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Oxidation behavior of CVD star-shaped TiN coating in ambient air

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Abstract

Star-shaped 800-TiN and 850-TiN coatings were deposited on the surface of 310S stainless steel foils by CVD and their oxidation behavior was investigated in ambient air, from 300 °C to 800 °C for 1800 s by XRD, SEM, EDX and Raman spectroscopy. Initial oxidation of 850-TiN coating with a partial color change occurs at 350 °C, remarkable oxidation of 850-TiN coating occurring between 400 °C and 450 °C. The EDX results show that obvious oxidation of 850-TiN starts at 400 °C with about 9 at% oxygen detected; no N atoms could be detected while the O content reaching a maximum of ca. 70% at oxidation temperature above 700 °C. The XRD and Raman results show that only rutile-TiO_2 formed on the surface of oxidized TiN coating. The oxidation of star-shaped TiN coating can be divided into three stages. In the case of mild oxidation (below 500 °C), TiN coating can maintain the star-shaped microstructure although oxygen diffuses into the TiN lattice resulting in replacement of N by O atoms. For moderate oxidation (550–600 °C), the star-shaped microstructures start to crack along the (111) twin planes, and the boundary of particles remains clear with oxide and oxynitride layer coexisting on the surface of 850-TiN coating. For severe oxidation (650–750 °C), the cracks of the star-shaped microstructures start to expand and become apparent, meanwhile the boundary of particles become uncertain. After oxidizing at 800 °C, the 850-TiN coating will lose efficacy due to the bad spalling resistance.
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Keywords: Star-shaped TiN; Oxidation behavior; Color changes; Rutile-TiO_2; Spalling resistance

1. Introduction

Over the past several decades, titanium nitride (TiN) has been received considerable interests, not only because of its excellent tribological property but also due to a good chemical stability. TiN is a face-centered cubic (fcc) interstitial compound of the NaCl type with a high melting point, thermodynamic stability, extreme hardness, low coefficient friction, good thermal and electrical conductivity [1–3]. Owing to these properties, TiN is used in a wide range of applications, such as protective materials for machine parts and cutting tools, wear-resistant coatings for orthopedic implants and diffusion barriers in semiconductor technology [4–6]. Recently, TiN coatings have been designed as anti-coking coatings for hydrocarbon steam cracking [7] and liquid hydrocarbon fuels pyrolysis [8], and exhibit a very good protective layer to prevent the substrate from metal dusting and severe coking. In our recent work [7], star-shaped TiN coatings were prepared by chemical vapor deposition (CVD) and their anti-coking ratios above 90% was obtained during cyclohexane pyrolysis at 770 °C for 1.5 h. For anti-coking applications, CVD TiN coating is an ideal material due to the following reasons: (i) CVD TiN coating has a good adhesive strength due to higher linear expansion coefficient. (ii) CVD TiN coating is well crystallized instead of amorphous, which lacks surface acid sites to form the catalytic coking. (iii), CVD TiN coating has a controllable thickness and compactness. (iv) The lower deposition temperature of the star-shaped TiN coating (below 850 °C) will not affect the performance of metal substrate. However, the oxidation of star-shaped TiN coating is often observed under the pyrolysis conditions. The reason is the dissolved O_2 in hydrocarbon fuels (often dozens to hundreds of ppm) [9], resulting in the formation of oxygenated products and the oxidation of TiN coating. Therefore, it is necessary to study the oxidation behavior

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of TiN coating, especially the star-shaped TiN coating under a lower deposition temperature.

The star-shaped TiN is a common microstructure in the CVD process. Staia et al. [10] deposited star-shaped TiN on stainless steel from a gaseous mixture of $TiCl_4$, H_2 and N_2 using a CVD process at a temperature of 1173 K and linear flow velocity in the range from 32.75 to 51.09 cm/min. Cheng et al. [11–14] published a series of articles about the CVD star-shaped TiN coatings, and systematically investigated the growth mechanism of star-shaped TiN crystal. Their results showed that the star-shaped TiN is grown from a multiple-twin particle (as a nucleus), then the five extrusion arms are the result of preferred growth at the five (111) twin boundaries. The oxidation of TiN coating has been extensively studied. Typically, Desmaison et al. [15,16] reported the oxidation of $TiN_{0.83}$ and $TiN_{0.79}$ plates at oxygen pressures in the range of 15–600 Torr, and then defined the oxidation mechanism of titanium nitride in oxygen. Saha et al. [17] used the X-ray photoelectron spectroscopy to investigate the oxidation mechanism of TiN at the initiation temperature of 350 °C. Recently, Hou et al. [18] discussed the oxidation kinetics of TiN-containing composites from theoretical aspect based on experimental data available in literatures. Despite so many investigations, the correlation of oxidation behavior of TiN among the deposition temperature, microstructure and anti-coking properties has seldom been concerned.

