

Review



Micro-Nano Scale Surface Coating for Nucleate Boiling Heat Transfer: A Critical Review

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Abstract: Nucleate boiling is a phase change heat transfer process with a wide range of applications i.e., steam power plants, thermal desalination, heat pipes, domestic heating and cooling, refrigeration and air-conditioning, electronic cooling, cooling of turbo-machinery, waste heat recovery and much more. Due to its quite broad range of applications, any improvement in this area leads to significant economic, environmental and energy efficiency outcomes. This paper presents a comprehensive review and critical analysis on the recent developments in the area of micro-nano scale coating technologies, materials, and their applications for modification of surface geometry and chemistry, which play an important role in the enhancement of nucleate boiling heat transfer. In many industrial applications boiling is a surface phenomenon, which depends upon its variables such as surface area, thermal conductivity, wettability, porosity, and roughness. Compared to subtractive methods, the surface coating is more versatile in material selection, simple, quick, robust in implementation and is quite functional to apply to already installed systems. The present status of these techniques for boiling heat transfer enhancement, along with their future challenges, enhancement potentials, limitations, and their possible industrial implementation are also discussed in this paper.

Keywords: nucleate boiling; phase change heat transfer; energy efficiency; surface coating; pool and flow boiling; heat exchangers

1. Introduction

Heat transfer is a thermophysical phenomenon and is involved in every energy conversion, utilization, and recovery process. Its enhancements require physical improvements in the heat transfer system, which will, in turn, decrease its size (material saving), pumping power and volume needs [1]. Any developments in this area would potentially lead to improvements in the overall energy efficiency and reduction in size and cost of the system and operations. The main advantage of the phase change heat transfer is its ability to transfer a large amount of heat energy within a given time and volume. Boiling is a multi-phase and efficient thermal energy transfer process due to its high latent heat [2]. Boiling heat transfer is applied in processes where high heat flux is needed to be removed i.e., nuclear power plant [3,4], desalination [5,6], or where space is confined such as electronic cooling and thermal management of data centers [7–10], thermal management of batteries [11], heat pipes [12,13] and microfluidic systems [14–17].

Available heat transfer enhancement techniques in literature can be broadly classified as active, passive and compound technique, as shown in Table 1. In the active techniques, the overall heat transfer of the system is improved by the help of external power while in passive techniques, no external

power is required. Compound techniques, on the other hand, are the combination of both active and passive techniques at the same time. Passive techniques have higher reliability, as compared to active techniques, due to the absence of moving components and auxiliary power [18]. Treated surfaces methods mainly deal with coating or alteration of the surface structure at fine, i.e., micro to nano, scale. Recent developments in the field of micro-nano scale manufacturing and surface functionalization expanded further the boundaries of heat transfer enhancement through surface treatment. Although micro-nano scale surface modifications are mainly used in the phase-change heat transfer process i.e., boiling, condensation, and freezing [19–22], they are also found effective for single-phase heat transfer convection [23–25].

Passive Techniques	Active Techniques				
Treated Surfaces	Mechanical Aids				
Rough Surfaces	Surface Vibration				
Extended Surfaces	Fluid Vibration				
Displaced Enhancement Devices	Electrostatic Fields				
Swirl Flow Devices	Injection				
Coiled Tubes	Suction				
Surface Tension Devices	Jet Impingement				
Additives for Liquids					
Additives for Gases					
Compound Enhancement					
Two or more passive and active techniques that are employed together.					

Table 1. Classification of Heat transfer enhancement techniques [1].

Working fluid and solid surfaces are two main variables to modify for enhancing boiling heat transfer [26–28]. Most of the time, the working fluid is not possible to modify due to restrictions that arise from applications i.e., water desalination, steam power generation cycles etc. Hence, the surface remains as a key variable to modify. This is where micro-nano scale surface enhancements through surface roughening (usually through fabrication and deformation) or surface coating techniques come into play. In almost all of the industrial applications, boiling is a surface phenomenon and depends on properties of the surface such as roughness, porosity, and wettability. In nucleate boiling heat transfer, nucleation, growth, frequency, and departure of vapor bubbles are strongly linked to topology and chemistry of the associated surface. The micro-nano scale coating provides an efficient solution for altering the surface parameters, according to the optimization conditions of the specific application [29]. Compared to subtractive methods, surface coating is simple, quick, more versatile in material selection and geometry, robust in implementation and quite functional to apply to already installed systems.

