Ultra Fine Grained Copper Prepared by High Pressure Torsion: Spatial Distribution of Defects from Positron Annihilation Spectroscopy

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1 Introduction

High-pressure torsion (HPT) and equal channel angular pressing (ECAP) are techniques based on severe plastic deformation (SPD). They are used to produce relatively large amounts of ultra fine-grained (UFG) materials without any porosity [1]. HPT-made metallic UFG specimens are typically disk shaped with a diameter of ≈ 10 mm and a thickness of ≈ 0.3 mm. In an ideal case, the specimens would exhibit axial symmetry of UFG structure. In real case, however, some deviations from axial symmetry of UFG structure may be expected. In addition, radial as well as depth variations of grain size and/or defect density may result from unequal degrees of plastic deformation during the preparation of specimens. In the ECAP technique, ingots of a diameter given by channel cross-section are produced. The shear deformation during ECAP pressing is the same along the whole ingot. It means that, contrary to the HPT-made specimens, variations of defect density and grain size with depth are not expected.

The investigation of lateral and depth distributions of grain size and defects in UFG materials prepared by SPD is very important for an understanding of processes which take place during the preparation procedure and underlie the formation of an UFG structure. Previous transmission electron microscopy (TEM) studies of UFG metals prepared by HPT [2,3] revealed a fragmented structure with high angle misorientation of neighbouring grains. Grain interiors are almost free of dislocations and separated by distorted regions (DRs) with a high-dislocation density situated along grain boundaries (GBs) [2,3]. Strong inhomogeneities in the dislocation distribution have also been confirmed by X-ray diffraction (XRD) [4], synchrotron radiation [5] and positron lifetime (PL) spectroscopy [3,6]. In our recent PL investigations of HPT-made UFG copper [3,6], two kinds of defects could be found in the material: (i) dislocations in DRs along GBs and (ii) microvoids of a size comparable to a few vacancies distributed homogeneously throughout grains.

The present contribution is concerned with the spatial distribution of defects in SPD-made UFG copper. For specimens produced by HPT, detailed data were collected on defect densities as functions of radial distance from specimen axis as well as the depth from the specimen surface. Two mutually complementary positron-annihilation spectroscopy (PAS) techniques were employed as a principal experimental tool in the present work: (a) slow positron implantation spectroscopy (SPIS) by measurement of Doppler broadening (DB) of annihilation radiation, and (b) conventional PL and DB measurements with a ^{22}Na positron source. Results obtained by these techniques were correlated with TEM, XRD and microhardness measurements. Since the results obtained for HPT-made specimens will be given in details elsewhere [7] they are only

briefly reproduced here. In addition, first PAS measurements on ECAP produced specimens are reported here and compared with those for the HPT technique.

2 Experimental

PAS makes use of the annihilation of electron–positron pairs in matter into which energetic positrons were implanted. The annihilation process results in an emission of annihilation photons, which convey desired information about the material studied. Basic PAS observables are the positron lifetime and the Doppler broadening of annihilation radiation. The former quantity reflects the local electron density scanned by a positron while the latter one depends on the electron momentum distribution near the annihilation site. Both observables can be used for a characterisation of open-space defects capable of capturing positrons into a localised state: vacancies, dislocations, a few-vacancy clusters, etc. PAS is nowadays widely recognised as an effective non-destructive tool for investigations of materials structure on an atomic level [8]. The potential of PAS for such studies arises from the facts that thermalised positrons penetrating through matter behave like a probe of the size of a few nanometers. Since positrons diffuse in metals to distances typically amounting to several hundreds of nanometers, an information from statistically significant volume is obtained.

SPIS experiments were performed on the magnetically guided positron beam system "SPONSOR" [9] at Rossendorf. Positron energies E varied between 30 eV and 35 keV. Within this energy range, a region from sample *surface* up to $\approx$ 1.5 μm depth is probed by the positron beam. The diameter of the beam spot was $\approx$ 4 mm within the whole positron energy range. Energy spectra of annihilation photons were measured by means of a HPGe spectrometer with an energy resolution of 1.25 keV at 0.511 MeV. The shapes of Doppler broadened annihilation peaks were characterised in terms of ordinary S and W parameters proportional to the central (low momentum) and wing (high momentum) parts of peaks, respectively. Hence, the larger S-values mean an enhanced role of positron trapping in open-volume defects and variations of S with energy E reflect the depth dependence of defect concentration and of positron back diffusion to the surface. The S(E) dependencies were analysed using the VEPFIT code [10].

