MODIFIED DLC-COATINGS FOR THE MITIGATION OF SCALING ON HEAT TRANSFER SURFACES

Wolfgang Augustin¹, Jiajie Zhang², Ingmar Bialuch³, Timo Geddert⁴ and Stephan Scholl⁵

¹,²,⁴,⁵TU Braunschweig, Institute for Chemical and Thermal Process Engineering, Braunschweig, Germany; ¹w.augustin@tu-bs.de; ²j.zhang@tu-bs.de; ⁴t.geddert@tu-bs.de, ⁵s.scholl@tu-bs.de
³Fraunhofer Institute for Surface Engineering and Thin Film, Braunschweig, Germany; bialuch@ist.fhg.de

ABSTRACT

Fouling is generally defined as the unwanted deposition (or growth) of suspended, dissolved or chemically generated species from process fluids onto heat transfer surfaces. These layers can lead to a drastic increase of the heat flux resistance, thereby decreasing the thermal efficiency of the equipment, e.g. heat exchangers. Efforts towards avoidance or reduction of the occurrence of fouling most times lead to only limited success, and in such cases, typically require great effort to achieve such.

A method to reduce fouling is an extension of the induction time by a defined modification of interfacial interactions between heat transfer surface and deposit. These interactions are caused by molecular and mechanical forces, so two approaches for fouling mitigation have been developed:

1. Modification of the energy related properties of the heat transfer surface.

2. Modification of the geometry-related properties of the heat transfer surface.

This work employs the first strategy, where the induction period is explored in detail to gain information about the conditions which prolong induction period. In this period, the formation of stable crystals on the heat transfer surface and their compaction to a fouling layer take place. This process is mainly dependent on the interfacial free energy crystal/heat transfer surface. For many industrial applications of compact heat exchangers the only possibility to influence this energy is to modify the energetic properties of the heat transfer surface, i.e. its surface energy. Various surface coatings have been examined by exposing the surface to a saline solution within a fouling test unit. All results were compared with standard stainless steel surfaces.

INTRODUCTION

The formation of fouling layers on heat transfer surfaces is a severe problem in process industry. Due to insulation these crystalline deposits contribute to the overall heat transfer coefficient, thereby deteriorating the thermal performance of heat exchangers considerably (Müller-Steinhagen, 2000).

In crystallization systems the fouling process can be divided into two periods, i.e. induction and fouling period, as shown in Fig. 1. For the crystalline deposit the fouling resistance, \( R_f \), was used:

\[
R_f = \frac{1}{k_f} - \frac{1}{k_0}
\]  

(1)

The formation of stable nuclei at the heat transfer surface and the crystal growth already take place within the induction period. Subsequently, the profile of \( R_f \) i.e. its variation with time in the fouling period can be measured.
Both induction and fouling period consist of a deposition and removal process, respectively described by the deposition mass rate $m_d$ and removal mass rate $m_r$. The deposition mechanism of the induction period is a function of the nucleation rate, whereas the removal mechanism is mainly influenced by the adhesion between crystals and heat transfer surface as described in Fig. 2.

Modern anti-fouling strategies are based on approaches to increase the duration of the induction period, hence decreasing the adhesive strength of the crystals (Förster et al., 2000). In order to relate physical properties of the interface crystal/heat transfer surface to adhesion, the interfacial interactions have to be analyzed (Zhao and Müller-Steinhagen, 2002).

The deployment of surface materials such as DLC (diamond like carbon) respectively a:C:H coatings proved to be a strategy to increase the duration of the induction period. The surface energy can be reduced significantly by the built-in of elements like silicon and oxygen (a-C:H:Si:O) or fluorine (a-C:H:F) which are both hydrophobic and oil repellent. Low surface energies correspond to high contact angles, see Fig. 3.

By modifying the DLC network with fluorine (a-C:H:F) the surface energy of DLC coatings can be reduced from 42 to 20 mN/m. Silicon and oxygen modified DLC (a-C:H:Si:O) can reduce the surface energy to 22 mN/m, but their wear resistance is more than 10 times higher than that of a-C:H:F coatings.

**EXPERIMENTS**

**Surface modification**

Such modified DLC films were deposited by plasma assisted chemical vapor deposition (PECVD) or physical vapor deposition (PVD), both at low substrate temperatures ($T < 200 °C$), in a vacuum chamber. Typical properties of DLC-coatings are high hardness, high wear resistance, low friction coefficient (e.g. vs. steel), low electrical conductivity, good chemical inertness and an adjustable surface energy.

