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The crystallite-size dependence of structural parameters in pure ultrafine-grained copper

K Zhang†, I V Alexandrov‡, A R Kilmametov‡, R Z Valiev‡ and K Lu†

 † State Key Laboratory for RSA, Institute of Metal Research, Academia Sinica, Shenyang 110015, People's Republic of China
 ‡ Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, K Marksa 12, Ufa 450000, Russia

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Abstract. Quantitative x-ray diffraction investigations were performed on ultrafine-grained copper samples with various crystallite sizes processed by severe plastic deformation. In the x-ray diffraction patterns, common features such as the relative maximum intensity, considerable broadening, long tails, centroid positions of Bragg reflections shifted to larger diffraction angles and increased background integrated intensities are revealed. The evolution of the shape of the Bragg reflections, background integrated intensity, microstrain, dislocation density, lattice parameter and atomic displacement with decreasing crystallite size was investigated. The obtained results are analysed and discussed in terms of the structural model of ultrafine-grained materials processed by severe plastic deformation.

1. Introduction

Many grain-size-dependent novel properties have recently been revealed in ultrafine-grained (UFG) materials (submicrocrystalline and nanocrystalline materials) processed by severe plastic deformation (SPD) [1]. Such properties include elastic, strength, microhardness, superplastic and magnetic properties [2]. The decrease of the grain size leads to a significant variation of properties in these materials.

X-ray diffraction is a powerful tool in the investigation of UFG materials. Recent investigations [3–7] indicated that the x-ray diffraction patterns (XRDPs) of the UFG materials differ significantly from those of their coarsegrained (CG) counterparts. This means that such structural parameters as the microstrain, dislocation density, lattice parameter and atomic displacement are considerably changed in UFG materials in comparison with those of CG materials. The goal of the present work is to carry out a detailed x-ray diffraction characterization of UFG Cu during the development of the UFG structure upon SPD.

2. Experimental details

2.1. The sample preparation of samples

Pure Cu (99.98%) samples were subjected to SPD by torsion straining with axial rotation under a pressure of several gigapascals at room temperature. The numbers and the angles of rotation were controlled so that UFG Cu

	Table 1.	The crystallite	e size of the	UFG C	u samples
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Crystallite size (nm)	А	В	С	D	Е
D ₁₁₁	116	94	94	94	91
D ₂₀₀	208	204	135	88	80
Ū	162	149	114	91	85
D ₂₀₀ ∕D ₁₁₁	1.8	2.2	1.4	≈ 1	≈ 1

samples with no residual porosity could be obtained after such treatment [2]. By use of this technique the range of crystallite sizes shown in table 1 was obtained.

The UFG Cu samples were discs of diameter 12 mm and thickness about 0.20 mm. The reference CG Cu sample [7] used in this work was cut from a massive sheet obtained by cold rolling and had the same shape as the UFG samples.

2.2. X-ray diffraction measurements

X-ray diffraction measurements of the Cu samples were performed on the wide-angle goniometer of a Rigaku D/MAX 2400 x-ray diffractometer. The rotating Cu target was operated at a voltage of 58 kV and a current of 180 mA. The x-ray wavelengths $\lambda_{K\alpha_1}$ (1.540 56 Å) and $\lambda_{K\alpha_2}$ (1.544 39 Å) were reflected by a graphite crystal using the (0002) reflection. With these wavelengths, the extinction depth in Cu was calculated to be less than 50 μ m, which



Figure 1. The intensity data (on a logarithmic scale of intensities) for the UFG Cu samples A and E and the reference CG Cu sample plotted against the diffraction angle 2θ .

was about a fifth of the thickness of the samples. The scans were collected over the 2θ range from $40^{\circ}-140^{\circ}$. Small angular steps of $2\theta = 0.02^{\circ}$ and a fixed counting time of 20 s were taken to measure the intensity of each Bragg peak. The angular intervals were chosen to be identical for the same (*hkl*) Bragg peaks of these samples. Then, it was possible to compare the integrated intensities of Bragg reflections and the background integrated intensities for these samples. Other regions of background intensity were measured using a step size of 0.1° and a counting time of 10 s.

