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AGING AND THERMAL CONDITIONING OF MODIFIED HEAT EXCHANGER SURFACES -IMPACT ON CRYSTALLIZATION FOULING

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ABSTRACT

In many research studies Diamond-like-carbon (DLC) coatings are used to change the wetting behavior by varying the solids' surface free energy of heat exchanger surfaces to mitigate crystallization fouling. For future industrial application the stability of their specific surface properties, exposed to fluidic, thermal and chemical stresses determines their efficiency. Therefore, fluidic thermal and cleaning stresses applied to the coating are investigated. Cleaning procedures with acid, base and heat treatment over multiple cycles were conducted, in order to investigate the solids' surface free energy over time and thereby the stability of the coating. From these information an optimal conditioning to set constant surface properties was derived. Furthermore, the fouling behavior of CaSO4 on new and conditioned coatings was investigated in order to identify repeatable and favorable surface properties for fouling reduction. For all coatings the cleaning treatments and fouling experiments provided changes in the energetic surface properties, dominated by the change of polar/ γ^{-} content. Most probably these changes may originate from varying elementary composition and structure of the coating.

INTRODUCTION

In the field of fouling thin (< 3 μ m) amorphous hydrogen containing carbon coatings (a-C:H or DLC) proved to mitigate fouling effectively in many applications (Müller-Steinhagen et al. 2000, Beuf et al. 2004, Zettler and Müller-Steinhagen 2005, Augustin et al. 2006, Geddert et al. 2007, Augustin et al. 2007, Bargir et al. 2009). Their interactive aims are: (i) to extend the induction phase by establishing unfavorable wetting behavior for the depositing material and (ii) decrease adhesive forces in the crystal growth phase; both by varying the solids' surface free energy (Trojan et al. 1994, Bargir et al. 2009). In industrial applications DLC-coatings acting as heat transfer surfaces for flowing liquids will be exposed to mechanical, thermal and chemical stresses during production and cleaning processes. Therefore the stability of the coating to retain its favorable conditions are investigated to qualify reliable process application in the future.

In fouling investigations the varying fouling behavior of new and used DLC coatings has to be addressed. The prediction of fouling in the induction and crystal growth phase is considered in many research studies (Förster et al. 1999, Grosfils et al. 2004), mostly for modeling or in flow simulations (Brahim et al. 2004, Bayat et al. 2012) to consider the additional heat transfer resistance caused by the fouling layer for the optimization of processing or the design of heat exchangers. For fouling experiments, well-defined repeatability through and constant experimental conditions and procedures is essential to relate a certain behavior or effect to the prediction of induction or crystal growth phase. For example a single SICON[®] plate was investigated, as described in detail in experimental procedure, at constant process conditions over multiple repetitions resulting in varying fouling behavior, see Fig. 1. Regarding Exp.1 a new untreated plate seems to be most unfavorable in terms of the shortest induction phase and the highest crystal growth rate. For all repetitions the induction phase is extended and the crystal growth rate is decreased compared to the new state. Therefore, a newly coated SICON[®] surface is not representative to describe reproducible fouling behavior. Though regarding all repetitions no clear repeatable behavior can be identified. despite a reduction compared to the new state. For some experiments the induction time is increased with or without a roughness controlled phase and for some the crystal growth rate is in the same order of magnitude. The following questions appear: (i) why do the crystals adhere more or less under the same fluidic stress, heat flux, super saturation and surface temperature, (ii) when is the surface modification suitable to avoid fouling at repeatable conditions and iii.) how long can this condition be preserved?



Fig. 1 Fouling resistance over time for one SICON[®] plate in multiple repetition experiments from new and used surface.

These questions should be addressed to the interaction between heat transfer surface and crystals and to the time dependent changes of these properties. Therefore the physical properties of the solid surfaces are considered in closer detail. If an adhesive or fouling behavior could be related to a certain surface free energy and the repeatability of fouling experiments is pursued, the solids' surface free energy should be kept constant. Therefore investigations on DLC coatings reaction to different types of treatment over time and how this impacts the fouling behavior become of interest. For predicting optimal surface conditions to avoid crystallization fouling, the changing conditions over time from new and multiple use are of interest.

