

Nucleation Effects in the Dropwise Condensation of Steam on Electroplated Gold Surfaces

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Dropwise condensation heat transfer coefficients were measured for steam on gold surfaces electroplated on copper and nickel substrates. The effect on the heat transfer of the activation of very small nucleation sites present on the gold plated copper surface was observed. In addition, the heat transfer coefficient of the gold plated nickel surface was lower than that of the gold plated copper surface.

SCOPE

The enhancement of shell side condensation heat transfer is becoming increasingly important. Currently, various mechanical means are employed to accomplish this enhancement, but these methods entail certain penalties which include increased cost, susceptibility to liquid flooding, and increased tube diameter. The use of dropwise condensing surfaces could eliminate most of the drawbacks associated with the mechanical enhancement of condensation heat transfer. At this time, however, there is no commercially acceptable dropwise condensing surface, although the motivation for producing such a surface is significant. It is important, therefore, to understand the mechanism of dropwise condensation.

There is general agreement that dropwise condensation is a heterogeneous nucleation process. In the particular case of steam condensation, specific sites on an otherwise hydrophobic surface act as points for the nucleation of liquid drops. Elementary nucleation theory predicts that the heat transfer behavior should depend on certain properties of these nucleation sites. In particular, the degree of subcooling required for a liquid drop to form on a given nucleation site is inversely proportional to the radius of curvature of that site. Thus, for a given vapor temperature, nucleation sites will become active at surface temperatures which depend upon the size of those sites. As a con-

sequence, the surface heat transfer coefficient should vary with surface subcooling until all the nucleation sites are activated. In previous work, surface nucleation sites have been larger than 10^{-4} cm in diameter and, therefore, were fully activated at surface subcooling values of less than 0.1°C . For this reason, the direct effect of nucleation site dimensions on the heat transfer rate has not been observed in previously performed experiments, which were not capable of accurate measurements at such low surface subcooling levels.

The objective of this work is to demonstrate the direct effect of nucleation site dimension on the dropwise condensation heat transfer rate. This has been accomplished by observing the heat transfer behavior of a surface possessing nucleation sites which are sufficiently small so that they require a measurable degree of subcooling for activation. The heat transfer associated with the condensation of steam has been measured on gold surfaces plated on copper and nickel substrates. No organic promoters were required to produce dropwise condensation on these surfaces. The gold plated on copper possessed surface nucleation sites with dimensions of approximately 10^{-6} cm. These nucleation sites were of sufficiently small size that the subcooling required to produce condensation was readily observable.

CONCLUSIONS AND SIGNIFICANCE

This work has experimentally demonstrated the effect of the size of surface nucleation sites on the heat transfer behavior during dropwise condensation. The experiments have verified the prediction of nucleation theory that in order to activate these surface sites, which function as nuclei for the formation of liquid drops, a degree of surface subcooling is required which increases as the size of the nucleation site decreases.

Surface heat transfer coefficients were measured for the condensation of steam at 1 atm pressure on electroplated gold surfaces deposited on copper and nickel substrates. Both gold surfaces were hydrophobic, and they did not require the application of promoters in order to maintain dropwise condensation.

The plating process resulted in the formation of pits and channels on the gold plated copper surface, and these surface features, which possessed dimensions of approximately 10^{-6} cm, acted as nucleation sites for the condensation of steam. The gold plated nickel surface, however, was devoid of these very small nucleation sites.

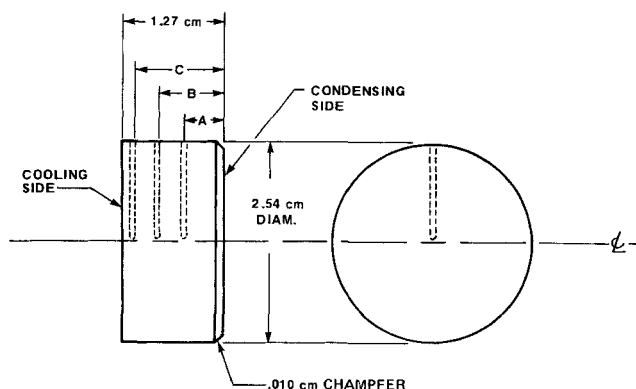
The difference in the microscopic topography of these surfaces resulted in a strikingly different behavior of the condensation heat transfer coefficient for each surface. In the case of the gold plated on copper, the very small nucleation sites which were present on the surface required a subcooling of 12°C in order to become active in nucleating drops. Below this level of subcooling, the heat transfer rate was relatively low, but at a surface subcooling of 12°C , the heat transfer coefficient increased abruptly to give the high values which are characteristic

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of dropwise condensation. The condensation heat transfer coefficient for the gold plated nickel surface, however, varied smoothly with surface subcooling up to the largest value of the surface subcooling which was studied. In addition, the absolute value of the heat transfer coefficient for the gold plated nickel surface was lower than that for the gold plated copper surface.

