Published online www.heatexchanger-fouling.com

# INFLUENCE OF SURFACE DEFECTS AND AGING OF COATED SURFACES ON FOULING BEHAVIOR

T. Geddert<sup>1</sup>, W. Augustin<sup>1\*</sup> and S. Scholl<sup>1</sup>

<sup>1</sup> Technische Universität Braunschweig Institute for Chemical and Thermal Process Engineering, Langer Kamp 7, 38106 Braunschweig, Germany; \*w.augustin@tu-braunschweig.de

## ABSTRACT

To avoid the negative effects caused by fouling in heat exchanger equipment, the heat exchanger surface can be modified energetically or mechanically. Thus mechanical, chemical and thermal stability of the coatings with respect to the fouling and cleaning conditions is crucial. The surface is typically characterized by the measurement of the contact angles of different wetting fluids to calculate surface energy and tactile roughness measurements. The influence of several cleaning and fouling cycles on surface energy and the composition of the coatings has been investigated. The experimental investigation of different cleaning methods from acid to base solution displays the influence of the interface reactions on the surface energy. Structural analysis of the PACVD (plasma activated chemical vapour deposition) coatings are showing a build-in of oxygen inside the a-C:H matrix with time resulting in higher surface energies and an increase of polar interactions. Also, structural defects of the coatings have been analyzed by a defined disturbance of the coating process or mechanical treatment of the already coated material. These defects are acting as a starting point for crystallization fouling due to reduced activation energy of nucleation. Depending on the interface and process conditions, defects can enhance fouling, if the crystals are able to adhere on the coated surface. The results should lead to a better understanding of interface reactions, stability of coatings and the aging of surfaces.

## INTRODUCTION

Fouling of heat exchanger surfaces reduces the heat transfer and leads to an increase of pressure drop. Although fouling results in higher capital and operating costs, the mitigation of fouling is still an unsolved problem.



Fig. 1 Deposition and removal on a heat transfer surface

One possibility to avoid fouling is the modification of the heat transfer surface. Mechanical modification can lead to smooth surfaces with a reduction of nucleation spots [*Geddert2008*] and energetic modifications like coatings can lead to "easy to clean" surfaces. The change of the interactions at the interface surface/fouling layer may cause longer induction times [*Förster1999, Geddert2008, Zhao2005*] resulting in longer operation times and shorter cleaning periods. The influencing factors on fouling and cleaning are numerous, see Fig. 1, and not all mechanisms are completely understood. Particularly the influence of the surface itself and especially the surface energy is still part of current research.

In crystallization fouling, the quantification of the decrease in heat transfer is displayed by the fouling resistance:

$$R_{f} = \frac{1}{k_{f}} - \frac{1}{k_{0}}$$
(1)

Fig. 2 shows a typical fouling curve for  $CaSO_4$  on stainless steel with an initial surface temperature of 75°C. The heterogeneous nucleation on the surface starts nearly immediately, but neither the crystal number nor size is reaching a critical value to affect the integral heat transfer.



Fig. 2 Fouling curve of calcium sulphate

After a certain period of time, the so called induction time, heat transfer is reduced due to the growth of the nucleation spots resulting in a positive value of the fouling resistance.

## **EXPERIMENTS**

#### Surface modification

Modification of the heat transfer surface can be achieved by different coating techniques. The additional layer can be formed by chemical reactions, adsorption or adhesion. The most prominent coating techniques in the field of surface modification are sol gel coatings, ion implantation or sputtering, physical vapour deposition (PVD) or chemical vapour deposition (CVD). In the case of surface modification for fouling mitigation, surface roughness, layer thickness and energetic properties are important. To achieve thin layer coatings with defined surface conditions, stainless steel (AISI304) was coated by plasma assisted chemical vapor deposition (PACVD) in a high vacuum chamber. The coating layer thickness is only  $3\mu m$ , therefore the influence of the additional layer on the heat transfer is negligible. By using PACVD, diamond like carbon (DLC or a-C:H:X) coatings can be precipitated under low temperature (< 200°C) conditions. The coating characteristic can be varied by different ratios of polymer, diamond or graphite as it is shown in Fig. 3.



Fig. 3 Types of carbon based coatings [Robertson1997]

DLC or amorphous carbon hydrogen (a-C:H:X) can be modified due to their composition inside the carbon triangle or by a defined build-in of different molecules inside the DLC matrix. The physical properties of the coating are a function of the composition as it can be seen in Fig. 4. Different structures or different precursor gases can change the wear and heat resistance as well as hardness and surface energy of the coating [*Hieke2001*].