Objectives of the presented work are to determine the influence of cleaning procedures and fouling experiments on the surface free energy of different DLC coatings utilized as heat exchanger surface. For cleaning procedures nitric acid, sodium hydroxide and a thermal treatment was investigated. The fouling experiments were conducted with CaSO₄. For comparing the impact of each treatment to the surface free energy, two analysis methods, OWRK and acid-base were consulted. A possible oxygen inclusion in processed coatings were analyzed with an EDX application of SEM measurement. The long-term stability of coatings compared to a stainless steel reference, impact on their fouling behavior and possible favorable conditions are discussed in the end.

EXPERIMENTAL INVESTIGATION

Surface free energy

The relation between a droplet and a solid surface can be expressed by the interfacial energy γ_{SL} as

where W_a is the adhesive work to separate the liquid and solid from contact (Bargir et al. 2009). The solids' surface free energy is given by the Young equation (Young 1804).

(2)

(3)

(1)

Referring to Fowkes (1964), the surface tension of liquids and surface free energy of solids are distinguished in the dispersive part, accounting for the London forces of molecular interaction and the polar content for all other molecular interactions, i.e. hydrogen bonding, Keesome (dipole-dipole interaction), Debye (dipole-induced dipole interaction), etc.. Owens and Wendt established a method to evaluate the interactive surface free energy from the contact angle measurement considering the geometrical mean of polar and dispersive content (Owens 1969). Kaelble (1971) extended this equation with the Young equation, getting rid of the unknown interfacial surface free energy using multiple liquids for contact angle measurement. Finally, Rabel (1971) gained access for the calculation of the two unknown parameter γ_{SV}^{d} and γ_{SV}^{p} through a linear regression.

Since both values are unknown, at least two different liquids with known physical properties of polar and dispersive contents are needed to evaluate $(\gamma_{SV}^{\ d})^{0.5}$ from the offset and $(\gamma_{SV}^{\ p})^{0.5}$ from the slope.

The approach of (van Oss et al. 1988) considers the polar and dispersive content in the surface free energy of liquids and solids as well. Since the London forces dominate the van-der-Waals-interactions, van Oss regards the whole Lifshitz-van-der-Waals (LW) interactions as the non-polar interaction. The acid-base (AB) content accounts for the acid-base interactions where the acid interaction is the electron acceptor γ^+ and the base content the electron donor γ^- .

(4)

Analog to the OWRK method the AB and LW contents are inserted in the Young equation eq. (2) resulting in:

To evaluate the three unknown parameters γ_{SV}^{LW} , γ_{SV}^+ and γ at least three different test liquids are needed to assess the surface free energy, of which two need to have acid and base contents greater than zero (van Oss et al. 1988), see Table 1.

Table 1 Physical properties for determination of the surface free energy via i) OWRK and ii) acid-base method.

| i) liquids OWRK | surface tension data [10 ⁻³ Nm ⁻¹] | | |
|--|---|------|------|
| | | | |
| water H ₂ O | 72.8 | 51.0 | 21.8 |
| ethylene glycol C ₂ H ₆ O ₂ | 47.7 | 16.8 | 30.9 |
| formamide CH ₃ NO | 58.2 | 23.1 | 35.1 |
| 1-bromnaphthalene C ₁₀ H ₇ Br | 44.6 | 0.9 | 43.7 |
| diiodmethane CH ₂ I ₂ | 50.8 | 2.3 | 48.5 |
| | | | |

| ii) liquids acid-base | su | rface tens | ion dat | ta [10 ⁻³ Nı | m ⁻¹] |
|--|------|------------|---------|-------------------------|-------------------|
| water H ₂ O | 72.8 | 21.8 | 51 | 25.5 | 25.5 |
| ethylene glycol C ₂ H ₆ O ₂ | 48 | 29 | 19 | 1.92 | 47 |
| formamide CH ₃ NO | 58 | 39 | 19 | 2.28 | 39.6 |
| 1-bromnaphthalene C ₁₀ H ₇ Br | 44.4 | 44.4 | 0 | 0 | 0 |
| diiodmethane CH ₂ I ₂ | 50.8 | 50.08 | 0 | 0 | 0 |

