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SEPARATE EFFECTS OF SURFACE ROUGHNESS, WETTABILITY AND POROSITY ON THE LEIDENFROST TEMPERATURE OF WATER

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Abstract

Quenching phenomena play a key role in LWR safety, particularly in the reflood phase of a large-break LOCA. It is well known that quenching phenomena are affected by the physico-chemical characteristics of the hot surface, such as surface roughness, wettability and porosity. However, while some general qualitative trends are known, there is a lack of quantitative data on the relative importance and magnitude of these effects. Therefore, we have conducted water-droplet Leidenfrost Point (LFP) tests using custom-fabricated surfaces for which roughness, wettability and porosity were controlled accurately and separately at the nanoscale. This approach reveals that nanoporosity is the crucial feature in efficiently increasing the LFP temperature by initiating heterogeneous nucleation of bubbles during short-lived solid-liquid contacts, which results in disruption of the vapor film.

Introduction

Quenching heat transfer refers to the rapid cooling of a very hot object by immersion in a cooler liquid. The process is initially dominated by film boiling in which a continuous vapor film completely separates the liquid phase from the solid surface. During film boiling, heat transfer from the surface to the liquid takes place by conduction and radiation through the vapor layer, and thus the liquid takes a significantly longer time to evaporate than it would on a surface held at lower temperature; however, as the temperature gets closer to the *Leidenfrost point (LFP)*, intermittent and short-lived liquid-solid contacts occur at discrete locations on the surface, thus creating liquid-vapor-solid interfaces once again. Ultimately, if bubble nucleation ensues at such contact points, the vapor film is disrupted and the heat transfer regime transitions from film boiling to transition boiling.

Quenching phenomena play a key role in LWR safety, particularly in the reflood phase of a large-break LOCA. Because during an accident the fuel can be initially very hot (>700°C), its rewetting occurs slowly through the development of a quench front which advances upward in the reactor core. The speed of the quench front and thus the peak temperature reached during the reflood transient depend on a combination of factors including film boiling heat transfer and the physico-chemical and micro-structural characteristics of the hot surface, such as surface roughness, wettability and porosity. Note that these surface parameters can change greatly during the in-core service due to the effects of crud deposition, clad oxidation, radiation-induced surface activation, etc.

In recent film boiling heat transfer studies with nanofluids, we demonstrated that deposition of nanoparticles on a surface significantly increases the nominal LFP up to ~500°C under atmospheric and saturated conditions, considerably accelerating the transient cooling of overheated objects [1,2].

However, such a high LFP could not be explained by the traditional LFP models based on hydrodynamic instability of the vapor film, e.g. Berenson's [3] model and Henry's model [4]. This suggested that the vapor film is destabilized and disrupted by a different mechanism associated with the thin nanoparticle deposition layer. Characterization of the deposition layer suggested changes in roughness, wettability, and nanoscale porosity as plausible causes for such a high LFP. Nevertheless, it was not possible to identify the exact physical mechanism of LFP enhancement because nanoparticle deposition in those experiments changed roughness height, wettability and porosity simultaneously.

In this study we investigated the *separate effects* of surface roughness, wettability and porosity on the Leidenfrost temperature of water droplets with custom-fabricated surfaces at the nanoscale. This approach revealed that nanoporosity is the crucial feature in efficiently increasing the LFP temperature by initiating heterogeneous nucleation of bubbles during short-lived solid-liquid contacts, which results in disruption of the vapor film.

