Surface & Coatings Technology 230 (2013) 39–45

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

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

# Scale-up design for industrial development of a PP-MOCVD coating system

Darryl Lee [a], Susan Krumdieck [a,*], Sam Davies Talwar [b]

[a] Advanced Energy and Material Systems Lab, Department of Mechanical Engineering, University of Canterbury, Christchurch, New Zealand
[b] Koti Technology, Inc., Christchurch, New Zealand

ARTICLE INFO

Available online 21 June 2013

*Keywords:*
PP-MOCVD
System design
Ceramic coatings
Industrial coatings
Scale-up

ABSTRACT

The scale-up of research results into industrial processes is a challenge for CVD commercialization. Pulsed-pressure metal-organic (PP-MOCVD) technology does not use a carrier gas. A low-concentration precursor liquid solution is injected into the deposition chamber in discreet, timed pulses. Previous research has indicated that three-dimensional, complex-shaped objects could be coated, and that the process could be scaled-up using simple geometric and time constant relations. This research presents the scale-up design process for a machine to coat a particular product, a stainless steel water pump impeller. Design relations to avoid choked flow and produce uniform coating thickness at high growth rate were estimated and verified experimentally. The pump was inductively heated to 450 °C and coated with $TiO_2$ from alkoxide precursor. The coating had good coverage and was estimated to be 5–6 μm thick.



## 1. Introduction

The industrial potential for oxide ceramic coatings on metal parts has always been promising. Developments in processing techniques, reactor system designs and new materials have provided some new opportunities in protective industrial coatings using CVD [1]. Plasma spray and PVD have the limitations of line-of-sight deposition. CVD could provide coatings for complex-shaped metal parts if cost-effective coating tools could be developed. The well-known trade-off problem for CVD processing is between low-pressure CVD with low growth rate and good coverage and atmospheric-pressure CVD with high growth rate but challenges for achieving uniformity [2].

This paper describes the scale-up design for an industrial coating system using the pulsed-pressure metal-organic chemical vapour deposition process (PP-MOCVD). The distinguishing feature of PP-MOCVD is that it does not use a carrier gas. The liquid precursor solution is delivered via an ultrasonic atomizing nozzle, directly into the continuously evacuated deposition chamber in discreet timed injections. Flash evaporation of the atomized droplets results in a sharp pressure pulse in the reactor. The rapid expansion of the precursor vapour into the chamber produces a "well-mixed" reactor condition that could result in reasonably uniform coatings on complex shapes. After the pressure pulse, a number of seconds are allowed before the next injection and the deposition chamber is pumped down to the base pressure by a rotary vacuum pump. All of the previous experience with PP-MOCVD has been carried out in a research-scale vertical tube, cold wall reactor with volume 1.67 L that could coat samples up to 2 $cm^2$. Numerical modelling studies have shown that the unique expansion-driven mass transport regime could be scaled up and that different chamber geometries could be used [3,4]. The research objective for this project was to demonstrate the design relations for scale-up and the capability of the PP-MOCVD method to coat a complex object.

## 2. Process engineering

Protecting a pump impeller with a ceramic coating could increase the wear resistance and service life. The pump impeller pictured in Fig. 1 has a diameter of 150 mm and a height of 75 mm. The impeller is cast from 304 stainless steel. It has polished external surfaces for installation purposes, but the vanes left as cast. The best fluid wear coating for a water pump is not known. $TiO_2$ was used as a model ceramic coating, largely due to our extended experience with deposition of $TiO_2$ from titanium isopropoxide (TTIP).

### 2.1. General design considerations for MOCVD

The design of conventional, carrier-gas MOCVD tools for industrial production focuses on the detailed fluid dynamics modelling in the reactor across the deposition zone [5]. The numerical modelling of the flow in a conventional MOCVD reactor has provided the understanding of the local mass transport phenomena inside the reactor during deposition [6,7]. Work has also been done on various MOCVD parameters to determine the effects on uniformity of the final coating [8–10]. The modelling of the fluid dynamics in steady-flow processes as well as heating mechanisms allow tool designers to further improve the throughput of the MOCVD system for both research applications and

* Corresponding author at: Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand. Tel.: +64 3 364 2987x724; fax: +64 3 364 2078.
*E-mail address:* susan.krumdieck@canterbury.ac.nz (S. Krumdieck).

0257-8972/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2013.06.064

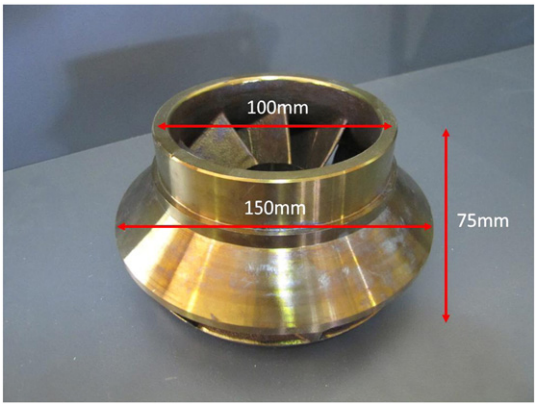


**Fig. 1.** The stainless steel pump impeller to be coated.

commercial development [11–13]. The appropriate modelling of reactor designs reduces the amount of time to develop operating conditions and processes once the system has been developed [14].

