Microstructure and yield strength of ultrafine grained aluminum processed by hot isostatic pressing

J. Gubicza\textsuperscript{a,}\textsuperscript{*}, G. Dirras\textsuperscript{b}, P. Szommer\textsuperscript{a}, B. Bacroix \textsuperscript{b}

\textsuperscript{a} Department of Materials Physics, E\'otv"{o}s Lor\'{a}nd University, P.O.B. 32, Budapest H-1518, Hungary
\textsuperscript{b} LPMTM-CNRS, Institut Galil\`ee, Universit\`e Paris 13, 99, Avenue J. B. Clement, 93430 Villetaneuse, France

Received 7 September 2006; accepted 21 December 2006

Abstract

The correlation between the microstructure and the yield strength of a specimen produced by hot isostatic pressing (HIP) of commercial purity aluminum nano-powder was studied. It was found that the bulk sample can be regarded as a composite containing microcrystalline grains embedded in an ultrafine grained matrix. The composite-like microstructure results in a bimodal hardness distribution as shown by nanoindentation. The yield strength values for both the ufg matrix and the mc grains were calculated from the characteristic parameters of the microstructure. The yield strength of the composite estimated by using a simple rule of mixture was in good agreement with the value determined by compression test. It was revealed that the majority of the strengthening can be attributed to the dislocations in the ufg matrix and the alumina dispersoids formed during HIP process.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Hot isostatic pressing (HIP); Ultrafine grained microstructure; Nanoindentation; Yield strength; X-ray line profile analysis

1. Introduction

Bulk nanocrystalline and ultrafine grained materials are the object of increasing attention since these materials have unique mechanical properties compared to coarse-grained counterparts [1–5]. The reduction of the grain size is especially effective in the increase of the flow stress of bulk metallic materials. A wide range of experimental techniques have been developed for producing ultrafine grained materials. There is one class of these procedures where the fine grain size is achieved by refinement of coarse grains in bulk materials by severe plastic deformation (SPD) [2–5]. These methods result in a very high density of dislocations progressively arranged into high-angle boundaries and thereby lead to an ultrafine grained structure. In the SPD processed materials crystallographic texture is often formed which makes the study of the effect of grain size on the strength difficult. The other class of methods is based on consolidation of nanopowders [6–8]. These procedures result in a texture-free, stable microstructure, but usually with a residual porosity. Hot isostatic pressing (HIP) is a promising method to obtain relatively large, bulk and near fully dense materials from nanometric metallic powders [7,8]. The samples processed by HIP have a potential for examining the effect of grain size on the mechanical behavior of nanomaterials. In this paper the correlation between the microstructure and the flow stress of a bulk Al sample produced from nano-powder by HIP is studied. It is revealed that the flow stress of this material cannot be related to one characteristic grain size value because of the strong inhomogeneity of the microstructure. The parameters of the ultrafine-grained (ufg) and the microcrystalline (mc) components of the microstructure are determined by TEM and X-ray line profile analysis and related to the flow stress.

2. Experimental procedures

The bulk Al sample was produced from ALEX nano-powder supplied by Argonide Corporation (USA). The processing route and the chemical composition of this powder is described elsewhere [9]. The nano-powder particles are characterized by a spherical shape and an average diameter of about 80 nm. It should be noted that the powder also contains a small amount of large particles with sizes between 1 and 60 \(\mu\)m. Fully dense bulk material was processed via HIP at 550 °C under a pressure of 200 MPa for 600 min. The detailed
description of the HIP procedure has been given in Ref. [9].

Phase composition of the HIP-processed sample was determined by X-ray diffraction using a Philips X’pert powder diffractometer with a Cu anode. The microstructure was examined using X-ray diffraction line profile analysis. The X-ray line profiles were measured by a high-resolution rotating anode diffractometer (Nonius, FR591) using Cu Kα₁ radiation. The scattered X-rays were detected by image plates with the angular resolution of 0.005° in 2Θ, where Θ is the angle of diffraction. The line profiles were evaluated using the multiple whole profile (MWP) fitting procedure described in detail in other reports [10]. The procedure is used to estimate the median (m) and the variance (σ) of crystallite size distribution, the mean size of crystallites (or coherently scattering domains) and the density of dislocations (ρ). The microstructure was also investigated using a JEOL-2011 transmission electron microscope (TEM) operating at 200 kV, under both conventional and energy-filtered TEM (EFTEM) conditions.