Fig. 4 Physical properties of modified DLC-based coatings [*Hieke2001*]

The modification of the wetting behaviour due to different molecules inside the DLC-matrix is a function of the type of molecule and its concentration as it is shown in Fig. 5. The water contact angle can vary due to interfacial changes from hydrophilic (nitrogen and oxygen) to hydrophobic (silicon and fluorine) behaviour.





The increase of silicon inside the a-C:H:Si coating is leading to surface energies from 40mN/m (0% Si, a-C:H) to 34mN/m (30% Si, a-C:H:Si). The combination of silicon and oxygen as modification elements decreases the surface energy to 25mN/m. All a-C:H:X coatings are produced by PACVD, Chromium nitride (CrN) was prepared by PVD and Ni-PTFE is a galvanic coating.

#### Surface characterization

In order to characterize the coating process and to describe the heat transfer surface, roughness measurements as well as surface energy measurements were performed. While PACVD coatings are nearly form fitting, PVD and galvanic coatings are changing topography as well as the energetic conditions at the interface. While roughness parameters like  $R_a$  and  $R_z$  of PACVD-coatings, stainless steel and PVD-coating are comparable [*Geddert2008*], galvanic coatings leads to higher roughness values due to the coating process.

The energetic conditions of the coatings have been measured by the sessile drop technique shown in Fig. 6. Droplets of six different liquids (1-bromnaphthalene, ethylene glycol, formamide, glycerine, methylene iodide, water) are generated on the surface and their contact angle is recorded by a data acquisition.



Fig. 6 Drop shape analysis for surface energy calculations

The equilibrium of forces at the interface droplet/surface leads to the Young equation:

$$\gamma_{23} = \gamma_{12} + \gamma_{13} \cdot \cos(\theta) \tag{1}$$

The missing parameter  $\gamma_{12}$  is replaced based on the theory of Owens and Wendt [*Owens1969*] by

$$\gamma_{12} = \gamma_{13}^{LW} + \gamma_{23}^{LW} - 2 \cdot \left( \sqrt{\gamma_{13}^{dis} \gamma_{23}^{dis}} + \sqrt{\gamma_{13}^{pol} \gamma_{23}^{pol}} \right)$$
(2)

and modified to a linear equation:

$$\frac{\gamma_{13} \cdot (1 + \cos \theta_{12})}{2 \cdot \sqrt{\gamma_{13}^{\text{dis}}}} = \sqrt{\gamma_{23}^{\text{pol}}} \cdot \sqrt{\frac{\gamma_{13}^{\text{pol}}}{\gamma_{13}^{\text{dis}}}} + \sqrt{\gamma_{23}^{\text{dis}}}$$
(3)

Fig. 7 exemplifies the calculation of the surface energy. The six mean contact angles have to been fitted linearly to calculate the polar and dispersive part of the surface energy.

## **Fouling experiments**

The fouling experiments were carried out in a slowly stirred, temperature controlled 2.81 vessel, illustrated in Fig. 8. A supersaturated aqueous solution containing 0.025 mol/l calcium sulphate (CaSO<sub>4</sub>) at 42°C was produced by adding the well dissolvable salts sodium sulphate and calcium chloride resulting in a saturation index SI=0,12.



Fig. 7 Surface energy calculation based on Owens, Wendt, Rabel and Kaelble

The heating element consists of an electrical rod heater inside a rectangular stainless steel tube. The coated plates with the dimension  $80x20x2 \text{ mm}^3$  can be clamped on two sides of the heating element. Under the coated plates thermocouples are positioned to measure the temperature over time.



Fig. 8 Batch test unit for crystallization fouling experiments

Due to the electric heating, a constant heat flux of  $\dot{q} = 30 \text{ kW } m^{-2}$  was used in all fouling experiments. Assuming a constant convective heat transfer coefficient the interface temperature remains constant during the 24h experiment. The additional layer, which forms due to the inverse solubility of CaSO<sub>4</sub> on the heterogeneous surface, causes an increase of the thermocouple temperature which can be transformed to the fouling resistance.

## RESULTS

#### **Energetic modification**

After several fouling experiments followed by acid cleaning cycles, the surface energy of stainless steel and coated plates was determined. In Fig. 9 the comparison between the surface energy of new and used coatings respectively substrates is shown.



