

Electrodeposition of Super Hard Ni–B/Diamond Composite Coatings

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Super hard Ni–B/diamond composite coatings were prepared by electrodeposition. Such extreme hardness (ca. 2500 Hv) was ascribed to a large content of diamond particles and hardness of Ni–B matrix. Thermal treatment of the coatings resulted in the formation of Ni–B alloys, which led to increase in film hardness. This method is much simpler than previously reported methods for preparing hard coatings.

Surface properties of materials (e.g., durability, tribological properties, corrosion resistance, and electric conductivity) are often controlled by coating technology. Hard coatings are used to improve the durability of products; for example, cutting tools are coated with hard materials such as diamond and TiN by dry processes (i.e., chemical or physical vapor deposition).^{1,2} Though the dry process produces high-quality hard coatings, it requires specialized and costly instrumentation (reactors, vacuum furnaces, heaters, or plasma generators), extreme reaction conditions, and precise control of gas flow. On the other hand, a wet process, which is an alternative coating method, is carried out under mild conditions and involves low-cost methodology, but its disadvantage is that these coatings show lower hardness than those produced by the dry process: hard TiN films prepared by dry processes show 2000–2700 Hv,^{2,3} while the hardest coating (Cr–C alloy film) prepared by wet processing show ca. 1700 Hv.^{4,5} Recently, the disadvantage is solved by combining two wet processes, in which diamond particles are deposited onto substrate by electrophoretic deposition, and then Ni–B fills the pores of the diamond particles by electroless deposition.⁶ Ni–B is a hard metal coating, and the two-step process enables a large amount of diamond particles to codeposit into the hard Ni–B matrix. As a result, the Ni–B/diamond composite coatings exhibit high hardness. The hardness of the Ni–B/diamond composite coatings is comparable to some hard coatings prepared by dry processes. This wet process is much simpler than dry processes; nevertheless, it requires two steps. Herein, we report a simple one-step process for preparing hard Ni–B/diamond composite coatings.

For a long time, the preparation of Ni–B coatings was limited to electroless deposition,^{7–11} but recently a few researchers have revealed that the Ni–B coatings can be prepared by electrodeposition.^{12,13} Electrodeposition, which is a typical coating method for thin metal or alloy films, is simple, low cost and can easily control growth rate. In addition, when particles are dispersed in electrodeposition baths, the particles are codeposited into electrodeposited metal matrix.¹⁴ In this study, we tried to use Ni–B electrodeposition baths containing diamond particles to prepare hard Ni–B/diamond composite coating. This method consists of a one-step wet process, which would be preferable to the dry processes and the two-step wet processes.

Table 1. Chemical composition of the plating bath and the operating conditions

Chemicals/parameters	
NiSO ₄ ·6H ₂ O	240 g L ⁻¹
NiCl ₂ ·6H ₂ O	45 g L ⁻¹
H ₃ BO ₃	30 g L ⁻¹
Trimethylamine borane	3 g L ⁻¹
Diamond particle	15 g L ⁻¹
Sodium dodecyl sulfate	1 g L ⁻¹
pH	3.5
Temperature	323 K
Current density	1 A dm ⁻²

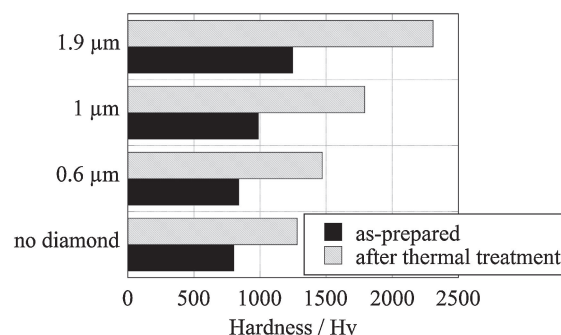


Figure 1. Microhardness of a Ni–B coating and Ni–B/diamond composite coatings before/after thermal treatments at 573 K.

Electrodeposition of Ni–B/diamond composite coatings was carried out by a conventional method. The composition of electrodeposition bath is shown in Table 1. Trimethylamine borane and sodium dodecyl sulfate were used as a boron source and a dispersing agent of diamond particles, respectively. Diamond particles (mean diameter: 0.6, 1, or 1.9 μm) were added into the baths. The pH values of the baths were adjusted using NiCO₃. The thickness of Ni–B/diamond composite coatings was controlled to be ca. 20 μm by adjusting electrodeposition time. Vickers microhardness of the coatings was measured by using a microhardness tester under the indentation load of 50 gf. The details of experimental procedures are described in Supporting Information (SI).¹⁷