The flow behavior of the specimen processed by HIP was studied by compression test performed at room temperature and at a strain rate of 2 × 10⁻⁴ s⁻¹. The hardness was tested by nanoindentation using an UMIS nanoindentation device with Berkovich indenter and applying a maximum load of 1 mN. The indentation rate was 0.03 mN/s. One hundred indentations were carried out arranging the indents in a 10 × 10 matrix. The distance between the neighboring indents was 4 μm. The hardness is characterized by the number determined as [11]:

\[ H = \frac{P_m}{24.5h_m^2} , \]

where \( P_m \) is the maximum load (1 mN) and \( h_m \) is the maximum penetration depth during indentation.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the TEM images taken on the bulk sample produced by the HIP technique. It can be seen from Fig. 1a that the microstructure consists of ultrafine grained volumes and large grains with a diameter of 1–10 μm, i.e. with respect to the aluminum grains, the material can be regarded as a two-phase composite of ufg and microcrystalline volumes. The average grain size in the ufg volume estimated from the TEM images is 150 nm. Fig. 1b shows a fine grain (160 nm) divided into subgrains with the size of about 50 nm.

In the X-ray diffractogram of Fig. 2, beside the aluminum phase a relatively small amount of γ-Al₂O₃ is also identified. The TEM image in Fig. 1a also shows alumina particles inside the mc grains with the diameter of about 20 nm. The Al₂O₃ dispersoids inside the aluminum grains are formed during HIP procedure from the alumina layer covering the nanoparticles in the initial alumina powder, as discussed in [9].

In the Debye–Scherrer rings detected by high resolution X-ray diffraction, sharp intensity spots are superimposed on the wide rings of the ufg matrix which are related to the reflect-
Fig. 3. The conventional (a) and the modified (b) Williamson–Hall plots for the ufg Al matrix.

\( K = 2 \sin \theta / \lambda \), where \( \lambda \) is the wavelength of X-rays) in Fig. 3a. The non-monotonic behavior of the line widths can be rationalized by the dislocation contrast factors, \( C \), as can be seen in the modified Williamson–Hall plot for the same data (Fig. 3b). This indicates that the lattice strains are caused by dislocations. For the detailed description of the dislocation contrast factors and modified Williamson–Hall procedure see Ref. [10]. The dislocation density was obtained from the evaluation of the line profiles by the MWP fitting method. The Fourier coefficients of the measured intensity profiles (open circles) and the fitted theoretical Fourier transforms (solid line) obtained by the MWP procedure are plotted in Fig. 4. The value of the dislocation density was found to be \( 13 \times 10^{14} \) m\(^{-2}\). The median and the variance of the crystallite size distribution function were obtained to be 48 nm and 0.38, respectively. The value of the median of the crystallite size distribution is consistent with the subgrain size observed in the TEM image in Fig. 1b (50 nm). This means that the subgrains can be identified as the domains scattering X-rays coherently.

The subgrain boundaries are most probably formed by the rearrangement of dislocations into low energy dense configurations, e.g. incidental dislocation boundaries (IDB) [12]. This process may be similar to the subgrain formation in metals during severe plastic deformation [13], but here the shear stresses necessary for the formation of dislocations are exerted by the contact edges of neighboring particles during HIP. It should be noted that the alumina particles probably have an important role in the development of substructure in the ultrafine grains. According to former investigations, SPD processing of pure Al resulted in the minimum diffracting domain size of about 200 nm [14]. The lower domain size achieved here can be attributed to the effect of alumina particles. These dispersoids act as obstacles against dislocation motion and enable the storage of dislocations in the ultrafine grains even after the releasing of pressure at the end of the HIP procedure. This effect together with the high temperature applied during the compaction resulted in the arrangement of dislocations into subgrain boundaries inside the ufg grains.