The aim of this paper is to review surface coating methods applied to nucleate boiling heat transfer, specifically with recently developed micro-nano scale coating techniques. A critical review of the present status of these methods, along with their future challenges, enhancement potentials, limitations and their possible industrial implementation are discussed in this paper.

2. Enhancement of Nucleate Boiling Heat Transfer: Overview

Heat is transferred from a solid surface to liquid during nucleate boiling, and convection is the main heat transfer mechanism due to the motion of the fluid [30]. Surface tension and difference in density, which results in buoyancy force, are two important parameters other than latent heat in this phenomenon. The buoyancy driven flow and latent heat of boiling heat transfer results in its high heat transfer rate, as compared to single-phase convection [31]. In boiling heat transfer, nucleate boiling is a desirable phenomenon due to its high thermal performance. Due to the involved phase-change heat transfer, the physics of this phenomenon is very complex and still not very well understood [32]. We will discuss these briefly in the coming sections.

It is important to understand the mechanism of how boiling phenomena transfer a huge amount of heat energy. During nucleate boiling, a bubble grows at nucleation site on the hot surface and moves up by overcoming the surface tension. Heat is being removed when the bubble departs from the hot surface. The rate of overall heat transfer is significantly affected by dynamic parameters of the bubble such as bubble nucleation density, departing diameter, frequency, growth rate and waiting period [33]. According to the vapor-liquid model, the amount of heat transfer with the bubble is equal to the heat energy required to raise the temperature of an equal amount of liquid from liquid temperature to the average of liquid and wall temperature [34]. Approximately 100 times more energy, in form of latent heat, required to boil 1 g of water than the energy required to raise its temperature by 5 K [35].

In order to understand the physical mechanism of how bubble transfers energy during nucleate boiling, other models such as the transient conduction model (TCM), the micro-layer heat model (MLM), and the contact line model (CLM) have been developed, as reported in the literature. According to TCM of Mikic et al. [36], when vapor is departing from the surface it takes away a superheated layer from its surrounding, equivalent to twice its diameter, and then cold water comes in contact with this surface and the process repeats. According to MLM of Sydney and Edwards [37], a thin liquid layer at the hot surface is trapped by a growing bubble, which evaporates and transfers a large amount of heat. The resultant decrease in temperature after evaporation of microlayer was also validated later by Moore and Mesler [38] and Hendricks and Sharp [39]. While CLM of Stephan and Hammer [40] states that the main cause of heat transfer in nucleate boiling is the evaporation of thin meniscus of the liquid layer at the contact point of three phases (solid substrate, gas bubble, and liquid). After studying of all three models, Kim [41] concluded that micro-convection and transient conduction are the main phenomenon in the heat transfer of a bubble during boiling. There are different opinions among researchers about these models. But all agree on the point that the resultant boiling bubble in nucleate boiling appears at the solid surface, which reflects the importance of surface modification as a key variable to enhance the overall phenomena.

Before going into detail about the boiling heat transfer enhancement through micro-nano scale surface coatings, the physics involved in the boiling phase-change heat transfer is reviewed here. Nukiyama [42] introduced the boiling curve, which describes different states of the nucleate pool boiling mechanism, as shown in Figure 1. The transition from Nucleate Boiling Heat Transfer (NBHT) to Film Boiling (FB), Critical Heat Flux (CHF), and Heat Transfer Coefficient (HTC or *h*) are the key factors to understand for efficiency improvement of this phenomenon. In addition, CHF and HTC are also the key parameters for the performance measurement of the boiling process. Increasing HTC and CHF have a substantial effect on the overall efficiency, cost, and safety of the process [43].

