Pool Boiling of Novec 7300 and Self-Rewetting Fluids on Electrically-Assisted Supersonically Solution-Blown, Copper-Plated Nanofibers

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Abstract

Pool boiling of Novec 7300 fluid and self-rewetting water-heptanol mixtures on bare copper surface and a copper surface coated with copper-plated nanofibers is studied experimentally. The experimental data revealed a significant increase in the heat removal rate up to the critical heat flux (CHF) on the copper-plated nanofiber surfaces in comparison with bare copper surfaces. Also, the critical heat flux increases on the copper-plated nanofiber surface, albeit it is reached at a lower surface superheat in comparison with bare copper surface. Prolong boiling in water facilitates oxidation of the layer of copper-plated nanofibers, and diminishes its roughness, albeit does not affect the heat transfer rate.
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1. Introduction

In the year 1965 Gordon E. Moore in his seminal paper\(^1\) had predicted that the number of transistors in a dense integrated circuit to be used for computing will double up almost every two years and that prediction is still holding true to keep up with the pace of computing, automation and boom in datacom industry. This resulted in an exponential increase in the number of computations per input power (MegaFlops per watt), as high as from 20 MFlops/watt in the year of 2004 to 600 MFlops/watt in 2010 \(^2\). Miniaturization of transistors posed an acute problem in heat dissipation and effective heat removal from microelectronic equipment became one of the biggest challenges. Several cooling technologies such as single-phase liquid cooling, flow boiling, jet impingement cooling, spray cooling, heat pipes, thermsyphons, and pool boiling with their advantages and drawbacks are used. Broadly speaking, cooling technologies can be subdivided into direct liquid cooling and indirect liquid cooling using both single- and two-phase media. Pool boiling is considered as one of the most promising remedies for the thermal management problem. It is used not only for thermal management and cooling of microelectronic devices, but also in nuclear power plants, air conditioners, refrigerators, for fluid handling and control, orbit storage and supply systems for cryogenic propellants and life support fluids.

Pool boiling regimes are dictated by the surface temperature and the heat flux and include consequently natural convective boiling, nucleate boiling, transitional boiling and film boiling. In
the nucleate boiling regime the heat flux from the surface increases with the wall temperature until it reaches the maximum heat flux called the critical heat flux (CHF). After the CHF, a vapor layer forms over the heater surface and the heat flux decreases as the surface temperature significantly increases. The challenge is to increase the heat flux at low wall temperature and several different mechanisms could be employed to achieve this. A thorough understanding of the boiling heat transfer and CHF is essential for developing the next generation of heat removal techniques.

Pool boiling of various coolants such as water, alcohol, Novec fluids, fluorinert fluids and refrigerants on different surfaces (wires or plane surfaces of different roughness) has been studied [3-8]. Several empirical and semi-empirical models were proposed to describe pool boiling under Earth gravity conditions [9-14]. Small concentrations of nanoparticles such as alumina, zirconia or silica in the boiling liquids were found to be an efficient way to enhance the CHF [15-18]. Nucleation rate, growth and departure of vapor bubbles are enhanced on superhydrophobic surfaces and thus heat removal is enhanced at lower degree of superheat [19-22]. Fluorinated compounds such as FC 72, FC 77, Novec 7100, Novec 7200, and Novec 7300 are of potential interest for microelectronics cooling due to the unique combination of low dielectric constant and high thermal and chemical stability. In addition to that, owing to their chemical inertness, unlike other fluids, FC fluids pose no harm for the microelectronics characteristics. Pool boiling of several fluorinerts, Novec fluids and other dielectric fluids have been reported earlier on different surfaces and in several mixtures [23-26]. As these fluorinerts and Novec fluids are used in direct liquid cooling of the electronic components, pool boiling study of these fluids is essential.
The influence of the electric field on bubble departure, bubble diameter and thus the heat flux was studied under various gravity conditions. It was found to be a reliable mechanism for bubble detachment and heater surface re-wetting in microgravity [27, 28].

