Investigation of micro- and nanostructured coatings for heat exchanger surfaces in an ice store

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Abstract. During loading ice stores an ice layer is forming on the heat exchanger surface when the surface temperature is coming below the nucleation temperature. The growing ice layer increases the heat conduction resistance and the loading performance decreases. With the application of micro- and nanostructured coatings the nucleation temperature of water drops on surfaces in an atmosphere of air can be decreased. If the coatings show similar characteristics under water, they can be used for heat exchanger surfaces in ice stores. Ideally the water in the ice store can be supercooled while ice growth is initiated at nucleation spots apart of the heat exchanger surface. Then a higher loading performance and storage capacity can be realized. First experiments have shown that the coatings can decrease the nucleation temperature.

Keywords: ice store, nucleation temperature, supercooling, coating

1. Introduction
Renewable energies should be used for the energy supply to minimize the climate change. The fluctuating supply of renewable energy sources requires energy storage to uncouple the energy demand from the energy supply. One possibility of energy storage is the usage of ice stores in combination with a cooling device for the air conditioning of buildings. They are used as thermal storage to increase the availability of the cooling provision. At the Institute of Thermodynamics and Thermal Engineering (ITW) an ammonia/water chiller for the application of solar cooling in combination with an ice store was developed. By using ammonia as refrigerant, cold water temperatures of less than 0 °C are reachable and ice growth is possible. The ice store uncouples the cooling provision from the solar radiation and allows a more regular operation of the absorption chiller. Ice stores can also be used for seasonal storage in combination with heat pumps [1–3]. Ice stores distinguish theirselves by a high storage capacity, because of the high enthalpy of fusion of water of 333 kJ/kg, and small thermal losses. During loading ice stores an ice layer is forming on the heat exchanger surface when the surface temperature is coming below the nucleation temperature. The growing ice layer increases the heat conduction resistance and the loading performance of the ice store decreases.

The idea in this work is to control the nucleation mechanism by surface modification. Suzuki et al. [4] investigated ice nucleation confined in nanoporous alumina. According to [4] the nucleation mechanisms of water are stochastic in nature but can be controlled by confinement with nanoporous alumina. With decreasing pore diameter, a transition occurs from heterogeneous nucleation to homo-
geneous nucleation. The Fraunhofer Institute of Interfacial Engineering and Biotechnology in Stuttgart develops micro- and nanostructured coatings that can be used on aircraft wings, wind power plants, cable cars and high-voltage power lines to prevent icing on the surface. The coatings enable a reduction of the nucleation temperature of water drops on surfaces in an atmosphere of air.

The Institute of Thermodynamics and Thermal Engineering (ITW) investigates whether these coatings show similar characteristics under water compared to water drops in an atmosphere of air. Then new application fields will arise, for example on heat exchanger surfaces of ice stores. By using the coatings, ideally, the water in the ice store can be supercooled while the ice growth is initiated at nucleation spots apart of the heat exchanger surface. Therefore, the usage of the coatings enables a higher loading performance of the ice store. The storage capacity is increased, because the ice store can be frozen with smaller heat exchangers.

In this work the application of coatings on the heat exchanger surface in demineralized water is investigated. The influence of the completely with water covered coatings on the nucleation temperature and the supercooling of the storage water during a loading procedure is examined. In the following the fundamentals, the experimental setup and first experimental results are presented and discussed.

2. Fundamentals

In this chapter the fundamentals of ice growth and surface coating technology are explained.

2.1. Fundamentals of ice growth

When water freezes, the three periods supercooling, nucleation and crystal growth are passed. As shown in Figure 1, liquid water can be cooled until it reaches the melting point (M.P.) at 0 °C and supercooled until it reaches the nucleation temperature (N.T.) at point A and nucleation occurs. From point A to point C crystal growth is taking place. In point C the whole amount of water is frozen and the ice can be supercooled. Liquid water with a temperature below 0 °C is called supercooled water and is in a metastable state. The supercooling is marked as ΔT and represents the difference between the melting temperature and the nucleation temperature [5].

