Available online at www.sciencedirect.com

SCIENCE DIRECT

Surface & Coatings Technology 194 (2005) 143–148

SURFACE & COATINGS TECHNOLOGY

www.elsevier.com/locate/surfcoat

Comparative study of the tribological behaviour of superhard nanocomposite coatings nc-TiN/a-Si_3N_4 with TiN

S. Ma[a,b], J. Procházka[b], P. Karvánková[b], Q. Ma[a], X. Niu[a], X. Wang[a], D. Ma[a,b], K. Xu[a], S. Vepřek[b,*]

[a] *State-Key Laboratory for Mechanical Behaviour of Materials, Xi'an Jiaotong University, Xi'an 710049, China*
[b] *Institute for Chemistry of Inorganic Materials, Technical University Munich, Lichtenbergstr. 4, D-85747 Garching, Germany*

Received 26 February 2004; accepted in revised form 14 May 2004

Abstract

Superhard nanocomposite nc-TiN/a-Si_3N_4 coatings were prepared by reactive magnetron sputtering (RMS) and pulsed dc plasma-induced chemical vapour deposition (PCVD) on stainless steel substrates. The tribological behaviour of these coatings at room and elevated temperature was compared with that of TiN coatings deposited by RMS and PCVD. The results show that the superhard nanocomposite nc-TiN/a-Si_3N_4 coatings have a somewhat higher friction coefficient of 0.55–0.7 at room temperature that decreases to about 0.4–0.5 at 550 °C. However, the friction coefficient of pure TiN coatings is 0.6 at room temperature and increases to 0.7 after a sliding distance of 0.1 km at 550 °C.

Keywords: Superhard nanocomposite coatings; Friction coefficient; Hardness

1. Introduction

Due to their high hardness (≥40 GPa), high elastic recovery of 80–94%, high oxidation resistance of ≥800 °C and high thermal stability of 1100–1200 °C, the superhard nanocomposite coatings consisting of a hard transition metal nitride and amorphous silicon or boron nitride, such as nc-TiN/a-Si_3N_4, nc-TiN/a-BN and nc-($Ti_{1-x}Al_x$)N/a-Si_3N_4, receive during the recent years an increasing attention for coating of machining and forming tools [1–5]. A variety of properties, such as hardness, elastic recovery, chemical composition, crystallite size and others were reported in these papers. The tribological behaviour of these hard coatings is very important for industrial application. In the present work we study the wear properties of superhard nanocomposite nc-TiN/a-Si_3N_4 coatings in comparison with TiN and nc-TiN/a-BN coatings.

2. Experimental details

The nc-TiN/a-Si_3N_4 coatings were prepared by reactive magnetron sputtering deposition (RMS) [6,7] and pulsed dc plasma-induced chemical vapour deposition (PCVD) [8] on stainless steel substrates of a diameter of 24.5 mm and thickness of 7.5 mm. The nc-TiN/a-BN coatings were deposited by PCVD in high frequency discharge operating at 13.56 MHz on the same type of substrates [9]. More details about the deposition conditions can be found in earlier papers [6–9].

The chemical composition of the coatings was determined by means of scanning electron microscopy (SEM) equipped with energy dispersive analysis of X-rays (EDX). The crystallite size was determined by means of X-ray diffraction (XRD) using Scherrer formula with the integral half width because using the full width at half maximum yields incorrect values. Because random strain contribution to the width of the Bragg reflection cannot be neglected for crystallite sizes larger than about 8 nm, the results were checked using the Warren–Averbach integral deconvolution method which allows one to separate the contribution of finite crystallite size and random strain [10]. The hardness measurements were conducted by means of automated

* Corresponding author. Tel.: +49-89-2891-3624; fax: +49-89-2891-3626.
E-mail address: veprek@ch.tum.de (S. Vepřek).

0257-8972/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2004.05.007

load–depth-sensing technique using indentometer Fischerscope 100 equipped with Vickers diamond indenter. At least six measurements were conducted at each maximum applied load, which was varied between 30 and 100 mN and only the load-independent value of hardness was taken as reliable [4,5]. Before the measurement, silicon and sapphire were used to calibrate the instrument for the tip rounding (for further details regarding the reliability of the measurement on superhard coatings, see Refs. [11,12]).

The adhesion of the coatings to the substrate was evaluated by conventional scratch adhesion test using a diamond tip on which the scratch force was continuously increased during the measurement. The adhesion failure was monitored by acoustic emission at the critical load when the delamination commenced. The validity of this method was illustrated elsewhere [13].

