CRYSTAL STRUCTURE AND NANOSTRUCTURE OF β-WC_{1-x}

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Thin films of tungsten carbide (t ≈ 1-3 μm) were prepared by DC magnetron sputtering of pure W target in admixture of C_6H_6 and Ar upon polycrystalline Cu or Au substrates, at room temperature(1). Electron microscopy (EM) and diffraction (ED) studies revealed the structure of deposited films as a compact aggregate of nanocrystallites of cubic β-WC_{1-x} high temperature phase(2).

The peel-off pieces of a tungsten carbide thin film were crushed and applied on Cu-grid. The EM & ED analysis was performed using Philips CM 20 equipped with double tilt holder.

Metal containing hydrocarbon film W-C:H consists of random packing of nanoparticles as imaged in Fig.1. Bright-field (BF) imaging of Fig.1(a) reveals irregular pattern of bright & dark dots representing crystallites with average spacing and dot size in the range of 2-3 nm. In contrast to the rather uniform dotty pattern of the BF imaging, the dark-field (DF) imaging shown in Fig.1(b) – obtained with the objective aperture at the first diffuse halo of selective area diffraction pattern of Fig.2. – reveals either separated or aggregated nanocrystallites with diameter size: 2 - 3 nm. The same imaging features, as these in Fig.1 (a) and (b), were observed for all specimen tilting angles ($-20° < \varphi < +20°$).

Selected area ED pattern of Fig.2. discloses remarkable diffraction maxima in the small-angle (SA) region – left trace (short exposure), besides the haloes of diffuse intensity in the large-angle (LA) regions – right trace (long exposure). The maximum at $q' = 2.3\ nm^{-1}$ is interpreted as a small angle electron scattering from close random packing arrangement of β-WC_{1-x} nano-particles; the corresponding inter-particle separation is d = 2.9 nm.

The ring pattern of diffuse intensity in the LA region is indexed by a series of broad fcc lines which belong to the crystal lattice of the β-WC_{1-x} phase with unit cell a_{fcc}= 0.42 nm. A sequence of four film plate exposures (4, 16, 32, 64 sec) were used to reconstruct the sensitivity curve, while the intensity curve was processed by the "ProcessDiffraction" Program(3). The obtained powder electron diffraction data were used for Rietweld analysis(4). Refinement results confirmed non-stoichiometric composition of the cubic β-WC_{1-x} high temperature phase, while the calculated crystallite size of 1 nm appears to be smaller then measured on the corresponding BF and DF micrographs, as expected(5).

High-resolution imaging of thin edge of tungsten carbide film, clearly reveals its crystalline structure as well as its "nano-structure". Dark patches of resolvable lattice fringes with spacing d_{111} = 0.23 nm, represent these crystallites for which their close packed planes are fairly well oriented "edge-on". The patches with the up to 10-12 lattice fringes running along various direction confirm uniform size distribution and isotropic orientation of β-WC_{1-x} nanocrystallites.

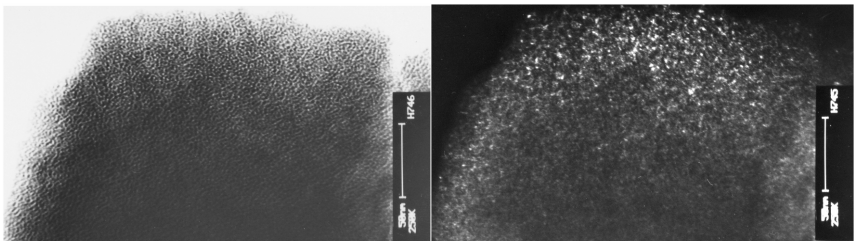

Fig.1 (a) - BF imaging and (b) - DF imaging of β-WC_{1-x} film. Random pattern of bright & dark dots discloses spherical shape of nanocrystallites and their monodisperse size distribution. (bar - 50 nm)

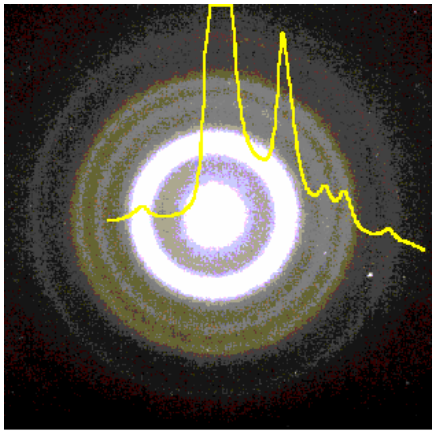

Fig.2. Selected area ED pattern of nanocrystalline tungsten carbide film: left trace reveals particle maxima in the SA region; structural haloes in LA region (right trace) reveal the β-WC_{1-x} fcc lines positions. Objective aperture for imaging of Fig.1(b) was positioned at the ring of the highest intensity maximum.

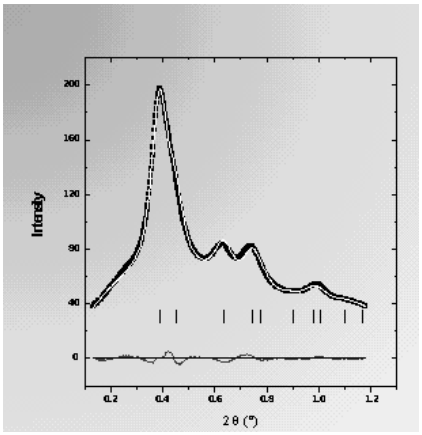

Fig.3. Powder ED pattern of nanocrystalline tungsten carbide film (black line) refined by the Rietweld method (white line); particle maxima in SA region are excluded; vertical bars mark the β-WC_{1-x} fcc lines positions; the deviation between the observed and calculated intensity is represented by the difference plot in the lower part.

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REFERENCES

(1) N. Radić, B. Gržeta, O. Milat, J. Ivkov, M. Stubičar, Proceedings of the 4th Croatian-Slovenian Vacuum Conference, Zagreb, April 18,'96, pp.17
(2) O. Milat, N. Radić, Proc. EUREM-11, Dublin 1996, pp.163
(3) J.L. Labar, Proc. EUREM-12, Brno 2000, I379-I380
(4) T.E. Weirich, S. Winterer, S. Seifrid, H. Hahn, H. Fuess, Ultramicroscopy, 81 (2000), 263
(5) T.E. Weirich, M. Winterer, S. Seiried, J. Mayer, Acta Crystallographica, A58 (2002), 308

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