Fig. 4 shows the scheme of the used PECVD deposition arrangement. The chamber was evacuated to a base pressure of $< 10^{-3}$ Pa. Before starting the DLC deposition, the substrates were cleaned by a sputtering
process with Ar ions for a few minutes. To achieve a good adhesion, first a silicon containing DLC (a-C:H:Si) interlayer (some 100 nm thick) using tetramethylsilane (TMS: Si(CH₃)₄) as a precursor gas was prepared. Then the gas composition was changed to a pure hydrocarbon gas, either methane (CH₄) or acetylene (C₂H₂) for pure DLC films and in some cases TMS or hexamethyldisiloxane (HMDSO) additionally. Table 1 shows the surface modifications used for the investigations.

Table 1 Surface modifications

<table>
<thead>
<tr>
<th>Surface</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>X5CrNi18 9 (1.4301)</td>
</tr>
<tr>
<td>DLC</td>
<td>a:C:H</td>
</tr>
<tr>
<td>Si-DLC</td>
<td>a:C:H:Si</td>
</tr>
<tr>
<td>SICON®</td>
<td>a-C:H:Si:O</td>
</tr>
<tr>
<td>SICAN®</td>
<td>a:C:H:Si</td>
</tr>
<tr>
<td>CrN</td>
<td>CrN</td>
</tr>
<tr>
<td>Sol-Gel with hydrophobic and oleophobic function</td>
<td>99.9% Copper</td>
</tr>
<tr>
<td>Cu</td>
<td>99.9% Copper</td>
</tr>
</tbody>
</table>

Chromium nitride (CrN) was prepared by a reactive magnetron sputtering process (PVD). The chromium material was emitted from a solid target during a sputtering process in a nitrogen atmosphere. In this case CrN was the coating with the highest surface energy.

The sol-gel process is a technology for the synthesis of inorganic and hybrid materials ranging from molecularly disperse precursors through nanoscale particles to thin films with several µm thickness. The main advantage of the sol-gel technology in comparison to a vacuum process is the low investment cost of the deposition equipment. In this case the sol-gel film was an anti-adhesive coating with hydrophobic and oleophobic function. It was the coating with the lowest surface energy in the ranking.

**Roughness and topography**

In order to elucidate the influence of mechanical interactions at the interface crystal/heat transfer surface on the induction period in crystallization fouling, measurements of roughness, micro contours and topography based on the tactile stylus method were conducted, see Fig. 5. For the evaluation of surface contour the R-profile (roughness profile) is deployed, resulting from filtering the original P-profile (primary profile).

Fig. 6 shows the results of the surface measurements. There is no significant difference in the mean roughness depth, Rₚ, for the stainless steel based substrates except the very smooth sol-gel coating which shows an mirroring surface. This results from the basically different coating technique. Also the copper plate is less rough but has directed longish structures due to the manufacturing process.
The AFM (atomic force microscope)-micrographs displayed in Fig. 7 for selected surfaces show the difference in topography. The topography of the stainless steel plate is dominated by the grain boundaries. These are expected to be the nucleation points for the crystallization because of the lower activation energy at sharp edges and narrow grooves.

The DLC-coating produces an additional layer on top of the stainless steel substrate but it is not leveling the surface roughness. The original structure of the substrate is reproduced by the surface of the DLC-coating. The valleys of the structure represent the former grain boundaries. In contrast to crystallization, the amorphous hydrocarbons prefer to deposit out of the plasma on plain areas. Even so the sharp edges and narrow grooves of the stainless steel were smoothed. The topography of the standard DLC-coating is representative of the whole set of different DLC-coating used in this experimental work.

The sol-gel-coating also creates an additional layer but because of the liquid application followed by the thermal hardening the original surface roughness is leveled. Visible to the naked eye is the mirroring effect of the surface finish which corresponds to roughness values < 0.2 µm, required for this effect.
**Surface energy**

In order to evaluate the dependence of fouling behavior on surface material during the induction period, the physical mechanisms occurring at the interface crystal/heat transfer surface have to be analyzed. An important parameter influencing molecular interactions is the interfacial free energy (Förster et al., 1999)

$$
\gamma_{ij} = \frac{\partial G}{\partial A}_{T,p}
$$

defined as the total reversible work to create an interfacial area at the interface of the phases i and j. Here, $G$ denotes the Gibbs free energy of the system, $T$ the temperature and $p$ the pressure.