![Figure 1. Cooling curve of a liquid with phase change in conditions of a constant rate of heat removal [5]](image)

There exists homogeneous, heterogeneous and secondary nucleation. Homogeneous nucleation occurs if ice is formed in water at low temperatures. The homogeneous nucleation temperature can be below -40 °C. Heterogeneous nucleation occurs if foreign undissolved objects are in the water. In supercooled water, water molecules build clusters with the same configuration as ice that are broken...
again. The water molecules are attracted among each other by hydrogen bridge bond. When the supercooling of the water increases the formation and growth of clusters exceeds the break-up of clusters. Nucleation starts if molecules form stable clusters of a sufficient size. With the presence of foreign objects, a crystal lattice is more easily formed as the formation of initial nuclei is supported. The heterogeneous nucleation starts at higher temperatures as the homogeneous nucleation. The foreign objects can be dirt, dust or in this case the heat exchanger surface itself in an ice store. Therefore, in technical applications mainly heterogeneous nucleation occurs. By an appropriate surface treatment of the heat exchanger, e.g. by reducing the nucleation points, the heterogeneous nucleation temperature can be decreased. If there is already ice in the water nuclei are formed from existing ice crystals. This is called secondary nucleation [5–9].

During crystal growth dissolved molecules from the water grow into the crystal. The molecules diffuse from the water through the boundary layer around the nucleus, incorporate into the crystal lattice and latent heat is transferred. Therefore during crystal growth a jump in the temperature to the melting temperature of 0 °C in point B occurs [5–9].

2.2. Surface coating technology

Low-pressure plasma technologies are used for the surface coating. When a gas is stimulated with external energy, e.g. by an electrical field, it ionizes and a plasma state originates. A plasma is an electrical neutral gas with free charge carriers, such as ions, electrons, excited molecules, radicals and photons. Important process variables are the type of the gas monomer, the gas pressure, the gas flow, the excitation frequency, the power and the processing time [10].

The used method to produce thin layers in the range of nanometres or micrometres on the surface of the heat exchanger is called “plasma-enhanced chemical vapour deposition” (PECVD). The PECVD uses for the plasma coating a gas monomer that is converted into a thin layer in the plasma. In the beginning of the process the object to be threatened - in this case the heat exchanger - is put into the reactor, where a vacuum is produced. Then a gas monomer is filled into the reactor until the process pressure is achieved. With a frequency generator the plasma is excited and ignited. By transferring the energy of the accelerated electrons the reaction gas is ionized, fragmented and activated. The low pressure is needed to avoid a collision of electrons with external particles. A chemical change process happens on the one hand within the plasma and on the other hand at the object surface. Due to the within the plasma existing ions and radicals the plasma polymers can be bind on the object surface and serve as coating. The properties of the coating such as thickness of the layer and the deposition rate can be determinated by the process parameters and the reaction gases. The properties of the coatings, e.g. wetting angle or surface energy, are quantified [10, 11].

The coating investigated in this work is produced by the Fraunhofer Institute of Interfacial Engineering and Biotechnology in Stuttgart. Fluorocarbons are used as reaction gases. A coating with C-F-compounds results.

3. Experimental Setup

To investigate the influence of the coatings on the heat exchanger surface on the nucleation process under water a test stand represented in Figure 2 is built up.

The model ice store is a box-shaped tank made of Macrolon filled with about 30 litres of demineralized water. It is completely – except for one display window – insulated by microporous pyrogenic silicic acid with a thermal conductivity of 0.02 W/(m K). An aluminium layer is attached on the outside of the insulation to protect the surface. Horizontal copper tubes are arranged in the centre of the model ice store. The tubes act as heat exchanger in the store. A refrigerant is flowing through the tubes. The temperature of the refrigerant at the inlet of the tube is controlled by the thermostat. The tubes can be replaced and different coatings and surface treatments can be investigated. The refrigerant temperatures (T1, T2) and the surface temperature (T3, T4) at the inlet and at the outlet of the tube are measured. The thermal stratification in the model ice store (T5 - T8) in different heights under and above the tube is recorded. An ice reference junction is used for the temperature measurement with
thermocouples. Isothermal blocks are used to avoid parasitic thermoelectric voltage. The mass flow (M1) and the density of the refrigerant (D1) are measured by a Coriolis measuring device.

