

# The structure and mechanical and tribological properties of TiBCN nanocomposite coatings

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Received 28 June 2009; received in revised form 19 October 2009; accepted 30 October 2009

Available online 11 December 2009

## Abstract

TiBCN nanocomposite coatings were deposited in a closed field unbalanced magnetron sputtering system using pulsed magnetron sputtering of a TiBC compound target with various Ar/N<sub>2</sub> mixtures. TiBCN coatings were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, nanoindentation, Rockwell C indentation and ball-on-disk wear tests. The coatings with a nitrogen content of less than 8 at.% exhibited superhardness values in the range of 44–49 GPa, but also showed poor adhesion and low wear resistance. Improvements in the coating adhesion, *H/E* ratio and wear resistance were achieved together with a decrease in the coating hardness to 35–45 GPa as the N content in the coatings was increased from 8 to 15 at.%. The microstructure of the coatings changed from a nano-columnar to a nanocomposite structure in which 5–8 nm nanocrystalline Ti(B,C) and Ti(N,C) compounds were embedded in an amorphous matrix consisting of BN, free carbon and CN phases. With a further increase in the N content in the coatings to levels greater than 20 at.%, the inter-particle spacing of the nanocrystalline compounds increased significantly due to the formation of a large amount of the amorphous BN phase, which also led to low hardness and poor wear resistance of the TiBCN coatings.

Published by Elsevier Ltd. on behalf of Acta Materialia Inc.

**Keywords:** TiBCN coating; Nanocomposite coating; Nanocrystalline coating; Pulsed magnetron sputtering; Wear

## 1. Introduction

The development of nanostructured nanocomposite coatings over the past decade has resulted in considerable improvements in comparison to traditional monolithic hard transition metal nitride coatings (TiN, CrN, TiAlN, etc.) in terms of their increased hardness, chemical inertness, and good thermal stability, which make these new coatings suitable for machining and metal-forming tools and for wear resistance applications [1–3]. Nanocomposite coatings can be used to combine nanometer-scale multicomponents,

including nanocrystalline and amorphous phases selected from various nitrides, carbides, borides, and silicides that may be engineered to provide a range of microstructures and physical and chemical properties in an effort to achieve multifunctional properties that are normally difficult to be obtained from conventional single-phase coatings. The strong interfaces between nanocrystalline and amorphous phases can increase the interface cohesive energy and therefore effectively restrain grain boundary sliding when the nanocrystallite size is less than 10 nm [4], thereby inhibiting the inverse Hall–Petch effect [5]. In this regard, superhard and ultrahard nanocomposite coatings with hardness values above 40 and 80 GPa, respectively, have been produced depending on the structural design and grain size control of the specific coating systems, e.g. TiSiN [6], TiSiB [7], TiBN [8], WC/DLC [9], CrSiN [10].

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The TiBN system is a promising nanocomposite coating that exhibits superhardness, coupled with high oxidation and corrosion resistance. This unusual combination of properties has been achieved by forming thermodynamically stable TiN, TiB<sub>2</sub> and other boride phases in an amorphous matrix [11–14]. However, high coefficient of friction (COF) values (0.7–0.9) of the TiBN coating sliding against various materials have been reported. For tribological applications, it is critical to decrease the COF while maintaining the strength and hardness of the coatings.

The COF largely depends on the selection and distribution of the phase compositions in the coating architecture as well as the counterpart material against which the COF of the coating is being measured. Since various carbides, silicides and amorphous phases in general exhibit lower sliding coefficients than nitrides, carefully adding optimized levels of C, S, B, and Si in the coating has resulted in a reduction of the COF and an increase in the wear resistance by forming low friction phases (e.g. a-C, a-Si<sub>3</sub>N<sub>4</sub>, a-BN, a-CN, WS<sub>2</sub>, MoS<sub>2</sub>) or layers due to tribochemical reactions that take place during sliding [15,16].

In this regard, TiCN and TiBC coatings have been widely studied in an effort to decrease the COF, and it was found that the COF strongly depended on the amount of C in the film [17–19]. However, an excessive addition of C will also lead to a reduction in the hardness and oxidation resistance of the coatings. Therefore, it was predicted that the formation of an optimized TiBCN nanocomposite coating would have considerable potential in providing a favorable combination of high hardness and good wear and oxidation resistance. Moreover, while the traditional development of hard tribological coatings has focused on maximizing hardness and strength, e.g. for cutting tools, most coating tribological applications require or would receive significant benefit from increased toughness [20].

