Materials Science Forum Vols. 426-432 (2003) pp. 4507-4512
online at http://www.scientific.net

CALORIMETRIC AND X-RAY MEASUREMENTS IN ULTRAFINE-GRAINED NICKEL

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Keywords: nickel, equal-channel angular pressing, high-pressure torsion, ultrafine-grain sizes, grain boundary misorientations

Abstract. The procedures of X-ray diffractometry and peak profile analysis, together with differential scanning calorimetry (DSC), were used to measure the grain size, dislocation density and corresponding elastic energy stored in ultrafine-grained (UFG) nickel processed by different methods: equal channel angular pressing, high pressure torsion and their combinations. It has been shown that grain growth in these samples begins at temperatures in the range from 500 to 700 K and the measured activation energy for grain growth is close to the activation energy for grain boundary self-diffusion. A difference between the released enthalpy in DSC experiments and the elastic energy evaluated by x-ray diffractometry is attributed to the decrease in surface energy during grain growth in UFG nickel. The grain boundary (GB) surface energy of high angle boundaries was also evaluated.

Introduction

Generally, grain refinement has been accomplished by using various thermo-mechanical processing treatments involving both heat treatments and mechanical working. But these procedures have the disadvantage that new and often complex procedures must be developed for each individual alloy. An alternative procedure is to use processes involving severe plastic deformation (SPD) [1-4] in which bulk materials with coarse grain sizes are subjected to very intense straining and the introduction of high densities of dislocations that re-arrange to form grain boundaries.

The highly strained microstructures produced by severe plastic deformation (SPD) can only be characterized locally by transmission electron microscopy. In this sense high resolution x-ray diffraction is a useful instrument for providing information on the mean grain size and the distribution of grain sizes, the internal microstrains and the related dislocation densities. It is especially useful in the case of UFG metals and alloys produced by SPD where measurements by transmission electron microscopy (TEM) reveal very high dislocation densities (10^{15}–10^{16} m^{-2}). In practice, a complete characterization of the microstructure can be achieved by simultaneous application of X-ray diffraction and TEM.

This paper is devoted to the results obtained in a study of pure nickel samples obtained from two different SPD processes: Equal Channel Angular Pressing (ECAP), High-Pressure Torsion (HPT) and their combination. The procedures of X-ray diffractometry [5, 6] and peak profile analysis together with differential scanning calorimetry were used to measure the grain size, dislocation density and the corresponding elastic energy stored in ultrafine-grained nickel.

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Experimental material and procedures

High purity nickel (99.99%) was selected for use in this investigation. There were two reasons for this choice. First, pure Ni was used in earlier investigations documenting the characteristics of ECAP and HPT [4, 7]. Second, it was established recently that pure Ni represents an ideal model material for investigations involving processing by severe plastic deformation because the stacking fault energy, which is lower than for pure Al but higher than for pure Cu, leads to a significantly smaller grain size than is generally achieved in aluminum and a more homogeneous microstructure than is achieved in copper [8].

The principles of processing by ECAP and HPT have been described elsewhere [1-4, 7, 9]. Briefly, nickel cylinders having diameters of 16 mm and lengths of ~100 mm were subjected to ECAP at room temperature using a die with an internal angle of 90°. Samples were pressed repetitively for 8 passes, equivalent to a total strain of ~8, and each sample was reversed from end to end and rotated by 90° about the longitudinal axis between passes. Earlier experiments showed this procedure produces an as-pressed mean grain size of ~0.30-0.35 μm [3, 10]. For processing by HPT, disks with diameter of 10 mm and thickness of ~0.3 mm were torsionally strained under a high pressure of 6 GPa for a total of 5 complete revolutions, equivalent to a true logarithmic strain of ~6. This procedure produces a mean grain size of ~0.17 μm [7]. One additional sample was prepared by using an electrodischarge procedure to cut disks from the central parts of rods prepared by ECAP and then subjecting this disk to high-pressure torsion for 5 revolutions under an applied pressure of 6 GPa: this sample is designated ECAP&HPT [11].

