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Microstructure and properties of ZrC-SiC multi-phase coatings prepared by thermal evaporation deposition and an in-situ reaction method

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ABSTRACT

A structurally controllable ZrC-SiC coating was prepared by thermal evaporation and an in-situ reaction on carbon materials at 2400 °C. The micro-mechanical properties, and friction and ablation properties of the coatings were studied. Results show that ZrC-SiC coatings have a multi-layered structure with a low content of Si, and a single ZrC_x-SiC layer with a high content of Si. The ZrC-SiC-C interface is spontaneously formed on the surface of the carbon matrix, which is useful to rectify the mismatch of the thermal expansion coefficient between ZrC and the carbon matrix. The mass and linear ablation rates of coating 50%Zr-50%Si were -2.43×10^{-3} mg/(cm^2·s) and −0.667 μm/s, respectively.

1. Introduction

Carbon materials are widely used in electronic components, high-temperature devices, and in the nuclear field because of their advantages such as low density, high specific modulus, good thermal conductivity, good electrical conductivity, and high corrosion resistance [1–3]. However, in actual service environments, carbon materials are usually protected by coatings to ensure their oxidation resistance [4, 5]. ZrC is a typical refractory carbide with many excellent properties, such as a high melting point, high hardness, and good physical and chemical stability, which makes it a good choice for use as a coating on carbon materials [6]. However, the combination of a single ZrC layer with a carbon substrate is not advantageous, because of the vast difference between the thermal expansion coefficients of the two materials [7]. SiC has many advantages, such as high hardness, high strength, good erosion resistance, and a thermal expansion coefficient similar to that of carbon, which may help improve the combination of a carbon substrate with a coating [8]. Therefore, a ZrC-SiC multi-layer coating protection system is an ideal choice for improving the ablation properties of coatings.

ZrC-SiC coatings are typically fabricated by chemical vapor deposition [9], brush painting [10], or plasma spraying [11]. However, these methods have some significant limitations: they involve complicated technology, and are time consuming, costly, cause environmental damage, and form poor bonds with carbon substrates.

In this study, a simple and efficient thermal evaporation deposition method and an in-situ reaction method were used to fabricate uniform, dense, and high-performance ZrC-SiC coatings. The thermal evaporation in-situ reaction method was developed on the basis of vacuum thermal evaporation technology. The traditional vacuum thermal evaporation technology has the following characteristics [12–15]:

1) Traditional thermal evaporation is usually used to deposit low-melting-point materials such as Zn, Al, ZnSe, or MoO_3 at low temperature (below 1000 °C) and under high-vacuum conditions (lower than 20 Pa).
2) The deposited atoms do not react with the matrix; moreover, the deposited film has poor bonding ability.

In this study, ZrC-SiC multi-phase coatings were fabricated by a novel thermal evaporation deposition and in-situ reaction method. This method overcomes the limitations of traditional vacuum evaporation, which is carried out at extremely high temperatures (> 2000 °C). The deposited atoms were highly active and could react with the carbon matrix to form carbides. For Zr—Si mixed evaporation atoms, Si first evaporates on the carbon substrate and produces a SiC layer which bonds well with the substrate, following which Zr evaporates and produces a ZrC outer layer. This multi-layer structure can strengthen the bond between the coating and the substrate, and resolves the mismatch between their thermal expansion coefficients.

The influences of parameters such as the temperature and composition of the evaporation materials, on the microstructure of the ZrC-SiC coatings, were systematically investigated. The micro-mechanical properties, friction properties, and ablation properties of the coatings

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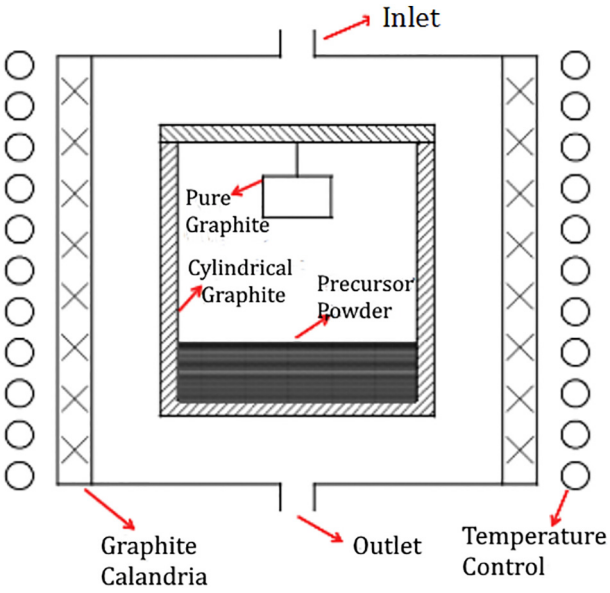

Fig. 1. Schematic diagram of evaporation system.

were also studied.

2. Materials and methods

2.1. Materials and characterization

Fig. 1 shows a schematic diagram of the evaporation system. Evaporation materials composed of a mixture of Zr and Si powders with a grain size of 200 mesh were placed at the bottom of a graphite crucible. The mass ratio of the thermal evaporation powder was Zr:Si = 1:0, 1:1, and 3:1. The C powder was not added to the mixed powders, so as to avoid reaction before evaporation and the subsequent formation of high-melting-point carbides. A graphite substrate was fixed 40 mm above the evaporation materials. The coatings were labelled according to the chemical compositions of the powder mixtures.

