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Synthesis and characterisation of Mo-B-C thin films deposited by non-reactive DC magnetron sputtering

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ABSTRACT

Thin films in the Mo-B-C system with varying carbon content (up to 37 at.%) were deposited using non-reactive DC magnetron sputtering. The phase composition and microstructure were determined and the potential use of the films in sliding electrical contact applications was evaluated. Films with lower than 23 at.% carbon content consisted of nanocrystalline MoB_{2-x} grains surrounded by an amorphous tissue phase (a-B for binary, and a-BC_x for ternary films). With increasing carbon content grain sizes was found to decrease (from 16 to 5 nm), and above 23 at.% carbon the films deposited at room temperature were X-ray amorphous. Scanning transmission electron microscopy and energy dispersive X-ray spectroscopy reveal that these films contain Mo-rich and Mo-poor regions, and thus are two-phase amorphous nanocomposites. Low-carbon content samples exhibited a friction coefficient against the steel counter surface of 1.1; this was reduced to 0.8 for high carbon-content films. Analysis of the tribofilm revealed formation of molybdenum oxide and amorphous carbon, however without significant lubricating effect at room temperature. Hardness and elastic modulus decrease with carbon content from ~29 to ~22 GPa and ~526 to ~326 GPa. These values give an H/E ratio of 0.06 to 0.07, indicating brittle material. Resistivity was found to increase with carbon content from ~175 μΩ cm for binary Mo-B to ~395 μΩ cm for Mo-B-C thin film with 37 at.% of C. Therefore all the above results suggest that the Mo-B-C films are not suitable for sliding electrical contacts.

1. Introduction

Transition metal diborides combine attractive properties which includes high hardness and wear resistance, high electrical conductivity and oxidation resistance [1,2]. The properties' enhancement can be further achieved if material is synthesized in the form of a thin film. Sputtered TiB_2 films have been observed to be were superhard with values more than twice that of the bulk crystal value, which was explained by Mayrhofer et al. [3], who attributed the hardening to (001)-textured TiB_2 grains surrounded by an amorphous tissue phase of boron. This tissue phase hinders dislocation movements, thus yielding the hardening. Recent studies of magnetron sputtered Nb-B and Cr-B films by Nedfors et al. have demonstrated the presence of such a boron tissue phase also in these materials systems, as well as a significant hardness increase compared to bulk materials [4,5]. We observed a similar behaviour in magnetron-sputtered Mo-B films [6]. Consequently, nano-sized diboride grains surrounded by a boron tissue phase seem to constitute the typical thin film microstructure for magnetron sputtered Me-B films.

A potential application for metal boride films is as sliding electric contacts, which require a low wear rate, a high electrical conductivity, a low contact resistance combined with a low friction coefficient. So far the limiting factor for magnetron sputtered metal diboride film applications as electric contacts – is the high friction coefficients (>0.5) which has been observed in several systems [5,7,8]. An exception is the Nb-B system where Nedfors et al. observed a friction coefficient of only 0.12 versus a steel counter surface, however these coatings also exhibited a high contact resistance due to their high hardness [4]. In our recent Mo-B study [6], we predicted, based on stability trends in the diborides, an extensive formation of molybdenum oxides, which potentially could reduce the friction in a tribocontact. An extensive molybdenum oxide formation was indeed observed but did not lead to reduced friction at room temperature in ambient environment.

