Available online at www.sciencedirect.com
ScienceDirect
Surface & Coatings Technology 202 (2008) 4011 – 4018
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Tribological behaviour of titanium carbide/amorphous carbon nanocomposite coatings: From macro to the micro-scale

J.C. Sánchez-López *, D. Martínez-Martínez [1], C. López-Cartes, A. Fernández

Instituto de Ciencia de Materiales de Sevilla, CSIC-Universidad de Sevilla, Avda. Américo Vespucio 49, 41092-Sevilla, Spain

Received 1 October 2007; accepted 12 February 2008
Available online 10 March 2008

Abstract

The tribological behaviour of nanocomposite coatings made of nanocrystalline metal carbides and amorphous carbon (a-C) prepared by PVD/CVD techniques is found to be very dependant on the film deposition technique, synthesis conditions and testing parameters. Focusing in the TiC/amorphous carbon-based nanostructured system, this paper is devoted to an assessment of the factors governing the tribological performance of this family of nanocomposites using a series of TiC/a-C films prepared by magnetron sputtering technique varying the power applied to each target (titanium or graphite) as model system to establish correlations between film microstructure and chemical compositions and tribological properties measured by a pin-on-disk tribometer. The film microstructure goes from a quasi-polycrystalline TiC to a nanocomposite formed by nanocrystals of TiC embedded in an amorphous carbon matrix as observed by transmission electron microscopy (TEM). The nanocrystalline/amorphous ratio appears to be the key-parameter to control the tribological properties and its quantification has been done by electron energy-loss spectroscopy (EELS). A significant change in the tribological performance is observed for nanocomposites with amorphous carbon phase contents above 60–65%. The friction coefficient decreases from 0.3 to 0.1 and the film wear rates by a factor of 10. Examination of the wear scars on ball and film surfaces by laser micro-Raman spectroscopy has allowed to determine the presence of metallic oxides and carbonaceous compounds responsible of the observed friction behaviour. The revision of the literature results in view of the conclusions obtained enabled to explain their apparent dispersion in the tribological performance.

Keywords: Nanocomposites; Wear; Tribology; Friction; a-C; TiC

1. Introduction

The development of multilayered and nanocomposite heterostructures allows tailoring material properties to a specific desired value by superlattice and grain size effects. In the field of protective coatings, superior mechanical properties have been reported in the last decade for systems combining various transition metal nitrides in nanostructured form (e.g. nc-TiN/a-Si_3N_4, nc-TiN/a-Si_3N_4/a- and nc-$TiSi_2$, nc-$(Ti_{1-x}Al_x)N$/a-Si_3N_4, nc-TiN/TiB_2, nc-TiN/BN, etc. [1–9]) displaying hardness values ranging from 40 to 60 GPa with excellent thermal resistance. These materials are excellent candidates for protective applications as cutting or drilling tools; however, for tribological applications other properties as low friction, wear resistance, toughness or load capacity are also needed in order to prevent the brittle fracture or delamination of the coating under severe conditions. One way to improve composite toughness is to combine the hard nanocrystalline phase with a soft matrix as TiC/a-C [10], ZrN/Cu [11] or ZrO_2/Cu [12]. This design maintains the crystallite size of the hard phase at the nanometric level (5–20 nm) to guarantee hardness separated by a second soft phase of several tens of nm of thickness that provides ductility. This configuration shows a large volume of grain boundaries which restricts initial crack sizes and helps to deflect and terminate growing cracks. Also the presence of an amorphous boundary phase facilitates grain boundary sliding introducing ductility and preventing fracture under severe load conditions. If this soft matrix has good tribological properties we can obtain simultaneously a continuous supply of lubricant at the contact increasing the tribo-mechanical performance in dry lubricated conditions. Voevodin et al. (2000) prepared a

* Corresponding author. Tel.: +34 954 48 95 79; fax: +34 954 46 06 65.
E-mail address: jcslopez@icmse.csic.es (J.C. Sánchez-López).
[1] Current address: Université libre de Bruxelles, Chemicals and Materials Department, Faculty of Applied Science, CP165/63, avenue F.D. Roosevelt 50, 1050, Brussels.

