EFFECTIVE CORROSION PROTECTION AND SCALING PREVENTION OF COMPLEX GEOMETRIES

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ABSTRACT

Atmospheric chemical vapour deposition technology (APCVD) though available for decades on the market is not widely used in technical applications. By optimizing precursor selection and mixtures, and introducing acid-catalyzed hydrolysis alkoxysilane-based APCVD has been brought to an industrial scale. Coated surfaces are successfully applied in heating and drinking water applications by protecting standard metals against corrosion (e.g. Cu, Al, steel). Based on its anti-fouling properties and the capability of the technology to coat surfaces of almost unlimited complexity further applications in additive manufacturing and for chemical process equipment are under investigation. Chemical modifications of the layers are opening up additional features including adhesion of polymers on metal and anti-stick properties.

INTRODUCTION

Beneficial characteristics of SiO_2-based solids are widely known, applied and in use for thousands of years in domestic ceramics, glassware or porcelain. In the 1960s and 1970s, emphasis was set on creating thin films by atmospheric chemical vapour deposition processes (APCVD), especially for the semiconductor industry (Heunisch, 1969; Osawa, Toyonaka-shi, & Yokozawa, 1971). APCVD setups are quite simple and basically consist of a precursor supply (gas or liquid), eventually an evaporator and carrier gas and a heated coating chamber. Such a setup has to be completed by an exhaust gas treatment. While Heunisch focused on the thermal decomposition of alkoysilane precursors and reported the deposition of useful films from a TEOS (tetraethoxy-silane) precursor at 617°C, Osawa et al. already described the next step towards alternative ways to provide the activation energy. By introducing acetic acid and water to the process film deposition yield was taking place well between 300 and 600°C. Other researchers followed this approach in consecutive process steps (Smith, Ramos, & Roderick, 2000) and continuously operated devices (Morita, 1994). An alternative APCVD approach uses ozone gas to provide the necessary activation energy (Kubo, Homma, & Kishimoto, 1998) (Fujino, Nishimoto, Tokumasu, & Maeda, 1990).

Lower activation energy by catalyzing agents (e.g. carboxylic acid) may also be introduced into the preparation step of the applied precursors. Hofman et al. applied more reactive precursors like diacetoxy-ditertiarybutoxy-silane (DAOBS) or aluminum tri-propoxides (ATI) which decompose into SiO_2 and Al_2O_3 respectively in the 300°C range (Hofman, Morssinkhof, Fransen, Westheim, & Gellings, 1993) and provided additional insight into the reaction mechanism (Hofman, Westheim, Pouwel, Fransen, & Gellings, 1996). While this approach created high-quality films for corrosion protection, the applied precursors are too difficult to handle and too expensive for industrializing the concept. This issue was successfully addressed by Biedermann who included the formation step of the highly reactive acetoxy-silanes into the coating process where the coating precursors were prepared in an initial liquid-phase reactor and evaporated before entering the coating chamber (Biedermann, 1998). The author speculates on a nucleophilic substitution of alkyl groups by acetoxy groups in the liquid phase which readily decompose into silanols in contact with water in the gas phase. These silanols tend to condensate on the surfaces of hot metal parts in the atmospheric coating chamber and form SiO_2 films

This reaction mechanism remains somewhat uncertain and improbable. When analyzing the literature on sol-gel processes where similar chemicals are applied in the liquid phase, no evidence was found for the existence of the acetoxy-silanes (Arkles, Steinmetz, Zazyczny, & Mehta, 1992) (Pierre & Rigacci, 2011). The liquid phase reaction follows a two-step mechanism where a S_N2-mechanism is followed by a subsequent condensation step. Brinker has studied the influence of different catalyzing agents and the effect of

functional groups in the silane precursors in both hydrolysis and condensation (Brinker, 1988).

