Ultra Fine-Grained Cubic Metals Prepared by Severe Plastic Deformation: A Positron Annihilation Study

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Keywords: Ultra fine-grained metals. Positron annihilation spectroscopy. Dislocations. Vacancy clusters.

Abstract. A review of the recent investigations of ultra fine-grained (UFG) cubic metals (Cu, Fe, Ni and Cu+0.5wt% Al_2O_3), which were carried out within a Prague-Rossendorf-Ufa collaboration, will be presented. Two techniques of severe plastic deformation were used for specimen preparation: the high-pressure torsion and equal channel angular pressing. Positron annihilation spectroscopy method including (i) the conventional lifetime and Doppler broadening (DB) techniques with ^{22}Na positron source and (ii) the slow-positron implantation spectroscopy with DB measurement was employed as a principal method in the present investigation. Other experimental methods were also involved: TEM, XRD and microhardness. First, the mean grain size was determined and defects were identified in the *as-deformed* materials. The spatial distribution of defects was studied in details. Dislocations situated in distorted regions along grain boundaries, and a few-vacancy clusters distributed homogeneously inside grains almost free of dislocations, were observed. In addition, the thermal evolution of the UFG structure during isochronal annealing was investigated.

Introduction

Ultra fine-grained (UFG) metals characterised with a mean grain size of several hundreds of nanometers are attracting much attention as perspective materials for technological applications. This is because a refinement of grain size of polycrystalline metals below one micrometer can lead to a significant improvement of their mechanical, electrical, thermal and other properties. Severe plastic deformation (SPD) is now a well-established process capable of producing macroscopic amounts of UFG materials with no porosity (for a review of SPD process, see Refs. [1,2]). The SPD-created UFG structures exhibit several typical structural components:

(i) *Grains* of the size of several hundreds of nanometers, which becomes comparable to typical diffusion lengths of positrons in perfect metallic lattices (~ 100 nm).

(ii) *Grain boundaries* (GB) which integrated volume constitutes, contrary to the ordinary polycrystalline metals, a significant fraction of the total volume of the material.

(iii) *Defects* introduced by SPD (dislocations, vacancies and vacancy clusters, GBs).

Two SPD-based techniques are currently being in use in order to produce UFG structures in a wide class of metallic systems [2]:

(a) The *high-pressure torsion* (HPT) is a technique that can usually provide disk-shaped specimens of the diameter of ~ 10 mm and thickness of a few tenths of mm. The HPT-made

specimens exhibit rather small grain size of ~ 100 nm, homogeneous UFG structure and a weak texture only.

(b) The *equal channel angular pressing* (ECAP) can produce more massive specimens, however, the mean grain size usually appears to be larger compared to HPT.

The SPD process leads to a highly non-equilibrium structure. Obviously, defects created by SPD play a key role in a formation of the UFG structure and underlie the unusual properties of these materials. Detailed defect investigations appear thus to be highly important both from the point of understanding the formation as well as thermal stability of the UFG structures. Positron annihilation spectroscopy (PAS) is now generally recognised as a powerful non-destructive technique of microstructural studies of a wide set of materials [3]. It was proved to be extremely sensitive to the small-sized open-volume defects. Another important feature of PAS is based on the fact that positron probe scans a volume of a size comparable with the positron diffusion length which in turn appears to be comparable with the grain size of UFG metals. From these two reasons, PAS becomes to be an ideal tool for the investigation of the above structural elements.

In the present contribution, recent investigations of the SPD-prepared UFG metals, performed within a Prague – Rossendorf – Ufa collaboration, will be reviewed. PAS was utilised as the principal experimental technique in these investigations, which involved

(1) the conventional lifetime and Doppler broadening (DB) measurements with ^{22}Na positron source and

(2) the slow-positron implantation spectroscopy (SPIS) combined with DB measurements.

Other experimental methods, complementary to PAS, were also included in these investigations: the transmission electron microscopy (TEM), x-ray diffraction (XRD) and microhardness measurements. The present paper will focuse on the results obtained for the UFG Cu, Fe, Ni metals and UFG Cu+Al_2O_3 composite. The Mg-based UFG metallic systems exhibiting a hexagonal structure have recently been studied within the above collaboration, too. These results will be presented separately at this Conference [4].

