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Microstructure and tribological behaviour of super-hard Ti–Si–C–N nanocomposite coatings deposited by plasma enhanced chemical vapour deposition

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Abstract

In this study, a series of new quaternary Ti–Si–C–N nanocomposite coatings have been deposited on HSS substrate at 550 °C using an industrial set-up of pulsed direct circuit plasma enhanced chemical vapour deposition (PECVD) equipment with a gas mixture of $TiCl_4/SiCl_4/H_2/N_2/CH_4/Ar$. The composition of the coatings can be controlled through the adjustment of CH_4 flow rate and the mixing ratio of the chlorides. Detailed structural and chemical characterisations using transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) suggest the formation of a Ti (C, N)/a-C/a-Si_3N_4 nanocomposite structure. Ti (C, N) films show a (200) texture, which change to random orientation of the crystallites when the silicon content reaches about 9 at.%. The tribological behaviour of these coatings was investigated at room and elevated temperature. The results show that the nanocomposite Ti–Si–C–N coatings with low Si and high C contents have a lower friction coefficient of 0.17–0.35 at room temperature. The Ti–Si–C–N nanocomposite coating containing 12 at.% Si and 30 at.% C shows excellent tribological properties with a low friction coefficient of 0.30 and a low wear rate of 4.5×10^{5} mm^{3} $N^{-1}m^{-1}$ at 550 °C.

Keywords: Carbon; Coatings; Hardness; Tribology

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1. Introduction

Ever-increasing requirements for high cutting speed and dry cutting applications are the drivers behind the development of high performance cutting tool materials. Notwithstanding the fact that traditional hard coatings, such as TiN single layer coatings, can improve the wear resistance of many cutting and forming tools [1,2], one of the drawbacks of TiN coatings is its limited oxidation resistance to high temperatures involved in high speed cutting and forming processes [3,4]. In order to improve the chemical and mechanical properties of TiN coatings at elevated temperature, great efforts have been made in recent years to explore such multi-component coatings as Ti–Al–N, Ti–Si–N, Ti–B–N and Ti–C–N [5–8]. Among them, Ti–Si–N nanocomposites coatings have received particular attention because of its much higher hardness (40–105 GPa), better thermal stability (up to ∼1000 °C) and higher elastic recovery (up to ∼80%) as compared with TiN coatings [9,10].

The generic concept for the design of novel, super-hard (>40 GPa) nanocomposite coatings, which are nanometer-size grains embedded in the matrix, was developed by S. Veprek in 1995 [11]. Their particular advantage over super-lattice coatings is that they are isotropic and, therefore, less sensitive to thickness non-uniformity. These properties make super-hard nanocomposite coatings an interesting prospect for a wide range of mechanical applications in an erosive, abrasive, corrosive, or high environment. Meantime, the method of PECVD has a merit of low temperature like Physical Vapor Deposition (PVD), and allows geometrically complex-shaped tools or dies to be coated homogeneously with super-hard nanocomposite coatings. In the present work, attempts have been made to explore the possibility of developing super-hard nanocomposite coatings by embedding TiCN nanoparticles

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into a hard matrix. Systematic materials characterization was conducted using scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), and the tribological properties of these novel coatings at room and elevated temperatures were evaluated.

2. Experimental details

Quaternary coatings based on Ti–Si–C–N were deposited on a high-speed steel substrate which is used for a typical tool steel by pulsed direct circuit plasma enhanced chemical vapor deposition (PECVD) using a gaseous mixture of $TiCl_4$ (flow rate 40 ml/min), $SiCl_4$ (5–15 ml/min), N_2 (400 ml/min), H_2 (800 ml/min), CH_4 (0–400 ml/min) and Ar (50 ml/min) at a total pressure of 200 Pa. A schematic diagram of the PECVD deposition system has been shown elsewhere in our earlier publications [12]. The cylindrical vacuum chamber, 450 mm in diameter and 650 mm in height, was heated with an auxiliary heating system and the temperature was measured by a thermocouple. The substrate was put directly on the charging plate (the cathode of the system) and the wall of the chamber was the anode of the system and earthed. The pulsed power supply was able to produce a voltage up to 1200 V and a frequency up to 33 KHz. The flow of the different gases was measured and controlled by mass flow controllers. $TiCl_4$ was led to the chamber by the flow of carrier gas (H_2) through the $TiCl_4$ tank at a constant temperature of 40 °C. $SiCl_4$ was led into chamber from the $SiCl_4$ tank at room temperature.

