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Deposition characteristics of titanium coating deposited on SiC fiber by cold-wall chemical vapor deposition

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HIGHLIGHTS

- Both thermodynamic analysis and experimental studies were adopted in this work.
- The transformation paths of $TiCl_4$ to Ti is: $TiCl_4 \rightarrow TiCl_3 \rightarrow Ti$, or $TiCl_4 \rightarrow TiCl_3 \rightarrow TiCl_2 \rightarrow Ti$.
- Typical deposited Ti coating on SiC fiber contained two distinct layers.
- Deposition temperature is important on deposition rate and morphologies.
- Appropriate argon gas flow rate has a positive effect on smoothing of the coating.

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ABSTRACT

The deposition characteristics of titanium coating on SiC fiber using $TiCl_4$-H_2-Ar gas mixture in a cold-wall chemical vapor deposition were studied by the combination of thermodynamic analysis and experimental studies. The thermodynamic analysis of the reactions in the $TiCl_4$-H_2-Ar system indicates that $TiCl_4$ transforms to titanium as the following paths: $TiCl_4 \rightarrow TiCl_3 \rightarrow Ti$, or $TiCl_4 \rightarrow TiCl_3 \rightarrow TiCl_2 \rightarrow Ti$. The experimental results show that typical deposited coating contains two distinct layers: a TiC reaction layer close to SiC fiber and titanium coating which has an atomic percentage of titanium more than 70% and that of carbon lower than 30%. The results illustrate that a carbon diffusion barrier coating needs to be deposited if pure titanium is to be prepared. The deposition rate increases with the increase of temperature, but higher temperature has a negative effect on the surface uniformity of titanium coating. In addition, appropriate argon gas flow rate has a positive effect on smoothing the surface morphology of the coating.

1. Introduction

Titanium coating has been prepared for a variety of applications, including corrosion-resistant, abrasion-resistant, electrodes or electronic contacts et al. [1–3]. There are many techniques to prepare titanium coating, which can be mainly divided into two kinds: physical and chemical ones. Physical methods are mostly used to deposit titanium film in different coating systems [4–8], such as magnetron sputtering [9–13], pulse biased arc ion plating [14,15], plasma immersion ion implantation and deposition [16], pulsed laser deposition [17], or cold spraying [18]. Chemical methods are much less used to prepare titanium film [19–22], and the relationships between deposition parameters and characteristics of the coating are still unclear.

Up to now, chemical vapor deposition (CVD) has got great development as a technique to prepare metal films for numerous applications in the electronics and coating industries [23]. Thin titanium films have been obtained by conventional CVD, plasma enhanced chemical vapor deposition (PECVD), or laser chemical vapor deposition (LCVD). For instance, Tan [24] prepared a Ti coating on SiC-coated boron fibers via CVD using $TiCl_4$-H_2 mixture at 1040 °C under atmospheric pressure. The titanium was found to react with the fiber surface, and the carbon-rich surface results in the formation of a protective TiC layer which could impede the diffusion of Ti into the SiC coating. Sang [25] applied Ti-I_2 powder mixture to prepare Ti coating in alumina foam by hot-wall CVD method. Their results showed that the obtained titanium coating had a high purity, and showed a good coverage and uniform distribution on the skeleton surface of the foam. Hedaiatmofidi [26]

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used PECVD method to deposit titanium film at 470 °C–530 °C with $TiCl_4$-H_2-Ar gas mixture. It was found that increasing hydrogen flow rate resulted in a decrease in oxygen and chlorine contents of the film. Moreover, applied plasma voltage had a severe effect on nanohardness of the coating, and pressure of the deposition chamber had a negative effect on titanium characteristics. Chou [27] prepared titanium film directly from the dissociation of $TiBr_4$ using a CO_2 laser beam in an argon atmosphere. Their results indicate that the coatings were relatively pure (90%) and uniform. In addition, both the film thickness and deposition rate of the films have been studied as a function of partial vapor pressure of $TiBr_4$, irradiation time, and chamber temperature, respectively.

Anyhow, few researchers have studied depositing titanium film employing $TiCl_4$-H_2-Ar system [26], and it mostly focused on experimental studies in order to prepare titanium coating with optimum parameters. Currently there is little information available concerning the thermodynamic analysis of the CVD reactions in $TiCl_4$-H_2-Ar system, but these theoretical data are vital to achieve a titanium coating which predicts the formation mechanism of the deposit. Accordingly, the theoretical and experimental analyses on the deposition characteristics of the coating are necessary to understand the phenomena involved in the CVD process.

In the present work, thermodynamic analysis was carried out based on the $TiCl_4$-H_2-Ar system in a cold-wall CVD chamber. Meanwhile, titanium coating was deposited systematically using $TiCl_4$-H_2-Ar as a reaction system under a temperature range from 1000 °C to 1200 °C. The deposition characteristics of titanium coating were studied through studying the microstructure of the deposits prepared by cold-wall CVD process under different temperatures and gas flow rates.