1. Experiments

1.1 Preparation of test surfaces

Surface roughness height was controlled in the range from 0 μm to 15 μm (with 5 μm increment) by fabricating cylindrical posts with 5 μm diameter on a nano-smooth silicon wafer (R_a < 0.5 nm; thickness 380 μm) (Fig. 1b). The posts were fabricated with a deep reactive-ion etching process, and were arranged on a square array of large pitch (500 μm), to prevent secondary effects, such as capillarity. The deep reactive-ion etching process to create the posts on silicon wafer was as follows. First, a layer of Hexamethyldisilazane (HMDS) primer was deposited on a silicon wafer via a vapor deposition at 150 ºC. Then, a layer of negative photo-resist, NR71-1000P, was coated on the wafer using a spin coater spinning at 3000 rpm for 30 seconds. The HMDS helped adhesion of the negative photo-resist to the wafer. Post baking on hot plate at 150ºC for two minutes helped drying the negative photo resist. Next, the wafer was exposed to ultraviolet (UV) light of wavelength 365nm to 400 nm for 20 seconds. A mask was inserted between the UV light source and the wafer to imprint pattern of square array of 5 μm circles at 500 μm pitch, where the UV light interacts with the negative photo resist. After exposure to UV, the wafer was dried again on a hot plate at 100 ºC for two minutes. The wafer was then developed in RD6 developer for 15 seconds. All the negative photo resist on the wafer, except for that which was exposed to UV light underneath the mask, was washed away by the RD6 developer. The remaining patterned negative photo-resist helped protecting the wafer underneath during reactive-ion etching, which created a square array of post 5-μm circles at 500 μm pitch. Subsequently, the wafer was cleaned with piranha solution to remove all negative photo-resist.

The surface intrinsic wettability was controlled by depositing a nano-smooth thin layer of gold (100 nm thick) or silicon oxide (20 nm thick) with a sputtering technique; the resulting contact angles for de-ionized water droplets were found to be 83° on the gold surface and 19° on the silicon oxide surface (see the insets of Fig. 1). Note that the presence of the micro-posts does not affect wettability (compare insets of Figs. 1a and 1b), which was expected, given the large pitch of the post array. Finally, to explore the effect of nano-porosity, we used a thin nano-porous layer (about 600 nm thick) made of silicon oxide nanoparticles (23 nm), deposited according to the layer-by-layer process described by Lee et al. [5]. The nano-porous layer causes a further enhancement in the apparent wettability (the contact angle decreases to ~0°, as shown in Fig. 1d) with respect to the smooth silicon

oxide surface (19°). This is due to the well-known Wenzel effect [6]. On the other hand, the roughness height change due to the nano-porous layer is negligible (≤ 0.016 μm). In summary, using a combination of spaced-out micro-posts, and smooth and nano-porous layers we were able to control surface roughness height, wettability and nano-porosity independently.

1.2 Measurement of LFP

A common technique used for determining the LFP consists in measuring the evaporation times of liquid droplets over a heated surface. A schematic of the experimental apparatus is shown in Fig. 2. The test surface is sandwiched between two independently heated and controlled copper blocks. The upper block has a through-hole in the shape of an inverted cone to place a droplet on the silicon wafer and keep the evaporating droplet on the silicon wafer. The temperature difference between the two blocks was controlled to be less than 1 K during the experiments. A water droplet of ~2.9 mm in diameter is released on the test surface from a height of 1.5 mm using a syringe, and the evaporation time is measured with a stopwatch. The uncertainty in the evaporation time measurement was found to be ~0.4 sec from a set of tests at representative conditions. The surface temperature stayed within ±1 K during evaporation of a droplet.

