The Hardness of Fe-Ni-P Alloy and Fe-Ni-P-Si_3N_4 Composite Coatings

by Liang Hui* & Zhang He-ling

The influence of process variables and deposit microstructure on the hardness of Fe-Ni-P alloy and Fe-Ni-P-Si_3N_4 composite electrodeposits have been studied. It is shown that the phosphorus content in the coatings has an important effect on the hardness. Because phosphorus deposition is induced by depositing nickel, the effect of nickel ion concentration on hardness is also significant. The hardness of the composite coatings was a little higher than that of the matrix alloy coatings. When the Si_3N_4 (2-μm; 79 μ-in.) particle content in the coating was above 4%, the hardness remained unchanged. The mechanisms of particle reinforcement, solution hardening, dislocation hardening, crystal stress and texture hardening have possible effects on the coating hardness.

Introduction

Alloy matrix composite coatings are an important part of research into the electrodeposition of composites,[1] and the major focus has been on Ni-P matrix composite coatings.[2,3] Because iron can codeposit with many other elements, including even non-metallic elements, there are a variety of iron-based alloy coating processes. The iron content can be continuously varied from 0 to 100%. For room temperature processes, the iron content is always greater than 85 wt% by varying the bath composition. The primary research focus has been the enhancement of hardness, wear-resistance and heat resistance. Iron-matrix composite coatings hardened by solid particles have also attracted much attention, including Fe-Al_2O_3 composite coatings and room temperature deposition of Fe-B_4C composites.[5] Nevertheless, studies on iron alloy matrix composite platings have been rarely reported except for Fe-P-Al_2O_3.[6] In this paper, the mechanical characteristics of Fe-Ni-P-Si_3N_4 composites deposited from room temperature solutions are reported.

Nuts & Bolts: What This Paper Means to You

Following on the nanocomposite theme of the previous paper, this work involves codepositing silicon nitride with iron-nickel-phosphorus. This material shows promise in applications where hardness and heat resistance are critical. The authors focus on how these properties derive from composition and structure.

Experimental procedure

The solution composition and operating conditions are given below.

Ferrous chloride ($FeCl_2 \cdot 4H_2O$)	400 to 600 g/L (53.1 to 80.1 oz/gal)
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	40 to 80 g/L (5.3 to 10.7 oz/gal)
Sodium Hypophosphite ($NaH_2PO_2 \cdot H_2O$)	2 to 18 g/L (0.3 to 2.4 oz/gal)
pH	0.5 to 1.5
Cathode current density	2.5 to 20.0 A/dm^2 (23.2 to 185.8 A/ft$^{2)}$
Solution temperature	20 to 50°C (68 to 122°F)
Anode material	A3 steel plate
Agitation	Mechanical

Fe-Ni-P alloy coatings and Fe-Ni-P- Si_3N_4 composite coatings were electrodeposited on-rectangular carbon steel blocks, with dimensions of 15 mm length and 7 mm width and 7 mm height (0.59 × 0.27 × 0.27 in.).

The coating composition was determined by analyzing the energy spectrum with an X-ray electron probe. Hardness was determined using a sclerometer. Each test was done for 5 sec with a 0.98 N (100 $g_{(f)}$; 0.22 $lb_{(f)}$) load. The test was repeated three times, and the average of the three readings was recorded.

In order to determine heat resistance, the electrodeposited specimens underwent heat treatment at different temperatures for 2 hr in a deoxidizing atmosphere, using graphite as reducing agent. They were then allowed to cool naturally. The hardness of each specimen was tested measured and compared before and after heat treatment. The heat resistance was estimated from this data.

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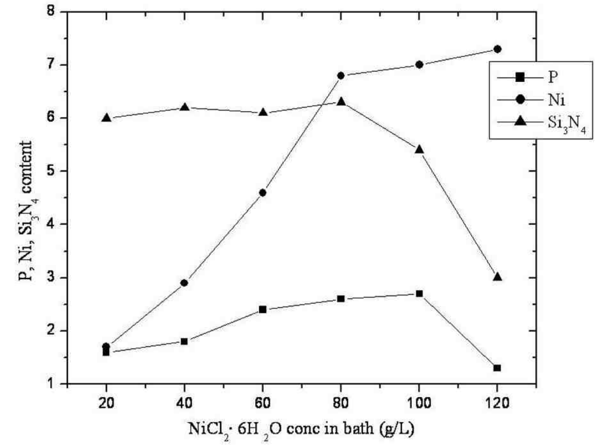

Figure 1—Effect of $NiCl_2 \cdot 6H_2O$ concentration on the coating composition. Bath and process conditions: $FeCl_2 \cdot 4H_2O$, 500 g/L (67 oz/gal); $NaH_2PO_2 \cdot H_2O$, 10 g/L (1.3 oz/gal); Ascorbinic acid, 2 g/L (0.27 oz/gal); Si_3N_4, 60 g/L (8.0 oz/gal); CD, 5 A/dm^2 (46.4 A/ft^2); T, 40°C (104°F); pH 1.0.

