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Effect of low-temperature annealing on tensile behavior of electrodeposited bulk nanocrystalline Ni–W alloys

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ABSTRACT

Relatively low-temperature thermal treatment of nanocrystalline metals results in grain boundary relaxation and the absence of clear grain growth. However, the manner in which the relaxation affects the tensile properties of bulk nanocrystalline metals is unclear. In this study, the effect of low-temperature annealing on the tensile behavior of nanocrystalline metals was studied using electrodeposited Ni–W alloys as a model system. Tensile tests were conducted using the electrodeposited bulk nanocrystalline Ni–W alloys in the as-deposited state and after annealing at 200–300 °C for 24 h. After annealing, the yield strength and tensile strength increased by 0.25–0.34 and 0.13–0.18 GPa, respectively, while uniform elongation decreased from 4.8% to 2.5%. Good local elongation of 6.0–7.0%, which was comparable with the value in the as-deposited state, was observed after annealing at 200 and 250 °C. However, annealing at 300 °C induced a degradation of local elongation to 2.6%. The results of this study indicate that reduction of excess boundary defects affects dislocation emission from grain boundaries, leading to increasing yield strength and decreasing uniform elongation, whereas the relaxation has no effect on the local elongation. In addition, discussion of the microstructures of Ni–W alloys also suggest the possibility that the failure mode changes at annealing temperatures near 250–300 °C by changing the shape of grain boundaries more linearly, in addition to a reduction of excess boundary defects.

1. Introduction

When grain size is decreased below 100 nm, grain boundaries begin to account for a significant volume fraction of a material [1]. Distinct changes are observed in the deformation characteristics when compared with coarse-grained metals, although plasticity is still dislocation-mediated in the grain size range of approximately 20–100 nm [2,3]. In the as-prepared state, these nanocrystalline metals often contain non-equilibrium grain boundaries with excess dislocations, misfit regions, or excess free volume [4–6]. The intra-grain dislocation sources widely available in coarse-grained metals are suppressed. Excess boundary defects may facilitate plasticity by acting as sinks and sources for dislocations [7]. These dislocation sources at the grain boundaries can be removed by thermal annealing, which is a low-temperature process that does not affect the grain size or texture [4]. As a result, unusual hardening phenomena with moderate annealing have been observed [8–15]. This is termed grain boundary relaxation strengthening [9]. In fact, several nanocrystalline metals show an unprecedented increase in hardness by up to 20% upon annealing [9,16].

Conversely, small amounts of impurity atoms also segregate to the boundaries during grain boundary relaxation. Thus, it remains an issue for hardening phenomena: a segregated solute might suppress dislocation emission from the boundaries, leading to higher stress levels for plastic deformation of nanocrystalline metals [17–19]. Recently, Renk et al. [16,20] conducted a detailed study, based on the mechanical and microstructural characterization by atom probe tomography, to clarify whether solute segregation at the boundaries can account for the hardening behavior with annealing. Their results reveal that the hardening phenomenon is apparently not related to solute segregation. These studies point to the fact that the relaxation state of the grain boundary plays a key role in the mechanical properties as well as grain sizes. Despite this progress, to date, very little is known about how the relaxation affects the tensile behavior, especially ductility, of bulk nanocrystalline metals. In a limited report, Wang et al. [21] investigated the effect of low-temperature annealing (100–300 °C) on the tensile properties of electrodeposited nanocrystalline Ni. This study clearly shows an increase in tensile strength as a result of the depletion of dislocation sources. They also reported that there was no clear

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Table 1
Bath composition for Ni–W alloys.

Chemicals	Amount (g/L)
Nickel sulfamate tetrahydrate	300.0
Sodium tungstate dihydrate	6.4
Nickel chloride hexahydrate	5.0
Sodium propionate	20.0
Sodium gluconate	4.2
Saccharin sodium dihydrate	1.0
Sodium lauryl sulfate	0.3

reduction of the total elongation after relaxation. However, the total elongation of electrodeposited Ni in their study was only 1–3%. Recently, an electrodeposition process has achieved a total elongation of approximately 10% in bulk nanocrystalline metals [22–26]. It is thus unclear if the phenomenon is common in bulk nanocrystalline metals. The purpose of this study is to connect the relaxation of the grain boundary structure to tensile behavior in electrodeposited bulk nanocrystalline metals. We electrodeposited bulk nanocrystalline Ni–W alloys with high tensile elongation, and the effect of grain boundary relaxation on the tensile behavior was explored.

2. Experimental procedure

Four plates of bulk nanocrystalline Ni–W alloys were electrodeposited under identical conditions. The details of the bath composition are given in Table 1. All samples were deposited onto copper substrates of commercial purity using two counter electrodes of nickel plates and tungsten rods in a 1-L system. The details of the system are described in Ref. [27]. Electrodeposition was performed at a current density of 20 mA/cm^2, a bath temperature of 55 °C, and a pH of 4.0. The pH values of the solutions during electrodeposition were maintained by the addition of drops of 1.0-mol/L sulfamic acid and 5.0-mol/L sodium hydroxide. The target electrodeposition thickness was typically 1 mm for mechanical testing [23], which requires approximately 96 h of deposition run time to achieve.

