Proceedings of the International Heat Transfer Conference
IHTC14
August 8-13, 2010, Washington, DC, USA

IHTC14-22936

DROPWISE CONDENSATION LIFE TESTING OF SELF ASSEMBLED MONOLAYERS

Richard W. Bonner III

Advanced Cooling Technologies, Inc.
Lancaster, Pennsylvania, USA

ABSTRACT

The increasing thermal demand of electronics devices has pushed the limits of current two-phase thermal technologies such as heat pipes and vapor chambers. The most obvious area for thermal improvement is centered around the high heat flux generating chips including improved evaporators, thermal interfaces, etc. However, heat fluxes in the sink/condensing regions have also risen as the size of electronics packages has decreased. One way to reduce the thermal resistance associated with condensation is to promote dropwise condensation. In previous work, the condensation performance improvement using self-assembled monolayer coated surfaces (to promote hydrophobicity) has been shown. However, the question of the life of the self-assembled monolayer coatings needs to be addressed before the technology is adopted, as this has plagued other dropwise condensation coatings in the past.

Presented here is a general use of self-assembled monolayer coatings to promote dropwise condensation in electronics device applications, including a summary of recent work regarding dropwise condensation on gradient surfaces. Also presented is experimental data from a life test of self-assembled monolayers on copper and gold plated surfaces. In the life test, the surfaces have been continuously exposed to saturated steam at 60°C. Both surfaces have continued to promote dropwise condensation for over 9 months under conditions representative of heat pipe electronics cooling applications.

BACKGROUND

As the electronics industry continues to push processor performance, the amount of power utilized by these devices grows. System integrators face challenges in thermal management as consumers continue to demand smaller, more portable, and more rugged devices. For these devices to maintain a nominal operating temperature, the thermal management techniques involved must continue to become more efficient and compact. An important process in the current thermal management architecture involves spreading the heat generated from these small electronics devices over a larger area so the heat can be dissipated to the ambient through traditional air cooled heat sinks. The use of two-phase heat transfer devices such as heat pipes and thermosyphons to help spread heat has become common [1,2]. As the overall device package shrinks the area for the heat sink also decreases, causing larger thermal gradients and heat fluxes through the condensing sections of the two-phase heat transfer devices. A need arises for technologies resulting in a decrease in condenser thermal resistance without additional power consumption or moving parts.

For over 6 decades dropwise condensation has been studied for its ability to produce heat transfer coefficients an order of magnitude higher than filmwise condensation [3]. The mechanism of dropwise condensation is still debatable and much discrepancy exists in the literature on this topic [4]. However, the ability of dropwise condensation to increase heat transfer coefficients over filmwise condensation is well established [5]. Research into dropwise condensation is inspired by economic incentives attainable if the heat transfer coefficients of dropwise condensation can be sustainable [6]. However, only recently have researchers been able to create surfaces which can maintain their properties and sustain the dropwise condensation mode over time [7]. Until recently, dropwise condensation has relied almost solely on gravitational forces to remove liquid droplets from the condensing surface causing the performance to be very sensitive to orientation with respect to gravity [8].

Performances in both filmwise and dropwise condensation are further degraded by the absence of gravity. In the absence of gravity only drag forces are able to remove condensing droplets from a surface for recirculation. In a filmwise mode, capillary wicks can also remove fluid from a condensing surface [9]. Dropwise condensation is not possible in the condensing regions of capillary driven heat pipes because the fluid must be able to wet the heat pipe wick surface. Implementing dropwise condensation in orientation insensitive heat pipes is not straight forward as dropwise condensation only occurs on non-wetting surfaces. Recent advances have been made regarding dropwise condensation on surfaces with graded wettability. This new technology has both the ability to minimize condenser thermal resistance and passively remove liquid from a surface [8,10-12]. Using a gradient surface the liquid can be moved to wicked regions in a heat pipe device. However, this new advancement can only be realized in commercial applications if the surfaces can exhibit their dropwise condensation properties over long periods of time.