Cleaning procedure

For all cleaning procedures plates of stainless steel 316L (SS) with the size of 80 x 20 x 1.5 mm³ with different surface modifications were investigated. For a number of plates the surface roughness was decreased to $S_Z \approx 1 \ \mu m$ by electro polishing (EP). The two different coatings are hydrogenated amorphous carbon a-C:H (DLC) and a-C:H:Si:O (SICON[®]) doped with silicon and oxygen (VDI, 1996). The acid and base treatments were carried out with 5% nitric acid (HNO₃) and 5% sodium hydroxide (NaOH) each for 30 minutes at 50 °C. The thermal treatment of all surface modifications was carried out in de-ionized water at 90 °C for 24 hours. All treating liquids were preheated to the desired temperature before the probes were immerged in a fluid-filled beaker, which was placed in a hot-air cabinet (Heraeus UT 5050). The contact angles were measured by drop shape analysis utilizing a Krüss DSA 100 expert. The contact angles of the test liquids, see Table 1, were measured with the dynamic progression method before and after surface treatment and the solids' surface free energy was calculated. At first four successive treatments were conducted obtaining all surface free energies before and after treatment. In order to investigate the long-term stability six consecutive treatments followed whereupon the surface energy was determined. For each treatment two plates (P1 and P2) with identical surface modification were placed in each treating liquid as parallel probes.

Fouling experiments

The fouling behavior on different surface modifications, utilized as heat exchanger surfaces, was investigated in a fouling test rig, see Fig. 2. Here a flow channel is composed of three partitions, inlet, heat exchanger and outlet section. All provide a rectangular cross sectional area with 18 mm in width and 7.3 mm in height, resulting in a hydraulic diameter of 10.39 mm. The inlet section provides a transition from circular to rectangular geometry and an inlet path of 230 mm. The inlet length provides the possibility for hydrodynamic development of the examined flow regime. A flow velocity of 0.3 m s⁻¹ at 42 °C results in a Reynolds number of Re = 4890. According to equation 11 (Herwig 2008) the chosen

inlet path is sufficient for the hydraulic development. The heat exchanger section consists of a copper block providing heat from nine cylindrical electric heating rods (each 30 W) ordered perpendicular to the flow direction for uniform heat distribution. A probe ($80 \times 20 \times 1.5 \text{ mm}$) is placed upon the copper block, clamped with two isolator blocks and

enclosed through a lid with additional optical access. The thermal fouling resistance R_f is measured via three thermocouples 2 mm beneath the probe in the copper block, arranged along the plate and calculated with equation 12.

Hereby T_0 is the temperature at clean state, T(t) the varying temperature over time during the experiment and \dot{q} the heat flux, which was set constant via the electrical heating. In a tank 25 L of de-ionized water with a CaSO₄ concentration of 0.027 mol L^{-1} were provided at the initial start of each fouling experiment. The liquid solution was pumped by a pump (Verder 35FX6PPP200000US-8) gear with (2.36 ± 0.01) L min⁻¹, controlled by an inductive flow meter (Krohne, OPTIFLUX 5000), through a pre-heater connected to a cryostat (Medingen, TC 250) to provide a constant inlet temperature of (42 ± 0.2) °C. Before and after the flow channel static mixers are placed to disturb the temperature profile for temperature measurement leading to accurate heat flow evaluation. The solution was constantly recirculated and heated up in the heat exchanger with (120 ± 1) W, resulting in initial surface temperatures \approx 78 °C. The solution was prepared by dissolving 95.88g of sodium sulfate (Na₂SO₄. CAS:7757-82-6) and 159.39g calcium-nitrate-tetra-hydrate(CaN2O64H2O, CAS:13477344) each in one Erlenmeyer flask with 2.5L of de-ionized water stirred and preheated to approximately 40 °C. Before adding the salts to the 20L water in the tank and starting the fouling experiment a degasification was realized by setting an absolute pressure of 85 mbar using vacuum pump P2 (Vacu-