Figure 1 shows hardness of a Ni–B and Ni–B/diamond composite coatings before/after thermal treatment in air at 573 K for 1 h. At first, we focus on coatings before thermal treatment. Obviously, the film hardness was enhanced by the codeposition of diamond particles, and the film hardness of Ni–B/diamond composite coatings increased with increasing the particle size of diamonds. The hardness of Ni–B/diamond (1.9 μm) composite

coatings was 1248 Hv, which is about 1.5 times higher than that of the Ni–B coating (804 Hv). The hardness of these coatings was increased by thermal treatment. For example, the thermal treatment of the Ni–B/diamond (1.9 μm) composite coatings raised its hardness to 2310 Hv, which is almost the same hardness as hard coatings prepared by two-step wet process (2494 Hv).⁶

The effect of thermal treatment on the film hardness can be explained based on previous studies on Ni–B coatings.^{9,12} During thermal treatment, amorphous structure of as-prepared Ni–B coatings is transformed into Ni–B alloy structure such as Ni₂B and Ni₃B. The Ni–B alloys have higher hardness than amorphous Ni–B; therefore, thermal treatment enhances the film hardness of Ni–B coatings. In this study, thermal treatment was carried out at 573 K, because Ni–B alloys hardly formed at lower temperatures than 573 K, and the strong growth of nickel crystallites which results in the decrease of hardness occurred at higher temperatures than 573 K. XRD patterns of Ni–B/diamond (1.9 μm) composite coatings are shown in SI.¹⁷ Before thermal treatment, relatively broad diffraction line of nickel was confirmed. After thermal treatment, formation of Ni₃B alloy and the growth of nickel crystallite were observed. The size of nickel crystallites after thermal treatment was 254 nm.

Figure 2 shows optical micrographs of a Ni–B coating and Ni–B/diamond composite coatings. The surface of the Ni–B coating was smooth (Figure 2a) so that we could observe it possessed metallic luster. The surface roughness (*Ra*) of the Ni–B coating was 0.035 μm . The surface flatness is an advantage of electrodeposition of Ni–B, because electroless deposition of Ni–B produces rough surface.⁷ The surface roughness (*Ra*) of Ni–B/diamond (1.9 μm) composite coatings was 0.28 μm . Although *Ra* was increased by the codeposition of diamond particles, the composite coating had relatively flat surface. The black areas in Figures 2b, 2c, and 2d represent the codeposited diamond particles in Ni–B matrix. From the images, we can see that a large amount of diamond particles was codeposited into Ni–B matrix. It seems that the black areas (i.e., the amount of codeposited diamond particles) increase with increasing particle size of diamonds. This would be the reason that hardness of Ni–B/diamond composite coatings increased with increasing particle size of diamond particles (Figure 1).

The hardness of Ni–B/diamond composite coatings depends on not only the amount of diamond particles but also the amount of boron atoms in Ni–B matrix. To examine the boron content in these coatings, ICP analyses for the coatings were carried out. The results of the ICP analyses suggested that boron content in the Ni–B matrix of these coatings was almost the same value (ca. 13 atom %). Therefore, it would be concluded that the hardness of these Ni–B/diamond composite coatings depends on the content of codeposited diamond particles which is determined by their particle sizes. At the present moment, we cannot explain why diamonds with larger sizes tend to codeposit more easily. It is reported that codeposition of diamond particle into metal matrix is affected by many factors such as applied voltage, stirring speed for baths, ζ potential of diamonds, and adsorbed species on diamond.^{15,16} In future work, we would like to study factors that determine the content of diamond particles in the coatings.

In summary, super hard Ni–B/diamond composite coatings were prepared by one-step electrodeposition. These coatings

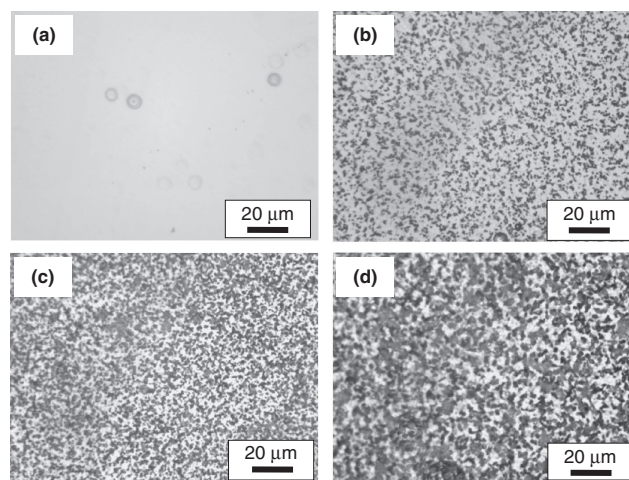


Figure 2. Optical micrograph images of (a) a Ni–B coating, and Ni–B/diamond coatings (mean particle size of diamond: (b) 0.6, (c) 1.0, and (d) 1.9 μm).

showed extreme high hardness. The hardness of the composite coatings was increased by increasing the particle size of diamonds because diamonds with larger sizes tend to codeposit into Ni–B matrix more easily. The hardness was enhanced by thermal treatments of the coatings. The hardest Ni–B/diamond composited coating in this study was comparable to TiN coatings prepared by dry process and Ni–B/diamond composited coatings prepared by two-step wet process.

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- 17 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.