The observed behavior of the condensation heat transfer on these surfaces as a function of surface subcooling is

consistent with both the existence of very small nucleation sites on the gold plated copper surface and with the higher thermal conductivity of copper compared to that of nickel. The results of these experiments graphically illustrate the role which heterogeneous nucleation plays in dropwise condensation. The requirement of a temperature difference between the vapor and the surface for the activation of drop forming nucleation sites has been established.



| CONDENSATION SAMPLE | DISTANCE A (cm) | DISTANCE B (cm) | DISTANCE C (cm) |
|---------------------|-----------------|-----------------|-----------------|
| GOLD PLATED COPPER | 0.4704 | 0.7925 | 1.0989 |
| GOLD PLATED NICKEL | 0.4788 | 0.8182 | 1.1375 |

Fig. 1. Details of the heat transfer samples showing the positions of the three thermocouples.

Interest in the dropwise condensation of steam has existed for nearly 40 yr., and this interest has been fueled by the large heat transfer coefficients which can be attained by means of this mode of condensation. Experimental studies, particularly those of McCormick and Baer (1963) and of McCormick and Westwater (1965), have established that dropwise condensation is a heterogeneous nucleation phenomenon. McCormick and Baer (1963) demonstrated that drops are nucleated on randomly situated nucleation sites on the condensing surface, and McCormick and Westwater (1965) identified and filmed natural nucleation sites on a surface. They were also able to artificially produce nucleation sites and concluded that nucleation sites with diameters of 2×10^{-4} — 30×10^{-4} cm were effective. It is to be expected that natural nucleation sites of this size range might be found on typical condensing surfaces. However, the degree of subcooling associated with the condensation of a drop of water 2×10^{-4} cm in diameter is approximately 0.08°C . Therefore, on typical dropwise condensing surfaces it will not be possible to observe the effect of the onset of nucleation since it occurs at values of the temperature difference between the vapor and the condensing surface, the surface subcooling ΔT_{sv} , which are much smaller than usually measured. If nucleation sites which are small enough exist on a surface, however, the onset of condensation on these sites and the associated effect on the heat transfer coefficient will be observable within the range of ΔT_{sv} which is observed during experiments. Thus, for nucleation sites of the proper size range, the behavior of the observed

condensation heat transfer coefficient h_c as a function of ΔT_{sv} will be influenced by the size distribution of the nucleation sites.

In the work described below, the heat transfer coefficient for dropwise condensation has been measured on gold surfaces electroplated onto copper and nickel substrates. In the former case, the preponderance of nucleation sites possessed dimensions of less than 10^{-6} cm. When ΔT_{sv} exceeded the level of subcooling necessary to cause condensation to occur at these sites, there was a sudden and dramatic increase in the measured heat transfer coefficient and a decrease in ΔT_{sv} . Below this critical value of ΔT_{sv} , the heat transfer coefficient was only slightly greater than the Nusselt value, but when the critical temperature difference was exceeded, heat fluxes an order of magnitude larger than Nusselt values were achieved. The gold plated nickel sample did not possess nucleation sites with dimensions less than about 10^{-4} cm in diameter, and the heat flux and heat transfer coefficient on that sample varied monotonically with the degree of subcooling.

EXPERIMENTAL PROCEDURE

The samples on which the heat transfer was measured are shown in Figure 1. They consisted of cylinders of copper and nickel 1.27 cm long and 2.54 cm in diameter. A gold coating approximately 2.5×10^{-5} cm thick was commercially electroplated on the front face of these cylinders. Both cylinders were prepared for plating in as similar a manner as possible. The surfaces were polished with increasingly fine grit and then buffed to a mirror finish. They were then degreased with organic solvents and washed with distilled water. The gold plating was performed by a commercial electroplater using a cyanide plating bath free of organic plating aids. The surfaces were acid dipped immediately prior to plating. The nominal purity of the deposited gold was greater than 99.9%. The gold surfaces were used in heat transfer measurements following a thorough solvent degreasing and distilled water rinse. No other treatment was performed on the surfaces prior to the heat transfer measurements.

Before the surfaces were electroplated, three thermocouple holes of diameter 0.03 cm were drilled along radii to the axes of the samples at three positions along their length. The axial positions of the bottoms of these holes were determined to an accuracy of $\pm 3 \times 10^{-3}$ cm. A traveling microscope was used to locate the positions of the tops of the thermocouple holes. Straight lengths of 0.03 cm. diameter drill rod were then placed in each hole, and the angles which the holes made with the axes of the samples were measured by using an optical comparator. The positions of the bottoms of the holes were then calculated from the measured depths and inclinations of the holes and the locations of the tops of the holes. Stainless steel sheathed chromel-alumel thermocouples of overall

outside diameter 0.025 cm were placed in each hole. Thermal contact was achieved with zinc oxide filled thermal grease, and the thermocouples were held in place mechanically with Duco cement.