Fig. 2 Fouling test rig with flow channel.

ubrand PC520NT). Herewith boiling was established for 30 minutes to remove dissolved gases within the liquid, thus avoiding bubble formation at the heat exchanger surface at the initial start. After the pressure was set back to atmospheric condition, both solutions were added to the water in the tank and the experiment was initiated. After the experiment the heat exchanger plate was removed from the plant, the fouling layer was washed-off with de-ionized water, cleaned with isopropanol and dried with pressure air for DSA analysis. The plant was cleaned with de-ionized water several times, where after a cleaning solution with 2% acetic acid for 5 hours was applied. Several consecutive water cleaning treatments were conducted, until a conductivity sensor in the tank measured values below $50\mu S \text{ cm}^{-1}$.

RESULTS

Cleaning stability of DLC coatings

Base treatment

The surface free energy (SFE) of the different modifications evaluated with OWRK and acid-base method for base treatments are present in Fig. 3. The measured pH values for the base treatment were pH 13.5 ± 0.2 . The shown tolerances are based on the R² of the linear equation of the measured liquids form Tab. 1 and are calculated with the maximum of the resulted overall surface free energy value. The dispersive and polar content which in addition is the overall SFE are presented in columns. From untreated state (new) over cleaning treatments from experiment 1 to 10 (E1...E10) both plates of the same modification (P1, P2) and their treatments are displayed next to another. Regarding the results with OWRK and acid-base method, both plates of the same modification mostly show similar trends for the overall, polar, dispersive, AB and LW contents. Therefore the parallel probes support validity of the results. The stainless steel modification (SS) seems not to be affected by the base treatment. The overall SFE for both methods remains within the calculated tolerances, which is expected since 316L should resist chemical stress of base treatment. Regarding all coating modifications four major outcomes from the OWRK method can be identified:

- 1) Decrease of dispersive content for unpolished coated surfaces and significant increase of the polar content for all coatings.
- 2) Constant surface conditions after 3 to 4 treatments, within experimental variation.
- 3) After four treatments, six more repetitions do not impact the overall SFE as well as the ratio between polar and dispersive content.
- 4) The first treatment shows the greatest impact on the change of the SFE, especially for SICON[®] surfaces.

Especially the change for SICON[®] and its EP modification is remarkable. The untreated surfaces have an almost immeasurable polar content which increases over multiple treatments to more than double the overall SFE. For SICON[®] the change of the dispersive content over multiple treatment is decreasing whereas for its EP modification only increases after the first treatment and remains constant afterwards.



Fig. 3 Surface free energy of surface modifications from new to treated in NaOH for 0.5h at 50 °C each treatment, for two identical plates P1 and P2.

Regarding the AB method, the change of the overall SFE is not as significant as seen for the OWRK method. In general the overall SFE and respected AB to polar content is less in absolute value. For SS the change of overall SFE is in the magnitude of deviation and confirms findings from OWRK. Interestingly, their base content decreases over time and becomes almost constant for both plates at (22.65 ± 0.11) 10⁻³ N m⁻¹. The overall SFE for DLC and EP-DLC vary by $\pm 3 \ 10^{-3} \ N \ m^{-1}$ and are regarded as constant, though their ratio of contents change. A slight increase of the AB content and decrease of LW over treatments for DLC is visible. The change for SICON[®] and EP-SICON[®] is more distinct. For both the LW-content is increased until the third treatment and remains constant afterwards. The AB content increases for SICON[®] from new ($\approx 0.6 \ 10^{-3} \ \text{N} \ \text{m}^{-1}$) to the first treatment ($\approx 6 \ 10^{-3} \ \text{N m}^{-1}$), afterwards changes until 10 10^{-3} N m⁻¹ are observed. For the EP-SICON[®] two treatments are sufficient to change the AB content from 2 to 10 10⁻³ N m⁻¹ and remain constant until the 10th treatment. The change of base content for all surface modification is most remarkable. Only for EP-SICON[®] it seems to reach constant values. Therefore the base treatment provides a clear effect on the increasing γ^2 content. The acid content has a minor effect in value, but clearly affects the calculation of the AB