The thermal behavior of these samples was investigated using DSC under an atmosphere of pure argon. All DSC measurements were performed in a Perkin-Elmer DSC7 calorimeter under continuous-heating conditions using heating rates of 20, 40 and 60 K/min. The activation energy of the relaxation processes occurring during heating has been evaluated using a Kissinger plot [11]

The diffraction profiles were measured by a special double-crystal diffractometer (Nonius FR591) with negligible instrument-induced broadening [5, 12]. It was operated at 40 kV and 70 mA with rotating copper anode. The symmetrical 220 reflection of a germanium monochromator was used for wavelength compensation at the position of the detector. The Kα2 peak of the Cu radiation was eliminated by placing a 0.16 mm slit between the source and the monochromator. The profiles were recorded by a linear position sensitive gas-flow detector (OED 50 Braun, Münich). The structure of UFG nickel samples was studied with a conventional X-ray diffractometer (Phillips 3050) using Cu K_α radiation, in the Bragg-Brentano geometry operating in a step scan mode.

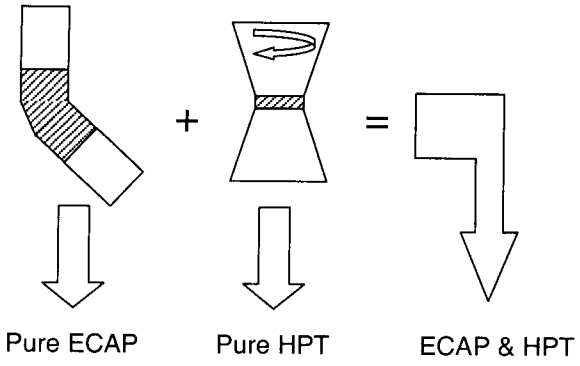

Fig. 1. Schematic representation of ultrafine-grained nickel processing.

Results and discussion

Differential scanning calorimetry. During continuous heating, the microstructures of the processed materials undergo significant changes in grain size. An example is shown in Fig. 2 for ultrafine-grained nickel obtained by ECAP, where Fig. 2(a) is a bright-field TEM image showing the as-processed grain size of ~350 nm and Fig. 2(b) is an optical micrograph showing the course-grained microstructure present in this material after three cycles at a heating rate of 60 K/min up to the temperature of 923 K. The activation energies derived from the Kissinger plots for all Ni samples [11] are very close to the activation energy for grain boundary self-diffusion [13]. Measured enthalpies, ΔH, released during DSC heating of ultrafine-grained nickel specimens are shown in Table 1. Released heat strongly depends on sample microstructure, increasing with decreasing of the mean grain size. The HPT nickel possesses 1.7 times higher heat release and the ECAP&HPT sample ~ 3.2 times compared to the ECAP nickel. The level of heat release of 102.7 J/mol measured in HPT nickel is the same order of magnitude as the value of 0.26 kJ/mol reported in an earlier paper [14].

X-ray measurements. A numerical procedure has been developed for fitting the Fourier transform of the experimental profiles by the product of the theoretical functions of the size and the distortion (strain) Fourier transforms (Multiple Whole Profile fitting - MWP) [5, 12]. The theoretical functions were calculated from a microstructural model with the following assumptions: (i) the crystallites are spheres and have a log-normal crystallite size distribution; (ii) the lattice distortions are caused by dislocations. The procedure has five fitting parameters for cubic crystals: the median (m) and the variance (σ) of the log-normal size distribution function, the dislocation density (ρ), the dislocation arrangement parameter M and q for determining the average dislocation contrast factors. An example of x-ray profiles for ECAP, HPT and ECAP&HPT samples recorded by conventional x-ray is presented in Fig.3. The insert shows the enlarged part corresponding to the 111-peak. It is seen that, as a consequence of deformation (ECAP, HPT, ECAP&HPT), there is an increase in the full width high maximum (FWHM). A fitting procedure permits an evaluation (under certain assumptions) of the average size of coherent domains, the elastic distortion of the crystalline lattice, the dislocation density and the elastic energy stored in the sample. All of the relevant experimental data are summarized in Table 1. There is a tendency for increasing of microstrain level, $\langle \varepsilon^2 \rangle^{1/2}$ and decreasing of the mean sizes of coherent domains ($d_{X\text{-}ray}$) and grains (d_{TEM}) with increasing of strain imposed on the nickel samples during SPD processing. The coherent domain size (CDS) for HPT nickel of 42 nm observed in the present work is in good agreement with the value of 35 nm measured in other work [15].