The samples were then placed in a Teflon sample holder with an O ring seal about the circumference of the sample, between it and the Teflon holder. This subassembly was mounted on the experimental vessel shown in Figure 2 which was constructed of Pyrex with Teflon seals. The entire apparatus was constructed to be helium leak tight in order to prevent the leakage of air into the experimental vessel during a run. Steam was generated by means of Pyrex immersion heaters which were sealed into the bottom of the glass vessel. In addition, a removable Pyrex sampling bulb was provided to facilitate the measurement of the level of noncondensables before and after each run.

Before each run the distilled water in the apparatus was thoroughly degassed. The water was brought to 100°C and boiled. It was then pumped on by means of a mechanical pump connected to the system through a liquid nitrogen filled trap and a large ballast chamber. The degassing procedure was repeated until the noncondensables were reduced to an acceptable level as measured by the following procedure.

The Pyrex sample bulb shown in Figure 2 was heated to a temperature slightly above 100°C and evacuated to a pressure of 2.5 to 4.0 N/m², as read on a thermocouple type of vacuum gauge. The Teflon valve on the sample bulb was then opened, admitting a sample of 100°C steam into the bulb. After valving off the bulb, it was removed from the condensing apparatus and attached to a vacuum line equipped with a thermocouple type of pressure gauge. The sample bulb was partially immersed in a dry ice-acetone bath in order to freeze out the water vapor and reduce its vapor pressure to approximately 53 mN/m². The residual pressure was determined by opening the Teflon valve on the sample bulb to the vacuum line which had previously been evacuated to a pressure of approximately 2.5 N/m² and then sealed off from the pump. The pressure rise, which was sensed by the thermocouple gauge when the sample bottle was opened to the vacuum line, gave the partial pressure of noncondensable gases in the steam after corrections for volume expansion and the ratio of the temperature at which the sample was taken to that at which the pressure rise was measured.

During a run the entire system was sealed off to prevent leakage of noncondensables into the system. The steam temperature and pressure were measured by a thermocouple in the vapor and a bonded strain gauge pressure transducer, respectively, and they were controlled at constant values. The heat flux \dot{q} and consequently the surface-vapor temperature difference ΔT_{sv} were varied by altering the flow rate and temperature of the cooling water to the rear surface of the sample. Depending upon the desired flow rate, the cooling water was either taken directly from the tap or else recirculated by means of a constant temperature recirculating bath. The level of noncondensables in the system was measured again after each run.

At each experimental point, the system was allowed to come to equilibrium, and the outputs from each of the three thermocouples on the sample were recorded. Two of the thermocouples were connected differentially with respect to the third, the output of which was referred to an electronic cold junction compensator which had been calibrated at 0°C. Prior to the experiments, all three thermocouples in the sample as well as the steam temperature thermocouple had been calibrated against a mercury bulb thermometer of 0.1°C accuracy at the freezing and boiling points of water and at the boiling points of

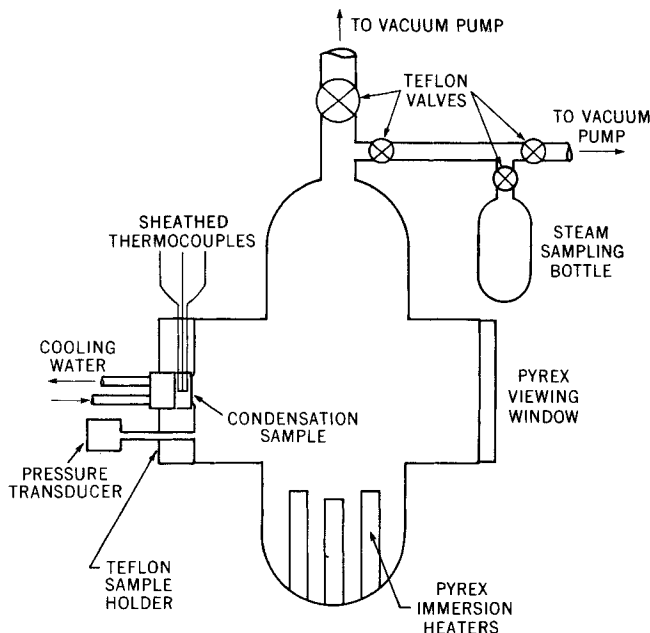


Fig. 2. Schematic drawing of the cell which was used for measuring surface heat transfer characteristics.

methanol and isopropanol.

The heat flux \dot{q} and surface temperature T_s were obtained from the experimental data by using a least-squares procedure to fit a straight line to the temperature as a function of position along the axis of the sample:

$$\begin{aligned} T &= T_s + bx \\ b &= \frac{dT}{dx} \\ \dot{q} &= kb \end{aligned} \quad (1)$$

In the expressions above, T_s and b are the least-squares values of the surface temperature and the temperature gradient in the sample, and k is the thermal conductivity of the sample material. The heat transfer coefficient was evaluated from the relationship

$$h_c = \frac{k}{T_v - T_s} \frac{dT}{dx} \quad (2)$$

in which T_v is the measured vapor temperature.

