Vacuum 89 (2013) 168–173

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Microstructure and tribological properties of Ti(Cr)SiCN coating deposited by plasma enhanced magnetron sputtering

Qiang Li [a], Fan-qing Jiang [a], Yong-xiang Leng [a,*], Rong-hua Wei [b], Nan Huang [a]

[a] *Key Laboratory of Advanced Technologies of Materials, Ministry of Education, Southwest Jiaotong University, Er round Road 111#, Chengdu, Sichuan 610031, China*
[b] *Southwest Research Institute, San Antonio, USA*

ARTICLE INFO

Article history:
Received 23 September 2011
Received in revised form
18 March 2012
Accepted 21 March 2012

Keywords:
TiSiCN
CrSiCN
TiCrSiCN
Microstructure
Wear
Ti6Al4V

ABSTRACT

Three kinds of hard coatings, TiSiCN, TiCrSiCN and CrSiCN were deposited on WC/Co alloys by plasma enhanced magnetron sputtering (PEMS) technique. Those coatings were comparatively studied with respect to their microstructure and mechanical properties. The sliding tribological behaviour of the coatings against Ti6Al4V counterpart was also studied by pin-on-disc tests. The results indicated that TiN and CrN were the main phase composition for the TiSiCN and CrSiCN coatings, respectively. While the TiCrSiCN coating consisted of $TiCrN_2$ phases or Cr be incorporated in TiN as a single solid solution. The TiCrSiCN coating showed higher hardness than the CrSiCN coating, better adhesion with substrate than the TiSiCN coating, and higher dry sliding wear resistance against the Ti6Al4V counterpart than both TiSiCN and CrSiCN coatings.

1. Introduction

Ti and Ti alloys have wide applications in the aerospace industry, but they are difficult to machine [1,2]. Rapid tool wear encountered in machining of these materials is a serious problem. In order to reduce tool wear, hard coatings are deposited to protect them from severe abrasion. Single-phased hard coatings such as TiN and TiC, which are commonly used for machining steels, can barely extend the service life of cutting tools for Ti alloys due to the high friction force and low thermal stability, especially in high speed and dry cutting [3–5]. Multi-component coatings based on transition metal nitrides may be good candidate cutting tools for Ti alloys. Studies have shown that additional of metal or metalloid elements to transition metal nitrides can improve the coating properties including wear, oxidation, and corrosion resistance [6–10].

Transition metal carbon nitride (TiCN or CrCN) is known for its superior combinational properties of high hardness of carbides and high ductility of nitrides [10,11]. Silicon containing coatings are also increasingly used as protective layers. The effect of Si addition into transition metal nitride coatings have been reported to achieve the formation of a composite microstructure comprising a nano crystalline metal nitride in a matrix of amorphous silicon nitride. And the Si-doped coatings such as TiSiN or CrSiN have shown both superior fracture toughness and high hardness, which are key properties for excellent wear resistance. TiSiCN and CrSiCN coatings are typical examples of multi-component coatings that provide superior properties to binary coatings. For example, the hardness value of the TiSiCN coatings is found to vary from 25 to 55 GPa [5,10,12] and the coatings maintained their high hardness up to 800–850 °C [5,10]. It is reported that the TiSiCN coating exhibited lower wear rates and lower coefficients of friction against aluminium and alumina counterparts than TiN when tested in air [12].

However, the TiSiCN based coatings are far from thoroughly investigated, especially their tribological properties with titanium alloy counterparts. In order to confirm their potential application on Ti cutting tool, the TiSiCN, TiCrSiCN and CrSiCN coatings were deposited on WC/Co alloys by a plasma enhanced magnetron sputtering (PEMS) technique. The microstructure and mechanical properties of those coatings were evaluated. Ti6Al4V balls were chosen as the wear counterpart during wear testing to investigate the tribological behaviour of the coatings.

2. Experimental

2.1. Deposition of SiCN based coatings

TiSiCN, TiCrSiCN and CrSiCN coatings were deposited on K40UF cemented carbide alloy (WC-Co) and silicon (100) wafer

* Corresponding author. Tel./fax: +86 28 87601149.
E-mail address: yxleng@263.net (Y.-x. Leng).

0042-207X/$ – see front matter © 2012 Published by Elsevier Ltd.
doi:10.1016/j.vacuum.2012.03.053

substrate by a plasma enhanced magnetron sputtering (PEMS) process at Southwest Research Institute [13]. Prior to coating deposition, substrates were sputtered with Ar plasma for 120 min at the substrate bias of −120 V and a discharge current of 10 A. The sputtering process was found to be sufficient to remove residual oxide and contaminant on the surface. After Ar ion sputter cleaning, the coating process was carried out in a gas mixture of Ar and N_2 at flow rates of 150 sccm and 55 sccm, respectively. In addition, trimethylsilane ($(CH_3)_3SiH$, TMS) was also admitted into the vacuum system to introduce Si into the coating composition. Ti and/or Cr targets were used to obtain the Ti, Cr or TiCr-based coatings. Two pure Ti targets (at the power of 4 kW for each target) were employed as the source of Ti for TiSiCN coating. Two Cr targets (at the power of 2 kW for each target) were used in CrSiCN coating, while a Ti target (at 4 kw) and a Cr target (at 2 kW) were used for the deposition of TiCrSiCN. The substrate bias voltage and the deposited time were fixed to −40 V and 1 h for all coatings. The detailed deposition parameters can be found in Table 1.