In the last decade there have been a few studies regarding dropwise condensation of surfaces prepared using self-assembled monolayers. Das et al. performed testing on a number of tubing surfaces suitable for industrial heat exchanger applications. Their data showed a 4-5 times enhancement over filmwise condensation for the SAM coated tubes of various orientations [13,14]. Vemuri et al. conducted dropwise condensation experiments using horizontal copper tubes prepared with stearic acid and n-octadecyl mercaptan. The n-octadecyl mercaptan promoted surfaces lasted for over 2600 hours, although a significant degradation in performance and contact angle was observed over time [15]. The longevity of the surface was attributed to the strong covalent bonding between the well oxidized copper surface and sulfur reactive group of n-octadecyl mercaptan. Chen et al. also investigated the effect of copper oxides prior to SAM formation [16]. Their measured dropwise condensation data compared favorably Vemuri et al. although no life testing was reported.

INTRODUCTION

Self-assembled monolayers are ideal for promoting dropwise condensation because of their ability to create low energy surfaces (non-wetting) while adding negligible thermal resistance as compared to thicker polymer based coatings, such as Teflon. The negligible thermal resistance is a result of the coating being one molecule (<2nm) thick. Using the SAM technique involves chemically reacting a molecule with a short polymer chain to a surface as demonstrated in Figure 1. The chemical used in these types of surface preparations are typically polymer chains with a backbone that ranges from approximately 8 to 20 carbon atoms long [8,10]. On one side of the polymer chain is a reactive functional group, capable of forming a chemical bond with a surface. In this study the copper and gold surfaces were prepared using a thiol (or sulfur) reactive group.

The other end of the polymer chain is a surface group with low surface energy, such as a methyl -CH_3 or fluoryl -CF_3 group. Surfaces with low energy are considered hydrophobic or non-wetting. SAMs form a one layer thick coating very readily because of the self-extinguishing nature of the reaction. Since the thiol (reactive) end group only reacts with the copper surface, and not the hydrophobic end group, the process cannot continue after one layer is created. The result of the SAM process is a surface which is chemically altered possessing only the surface properties of the hydrophobic functional end group of the molecule.

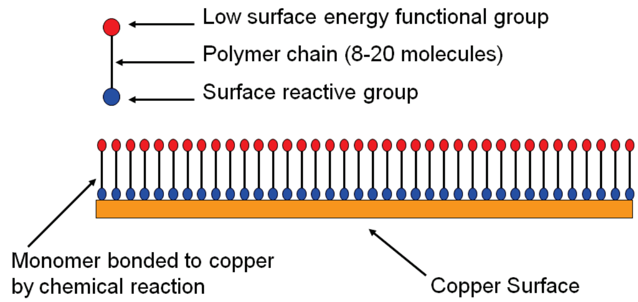

Fig. 1 Illustration of non-wetting surface preparation using self-assembled monolayer technique. While one end of the molecule chemically reacts with the surface, the hydrophobic (non-wetting) side of the molecule points away from the surface creating a surface that is entirely non-wetting.

Self-assembled monolayers can also be used to surface engineer more advanced surface structures with unique properties. One of the unique surface structures more useful to dropwise condensation are surfaces that possess graded hydrophobicity (or wettability). Surface energy gradients (or wettability gradient) have the ability to move droplets placed on the hydrophobic side of the gradient to the hydrophilic side. In fact, droplets placed on the surfaces can even move "uphill" against gravity. When condensing on a gradient surface, condensing droplets can move away from the condensing surface without gravity [8].

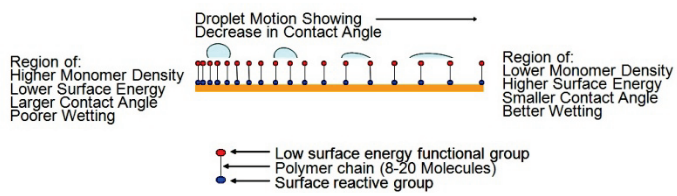

Fig. 2 The motion of droplets from the hydrophobic to hydrophilic side of a surface gradient is depicted. The creation of a surface energy gradient by varying areal concentration of molecules with low surface energy is also depicted.

