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High-speed deposition of titanium carbide coatings by laser-assisted metal–organic CVD

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ABSTRACT

A semiconductor laser-assisted chemical vapor deposition (LCVD) of titanium carbide (TiC_x) coatings on Al_2O_3 substrate using tetrakis (diethylamido) titanium (TDEAT) and C_2H_2 as source materials were investigated. The influences of laser power (P_L) and pre-heating temperature (T_{pre}) on the microstructure and deposition rate of TiC_x coatings were examined. Single phase of TiC_x coatings were obtained at P_L = 100–200 W. TiC_x coatings had a cauliflower-like surface and columnar cross section. TiC_x coatings in the present study had the highest R_{dep} (54 μm/h) at a relative low T_{dep} than those of conventional CVD-TiC_x coatings. The highest volume deposition rate (V_{dep}) of TiC_x coatings was about 4.7×10^{-12} m^3 s^{-1}, which had 3–10^5 times larger deposition area and 1–4 order lower laser density than those of previous LCVD using CO_2, Nd:YAG and argon ion laser.

1. Introduction

Titanium carbide (TiC_x) coatings exhibit very high melting point and thermal stability, high hardness and excellent wear resistance, low coefficient of friction, high electrical and thermal conductivities [1,2], which can be used as wear resistant coatings for cutting tools and inserts, thermal barrier coatings in fusion reactors and diffusion barrier in semiconductor technology [3,4].

Thin films of titanium carbide have been grown from the vapor phase using several techniques, either chemical or physical [5,6]. The need for lower deposition temperature together with the need for local deposition led to those investigations using laser-assisted chemical vapor deposition (LCVD) [7]. It is well known that LCVD technique can be divided into two main categories depending on whether the laser beam interacts with the reactant gases or the substrate material. In photolytic LCVD the laser beam is absorbed by the reactant gases, which undergo photo dissociation, whereas in the pyrolytic LCVD the substrate is heated locally by the laser beam and the chemical reaction is thermally induced [8]. A few researches on the LCVD of TiC_x coatings on different substrate materials by employing different types of lasers have previously been published in the literature [9–12]. High-powered CO_2 laser, which is often called pyrolytic LCVD, has often been applied to CVD of TiC_x coatings, however, due to a small beam size of laser (usually less than several mm) and nonuniform radial distribution of intensity (namely Gaussian distribution), LCVD using CO_2 laser would not be appropriate for uniform coatings on large-scaled substrates [13]. Nd:YAG laser and argon ion laser have also been applied for preparing CVD-TiC_x films, intending to prepare thin films under high deposition temperature (1273–2030 K) for small deposition areas [11,14]. Since the heated area is small and the temperature varies across the laser spot on the substrate surface, temperature measurements are very difficult to perform in focused laser beam in the previous LCVD-TiC_x reports.

In the present study, a semiconductor laser with a wavelength of 808 nm, which has the wavelength in-between CO_2 laser and excimer laser, was first used with the goal of preparing wide-area TiC_x coatings with high deposition rate at a low deposition temperature. Among common hydrocarbon sources, carbon is most readily dissociated from C_2H_2 and least readily from CH_4 [15]. Thus, the use of C_2H_2 and organometallic precursor could potentially reduce deposition temperatures significantly. Differences in deposition parameters, mainly laser power (P_L) and pre-heating temperature (T_{pre}), on the composition, microstructure, and deposition rate of TiC_x coatings achieved with these sources were explored. The effect of laser for the deposition of TiC_x coatings was also discussed.

2. Experimental

TiC_x coatings were prepared on Al_2O_3 substrates by a semiconductor (InGaAlAs) laser assisted CVD with a spot area of

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Table 1
Laser characteristics and deposition parameters of TiC_x coatings prepared by LCVD.

Laser characteristics	Deposition condition	
Source: InGaAlAs	Total pressure in chamber, P_{tot}	200 Pa
Mode: continuous wave mode	Substrate	Al_2O_3 (Nikkato, 99.99%, α-phase)
Wave length: 808 nm	Pre-heating temperature, T_{pre}	293–873 K
Power, P_L: 100–200 W	TDEAT vaporizer temperature	403–413 K
	Gas line temperature	423 K
	Nozzle temperature	423 K
	Flow rate of C_2H_2	1.32×10^{-6} m^3 s^{-1}
	Flow rate of Ar	1.65×10^{-6} m^3 s^{-1}
	Nozzle-to-substrate distance	23 mm
	Deposition time	1.2 ks

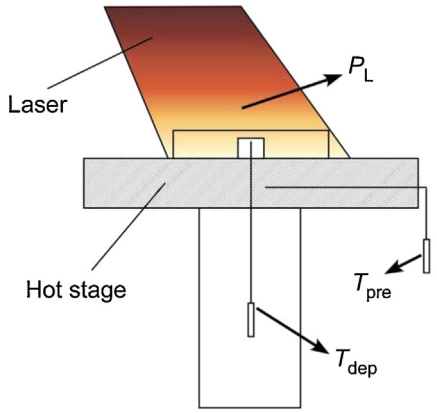

Fig. 1. Schematic diagram of LCVD deposition temperature.