Resolving the interfacial free energies given in Fig. 8 in horizontal direction leads to the Young equation:

$$
\gamma_{23} = \gamma_{12} + \tilde{\gamma}_{13} \cdot \cos \theta_{12}
$$

In order to calculate the surface free energy $\gamma_{23}$ of the heat transfer surface, the following procedure has to be carried out:

1. Determination of $\tilde{\gamma}_{13}$ which is the surface tension of the test liquid (pendant drop method or literature data).

2. Measuring the contact angle $\gamma_{12}$ by DSA (drop shape analysis) as outlined in Fig. 9. Here, a droplet of a test liquid is placed upon the surface to be characterized. By means of a CCD camera and a data processing system the image of the liquid droplet is digitized. Afterwards, the contour of the droplet is analyzed with respect to the determination of $\gamma_{12}$ which is the contact angle corresponding to the wetting equilibrium.

3. Substitution of the interfacial free energy between droplet and heat transfer surface $\gamma_{12}$ in Eq. (3) using the geometric/harmonic mean or the Lewis acid-base approach according to Table 2.

Table 2 Calculation of $\gamma_{12}$

<table>
<thead>
<tr>
<th>Approach</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Owen-Wendt-Kaeble approach</td>
<td>$\gamma_{12} = \gamma_{13}^{\text{LW}} + \gamma_{23}^{\text{LW}} - 2 \left( \sqrt{\gamma_{13}^{\text{dis}} \gamma_{23}^{\text{dis}}} + \sqrt{\gamma_{13}^{\text{pol}} \gamma_{23}^{\text{pol}}} \right)$</td>
</tr>
<tr>
<td>Lewis acid-base approach</td>
<td>$\gamma_{12} = \gamma_{12}^{\text{LW}} + \gamma_{12}^{\text{AB}} = \left( \gamma_{12}^{\text{LW}} - \gamma_{23}^{\text{LW}} \right)^2 + 2 \left( \sqrt{\gamma_{13}^{\text{LW}} \gamma_{23}^{\text{LW}}} - \sqrt{\gamma_{13}^{\text{dis}} \gamma_{23}^{\text{dis}}} - \sqrt{\gamma_{13}^{\text{pol}} \gamma_{23}^{\text{pol}}} \right)$</td>
</tr>
</tbody>
</table>

The restrictions of Eqs. (4) and (5) and the corresponding assumptions are discussed in detail by Förster and Bohnet (2000).

4. Calculation of $\gamma_{23}$. DSA-measurements with at least two (geometric/harmonic mean approach) or three test liquids (Lewis acid-base approach) enables to solve the system of equations.

There is a significant difference in the surface energy for the different materials as shown in Fig. 10 with stainless steel having the lowest and CrN the highest value. Also the ratio of the disperse and polar part differs significantly. Sol-gel and SICON® show a
polar part of almost zero, the ratio for standard DLC is equal and for CrN the polar part prevails.

The choice of the approach for the calculation of the surface energy has only a minor effect on the results except for stainless steel where they disagree. The calculation with the Lewis acid-base approach was not possible for CrN because of not enough feasible test liquids due to the very low contact angle.

![Surface energy graph](image)

**Fig. 10 Surface energy**

**Fouling experiments**

Fouling experiments were carried out in a temperature controlled 2.8 l vessel, illustrated in Fig. 11. A slowly rotating stirrer equalizes temperature and concentration gradients without introducing high shear stress on the surface. A supersaturated aqueous solution of calcium sulfate with a concentration of 3.4 g/l and a temperature of 42 °C was produced by adding the well dissolvable salts sodium sulfate and calcium chloride. The concentration was quantified by titration and the electrical conductivity was calibrated.

![Fouling test unit](image)

**Fig. 11 Fouling test unit**

A heating element, as shown in Fig. 12, was immersed in the salt solution. It consists of a electrical rod heater that was molded with lead in a rectangular pipe made of stainless steel. Two thermocouples with a diameter of 1 mm are fixed in grooves on two sides of the heating element. The actual heated plates with the
different surfaces can be clamped with brackets on the sides with the thermocouples. This allows a simple design (80 mm × 20 mm × 2 mm) and an easy assembly of the test items. The surface temperature is adjusted to 75 °C.

Measuring quantities are solution temperature, pH and electrical conductivity as gage for the salt concentration as well as the surface temperature of the heating elements. Knowing the change of temperature difference between bulk and surface over time allows the calculation of the fouling curves.

Figs. 13 and 14 display the fouling curves for all tested surfaces subdivided into surfaces with a water contact angle $\Theta$ of around 90° and less than 90°. The curves show the typical run. After a short time there is a more or less high negative value of the fouling resistance, i.e. an increase of the heat transfer, caused by the greater turbulence due to first crystals growing on the surface.

