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Internal friction, thermal and structural analysis of nanocrystalline aluminium

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Abstract

Elastic energy dissipation and dynamic elasticity modulus measurements were performed on nanocrystalline aluminium obtained by mechanical attrition and cold consolidation. Information has so far been obtained on the structural stability of the specimens with different grain sizes and defect contents. The anelasticity spectra from specimens where the ultimate grain size was reached (20 nm) show a well-defined relaxation process with an activation energy of 0.8 ± 0.1 eV. Differential scanning calorimetry and transmission electron microscopy observations confirmed the defect density dependence and behaviour of the anelastic spectra.

1. Introduction

Recently it has been demonstrated that nanocrystalline pure metals and alloys can be obtained by mechanical attrition [1–3].

Two parameters are of major concern in determining the formation of the nanocrystalline alloys or pure metals at their ultimate grain size after severe deformation induced by mechanical attrition. These are the amount of "stored enthalpy" during the milling process and the structure of the disordered interfacial regions, the "grain boundary phase", constituting in nanocrystalline materials a relevant fraction [3–6].

The observed high density of defects generated during the early stages of cold deformation by mechanical attrition and their subsequent dynamics, with formation of dislocation substructures, and moreover the dynamic equilibrium reached during the milling between defect production and recovery are essential steps in understanding the formation and behaviour of the nanocrystalline materials and in particular the reaching of the ultimate grain size and the structural stability [4].

Recently spectroscopy techniques were fruitfully employed to gain insight into the structure of nanocrystalline materials [7–9]. The anelasticity spectra showed significant difference from those corresponding to similar coarse-grained materials.

On the contrary, it is well known that the above techniques in the past have provided significant results in understanding the details of grain and subgrain boundary sliding and/or dislocation boundary interactions in coarse-grained materials [10–12]. Since for a deep knowledge of the mechanical properties of nanocrystalline materials it is necessary to understand their intimate connection with the grain size and "grain boundary" structure, in this work we have investigated the anelastic behaviour of pure nanocrystalline aluminium obtained by mechanical attrition. Particular attention was paid to search for a connection of the specific features of the anelasticity spectra with the structural evolution at different milling times, *i.e.* for different grain sizes and defect densities. Moreover the search was also intended to show the specific anelastic relaxation processes linked to defects and/or disordered interfaces.

Differential scanning calorimetry (DSC) analysis was performed to study the thermal behaviour of nanocrystalline aluminium, and in particular the enthalpy content *vs.* the milling time. Field emission transmission electron microscopy (TEM) observations have been employed to follow the nanostructural modifications of the aluminium powders after different amounts of mechanical attrition.

2. Experimental details

Pure Al powders (Alfa products; 99.99% purity) were employed in the present research. Mechanical attrition was performed by ball milling in a Spex mixer mill model 8000, with hardened steel balls and a tungsten

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carbide vial. The process was conducted under an argon atmosphere with an oxygen content below 5 ppm. 10 g of powders were milled and the ball-to-powder weight ratio was 8 to 1. The grain size and the atomic level strain variations during milling were followed by X-ray diffraction (XRD) procedures as reported elsewhere [13]. For the measurements of mechanical properties the milled powders were cold consolidated by means of a specifically constructed die under an axial pressure of 1.5–2.0 GPa. In this way, bar-shaped samples with dimensions of 4 mm×1 mm in section, and a length of 20 mm were obtained. The internal friction and dynamic modulus measurements were performed by an inverted torsional pendulum operating in the 3–10 Hz range at a strain amplitude of less than 10^{-5}. Some measurements were also performed by a vibrating-reed technique in the 10^2–10^4 Hz range at a strain amplitude less than 10^{-6}. All data acquisition and processing were completely computer controlled.

Specimens for TEM observations were prepared either by retrieving the as-milled aluminium powders, which are transparent to the electron beam on their edge, on lacey carbon-film-covered grids, either by retrieving on the same films after chemical thinning the powders by means of a solution of hydrofluoric acid at room temperature. Observations have been performed with an FEG Philips EM 400T electron microscope operating at 100 kV.

