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Characterization of Ta-B-C nanostructured hard coatings

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Abstract. Microstructure and mechanical properties of Ta-B-C nanocrystalline layers prepared by magnetron sputtering were studied. DC magnetron sputtering was used to prepare thin layers on rotated substrates. Various deposition parameters were tested. Microstructure of layers was studied by means of scanning and transmission electron microscopy on thin lamellar cross sections prepared using a focussed ion beam. Both undisturbed layers and the volume under relatively large indentation prints (load of 1 N) were observed. The microstructure observations were correlated with mechanical properties characterized by means of nanoindentation experiments in both the static and the dynamic loading regime. Elastic modulus, indentation hardness and fracture resistance of prepared nanostructured coatings were evaluated and discussed.

1. Introduction

Hard coatings are commonly deposited on cutting tools to protect the tool surfaces from mechanical and chemical damage and hence to improve lifetime and performance. Protective coating materials used for cutting require high stiffness and hardness to lower wear rates. On the other hand, since crack initiation and growth have to be avoided, the protective coating materials should also possess a moderate ductility. There are two criteria which are generally used for determination if the material is brittle or ductile. Pugh [1] 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 [2] 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, material is brittle. Positive Cauchy pressure, on the other hand, implies ductile behaviour.

In the last decade, a proposal for an unusually stiff and moderately ductile hard coating material Mo_2BC was proposed by Emmerlich et al [3] based on *ab initio* calculations and supported also experimentally. The calculated bulk modulus of 324 GPa was 45% larger than that of $Ti_{0.25}Al_{0.75}N$ and only 14% smaller than that of c-BN, indicating a highly stiff material. The calculated B/G ratio was 1.72 at the transition from brittle to ductile behaviour. This, in combination with a positive Cauchy pressure, suggested moderate ductility. The authors [3] showed that these properties can be understood by considering the electronic structure and particularly the extreme anisotropy (ortorhombic crystal lattice with a=0.309nm, b=1.735nm, c=0.305nm, space group *Cmcm* [4], ICSD entry no. 043318 [5]). The presence of stiff Mo-C and Mo-B layers with metallic interlayer bonding enables the intriguing and unexpected property combination. Excellent mechanical properties of Mo_2BC coatings were recently confirmed by several experimental works [6-10].

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The Aachen group continued the work later by preparing Mo_2BC thin films at lower temperatures using high power pulsed magnetron sputtering [11] 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 [12]. All compounds were shown to be stable with the similar orthorhombic lattice parameters with a high aspect ratio. It was shown that systems with higher valence electron concentration appear to be stiffer and ductile as inferred from both the more positive Cauchy pressure and the larger value of the B/G ratio. On the other hand, the calculated phase stabilities decrease as the valence electron concentration is increased. The combination of high stiffness and moderate ductility renders X_2BC compounds with X = Mo, Ta and W as the most promising candidates for protection of cutting and forming tools.

In this work we studied microstructure and mechanical properties of Ta-B-C nanocrystalline layers prepared by magnetron sputtering. Microstructure of layers was studied by means of scanning and transmission electron microscopy on thin lamellar cross sections prepared using a focussed ion beam and correlated with mechanical properties characterized by means of nanoindentation experiments.

2. Experimental

A custom built magnetron sputtering device equipped with four magnetron sputtering heads in a balanced magnetic field configuration was used for the Ta-B-C coating depositions. Samples of about 0.5 μm thin layers were deposited using magnetron sputtering of three DC driven targets: B_4C, C and Ta. 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. The deposition pressure was 0.3 Pa. Substrates were not heated.

Microstructure of layers was studied using a Tescan LYRA 3XMU FEG/SEM×FIB scanning electron microscope (SEM) and a Philips CM12 STEM transmission electron microscope (TEM). 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 1N. TEM observations were correlated with mechanical properties measured by means of nanoindentation technique using a Hysitron dual head TI950 triboindenter equipped with diamond Berkovich tip in the load range from 50 μN to 11 mN. The hardness and reduced elastic modulus values were determined at indentation depths where the substrate influence was negligible. Moreover, microindentation using a Fischerscope H100 microindenter equipped with diamond Berkovich tip was used to study the fracture resistance of the coatings in the load range from 0.01 to 1 N.

