Investigation of condensation mode on PTFE-based coatings

Internship report

Thomas Gaudelet°, Ken Suwabe, Kyu-Hong Kyung, Seimei Shiratori

The enhancement of heat transfers during condensation is at the core of numerous researches as it will lead to increased efficiencies and productivities for various fields especially for power generation. One of the main solutions explored at the current time is to engineer a surface coating in order to promote dropwise condensation, in opposition of the filmwise condensation generally observed in actual condensing systems. With this goal in mind, we investigate the use of polytetrafluoroethylene-coated (PTFE) surfaces to improve heat transfers.

Contents

Introduction	2
Fabrication methods	
Coatings' characteristics	5
Conclusion	11
Annexe : Environnement de travail	12
Bibliography	13

Introduction

Condensers are keys components of numerous systems, especially in power plants where the condenser is found as part of the secondary circuit. The purpose of the condenser is to transform a substance, typically water, from its gaseous form to its liquid state. Generally, a cooled down surface is used as medium, for power plants it is the outer surface of cylindrical tubes cooled down by running water flowing inside. This study concerns the development of a coating for the cooling surface as a mean to lead to enhanced heat transfers and a faster condensation process. The underlying consequences of such coatings would be improved efficiencies and productivities.

One of the existing limitations in current systems, and subsequently one of the ways to improved them, is linked to the condensation mode observed on the cooling surface: a film of condensate form on the surface. The limitations implied by the filmwise condensation mode come from the added thermal resistivity and the cohesion of the condensate film. The former slows the heat transfers, hence the cooling process of the vapour and the condensation rate, the latter keeps the water layer by limiting the shedding of the water under the effect of gravity. A widely accepted, and researched, solution to this issue is to enable a different condensation mode by using coatings and topography structuration at micro- and nanoscale: the dropwise condensation mode.



Figure 1 : (a) filmwise condensation, (b) dropwise condensation

In this configuration, throughout the process, the condensate keeps the shape of droplets. This is made possible by a fast removal of the condensate preventing the coalescence of droplets leading to the formation of a film. This remark has led the scientific attention on hydrophobic and superhydrophobic coatings with low hysteresis angles, meaning that the water slide off with a slight inclination of the surface. In their study, Kim et al. [1] showed that theoretically, the heat transfer coefficient is an increasing function of the contact angle. However the reality differs from this theoretical result. The condensation phenomenon is particularly complex and not yet fully grasped. Miljkovich et al. [2] have notably shown that the droplet state during condensation has a huge impact on the condensation mode and the heat transfer coefficient.

In the light of the different challenges raised by the improvement of condensation, we chose to study one means of surface tempering in order to enable dropwise condensation. We investigate the use of polytetrafluoroethylene (PTFE) as a coating layer and meshes as a mean to alter the topography of the layer of PTFE. The study follow two step, the first one was

realized on flat stainless steel substrate, and the goal was to determine the viability of the method as well as investigate the characteristics of the coating, the second step used aluminium tubes as substrates as a mean to measure the evolution of heat transfer depending on the mesh step used. The choice of PTFE was based on its low surface energy and high thermal resistance taking into account the major role of high contact angle and the nature of the wide range of temperature that the coating might have to withstand. However, we remark here, that PTFE poor thermal conductivity and the low physical resistance of the coating might harm the implementation of such coatings, as it is here, in the industry.

Fabrication methods

Considering the fact that two substrates were used - flat and cylindrical – the fabrication method had to be adapted for each. However, the guiding line of the process stays the same. It starts with rinsing then depositing a first layer of PTFE, which is annealed at 370°C in order to get a smoother surface and improve the bonding of the geometry altered layer with the surface. Then we deposit the second layer, which will hold the topography alteration as explained earlier. We finish by annealing again in order to strengthen the final coating and increase durability, the weak physical resistance being one of the issues as stated in the introduction.

Flat stainless steel substrate

For this first experiment, we used dipping as a mean to deposit the layers of PTFE and mechanical press as a mean to imprint the geometry of the meshes onto the final layer.



Two different annealing temperatures were used for the final part, 250°C or 370°C, the idea was to study the effect on the coating of temperatures below and above the melting point of PTFE which is at 343°C. In the second experiment the annealing was made at 370°C as the results obtained on flat substrate shown, as we will discuss in the following, it was more efficient.