content over the geometrical mean. Therefore γ^- seems to provide the dominant impact for changing the AB content, since the first two treatments impact this value the most for all coating modifications. Especially for the treatments of SICON[®] modification a major impact on γ^- can be observed.

In summary, the overall SFE changes over a severe base treatment, most impacted by increasing changes in the polar and γ^{-} content. Regarding the OWRK method only decreasing changes of dispersive forces after first treatment may be observed. Regarding acid-base method an increase of the LW content could only be observed for SICON[®] modifications. For all coating modifications, the AB content is primarily impacted by the dominant change of the γ^{-} content throughout the treatments, whereas SS seems not to be impacted by base treatment. Since both methods predict significant changes in polar contents and γ^{-} could be identified to provide the major impact on the acid-base content, the acid-base method is more distinct to evaluate the SFE behavior over multiple treatment. Therefore, in the following only the acid-base method will be presented.

Since it was observed that both plates of the same modification (P1 and P2) obtain similar results for base treatment, as well as for acid and temperature treatment only P1 is displayed in the following.

Acid treatment

For the acid treatment the measured pH values were 0.3 ± 0.2 . For SS only small changes in SFE can be observed, see Fig. 4. From new state to first treatment a small decrease of AB and LW content are obtained. Afterwards only minor changes of AB and LW contents over treatments conclude almost no impact through acid treatment, excluding γ^{-} which slightly increases. DLC and EP-DLC show minor effects in their overall SFE and remain within the calculated deviation. Again an increase of the AB content mainly results from an increasing γ^{-} and small changes in LW content are obtained. After third treatment γ^{-} of EP-DLC varies about $\pm 1.55 \ 10^{-3} \ N \ m^{-1}$ of an estimated mean value of 21.68 10⁻³ N m⁻¹. For this reason a nearly constant behavior with minor impacts due to longer acid treatments can be assumed. For SICON[®] the overall SFE is almost doubled from new state to the first treatment. A great change of AB and LW content is obvious. All further treatments lead to minor increments of both contents. The change of γ^{-} is not as dominant as seen for the base treatment, though again most responsible for AB's content increase. EP-SICON® provides similar results, though compared to SICON[®] three treatments are needed be in the range of constant overall SFE. For all coatings after third treatment no significant increase of γ^{-} or overall SFE can be observed. Comparing the tenth and 4.th treatment, minor changes in γ^{-} and overall SFE are obtained. Consequently, this could be interpreted as the surface property of an "aged" surface through acid treatment.

In summary the acid treatment has minor effects on the coatings' surface free energies compared to base treatment. The overall SFE values are below base treatment as well as their changes over multiple treatment. The change of γ^{-} is not as distinct as seen for base treatment. Clearly the gradient of γ^{-} is decreased with increasing cleaning cycles.

Fig. 4 Surface free energy of surface modifications from new to treated in HNO_3 for 0.5h at 50 °C each treatment.

Temperature treatment

For temperature treatment changes in SFE properties can be observed, see Fig. 5. The highest achieved overall SFE and γ^{-} content compared to all treatments and for all modifications is seen here. Except for EP-SICON[®] the first treatment provides the greatest change in γ^{-} value for all modifications. Again three treatments are sufficient to establish a state of SFE property where after only minor changes can be observed.

treated in H_2O for 24h at 90 °C from new to 10 treatments.

