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Tool steel coatings based on niobium carbide and carbonitride compounds

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ABSTRACT

Although Physical Vapor Deposition (PVD) is extremely versatile in the palette of coating materials and substrates to which it can be applied, many potentially viable hard coating materials have yet to be explored for deposition on tool steels via PVD processing. Here one family of such coatings is explored: the niobium carbide and carbonitride system. By changing process variables, including bias voltage and working pressure, evaluating the mechanical properties through nanoindentation and correlating the results to microstructural observations by transmission electron microscopy, a preliminary survey of these coating materials and the preferred conditions for their production is presented. Under some conditions of deposition bias and pressure, niobium carbide can be produced with hardness and elastic modulus superior to titanium nitride films, reaching up to 37 GPa and 400 GPa, respectively, for coatings produced under deposition conditions that reduce intrinsic porosity. Nitrogen substitution for carbon leads to intermediate carbonitride compositions with mechanical properties that depend roughly linearly on composition, permitting a degree of tunability of the coating properties.

1. Introduction

Since the 1960s, hard coatings have been applied to reduce wear and improve friction characteristics of tool steels, especially in, e.g., cutting tools [1]. Due to its high hardness, one of the first compounds used in such applications was titanium carbide. TiC was first applied by Chemical Vapor Deposition, CVD [2,3], although the high temperature of this process proved unsuitable for many steel substrates, restricting its application mainly to solid carbide tools. Physical Vapor Deposition (PVD) was developed as an effective way to reduce the processing temperature to less than 550 °C, enabling coatings on high alloy steels [4–6]. In the PVD chamber, nitriding reactions are induced more easily than are carburizing reactions, so nitrides gradually replaced carbides, with titanium nitride (TiN) being the most widely used compound [7] due to its similarity to TiC. Today PVD TiN compounds are often modified with Al to increase thermal stability [7]. In fact, due to the large number of studies on TiN or TiAlN coatings and their extensive use in industry for tool steels applied to cutting or forming tools [8], these compounds are used as a baseline reference for the results of the present paper.

As a result of the above trend, most of the literature on PVD coatings over tool steels is directed at the study of nitrides, with the number of studies on carbides being much smaller. However, based on the requirements of hard coatings (high strength and thermal stability) [9], there are a number of carbide systems that seem potentially suitable even though they have not been widely studied as yet. Examples of specific interest to the present work are niobium carbide and niobium carbonitride. NbC seems a natural candidate hard coating material, since as a bulk compound it exhibits a hardness beyond 20 GPa and a melting point above 3000 °C [10]. NbN exhibits full mutual solubility in NbC [11], so a wide range of carbonitride materials could also be fashioned within this family. This could permit, e.g., tuning of toughness, thermal expansion coefficient and other secondary properties needed for high performance applications.

Despite these generally positive expectations for NbC and NbCN as potential coating materials, to the authors' knowledge there are no systematic reports in the literature on the effect of processing parameters upon even the most basic of mechanical properties of such materials produced by sputtering PVD, such as, e.g., hardness and elastic modulus. One report in this sense is on vacuum cathode arc deposition of NbC [12], showing exceptional properties, with hardness values above 40 GPa. For mechanical properties of sputtered NbC coatings, only one reference was found [13], but the hardness values obtained were below 25 GPa, which is below the hardness of traditional TiN sputtered coatings (~30 GPa) applied to tool steels; we are also not aware of published results on the mechanical properties of niobium carbonitride coatings applied specifically to tool steels.

The purpose of the present paper is therefore to present a study on the fabrication, mechanical properties and microstructure of niobium carbide and carbonitride coatings on H13 hot work tool steel, produced by PVD using direct sputtering of NbC and reactive sputtering with N_2 atmospheres. Beginning with studies on binary NbC, traditional PVD variables such as the deposition pressure and bias are changed to

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evaluate their effect on hardness and microstructure. Subsequently, nitrogen is introduced and nitrogen content is used to tailor the coating structure and properties. For the preferred conditions, we identify coatings with hardness and elastic modulus values either similar to or higher than those of conventional TiN. By using transmission electron microscopy, these properties are correlated to the films' microstructure.

2. Experimental details

PVD films were produced by magnetron sputtering, in a system from AJA International (ATC 2000 UHV), with balanced design. This system operates via co-sputtering with up to 6 targets, with 2 targets being used in the present paper: NbC, sputtered under radio frequency (RF) conditions due to its non-conductive and brittle behavior, and metallic Nb, sputtered with direct current (DC). The targets, of 50.4 mm diameter, are placed with a focusing arrangement, with the substrates located at the focal point and rotating at 15 rpm. The distance from target to substrate was maintained at approximately 200 mm.

A base pressure of less than 3.10^{-5} Pa (2.10^{-7} Torr) and working pressures of 0.40 Pa and 0.67 Pa (3 and 5 mTorr) were employed; throughout the text, working pressure refers to the total pressure in the chamber. Ar was the main process gas, but N_2 was also used for the carbonitride compositions. The system substrate bias was varied between 0 and 150 V. All depositions were conducted using a 400 °C substrate temperature, as measured by a k-type thermocouple in contact with the sample holder; temperature was constant throughout the process, with variation of less than 0.5 °C.