Figure 2 shows a physical description of how droplet motion is generated on a surface with graded hydrophobicity. Since the surface is steadily decreasing from hydrophobic to hydrophilic, a droplet placed on the graded energy surface experiences two differing contact angles with the higher contact angle located on the more hydrophobic side of the droplet. The difference in contact angle across the droplet creates a driving force to push the droplet in the direction of increased wettability. It should also be noted that in order for a droplet to move on the gradient surface the advancing contact angle on the front side (more hydrophilic side) of the droplet must be less than the receding contact angle on the back side. Otherwise, the droplet will remained pinned on the surface. In other words, the gradient surface must have a low hysteresis (difference between advancing and receding contact angles) at all positions along the gradient for droplet motion to occur.

Previous research has shown that droplets condensing on a gradient surface can attain very high speeds. The fast movement of condensing droplets on a sub-cooled surface exposed to saturated steam was demonstrated by Lehigh University researchers using a chemically produced surface gradient [8]. The movement of these droplets was demonstrated on a 5 cm diameter copper disk with a radial gradient surface oriented horizontally. Droplets condensing on the surface moved from the center of the disk to the outer edges by the surface gradient. Due to the coalescence of droplets and constant addition of fluid to the surface by condensation, the droplets accelerate to very high speeds. Droplet speeds of over 30 cm/s were measured on the horizontal surface. The fast motion of the droplets on the surface causes an increase in the condensation heat transfer coefficient as compared to falling droplets. The motion of the droplets is much less sensitive to gravity as the driving force is inherent in the energy of the surface. Due to the gravity independence, the heat transfer coefficient values are higher in comparison to traditional dropwise condensation surfaces oriented horizontally.

More recently, work was conducted with one-dimensional surface gradients[12]. By condensing on the gradient surface, a 35% improvement in heat transfer coefficient was observed as compared to a traditional dropwise condensation surface in the vertical orientation. The improvement in the vertical orientation was not expected to be excessive, since gravity alone is able to pull condensing droplet on a vertical surface rather quickly. The result does show evidence that a surface gradient adds some additional force to move the droplet in addition to gravity, resulting in increased performance. Horizontally and against gravity, the gradient performed much better than the "traditional" non-wetting surface as the non-wetting and wetting surfaces flood without gravity to remove condensing liquid. The flooding resulted in heat transfer coefficients approaching 500W/m^2-K for the non-wetting and filmwise surfaces. Heat transfer coefficients on a horizontal surface of 3.5W/cm^2-K were measure with a gradient surface. Against gravity (at an inclination of 5°), heat transfer coefficients of 2.0W/cm^2-K were measured with a gradient surface. Although these values were lower than values obtained for the vertically orientated dropwise condensation surface (~10W/cm^2-K), they were still higher than vertically oriented filmwise condensation surfaces (~1.0W/cm^2-K).

EXPERIMENTAL SETUP

A thermosyphoning two-phase test loop was fabricated to measure the condensation heat transfer coefficients attained from the condensation of saturated steam. A test loop schematic is shown in Figure 3. The loop consisted of a boiling chamber, condensation test section, transport lines and a valve for filling, venting and vacuuming. The boiling chamber evaporated liquid returning from the condensation test section. Vapor travels up the transport line above the liquid puddle in the condenser. Liquid from the condensing section first puddles in the bottom of the test section before travelling down the transport lines to the boiling chamber. A close up of the condensation test section is shown in Figure 4. The device shown in Figure 3 was used for performance testing and the life testing.

