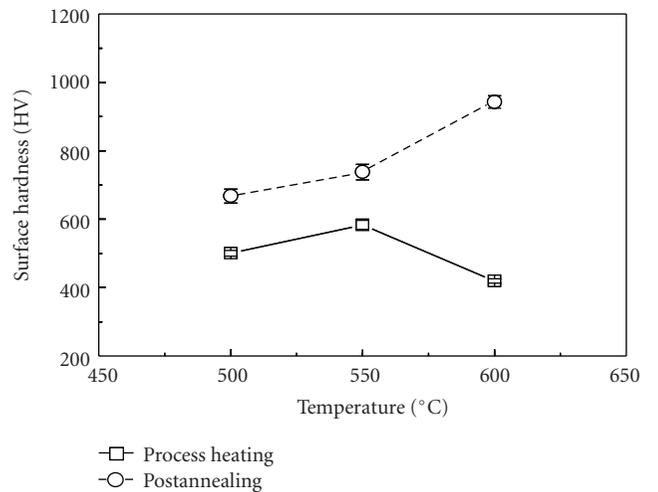


FIGURE 7: Surface hardness of the Ni-P-Al coatings under process heating and postannealing.

coatings could be referred to a previous work [6]. It should be pointed out that all the postannealed coatings exhibited superior hardness than those under process heating. Due to volumetric constraint, the precipitation hardening was suppressed to higher temperature region. Even annealed at a higher temperature of 600°C, the Ni-P-Al coating showed metastable phases of  $Ni_xP_y$ . As a result, the hardness kept increasing with respect to temperature. To sum up, the substrate heating during deposition of Ni-P-Al coatings forced the crystallization and precipitation at 550°C and resulted in an overaging phenomenon using process temperature of 600°C. Meanwhile, the postannealed Ni-P-Al coatings exhibited a superior thermal stability and higher hardness of approximately 900 HV up to 600°C owing to the suppression in precipitation by volumetric effect.

#### 4. Conclusions

- (1) The Ni-P-Al alloy coatings were successfully fabricated by sputtering technique with various thermal histories including process heating and postannealing. Through in-situ X-ray phase identification, amorphous to transient nanocrystalline phases were observed below 550°C, while a fully transformed microstructure of Ni matrix with  $Ni_xP_y$  and  $Ni_pAl_q$  compounds was found above 550°C for the Ni-P-Al coatings. A thermal stability of 550°C was concluded for the ternary sputtering Ni-P-Al coatings.
- (2) The process heating at 500 to 600°C during deposition provided sufficient energy and hastened the crystallization and precipitation. Since the film formation of the Ni-P-Al coating was accompanied by growth of crystallization and precipitation crystalline grains, the loose coating structure and rougher surface morphology were expected. Contrarily, under postannealing at higher temperatures of 550 to 600°C, slower compound formation and smoother morphology of Ra less than 3.2 nm were obtained for the Ni-P-Al coatings owing to the volumetric constraint on nucleation and growth due to phase transformation.
- (3) By postannealing process, a superior hardness up to 920 HV could be deduced for the Ni-P-Al coatings as compared to that under process heating. The overaging phenomenon of the process heating films was attributed by the well developed crystallization of  $Ni_xP_y$  and  $Ni_pAl_q$  compounds at 550°C. Using postannealing, the precipitation and crystallization were postponed toward high temperature. As a consequence, the Ni-P-Al coatings exhibited an ever increase hardness from 500 to 600°C.

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