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Plating of Ni/c-BN composite film in two steps

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In recent years, advanced new metal composites, metal-ceramic composites, and other hard and wear resistant materials have been used more widely as machinery parts in industry. In order to machine these advanced materials, ultra hard and ultra wear resistant tools are required to supply the demands of a higher productivity accompanied by the accuracy of geometry and dimensions of work-pieces as well as the fine finishing of working surfaces of the machined pieces. These requirements have been fulfilled by tools coated with super-hard materials such as diamond and cubic boron nitride (c-BN). Although diamond is known as the hardest material, diamond tools cannot apply to machining ferrous materials where relatively higher temperature is generated due to the problem of the dissolution of carbon in iron at higher temperature [1]. In contrast, c-BN known as the second hardest material after diamond has good thermal stability and chemical inertness regarding iron [2]. These advantages of c-BN have opened up the ferrous machining markets. Nowadays, c-BN coated tools are widely used to machine iron and iron based alloy materials in the field of automotive and aerospace industries. Although c-BN can coat on cutting, drilling and grinding tools using various modified physical and chemical vapor deposition methods [3–6], the deposits by these methods are usually contaminated with the hexagonal phase (h-BN) [2, 3]. Additionally these methods are expensive and therefore, have been commercially substituted with the electrolytic composite plating technique in which particles of c-BN are codeposited with metals such as nickel, cobalt, etc. However, the performance of these coatings depends upon the particle content in the metal matrix, and generally, high particle content is required. In an attempt to incorporate high amount of organic [7] and inorganic [8–11] particles into a nickel matrix, various techniques have been developed in our laboratory. Previously, we have demonstrated that the composite coatings prepared by a two step electrolytic method are rich in particle content and these composites exhibited good anti-wear performance [8]. In the present investigation, we carried out the coating of Ni/c-BN composite film by the two step method and its anti-wear performance was studied.

In the first step, c-BN particles were electrophoretically deposited on a copper substrate. Then, electrodeposition of nickel on this substrate was carried out in the second step. For the electrophoretic deposition, 5 g dm^{-3} of the c-BN powder (0–2 μm, BORAZON, GE Micron Products, USA) was dispersed in an ethanol bath containing 6 mM $MgCl_2{\cdot}6H_2O$ using an ultrasonic disruptor (TOMY, UD-200) for 10 min. The c-BN particles were deposited electrophoretically on a copper cathode placed vertically at a distance of 0.01 m parallel to a graphite electrode under an electric field strength of 4 kV m^{-1} for 3 min. After air-drying, the copper substrate covered with the electrophoretic deposits was subjected to the electrodeposition of nickel using a chloride bath containing 50 g dm^{-3} $NiCl_2{\cdot}6H_2O$ and 10 g dm^{-3} NH_4Cl. The pH of this bath was initially adjusted to 6.6. Controlled potential electrolysis of this bath was carried out at −0.82 V vs. SCE for 400 k coulomb m^{-2} of the electrical charge passing through the cathode. The electrophoretic as well as nickel deposition was carried out without agitation of the baths. After depositing nickel in the second step, the deposit was washed with running water, and then ultrasonic cleaning in acetone was applied for 10 min followed by another 10 min in distilled water. The surface and cross sectional morphologies of the coating were examined using a scanning electron microscope (SEM) and the composition of the deposits was determined using an energy dispersive X-ray micro-analyzer (EDX) coupled to the SEM. Wear resistance of the coating was examined using an abrasion tester (NUS-ISO3, Suga Abrasion Tester) fitted with a counter surface of a SiC abrader under dry sliding friction conditions for 300 cycles at various applied loads. All the above experiments were carried out at 25 °C.

SEM images of the surface and cross-section of an electrophoretic deposit prepared in the first step are shown in Fig. 1. This surface image (Fig. 1a) reveals the uniform and dense deposit of c-BN particles. As shown by the cross section image (Fig. 1b), the thickness of this electrophoretic deposit was approximately 30 μm. The growth of the electrophoretic deposits was found to increase with the deposition time, electric field strength, particle loading and the concentration of $MgCl_2$. However, higher concentrations of $MgCl_2$ produced rough deposits, which developed cracks on drying. Therefore, the ratio of particles loading and the concentration of $MgCl_2$ should be in the correct proportions in order to produce crack-free, thick and stable electrophoretic deposits. The deposition potential for nickel in the second step was determined using a voltametric technique. When linear sweep voltametry of an aqueous bath containing 1 mM $NiCl_2$ and 0.1 M NH_4Cl was carried out using the above substrate covered with the c-BN particles as the cathode, the peak potential for nickel deposition was observed to be approximately at −0.82 V vs.