It is important to control the growth rate and phase compositions of the coating. For the thermal-evaporation coating, growth rates of the SiC and ZrC coatings are controlled not only by the evaporation rates of Si and Zr, but also by the carbonization and diffusion rates of Si, C, and Zr. However, SiC and ZrC were formed in a very short time due to the rapid diffusion of carbon atoms above 2000 °C [16, 17]. The deposition rate is controlled by the slowest step during the preparation of the coating, that is, by the number of heated evaporation atoms. Moreover, the number of evaporated Zr and Si atoms is related to the vapor pressure and temperature.

The relationship between the heat of vaporization and the vapor pressure and temperature is described by the Clausius–Clapeyron equation [18]:

$$\frac{dl(P_s)}{dT} = \frac{\Delta H_v}{RT^2} \tag{1}$$

where P_s and ΔH_v are the saturated vapor pressure and heat of vaporization, respectively, for a temperature T, and R is the gas constant. Assuming that ΔHv is a constant within a narrow temperature range:

$$\ln(P_s) = \frac{\Delta H_v}{RT} + const \tag{2}$$

From Eq. (2), we can see that $\ln(P_s)$ is linear with respect to $1/T$. Using the data collected by Weast et al. [19], the vapor pressures of Si and Zr can be calculated, and the deposition rate on a coating can be shown to be related to the evaporation rate of a component of the evaporation materials (Zr or Si). When a component of the evaporation material fails to attain its saturated vapor pressure, pan evaporation occurs. In this case, the evaporation rate of the evaporation materials, U_A, can be expressed as follows [19]:

$$U_A = aP_s\left(\frac{M_A}{2\pi RT}\right)^{1/2} \tag{3}$$

where M_A is the gram mole weight of a component in the evaporation material, and a is a constant between 0 and 1. When a component of the evaporation material reaches its saturated vapor pressure, Si undergoes boiling evaporation, and the maximum evaporation rate of the component of the evaporation material, U_{max}, becomes:

$$U_{max} = P_s\left(\frac{M_A}{2\pi RT}\right)^{1/2} \tag{4}$$

Calculations using Eqs. (3) and (4) for a temperature of 2083 °C provide a saturated vapor pressure of Si of 1.333×10^4 Pa and maximum evaporation rate of Si of 1.92×10^{-2} g/(cm^2·s). However, at 2459 °C, the saturated vapor pressure of Zr is 1.333×10^4 Pa, and the maximum evaporation rate of Zr is 3.37×10^{-4} g/(cm^2·s). In addition, Zr and Si atoms react to form $ZrSi_2$ [20]. It is therefore necessary to diminish the influence of the reaction between Zr and Si and C (from the graphite crucible) in the masterbatch, to enable a gradual decrease in the fractional pressure of Zr and Si atoms. Excess amounts of Zr and Si powders are needed to ensure thermal evaporation.

Zr in the evaporation materials will melt, but can hardly evaporate because of its low evaporation rate at 2100 °C. Therefore, a SiC coating was prepared at this temperature to analyze the mechanism of evaporation, and its microstructure was compared to that of a ZrC-SiC coating prepared at 2400 °C. The evaporation temperature was 2100 °C or 2400 °C, and the pressure was 133.3 Pa.

The phase composition of the coating was identified using a rotating-target X-ray diffraction analyzer (XRD, D/max 2550 vb + 18 kW, Rigaku Co., Japan). The surface and cross-sectional morphologies of the coating were observed by scanning electron microscopy (SEM, NanoSEM230, Novtma, Holland). The microstructure of ZrCx was observed by using a spherical aberration-corrected electron microscope (HRTEM, Titan G2 60-300). A TEM sample was prepared using a focused ion beam (FIB, FEI Quanta 3D) on a cross-section of a 75%Zr-25% Si coating. The element distribution on the surface and cross-section of the coatings was investigated by electron probe micro-analysis (EPMA, JXA-8530F, JEOL, Japan).

2.2. Test for micro-mechanical properties

The hardness and elastic modulus of the coating were tested using a UNHT + MCT nano-mechanical properties comprehensive test instrument (CSM, Swiss). Two to five points were selected for testing on every sample. The maximum load during the test was 10 mN, which was unloaded after 15 s. was unloaded after 15 s. The hardness and elastic modulus were calculated from the elastic–plastic deformation depth, according to the Oliver–Pharr elastic contact theory [21].

2.3. Friction test

The friction properties of the coatings were tested using a friction testing machine (UMT-3, Bruker Daltonics, Inc., USA). Friction was measured in a ball-on-disc contact at room temperature with a load force of 5 N, spin speed of 180 r/min, and friction time of 30 min. A chromium steel ball with a diameter of 9.5 mm and hardness of 62 HRC was used.

2.4. Ablation test

The ablation properties of the ZrC-SiC coatings were tested using a DR6130 oxyacetylene torch system, in accordance with the Chinese