ULTRA-FINE GRAINED COPPER PREPARED BY HIGH-PRESSURE TORSION: A POSITRON ANNIHILATION STUDY OF MICROSTRUCTURE EVOLUTION AND LATERAL DISTRIBUTION OF DEFECTS

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Abstract

A defect study of ultra-fine grained (UFG) Cu prepared by high-pressure torsion (HPT) will be reported. HPT introduces a huge amount of defects (vacancies, dislocations) what makes HPT-made materials a challenge for positron annihilation spectroscopy (PAS) because of PAS non-destructivity and excellent sensitivity to open-volume defects. Thus, conventional PAS including positron lifetime (PLT) and Doppler broadening (DB) techniques was the main experimental tool. PAS was combined with transmission electron microscopy, X-ray diffraction and Vickers microhardness (HV) measurements. Lattice defects introduced by HPT were characterized first. A very high concentration of defects created during HPT deformation was observed and the two kinds of defects could be identified: dislocations and small vacancy clusters (microvoids). Because of a significant increase in imposed shear strain with radial distance, microstructure of a HPT-deformed sample at the centre is expected to differ from that at the sample periphery. Therefore, further investigations focused on (i) development of microstructure with HPT turns and (ii) radial distributions of defects. The results are consistent with torsion-induced strain increase from the sample centre toward its edge and predictions of strain gradient model. Extended lateral mapping of microstructure was performed using HV and DB techniques. The latter one could reveal significant non-uniformity of defect distribution which was less pronounced in the HV measurements.

Keywords: ultra-fine grained copper, high-pressure torsion, lateral distribution of defects, dislocations, vacancy clusters, positron annihilation spectroscopy.

1. INTRODUCTION

Ultra-fine grained (UFG) materials are characterised with a typical grain size lowered down to 100 nm scale. Such a grain refinement usually leads to significantly improved mechanical properties of UFG materials, like e.g. a high strength combined with a reasonable ductility [1]. Grain boundaries (GB's) become important in UFG materials and substantially contribute, for example, to an enhancement of their ductility [2] and atomic diffusion activity [3]. Grain refinement to a mean grain size of ≈ 100 nm was succeeded in a variety

of metals or metallic alloys by means of high-pressure torsion (HPT) [1]. UFG copper may be regarded as a suitable model system for the investigations of HPT processing and its influence on final microstructure of the deformed material: pure copper specimens can easily be obtained and, moreover, various characterization methods can be utilised. Potential applications of UFG Cu (e.g. body-friendly implants) make also this material attractive for research.

HPT technique provides bulk specimens of disk shape sized typically to ≈ 10 mm in diameter and ≈ 0.3 mm in thickness. Besides grain refinement, however, a vast amount of lattice defects (vacancies, dislocations) is induced by severe plastic deformation during HPT treatment. Obviously, the HPT imposed shear strain is increased with an increasing number of torsion turns, *N*, and a radial distance from the disk centre, *r* [1]. Radial variations of the microstructure of HPT deformed materials are naturally expected and, indeed, were reported earlier. A lower hardness at the disk centre, compared to its periphery, was found [4] in HPT made Ni. On the other hand, the microstructure differences between the sample centre and its periphery were indicated to diminish with an increasing number of turns and under a higher pressure applied during HPT deformation [5]. Any effort to understand extraordinary features of HPT made UFG materials and to optimize HPT procedure have to rely upon a detailed knowledge of microstructure and its evolution during HPT processing. In particular, (i) the degree of grain refinement and (ii) the type of HPT induced defects should be thoroughly investigated, including lateral variations of these two principal characteristics of UFG materials.

