Thermal management of metallic surfaces: evaporation of sessile water droplets on polished and patterned stainless steel

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Abstract. This communication focus on the evaporation of sessile water droplets on different states of austenitic stainless steel surfaces: mirror polished, mirror polished and aged and patterned by sputtering. The evolution of the contact angle and of the droplet diameter is presented as a function of time at room temperature. For all the surface states, a constant diameter regime (CCR) is observed. An important aging effect on the contact angle is measured on polished surfaces due to atmospheric contamination. The experimental observations are compared to a quasi-static evaporation model assuming spherical caps. The evolution of the droplet volume as a function of time is almost linear with the evaporation time for all the observed surfaces. This is in accordance with the model prediction for the CCR mode for small initial contact angles. In our experiments, the evaporation time is found to be linearly dependent on the initial contact angle. This dependence is not correctly described by the evaporation model.

1. Introduction
Heat production accounts for about 70% of the world's primary energy consumption. Better thermal management in industrial processes would be an advance in the energy transition process. In this context, the development of efficient extractors, heat exchangers, condensers, sufficiently compact and affordable constitutes an important industrial challenge. Studying the evaporation of droplets on a solid surface is a way to fulfil this objective.

When the temperature of a solid surface is lower than the saturation temperature of the liquid ($T_{\text{sat}}$), heat transfer is dominated by heat conduction from the substrate to the liquid, and evaporation occurs at the liquid-gas interface [1-3]. This evaporation regime is called “film evaporation”. When the substrate temperature exceeds $T_{\text{sat}}$, the droplet boils and small bubbles nucleate at the liquid-solid interface. The corresponding evaporation regime is “nucleate boiling”. However, a limiting heat flux, the so-called critical heat flux, is reached at a critical temperature, for which the total evaporation time of a droplet is at its minimum. When vapour bubbles burst at the liquid-gas interface, small droplets can be ejected from the drop. The corresponding heat transfer regime is the transition boiling regime [2]. For higher temperature, a thin micrometre-scale vapour layer interface formed between the water
droplet and the wall. The transition temperature between transition and film boiling is called the steady Leidenfrost temperature ($T_{\text{le}}$). In many industrial processes, it is not desirable to work in the film boiling regime (above the Leidenfrost temperature) due to the inhibition of heat transfer. The Leidenfrost temperature thus limits the efficiency of metallurgical processes such as quenching and spray cooling, high heat flux microelectronics cooling systems and fire-fighting equipment [4]. An improvement of heat transfer performances can be obtained by enhancing the surface area. This can be achieved by roughening the surface, or by surface patterning. Surface patterning (surface structuration) allows the production of a “patterned” surface with some regular array of surface height features on the size scale of several micrometres to some nanometres. Robust and efficient surface patterning manufacturing methods are existing but alternative cheap and flexible technologies are required, especially for metallic surfaces. Plasma technologies such as nitriding, carburizing and etching by ion bombardment are well adapted technologies for that purpose [5-6]. Evaporation on textured surfaces is intensively studied, especially on textured surfaces having superhydrophobic properties [7-11]. However, it is not the case for plasma nitrided or plasma patterned by sputtering metallic surfaces. This communication will focus on the evaporation of sessile water droplets on different states of austenitic stainless steel AISI 316 L surfaces modified or not by plasma treatments: mirror polished and patterned by ion sputtering using masks. The experimental results will be compared to a simple quasi-static evaporation model assuming spherical caps for the evaporating droplets.