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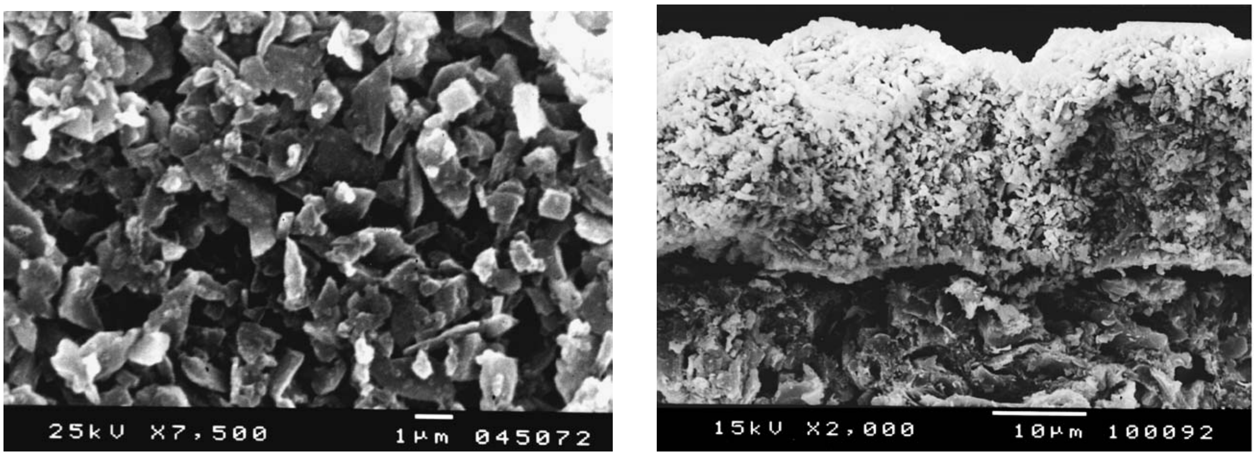
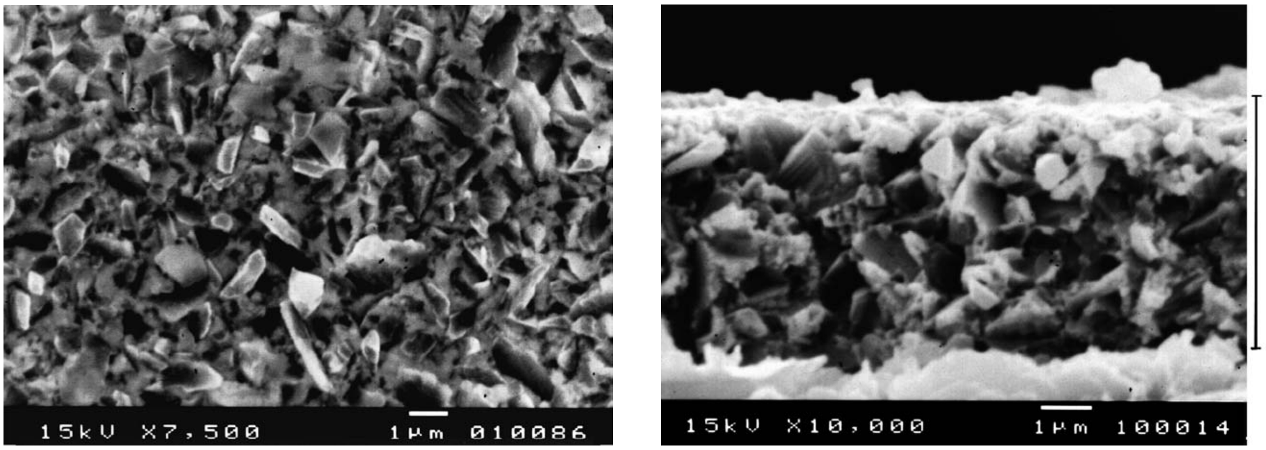


(a) (b)

Figure 1 SEM images of the (a) surface, and (b) cross section, of an electrophoretic deposit of c-BN on a copper substrate using an ethanol bath containing 6 mM $MgCl_2 \cdot 6H_2O$ and 5 g dm^{-3} c-BN particles for 3 min under 4×10^3 V m^{-1}.



(a) (b)

Figure 2 SEM images of the (a) surface, and (b) cross section, of the composite film of Ni/c-BN prepared by depositing nickel on the substrate of Fig. 1.