2.1. The Transition from Nucleate Boiling Heat Transfer (NBHT) to Film Boiling (FB)

The phenomena of NBHT can be best understood by the well-known boiling curve, Figure 1. In this curve, q''_s represents the heat flux, T_s is the surface temperature, T_{sat} is the saturation temperature and h is the heat transfer coefficient. The nucleation of bubbles on hot surface, and hence the boiling process, starts when T_s exceeds T_{sat} . Nucleate boiling heat transfer (NBHT) is a boiling regime where more mature vapor bubbles nucleate on the surface and are quickly removed. New bubbles appear at nucleation sites just after the departure of these bubbles and the process continues. This motion of bubbles produces more advanced fluid mixing in the region near the surface and enhances q''_s and h [31]. The number of nucleation sites increase and bubbles merge until its maximum limit called critical heat flux q''_{max} .

By increasing heat flux above a certain limit, the rate of bubbles generation overcomes its rate of departure. The bubbles start to merge together and form a film of vapors. As the thermal conductivity of vapor is less than that of the liquid, q''_s starts to decrease after this point and a layer of bubbles covers the whole surface forming a vapor film, which forces the transformation from NBHT to Film Boiling (FB) regime. Due to transition from convection to radiation, heat transfer from the surface decreases, which results in a significant increase in surface temperature. The transition from nucleate to film

boiling is an undesirable state, however, there is always a limit for every boiling above which this conversion occurs. Improvement in NBHT and delaying FB are two common goals in enhancing the performance of boiling heat transfer devices. Nucleate boiling and film boiling, for the same surface and working fluid at different working conditions, are shown in Figure 2.



Figure 1. Boiling heat transfer curve, q_s'' heat flux as a function of (Ts – Tsat) [31].



Figure 2. For same substrate and boiling fluid, two different conditions: (**a**) Nucleate boiling; (**b**) Film boiling [31].

2.2. Critical Heat Flux (CHF)

CHF was first introduced in the hydrodynamic model centered on the principle of Kelvin–Helmholtz instability [44,45]. CHF is the maximum limit of NBHT occurring when $q''_s = q_{max}$ and is also performance parameter. Due to high efficiency of the boiling process near CHF, every design process' goal is to work near this limit. But care needs to be taken, as a little increase in surface temperature can lead the process to inefficient film boiling zone [31].

For the efficient and safe operation of boiling heat transfer system, it is very important to know the precise value of CHF [46,47]. High CHF value with low surface temperature is the goal of every design of NBHT. The very high value of CHF but at a very high surface temperature (i.e., low *h*) or vice versa are not suitable conditions for the nucleate boiling process. Although the phenomenon of CHF is not still well understood, however, there are studies in literature trying to predict CHF value and attempt to explain. The review of such studies is presented by Liang and Mudawar [48,49]. For example, Kandlikar [50] reported that vapor recoil force causes the bubbles to make a film on the substrate surface. This study also presented a theoretical model for CHF and verified with experimental data.

2.3. Heat Transfer Coefficient (HTC/h)

Thermodynamic efficiency of NBHT can be best reparented by HTC [35], which can be seen as the slope of the NBHT curve. If q_s'' increased beyond CHF, HTC decreased drastically due to formation of vapor film on hot surface. This increases the surface temperature undesirably and often reached up-to destructive level, known as "dry out" condition.

3. Surface Coatings for Boiling Heat Transfer Enhancement

Ho et al. [51] reported for the first time the effectiveness of surface roughness in NBHT process. Topography is a geometric property of a surface that varies with pitch, shape, height, depth, etc. and each one of them significantly affects the function of the surface. This indicates infinite possibilities for surface modification and provides ample room for improvement of boiling heat transfer [35,52]. Surface coatings provide a robust and efficient solution to modify surface according to the requirement of the heat transfer phenomena. Researchers have used different coating techniques for boiling heat transfer enhancement i.e., sintering [53], spraying [54], plasma coating [55] and electrochemical deposition [56]. They have used materials such as metals, polymers, ceramics and composites for complex geometries and shapes, i.e., 3D porous structures, pyramids, bumps, pillars in micro-nano-scales. This modification of micro-nano scale affects different parameters in boiling heat transfer such as nucleation sites, roughness, wettability, and porosity.