Concentration-driven Marangoni effect and the thermocapillarity oppose liquid flow in a thin layer between the bubble and the heater surface for most pure liquids and binary mixtures. Dilute aqueous solutions of high carbon alcohols (number of carbon atoms ≥ 4) also called self-rewetting fluids, used in indirect liquid cooling of electronic components reveal an increase in surface tension with temperature after a certain point. This allows both the concentration-driven Marangoni effect and thermocapillarity to pull liquid in the same direction and drive the flow towards the heated surface, thus removing the bubbles. Pool boiling of self-rewetting fluids showed an enhancement of cooling performance and prevented the dry-out phenomenon [29-31].

Nano-textured surfaces formed by metal-plated nanofibers revealed attractive features for such applications as spray cooling and pool boiling [32-36]. The dramatic increase in the bubble nucleation rate and projected area density on metal-plated nanofiber mats is due to the increased temperature of the liquid entrapped in the fluffy surface provided by nanofiber mats. Moreover, the nano-textured surfaces provide numerous nucleation points for the bubble nucleation and growth. An increased nucleation rate due to the multiple nucleation sites on nano-textured surfaces, results in the enhanced bubble formation. This causes an increased mixing within the bulk fluid, and thus contributes to higher heat transfer rate. In addition, the increased surface area of the nano-textured surfaces provides a greater heat flux according to the Newton’s law of cooling. The increased surface area associated with metal-plated nanofiber mats located at the heater surface is also beneficial for the enhanced cooling by impinging jets of air [37]. Overall,
inexpensive nano-textured surfaces hold great potential of solving an acute thermal management problem, which surmount to billions of dollars [38, 39].

In the present work pool boiling of Novec 7300 and water-heptanol (0.1% by vol.) mixture is studied on both bare copper surface and copper-plated nanofiber surface. Section 2 describes preparation of nano-textured surface. Pool boiling experiments are detailed in section 3. The experimental results are discussed in section 4 and conclusions are drawn in section 5.

2. Preparation of Nanofiber Mats on Heater Surface

2.1. Materials

Polymer polyacrylonitrite (PAN; molecular weight $M_w=150$ kDa) was obtained from Polymer Inc. Solvent N,N-Dimethyl formamide (DMF) anhydrous-99.8%, and compounds used for copper-plating (sulfuric acid, hydrochloric acid, copper sulfate-pentahydrate, and formaldehyde), as well as the working fluid n-heptanol were obtained from Sigma-Aldrich. Novec 7300 fluid was purchased from 3M. Oxygen-free high-conductive (OFHC) 101 grade copper plates and rods were purchased from McMaster-Carr to use as anode for copper-plating. They were cut into cylindrical pieces and used as substrates. Prior to deposition of nanofiber mats, copper plates were roughened using a 3M Pro Grade sand paper P600.

2.2. Electrically-Assisted Supersonic Solution Blowing and Electroplating

Electrically-assisted supersonic solution blowing was conducted with 6 wt% PAN solutions in DMF as in the previous work of this group [36]. Cu substrates used in the experiments, were employed as nanofiber collectors. Polymer nanofibers were deposited on them directly for 10
min. The obtained polymer nanofiber mats were then copper-plated to enhance their thermal conductivity. For copper-plating a nanofiber mat was first sputter coated with 7.5 nm Pt-Pd layer using Cressington Sputter Coater to establish electrical path between Cu ions and insulating polymer nanofibers. At the following stage such sputter-coated layer acted as a conductive “mask” for the nanofibers for successful copper plating. The electroplating bath was filled with a mixture of sulfuric acid (5 g), hydrochloric acid (0.5 g), copper sulfate-pentahydrate (16 g) and formaldehyde (10 g) in 100 mL of deionized (DI) water. Electroplating was conducted using the Electroplating Station HSEPS-10 following the procedure as described in Ref. 36.

2.3. Characterizations

Scanning electron microscopy (SEM) of copper-plated nanofiber mats was done using JEOL JSM-6320F with a cold emission source, while the optical images were taken using optical microscope Olympus BX-51. The surface roughness of both bare copper and nanofiber-coated copper surface was analyzed with the Bruker 3D Optical Microscope GTK1. The high-speed imaging was done using a Phantom V210 camera, and Nikon D3100 camera was used to record long-time videos illustrating the CHF patterns. The X-ray Diffraction analysis of the copper-plated nanofiber surface was conducted using Siemens X-ray machine.