RESULTS

Although the work of Erb and Thelen (1965) and that of Wilkens and Bromley (1973) indicate disagreement over the true nature of the condensation phenomenon on a pure gold surface, the particular gold plated surfaces upon which these heat transfer measurements were made remained dropwise throughout the course of the experiments. The steam temperatures and noncondensable levels for each experiment are given in Table 1. All experiments were run under conditions of low noncondensable levels in the steam. The maximum level of noncondensables at the start of an experimental run was 30 p.p.m. mole fraction, and the maximum level at the end of an experimental run was 133 p.p.m. mole fraction. More typically, the noncondensable level was in the range 10 to 20 p.p.m. mole fraction.

The temperature distribution measured in the sample by the thermocouples along its axis was linear. The maximum

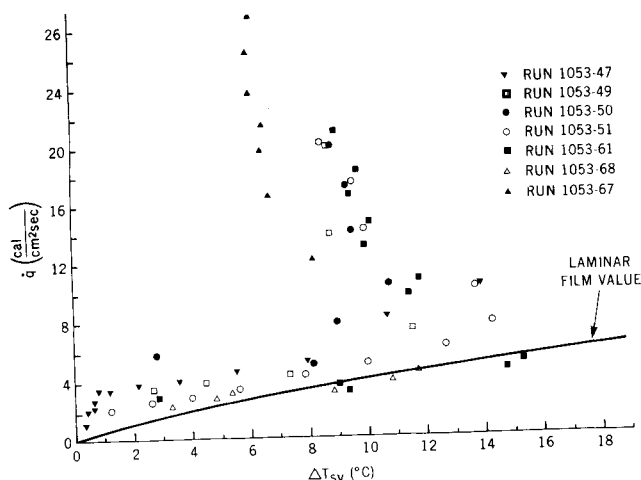


Fig. 3. Measured heat flux on the gold surface plated on a copper substrate as a function of the surface subcooling.

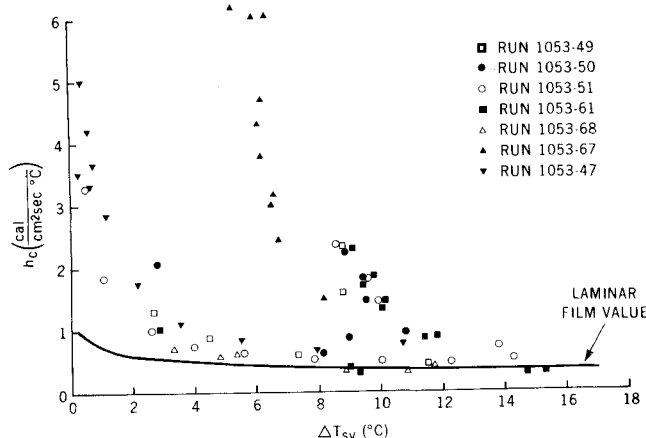


Fig. 4. Measured values of the condensation heat transfer coefficient on the gold surface plated on a copper substrate as a function of the surface subcooling.

deviation of a thermocouple temperature from the least-squares fit straight line through the three temperature points was 0.05°C.

The heat transfer behavior on the copper substrate sample exhibited a unique type of behavior with respect to varying ΔT_{sv} . As Figure 3 indicates, the heat flux at first increased gradually with ΔT_{sv} . At a surface temperature-steam temperature difference of approximately 12°C, the heat flux rose sharply from 6 cal/cm² · s to 30 cal/cm² · s, and the extrapolated surface temperature increased by approximately 5°C, giving rise to lower values of ΔT_{sv} . This behavior was traced out with both increasing and decreasing coolant temperatures at several constant coolant flow rates and with increasing and decreasing coolant flow rates at several constant coolant temperatures. The cooling water flow rates varied from 21 to 120 gal/hr. and the cooling water temperature from 20° to 94°C. In all cases, the flow in the cooling chamber was fully turbulent, and the temperature rise of the cooling water was less than 2°C.

Figure 4 depicts the heat transfer coefficients associated with the heat flux behavior described above. On the lower branch of this curve, the heat transfer coefficients exceed the values of the laminar film condensation coefficient calculated from the relationship of Nusselt (1916) at the lower subcooling levels but approach the Nusselt values

TABLE 1. STEAM TEMPERATURES AND NONCONDENSABLE LEVELS

| Experiment number | Substrate | Steam temperature (°C) | Noncondensables (p.p.m. mole fraction) | |
|-------------------|-----------|------------------------|--|----------|
| | | | pre run | post run |
| 1 053-27 | Ni | 100.1 | 26 | 66 |
| 1 053-28 | Ni | 100.2 | 14 | 133 |
| 1 053-32 | Ni | 100.2 | 25 | —* |
| 1 053-34 | Ni | 100.4 | 21 | 28 |
| 1 053-47 | Cu | 101.4 | 30 | 23 |
| 1 053-49 | Cu | 100.4 | 12 | 18 |
| 1 053-50 | Cu | 100.6 | 18 | 23 |
| 1 053-51 | Cu | 100.4 | 9 | 39 |
| 1 053-61 | Cu | 100.4 | 16 | 23 |
| 1 053-67 | Cu | 100.4 | 12 | 7 |
| 1 053-68 | Cu | 100.3 | 7 | 28 |

