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Improved thermal stability, mechanical and tribological properties of reactively sputtered Si doped TiAlC nanostructured hard coatings

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ABSTRACT

The influence of different Si contents on TiAlSiC nanocomposite coatings deposited on stainless steel and silicon (100) substrates using reactive unbalanced direct current magnetron sputtering has been studied. A comprehensive study of microstructure, mechanical, tribological and thermal stability of Si doped TiAlC has been carried out. X-ray diffraction (XRD) analysis reveals that the TiAlSiC coating exhibits *fcc* NaCl type TiC phase. The presence of *a*-AlC and *a*-Si phases was observed by correlating the X-ray photoelectron spectroscopy and XRD data. Moreover, micro-Raman spectroscopy studies indicate the existence of graphitic rich layer of *a*-C in the coating which limits the columnar growth on account of *a*-Si. Friction coefficient, adhesion, toughness and mechanical properties of the TiAlSiC coatings were characterized by nanoscratch tester and nanoindentation measurements. A high hardness ~28 GPa and a friction co-efficient of ~0.49 was achieved for TiAlSiC coatings prepared at a Si contents of 8 at.%. The maximum toughness of 2.14 MPa $m^{1/2}$ was obtained for the optimized coating due to grain boundary strengthening. Although, increase in the Si content deteriorates the mechanical and tribological performance, but it improves the thermal stability of the coatings. A remarkable thermal stability up to 1000 °C in air for 4 h has been observed for higher Si contents (>12 at.%).

1. Introduction

Nowadays microstructural design of nanocomposite thin films is highly demanding to achieve multifunctional coatings with outstanding properties. The conventional cutting tools coated with TiC, TiN, WC, etc. are commonly used to enhance the wear resistant properties [1,2]. However, these coatings offer low oxidation resistance and relatively low hardness, which are not satisfactory for advance engineering applications [3,4]. In recent years, ternary composite materials such as TiAlN, TiAlC, TiSiN, TiCN, and TiBN, and also quaternary materials such as TiAlSiN, TiSiCN, and TiAlSiCN, have attracted attention due to their high hardness (H), thermal stability and good adhesion to the substrate [5–9]. It is well known that C-based or Me–C–N (Me = transition metal, C = carbon, N = nitride) based coatings exhibit low friction coefficient and better wear properties compared to Me-N coatings depending upon the different C/Me ratio [3,10–15]. In recent years, Ti_3SiC_2 a so called MAX phase, was also investigated which displays very interesting deformation mechanism [16]. Ti_3SiC_2 MAX phase has been synthesized at temperature above 700 °C [16]. However, it has been lately observed by Vishnyakov et al. [17] that Ti_3SiC_2 MAX phase can also be obtained at a low T_{sub} = 650 °C on the Si substrate by sequential process.

Nanocomposite hard coatings can be synthesized by plasma enhanced chemical vapor deposition technique [1], hybrid PVD processes [7], magnetron sputtering [9], cathodic arc ion-platting [18], ion beam deposition processes [19], etc. Among various deposition techniques, magnetron sputtering is a conventional and versatile technique to develop hard coatings [20,21].

The present work reports the influence of Si content on the microstructure and mechanical properties of the TiAlSiC coating. The endurance of the coating is also discussed in terms of the friction coefficient and adhesion properties, correlated with the composition and the microstructure of the TiAlSiC coating. Finally, the detailed investigation is carried out to study the thermal stability of the coating for different Si contents. The deposition conditions and the process parameters are optimized based on the mechanical properties of the film.