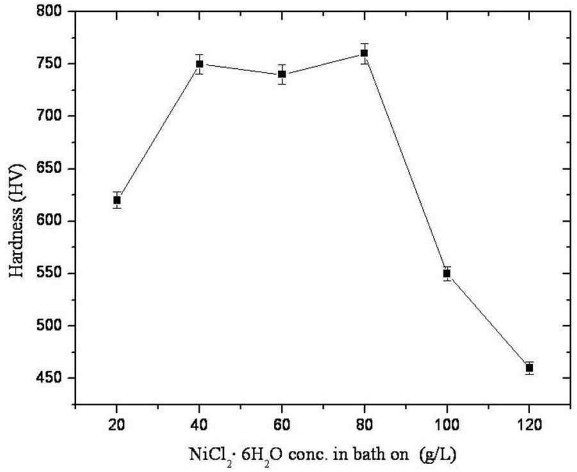

Figure 2—Effect of $NiCl_2 \cdot 6H_2O$ concentration on the coating hardness. Bath and process conditions: same as in Fig. 1.

Results and discussion

Effect of nickel chloride

The effect of $NiCl_2 \bullet 6H_2O$ concentration on the composition and hardness of the deposit are shown in Figs. 1 and 2, respectively. When the nickel chloride concentration was increased from 20 to 80 g/L (2.67 to 10.68 oz/gal), the phosphorus content increased slightly, while the nickel content increased more significantly. No significant change in Si_3N_4 was observed. Over this relatively wide range of coating composition, the hardness remained relatively constant, at 730 to 780 VHN_{100}. When the $NiCl_2 \cdot 6H_2O$ concentration was raised above 100 g/L (13.4 oz/gal), the P and Si_3N_4 composition in the deposit greatly decreased. As well, the hardness decreased significantly. Below 20 g/L (2.67 oz/gal) $NiCl_2 \cdot 6H_2O$ in the bath, the hardness was also lower.

The reasoning behind this is as follows. When the nickel chloride concentration strayed from the 20 to 80 g/L (2.67 to 10.68 oz/gal) range, the deposition rate significantly decreased,[7] owing to increased hydrogen evolution, hydrogen embrittlement and the resultant blocking of Si_3N_4 incorporation into the deposit. It is also indicated that the codeposition of phosphorus was induced by nickel electrodeposition, and the percentages of P and Si_3N_4 particles in the coatings would possibly have notable influences on the hardness.

Effect of sodium hypophosphite

Figures 3 and 4 show the influence of varying the sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) concentration on the composition and hardness of the coating, respectively. It can be seen from Fig. 3 that the phosphorus concentration in the coating increased with increasing $NaH_2PO_2 \cdot H_2O$, while the nickel and Si_3N_4 compositions slightly decreased. Corresponding to the increasing phosphorus in the deposit, the hardness increased from 630 to 770 VHN_{100}.. The data showed that the concentration of P in the coating had an evident influence on hardness. Further, it was noted that, when the amount of $NaH_2PO_2 \cdot H_2O$ reached 18 g/L (2.4 oz/gal), large amounts of hydrogen evolved at the cathode, and high quality coatings could not be obtained.

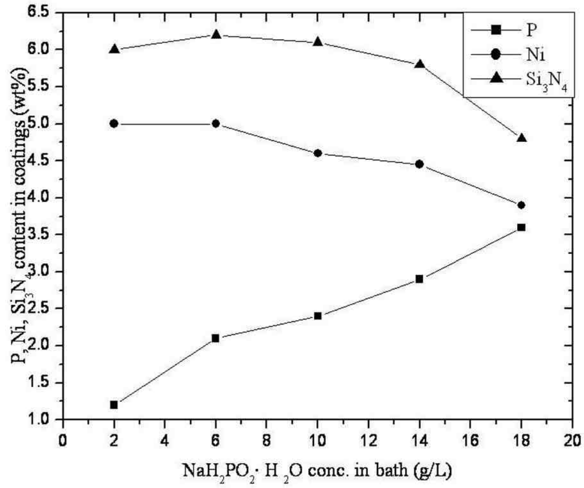

Figure 3—Effect of $NaH_2PO_2 \cdot H_2O$ concentration on the coating composition. Bath and process condition: $FeCl_2 \cdot 4H_2O$, 500 g/L (67 oz/gal); $NiCl_2 \cdot 6H_2O$, 60 g/L (8.0 oz/gal); Ascorbinic acid, 2 g/L (0.27 oz/gal); Si_3N_4, 60 g/L (8.0 oz/gal); CD, 5 A/dm^2 (46.4 A/ft^2); T, 40°C (104°F); pH 1.0.