3. Pool Boiling Experiments

3.1 Experimental Setup

The experimental setup used in the present work was based on our previous design [36] with many modifications. The main parts of the experimental setup are the primary Teflon casing, the secondary Teflon casing, the main copper rod, the copper substrate, the glass chamber, the recuperating unit, the back cover and the cartridge heater assembly. The schematic of the experimental setup is shown in Fig. 1. The primary copper rod of length 3” was machined
into three step-sections of different diameters of 0.75”, 1.75” and 1.5”, respectively. The reduction of cross-section of the primary copper rod was done to intensify the heat flux at the surface. The primary copper rod was bolted to the primary Teflon casing. An air gap of radius 0.125” was allowed to insulate the copper rod with the primary Teflon casing to avoid the conduction losses. Five 200W cartridge heaters, purchased from Omega (3/8” x 1.50”) were used as heat source and were placed inside the holes drilled in the copper rod. Springs were placed on the rear side of each cartridge heater and were then pressed with the back Teflon cover. This ensured a proper contact of the heater with the copper rod surface minimizing heat losses through the system.

The copper substrate was a cylindrical piece of diameter 0.75” and height 0.75”, where 0.25” of its height was threaded to a diameter of 0.25”. The copper substrate was screwed into the copper rod. A thin layer of thermally-conductive silver paste was applied in-between the copper substrate and the copper rod to eliminate any air gap and facilitate proper heat transfer across the interface. Two holes were drilled within the copper substrate at a distance of 6.25 mm between them. The holes were drilled to the center of the copper substrate.

The secondary Teflon casing was attached to the glass chamber, the outer casing of which was made from aluminum. The boiling chamber was a parallelepiped of size 1.5”x1.5”x 3.25” and was made of glass. The secondary Teflon casing with the boiling chamber was then placed on the copper substrate. An O-ring was used to seal the gap between the copper substrate and the secondary Teflon casing. The vapor recuperating unit was then placed on top of the boiling chamber. Cold water flowing through the recuperating unit kept the temperature of the unit well below the room temperature and allowed the vapor formed inside the chamber to condense within it. A small hole of 1 mm was drilled at the top of the vapor recuperating unit.
which allowed the excess vapor formed inside the chamber to escape out to avoid pressure rise inside the chamber. A 100 W immersion heater was inserted inside the boiling chamber to keep the temperature of the test fluid up to the saturation conditions and also to degasify the liquid as much as possible.

**Fig. 1.** The section view of the assembled experimental set-up used for the pool boiling experiments.

### 3.2 Experimental Procedure
The copper substrates, either a bare one or the one coated with copper-plated nanofibers, was placed over the primary copper rod. The T-type thermocouples were then inserted into the copper substrate and connected to the HH806AW microprocessor thermometer purchased from Omega. The thermocouples were covered with conductive silver paste to ensure good thermal contact with the copper substrate. The five cartridge heaters inside the primary copper rod were all connected in parallel and powered using a variable autotransformer. The variable autotransformer provided variable voltage and current output at varied percentage setting. The voltage and current at different percentage settings of the autotransformer were recorded using Fluke 115 true RMS multimeter. Test liquid (90 ml) was poured into the boiling chamber in each experiment. The variable transformer was turned on at 16% setting along with the immersion heater being on too. They were kept at this setting for 50 min. This procedure was used to degasify the liquid inside the chamber. Then the input of the variable transformer was increased with an interval of 4%. After 10 min of changing the percentage setting, the thermocouple reading did not show any variation indicating that the system had reached a steady state. The temperature values at the thermocouple locations were then recorded.

4. Results and Discussion

4.1. Pool Boiling of Novec 7300

The pool boiling experiments with Novec 7300 fluid were conducted using both bare copper surfaces and copper surfaces coated with copper-plated nanofibers. The working fluid (90 ml) was located in the boiling chamber with both the immersion heater and the variable autotransformer (16%) kept on for 50 min. This partially degasifies the fluid without any nucleation from the surface of the copper substrate. The autotransformer setting was then
increased with an interval of 4% and kept at that setting for the next 10 min. This is the maximum time it takes the system to reach steady state. The voltage, current and the thermocouple readings were taken at each setting after the system had reached steady state. The power input to the cartridge heaters P which was transferred to the copper rod was calculated as $P=VI$, where V is the voltage applied across each identical cartridge heater and I is the total current through all the heaters.