THE WICOATEC PROCESS

As a conclusion from the study of the existing literature, a simplified APCVD setup was created where available precursors like alkoxy-silanes (e.g. TEOS), carboxylic acid – in this case acetid acid and water are directly and independently evaporated and directed into the coating chamber using an inert carrier gas – the Wicoatec process. Initial mass spectrometry results point to the fact that hydrolysis and condensation take place in the gas phase forming dimeric and oligomeric condensates. By adapting the gas composition, flow rates, residence time and temperature regime in the evaporation process and in the coating chamber, it was possible to create high quality films on metal substrates while reducing process times from days (Biedermann, 1998) to some hours in our process.
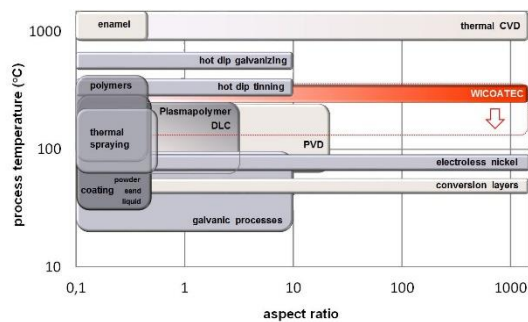
Figure 1
Benchmark on available coating technologies where typical process temperatures and achievable aspect ratios are plotted.
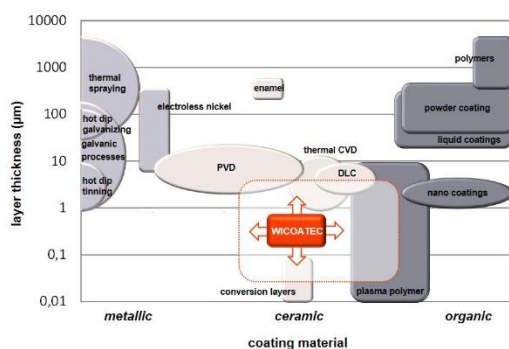
Figure 2
Benchmark on available coating technologies where typical layer thickness and coating substrates are plotted.

Major characteristics of the Wicoatec process are represented in two benchmark figures. Most coating technologies are 'line-of-sight processes' where flat geometries can be coated with good results – see Figure 1 where most of the coating processes are located at low aspect ratios on the left hand side. Theoretically, the atmospheric CVD process 'wicoatec' has no limitations for coating complex geometries like pipes, brazed plate heat exchangers or equipment for the chemical industry. Lowering the process temperature is subject to future developments which may open up additional applications apart from most aluminum, copper and steel alloys.

Many organic functionalities may be introduced into the SiO_2-based coatings created by the Wicoatec process placing it somewhere between metals and organics (Figure 2). Providing adhesive or anti-stick properties to metal substrates is one key element of ongoing R&D activities.

PROCESS EQUIPMENT FOR INDUSTRIAL PRODUCTION

As outlined above recent advances in APCVD technology bring the coating deep inside complex structures and reach surfaces no other technology can explore. Customized compositions of the thin layer components help to solve key challenges of industry participants. Major fields of interest are fouling reduction, chemical adhesion and inertization in combination with reduction of corrosion. By scaling up an atmospheric CVD process from 200 liter lab-scale furnace to 3 cubic meter series production, the beneficial anti-scaling features of silica-based coatings have been made available for large scale applications.
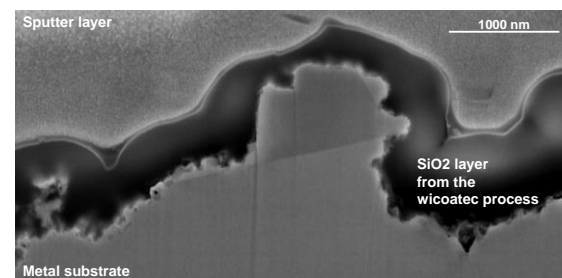
Figure 3
FIB image (fast ion beam) of a micro-etched copper surface with a SiO_2 layer from the Wicoatec process

Coating high aspect ratios by CVD processes is possible at temperatures well above 900°C where alkoxysilane precursors like TEOS thermally decompose (see thermal CVD in Figure 1) significantly limiting the metal substrates to small parts made of a very limited number of high temperature alloys. Alternative CVD processes work at temperatures as low as room temperature. For example, DLC coatings are deposited in plasma-enhanced CVD processes (PECVD) where

accessible aspect ratios are around 1 (Figure 1). The Wicoatec process operates between 200 and 300°C, deposition from the gas phase takes place wherever the precursor gas has access to. Where natural or forced convection do not work (e.g. in pores and micro and nano structures) diffusion will do the job providing uniform coating on a microscopic scale (Figure 3) as well as one macroscopic parts (Figure 4 + Figure 5).

Figure 4
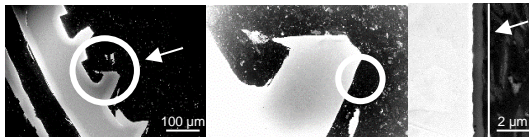CVD modified finned tube for reduced fouling.

