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Influence of annealing on the mechanical property of iron- and nickel-based nanocrystalline alloys

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ABSTRACT

In plastically deformed coarse-grained metallic materials, recovery annealing largely decreases their strength because of the annihilation of the stored dislocations. In contrast, the subsequent grain growth only slightly decreases their strength. We have found an exactly opposite change in the strength of our annealed nanocrystalline iron- and nickel-based alloys prepared by a severe plastic deformation method – mechanical alloying. In the recovery stage, the microhardness is almost constant and even slightly increases just before the grains start to grow because of the segregation of solutes in the grain boundary. Our experiment results suggest that the dislocations – mainly taking the form of dislocation dipoles – stored in the grain interiors of our mechanically alloyed nanocrystalline alloys do not influence the microhardness. At the grain growth stage, microhardness decreases as the grains grow. In addition, the microhardness of furnace-cooled nanocrystalline alloys is higher than that of air-cooled nanocrystalline alloys, further supporting that the grain boundary segregation influences the microhardness of nanocrystalline alloys. Our experimental results suggest that it is the grain size and the grain boundary structure, rather than the dislocations stored in the grain interiors, that determine the strength of the deformed and annealed nanocrystalline alloys.

1. Introduction

For conventional single crystalline and large-grained (grain size > 10 μm) polycrystalline materials, hardening by plastic deformation is one of the widely used strengthening methods. The plastic deformation forms a large number of stored dislocations, which usually leads to a long-range stress field that is the major resistance needed to be overcome upon further deforming. The well-known work hardening theory predicts that the shear strength τ of a plastically deformed metal increases with dislocation density ρ according to [1]

$$\tau = \tau_0 + \alpha G b \rho^{1/2} \quad (1)$$

where τ_0 and α ($\approx$ 0.2 to 0.3) are material constants, G is the shear modulus and b is the magnitude of Burger's vector of dislocations. Plastic deformation significantly increases strength τ because of the largely increased ρ. If the plastically deformed polycrystalline metal is annealed, recovery and recrystallization (accompanied by grain growth) are anticipated. During the recovery stage, the strength largely decreases because of the annihilation of stored dislocations. In contrast, during the grain growth stage, the strength decreases only slightly. These facts have been well known in coarse-grained metals since the 1960s [2].

For our nanocrystalline (grain size < 100 nm) $Fe_{85}Al_4Si_{11}$ and $Ni_{99}Fe_1$ alloys, exactly the opposite effect has been observed. The strength is almost constant during the recovery stage and significantly decreases during the grain growth stage. Immediately before the grain growth, the strength of our nanocrystalline alloys can even increase slightly! Our previous studies [3] ascribe the increase in strength to the segregation of solutes in the grain boundary.

The mechanical property of nanocrystalline materials has been extensively studied during the past decades [4]. Many mechanisms have been proposed for the deformation of nanostructured materials. These include pile-up breakdown [5,6], grain boundary sliding [7,8], core and mantle models (i.e., grain interior and grain boundary region models) [9,10], grain-boundary rotation/grain coalescence [11–13], shear-band formation [14], gradient models [15], twinning [16], and grain-boundary dislocation creation and annihilation [17–19]. It is difficult to judge which of the above mechanisms actually dominates the deformation of the given nanostructured materials. In addition, most of the above mechanisms only consider the effect of grain size, without taking into account the grain boundary and interior structures. The present paper discusses the influence of grain size, grain interior structure, and grain boundary structure on the mechanical property of

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nanocrystalline $Fe_{85}Al_4Si_{11}$ and $Ni_{99}Fe_1$ alloys in the recovery and grain growth stages during annealing, hoping to shed light on the unique deformation behaviors of the nanostructured materials.

2. Experimental

Experimental procedures for the synthesis of our nanocrystalline $Fe_{85}Al_4Si_{11}$ and $Ni_{99}Fe_1$ (at%) alloys have been explained in a previous paper [3]. In brief, the nanocrystalline powders were prepared by mechanical alloying using a SPEX 8000 mill operated inside an argon-filled glove box containing less than 1 ppm oxygen. Aliquots of these powders were isothermally annealed in the above glove-box at selected temperatures for one hour, then either air cooled or furnace cooled, and finally studied by X-ray diffraction, neutron diffraction, microhardness measurement, and transmission electron microscopy [3]. Grain size and dislocation density of our nanocrystalline alloys were derived from the collected X-ray diffraction and neutron diffraction patterns using the method proposed by Ungar and co-workers [20–22].

In order to examine if the dislocation density derived from the diffraction patterns is reasonable, we also used a Perkin-Elmer (Pyris Diamond) Differential Scanning Calorimetry (DSC) to measure the heat release during annealing the as-synthesized nanocrystalline $Fe_{85}Al_4Si_{11}$ at 250 °C for an hour. Two experimental procedures were utilized in the DSC to measure the heat release:

Procedure 1: the as-mechanically alloyed (as-MA) nanocrystalline $Fe_{85}Al_4Si_{11}$ powder was heated from 50 to 250 °C at a rate of 10 K/min and then isothermally annealed at 250 °C for an hour (Scan 1). These heating and isothermal treatments were repeated (on the same specimen) to obtain a baseline (Scan 2). The heat flow signals in Scan 1, after being subtracted from those in Scan 2, were integrated to obtain the enthalpy release.

Procedure 2: the as-MA nanocrystalline $Fe_{85}Al_4Si_{11}$ powder (Specimen 1) was heated from 50 to 250 °C at a rate of 10 K/min, isothermally annealed at 250 °C for an hour, and cooled from 250 °C to room temperature at a rate of 40 K/min to obtain an annealed specimen (Specimen 2). Specimens 1 and 2 were then (separately) heated from 50 to 600 °C at a rate of 10 K/min to obtain Scans 3 and 4, respectively. These heating treatments were repeated to obtain baselines. The area between the heat flow signals in Scan 3 (after being subtracted from its baseline) and those in Scan 4 (after being subtracted from its baseline) should be the enthalpy release.