Comprehensively, surface (s), temperature (T) and pressure (P) conditions along with working fluid properties (i.e., viscosity, thermal conductivity and heat capacity) are main parameters for NBHT [27], expressed as:

$$q''_{NB} = f(\text{fluid property, surface characteristics}) * [T_{wall} - T_{sat}(PI)]^{\text{constant}}$$
 (1)

In NBHT, important properties of working fluid are density, viscosity, surface tension, thermal conductivity; properties of the surface include geometry, wettability, and roughness, whereas process conditions include operating temperature and pressure [57,58]. Engineered surfaces at micro-nano scale for boiling heat transfer facilitate nucleation and maximize CHF by preventing or delaying film boiling [59–61]. For example, the cavities on the surface originate bubbles and entrap them inside [62–66]. Similar studies also substantiated that surface roughness and cavities increase the number of nucleation points during NBHT [67,68].

Surface modification techniques for NBHT enhancement can be classified as (1) mechanical shaping processes i.e., machining, deforming using roughness tools, CNC, laser machining and sandblasting techniques [51,69,70], (2) surface coating processes i.e., chemical vapor deposition (CVD), physical vapor deposition (PVD), spraying, plasma, (3) chemical processes i.e., oxidation,

etching and photochemical etching [71–74] and (4) micro-electro-mechanical systems (MEMS) and nano-electro-mechanical systems (NEMS) techniques [46–48]. In the literature, the performance of any modified coated surface is evaluated by comparing its heat transfer coefficient (HTC) and critical heat flux (CHF) with the corresponding untreated surface [75–77]. In the coming sections, we will discuss different types of surface coatings to enhance boiling heat transfer. The classification of the coating can be summarized as follows: (a) Nanoparticle coating (NPC): metals and ceramics; (b) Micro-scale surface coatings (MSSC); (c) Hydrophobic and hydrophilic surface coating to control wettability; and (d) Carbon-based nanoparticles coating (CbNPC). The hybrid coating as combination of above coatings are covered in this section.

3.1. Nanoparticle Coatings: Metals and Ceramics

Apparent properties of nanofluids such as high thermal conductivity, a non-linear relationship between the particles concentration and thermal conductivity, and high HTC make it an interesting medium for boiling heat transfer [78–83]. You et al. [84] investigated for the first time the effect of nanofluids for boiling heat transfer. They studied alumina-water nanofluids (concentration up to 0.01 vol.%) vs. pure water for pool boiling heat transfer and stated an increase in CHF up to 200%. Later on, the focus of research changed when Vassallo et al. [85] reported the deposition (settlement) of nanoparticles on the substrate, during the study of pool boiling for silica nanofluids and silica micro-solution. They explained that it was not the gravitational force, which caused their settlement, but rather, was the evaporation of fluid during bubble departure. During the growth of the bubble, the nanoparticles settled down and attached to the hot surface. The concentration of these particles increased with time and formed a porous layer. This observation has been confirmed recently by optically observing the active nucleation site, by Kim [86], Figure 3.

Kim et al. examined surface modification with nanofluids (alumina, zirconia, and silica nanoparticles) and its effect on overall heat transfer [87–90]. They found that there was no considerable difference between the samples treated with different nanofluids. The deposition (settlement) of nanoparticles on the heated surface caused porous coatings, which increased the overall surface area and wettability of the surface, and decreased its static contact angle as shown in Figure 4. Hence, an increase in wettability and overall surface area caused an appreciable increase in nucleate boiling CHF. Many other researchers have investigated the role of nanoparticle coatings on a substrate surface and reached the same conclusion [91–93]. Watanabe et al. [94] investigated the adhesion of the deposited nanoparticle coating and its detachment effect on NBHT performance. They reported that adhesion force of nanoparticle coating highly depends on the type, size and distribution of the nanoparticle material. Both CHF and HTC values were reported to increase with the nanoparticle coating.