In order to determine the instrumental broadening, a powder sample of Cu (particle sizes about 30 μ m) annealed at 773 K for 60 min under a vacuum of 10^{-3} Pa was used. This sample had an almost perfect structure and its Bragg reflections were taken as the instrumental broadening.

3. Experimental results

3.1. The Bragg peak shape and background intensity analysis

The x-ray diffraction intensities including the (111), (200), (220), (311), (222), (400) and (331) Bragg reflections are plotted on a logarithmic scale for UFG Cu samples A and E (with the most different crystallite sizes) and the reference CG Cu sample in figure 1. From the relative maximum intensities of Bragg reflections, different types of crystallographic texture were obviously observed (see also [7]). The (111) and (331) textures were revealed in the UFG Cu samples A and E. However, the reference CG sample exhibited the (200) texture.

The Bragg-reflection broadenings from the UFG Cu samples A and E were significantly larger than that from the reference CG Cu sample. Simultaneously, the broadening was larger for sample E than that for sample A. This reflected the microstructural evolution in these samples when they had been subjected to different ranges of SPD.

Taking into account the kinematical x-ray diffraction theory [8], the intensity measurements are represented as a function of the diffraction angle 2θ . The pseudo-Voigt function which is a linear combination of a Lorentzian and Gaussian function was used in order to obtain the information about the shapes and integrated intensities of Bragg reflections for the investigated Cu samples.

The results of a pseudo-Voigt fitting for Bragg reflections of these samples are shown in figure 2. For all Bragg reflections of the UFG Cu samples, the averaged Lorentzian fractions η were above 0.95. This means that the shapes of Bragg reflections from the UFG Cu samples were represented better by the primarily Lorentzian function. However, in the case of the reference CG Cu sample, the averaged Lorentzian fraction η of Bragg reflections was about 0.46. Therefore, the shape of Bragg reflections for the reference CG Cu sample was represented by a sum of the Gaussian and Lorentzian functions with a relatively large Gaussian component.

The background intensity included diffuse scattering both from the sample and from the instrument, for example scattering by air [9]. In the present experiments, because the scattered intensities associated with the instrument were the same for all samples, the information about the diffusescattering intensities from these samples could be estimated.

In order to separate the background intensities from the intensity data which had been fitted by the pseudo-Voigt function, base lines were used. The base line connected the edge points which were located at both corners of each Bragg reflection and corresponded to the background intensity. The intensity above the base line was removed for all Bragg reflections. The remaining parts were taken as the background intensity. The integrated background intensity W was calculated over the measured range ($40^{\circ} \le 2\theta \le 140^{\circ}$).

As a result, the integrated background intensities from the UFG Cu samples were slightly larger than the corresponding value from the reference CG Cu sample. The values $\Delta W/W$ relative to W of the reference CG Cu sample are plotted versus the inverse crystallite size in figure 3. In this way, a tendency of $\Delta W/W$ to increase from 6% to 8% was derived.



Figure 2. The average Lorentzian fraction η of the Bragg reflections from the UFG and reference CG Cu samples versus the inverse crystallite size.

3.2. The lattice-parameter analysis

The Bragg intensities consisted of two components with the wavelengths $\lambda_{K\alpha_1}$ and $\lambda_{K\alpha_2}$ with an intensity ratio of 2:1. With the modified Rachinger method [10, 11], the corrected $\lambda_{K\alpha_1}$ Bragg reflection profile was obtained by eliminating the $\lambda_{K\alpha_2}$ component. The corresponding lattice parameters were calculated from the centroid positions of peaks. In order to remove the systematic error arising from the geometrical arrangement of the instrument, a standard Si sample was used to calibrate the peak centroid positions.

The averaged lattice parameter for each sample was calculated using the least-squares method with a weighting function $\sin^2(2\theta)$. The rates of variation of the lattice parameters $\Delta a/a$ and the unit cell volume $\Delta V/V$ for these samples are shown in figure 4. The values both of $\Delta a/a$ and of $\Delta V/V$ for the UFG Cu samples were below zero. The decrease in crystallite size resulted in a significant increase in this deviation. For the reference CG Cu sample, its lattice parameter approached the literature value and the rate of variation was close to zero.