Figure 5
Scanning electron microscopy image on the inside of a CVD coated finned tube (as shown above). Metal is shown in white. On the right side the 500 nm thick coating is visible.

One of the main challenges was the implementation of the new CVD technology into a series production environment where several ten thousands of heat exchangers are coated each year. Besides recent process and precursor developments market demands the next development steps in plant technology: mobile production concepts to be operated close to the customers' premises or inside the factory. Future advances in technology might allow the coating of new and existing XL process equipment on site.

MODIFICATION OF CVD THIN LAYER COATINGS OPEN UP NEW APPLICATIONS

Recently, functionalized alkoy-silane precursors were introduced in the SiO_2 layers. By adding these precursors the properties of the coating can be customized to specific applications in many industries where the functionalities created improved properties with respect to elasticity and thermal stress resistance. From high to low surface energy, ranging from low to high chemical functionality and from alkaline to acid resistance in oil and water based systems, all these functions can be built into the silica based layer. Permanent R&D efforts on improving are supported by analytical tools and state-of-the-art testing facilities.

FOULING REDUCTION

Fouling inside complex designs, e.g. brazed plate heat exchangers, where outside dimensions range from centimeters to meters, remains an unsolved challenge for designers, manufacturers and end users of process equipment. Fouling is causing high cost and losses in production due to reduced energy efficiency and extra service time. CVD technology reduces adhesion of impurities and improves the self-cleaning ability of the metal surface. Even if small particles migrate to the coated surface they will pop off and the surface will remain clean and functional. In addition, the thin ceramic layer reduces corrosion by covering the whole surface of parts like condenser, heat exchanger, distillation, metal filter and pipes. Ongoing applications in heat exchangers and metal filters show positive long-term results and prove the functionality of the technology. Over 50,000 pieces are out in the field.
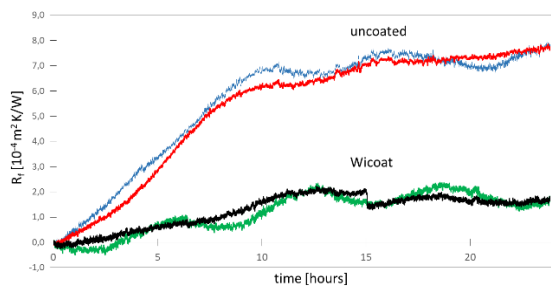

Figure 6
Scaling test in saturated $CaSO_4$ solution after 24 h
Left: CVD-coated shiny aluminum plate without deposits
Right: crystal growth on the entire surface of the uncoated reference piece

In a laboratory setup, aluminum plates were exposed to a saturated calcium sulphate solution. While solution temperature was kept at 40°C (corresponding to maximum solubility of $CaSO_4$), the aluminum plates were heated to about 80°C. Thus, formation of crystals appeared on uncoated surfaces like sample holders and reference aluminum plate (see right hand side in Figure 6). On the surface of the CVD-coated aluminium plate (left hand side in Figure 6) no deposits form – the surface keeps its shiny appearance. The experimental setup

is based on the methods described in (Augustin, 2006).

In parallel, the development of the thermal heat transfer fouling resistance R_f of both coated and uncoated parts was monitored. R_f values for CVD-coated aluminum plates stayed well below 1.4×10^{-4} m² K/W. Uncoated surfaces developed a six fold higher heat transfer resistance of 8.0×10^{-4} m² K/W (Figure 7). Benchmark studies with alternative surface treatments yielded best R_f values for certain DLC coatings (diamond like carbon from PECVD processes) and electropolished surfaces in the range of 2.0×10^{-4} m² K/W (Augustin, 2006).
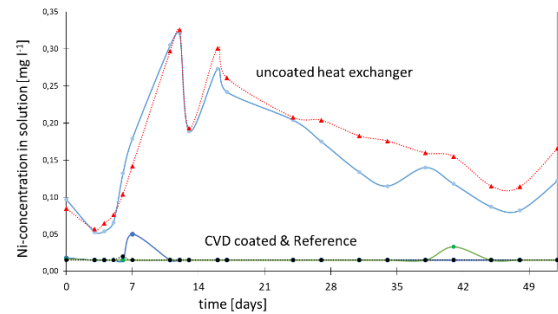
Figure 7
Development of the thermal heat transfer resistance R_f in an inorganic fouling experiment in saturated CaSO4 solution. CVD-coated plates (wicoat) are shown in black and green, uncoated references in red and blue.