For nanofluids in NBHT, researchers also reported both enhancement and decline of CHF and HTC [95–97]. The settlement of nanoparticles increased the surface roughness [98] and wettability [99], and hence boiling performance but on the other hand suspended nanoparticles in nanofluid might have hindered the movement of the bubbles and caused a decrease in the overall heat transfer performance [100,101]. In all these and similar investigations, the results were always compared by changing the surface from clean to nanoparticle-deposited surface and keeping the nanofluid same. To get a clear understanding of the contribution of nanofluids and of the suspended nanoparticles, White et al. [102] performed experiments by changing the base liquid from pure to nanofluid. They found that increased surface roughness due to nanoparticle deposition significantly increased the performance for base fluid and declined slightly for nanofluid. The increase is attributed to surface roughness and decline to the suppression of the bubble formation and motion of suspended nanoparticles. Nanofluid boiling is considered widely for the nanoparticle coating in pool boiling heat transfer. However, the deposition or settlement of nanoparticles using boiling technique is difficult to control. White et al. [103] used electrophoretic deposition (EPD) technique to coat stainless steel plate.

EPD have a high level of automation and control where charged particles are attracted by a conducting substrate using an external electric field.



Figure 3. Nanoparticle coating during nucleate boiling heat transfer [86].



Figure 4. Wettability changes of stainless steel surface by the representation of contact angle: (**a**) Drop of pure water on stainless steel surface boiled in pure water; (**b**) Drop of alumina nanofluid on stainless steel surface boiled in pure water; (**c**) Drop of pure water on stainless steel surface boiled in alumina fluid; (**d**) Drop of alumina nanofluid on stainless steel surface boiled in alumina fluid; (**d**) Drop of alumina nanofluid on stainless steel surface boiled in alumina fluid.

Nanoparticles are also used with other micro-nano coatings as a hybrid coating due to its properties of act as nucleation points for bubble generation and also increase an overall surface area [104–106]. Using this concept, nanoparticles can be used to increase bubble nucleation. Jaikumar and kandlikar [107] investigated the effect of nanoparticle coating on selectively open microchannel for pool boiling heat transfer. Three different coating patterns, i.e., overall coating, the coating on fin tops and coating between the fins (channels) were analyzed as shown in Figure 5. The nanoparticle coated areas appeared as the source points for bubble nucleation and enhanced the heat transfer, i.e., both CHF and HTC. The greatest enhancement out of these three configurations was noted for the channel coatings. The uncoated fin top worked for the water supply as a jet impingement mechanism, for nucleation points inside the channels. Nanoparticle coating can also be applied for controlling surface wettability to enhance NBHT. Kim et al. [108] investigated hybrid Al₂O₃ and reduced graphene oxide (RGO) colloids, and compared their performance with that of RGO and Al₂O₃ nanofluid. The maximum increase in CHF for RGO and Al₂O₃ suspension were 37% and 54%,

respectively. However, Al_2O_3 and RGO composite resulted in the highest enhancement in CHF with 473%. In a similar study, Gupta and Misra [109] reported 260% and 68% enhancement in HTC and CHF for hybrid Cu and Al_2O_3 colloids.

Forrest et al. [110] coated nickel wire and stainless-steel plate with silica nanoparticles using the method of the layer by layer assembly. This study reported a significant increase in CHF and HTC. Depending upon final treatment, both hydrophilic and hydrophobic surfaces were obtained and reported enhanced results for CHF and HTC. Also, calcination was applied to make the coating porous, which might affect CHF as the overall area was increased. The comparative analysis of CHF enhancement using metals and ceramics nanoparticles coating, among referenced articles, can be seen in Figure 6. Similar studies of surface coating with nanoparticles, NBHT, are summarized in Table 2.



Figure 5. Proposed mechanism of selectively coated micro channel's heat transfer [107].



Figure 6. Maximum enhancement of Critical Heat Flux (CHF) by modification of the substrate with nanoparticles. Refer to Table 2, for detailed conditions of the studies listed on the *X*-axis. On *Y*-axis, "m" represents coated modified surface and "un" represents the uncoated untreated surface.