Experimental procedures

Specimens. The UFG specimens studied within the present investigations are listed in the first column of Table 1. The specimens of the UFG Cu, Fe, Ni metals and Cu+Al_2O_3 composite were HPT deformed at room temperature (RT) using a technique described in Ref. [2]. Torsion was performed up to a true logarithmic strain of $\varepsilon = 7$ with a simultaneously applied high pressure of 6 GPa. An additional set of the UFG Cu specimens deformed by HPT under a pressure of 3 GPa was prepared, too. All the HPT-made specimens were disk-shaped with a diameter of 10÷12 mm and thickness of 0.2÷0.4 mm. Another set of the UFG Cu specimens produced by the ECAP technique [2] at RT (route Bc, 12 passes) was also investigated in the frame of the present work.

Isochronal annealing experiments were performed at temperatures ranging from 80 °C up to a temperature well above the start of recrystallisation stage in steps 30 °C / 30 min. Each annealing step was finished by a quenching to water of room temperature.

Apparatus. For the conventional positron lifetime measurements, a BaF_2 spectrometer described in Ref. [5] was used. The spectrometer exhibited a time resolution of 150÷170 ps (FWHM) for ^{22}Na and a coincidence count rate of ~ 100 events per second. Positron sources of ~ 1.5 MBq strength were used (a carrier-free ^{22}NaCl purchased from Amersham or iThemba were sealed between 2 μm mylar D foils obtained from DuPont). The diameter of radioactive spot was ≈ 3 mm. At least 10^7 counts were collected in each lifetime spectrum. Using the maximum-likelihood procedure [5], the measured spectra were decomposed in up to five exponential components (two of them of ~ 7 % sum intensity were arising from annihilation in the source and covering foils).

The conventional DB measurements were performed by means of a HPGe spectrometer (1.7 keV FWHM at 511 keV).

The SPIS measurements were performed on the magnetically guided positron beam facility "SPONSOR" at FZ Rossendorf [6]. Doppler broadened line shapes of annihilation γ-rays were measured with a HPGe spectrometer having an energy resolution (FWHM) of 1.09 keV at 511 keV. The beam diameter at the sample surface was ≈ 4 mm. The dependencies of annihilation line shape parameters S on positron energy E were determined in the interval of E = 30 eV ÷ 35 keV and analysed with the aid of the VEPFIT code [7].

The TEM observations were performed using a JEOL 2000 FX electron microscope operating at 200 kV. The XRD investigations were carried out on XRD7 and HZG4 (Seifert-FPM) powder diffractometers using Cu K_α radiation. The microhardness H_V was measured by the Vickers method by means of a LECO M-400-A hardness tester with a load of 100 g applied for 10 s.

Results and discussion

The main results obtained using PAS on SPD-prepared UFG Cu, Ni, Fe and Cu + Al_2O_3 will be briefly presented in this section below while a complete description of these investigations has been given in separate publications [8-13].

Positron lifetimes in the *as-deformed* materials. The results of positron lifetime measurements on the as-deformed UFG specimens are summarised in Table 1. All the UFG materials listed in column 1 of the Table exhibited two lifetime components. Corresponding lifetimes τ_i and intensities I_i (i=1,2) are shown in columns 2 thru 5 of the Table. Both the observed components should be attributed to positrons trapped at defects since the observed lifetimes remarkably exceed the respective bulk ones. The saturated positron trapping therefore takes place in the as-deformed specimens what is a clear indication of high defect densities created by SPD.

Table 1. Positron lifetimes τ_i and relative intensities I_i (i=1,2) observed in the *as-deformed* UFG samples [a].

UFG material	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	R_g [nm] [b]	n_v [c]
HPT deformed Cu, p = 6 GPa	161(3)	64(4)	249(5)	36(4)	70(10)	4.8(3)
HPT deformed Cu, p = 3 GPa	164(1)	83(4)	255(4)	17(3)	90(5)	5.2(3)
HPT deformed Cu+0.5 wt.% Al_2O_3 (GlidCop), p = 6 GPa	161(3)	60.4(5)	257(1)	39.6(5)	64(4)	5.31(7)
ECAP deformed Cu, route Bc, 12 passes	164(3)	80(6)	240(10)	20(6)		4.2(6)
HPT deformed Ni, p = 6 GPa	157(1)	88.9(6)	336(8)	11.1(6)	80(10)	13.1(6)
HPT deformed Fe, p = 6 GPa	150.9(4)	90.6(3)	352(6)	9.5(3)		13.2(5)

[a] The one standard deviation errors are given in parentheses in units of the last significant digits.
[b] Mean grain size estimated from PAS data using the diffusion trapping model [8].
[c] Number of vacancies constituting vacancy clusters (microvoids), see the text for details.