At first sight the difference in induction time comes apparent. This ranges from stainless steel with an induction time of 3 h to SICAN® with 12 h. This confirms the assumption that the surface material affects the nucleation and the crystal growth in some way.

At the end of the induction period the normal growth of the crystal layer begins with nearly the same slope for all experiments. Deviations particularly at the end of a test run are caused by the decrease of the supersaturation. Because of the interest in the induction time this effect can be neglected.

Fig. 13 Fouling curves for different surface materials ($\Theta \approx 90^\circ$)

Fig. 14 Fouling curves for different surface materials ($\Theta < 90^\circ$)

Fig. 15 Surface energy and induction time
Fouling behavior and surface energy are compared in Fig. 15. The different surface materials are listed with ascending induction time, i.e. better fouling behavior, from left to right. The comparison of total surface energy data with induction time yields no correlation between surface energy and fouling behavior. Also the consideration of the polar and disperse parts shows no clear tendency.

CONCLUSIONS AND PROSPECT

The experimental results display the possibility to change the fouling behavior of heat transfer surfaces by modifying of the surface properties. New DLC-coating tailored with the variable build-in of additional elements show promise. The induction period could be extended four times.

Comparing gageable surface properties such as roughness and surface energy with the induction time yield no clear-cut tendencies for the prediction of the fouling behavior. This can also not be explained by the nature of the chemical elements added to the surface, i.e. the build-in of Silicon (Si-DLC, SICAN®, SICON®) extends the induction time variably. Here the combination of elements and the distribution is determining.

Thus, the choice of surface material with respect to least fouling occurrence cannot be solely based on surface properties of the heat transfer surface. In order to find the optimal surface material the adjacent crystalline deposit has to be taken into account since the latter phase also influences molecular interaction at the interface crystal/heat transfer surface.

Further investigations will focus on the nucleation. A new test rig was build at TU Braunschweig to visualize the nucleation on different surfaces in-situ with the application of an AFM. Fig. 16 shows one of the preliminary results. The micrograph displays a 5 by 5 µm section of a stainless steel surface after 30 min of application in a flowing salt solution. The groove in the middle is a ca. 1.1 µm deep grain boundary. The visible structures in the groove are growing crystals which was verified by XRD (x-ray diffraction) measurements. A significant number of experiments with different surface coatings and topography will result in a better understanding of the interactions between heat transfer surface and crystals.

Future research should also contribute to the improvement of the description of interfacial interactions. Here, the theoretical treatment of the induction period is based on the assumption that a static lattice constitution of the deposit can be expected since the heat flux density \( \dot{q} \) is rather low during the fouling experiments. However, in the case of higher values of \( \dot{q} \), crystalline deposits made of calcium sulphate may be subject to an ageing process. That means that during crystallization the system does not necessarily transform into the most stable state but into one which is accompanied by the smallest loss of free energy (Mullin, 1993). In a succeeding ageing process the thermodynamic stable state is achieved after a more or less long period of time. The ageing process at the interface crystal/heat transfer surface leads to a loss of constitutional water reducing the adhesive strength (Fürster and Bohnet, 2000). The understanding of the physical principles of ageing, i.e. its impact on adhesion, is a crucial premise for the development of a comprehensive model describing the induction period.

ACKNOWLEDGEMENTS

Financial support for this research work has been granted by „Arbeitgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V. (AIF)“, „Europäische Forschungsgesellschaft Dünne Schichten e.V. (EFDS)“ and „DECHEMA“.

Fig. 16 AFM micrograph of growing crystals
NOMENCLATURE

A  area, m²

A  concentration, g l⁻¹

G  Gibbs free energy, J

h  enthalpy, J

k  heat transfer coefficient, W m⁻² K⁻¹

ṁ  mass flow rate per unit area, kg m⁻² s⁻¹

p  pressure, Pa

Rf  fouling resistance, m² kW⁻¹

Rz  mean roughness depth, m

T  temperature, K

t  time, h

w  flow velocity, m s⁻¹

γij  interfacial free energy between two adjacent phases i and j, J m⁻²

θ  contact angle, degree

τ  wall shear stress, N m⁻²

ζ  adhesive strength, N m⁻²

0  clean surface

1  adhesive phase

2  substrate phase

3  surrounding phase

~  test liquid

+  electron acceptor

−  electron donor

SUBSCRIPT

AB  Lewis acid-base

d  deposition

dis  disperse

f  fouling

ind  induction period

LW  Lifshitz - van der Waals

pol  polar

r  removal

w  wall

REFERENCES