The temperature gradient across the thermocouples at locations $T_2$ and $T_3$ (cf. Fig. 1) was used to obtain the surface temperature of the copper substrate $T_s$ using the following expression

$$T_s = T_3 - \left( \frac{T_2 - T_3}{\Delta x_{23}} \right) \Delta x_{3s}$$  \hspace{1cm} (1)

where $\Delta x_{23}$ is the distance between the thermocouple locations $T_2$ and $T_3$ and $\Delta x_{3s}$ is the distance between the thermocouple location $T_3$ (cf. Fig. 1) and the surface. The degree of superheat $\Delta T$ was obtained as the difference of the surface temperature $T_s$ and the saturation temperature of the boiling liquid $T_w$. The heat transfer to the boiling liquid from the surface of the copper substrate is then found using the Fourier law as

$$q = -k_{cu} \frac{T_1 - T_2}{\Delta x_{23}}$$  \hspace{1cm} (2)

where $k_{cu} = 401 \text{ W/(m} \times \text{K)}$ is the thermal conductivity of copper.

The pool boiling data for Novec 7300 fluid on both bare copper surface and the copper surface coated with copper-plated nanofibers are depicted in Fig. 2. At the same surface superheat, the heat flux, as well as the heat transfer coefficient, is higher on the copper-plated nanofiber surface than on the bare copper surface, as is evident from Fig. 2. The experimental data for two representative trials conducted on both surfaces are shown in the figure and reveal
good repeatability. In the case of the copper-plated nanofiber surface, nucleation begins at a very low superheating in comparison to the bare copper surface. The temperature at which nucleation begins is reduced by 6 °C on copper-plated nanofibers. The heat transfer coefficient \( h \) was calculated as \( h = q''/\Delta T \). The robustness of the samples and repeatability of the results on each of them was additionally verified by conducting several trials on the same copper-plated nanofiber surface. No decay in the heat removal rate was observed due to aging of the nano-textured surfaces. Figure 3 shows the optical microscope and SEM images both before and after pool boiling experiments. The actual copper sample used in the experiment is too big to be observed in SEM. To observe the effect of pool boiling on the nanofibers a smaller copper disc was used for depositing the nanofibers and subsequently copper plating them under the conditions identical to the actual samples. The smaller copper disc was then used in pool boiling experiments with the setup described in [35]. No visual delamination was observed during such pool boiling experiments indicating the robustness of the nano-textured surface. This, ensures that the surface does not deteriorate after repeated pool boiling experiments on it which last for several hours. The robustness of the samples is also corroborated by the repeatability of the results of the actual pool boiling experiments in the present work (e.g. in Fig. 2).
Fig. 2. Pool boiling data for Novec 7300 fluid on bare copper surface and copper surface coated with a thin (15-20 µm) layer of copper-plated nanofibers. The experiments have been repeated twice on the same surface and the results for trials 1 and 2 are shown by the corresponding filled and open symbols. (a) Heat flux versus surface superheat, and (b) the corresponding heat transfer coefficient versus surface superheat. Notation: Bare corresponds to bare copper surface, NT-to nano-textured surface of copper-plated nanofibers.

The remarkable steepness of the boiling curve measured on the nano-textured surfaces (cf. Fig. 2a) reveals a sharp rise of the heat removal rate at very low surface superheat. It was possible to reach the critical heat flux (CHF) with the present setup and it increased by 33% on the copper-plated nanofiber surface compared to the bare copper surface. Moreover, the CHF on the copper-plated nanofiber surface was reached at a lower (by 10 °C) surface superheat than on the bare copper surface. A similar result (the CHF reached at a surface superheat lowered by 5.3 °C) was reported in [25] for pool boiling of Novec 7300 fluid on sintered copper surfaces with carbon nanotubes. Pool boiling is an efficient cooling technique in a wide range of the degree of
superheat. Most of the electronic devices operate at variable percentage of their maximum capacity and thus produce various heat fluxes. In the case of cooling of high-power microelectronics one of the objectives is to remove high heat flux even at a relatively low degree of superheat. Early boiling from a nano-textured surface at lower degree of superheat facilitates enhanced cooling as the phase change heat transfer is higher than the conductive and convective heat transfer characteristic of lower degrees of superheat.

