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Structure and wear characteristics of TiCN nanocomposite coatings fabricated by reactive plasma spraying

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ABSTRACT

In this present work, titanium carbonitride (TiCN) coatings were successfully fabricated by reactive plasma spraying from agglomerated Ti-graphite feedstock under reactive nitrogen atmosphere. The microstructure and morphology were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution TEM. The mechanical and tribological performances were measured using a nanoindentation tester, tensile tester and block-on-ring tribometer. Results show that typical equiaxed grains with size about 40–90 nm is obtained. The as-sprayed coating consists of nano scaled $TiC_{0.7}N_{0.3}$, $TiC_{0.3}N_{0.7}$ and Ti_2O crystalline phases with some amorphous phases (graphite and CN_x), which would influence the mechanical and tribological properties of coating directly. When compared with TiN coating, TiCN coating exhibits a higher hardness and higher H/E and H^3/E^2 ratios with values of 27.1 GP, 0.1 and 0.3 GPa, respectively. This could benefit TiCN coating possessing high deformation resistance and large elastic recoverability to reduce the damage by impact and wear. Furthermore, the main wear mechanism of TiCN coating is tribo-oxidation wear and abrasive wear.

1. Introduction

Nanocomposite materials are multi-phase materials in structure which the grain/particle size is < 100 nm in at least one dimension. In the last few decades, nanocomposite coatings have gained considerable interests in protective coatings of industry fields (e.g. automobile, aerospace and petroleum chemical), which is due to their extraordinary physical, chemical and mechanical properties as compared with conventional macro-grained counterparts [1–4].

Numbers of techniques have been attempted to produce nanostructured composite coatings, for instance physical vapor deposition (PVD), ion implantation, magnetron sputtering and thermal spraying [5–8]. Among these techniques, reactive plasma spraying (RPS), which combines plasma spraying with self-propagating high-temperature synthesis into a single step, has attracted widely attention [9–11]. RPS which is based on the reactions between feedstock materials or between feedstock materials and surrounding active species (e.g. atom, ion, and radical) in plasma jet has shown a great deal of advantages [12–15]: high deposition rate (8 kg/h) to deposit thick coatings; rapid cooling rate (10^5–10^6 K/s) to reduce production cost; simplicity of the process and improved cohesion strength with clean interface due to in situ synthesis.

Over the past decades, TiC and TiN coatings acting as two important transition metal carbide and nitride coatings have been deeply studied. Owing to the high brittleness of TiC coating and limited hardness of TiN coating, the further development applications of them are limited [16–18]. Titanium carbonitride (TiCN) acts as a continuous solid solution of TiC and TiN, which combines high hardness and low friction coefficient of TiC, and high toughness and bonding strength of TiN. In recently years, TiCN coating has been extensively studied, and found that the performances of TiCN coatings are closely related to its composition and structure [19,20]. For instance, Chen et al. [16] found that TiCN films possessed a high hardness and good wear resistance with high sp^2 carbon content. Shan et al. [18] reported that TiCN coating presented a better wear resistance in artificial seawater than that of TiN coating, and it is ascribed to the dense structure with high hardness. Cheng et al. [19] indicated that the defect density in TiCN coatings increases with the increasing CH_4 fraction, leading to a decrease in hardness and elastic modulus, as well as tribological performance. However, information about the microstructural characteristics of TiCN

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coating prepared by RPS technique and the mechanical and tribological behavior are still very shortage.

In the present study, nanocomposite TiCN coatings were fabricated by RPS through the reactions between Ti-graphite feedstock and nitrogen. The attention has been focused on establishing the correlation between the microstructure (phase composition, grains) and tribological properties of TiCN coatings.

2. Experimental details

2.1. Materials and coatings preparation

Commercially Ti powder (99.9% in purity, 20–35 μm) and graphite powder (99.9% in purity, 2–5 μm) were used as raw materials. Ti powder and graphite powder with mass ratio of 6:1 were mixed with distilled water, sodium carboxymethyl cellulose and gum arabic to form slurry. Subsequently, the dispersed slurry was sprayed into a centrifugal spray-dried facility (LPG-50, Changzhou, Jiangsu, China) equipped with a high speed rotation atomizer systems to obtain agglomerated Ti-graphite powders. Mild steel specimens with dimension of 10 mm × 10 mm × 10 mm were used as substrate materials. Before deposition, the substrate were firstly ultrasonically cleaned in acetone for 10 min and dried by alcohol, and then each sample was grist-blasted by corundum to obtain a surface with certain roughness. To enhance coating adhesion to the substrate, a thin Ni/Al alloy bond coat was sprayed onto the treated substrate surface [21].

Atmospheric plasma spray equipments (GP-80, Made in Jiujiang, China) were employed to prepare TiCN coating. During RPS process, the feedstock (Ti-graphite or Ti) were directly injected into plasma jet and reacted with surrounding N_2 to synthesize TiCN or TiN products. The used parameters were displayed in Table 1. In this paper, the thickness of Ni/Al bond coat and TiCN coating was 50–100 μm and 300–400 μm, respectively.