Thermal analysis was performed before and after the mechanical attrition with a computer-controlled Perkin–Elmer DSC7 differential scanning calorimeter. The temperature was calibrated within 1 K, and the samples were cold welded on aluminium pans under an argon atmosphere. The enthalpy was measured at a heating rate of 10 K min^{-1} in a temperature range from 320 to 870 K under flowing argon and nitrogen.

3. Results

Figures 1–3 show the elastic energy dissipation coefficient Q^{-1}, as a function of temperature, measured during a constant-heating-rate run (2 K min^{-1}) on as-prepared specimens. The different curves refer to cold consolidated specimens obtained from powders milled for different times. Some specific features are worth noting.

(1) The background damping is generally higher in specimens obtained from powders milled for short times (less than 5 h) and reaches a constant value for milling times in excess of 10 h. Taking into account the inverse dependence of the grain size on milling time, as previously observed [9], it turns out that the low background damping values are reached at the ultimate grain size.

(2) A damping peak can be observed in specimens milled for times longer than 5 h. The peak relaxation strength is maximum for specimens milled for 10–24 h. This peak is of relaxational type, as can be deduced by the shift in peak temperature with frequency (Fig. 2).

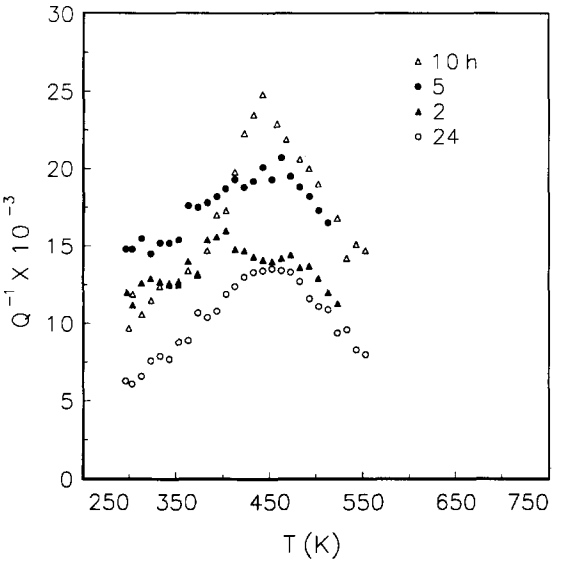

Fig. 1. Internal friction *vs.* temperature behaviour for nanocrystalline aluminium specimens obtained after consolidation of the powders milled for the indicated times (frequency, 3 Hz).

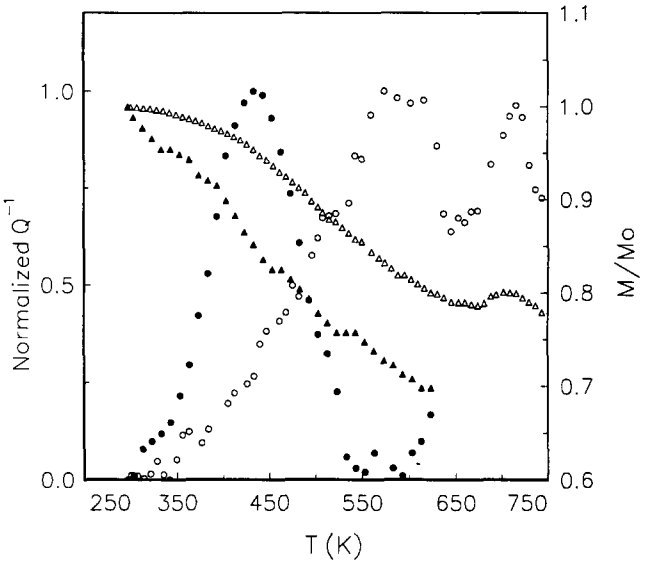

Fig. 2. Internal friction (circle) and modulus (triangle) *vs.* temperature for specimens obtained from powders milled for 10 h, measured at two different frequencies: ●, ▲, 4 Hz; ○, △, 3000 Hz. Note the anomalous modulus behaviour at temperatures higher than 600 K due to the nanostructure destabilization.