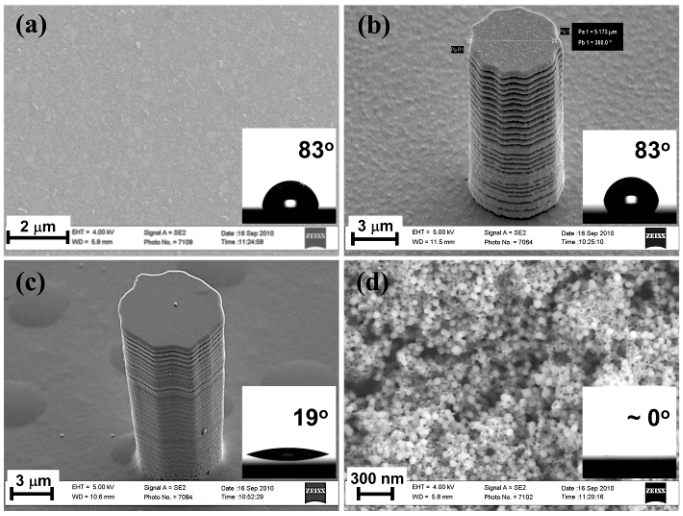

Figure 1. Scanning Electron Microscope (SEM) images of fabricated samples for LFP tests: (a) smooth Au layer; (b) 15 μm posts on smooth Au layer; (c) 15 μm posts on smooth SiO_2 layer; (d) layer-by-layer (LBL) SiO_2 layer. Insets show static contact angle on the fabricated samples for 10-μL water droplets on (a) smooth Au (83^o), (b) Au with micro-posts (83^o), (c) SiO_2 layer (19^o), (d) nano-porous SiO_2 layer (~0^o).

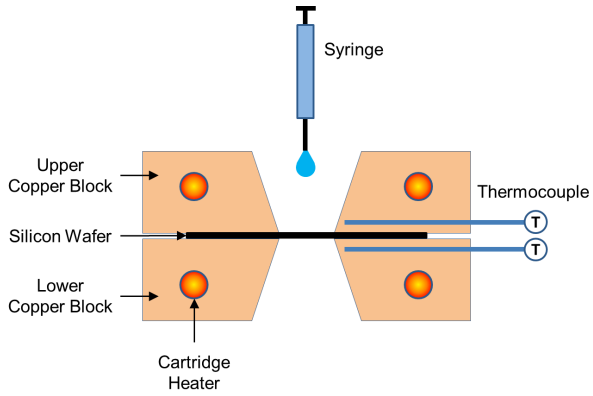

Figure 2. Schematic of the apparatus used to measure droplet evaporation time.

2. Results

The data obtained from the droplet experiments for the surfaces without micro-posts and with the highest posts of 15 μm are displayed as droplet evaporation time vs surface temperature in Fig. 3. In this curve, the temperature corresponding to the longest evaporation time is the LFP. The LFP on the smooth gold surface without micro-posts is ~264°C, reasonably closed to the values found in the literature [7]. The LFP is slightly higher (~274°C) for the smooth silicon oxide surface without micro-posts, but is significantly higher (~359°C) for the porous silicon oxide surface without micro-posts. This result suggests that nano-porosity has a stronger effect than intrinsic surface wettability on the LFP.

Figures 4-6 shows the effect of roughness height (micro-posts) respectively for the gold, silicon oxide, and porous silicon oxide surfaces; everything else being the same, the presence of the micro-posts consistently enhances the LFP on all surfaces tested in this study, but the magnitude of the enhancement is distinctively higher on the nano-porous surface. As a result, the nano-porous surface with micro-posts can be considered an optimum (within the limits of our study), exhibiting the highest LFP at 453°C, which is even beyond the critical point of water (374°C). Note that the reported values of LFP are the nominal temperatures of the test surface. Obviously, the local temperature at which the liquid-solid contact occurs must be below the critical point.

