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Investigation of low temperature thermal stability in bulk nanocrystalline Ni

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Abstract

Grain growth behavior of bulk nanocrystalline Ni, prepared by an electrodeposition technique with average grain sizes of 20 and 15 nm was investigated in the homologous temperature (T/T_m) range of 0.20–0.40. In studying grain growth, the techniques of X-ray diffraction and transmission electron microscopy were used. The results show that in the temperature range of 0.20–0.30T_m, there is no appreciable grain growth, even after long annealing times. However, in the temperature range of 0.3–0.4T_m, the rate of grain growth was rapid during the initial period of annealing, which decreases with increase in time. The value of time exponent, n, deduced from the grain growth equation of the general form $D^{1/n} - D_0^{1/n} = Kt$ was found to be approximately 0.1 for both grain sizes of Ni. At temperatures higher than 0.3T_m, an approximate activation energy of 105 ± 3 kJ/mol, which is close to the activation energy for grain boundary diffusion in polycrystalline Ni, was measured. At temperatures lower than 0.3T_m, an approximate activation energy of 11 ± 3 kJ/mol was found. It is suggested that this low activation energy represents the energy for the re-ordering of the nanocrystalline grain boundaries.

Keywords: Nanocrystalline Ni; Grain growth; XRD; TEM; Impurity segregation; Electrodeposition

1. Introduction

Nanocrystalline materials (nc-materials) that are characterized by a grain size in the range of 1–100 nm [1,2] have been found to exhibit unusual physical and mechanical properties. Since these unique properties are closely related to the extremely fine grain size and the large volume fraction of grain boundaries associated with nc-materials, it is of importance to maintain the microstructure at a nanometer scale during the structural applications of these materials at the elevated temperatures. Therefore, it is not surprising that the research on thermal stability of nc-materials has recently received considerable attention.

Gleiter [3] reported that nc-Fe with a starting grain size of approximately 10 nm was thermally stable up to 0.26T_m (where T_m is the melting temperature of pure metal). After increasing the temperature to 0.37T_m and annealing for 10 h, the grain size of nc-Fe increased by five times, while the material became microcrystalline when annealed at 0.42T_m. Annealing studies on nc-Ni–1.2 wt.% P [4] revealed that up to 0.28T_m, nanocrystalline structure was retained, whereas the material transformed rapidly into a microcrystalline structure above 0.4T_m. Klement et al. [5] investigated the thermal stability of nc-Ni with an average grain size of 10 and 20 nm by differential scanning calorimetry (DSC). They reported that in nc-Ni, nucleation and abnormal grain growth took place in the temperature range of 0.2 and 0.32T_m, that normal grain growth took place in the range of 0.32 and 0.34T_m, and that grain growth approaches equilibrium in the range of 0.37 and 0.45T_m. Lee et al. [6] studied the grain growth of nc-Ni powders prepared by cryomilling with an average grain size of 22 nm. They reported that a grain size of 150 nm remained unchanged even after very long annealing times when annealed at 0.56T_m due to the presence of dispersions, which acted as a grain growth inhibitor. They also reported that the activation energy for the grain growth in nc-Ni to be 113 kJ/mol, a value that is close to the activation energy for the grain boundary diffusion of polycrystalline Ni. More recently, Kobayashi and Kashikura [7] examined the grain growth behavior of nc-Ni–4.4 mass% P. They reported the grain growth exponent in Ni to be around 4.5–5.9 (time exponent to be around 0.16–0.22).

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The present investigation was carried out in order to study the static grain growth behavior of bulk nc-Ni prepared by an electrodeposition procedure at relatively low homologous temperature (less than $0.4T_m$, where T_m is the melting temperature of pure Ni). It is the purpose of this paper to report and discuss the results of the investigation.

2. Experimental procedure

Nc-Ni with average initial grain sizes of 20 and 15 nm that was prepared by an electrodeposition technique was used. The chemical composition of as-electrodeposited Ni is tabulated in Table 1. The metal was provided by two sources: (a) Integran Technologies Inc., Toronto, Canada, in the form of sheet with an average initial grain size of 20 nm and a thickness of 0.5 mm, and (b) the Lawrence Livermore National Laboratory, CA, in the form of sheet with an average initial grain size of 15 nm and a thickness of 0.3 mm. Nc-Ni from the former source was tested to obtain experimental data while nc-Ni from the latter source was selectively used to check experimental trends.