Due to higher initial energies of positrons, conventional PL and DB measurements probe *volume* properties of specimens. These measurements were conducted at Prague. A 1.3 MBq ^{22}NaCl source sealed between 2 μm thick mylar foils was used (the diameter of the activity spot was $\approx$ 3 mm). A high-resolution BaF_2 spectrometer [11] was utilised in PL measurements (time resolution of $\approx$ 150 ps FWHM at $\approx$ 75 s^{-1} coincidence count rate). At least 10^7 counts were collected in each spectrum. The spectra were decomposed into exponential components by means of a maximum likelihood procedure [11]. Conventional DB measurements were performed using a standard HPGe spectrometer with an energy resolution of 1.2 keV FWHM at 0.511 MeV.

XRD measurements were carried out with the aid of powder diffractometers using Cu K_α radiation, for which penetration depth in Cu amounts to $\approx$ 6–7 μm. Thus a layer, still relatively close to the specimen surface, was probed. A full description of XRD studies as well as TEM and microhardness measurements performed in this study will be given elsewhere [7].

HPT specimens with UFG structure were made of high purity copper (99.99 %) subjected to torsion under a pressure of 6 GPa at room temperature (true logarithmic strain $e = 7$). In order to increase the depth range of SPIS and XRD, some of the UFG Cu specimens were, after charac-

terisation of the as-prepared state, subjected to a controlled chemical etching in a solute of HNO_3 (25 %), H_3PO_4 (12.5 %), CH_3COOH (12.5 %) and H_2O (50 %) at room temperature.

ECAP specimens for PAS measurements were obtained by cutting discs of ≈ 1 mm thickness from the virgin ingot. In order to remove defects introduced by cutting, a similar etching procedure as described above was applied.

3 Results

Conventional PL and SPIS measurements of S parameter vs. positron energy E, S(E), were performed with a well annealed (850 °C/30 min) pure Cu (99.999 %) *reference* specimen. A single (bulk) lifetime of 114.5 ± 0.1 ps and the diffusion coefficient of positrons in Cu, $D_+ = 1.86 \pm 0.08$ cm^2 s^{-1}, were obtained in accordance with the literature data [12,13].

3.1 HPT-made UFG Cu

As-received specimen. The $S(E)$ dependence measured by SPIS with the beam hitting the centre of the disk is shown in Figure 1 and compared with the reference Cu. The S values of Figure 1 are higher for UFG Cu than for the reference Cu above 5 keV positron energy. This is a clear evidence of positron trapping at open volume defects in the HPT-made UFG Cu. The absence of any plateau of the observed $S(E)$ curve for the UFG Cu, which remained slightly decreasing up to the highest positron energy measured (see Figure 1), implies a decrease of defect density with depth. The two kinds of defects in HPT-made UFG copper were identified in our recent study [6]: dislocations inside the DRs along GBs, and microvoids inside grains. Thus the observed decrease in $S(E)$ may occur due to a decrease in the concentration of microvoids or the dislocation density, and also due to increase in the mean crystallite size (decrease in the volume fraction of DRs).

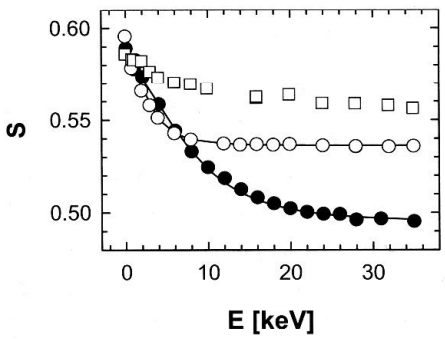

Figure 1: $S(E)$ dependencies measured for as received (□), etched (◊) UFG Cu and annealed Cu (•). VEPFIT results are shown by the solid line.

To study the local variations of defect density, the S(E) dependencies were measured with the beam centred at several positions in radial distances of r = 3 mm from the specimen axis. Local changes in S values were observed. Generally the S parameters appeared to be lower at "outer" positions than at the "centre" one. XRD has indicated [7] no significant changes of the

dislocation density or the mean crystallite size with r . Therefore, the lowering of S parameter observed in the subsurface layer indicates a decrease in concentration of microvoids with increasing r.

Conventional PL and DB measurements were carried out for several values of r with the same specimens. Two components, arising from positron trapping in dislocations and at microvoids, were identified in the PL spectra as shown in Fig 2. The lifetime of the microvoid component, τ_2 , which exhibited a slightly non-monotonic variations with r, reflects the size of microvoids. From theoretical results of Ref. [6], the mean volume of microvoids was estimated to be 3-4 agglomerated vacancies. A slight increase of the size of microvoids occurs for $r > 3.5$ mm, see Figure 2. The intensity of microvoid component, I_2 , shows a remarkable increase in the interval $0 < r < 2$ mm. No variations of dislocation density with r were indicated by TEM and XRD [10]. Thus a radial increase of the concentration of microvoids towards higher r is implied by observed I_2's. It is further supported by: (i) an increase of S parameters with r found by means of conventional DB, and (ii) the measured increase of microhardness with r (see Ref. [10] for details). On the other hand, SPIS results for a thin layer close to surface indicate slightly lower S values at r = 3 mm than at the sample centre. It means that spatial distribution of defects very close to the surface can be different from that at larger depth seen by the conventional PAS.