* Not measured.

as ΔT_{sv} increases to about 12°C, at which point h_c begins to rise sharply. The heat transfer coefficient increases from 0.4 cal/cm² · s · °C to more than 6 cal/cm² · s · °C at surface subcooling levels in the neighborhood of 12°C. On the upper branch of this curve, values of h_c an order of magnitude greater than the laminar film values are achieved. Furthermore, both the heat transfer coefficient and the heat flux were rising sharply with increasing cooling rate, and the maximum values which are reported were limited by the ability to extract heat from the rear of the sample.

Figure 5 shows an electron micrograph of a carbon replica of a portion of the condensing surface. The micrograph indicates that the surface is rich in grooves and channels with widths typically 10⁻⁶ cm. It will be shown

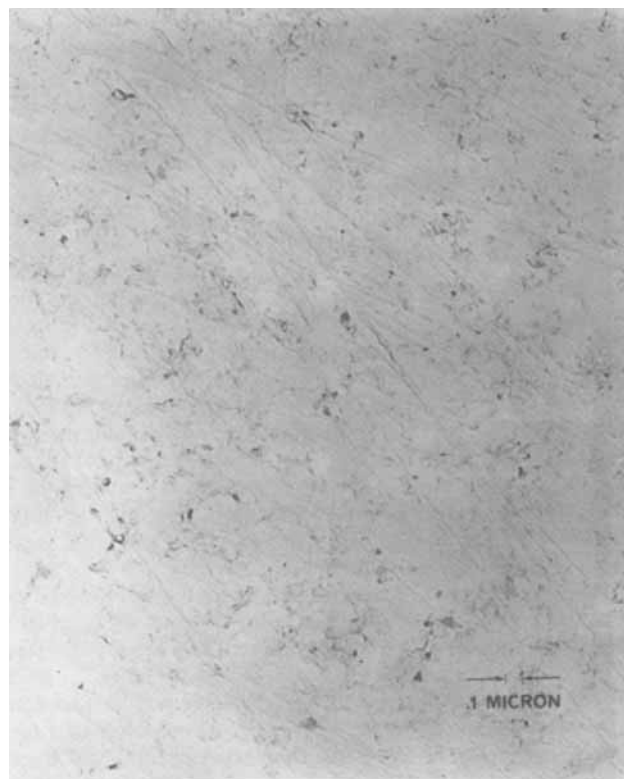


Fig. 5. Electron micrograph of a carbon replica of a portion of the condensation surface manufactured by plating gold onto a copper substrate.

below that the observed condensation heat transfer behavior is consistent with the nucleation behavior to be expected on a surface possessing this kind of structure.

The microscopic topography of the gold plated nickel sample surface was very different from that of the gold plated copper surface. The gold plated onto nickel was devoid of the very small surface features which characterized the gold-copper sample. The only surface features observable were scratches greater than 10^{-4} cm in width. Since both samples were given identical preplating treatment, the different surface topography is most likely due to a preferential etching of the copper sample during the plating process or during the acid dip which directly preceded the plating.

This difference in surface structure is reflected in the heat transfer data for the gold plated nickel surface which is shown in Figures 6 and 7. The heat flux is characterized by a single branch along which the heat flux increases monotonically with ΔT_{sv} . Furthermore, the heat flux is less than that on the lower branch of the curve for the gold plated copper sample, and this difference varies from approximately 25% at ΔT_{sv} equal to 10°C to approximately a factor of 2 at ΔT_{sv} equal to 1°C . The heat flux significantly exceeds that calculated for laminar film condensation only for temperature differences less than about 3°C .

DISCUSSION

Error Analysis

The primary source of error in the analysis of the data from these experiments lies in the determination of the surface temperature T_s and the temperature gradient in the sample b by fitting a straight line to the measured temperature distribution in the sample. This procedure gives rise to uncertainties in both T_s and b which are due ultimately to uncertainties in the thermocouple temperatures and the thermocouple positions. These temperature and position measurements are characterized by standard deviations σ_T and σ_x , respectively. If it is assumed that the uncertainties in the temperature and position measurements represent uncorrelated sources of error, then the following expressions for the standard deviations in T_s and b , respectively, are obtained by the standard techniques used to estimate the uncertainties of the coefficients in a linear least-squares fit (Bevington, 1969):

$$\sigma^2(T_s) \cong \frac{\sum x_i^2}{\Delta(x)} \sigma_T^2 + \frac{b^2 (\sum T_i^2 + N T_s^2)}{\Delta(T)} \sigma_x^2 \quad (3)$$

$$\sigma^2(b) \cong \frac{N}{\Delta(x)} \sigma_T^2 + \frac{b^4}{\Delta(T)} \sigma_x^2 \quad (4)$$

$$\Delta(x) \cong N \sum x_i^2 - (\sum x_i)^2$$

$$\Delta(T) \cong N \sum T_i^2 - (\sum T_i)^2$$

In the expressions above, i varies from 1 to N , and in these experiments N equals 3.

