CHARACTERIZATION OF MO-B-C NANOSTRUCTURED COATING MICROSTRUCTURE BY MEANS OF AEM AND GDOES

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Abstract

A Mo-B-C nanostructured coating was prepared on WC-Co hard-metal substrate by magnetron sputtering. The details of microstructure of deposited thin layer as well as elements redistribution caused by subsequent annealing at 1000 °C were studied by several experimental techniques, namely scanning electron microscopy, transmission electron microscopy and glow discharge optical emission spectroscopy. A strong effect of Co diffusion from substrate to the coating was detected resulting in the formation of interlayer at coating/substrate interface.

Keywords: Coating, nanostructure, analytical electron microscopy, GDOES

1. INTRODUCTION

During the past years a substantial progress has been achieved in the development of hard protective nanocomposite coatings. Numerous nanostructured coatings exhibiting excellent mechanical properties substantially different from their bulk constituents have been designed and successfully used in industrial applications [1-3]. Hard coatings are deposited on cutting tools to protect their surfaces against mechanical and chemical damage and hence to improve lifetime and performance. Protective coating materials for cutting require high stiffness and hardness to lower wear rates. At the same time they should possess also a moderate ductility to avoid crack initiation and growth. There are two criteria generally used for assessment of material's ductility or brittleness. Pugh [4] showed that if the ratio of bulk modulus to shear modulus B / G is greater than 1.75, the material exhibits ductile metal-like behaviour. Otherwise, the material is considered brittle. Pettifor [5] showed that the value of the Cauchy pressure can also give information about ductility. Cauchy pressure is determined as the difference between elastic constants C_{12}-C_{44}. If it is negative, the material is brittle. Positive Cauchy pressure implies ductile behaviour.

Regarding the above mentioned trends and criteria, a proposal for an unusually stiff and moderately ductile hard coating material Mo_2BC was proposed by Emmerlich et al [6] based on *ab initio* calculations and supported also experimentally by coatings prepared at 900 °C. Orthorhombic crystal lattice of Mo_2BC with a high aspect ratio (a = 0.309 nm, b = 1.735 nm, c = 0.305 nm, space group *Cmcm* [7], ICSD entry no. 043318 [8, 9]) constitutes a structure of stiff Mo-C and Mo-B layers with metallic interlayer bonding. The authors [6] showed that calculated properties (B = 324 GPa, B / G = 1.72, C_{12}-C_{44} = 43 GPa) can be understood by considering the electronic structure and particularly the extreme anisotropy. Excellent mechanical properties of Mo_2BC coatings were recently confirmed by several experimental works [10-13]. The authors of [6] continued their work by preparing Mo_2BC thin films at lower temperatures using high power pulsed magnetron sputtering [14] and by systematic theoretical study on the electronic structure and mechanical properties of broader class of similar X_2BC nanolaminated materials where X = Ti, V, Zr, Nb, Mo, Hf, Ta and W [15].

After we successfully prepared Mo_2BC coatings by magnetron sputtering and assessed their microstructure and mechanical properties in the as deposited state [11-13] we addressed thermal stability of the coatings up to 1000 °C. First results [14] indicate that annealing process significantly improves the hardness and elastic

modulus of coatings while keeping their resistance to fracture sufficiently high. In this work we combine several experimental methods to study in detail microstructural changes in Mo_2BC coatings on WC-Co substrates caused by annealing at 1000 °C.

2. EXPERIMENTAL

A custom built magnetron sputtering device equipped with four magnetron sputtering heads in a balanced magnetic field configuration was used for the Mo-B-C coating depositions. Samples of about 2 μm thick layers were deposited using magnetron co-sputtering of three targets: B_4C, C and Mo. The hard-metal (cemented tungsten carbide, WC-Co) substrates were ultrasonically cleaned in a degreasing agent and then placed in the chamber using a load-lock system. Prior to the deposition process the substrates were cleaned in argon plasma for 20 min. B_4C and Mo targets were DC driven, a pulsed power was applied on the C target. Substrates were not heated. More details on preparation can be found in [13, 14].

The prepared coatings were annealed in the resistively heated laboratory furnace Classic Clare 4.0 to 1000 °C with constant heating rate of 5 K / min. The furnace chamber was evacuated to the base pressure of about 10^{-5} Pa. After achieving the desired temperature it was kept constant for 30 minutes and then the samples cooled down in vacuum for approximately 12 hours.