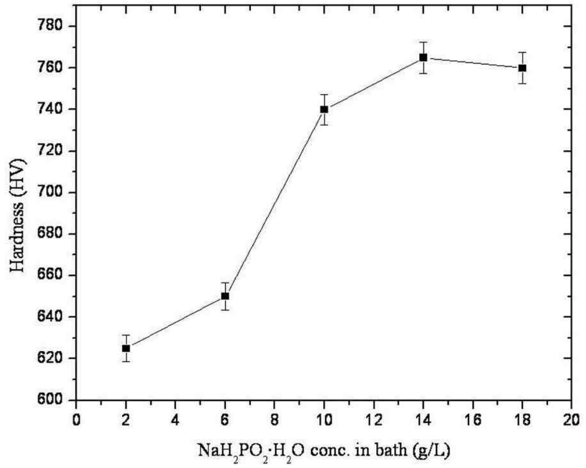

Figure 4—Effect of $NaH_2PO_2 \cdot H_2O$ concentration on the coating hardness. Bath and process conditions: same as in Fig. 3.

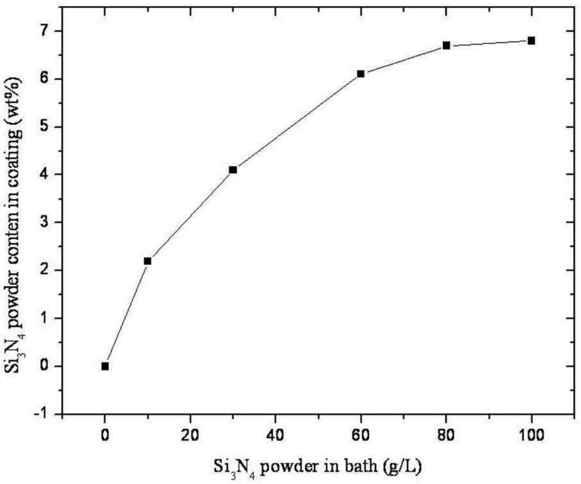

Figure 5—Effect of Si$_3$N$_4$ powder concentration on the coating hardness. Bath and process conditions: FeCl$_2$ · 4H$_2$O, 500 g/L (67 oz/gal); NiCl$_2$ · 6H$_2$O, 60 g/L (8.0 oz/gal); NaH$_2$PO$_2$ · H$_2$O, 10 g/L (1.3 oz/gal); Ascorbinic acid, 2 g/L (0.27 oz/gal); CD, 5 A/dm^2 (46.4 A/ft^2); T, 40°C (104°F); pH 1.0.

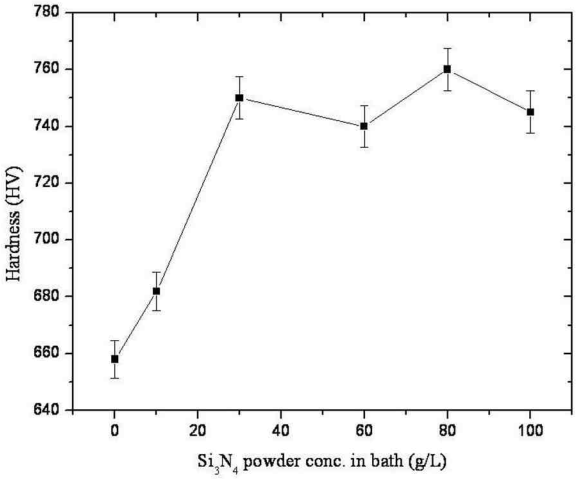

Figure 6—Effect of Si$_3$N$_4$ powder concentration on the coating composition. Bath and process condition: same as in Fig. 5.