SCE. Therefore, the deposition of nickel on a substrate covered with the c-BN particles was carried out at this potential value. At a potential higher than this value, hydrogen gas was evolved on the working electrode and stripped the c-BN particles layer. At the optimum condition of depositions as described above, the composite coating looked smooth. The surface and cross sectional morphologies of the composite film are shown in Fig. 2. This SEM image of the surface (Fig. 2a) reveals a uniform distribution of the particles throughout the coating and this finding is also supported by the SEM image of the cross section of the coating (Fig. 2b). As evident from this cross sectional image, the composite coating had a thickness of about 5 μm. The particle content in this composite film estimated by EDX was approximately 67 vol% with an error corresponding to about 4 vol%. Thus, using only 5 g dm^{-3} of particles in the electrophoretic bath, the two-step method co-deposited more than 60 vol% of the c-BN particles into a nickel matrix. Similar results were obtained with other types of ceramic particles in our previous experiment [8]. These results show that the two-step method can be used to incorporate a high vol% of a variety of particles into a nickel matrix using relatively low amount of particles in a bath compared to that of a single-step classical plating bath. Moreover, the amount of particles deposited from the single-step technique is often less than the amount of particles needed in a coating for most

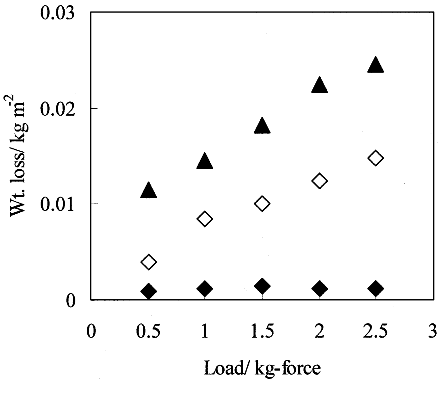


Figure 3 Weight loss of material worn out from the (♦) Ni/c-BN composite film of Fig. 2, (◇) a stainless steel plate, and (▲) an electrodeposited nickel coating during a wear experiment.

engineering work. In such cases, the proposed two-step technique of composite plating may be a promising technique.

During the wear test, the specimen was moved to-and-fro against the counter surface under various applied loads. This back-and-forth movement of the specimen produced a constant worn surface area with dimensions of 33 mm × 10 mm. The wear resistance of the composite film was measured here in terms of the weight loss per square meter of the material against different applied loads (Fig. 3). The wear resistances of a stainless steel plate and the particle-free electrodeposited nickel obtained from the same bath and conditions as that for the two-step coating are also shown in Fig. 3. As evident from this figure, the wear resistance of the Ni/c-BN composite film is much higher than that of the stainless steel and the particle-free electrodeposited nickel. Weight loss of the wear of the Ni/c-BN coating was negligible and did not increase significantly with the applied load as in the case of steel and nickel. This better wear performance of the Ni/c-BN coating might be due to the presence of a high vol% of the c-BN particles, which have super hard and super abrasive nature. As a result of its extremely good wear performance, the Ni/c-BN composite film prepared by the proposed two-step method may be applied to various tools for cutting, drilling and grinding super hard alloy of steel and other materials.

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References

1. A. SCHUTZE, K. BEWILOGUA, H. LUTHJE, S. KOUPTSIDIS and M. GAERTNER, *Surf. Coat. Technol.* **97** (1997) 33.
2. J. ULLMANN, D. HEYDEN, G. SCHWARZ, G. K. WOLF, K. BABA and H. HATADA, *ibid.* **97** (1997) 281.
3. R. FREUDENSTEIN, S. REINKE and W. KULISCH, *ibid.* **97** (1997) 270.
4. P. LIN, C. DESHPANDEY, H. J. DOERR, R. F. BUNSHAH, K. L. CHOPRA and V. VANKAR, *Thin Solid Films* **153** (1987) 487.
5. N. TANABE and T. HAYASHI, *Diam. Related Mater.* **01** (1992) 883.
6. S. P. S. ARYA and A. D'AMICO, *Thin Solid Films* **157** (1988) 267.
7. N. K. SHRESTHA and T. SAJI, *J. Jpn. Colour Mater. Soc.* **73** (2000) 227.
8. N. K. SHRESTHA, K. SAKURADA, M. MASUKO and T. SAJI, *Surf. Coat. Technol.* **140** (2001) 175.
9. N. K. SHRESTHA, I. MIWA and TETSUO SAJI, *J. Electrochem. Soc.* **148** (2001) C106.
10. N. K. SHRESTHA, M. MASUKO and T. SAJI, *Wear* **254** (2003) 555.
11. T. TAKEBE, T. MATSUZAKI, N. K. SHRESTHA and T. SAJI, *J. Surf. Fin. Soc. Jpn.* **54** (2003) 610.

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