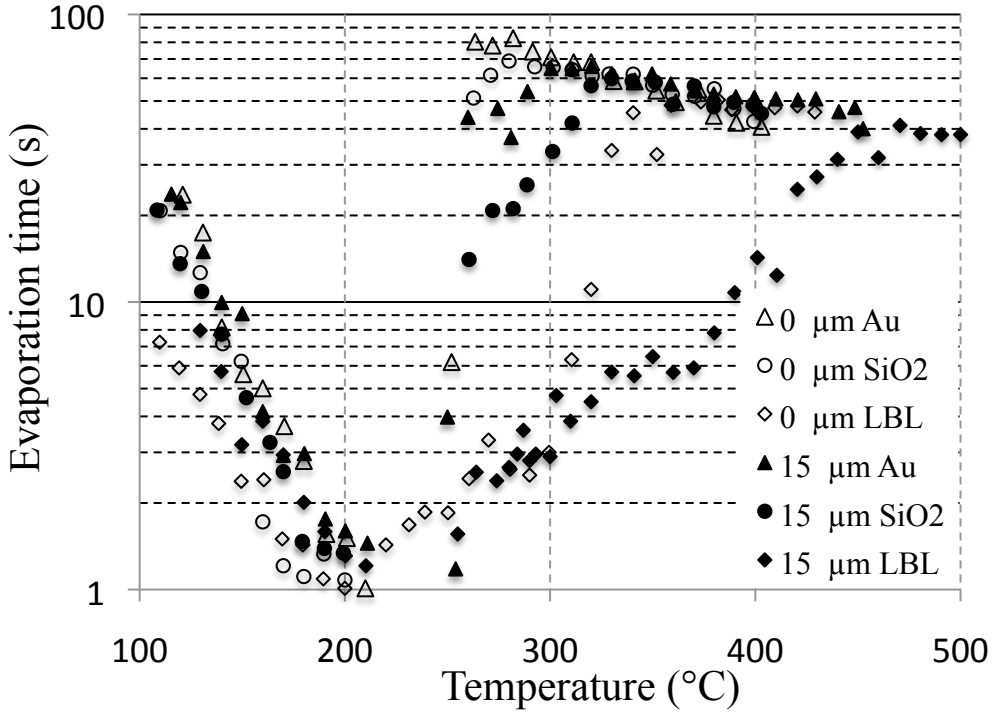

Figure 3. Water droplet evaporation time vs. surface temperature. The nominal uncertainty in the measurement of the LFP temperature was found to be less than ±5°C.