The tungsten content of the electrodeposited Ni–W alloys was determined by energy-dispersive X-ray spectrometry (EDX, Shimadzu EDX-8000). The carbon and sulfur contents were quantified by infrared absorption after combustion in a high-frequency induction furnace (LECO CS-LS600). X-ray diffraction (XRD, Rigaku MiniFlex600) analysis was performed using Cu Kα radiation to confirm orientation and estimate grain sizes. Transmission electron microscopy (TEM) specimens were prepared by ion milling. TEM specimens were examined using a JEOL ARM-200FC (Cs-corrected) operated at 200 kV for microstructure observation. To evaluate the hardness of the electrodeposits, micro-Vickers hardness tests were conducted on bulk samples using a load of 500 g for 10 s. Each reported data point represents the average value for at least 12 indentations. Dog-bone specimens with a gauge length of 12 mm, width of 3.0 mm, and thickness of approximately 1.0 mm were machined by electrical discharge machining for tensile tests. The copper substrate and affected layer were removed using a surface grinding machine. In total, 12 tensile specimens were cut from four plates of bulk nanocrystalline Ni–W alloys. Nine of these specimens were heat-treated at 200, 250, or 300 °C for 24 h. The tensile tests were carried out at room temperature and a strain rate of $1 \times 10^{-3}\,s^{-1}$ using a universal testing machine (Shimadzu AUTOGRAPH AG-X plus). Each reported data point represents the average of three measurements. After the tensile tests, the fracture surfaces were examined by scanning electron microscopy (SEM, Hitachi S-4800).

3. Results

3.1. Microstructural characterization

Four samples of electrodeposited Ni–W alloy were prepared under identical conditions. The prepared samples showed constant solute and

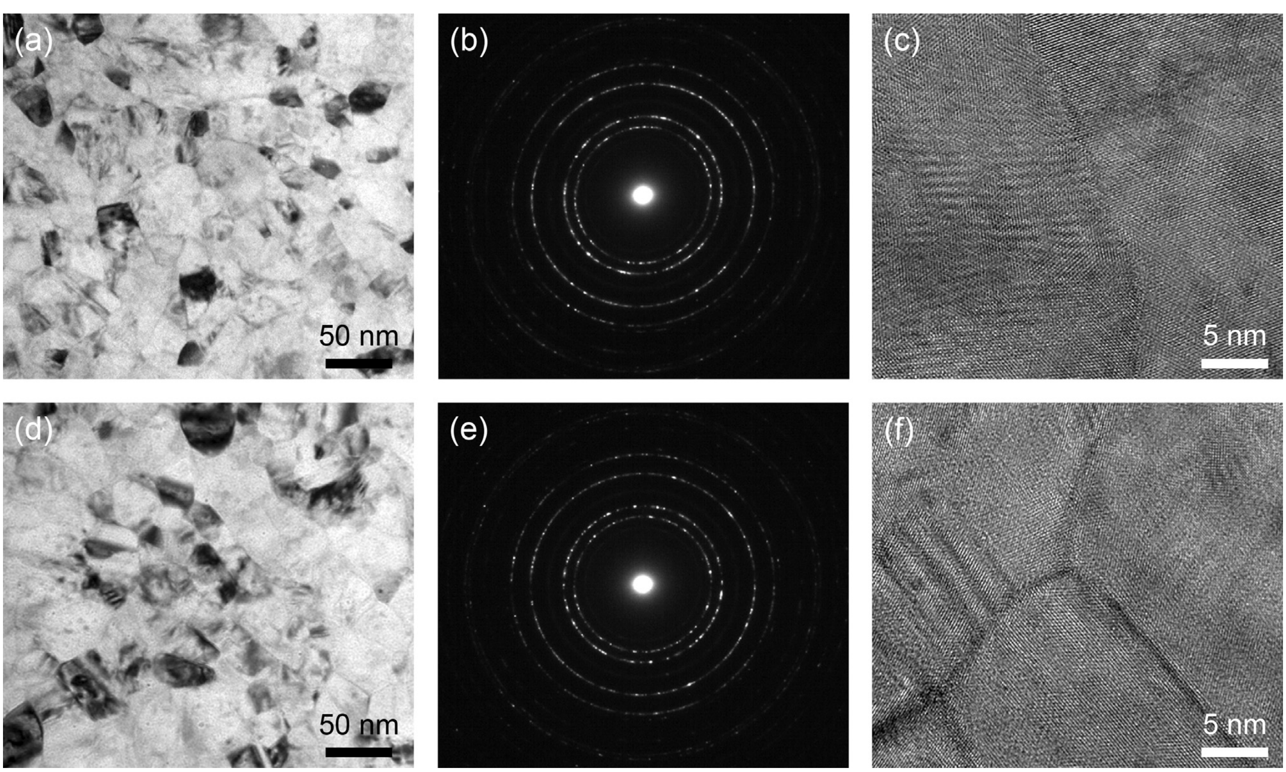

Fig. 1. TEM characterization data for bulk nanocrystalline Ni–W alloys (upper) in the as-deposited state and (lower) after annealing at 300 °C for 24 h. (a and d) Bright-field images show a nanocrystalline structure with a grain size of approximately 30 nm. (b and e) The electron diffraction patterns provide evidence of the fcc structure. (c and f) Precipitate and amorphous phase are not observed at grain boundaries in high-resolution observations.