The dominating components are those with the shorter lifetimes τ_1.These are by about 20 ps lower than the lifetimes of positrons trapped in monovacancies in respective materials. Such a behaviour is typical for positrons trapped at dislocations. The TEM observations on UFG Cu, Ni and Fe performed within present investigations revealed a strongly non-uniform spatial distribution of dislocations over the grain volume: grain interiors almost free of dislocations are separated by distorted regions along GBs with a high dislocation density. On the basis of these TEM results, we attribute the τ_1-component in the UFG materials of Table 1 to positrons trapped at dislocations situated in the distorted regions along GBs. However, such a kind of inhomegeneity in the distribution of dislocations is not a general feature of UFG structures. A uniform distribution of

dislocations over a grain was found in the HPT-processed UFG Mg-10%Gd alloy [4]. Such a uniform distribution of dislocations seems to be present in HPT-deformed metals with the hcp structure as a consequence of a lower number of slip systems compared to the fcc or bcc metals [4].

The positron lifetime data of Table 1 were analysed within the diffusion trapping model [8] allowing to deduce several important physical characteristics of the UFG structures: the average grain size R_g, the volume fraction of distorted regions η and the mean dislocation density. Generally, a reasonable agreement of these parameters with the TEM and XRD results obtained within the present work was observed. The R_g-values resulting from such an analysis were included in the sixth column of Table 1.

The longer lifetime τ_2 originates from a contribution of positrons trapped in a few-vacancy clusters referred to as *microvoids* below. Since a large number of vacancies are created during SPD, the formation of vacancy clusters in these materials becomes to be likely. Vacancies in the metals under study attain a substantial mobility [14] so that they can easily diffuse to GBs, decorate dislocations present in the vicinity of a GB or disappear in sinks at GBs. On the other hand, a portion of vacancies can form small vacancy clusters. The latter process seems to be more probable inside the dislocation-free grain interiors and it was shown to be suppressed in HPT-deformed Mg-10%Gd alloy with homogeneously distributed dislocations [4]. The average number of vacancies n_V constituting the clusters, which is a measure of the average size of microvoids, can be estimated from the comparison of the measured lifetime τ_2 with *ab-initio* calculations based on the density functional theory. Such calculations for Cu, Ni and Fe were given elsewhere [8,10,15] and n_V-values resulting from this comparison were included in the last column of Table 1. The values shown in the Table suggested a conclusion that the size of microvoids depends primarily on the material studied (due to the different mobility of vacancies in different metals) while its dependence on the type and parameters of the deformation process itself is of less importance [12].

Spatial distribution of defects. Radial and depth distribution of defects resulting from HPT deformation may provide a valuable knowledge on the deformation process itself. A depth variation of defects was investigated on a HPT-made Cu specimen (6 GPa) by means of SPIS and conventional PAS supplemented by TEM, XRD and microhardness measurements [10,12]. In order to enlarge the depth scale probed by SPIS, the specimen was subjected to a controlled chemical etching. The S-parameter values corresponding to positron annihilation in the bulk were found to decrease gradually up to an 18 μm layer removed by etching. Then, no further decrease in the bulk S-values was observed. Such a decrease in S indicates a decrease in defect density. It comes primarily from the decrease in concentration of microvoids with depth and also from a slight increase in grain size with depth, which is suggested by the XRD investigations (see Ref. [10] for details). One should then conclude that the defect concentration decreases with depth in a surface layer of ~ 18 μm thickness while at deeper layers remains unchanged.

Radial dependence of defect concentrations was also inspected by the conventional PAS and SPIS. In a reasonable agreement with the XRD and microhardness findings, no significant changes in the mean grain size and the dislocation density with radial distance from the centre of disk were found. On the other hand, the size and density of microvoids were shown to vary with the radial distance from the centre of the sample.

Thermal recovery of UFG structure. The investigation of the thermal stability of the UFG structure is an important factor for the industrial application of these materials and can contribute to an understanding the physical processes in these materials. Isochronal annealing curves were measured by means of positron lifetime technique on the HPT-made UFG Cu (two specimens prepared under 3 and 6 GPa pressure) and Cu+Al_2O_3 composite. Note that the higher pressure resulted in a slightly finer grains of the UFG Cu specimen, see Table 1. A detailed description of annealing experiments was given elsewhere (see Refs. [9,12,16]). The thermal evolution of UFG structure was illustrated in Figure 1, where the temperature dependence of the volume fraction η of distorted regions along GBs, deduced from positron lifetime data using the diffusion trapping model

