INVESTIGATION OF ICEPHOBIC COATINGS FOR SUPERCOOLING HEAT EXCHANGERS UNDER SUBMERGED CONDITIONS USING ICE DETECTION EQUIPMENT

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ABSTRACT

By using ice slurry generated through a supercooler as storage, it is possible to reduce energy consumption due to high energy density and heat transfer rate along with the phase change. The supercooled water will then be disturbed to create ice crystals in a crystalizer. The main challenge is to prevent the formation of ice in the supercooler since this leads to its blockage. One aim of the European H2020 TRI-HP project is to develop icephobic coatings for supercoolers, that promote high-water supercooling and avoid the formation of ice. In this study, three coatings to prevent or depress freezing in supercoolers are investigated. Specialised equipment for testing freezing on submerged surfaces has been developed, and the results have been correlated to standard surface properties like roughness and contact angle. It was found that the submerged surfaces do not necessarily follow normal icing theory, where freeze depression is related to contact angle. Instead, it is believed that the mobility of surface additives in amphiphilic coatings has an important role.

INTRODUCTION

Air conditioning accounts for about 42% of household GHG emissions. More energy-efficient and climate-friendly appliances could make a huge dent in environmentally harmful emissions. To produce cold, the choice of the appropriate refrigerant is limited since most available fluids are greenhouse gases [1]. In the last 30 years, there has been a growing interest in two-phase refrigerants, particularly for ice slurries, which represent an interesting alternative to secondary fluid in conventional refrigeration systems [2]. Ice slurry is a mixture of fine ice particles with a diameter of 0.1 mm to 1 mm and a carrier liquid. Ice slurry has a high energy storage density because of the latent heat of the fusion of its ice crystals. It also has a fast cooling rate due to the large heat transfer surface area created by its numerous particles.

Ice slurries are used in multiple applications such as comfort cooling of buildings, mine cooling, food cooling and others [3]. The most widely accepted method for ice slurry production is the scraping method [4] which requires high investment and maintenance costs. A cheaper and more efficient alternative is to produce ice slurry by the supercooling method [5], where a stream of water that is flowing into an evaporator is cooled by a few degrees below the normal freezing point. Upon leaving the evaporator, the supercooled water flow is disturbed to generate ice crystals. The water/ice fraction depends on the supercooling of the liquid leaving the evaporator (supercooled) and increases by approximately 1.25% / °K. The main advantage of this technique is that it uses simple technology without extra energy to operate, thus reducing maintaining cost and efficiency is kept high since no ice on the heat transfer surfaces. However, the heat exchanger for supercooling must ensure that there is no crystallization happening inside, otherwise, the slurry generation may stop due to the blockage [6] [7]. The best way to realize the continuous ice generation with supercooling water is to find an effective way to prevent the nucleation of ice on the surface of the supercooling heat exchanger.

Herein, we present a study to evaluate the use of three coatings to prevent or delay the formation of ice on supercooling heat exchangers using demineralized water, via a specialised test setup and software. Specially developed equipment will be used to test under different flow conditions while the surfaces will be monitored. Last the coatings will be evaluated based on their surface properties.

MATERIALS AND METHODS

Coatings

Three coatings with different proven properties, developed by the Danish Technological Institute, were chosen. All coatings were organic/inorganic hybrid, synthesized via the sol-gel method with a siloxane backbone, organic compounds and different additives added for functionality. The coatings used are described in Table 1 and named according to their coating properties.

Table 1: Coatings provided by Danish Technological Institute and their key differences.

Coating	Remarks
HPO	Smooth hydrophobic coating with excellent repellent properties, is often used for antifouling purposes.
API	Smooth amphiphilic coating with hydrophilic Polydimethylsiloxane (PDMS) chains migrating through

	the surface based on surrounding surface energy.
NoAdd	Smooth coating with siloxane backbone without any repellent additives. Nanoparticles were added for increased thickness and flexibility.

Substrates and application

All coatings were spray-coated upon round aluminium discs with a thickness of 0.7 mm and area of 177 cm^2, with a target layer thickness between 5-15 µm and one coating-free disk was used as a reference. The coatings were cured between 50 °C to 300 °C for 1-2 hours, depending on the coating.

Testing methods

The properties, roughness, static contact angle, residing contact angle and surface energy of the coated and non-coated references were measured. A special test setup for measuring freeze depression (FD) was constructed as well.

Roughness

The roughness of the coatings and reference disk was measured with a Mitutoyo Surftest SJ-210. Each dish was measured at five different spots and the average results and standard deviation were recorded.