3.3. The crystallite-size and microstrain analysis

Integral widths of the Bragg reflections from the UFG and reference Cu samples were derived using the integrated intensity of each Bragg reflection divided by the corresponding maximum intensity (an example is shown in figure 5). That the integral widths for the UFG Cu samples were larger suggests that a physical broadening caused by the small crystallite and structural defects in these samples had occurred.

The physical profiles were obtained by the deconvolution of the experimental profiles with the instrumental broadening profiles [8]. Because the experimental profiles were represented better by the Lorentzian function and the instrumental broadening was more of Gaussian type for the UFG Cu samples, one may suppose that the physical profile was a Lorentzian one [12–14]. Bearing in mind that size-broadening profiles are usually represented by the Lorentzian function [15] and that the physical profiles of the Bragg reflections from the UFG Cu samples were also described by the Lorentzian function, we chose to use a Lorentzian-shaped profile to represent the microstrain broadening. Then, the integral width of the physical profile β_p was taken as the sum of the integral widths of the size broadening and the distortion broadening. By using the Scherrer and Wilson equation [16], the physical width of the (*hkl*) Bragg reflections was taken as the following:

$$\beta_{\tau} = \pi / D_{hkl} + \langle \epsilon_{hkl}^2 \rangle^{1/2} \tau \tag{1}$$

where β_{τ} is equal to $\beta_p \pi \cos(\theta)/\lambda$ and β_p is the integral width of the physical profile, the scattering vector $\tau = 4 \sin(\theta)/\lambda$ and D_{hkl} and $\langle \epsilon_{hkl}^2 \rangle^{1/2}$ represent the volume-averaged crystallite size and the microstrain inside the grains and interfacial regions in the $\langle hkl \rangle$ direction, respectively.

The increase in β_{τ} with τ was related to the magnitude of the microstrain, because the size broadening was independent of the magnitude of τ . The pairs of the (111)–(222) and (200)–(400) Bragg reflections were used to calculate the crystallite size and microstrain (table 1 and figure 6).

Table 1 shows that the volume-averaged crystallite sizes for UFG Cu samples differed significantly. Simultaneously, the crystallites in different texture components were anisotropic in samples A, B and C and approximately identical in samples D and E. The decrease in crystallite size on going from A to E was more pronounced in the $\langle 200 \rangle$ than it was in the $\langle 111 \rangle$ direction.

The evolution of the microstrain with the reduction in crystallite size is shown in figure 6. The values of the microstrain for the (111) and (200) families of the Bragg peaks from the UFG Cu samples were sufficiently large and significantly different. The values of the microstrain in the



Figure 3. The variation $\Delta W/W$ of the background integrated intensity relative to *W* of the reference CG Cu sample against the inverse crystallite size \overline{D}^{-1} .



Figure 4. The variations $\Delta a/a$ of the lattice parameter (full circles) and $\Delta V/V$ of the volume of the unit cell (open circles) versus the inverse crystallite size \overline{D}^{-1} . The full curve stands for the variation of $\Delta a/a$ and the broken curve for $\Delta V/V$.

(200) direction were at least three or four times larger than those in the $\langle 111 \rangle$ direction. Furthermore, together with the decrease in grain size, the values of the microstrain in the $\langle 111 \rangle$ direction remained approximately the same, whereas those in the $\langle 200 \rangle$ direction decreased a little. So, a large lattice distortion occurred and, simultaneously, an anisotropic distribution of the microstrain developed in the UFG Cu samples.

3.4. The estimation of the dislocation density

The dislocation density ρ_{hkl} can be represented in terms of the crystallite size and microstrain derived from Bragg-reflection-profile analysis as follows [17, 18]:

$$\rho_{hkl} = (\rho_D \rho_S)^{1/2} = 2\sqrt{3} \langle \epsilon_{hkl}^2 \rangle^{1/2} / (D_{hkl}b)$$
(2)

where D_{hkl} and $\langle \epsilon_{hkl}^2 \rangle^{1/2}$ are the volume-averaged crystallite size and the microstrain in the directions perpendicular to the (hkl) families. *b* is the Burgers vector of the dislocations (for Cu, *b* is approximately 0.256 nm).

