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Deposition and characterization of TiAlSiN nanocomposite coatings prepared by reactive pulsed direct current unbalanced magnetron sputtering

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ABSTRACT

This work reports the performance of high speed steel drill bits coated with TiAlSiN nanocomposite coating at different Si contents (5.5–8.1 at.%) prepared using a four-cathode reactive pulsed direct current unbalanced magnetron sputtering system. The surface morphology of the as-deposited coatings was characterized using field emission scanning electron microscopy. The crystallographic structure, chemical composition and bonding structure were evaluated using X-ray diffraction, energy-dispersive X-ray analysis, X-ray photoelectron spectroscopy, respectively. The corrosion behavior, mechanical properties and thermal stability of TiAlSiN nanocomposite coatings were also studied using potentiodynamic polarization, nanoindentation and Raman spectroscopy, respectively. The TiAlSiN coating thickness was approximately 2.5–2.9 μm. These coatings exhibited a maximum hardness of 38 GPa at a silicon content of approximately 6.9 at.% and were stable in air up to 850 °C. For the performance evaluation, the TiAlSiN coated drills were tested under accelerated machining conditions by drilling a 12 mm thick 304 stainless steel plate. Under dry conditions the uncoated drill bits failed after drilling 50 holes, whereas, TiAlSiN coated drill bits (Si = 5.5 at.%) drilled 714 holes before failure. Results indicated that for TiAlSiN coated drill bits the tool life increased by a factor of more than 14.

1. Introduction

High speed steel (HSS) is used in the manufacturing of cutting tools (such as drill bits) as it can withstand high temperatures. When uncoated drill bits advance into the metallic work piece, the material is removed in the form of chips which bind around the drill bits and cause breakage. In case of coated drill bits, the chip moves over the coating and can be easily removed, preventing the jamming and breakage of the drill bits. Also while drilling, the temperature at the contact point between tool and work piece increases up to 1200 °C [1,2]. Uncoated tools cannot be used for such high temperature applications. To meet these conditions, it is necessary to develop coatings which are wear-resistant and thermally stable at high cutting temperatures.

TiN coatings have been widely used as a protective layer to enhance the lifetime and performance of cutting tools. But the oxidation resistance of TiN is limited up to approximately 500 °C [3,4]. TiAlN coatings show an improvement in the oxidation resistance when compared to TiN coatings (approximately 700 °C) [5,6]. Increasing requirements on high speed and dry cutting applications at elevated temperatures are of great importance. This opens up demand for the quality of wear resistant coatings at high temperatures. Incorporation of Si into the TiAlN system increases the hardness as well as thermal stability (approximately 900 °C) [7,8]. Therefore, coatings with quaternary system (e.g., TiAlSiN) are of special interest for high temperature cutting tool applications [9,10].

In the present study, TiAlSiN nanocomposite coatings with different Si contents ranging from 5.5 to 8.1 at.% were deposited on various substrates such as HSS drill bits, silicon and mild steel (MS) by four-cathode reactive pulsed direct current unbalanced magnetron sputtering system. We present the mechanical properties, structural and microstructural characterization, chemical composition and corrosion behavior of the TiAlSiN coatings. We have also studied the performance of the TiAlSiN coated HSS drill bits.

2. Experimental details

2.1. Preparation of TiAlSiN coatings

TiAlSiN coatings were deposited on HSS drill bits, silicon (1 0 0) and mild steel substrates using a four-cathode reactive unbalanced pulsed direct current magnetron sputtering system. The details of the sputtering system are described elsewhere [11]. Four direct-cooled unbalanced magnetron cathodes (2 Ti, 1 Al and 1 Si) with feed-throughs mounted horizontally in opposed-cathode configu-

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Table 1
Process parameters for the deposition of TiAlSiN coatings.

Diameter of sputtering gun	0.1524 m
Ar flow rate	35 sccm
N_2 flow rate	15 sccm
Operating pressure	5.0×10^{-4} Pa
Ar + N_2 pressure	5.0×10^{-1} Pa
Substrate temperature	200 °C
Ti target power	500 W
Al target power	250 W
Si target power	150–200 W
Bias voltage	−75 V
Thickness of the coating	2.5–2.9 μm
Substrate holder rotation frequency	1 rpm

ration were used for co-sputtering. The diameter of the sputtering guns was 0.1524 m. In order to deposit TiAlSiN coatings, the substrates were first degreased using acetone, isopropyl alcohol and trichloroethylene. The substrates were finally dried with dry nitrogen. After loading, the vacuum chamber was evacuated to a base pressure of 5.0×10^{-4} Pa. This was followed by argon–hydrogen plasma cleaning under an operating pressure of 1.34 Pa for 45 min at a discharge voltage of −800 V, which helps to remove the oxide layer effectively from the metallic substrates [12,13]. To achieve better adhesion between the coating and the substrate, an interlayer of Ti with a thickness of approximately 0.3 μm was deposited on the substrates. During Ti interlayer deposition, argon flow was maintained at 35 sccm and the voltage was maintained at −125 V. In order to deposit TiAlSiN coatings, two Ti targets (99.99% purity), an Al target (99.99% purity), and a Si target (99.99% purity) were sputtered in Ar (99.999% purity) and N_2 (99.999% purity) plasma at an operating pressure of 5.0×10^{-1} Pa. The flow rate of N_2 was kept constant at 15 sccm. All the coatings were prepared at a substrate temperature of 200 °C and an infrared lamp, fixed behind the substrate holder, was used for substrate heating. Coatings were prepared at different Si contents by varying power to the Si target. The coating thickness was approximately 2.5–2.9 μm. In order to obtain uniform coating on drill bits and other substrates a planetary substrate rotation was employed. The deposition conditions for TiAlSiN coatings are listed in Table 1.