Positron annihilation spectroscopy (PAS) has proven itself to be a very efficient method of investigation of microstructure on a nanoscopic scale, in particular, of open-volume lattice defects, capable of positron trapping, and GB's which positron can reach by diffusion. Basic PAS experiments involve the measurements of the positron lifetime (PLT) and the Doppler broadening of annihilation radiation (DB). PAS can provide information about the types and the concentrations of defects. Positron range of at least ≈ 0.1 mm occurs in most materials. In conventional PAS, positrons from a radionuclide, e.g. ^{22}Na, are directly implanted to the material studied. Microstructure information, averaged over the bulk volume scanned by positrons, is revealed by PAS in this case. Basics of the PAS method were presented in previous NANOCON Conferences together with examples of PAS applications to various materials (Refs. [6,7] and citations quoted therein).

In the present Contribution, a defect study of UFG Cu prepared by HPT is reported as an extension of our recent investigations [8,9]. Conventional PAS was involved as the main experimental technique and combined with X-ray diffraction (XRD), transmission electron microscopy (TEM) and Vickers microhardness (HV) measurements. The Contribution is concerned on characterization of defects introduced by HPT, microstructure evolution during HPT processing, and extensive mapping of lateral distribution of defects by HV and DB techniques.

2. EXPERIMENTS

Samples. Copper of 99.95 % purity was subjected to HPT deformation at room temperature. HPT processing resulted in disk-shaped specimens of ≈ 9 mm in diameter and ≈ 0.3 mm thickness. Influence of compressive pressure was tried using samples deformed under 2 and 4 GPa. Evolution of microstructure with increasing number of HPT revolutions was followed on a series of Cu samples which underwent *N* = 1, 3, 5, 10, 15 and 25 revolutions. For HV measurements, sample surface was polished to mirror-like quality.

HV measurements. Microstructure homogeneity of samples was characterized by HV measurements using a STRUERS Duramin 300 hardness tester with a load of 100 g applied for 10 s. HV data were taken on a rectangular grid with an incremental spacing of 0.5 mm. HV results were represented as colour-coded maps of microhardness constructed to provide pictorial displays about homogeneity of microstructure across the sample.

PAS measurements. Positron sources were prepared of carrier-free ^{22}Na carbonate salt (iThembaLABS) deposited and sealed between two 1.5 μm thick mylar C foils (Dupont). Positron source was tightly sandwiched between two identical disks of material studied. The two sources were employed: a stronger source for PLT measurements, having ≈ 1 MBq strength and an activity spot of ≈ 3 mm diameter, and a weaker source for DB experiments (≈ 0.5 MBq strength, < 1 mm spot diameter).

PLT measurements were performed using a fast-fast spectrometer [10] exhibiting a time resolution of 150 ps (FWHM) and a coincidence count rate of ≈ 100 s^{-1} for the above positron source. To characterise radial changes of microstructure, PLT measurements with the positron source positioned at the sample centre (i.e. at a radial distance of $r \approx 0$) and at a periphery position ($r \approx 3$ mm) were conducted. Positron annihilations in the source (including salt and cover foils) contributed to PLT spectra with two weak components exhibiting lifetimes (intensities) of 0.368 ns (8 %) and 1.5 ns (1 %).

DB experiments were carried out using a conventional HPGe γ-ray spectrometer having an energy resolution of 1.3 keV (FWHM) at 511 keV γ-ray energy. Lateral variations of microstructure were mapped using DB measurements were performed for source positions changed along a rectangular grid incremented in 1 mm steps. A micrometer x – y shift was used to adjust source positions with a precision of ≈ 0.1 mm. Doppler profiles were described in terms of usual sharpness and wing parameters, S and W, respectively, normalised to the shape parameters measured at the centre of the sample after one HPT revolution (S_0 and W_0).

TEM and XRD measurements. Details of apparatus and data acquisition are given in our recent papers [8].

3. RESULTS

TEM. In TEM observations of HPT Cu, a heavily deformed structure with a high dislocation density over the whole sample is displayed already after 1 turn with initial stage of dislocation rearrangement at the sample centre and a more refined microstructure at the sample edge [8]. In the sample subjected to 15 revolutions and 4 GPa pressure, grain refinement to a mean grain size of 200 – 300 nm is seen at the sample periphery. Different picture still takes place, however, at the central region where dislocation cells and subgrains separated by tangled dislocations are observed by TEM after 15 revolutions [8].

