Electrodeposition with intermittent addition of trimethylamine borane to produce ductile bulk nanocrystalline Ni–B alloys

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ABSTRACT

We developed a technique to dope electrodeposited Ni with B to produce ductile bulk electrodeposits of Ni–B alloys. The conventional method, in which TMAB is added as a source for B-doping to the deposition bath before electrodeposition, affected only the first layer, producing two layers of Ni–B alloys and pure Ni in the bulk electrodeposits. These inhomogeneous specimens showed poor tensile properties, because of processing-defects presented in the layer of Ni–B alloys. These defects were produced because TMAB immediately decomposes during electrodeposition, generating hydrogen gas. In contrast, the developed technique for B-doping, in which TMAB is added intermittently during electrodeposition, produced a more-uniform B content of 0.04 at.% in the growth direction. This B distribution resulted in a uniform nanocrystalline structure with a grain size of ~28 nm. The sample of bulk nanocrystalline Ni–B alloys exhibited a good tensile elongation of 7.6% with a high tensile strength of 1.45 GPa. The developed B-doping technique avoids the harmful effects of the hydrolysis of boron compounds, and it can produce electrodeposited bulk nanocrystalline Ni–B alloys with good ductility.

1. Introduction

Electroforming is the preferred way to fabricate molding tools because it can controllably reproduce microscale geometries [1,2]. Ni is widely used in electroforming, because electrodeposited Ni has a grain size less than 100 nm and exhibits high strength due to its nanocrystalline structure [3–6]. However, electrodeposited pure nanocrystalline Ni cannot withstand relatively high temperatures without losing its hardness due to recrystallization [7]. Because alloying increases thermal stability [8], studies on electrodepositing Ni alloys have been done in recent years [9–13]. Among the Ni alloys, Ni–B alloys are a promising candidate because they have higher mechanical strength [14–17] and corrosion resistance [18,19].

Several authors have electrodeposited Ni–B alloys [14,17,18,20–28]. These processes are often accomplished by using a B source such as dimethylamine borane [14,29] or trimethylamine borane (TMAB) [30,31]. Unfortunately, these boron compounds immediately decompose by hydrolysis in acid solutions, generating hydrogen gas [32]. Thus, boron compounds affect only the first electrodeposited layer [33]. Moreover, repeated trapping and desorption of hydrogen gas introduces high internal stress and defects in

electrodeposited materials [34], decreasing ductility [33]. Thus, producing defect-free bulk electrodeposited Ni–B alloys is difficult by the conventional methods of adding boron compounds, making it desirable to find a new type of electrodeposition that can produce ductile bulk electrodeposits of nanocrystalline Ni–B alloys. Thus, we developed a technique for B-doping of electrodeposited Ni that suppresses the harmful effects of hydrogen gas caused by decomposition of boron compounds. In this paper, we electrodeposited two types of bulk Ni–B alloys with the conventional and developed techniques of adding TMAB. Then, we examined their microstructures and mechanical properties.

2. Experimental procedure

2.1. Electrodeposition

Samples were electrodeposited using either the conventional or the developed method for B-doping. Both types of samples were prepared using a basic bath with the composition shown in Table 1. In the conventional method, TMAB is added as the source for B-doping to the basic bath before electrodeposition. The amount of TMAB added to the

Table 1
Composition of basic bath.

Chemicals	Amount (g/L)	Purpose
Nickel sulfamate tetrahydrate	300.0	Ni source
Nickel chloride hexahydrate	5.0	Passivation inhibitor
Sodium propionate	20.0	Complexing agent
Sodium gluconate	4.2	Complexing agent
Saccharin sodium dihydrate	1.0	Stress reliever
Sodium lauryl sulfate	0.3	Pit prevention agent

deposition bath was 0.6 g/L. To produce the bulk electrodeposits, simply adding TMAB would produce a gradient of B content in the growth direction [33] because TMAB experiences immediate hydrolysis in an acid solution [32]. We thus invented a new method for B-doping.

In the new method, TMAB at 2.0 g/L was first dissolved into an aqueous solution with sodium saccharin at 5.0 g/L. The sodium saccharin was added to maintain the pH of the aqueous solution at 5.5 and to suppress the hydrolysis of TMAB. This solution, which was the B source, was intermittently added to the basic bath during electrodeposition. This intermittent addition was done automatically by a tubing pump with an on-time of 6 s and an off-time of 194 s. The average amount of solution dropped was 2.2 mL/h, and the total amount was 207 mL, equating to ~0.6 g/L TMAB. Note that this intermittent addition did not lead to overflow, since the evaporation of the solution is much higher. Also, water level was kept constant for both methods by monitoring the water level gauge and dropping pure water, suppressing fluctuation of the bath composition.

All samples were deposited on copper substrates of commercial purity by using nickel plates (99.98%) as a counter-electrode. Electrodeposition was performed using 1-L deposition systems at a current density of 25 mA/cm^2, bath temperature of 55 °C, and pH of 4.0. The details of these deposition systems are described in a previous paper [35]. The pH values of the solutions during electrodeposition were maintained by adding drops of 1.0 mol/L sulfamic acid. The target thickness of the electrodeposits is typically 1 mm for mechanical testing [36], which required us to deposit for approximately 96 h.