So in conclusion all treatments do lead to energetic surface property changes compared to newly coated surfaces. The greatest impact of this change can be related to the temperature treatment, where in comparison to the acid treatment provides the lowest impact. The increments of polar and γ content of the used evaluating methods seem to be considerably important. Mostly 3 to 4 treatments are sufficient to establish constant surface properties for the overall SFE. Further treatments lead to minor changes, indicating this to be the "altered" or "aged" state established by each cleaning procedure. The question why the energetic properties of the coating change through cleaning treatments should be directed to the coatings composition and structure. Since temperature treatment in water provides the highest impact a chemical reaction of the coating is questionable. The hydrogenated a-C:H (DLC) coating is a metastable material, which may change in composition through thermal activation (Grill 1999). The general thermal instability is associated with the loss of hydrogen, causing collapses in the bonding structure (Grill 1999). Critical temperatures for hydrogenated DLC coatings start at about 400 °C or lower and strongly depend on the deposition conditions and the coatings' dopant (Grill 1999). Modifying hydrogenated DLC coatings with incorporating oxygen or nitrogen in the deposition process leads to smaller water contact angles and therefore favorable wetting condition, while silicon or fluorine will increase the water contact angle to minor wettability (Grischke et al. 1995). Including oxygen to a deposition process of hydrogenated DLC increases the overall SFE, mostly by increasing its polar content (Grischke et al. 1995). Therefore a possible oxygen inclusion through cleaning treatments should be considered for the observed changes of γ^{-} . Combining oxygen and silicon in the deposition process to form a-C:H:Si:O (SICON[®]), enables to reduce the surface free energy to as low as 21 10⁻³ N m⁻¹ (Grischke et al. 1995). Changing compositions of DLC layers over time could affect the overall SFE, which might explain the exceeding behavior of cleaning treatments to SICON® surfaces. A change through nitrogen and oxygen inclusion during air storage of the coatings between investigations could be neglected, as shown by (Geddert et al. 2011). Therefore the thermal instability of DLC coatings, even at treatments of 90 °C, could impact the coatings composition. A reduction of silicon could also lead to improving wetting conditions. (Geddert et al. 2011) revealed that the state of SFE and its' contents for DLC and SICON® change from new over multiple alternating fouling and acid cleaning procedures, as well as different storage conditions. Hereby stainless steel proved to be inert against alternating fouling and acid treatments, which is in accordance to findings of the presented acid treatments in Fig. 4. Decreasing dispersive and increasing polar contents are a general trend for hydrogenated DLC as well as SICON[®] (Geddert et al. 2011). Water storage for 24 h revealed to increase the polar content around 4...7 10⁻³ N m⁻¹ for all investigated surfaces (Geddert et al. 2011). Heat treatments at 150 °C, cleaning procedures with 6 wt.-% HCl for 24 h and 6wt.-% NaOH for 24 h revealed decreasing dispersive and increasing polar

contents, which can be confirmed this study. With SIMS in (secondary ion mass spectrometry) (Geddert et al. 2011) could show the influence of fouling and acid treatments on the coating's elementary composition. When comparing the upper layer (first 120 nm from the top) of new and used a-C:H and a-C:H:Si coatings stainless steel. both on modifications showed a reduction of hydrogen concentration and increase of oxygen in the first 20 nm, which affected the overall SFE. Additionally for a-C:H:Si, а

decrease of silicon in composition over the first 20 nm could be observed (Geddert et al. 2011). These findings imply that changes in composition, especially directly at the interface solid/liquid could be most responsible for the change of energetic properties.

Conditioning of DLC coatings

If changes in composition of DLC coatings appear, three major questions should be investigated.

- 1) To which extent do changes in energetic surface properties appear, by which process?
- 2) When energetic surface properties become constant, is this the altered surface state and/or to which extent can this state be preserved?
- 3) Which state is most favorable to mitigate fouling?