2.2. Characterization of the coatings

As described, three coatings were deposited on two different substrates. The coatings on silicon wafer substrate were used to examine surface morphology and coating phase structure while microhardness, scratch adhesion and wear testing were performed on the samples with cemented carbide alloy substrate. The coating surface morphologies were examined using scanning electron microscopy (SEM) (JEOL JSM-7001F) and the chemical compositions of the coatings were measured with energy dispersive X-ray spectroscopy (EDS). Coating phase structure was characterized using X-ray diffraction (Philips X'Pert X) with a Cu K_α Source, and the scanning was performed from 20° to 70° with a grazing angle 0.5°. Microhardness testing was carried out using an ultra-micro-hardness tester Shimadzu DUH 211S with a Vickers shaped diamond indenter and the maximum load was 25 mN.

For the scratch adhesion testing, a MTF-4000 multifunctional material surface performance test instrument was used. A Rockwell diamond was drawn over the coatings with a linear dynamic loading at a speed of 5 mm/min. The maximum load was 50 N or 100 N and the scratching distance was fixed to 5 mm. The surface morphology of the coatings was examined using optical microscopy (OM) (Leica DM4000M).

Wear properties were analyzed using pin-on-disc testing under dry sliding conditions on a CSEM tribometer (CSEM Instrument, Switzerland). During the test, the coating sample was rotated against a 6 mm diameter Ti6Al4V ball under a load of 5 N and at a sliding speed of 5 cm/s. Optical microscope (OM) was also used after wear test to examine the wear tracks to study the wear mechanisms. To calculate the wear volume of the coatings after testing, the cross-sectional areas (A) of the wear tracks on the coatings were measured using a surface profilemeter (AMBIOS XP-2). The volume wear rates ($k_{coating}$) of coatings were obtained by normalizing the wear volume (V) over the total sliding distance (L) and the applied load (N) based on the following relationship:

$$k = \frac{V}{N \cdot L} = \frac{\pi dA}{N \cdot \pi dl} = \frac{A}{Nl} \quad (1)$$

where l is the total sliding laps during wear test.

Table 1
Process conditions for the coating samples.

Coatings	Target power (kW)				Substrate bias voltage (V)	Gas flow rate (sccm)			Coating time (h)
						TMS	N_2	Ar	
TiSiCN	Ti	4	Ti	4	−40	7.5	55	150	1
TiCrSiCN	Ti	4	Cr	2					
CrSiCN	Cr	2	Cr	2					

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows the surface morphologies of the three coatings. All coatings exhibit dense cellular with each one consisting of fine grains. TiCrSiCN coating (Fig. 1b) reveals a more dense structure than the other two coatings, especially the CrSiCN coating (Fig. 1c) with much rougher surface. Localized defects are also observed on all three samples. CrSiCN has more nodule typed defects than TiSiCN and TiCrSiCN coatings. The type of defect look likes embedded nodule. These defects often occur during PVD process and the origin is foreign particles or large droplets deposited on the coating surface [13–15].

3.2. Chemical and phase compositions

The thickness of three coating samples coatings is around 5 μm. The chemical compositions of each coating sample are measured at three different locations using EDS and presented in Table 2. Fig. 2 shows the X-ray diffraction patterns for three coating samples. The XRD pattern for TiSiCN coating consists TiN (ICCD card No.03-065-0715) and TiC (ICCD card No.03-065-8804) structures, corresponding to (111), (200) and (220) planes of TiN, and (111) and (200) planes of TiC. The broadened diffraction peaks in the XRD pattern for TiSiCN coating may imply that C is incorporated in TiN as a solid solution [12]. For TiCrSiCN coating only $TiCrN_2$ (ICCD card No.03-065-9002) can be recognized. CrSiCN coating has typical CrN (ICCD card No.01-077-0047) structure with plane orientations of (111), (200) and (220). The XRD results in our study do not show any crystalline silicon-containing phase (e.g. CrSi, TiSi, Si and Si_3N_4), indicating that the Si may exist in an amorphous form as commonly observed in other published research [16–19]. Zhang et al. [16] confirmed the present of amorphous Si_3N_4 phase through both FITR and XPS analyses in CrSiN films with different Si contents (1.8 at.%–47.0 at.%). In this paper, the peak broadening phenomenon is also observed in all coatings, especially in CrSiCN coating. In addition to the solid solution formation as mentioned above, the small size of crystallite grains in three coatings is also a possible reason for broadening phenomenon. The fine grains are attributed to the formation of a composite microstructure consisting of fined TiN (or TiC, CrN) crystal grain and amorphous SiN_x (or SiC) phase, which is confirmed by other workers [16,17].

3.3. Hardness and scratch adhesion

The indentation hardness (H_{it}) and elastic modulus (E_{it}) are measured on an ultra-micohardness tester using the load-unload mode. The results summarized in Table 3 are based on an average of 6–8 tests. The TiCrSiCN coating exhibits higher hardness and elastic modulus than the TiSiCN and CrSiCN coatings. An explanation of the high hardness of the TiCrSiCN coating is the solid solution hardening. The XRD results of the broadened diffraction peaks of TiN (or TiC) and CrN imply that Cr be incorporated in TiN as a solid solution. Part of Cr atoms instead of Ti atoms position, where the lattice distortion in the coatings is developed and this distortion