XRD. XRD pattern of HPT deformed Cu allowed to estimate the mean size of coherently scattering domains to become as low as ≈ 100 nm already after the first turn. The domain size seen by XRD is always smaller than the grain size estimated by TEM. This is because XRD responds to a mean size of coherently diffracting crystallites with almost perfect structure free of microstrains (like e.g. dislocation cells and subgrains) while the grains separated by well-defined GB's are recognised by TEM. After the third turn, the coherent domain size is somewhat diminished and appears to be slightly smaller for 4 GPa applied pressure compared to that of 2 GPa (≈ 50 and ≈ 70 nm, respectively). Then it remains roughly constant with increasing number of HPT turns [6]. From the XRD line profile analysis, a high dislocation density averaged over the sample, $\rho_D \approx 7\times10^{15}$ m^{-2}, could be deduced. No significant variations of ρ_D with applied pressure and only a very slight increase of the mean dislocation density with number of turns could be implied by XRD [8].

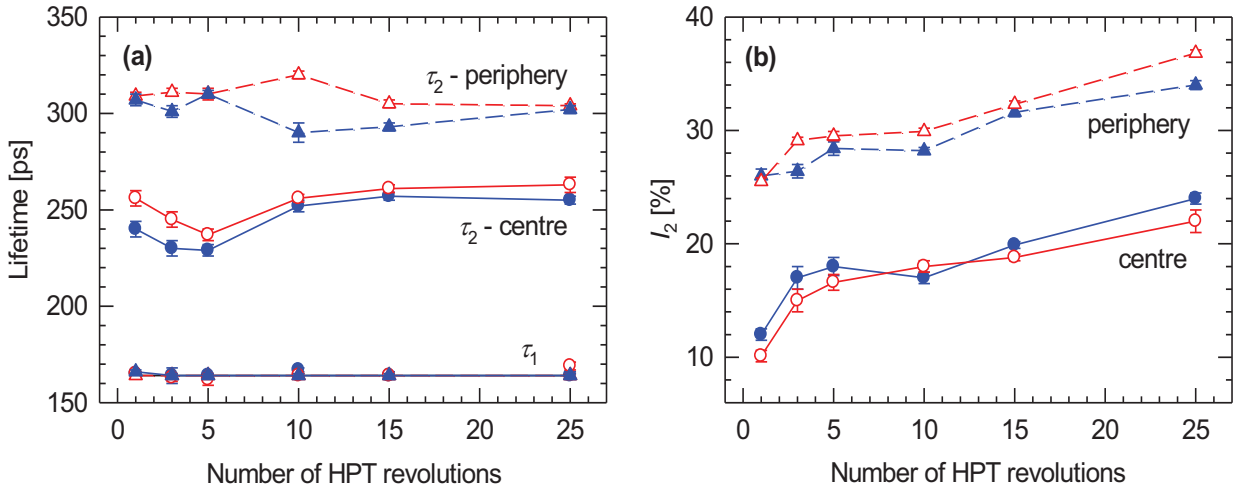

Fig. 1 Results of PLT investigations plotted as a function of the number of HPT revolutions: (a) lifetimes of exponential components resolved in PLT spectra, (b) relative intensity I_2 ($I_1 + I_2 = 100\%$) of the contribution of positrons trapped in vacancy clusters. Results of measurements taken at the centre of the sample ($r \approx 0$ mm) are plotted by circles while those performed at the periphery ($r \approx 3$ mm) are plotted by triangles. Data obtained on samples deformed under the pressure of 2 and 4 GPa are plotted by full and open symbols, respectively.