3. Results

The dependence of microhardness H_v, dislocation density ρ, and grain size D on annealing temperature has been provided in our previous paper [3]. For clarity we re-plot this dependence in Fig. 1. For nanocrystalline $Fe_{85}Al_4Si_{11}$ (Fig. 1a), the as-MA alloy has a grain size of ~11 nm, which does not grow until the annealing temperature reaches 450 °C. The dislocation density ρ in as-MA nanocrystalline $Fe_{85}Al_4Si_{11}$ alloy is extremely high, ~0.14 nm^{-2} (=1.4×10^{17} m^{-2}), which decreases by a factor of ~10 to 0.012 nm^{-2} at 450 °C. Above 450 °C, grain size increases whereas dislocation density decreases. These results indicate that recovery occurs below 450 °C whereas grain growth occurs above 450 °C. Microhardness (H_v) does not change with annealing for temperatures < 400 °C, slightly increases between 400 and 450 °C, and decreases with annealing for temperatures > 450 °C.

A similar effect is seen in Fig. 1b for nanocrystalline $Ni_{99}Fe_1$ alloys. The as-MA $Ni_{99}Fe_1$ has a grain size D of ~14 nm, which is almost constant below 300 °C. The dislocation density ρ in the as-MA nanocrystalline $Ni_{99}Fe_1$ alloy is ~0.053 nm^{-2} (=5.3×10^{16} m^{-2}),

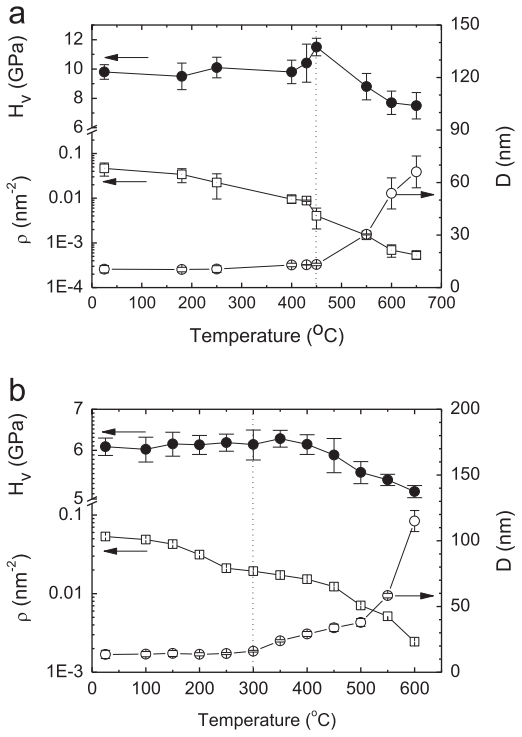

Fig. 1. Microhardness H_v (•), dislocation density ρ (▫), and grain size D (○) as a function of temperature for nanocrystalline $Fe_{85}Al_4Si_{11}$ (a) and $Ni_{99}Fe_1$ (b). Dashed vertical lines separate the recovery and grain growth stages.

which decreases by a factor of ~3 to 0.019 nm^{-2} at 300 °C. Above 300 °C, grain size increases whereas dislocation density decreases. Microhardness (H_v) remains almost constant for temperatures < 300 °C, slightly increases at around 350 °C, and decreases with annealing for temperatures > 350 °C.

Fig. 2a shows the TEM image of the as-MA $Fe_{85}Al_4Si_{11}$. The grain interior is significantly defected, as revealed by the black/white contrast. The Fourier filtered image (Fig. 2b) indicates that there are many dislocation dipoles. After the $Fe_{85}Al_4Si_{11}$ is annealed at 450 °C, the corresponding TEM image (Fig. 2c) shows well-ordered lattice arrangements and no dislocations in the grain interiors can be observed. Note further from Fig. 3c that annealing at 450 °C for one hour does not cause grain growth. In addition, the grain size obtained from the TEM images agrees well with that derived from the X-ray diffraction patterns.

Surprisingly, annihilation of the dislocations stored in the grain interiors does not change the microhardness. Fig. 3 shows the microhardness (H_v) as a function of the square root of dislocation density ($\rho^{1/2}$) for annealed $Fe_{85}Al_4Si_{11}$ (Fig. 3a) and $Ni_{99}Fe_1$ (Fig. 3b). In the recovery stage (i.e., the data between the as-MA and 450 °C in Fig. 3a and the data between the as-MA and 300 °C in Fig. 3b), H_v does not increase with $\rho^{1/2}$. Clearly, the dislocation dipoles stored in the grain interiors contribute little to the strength of our annealed nanocrystalline alloys. In the grain growth stage – which corresponds with the data between 450 and 600 °C in Fig. 3a and the data between 350 and 600 °C in Fig. 3b – H_v increases linearly with $\rho^{1/2}$. Linearly fitting the data in the grain growth stage gives a slope of 54.6 ± 8.4 GPa nm for $Fe_{85}Al_4Si_{11}$ (Fig. 3a) and 13.7 ± 0.7 GPa nm for $Ni_{99}Fe_1$ (Fig. 3b).

In order to further support our viewpoint that dislocations stored in grain interiors contribute little to the strength, we re-milled the nanocrystalline $Fe_{85}Al_4Si_{11}$, which had been annealed at 400 °C for an hour (Specimen A), for 10 h to obtain Specimen B. We then used X-ray diffraction and nanoindentation techniques to examine the grain size, dislocation density, and microhardness of these two specimens. We