Vacuum 110 (2014) 190–195

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Photo-catalytic titanium oxide film deposition by atmospheric TPCVD using vortex Ar plasma jet

Yasutaka Ando [a,*], Yoshimasa Noda [b], Akira Kobayashi [c,d]

[a] Division of Renewable Energy and Environment, Ashikaga Institute of Technology, 268-1 Omae, Ashikaga, Tochigi 326-8558, Japan
[b] Collaborative Research Center, Ashikaga Institute of Technology, 268-1 Omae, Ashikaga, Tochigi 326-8558, Japan
[c] Malaysia Japan International Institute of Technology, University of Technology Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia
[d] Graduate School of Eng., Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form
22 June 2014
Accepted 4 July 2014
Available online 11 July 2014

Keywords:
Titanium oxide
Thermal plasma chemical vapor deposition (TPCVD)
MOCVD
Photo-catalyst
Surface modification
Vortex flow
Spray pyrolysis

ABSTRACT

In order to generate the vortex plasma jet, the vortex flow creation nozzle (vortex nozzle) was equipped at the head of the plasma torch. Consequently, by equipment of the vortex nozzle, plasma jet released from the plasma torch ran along the inner wall of the vortex nozzle and the plasma jet was changed into vortex plasma jet in the vortex nozzle. As for the titanium oxide film deposition, anatase rich titanium oxide film with uniform thickness distribution could be obtained on the 304 stainless steel substrate. The film deposition rate at the center on the condition of 30 mm in deposition distance was approximately 8 μm/min. Besides, since the anatase rich film indicated hydrophilic and methylene-blue droplet on the film was decolored by UV irradiation in cases of methylene-blue wettability and decoloration tests, it was proved that the anatase rich film have photocatalytic properties. Especially, in case of the film deposited on the condition of 30 mm in deposition distance, methylene-blue droplet was perfectly decolored by 48 h UV irradiation. From these results, this technique was found to have high potential for uniform film deposition by TPCVD.

1. Introduction

Thermal Plasma chemical vapor deposition (TPCVD), recently sometimes called SPPS (Solution Precursor Plasma Spray), is a rapid film deposition process using thermal plasma spray equipment. Because the film is deposited by utilizing chemical reactions among feedstock materials in thermal plasma jets in this process, high rate film deposition with control of the film structure and component can be conducted. Since this process was developed in 1980s', various functional films such as diamond [1-4], SiC [5,6], Si_3N_4 [6], Ti—B—N—C [7], TiO_2 [8-10] and so on have been successfully deposited. Therefore, this process is hoped to be a low cost functional film deposition process. Especially, as for the oxide film, since the pollution of the film by oxygen derived from ambient air do not need to be taken into account seriously, the oxide film can be deposited by atmospheric TPCVD with lower equipment and running costs in comparison with the conventional low pressure TPCVD. In our previous studies, titanium oxide films and zinc oxide films were successfully deposited by atmospheric TPCVD [11-15].

As thermal plasma type for TPCVD, arc jet type and RF discharge type have been mainly used. The RF discharge type plasma has some advantages such as no electrode abrasion, smooth plasma spatial distribution, high controllability of plasma flow speed and so on. Actually, as for the atmospheric TPCVD, though crystal growth was successfully conducted by RF discharge type plasma in the study of diamond particle deposition [16], there is no report on crystal growth by using arc jet type plasma due to difficulty of estimation of the proper deposition condition. However, since the RF discharge type plasma has some disadvantages such as expensive RF power source, difficulty of impedance matching of the circuit and so on.

As the solution for generation of the plasma with smooth plasma spatial distribution in case of the arc jet type, the gas tunnel type plasma jet torch developed by Kobayashi et al. has been successfully utilized [17-21]. In this case, since vortex plasma

* Corresponding author. Fax: +81 0284 62 9802.
E-mail address: yando@ashitech.ac.jp (Y. Ando).

http://dx.doi.org/10.1016/j.vacuum.2014.07.002

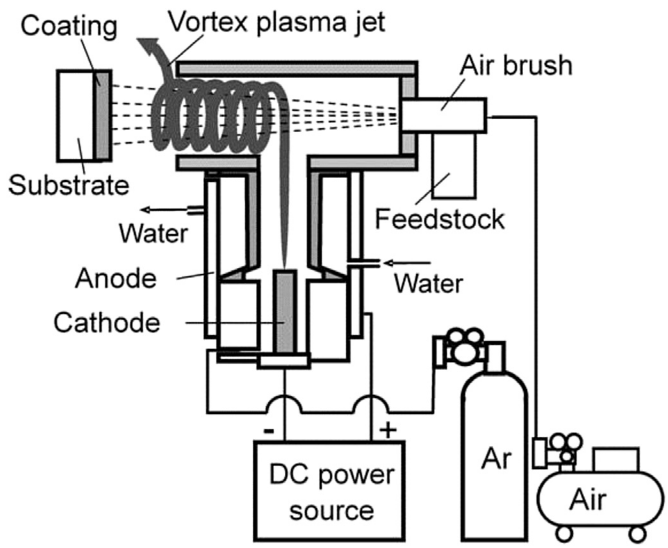

Fig. 1. Schematic diagram of the atmospheric TPCVD equipment.

flow can be generated by discharge of vortex working gas flow with DC power source, radial distribution of the plasma is much smoother than that of the conventional DC arc plasma jet. In the previous studies, it was confirmed the Al_2O_3 and YSZ films deposited by this technique were denser than the conventional thermal spray films and deposition efficiency was promoted in comparison with the conventional plasma spray techniques. However, the contamination derived from the cathode is not evitable even in this technique.