S. No	Substrate	Type of Nanoparticles	Preperation Techniques	Working Fluid	Enhancement	Ref.
1	Nickel wires	Silica nanoparticles	Layer by layer (lbl) assembly method	Water	100%	[110]
2	Cu plate	Al ₂ O ₃	Nanofluid boiling	Water	Enhanced	[111]
3	Cu	TiO ₂	Nanofluid boiling	Distilled water	HTC by 38%	[112]
4	Cu	Al, Cu, Ag and diamond particles	Dipping and backing	FC-72	Enhancement: up to 4.5 times in HTC and 2 times in CHF	[113]
5	Platinum	Diamond	DOM coating	FC-72	$\simeq 100\%$ CHF enhancement	[114]
6	Cu plate	ZrO ₂	Nanofluid boiling	Water	Enhanced	[115]
7	Stainless stell disk	ZnO	Electrophoretic deposition	ZnO-propylene	200%	[103]
8	untreated rectangular heater	Al_2O_3	Nanofluid boiling	Water	32%	[116]
9	Nicr wire	SiO ₂	Nanofluid boiling	Water	Enhanced by 3 times	[85]
10	Aluminum and copper	Cu, Al, bronze, and corundum particles	Plasma sprayed coating	Freon	Max. Enhancement up-to 32%	[117]
12	Small horizontal tube with diameter 4 to 6.5 mm	Al ₂ O ₃	Boiling nanofluid	Water	Enhanced	[65]
13	Pt Wire And Heater(Square)	Al ₂ O ₃	Nanofluid Boiling	Water	CHF By 200%	[84]
14	Cu machined surface and polished surface	Al ₂ O ₃	Nanofluid Boiling	water	Enhancement up-to: 7% in CHF, and 37% in HTC	[118]
15	Cu surface	Cu-Al ₂ O ₃	Electrochemical deposition	DI water	Enhancement up-to: 68% in CHF, and 260% in HTC	[109]
16	Cu surface	GO and Cu particles coating	Screen printing and electrodeposition	water	Enhancement up-to: 1.8-fold in CHF, and 2.4-fold in HTC	[119]
17	Cu surface	Micro-nanostructured surfaces	Femtosecond laser processing	N-pentane	Enhancement up-to: 60% in CHF, and 300%in HTC	[120]
18	Cu surface	TiO ₂ nanoparticles film	Electron beam evaporation method	R134a	HTC increased by 87.5%	[121]
19	Cu surface	SiO ₂ nanoparticles film	Electron beam evaporation technique	water	HTC increased by 80%	[122]
20	Cu surface	Cu-TiO ₂ nanocomposite	Electrocodeposition	DI water	CHF increased up to 92%	[109]
21	Flat Stainless steel surface	Al ₂ O ₃ nanoporous surface	Electrophoretic deposition	Pure SES36 fluid	Maximum HTC increased by 76.9%	[123]

Table 2. Nanoparticle coatings for boiling heat transfer.

3.2. Wettability: Hydrophobic and Hydrophilic Coatings

Recent studies showed that hydrophilic and hydrophobic surfaces have significant abilities for boiling heat transfer enhancements [124–128]. Modified surfaces with the ability to enhance HTC (Heat Transfer Coefficient) and CHF (Critical of Heat Flux) values show at least one of the following properties: (a) increase in the frequency of the bubbles, (b) increase in the nucleation sites, (c) reduction of bubble's contact area, (d) low onset superheat for nucleate boiling [129,130].

Betz et al. [131] reported wettability behavior for boiling heat transfer, i.e., hydrophilic surfaces delay film formation while hydrophobic increase the number of nucleation density. They studied different patterns including hydrophilic and hydrophobic networks for pool boiling, as shown in Figure 7. For all the patterns, higher results of heat transfer coefficient (HTC) and critical heat flux (CHF) were reported. The maximum enhancement of 65% and 100% were achieved for HTC and CHF, respectively. In another study, Betz et al. [132] studied hydrophilic, hydrophobic, superhydrophilic, superhydrophilic coated surfaces as shown in Figure 8 Superhydrophilic

(SPHi) are the surfaces with close to zero contact angle and superhydrophobic (SHPo) are surfaces with a contact angle of larger than 150° with water. While biphilic are surfaces of hydrophilic and hydrophobic collocate and superbiphilic are surfaces with juxtaposing of SPHi and SHPo surfaces. Interestingly, enhanced results for CHF and HTC were achieved for biphilic surfaces as compared those of surfaces of uniform wettability. Very high values of CHF over 100 W/cm² and HTC over 100 kW/m²K were obtained for superbiphilic surfaces. They developed an analytical model to describe the enhanced behavior of these surfaces.