2.2. Characterization

The phase composition of coating was investigated by X-ray diffractometer (XRD, Bruker D8 Focus-X) with Cu Kα radiation (λ = 1.542 Å). The data was collected in a scattering angle (2θ) ranging from 10° to 90° with a scanning speed of 5°/min, voltage of 40 kV and current of 35 mA. The coating's surface and cross-section morphologies were observed by a field scanning electron microscope (FESEM, Hatachi S-4800) with acceleration voltage of 15 kV. The microstructure of coating was studied in detail by a transmission electron microscopy (TEM) and high resolution transmission electron microscope (HRTEM) using a Tecnai G2 TF20 Transmission Electron Microscope operating at voltage of 200 kV. The chemical composition of coating and wear track were identified by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250xi) with Al Kα radiation. All spectra were referenced to C 1s line of adventitious carbon set at 284.6 eV, and all the spectra fitting were carried out using a non-linear least-squares fitting method employing Gaussian–Lorentzian function and Shirley type back–ground.

The hardness (H) and elastic modulus (E) were measured using an MTS Nano Indenter G200 system equipped with a Berkovich indenter under continuous stiffness measurement (CSM) mode, and values were calculated by Oliver-Pharr method. In order to avoid the deformation behavior from the underline substrate and reflect the mechanical behavior of the coating accurately, the indentation depth of coatings should be below 10% thickness of coating. The indentation load is 75 mN, and the results from 15 indentation tests to obtain reliable statistics. Based on GB/T8542-2002 [22], the bonding strength was performed on a 100 KN Universal Tester (WE-100B, Jinan, China) with the ratio of tensile force (F) to cross-section area (S). For each testing, the average of three was used to reduce the random error.

Table 1
The detailed spray parameters for TiCN and TiN coating during RPS.

Parameters	Values	
	TiCN coating	TiN coating
Current (A)	500	500
Power (kW)	35	35
Primary gas flow rate (Ar, L/min)	40–50	40–50
Carried gas flow rate (N_2, L/min)	3–5	3–5
Reactive gas flow rate (N_2, L/min)	20–30	20–30
Spraying distance (mm)	80–100	80–100

Friction and wear characteristics of coating were tested by dry sliding wear on a block-on-ring tribometer (MM-200, Xuanhua, China) with GCr15 rings counterparts (Φ40 mm × 10 mm, 63.5 HRC). The applied load ranged from 100 N to 500 N. The wear tracks were examined by a profile meter and the wear volume of coating were calculated according to [23]:

$$\Delta V = B \times \left[r^2 \sin^{-1}\left(\frac{b}{2r}\right) - \frac{b}{2}\left(r^2 - \frac{b^2}{4}\right)^{\frac{1}{2}} \right] \tag{1}$$

where ΔV is the wear volume of the coating specimen; B is the thickness of the ring; r is the radius of the ring; b is the width of the worn scars.

3. Results and discussion

3.1. Characterization of powders

Fig. 1 shows the SEM images of raw Ti powder and graphite powder, and agglomerated Ti-graphite feedstock as well as the corresponding XRD pattern. As seen from Fig. 1(c), irregular Ti powders (Fig. 1(a)) are cladded by flank graphite (Fig. 1(b)) compactly to form subsphaeroidal feedstock. As seen from Fig. 1(d), it can be found that only Ti and graphite diffraction peaks are detected, indicating that no impurities were formed during spraying granulation.

3.2. Composition and structure of plasma sprayed TiCN coating

Fig. 2 shows the SEM images of non-polished surface and polished cross-sectional morphology of TiCN coating. As shown, typical surface spread out morphology and cross-sectional layered structure are obtained with some defects (cracks and pores), and the thickness of coating is about 300–400 μm. Similar micrographs are obtained for TiN coating [8]. The formation of cracks is attributed to the release of thermal stress [24]. For RPS, the formation of pores is mainly explained from following three aspects. Firstly, gases are inevitably carried onto feedstock during spraying granulation. Secondly, plasma gases (or air) are trapped and dissolved into molten droplets, and cannot be released completely due to high cooling rate during RPS [25]. Finally, irregular stack and incomplete spread out occurs.

Fig. 3 shows the XRD patterns of as-sprayed TiN and TiCN coatings. As seen from Fig. 3(a), a small amount of Ti_2O is detected in both TiN and TiCN coatings, owing to the oxidation of Ti atoms during spraying. Both the coating present (111), (200), (220), (311) and (222) multiple orientations of face-centered cubic (FCC) structure, and (111) and (200) diffraction planes are the preferred orientations. The peak for TiCN coating shift toward lower Bragg angles slightly compared with the TiN peak positions. This shift can be attributed to the addition of C atoms in TiN lattice and give rise to the lattice strain. In addition, the full width at half maximum of TiCN peaks is broader than that of TiN peaks. This may derive from the solid solution of C atoms in TiC lattice occupied by N atoms in any proportion or N atoms in TiN lattice replaced by C atoms in any proportion to form TiC_xN_{1-x} ($0 \le x \le 1$). Similar phenomenon was also observed by Peng et al. [24]. Owing to the atom radii of C and N are too close, thus it difficult to distinguish them. In order to further identify the phase composition of coating, a method of deconvolution