The samples were annealed in air at four different temperatures, varying from 0.2 to $0.4T_m$, i.e., 393, 493, 593 and 693 K, for five different annealing times ranging from 0.5 to 25 h. After annealing the samples were rapidly cooled in air and characterized using X-ray diffraction (XRD) to calculate the grain size.

XRD measurements were conducted using a Siemens D5000 diffractometer equipped with a graphite monochromator using copper Kα ($\lambda = 0.15406$ nm) radiations. General scans with a step size of 0.01 degree (2θ) and with a step time of 2 s were conducted for grain size determination. Following subtraction of the instrumental broadening and $K\alpha_2$ components, integral breadth for five strong FCC Ni peaks ({1 1 1}, {2 0 0}, {2 2 0}, {3 1 1} and {2 2 2}) was measured.

For grain size measurement, the method of integral breadth (IB) [8] was adopted since the results of an analysis of grain size in bulk nc-materials have shown [9] that this method provides the closest approximation to the average grain size determined by transmission electron microscopy (TEM). In the method of IB [8], the average crystallite size and the lattice microstrain were estimated by XRD line broadening. This broadening of Bragg's peaks is caused by the small size of the diffracting grains and by lattice strain. When the size and strain broadening are simultaneously present, the separation of the size and strain broadening by the method of IB can be presented by the equation given below:

$$\frac{(\delta 2\theta)^2}{\tan^2\theta_0} = \frac{K\lambda}{L}\left(\frac{\delta 2\theta}{\tan\theta_0 \sin\theta_0}\right) + 16e^2 \quad (1)$$

where $\delta 2\theta$ is IB (in radians), λ the wave length of copper Kα radiations, K a constant taken as 1, L the mean grain size, θ_0 the position of the peak maximum and e is equivalent to one-forth of the root-mean-square strain:

$$e = \frac{1}{4}\langle \varepsilon^2 \rangle^{0.5} \quad (2)$$

By performing a least-square fit to $(\delta 2\theta)^2/\tan^2\theta_0$ plotted against $(\delta 2\theta/(\tan\theta_0 \sin\theta_0))$ for all the measured peaks of a sample, L and e can be estimated from the slope of the straight line and y intercept, respectively.

In addition to applying the method of IB, TEM investigation on as-received and post annealed samples was conducted using a Philips CM 20 TEM at 200 kV. The investigation by means of TEM serves two purposes: (a) to check the data on grain growth that are obtained from the IB method, and (b) to provide information on grain size distribution in both as-received and post annealed samples. The TEM sample preparation was carried out in two steps. First, the sample was mechanically mirror polished down to a thickness of less than 50 μm and a punch was used to cut 3 mm disc from it. The 3 mm discs were then chemically polished using a twin jet polisher, in which the surface exposed to the twin jets was chemically etched until the thinned area was transparent to the optical sensor. The solution used was a mixture of 75% CH_3OH and 25% conc. HNO_3. The voltage used was 8 V and the ampere reading was 4 mA. The temperature of the chemical solution was maintained below 243 K.

Differential scanning calorimetry (DSC) investigation was performed on 20 nm nc-Ni samples in a commercial laboratory, OCM Test laboratories, Anaheim, CA. The scan was performed in Universal TA Instruments using nitrogen as a purge gas. Measurements were done between 323 and 973 K at a heating rate of 10 K/min.

Table 1
Chemical composition of as-electrodeposited nc-Ni

Elements	Wt.%
C	0.013
Si	<0.001
P	0.003
S	0.058
Cu	0.023
Co	0.071
B	0.0091
Ni	Balance

3. Results

3.1. As-received material

Fig. 1(a and b) shows the XRD pattern for an as-received electrodeposited nc-Ni specimens of 15 and 20 nm, respectively. The XRD pattern for both 15 and 20 nm specimen shows strong orientation around (1 1 1) followed by (2 0 0), indicating a preference for the planes with the lowest surface free energy to lie in the plane of the specimen [10]. For 15 nm specimens, the orientation around (2 0 0) is much stronger in terms of the relative peak intensity as compared with the standard JCPDS pattern (04-0850), whereas 20 nm specimens show an extra peak of (3 0 0), which is not a standard reflection plane for FCC metals. This observation reveals the presence of strongly preferred texture with the (1 0 0) planes oriented predominantly in the as-electrodeposited samples.