2.2. Characterization of the coatings

The bonding structure of the coatings was characterized by X-ray photoelectron spectroscopy (XPS, V.G. Microtech) using an ESCA 3000 system with a monochromatic Al K_α X-ray beam (energy = 1486.5 eV and power = 150 W). The C 1s peak with a binding energy of 285.0 eV was used to make correction for the charge shift. Sputter cleaning was not performed for the XPS measurements. X-ray diffraction (XRD) patterns of the coatings were recorded in a Rigaku D/max 2200 Ultima thin film X-ray diffractometer using a Cu K_α radiation (λ = 0.15418 nm). Microstructural studies and thickness measurements were carried out using field emission scanning electron microscopy (FESEM, Carl Zeiss). The composition of the coatings was measured using an Oxford Instruments energy dispersive X-ray analysis (EDAX). The detector area for EDAX measurements was 30 mm^2, which provided large signal/noise ratio. The hardness measurements were performed in a nanoindenter (CSEM Instruments) at a load of 5 mN using a Berkovich diamond indenter. Before indentation, the samples were observed under an optical microscope and a suitable area was chosen. Ten indentations were made on the sample and the values reported herein represent the average of ten values. More details of the nanoindentation measurements are described elsewhere [14].

The corrosion behavior of the coatings deposited on mild steel substrate was studied using potentiodynamic polarization in 3.5% NaCl solution under free-air condition at room temperature. The experimental conditions for the polarization measurements are described elsewhere [15]. The corrosion potential (E_{corr}), the corrosion current density (i_{corr}) and the polarization resistance (R_p) were deduced from the Tafel plots ($\log i$ vs. E). In order to test the thermal stability of the coatings, silicon substrates coated with TiAlSiN were heated in air in a resistive furnace at temperatures in the range 750–1000 °C. The structural changes of the coatings as a result of heating were measured using micro-Raman spectroscopy. A DILOR-JOBIN-YVON-SPEX integrated micro-Raman spectrometer was used for the present study [16]. Drilling tests were carried out using an automated Oerlikron make radial drilling machine. In order to determine the performance, the uncoated drill bits and the drill bits coated with TiAlSiN were used to drill a 12 mm thick SS 304 plate. The standard test parameters are summarized in Table 2. After drilling operation, the TiAlSiN coatings on the margins, cutting edges, and lips of the drills were observed under an optical microscope.

Table 2
Standard parameters for testing of TiAlSiN coated HSS drill bits.

Testing material	SS 304
Drill speed	800 rpm
Feed rate	0.08 mm/rev
Drill diameter	8 mm
Drilling depth	12 mm
Time for drilling each hole	11 s
Penetration rate	64 mm/min

3. Results and discussion

3.1. Chemical composition and chemical structure

TiAlSiN nanocomposite coatings prepared at Si contents of 5.5, 6.9 and 8.1 at.% are denoted as Sample nos. 1, 2 and 3, respectively. The relative composition of the as-deposited TiAlSiN coatings with different Si contents as determined from EDAX is presented in Table 3. The EDAX data also showed trace amounts of argon and oxygen in the coatings.

Fig. 1 shows the high-resolution core level spectra for the TiAlSiN coatings with Si content of 5.5 at.%. In Fig. 1(a), deconvolution of the Ti 2p peak indicated that it was composed of four peaks centered at binding energy values of 456.9, 458.7, 461.6 and 464.0 eV. The peaks centered at 456.9 and 461.6 eV originate from Ti $2p_{3/2}$ and Ti $2p_{1/2}$ electrons in titanium oxynitride [11,17]. The two peaks centered at 458.7 and 464.0 eV correspond to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ electrons respectively in TiO_2 [18,19]. Fig. 1(b) shows the XPS core level spectrum of Al 2p with a peak centered at 74.1 eV, which corresponds to AlN [17,20]. The Si 2p spectrum showed a characteristic peak of Si_3N_4 at a binding energy of 100.8 eV as shown in Fig. 1(c) [20–22]. The origin of a very low intensity peak centered at a binding energy of approximately 97.0 eV, shown in Fig. 1(c), may be attributed to the formation of $SiTi_x$ phase as the Si 2p component shifts gradually to lower binding energies relative to that of Si–Si bond (99.15 eV) due to the formation of Si–Ti bond structure [22]. Fig. 1(d) associated with N 1s spectrum of the TiAlSiN coating revealed the presence of two peaks at 396.6 and 398.3 eV. The peak at 396.6 eV corresponds to nitrogen in TiN or AlN, as the binding

Table 3
Composition of TiAlSiN coatings determined using EDAX analysis.

Sample no.	Composition					
	Ti	Al	Si	N	Ar	O
1	24.5 at.%	11.9 at%	5.5 at%	56.7 at.%	1.0 at.%	0.4 at.%
2	23.1 at.%	11.9 at.%	6.9 at.%	56.5 at.%	1.6 at.%	–
3	21.2 at.%	10.8 at.%	8.1 at.%	57.2 at.%	1.8 at.%	0.9 at.%