An alternative approach is to tailor the properties by introducing a third element like carbon [5,8–11] or nitrogen [11–13]. In general the introduction of carbon or nitrogen to a material based on a metal diboride has led to a decrease in grain-size and eventually an amorphisation of the material. This has been coupled with a decrease in hardness [5,10–13]. The approach of studying increasing carbon content of coatings around the MeB_2-C tie line has been explored in several systems in connection with possible applications in electrical contacts:

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Nb-B-C [10] and Cr-B-C [5]. It was found that the ternary films exhibited a slightly lower hardness than the binary Me-B films but lower contact resistances and friction coefficients making them more suitable for a contact application. Also the Ti-B-C system has been studied with regards till electrical contact applications, but then the starting point was TiC and the tie-line TiC-TiB_2 was investigated [9]. The reduced friction coefficients for the Me-B-C films could be explained by the formation of a thicker a-BC_x tissue around the crystalline grains thereby softening the material (hardness ~20 GPa [14]), and increasing ductility, thus preventing brittle fracture and the formation of debris in the wear track [8,10]. Furthermore, carbon is well-known to be able to form lubricating tribolayers, which further can reduce the friction coefficients [8,9,15]. There are also some studies on thin films from the Mo-B-C system, however these have been centred on the ternary phase Mo_2BC, and thus not on studying the effect of carbon alloying on a MoB_2 material. Furthermore, the Mo_2BC phase is not on the tie-line MoB_2-C, and generally requires high substrate temperature (or an energetic process) to be formed [16–18]. At lower temperatures, amorphous or poorly crystalline coatings have been formed, in agreement with the other Me-B-C systems mentioned above [17,18].

In the present study the microstructure and properties of DC magnetron sputtered Mo-B-C thin films were investigated, and are presented together with data from previously deposited binary Mo-B coatings [6] in order to clearly demonstrate the effect of carbon alloying. The aim is to investigate if the added carbon can improve the tribological and mechanical properties (COF < 0.6 and H/E > 0.1) of the Mo-B films for a potential use as sliding electric contacts. Mo-B-C films were grown with varying carbon contents and at two different temperatures (300 °C and 600 °C), using a compound $MoB_{1.5}$ and a graphite targets. Structures, as well as mechanical and tribological properties of these materials, were evaluated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission and scanning electron microscopy (TEM and SEM), Raman spectroscopy, nanoindentation and tribological ball-on-disk tests. A single high temperature experiment was carried out in order to investigate the temperature effect to film structure and properties.

2. Experimental details

The Mo-B and Mo-B-C films were deposited by non-reactive DC-magnetron sputtering from circular targets (diameter 51 mm, thickness 3.2 mm): $MoB_{1.5}$ (stated composition of 2:1 could not be confirmed by our analysis of the target, nor the stated purity of 99.9%, see below) and C (stated purity 99.9%). XRD showed that the $MoB_{1.5}$ target consisted of the rhombohedral hR18-MoB_2 phase. However, elastic recoil detection analysis (ERDA) of the target showed B/Mo ratio ~1.5 (equivalent to 61 at.% of B). The ERDA analysis also showed that target contains carbon, oxygen and hydrogen, therefore it is assumed to originate from adsorption of water and other oxygen-containing species in pores as observed in SEM. The significant outgassing in the sputter chamber from a freshly mounted target supports this conclusion. All experiments were carried out after baking and outgassing of the targets and chamber. A DC-magnetron sputtering system (ultra-high vacuum chamber with base pressure $<1 \cdot 10^{-7}$ Pa) with a confocal sputter-down configuration with three targets and a target to substrate distance of 150 mm was used. The targets were mounted with 24° angle between substrate and target normal. The substrates were mounted on rotational table with integrated heater, preheated before deposition and kept at constant temperature of 300 °C, as measured by thermocouple (calibrated with optical pyrometer). To investigate if a full temperature study was called for, a single deposition at high temperature the substrates was conducted, in this case the substrates were kept at 600 °C. An Ar^+ plasma was ignited at 0.4 Pa, using a 42 sccm Ar gas flow. The $MoB_{1.5}$ target current was kept constant at 150 mA (yielding ~2.2 W/cm^2), while the C target current was varied between 0 and 250 mA (yielding 0 to ~8.5 W/cm^2) to attain the ternary alloys with different carbon content. Prior to deposition the substrates were plasma etched using a DC-bias of −300 V and plasma ignited on Mo target (stated purity 99.95%) which were run at 25 mA, thereafter a thin adhesion layer of Mo was deposited, by lowering the bias to −50 V and increasing the current on Mo target to 100 mA. All depositions were performed with a DC bias voltage of −50 V on the substrate table with low ion current (<0.2 mA/cm^2). Coatings were deposited simultaneously on Si(001), α-Al_2O_3(001) and 316L stainless steel substrates for structural properties (Si(001) 0.5 mm thick), stress measurements (Si(001) 0.3 mm thick); mechanical properties (α-Al_2O_3) and tribological (316L steel) analysis, respectively. To attain a coating thickness of around 1 μm the deposition time of the Mo-B-C coating was varied between 250 and 350 min. The binary Mo-B sample was studied in-depth and the results have been published in [6], but are included in this paper acting as a reference in order to reveal the effect of carbon alloying into the Mo-B system.

