Investigation of cryogenic quenching of metal surfaces with various coatings

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Abstract. Cryogenic quenching is frequently encountered in many applications like LNG technology, cryogenic preservation of biomaterials, cryogenic material machining etc., in which one key issue is to accelerate the temperature decrease so as to achieve large cooling rate. In the present study, the cryogenic quenching experiments are conducted by immersing the metal rodlets with various coating layers at room temperature into a liquid nitrogen bath. It is found that fast cryogenic quenching of the aluminium alloy rodlet with a higher Leidenfrost temperature is achieved by coating a thin layer of nano-structure with nanopores on the outer surface. In addition, the similar method of surface fabrication is applied to the stainless steel rodlet and a moderate reduction of quenching time in liquid nitrogen is achieved. Furthermore, the cryogenic quenching of stainless steel rodlets coated with the Teflon layers is also investigated.

1. Introduction

With the fast development of cryogenic technologies, the applications of cryogenic fluids have been spreading to many industrial fields. For examples, to fully fill a cryogenic tank with cryogenic liquids, it will experience a temperature decrease period which generally takes a very long time. Such a situation is also encountered in materials processing where a very fast temperature decrease is necessary to generate appropriate metallurgical structures so as to modulate mechanical or surface properties. In those applications, cryogenic quenching is often encountered. However, in practice, the efficiency of cryogenic quenching is estimated to be extremely low, i.e., only around 8%, which implies that the cold energy supplied by the cryogen is not fully utilized, resulting in a huge waste of cryogenic fluids. Apparently, understanding the mechanisms and improving the quenching efficiency is of great significance. There are many potential factors that may affect quenching heat transfer, such as surface roughness, surface wettability, surface thermal resistance, surface structures and so on, among which fabricating surface structures or coating layers that can enhance the quenching heat transfer have been focused by many recent investigations.

Nano-structures can be fabricated on metal surfaces, including nanoscale particle-coated surfaces, surfaces coated with nanotubes, nanoporous surfaces and etc. By fabricating nano-structures on the surfaces, the morphology, the properties of wettability and thermal resistance are accordingly changed, and consequently the quenching performance might be altered. Many researches have made the endeavors to investigate the quenching heat transfer characteristics and mechanisms of such surfaces.
on which the nano-structures are fabricated. Liter and Kaviany [1] reported a nearly-three-time improvement of heat transfer performance by a nanoporous-layer coating over a conventional plain surface. Singh et al. [2] fabricated several nanoporous anodic aluminium oxide (AAO) substrates with different pore distribution morphologies and pore sizes to investigate the wetting and evaporation of sessile water droplets. The results showed that nano-structured surface was a practical way to vary the wettability as well as to adjust the diffusive evaporation of liquid droplet to improve the quenching performance. Hu et al. [3] coated a layer of AAO on an aluminium alloy rodlet and conducted the quenching experiments by using liquid nitrogen, and the results showed significant improvement of heat transfer. However, the comprehensive knowledge about the effect of nano-structures on the quenching process were all attributed to the effect of the surface wettability, because most of the current experiments were conducted with conventional fluids, like water, which showed different contact angles between surfaces with different materials and surface morphologies. And the effect of surface thermal resistance due to surface nano-structures was generally neglected in the quenching investigation.

Apparently, the quenching is profoundly influenced by the surface nano-structure and the thermal resistance of such coating. Therefore, the experiments to investigate the effect of the structure and thermal resistance should be designed and conducted. It is well known that the contact angles of liquid nitrogen on metal surfaces are reported to be relatively small (less than 7°) [4], thus liquid nitrogen can be applied as the coolant to eliminate the influence of surface wettability imposed by the nano-structure of the surfaces. Furthermore, the thickness of the coating layer is apparently of investigation interests since the thermal resistance of the coating layer shows significant effect on cryogenic quenching [5]. Furthermore, it is more practical to apply the comparatively facile approach of fabricating coating layer to industrial application, thus the spray coating layer is also expected to play a role in cryogenic quenching application.