PLT spectra., Two exponential components (lifetimes τ_i , intensities I_i , i = 1,2) were resolved in PLT spectra of HPT deformed Cu after subtraction of the positron source contribution. In Fig. 1a, observed lifetimes τ_1 , τ_2 were plotted as functions of number of HPT revolutions for the two pressures used, 2 and 4 GPa, and the two positions of the positron source, central ($r \approx 0$) and peripheral ($r \approx 3$ mm). Intensity I_2 as a function of HPT turns is represented in Fig. 1b. Positron lifetimes τ_1 , τ_2 were found to be substantially higher than lifetime $\tau_b = 114$ ps known [10] for well-annealed Cu reference material. Therefore, lifetimes τ_1 , τ_2 arise due to positron trapping in defects. Lifetime τ_1 appear to be close to a value of 164 ps known as the lifetime of positrons trapped at dislocations [11]. Thus, τ_1-component which most intense in PLT spectra of HPT deformed Cu originates from positron trapping at dislocations created during severe plastic deformation. The longer component (lifetime τ_2) comes from positron trapping in larger defects (microvoids) of open volume equivalent to a cluster of several vacancies. Comparing the experimental τ_2-values with those calculated in Ref. [10], the size of clusters was estimated as 4 to 5 vacancies at the sample centre and 7 to 9 vacancies at the sample periphery [8]. It can be seen in Fig. 1 that the number of HPT revolutions does not influence significantly the cluster size. A well-pronounced effect of positron trapping in vacancy clusters can be regarded as a strong evidence of a high number of vacancies formed by HPT deformation in Cu [8]. These vacancies are mobile at room temperature and, hence, they either disappear via diffusion to sinks or aggregate into small clusters.

HV mapping of microstructure. Fig. 2 shows colour coded maps of HV distribution across the sample subjected various number of HPT revolutions. The sample subjected to one HPT revolution exhibits lowered HV ≈ 116 in the centre while the periphery is characterized by a high HV ≈ 150. With increasing number of HPT revolutions HV in the centre increases and the difference between the centre and the periphery becomes smaller. Obviously high HV at the periphery already after the first HPT revolution is caused by the fact that this region is subjected to the highest strain. With increasing number of HPT turns the region