Simultaneous optical inspection revealed that the SiO$_2$-based coatings significantly inhibit scale growth by their self-cleaning ability and prevents fouling in the induction phase of the process. Any gypsum deposits forming on the surface may cover small areas of heat transfer surface for short periods of time only. Due to the surface characteristics theses deposits show poor adhesion and easily flip off even though the experiment is performed in almost stagnant water. These observations are available in an internet video (Wieland Wicoatec GmbH, 2019).

CORROSION REDUCTION

Preventing metals from corrosion is a big challenge, especially in aggressive media like saltwater, hot acids or organic solvents. By creating a separation between the metal and the liquid phase CVD coatings prevent the migration of metal ions between systems. This protects the coated metal from leaching and the whole system from metal contamination (Figure 3). This concept also works for preventing metal ions from migrating into water. The separation between the metal and the medium

reduces reactions of metal ions involved in corrosion reactions. Tests performed with tab water on coated versus uncoated heat exchangers show no metal transfer for coated products. On the other hand a significant level of nickel for the uncoated heat exchangers was observed (Figure 8).

Figure 8
Metal leaching: Comparison of nickel migration from heat exchangers into drinking water. CVD-coated products are represented in green and black, uncoated references in red and blue.

CHEMICAL ADHESION

The implementation of chemical modifications on the surface shifts the bonding of glues from physical bonding to far stronger chemical bonding. By changing from adhesion to chemical bonding, new applications for glue-producers and end users arise. Glue-systems become independent from the metal surface because the surface can be modified to fit the specific demands of the respective glue. Thus modified CVD coatings open up possibilities for a huge variety of metals, e.g. nickel, copper or titanium. An example is the modification of copper that can be bound to a resin. In a pull-off test the uncoated system (3.78 MPa) was compared to a CVD coated system (5.60 MPa). The experiment reveled a stability increase of 47 % under standard conditions. A special feature is the temperature and climate change resistance. In a controlled climate change test (-30 to 160°C with maximum humidity) the adhesive force between the resin and the metal substrate was not affected for CVD-coated parts while uncoated references pieces fell apart without external force.

These experimental findings were confirmed by long-term tests where the quality of the bonding between resin and metal substrate was tested with helium leakage testing.

INERT SURFACES

As mentioned above it is possible to reduce reactivity of metal surfaces. Two interesting applications are aluminum calibration gas cylinders and semiconductor production equipment. The Al calibration gas cylinders are coated to reduce metal catalyzed reactions and double the storage time of the test gas.

In the semiconductor production composition and purity of materials in contact with process chemicals is key to achieve performance levels and guarantee functionality. Modified CVD coatings reduce the adhesion of gas molecules and suppress unwanted site reactions on metal components. Thus it is possible to dose different gases at the right time without mixture or reaction of the different gas types.

CVD coatings are also applied in devices for gas analysis where two issues can be addressed successfully. Vulnerability to corrosion can be significantly reduced in dehumidifiers, and memory effects in hand-held devices for gas analysis are minimized which enhances the analytical sensitivity up to an order of magnitude. An example for a coated part in gas analysis is shown in Figure 8. The coating is applied to the inside and outside surface. The internal diameter of the needle is about 3 mm, total height about 10 mm.

Figure 9
Inert gas needle for use in analytical devices.
Left: uncoated, right: coated. The thin, modified silica layer creates a rainbow colour effect on the metal surface.

CONCLUSIONS AND PERSPECTIVES FOR FUTURE DEVELOPMENT

Bringing the Wicoatec process from lab scale into series production was the major issue over the last years. Successful applications in gas-fired boilers, drinking water applications and gas

analytics prove that the improved APCVD can add value to metal surfaces. The unique selling proposition is the coating of complex geometries and inside surfaces. By introducing functionalized precursors into the CVD layers temperature resistance, elasticity and pH stability will further increase. Reactive groups in the layer will improve chemical adhesion of polymers to metal surfaces. Reduced process temperatures may open up additional applications for corrosion protection of electronics.

NOMENCLATURE

APCVD	atmospheric chemical vapor deposition
CVD	Chemical vapor deposition
FIB	Fast ion beam
MPa	Mega pascal
PECVD	plasma-enhanced chemical vapor deposition
PVD	physical vapor deposition
R&D	Research and Development
REM	Reflection electron microscopy
R_f	Heat transfer resistance, m² K/W
TEOS	tetraethoxy-silane

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