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Relationship between grain boundary relaxation strengthening and orientation in electrodeposited bulk nanocrystalline Ni alloys

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ABSTRACT

Many studies have been performed to better understand the Hall–Petch effect at the nanometer scale. Hardening can be caused not only by a reduction of the grain size, but also through the relaxation of the nonequilibrium grain boundary structure. Despite considerable effort, there is still a large discrepancy among the available data for the strength values of nanocrystalline metals because of the difficulty in quantitatively evaluating the state of grain boundary relaxation. In this study, we used electrodeposited bulk nanocrystalline Ni–Fe and Ni–W alloys to develop a better predictive method of the grain boundary relaxation behavior. Relatively low-temperature thermal treatment resulted in grain boundary relaxation and thus increased the hardness by 0.07–0.74 GPa. We found that the increase in hardness decreased with increasing orientation index for the (200) plane. Specifically, we concluded that electrodeposited Ni alloys with an orientation index for the (200) plane greater than 3.0 do not exhibit grain boundary relaxation strengthening, because these alloys do not have a nonequilibrium grain boundary structure even in the as-deposited state. The relationship also enables the prediction of the grain boundary relaxation state of electrodeposited bulk nanocrystalline Ni alloys.

1. Introduction

When the grain size is reduced below 100 nm, grain boundaries begin to account for a large volume fraction of the crystal structure of a material [1]. In such nanocrystalline materials, the grain boundary structure has a key determining role in the mechanical properties in addition to the grain size. Much attention has been focused on studying the atomic structure of grain boundaries in these materials. Several studies [2–4] have reported that nanocrystalline metals often contain nonequilibrium grain boundaries with excess dislocations, misfit regions, or excess free volume in their as-prepared states. Low-temperature annealing has been shown to release excess defects without any measurable change in grain size or texture; this is termed grain boundary relaxation [2]. Grain boundary relaxation has been reported to increase the hardness [5] and tensile strength [6], which is thought to be the result of a reduction in the number of dislocation sources [5].

In recent studies using electrodeposited nanocrystalline Ni and Ni alloys as a model system, the effect of grain size on the strength has been investigated [7,8]. Unfortunately, these studies were generally unable to separate the effects of the state of grain boundary relaxation and the grain size. This is because it is practically difficult to quantitatively evaluate the grain boundary relaxation state. Thus, the development of a convenient method to predict the grain boundary relaxation state would provide a deeper understanding of the hardening effect in nanocrystalline metals. In this study, we examined the effect of grain boundary relaxation on the hardness of electrodeposited bulk nanocrystalline Ni–Fe and Ni–W alloys towards this goal. We prepared a set of 39 samples by electrodeposition. The hardness of these alloys was measured in the as-deposited state and after annealing to investigate the grain boundary relaxation strengthening behavior. We found that the grain boundary relaxation strengthening could be estimated on the basis of the orientation index of the (200) plane.

2. Experimental procedure

A set of 39 bulk nanocrystalline Ni alloys was prepared. All alloys were synthesized using an electrodeposition technique that is described elsewhere [9–12]. The experimental setup for electrodeposition is described in Ref. [13]. The samples were deposited onto Cu substrates of commercial purity. Electrodeposition for Ni–Fe alloys was performed at a current density of 10–30 mA cm^{-2}, bath temperature of 50–55 °C, and pH of 2.0–2.2. Electrodeposition

