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Microstructure and growth mechanism of tungsten carbide coatings by atmospheric CVD

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ABSTRACT

A tungsten carbide coating was prepared by atmospheric chemical vapor deposition (CVD) with tungsten hexafluoride (WF_6), hydrogen, and dimethyl ether (DME) as the reaction gases, under a dimethyl ether partial pressure (P_{DME}) of 3.2–21.0 kPa and a temperature of 550–600 °C. The phase compositions of the coatings are W_2C + W and W_3C + W, and it is found that when P_{DME} is low, the coating has a lamellar structure, but at a high P_{DME}, the lamellar structure and fibrous tissue are simultaneously present in the scanning electron microscope (SEM) image. In the latter case, no delamination was found, which was visible at a low P_{DME}. In addition, as the P_{DME} increases, the deposition rate of the coating decreases, and ultimately, the coating cannot continue to grow. The growth model of the tungsten carbide coating based on the kinetics of the chemical vapor deposition of tungsten by the hydrogen reduction of tungsten hexafluoride was proposed, and the influences of P_{DME} and temperature on the coatings were discussed and the orientation relationship between W and W_2C in high resolution transmission electron microscopy (HRTEM) was analyzed.

1. Introduction

Tungsten carbide has extreme hardness, high melting point, thermal stability, and low resistivity [1–5] combined with its exceptional inertness to chemical attack of acid, alkali, and corrosive gas [6,7]. Therefore, it exhibits excellent abrasion resistance, corrosion resistance, and erosion resistance and can thus be used as a protective coating in aerospace and petrochemical industries for devices that include impellers, valves, turbodrills, and metal–metal seals et al. [8,9].

Methods for preparing tungsten carbide coatings include chemical vapor deposition (CVD) [10–15], physical vapor deposition (PVD) [16,17], thermal spraying [18], and other methods [19,20]. Tungsten carbide coatings are difficult to deposit on complex-shaped substrates through PVD and thermal spraying, which are “line-of-sight” processes. However, the deposition rate of the PVD method is low, and the resulting coating exhibits great internal stress. In addition, the as-deposited surface of the coating obtained by the thermal spraying method is rough and needs to be processed later [11–13,21]. The CVD process eliminates these disadvantages and can rapidly form dense coatings on complex substrates.

Phases of tungsten carbide, including $W_{12}C$, W_3C, W_2C, and WC, and their crystal structures are cubic, cubic, rhombic and hexagonal respectively while W is cubic structure [21]. W_3C and $W_{12}C$ are metastable compounds and have higher brittleness than WC and W_2C which are stable phases [22]. The plasticity of WC is the best, but the compound's growth rate is the lowest under the same conditions, and the internal stress gradient is the highest. W_2C has the highest hardness in these four tungsten carbides [21]. There are many variables in the CVD process, in which the deposition temperature and the carbonaceous gas partial pressure have a significant influence on the phase composition [23,24]. In a study by Garg [11–13,25,26], the pressure at which tungsten carbide coatings can be obtained is 1–1000 Torr, and the graph about the dependence of phase on the temperature and n(WF_6)/n(DME) was plotted at the pressure of 20–100 Torr. In addition, as the ratio decreases, the coating is changed from W_3C + W to W_2C + W_3C + W to W_2C + W. The coatings formed by Lakhotkin [9,21] changed from $W_{12}C$ + C to WC as $P(C_3H_8)/P(H_2)$ increased gradually and C_3H_8 was heated in advance, and the deposition pressure was 2–150 kPa. It was found that WC can be obtained when the deposition temperature is higher than 700 °C generally [10–15,21,23–27]. In addition, lower deposition temperature favored the formation of tungsten-rich films and amorphous tungsten carbide [1]. It is clear that both of low pressure and atmospheric CVD can be used to prepare tungsten carbide coatings. The deposition rate at atmospheric pressure

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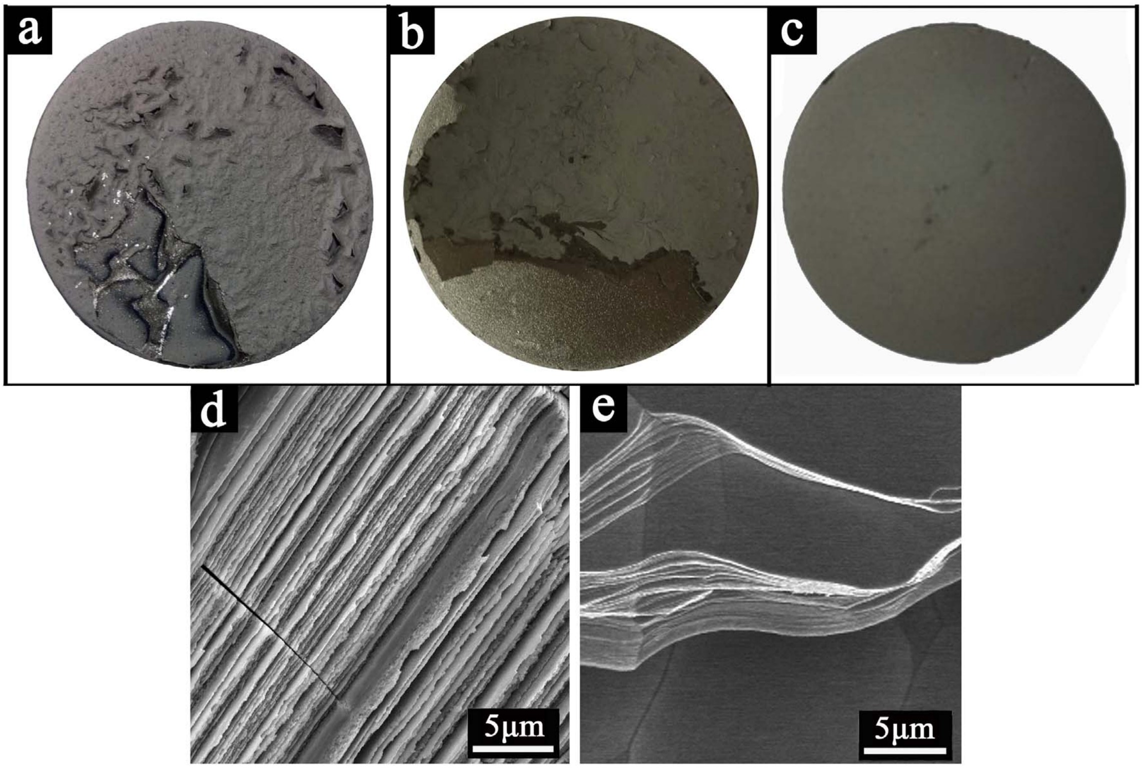