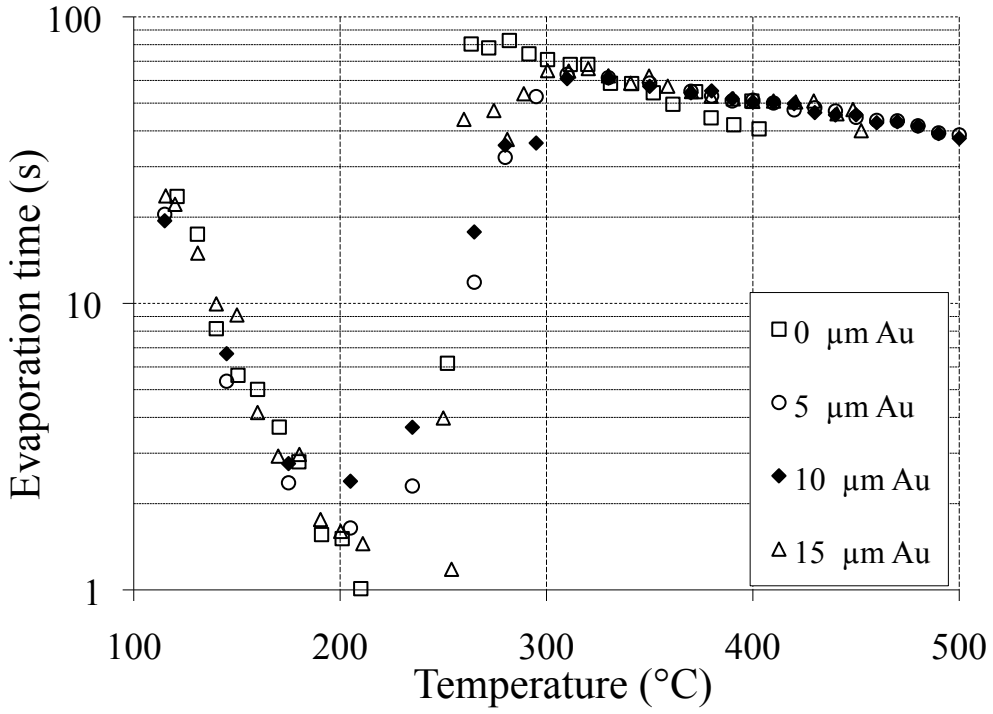

Figure 4. Surface roughness effect on the LFP for gold coated surfaces

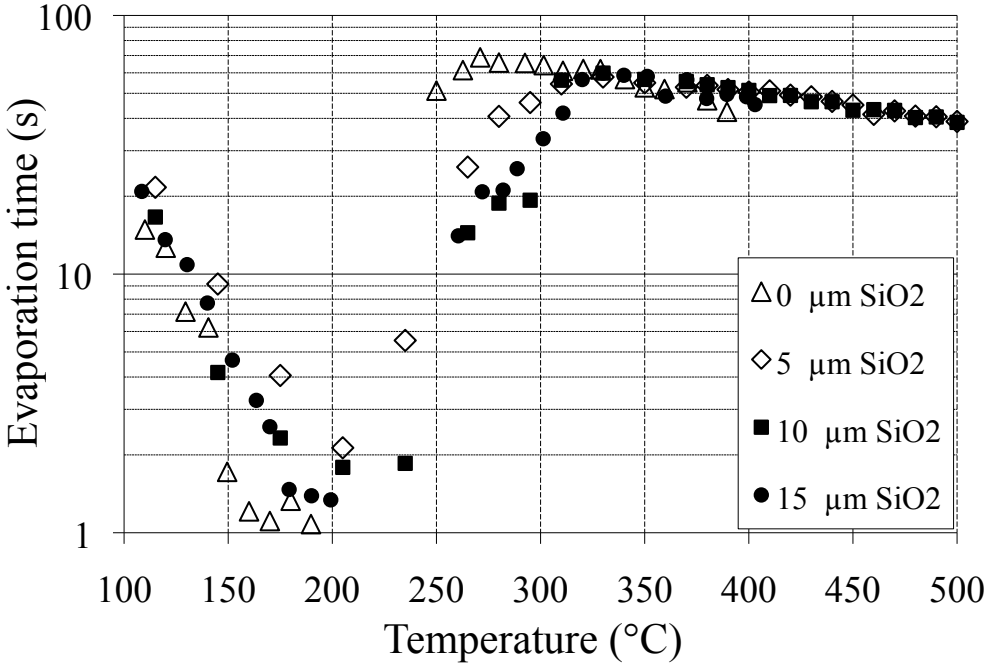

Figure 5. Surface roughness effect on the LFP for silicon oxide coated surfaces

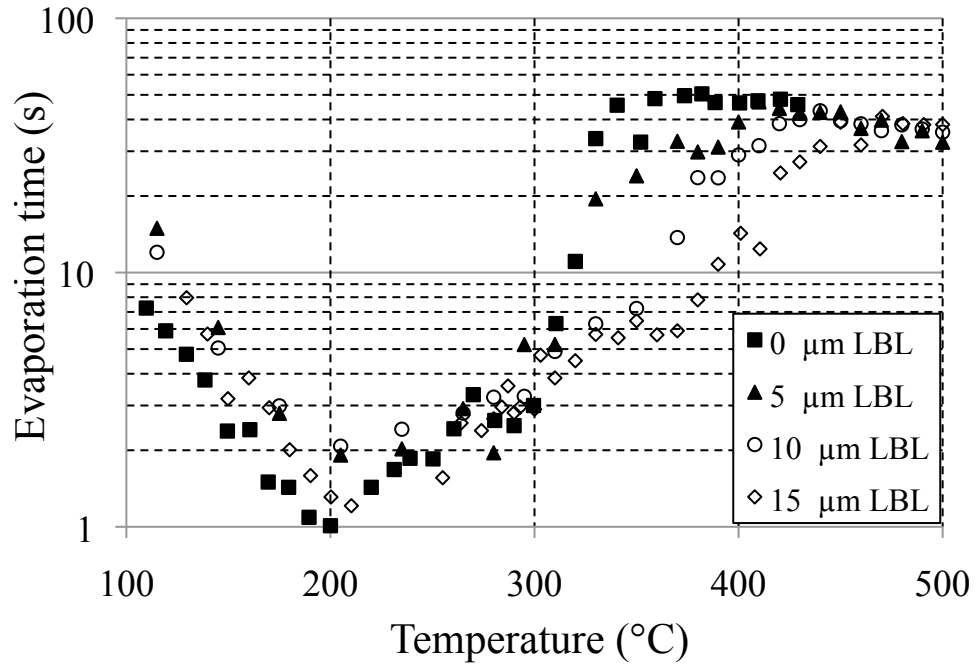

Figure 6. Surface roughness effect on the LFP for SiO_2 nanoparticle layer-by-layer coated surfaces