In the present study, two types of nano-structured coatings are fabricated on the outer surface of aluminium alloy rodlet by anodic oxidation, i.e., anodic aluminum oxidation (AAO) surface which has the nanopores exposed on the outer surface and raw anodic aluminium oxide (RAAO) surface which has nanopores end-covered by a thin layer of alumina, and they have approximately the same surface thermal resistance. Furthermore, in order to facilitate the cryogenic applications in engineering practice, the stainless steel rodlets are also involved in the experiments as well, which are bare stainless steel rodlet, anodic stainless steel rodlet and the Teflon-coated stainless steel rodlet. Then we conduct the cryogenic pool quenching experiments on those metal surfaces in a bath of liquid nitrogen. In the experiments, the focus is placed on investigating the effect of nanopore structure and thickness of the Teflon coating layers on the cryogenic quenching.

2. Fabrication of the metal surfaces with various coatings
The AAO surface was fabricated using the 6061 aluminium alloy rodlet. The fabrication process consists of four steps. The aluminium alloy rodlet was firstly ground serially by silicon carbide sandpapers of 400Cw, 800Cw, 1200Cw, 1500Cw, 2000Cw, 3000Cw and 5000Cw and mechanically polished with water-soluble granular diamond paste of granularity of W2.5 and W1. Afterwards, it was cleaned by using ethanol and de-ionized water. Secondly, a carbon hollow cylinder was used as a cathode, and an aluminium alloy rodlet was used as an anode, and the electropolishing was carried out in an acidic solution (ethanol: water: perchloric acid was 360:63:27 in volume ratio) for 40 s at around 0-1 °C with voltage and electric current maintained at 18 V and 2.7 A, respectively. Afterwards, the rodlet was anodized in 0.3 mol/L Oxalic acid solution at 6-7 °C for about 3 hours, and the voltage and electric current were maintained at 60 V and 0.1 A during the anodic oxidation process, respectively. Then, the rodlet was immersed in a solution of 5 wt% phosphoric acid at room temperature for about 30 minutes to open the pores, and finally the AAO surface was obtained. The RAAO surface was fabricated in the same way as the AAO surface except the final pore-opening step. The AAO surface shows the evenly distributed nanopores of approximately equal size of the diameter of about 50 nm on
the surface [6]. On the RAAO surface, the top of the nanopore is covered with a layer of alumina, resulting in the end of the nanopore being closed.

Stainless steel (316L) was also used as a substrate material for the rodlets. Prior to anodization, the stainless steel rodlet was mechanically polished to a roughness of 0.3 μm and ultrasonically degreased in ethanol. Anodization was performed at a constant current density of about 200 A/m² in 5 mol/L H₂SO₄ with 2 mol/L H₂O₂ for about 120 minutes. A hollow carbon cylinder was used as a counter electrode. The temperature of electrolyte was maintained at 60 °C and the solution was well stirred using a magnetic stirrer to maintain the temperature uniform. It has been observed that there are many tiny pits and dents on the surface, which denote for the nanopores. However, the nanopore on the stainless steel surface is in general very shallow compared with those on the AAO surface.

We used spray coating to fabricate the Teflon coating layer on the 316L stainless steel rodlet. After the Teflon was sprayed on the outer surface of the stainless steel rodlet, it was put into an oven to bake at about 250 °C for about 30 min. Then, such a procedure was repeated for several times to increase the thickness of the Teflon coating layer if necessary. In general, the porous cavity and irregularity on the Teflon-coated surface are apparently more visible.

In order to clarify the effect of the surface thermal resistance on the quenching, the thickness of the alumina layer was determined. To compare the thermal resistances of the AAO and RAAO surfaces, the average thickness of both the AAO and RAAO surfaces were measured to be 15 μm by scaling the SEM images of cross section of those two surfaces at three different positions and averaging the thicknesses [6]. Then, the thermal resistance of these two surfaces are estimated approximately the same because they are of the same interior structures and equal thickness, and the alumina coverings on nanopores of the RAAO surface are much thinner than the thickness of the anodic layers.