Direct sputtering from a NbC target (99.5% pure) was used for both the NbC and NbCN coatings, with the N additions effected by sputtering under a N_2-rich atmosphere, with the following conditions: NbC sputtering under 0.08 Pa N_2 partial pressure (20% of total pressure) and simultaneous sputtering of NbC and metallic Nb (99.9% pure) targets, under the same N_2 atmosphere. For the NbN, traditional reactive Nb sputtering under N_2 was used, with 0.07 Pa partial pressure of N_2. The details for all conditions are given in Table 1. Before sputtering, substrates were polished down to 1 μm with diamond media, leading to Ra roughness of about 0.02 mm. Before sputtering, samples were cleaned in acetone, dried with nitrogen and plasma cleaned using 25 W and 150 V bias for 10 min. Due to the low deposition rate (of about 100 nm/h), the sputtering time was between 4 and 5 h for each condition. This slower deposition process is related to the confocal arrangement and also to the small target diameter and sputtering power. However, it is important to mention that the AES results showed no important contaminants, such as oxygen or other gases, during such long deposition times. After sputtering, the thickness of all coatings was measured to be around 400 nm, the only notable exception being the 0 V bias NbC film with a thickness of about 700 nm.

All films were deposited on glass and on H13 tool steel substrates. The tool steel samples were heat treated before deposition, through hardening at 1020 °C and double tempering at 600 °C for 2 h each, leading to a hardness of 45 HRC. This procedure is common for hot work tool steels [13], and leads to a stable dispersion of secondary hardening carbides that only show extensive coarsening and hardness loss at temperatures above 600 °C [14].

Mechanical properties were characterized by nanoindentation, using a Hysitron nanoindenter with a Berkovich tip. The same tip was used for all experiments, with an area function carefully calibrated for indentation depths between 20 and 80 nm; the error in relation to the fused silica calibration standard was below 5% in terms of hardness and modulus, as can be observed in Fig. 1. These low indentation depths were used to preserve the accuracy of hardness and modulus measurements, as the thickness of the coatings varied between 300 and 600 nm. Therefore, indentation depths between 30 and 50 nm were used in all experiments to ensure a bulk measurement free of interference from the substrate. The indentation load was adjusted (between 600 and 3000 μN) to achieve these depths depending upon the coating hardness. The same nanoindenter was used to determine surface roughness in scanning contact-imaging mode.

Phase characterization was performed initially by X-ray diffraction (XRD) using a Rigaku H3R Cu-source Powder Diffractometer, operating at 50 kV and 200 mA with Cu Kα radiation. A scatter slit and divergence slit of 0.5° were used to concentrate the diffraction beam on the small samples (about 1 cm^2) and to increase the signal/noise ratio respectively. All patterns were then analyzed using Rietveld refinement, leading to precision on lattice parameters (a) better than 0.0005 nm. This accuracy level was obtained by the use of an external standard Si powder sample and also by the use of substrate iron peaks as an internal standard. Differences in lattice parameter (Δa) were used to calculate the residual elastic macro strain via Hooke's law for a state of plane stress: $\sigma = -E \cdot \varepsilon / (2\upsilon)$, where E is the Young's modulus, $\varepsilon = \Delta a / a_0$ the residual strain calculated with respect to the lattice parameter of NbC, $a_0 = 0.447$ nm [15,16], and $\upsilon = 0.235$ [17] the Poisson ratio for NbC. This method was preferred to the sine-square psi traditional XRD method, due to the low intensity in high angle reflections and considerable broadening observed in many of the conditions. The method has been previously validated for coatings [18] when the stress-free compound lattice parameter is known and the sample lattice constant is determined with high accuracy. In the present case, both conditions were satisfied, with the lattice constant for NbC calculated from sources of high quality with variation between them less than 0.00006 nm [15,16].

The XRD data were also used to estimate the C to N ratio in Nb(C,N) films based on the lattice parameter (determined by Rietveld refinement) and Vegard's law, with an apparent accuracy better than 0.001 nm. The Vegard reference relationship for this calculation is based on patterns of high quality for the pure NbC [15,16] and NbN [19–21] compounds and three indexed patterns for intermediary $NbC_{0.5}N_{0.5}$ (average of literature determinations [22,23]). We note that most of the available powder diffraction files for NbN represent a stoichiometry of $NbN_{0.9}$, but here the ideal 1:1 ratio was assumed. This indirect, structural means of determining N content was also augmented with results from Auger Electron Spectroscopy (AES), Physical Electronics Model 700 Scanning Auger Nanoprobe (LS). The N content calculated by XRD and AES was in agreement, as presented in Table 1.

The results of hardness and residual stresses were correlated to sample surface topography by analyzing the as-coated surfaces under a field emission scanning electron microscope (SEM), Zeiss Nvision 40. This apparatus has also a focused ion beam (FIB) source, with Ga+

Table 1
Conditions used to produce the various compositions of $NbC_{(1-x)}N_x$ coatings. The errors for both methods of nitrogen content determination are around 15% of measured values, calculated from the Rietveld error on the lattice parameter determination or by the AES analysis uncertainty.

Designation	Sputtering conditions (targets, power, time)	N partial pressure (Pa)	x calculated by XRD	x measured by AES	Bias and total pressure
NbC	NbC: RF 200 W, 5 h	–	–	–	Low: 0 V, 0.40 Pa High: 70 V, 0.67 Pa
$NbC_{0.6}N_{0.4}$	NbC: RF 200 W, 3 h	0.08	0.40	0.35	Low: 0 V, 0.40 Pa High: 70 V, 0.67 Pa
$NbC_{0.4}N_{0.6}$	NbC: RF 200 W, 3 h Nb: DC 250 W, 3 h	0.08	0.61	0.56	Low: 0 V, 0.40 Pa
NbN	Nb: DC 250 W, 1 h	0.07	–	–	Low: 0 V, 0.40 Pa High: 150 V, 0.40 Pa