Fig. 9 Influence of fouling and cleaning cycles on the change of surface energy of a-C:H based coatings

Due to the scaling and cleaning process, the interface substrate/liquid drop has been changed. While stainless steel seems to be inert related to energetic changes, PACVD and PVD coatings are significantly affected. Apart from unmodified a-C:H, silicon based coatings as well as CrN are showing similar behaviour. While the dispersive part of the surface energy is reduced, the polar interactions have been enforced. This change of the surface energy is based on several processes taking place at the interface surface/crystal or surface/solution at different time steps during the fouling and cleaning process. To separate the different influencing factors, experiments with unused coatings were conducted with the conditions:

- Storage at ambient conditions (four weeks)
- Storage in pure water (24h)
- Heat treatment at 150°C (24h)

Additionally, the cleaning cycles were simulated by:

- Cleaning with acid solution (HCl, 6 wt-%, 24h)
- Cleaning with base solution (NaOH, 6 wt-%, 24h)



Fig. 10 Influence of storage conditions and heat treatment on the change of surface energy of a-C:H based coatings

Before and after the experiment, all surfaces were investigated focusing on their surface properties. Fig. 10 shows the influence of the storage conditions on surface energy related to the original energetic properties. The different storage conditions are resulting in different interface characteristics. While four weeks at ambient conditions have no influence on the surface properties within the experimental standard derivation ( $\pm$  3mN/m), water storage increases the polar part of the surface energy due to interfacial changes. By contrast the dispersive part is reduced in the same order of magnitude. Heat treatment influences the oxide layer of stainless steel resulting in a change of the polar and dispersive part.

The simulation of the cleaning process, treatment with acid and base solution, shows similar behaviour, displayed in Fig. 11. Except for stainless steel, the surface energy is significantly increased caused by the adsorption processes at the surface.



Fig. 11 Influence of different cleaning solutions on the surface energy of a-C:H based coatings

Silicon modified a-C:H:X coatings are strongly influenced by the cleaning solution. Due to the silicon atoms at the interface, hydroxyl as well as oxygen bonds are possible, resulting in an increase of polar interaction [*Trojan1994*]. The CrN-coating is not acid-resistant and is damaged in the course of cleaning. For more detailed information on the influence of fouling and cleaning, secondary ion mass spectrometry (SIMS) was used to gain depth composition data of the investigated coatings. Fig. 12 shows the change in the depth profile due to fouling and acid cleaning of a a-C:H coating.



Fig. 12 Depth composition profile of an a-C:H coating from SIMS analysis

Inside the a-C:H matrix, the hydrogen concentration at the interface is reduced, replaced by an increase of oxygen bonds in the first 20 nm of the surface. Due to the higher amount of oxygen, the interface potential and hence the surface energy is changed.



Fig. 13 Depth composition profile of an a-C:H:Si coating from SIMS analysis

Silicon containing a-C:H:X coatings, displayed in Fig. 13, seem to have a higher potential to replace hydrogen and silicon by oxygen. Due to the fact that hydrogen as well as silicon bonds are replaced by oxygen, the higher reactivity with the cleaning solutions is explainable. The results of the depth profile show that not only interface conditions are important but also changes in the composition of the coating must be considered.

#### Structural defects

Besides energetic modifications and the examination of the long time stability of the coatings, the influence of structural defects is crucial. After the coating process, which most times take place before assembling the heat exchanger, the coated part must be integrated. On the other hand coating can be done before the forming step of the plates for plate heat exchangers. In both cases the influence of structural defects on the fouling behavior is crucial. Unwanted structural defects can result from damaging through mechanical or chemical cleaning or problems of long time stability including cohesion failure.

Ni-PTFE is a galvanic coating which includes PTFE for minimum adhesion and nickel to avoid crystallization fouling. Referring to Zettler [*Zettler2005*], Ni-PTFE coating are unstable due to dissolving processes of nickel at the interface coating/liquid. In the presence of nickel ions crystallization of calcium salts is inhibited. In long term experiments the continuous diffusion of nickel inside the liquid solution results in a damage of the structural integrity of the coating. As a result of the disorganization parts of the coating are detached through structural failures, creating new nucleation spots as well as a higher surface roughness. The results of several fouling experiments with the identical Ni-PTFE coating are displayed in Fig. 14. The fouling curve is showing a decrease of induction time and an increase of the slope of the fouling curve with higher utilization.



Fig. 14 Fouling curves of Ni-PTFE

To isolate the influence of structural defects from dissolving processes or continuous changes of the macroscopic roughness, two different defined structural defects were created on a-C:H:Si:O coatings. Circular defects have been created by masking the substrate before coating, oblong defects by destroying the coating with a nanoindentor. The area of all defects related to the coated area is less than 1%. Fig. 15 displays the fouling plots of a stainless steel surface, a-C:H:Si:O (SICON<sup>®</sup>) coating and two a-C:H:Si:O coating with defects. Neither the induction time nor the initial slope of the fouling curves seems to be influenced by the defects of the coating. But the increase of the fouling resistance after 10 to 15h is forced by the structural defects of the coatings.



Fig. 15 Fouling curves of stainless steel and a-C:H:Si:O with structural defects

A more detailed analysis within the induction period, displayed in Fig. 16, shows the influence of the defects on the nucleation. While crystals are not able to form neither on the coated surface nor the substrate (stainless steel), the heterogeneous crystallization is forced at the contact points of coating and substrate. This part of the surface is energetically as well as topographically heterogeneous and shows a fractal surface.