Sample compositions were determined by Time-of-Flight Energy ERDA (ToF-E-ERDA) experiments, performed at the Tandem Accelerator Laboratory at Uppsala University. Experiments were performed in a vacuum chamber at a base pressure of $<1 \cdot 10^{-4}$ Pa. 36 MeV $^{127}I^{8+}$ ions were used as primary projectiles. Scattered recoils were detected in an angle of 45° with respect to the primary beam, with both incidence and exit angle of beam and detected particles at 22.5° with respect to the sample surface. Further details on the detection systems can be found in Ref. [19]. Calculation of depth profiles from time-energy coincidence spectra of recoils was done using the CONTES program package [20].

The chemical bonding in the films was analysed with XPS using a Physical Electronics Quantum 2000 with monochromatic Al Kα radiation and a 45° photoelectron take-off angle. High resolution spectra were acquired on the surface (to analyse tribological behaviour) as well as after sputter-etching (1 keV Ar^+ ions for 10 min, yielding an approximate depth of 42 nm) to analyse the bulk of the coating material, i.e. below the surface oxidised region. The analysis region was 200 μm in diameter and the ion beam for sputter-etching was rastered over a 1 × 1 mm area. Compositional and chemical bonding analysis was carried out on coatings deposited on Si(001)-substrates.

For analysis of crystalline phases XRD was performed with a Philips X'Pert MRD diffractometer with Cu Kα radiation and parallel beam geometry using a Göbel mirror on the primary side and a parallel plate collimator with an 0.27° acceptance angle on the secondary side. Both θ/2θ and grazing incidence scans performed, the latter with a 2° incident angle. Peak positions and widths were determined by curve fitting of the peaks and measured full width at half maximum. Grain sizes were estimated using Scherrer's equation, assuming spherical grains [21]. Lattice parameters were determined using the observed (001) and (100) peaks, assuming a hexagonal crystal structure.

Coating morphology and wear were studied using a Zeiss Merlin SEM instrument. As-deposited samples on Si(001) were used to attain fractured cross-sections. Surface morphology as well as wear was studied on coatings deposited on steel substrates. In both cases in-lens detector and a 5 keV beam were used. EDX (energy dispersive X-ray spectroscopy) analysis was performed at 20 keV beam energy and collected with EDX X-Max 80 mm^2 Silicon Drift Detector with high sensitivity and analysed with AZtec (INCA energy) software for X-ray mapping and element analysis. Raman spectroscopy was carried out with Renishaw Invia Raman spectrometer equipped with 532 nm laser to identify Raman-active phases at the surface of the films. Raman spectra were normalised according to the highest intensity in each spectrum.

Electron transparent cross-section TEM samples were prepared from as-grown films using the traditional "sandwich" method. The films were cut into small pieces, mounted into a Ti grid, glued with a high temperature glue (Gatan G-1 epoxy) and polished to a thickness of approximately 50 μm. Ar^+ ion milling followed with 5 keV and 2 keV (to minimize the damage) ion energy at a 5° milling angle from both sides in a Gatan precision ion polishing system (PIPS). TEM images