Industrial MOCVD tool design has to make trade-offs between the number of units that can be processed and the reliability and uniformity of the coating process. Factors that affect these trade-offs are the reactor size, heating strategies like using hot or cold wall, and the conversion efficiency of precursor to film [15]. The cost per component is a function of capital costs of the coating tool, personnel costs, maintenance, consumable costs and whether the product is suitable for batch or continuous production [16]. These process design factors have been examined individually [17], as specific subsystems of an MOCVD system and as a whole [18,19].

### 2.2. PP-MOCVD process design considerations

The PP-MOCVD process utilizes direct liquid precursor injection of a metered liquid volume at timed intervals through an ultrasonic atomizer into a continuously evacuated reactor [20]. PP-MOCVD is distinguished from other MOCVD approaches in that it does not use a steady flow of carrier gas to transport low volatility precursor to the substrate [21]. The expansion of the precursor and solvent vapour into the evacuated reactor volume results in a well-mixed reactor condition [22], which in turn can result in mass-transport limited growth and potentially high deposition efficiency, sufficient thickness, and reasonable processing time [23]. The well-mixed reactor condition means that a relatively simple modelling approach to the deposition kinetics can be considered [20]. A research scale PP-MOCVD system constructed at a cost of less than $30,000 USD and reliably operating for more than 7 years and has been used to deposit micro and nano-scale conformal layers [24,25].

### 2.3. Precursor vaporization

Fig. 2 shows a typical pressure pulse when precursor is atomized into a continuously evacuated vacuum chamber. A sharp spike is observed in the reactor pressure as the mist of fine droplets are vaporized [26,27]. The deposition chamber is then pumped down, and the next injection occurs. The liquid injection must be done rapidly so that droplets are exposed to the lowest vessel pressure. If the injection continued from time A to time B shown in Fig. 2, then the droplets entering the vacuum chamber at time B would be more likely to evaporate in a continuous manner, shrinking in size while remaining intact, which can lead to aerosol formation.

Fig. 3 shows the two different vaporization modes: (A) instantaneous phase change and (B) aerosol formation. The liquid delivery system and atomizer would ideally to provide 100% vaporization of the injected precursor. The vaporization efficiency is defined as the percentage of precursor in the pulse volume, which is converted to vapour. Large drops that survive for even a short time will have solvent preferentially evaporate from the surface, and the resulting higher concentration solution, exposed to a higher chamber pressure, is likely to continue, simply drying out and forming an aerosol of dried precursor solid. Thus, smaller droplets are desired. A high vapour pressure solvent, with low surface tension and low viscosity, can also help increase the vaporization efficiency. However, chemical compatibility of the solvent with the particular precursor being used is the over-riding consideration. The main operational parameters for evaporation are the concentration of the precursor in the solvent and the minimum chamber pressure. Higher concentration increases growth rate because more precursor is injected in each pulse. However, higher concentration solution also decreases vaporization efficiency because of a greater tendency to form aerosols during evaporation. The best solution given these trade-offs is determined experimentally, and the concentration from the research-scale experiments is used in the scale-up process.

### 2.4. Mass transport

The Knudsen number is a key design variable for conventional steady-flow CVD process design. At Knudsen number near or greater than one, vapour molecules are as likely to collide with the walls of

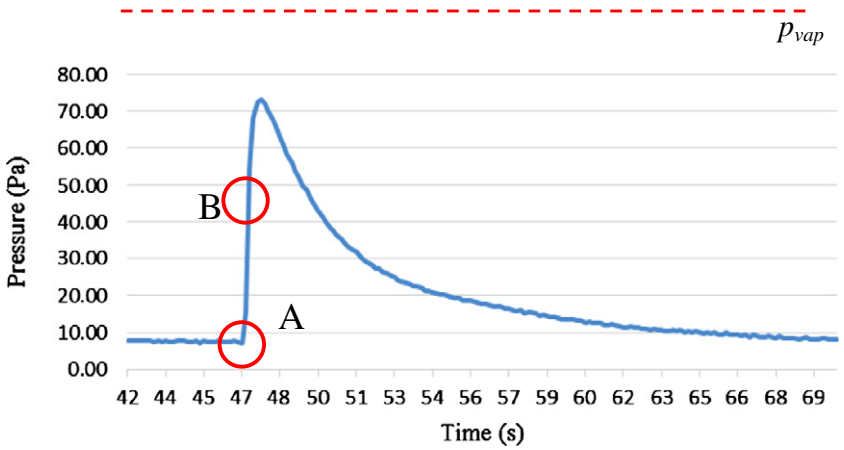


**Fig. 2.** Example of a typical pressure plot of one injection into a continuously evacuated vessel. (A) majority of the precursor enters reactor and flash-evaporates. (B) The evaporation process may be slower as it gets closer to its vapour pressure and aerosols are formed.