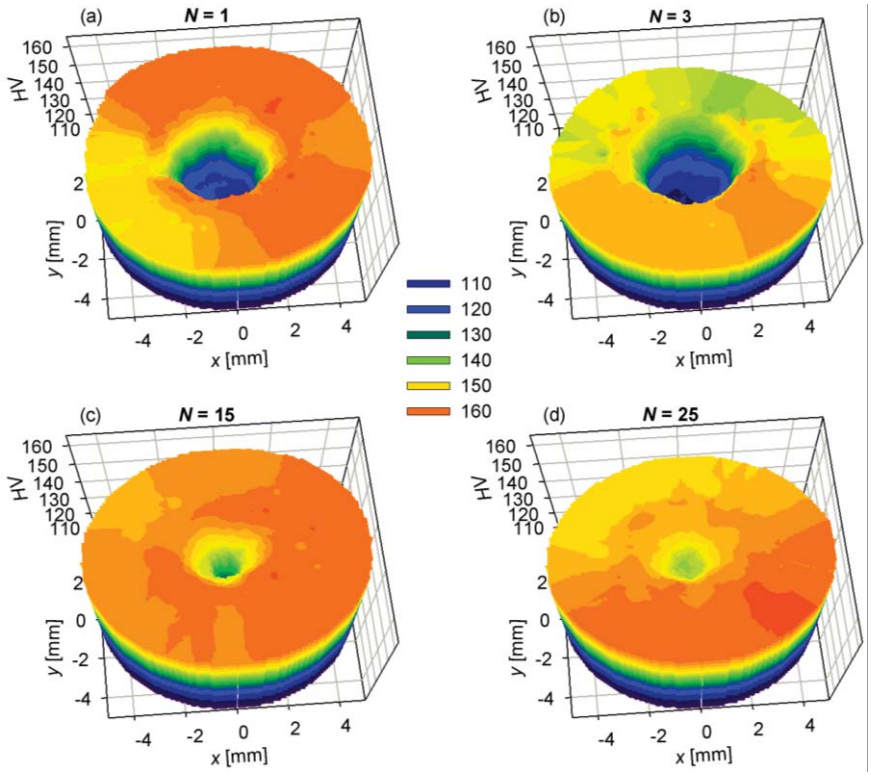

Fig. 2 Colour-coded map constructed from HV values measured on a rectangular grid (incremental spacing 0.5 mm) for HPT deformed Cu subjected to *N*=1, 3, 15 and 25 revolutions.

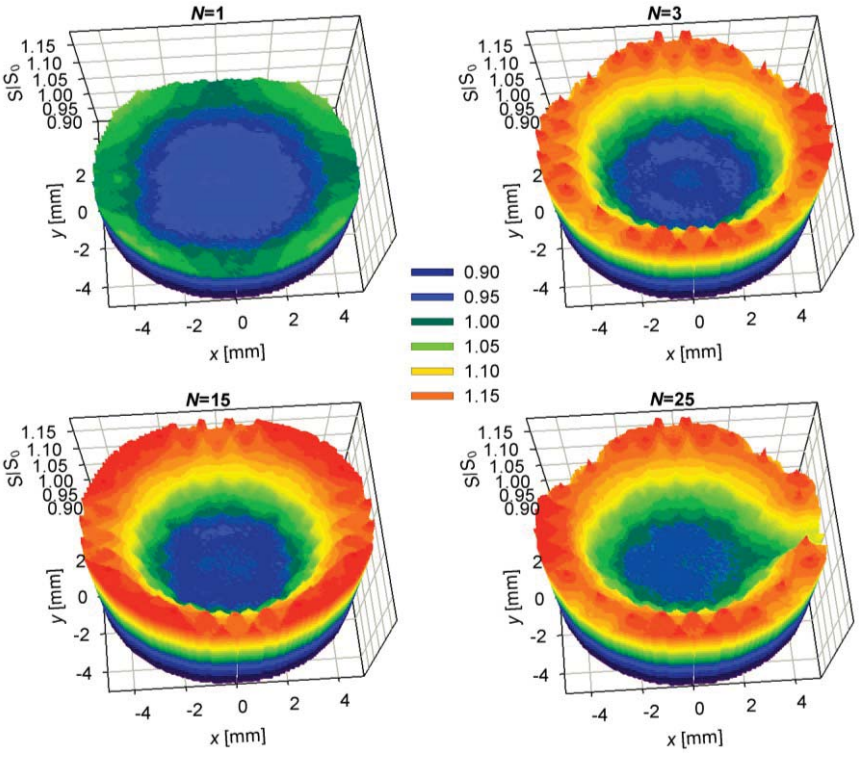

Fig. 3 Colour-coded map constructed from *S* values measured on a rectangular grid (incremental spacing 1 mm) for HPT deformed Cu subjected to *N*=1, 3, 15 and 25 revolutions.

characterized by high HV extends gradually toward the centre. The sample subjected to 25 HPT turns shows almost uniform HV everywhere at $r > 1$ mm. However, the centre still exhibits a slightly lower HV.

DB results. Lateral distri-bution of defects in HPT deformed Cu was mapped for samples subjected to $N = 1$, 3, 15 and 25 turns under 4 GPa pressure. Fig. 3 shows colour coded maps constructed from the *S*-parameter values. The Figure illustrates a radial symmetry of defect distribution (dislocations and microvoids) over the disk plain. Radial dependences of *S* parameter are plotted in Fig. 4a, while Fig. 4b shows the DB data arranged into the *S*–*W* plot.