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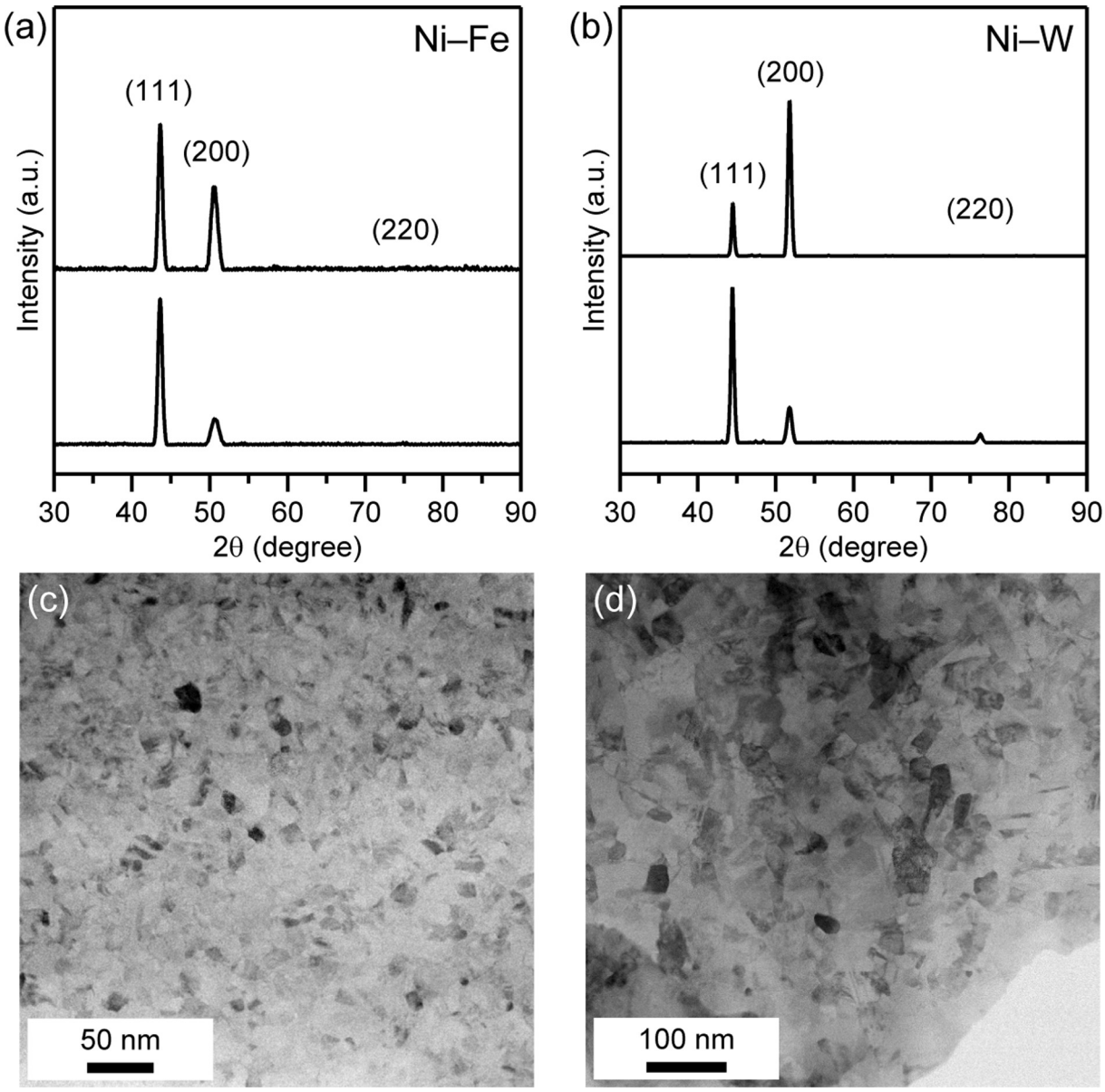

Fig. 1. Representative XRD patterns (a,b) and STEM images (c,d) of electrodeposited bulk nanocrystalline (a,c) Ni–Fe alloys and (b,d) Ni–W alloys.

for Ni–W alloys was performed at a current density of 30–40 mA cm^{-2}, bath temperature of 50–60 °C, and pH of 4.0. The pH values of the solutions during electrodeposition were maintained by adding drops of 1.0 mol L^{-1} sulfamic acid and 5.0 mol L^{-1} sodium hydroxide.

After electrodeposition, the following analyses were conducted. The Fe and W content of the electrodeposits was determined by energy-dispersive X-ray spectrometry (EDS) using a scanning electron microscope (HITACHI S-4800). To calculate the orientation index [14] and estimate the grain size, X-ray diffraction (XRD, RIGAKU Ultimate IV) was performed using Cu Kα radiation. Transmission electron microscopy (TEM) specimens were prepared by ion milling and were examined using a JEOL ARM-200FC (Cs-corrected) transmission electron microscope, operated at 200 kV for microstructure observation. To evaluate the hardness of the electrodeposits, micro-Vickers hardness tests were conducted using a load of 500 g for 10 s. Each reported data point represents the average of at least 12 indentations. To demonstrate grain boundary relaxation strengthening, all electrodeposited samples were annealed at 200 °C for 2 h, after which the hardness was measured again.

3. Results and discussion

The electrodeposited Ni–Fe and Ni–W nanocrystalline alloys contained 45–60 at.% Fe and 2–5 at.% W, respectively. To estimate the grain size, we conducted XRD analysis. Representative XRD patterns of bulk nanocrystalline Ni–Fe and Ni–W alloys are shown in Fig. 1a and b, respectively. All patterns are indicative of a single face-centered cubic (fcc) structure. The grain sizes of each sample were estimated from the (111) diffraction peak width using the Scherrer equation. The grain sizes of the Ni–W and Ni–Fe alloys ranged 13–16 nm and 17–24 nm, respectively. We also confirmed the grain sizes by TEM observation; representative scanning transmission electron microscope (STEM) images of bulk nanocrystalline Ni–Fe and Ni–W alloys are shown in Fig. 1c and d, respectively. These images reveal that the nanocrystalline structure of