The calculated data of the averaged dislocation densities $\bar{\rho}$ obtained from the Bragg reflections (111)–(222) and (200)–(400) are shown in figure 7. The dislocation density $\bar{\rho}$ increased linearly with the reciprocal crystallite size.

3.5. The estimation of the Debye-Waller parameter

The Debye–Waller parameter B which is related to the displacements of the atoms from their ideal lattice positions may be separated into two components B_T and B_S , where B_T is the contribution from the thermal vibrations of the atoms and is temperature dependent, while B_S is



Figure 5. The experimental integral widths β of Bragg reflections against the scattering vector τ ($4\pi \sin(\theta)/\lambda$) for the UFG Cu samples A (open triangles) and E (full triangles) and the reference CG (open circles) Cu sample. The full curve which was fitted to the data from the powder Cu sample (crosses) represents the instrumental broadening of the x-ray diffractometer.



Figure 6. The microstrain $\langle \epsilon^2 \rangle^{1/2}$ in the $\langle 111 \rangle$ (full circles) and $\langle 200 \rangle$ (open circles) directions of the UFG Cu samples against the inverse crystallite size \bar{D}^{-1} .

the temperature-independent term due to static atomic displacements [5].

The Debye–Waller parameter is usually obtained from the XRPDs using the Warren [8] and other methods [19, 20]. These methods rely on one's having texture-free samples. However, the samples processed by SPD exhibit $\langle 111 \rangle$ and $\langle 331 \rangle$ textures. Therefore, these methods cannot be used to calculate the Debye–Waller parameter for the UFG Cu samples.

In order to obtain the information about the Debye– Waller parameter for the textured materials, the equation based on kinematical x-ray diffraction theory [8], namely

$$\ln[\Phi_{obt_{hkl}}/\Phi_{cal_{hkl}}] = -2B[\sin(\theta_{hkl})/\lambda]^2$$
(3)

where $B = B_s + B_T$ and $\Phi_{obt_{hkl}}$ and $\Phi_{cal_{hkl}}$ are the experimental and theoretical integrated intensities of (hkl) Bragg peaks, respectively, may still be used.

For the textured UFG Cu samples, the first- and secondorder Bragg reflections from the same family of (hkl) planes are not related to the texture. So, pairs of (111)–(222) or (200)–(400) Bragg peaks were used to calculate the Debye– Waller parameter *B*. The averaged value \overline{B} for each sample was obtained by taking an average over the values B of the (111) and (200) Bragg reflections (figure 8).

The Debye–Waller parameters \bar{B} of the UFG Cu samples are larger than those of the reference CG Cu sample which was equal to 0.72 ± 0.08 Å² [7] and are linearly proportional to the inverse crystallite size \bar{D} . The increase in \bar{B} with decreasing the crystallite size illustrates the enhancement of the atomic displacements from their ideal lattice positions that had occurred. In the present work, we assumed that the atoms in the UFG Cu samples had been shifted isotropically from their ideal lattice positions. So, the atomic displacements $\langle \mu^2 \rangle^{1/2}$ were calculated from \bar{B}



Figure 7. The averaged dislocation density $\bar{\rho}$ against the inverse crystallite size \bar{D}^{-1} . The full line represents the least-squares fit of the measured data.



Figure 8. The Debye–Waller parameter *B* against the inverse crystallite size D^{-1} . The full line represents the least-squares fit of these data.

with the relation $\langle \mu^2 \rangle^{1/2} = [\bar{B}/(8\pi^2)]^{1/2}$ [8]. Fitzsimmons *et al* [21] have shown that this isotropic condition may not be true for the atoms in the interfacial regions near the GBs, but the resulting errors in this case are expected to be small [22]. The calculated data of the atomic displacements $\langle \mu^2 \rangle^{1/2}$ along the scattering vector τ for the UFG Cu samples are shown in figure 9. The displacements $\langle \mu^2 \rangle^{1/2}$ increased gradually together with the decrease in crystallite size, from 0.034 ± 0.002 Å in sample A to 0.061 ± 0.003 Å in sample E.