The static contact angles of these surfaces together with a plain aluminium surface were measured to characterize the wettability. The average contact angles of the AAO, RAAO and the plain aluminium surfaces are 22.8°±1.8°, 54.9°±4.6° and 64.2°±2.7°, respectively, which shows that the hydrophilicity of the AAO and RAAO surfaces is better than that of plain aluminium surface. Because the contact angles for liquid nitrogen on conventional plain aluminium surfaces are reported to be relatively small (less than 7°) [4], the AAO and RAAO surfaces tend to bear even smaller contact angles of the liquid nitrogen as compared to the plain aluminium surface. For the stainless steel surface that was subjected to anodic oxidation, it shows similar characteristics to that of the AAO surface, but with very shallow depth of the nanopores. The contact angles of the water droplet on the anodic stainless steel surface is less than 90.0°, and that on the Teflon-coated surface is about 125.9°±2.4°. It can be understood from the contact angles of various coating layers that the Teflon-coated layer shows superhydrophobicity while the rest of the surfaces show hydrophilicity. However, as liquid nitrogen shows superhydrophilicity on nearly all the surfaces, therefore the effect of wettability on cryogenic quenching can be reasonably ruled out when comparing different coating layers.

3. Experiments and methods

3.1. Experimental set-up and procedure

The experimental setup is shown in Figure 1(a). A cryostat with visualization windows is used as the experimental vessel, which works at the atmospheric pressure through an outlet opening on the top flange. The test section is a thin metal rodlet (6061 aluminium alloy or 316L stainless steel) with a diameter of 10.0 mm and a length of 100.0 mm. A half-through hole with a diameter of 1.0 mm was drilled along the central axis, in which a thermocouple was inserted to measure the temperature history during the quenching process, as shown in Figure 1(b). The quenching experiment was performed in an air-conditioned room with an initial temperature of around 296.0 K. At least three independent experimental runs were performed on each rodlet to guarantee the repeatability. The rodlet was dropped into liquid nitrogen bath where it was maintained until the temperature was stabilized,
equalling the saturation temperature of the liquid nitrogen at one atmosphere pressure. The rodlet was then thoroughly dried and recovered to room temperature for the next experimental run.

![Figure 1](image)

**Figure 1.** Schematics of experimental set-up and test section. (a) Experimental set-up. (b) The metal rodlet

### 3.2. Data reduction and uncertainty analysis

In general, the inverse heat conduction equation was solved to obtain the transient surface temperature and surface heat flux through the measured temperature history at the centre of the rodlet. The analysis is conducted by solving the heat conduction equation with the constant thermo-physical properties [7] so that the outer surface temperature and heat flux of the rodlet can be consequently obtained. However, such simple calculation neglects the variation of the thermo-physical properties with the temperature and the thermal resistance between the substrate and the coating layer, which inevitably leads to a certain of uncertainties in results. Therefore, in the present study, the inverse heat transfer analysis [8] was carried out by numerically solving the following equations iteratively to estimate the surface temperature and surface heat flux. In the calculation, only one-dimensional inverse heat conduction was considered because the length of the rodlet was far larger than that of the diameter.

\[
\frac{\partial q}{\partial r} = -\frac{q}{r} + c_p(T) \rho(T) \frac{\partial T}{\partial t} \quad 0 < r < R + \delta \tag{1}
\]

\[
\frac{\partial T}{\partial r} = -\frac{q}{\lambda(T)} \tag{2}
\]

where, \( q_0(t) = 0, \quad T_0(t) = f(t) \)

The uncertainty analysis was conducted by using the uncertainty propagation theory. The uncertainties of the measured parameters and the derived parameters were obtained and it is shown that the uncertainty for the central temperature is about 0.76 % and those of the surface temperature and heat flux were estimated to be 0.83% and 9.3%, respectively.