0257-8972/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2008.02.012

TiC/DLC nanocomposite which showed a pseudoplastic behaviour when dragging its surface with a diamond tip of 0.2 mm radius loaded with 50 N (contact stress ~7 GPa) [13]. Also, the observation of the cracks by high resolution scanning electron microscopy revealed that sliding cavitation were maintained in the nanometric regime due to the reduced size of the grains and enhanced mobility of boundaries. Many groups have later synthesised TiC/C tough composites for tribological applications [14–20] although the correlation of the friction properties with their chemical composition is quite unclear. Thus, for instance, Gulbinski et al. [15] finds friction a variation from 0.6 to 0.1 when total carbon content increases with a plateau around 0.45 for medium contents. Stuber and co-workers [16] sees no differences between TiC/C composites prepared with carbon content of 30 or 50% (average friction ~0.45) while a sample with a ratio 70%(TiC):30%(C) exhibits value below 0.1. Other authors expressed the friction values as a function of the titanium content [17,18]. It is observed that friction below 0.3 are achieved when at. Ti % is below 45. Higher incorporation of titanium led to a sharp increase to 0.6 mean values. This lack of correlation could be partially attributed to the employment of different deposition techniques and synthesis conditions together with the difficulties inherent to the evaluation of tribological properties which are controlled by a nonlinear interaction of several different parameters. Also, the different way of displaying the friction properties in respect to the chemical composition does not help to compare the data among different works. The main motivation of this paper is to understand the tribological behaviour of this type of nanocomposites by the establishment of correlation between phase composition, film microstructure and tribological properties. To achieve this goal a family of TiC/a-C coatings has been prepared by magnetron sputtering with controlled chemical composition and microstructure that serves as base material to propose a friction mechanism that can be extrapolated to explain the reported literature data.

2. Experimental details

TiC/a-C nanocomposite coatings were prepared by Ar^+ sputtering of Ti (Goodfellow, 99.99% purity) and graphite targets. The magnetron sources were d.c. (graphite) and r.f. (Ti) working at sputtering power ratios (SPR), defined as the ratio of sputtering power applied to graphite target in respect to Ti one, from 1 to 4. The pressure of the vacuum chamber was measured before deposition in 6.5×10^{-4} Pa and 0.75 Pa while growing. The substrate were mounted in a rotary sample-holder (10 rpm) to ensure homogeneity and the temperature was found to vary in the range of 150–200 °C under the effect of the plasma. No additional heating or biasing of the substrate was done. Further experimental details concerning the synthesis conditions can be found in reference [21]. The crystal structure of the films was examined by X-ray diffraction analysis (XRD) at a low incidence angle of 1° in order to increase the signal from the coating compared with the substrate. Transmission electron microscopy (TEM) observation of the samples coupled with electron energy-loss spectroscopy (EELS) analysis were carried out in a Philips CM200 microscope operating at 200 kV and equipped with a parallel detection EELS spectrometer from Gatan (766–2 kV). The C K-edge was recorded in the diffraction mode with a camera length of 470 mm and a 2 mm-spectrometer entrance aperture yielded an energy resolution at the zero-loss peak of 1.4 eV. Tribological tests were carried out using 6 mm-diameter 100Cr6 steel balls in a pin-on-disk CSM tribometer with a sliding speed of 10 cm/s and 5 N of applied load in ambient air (30–60% of relative humidity). Normalized wear rates of the coatings ($mm^3\ N^{-1}\ m^{-1}$) were evaluated from cross sectional profiles taken across the disk wear track after testing by means of stylus profilometry. Micro-Raman measurements were performed using a LabRAM Jobin Yvon spectrometer equipped with a microscope. Laser radiation ($\lambda=532$ nm) was used as excitation source at 5 mW. All measurements were recorded under the same conditions (10 s of integration time and 10 accumulations) using a 100× magnification objective and a 100 μm pinhole.

3. Results and discussion

In a previous work [21] we have shown the preparation of nc-TiC/a-C by changing the sputtering power ratio applied to two targets (carbon and titanium). Varying this parameter from 1 to 4 (i.e. SPR = 4 means power applied to C target is four times that of Ti) we could obtain film microstructures going from densely packed crystals, with a thin separation among them, to small spherical grains randomly distributed in an amorphous

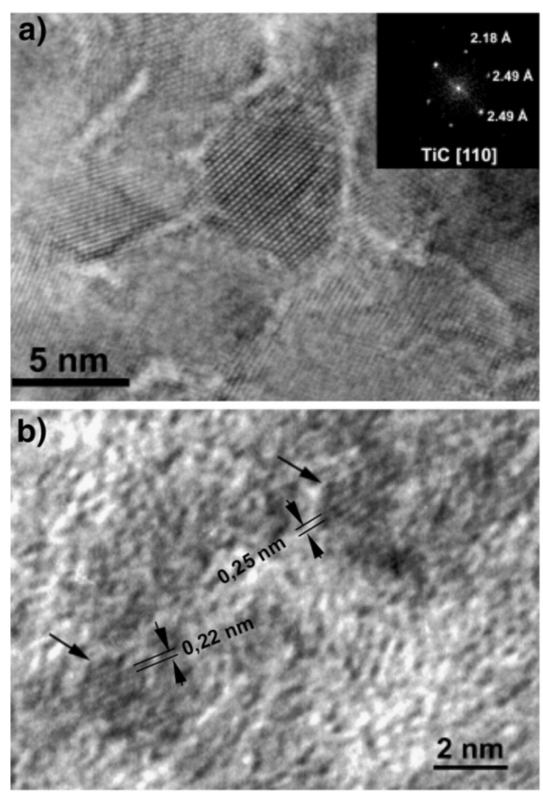

Fig. 1. HRTEM micrographs and corresponding electron diffraction patterns for nc-TiC/a-C nanocomposite coatings prepared at sputtering power ratios of 1 (a) and 4 (b) respectively.