In the present work, the star-shaped TiN coatings were prepared by CVD and their oxidation behavior was investigated in ambient air, from 300 °C to 800 °C for 1800 s by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy.

2. Experimental details

The star-shaped TiN coatings were deposited on the surface of 310S stainless steel foils (10 mm × 10 mm × 0.9 mm) in a horizontal and tubular hot-wall reactor with 11 mm i.d. and 300 mm in length under atmospheric pressure. The conditions used for the deposition of star-shaped TiN coatings by CVD were summarized in Table 1, wherein the TiN coatings with deposition temperature of 800 °C and 850 °C were denoted as 800-TiN and 850-TiN, respectively. It is noteworthy to point out that the estimated $TiCl_4$ flow rate was 16 ml/min. The elemental composition of 310S substrate in weight percentage (wt%) used in this study is 20.4% of Cr, 22.0% of Ni, 2.0% of Mn, 0.9% of Si, 0.08% of C, 0.03% of S, 0.03% of P and 54.56% of Fe. Before the CVD experiment, the 310S foils were washed in soap solution, rinsed with acetone and ethanol, and then dried in a vacuum drying oven at 120 °C for 1 h. After deposition, the substrates were kept at high purity nitrogen atmosphere and cooled down to room temperature. More details were described elsewhere [7,19].

Table 1
Experimental conditions used to deposit star-shaped TiN coatings by CVD.

Sample	800-TiN	850-TiN
Substrate temperature (°C)	800	850
$TiCl_4$ evaporator temperature (°C)	21	21
H_2 carrier gasflow rate (sccm)	1200	1200
N_2 reactant gasflow rate (sccm)	1400	1400
Experimental period (h)	2.5	2.5

The oxidation experiments were carried out in a muffle furnace in ambient air. Before oxidation, the coated TiN samples were cleaned in acetone and alcohol by ultrasonic treatment, and then dried in a vacuum drying oven overnight. The samples were placed in a quartz boat to avoid any pollution by the furnace environment before pushed it into muffle furnace. The temperature of muffle furnace was fixed at a target temperature ranging from 300 °C to 800 °C for 1800 s. To simulate the quenching of anti-coking coating and test the resistance to heat shock of the TiN coating, samples were taken from the furnace immediately after each oxidation period.

The microstructure and chemical composition of the oxidized samples were characterized by SEM (Hitachi-S-4800, Japan) and EDX (Oxford-IE-250, Germany) which attached to the SEM. For EDX analysis, three parts of a sample were analyzed under lower magnification, and the average value was obtained by means of selecting and measuring at least three different areas on surface of the sample. Phase identification was carried out by XRD analysis (DX-2500 rotating anode X-ray diffractometer, Dandong Fangyuan Instruments Co., Ltd., China) using Cu *Ka* (λ=0.15406 nm) radiation. The tube voltage and current were 40 kV and 100 mA, respectively. The X-ray diffractogram was recorded at a 0.03°/s interval in the range of 20–80°. Raman spectra were measured using Lab-RAM HR (HORIBA Co., Ltd., France) with 532 nm radiation from an Nd:Yag laser as the excitation source. The system was operated with an output power of 5 mW and a focal spot of the order of a few micrometers (1–2 μm^2). The back-scattered Raman signals were collected and recorded from 100 to 900 cm^{-1}.

3. Results and discussion

Fig. 1 shows the SEM images (10,000:1) of as-deposited TiN coatings. The star-shaped microstructure is scattered almost uniformly on the surface of 800-TiN and 850-TiN. As the deposition temperature increased, the star-shaped size of 850-TiN (average of 1 μm in diameter) is bigger than that of 800-TiN (0.6 μm). Both of them show a fully stoichiometric composition (Ti/N ratio is very close to 1:1) by EDX analysis. Moreover, it is clear that most of the star-shaped crystals are isolated because the five ideal tetrahedra cannot completely fill 360°. The whole TiN coating appears star-shaped crystals intermix with lenticular crystals and presents irregular arrangement. The calculated thickness of 800-TiN and 850-TiN coatings is 3 μm and 7 μm, respectively. The result implies that the deposition rate of 850-TiN coating is about two times of 800-TiN coating.

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