The most pronounced feature of DB results is an increase in *S* parameter (and corresponding decrease in *W* parameter) from sample centre toward its edge. Note that no significant variations of dislocation density were indicated by XRD measurements on HPT deformed Cu [8]. Then observed radial changes of *S* and *W* parameters are obviously due to an enlarged size of vacancy clusters at the sample periphery compared to its centre, as suggested also by the PLT measurements (7 – 9 compared to 4 – 5 vacancies, respectively). Not only the *S* parameter for positrons trapped in microvoids but also the trapping rate (i.e. the

positron fraction) to microvoids is increased at the sample periphery. Similarly, a decrease of *W*-values accompanying an increase of *S*-values at the sample periphery can be understood. Amount of defects introduced by HPT deformation is increased with increasing number of turns what is reflected by a general trend of a growth of *S*- and a drop of *W*-values seen in Fig. 4a. Similarly to PLT results this effect is pronounced for lower number of turns. It can be read from the *S*–*W* plot on Fig. 4b that *S*- and *W*-values become placed roughly along a straight line which testifies that the nature of positron traps does not change substantially but the defect concentration does. With increasing radial distance, *S* is increased and *W* decreased which results in negative slope of the plot. On the other hand, radial variations in size of vacancy clusters cause an increase of trapping rate as well as a growth of *S* and, correspondingly, a drop of *W*. This is likely a reason for small but systematic deviations from linearity of the data plotted in Fig. 4b.

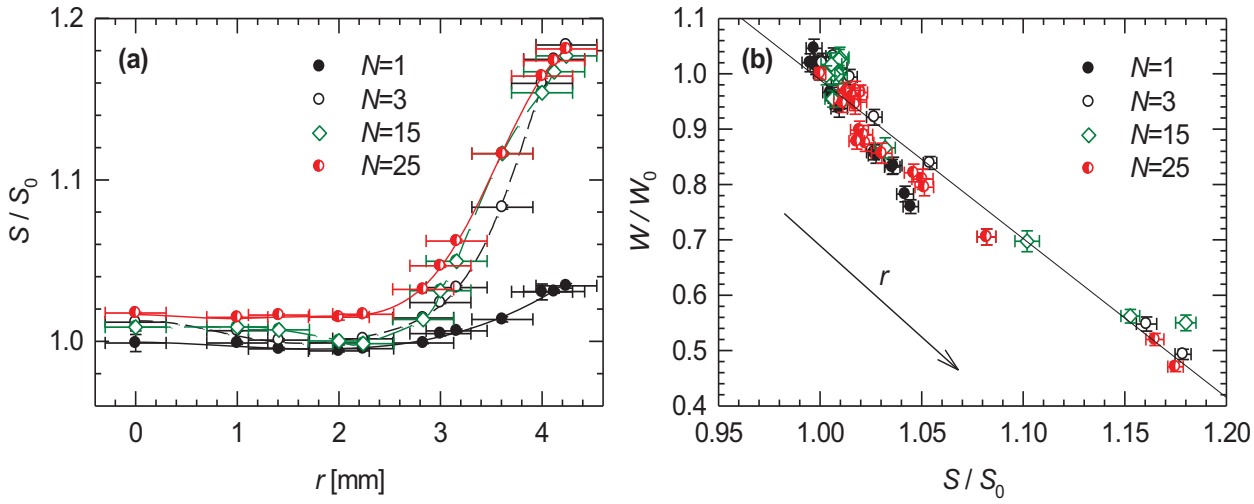

Fig. 4 (a) The dependence of the *S* parameter on the radial distance *r* from the sample centre. Each data point in the panel is an averaged value over all nodes of the rectangular grid with the same distance from the centre. (b) The *S*-*W* plot constructed from the S and W values of panel (a). The straight line in panel (b) is a linear fit to all points of the panel. The arrow in panel (b) points in the direction of increasing *r*. *N* denotes the number of HPT revolutions.

One can note that general trends displayed by the HV and the *S*-parameter mapping are similar as they reflect increasing defect densities and decreasing grain size due to a higher imposed strain. However, the HV data are influenced by grain size and dislocation density, while the DB parameters conveys information on deformation-induced vacancies which have a relatively low impact on hardness, but influence other physical properties of the UFG material (diffusion, phase transformations etc.). Hence, both methods of mapping are complementary, since they respond to different aspects of microstructure.

