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Thermal stability of hard nanocomposite Mo-B-C coatings

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ABSTRACT

In the present work, nanocomposite Mo-B-C coatings were deposited on high speed steel and hard metal substrates by magnetron sputtering of three targets. These coatings were subjected to annealing to final temperatures in the range from 500 °C to 1000 °C. It was found that the as deposited Mo-B-C coatings exhibited hardness of ~20 GPa, nanocomposite microstructure with very fine grains (~2 nm) and low degree of crystallinity. The X-ray diffraction and transmission electron microscopy together with selective area electron diffraction were used to study the temperature induced changes of the microstructure of the coating and its crystallinity. The annealing process significantly improved the hardness (from ~20 GPa to ~30 GPa) and effective elastic modulus (from initial 330 GPa–500 GPa) of coatings while their resistance to fracture was kept sufficiently high.

1. Introduction

Recently, there has been an increased interest in boron and carbon based nanolaminate coatings such as Mo_2BC with similar structure to the so-called MAX phases [1,2] (M = transition metal, A is a group A element and X is either boron or carbon). The Mo_2BC material exhibits orthorhombic structure with the *Cmcm* space group (unit cell with large ratio of $b/a = 5.6$) and consists of face-sharing Mo_6B trigonal prismatic and Mo_6C octahedral (cubic rock-salt coordination) building blocks. Previous *ab initio* calculations [3,4] and subsequent experimental work [3,5,6] proved that Mo_2BC coatings exhibit a highly demanded combination of high hardness and Young's modulus which is accompanied by moderate ductility. These properties enable to reduce the crack initiation and propagation in the coating. Emmerlich et al. [3] synthesized crystalline Mo_2BC thin films on Al_2O_3 substrate using DC (direct current) magnetron sputtering with the deposition temperature of 900 °C. The Young's modulus of 460 ± 21 GPa and hardness of 29 ± 2 GPa were measured by nanoindentation using a load of 5 mN. Bolvardi et al. [7] managed to prepare crystalline Mo_2BC thin films using high power pulsed magnetron sputtering (HPPMS) with synthesis temperature of 380 °C while the synthesis temperature in case of standard DC magnetron sputtering was found to be at least 550 °C. In our previous papers [5,8], we reported on a low temperature deposition of Mo-B-C coatings using HPPMS and DC magnetron sputtering of either one Mo_2BC target or three targets: B_4C, C and Mo with or without additional substrate heating. In case of Mo_2BC target it was difficult to control the stoichiometry of the deposited samples, most of the coatings prepared by employing only the Mo_2BC target showed amorphous microstructure. Using sputtering of three targets we were able to control better the stoichiometry and the related microstructure of growing coatings. In general, the synthesized coatings exhibited different mechanical properties: their hardness ranged from ~19 GPa for amorphous coatings to ~32 GPa for nanocomposite coatings. According to our previous TEM study [5], the nanocomposite coatings consisted of nanosized Mo_2BC grains (2–10 nm) embedded in amorphous matrix. The as deposited coatings showed very good resistance against fracture due to their moderate ductility, predicted and calculated in previous studies [3,4]. It was concluded that these coatings have potential application as protective coatings for cutting tools.

However, for cutting tool applications the hardness and toughness are not the only important characteristics. The tools protected by hard coatings often operate at elevated temperatures and thus their thermal stability is also crucial. In general, the thermal activation can lead to the enhancement of diffusion, e.g. outward diffusion of hydrogen in case of hydrogenated DLC coatings [9–12] or inter-diffusion at the interface [13], changes in size, shape or

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composition of grains such as recrystallization, segregation or grain growth processes [14,15], phase transitions [16] or stress relaxations [17]. These undesired effects often act as limiting factors in applications of protective coatings and, moreover, the mismatched coefficients of thermal expansion (CTE) of the substrate and the coating can often lead to adhesive failure. On the other hand, the thermal treatment can also improve some of the mechanical properties, e.g. age hardening of TiAlN due to phase decomposition [16].

Although Mo_2BC material in its bulk form is known from 1960s [18], only few research papers have been published so far in the area of thermal stability of Mo-B-C coatings. Bolvardi et al. [7] discussed the thermal annealing of amorphous Mo_2BC powder which was studied by differential scanning calorimetry and X-ray diffraction. It was shown that from 820 °C the bulk diffusion induced crystallization occurred which resulted in several distinguished Mo_2BC and Mo_2C diffraction peaks. However, the crystallization temperature was significantly lower for HPPMS or DC sputtering where the surface diffusion induced by ion bombardment was reported to be the main reason for this decrease of the crystallization temperature.

As it was shown by Bolvardi et al. [7], the annealing of the Mo_2BC powder resulted in the increase of the degree of crystallization. One of the goals of the present work was to determine whether the crystallization mechanism is performed in the same way in the case of thin Mo-B-C coatings. In order to study the influence of the annealing temperature on the degree of crystallization and the subsequent changes in the mechanical properties, several Mo-B-C coatings were prepared using HPPMS and DC magnetron sputtering. The deposition conditions were chosen in order to prepare coatings with similar initial properties and microstructures as in our previous study [5], i.e. coatings with nanocomposite microstructure, lower degree of crystallinity and hardness of ~20 GPa. In order to study the thermally induced changes the samples were measured using nanoindentation, scanning electron microscopy (SEM) to study the potential fracture around the residual imprints made by nanoindentation and GI-XRD to study the crystallinity changes after the annealing process.

