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Preparation of a gradient nanostructured surface TaC layer-reinforced Fe substrate by in situ reaction

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ABSTRACT

A gradient nanostructured surface tantalum carbide (TaC) layer was prepared by a general heat-treatment process on the surface of grey cast iron at 1135 °C for 15 min. X-ray diffraction (XRD) and transmission electron microscopy (TEM) results reveal that the topmost surface of the layer consists of dense TaC ceramic grains; the average grain size is less than 10 nm and increases with depth. The chemical composition also presents a gradient distribution. The investigation indicates that the formation of the TaC layer can be attributed to a reaction between tantalum atoms provided by the tantalum plate and carbon atoms supplied by the graphite phase in the substrate. Furthermore, microhardness, elastic modulus and fracture toughness tests have been performed on the TaC layer under nano-indentation mode. The microhardness, in the range of 21.3–28.1 GPa, is 3–4 times that of the substrate. The fracture toughness is calculated to be 3.9 ± 0.2 MPa $m^{1/2}$. The results emphasize that the gradient nanostructured TaC layer improved the comprehensive mechanical properties of the substrate surface by its ultrafine microstructure.

1. Introduction

In recent decades, superhard and refractory coating materials of transition metal carbides, nitrides, and borides have been widely investigated. Among coating materials, tantalum carbide (TaC) has broad applications [1–3], such as cutting tools, wear-resistant components and high temperature structural materials [3,4], due to its high hardness, good wear resistance and high melting point (3950 °C) [1,5,6]. Although wear of substrate material surfaces has traditionally been conquered by increasing hardness, this inevitably leads to a decrease in toughness [7]. Owing to the lack of adequate toughness [8], however, tantalum carbide tends to exhibit brittle failure under extreme working conditions. The possession of both strength and toughness is a vital requirement for most structural materials; unfortunately, these properties are generally mutually exclusive [9]. Therefore, to overcome this limit and simultaneously improve toughness and other mechanical behaviours, several researchers have focused their attention on nanostructured materials. It is well known that some nanocrystalline metals, ceramics, and even alloys exhibit excellent plasticity at relatively low temperatures and high strain rates [10]. One study [11] indicated that nanostructured TiC composite coatings possess superior wear resistance and excellent toughness. Consequently, it is necessary to develop new preparation techniques for nanostructured coating materials owing to an interest in toughness, wear resistance and extended applications.

Recently, production methods of nanoscale TaC have been developed by several researchers. Several investigations [3,4,6,12,13] have fabricated TaC nanoparticles by chemical processes. Hot-filament chemical vapour deposition was used to deposit tantalum carbide-graphite composite films on etched silicon with an average grain size of 30 nm at 60 Torr [14]. A previous report conducted by W. Ronget al. [15] deposited a nanostructured Ta_xC (Ta_2C and TaC) interlayer on a cemented carbide (WC-Co) substrate by double glow plasma surface alloying to improve the adhesion of a diamond coating with the substrate. Furthermore, a femtosecond pulsed laser has been used to ablate a TaC target and to deposit carbide thin films on silicon by R. Teghil et al. [16]. The results show a nanostructure consisting of a large number of spherical particles with a mean diameter of approximately 50 nm and a stoichiometry corresponding to Ta_2C. Whilst these techniques can obtain relatively uniform and ultrafine TaC ceramic

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particulates, complex processes and high costs may greatly restrict their wider industrial applications. Developments in the in situ reaction (ISR) technique have shown that this inexpensive and general approach can produce fine ceramic grains, strong interfacial bonds, and excellent mechanical properties [17,18].

The ISR technique is a surface modification approach. It can be developed to prepare a gradient nanostructured (GNS) surface ceramic layer on a grey cast iron (Fe) substrate by means of heat treatment. In the GNS surface ceramic layer, the grain size is at the nanometre-scale on the topmost surface and gradually increases with depth to the submicrometre-scale. In addition, the distributions of chemical composition also present gradient variations. In comparison with conventional ceramic coatings on metal substrates, ISR produces a GNS surface ceramic layer with a higher surface hardness and a good toughness. In particular, the GNS surface ceramic layer creates a gradual transition in interfacial properties, which can improve the adhesion of the ceramic layer/metal substrate [15,19]. Previous investigations suggested that formation of a GNS surface (metal or ceramic) layer remarkably improved mechanical properties and interfacial behaviours [19–22].

In this paper, we have proposed the ISR technique to prepare a gradient nanostructured surface TaC layer-reinforced Fe substrate. This process is dependent on the carbon (C) diffusing to react with a thin tantalum (Ta) plate covering the Fe substrate, leading to the formation of the TaC layer under conventional heat treatment. The Fe substrate contains a graphite phase, which provides an abundant C source for ISR. In addition, the physical and chemical characteristics, microstructure, and mechanical behaviours of the TaC layer were investigated.