2. Experimental devices

Samples used in this communication are AISI 316L stainless steel cylinders (see table 1 for composition). The samples were cut from a cylindrical rod (20 mm of diameter) with a thickness of 5 mm. The samples were polished with a mirror-like finish that guarantee the parallelism between the two faces of each ring. The patterning treatment was done using a multi-dipolar electron cyclotron resonance system (MDECR) [5] in an argon-hydrogen gas mixture. The analysis of the traces on the samples was performed by optical microscopy. The confocal laser scanning microscope was a Zeiss LSM 700 (solid laser, 405 nm, 5 mW) and the spatial and time resolutions were respectively 70 μm (field of view 1248 × 1268 μm) and 0.64 fps. Contact angle measurements were performed with a Digidrop equipment at room temperature (22-23°C) with a humidity of 51-52%. Drops of ultrapure water were deposited with minimal influence of external forces and the process was recorded until the drop was fully evaporated, with 1 picture taken per second. The contact angle measurements were done without doing any surface cleaning before the test.

Table 1. Composition of the two AISI 316L stainless steel in wt%.

|           | Fe | Cr | Ni | Mn | Mo | Si | Cu | Co | N   | P   | C   | S   | N   |
|-----------|----|----|----|----|----|----|----|----|-----|-----|-----|-----|-----|
| AISI 316L sample 1 | 67 | 16.8 | 10.1 | 2.2 | 2 | 0.8 | 0.5 | 0.2 | 0.09 | 0.05 | 0.02 | 0.03 | 0.1 |
| AISI 316LM sample 2 | 67.5 | 16.2 | 9.4 | 2.3 | 2 | 0.9 | 0.7 | 0.2 | 0.1  | 0.05 | 0.02 | 0.02 | 0.2 |

3. Evaporation of sessile droplet on stainless steel surfaces

3.1. The different evaporation regimes

Figures 1, 2 and 3 respectively show the evolution of the contact angle and drop width (2 R) as a function of time for polished austenitic stainless steel exposed to air for a long time, a patterned sample and polished austenitic stainless steel exposed to air after different ageing times. These figures illustrate the four possible evaporation regimes that can exist for a drop of liquid on a surface in the partial wetting situation [12-15]:
• Initial regime (propagation step): during this short initial spreading period (generally less than one minute), the contact angle and the radius R change simultaneously to reach the initial considered values for the next step (see the early beginning of figures 2 and 3).
• CCR Regime: the contact angle $\theta$ decreases while the radius R of the drop remains constant. This step is known as the constant contact radius evaporation regime (CCR). In this configuration, the triple line remains pinned (pinning mode).

Figure 1. Evolution of the contact angle and drop width (2 R) as a function of time for a 3 $\mu$l water drop on polished stainless steel sample 1 exposed to air for a long time. The onset shows the definition of the contact angle.
CCA Regime: the contact angle $\theta$ remains constant while the radius $R$ of the drop decreases. This step is known as the constant contact angle evaporation regime (CCA). In this configuration, the triple line moves (depinning mode).

Mixed Regime: the contact angle $\theta$ and the radius $R$ of the drop decreases until the droplet completely disappears (mixed regime).

Stick-slip regime: in this mode, consisting of one or more stages, the triple line is pinned ($R$ is constant) and one or more "sliding" phases in which the triple line is moving ($R$ varies) happens.

As seen on figure 1, three different regimes for the evaporation exist on austenitic stainless steel AISI 316L: a constant diameter regime, a constant contact angle regime and a mixt regime in which both diameter and contact angle are evolving with time. Sharp transitions from CCR to CCA (figure 1) are only observed for large volume drop. For volume drop less than 3 $\mu$L, a continuous transition from CCR to mixed regime is observed most of the time. As it can be seen on figure 3, the existence of pure CCR is also debatable and we are facing mixt regimes most of the time. For patterned surfaces (figure 2) we observed many small transition regimes, corresponding to local jump of the triple line. This is the stick-slip regime.

Figure 2. Evolution of the contact angle and drop width (2 R) as a function of time for a 1.9 $\mu$L water drop on a negatively patterned substrate sample 1 (squares of 100 $\times$ 100 $\mu$m separated by 200 $\mu$m from each other with a depth of 0.7 $\mu$m). The onset shows the trace remaining after the evaporation of a 3 mm in diameter water drop on the patterned surface.