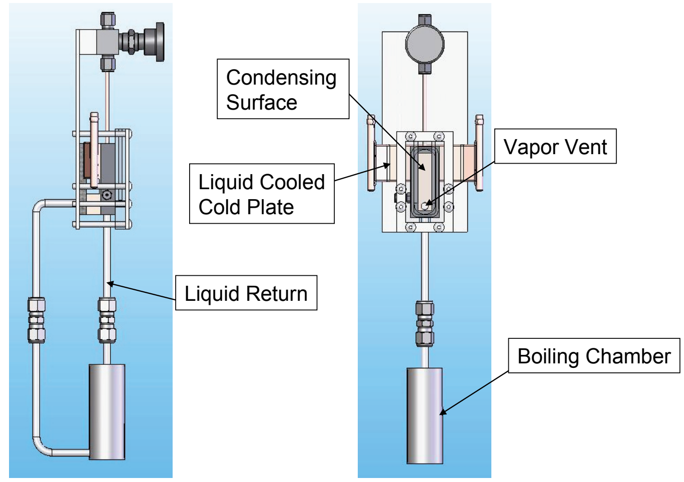

Fig. 3 A solids model of the thermosyphoning test system is shown.

The heat flux and heat transfer coefficients along the condenser were measured using a series of thermocouples as shown in the side view photograph of the test article in Figure 5. The sets of thermocouples allow for calculation of the heat flux by conduction calorimetry. Conduction calorimetry was performed by using Fourier's Law to calculate the heat flux at each location. By using the three thermocouple measurements at each location, the distance between the thermocouples and the known thermal conductivity of copper, the local heat flux was calculated using Equation 1. The temperature gradient, $\frac{dT}{dx}$, was found by plotting the thermocouple measurements versus position and using the slope of the linear regression curve fit through the data. The surface temperature used in Equation 2, was the y-intercept of the curve fit described above. The temperature of the saturated vapor was measured with a thermocouple located in the vapor space of the test section. The local heat transfer coefficient could then be calculated using the locally measured heat flux, surface temperature and saturated fluid temperature. The data acquired at the three positions was then averaged.

$$q'' = k\frac{dT}{dx} \quad \text{Equation 1}$$

$$h = \frac{q''}{T_\infty - T_s} \quad \text{Equation 2}$$

It should be noted that a gap was machined in the copper plate between the connection port and condenser regions to prevent a thermal link between the two regions which would complicate heat transfer coefficient measurements due to conduction effects (Shown in Figure 5).

PERFORMANCE TESTING

All of the condensation performance data was obtained using water as the working fluid. All tests were taken at a saturation temperature of 100°C under vacuum (not in open atmosphere). Data was acquired at four input powers (25W, 50W, 75W and 100W) over the 2.54cm by 1.27cm heat input section (heat fluxes ranged between 7.75 W/cm^2 and 31 W/cm^2). Data was acquired for three surfaces (filmwise, dropwise, and gradients) at four orientations (vertical, angled 45° gravity aided, horizontal and 5° against gravity). A plot of the four orientations tested is shown in Figure 6.

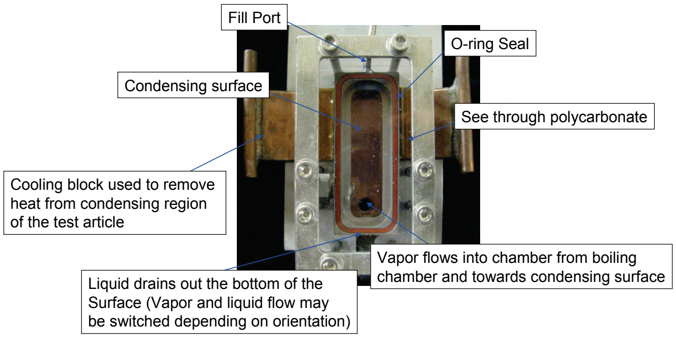

Fig. 4 A close up view of the condensation test section is shown.

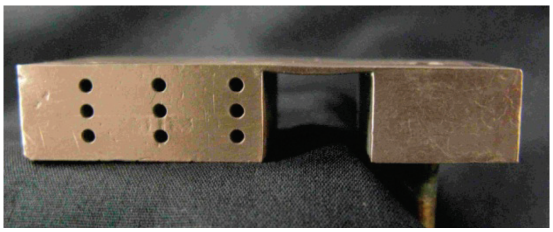

Fig. 5 A side view of the test section is shown. Thermocouples inserted in the 9 holes are used to measure the heat flux and surface temperature of the condensing surface. A gap was also machined to prevent heat from leaking in through the vapor/liquid ports.