**Fig. 3.** Optical microscope image (a-b) and SEM image (c-d) of copper plated nano-textured surface on copper substrate both before (a, c) and after (b, d) pool boiling experiments in the setup of [35]. Scale bars are 10 µm in panels (a, b) and 1 µm in panels (c, d). No deterioration of the nanofibers had been observed after the pool boiling experiments.
At CHF a vapor film forms over the heater surface which acts as an insulating layer between the bulk fluid and the heater, as a result of which the temperature at the thermocouple locations $T_2$ and $T_3$ keep rising continuously. Both the cartridge heaters and the immersion heater were kept on and the temperatures of the thermocouples were monitored and recorded until the temperature at the location $T_2$ had reached 210 °C, a safety limit for the Teflon casing in this setup. The heat flux measurements were conducted using the temperature gradient even after the CHF had been reached. The heat flux beyond CHF decreases slowly in case of copper-plated nanofiber as is evident from the slope of the pool boiling curve after the CHF had been reached (cf Fig. 2a). The boiling curve after CHF is steeper on the bare copper surface than on the copper-plated nanofiber surface, which is similar to the observations in [35]. This is due to the fact that as the CHF has been reached and a vapor film formed over the copper surface, the roughness of the copper-plated nanofiber surface facilitated film destabilization and break-up into separate bubbles. The high-speed videos of the pool boiling at the CHF and beyond were recorded using Phantom V210 camera on both types of surfaces (cf. the Supporting videos S1 and S2). It can be seen from the video how the intact vapor film is destroyed locally and then followed by spreading of nucleate boiling over the entire heated surface, either a bare copper or a copper surface coated with copper-plated nanofibers. The pool boiling of Novec 7300 fluid at the CHF and beyond was also recorded using a DSLR camera on both types of surfaces at 33 fps (cf. the Supporting videos S3 and S4). Figure 4 shows how the thick vapor film is destabilized after the CHF has been reached and the heaters turned off at the temperature $T_1 = 210$ °C. It is seen how the vapor film subsequently breaks up into trains of small individual bubbles. The
comparison in Figs. 4 (a)-4(c) shows that the vapor film is more unstable on the copper-plated nanofiber surface due to inherent destabilizing effect of its nano-texture.

Fig. 4. Formation of bubbles at the CHF and subsequent destabilization and break-up of the vapor layer into tiny bubbles on both the bare copper surface and copper-plated nanofiber surface. The high speed images of destabilization of the vapor film on both surfaces are compared at the same time instants in panels (a)-(e), and at the same degree of superheat in panel
(f). Each panel contains two images: the left one corresponds to the bare copper surface, and the right one to the copper-plated nanofiber surface. The time $t = 0$ corresponds to the moment when the cartridge heaters and the immersion heater were turned off. Scale bar is 1cm.

The images shown in each panel in Fig. 4 were shot at the same time instant, and the surface superheat was found to be less at the nano-textured surface than at the bare copper surface. When the entire vapor film is destabilized due to the Rayleigh-Taylor instability (with the denser liquid being supported by a lighter vapor layer with the gravity acceleration being directed toward the lighter layer), isolated vapor columns are formed and break up into trains of individual bubbles (due to the Rayleigh capillary instability) [40], which subsequently decrease in size. As the heater was turned off, these vapor bubble trains facilitate surface cooling and thus reduce the wall superheat. The size of the bubbles is smaller and their area density on the nano-textured surface is higher than those on the bare copper surface which is evident from Fig. 4 (d-f), especially in the case of $\Delta T=2.5$ °C.