3. Results and discussion

SEM micrographs in figure 1 show one of the large indentation prints produced with a load of 1N and two stages of thin lamella preparation. Cracks at the indentation print perimeter were often observed (see figure 1a). According to indentation loading curves the cracking started only after the maximum indentation depth was reached. The Pt protective layer for thin lamella was deposited across the central part of the indentation print (figure 1b). On the lamellar cross section (figure 1c) one can observe the large indentation depth (more than twice the layer thickness) without any visible defects at the layer/substrate interface and with the only crack at the indentation print perimeter marked by an arrow.

TEM micrographs in figure 2 depict details of the Ta-B-C layer microstructure in the indented region. The crack at the perimeter of the indentation print (figure 2a) is shown to be absorbed in the layer interior. The layer itself reveals a columnar structure of fine grains (see figure 2b and a detail in figure 2c). A thorough inspection of the lamella did not find any defects (except the crack described above) inside the layer or at the layer/substrate interface even though both the shape of the interface under indentation print and a high dislocation density in WC grains evidence heavy plastic deformation.

The depth profiles of hardness and elastic modulus in figure 3 were obtained using quasistatic nanoindentation tests with 20 partially unloading segments. The maximum load was 10 mN. The basic parameters characterizing mechanical properties of the deposited layer are hardness H=28±1 GPa and effective elastic modulus $E_{eff}=E/(1-\nu^2)$=442±2 GPa, where E is the Young modulus and ν is the Poisson ratio. Substituting the Poisson ratio 0.254 calculated *ab initio*for Ta_2BC [12] into the formula for E_{eff} the Young modulus value E=414 GPa is obtained, which is very close to the Young modulus value of 421 GPa predicted for Ta_2BC [12].

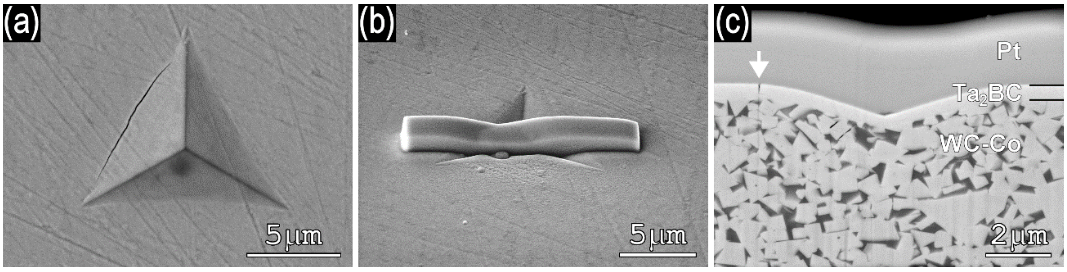

Figure 1. SEM micrographs, signal of backscattered electrons. Plan view of indentation print with a crack at the perimeter (a), a protective Pt block across the central part of indentation print defining the thin lamella position, sample surface is tilted by 55 degree (b), the lamella prior to final thinning, surface is tilted by 35 degree, a crack is marked by an arrow (c)

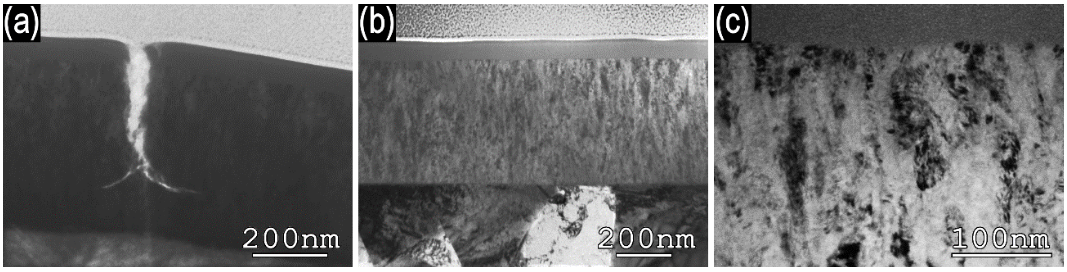

Figure 2. TEM micrographs: a crack at the indentation print perimeter (a), columnar structure of the layer (b) and a detail of fine grains of the layer (c)