Figure 3. Evolution of the contact angle and drop width (2 R) as a function of time for a 1.9 $\mu$L water drop on a negatively patterned substrate sample 1 (squares of 100 $\times$ 100 $\mu$m separated by 200 $\mu$m from each other with a depth of 0.7 $\mu$m). The onset shows the trace remaining after the evaporation of a 3 mm in diameter water drop on the patterned surface.

Evolution of the contact angle and drop width (2 R) as a function of time for different ageing times on polished stainless steel sample 2 exposed to air: (a) freshly polished, (b) 3 days, (c) 7 days and (d) 10 days of air exposure. The onset in (c) shows the early beginning of the drop evaporation.
3.2. Tracking the traces

Another important finding on polished stainless steel is the important aging effect on the contact angle. Kim et al [16] recently report on such an effect for polished and aged AISI STS 304 samples. Time-dependent wettability transitions were observed after laser [17-18] or electrochemical processing [19]. Oxygen, carbon dioxide, and organic matter in the atmosphere have been proposed to explain such ageing effect [16-18]. The contamination layer seems to dissolve in water producing tracks visible at the end of the evaporation (onsets in figure 1 and 2). Such a phenomenon must also be connected to the rapid decrease of the contact angle observed at the beginning of the evaporation process on contaminated surfaces (figure 3). We have to note that this phenomenon is not observable on freshly polished surfaces. Figure 4 shows the evaporation of a sessile droplet seen from the top by confocal microscopy.

![Figure 4](image_url)

**Figure 4.** Evolution of the contact surface as a function of time for a 0.3 µl water drop on polished stainless steel sample 2 exposed to air for a long time as observed by confocal microscopy. Scale bar (200 µm)
Figure 5. (a) Evolution of the drop width for drops of 0.3 μl as a function of time (data from fig.4), (b) traces remaining after the evaporation of a 3 mm in diameter water drop (approximately 4.2 μl). Both are for polished stainless steel samples exposed to air for a long time.

The triple line is almost circular during the evaporation process. The evolution of minimum and maximum radius of the triple line on the assumption of elliptical shapes are depicted on figure 5a. For such a small volume droplets (0.3 μl), the decrease of the diameter is more soft compared to larger drop volume (figures 1 and 3). Another interesting observation is in the kinetics of the triple line movement. It is not fully continuous, but instead is constituted by numerous stick-slip micro-events (see arrows in figure 4). It is difficult to say to which type of discontinuities these events are associated. It can be due to dust or to other defects like grain boundaries. It can be noted that, on most of the observations made with the confocal microscope, a pinning of the triple line on the initial position of the perimeter is observed. This is illustrated by the white ellipse drawn on the last snapshot of figure 4, which allows a comparison of the trace of the evaporated droplet and its initial position. For small volumes of droplets, there is no multiple elliptical traces, as observed for larger volume (figure 5b). The mixt regime occurs quasi-continuously for small volumes, whereas sharp transitions from the CCR to CCA modes occurs for larger volumes, which can be seen by the multiple traces remaining on the surface at the end of the evaporation process (figure 5b).

3.3. Comparison between experimental and theoretical aspects for the evaporation of sessile droplets

The process of evaporation corresponds to the progressive transfer of a liquid into its own vapour. Such a mechanism is possible as long as the thermodynamic equilibrium is not established by the transition of the water molecules between the liquid and the gaseous phase. When the gaseous phase is saturated, there are as many incoming molecules as leaving the liquid phase and the equilibrium condition is realized. If the gaseous phase is not saturated, there are more molecules which pass into the gas phase and the evaporation phenomenon is present. The evaporation of a drop can be considered as a quasi-stationary phenomenon when the diffusion time is very small compared to the evaporation time. The concentration of vapour then readily adjusts with respect to the time required for evaporation. This is true when the density of the vapour at the surface of the drop is much lower than the density of the liquid (ratio of 10^{-5} for water). The mass flow of evaporation which is established on the surface of the drop is then modelled by the diffusion of molecules of the liquid-gas interface to the surrounding gas phase. When a drop evaporates in contact with a substrate, the problem is complex to solve because of the loss of symmetry and the appearance of a triple line. Droplets small enough to be associated with spherical caps (valid when the radius R of the tip is less
than the capillary length: 2.7 mm for water) will be considered hereafter. Hence the volume variation is given by [20]:

$$\frac{dV}{dt} = \frac{\pi R^3}{(1+\cos \theta)^2} \frac{d \theta}{dt} + 3 \pi R^2 g(\theta) \frac{d \theta}{dt} \text{ with } g(\theta) = \frac{\cos^2 \theta - 3 \cos \theta + 2}{3 \sin^3 \theta}$$ \hspace{1cm} (1)

Popov [20] has shown that equation (1) can be given by:

$$\frac{dV}{dt} = -\pi R \frac{D (C_v - C_S)}{\rho} f(\theta) \text{ with } f(\theta) = \frac{\sin \theta}{1+\cos \theta} + 4 \int_0^\pi \frac{1+\cosh 2\theta \tau}{\sinh 2\theta \tau} \tanh \left[ \frac{\pi}{2} (\pi - \theta) \right] d\tau \hspace{1cm} (2)$$

$\rho$ is the fluid density, $f(\theta)$ is a function of the contact angle $\theta$, $D$ is the diffusion constant for vapour in air, $C_S$ is the vapour saturation concentration just above the liquid-air interface, $C_v$ is the ambient vapour concentration. This last relation is relevant for all the $\theta$ values. When $\theta \to 0$, relation (2) gives [20]:

$$\theta = \theta_i (1 - \frac{t}{t_f}) \text{ and } V = \frac{\pi R^3 \theta_i}{4} \left( 1 - \frac{t}{t_f} \right) \hspace{1cm} (3)$$

$$t_f^{CCR} = \frac{\pi \rho R^3 \theta_i}{16 D (C_v - C_S)} \hspace{1cm} (4)$$

In relations (3) and (4), $\theta_i$ is the initial contact angle and $t_f^{CCR}$ is the evaporation time in the CCR regime. Relation (2) has no simple analytical solutions but some analytical expressions have been proposed for $f(\theta)$ [21]. In the CCR mode, the obtained behaviours for $\theta$ and $V$ are similar to those given by relations (3) and (4). In the CCA mode, relations (5) and (6) are obtained:

$$R = \sqrt{R_0^2 - \psi(\theta_0) t} \text{ and } V = V_0 - 2 \pi \left( \sqrt{R_0^2 - \psi(\theta_0)} \right) \left( \frac{D (C_v - C_S)}{\rho} f(\theta_0) \right) \frac{1}{t^2} \hspace{1cm} (5)$$

$$t_f^{CCA} = \frac{R_0^2}{\psi(\theta_0)} \text{ with } \psi(\theta_0) = \frac{4}{3} \frac{D (C_v - C_S)}{\rho} \frac{f(\theta_0)}{g(\theta_0)} \hspace{1cm} (6)$$

In relation (5) and (6), $\theta_0$ is the contact angle at the beginning of the CCA mode and $t_f^{CCA}$ is the evaporation time in the CCA regime. As a general rule, the simple evaporation model gives the following power law for the droplet volume evolution as a function of time ($V_i$ is the initial volume of the droplet):

$$\left( \frac{V}{V_i} \right)^{\beta} = \left( 1 - \frac{t}{t_f^{CCA}} \right)$$ \hspace{1cm} (7)

Works from Nguyen et al [21] and Hu et al [22] show that the $\beta$ factor is evolving between 1 and 2/3 for the CCR mode and is equal 2/3 for the CCA mode.