Noticeable modification of the anelastic spectra can be observed in the second thermal run after returning to room temperature from approximately 600 K (Fig. 3). The background damping is strongly reduced, and peak-shifts of 10–20 K are seen at higher temperatures.

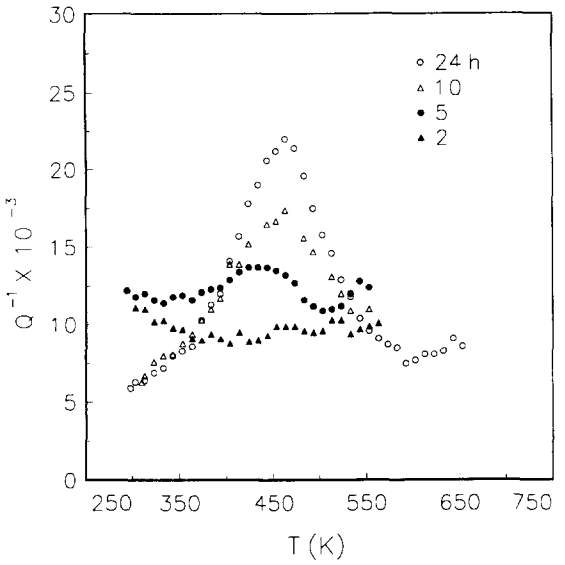

Fig. 3. Same as in Fig. 1 during the second thermal run.

TEM showed a strong increase in the defect density in the early mechanical attrition stages. For a milling time of 5 h a high density stressed defective morphology is present in the samples and is clearly evident in the micrograph in Fig. 4(a). In addition, from the electron diffraction pattern (Fig. 4(b)), it is possible to observe textured (111) and (002) zones in the sample. Aluminium crystals with sizes of 50–100 nm are still present.

At longer milling times, *e.g.* 10 h, the defect density decreases, with a concomitant homogenization of the crystallite sizes to about 15–20 nm, in agreement with XRD analysis.

Figure 5 shows the stored enthalpy H, measured by DSC, as a function of the grain size d. It must be observed that these data represent a lower estimation of the total stored enthalpy since the DSC scannings were performed only up to 870 K. It is note worthy that the stored enthalpy reaches a maximum value for $d \approx 20$–25 nm and decreases during further refinement of the nanostructure with $d \approx 15$ nm.

