Supplementary information

Experimental

Materials

Ethanol (Kanto Chemical Co., Inc.), diamond particles (Tomei Diamond Co. Ltd.), $MgCl_2 \cdot 6H_2O$ (Kanto Chemical Co., Inc.), poly(vinyl butyral) (MW = 8500, Scientific Polymer Products, Inc.), $NiCl_2 \cdot 6H_2O$ (Kanto Chemical Co., Inc.), ethylenediamine (Kanto Chemical Co., Inc.), potassium sodium tartrate (Kanto Chemical Co., Inc.), NaOH (Kanto Chemical Co., Inc.), and CH_3COOTl (Aldrich) were used as-received.

Pretreatment of substrates

Iron plates (40 × 20 × 1 mm) were used as substrates. Prior to coating, the plates were polished and cleaned as follows. The substrates were physically polished with Al_2O_3 powder, and then ultrasonicated in acetone for 10 min. The treated substrates were immersed in HCl aqueous solution (10 vol%) for 10 min and then rinsed with water.

To prevent corrosion, the polished and cleaned substrates were pre-coated with Ni-B thin films. Ni-B was deposited on the substrates by electroless plating. The composition of the plating bath and the coating parameters are given in Table S1. Electroless plating was started by adding $NaBH_4$ (1.25 g/L) as a reductant into plating bath. Pre-coating with Ni-B was carried out for 15 min.

Electrophoretic deposition

Ethanol (60 mL) containing 50 mg of $MgCl_2 \cdot 6H_2O$ and 300 mg of diamond particles was sonicated for 10 min, and then 60 mg of poly(vinyl butyral) was added to the resulting solution, followed by sonication for 20 min. Electrophoretic deposition of diamond particles on Ni-B pre-coated substrates was conducted at constant voltage (30 V/cm) using a carbon plate as counter-electrode and with a deposition time of 16 min. After drying at room temperature, diamond films were observed on the substrates.

Electroless plating

The resulting diamond film coated substrates were immersed into an electroless plating bath. The composition of the coating bath and the coating parameters are given in Table S1. Electroless plating was started by adding $NaBH_4$ (1.25 g/L) as a reductant. The coating of Ni-B was carried out for 3 h. The samples obtained were then ultrasonicated in ethanol for

Table S1 Chemical composition of electroless deposition bath and operating conditions

Chemicals/parameters	
$NiCl_2 \cdot 6H_2O$	30 g/L
Ethylenediamine	15 g/L
Potassium sodium tartrate	40 g/L
NaOH	40 g/L
CH_3COOTl	16 mg/L
pH	>13
Temperature	323 K

20–30 min to remove excess diamond particles which was not embedded in the Ni-B matrix. For diamond films prepared by electrophoretic deposition, diamond particles were not connected strongly. Therefore, diamond particles above Ni-B/diamond coatings were easily removed by the sonication method.

Heat treatment

Ni-B/diamond coatings were heated in air at 673 K for 1 h using an electric furnace. The heated coatings were cooled in air.

Characterization

Vickers micro-hardness of the coatings was measured using a micro-hardness tester (MHTZ, Matsuzawa Co. Ltd., Japan) under an indentation load of 0.49 N at eight different locations on a specimen, and the mean value was determined as the coating hardness. X-ray diffraction (XRD; RINT 2500V, Rigaku) patterns were measured at room temperature using Cu-Kα radiation. The cross-section specimen was prepared using a cross-section polisher (JEOL, SM-09010). Etching of samples was carried out with an Ar ion beam at 6 kV for 8 h.

The Ni, B, and diamond contents in the coatings were estimated by the following methods. The Ni-B/diamond coatings were immersed in concentrated nitric acid solution to dissolve Ni and B. The resulting solution was filtered with a membrane filter unit. The filtrate was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine the composition of Ni and B. The residual diamond particles on the dried filter paper were directly weighed._

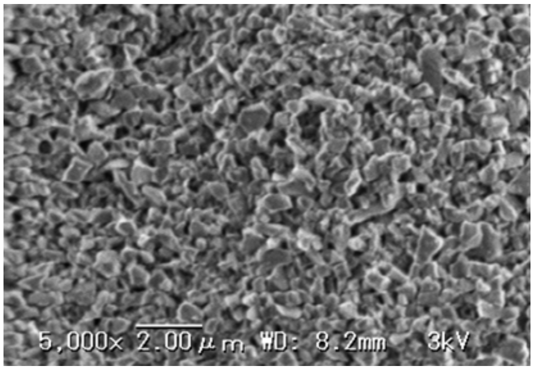

Fig. S1 A SEM image of diamond particle films prepared using electrophoretic deposition.