2.2. Analyses

After electrodeposition, we performed the following analyses. The B content was quantified by glow-discharge optical emission spectrometry (GD-OES, Horiba GD Profiler2), obtaining the B distribution in the growth direction. The C and S contents were quantified by IR absorption after combustion in a high-frequency induction furnace (LECO CS-LS600). X-ray diffraction analysis (XRD, Rigaku MiniFlex 600) using Cu Kα radiation was carried out to confirm the orientation and estimate the grain size. To estimate the grain size, we used a single-line method to separate the size and strain broadening [37,38]. A diffraction line is conceived as a convolution of Gaussian and Lorentzian profiles as a pseudo-Voigt function. In addition, to confirm the uniformity of the electrodeposits on the growth direction, XRD patterns were obtained from several layers (Fig. 2c) by alternating XRD and mechanical polishing. Transmission electron microscopy (TEM) specimens were prepared by ion milling. TEM specimens were examined using a JEOL JEM-ARM200F operated at 200 kV. To evaluate the hardness of the electrodeposits, micro-Vickers hardness tests were conducted on the cross-sections and surfaces of the bulk samples, using a load of 500 g for 10 s. The cross-sectional hardness was measured at intervals of ~0.3 mm from the interface to the surface. Each reported hardness value is the average of 10 measurements. Dog-bone specimens, for tensile tests, with a gauge length of 12 mm, width of 3.0 mm, and thickness of ~1.0 mm were machined by electrical discharge machining. Note that the surface grinder removed the copper substrate and the layer affected by electrical discharge machining (EDM). The tensile tests were performed at room temperature and at a strain rate of 1×10^{-3} s^{-1} using a universal testing machine (Shimadzu AUTO-GRAPH AG-X Plus). Each reported data point is the average of three measurements. The fracture surfaces of the tensile specimens were observed using scanning electron microscopy (SEM, JEOL JSM-IT300HR).

3. Results and discussion

3.1. Microstructure characterization

The electrodeposition was run for 96 h using the basic bath with two types of TMAB addition. Both types of electrodeposition showed a high current efficiency of ~90% and produced bulk electrodeposits with a thickness of 1.4 mm. For these bulk samples, to address how the method of TMAB addition affects the B distribution, we performed GD-OES on the substrate side and surface side. Fig. 1 shows the depth profiles of B content for both samples, measured from (a) the interface side and (b) the surface side. Conventional TMAB addition introduced a gradient in B content, which decreased from 0.046 to 0.005 wt% along the growth direction of the deposits up to 0.1 mm (Fig. 1a). Moreover, B was not detected in the analysis from the surface side (Fig. 1b). This result means that conventional TMAB addition produced multilayer electrodeposits consisting of Ni–B alloys and pure Ni. This result agrees with a
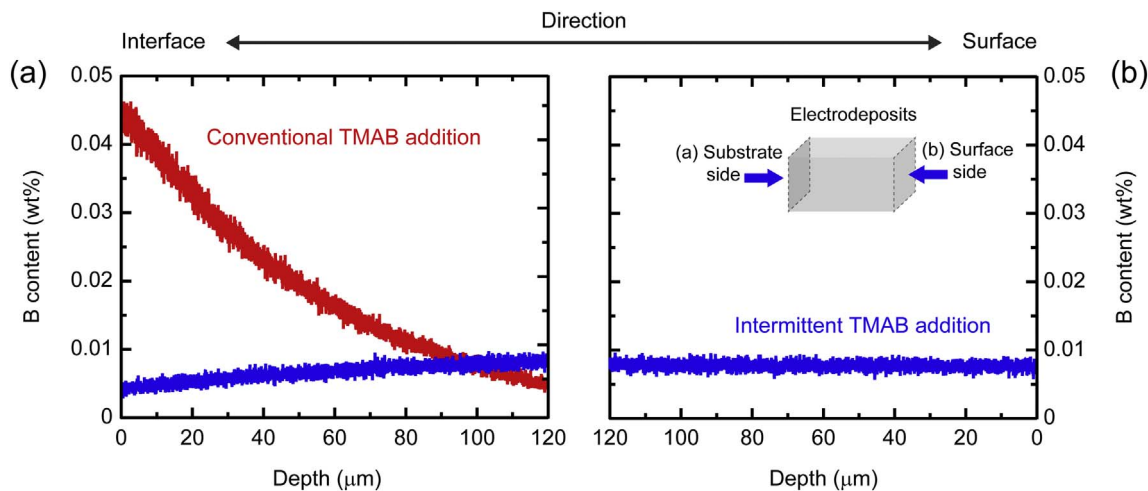

Fig. 1. B content measured by GD-OES of samples electrodeposited with conventional and intermittent TMAB addition: GD-OES was performed on (a) the substrate side and (b) the surface side as shown in inset image. B did not appear at the surface for the sample electrodeposited with conventional TMAB addition.