Microstructure of layers was studied using a Tescan LYRA 3XMU FEG/SEM×FIB scanning electron microscope (SEM) with an X-Max80 energy dispersive X-ray (EDX) analyser by Oxford Instruments and a Philips CM12 STEM transmission electron microscope (TEM) with an EDX analyser by EDAX. Thin lamellar cross sections for TEM observations were prepared using a focused ion beam (FIB) in SEM from two locations in each sample: an undisturbed layer and a central region of indentation print made with Berkovich tip with a load of 1 N. Depth profiles showing the elements redistribution due to annealing were measured by glow discharge optical emission spectroscopy (GDOES) at 650 Pa and power of 35 W using a HORIBA Jobin Yvon GD-Profiler 2 by HORIBA Scientific.

3. RESULTS AND DISCUSSION

Figure 1 summarizes the results of SEM and TEM observations after annealing at 1000 °C. The SEM image of thin lamella from the region of large indent (**Figure 1a**) shows the cross section through protective Pt layer, deposited layer and WC-Co substrate. A darker thin interlayer is visible near the coating/substrate interface.

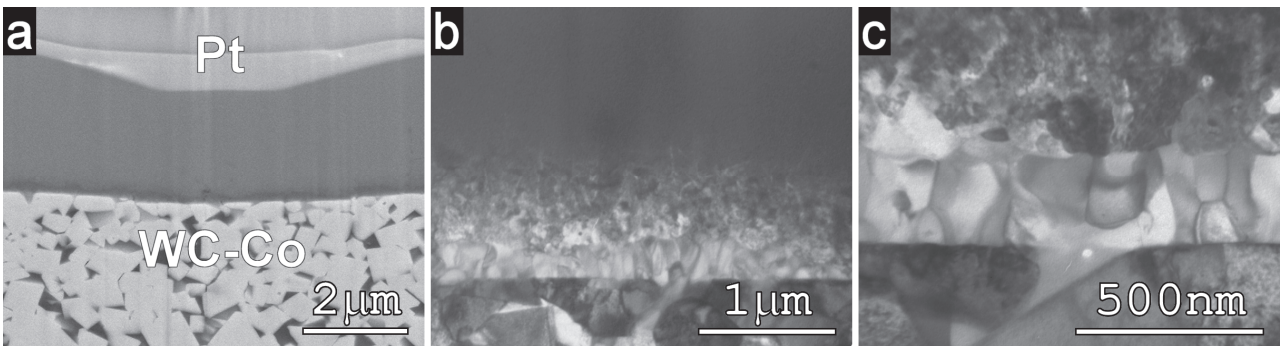

Figure 1 Electron micrographs: SEM, signal of backscattered electrons (a) and TEM (b, c)

Closer inspection on thin lamella in TEM shows clearly the remarkable grain size gradient in the coating (**Figure 1b**). Near the interface grains of size up to 200 nm appear and subsequently the grain size decreases with increasing distance from the interface. At the upper part of the layer the grain size reaches units of nanometres. Higher magnification (**Figure 1c**) reveals in the coating an interlayer of grains sized over 100 nm.

EDX in TEM detected a presence of Co in the interlayer which led us to closer examination of concentration profiles using different method sensitive also to light elements, namely GDOES.

GDOES method uses radio frequency glow discharge for a uniform and rapid sputtering of the sample and hence detecting chemical composition possibly varying with depth [17, 18]. The crater about 4 mm in diameter and 40 µm in depth produced by glow discharge (GD) is shown in **Figure 2a**. A brighter outer rim (of presumably redeposited material) is seen, which we decided to inspect closer by EDX in SEM to obtain a better notion of processes accompanying GDOES measurement. **Figure 2b** shows the crater edge region with marked spots of EDX analyses plotted in **Figure 2c** (due to low accuracy of EDX for light elements quantification only metallic constituents were quantified). We can learn that the wide (over 600 µm) outer ring of surface is dominated by redeposited W and Co from the crater and not until about 1 mm apart from the crater edge the surface is free of redeposited elements. The fluctuation of W and Co at the crater bottom reflects alternating WC grains and Co binder. It is also worth to notice that redeposited elements are not distributed uniformly; W hits higher radius than Co and more so, its content is not monotonous.