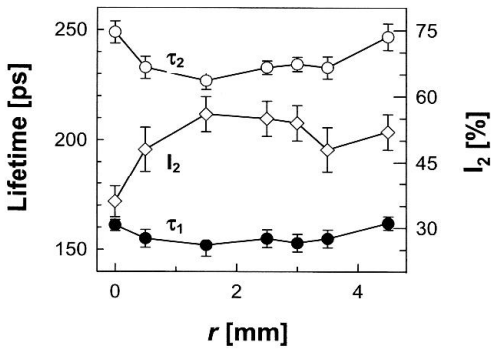

Figure 2: Positron lifetimes τ_1 and τ_2 and intensity I_2 as a function of radial distance r

An *etched specimen* was then used in SPIS and XRD where layers of ≈ 35 and ≈ 50 μm thickness were removed, respectively. The measured $S(E)$ dependence was included in Figure 1. The S values intermediate between the as prepared and reference states were observed for high positron energies. This is a manifest of a decreased but still existing positron trapping at ≈ 35 μm depth. A clearly visible plateau for $E > 15$ keV means that, contrary to the subsurface layer, no significant changes of the defect density, or the grain size, with depth occur at ≈ 35 μm depth. VEPFIT analysis provided an effective positron diffusion length of $L_+ = 35 \pm 1$ nm. This value does allow to estimate the mean dislocation densities to be $(1.1 \pm 0.3) \cdot 10^{15}$ and $(7.0 \pm 0.5) \cdot 10^{14}$ m^{-2} for the subsurface layer and $t \approx 35$ μm, respectively. XRD results for the etched specimen suggest an increased coherent domain size (i. e. a decreased volume fraction of DRs and hence the mean dislocation density) compared to the as received state (see Ref. [10] for details). One can also note a reasonable agreement of XRD data on coherent domain size with TEM results regarding the estimated mean grain size [10]. No more changes of S with r were detected at $t \approx 35$ μm .

3.2 ECAP made UFG Cu

SPIS measurements were carried out with the beam hitting the centre of the specimen and the two opposite edge positions (r 3 mm). In all cases, exactly the same S(E) curves were obtained. This suggests that there are no significant radial changes of the defect density. In Figure 3, $S(E)$ curves measured for etched HPT and ECAP specimens are shown. A plateau of the $S(E)$ curve is clearly visible for E > 15 keV for both specimens. The bulk S value is lower for the ECAP specimen, indicating a lower degree of positron trapping at open volume type defects compared to the HPT specimen. The same conclusion follows also from effective positron diffusion lengths obtained by VEPFIT: $L_+ = 42 \pm 2$ and 35 ± 1 nm respectively, for ECAP and HPT samples. This seems to indicate that a larger mean grain size may result from the ECAP compared to the HPT procedure.

Conventional PL measurements performed for the ECAP specimen (central position of the positron source) revealed two components with lifetimes similar to those observed in the HPT case. This suggests that positron trapping at dislocations and in microvoids in the ECAP sample takes place. However, the intensity I_2 of the microvoid component is lowered to about 20 %. This is less than half of the value observed in the HPT specimen and may be regarded as a result of a higher concentration of microvoids in HPT specimen.

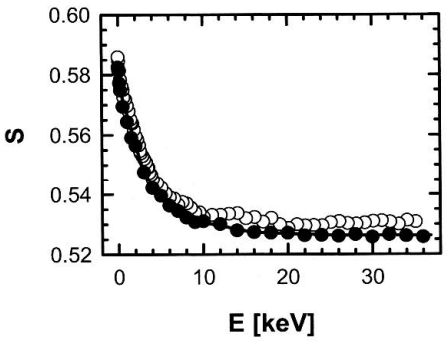

Figure 3: $S(E)$ dependencies measured for etched HPT (○) and ECAP (●) UFG Cu. VEPFIT results are shown by the solid line

4 Conclusions

Details of lateral and depth distributions of defects in HPT-made UFG Cu could be investigated using PAS techniques (SPIS, conventional PL and DB) in combination with other methods, like TEM, XRD and microhardness. It is known that UFG Cu prepared by HPT contains two types of lattice defects: dislocations in DRs along GBs, and microvoids of a size of a few vacancies inside grains [3,6]. These findings were confirmed by PAS in the present work. Moreover, mean dislocation densities derived from the present PAS data agree well with those given by XRD. Furthermore, PAS has provided a unique information about the size and concentration of microvoids formed, and, differences between HPT and ECAP-made specimens could be reflected.

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6 References

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