Fig. 1. Surface of the coatings: (a) macrograph when the P_{DME} was 3.2 kPa, (b) macrograph when the P_{DME} was 4.4 kPa, (c) macrograph when the P_{DME} was 11.7 kPa, (d) SEM image when the P_{DME} was 3.2 kPa, (d) SEM image when the P_{DME} was 4.4 kPa.

is high, and the requirements for equipment are simple, which results in lower production costs. However, there is only a small amount of research on the common impact of temperature and carbon gas partial pressure on the phase composition of tungsten carbide systematically in atmospheric CVD.

The practical application of CVD tungsten carbide coatings in industry is closely related to its microstructure, in addition to phase composition. Tungsten carbide coatings of columnar and fine-grain lamellar structures can be obtained by CVD. The hardness of the columnar tungsten carbide is generally 20 to 25 GPa, with good wear resistance, but the adhesion between adjacent grains is weak, so cracks are prone to occur in the presence of erosive or corrosive media [7,28]. The fine-grain lamellar tungsten carbide coating has a hardness of 24 to 30 GPa [10,11], and in the high- and low-angle impact, it exhibits a good resistance to erosion corrosion resistance. However, the weak binding force between the layers and the high internal stress in lamellar structure formed by competitive reaction could result in a cracking and delamination phenomenon when the coating reaches a certain thickness. It is certain that different engineering applications require different microstructures, whereas the question how the desired microstructure can be obtained by adjusting the process parameters has not been answered.

In this paper, tungsten carbide coatings with the phase composition of $W_3C + W$ and $W_2C + W$ were produced by atmospheric CVD at 550–600 °C. The influence of deposition temperature and P_{DME} on the phase composition and microstructure were investigated and growth model and kinetics of tungsten carbide coating were discussed. Moreover, the orientation relationship between W_2C and W was focused and studied through HRTEM.

2. Experimental

2.1. Material preparation

The tungsten carbide coating was deposited with WF_6 (purity: 99.999%), H_2 (99.999%) and DME (99.9%) by CVD under atmospheric pressure. Deposition was carried out in a vertical stainless steel cold-wall furnace that was heated by a resistance wire; the power of the deposition system in the furnace was controlled by a thyristor regulator. The nickel–chromium/nickel–silicon thermocouple was used to measure the substrate's temperature, and the deposition was carried out at a temperature of 550 to 600 °C. The gas flow rates of H_2, WF_6, and DME were controlled by needle valves and mass flow meters, in which the partial pressure ratio of WF_6 to H_2 was 1:3 and P_{DME} was from 3.2 kPa to 21.0 kPa. The substrate was copper ($\Phi 37 \times 2$ mm), which was sandblasted and ultrasonically cleansed in ethanol and acetone prior to deposition. Then, it was placed into the reactor under argon flow to minimize contamination and remove air, and the substrate was perpendicular to airflow in which all of the gases had mixed in advance. In addition, before deposition of tungsten carbide coatings, the tungsten coating was formed on the substrate by the reaction of WF_6 and H_2 for 10 min, and its thickness was approximately 70–100 μm. Then, DME gas was passed for one or two hours. Finally, the flows WF_6 and DME were closed at the same time. During the cooling process, the H_2 was retained until the Ar gas was introduced 10 min before the furnace was opened; thereafter, H_2 was turned off.

2.2. Characterization

The phase compositions of the coatings were analyzed by X-ray diffraction (Bruker D8) recorded in Bragg-Brentano geometry using Cu Kα1 radiation. Microstructures were observed using the field-emission scanning electron microscope (FEI QUANTA 200 FEG) as well as the cold field-emission high-resolution electron microscope (HITACHI SU8220), and the orientation relationship between tungsten and tungsten carbide was surveyed by transmission electron microscopy (Tecnai G2 F20 S-Twin) in which the samples were viscous with M-bond 610 and were ground from both sides in order to thin to below 20 μm firstly, and in the the Gatan691 ion-thinning instrument that gun current gradually reduced from 4.8 kV to 3.2 kV was used. The tilt of gun from