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The effects of heat treatments on hardness and wear resistance in Ni–W alloy coatings

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ABSTRACT

The relationship of processing parameters, microstructure, and mechanical responses of the electrodeposited nickel–tungsten alloys exposed to elevated temperatures in the range 700–1100 °C are investigated. Reverse pulse electrodeposition technique is employed to control the tungsten content and nanocrystalline grain size of the deposits. The application of heat treatment at 700 °C on the alloy with high tungsten content (22 at.%) and small grain size (3 nm) gives hardness enhancement and a small decrease in wear resistance. Prolonging annealing duration and increasing annealing temperature promote more grain growth and reductions of both hardness and wear resistance, despite the formations of secondary phases. For alloys with lower tungsten contents (6% and 13%) and larger grain sizes (13 and 56 nm), higher degrees of grain growth coupled with monotonic decline of hardness are observed. The study indicates that the electrodeposited nickel–tungsten alloys with a high tungsten content potentially serve as strong candidates for high temperature applications.

1. Introduction

Electrodeposited nickel (Ni) has been widely employed for protecting metal surfaces from mechanical damages and corrosion. With the needs for high hardness nickel-based coatings for the electronic and automotive applications, nickel–tungsten (Ni–W) alloy deposits which exhibit nanocrystalline structure have been developed [1–4]. In addition to the relatively high hardness of the materials which can be reached up to ~7 GPa [5], as compared to ~2 GPa found in the conventional Watt's bath Ni deposits [6], the Ni–W alloy coatings also show excellent wear resistance [7]. The recent study by Rupert and Schuh has illustrated that, owing to nanocrystallinity and microstructural stability of the as-deposited Ni–W alloys, improvements of both hardness and wear resistance, markedly deviating from what would have been predicted by Hall–Petch and Archard scaling, are observed [8]. Furthermore, the fine crystalline structure of the materials also contributes to high enhancement of the localized corrosion resistance [9,10].

While most studies on the electrodeposited Ni–W alloys have been concentrated on the as-deposited properties, studies of the materials' responses to elevated temperatures are rather limited [11–15]. An understanding on the behavior of the deposits exposed to high temperatures is crucial because the alloy coatings may be exposed to such conditions upon using in service, for example, in the welding or machining environments. Under high temperature conditions, grain growth, grain relaxation, and intermetallic formation in the alloy coatings may develop, and in turn, affect the mechanical integrity of the coatings. This also conversely suggests that, if the change in the deposits' characteristics as induced by elevated temperature is positive, heat treatment may serve a potential route for improving the properties of the alloys as well.

The relevant prior works in this area include that of Detor and Schuh [16], which explores the effect of annealing, in the temperature range of 150–900 °C, on microstructural development and corresponding hardness of electrodeposited Ni–W alloys (6–21 at.%W and grain size of 3–70 nm). The study illustrates that, when using annealing temperature below ~500 °C, the grains of the nanocrystalline deposit are generally well-stabilized, yet the increase of hardness from 6 to 9 GPa due to grain relaxation is observed, especially in the Ni–21%W annealed at 300 °C for 24 h. Grain growth however becomes dominant when heat treatment is performed at higher temperatures in the range of 600–900 °C. In such range of temperature, the formation of Ni_4W intermetallic is also observed. Similar results are later obtained in the work by C. Borgia et al. [17], which examines the effect of heat treatment on magnetron-sputtered Ni–W alloys containing 25–75 at.%W. The relatively high contents of W lead to the development of intermetallics, including Ni_4W and NiW, at the annealing temperature of merely 530 °C, and the hardness of the materials is found to rise from ~8 to 11 GPa. The study on wear resistance of as-annealed Ni–W is even more limited. In 2010, K.H. Hou et al. [11] analyze wear resistance of electrodeposited Ni–32%W alloy, which has been annealed at 700 °C for 1 h in vacuum. The ring on disk method, with SKD-11 as a sliding ring, was employed for wear test. Following the sliding distance of 1000 m, the test deposit exhibits

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minimal mass loss of 10.5 mg, approximately half of what was observed from the as-deposited specimen.

In the present study, we extend the prior works on heat treatment and mechanical response of the electrodeposited Ni–W alloys and examine the relationship between processing parameters, microstructural development, hardness and wear resistance of electrodeposited Ni–W alloys, exposed to annealing temperatures of 700–1100 °C. Employing the reverse pulse electrodeposition technique, the nanocrystalline alloy deposits with a broad range of the W content (6–22 at.%) and grain size (3–56 nm) are available for the analysis. Factors that influence the mechanical properties of the deposits, including composition and grain size, are systematically analyzed. The understanding gained from the study would lead to developments of Ni–W alloys that can well-withstand high temperatures or of those whose properties can be enhanced with high temperature treatments.

