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New strategy to grow TiC coatings on titanium alloy: Contact solid carburization by cast iron

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ABSTRACT

A contact solid carburization method to fabricate TiC coatings on titanium alloy by a "carbon sponge" – cast iron is proposed. When titanium alloy (Ti6Al4V) and cast iron contact in atomic scales at high temperatures below the melting point of the cast iron (e.g. 1100 °C), the interstitial carbon atoms in the cast iron diffuse into titanium alloy forming a TiC layer. Meanwhile, due to the ignorable interdiffusion of metallic atoms, the iron can be easily taken off, leaving a TiC coated titanium alloy. The coating is composed of equiaxed TiC grains and it is completely dense (no porosity). The microstructure is gradient in TiC grain size which increases exponentially from about 100 nm to 1 μm with depth. The inward growth of the coating is diffusion-controlled, and the coating thickness reaches 23 μm when annealed for 10 h. The coatings exhibit high hardness (2400 $HV_{0.05}$) and excellent coating-substrate adhesion strength. This strategy could have a wide application: to grow ceramic coatings on carbide-forming metals by solids having good carbon solubility.

1. Introduction

Titanium and its alloys, due to their low density, high specific strength, good corrosion resistance, excellent crack resistance, and high creeping resistance, are widely used in aerospace, military and biomedical industries [1, 2]. Their applications often require high hardness and good wear resistance at the surface. Therefore, to improve the surface properties of titanium alloy is of great importance. A commonly adopted approach is to fabricate ceramic or cermet coatings [3].

Numerous techniques have been exploited for the preparation of hard coatings on titanium and its alloys [4, 5]. In thermal spraying [6, 7], the coating materials are thermally melted into liquid droplets and coated to the substrate at a high speed. It is highly efficient, but the low adhesion strength has greatly restricted its application in some specific circumstances. Laser surface modification [8], such as laser cladding [9-11], melts the surface and embeds the ceramic powders into the metal substrates. These techniques may obtain uniform distribution of fine ceramic particulates, but the volume fraction of ceramics is limited [12]. Using physical vapor deposition (PVD) [13-16] and chemical vapor deposition (CVD) [17, 18], ceramic coatings grow epitaxially, the residual stress at the interface associated with the lattice mismatch is sensitive to the process parameters. Micro-arc oxidation (MAO) has been intensively studied owing to the advantages of in-situ chemical reactions and the inward growth of oxides. The obtained coatings have high adhesion strength but are inevitably porous [19-21]. Carburization is another feasible in-situ approach for titanium and its alloys since Ti is a strong carbide forming element [22-24]. Carbon atoms diffuse into the titanium substrate forming TiC coating growing towards the matrix so that the adhesion strength of the coating is high. The generated cermet coatings usually have gradient microstructures with increasing TiC grain size and decreasing ceramic volume fraction as the distance increases from the surface. The ceramic particulates are usually coarse, especially in the vicinity of coating-substrate interface [24].

Traditional carburization refers to gaseous, liquid and solid carburization. Though the initial states of the carbon source are different, their principles are indeed quite similar [23]. The carbonaceous gas is firstly decomposed from the heated carbon source, the consequent reduction reaction generates free atomic carbons which are absorbed by the sample surface and diffuse into the

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substrates.

In the present paper, we propose a new idea to carburize titanium alloy by a solid "carbon sponge" −cast iron. The interstitial carbon atoms in the cast iron diffuse into titanium alloy when they contact in atomic scales, TiC coating grows inside the titanium alloy substrate. The cast iron can be easily taken off for recycle due to the weak bonding strength at the interface. Then the TiC coating on titanium alloy is obtained, which is dense and of gradient structures. The high volume fraction of TiC leads to remarkable surface hardness and adhesion strength. The advantages of this approach are discussed in this paper.

2. Materials and methods

2.1. Raw materials and experimental procedure

To carburize the titanium alloy, commercial TC4 with a chemical composition (in wt%) of Ti-6.0Al-4.0V-0.3Fe-0.1C-0.05N-0.015H-0.2O (Ti6Al4V for short) was sized to 10 × 5 × 1 mm and gray cast iron (HT300, with a chemical composition of Fe-3.21C-1.32Si-1.05Mn-0.077P-0.045S-0.014Cu, in wt%) of the same size was chosen as the solid "carbon sponge" containing interstitial carbon atoms. The cast iron was then placed on top of Ti6Al4V substrate and annealed together at constant temperature and uniaxial pressure (as shown schematically in Fig. 1). The detailed experimental procedure is described as follows. In order to enable the atom diffusion between the two materials, two surfaces should contact in atomic scale. Therefore, to reduce the surface roughness, the contact surfaces of Ti6Al4V and the cast iron were firstly ground with SiC sandpaper till 2000# and polished until no scratch was visible before annealing. Then, Ti6Al4V with cast iron on the top was placed in a hot pressing furnace. The sample was heated up to 1100 °C and then the temperature was hold for 2 h, 4 h, 6 h, 8 h and 10 h at 1100 °C before being cooled to room temperature. The heating rate is 5 °C/min and the cooling rate is 4 °C/min. The annealing temperature was set to 1100 °C to facilitate the carbon diffusion with the iron unmelted. Constant uniaxial pressure of 7Mpa was implemented within the temperature holding time to overcome the surface roughness. A modest flow of argon gas (15 ml/min) is maintained during annealing to prevent oxidation. In addition, bulk graphite and high-carbon steel were also used as the solid carbon sources for comparison.