The standard deviations in the thermocouple temperatures and positions are approximately 0.1°C and 0.003 cm, respectively. Using these values in Equations (3) and (4), we find that $\sigma(T_s)$ and $\sigma(b)$ vary from 0.96°C and $0.22^\circ\text{C}/\text{cm}$ to 0.84°C and $0.23^\circ\text{C}/\text{cm}$ over the range of experiments performed on the gold plated copper sample. In the case of the gold plated nickel sample, $\sigma(T_s)$ and $\sigma(b)$ vary from 0.90°C and $0.22^\circ\text{C}/\text{cm}$ to 0.70°C and $0.25^\circ\text{C}/\text{cm}$ over the experimental range. The main contribution to the uncertainties in both the surface temperature and the temperature gradient arises from the uncertainty in the positions of the thermocouples.

While the heat transfer data obtained at values of ΔT_{sv} less than 2°C are subject to considerable uncertainty, the

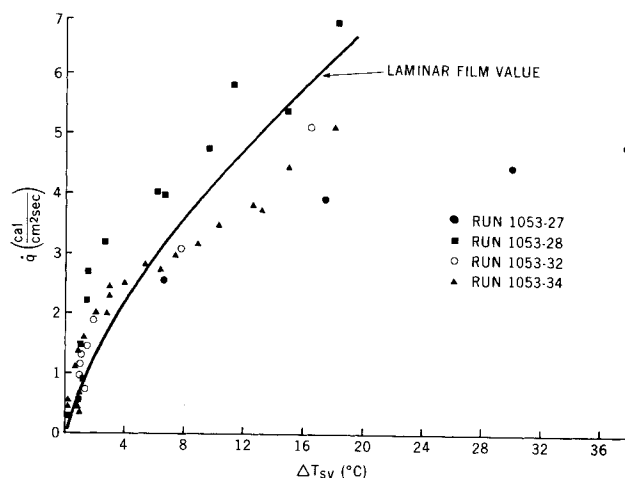


Fig. 6. Measured heat flux on the gold surface plated on a nickel substrate as a function of surface subcooling.

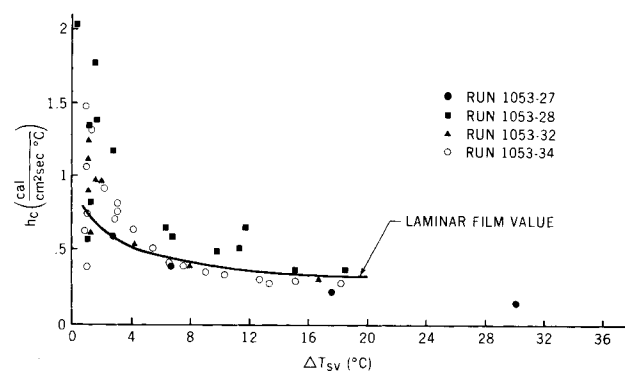


Fig. 7. Measured values of the condensation heat transfer coefficient on the gold surface plated on a nickel substrate as a function of surface subcooling.

fractional uncertainty diminishes with increasing surface subcooling and is negligible under the conditions for which the sharp rise in heat transfer was observed on the gold plated copper sample.

Effects of Noncondensable Gases

LeFevre and Rose (1965) and Tanner et al. (1964) have demonstrated that the presence of a significant quantity of noncondensable gases in the steam during dropwise condensation imposes a substantial mass transfer impedance in front of the condensing surface and therefore decreases the measured heat transfer coefficient. While the primary purpose of this paper is the illustration of the fundamental role which nucleation sites play in dropwise condensation rather than the accurate determination of specific heat transfer coefficients, noncondensable levels were nonetheless kept below a point at which they would substantially interfere with the heat transfer.

There are two convincing pieces of evidence to indicate that the noncondensable levels shown in Table 1 are not sufficient to significantly influence the heat transfer measurements. LeFevre and Rose (1965) and Tanner, et al. (1964) have shown that the presence of noncondensable gases in amounts great enough to interfere with the heat transfer gives rise to large fluctuations in the surface temperature. The fact that no such fluctuations were observed in this work is evidence that noncondensables were not present in significant amounts in these experiments. Furthermore, Tanner et al. (1964) have measured the decrease in the dropwise condensation heat transfer coefficient as a function of added noncondensables. Their data indicate that even at very low steam velocities, the reduc-

tion in the heat transfer coefficient at a heat flux of $13 \text{ cal/cm}^2 \cdot \text{s}$ would be no more than 20% at a noncondensable level of 20 p.p.m., which is typical of these experiments.