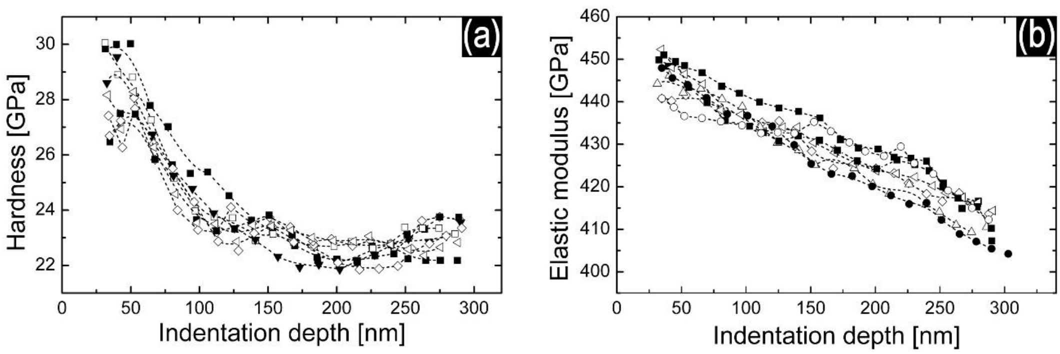

Figure 3. The depth profiles of hardness (a) and elastic modulus (b)

There exist yet other useful empirical parameters for characterization of protective coatings, such as the H/E and H^3/E^2 ratios, which are measures of the toughness and resilience of the coatings, respectively. Toughness can be defined as the ability of a material to absorb energy during deformation up to fracture. In the case of our Ta-B-C layer H/E=0.07 value indicates promising fracture toughness. The prediction of the wear resistance of the coatings can be related to the resilience of the coating, which is defined as the resistance of a material against plastic deformation. Measured value H^3/E^2=0.13GPa indicate improved wear resistance of the Ta-B-C coating.

Conclusions

Hard and ductile Ta-B-C coatings with an excellent resistance against indentation induced cracking were successfully prepared by magnetron sputtering. Complex characterisation of the local mechanical properties and microstructure was carried out showing very favorable combination of high hardness and elastic modulus together with high fracture toughness. The nanocomposite Ta-B-C coatings hardness reached 28 GPa and its effective elastic modulus was 442 GPa. TEM observations of the area under the indentation prints proved that there was no delamination at the film/substrate interface. The cracks appeared in the vicinity of the imprints only after the indentation depth substantially (more than twice) exceeded the film thickness.

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References

[1] Pugh S F 1954 *Phil. Mag.* **45** 823
[2] Pettifor D G 1992 *Mater. Sci. Technol.* **8** 345
[3] Emmerlich J, Music D, Braun M, Fayek P, MunnikF and Schneider J M 2009 *J. Appl. Phys. D: Appl. Phys.* **42** 185406
[4] Jeitschko W, Nowotny H N and Benesovsky F 1963 *Monatsh. Chem.* **94**565
[5] Bergerhoff G and Brown I D 1987 *Crystallographic Databases* ed F H Allen et al. (Chester, International Union of Crystallography)
[6] Djaziri S, Gleicha S, Bolvardi H, Kirchlechner C, Hans M, Scheu C, Schneider J M and Dehm G 2016 *Surf. Coat. Technol.* **289** 213–218
[7] Buršík J, Kuběna I, Buršíková V, Souček P, Zábranský L and Vašina P 2016 *Def Diff Forum* **368** 107
[8] Buršík J, Buršíková V, Souček P, Zábranský L and Vašina P 2016 *Rom. Reports Phys.* **68** 1069
[9] Zábranský L, Buršíková V, Souček P, Vašina P and Buršík J 2016 *Eur. Phys. J. Appl. Phys.* **75** 24716
[10] Buršíková V, Buršík J, Zábranský L, Souček P and Vašina P 2016 *Def Diff Forum* **368**111
[11] Bolvardi H, Emmerlich J, Mraz S, Arndt M, Rudigier H and Schneider J M 2013 *Thin Solid Films* **542** 5-7
[12] Bolvardi H, Emmerlich J, to Baben M, Music D, von Appen J, Dronskowski R and Schneider J M 2013 *J. Phys.: Condens. Matter* **25** 045501