Amorphous versus nanocrystalline structure of sputtered tungsten carbide thin film

O. Milat[1], **K. Salamon**[1] **and N. Radic**[2]

[1]Institute of Physics, Bijenicka c. 46. HR-10001 Zagreb, Croatia
[2]Institute "Rugjer Boskovic", Bijenicka c. 54, HR-10001 Zagreb, Croatia
e-mail: milat@ifs.hr

The structure of tungsten carbide thin films (prepared by magnetron sputtering deposition) was found to be apparently amorphous following the observed typical diffuse XRD patterns[1]. In contrast, this extended EM&D investigation discloses its prominent crystalline feature in a form of dense compact aggregate of randomly oriented nanocrystals of rather globular shape and uniform size (D≈2-3nm).

The EM samples were prepared by peeling the deposited material of the substrate and crushing. The selected area ED patterns were recorded on traditional photographic plates in a series of exposures, using Philips CM 20 microscope[2], and processed by ProcessDiffraction[3], to be finally analysed by FullProf[4] software modified with scattering factors for electrons[3].

Dense uniform packing of aggregated particles is imaged in Fig.1(a)&(b) as irregular pattern of bright & dark dots with average size and spacing in the range of 2-3 nm. Dark field imaging of Fig.1(b) (aperture position indicated in Fig 2(b); rcp. spacing $1/d = (0.3^{-1} – 0.2^{-1})$ nm^{-1}) clearly discloses crystalline features, while high resolution imaging of Fig 1(c) reveals isotropic crystallites orientation evidenced by patches of lattice fringes running along various directions. Therefore, although the observed ED patterns could be tentatively assigned to diffuse haloes of the structure factor variation of an amorphous W-C phase, they have to be attributed to the sequence of broad diffraction rings indexed by the fcc unit cell (a_{fcc}= 0.41 nm) of the crystalline β-WC_{1-x} phase. In addition, the Rietveld structure refinement[5], shown in Fig. 2(c), in the *F43m* space group confirmed the non-stochiometric composition (x≈0.3), and the crystallite size of ≈10^0 nm.

Peculiar feature was observed for shortest exposure times in a form of intensity maximum clearly discernible out of the central spot in ED pattern of Fig. 2(a). As its reciprocal position corresponds to the direct distance of d ≈ 2-3 nm, it can be consistently interpreted as an effect of particle scattering; the shape and size distribution of nanocristalline particles could be deduced; the interparticle separation is comparable to particle diameter.

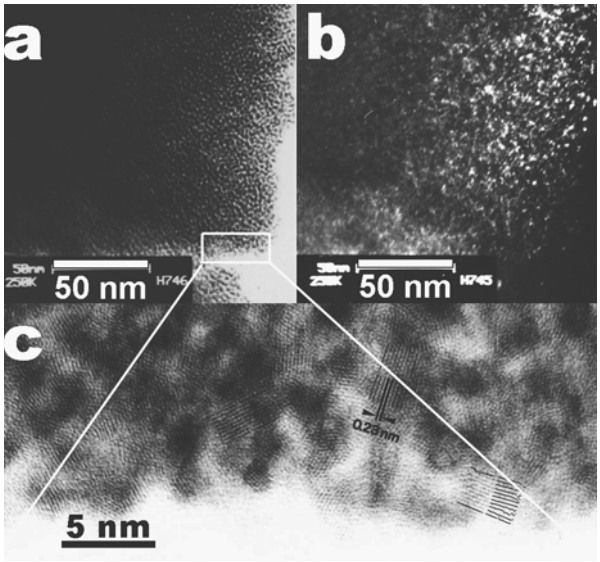

Fig 1. Imaging of W-C thin film consisting of dense aggregates of β-WC_{1-x} nanocrystals; (a) BF, (b) DF, (c) HR; position of objective aperture for (b) is indicated by circle in Fig 2(b). Particles are visible as dark dots in (a) or bright dots in (b), while their crystalline feature is revealed by 0.23 nm lattice fringes in (c). Patches consisting of 10-13 parallel fringes running in all directions are consistent with the average crystallite size of 2.8 nm, uniform spherical shape, and isotropic orientation.

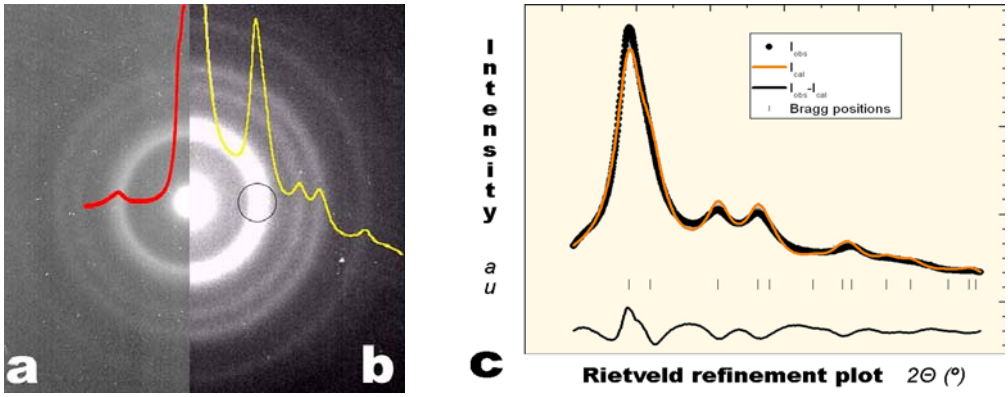

Fig 2. Diffuse EDP of β-WC_{1-x} nanocrystals recorded with exposure time 4 sec. – (a), and 64 sec - (b), respectively, and Rietverld refinement plot – (c). One dimensional photometric traces are indicated in (a) and (b); position of objective aperture for BF image in Fig 1(b) is marked by circle in (b).

[1] N. Radić at al.;Strojarstvo, 38 (1996), 265-274
[2] A. Migliori and G. Calestani at CNR-Lamel, Bologna, Italy, are acknowledged for use of the microscope.
[3] J.L. Labar, Proc. EUREM-12, Brno 2000, I379-I380; www.mfa.kfki.hu/~labar/ProcDiff.html
[4] www.ill.fr/dif/Soft/fp/index.html
[5] T.E. Weirich, et al, Ultramicroscopy, 81 (2000), 263