Aluminium tubes

Here, we chose a method more adapted to the cylindrical shaped substrate: spraying. To introduce the change in topography, we spray through the meshes, using them as a canvas.



We assumed that the characteristics of the coated surface were amost the same for the two methods for a given mesh.

To insure that the spraying was homogeneous, we used a rotating device on which the tubes were mounted and we used a spray-gun with small diameter outlet.



Figure 2 : Rotating device and spray-gun

To investigate the condensation behaviour and heat transfers, we designed a chamber using a water heater as vapour source and running water at room temperature as cooling fluid inside the tubes. The chamber is a plexiglas box which has been pierced in order to let the tube go through. The vapour source is placed inside the box. Once closed the chamber is hermetic.



We measure the inlet and outlet temperature of the cooling water using thermocouples as a way to calculate condensation heat transfers as we will discuss later on.

We observe that there is condensation not only on the tubes but also on the walls of the chamber which hamper our vision of what is happening inside the chamber. To tackle this issue, we used a hydrophilic coating on the inside walls in order to prevent the formation of small droplets and preserve the visibility. The coating was made in three steps, non-including the ethanol cleaning. The first was to spray a KOH solution, then after drying this first layer we spray a layer of pure water. This first steps were taken in order to deposit a thin layer of water molecules on the wall to facilitate the adhesion of the hydrophilic agent which was a lenses cleaning solution.

Coatings' characteristics

Here we present the results of the different measurements taken on flat samples. Measurements were made through laser microscopy, scanning electron microscope (SEM), VHX microscope and a classical contact angle measurement setup (light, cross, lenses, rotating support).

Four different meshes were used for this experiment, three were made out of polymer –mesh step of $30\mu m$, $60\mu m$ or $105\mu m$) and the last one was a stainless steel mesh (step of $20\mu m$). Two annealing temperatures were investigated as pointed out earlier: $250^{\circ}C$ and $370^{\circ}C$. The differences appear at microscale, when the temperature is above the melting point of PTFE the nano-particles melt and form filament structures as the following SEM images underline.



250°C annealing



370°C annealing

SEM images

First we note that we can observe the filament structures on the 370°C-annealed samples. Then we remark that the pores have roughly similar areas, we will take a closer look at those through laser microscopy. Finally we can infer from the pictures, that the higher the annealing temperature the more the surface is levelled as it appears that the pores are deeper after a 250°C annealing than for the 370°C annealed samples.



The above graph represents the RMS factor with respect to the mesh step. From this result we cannot draw conclusion concerning the link between the two characteristics. The graph below shows that the pores' area is an increasing function of the mesh step.



For both this graph, we observe that when we increase the annealing temperature, the RMS factor decrease but the pore surface increase.

We then took a look at the contact angle values for the different samples. To put the different measurements into perspective, we draw here the graphs of contact angles with respect to the mesh step then to the RMS factor.



First, we note that the contact angles decrease when the annealing temperature is above the melting point of PTFE. This is consistent with the smoother topography at nanoscale for the 370°C annealed samples. Then, we remark a slight decrease in contact angle as the RMS factor increase, putting aside the smooth coated sample.

Condensation behaviour

Next, we investigate the condensation behaviour on the flat coated samples. To achieve this we used the plexiglas box introduced earlier. However as a cooling method we used a peltier module set to 5° C. The samples are taped to the peltier module which is placed at 60° from the horizontal plane in order to facilitate the departure of the condensate.

The picture below was taken after 45 minutes in the vapour chamber. Starting at the top row and going from left to right, the two first samples are, in that order, the bare substrate and the smooth coated samples. Then the three next samples are 370° C annealed samples pressed with respectively the stainless steel mesh, the 30μ m mesh and the 64μ m mesh.

Finally we have the 250°C annealed samples pressed in the same fashion that the previous three.



Figure 3 : Condensation state after 45 minutes

We observe that we have dropwise condensation on each of the pressed samples, however a film of condensate has formed on the smooth coated sample and a film is in the process of forming for the bare substrate.

The next step is to evaluate the condensation density on each of the six samples presenting dropwise condensation in order to evaluate the efficiency of each sample. Therefore, using the software ImageJ and pictures after 30 and 45 minutes of experiment, we measure the wetted area (in percentage), below is the graph of this measurements vs the RMS factor.