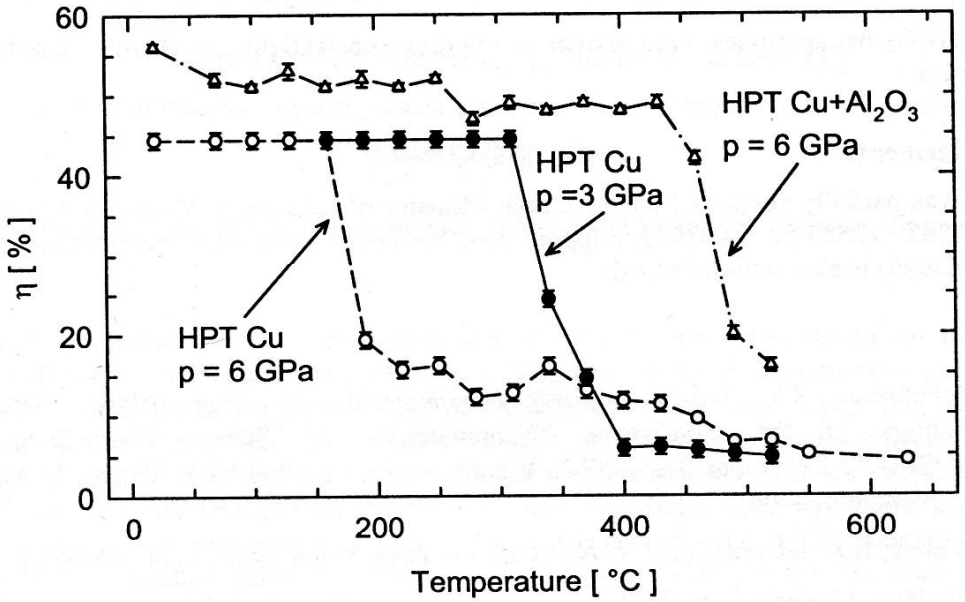

Fig. 1. The evolution of volume fraction η of distorted regions along GBs, obtained using diffusion trapping model [8], with annealing temperature for the UFG Cu (6 GPa) – open circles, UFG Cu (3 GPa) – filled circles and UFG Cu+0.5 wt.% Al_2O_3 composite – open triangles.

[8] is shown. The main results of these annealing experiments, which are also supported by the TEM and XRD observations, are summarised below:

- In both pure Cu specimens, the recovery of the UFG structure proceeds by the same sequence of processes. The abnormal grain growth when isolated recrystallised grains appear in virtually unchanged deformed matrix is followed at higher temperatures by recrystallisation in the whole volume of the specimen.
- The recrystallisation process was found to start at around 300 °C in the HPT-made Cu prepared under 3 GPa (R_g = 90 nm). In the case of the Cu HPT-deformed under 6 GPa (finer grains of R_g = 70 nm), the onset of recrystallisation is moved by about 130 °C towards the lower temperature (see Fig. 1).
- The activation energy of recrystallisation in the UFG Cu, deduced from the present annealing experiments, corresponds reasonably well with the activation energy of the migration of equilibrium grains in the coarse-grained Cu.
- The same sequence of recovery processes as in the UFG Cu appears also in the UFG Cu+Al_2O_3 composite, however, the recrystallisation stage is shifted by almost 300 °C towards the higher temperatures in the composite with respect to the UFG Cu (6 GPa), see Fig. 1.

Summary

A combination of PAS techniques with the TEM, XRD and microhardness measurement appeared to be an effective tool for detailed investigations of UFG structures in the SPD-processed cubic Cu, Fe, Ni metals and Cu+0.5wt.%Al_2O_3 composite. Defects were identified and their concentrations and spatial distributions were investigated. The dislocations were found to be located with a high density in the distorted regions along GBs. The small vacancy clusters distributed homogeneously inside dislocation-free grain interiors were observed and their size was found to depend primarily on the material studied. In the HPT-made Cu, the size and density of vacancy clusters were found to vary with depth and radial distance from the sample centre. The thermal stability of the UFG structure in Cu was found to be better in the material with a larger grain size in the as-deformed

state. The Al_2O_3 nanoparticles were shown to improve substantially the thermal stability of the HPT-made Cu.

Acknowledgements

This work was partially supported by the Czech Ministry of Education, Youths and Sports under contracts COST OC523.50, 1K03025. Support from The Grant Agency of Czech Republic (project GA 106/01/D049) is also acknowledged.

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