The temperature rise at the thermocouple locations $T_2$ and $T_3$ was recorded every 10 s after the CHF was reached for both the bare copper surface and copper-plated nanofiber surface, with the results being shown in Fig. 5. The objective in this case was to see how the temperature of the sample rises even after the CHF is reached. Both the immersion heater and the cartridge heaters were kept on. The temperature rise is steeper and the cut-off limit for the temperature is reached much earlier in the case of the bare copper surface than for the copper-plated nanofiber surface. This suggests that the nanofiber surface delays the temperature rise or in other words allows higher heat removal rate across the vapor film formed on the surface even after the CHF.
It should be emphasized that as thermocouples measuring $T_2$ and $T_3$ are placed close, the temperatures $T_2$ and $T_3$ for each surface may look almost indistinguishable. For better representation, the variation of temperature gradients with time for both the surfaces is shown in Fig. 5c and the higher gradient in the case of copper-plated nanofibers is clearly evident. This probably happens due to a much higher surface area of the copper-plated nanofiber surface compared to the projected bare copper surface.

**Fig. 5.** The temperature increase at the thermocouple locations $T_2$ and $T_3$ (cf. Fig.1), respectively, panels (a) and (b), after the CHF has been reached. (c) Variation of the temperature gradient with time after the CHF has reached. Notation: Bare corresponds to bare copper surface, NT-to nano-textured surface of copper-plated nanofibers.
As soon as the temperature $T_1$ reaches a limit of 210 °C, the power of the immersion heater and the variable autotransformer was turned off and the temperature of the thermocouples $T_2$ and $T_3$ were recorded then after every 10 s. These temperatures start decreasing as the vapor layer breaks up and bubble trains released from the surface remove heat from it. The rate at which the temperature decreases is higher on the nano-textured surface than the bare copper surface which can be seen in Fig. 6c. The nano-textured surface of the copper-plated nanofibers facilitates higher bubble nucleation and thus reduces temperature more efficiently.

**Fig. 6.** Decrease in temperatures $T_2$ and $T_3$ (cf. Fig.1), respectively, panels (a) and (b), after the heat source has been turned off after temperature $T_1$ reached the cut-off limit of 210 °C. (c)
Variation of the temperature gradient with time after the CHF has reached. Notation: Bare corresponds to bare copper surface, NT-to nano-textured surface of copper-plated nanofibers.

4.2. *Pool Boiling of Water-Heptanol Mixture*

Pool boiling of pure water and water-heptanol mixture (0.1% by vol, which is the maximum solubility of heptanol in water) was conducted following the approach described in the previous section. Several trials were done on many surfaces and two of them are shown in the figures in the present section as the representative cases. The pool boiling data for pure water is shown in Fig. 7. At the same degree of superheat, the heat flux and the heat transfer coefficient on the copper-plated nanofiber surface was higher than those on the bare copper surface. The inception of bubble nucleation from the nano-textured surface was found at the surface superheat of 1.5 °C.

![Fig. 7. Pool boiling data of water on bare copper surface and copper-plate nanofiber layer. The experiments have been repeated twice on the same surface and the results for trials 1 and 2 are shown by the corresponding filled and open symbols. (a) Heat flux versus surface superheat, and](image-url)
(b) the corresponding heat transfer coefficient versus surface superheat. Notation: Bare corresponds to bare copper surface, NT-to nano-textured surface of copper-plated nanofibers.

The pool boiling experiments with water and water-heptanol mixture were not allowed reaching the CHF due to the safety concerns related to the construction of the experimental setup. Therefore, the transformer setting was limited to 60% of its maximum rating. The surface superheat at which the maximum heat flux on the nano-textured surface was reached was by 4.5 °C lower than on the bare copper surface. At any surface superheat the heat flux on the copper-plated nanofiber surface was 2-3 times higher than that on the bare copper surface. The pool boiling data for water-heptanol mixture is depicted in Fig. 8. The heat flux and the heat transfer coefficient were higher on the copper-plated nanofiber surface than those on the bare copper surface. The surface superheat at which the vapor bubble nucleation was observed from the nano-textured surface was by 2 °C lower than that for the bare copper surface. The surface superheat at which the maximum heat flux was reached on the nano-textured surface was by 4.5 °C lower than that on the bare copper surface.
Fig. 8. Pool boiling data for 0.1 % vol water-heptanol mixture on bare copper surface and copper-plated nanofiber surface. The experiments have been repeated twice on the same surface and the results for trials 1 and 2 are shown by the corresponding filled and open symbols. (a) Heat flux versus surface superheat, and (b) the corresponding heat transfer coefficient versus surface superheat. Notation: Bare corresponds to bare copper surface, NT-to nano-textured surface of copper-plated nanofibers.