Early work on sputtered TiBCN coatings were focused either on sputtering of a TiB<sub>2</sub> target in methane and nitrogen [21–23] or on sputtering a compound target with different mole fractions of TiB<sub>2</sub> and TiC in an Ar/N<sub>2</sub> mixture [18,24,25]. However, relatively few papers have provided a detailed study of the influence of chemical composition, phase content, and coating microstructure on the mechanical and tribological behavior of TiBCN coatings.

In the present study, the focus of attention has been on the reactive sputtering TiBCN nanocomposite coatings from a TiBC compound target with a TiB<sub>2</sub> to TiC mole fraction ratio of 80:20 in various Ar/N<sub>2</sub> gas mixtures. The N content was varied in an effort to produce different phases and microstructures of the coatings using a pulsed closed field unbalanced magnetron sputtering (P-CFUBMS) system. The relationship between the microstructure, mechanical and tribological properties of TiBCN coatings was investigated in an effort to understand how to optimize the volume fractions of the nanocrystalline and amorphous phases by controlling the N content to achieve a combination of high hardness and good wear resistance.

## 2. Experimental details

TiBCN coatings were deposited in a P-CFUBMS system equipped with four rectangular unbalanced magnetrons (320 mm × 127 mm). A schematic diagram and detailed description of the system were reported in an earlier publication [26]. A TiBC compound target with a TiB<sub>2</sub>:TiC mole fraction ratio of 80:20 had been synthesized by the self-propagating high-temperature synthesis technique [27] using Ti, B, C powders. The pulsed DC power was provided by an Advanced Energy 5 kW Pinnacle Plus power supply.

AISI 304 stainless steel coupons (76 mm × 25 mm × 1 mm) and (1 0 0) silicon wafers were used as the substrates, which were ultrasonically cleaned in acetone and ethylene for 15 min, respectively. The substrates were mounted on a substrate holder and installed at a distance of 127 mm from the target. A base pressure of less than  $1 \times 10^{-4}$  Pa was reached prior to all coating depositions. The substrates were DC sputter-etched by Ar plasma bombardment at a bias voltage of –400 V to remove the surface contaminants. Prior to the TiBCN coating deposition, a thin Cr adhesion layer was first deposited by sputtering from a Cr target using a  $5.7 \text{ W cm}^{-2}$  target power density and a –50 V DC substrate bias. Subsequently, the TiBCN coatings, with a thickness of 2–3 μm, were deposited in various Ar/N<sub>2</sub> mixtures using a target power density of  $5.7 \text{ W cm}^{-2}$ . The pulsed voltage applied to the target was in an asymmetric pulse shape with a frequency of 100 kHz and a duty cycle of 50% (the duty cycle is defined as the negative pulse time divided by the time of the pulsing cycle). During coating depositions, the total gas flow was maintained constant at  $20 \pm 1$  sccm together with a fixed pumping speed to achieve a constant working pressure of 0.27 Pa. The flow of N<sub>2</sub> was increased from 0 to 7 sccm with simultaneous changes in the Ar flow controlled by the MKS 146C vacuum gauge measurement system together with separate MKS 100 sccm mass flow controllers. The deposition temperature was measured to be about 250 °C. A DC substrate bias of –50 V was used for all depositions.

X-ray photoelectron spectroscopy (XPS) (PHI model 5600LS) using an Al K $\alpha$  X-ray source (13 kV and 15 mA) was used to investigate the chemical composition and state of each component in the coatings. The crystal structure of the coatings was characterized using monochromatic Cu K $\alpha$  radiation on a Siemens X-ray diffractometer (Model Kristalloflex-810) operated at 30 kV and 20 mA. Cross-sectional TEM samples were prepared by gluing two coated Si wafers face to face into a “sandwich”, which was then polished down to 20–30 μm using the conventional “tripod” grinding method followed by Ar<sup>+</sup> ion milling to electron transparency (Gatan Duo-mill). A Philips/FEI CM200 transmission electron microscope (TEM) operated at 200 kV was used to examine the coating microstructure.

The hardness and Young’s modulus of the TiBCN coatings were determined using nanoindentation. The measure-

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