Thus, while variations in the noncondensable level from run to run may account for a portion of the scatter in the experimental data, the coefficients measured are close to the true dropwise condensation heat transfer coefficients. More importantly, the presence of noncondensables cannot account for the most salient feature of the data, which is the sharp increase in heat transfer that occurred on the gold plated copper sample at a surface subcooling of approximately 12°C and which was reproduced in seven independent runs with that sample.

Surface Nucleation Effects

The condensation heat transfer behavior which has been described above for the gold plated surface on a copper substrate is a graphic illustration of the nucleation phenomenon which occurs during dropwise condensation. The observed behavior arises from the nature of the nucleation sites on the surface, and the heat transfer results are consistent with an electron microscope study of the surface geometry.

In the general case of nucleation condensation, the degree of subcooling necessary to form a liquid drop of radius r from the saturated vapor is given by a combination of the Clausius-Clapeyron relationship and the Kelvin equation:

$$\frac{dP}{dT} = \frac{\Delta H}{RT^2} P \quad (5)$$

$$\ln \frac{P}{P_e} = \frac{2 v \gamma}{r RT} \quad (6)$$

The required degree of subcooling for a drop of radius r is, therefore

$$\Delta T_r = T_v - T \approx \frac{2 v \gamma}{r \Delta H} T_v \quad (7)$$

Using macroscopic values of the variables in Equation (7) for water at 100°C , we get

$$\Delta T_r \approx \frac{20.2}{r} \times 10^{-7}$$

in which r is the drop radius in centimeters and ΔT_r the required subcooling in degrees Centigrade. Generally, active nucleation sites and drops in dropwise condensation possess radii which lie in the neighborhood of $1 \times 10^{-4} \text{ cm}$, and the required degree of subcooling is, therefore, approximately 0.02°C .

Carbon replication and electron microscopy of this particular gold plated surface, however, revealed that it was covered by pits and channels with typical widths of 10^{-6} cm . This surface morphology is shown in Figure 5, which is an electron micrograph of a carbon replica of the surface. The required degree of subcooling necessary to initiate condensation on these surface features depends upon their detailed shape and the contact angle between the growing liquid phase and the solid. If Equation (7) and the macroscopic values of the parameters which it contains are applicable at liquid drop dimensions of less than 10^{-6} cm , then a radius of curvature of $0.17 \times 10^{-6} \text{ cm}$ is associated with a subcooling of 12°C , the value of ΔT_{sv} at which the sharp upturn in h_c and \dot{q} was observed. It is reasonable to expect radii of curvature of this magnitude to exist at the base of pits in the surface which have a lateral dimension of approximately $1 \times 10^{-6} \text{ cm}$ at their tops, such as occur on the gold plated copper sample.

This discussion indicates that the behavior of the condensation phenomenon observed in the experiments carried out on this surface is consistent with the general view of dropwise condensation as a nucleation phenomenon. With increasing ΔT_{sv} , the heat flux rises from zero at $\Delta T_{sv} = 0$, sharply at first and then much more gradually. This initial sharp rise, which terminates at a surface subcooling of approximately 0.8°C , represents the activation of nucleation sites ranging in diameter down to approximately 10^{-5} cm . At a surface subcooling of approximately 12°C , the very small nucleation sites which lie at the base of the surface pits and channels and which have nominal diameters of $0.34 \times 10^{-6} \text{ cm}$ are activated and rapidly fill with liquid. As the pits and channels fill with liquid, the radius of curvature of the liquid-vapor meniscus increases in a manner determined by the local contact angle and the particular geometry of the pit or channel. As the radius of curvature of the liquid meniscus increases, the liquid is able to initiate and maintain condensation at lower subcooling values. In fact, the curvature could become negative, in which case the site would act as a spontaneous condensation point requiring no subcooling. As more and more of these sites become active and require lower levels of subcooling, the effective thermal resistance between the surface and the steam will decrease, and this is reflected in the steep negative slope of the upper branches of the heat flux and heat transfer coefficient curves in Figures 3 and 4. We postulate that these surface sites remain filled with liquid between each successive drop departure cycle and therefore remain as activated nucleation sites requiring a subcooling corresponding only to the liquid radius in the filled channel or pit.

