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Reduction of the coefficient of friction of niobium nitride coatings by the addition of bismuth

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Composite coatings of niobium nitride containing bismuth inclusions were deposited using a dual magnetron sputtering system with independent power suppliers for each targets; Bi and Nb. The deposition was performed under and Ar/N_2 atmosphere at a 2.3 flow rate ratio, which allows the stoichiometric NbN phase to be obtained. The aim of this work was to evaluate the effect of increasing concentrations of Bi, proposed as a lubricous second phase, in the structural, mechanical and tribological properties of niobium nitride (NbN) coatings, searching for a reduction in the coefficient of friction but trying to keep hardness values larger than the tool steels (>10 GPa). The power applied to the Nb target was fixed, while the power on the Bi target was increased; obtaining Bi atomic percentage values of 1.7, 4.9 and 8.4 at%. The Bi inclusions showed different sizes and distribution in the volume and surface of the coatings. The results indicated a reduction in the hardness from 30 GPa of the NbN coating to 13.9 GPa for the highest Bi concentration. However, a more significant reduction was observed for the coefficient of friction (CoF) from 0.8 of the NbN to 0.3 for Bi concentrations between 4.9 and 8.4 at%.

1. Introduction

Niobium nitride (NbN) is a hard coating which has been proposed as a candidate for protective tool steels since there is a good matching between the thermal expansion coefficients of the substrate and the NbN; it also present high chemical resistance and high melting point [1–3]. NbN thin films with compositions around 1:1 (Nb:N) have different crystalline phases; one face centered cubic (fcc) phases δ-NbN and three hexagonal phases (δ′-NbN, ε−NbN and η−NbN) [4–6]. For sputtering deposition, it has been shown that the structure and properties strongly depend on the synthesis conditions, such as the N_2 flow rate. Generally, the hexagonal δ′-NbN is harder than the δ-NbN cubic structure. The hardness of the NbN coatings has been reported between 25 and 35 GPa for the δ-NbN [7–10] and around 40 GPa for δ′-NbN [11–13]. However, very few have been studied about its tribological properties; friction and wear. The reported coefficients of frictions (CoF) are relatively high to mitigate the friction consequences. Havey et al. [7] and Zhang et al. [14] showed that the CoF of NbN against Si_3N_4 and WC was 0.6 and 0.75, respectively.

In order to improve the tribological performance of hard coatings, the production of nanocomposites [15,16] or the “chamaleon” structure [17,18] have been proposed. The nanocomposites consisting of at least two separate phases with one being nanocrystalline or amorphous phase have been used to enhanced hardness [11,19], while the addition of a soft metal or a lubricous second phase into the hard matrix have been suggested for tribological applications [20]. Good tribological performance requires a wear resistant hard matrix, such as the metal nitrides or carbides, with a lubricous solid. Solid lubricants must fulfill three conditions: low shear in the sliding direction, high compression strength in the direction of the load and good adhesion to the substrate [21,22]. Covalently bonded lamellar structures, such as graphite and MoS_2 fulfilled the first two conditions and so are widely used as solid

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lubricants [22]. Other group of solid lubricants is constituted by some soft metals, due to the low shear strength and high plasticity, such as Pb, Sn, Bi, Cd, In, Cu and Ag. These metals and their alloys are used as the overlay material in engine bearings [23]; however, as a result of new regulations and also the general environmental awareness to eliminate the use of toxic metals (Pb, Cd), new compounds are constantly investigated. Bismuth is considered as a green metal [24,25] that besides the low shear strength has a semi-layered structure [26], which makes it attractive as a solid lubricant [27]. Nevertheless, it has not been deeply investigated and definitely not as an addition in hard coatings, one possible disadvantage is the low melting point of metallic bismuth (270 °C).

Nanocomposites films based on NbN and a lubricous second phase have been performed by few authors [14,28,29]. Stone et al. [28] reported the synthesis and tribological evaluation of NbN–Ag nanocomposite coatings, and these had reduced CoFs between 0.2 and 0.4. Also, they proposed the addition of MoS_2 to NbN–Ag composite coatings [28]; the results indicated a reduction in the CoF only at high temperatures (0.05 at 750 °C). Ezirmik and Rouhi [29] produced coatings of NbN–Cu with different copper contents, but the CoF did not change in comparison to the NbN coefficient.

The proposal of this work was to study the effects of the addition of bismuth as the second phase in a NbN matrix, on the mechanical and tribological properties. To date the combination of these materials has not been studied, so it was necessary to define suitable deposition conditions to achieve stable and adherent coatings. This paper reports the deposition, structural changes and the evaluation of the hardness and CoF of niobium nitride films with bismuth inclusions; three different Bi concentrations were tested.