In this study, in order to develop the arc jet type generation system of the contamination free plasma with smooth plasma spatial distribution, vortex thermal plasma jet generating equipment was developed and titanium oxide film deposition by TPCVD using this equipment on the condition of Ar working gas was carried out. Previously, we conducted titanium oxide film deposition by using this equipment and confirmed titanium oxide film deposition. However, since whether the vortex flow was created or not and photo-catalytic property of the deposited film were not presented in the previous paper [22], these data were mainly discussed in this paper.

2. Experimental procedure

Fig. 1 shows TPCVD equipment with vortex plasma jet generator. The equipment consisted of plasma torch, DC power supplying system, micro tube pump (feedstock supplying system) and working gas supplying system. The nozzle for vortex plasma jet generation (vortex nozzle) was equipped at the head of the plasma torch. As feedstock feeding system, a commercial airbrush was used. Table 1 shows deposition conditions. The plasma torch had water cooled electrodes. The anode, which was made from copper, had the constrictor which is 6 mm in diameter. A cylindrical cathode made from tungsten had a diameter of 3 mm. Ar was used as working gas. Working gas flow rate was varied from 1 l/min. to 20 l/min. in case of observation of the vortex plasma jet and was fixed at 20 l/min. in case of film deposition. Carrier gas flow rate was fixed at 3 l/min. which had a potential for 14.24 ml/s. in feedstock feed rate. As the feedstock for titanium oxide film deposition, ethanol diluted titanium tetra iso butoxide ($Ti(OC_4H_9)_4$) was used. Substrates were grit blasted 15 mm × 15 mm × 1 mm^t 304 stainless steel plates. Film depositions were conducted on the conditions of 30 mm, 50 mm and 100 mm in spray distance (the distance between the nozzle outlet of the plasma torch and the surface of the substrate). The discharge power was 100 A/25 V. After titanium oxide films deposition, the microstructures of the films were investigated by optical microscope and X-ray diffraction (CuKα, 40 kV, 100 mA). Besides, in order to confirm photo-catalytic property of the film, methylene-blue wettability and decoloration test using UV irradiation equipment (Fig. 2) were carried out.

Table 1
Film deposition conditions.

Working gas (flow rate)	Ar (1–20 l/min)
Carrier gas (flow rate)	Air (3 l/min)
Discharge power	100 A, 25 V
Deposition distance	30, 50, 100 mm
Feedstock	C_2H_5OH diluted TTIB[a] solution
Feedstock quantity	20 ml
Substrate	304 stainless steel

[a] TTIB: Titanium tetra iso butoxide.

3. Results and discussion

3.1. Influence of working gas flow rate on vortex Ar plasma jet flow

In case of the conventional TPCVD using arc jet type plasma, as the working gas flow rate is increased, transition from laminar flow to turbulence flow occurs and flame length and temperature distribution of the plasma jet is dramatically changed during the transition. Since the vortex flow used in this study is created by making the plasma jet run along the inner wall of the vortex flow generation nozzle, appearance of the vortex flow is thought to be influenced by working gas flow rate. Therefore, first of all, influence of working gas flow rate on vortex Ar plasma jet flow is investigated. Fig. 3 shows the front view of the vortex plasma jets. As shown in this figure, it was proved that the vortex plasma jet could be created by using vortex flow generating nozzle. As for the transition from laminar flow to turbulence flow, in our previous study, in case of arc jet plasma,

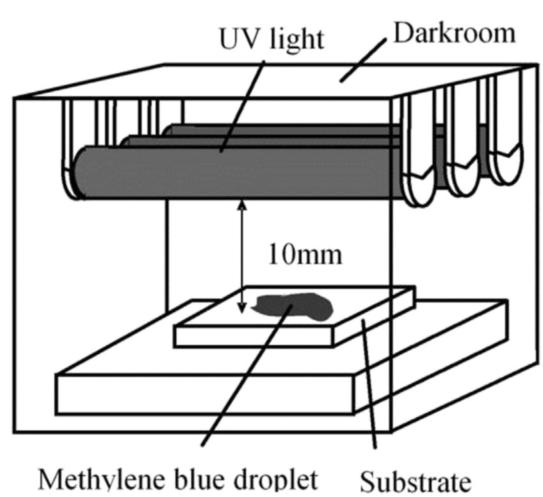

Fig. 2. Schematic diagram of the equipment for methylene-blue decoloration test.