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Effect of boron content and crystalline structure on hardness in electrodeposited Ni–B alloy films

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ABSTRACT

Ni–B alloy films were electrodeposited using a conventional Ni plating bath containing dimethylamine borane (DMAB) or trimethylamine borane (TMAB) as boron sources. Properties (hardness, boron content, and crystalline structure) of the electrodeposited Ni–B alloy films were significantly affected by electrodeposition conditions (current density, pH, and the amount of boron sources in plating bath). X-ray amorphous Ni–B alloy films showed high hardness, whereas hardness of Ni–B alloy films that consisted of large crystallites was low. In TMAB bath, the crystalline structure of Ni–B alloy films was controlled by the amount of co-deposited boron atoms; however in DMAB bath, clear relationship between film hardness and boron content was not confirmed. The crystalline structure of Ni–B films was drastically changed by heat-treatment and the effect of structural changes on hardness was discussed.

1. Introduction

Coating of substrates is an important industrial process and huge amounts of industrial products coated with functional thin films are processed. A Ni–B alloy film is one of the functional coatings and is applied in aerospace, automotive, chemical and electrical industries due to their high hardness, high wear and corrosion resistances and good solderability.

Electroless deposition has been used to produce the Ni–B alloy particles or films [1–7]. In this process, dissolving reducing agents such as borohydride, release electrons which are received by metal cations, forming a metal thin film on substrates. Electrodeposition is also well-known as a typical coating method of metal or alloy thin films. The method is simple, low cost, and easy to control growth rate [8,9]. However, electrodeposition of Ni–B films has been hardly reported. Onoda et al. demonstrate that Ni–B films can be prepared from electrodeposition of Ni, in the presence of trimethylamine borane (TMAB) which acts as boron sources [10]. Based on this study, a few reports about electrodeposition of Ni–B films and applications of them are reported [11–15]. Lee et al. analyzed the properties (e.g., crystalline structure, micro hardness and internal stress) of the electrodeposited Ni–B films [11]. Krishnaveni et al. reported that dimethylamine borane (DMAB) can also be used as a boron source in electrodeposition of Ni–B films [12]. Bekish et al. examined the relationship between corrosion resistance and structure of electrodeposited Ni–B films [15].

The previous reports show that hardness of electrodeposited Ni–B films depends on plating condition, but factors that determine hardness are not sufficiently understood. Herein, we prepared Ni–B films under various plating conditions, and discuss the factors determining film hardness based on their crystalline structure and boron content.

2. Experimental

2.1. Electrodeposition

A conventional Ni plating bath (Watt's type bath) containing DMAB or TMAB was used in electrodeposition of Ni–B films (Table 1). Hereafter, the two types of plating baths will be referred to as a DMAB bath or a TMAB bath. The pH values of the baths were adjusted by H_2SO_4 or $NiCO_3$. A Cu substrate was polished using metal polishing reagent (PIKAL, Nihon Maryo-Kogyo Co. Ltd.), and was washed in acetone under ultrasonic radiation for 10 min. The Cu substrates were masked with insulated tapes to be 20×20 mm. A Ni plate was used as a counter electrode.

The Cu and the Ni plates were vertically immersed into 50 ml of plating baths. The temperature of the plating bath was controlled with a water bath. Electrodeposition was carried out under constant current density (0.5–10 A/dm^2) at 323 K with stirring. The electrodeposited films with the same thickness (ca. 20 μm) were prepared by adjusting plating time. The resulting Ni–B films were washed with ion-exchanged water and dried in air at room temperature.

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

Chemicals/parameters	
$NiSO_4 \cdot 6H_2O$	240 g/L
$NiCl_2 \cdot 6H_2O$	45 g/L
H_3BO_3	30 g/L
DMAB or TMAB	0–10 g/L
pH	1.0–5.5
Temperature	323 K

2.2. Electrochemical analyses

Polarization curves for aqueous solutions of $Na_2SO_4 \cdot 10H_2O$ (0.16 M), $Na_2SO_4 \cdot 10H_2O$ (0.16 M) + DMAB (22.8 mM), and $Na_2SO_4 \cdot 10H_2O$ (0.16 M) + TMAB (22.8 mM) were measured in a one-compartment cell consisting of three electrodes system using an electrochemical workstation (CV-50W, BAS Co. Ltd.). Ni–B films which were prepared by electrodeposition under 1 A/dm^2 and 3 g/L of TMAB were used as working electrodes. The Ni–B films were masked with insulated tapes to be 0.5 × 0.5 cm. Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively. Prior to the measurement, the solution was bubbled with nitrogen for 10 min and −1500 mV vs. Ag/AgCl was applied to the Ni–B electrodes for 10 s to clean their surface. The electrode potential was scanned at 25 mV/s.

2.3. Characterization

The chemical composition in Ni–B films was determined by using inductively coupled plasma (ICP) spectroscopy (Prodigy ICP, Leeman Labs, INC U.S.A.). Samples for ICP analyses were prepared as following procedures. A plating film was dissolved in conc. HNO_3, and the resulting solution was diluted with ion-exchanged water. ICP system was calibrated using boron and nickel standard solutions (Kanto Chemical Co., Inc.). Hereafter, a Ni–B film contains X at.% of boron atoms which is prepared in a DMAB or a TMAB bath will be referred to as a Ni–B (X%, DMAB or TMAB) film. Vickers's micro-hardness was measured using a micro-hardness tester (MHTZ, Matsuzawa Co. Ltd.) under the indentation load of 50 gf at five different locations of a specimen and the average value of the three measurements except the maximum and minimum values was quoted here as the hardness of the film. XRD patterns were measured with a Rigaku RINT 2500 V diffractometer using Cu-Kα radiation at room temperature. Optical micrograph images were measured by using an optical microscope (Digital Microscope VHX-200, Keyence).

