Applied Surface Science 257 (2011) 8722–8727

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synthesis and microstructure observation of titanium carbonitride nanostructured coatings using reactive plasma spraying in atmosphere

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ARTICLE INFO

Article history:
Received 26 November 2009
Received in revised form 11 May 2011
Accepted 12 May 2011
Available online 19 May 2011

Keywords:
Titanium carbonitride
Reactive plasma spraying
Nanostructured coating
Microhardness
Toughness

ABSTRACT

In the present study, nanostructured titanium carbonitride (TiCN) coatings were successfully deposited by reactive plasma spraying (RPS) technology using a self-designed gas tunnel mounted on a normal plasma spray torch. The phase composition and microstructure of the TiCN coatings were characterised by XRD, SEM and TEM. The results indicated that the main phase of the coatings was FCC $TiC_{0.2}N_{0.8}$ with a small amount of Ti_3O. The coating that was deposited using 35 kW displayed better microstructure and properties. The coating exhibited a typical nanostructure including 90 nm diamertrical equiaxed grains and 400 nm long columnar grains by TEM images. The SEM observation further revealed that the equiaxed grains in parallel direction to the substrate surface in TEM images were actually the columnar grains perpendicular to the substrate surface. The formation mechanism of the nanostructured coatings was also discussed. The measured microhardness value of the coating was approximately 1659 $Hv_{100\,g}$, and the calculated crack extension force was about 34.9 J/m^2.

1. Introduction

Nanocrystalline materials, with an average typical grain size of 10–100 nm, are of prime importance in today's materials research due to their extraordinary mechanical, thermal, optical, electrical characteristics and various applications [1,2]. Recently, thermal spraying technology has been commonly accepted as one of the most effective and economical methods to elaborate nanostructured coatings [3]. Nanostructured coatings, including TiO_2–Al, ZrO_2, WC–Co, FeAl, etc. [4–8], have been successfully prepared by APS or HVOF processes in previous studies, and displayed superior properties in comparison with their micron-sized counterparts. However, most nanocoatings were deposited using micron-sized powders that were manufactured by reconstituted nanosized particles, since raw nanosized ultra-fine particles cannot be directly introduced into the thermal spray plume by means of a standard powder feeding system due to their low inertia. As a result, the manufacturing of these micro-sized powders has to induce costly and complicated powder processes.

Alternatively, reactive plasma spraying (RPS) technology is thereby involved as a more economical solution for the deposition of nanostructured coatings. It can significantly combine normal plasma spray process and material synthesis into one step, and remarkably simplify powder process and reduce cost. Usually, RPS process can be principally classified into two modes. The first one is based on a solid–solid reaction between composite powders (reconstituted two or more powders) for in situ synthesized composite coating materials [9–12]. The gas-solid reaction between particles and injected reactive gases as the second mode can be dedicated to form mono- or multi-phase coatings [13–15]. Moreover, RPS has plenty of advantages: (i) high deposition rate; (ii) simple process; (iii) high pure, refractory, or super-hard coating products; (iv) lower operation cost; (v) good adherence with substrate; (vi) the opportunity to synthesize metastable or transitional phases. However, this technique has not drawn extensive attention and only a few studies were reported on RPS nanostructured coatings so far [16,17].

TiCN cermet is a suitable coating material with outstanding characteristics, i.e., ultra-high hardness, high wear and corrosion resistance, high thermodynamic stability, and comparatively good toughness [18,19]. Generally, TiCN films were often elaborated as a protective layer by physical or chemical vapor deposition techniques (PVD or CVD) for the anti-friction applications on bearings, gears, cutting-tools, drills, moulds, etc., whereas low deposition rate, extremely thin thickness, as well as poor adhesion between film and substrate [20] are unavoidable. Accordingly, this research

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doi:10.1016/j.apsusc.2011.05.056

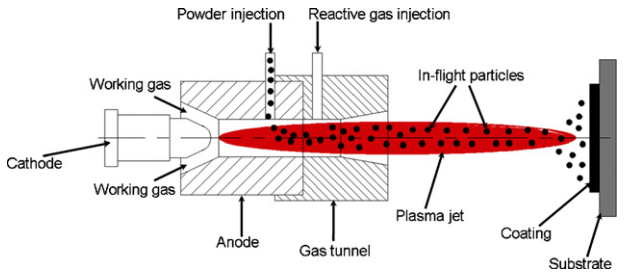

Fig. 1. Schematic plan of the gas tunnel mounted on a plasma gun.

aims at using RPS process to prepare TiCN high-quality nanostructured coatings by an exothermal reaction between Ti particles and reactive gases of nitrogen and acetylene (N_2 and C_2H_2). A reactive gas tunnel was made and installed in the front of plasma torch for promoting the reaction between particles and gases. Phase composition, microstructure, and mechanical properties of the coatings were carefully determined.