Contact angle

For Static contact angle (SCA) a 20 µl droplet demineralized water was deposited at the surface and a picture was taken. The image was analysed using the ImageJ Contact_Angle plugin. This was repeated five times for each surface and the average and standard deviation were reported. For receding contact angle (RCA) a cannula was used to retract the water droplet while a video was recording the droplet. A still frame from the video, right after the edge of the droplet started to move, was used for RCA measurement. The process was repeated five times and the image was analysed using the ImageJ Contact_Angle plugin.

Surface energy

Surface energy (SE) was measured with Tigres Test ink, using nonpolar ink with surface tension values of 16, 18, 20, and 25 mN/m^2. The recorded surface energy is the interval between where the droplet spreads out or contracts on the surface.

Submerge free depression

To investigate how freezing occurs in a submerged environment, a new setup was constructed, illustrated in Figure 1a, where the sample was pressed tight in between a top and bottom chamber with a silicon rubber layer to ensure a tight seal. The top chamber could hold the liquid and provide access to mechanical stirring equipment (Hei-TORQUE Core) and visual monitoring through up to two USB microscopes (Andonstar Digital Microscope V160). Extra bolts were added around the chamber for new equipment to be added in the future. The bottom chamber contained an LHP-300 CP Peltier cooler which was pressed towards the backside of the sample. The peltier cooler was equipped with a thermocouple measuring the backside of the sample and allowed to measure the temperature and control the peltier unit via SpecView software. To ensure good thermal contact between the peltier module and the sample, a thermal conducting pad (DiaTherm DT30-05) of 0.5 mm with thermal conductivity of 3 W/mK was used, as seen in Figure 1c. The whole setup was placed in an insulated environment to avoid outside influence, as seen in Figure 1b. The software could be programmed depending on what the test required.

Before testing, to ensure that there was good thermal contact, a droplet was frozen to the surface. The peltier was then set to heat at 3 °C/h, while the droplet was observed. At the moment the droplet started to melt, it was assumed that the surface was 0 °C. If the temperature difference of the peltier element was less than 0.5 °C, it was categorized as a good thermal contact.

During testing, the top chamber was filled with 500 ml of demineralized water, and the temperature was set to 2 °C. The agitator was set to 60 rpm to distribute the water and remove any temperature gradient between the top and bottom. After two hours the water had reached an equilibrium and the test could start.

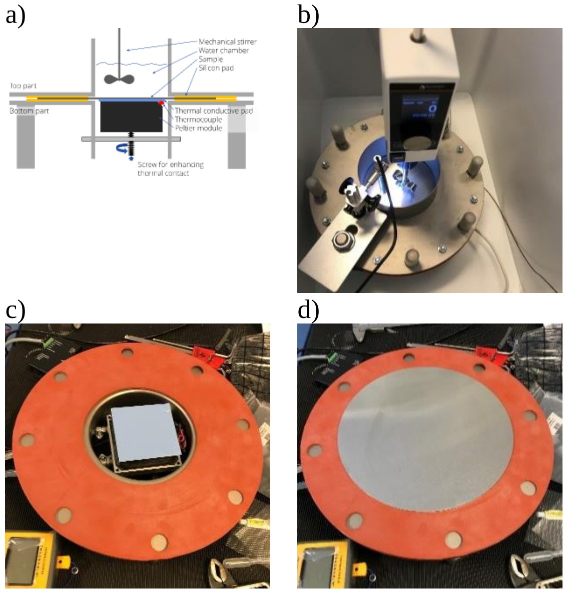

Figure 1: Setup of the submerge freeze depression test chamber.

RESULTS

Ice detection via software

The detection of ice was important to control the freezing and heating cycles automatically.

The SpecView software was set to cool at a rate of 3 °C/h and monitor the temperature continuously. When the water freezes there will be a heating spike due to the phase change of the water, which could be detected by the thermocouple. The coldest recorded temperature before the spike would be noted as the freezing temperature. This was followed by automatic heating of the chamber to 2 °C where it was left for 2 hours to reach equilibrium in the system and a new test could start again. This process was set up to be done automatically for further testing. The heating spice, introduced by ice formation can be seen in Figure 2, where the program is set up to heat right after the detection.

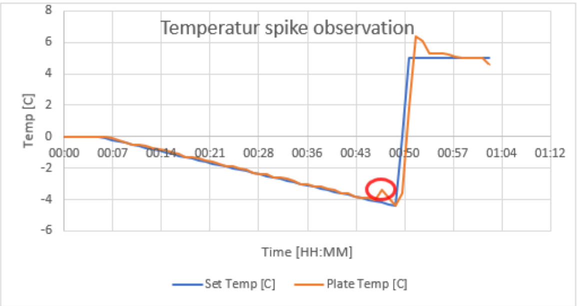

Figure 2: The ice formation in the chamber is detected and can be observed as a 0.5 K increase in temperature.