![Diagram of test stand](image)

**Figure 2. Test stand**

Furthermore, the beginning of ice growth, the ice growth itself and the thickness of the ice layer are captured optically with a camera. The thickness of the ice layer is measured by an implemented scale. The measured data are gathered by an Agilent digital multimeter and processed by LabView.

4. **Results and Discussion**

To investigate the influence of the different coatings on the copper heat exchanger surface on the nucleation process, loading procedures of the model ice store are conducted. A test with uncoated copper heat exchanger tubes is made as a reference, whose results are represented in Figure 3.

![Cooling curve of model ice store](image)

**Figure 3. Cooling curve of the model ice store using a copper heat exchanger tube without coating**

The temperature in the upper (T8) and in the lower part (T5) of the model ice store, as well as the temperature in the middle part of the model ice store next to the heat exchanger tube (T6) are plotted over the duration of the test. Furthermore, the temperature of the refrigerant at the inlet of the heat ex-
The refrigerant tube (T1) is listed. The refrigerant temperature determines the heat exchanger tube surface temperature that is equal to the nucleation temperature when ice growth starts. At the beginning of the test the model ice store has a homogeneous water temperature of 7 °C. The refrigerant temperature is -3 °C. The temperature in the upper part of the model ice store increases slightly at the beginning. The store is not completely filled with water and free convection is taking place between the water surface and air. The temperatures in the middle and in the lower part of the store decrease. When the highest density of water is reached at 4 °C convection currents occur and the temperature stratification in the store is inversed. The water cooler than 4 °C rises and the temperature in the middle and upper part of the store decreases. From minute 250 on the water in the model ice store is supercooled. After 1000 minutes no ice growth occurred in the store while steady conditions exist. That means the heat losses from outside are equal to the heat transfer rate of the heat exchanger tube and the temperatures in the store are constant. The maximal supercooling of the water in the store before the onset of ice growth should be determined. To initiate ice growth, the refrigerant temperature is decreased in steps of 0.5 K in an interval of 60 minutes until ice growth starts. By decreasing the refrigerant temperature, the water temperatures in the store decrease. At a refrigerant temperature of -4 °C and a supercooling of the water in the store of 2.5 K ice growth starts from the heat exchanger surface, that is pictured in Figure 4. The start of ice growth is characterized by a jump in the temperature to the melting temperature of 0 °C by minute 1080.

In Figure 4 ice growth in supercooled water starting from the cold heat exchanger surface is shown. When the ice growth is initiated - when the heat exchanger surface temperature comes below the nucleation temperature by applying a sufficient low refrigerant temperature - ice dendrites grow within seconds in different angels to each other from the heat exchanger surface through the complete supercooled water.

In Figure 5 a cooling curve of the model ice store using a coated copper heat exchanger tube is plotted. With the temperature in the upper (T8), in the middle (T6) and in the lower part (T5) of the store and the temperature of the refrigerant at the inlet of the copper heat exchanger tube (T1) the same measurement parameters as in Figure 3 are shown.