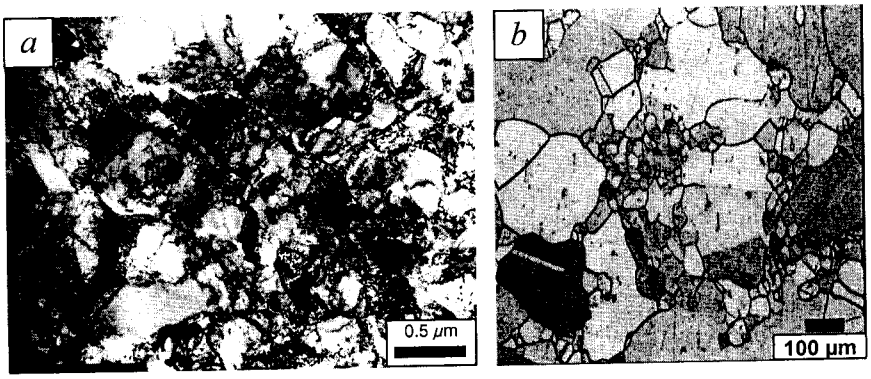

Fig. 2. ECAP nickel: (a) – in bright field TEM as received [10] and (b) – using optical microscopy after 3 runs at heating rate of 60 K/min up to a temperature of 923 K.

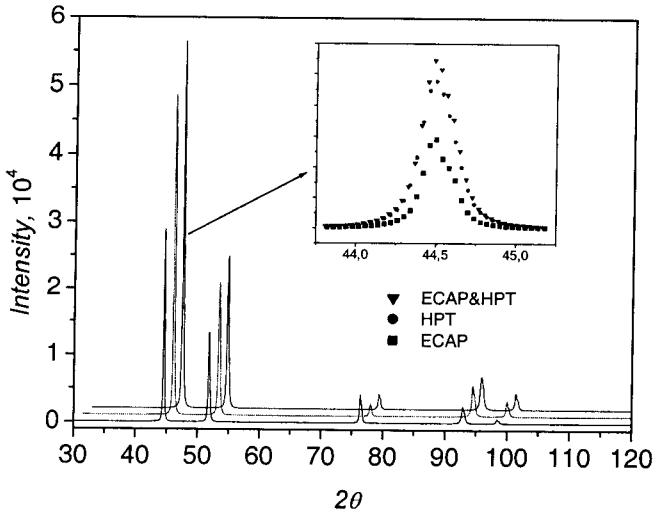

Fig. 3. X-ray profiles for ECAP, HPT and ECAP&HPT samples.

GB surface energy. There is a difference in enthalpy released during DSC and elastic energy measured by X-ray and this is related to the liberation of GB surface energy. It is shown in the last column of Table 1. It is possible to deduce the total GB surface energy normalized per unit area using the following procedure. The grain boundary energy, W_{GB}, can be represented (in units of J/mol) as [11]:

$$W_{GB} = \alpha \frac{\gamma}{d_0} \Omega \cdot N_A, \tag{1}$$

where γ is the GB surface energy per unit area (J/m^2), α is a geometrical factor (for an idealized model of spherical grains, α=3), d_0 is the initial grain size, Ω =1.09·10^{-29} m^3 is the atomic volume and N_A is Avogadro's number. Then, γ can be estimated from the equation

$$\gamma = \frac{d_0 \cdot W_{GB}}{3 \cdot \Omega \cdot N_A}. \tag{2}$$

The results obtained are depicted in Fig. 4. The GB surface energy varies from 0.8 J/m^2 for the ECAP nickel to 1.0 J/m^2 for the HPT nickel giving an average value of 0.9 J/m^2 that corresponds to the sample obtained by a combination of ECAP and HPT. The values calculated by this approach are in good agreement with known literature data that gives values for the GB surface energy