2. Experimental procedure

2.1. Preparation of the TaC layer

A Ta plate and Fe substrate were used as preparation materials. The chemical compositions of the Fe and the Ta plate are presented in Table 1, which were determined using a spectrum analyser (EXF9600, Xifan, China). To select an appropriate heat-treatment temperature, an experiment was carried out by differential scanning calorimetry (DSC, HCCR-3000, China), as shown in Fig. 1a. Specimens with the radius (1.5 mm) and the thickness (0.5 mm) were used as DSC analysis under argon (Ar) atmosphere (5 ml/min) and at a heating rate of 10 °C/min. Based on the DSC experiment, 1135 °C was selected as the final choice. The heat treatment was performed to facilitate the reaction of Ta and C atoms forming the carbide layer. First, the Ta plate (10 × 5 × 1 mm) was ultrasonically cleaned in acetone for 15 min before being placed at the surface of the Fe (10 × 5 × 5 mm). Subsequently, the specimen was placed in a horizontal tube furnace with a modest flow of Ar gas (5 ml/min) at 1135 °C for 15min, as shown in Fig. 1b. Finally, the specimen was immediately quenched in water and cooled to room temperature.

2.2. Characterization of the layer

To observe the microstructure, the specimen was cut along the cross-section by wire-cutting into a size of 5 × 5 × 6 mm. The profile and surface of the specimen were polished with a diamond paste and ultrasonically cleaned in acetone. The morphologies and elemental distributions were examined using a scanning electron microscope (SEM, EVO18 ZEISS, Germany) installed with an energy dispersive spectral (EDS) analyser. The microstructure of the layer was characterized using a field emission transmission electron microscope (TEM, JEM-3010). The sample obtained was a thin foil that was prepared by cutting, grinding, and dimpling, followed by ion thinning at low temperature. X-ray diffraction (XRD) data of the profile and surface of the layer were obtained using an XRD-7000 X-ray diffractometer (Shimadzu, Japan) with Cu $K\alpha$ radiation at 40 kV and 40 mA in the 2θ range of 20°–90°. Chemical bonding states were investigated by X-ray photoelectron spectroscopy (XPS) (AXISULTRA, Kratos, UK). XPS spectra were obtained with monochromatic Al $K\alpha$(1486.71eV) line at a power of 100 W (10 mA, 10 kV) under vacuum of approximately 10^{-8} Torr. The charge neutralizer was used to compensate for surface charge effects, and binding energies were calibrated.

Table 1
Chemical compositions of Fe substrate and tantalum plate in wt.%.

Element	C	Si	Mn	P	S	Cu	Al	Fe	Ta
Substrate	3.21	1.23	1.05	0.047	0.045	–	–	Balance	–
Ta plate	–	0.06	<0.03	–	–	0.03	0.06	–	Balance

2.3. Property testing

The microhardness and elastic modulus for the polished profile of the carbide layer were obtained using a Nanoindenter G200 (Agilent Technologies, Oak Ridge, TN, USA) with a diamond Berkovich tip. A maximum load of 450 mN was used for each loading-unloading cycle. Loading and unloading lasted for 15 s each, and a dwell time of 10 s was executed at peak load. The fracture toughness of the TaC layer was measured by means of nanoindentation testing. For the Palmqvist crack configuration, the following expression has been developed to calculate K_{IC} [7]:

$$K_{IC} = k\left(\frac{a}{l}\right)^{\frac{1}{2}}\left(\frac{E}{H}\right)^{\frac{2}{3}}\frac{P}{C^{3/2}} \quad (1)$$

where E is the elastic modulus, H is the hardness, P is the indentation load, k is a constant with the value of 0.016 for a Berkovich tip, and C is the total length of a and l, where a and l are the dimensions of the nanoindentation imprint and the crack, respectively.

3. Results and discussion

3.1. Characterization and microstructure of the TaC layer

Fig. 2 shows the DSC curve of the tantalum and Fe substrate in the heating process. It can be observed that two primarily endothermic peaks (EP) present at 831 °C and 1165 °C. The first EP at 831 °C is due to an allotropic transformation: $\partial - Fe \rightarrow \gamma - Fe$. The range of the initial and terminal temperature of the second EP is approximately between 1135 °C and 1180 °C (Fig. 2). Within this temperature range, there may be liquid phase in the interface of the Ta plate/Fe substrate. Therefore, part of regions at the interface of the Ta plate/Fe substrate can be regarded as Fe-Ta-C system. In this case, the second EP at 1165 °C is a result of the reaction [23]: $L \rightarrow \gamma - Fe + TaC + Graphite$. The heat-treatment parameters were selected to be 1135 °C for 15 min. There are several reasons needed to be considered. (i) The TaC can be formed at 1135 °C [18,23]. (ii) Since 1135 °C is close to the melting point of 1148 °C for Fe, a rapid diffusion of C atoms can be anticipated, resulting in a high productivity. (iii) At 1135 °C, the Fe substrate and Ta plate are still in solid state, except the interface in the liquid phase, which guarantees that the ISR leading to the carbide layer is controlled by the diffusion of atoms from the solid-state Ta plate and Fe substrate. The XRD patterns of the cross-section of the specimen revealed