Ice detection via camera

To observe ice formation, the two USB microscopes were attached to the setup and connected to a PC, which made it possible to record video and take pictures at a set interval. A spot on the sample surface was chosen and the microscope was placed directly above, with a focus on the surface. It was important that no part of the microscope directly touched the water, to prevent ice nucleation from the microscope itself. The ice formation can be seen in Figure 3 where the ice is spreading along the surface from the bottom right to the top left. The spreading of the ice is fast and covers the full container in less than 15 s. Two obvious drawbacks of this method are that the nucleation point is stochastic and can only be found with the camera by chance unless you modify the surface to have a fixed point of nucleation. The other is, that you can only observe the ice spreading in the x, and y plane and not spreading towards the camera.

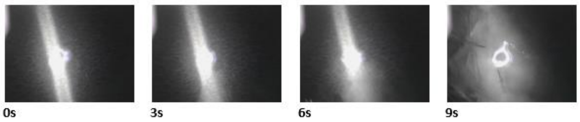

Figure 3: 0s: Last ice-free frame, 3s: Ice starts appearing at the bottom, 6s: Ice is spreading, 9s: The whole view is blocked by ice

Freeze depression during flow conditions

To observe if flow in the water had an effect on freezing temperature, two samples, one coated and one ref was tested under different flow conditions. With the stirrer, it was possible to observe freeze depression (FD) with differences in the agitation of the water. Initial tests with the aluminium reference sample and a HPO sample was done, and the water was stirred at 0 rpm (still water), 60 rpm (laminar) and 200 rpm (turbulent) while the water was being cooled. in the freezing chamber. This test was repeated five times for each RPM and the freezing temperature was recorded, as shown in Figure 4. It can be seen that no fluctuation in the water leads to higher FD for both samples. The alu ref does have an overall greater standard deviation. It is believed that the trend with lower freeze temperature with higher flow continues with different coatings.

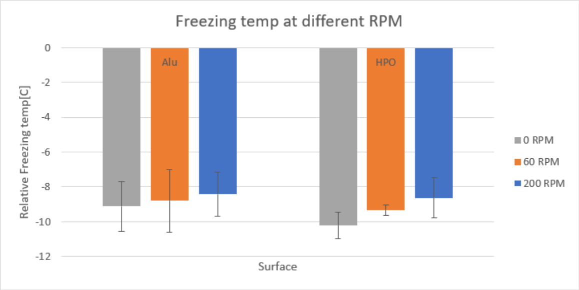

Figure 4: Freezing temperature with different agitation.

General properties of the coatings

Results for general surface properties can be seen in Table 2. The results measured for API, SE, SCA and RCA were done after the surface had been exposed to air and will change under submerged conditions due to the changing nature of the surface in contact with different environments. It is safe to say that in contact with water, the surface becomes hydrophilic which will result in a small SCA and RCA.

Table 2: Roughness, surface energy (SE), Static contact angle (SCA) and Receding contact angle (RCA). API was measured in atmospheric conditions and SE, SCA and RCA will change when submerged.

Coating	Roughness [Ra]	SE [mN/m^2]	SCA [°]	RCA [°]
Alu ref	0.73±0.06	20-25	90.6±5,4	48±3.9
HPO	0.04±0.01	20-25	104.2±0.5	92.6±1.1
API	0.05±0.01	20-25	88.9±3.1	70±5.4
NoAdd	0.40±0.05	> 25	83.5±4.9	72.6±4.6

Freeze depression

To compare the freeze depression on different surfaces, the agitator was set to 60 rpm, where a vortex was formed, but the flow was not turbulent. The test was repeated at least five times for each surface.

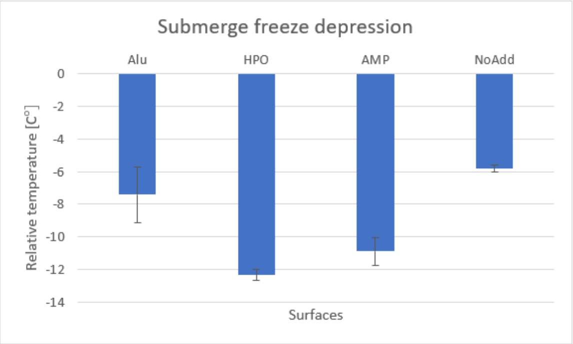

Figure 5: Submerge freezing temperature, where the average freezing can be compared to one another.

In Figure 5 it can be seen that the NoAdd coating without repellent additives has the lowest FD, but with very little standard deviation. Both HPO and API had high FD, but API had a much higher standard deviation. The aluminium reference both has low FD and the highest standard deviation.