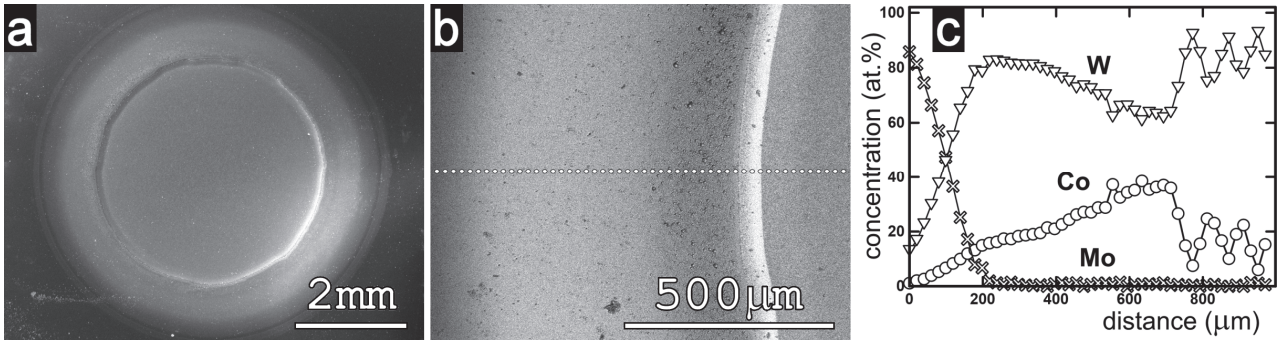

Figure 2 SEM micrographs of GDOES crater (a), a detail of crater edge (b) and EDX analyses (c)

After the excursion towards instrumental matters we finally present quantitative depth profiles in **Figure 3**. Without using specific standards GDOES reproduces very well the layer thickness and stoichiometry of WC grains in the substrate. The elemental fractions in the coating will need further check using a boron-containing standard. The interfacial layer observed after annealing on SEM and TEM micrographs in **Figure 1** is well pronounced also on depth profiles: Co diffuses from substrate into Mo-B-C layer and forms a peak in a narrow interlayer at depths from 2.1 to 2.3 µm, where at the same time C is locally decreased and B is increased. Next to it (between 1.7 and 2.1 µm) there is another zone (also apparent at TEM micrograph in **Figure 1b**) where Co gradually vanishes, C reaches a local maximum and B shows local minimum. All these interesting features as well as study of local mechanical properties of particular sublayers are subject to further work.

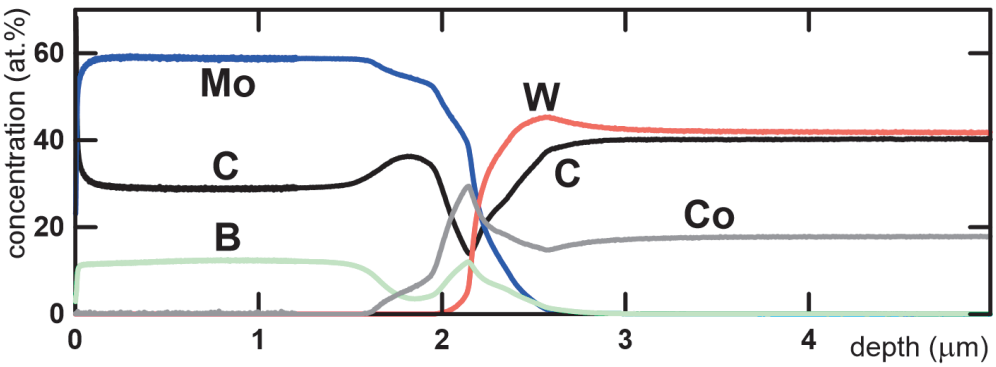

Figure 3 Composition depth profiles on the Mo-B-C / WC-Co system

4. CONCLUSION

Hard and ductile partially crystalline Mo2BC coatings were successfully prepared on hard-metal substrates by magnetron sputtering of three targets. The samples were then subjected to annealing at 1000 °C. Transmission electron microscopy revealed development of an interlayer in the coating formed by coarsened grains. Grain size gradually decreases down to units of nanometres at the free surface. Glow discharge optical emission spectroscopy supported TEM results and disclosed a complex element redistribution in the coating / substrate system due to annealing. The effect of element redeposition during glow discharge measurement was briefly addressed.

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