The friction coefficient and wear rate were evaluated by means of the pin-on-disk test in 45% humid air at room (25 °C) and elevated (550 °C) temperature without lubricant. The counterpart was a ∅ 3 mm GCr15 steel ball with a hardness of HRC 60–62. A load of 5 N was maintained at a sliding speed of 20 cm/s. The wear scars were studied using optical microscopy. For each sample, the depth of the wear track, t, was determined using a surface profilmeter, TR240, and the width of the wear track, b, was observed with an optical microscope. Thereafter, the wear volume, W_S, was calculated using

$$W_S = \frac{t}{6b}(3t^2 + 4b^2)2\pi \cdot r \quad (1)$$

where r is the radius of the wear track. Then the dimensional wear coefficient, W_R, was calculated using the equation

$$W_R = \frac{W_S}{F_n \cdot S} \quad (2)$$

where S is the sliding distance and F_n is the nominal load.

3. Results and discussion

As already shown in our earlier papers for PCVD coatings [1,4,14] the crystallite size of TiN decreases with the addition of silicon. The crystallite size of the present RMS coatings decreases to 3–6 nm when the silicon content is more than about 9 at.% as well [6] (see Fig. 1). The decrease of the crystallite size with increasing silicon content is due to the formation of stable nanostructure, composed of stoichiometric TiN and Si_3N_4 [4,5,15].

By analogy with PCVD coatings [4] the hardness of nc-TiN/a-Si_3N_4 coatings reaches a maximum value of about 43 GPa when the Si content is about 8–10 at.% [6,7] (see Fig. 2). This hardness is much higher than that of TiN (20–25 GPa). According to the generic design concept [4,5], this high hardness is based on the combination of the absence of dislocation activity in the small TiN nanocrystals and blocking of grain boundary sliding by the formation of a strong interface between the two phases, as shown also for nc-W_2N/a-Si_3N_4, nc-VN/a-Si_3N_4 and nc-TiN/a-BN [4,5,9].

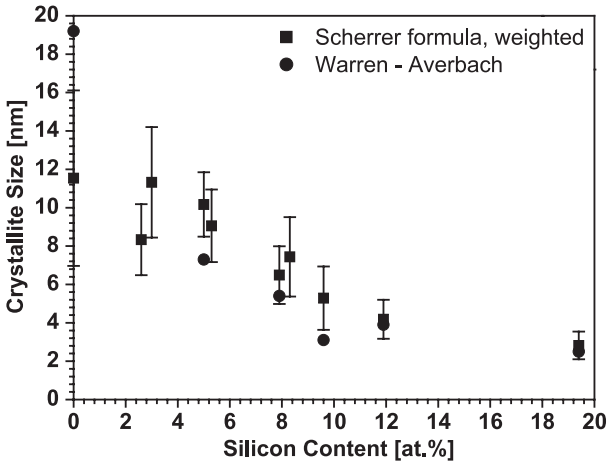

Fig. 1. Dependence of the crystallite size of nc-TiN/a-Si_3N_4 coatings deposited by RMS on the silicon content.

For industrial application of superhard nanocomposite coatings, a good adhesion between the substrate and the coating is important. Therefore, the standard scratch test was conducted on the present coatings deposited by RMS and PCVD (pulsed dc and hf discharge). The results are shown in Fig. 3. One can see that the interfacial adhesion of the present nc-TiN/a-Si_3N_4 coatings decreases with increasing silicon content and it is not sufficient for industrial application that usually requires more than 60–90 N measured by scratch test. This is due to the fact that these coatings are not optimised for adhesion and there is no interlayer between substrate and coating, which increases the adhesion, as usually introduced by the industry. The reason of worse adhesion at high silicon content of the nc-TiN/a-Si_3N_4 coatings deposited by RMS is likely due to a higher compressive stress together with a higher contamination of the substrate-coating interface due to an increasing amount of silicon on the target [6]. The worse adhesion of the coatings deposited by PCVD can originate from a relatively high chlorine content in the coatings ([Cl] ≤ 2.2 at.%).

3.1. Friction coefficient of nc-TiN/a-Si_3N_4 coatings measured at T=25 °C

The room temperature friction coefficient of different Ti–Si–N coatings against steel ball was found to be in the range of 0.5–1.2 [16–19]. The decrease of the friction coefficient with increasing content of silicon was usually observed and this behaviour was attributed to the formation of self-lubricant tribo-layers such as SiO_2 or $Si(OH)_2$, which would be more activated with increasing silicon content [16–18]. This assumption is supported by results of Kim et al. [16]. They found that with increase of the relative