Table 1 Summary of LFP temperatures for water on the test surfaces (°C).

Micro post height	Au	SiO_2	nano-porous SiO_2
0 μm	264±5	274±5	359±5
5 μm	295±5	330±5	410±5
10 μm	295±5	330±5	440±5
15 μm	290±5	325±5	453±5

3. Data Interpretation

Why do nano-porosity and micro-posts result in such a high LFP (Table 1)? High-speed imaging of the evaporating droplets shed light on the mechanisms, when we focused on the intermittent solid-liquid contacts in film boiling, as suggested by previous researches [8]. Actually, we observed thin liquid filaments intermittently connecting the droplet to the solid surface on the samples with micro-posts (Fig. 7b), whereas the filaments were not observed on the surfaces without micro-posts (Fig. 7a). However, even in the presence of liquid filaments, the evaporation process was quite different depending on whether the surface was nano-porous or not. The gold and silicon oxide surfaces without nano-porosity stably sustained the liquid filaments, typically for a few milliseconds, without triggering any perturbation (Figs. 7b and c). By contrast, the nano-porous surfaces instantaneously reacted to the filament contacts with violent splashes of tiny droplets around the large evaporating droplet (Fig. 7d). This splashing severely disturbed the liquid-vapor interface and prevented the establishment of a stable vapor film at nominal surface temperatures as high as ~453°C.

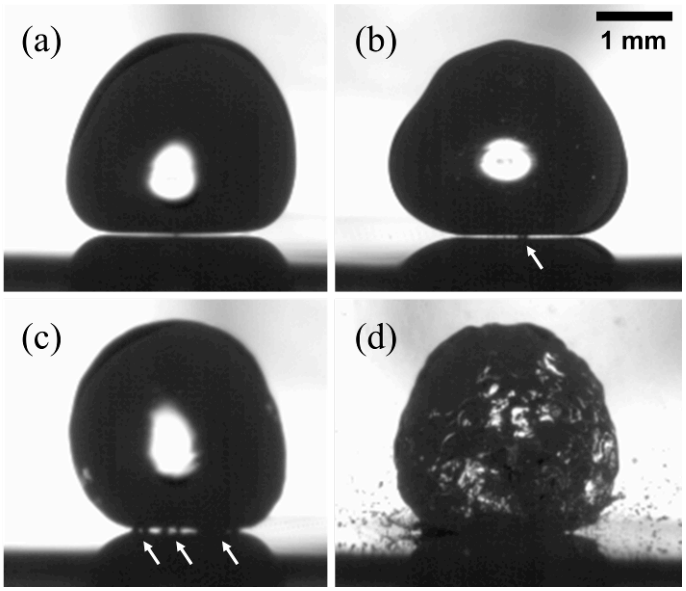

Figure 7. Photographs of evaporating water droplets on test surfaces held at 400°C: (a) Au without posts; (b) Au with 15 μm posts; (c) SiO_2 with 15 μm posts; (d) nano-porous SiO_2 layer with 15 μm posts. Arrows show location of droplet-to-surface bridging by liquid filaments.