The pool boiling curves for water on the bare copper surface and copper-plated nano-textured surface are compared with those for the 0.1% vol water-heptanol mixture in Fig. 9. The pool boiling curve for water on the nano-textured surface shows enhancement in heat removal in comparison with the pool boiling curve of water-heptanol mixture on bare copper surface. The heat flux removed by water-heptanol mixture from nano-textured surface at any surface superheat was higher than the heat flux removed by water from the copper-plated nanofiber surface, even though the latent heat of evaporation of heptanol is lower than that of water, 439 kJ/kg versus 2256 kJ/kg, respectively. This shows that the self-rewetting water-heptanol mixture
[29] results in a higher heat removal rate from nano-textured surface than pure water. This is attributed to a higher bubble removal rate and thus higher heat flux. In this case both the thermocapillary and concentrational Marangoni flow (the latter is due to faster evaporation of heptanol than water) act in the same direction, which assists to vapor bubble removal in self-rewetting fluids (one of them is the present water-heptanol mixture). It should be emphasized that the self-rewetting liquid promotes early removal of bubbles as both the thermocapillary and the concentrational Marangoni flow deliver the liquid toward the bubble interface and the heater surface, to which the bubble is attached. As soon as a bubble detaches from the surface, the site is again available for the nucleation and growth of a new bubble. In other words, the early bubble removal facilitates the nucleation and growth of the next “generation” of bubbles. Overall, the number of bubbles, which have nucleated and detached per unit time is higher in the case of self-rewetting liquid. Thus, the self-rewetting liquid promotes bubble formation by removing them quickly from the surface and thus yielding a higher heat flux.
Fig. 9. Pool boiling data of water and self-rewetting water-heptanol mixture on bare copper surface and copper-plated nanofiber surface. The experiments have been repeated twice on the same surface and the results for trials 1 and 2 are shown by the corresponding filled and open symbols. (a) Heat flux versus surface superheat, and (b) the corresponding heat transfer coefficient versus surface superheat. Notation: Bare corresponds to bare copper surface, NT-to nano-textured surface of copper-plated nanofibers, and SRW to self-rewetting fluid.

4.3. Effect of Prolong Boiling on Nano-Textured Surfaces

The surfaces used in the pool boiling experiments were inspected under a 3D Optical Microscope. This was done to evaluate the effect of boiling on nano-textures of the surface. The measured roughness average (Ra) and the root-mean square (RMS) roughness (Rq) averaged over fifteen different spots on different samples before and after boiling are listed in Table 1.

Table 1: Roughness average (Ra) and root mean square roughness (Rq) of bare copper surface and copper surface with deposited nanofibers both before and after pool boiling experiments.
The roughness average represented by $R_a$ is the average of the absolute values of the surface deviation from the reference plane. The three-dimensional approximation of $R_a$ is

$$R_a = \frac{1}{XY} \sum_{i=1}^{X} \sum_{j=1}^{Y} |Z_{ij}|$$

where $X$, $Y$ are the number of data points in the x,y direction and $Z$ is the surface elevation relative to the reference plane. It is used to measure the roughness of a surface. The root mean square (RMS) roughness $R_q$ is calculated in the three-dimensional approximation as

