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Microstructure and wear behavior of nano C-rich TiCN coatings fabricated by reactive plasma spraying with Ti-graphite powders

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ABSTRACT

In the present study, nanostructured titanium carbonitride (TiCN) coatings were prepared by reactive plasma spray (RPS) from Ti-graphite powders under nitrogen atmosphere. The phase composition, microstructure and wear resistance of the TiCN coatings were characterized by X-ray diffractometer (XRD), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscope (TEM), microhardness tester and block-on-ring tribometer. Results showed that the as-obtained coatings are mainly consisted of C-rich $TiC_{0.7}N_{0.3}$ phase. The occurrence of C-sp^2 bond indicated the existence of residual graphite in $TiC_{0.7}N_{0.3}$ coatings. The coating exhibited a typical nanostructure including 90 nm equiaxed grains. The as-obtained TiCN coating had the hardness of ~1674 HV and exhibited better wear resistance than TiN coatings, showing low coefficient of friction of 0.28 under 980 N. The wear mechanism of TiCN coatings showed the mixture of adhesive wear and oxide wear under low load while mainly abrasive wear under heavy load.

1. Introduction

Titanium carbonitride cermet (TiCN) has aroused increasing interest for coating materials due to its outstanding characteristics, i.e., high hardness, good wear resistance, high thermal stability, and comparatively good toughness [1–4]. The TiCN coating has combined properties of TiC and TiN, which was suitable for complex working conditions requiring high abrasion and wear resistance. Generally, TiCN coatings could be produced successfully by various deposition techniques, such as chemical vapor deposition (CVD) [5], plasma enhanced chemical vapor deposition (PECVD) [6] and physical vapor deposition (PVD) [7]. Each technology has its own advantages. Recently, reactive plasma spraying (RPS) technology has been successfully applied to prepare high-performance structural oxide and nitride coatings [8–9], which provides an efficient way to prepare TiCN coatings.

RPS provides a simple processing to rapidly produce thick coatings (from tens of micrometers to hundreds of micrometers even to one millimeter) with good coating/substrate adherence. Usually, RPS process can be principally classified into two modes, i.e., solid-solid reaction between composite powders for in situ synthesized composite coating materials [10–11], gas-solid reaction between particles and injected reactive gases to form mono- or multi-phase coatings [12–13]. Previous studies found that TiCN phase formed by the substitution of C atoms for N atoms in the crystal lattice of TiN in any proportion [14,15], implying rather broad composition of TiCN phase. Pure TiC phase exhibits higher hardness and lower coefficient of friction, while the TiN phase shows higher toughness [16–17]. Thus, the carbon content has a significant effect on the mechanical properties of TiCN coatings [18]. Based on the study of deposited $TiC_{1-x}N_x$ films, Huang et al. [19] found that the coefficient of friction of TiCN films decreased with increasing the carbon content. In our previous study, nanostructured N-rich $TiC_{0.2}N_{0.8}$ coatings were produced by using C_2H_2 as carbon source, yielding high hardness of 1659 HV [20]. However, these studies mainly concern the carbon content by adjusting the fraction of C-containing gas (CH4 or C_2H_2) in the mixture gas as well as the flow rate.

Few studies have been reported on preparing TiCN coatings by using the solid carbon source. Actually, due to the high temperature plasma in the inject chamber, RPS technique provides the possibility to facilitate the reaction between Ti molten and solid carbon source. Thus, the present study concerns about producing C-rich TiCN coatings by using reactive plasma spray method with graphite as carbon source. The microstructure and wear behavior of C-rich TiCN coatings are investigated.

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2. Experimental details

2.1. Materials and coating process

The raw materials used in the present study are commercial Ti powder (99.9% in purity, 30–45 μm, Fig. 1a) and graphite powder (5 μm, Fig. 1b). The feedstock used for APS are prepared by mixing Ti and graphite powders with the ratio of 1:4. As shown in Fig. 1c, the irregular Ti particle is surrounded with graphite powders compactly, leading to the subsphaeroidal feedstock. Mild steels (ASTM 1015, dimension of 10 mm × 10 mm × 10 mm) are used for substrate materials.

The GP-80B atmospheric plasma spray equipment (Made in Jiujiang, China) was employed for preparing TICN coatings. A BT-G3 plasma-spray torch and a homemade reactive gas tunnel were assembled as a reactive spraying system [20,21]. Ni-10 wt% Al alloy was firstly sprayed onto the substrate as a bond layer to improve the adherence between coating and substrate. The feedstock was introduced into plasma jet and reacted with N_2 in the reactive gas tunnel, and then the TiCN coatings with the thickness of more than 200 μm were obtained within a few minutes. The used plasma spray parameters are listed as follows: current (400 A), power (30 kW), N_2 flow (40 L/min) and the spraying distance (50 mm).