3.2. Mechanical characterization

Fig. 5a shows an atomic force microscopy (AFM) picture of the impressions made by nanoindentation. This image reveals that there is a bimodal distribution of the indentation sizes which corresponds to the two-phase composite model of the microstructure. The large indents can be found in the softer mc grains. On the right hand side of Fig. 5a, a large grain can be seen where the size of indents is approximately two times larger than the size of indentations in the ufg volume. The hardness was calculated according to Eq. (1) and the statistics for the hardness values are plotted in Fig. 5b. The mean hardness of the ufg matrix is about four times higher than that for mc grains. However, several caveats regarding this measurement should be noted: (i) as the size of the fine and the mc grains have a distribution, the hardness can differ in different mc grains or in different positions in the ufg matrix, i.e. the mentioned ratio between hardnesses is valid only for the mean values; (ii) the hardness calculated by Eq. (1) is generally different from the value obtained from the indent size determined by microscopy methods owing to the distortion of the shape of residual indentation pattern after removing the tip from the surface of probe material [15]; (iii) generally, the hardness measurement results in an additional 8% plastic deformation [16], i.e. the flow stress corresponds to 8% strain can be determined as a one-third of the hardness measured at relatively high load (\( 2 \ N \leq P_{\text{max}} \)); (iv) Nanohardness value cannot be used directly for the determination of the flow stress because of the so-called indentation size effect. This means that the hardness...
of a material increases with the decrease of indentation size and the flow stress can be determined only from the macrohardness value. Nevertheless, the difference between the flow stress values of the ufg and the mc volumes is manifested in the bimodal distribution of nanohardness values.

Fig. 6 shows the true stress–true plastic strain curve obtained by compression test. The yield strength is about 390 MPa, the flow stress at 0.2% plastic strain is 440 MPa, and the maximum strength occurs around 490 MPa. In the following section the yield strength is calculated from the characteristics of the microstructure and compared to the value determined by compression.

3.3. Calculation of the yield strength

Using a simple composite model, the yield strength ($\sigma_Y$) can be calculated as the volume-weighted sum of yield strength values of the two components (rule of mixture):

$$\sigma_Y = \sigma_{Y_{\text{ufg}}} V_{\text{ufg}} + \sigma_{Y_{\text{mc}}} V_{\text{mc}},$$  \hspace{1cm} (2)

where $\sigma_{Y_{\text{ufg}}}$, $\sigma_{Y_{\text{mc}}}$, $V_{\text{ufg}}$ and $V_{\text{mc}}$ are the yield strength values and the volume fractions of the ufg and mc components, respectively. From the frequency distribution of hardness (see Fig. 5b) it is revealed that 30% of the indents are situated in a relatively soft region ($H \leq 6$ GPa) and the rest (70%) are placed into hard volumes. These percentages can be regarded as the volume fractions of the soft mc and hard ufg regions which is also supported by TEM images (not shown here). In order to estimate the yield strength of the composite by using Eq. (2), the values of $\sigma_{Y_{\text{ufg}}}$ and $\sigma_{Y_{\text{mc}}}$ are determined.

According to Hansen [17] the yield strength can be given as:

$$\sigma_Y = \sigma_0 + \sigma_{\text{LAGB}} + \sigma_{\text{HAGB}},$$  \hspace{1cm} (3)

where $\sigma_0$, $\sigma_{\text{LAGB}}$ and $\sigma_{\text{HAGB}}$ are the friction stress, the yield strength components related to the low- and high-angle grain boundaries. For the mc grains $\sigma_0$ is the sum of the friction stress for pure Al ($\sigma^0_p = 20$ MPa [14]) and the yield strength related to the dispersion hardening caused by the alumina particles [18]:

$$\sigma_0 = \sigma^0_p + 0.85 M^T G b \ln(x/b) \frac{2\pi(l-x)}{2\pi(l-x)},$$  \hspace{1cm} (4)

where $G$ is the shear modulus ($G = 26$ GPa), $b$ is the Burgers vector ($b = 0.2865$ nm), $M^T$ is the Taylor factor (where $M^T = 3$ for untextured polycrystalline materials), $x$ is the average size of the dispersoids and $l$ is the inter-particle spacing. According to Fig. 1a, the average size of the alumina particles in mc grains is about 20 nm while the distance between them can be approximated as 200 nm. Substituting these data into Eq. (4), $\sigma_0$ is obtained to be 91 MPa. The contribution of the low-angle grain boundaries to the yield strength can be expressed by the Taylor-equation as these boundaries are formed by the rearrangement of dislocations into subgrain boundaries [12]:

$$\sigma_{\text{LAGB}} = \alpha M^T G b \rho^{1/2},$$  \hspace{1cm} (5)

According to Hansen [17] the yield strength can be given as:
where $\alpha$ is a constant (taken as $\alpha = 0.33$), and $\rho$ is the dislocation density. The yield strength resulted from the high-angle grain boundaries can be given by the Hall–Petch formula as:

$$\sigma_{\text{HAGB}} = kD_{\text{HAGB}}^{-1/2},$$  \hspace{1cm} (6)$$

where $k$ is a constant ($k = 0.04 \text{MPa m}^{1/2}$ \cite{17}) and $D_{\text{HAGB}}$ is the size of the grains surrounded by high-angle grain boundaries. For mc grains the yield strength contribution expressed in Eq. (5) can be neglected owing to the very low dislocation density. In the mc grains the dislocation density should be less than the limit detectable by X-ray line profile analysis ($10^{13} \text{m}^{-2}$) as the breadths of the line profiles for mc grains agree with the instrumental broadening. The average value of $D_{\text{HAGB}}$ for mc grains is found to be 5 $\mu$m which gives 18 MPa for $\sigma_{\text{HAGB}}$. The sum of the yield strength components gives 109 MPa for mc grains.