For the first question the cleaning procedures already indicate a thermal instability of the coating. Besides, the temperature treatment at 90 °C for 24 h provides information of the mean thermal stress on the coating exposed to in fouling experiments. These start with a surface temperature of the test plate at ≈ 78 °C and end up at ≈ 105 °C after 24 to 48 h. However, a fouling process is different, since the coating may be covered with fouling material, hence leading to different interface conditions from solid/liquid to solid/solid which may affect changes in the coatings composition or structure. Though if the crystal layer doesn't impact the energetic surface properties, the temperature treatment could be a sufficient procedure to condition the coated surface to constant surface properties. A fast thermal conditioning for DLC and SICON® was investigated by hot air treatment between 150 and 500 °C with fast cool down in a water column. In many conditioning experiments DLC showed defects to the point of destruction over 250 °C and minor changes in energetic surface properties below 250 °C. Therefore a conditioning in water at 90 °C for 72 h, according to findings in Fig. 5, was chosen for DLC. Though SICON[®] proved to resist the thermal stress at 500 °C, enabling for a shorter conditioning of 2 h to be sufficient to establish constant absolute SFE values in the magnitude of thermal treatments, see Fig. 5. Referring to question two and three a test procedure was established, see Fig. 6. Here fouling experiments with EP-DLC and EP-SICON[®] coatings at new state and after

Fig.6 Fouling test procedure.

conditioning, followed by multiple fouling experiments

were conducted. Before and after every experimental stage the energetic surface properties were investigated with DSA and the elementary composition in the coating with EDX of SEM measurements to reveal the impact of each treatment. Ultimately, conditioning should establish constant energetic surface properties of the coating with no or minor changes through fouling experiments, thus enabling to identify favorable or unfavorable nucleation and/or crystal growth behavior.

Fouling experiments

In the following the results from the test procedure shown in Fig. 6 are presented. For both fouling experiments with EP-SICON[®] at new state similar fouling behavior with beginning crystal growth phase at 45h and similar gradients around $0.1 \cdot 10^{-4}$ m²KW⁻¹h⁻¹ are obtained, implying repeatability of fouling experiments, see Fig. 7. The increase of surface free energy for both plates through fouling experiment is identical, but clearly decreased in comparison to thermal treatment in water. Therefore the fouling process could be responsible to hinder the increase of energetic surface properties, hence changes in composition or structure. After both conditioning procedures on EP-SICON[®], the SFEs increase to the maximum observed values from thermal treatment. For the following fouling experiments E2 the crystal growth phase is suppressed, compare fig. 8a and 8b, implying decreased adhesive strength of the fouling layer, if a roughness controlled phase is interpreted in fig. 8. In the following fouling experiments the mitigation effect of the coating after conditioning can be repeated, except for E4 (C = 90° C), though the fouling experiments decrease the energetic surface properties of SICON®. For DLC the SFE is increased with the first fouling experiment, and again below findings from thermal conditioning. For its fouling behavior the conditioning provides negative effects in terms of decreasing induction period and increasing crystal growth rates compared to the new state. After conditioning the SFE remains within small deviations, especially in the γ^{-} content, for all further fouling experiments.

These observations conclude an increase of SFE from new state through fouling experiment to be below findings from thermal treatment, especially for γ^{-} , though the fouling process itself is a similar thermal treatment. The deposition of a CaSO₄ layer could be responsible for hindering oxygen, hydrogen or silicon exchange or structural changes. A decreasing impact on the SFE properties through fouling after conditioning can only be observed for SICON[®]. For conditioning at 500 °C SICON® shows an increase of oxygen content, whereas the conditioning at 90 °C does lead to minor changes. Interestingly, the fouling behavior after conditioning changes to longer induction times and decreased or suppressed crystal growth rates. For DLC the conditioning in water increases the oxygen content which in further fouling experiments is decreased to about the starting condition. Here the change of SFE is dominated by increasing γ^{-} content.