about 3 cm^2 in a cold-wall chamber. TDEAT ($C_{16}H_{40}N_4Ti$, Aldrich, 99.999%) and C_2H_2 (Japan Air Gas, 99.9995%) were used as the source materials. The vaporization temperature of TDEAT (T_{vap}) was controlled at 403–413 K and the vapor was carried by Ar (99.99%) gas into the chamber. The gas delivery line was heated to prevent condensation of the precursor. The laser power (P_L) was changed from 100 to 200 W and the pre-heating temperature (T_{pre}) ranged from 293 to 873 K. The total pressure in the chamber (P_{tot}) was fixed at 200 Pa. A thermocouple was inserted into a slot in the substrate (2 mm in depth) to measure the deposition temperature (T_{dep}). The T_{dep} in the present study could be controlled by the combination of T_{pre} and P_L, which was shown in Fig. 1. Table 1 summarizes the characters of semiconductor laser and deposition parameters for preparing TiC_x coatings by LCVD.

The crystal structure was examined by X-ray diffraction ($\theta/2\theta$ scan) with Cu Kα radiation (Rigaku, RAD-2C). The lattice parameters were calculated from a program based on a least squares analysis. Ex situ X-ray photoelectron spectroscopy (XPS) was utilized to determine the bonding character of the coatings using Al Kα radiation (1486.6 eV) as the X-rays source. The surfaces of the coatings were sputtered using an Ar ion bombardment for 300 s (4 keV, current density 10 μA/cm^2) to remove contamination from the surface. The residual pressure in the chamber of the XPS system was about 2×10^{-6} Pa before the ion bombardment. Scanning electron microscopy (SEM, Hitachi, S-3100H) was used to observe the surface morphology and cross section. The deposition rate (R_{dep}) was calculated from the film thickness and the deposition time.

3. Results and discussion

Fig. 2 shows the effect of P_L on the X-ray diffraction (XRD) patterns of TiC_x coatings at T_{pre} = 298 K. The standard XRD patterns of TiC and Al_2O_3 substrate were also shown in Fig. 1 for comparison. TiC_x coatings in a single phase were obtained at $P_L > 100$ W, and the crystallity of TiC_x coatings improved with increasing P_L. The lattice parameter of TiC_x coatings prepared at P_L = 200 W was 0.4324 nm based on an average from the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffraction peaks, consistent with a previously reported value of 0.4327 nm for stoichiometric TiC [16]. However, care must be taken in using this as the only evidence for stoichiometery since the lattice parameter for TiC does not vary monotonically with C/Ti ratio [15].

The XPS scan spectra exhibiting the chemical structural and bonding states in the TiC_x coating is shown in Fig. 3. Dominant signals of Ti and C were detected. Except the dominant signals, the low signal intensity of O and Ar was also detected. The presence of oxygen can be understood either as the result of surface adsorption/oxidation of the samples as they are exposed to atmosphere while being transferred from the deposition chamber to the XPS system, or it can be present in the bulk of the films due to the residual pressure in the deposition chamber [19]. The signal of Ar can be attributed to the selection of Ar ion as the bombarding ions for the XPS analysis. Nitrides were not detected with XPS indicating that significant concentrations of nitride from TDEAT precursor were not incorporated into the films. The detected oxygen content was about 5 at.% after ion erosion.

Fig. 4 shows the typical XPS spectra for C 1s region from TiC_x coating at P_L = 150 W, T_{dep} = 1063 K. The binding energy of carbon

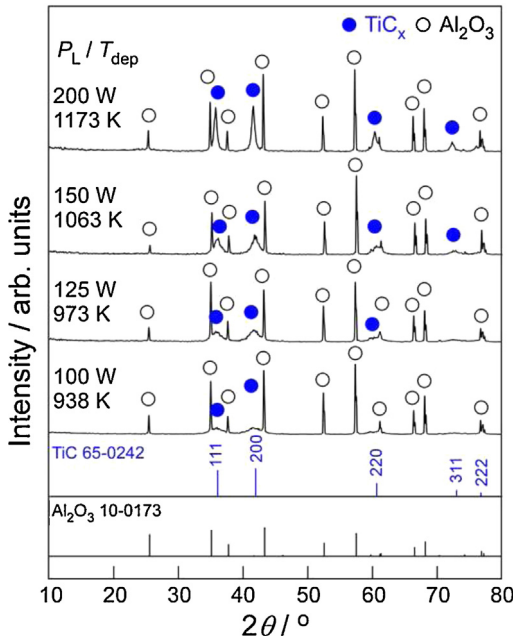

Fig. 2. XRD patterns of TiC_x coatings prepared at T_{pre} = 298 K, P_{tot} = 200 Pa and P_L = 100–200 W.