For the ufg matrix the yield strength contributions resulting from the low- and high-angle grain boundaries were calculated using the dislocation density $\rho = 13 \times 10^{14} \text{m}^{-2}$ and the mean size of ufg particles $D_{\text{HAGB}} = 150 \text{nm}$, respectively. Applying Eqs. (5) and (6) $\sigma_{\text{HAGB}} = 268 \text{MPa}$ and $\sigma_{\text{HAGB}} = 103 \text{MPa}$ were obtained. In the determination of $\sigma_0$ for ufg matrix, the dispersion hardening also should be taken into account as TEM images of ultrafine grains show alumina particles inside these grains (e.g. see the upper right corner of the 160 nm grain in Fig. 1b). It seems that the distribution of alumina particles between the different subgrains is rather inhomogeneous, therefore the determination of the inter-particle spacing is uncertain. Nevertheless, an average distance between alumina dispersoids was estimated by the following procedure. First, we counted the number of alumina particles in a relatively large volume of the ufg matrix and then the average volume of the ufg matrix per alumina particle was determined. The average inter-particle spacing was calculated as the cube root of this volume. For the mean size and the average inter-particle spacing 4 and 56 nm were obtained, respectively. Substituting these values into Eq. (4) and using the friction stress for pure Al ($\sigma_0 = 20 \text{MPa}$) 173 MPa was obtained for $\sigma_0$ of ufg matrix. The sum of the yield strength components gives 544 MPa for ufg matrix. We have calculated the total yield strength of the composite from the theoretically determined values of the two components (109 and 544 MPa) and from their volume fractions using Eq. (2). From this calculation 414 MPa was obtained for the yield strength which is in relatively good agreement with the experimentally determined value of 390 MPa.

In the following the flow stress corresponding to 8% plastic strain is also calculated for both ufg and mc components and their ratio is compared to the ratio of their hardness numbers determined by nanoindentation. In this calculation, the strain hardening ($\sigma_{\text{sh}}$) resulted by 8% strain should be added to the yield strength. The value of $\sigma_{\text{sh}}$ for the mc grains is determined as the difference between the flow stress at 8% strain and the yield stress on the stress–strain curve measured on bulk Al sample produced by HIP of mc powder (see Fig. 4a in \cite{9}). From this procedure 50 MPa was obtained. Using the values of $\sigma_{\text{sh}}$ determined for the mc grains (50 MPa) and for the composite (90 MPa, from Fig. 6) and assuming the rule of mixture (Eq. (2)), $\sigma_{\text{sh}}$ for the ufg matrix is obtained to be 107 MPa. Adding $\sigma_{\text{sh}}$ to the yield strength, 159 and 651 MPa are obtained for the flow stress at 8% strain in the cases of mc and ufg volumes. The ratio of the calculated flow stresses of the ufg and mc components is 4.1 which agrees well with the ratio of the hardness values ($\sim 4$) determined by nanoindentation.

4. Conclusions

The microstructure of the bulk sample obtained by HIP of Al nano-powder is rather inhomogeneous, which resulted in a bimodal distribution of hardness values measured by nanoindentation. On the basis of the TEM and nanoindentation observations, the microstructure is modelled by a two-phase composite of the microcrystalline grains and the ultrafine grained matrix. The yield strength was determined from the grain size, the dislocation density and the size and dispersion of alumina particles in the two components of microstructure. This calculated value of the yield strength was in relatively good agreement with that determined by compression test. It was found that the majority of the hardening can be attributed to the high dislocation density and the finely dispersed alumina particles in the ufg matrix.

Acknowledgements

This work was supported by the Hungarian Scientific Research Fund, OTKA, Grant No. F-047057. JG is grateful for the support of a Bolyai Janos Research Scholarship of the Hungarian Academy of Sciences. G. Dirras is grateful for the support of Direction Générale à l’Armement (DGA), Ministère de la Défense.

References