Comparison of the Heat Transfer on the Gold Plated Copper and Nickel Samples

In comparing the observed condensation heat transfer behavior of the gold plated nickel sample to that of the gold plated copper sample, two factors which differ for each sample must be considered. These are the nature of the geometry of the nucleation sites on the surface and the thermal properties of the substrate. The absence of observed structure in both the heat flux and heat transfer coefficient as a function of subcooling in the case of the nickel substrate sample as compared to that which was observed in the case of the copper substrate sample can most likely be attributed to a lack of sufficiently small nucleation sites on the surface of the former sample. The lower values of the heat transfer coefficient which were measured on the nickel substrate sample most likely arose from the greater nonuniformities in surface temperature associated with the lower thermal conductivity of nickel. The heat transfer coefficients which were measured in the case of the nickel backed gold surface were significantly lower than both those measured on the copper backed surface and also those reported in the literature for organically promoted copper surfaces. Tanner et al. (1964) and Westwater (1969) have reported values of the dropwise condensation heat transfer coefficient on copper substrates which range between 2 and $5 \text{ cal/cm}^2 \cdot \text{s} \cdot ^\circ\text{C}$ as compared to the maximum value of $1.5 \text{ cal/cm}^2 \cdot \text{s} \cdot ^\circ\text{C}$ measured in this work for a 1°C surface subcooling of the nickel substrate sample.

While it is possible that the relatively low values of the heat transfer coefficient on the nickel backed gold surface may be due to the nature and population of nucleation sites on that surface, the preponderance of existing experimental evidence indicates that a more likely cause is the lower thermal conductivity of nickel compared to that of copper ($0.14 \text{ cal/cm} \cdot \text{s} \cdot ^\circ\text{C}$ for nickel compared to $0.92 \text{ cal/cm} \cdot \text{s} \cdot ^\circ\text{C}$ for copper at 20°C). Thus, Tanner, et al.

(1964), Griffith and Lee (1967), and Wilkins and Bromley (1973) have reported significantly lower values of h_c on surfaces deposited on relatively low thermal conductivity metal substrates as compared to values of h_c which have been measured on copper substrates. Tanner et al. (1964) reported a heat transfer coefficient for an organically promoted stainless steel sample which was approximately one-fifth the value of the coefficient measured on a copper surface which was supposed to be identically promoted. A similar trend was reported by Griffith and Lee (1967) for gold plated copper, zinc, and stainless steel substrates which were promoted with oleic acid. The heat transfer coefficients decreased in the order of decreasing thermal conductivity of the substrate metal. The latter workers concluded that the thermal conductivity of the substrate material was limiting in the case of relatively low thermal conductivity metals. They attributed this effect to a thermal constriction resistance due to the substantial nonuniformities in surface temperature which can exist during dropwise condensation on a material with a relatively low thermal conductivity. The surface temperature under an actively condensing drop can be significantly higher than the average surface temperature which is measured by the usual experimental procedure of extrapolating a measured linear temperature profile in the sample to the surface. This fact gives rise to an effective resistance in series with the overall heat transfer process.

Mikic (1969) has developed a theory to account for this constriction resistance which depends upon the details of the drop size distribution on the surface. Mikic's theory has been supported by the work of Wilkins and Bromley (1973) and of Horowitz and Mikic (1974). The constriction resistance calculated by Mikic (1969) is given approximately by

$$R_s \cong \frac{1}{3} \frac{\beta}{(1 - \beta)^{0.5}} \frac{c}{k} \quad (8)$$

Taking $\beta = 0.5$ and $c = 0.1$ cm, we get a value of R_s equal to $0.02/k$. It is only for values of k which are approximately 0.1 cal/cm \cdot s \cdot °C or less that $1/R_s$ approaches the values of the heat transfer coefficient associated with dropwise condensation, that is, 2 to 5 cal/cm 2 ·s \cdot °C, and the constriction resistance can begin to play a limiting role in the heat transfer process.

Since nickel has a thermal conductivity of 0.14 cal/cm \cdot s \cdot °C, it is probable that the substrate thermal conductivity played a limiting role in condensation heat transfer on the nickel backed gold surface. Because of the known difference in the nature of the nucleation sites on the two surfaces studied, however, it is not possible to definitely attribute the relatively low heat transfer coefficient measured on the nickel backed surface to the presence of a constriction resistance. It should be noted that recent work by Askan and Rose (1973) is at variance with the existence of a thermal constriction resistance in dropwise condensation. If, in fact, the postulated thermal constriction resistance does not exist, then the difference in the behavior of the two surfaces would have to be attributed solely to differences in their nucleation site geometries.

NOTATION

- b = temperature gradient in the sample
 c = mean radius of inactive drops on a dropwise condensing surface
 h_c = condensation heat transfer coefficient
 k = thermal conductivity

- P = vapor pressure over the liquid
 P_e = equilibrium vapor pressure over a plane liquid surface
 \dot{q} = heat flux
 r = drop radius
 R_s = thermal constriction resistance
 T = temperature
 T_s = temperature of condensing surface
 T_v = temperature of the saturated vapor
 v = specific volume of the liquid
 x = axial displacement in heat transfer sample

Greek Letters

- γ = surface tension of the liquid
 ΔH = heat of vaporization
 ΔT_r = subcooling required to condense a drop of radius r
 ΔT_{sv} = temperature difference between the vapor and the condensing surface, surface subcooling
 β = fraction of a dropwise condensing surface that is covered with inactive drops

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