4. Discussion

The experimental results show that x-ray diffraction supplies important information concerning the formation of the microstructure in the Cu processed by SPD. The XRDPs of the UFG Cu samples differed significantly from that of the reference CG Cu sample. The XRDPs of the UFG Cu samples exhibited a change in the relative maximum intensity, a shift of the centroid position to larger diffraction angles, considerable broadening, long tails of Bragg reflections and an increase in the integrated background intensity. The smaller the crystallite size the more significant these features.

The changes in the relative maximum intensities of Bragg reflections were a result of the intense plastic deformation of the refinement of the microstructure. The high values of the microstrain, the large density of the dislocations and the increases in background integrated intensity, Debye–Waller parameter and atomic displacements are attributed to the high distortion of the crystal lattice in the UFG Cu samples. Furthermore, the Lorentzian-shaped Bragg reflections and large atomic displacements showed that the defect structure was rather



Figure 9. The atomic displacement $\langle \mu^2 \rangle^{1/2}$ versus the inverse crystallite size \overline{D}^{-1} . The full line stands for the least-squares fit of these data.

specific to these samples.

The averaged dislocation density $\bar{\rho}$ estimated from the present experiments was high and increased significantly with decreasing crystallite size. This implies that there were high levels of lattice distortion and large static atomic shifts from the ideal lattice positions. According to the diffraction theory developed by Krivoglaz [23], the existence of static atomic displacements in the UFG Cu samples can be explained by the presence of defects having strain fields that decay with distance γ from the defect at a rate faster than $1/\gamma^{3/2}$. Examples of these types of defects include vacancies, interstitials and dislocation loops. Since any vacancies and interstitials contribute much less to the observed features, dislocations are the main element leading to elastic stress fields and static atomic displacements.

According to a recently developed model [2], the process of SPD leads to the formation of a microstructure which can be characterized in terms of non-equilibrium GBs. The non-equilibrium state of the GBs is caused by the presence of extrinsic GB dislocations of very high density. These dislocations create the long-range stress fields resulting in strong elastic distortions that are especially high in the vicinity of the GBs [24–26].

Eastman *et al* [27] pointed out that the average concentration of defects can be presented as the following:

$$c = c_0 + (c' - c_0) \times 3\delta/\bar{D} \tag{4}$$

where c_0 is the defect concentration inside a grain, c' is the defect concentration in the region near the GBs and δ is the thickness of this region.

From the present results, the positive slope in figure 7 suggested that c' is larger than c_0 ; that is, there was a higher dislocation density and a higher concentration of defects in the distorted layers near the GBs than there was inside the grains in the UFG Cu samples. Therefore, the present result obtained by the x-ray diffraction confirmed the existence of highly distorted layers near the GBs in the samples produced by SPD [24, 25].

The Lorentzian-shaped Bragg reflections in the UFG Cu samples implied that the distribution of defects was concentrated in some regions, due to the contribution of the GB dislocations. So the obtained Lorentzian-shaped Bragg reflections and the highly distorted layers near the vicinity of GBs are the main characteristics of the UFG materials made by SPD.

A possible reason for the decrease in lattice parameters in the UFG Cu samples is that a decrease of the interplanar spacings occurred due to the atomic displacements inside the grains caused by compressive long-range stress fields of the extrinsic GB dislocations. The decrease in crystallite size resulted in the increase of the influence of the longrange stress fields.

Increases both in the thermal atomic displacements and in the static atomic displacements due to the defects, namely dislocations, may have contributed to the enhancement of the Debye–Waller parameters for the UFG Cu samples. The linear enhancement of the Debye–Waller parameters obtained in the present work suggests that the atomic displacements increase correspondingly, so we propose that the influence of the long-range stress fields in the GBs is enhanced with decreasing grain size.

5. Conclusions

(i) Peculiarities in the formation of the UFG microstructure in pure Cu during the process of SPD were revealed by x-ray analysis.

(ii) It was found that the UFG Cu samples possessed a highly distorted microstructure with a specific defect distribution. Furthermore, the smaller the grain size the larger the effect of long-range stress fields.

(iii) The obtained results are in agreement with the recently developed structural model of UFG materials processed by SPD.

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