Table 1. Microstructure parameters for the nickel samples processed by different methods

Nickel samples	$d_{X\text{-}ray}$, nm [6]	d_{TEM}, nm [9, 10]	$\langle\varepsilon^2\rangle^{1/2}$, 10^{-3}	ρ, 10^{14} m^{-2}	W_{EL}, J/mol	ΔH, J/mol	W_{GB}, J/mol
ECAP	71±5	350	2.5±0.3	9±1	17.6	59.3	41.7
HPT	42±4	170	3.1±0.3	17±2	23.3	102.7	79.4
ECAP&HPT	48±4	140	3.7±0.4	25±2	42.5	187.9	145.4

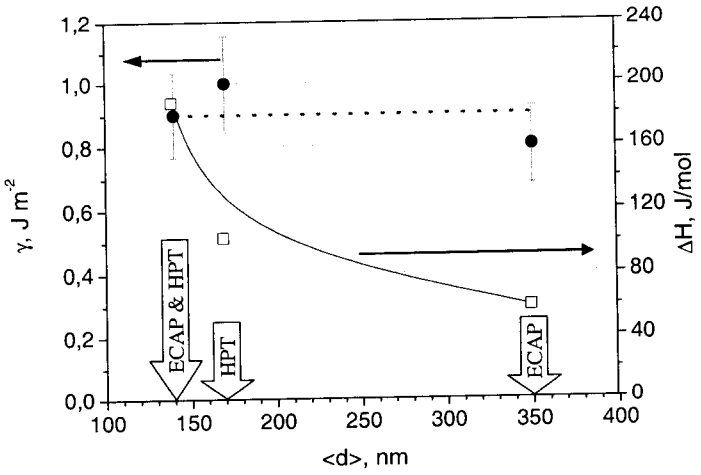

Fig. 4. Grain boundary surface energy and released enthalpy in UFG nickel samples under study.

between 0.7 and 1.0 J/m^2 [16]. It should be noted that the present evaluation has been made using significant simplification: namely, the microstructure consists of spherical grains and identical high-angle grain boundaries. Taking into account that the real microstructure will decrease the geometrical parameter α to a value of about 1.3 (see for example Appendix A in [17]) and respectively increase the GB surface energy, and considering the fact that not all grain boundaries have high angles of misorientation, the evaluated energy will be even higher. For example, Orientation Image Microscopy (OIM) experiments [18] have shown that ECAP nickel has only 60% high-angle grain boundaries and HPT nickel has 68.1 %.

Summary and Conclusions

By means of differential scanning calorimetry and high-resolution x-ray diffraction, the microstructural parameters and released enthalpy have been measured in ultrafine-grained nickel processed by ECAP, HPT and their combination. Using data obtained by x-ray, the elastic stored energy has been evaluated for all nickel specimens under study. The difference between the released DSC enthalpy and the elastic energy is attributed to the GB surface energy and the normalized surface energy has been evaluated. All nickel samples show GB surface energies in the range of 0.8-1.0 J/m^2 and this is consistent with the known literature data. Extension of the analysis to incorporate the real microstructure and the grain boundary statistics will lead to an increase in the calculated value. This is attributed to the non-equilibrium state of GBs existing in UFG materials obtained by severe plastic deformation as claimed earlier in several papers [3, 4, 19].

Acknowledgements

This work was supported in part by the U.S. Army Research Office Under Grant No. DAAD19-00-1-0488 and Spanish grant CICYT (MAT2001-2555). One of the authors (APZ) thanks the Spanish government (SAB 2000-0390) for financial support. Another author (JG) is grateful for the support of the Magyary Zoltan Postdoctoral Program of the Foundation for Hungarian Education and Research (AMFK).

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