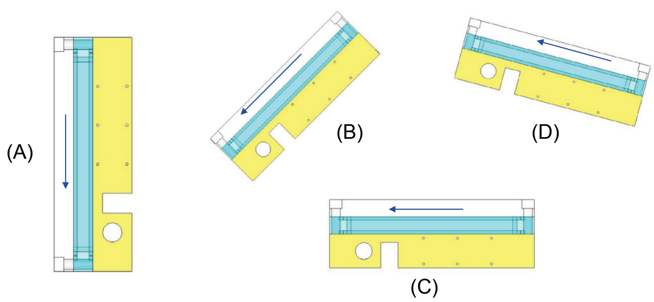

Fig. 6 This figure shows the various orientations to be tested including vertical (A), 45° angle gravity aided (B), horizontal (C) and 5° against gravity (D).

The vertical orientation on a wetted surface (Figure 6a) was tested first. A plot of the experimental results is shown in Figure 7. The most important piece of information in Figure 7 is the agreement of the filmwise test data with the Nusselt filmwise condensation model. The near perfect agreement validates the test section and method of heat transfer coefficient measurement for this study. The model verification also adds credibility to the often hard to accurately acquire dropwise condensation data. Dropwise condensation on the non-wetting surface produced heat transfer coefficients that were 5-8 times higher than filmwise condensation, a significant improvement. By condensing on the gradient surface, a 35% improvement in heat transfer coefficient was observed as compared to the dropwise condensation surface. The improvement in the vertical orientation was not expected to be excessive, since gravity alone is able to pull condensing droplet on a vertical surface rather quickly. The result does show evidence that a surface gradient adds some additional force to move the droplet in addition to gravity, resulting in increased performance.

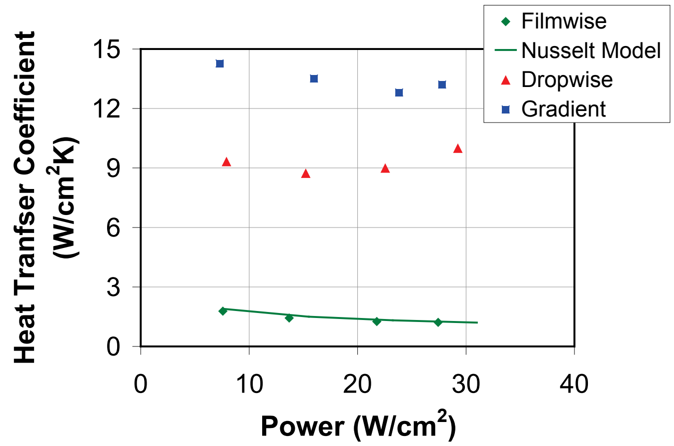

Fig. 7 A plot of experimentally measured heat transfer coefficients for a non-wetting, gradient and wetting surface in the vertical orientation (Figure 6A) are shown. The filmwise data compared well to the Nusselt model, validating the acquired data from the test section.

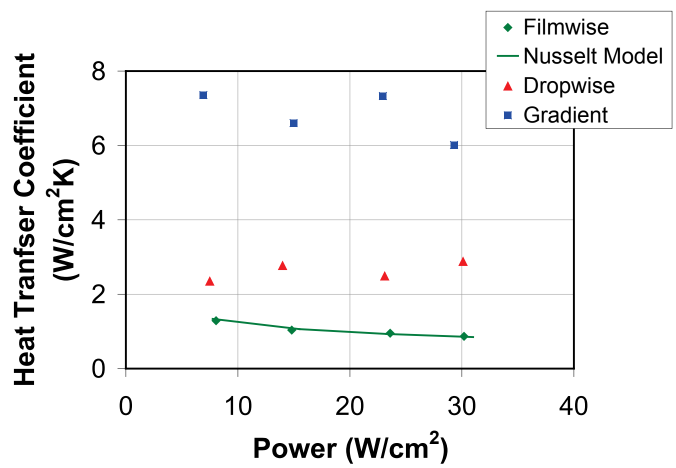

Fig. 8 A plot of experimentally measured heat transfer coefficients for a non-wetting, gradient and wetting surface angled at 45° (Figure 6A) are shown.