Figure 7. Patterns of hydrophobic and hydrophilic as gray and black colors coating [131].



Figure 8. Four different types of hydrophilic, hydrophobic, super hydrophilic, super-hydrophobic, biphilic and superbiphilic surfaces [132].

Hsu and Chen [133] used a coating of nano-silica particles on Cu surface to change wettability from superhydrophilic to super-hydrophobic. Wettability of the surface was modified by changing its chemistry and topography. This study presented a simple model for the relation between bubble growth and wettability of the surface. Zupančič et al. [129] introduced a new method of using pulsed neodymium-doped yttrium aluminum garnet (Nd:YAG) laser for biphilic hydrophobic/superhydrophilic pattern coating from polydimethylsiloxane-silica. Biphilic surfaces were developed with different spots sizes on stainless-steel foil, Figure 9. Results showed that smaller hydrophobic dots increased the bubble's nucleation frequency and decreased its diameter.

While surfaces with larger dots promoted NBHT and have high HTC at low heat flux. Highest CHF of 200% higher was achieved as compared with an untreated stainless-steel surface. An optimum-sized biphilic pattern was suggested in this study.

A network of hydrophobic on hydrophilic surfaces gives enhanced results for boiling heat transfer as reported by many researchers. However, hydrophobic and superhydrophobic coated surfaces do not show improved results as they promote the transition from nucleate to film boiling. In order to understand this phenomena, Takata et al. [134] prepared superhydrophobic surfaces by coating fine particles of nickel and PTFE. A static contact angle of 152° was achieved. The results showed the formation of a vapor film on the heated surface even before the starting of nucleate boiling. At saturation temperature, bubbles appeared and combined with each other to form a film of vapor. However, it is worth noting that in some cases hydrophobic coating with very high conductivity gives enhanced performance. For example, carbon nanotubes (CNT) are highly hydrophobic and conductive in nature: studies proved that their coating gives significant enhancement results in boiling heat transfer [134].

Takata et al. [135] reported the superhydrophilic surface as an ideal heat transfer surface. TiO_2 coating has high affinity to the liquid and its contact angle reaches to almost zero in ultraviolet light. Using this concept, they studied TiO_2 coating on Cu and glass for pool boiling and reported 2 times enhancement in CHF. The durability of such modified surfaces in intense boiling conditions is still a major challenge. Further work needs to be performed with respect to durability, cost and a better understanding of boiling heat transfer behavior on biphilic surfaces [129]. For wettability alteration, various other coating material and techniques have been designed, developed and tested in literature and enhanced results are reported, as summarized in Table 3.



Figure 9. Hydrophilic and hydrophobic coating using pulsed neodymium-doped yttrium aluminum garnet (Nd:YAG) laser technique [129].

S. No	Substrate	Coating Material	Coating Technique	Nature (Hydrophilic/Hydro-Phobic)	Ref.
1	Heating surface	Nickel with polytetrafluoroethylene (PTFE) particles	Electrolytic nickle coating with PTFE particles	Hydrophobic	[134]
2	Ni Wires of 0.25 mm	PAH/SiO ₂	Layer by layer assembly method	Hydrophilic, hydrophobic and super hydrophobic	[110]
3	Stainless-steel foil	Polydimethylsiloxane-silica coating	Pulsed Nd: YAG laser	Biphilic (hydrophobic/superhydrophilic patterns)	[129]
4	Sapphire substrate	SiO ₂ nanoparticles and monolayer thickness fluoro silane	Layer by layer deposition	Hydrophilic and hydrophobic matrices	[136]
5	Cu substrate	Teflon layer (hydrophobic), TiO ₂ (hydrophilic)	Hydrophobic: photolithography. Hydrophilic by two step process: layer by layer self-assembly and liquid phase deposition	Hydrophobic, hydrophilic and mixed hydrophobic/hydrophilic	[125]
6	Stainless-steel	Silicon oxide and silicon carbide	Pulsed Nd: YAG laser	Hydrophobic and superhydrophobic patterns	[137]
7	Copper	Fe-Doped Al ₂ O ₃ -TiO ₂ Composite	Spray coating	Hydrophilic	[138]
8	Glass	Octadecyltrichlorosilane (OTD) to add hydrophobic layer	Immersion in ots mixture	Hydrophilic and hydrophobic	[139]
9	Copper	Cuprous and cupric oxides	Using alkali solution	Hydrophilic surfaces	[140]
10	TiO ₂	Photo-induced wettability	Ultraviolet light irradiation	Enhanced wettability	[141]
11	Metal tube	FeCrAl and Cr	Direct current magnetron sputtering	Hydrophilic and superhydrophilic	[142]