Fig. 16 SEM micrograph during the induction period

This generates starting points for the nucleation and should reduce the induction time. Because a-C:H:Si:O has a short induction time in batch conditions, the influence of defects on the induction time is small. With higher flow velocities, the influence of defects depends on the coating material. If the coating is less adhesive, it can be expected that the crystals are not able to connect between different defects due to removal processes. With more adhesive coatings, the potential of crystal bridge building is higher resulting in a greater influence of the defect on the whole fouling process.

## CONCLUSIONS AND PROSPECTS

Due to the significance of the surface energy in terms of fouling mitigation with tailor made coatings, the long term stability and the influence of different cleaning solutions on the contact angle has been investigated. The surface energy experiments show the influence of several fouling and cleaning runs on the measured surface energy. The isolation of the different surface effects during fouling and cleaning are showing negligible influence of air and water storage as well as heat treatment (150°C) on the energetic properties of the different coatings. The simulation of cleaning cycles are showing strong interactions between acid or base solution and the silicon containing interface of a-C:H:Si coatings. Due to hydroxyl or oxygen bonds at the interface the surface energy increases about 30%. Concentration profiles of the coatings are showing an increase in the oxygen content, which is corresponding to a decrease of silicon in the surface near the coating layers. Due to these results, correlations between surface energy and fouling behaviour are only valid for the current energetic conditions.

Besides energetic changes, the influence of structural defects like scratches or heterogeneous coatings was investigated. The results with a-C:H:Si:O show a negligible

effect of defects on the fouling process, but SEM micrographs inside the induction period are showing first crystallization at the intersection substrate/coating. Due to these experimental results, the influence of structural defects on the fouling behaviour is depending on the defect area, the coated surface and the process conditions. Only when the crystals are not able to connect between uncoated areas, small structural defects can be neglected.

Further research should focus on the chemical processes at the interface coating/cleaning solution as well as a systematic study of the influence of different defects on the fouling behaviour.

## ACKNOWLEDGEMENT

The author would like to thank the Fraunhofer Institute for Surface Technology, Braunschweig (Germany), especially Ingmar Bialuch, for the coating process and the SIMS analysis.

## NOMENCLATURE

- k heat transfer coefficient, W m<sup>-2</sup> K<sup>-1</sup>
- $\dot{q}$  heat flux, W m<sup>-2</sup>
- $R_{\rm f}$  fouling resistance, m<sup>2</sup> K W<sup>-1</sup>
- SI saturation index
- $\gamma_{i,j}$  interfacial free energy between two adjacent phases i and j,  $N m^{-1}$
- $\theta$  Contact angle, °

## Subscript

- 0 clean
- l liquid
- 2 solid
- 3 gas
- f fouling
- ind induction

## Superscript

- LW Lifshitz-van der Waals part
- pol polar
- dis dispersive

## REFERENCES

Förster, M., Augustin, W., Bohnet, M., "Influence of the Adhesion Force Crystal/Heat Exchanger Surface on Fouling Mitigation", Chem. Engng. Process. Vol. 38, pp. 449-461, 1999.

Geddert, T., Augustin, W., Bialuch, I. and Scholl, S., "Extending the induction period of crystallization fouling through surface coating," Heat Transfer Eng., vol. 30, no. 10-11, in press, 2009.

Hieke, A., "Verschleissfeste Antihaftschichten auf Basis modifizierter diamantähnlicher Kohlenstoffschichten" Vakuum in Forschung und Praxis, vol. 13, no. 1, pp. 9-14, 2001. Owens, D. and Wendt, R., "Estimation of the free surface energy of polymers" J. Appl. Polym. Sci., no. 13, pp.1741-1747, 1969.

Robertson, J., "Amorphous carbon cathodes for field emission display" Thin solid films, vol. 296, pp. 61-65, 1997.

Trojan, K., Grischke, M. and Dimigen, H., "Network Modification of DLC Coatings to Adjust a Defined Surface Energy" Physica status solidi / A. - Berlin : Wiley-VCH, vol. 145, pp. 575-586, 1994. Zettler, H., Weiß, M., Zhao, Q. and Müller-Steinhagen, H., "Influence of Surface Properties and Characteristics on Fouling in Plate Heat Exchangers" Heat Transfer Eng., no. 26, pp. 3-17, 2005.

Zhao, Q., Liu, Y., Wang, C., Wang, S. and Müller-Steinhagen, H., "Effect of surface free energy on the adhesion of biofouling and crystalline fouling" Chem. Eng. Sci., vol. 60, no. 17, pp. 4858-4865, 2005.