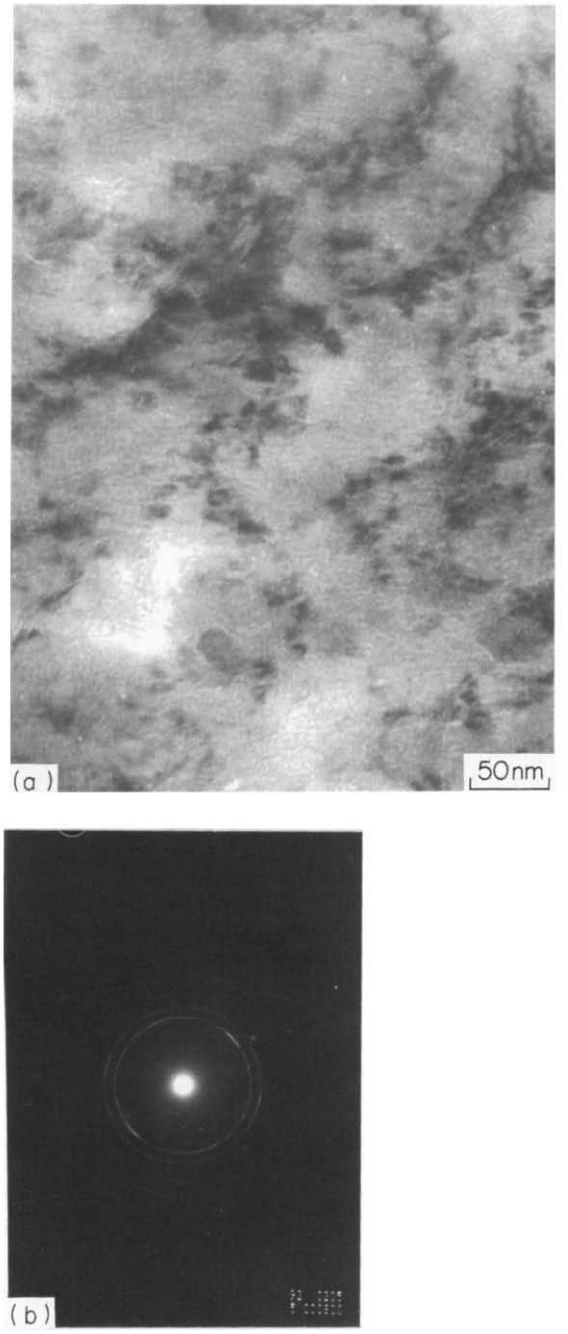

Fig. 4. (a) Detail of the defective structure developed after 5 h of mechanical attrition in pure aluminium. Extended strain contrast and high dislocation density is present. (b) The corresponding electron diffraction pattern indicates, in addition, (111) and (002) textures.

4. Discussion

Prolonged milling induces noticeable structural modifications. The grain size displays a significant reduction during the first hours of milling (Figs. 4(a) and 5). At milling times in excess of 10 h the grain dimension approaches the ultimate value (20 nm). No further grain refinements were observed for times up to 40 h. The r.m.s. atomic level strain, determined by XRD analyses [8, 9, 13], increases strongly up to 5–10 h milling and subsequently reaches a constant value.

The strong increase in the r.m.s. microstrain in the early stages of milling is mainly determined by the mechanical deformation with high energy transfer. The strong cold plastic deformation considerably enhances the dislocation density, when the grain size at the beginning of the process is still relatively large (Fig. 4(a)).

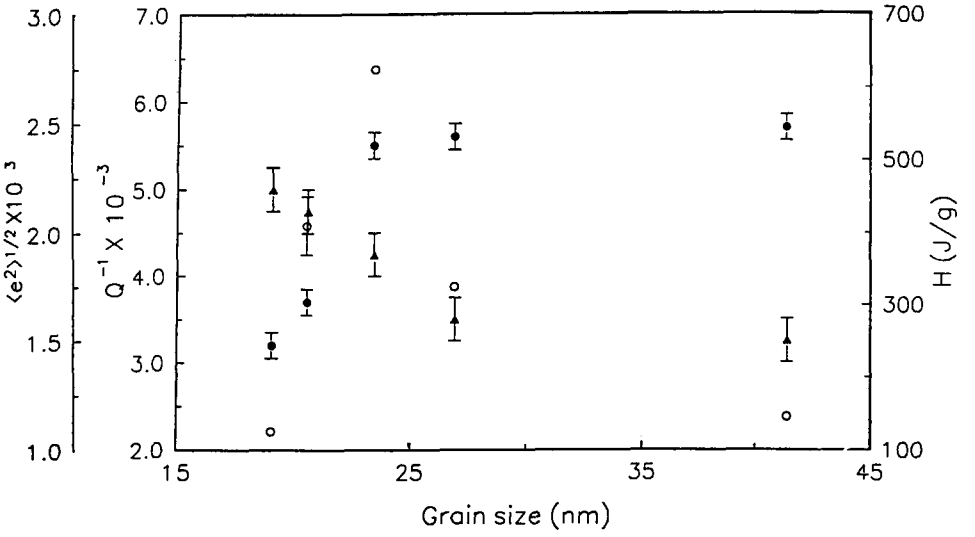

Fig. 5. Evolution with grain size respectively of background damping (●), microstrain ϵ (▲) and the stored enthalpy H (○).