Effect of silicon nitride

The data show that the concentration of Si$_3$N$_4$ in the bath had little influence on the metal composition of the composite coatings.[7] Figures 5 and 6 show the effect of the Si$_3$N$_4$ bath content on the coating composition and hardness, respectively. As can be seen, the Si$_3$N$_4$ content in the coating increased with that in the bath. Above 80 g/L (10.7 oz/gal) however, the Si$_3$N$_4$ content in the coating remained unchanged. When either the Si$_3$N$_4$ content in the bath was over 30 g/L (4.0 oz/gal) or that in the coating was over 4 wt%, there was virtually no change in coating hardness. In other words, the Si$_3$N$_4$ content did have an effect on the coating hardness to some degree, but when the silicon nitride content reached certain limits, further increases in hardness could not be realized.

Effect of heat treatment temperature on the coating hardness

The curves in Fig. 7 show the influence of heat treatment temperature on the hardness of the alloy coating and that of the alloy composite strengthened by silicon nitride. In the composite coating, the Si$_3$N$_4$ concentration was 6.1 wt%. The zero point on the abscissa (temperature scale) represents the specimen that did not receive heat treatment.

It is clear that when the heat treatment temperature was below 300°C (572°F), the coating hardness increased instead of decreasing. Comparing the curves, we can see that the heat resistances of the two coatings (non-composite and silicon nitride composite) were similar. In another study,[8] after an annealing treatment at 200°C (392°F) for 2 hr, the room temperature hardness of an iron- plated coating decreased from 790 to 590 VHN$_{100}$. The heat resistances of the specimens in Fig 7 are comparatively better than those of the specimen in the other study.[8] It would appear that the key factor in determining the heat resistance is the composition of the alloy matrix.

Hardening mechanism

Solid-solution hardening

Figure 8 shows the x-ray diffraction pattern of a plated Fe-Ni-P alloy specimen. It is known that the nickel and phosphorus in Fe-Ni-P coatings are dissolved into the α-Fe crystal lattice, and, to varying degrees, they have solid-solution hardening effects.[9]

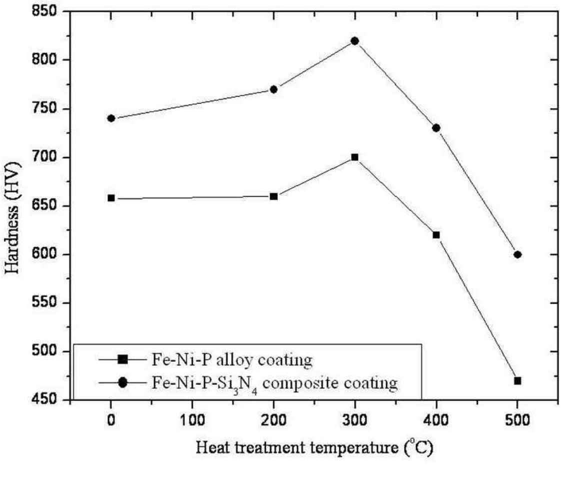

Figure 7—Effect of heat treatment temperature on the coating hardness.

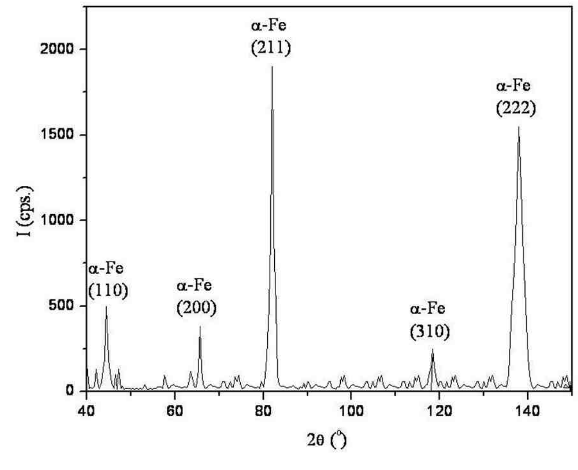

Figure 8—X-ray diffraction pattern for a Fe-Ni-P alloy deposit. Bath and process conditions: NaH$_2$PO$_2$ · H$_2$O, 6 g/L (0.8 oz/gal); other conditions are the same as those in Fig. 3.