2. Experimental details

2.1. Synthesis of TiAlSiC coatings

TiAlSiC films were deposited on stainless steel (SS304) and silicon (100) substrates using four-cathode reactive unbalanced direct current magnetron sputtering. The details of the sputtering system can be found elsewhere [22,23]. Deposition was carried out using two Ti (99.9% purity), one Si (99.9% purity) and one Al (99.9% purity) targets of 0.1524 m diameter. The SS substrates were manually polished and ultrasonically cleaned in 2-propanol and acetone for 15 min simultaneously. The hardness and average roughness values of SS304 substrates were ~4 GPa and ~9 nm, respectively. Finally, the samples

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were loaded in the chamber and the base pressure of 8.5×10^{-4} Pa was achieved. Argon plasma cleaning under an operating pressure of 1.9 Pa and at a bias voltage $|V_b| = 1000$ V was carried out to remove the impurities present on the surface of the substrate. For better adhesion between the coating and substrate, a Ti interlayer was deposited with Ar flow rate of 35 sccm and bias voltage of $|V_b| = 100$ V. To ensure a homogeneous composition the substrates were rotated over the planar targets with the surface to be coated facing towards the target. TiAlSiC deposition was performed using Al, Si and Ti targets, sputtered in Ar (99.99% purity) and C_2H_2 (99.99% purity) atmosphere at an operating pressure of ~1.72 Pa. The substrate temperature was kept constant at ~300 °C throughout the deposition. The other operating process parameters are listed in Table 1.

2.2. Characterization of TiAlSiC coatings

2.2.1. Microstructure, composition and thermal analysis

The effect of Si on the surface morphology and the thickness of the coating deposited on Si substrate was studied by Field Emission Scanning Electron Microscope (Carl Zeiss, Supra 40 VP). The compositional study of TiAlSiC coatings, prepared at different Si contents was obtained using Oxford Instruments Energy Dispersive X-ray Analysis (EDAX, Model 7426) at an accelerating voltage of 10 kV and beam current of 110 pA so as to avoid the substrate effect. The microstructural analysis of the coating deposited on stainless steel substrates was investigated by X-ray diffraction (XRD). The XRD patterns were recorded in Bruker D8 Advance X-ray diffractometer using a Cu K_α radiation ($\lambda = 0.154060$ nm). Furthermore, the bond formation of the TiAlSiC coatings, deposited on the Si substrate was studied using X-Ray Photoelectron Spectroscopy (XPS, SPECS) with non-monochromatic Al K_α X-ray beam (energy = 1486.6 eV, power = 150 W (12.5 kV and 12 mA)). The binding energies reported here were calibrated with reference to C1s peak at 284.6 eV. All the spectra were obtained with pass energy of 40 eV and step increment of 0.05 eV. For XPS analysis, coatings were mounted on the sample holders after cutting into small pieces (10 mm × 10 mm) and they were kept in the load-lock chamber with ultrahigh vacuum (UHV) at 2.7×10^{-7} Pa for 5 h in order to desorb any volatile species present on the surface. After 5 h, samples were transferred into the analyzing chamber with UHV at 6.6×10^{-8} Pa. Before recording the spectra, coatings were sputter-cleaned with focused Ar^+ ion beam using IQE12/38 ion gun by applying energy of 2 keV with Ar gas pressure of 6.6×10^{-5} Pa for 3 min with 1 μA current to remove surface oxide layer. CasaXPS program was employed for curve-fitting of Ti2p, Al2p, Si2p and C1s core level spectra into several components with Gaussian-Lorentzian peaks after Shirley background subtraction. Peak positions, spin-orbit splitting and doublet intensity ratios were fixed according to the reported literature [24,25]. A DILOR-JOBIN-YVON-SPEX integrated micro-Raman spectrometer (Model Labram) was used to study the presence of oxide phases and the thermal stability of Si doped TiAlC coatings. The samples were annealed in vacuum and air in a furnace ex-situ with a heating rate of 5 °C/min and the samples were soaked at a given temperature for 4 h. The samples were allowed to cool down naturally. Subsequently, the Raman spectra of the samples were recorded.

Table 1
Deposition conditions for the studied samples.