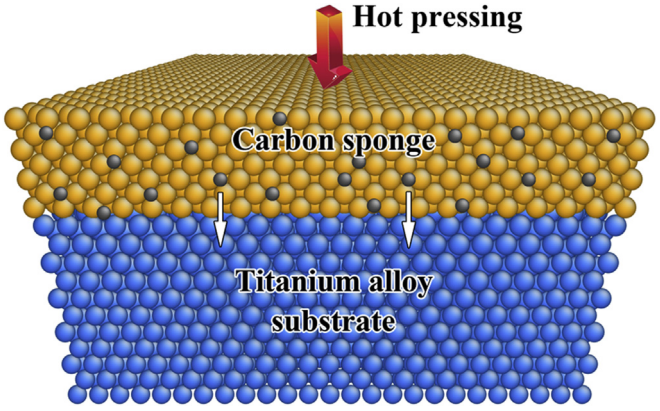

Fig. 1. Schematic illustration of the contact solid carburization. Solid titanium alloy (blue) and "carbon sponge" (yellow) contact in atomic scale at high temperatures to enable the directional diffusion of interstitial carbon atoms (black) from "carbon sponge" to the substrate. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2.2. Characterization

The phase constituents of the samples were analyzed by X-ray diffractometer (XRD) (XRD-7000, Shimadzu) with Cu Kα radiation at 40 kV and 40 mA in the 2θ range of 20°–90°.The microstructure and the element distributions were examined using a scanning electron microscope (SEM, JSM-6700F JEOL) equipped with an energy dispersive spectral (EDS) analyzer. The crystal orientation was investigated by means of electron backscattered diffraction (EBSD, NordlysNano, Oxfordshire, UK). The grain morphologies and the selected area electron diffraction patterns were characterized by using a field emission transmission electron microscope (TEM, JEM-3010). The hardness of the coating was measured on polished coating surface using Vicker's indenter (TUKON2100) with the load of 50 g. The hardness gradient in the cross section was measured by a Nanoindenter G200 (Agilent Technologies, USA) with a diamond Berkovich tip and a maximum load of 50 mN. The scratch tests were performed on the polished coating surface at room temperature using a WS-2005 automatic scratch tester (WS-2005, China). The load was linearly increased from 0 N to 100 N with a loading rate of 100 N/min and a constant scratching speed of 0.05 mm/s.

3. Results

The as-fabricated sample has a sandwich configuration containing a newly generated layer between iron and Ti6Al4V (Fig. 2(a)). The EDS line scan profile perpendicular to the interface shows sharp changes of Fe, Ti and C content at the initial interface,

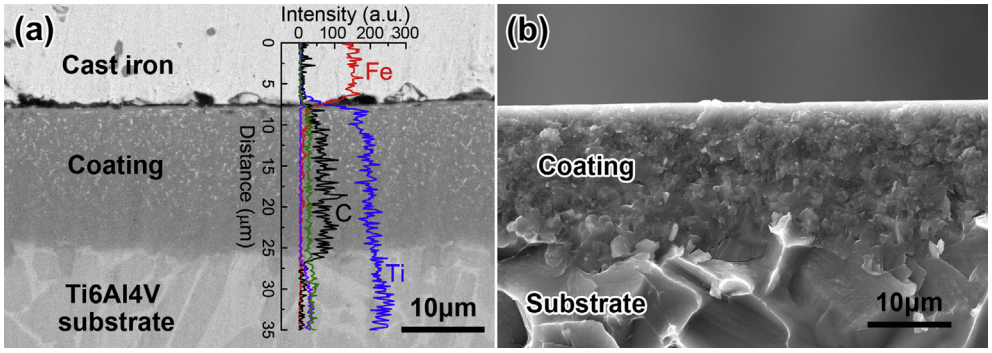

Fig. 2. (a) The cross-sectional SEM micrograph of the as-fabricated sample and the element distribution perpendicular to the interface (the inset), the carbon intensity in the EDS line scan profile is amplified by a factor of 5 for clarity. The violet and green line illustrates the distribution of Al and V, respectively. (b) The SEM micrograph of low-temperature cross-sectional fracture surface showing the dense microstructure with fine ceramic grains. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)