The result shows no dependency between the wetted area and the RMS factor. Therefore, from these data we cannot determine the most suited mesh.

However, VHX microscope measurement shows that the droplet density is higher on the 370°C annealed samples as we can observe on the figure below. The sample were cooled down to 5°C using the peltier module, we then used a vaporizer to place them in a water saturated atmosphere. The pictures were taken after 2 minutes.



Figure 4 : (left) 250°C annealed and (right) 370°C annealed samples (30µm mesh)

Tubes experiment

Here we present the result of the experiments on the tubes. All along the experiments we monitored the evolution of the inlet and outlet temperature. And we recorded each experiment to insure that the condensation mode was sustained.



Figure 5 : Experiment after (a) 0, (b) 15, (c) 30 and (d) 60 minutes

The above pictures were extracted from the movie recorded during the experiment using the $100\mu m$ mesh. However, more generally, the dropwise condensation mode was sustained for more than two hours on every sample, even on the bare and smooth coated ones despite the expectation of filmwise condensation mode from the previous results.

Heat transfers data

To conclude on the interest of this experiment, we evaluate the heat transfer coefficients for each sample. In order to achieve this we used the same method as Lee *et al.* [8].

First, we calculate the heat transfer rate Q_W directly from the measure of the inlet and outlet temperature through the following formula:

$$Q_w = m_w c_p (T_{out} - T_{in})$$

Where m_W is the mass flow of coolant fluid, c_p is the specific heat and T_{out} , T_{in} are respectively the outlet and inlet temperatures. This equation expresses the fact that the heat transfer is directly linked to the temperature rise of the coolant when it flows through the tube.

Then, the following equation gives us the overall heat transfer during the experiment:

$$K = \frac{Q_w}{A_0 T_{LMDT}}$$

Where T_{LMDT} is the log mean temperature as follows:

$$T_{LMDT} = \frac{(T_{out} - T_{in})}{ln\left(\frac{T_s - T_{in}}{T_s - T_{out}}\right)}$$

And A_0 is the outside area of the tube.

The heat transfer coefficient of condensation is finally obtained through the equation:

$$h = \frac{1}{\frac{1}{\frac{1}{K} - \frac{A_0}{A_i h_w} - \frac{A_0 \delta}{A_m \lambda_s}}}$$

Where A_i is the inner area of the tube, A_m is the mean value of A_0 and A_i , h_w is the heat transfer coefficient of the pipe wall, λ_s is the fluid thermal conductivity at saturation and δ is the wall thickness.

The terms $\frac{A_0}{A_i h_w}$ and $\frac{A_0 \delta}{A_m \lambda_s}$ corresponds to the heat transfer coefficients inside the tube and in the bulk of the coolant.

Discussion

The results obtained are represented in the graph below with respect to the coating/mesh used.



The experiment shows that the smooth coating leads to a slight decrease of the heat transfer coefficient. This can be explained by the added thermal resistance from the layer of PTFE – which has low thermal conductivity – and the fact that the contact angle for the bare substrate is close to the one for the smooth coated sample (around 100°).

However, with the use of mesh, we remark an increase between 120% and 200% of the heat transfer coefficient. The interpretation of the data for the sample coated through meshes is problematic though. Indeed, considering the fact that the sole difference between the meshes comes from the step, we expected the result to be decreasing with the increase of the mesh step. So far, we cannot explain the evolution of the data observed and we need to rerun the experiments as a mean to corroborate these first values. Furthermore, the heat transfer coefficient values are really low, which is linked to the slow mass flow of the coolant due to the capacity of the pump used.

Conclusion

This study has shown the interest of sprayed through mesh PTFE-coatings as we observe a neat increase of the heat transfer coefficient during condensation, up to 200%.

However, as noted, it is difficult to underline a pattern in the different measurements made, on tubes and flat substrates as well, which makes it hard to draw definite conclusion concerning the optimization of the coating structure. Further studies will be needed to fully understand the phenomena. In following studies, we will also develop the test set as it is needed to gain more control over the different parameters playing a role in order to get more insights and more accurate and general results. Notably, control over the mass flows of the coolant and the vapour is essential as well as controlling the atmosphere inside the box (pressure, temperature, humidity).