2. Experimental

2.1. Processing

Ni–W alloy specimens were prepared by electrodeposition using a pulse rectifier (DuPR10-3-6w/M-2μSTAR). The plating bath contained 147 g/l $Na_3C_6H_5O_7 \cdot 2H_2O$, 26.7 g/l NH_4Cl, 15.8 g/l $NiSO_4 \cdot 6H_2O$, 46.2 g/l $Na_2WO_4 \cdot 2H_2O$ and 15.5 g/l NaBr, and the bath temperature was maintained at 75 °C. Platinum and nickel (1.5×2.5 cm^2), polished to a mirror-like finish and activated by 10 vol.% H_2SO_4, were used as an anode and a cathode, respectively. The electrodeposition process was performed in the reverse pulsing mode with the forward and reverse current densities of 0.2 and 0.05 A/cm^2, respectively. The forward pulse duration was controlled at 20 ms, whereas reverse pulse durations of 1, 6, and 9 ms were employed to tailor the content of W atoms alloyed in Ni matrix. These groups of as-deposited specimens will be termed A, B, and C, as detailed in Table 1. The electrodeposited specimens were subsequently subjected to heat treatment at 700 °C, 900 °C and 1100 °C for 0.5–3 h, under a controlled nitrogen atmosphere. For referring to these groups of specimens, the employed annealing temperature and duration will be prescribed to A, B or C (e.g., A-700-3 for the 700 °C and 3 h annealing condition).

2.2. Characterization

The surface morphology, microstructure and chemical composition of the deposits were characterized using a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). The X-ray diffractometer (XRD) was used to analyze phase composition of the materials. For nanocrystalline deposits (grain size <100 nm), their grain sizes were determined using the X-ray integral breadth method, whereby full width at half maximum (FWHM) of XRD peaks were measured, corrected the instrumental factor as obtained from a LaB_6 standard, and subsequently employed in the Scherrer's equation [18]:

$$d = (0.9\lambda) / (B \cdot \cos\theta) \tag{1}$$

where d is the average grain size, λ wavelength of X-ray, B FWHM, and θ scattering angle. The grain sizes of microcrystalline deposits were estimated with the linear intercept method by prescribing a line of specified length (L) on a micrograph that shows grain structure of the deposits, and counting number of grains intercepted by the line (n). The average grain size can be calculated from [19]:

$$d = 3\,L / 2n. \tag{2}$$

A chromic acid-based etchant was used to help reveal the grain structures of the materials.

2.3. Mechanical testing

Hardness of the alloys was assessed by a Vickers micro-indenter, using a 100 g load. Wear resistance of some selected deposits was characterized with the ball-on-disk method, where Ni–W testing pieces and tungsten carbide (WC) were used as a disk and a ball, respectively. The tests were conducted using a 5 N load, a 200 rpm sliding speed, and a 5 mm ball rotation radius. The friction coefficient (μ) was measured during the test and a profilometer (TalyScan 150, Taylor Hobson Ltd.) was employed to determine wear track area, from which volume loss of the worn deposits can be analyzed. The appearance of wear track before and after the tests was examined with SEM and an optical microscope.

Table 1
Characteristic of the as-deposited Ni–W specimens.

Specimen-set	Reverse pulse duration (ms)	Ni (at.%)	W (at.%)	Grain size (nm)
A	1	78	22	3
B	6	87	13	13
C	9	94	6	56

3. Results

The characteristics of the as-deposited Ni–W specimens from group A, B, and C are presented in Table 1. It is observed that the increase of reverse pulse duration results in reduction of W content in Ni matrix, and correspondingly, increment of grain size, which is in agreement with the prior works [10,20,21]. The average grain sizes of specimens A, B, and C are 3, 13, and 56 nm, respectively. The surface morphology of these as-deposited specimens, which is characterized by nodules which represent a cluster of nanocrystalline grains [22], is shown in Fig. 1. Fig. 2a illustrates relatively broad XRD profiles of these specimens, suggesting the presence of fine grain structures.

After performing heat treatment on the as-deposited specimens in the range of 700–1100 °C for 0.5–3 h, the microstructures of the specimens of the different groups are transformed in various fashions. This includes changes in surface morphology, phase compositions, and grain size, as illustrated by Figs. 1 and 2. Specifically, the average grain sizes of all specimens appear to increase following heat treatment at 700 °C. Performing heat treatment at 900 °C, the development of secondary phases, including Ni_4W and NiW, is detected in group-A specimens. The surface morphology of group-B and C specimens has by now transformed to that of a conventional microcrystalline electrodeposits, where each nodule corresponds to a single grain [22]. When heat treatment is performed at 1100 °C, NiW and W phases are observed in group-A specimens, whereas those in groups B and C remain precipitate-free. Furthermore, unlike B and C, group-A specimens still exhibit nanocrystalline structure at this stage, as illustrated in Fig. 1.

Figs. 3 and 4 illustrate the relationships of annealing temperature and duration, grain size, and hardness of the specimens. Relatively high hardness of 7 GPa with grain size of 3 nm are observed in the as-deposited A, whereas the reduction of W content from 13% to 6% leads to an increase of grain size, accompanying by a decrease of hardness from 6 to 4.5 GPa in the as-deposited B and C respectively. Grain growth is generally observed in all specimens following the heat treatment protocols, with specimens in B and C groups experiencing relatively large degree of grain growth. With an increasing grain size, specimens in B and C groups show monotonic reduction of hardness. On the other hand, specimens A-700 and A-900 exhibit hardness enhancement in spite of grain growth. Prolonging heat treatment duration from 0.5 h to 3 h, the group-A specimens experience grain growth and slight reduction of hardness (Fig. 4).