Biance et al. [9] derived an analytical solution for the film thickness of a stationary evaporating droplet of radius, R, smaller than the capillary length, ($R<a=\sqrt{\sigma/\rho g}$), for a given surface superheat, ΔT,

$$e = C\left(\frac{k\Delta T\mu\rho g}{h_{fg}\rho_v\sigma^2}\right)^{1/3} \tag{1}$$

where C, σ, k, μ, ρ, ρ_v, and h_{fg} are, respectively, an adjustable coefficient, surface tension, thermal conductivity, dynamic viscosity, density of liquid, density of vapor, and latent heat of evaporation. For an evaporating droplet of 2R ~ 2.9 mm on a surface of 400°C (ΔT=300°C), the initial film thickness is estimated to be approximately 36 μm and then decreases monotonically as $R^{4/3}$. Thus, at 15-μm height, the micro-posts can initiate solid-liquid contacts, as shown in Fig. 7.

Once the liquid filaments are established, heterogeneous nucleation of bubbles can occur at the contact points, if there are cavities available for nucleation. Bernardin and Mudawar [10]'s heterogeneous nucleation model of the LFP focuses on the surface superheat temperature required to initiate the growth of hemispherical vapor bubbles from the pre-existing surface cavities. The nano-sized pores act as cavities for heterogeneous nucleation of bubbles. The pressure drop across a spherical bubble interface of radius r can be estimated using Young-Laplace equation as

$$P_g - P_f = 2\sigma/r \tag{2}$$

In combination with the Clausius-Clapeyron equation, Eq. (2) gives the following expression for the temperature required to initiate the nucleation of a hemispherical vapor bubble [10],

$$T_{nucl} = T_{sat}\exp\left(\frac{2\sigma v_{fg}}{rh_{fg}}\right). \tag{3}$$

where v_{fg} is the difference in vapor and liquid specific volumes. There exists a large difference in temperature for heterogeneous nucleation of bubbles between the nano-porous and non-porous surfaces, i.e. $T_{nano\text{-}porous}$ ~ 218°C vs $T_{non\text{-}porous}$ ~ 336°C, where nucleation diameter of 23 nm and 1 nm were assumed, respectively. Therefore, bubbles more easily nucleate on the nano-porous surface and very rapidly grow in the highly superheated liquid. Note that these values of nucleation superheat are much higher than those normally encountered on engineering surfaces where micro-cavities are present. The calculated value of the heterogeneous nucleation temperature at d = 1 nm (order of magnitude of the 'roughness' on the nano-smooth surface) is higher than the homogeneous nucleation temperature (~300°C for water at atmospheric pressure) because the size of the vapor embryos responsible for homogeneous nucleation is of the order of a few nm. Therefore, the fluid nucleates homogeneously before it does so heterogeneously.

Starting from the Rayleigh equation for the inertia-controlled phase of bubble growth, it can be shown that $\Delta P \sim \rho V^2$, where V is the velocity of the expanding vapor interface and ΔP is the value of the pressure difference across the interface at the point of nucleation. For a bubble with a diameter of 23 nm (which is the order of magnitude of the pore size on the nanoporous surface), the estimated velocity, V, is of the order of 10 m/sec. When the vapor phase velocity is greater than the critical velocity of Kelvin-Helmholtz instability, the liquid-vapor interface can be disrupted. For the steam and water at atmospheric pressure, the critical velocity is approximately 8 m/sec [11]. Therefore the

velocity of the expanding vapor interface for the 23 nm-diameter bubble is fast enough to generate the splashes shown in Fig. 7d.

4. Conclusions

Water-droplet Leidenfrost Point (LFP) tests were carried out using custom-fabricated surfaces which separate the effects of surface roughness, wettability and porosity. The findings from the results are as follows:

- Nano-porosity (not solely high surface wettability) is an essential feature to enhance the LFP, and such enhancement occurs via prevention of the stable vapor film establishment, caused by heterogeneous nucleation of bubbles;
- Micro-posts on the surface intensify such effects by promoting intermittent liquid-surface contacts.

These findings can be used as the starting point for accurate mechanistic models of quenching heat transfer in reactor environment. Future work may include investigation of surfaces with a more dense lattice of posts to evaluate the effect of capillary wicking on quenching.

5. Acknowledgements

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6. References

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