2. Experimental

2.1. Preparation of the coating

$TiCl_4$ (purity 99.99 wt%) was adopted as Ti resource, and high purity H_2 (purity 99.99 wt%) was used as dilution and carrier gas which delivers $TiCl_4$ from the bubbler to the reactor, meanwhile high purity Ar (purity 99.99 wt%) was used as dilution gas. The deposition substrate was a 100 μm diameter SiC fiber with a tungsten core of about 16 μm in diameter. To avoid the effect of surface contamination on the deposition process of titanium coating, the surface of SiC fiber was cleaned by alcohol and dried in a drying oven which was set at 30 °C for 30 min before starting deposition experiments.

Fig. 1 shows a schematic of the experimental system used for the preparation of titanium coating. The experimental system contains a mixture of $TiCl_4$, H_2 and Ar reagents in which all kinds of reagents were delivered through float flow meters. Reagents were carried to the reactor through rubber tubes. The deposition reactor was a horizontal, cold-wall deposition chamber. The substrate was heated to certain temperature by controlling a DC power device, and the temperature of the substrate was measured using a WGG2 optical pyrometer. Typical deposition process parameters are listed in Table 1. After deposition, the deposited coatings were cooled to room temperature by air cooling.

The reactant $TiCl_4$ was carried into the reactor by H_2. According to the Dalton's Law of Partial Pressures, the relation between the amount of $TiCl_4$ and the carrier gas H_2 can be described by the following formula:

$$F_T = \left(3.06 \times 10^{-2} P_T F_H\right) \Big/ RT \tag{1}$$

where F_T refers to the flow of $TiCl_4$ in the reactor, ml/min; P_T refers to saturated vapor pressure of $TiCl_4$ at a certain temperature, Pa; F_H refers to the flow of H_2, ml/min; R refers to the gas constant, J/(mol K); and T refers to the temperature of $TiCl_4$, °C. In this work, T was controlled to 100 °C.

2.2. Characterization methods

After the coating was deposited on SiC fiber, the surface and cross-sectional morphologies of the deposited coating were observed using scanning electron microscopy (SEM, Zeiss SUPRA 55, Germany). In order to acquire average thickness and calculate deposition rate, ten different positions around cross-sectional edge were measured by SEM. The distributions of ten positions are uniform around cross-sectional edge.

Deposition rate was calculated through Eqs. (2) and (3):

$$S_a = (S_1 + S_2 + S + \ldots + S_{10})/10 \tag{2}$$

$$V = S_a/t \tag{3}$$

In Eqs. (2) and (3), S_a refers to average thickness of deposits, μm; S_i (i = 1, 2, 3 … 10) refers to thicknesses of deposits at different positions on substrates, μm; V refers to average deposition rate, μm/min; and t refers to deposition time, min.

The phase composition was characterized by X-ray diffraction (XRD, X'Pert Pro, Philip), and X-ray energy dispersive spectrometer (EDS, Oxford INCA Energy 350) was used to qualitatively analyze the chemical composition of the deposited coating.

3. Thermodynamic analysis

It is known that CVD reaction process is governed by both thermodynamics and kinetics. Thermodynamic analysis has great significances for guiding and determining a practical CVD process [28], which is accomplished by calculations of the thermodynamic equilibrium of the CVD reactions. Thermodynamic analysis would provide useful information about the characteristics and behaviors of the reactions, and can help optimize deposition conditions. In general, a complete thermodynamic calculation must include all chemical reactions involved in the actual process. Through the calculated results, researchers can analyze and predict the feasibility of the practical chemical reactions. Therefore, before starting the experiment, we attempted to make a complete understanding and an optimal prediction of the CVD reactions in the $TiCl_4$-H_2-Ar system through thermodynamic investigation. In this work, HSC Chemistry 5.1 chemical reaction and equilibrium software was used.

From the reactor in Fig. 1, it is easy to know that a temperature gradient would be produced from substrate to the cold-wall when the substrate is heated. In the cold-wall CVD chamber, gas sources may transform into other forms when adequate energy is provided for corresponding reactions at certain temperatures. Table 2 shows physical characteristics of different titanium chlorides, including their colors, molar mass, melting points and boiling points, which indirectly indicate their lowest energy state at certain temperatures. For example, $TiCl_4$ is gaseous while $TiCl_3$ is solid at 200–1300 °C. Titanium chlorides mainly include three kinds, $TiCl_4$, $TiCl_3$ and $TiCl_2$, whereas TiCl is ruled out because of its unstable and easy decomposition characteristics. As temperature changes, $TiCl_4$ may decompose into subchlorides such as $TiCl_3$ and $TiCl_2$ before it reaches the substrate, since heated substrate will radiate a large amount of heat to provide enough energy for chemical reaction.

In the $TiCl_4$-H_2-Ar system, $TiCl_4$ and H_2 are the reactant gases. The main reaction equations that will probably take place are shown as the following:

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