4. SUMMARY

The two kinds of lattice defects could be resolved in HPT deformed Cu – dislocations and small vacancy clusters formed by agglomeration of deformation-induced vacancies. Microstructure inhomogeneity of HPT deformed Cu was characterized by HV and DB mapping. It was demonstrated that DB mapping carries information about spatial distribution of dislocations and vacancy clusters. Hence, DB technique should be considered as a valuable tool complementary to the standard HV characterization. It was found that the *S*

parameter strongly increases with the radial distance from the centre due to increasing size of vacancy clusters. Although the HV mapping showed only a slight difference between the centre and the periphery in the sample subjected to 25 HPT revolutions, the DB mapping revealed that lateral distribution of vacancy clusters is still far from being uniform.

ACKNOWLEDGEMENTS

This work was supported by the Academy of Sciences of the Czech Republic in frame of projects KAN300100801 and IAA101120803 and by the Ministry of Education, Youths and Sports of the Czech Republic (scientific plan MSM 0021620834).

LITERATURE

[1] R.Z. Valiev, R.K. Islamgaliev, I.V. Aleksandrov, Prog. Mater. Sci. 45 (2000) 103.

[2] R.Z. Valiev, I.V. Aleksandrov, R.K. Islamgaliev, in G.M. Chow, N.I. Noskova (eds.), *Nanocrystalline materials: science and technology*, Kluwer, Dordrecht., 1998, p. 121.

[3] R.Z. Valiev, R.Sh. Musalimov, N.K. Tsenev, Phys. Status Solidi (a) 115 (1989) 451.

[4] A.P. Zhilyaev, G.V. Nurislamova, B.K.Kim, M.D. Baro, J.A. Szpunar, T.G. Langdon, Acta Mater 51 (2003) 753.

[5] M. Kawasaki, R.B. Figueiredo, T.G. Langdon, Acta Mater. 59 (2011) 308.

[6] I. Prochazka, J. Cizek, R. Kuzel, Z. Matej, M. Cieslar, G. Brauer, W. Anwand, R.K. Islamgaliev, Proc. 1st Internat Conf. NANOCON 2009, Roznov p. Radhostem, 20 – 22 Oct. 2009, TANGER, Ostrava (2009) p. 45.
See also http://www.nanocon.cz/data/nanocon2009/sbornik/index.htm , paper 63.

[7] I. Prochazka, J. Cizek, O. Melikhova, J. Kuriplach, T.E. Konstantinova, I.A. Danilenko, Proc 2nd Internat. Conf. NANOCON 2010, Olomouc, 12 – 14 Oct 2010, TANGER, Ostrava (2010) p. 151.
See also http://www.nanocon.cz/data/nanocon2010/sbornik/index.htm , paper 437.

[8] J. Cizek, M. Janecek, O. Srba, R. Kuzel, Z. Barnovska, I. Prochazka, S.V. Dobatkin, Acta Mater. 59 (2011) 2322.

[9] J. Cizek, O. Melikhova, M. Janecek, O. Srba, Z. Barnovska, I. Prochazka, S.V. Dobatkin, Scripta Mater. 65 (2011) 171.

[10] F. Becvar, J. Cizek, L. Lestak, I. Novotny, I. Prochazka, F. Sebesta, Nucl. Instr. Meth. A 443 (2000) 557.

[11] J. Cizek, I. Prochazka, M. Cieslar, R. Kuzel, J. Kuriplach, F. Chmelik, I. Stulikova, F. Becvar, O. Melikhova, Phys. Rev. B 65 (2002) 094106.

[12] B.T.A. McKee, S. Saimoto, A.T. Stewart, M.J. Scott, Canad. Journ. Phys. 54 (1974) 759.