Until minute 1000 the temperature profile of Figure 5 is almost equivalent to Figure 3. It represents a typical cooling curve of an ice store. There is an inversion of the temperature profile when the highest water density is reached at 4 °C. A supercooling of the water in the model ice store is achieved at minute 275. After 1000 minutes there is no ice growth in the store. There are steady conditions, the water temperatures in the store are constant. Therefore, the refrigerant temperature is decreased in steps of 0.5 K in an interval of 60 minutes until ice growth starts at the heat exchanger surface analogous to Figure 4, characterized by a temperature jump to the melting temperature at minute 1200. In doing so the refrigerant temperature is -4.5 °C and the supercooling of the water in the store is 3 K.
To accentuate the differences in the application of uncoated or coated copper heat exchanger tubes the temperature profiles of the loading procedure of the model ice store beginning from minute 900 out of Figure 3 and Figure 5 are represented in Figure 6.
The temperature in the upper part of the store (T8) and the refrigerant temperature at the inlet of the copper heat exchanger tube (T1) are represented. It is obvious that by using a coated copper heat exchanger tube a 0.5 K higher supercooling of the water in the store by a 0.5 K lower refrigerant temperature can be reached compared to an uncoated copper heat exchanger tube. The refrigerant temperature determines the heat exchanger tube surface temperature that is equal to the nucleation temperature when ice growth starts. That means that the nucleation temperature is lower, if coated copper heat exchanger tubes are used. Ice growth starts at a lower heat exchanger tube surface temperature. Lower refrigerant and heat exchanger tube surface temperatures lead to a higher supercooling of the water in the model ice store.

A higher supercooling of the water in the store leads to a greater mass of ice produced when ice growth is initiated. The heat of fusion $Q_{\text{fus}}$ is equal to the sensible heat $Q_{\text{sens}}$ (1). The heat of fusion is the product of ice mass $M_{\text{ice}}$ and enthalpy of fusion $\Delta h_{\text{fus}}$ of water. The sensible heat is the product of water mass $M_w$, specific heat capacity of water $c_w$ and supercooling of the water $\Delta T$ in K (2).

$$Q_{\text{fus}} = Q_{\text{sens}} \quad (1)$$
$$M_{\text{ice}} \cdot \Delta h_{\text{fus}} = M_w \cdot c_w \cdot \Delta T \quad (2)$$
$$\frac{M_{\text{ice}}}{M_w} = \frac{c_p}{\Delta h_{\text{fus}}} \cdot \Delta T \quad (3)$$

For water the enthalpy of fusion $\Delta h_{\text{fus}}$ is 333 kJ/kg and the specific heat capacity $c_p$ is 4.2 kJ/(kg K). Therefore, per Kelvin supercooling of the water 0.0126 kg ice can emerge per kg water.

As described in the introduction, ice growth is desirable because of the high storage capacity during phase change, but the ice should grow apart from the heat exchanger surface to retain a high loading power. To initiate the ice growth apart of the heat exchanger surface, an ice cube is placed in the upper part of the water in the store. As a coated heat exchanger is used, the water in the store is supercooled but at the same time the store is free of ice when inserting the ice cube. As shown in Figure 7, ice dendrites grow around the ice cube into the supercooled water, while the heat exchanger surface remains free of ice.

**Figure 7.** Initiation of ice growth in the model ice store apart of the heat exchanger surface by inserting an ice cube into the supercooled water
5. Conclusion and Perspective

By using the previously examined coatings on the surface of a copper heat exchanger tube in an ice store, the water in the store can be more supercooled than without coating. The higher supercooling results from a lower refrigerant temperature. The refrigerant temperature can be set lower without having ice growth on the heat exchanger surface, as the coatings reduce the nucleation temperature. The nucleation temperature is equal to the heat exchanger tube surface temperature when ice growth starts. With a higher supercooling of the water in the store, a greater mass of ice can be produced and the storage capacity can be increased.

It is possible to initiate the ice growth apart of the heat exchanger surface, while the heat exchanger is still working with a high loading power. As a result, less heat exchanger surface is needed to freeze the water in the ice store.

In further investigations the refrigerant temperature has to be decreased in smaller steps over longer time intervals, to detect the minimal nucleation temperature and the maximal supercooling of the water in the store, before the onset of ice growth. Furthermore, different kinds of coatings and heat exchanger materials have to be tested, to find the most suitable combination of coated heat exchanger tubes for ice stores. Additionally, the loading procedure of an ice store depending on the nucleation temperature will be modelled using different nucleation theories.

6. References

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