The test section was then tilted at a 45° angle (as shown in Figure 6B) and tested. The experimental data for the 45° orientation is shown in Figure 8. Again the filmwise heat transfer coefficient data matched well with the Nusselt model when modified for the partial loss of gravity. All modes of condensation showed reduced performance as compared to the vertical testing. The performance of the non-wetting surface fell about 65%. The gradient surface fell about 50%. However, the performance of the gradient surface was 200% better than the non-wetting surface at 45° as compared 35% in the vertical orientation. It seems that as gravity is reduced, the gradient surface is still able to maintain high droplet velocities required to keep the heat transfer coefficient high. Since the non-wetting surface relies solely on gravity for droplet motion, the reduction in performance is more rapid as gravity is removed.

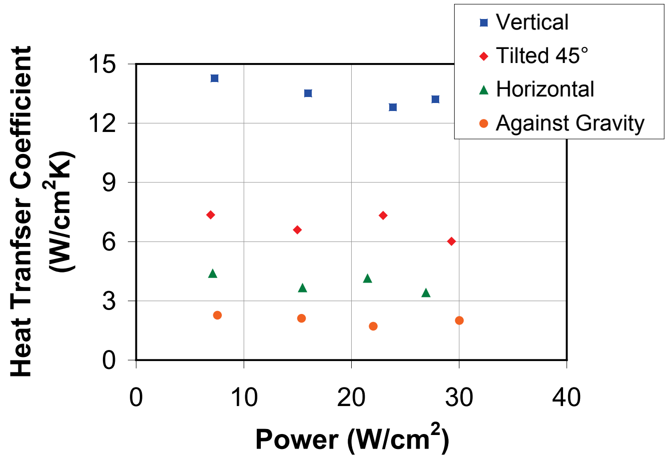

Fig. 9 A plot of all of the gradient surface condensation test data at multiple inclinations is provided.

The next test was performed in the horizontal orientation (Figure 6C). Data was only acquired with the gradient surface, although gathering data with both the uniformly non-wetting and wetting test articles was attempted. Without gravity to return condensing fluid to the boiling section, liquid just flooded the condensing region of both the uniformly non-wetting and wetting test articles. The heat transfer coefficients measured were <<500W/m^2-K at very low heat fluxes (less than 5 watts of power) since not enough driving forces was present to move heat through the poorly performing flooded heat transfer surfaces. The gradient surface was still able to move liquid droplets without the aid of gravity. The result was a heat transfer coefficient in excess of 3.5W/cm^2-K. As a reference this is approximately 3 times greater than the heat transfer coefficients measured on a wetting surface with the full aid of gravity. The data for the horizontal gradient surface test is plotted along with other gradient surface test data at other inclinations in Figure 9.

The final test was performed with the condenser operating against gravity (Figure 6D). The data is plotted in Figure 9. In this orientation the droplets have to be moved uphill in order to reach the end of the condensing section. A wick was inserted at the end of the condensing section to move liquid against gravity from the end of the gradient to the liquid return port. This could be avoided if the gradient ended at the liquid return port. However, the adiabatic gap section machined in the test article prevented the gradient from being close enough to the liquid return port. Inserting a piece of copper screen mesh worked well in transporting fluid from the gradient over the gap to the liquid return port. The measured heat transfer coefficients were much higher than the flooded dropwise and filmwise surfaces. However, there was some degradation in performance as compared to the horizontal testing. In order for the droplet to move uphill, they needed to grow until they spanned larger portions of the gradient to get additional driving force. The larger droplets required to move uphill resulted in more of the surface being coated with fluid, lessening heat transfer coefficients. However, the 2W/cm^2-K condensation heat transfer coefficients still exceed gravity aided filmwise condensation.