This strong modification of dislocation density and dislocation link length distribution might reasonably induce strong anelastic effects. In the near kilohertz frequency range, the elastic energy dissipation coefficient which expresses dislocation anelasticity, may be written in the form [14]

$$Q^{-1} = C\Lambda l^3 B\omega$$

where C is a constant for a given specimen at a fixed temperature, l is the effective average dislocation loop length, Λ is the dislocation density, B is the quasi-viscous damping constant for dislocation motion and ω is the frequency.

The observed background damping trend (Fig. 5), which decreases when the ultimate grain size is reached, may be connected to the decrease in both Λ and l. A dislocation density decrease in the grain by reducing the grain size was experienced in ball-milled Al [9] and observed in Ni–Mo by TEM [15]. Moreover, DSC analyses indicate that a strong reduction in the stored enthalpy of the milled products occurs when reaching the ultimate grain size (Fig. 5), in agreement with the hypothesis of a defect density and stress reduction.

The states of equilibrium induced by milling are intrinsically of metastable type. At temperatures as low as 350 K, thermally induced structural modification may occur in the course of an isochronal measurement at constant heating rate. These structural variations are brought into evidence by irreversible modulus enhancement during isothermal measurements [7]. In this regard, Weller *et al.* observed an irreversible increase in the shear modulus by aging nanocrystalline Pd at 400 K; the underlying activation energy was 0.65 eV. This modulus increase was ascribed to interatomic rearrangement in the interfaces with free volume reduction. Only the specimens milled for a long time (greater than 24 h) when saturation of the grain size has been reached (Fig. 5) show a relatively stable structure with small modifications of the anelasticity spectra after successive thermal runs up to 600 K. On account of the experimental results obtained from XRD which do not show a significant grain size increase for aging below 550 K, the structural modifications responsible for the modulus increase should mainly involve the structure of the disordered interfacial regions.

The damping peak observed at about 450 K (4 Hz) is of relaxational type (Fig. 2). Thus an averaged activation energy H may be obtained from the peak shift in temperature by changing the measurement frequency from ω_1 to ω_2 using the equation

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{k}{E} \ln\left(\frac{\omega_2}{\omega_1}\right)$$

where T_1, T_2 are the peak temperatures and k is the Boltzmann's constant. However, in our case it must be pointed out that the conditions both for a Debye-type relaxation and of the relaxation time temperature independence are not fulfilled.

Repeated measurements on several (ten) specimens milled for times in excess of 10 h showed statistically reproducible Q^{-1} curves of which Fig. 2 reports typical trends. The calculated mean activation energy resulted:

$$E = (0.8 \pm 0.1)\ \text{eV}$$

with a pre-exponential factor $\tau_0 = 10^{-12}$ s.

It is note worthy that this value is close to the activation energy for grain boundary diffusion in Al [16]. A similar value was obtained by Berry and Pritchet [17] for a peak observed in Al thin films with a grain size of 100 nm deposited onto fused silica substrate. In coarse-grained polycrystalline aluminium, higher

values of the activation energy (about 1.4 eV) for the "orthodox" grain boundary peak or "Ke peak" was observed [1]. This value is close to that for lattice diffusion. The difference in mean activation energy between pure nanocrystalline and coarse-grained aluminium should indicate that sliding by a vacancy mechanism becomes important at smaller grain sizes. This hypothesis is in agreement with the reported transition from a deformation behaviour controlled by dislocation to a diffusion-controlled mechanism when entering the nanometre range [18].

5. Conclusions

The anelasticity measurements on nanostructured pure Al obtained by mechanical attrition have shown specific features when the ultimate grain size is reached. These are a strong reduction in the background damping with concomitant evidence of a well-defined anelastic relaxation peak.

TEM observations and DSC analyses indicate that in the course of the milling process a strong initial dislocation density and atomic level strain increase occur as well as a strong increase in the stored enthalpy. In this condition, higher background damping is experienced. The following strong reduction in defect density and enthalpy for times in excess of 10 h when reaching the ultimate grain size corresponds to the nanostructural conditions, giving evidence of the relaxation peak.

Acknowledgments

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