2.2. Characterization

The thermal analysis of the feedstock was investigated by the thermal gravimetric and differential thermal analysis (TG/DTA, Netzsch STA 449C, Germany) in alumina crucibles at the rate of 10 °C/min in N_2 flow from 25° to 1400 °C. The phase compositions of the TiCN coatings were examined by X-ray diffraction (JEOL 2500 PC instrument, Japan) with Cu-Kα radiation. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI 5700 ESCA System with high resolution X-ray photoelectron spectrometer. A scanning electron microscope (SEM) (PHILIPS XL30-TMP) was used to observe the cross-section, polished and etched surface of the TiCN coatings. A transmission electron microscope (TEM, TECNAI G2 FEG, 200 kV) was employed to observe the fine structures of the TiCN coating.

2.3. Mechanical tests

The microhardness of the TiCN coating was measured by using a digital Vickers microhardess indenter (HXD-100, Shanghai, China), with the applied load of 100 N and dwelling time of 15 s. 10 points were randomly made and the average value was applied to estimate the coating hardness. Tribological tests were conducted under nonlubricated condition by MM-200 tribometer with a block-on-ring sliding mode that was described by Feng et al. [22]. According to previous studies on the wear test for hard coatings [23–26], the ASTM E52100 stainless steel with an average hardness 63.5 HRC after heat treatment was used as friction counterpart. The sliding speed was 0.4 m/s, and the loads ranged from 98 N to 980 N. The wearing time was during 30 min for each specimen. The mass loss of the test samples was measured by weighing the specimen before and after the wear test using an electronic balance of 0.01 mg accuracy [27].

3. Results and discussions

3.1. TG/DTA analysis of the feedstock

In order to understand the reaction process of the feedstock, TG/DTA was employed. Fig. 2 shows the thermal gravimetric (TG, Fig. 2a) and differential thermal analysis (DTA, Fig. 2b) curves of feedstock under N_2 atmosphere at the heating speed of 10 °C/min. As seen in Fig. 2a, slight mass loss can be observed at the initial stage (room temperature, RT ~ 100 °C), which is ascribed to the evaporation of the residual water. At the stage of 100 ~ 700 °C, the mass of the feedstock keeps nearly stable. However, a sharp increase is observed when the temperature is higher than 700 °C, which may result from the crystal structure transformation of Ti [28]. The transformation of HCP structure to BCC structure could bring the volume expansion of Ti [28], which might lead to the occurrence of cracks on surface of Ti particles in the feedstock. The absorption of N_2 results in the mass increase. The mass of feedstock increases up to the maximum at 1400 °C. As displayed in Fig. 2b, the exothermic reaction occurs at the region from 1150 °C to 1520 °C, indicating the reaction of the Ti-graphite feedstock under N_2 condition, which is

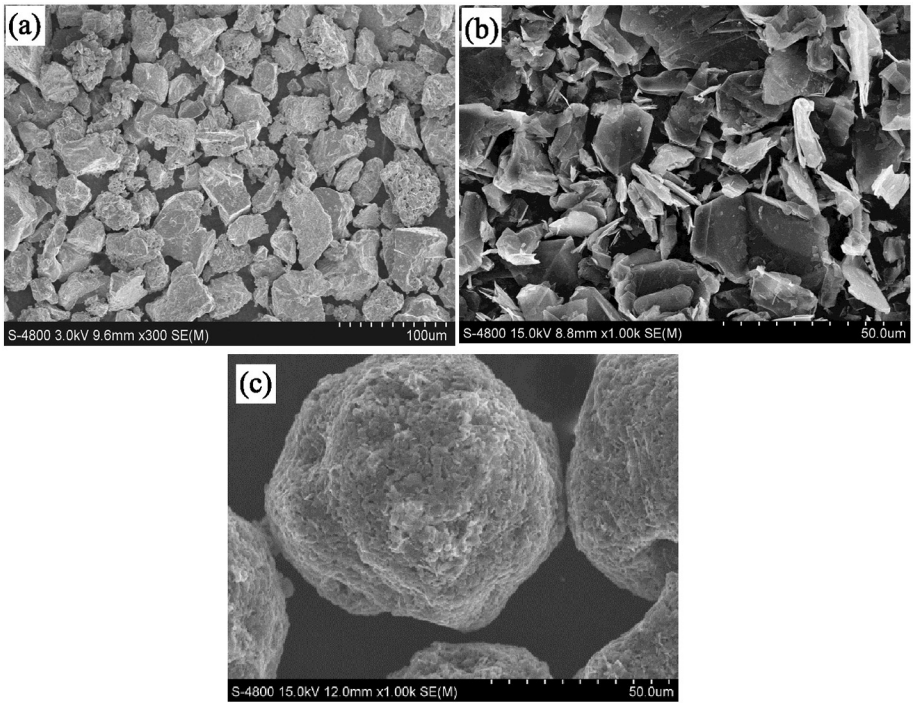

Fig. 1. SEM morphologies of (a) raw Ti powders, (b) raw graphite powders and (c) composite powders.