C_2H_2 flow rate	2.0 sccm
Operating pressure	1.72 Pa
Substrate temperature	~300 °C
Ti target power	300 W
Al target power	100 W
Si target power	0–300 W
Substrate holder rotation speed	2 rpm
Deposition time	2 h
Target area	266.2 cm^2
Distance between target	10 cm

2.2.2. Tribological and mechanical properties

The friction coefficient for TiAlSiC coatings with different Si contents was studied on SS substrate by using E52100-Cr-steel ball (4 mm diameter) at a contact load of 1 N with ~870 MPa contact pressure and a sliding speed of 6 mm/s at an ambient temperature (24 °C) under 53 ± 2% R.H., by using CETR-UMT (Bruker) Nano-tribometer in ball-on-flat reciprocating configuration without the use of any lubricant. The standard hardness of the Cr-steel ball was ~63 HRC and the average surface roughness of the Cr-steel ball was ~3 nm as determined by atomic force microscopy (AFM, Bruker Nano). For each sample, the sliding distance (108 m) was kept constant to determine the friction coefficient of the coating. The wear tracks generated during the sliding wear tests were characterized using NanoMap 500 LS 3D surface profilometer.

The effect of Si variation on the hardness of TiAlSiC coatings was studied using a nanoindentation hardness tester (CSM Instruments) at a load of 5 mN using a Berkovich diamond indenter. From the observed data, the Young's modulus (E^*), elastic strain to failure (H/E^*) and resistant to plastic deformation (H^3/E^{*2}) values were calculated. The adhesion evaluation was carried out by using CETR-UMT (Bruker) nanoscratch tester with a spherical diamond tip (radius 5 μm). The coatings were scratched with an increasing normal load until a maximum load of 3 N (loading rate 3 N/min and the scratching speed of 0.1 mm/s) for all Si contents. Finally, the fracture toughness was measured by using nanoindenter instrument at 50 mN load for different Si contents. A cube corner indenter was used to study the toughness on Si substrates for TiAlSiC coating.

3. Results and discussion

3.1. Compositional and structural characterization

3.1.1. Compositional analysis

Table 2 shows the relative compositions of the as-deposited TiAlSiC coatings for different Si contents obtained by EDAX measurements. From the table, it is observed that the Si content increases from 3 to 34 at.% when the sputtering power of Si target was increased from 60 to 300 W. Accordingly, the relative concentrations of Ti and Al also change. It is believed that the C atoms are replaced by Si atoms as also reported by Tengstrand et al. [26]. They reported that at low substrate temperature (T_{sub} < 500 °C), Si atoms hinder the growth of TiC and start incorporating into the TiC_x matrix replacing C [26]. Similar results have been presented by other researchers also [27–31].

3.1.2. X-ray photoelectron spectroscopy study

Ti2p, Al2p, Si2p and C1s core level spectra of TiAlSiC coatings with 3 and 34 at.% of Si are shown in Fig. 1. Broad spectral envelops of Ti2p core levels of the coatings (Fig. 1(a)) indicate that Ti is present in different oxidation states and it can be curve-fitted into sets of spin-orbit doublets. Accordingly, in the coatings, $Ti2p_{3/2}$ and $2p_{1/2}$ peaks at 454.8 and 460.4 eV with spin-orbit separation of 5.6 eV correspond to C bonded Ti species in the form of Ti–C, whereas peaks at 456.9 and 462.5 eV are attributed to Ti_2O_3 phase [14,22,32,33]. The possibility of oxidized Ti is attributed to the inducement of surface oxidation of low residual

Table 2
Composition of the TiAlSiC coatings determined from EDAX measurements, with varying Si content at constant Al power (100 W), Ti power (300 W) and bias voltage (−100 V).

Si power (W)	Ti (at.%)	Al (at.%)	Si (at.%)	C (at.%)
0	51	14	0	35
60	45	17	3	35
90	43	17	8	32
120	44	16	12	28
180	41	16	20	23
240	38	15	25	22
300	33	14	34	19