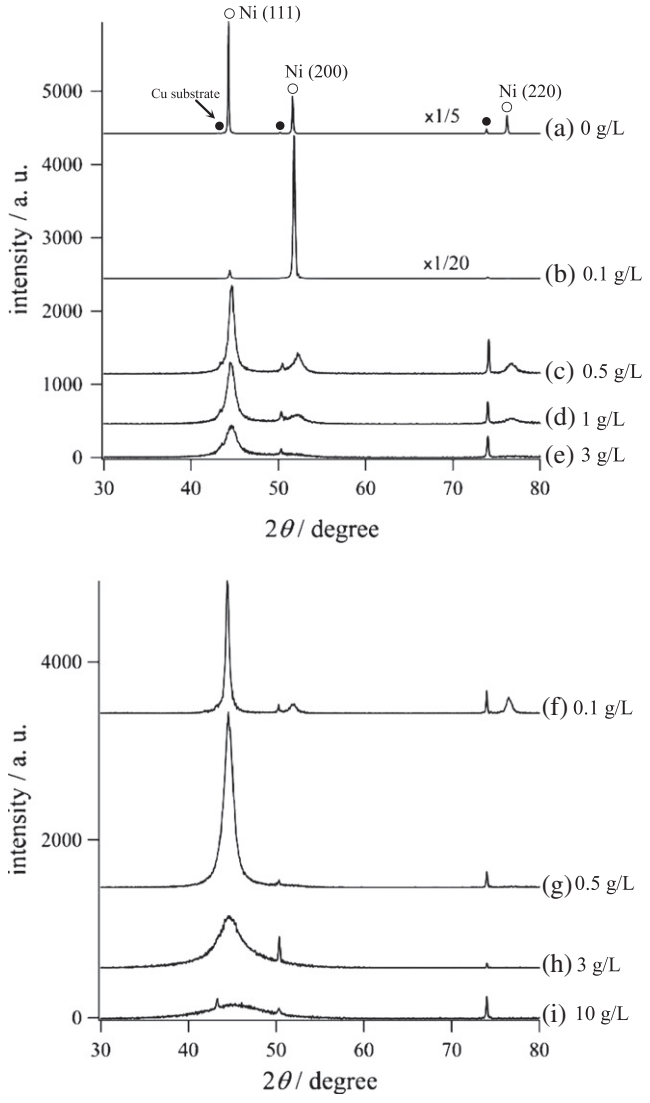

Fig. 1. XRD patterns of (a) a Ni film, and Ni–B films prepared from (b–e) DMAB baths or (f–i) TMAB baths containing different amount of boron sources. Current density = 6 A/dm^2 (DMAB) and 1 A/dm^2 (TMAB); pH = 3.5.

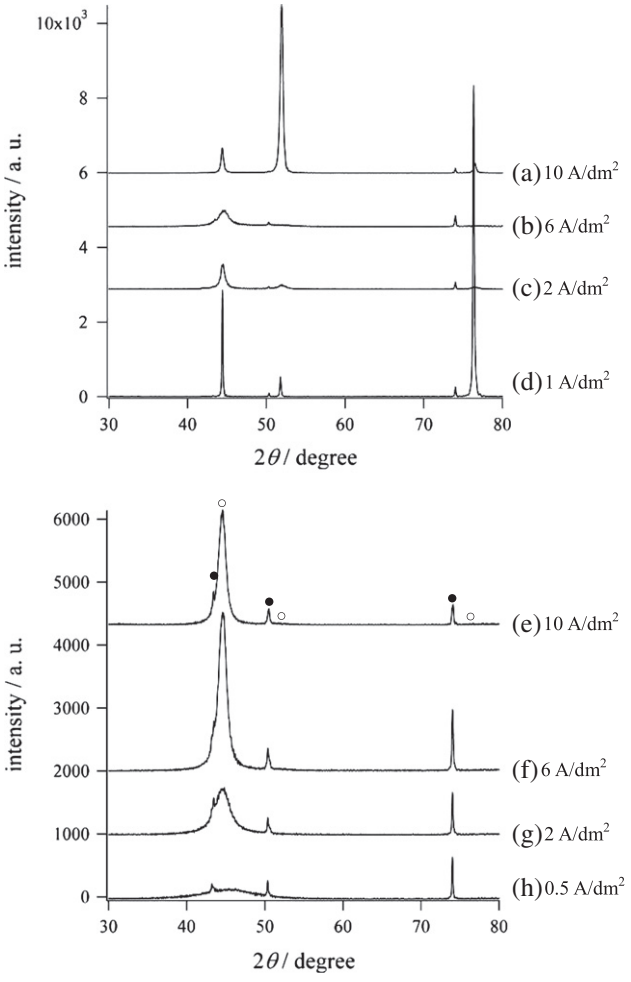

Fig. 2. XRD patterns of Ni–B films prepared from (a–d) DMAB baths or (e–h) TMAB baths at different current densities. pH = 3.5; the amount of DMAB or TMAB = 3 g/L.