### 4. Results and discussions

#### 4.1. Quenching of the anodic aluminium alloy rodlets

Shown in Figure 2(a) are the temperature evolutions on the outer surface of the AAO and RAAO samples, and the cryogenic quenching curve of the smooth surface is also shown for comparison. In general, there exists a film boiling regime that takes quite a long time for which the enhancement is endeavoured. Apparently, there is significant difference among the smooth, AAO and RAAO rodlets. At the beginning of quenching, the temperatures of the rodlets decrease slowly without evident differences, which corresponds to the film boiling regime. Then, the slope of the curve for the AAO surface increases sharply at a much earlier time than those of the RAAO and smooth rodlets, and the
temperatures are finally stabilized at liquid nitrogen temperature at the end of the quenching. The point, at which the quenching rate suddenly increases is known as the Leidenfrost point (LFP). Ahead the appearance of the LFP, the film boiling takes place, and then the heat transfer state on the rodlet enters transition boiling with a quite large increase in quenching rate. This change of quenching rate takes place at around 210 K on the AAO rodlet, at around 139 K on the RAAO rodlet and at around 114 K on the smooth rodlet based on the outer surface temperature. Thus, it can be understood from the quenching curves in Figure 2 that the higher LFP temperature resulting in shorter film boiling regime of the AAO rodlet leads to a shorter total quenching time to complete the quenching process.

![Figure 2](image.png)

Figure 2. Quenching curves (a) and heat transfer curves (b) of the AAO and RAAO rodlets. The superheat is defined as the surface temperature subtracting the saturation temperature of liquid nitrogen.

As indicated in the above text, the effective surface thermal resistance of the AAO and RAAO samples are approximately the same. Thus it is possible to demonstrate the effect of the nanopore structure on quenching clearly by comparing the experimental results of the AAO and RAAO rodlets. The curves of quenching heat flux versus temperature are shown in Figure 2(b), where that of the smooth surface is also presented. It is found that the LFP temperature of the AAO rodlet is about 71 K higher than that of the RAAO rodlet, and the heat transfer in nucleate boiling regime is reduced as demonstrated by smaller heat flux on the AAO rodlet than that on the RAAO rodlet, as shown in Figure 2(b).

In the present study, film boiling occurs at the beginning of quenching process due to high initial surface superheat (~220K), as shown in Figure 2(b), where there is little difference between the AAO and RAAO rodlets due to the fact that the nanopores on the AAO rodlets have little effect on the heat transfer of the film boiling. In the film boiling regime, liquid nitrogen is separated by a layer of vapour film which serves as the main thermal resistance for heat transfer, where nanopores do not impose large effect on the heat transfer due to the presence of vapour phase. When the surface temperature of the AAO rodlet decreases to below the LFP temperature, the liquid-vapour interface is formed above the nanopores at the local position where intermittent liquid-solid contacts start to occur. The existence of the liquid-vapour interface reduces the liquid-solid contact area at the local position, which leads to insufficient vapour generated locally to maintain the vapour film from collapsing. Therefore, the LFP on the AAO rodlet occurs at a much higher surface temperature than that on the RAAO rodlet. As the surface temperature decreases, the heat transfer state enters transition boiling, as shown in Figure 2(b), where the surface area allowing liquid-solid contact increases, as a result, the heat flux increases. When liquid contact eventually overcomes the dry area on the sample surface, the critical heat flux (CHF) point appears and then it appears the developed nucleate boiling, as shown in Figure 2(b). Afterwards, as the temperature decreases, the number of the activated nucleation sites decreases,
which results in the heat transfer entering partial nucleation boiling state. With the further decrease of surface temperature, the heat transfer is mainly dominated by natural convection when the bubble disappears. Because the rodlet surface is superhydrophobic to liquid nitrogen, and the nucleation of bubbles on the surface is greatly inhibited, natural convection occurs at a higher surface temperature. Therefore, as the surface superheat decreases further to below around 14 K, as shown in Figure 2(b), where the heat flux reaches the local minimum. Afterwards, liquid nitrogen penetrates into the nanopores with the decrease of the surface superheat, where the heat flux on the AAO rodlet increases again due to the increase of the liquid-solid contact area. As a consequence, a secondary heat flux peak appears.