LIFE TEST RESULTS

A life test was performed to determine the durability of thiol based SAM on coinage metal (copper and gold plated copper) surfaces. The life test was performed under vacuum at a saturation temperature of 60°C. The saturation temperature was chosen to mimic the vapor temperature of heat pipe systems designed for electronics cooling. The temperature is also associated with operation at the higher end of environmental conditions expected for commercial applications. This life test is not considered to be directly applicable to industrial operations, such as distillation, where a continuous supply of fresh fluid (with fresh contaminants) occurs and operation at higher temperatures is typical.

The copper and gold plated copper surfaces life tested in this study were prepared with a heptadecafluoro-1-decanethiol SAM. The surfaces were first polished until an optical quality (mirror) surface was attained. The surfaces were then ultrasonically cleaned with methanol. The native copper oxides on the surface were removed with nitric acid. The surface was then exposed to an oxidizing solution to create hydroxyl groups on the copper surfaces. The SAM was then created by placing the surface in a dilute solution of IPA and heptadecafluoro-1-decanethiol overnight. The surface was also rinsed with IPA and blown dry with nitrogen after every step of the preparation. Immediately after preparation the contact angle was visually inspected at various locations on the surface to be ~110°.

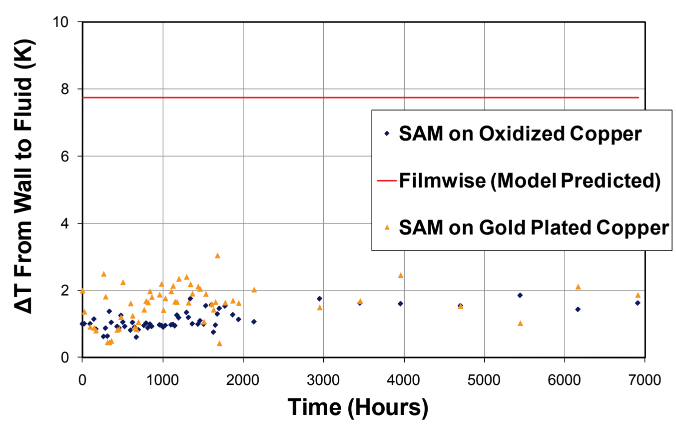

Fig. 10 Life test data for copper and gold surfaces prepared with SAM's is shown.

The same apparatus used in the performance testing was used for the life test. The life test data reported here is a numerical average of the extrapolated surface temperatures. Surface temperature was chosen as the reported variable because significant scatter results since the measured ΔT is very small at the low heat fluxes encountered with life test. The life test results are plotted in Figure 10. Both of the surfaces have been viable for over 9 months and the test is continuing. The longer duration between data after 2000 hours coincides with the funded project end date. Visual inspection of the surface shows both surfaces are still exhibiting full dropwise condensation. It should be noted that the gold surface appears to be producing better droplets than the copper surface (less pinning, smaller sizes), but this is not evident in the heat transfer measurements. The gold plated surfaces are expected to outperform the copper surface, as gold forms stronger bonds to the sulfur reactive group of the SAM.

CONCLUSIONS

Self-assembled monolayers are very promising for promoting dropwise condensation because of their ability to convert metal surfaces (that typically wet) from hydrophillic to hydrophobic. Some researchers have shown dropwise condensation heat transfer coefficients promoted with self-assembled monolayers to be almost 10 times that of filmwise condensation. Life testing of the surfaces has shown promising results, but more work is needed in this area. The use of self-assembled monolayers to surface engineer more exotic surface structures, such as wettability gradient is even more promising. These gradient surfaces could be integrated into passive two-phase heat transfer devices such as heat pipes and vapor chambers to improve heat transfer in non-gravity aided conditions (including zero-g aerospace applications).

A life test was also performed to test the durability of SAM coating under dropwise condensation conditions suitable for electronics cooling. The results demonstrated copper and gold plated copper surfaces that have lasted over 9 months.

ACKNOWLEDGMENTS

This work was funded by the National Science Foundation under a Phase I STTR grant, award number 0740350. The author would like to thank Professor Manoj Chaudhury from Lehigh University (RI on the NSF award), for advisement throughout the work. The author would also like to thank Jesse Campbell for fabrication and testing support throughout the project.

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