2. Experimental

All discussed Mo-B-C thin films were prepared using magnetron co-sputtering of three targets: B_4C, Mo and C using sputtering system with a cylindrical chamber ø 50 cm × 50 cm. The hard metal (cemented tungsten carbide WC-Co, with [Co] = 10 at.%) and high speed steel (HSS) were ultrasonically cleaned in a degreasing agent and then placed in the chamber using a load-lock system. Prior to the deposition process all substrates were cleaned in argon plasma (pressure 0.3 Pa) for 20 min, here the radiofrequency (RF, 13.56 MHz) power of 100 W was applied on the substrate holder. After the cleaning of the substrate, the deposition commenced. The biasable substrate holder was located 28 cm below the targets and its rotation was set to 5 rpm during the whole deposition process in order to ensure good homogeneity of the growing films. The deposition conditions were: 128 W DC power on the B_4C target, 110 W DC on the Mo target and pulsed power of 250 W with repetition frequency of 350 kHz and off-time of 1 μs (duty cycle of 45%) applied on the C target. The deposition pressure was 0.1 Pa and the duration 480 min. Neither additional external heating on the substrate nor bias voltage were used during the deposition of the studied coatings as well as no interlayer enhancing the adhesion to above mentioned substrates was introduced.

The thermal stability of the films was investigated as a function of thermal annealing under UHV conditions. The furnace chamber was evacuated to the base pressure of about 10^{-5} Pa. The films were annealed in the resistively heated laboratory furnace Classic Clare 4.0 to several different final temperatures depending on the substrate material. The studied samples were subjected to annealing with constant heating rate of 10 °C/min. The coatings on hard metal substrate were annealed up to 1000 °C and in case of the HSS substrate, because of its lower thermal stability [15], the coatings underwent annealing up to 500 °C, 600 °C and 700 °C. After achieving the desired temperature, it was kept constant for 30 min in case of all experiments. Then the samples cooled down in vacuum for approximately 12 h. Afterwards, the nanoindentation measurements, X-ray diffraction, SEM and TEM studies were performed in order to determine changes in microstructure and mechanical properties.

The hardness and reduced elastic modulus were measured and evaluated using a depth sensing indentation method performed on a Hysitron TI950 Triboindenter equipped with a Berkovich tip. The mounted nanoscale measuring head with resolution of 1 nN and load noise floor lower than 30 nN allow to measure in the load range from 50 μN to 11 mN. Several testing methods were used, e.g. classic quasistatic test or quasistatic test with several partially unloading segments. The quasistatic indentation tests were carried out in load controlled regime using a constant loading rate of 0.2 mN/s. The indenter tip calibration was carried out for low loads (indentation depths < 100 nm). For the evaluation of the measured data, the standard procedure proposed by Oliver and Pharr [19] was used. The differential hardness H_{dif} [20,21], calculated as $H_{dif} = k\partial L/\partial(h^2)$, where L is the applied load, k is a constant depending on the indenter and h is the indentation depth, was measured using Fischerscope H100 microindentation tester equipped with a Berkovich tip. The quasistatic test with the load of 1 N was used in order to determine the loads or depths where the substrate starts to influence the measurement of the hardness or to detect cracking possibly emerging during deformation. The residual imprints after microindentation tests with the Fischerscope H100 and the surface of coatings as deposited and after annealing were analyzed on scanning electron microscope MIRA 3 FEG SEM with the accelerating voltage of 15 kV.

The coating microstructure was studied by means of electron microscopy using a Tescan LYRA 3XMU SEM × FIB scanning electron microscope (SEM), a Philips CM12 STEM transmission electron microscope (TEM) operating at 120 kV and a JEOL 2100F high resolution TEM. Thin lamellar cross sections for TEM observations were prepared using a focussed ion beam (FIB) in SEM.

Scratch tests were carried out with a Revetest Scratch Tester (Anton Paar) equipped with a 200 μm diamond Rockwell indenter. A progressive scratch of load with loading rate of 15 N/min from 1 N to 16 N on a 8 mm path was applied to all samples. X-ray diffraction was used in order to determine the inner structure and level of crystallinity of coatings. The measurements were performed on Rigaku Smartlab X-ray diffractometer with a grazing angle of incidence configuration with an incidence angle of 0.5°. The Rutheford backscattering spectroscopy (RBS) using ion beam provided by the tandem accelerator Tandetron MC 4130 was applied to determine the atomic composition of the studied samples. For this purpose, the proton projectiles with energies of 1740 (higher sensitivity to C content) and 2700 keV (higher sensitivity to B content) impinging vertically on the samples were utilized. The backscattered protons were analyzed at the scattering angle of 170°.

3. Results and discussion

The atomic composition of Mo-B-C coatings on carbon substrates was determined using RBS. The deposition conditions resulting in coatings with composition near to stoichiometric Mo_2BC ([Mo] = 49.9 at.%, [B] = 23.2 at.%, [C] = 23.2 at.%,