4.2. Quenching of the stainless steel rodlets with different coating layers

A smooth stainless steel (SSS) rodlet and an anodic stainless steel (ASS) rodlet were quenched in liquid nitrogen under the same condition. As shown in Figure 3(a), the LFP takes place at around 117.7 K on the ASS sample, and is higher than that of the SSS sample which is about 100.8 K. The improved LFP temperature by the anodic layer on the ASS rodlet reduces the quenching time from about 115.1 s to 104.0 s, which demonstrates the feasibility of the application of anodic oxidation method on the commercial available stainless steel to improve the quenching heat transfer in practice. As compared with anodic aluminium alloy rodlet, the quenching time is considerably longer for the stainless steel rodlet to drop from room temperature to liquid nitrogen temperature, and the LFP temperature on the stainless steel rodlet is much lower as well, which might be due to the reason that the comparatively much lower thermal conductivity of the stainless steel as compared to that of aluminium alloy, resulting in the evidently prolonged time duration of the film boiling. Shown in Figure 3(b) are the heat transfer curves for the SSS and ASS rodlets, where the CHF of the ASS rodlet is much larger than that of the SSS rodlet. However, as compared to the case of the aluminium alloy rodlet, the anodized coating layer on the stainless steel does not show so evident enhancement as the AAO rodlet, which might be attributed to the thin thickness of the anodized coating layer. Therefore, we further appeal for the Teflon coating layer on the stainless steel rodlet for possible cryogenic quenching enhancement.

Figure 3. Quenching curves (a) and heat transfer curves (b) of the anodic stainless steel rodlet and smooth stainless steel rodlet.

Shown in Figure 4 are the quenching curves and the heat transfer curves of the Teflon-coated stainless steel rodlets. It is apparent that the quenching times are much shorter than that of the smooth stainless steel rodlet shown in Figure 3(a). As reported in the previous study [5], a thin coating layer with low thermal conductivity can effectively enhance the cryogenic quenching. Therefore, a thin layer of the Teflon coating can largely enhance the LFP temperature and therefore shorten the total
quenching time. With the increase of the thickness of the Teflon coating layer, it appears that the film boiling regime is even absent on the quenching curve, and the initial cooling rate is very large, as shown by the result of the rodlet with 120 μm thickness in Fig. 4(a). However, the cooling rate of the rodlet with thicker coating layer decreases at the latter stage where the nucleate boiling dominates, see Figure 4(b), thus resulting in the similar total quenching time compared to the rodlet with 60 μm thickness, as shown in Figure 4(a). Therefore, it can be conjectured from such results that there might exist an optimum thickness of the Teflon coating layer which can lead to the shortest cryogenic quenching time.

![Figure 4. Quenching curves (a) and heat transfer curves (b) of the Teflon-coated rodlets with different coating layer thicknesses](image)

5. Conclusions
In the present study, the cryogenic quenching experiments are conducted on the aluminium alloy and stainless steel rodlets with various coating layers. An increase of 71 K of the LFP temperature and a more than 50% reduction of total quenching time are realized by the nanopore structure on the AAO rodlet, as compared with the RAAO rodlet. This is because that the nanopore structure on the AAO rodlet reduces the local vapour generation rate which results in a higher LFP temperature. In addition, the vapour filled nanopores in the nucleate boiling regime decrease the heat flux on the AAO rodlet and a unique secondary heat flux peak is observed as the temperature drops which is due to liquid nitrogen infiltrating into the nanopores. Moreover, the feasibility of the application of anodic oxidation method to the stainless steel rodlet to improve the quenching performance in practice is verified in the present study. The further investigations on the Teflon-coated rodlets show that such a simple coating layer can effectively enhance cryogenic quenching and reduce the total quenching time up to more than 50%. More experimental investigations about an optimum thickness of the Teflon coating layer can pave the way towards the practical application.

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