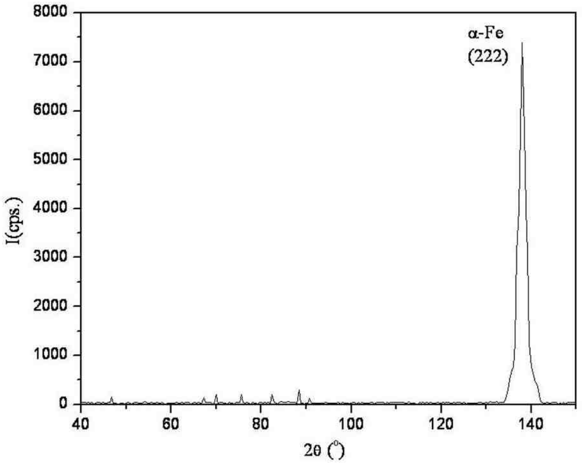

Figure 9—X-ray diffraction pattern for a Fe-Ni-P alloy deposit. Bath and process conditions: $NaH_2PO_2 \cdot H_2O$, 10 g/L (1.3 oz/gal); other conditions are the same as those in Fig. 3.

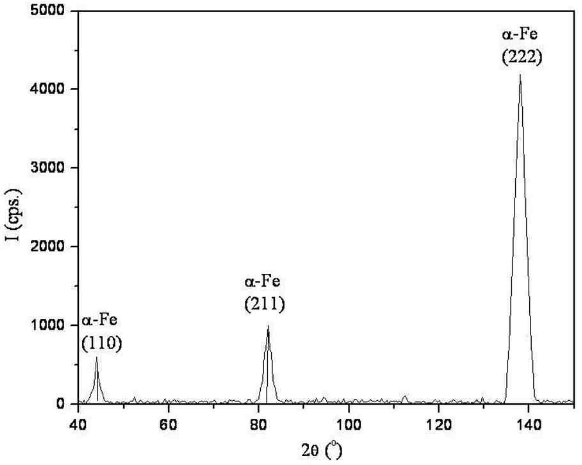

Figure 10—X-ray diffraction pattern for a Fe-Ni-P-Si_3N_4 composite deposit. Bath and process condition: Si_3N_4, 60 g/L (8.0 oz/gal); other conditions are the same as those in Fig. 5.

Because phosphorus has a higher value of electronegativity (χ = 2.1) than do Fe (χ = 1.64) or Ni (χ = 1.75), and the latter two have similar χ values, it tends to exist in the trivalent state(P^{-3}), while nickel keeps its neutral chemical state in the crystal lattice. According to the strengthening theory of solid solutions at low concentrations,[10,11] when there are residual charges of alloy atoms in the crystal lattice, charges of opposite character will be induced in the surrounding lattice. In this way, appending polarized bonding will emerge around the atoms of the alloy and the matrix, and the atomic bonding of metals will be strengthened as a result. This kind of bonding can prevent crystal dislocation slip. According to this theory, phosphorus has the greater strengthening function in an α-Fe crystal lattice than does nickel. What is more, a great number of experiments[11] have made clear that the re-crystallization temperature of the material would be significantly enhanced when only a small amount of alloying material entered the crystal lattice of the metal. Therefore, the alloy will exhibit high rigidity at high temperature. This also explains the relatively high heat resistance of the iron-alloy coating.

Texture hardening

Figures 9 and 10 show the x-ray diffraction patterns of the Fe-Ni-P alloy and Fe-Ni-P-Si_3N_4 composite coatings, respectively. The patterns in Figs. 8-10 clearly show texture character. From the figures, the effect of process conditions on the crystal orientation of Fe-Ni-P coatings is evident. Increasing $NaH_2PO_2 \cdot H_2O$ concentration in the bath favors growth on the (222) plane. Thus, a texture mechanism will influence the hardening of this type of coating.

Particle hardening

A comparison of Figs. 5 and 6 indicates that the Si_3N_4 particle concentration has some effect on coating hardness. Actually, there are two strengthening mechanisms operative here: dispersion strengthening and particle strengthening. The particle dimension in particle-strengthened composite materials is usually greater than 1 μm (~40 μ-in.). Both the matrix and the particles will bear the weight of a load. Through mechanical restriction of particles, distortion of the matrix can be controlled, and the strengthening effect is greatly influenced by the solid particle concentration in the material.

Conclusions

- The concentration of phosphorus in Fe-Ni-P-Si_3N_4 composite coatings had a clear influence on the hardness of coating.
- The hardness of the composite coating was slightly higher than that of alloy matrix coating, and the hardness reached a maximum when the concentration of Si_3N_4 reached about 4 wt%.
- The heat resistance of both the electrodeposited Fe-Ni-P-Si_3N_4 composite and the Fe-Ni-P alloy were all higher than that of a plated iron coating prepared at room temperature.
- Besides particle strengthening and solid-solution hardening in the Fe-Ni-P-Si_3N_4 composite coating, texture strengthening was also an important influence on coating hardness.

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