2. Experimental procedures

2.1. Materials and coating process

A commercialized titanium powder with a size distribution of 30–45 μm was selected as feedstock material. The used substrate material was mild steel ASTM 1015 with the dimension of 10 mm × 10 mm × 10 mm, and Ni–10 wt%Al alloy was firstly sprayed onto the substrate as a bond layer to improve the adherence between coating and substrate. The GP-80B atmospheric plasma spray equipment (Made in Jiujiang, China) was employed to deposit TiCN coatings. A BT-G3 plasma-spray torch and a homemade reactive gas tunnel were assembled as a reactive spraying system [21,22], as shown in Fig. 1. The pure Ti powder was introduced into plasma jet and reacted with N_2 and C_2H_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 in Table 1.

2.2. Characterisation

X-ray diffractometer (XRD) was performed on the polished surface of the coatings by JEOL 2500 PC instrument with a CuKα target (wavelength λ = 1.5406 Å). It is well-known that RPS process has to involve high stress which can produce high strain in the formed coating. Thus, the Williamson–Hall method [23–25] was used to estimate the grain size (d) of the coating, which can correct lattice stain broadening effect and be described by following Eq. (1):

$$B\cos\theta = \frac{0.9\lambda}{d} + 4\varepsilon\sin\theta \quad (1)$$

where λ is the wavelength of the used radiation, B is the full width at half-maximum of the diffraction peak after the correction of the instrumental line broadening at the diffraction angle 2θ, ε is the lattice microstrain. A scanning electron microscope (SEM) (PHILIPS XL30-TMP) was used to observe the cross-section, fracture and grain morphologies of the coatings. Coating foils were flaked from the substrates, and finally thinned to electron transparency and examined using transmission electron microscope (TEM) (PHILIPS TECNAI F20) with a maximal accelerating voltage of 200 kV.

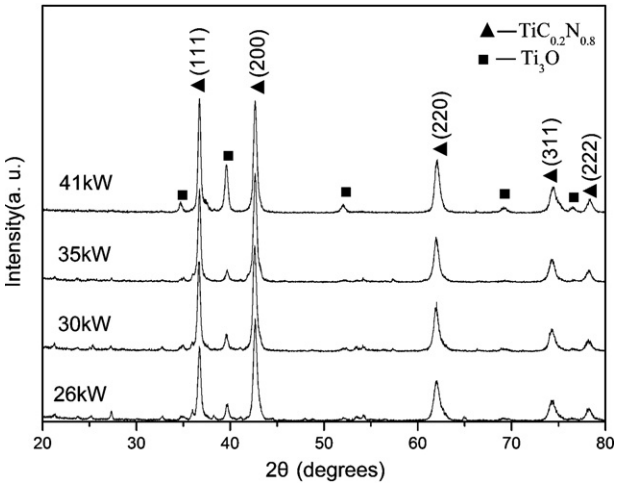

Fig. 2. XRD patterns of the TiCN coatings using different spray powers.

2.3. Microhardness and fracture toughness test

The microhardness of the coating was measured at the cross section of the coating by means of a digital Vickers micro-hardometer HXD-100 (Shanghai, China). The applied loads ranged from 100 to 1000 g, and a duration time of 15 s was selected. 10 indentations were made randomly for each load, and the average microhardness values were calculated to estimate the coating hardness. The coating toughness can be evaluated by crack extension force (G_c (J/m^2)) calculated from following Eq. (2) [26]:

$$G_c = 6.115 \times 10^{-4}\left(a^2 \cdot \frac{P}{c^3}\right) \quad (2)$$

where a is the impression half-diagonal (m), P is the indentation load (N), c is the half of the total length (tip-to-tip) of the major crack (m).

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the TiCN coatings deposited by different spray powers from 26 kW to 41 kW are presented in Fig. 2. It is clearly observed that the coatings are mainly composed of $TiC_{0.2}N_{0.8}$ phase (See JCPDS: # 76-2484) in all specimens, and exhibit a face centered cubic (FCC) similar to NaCl structure and belonging to the Fm-3 m space group. The similar results have been obtained by other researchers [27,28], and it is also in good agreement with our previous research [22]. According to G. Levi et al. [29], the crystal structure of TiCN could be described by TiN prototype with partial occupation of N sites by C. Exactly speaking,

Table 1
The used RPS parameters.

Parameters	Current (A)	Power (kW)	Ar (l/min)	N_2 (l/min)	C_2H_2 (l/min)	Standoff distance (mm)
1	400	26	40	40	2	100
2	450	30	40	50	4	100
3	500	35	40	60	4	100
4	550	41	50	70	8	100