According to these observations no clear fouling behavior can be related to a certain SFE. For SICON^{$\ensuremath{\mathbb{R}}$} an

almost unpolar surface seems to be most unfavorable for fouling mitigation. Increasing the AB content, mostly through γ , leads to improved mitigation behavior. In case of DLC the findings for SICON[®] cannot not be confirmed. Conditioning in air at 500 °C is most efficient to retain the mitigation properties of SICON[®] over the shown number of experiments.

The surface free energy clearly seems to effect fouling mitigating properties considering the conditioning step. Yet, more experiments need be conducted to achieve constant surface properties for SICON[®]. Great potential for SICON[®] lies in the small crystal growth rates, which were always below findings for hydrogenated carbon (DLC). Therefore, future effort should focus on the different effects when varying the ratio of oxygen and silicon of the coatings' composition, as well as their time dependent changes.

Fig. 8 Fouling curves over time a.) conditioned in air for 2h at 500 °C EP-SICON[®], b.) conditioned in water for 72 h at 90 °C for EP-SICON[®] and c.) EP-DLC.

CONCLUSIONS

Chemical and thermal cleaning treatments with liquids over multiple repetitions affect the surface free energy of DLC and SICON[®] coatings with increasing the overall surface free energy. The increase of γ^2 content could be identified to be the dominant influence for this. After three to four treatments almost constant surface properties could be established. Thereby thermal treatments in water at 90 °C provided the highest increase in overall SFE and γ^2 content. The loss of hydrogen and silicon as well as oxygen inclusion in the coating seems to have an influence on the varying surface properties. To obtain reproducible and constant surface conditions, a thermal conditioning in water (90 °C, 72 h) and in a hot air cabinet (500 °C, 2 h) was investigated. For SICON®, the conditioning in both cases was able to reduce the crystal growth rate significantly. The increase of the γ^{-} content seems to have a dominant effect by increasing the overall SFE and hence improving wetting conditions. A conditioning of DLC at 90 °C for 72 h revealed to be insufficient for fouling mitigation. The fouling process itself contributes to the changes of the energetic surface properties. Therefore more fouling experiments need be carried out, to identify if and when constant surface properties may be obtained. The conditioning itself proved to be a sufficient way to establish surface properties for SICON[®] with mitigating fouling effects. This effect could also be achieved by applying the desired amount of elements in the coating process. Either way, conditioning or retrofit of coating process, may lead to coating compositions and ratio of elements to be most vulnerable to fouling. An analysis of the conditioned coating composition could lead to favorable SICON® compositions to be established by the coating process. Fouling mitigation with decreasing the surface free energy could not be observed. Moreover an increasing γ content for SICON[®] improves fouling mitigation by extending induction time and decreasing crystal growth rate.

NOMENCLATURE

| Symbols used | | | | | |
|----------------|---------------------|--------------------------------------|--|--|--|
| d _h | [m] | hydraulic diameter | | | |
| L | [m] | length | | | |
| | $[Wm^{-2}]$ | heat flux | | | |
| Re | [-] | Reynolds number | | | |
| R_{f} | $[m^2 K W^{-1}]$ | thermal fouling resistance | | | |
| t | [s] | time | | | |
| Т | [°C] | temperature | | | |
| Greek symbols | | | | | |
| γ | [Nm ⁻¹] | surface free energy, surface tension | | | |
| θ | [°] | contact angle | | | |
| Subscripts | | | | | |
| AB | acid base | | | | |
| d | dispersive | | | | |
| i | variable | | | | |
| ind. | induction | | | | |
| j | variable | | | | |
| L | liquid | | | | |
| LW | Lifshits-van-de | er-Waals | | | |
| р | polar | | | | |
| S | solid | | | | |
| turb. | turbulent | | | | |
| V | vapor | | | | |
| Abbreviations | | | | | |
| С | [-] | conditioning | | | |
| E | [-] | experiment | | | |
| EP | [-] | electro polished | | | |
| Р | [-] | plate | | | |
| SS | [-] | stainless steel | | | |

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