DISCUSSION

The temperature measured during FD corresponds to what is measured by the peltier device and does not directly compare to the water temperature. The step to ensure good thermal contact during setup and the step to reach equilibrium temperature between the peltier module and water container is used to minimize the temperature difference between the peltire cooler and sample surface. With this, it is possible to compare the coatings to each other, only in this setup. To avoid this, one possibility would be to measure the water temperature directly, but since every small defect would be a catalyst for ice nucleation, this is not possible when the water reaches temperatures below 0°C. To get around this, a setup could be made, where the water temperature is measured when the temperature is above freezing, and a tendency line can be calculated thus a more precise temperature could be achieved. Other factors to consider are the substrate and thickness, where it is important that, for all tests, they stay similar. The coating thickness only consists of a fraction of the full thickness and would thus be negligible.

It is clear that the higher agitation also leads to a higher freezing point. While the stirrer is active, it is not obvious exactly where the ice is originating due to surface fluctuation, preventing the camera to get a clear shot at the sample. Combined with the water having a more homogenous temperature, it cannot be dismissed that the freezing could be originating from the side of the chamber or the stirrer itself. Nevertheless, it could be seen that an even faster RPM would decrease the freezing temperature even further and that the coated surface still had the lowest freezing temperature. This indicates, that in this case, the freezing was probably linked to the agitation of the water, rather than the contact with uncoated surfaces. The difference in freeze temperature for the HPO coating in Figure 4 and Figure 5 could be due to small adjustments in the testing procedure between the two tests.

In Figure 6 FD against, roughness, SE, SCA and RCA are plotted. There was no clear trend for all the coatings. Earlier studies found that CA and FD correlate [9], especially when studying droplets, where only a small area is in contact with the surface. In our case, the surface is fully submerged, exposing all defects and inhomogeneities of the surface to the supercooled water.

For roughness, one would expect a rougher surface, to have more defects to start the ice nucleation. The alu surface has the roughest surface, but not the lowest FD, though it has the highest standard deviation in FD. The API coating does also have a high standard deviation, but also high FD, leading to that other factors may play a role in the FD.

There appears to be some correlation with the FD and SCA when looking at HPO, Alu and NoAdd, but not for API. It is important to note, that the SCA for API was measured in atmospheric conditions, and during FD testing, would have an even lower CA. Again, this indicates that other factors than roughness and CA have an impact on FD. Even though that RCA appears to have a trend, this could not be the case, due to the further decrease of CA under submerged circumstances for API. Furthermore, the NoAdd falls completely outside this trend.

More investigation is needed to get a clear picture of what factors impact the FD in submerged conditions, and more factors than just CA and roughness have an influence. HPO coating appears to have the best results for freeze depression in submerged conditions.

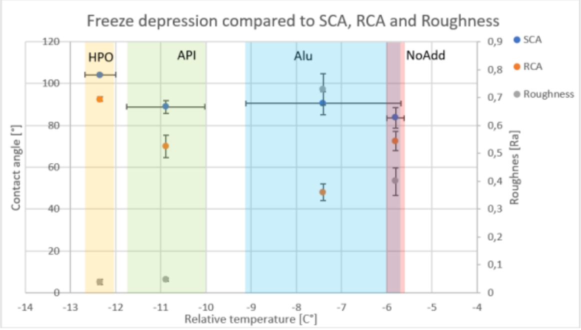

Figure 6: Correlation between freeze depression and SCA, RCA and roughness. The colours indicate the standard deviation for freeze depression for each of the coatings, with HPO being yellow, API being green, Alu being blue and NoAdd being red.

CONCLUSION

In this study, freezing in submerged conditions was studied using the versatility of newly developed equipment. It was shown that it was possible to investigate surfaces under different flow conditions, together with the possibility of observing the freezing process through a microscope. Software of the experimental setup was used to repeat tests automatically and reliably, under different conditions and with different surfaces. Microscopes were attached to investigate the ice formation, which showed ice crystallizing along the sample surface.

Three coated surfaces and one uncoated aluminium surface were measured with surface roughness, static and receding contact angle and compared to the freeze depression. No clear connection between the roughness, contact angles and freeze depression was found. The hydrophobic coatings showed the best freeze depression results, followed by the amphiphilic coating.

Outlook

Due to the versatility of the test equipment and software, there is a wide range of possibilities for further testing, with a change in setup, depending on what kind of investigation is wanted. It is important to note that only tests that are done with the same setup can be compared. At the current setup many different coatings, surfaces and materials can be compared if the thermal conductivity is comparable, and a good thermal connection is ensured. A setup for precisely determining the water temperature or temperature gradient through the water would be a great benefit for further studies.

NOMENCLATURE

GHG	Green House Gasses
HPO	Hydrophobic
API	Amphiphilic
NoAdd	No Additive
PDMS	Polydimethylsiloxane
Alu ref	Aluminium reference
FD	Freeze depression
CA	Contact Angle
SCA	Static Contact Angle
RCA	Receding Contact Angle
SE	Surface Energy
Ra	Roughness [µm]

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