2. Experimental procedure

The NbN–Bi composites coatings were deposited on both silicon substrates (100) and disks of polished M2 steel using a co-sputtering system containing two balanced magnetrons. The 5 cm targets were of Nb (99.95% purity) and Bi (99.999% purity). The system base pressure was $<6 \times 10^{-4}$ Pa and the working pressure was 0.4 Pa. A direct current, DC, power of 400 W was applied to the Nb target, and a variable radio frequency (RF) power of 6, 10 and 20 W was applied to the Bi target. The deposition atmosphere was a mixture of Ar (99.95% purity) and N2 (99.99% purity), at flow rates of 14 standard cubic centimeters per minute (sccm) and 6 sccm, respectively. Both plasmas were operated simultaneously; however, the M2 steel substrates were initially coated with a 150 nm Nb interface layer in order to enhance the coating-substrate adhesion. The substrates were pre-heated to 200 °C for 30 min on an 8 cm diameter rotating substrate holder at a speed of 0.5 Hz. Deposition times of 15 and 60 min were used to obtain different film thicknesses for the different tests. The thickness of the coatings was measured using a Veeco Dektak 150 profilometer.

The characterization of the crystalline structure was performed by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer (CuKα 1.5406 Å) in the Bragg Brentano scan configuration and θ-2θ mode from 20 to 60°. The surface morphology and the composition of the coatings were observed using a JEOL7600F Field Emission-Scanning Electron Microscope (FE-SEM) with 2 kV of acceleration voltage, and with a coupled Oxford INCAX-ACT Energy Dispersive X-ray Spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) was performed using a VG Microtech Multilab ESCA 2000 spectrometer with CLAM MCD detector, under a vacuum better than 5×10^{-7} Pa, using Al Kα ($h\nu = 1453.6$ eV) radiation and constant pass energy 50 and 20 eV for the acquisition of the normal and high resolution spectra, respectively. Ar-ion etch cleaning of the coatings was not performed because problems with the ion gun. However, the main purpose of the XPS analysis was to observe possible bonding between Bi and Nb or Bi and N, which have not been reported, as well as possible segregation of Bi into a surface layer, as has been observed for silver containing coatings [30].

The hardness and elastic modulus of the coatings were evaluated by nanoindentation using a CSM Instrument model TTX nanoindentator with a Berkovich-type pyramidal diamond tip. For each sample, six measurements were carried out, and the maximum load was chosen such that the penetration depth was <10% of the coatings thickness [31]; the load range was between 1.5 and 4 mN. The hardness was calculated using the Oliver-Pharr model [32] and 10 indentation were done for each sample. The statistical analysis applied was the Kurskall-Wallis approach, with a previous evaluation by the Shapiro–Wilk test, which determined that data distribution was not normal, so non-parametrical probes were used. The CoF of the grown coatings on M2 steel was measured using a CSM Instrument pin-on-disc tribometer with 6 mm diameter Al_2O_3 balls. Tribological tests were carried out using 5 N load, using a linear speed of 0.5 m/s and 500 m of sliding distance at room temperature. For each sample; NbN, NbN–Bi6W, NbN–Bi10W and NbN–Bi20W, the CoF was measured in three different samples in order to verify the reproducibility of the test. The wear tracks after the pin-on-disk tests were observed by 3D optical microscope and measured using an optical profilometer.

3. Results and discussion

3.1. Composition and morphology

Fig. 1 shows, as an example, the XPS spectrum of the NbN–Bi20W coating, where the presence of the bismuth is clear, in addition to the nitrogen and niobium. There is also oxygen and considerable carbon signal which is characteristic of unclean surfaces. The high resolution scans were recorded and analysed on the areas around the peaks of N 1s, Bi 4f, Nb 3d and O 1s in all samples. The Bi 4f peak deconvolution for the three different samples (Bi rf-powers 6 W, 10 W and 20 W) are shown in Fig. 2a. Each spectrum was deconvoluted into four Gaussians centred at 158.9 eV (Bi $4f_{7/2}$) and 164.2 eV (Bi $4f_{5/2}$) characteristic to Bi^{3+} related with Bi_2O_3, and the binding energies assigned to metallic bismuth Bi° (ref. 16) were found at 156.5 eV (Bi $4f_{7/2}$) and 161.8 eV (Bi $4f_{5/2}$). The intensity of both Bi photoelectron signals increased continuously as the Bi

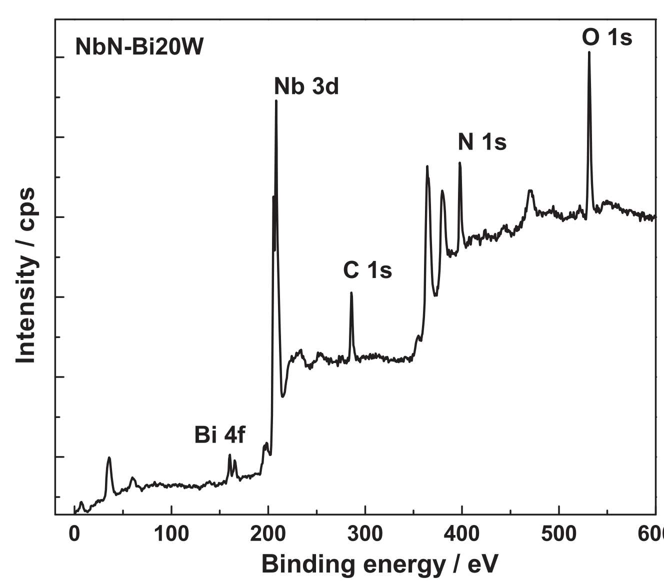

Fig. 1. Survey scan of the NbN–Bi coating deposited using 20 W at the Bi target.