After deposition, XRD (Philips X'pert) was performed in the grazing angle (0.5°) geometry using a Cu Kα radiation source to identify phases in the coatings. Some coatings were sectioned and their thickness was measured from the cross-sections using SEM at 20 kV operating voltage, (JSM-6460), and the elementary composition of these Ti–Si–C–N coatings was identified using energy dispersive spectroscopy (EDS) attached to the SEM. The chemical shifts of Si and C in the Ti–Si–C–N coatings were assessed by XPS using a VG Escalab 3 Mark II instrument with a non-monochromated MgKα source (1253.6 eV) and a 0.8 eV resolution. Low energy Ar sputtering was used to partially eliminate surface contaminants, especially oxygen. Very mild bombardment conditions were chosen (1.5 keV, 2 $\mu A/cm^2$ for 5 min) in order to avoid preferential sputtering. The detailed microstructure of Ti–Si–C–N coatings was examined by plane-view TEM at 160 kV operating voltage (200-CX).

A Fischerscope 100 indentometer equipped with a microscope and possibility to program a series of indentation at different lateral positions on the coatings was used.

The hardness measurements were done by means of the automated load-depth sensing technique employing the Fischerscope 100 indentometer with a Vickers diamond indenter. A maximum load of 30 mN was used in order to assure that the indenter depth is within the 5–10% of the coating thickness. The hardness values obtained from the Fischerscope was verified by measuring the size of remaining indentation under SEM and calculating the hardness from the equation $H=0.927L/A_P$, where L is the applied load and A_P is the projected area of indentation. Six repeated measurements were made for each specimen and the average hardness was reported.

The friction coefficient and wear rate were evaluated using a conventional pin (ball)-on-disk tribometer under a load of 5 N at a sliding speed of 20 cm/s. The tests were conducted using 3 mm hardened (HRC 60–62) GCr15 steel ball as counterpart at 25 °C and 550 °C in 45% humid air without lubricant. The temperature of samples was measured directly using a thermocouple. After tests, the depth of the wear track, t, was determined using a TR240 surface profilmeter, and the width of the wear track, b, was measured using an optical microscope. Thereafter, the wear volume, Ws, was calculated using the following formula:

$$W_{\mathrm{s}} = \frac{t}{2b}\left(3t^2 + 4b^2\right)2\pi r$$

Where r is the radius of the wear track. The dimensional wear coefficient, W_{R}, was then calculated using the following formula:

$$W_{\mathrm{R}} = \frac{W_{\mathrm{s}}}{F_{\mathrm{n}}S}$$

where S is the sliding distance and F_{n} is the applied normal load.

3. Results and discussion

3.1. Structural and hardness characterization

The effect of the addition of CH_4 and $SiCl_4$ on the overall elemental concentration was evaluated by EDS analysis and the results are shown in Table 1. In general, both the carbon and silicon content in the coatings increased with increasing the flow rate of CH_4 and $SiCl_4$, respectively. For instance, increasing the flow of CH_4 from 0 to 400 ml/min caused an increase of C content from 0 to about 30 at.%. The correlation analysis results show that there is a linear relationship between the flow rate of CH_4 and the carbon content, and the flow rate of $SiCl_4$ and the silicon content in the coatings; the correlation coefficients are 0.94 and 0.97, respectively, which are will larger than the corresponding threshold valve of 0.8471 ($n=9$, $p=0.01$). Clearly, the concentration of Si and C in these coatings is proportion to the flow rate of $SiCl_4$ and CH_4, respectively. The Cl content in these coatings was found to be less than 1 at.%.

Cross-sectional SEM micrographs of Ti–Si–N coatings with different silicon and carbon contents adjusted by $CH_4$and $SiCl_4$ flow rate are shown in Fig. 1. At low Si and C content in coating, the Ti–Si–C–N coating shows a columnar structure (Fig. 1a). However, the columnar structure was modified by increasing of C and Si content (Fig. 1b) and microstructure was dense and fine. The thickness of coatings was variable from 4 to 6 μm and increased with increasing of Si and C content.

The XRD spectra of some selected samples are shown in Fig. 2, revealing a crystalline structure of the Ti–Si–C–N