Annexe : Environnement de travail

Ce stage a été réalisé au sein du laboratoire du Professeur Seimei Shiratori de l'université de Keio. Le laboratoire est constitué par une grande majorité d'étudiants, leur travail au sein du laboratoire fait partie intégrante de leur cursus à partir de leur dernière année de licence jusqu'à la fin de leur deux année de master. Plus précisément, les étudiants sont amenés à choisir un laboratoire durant leur troisième année de licence afin de réalisé la composante de recherche nécessaire pour compléter leur cursus. Ceux qui choisissent de continuer les études par un master poursuivent généralement leur travail au sein du même laboratoire, il est toutefois possible de choisir un autre laboratoire ou un autre sujet. Le laboratoire du professeur Shiratori sélectionne chaque année six à sept nouveaux étudiants parmi les postulants. Ce qui fait environ une vingtaine d'étudiants en comptant les doctorants.

Les bureaux et salles d'expériences sont répartis sur deux campus : le campus Yagami et le campus K2. Compte-tenu du fait que le travail de recherche s'effectue en parallèle des cours constituant le cursus respectif de chaque étudiant, la gestion des horaires est laissée à chacun, l'accent étant mis sur la progression et l'obtention de résultats. Pour contrôler l'avancée et permettre les échanges d'idées deux réunions de groupes par semaine sont planifiées – le mercredi matin et le samedi matin – durant lesquelles cinq étudiants sont amenés à soit présenter l'avancée de leur travaux, soit à présenter un article en rapport avec leur sujet.

En ce qui me concerne, je suivais en parallèle un cours de japonais le mercredi aprèsmidi ce qui signifie que je passais la majorité de mon temps au laboratoire au campus Yagami. Les trois premiers mois se résumèrent à la prise en main du matériel et à une phase de bibliographie sous la tutelle d'un élève en première année de master Ken Suwabe, dont le sujet porte aussi sur l'hydrophobie, et le suivi du professeur Shiratori. La seconde partie à débuter lorsque mon sujet a été précisément défini. Il m'a fallu alors réfléchir à un banc d'essai réalisable avec les moyens mis à ma disposition puis à la réalisation des différentes expériences avec l'aide précieuse du doctorant Kyu-Hong Kyung et les conseils du professeur Shiratori. L'ensemble de mon travail s'est conclu par une présentation de poster à la conférence JSAP. Durant le dernier mois, en dehors de la préparation pour la conférence, j'ai été amené à former l'un des nouveaux membres du laboratoire, Hirotaka Tsuchiya, qui souhaitait reprendre et approfondir le sujet.

Bibliography

[1] Kim, S., & Kim, K. J. (2011). Dropwise condensation modeling suitable for superhydrophobic surfaces. *Journal of heat transfer*, *133*(8)

[2] Miljkovic, N., Enright, R., & Wang, E. N. Modeling and Optimization of Superhydrophobic Condensation.

[3] Chen, C. H., Cai, Q., Tsai, C., Chen, C. L., Xiong, G., Yu, Y., & Ren, Z. (2007). Dropwise condensation on superhydrophobic surfaces with two-tier roughness. *Applied Physics Letters*, *90*(17), 173108-173108.

[4] Xu, X., Zhang, Z., & Liu, W. (2009). Fabrication of superhydrophobic surfaces with perfluorooctanoic acid modified TiO₂/polystyrene nanocomposites coating. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 341(1), 21-26.

[5] Chen, H., Zhang, X., Zhang, P., & Zhang, Z. (2012). Facile approach in fabricating superhydrophobic SiO₂/polymer nanocomposite coating. *Applied Surface Science*.

[6] Singh, E., Chen, Z., Houshmand, F., Ren, W., Peles, Y., Cheng, H. M., & Koratkar, N. (2013). Superhydrophobic Graphene Foams. *Small*, *9*(1), 75-80.

[7] Enright, R., Miljkovic, N., Dou, N., Nam, Y., & Wang, E. N. (2012). Condensation on Superhydrophobic Copper Oxide Nanostructures. *Journal of Heat Transfer*, *10*(1.4024424).

[8] Lee, S., Cheng, K., Palmre, V., Bhuiya, M. D., Kim, K. J., Zhang, B. J., & Yoon, H. (2013). Heat transfer measurement during dropwise condensation using micro/nano-scale porous surface. *International Journal of Heat and Mass Transfer*, 65, 619-626.