Figure 6a and 6b respectively shows the evolution of the logarithm of the normalized drop volume as a function of $\ln (1 - t/t_i)$ for the data of figures 1 and 2. During most of the evaporation process, the evolution of $V_{norm}$ as a function of $\ln (1 - t/t_i)$ is linear for both the polished and the patterned stainless steel samples (with respective slopes of 1.08 and 0.9). A slope of 0.8 was found for smaller droplet volumes (data of figure 3). It can be concluded that relation (3) for the evaporation in the CCR mode is effective in both cases. However, the final part of the evaporation process is not correctly described by relation (3) as noted by Popov [20]. We also note that the theoretical value for the CCA
mode (3/2) is not observed for the end of the evaporation process (0.2 for the patterned sample). This is illustrated in the evolution of the droplet volume as a function of the evaporation time represented in figure 6c. If the initial volume evolution is correctly described by a linear law, it is not the case for the end of the evaporation process. From figure 6c, it can be also shown that the decrease of both contact angle and drop radius observed in the CCR mode of figure 2 (between 240 and 280 s) has not physical signification. As a matter of fact, during this time, the temporary decrease in volume of the droplet observed is followed by an increase in the droplet volume correctly adjusted to the linear evolution as a function of time. This event is probably connected to a temporary non symmetric change in the shape of the sessile droplet that cannot be correctly recorded by our experimental device.

![Figure 6](image)

**Figure 6.** Evolution of the logarithm of the normalized droplet volume as function of the logarithm of (1 - t/τ) for (a) data of figure 1, (b) data of figure 2. (c) Evolution of the volume as function of time for the corresponding two cases.

The evolution of the volume of the drops is correctly described by the theory of evaporation in CCR mode, what is about the evaporation time τ? From relation (4) it should depend on (R_i)^2 θ_i in the CCR mode. Figures 7a and 7b respectively show the evolution of the initial droplet radius (R_i) and of the initial contact angle (θ_i) as a function of the evaporation time τ for different polished and aged stainless steel samples and for the data of figures 1 and 2. For these data, different drop volumes are taken into account (1 µl for the polished and aged samples of figure 3, 1.9 µl for the patterned sample from figure 2 and 3 µl for the polished and aged sample from figure 1). From figure 7a, it is clear that the evaporation time does not strongly depends on the initial radius of the droplets. However, the evaporation time is linearly depend on the evaporation angle as it can be observed from figure 7b. Such an observation, which is very important for the improvement of the evaporation processes at industrial scale, has no correct interpretation for the moment. Such a dependence of τ_i on θ_i will be interesting to consider in order to improve the modelling of the evaporation process.
4. Conclusion

Evaporation of sessile water droplets was studied on different surface states of austenitic stainless steel: mirror polished, mirror polished and aged and patterned by sputtering. The evolution of the contact angle and of the droplet diameter was presented as a function of time at room temperature. For all the surface states, a constant contact radius evaporation mode (CCR) was observed. On polished and aged surfaces, it was sometimes followed by a nearly constant contact angle regime (CCA) for large volume droplets. In most case, a mixed regime, in which both the contact angle $\theta$ and the radius $R$ of the drop decreases with time, was observed. For the patterned surface and for small droplet volumes a stick-slip mode was recorded. An important aging effect on the contact angle was measured on polished surfaces. It was attributed to atmospheric contamination. Confocal microscopy observations from the top of the drop have shown that the triple line is almost circular during the evaporation process. A pinning of the triple line on the initial position of the perimeter was observed for polished and aged surfaces.

The experimental observations were compared to a quasi-static evaporation model for which the droplets are small enough to be associated with spherical caps. In our experiments, the evolution of the droplet volume as a function of time is almost linear with the evaporation time for all the observed surfaces. This is in accordance with the model prediction for the CCR mode for small initial contact angles ($\theta_i$). However, the final part of the evaporation curves is not correctly described by the model. Also, the evaporation time ($t_f$) is not correctly described by the evaporation model which involves a $R_i^2 \theta_i$ dependence for $t_f$, whereas a $\theta_i$ dependence is observed for the studied surfaces. It will be interesting to consider this dependence in order to improve the modelling of the evaporation process.

5. References

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