$$R_q = \sqrt{\frac{1}{XY} \sum_{i=1}^{X} \sum_{j=1}^{Y} Z^2(x_i, y_j)}$$

It is used to represent the finish of surfaces and thus represents the standard deviation of the surface heights. Table 1 reveals that the change in $R_a$ and $R_q$ between the bare copper surface and the surfaces with deposited electroplated nanofibers is insignificant. Figure 10a shows representative 2D and 3D images of the bare copper surface. The scratches on the bare copper surface result from rubbing the sample with sandpaper. The roughness of the copper-plated nanofibers deposited on the copper surface is higher, cf. Table 1. Three samples were observed under the 3D optical microscope both before and after pool boiling experiments and 15 different spots over each sample were chosen for statistical averaging of the roughness parameters. Plating of copper crystals on nanofibers resulted in an increase in roughness of the nanofiber layer which can be seen in Fig. 10b. After pool boiling on the same sample for several hours the roughness of the nanofiber layer slightly (statistically insignificantly) decreased. It should be emphasized that such decrease in roughness did not cause any change in the heat transfer characteristics of the samples which is clearly evident from the repeatability of the boiling curve in Fig. 2a. Differences in the corresponding values of $R_a$ and $R_q$ in Table 1 signify the unevenness of the underlying bare copper surface and copper-plated nano-textured surface.
The above-mentioned slight decrease in roughness of the copper-plated nanofiber layer can be attributed to the following reasons. First, during the initial degasification process when the copper substrate is heated for 50 min, the nano-textured nanofiber layers get partially sintered [41-43], which causes a decrease in thickness. Second, due to prolong pool boiling experiments the metallic Cu on the nanofibers can be oxidized to form copper (I) oxide. The formation of Cu$_2$O from Cu can facilitate lattice diffusion [44], later favoring annealing of the oxide layer to form large grains and a smoother surface. This is also seen as a reduction of the elevation of Cu plating on the nanofibers (cf. Table 1). Both reasons can cause an overall decrease in the thickness of the metal coating on nanofibers to some extent.
Fig. 10. 3D Optical Microscope image of (a) bare copper surface, and (b) copper-plated nanofiber-coated copper surface. Both 2D and 3D views of the scan are shown in the left-hand side and right-hand side columns, respectively.

4.4. X-Ray Diffraction (XRD) Analysis

Formation of copper oxide on the copper-plated nano-textured surface was investigated using XRD analysis. Electrospun nanofiber mats were deposited on stainless steel foil and were copper-plated using the method described in section 2.2. In this case stainless steel foil was chosen instead of copper plate as a substrate to eliminate background noise. Copper-plated nanofiber mats on stainless steel foil were dried after copper plating either in air, or nitrogen separately. The XRD analysis was conducted on such samples with the results being shown in Fig. 11.
Fig. 11. XRD analysis of copper-plated nanofibers collected on stainless steel foil and dried after copper-plating in (a) air, or (b) nitrogen atmosphere. The presence of peaks corresponding to d-spacing of 2.465 Å and 1.509 Å indicates formation of cuprite (Cu$_2$O), an oxide of copper.

The formation of copper oxide in contact with air is evident from the characteristic peak of cuprite (cf. Fig. 11a) in distinction from the sample dried in nitrogen atmosphere where the cuprite peak is absent (cf. Fig. 11b). However, after a copper-plated nanofiber mat dried in
nitrogen atmosphere was subsequently dipped in boiling water for 30 min and then dried in air, the XRD analysis revealed the presence of cuprite (cf. Fig 12). Boiling in water facilitates oxidation of copper-plated nanofibers.

**Fig. 12.** XRD pattern of copper-plated nanofibers collected on a stainless steel foil, dried in nitrogen atmosphere and subsequently immersed in boiling water for 30 min and then dried in air. The presence of a peak corresponding to a d-spacing of 2.465 Å in panel (a) indicates
formation of cuprite (Cu$_2$O). The XRD pattern of bare stainless steel foil without such a peak is shown for control in panel (b).

5. Conclusion

Pool boiling of Novec FC 7300 fluid, pure water and self-rewetting water-heptanol mixture was conducted on both bare copper surface and copper-plated nanofiber nano-textured surface. The heat flux (the heat removal rate) and the corresponding heat transfer coefficient were found to be higher on the copper-plated nanofiber surface. The pool boiling data for the self-rewetting fluid revealed a higher heat removal rate from the nano-textured surfaces than even the one for pure water. The XRD analysis of the copper-plated nanofiber surfaces before and after pool boiling of water revealed oxidation of copper and formation of copper oxide on the surface. The nature of the plated material (either copper oxide or copper) on nanofiber surface did not affect the characteristics of pool boiling over such surface. The roughness of the copper-plated nanofiber surface slightly (and statistically insignificant) decreases as a result of prolong pool boiling experiments due to both sintering of the nano-textures and formation of the oxide layer over the nano-textures.

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