Table 3. Studies of hydrophilic and hydrophobic coating for boiling heat transfer study.

3.3. Micro-Scale Coatings

Micro scale surfaces result in better heat transfer performance by increasing CHF and by reduction of surface superheat [143–147]. According to different phenomenological theories, this enhancement is attributed to increasing the density of nucleation site, surface area, the capillary effect to assist liquid flow, and vapor escape paths [148,149]. Porous and modulated coating layers reduce the resistance of vapor and liquid opposite flow by separation of two phases. Optimal results can be obtained for the surfaces, which can ensure completely separate pathways for liquid and vapors. Figure 10, represents the ability of surface modification for heat boiling heat transfer as collected from experimental data of Litter and Kaviany [148]. They developed porous coating using spherical particles of copper, with an average diameter of 200 µm, on a copper substrate as shown in Figure 11. They compared the developed porous surfaces with untreated surfaces for pool boiling and reported enhancement of CHF up to 3 times. Hwang and Kaviany [150] studied pool boiling for different Cu particle diameter (40 to 80 µm), characteristics (hollow or solid particle) and fabrication process (pressed, shaken or loosely packed). In addition to the theoretical study of different configurations, they showed that completely separated liquid and vapor flow paths could result in significant enhancement [148]. Figure 12, represents the CHF enhancement capability of different surfaces with respect to plain untreated surface (p), deep porous layer coating indicates lower performance as compared to the plain surface, due to its reduced ability of liquid and vapor phase separation during boiling. The highest performance is indicated for the artery-evaporator configuration with the ability to completely separate the vapor and liquid phase. In order to achieve separate pathways for vapor and working liquid Jaikumar and Kandlikar [7] designed new surface geometry. Porous coating has been applied on fin top of copper surfaces. Bubbles were observed to appear on fin top and channel worked as a source of liquid for these vapors. They also reported channel width to depth ratio as an important parameter for the enhancement of the overall process.



Figure 10. Potential of surface modification for heat transfer [148].



Figure 11. (a) Conical stacks from Cu powder with average diameter of 200 μ m (b) porous layer with Cu particle of d = 200 μ m (average) with single height (SEM) [148].

Min et al. [151] developed a new method of hot powder compaction for 2-D and 3-D porous coated surfaces with different aspect ratio, pitch (modulation wavelength), particle sizes, and porosity. They reported the strong influence of wavelength and little effect of porosity and particle size on CHF,

during pool boiling experiments. Maximum enhancement in CHF of coated surfaces was reported 3.3 and 2.0 times higher as compared to plain surfaces. To control the vapor and liquid flow for efficient phase separation, Nasersharifi et al. [152] developed and tested several multilevel modulated wicks such as columnar, monolayer and mushroom posts wicks as shown in Figure 13. The surface was fabricated using 200 μ m copper particles by multi-step sintering process. The study reported up-to 250% of improvement in CHF value for n-pentane as working fluid.



Figure 12. Boiling heat transfer enhancement abilities with different configurations, the *y*-axis represents the increase in the CHF with respect to plain surface [148].

Similar to particle-based coating, direct coating of foam on the substrate also showed enhanced results for heat transfer enhancement. Yang et al. [153] studied Cu foam welded on Cu substrate for pool boiling, shown in Figure 14. They reported the enhancement of CHF pool boiling up to three times and a significant decrease in the onset of nucleate boiling as compared to the plain surface. Similarly, Xu and Zhao [28] studied Cu foam with nanoparticles for pool boiling. Coursey et al. [154] applied graphite and reported significantly enhanced results for pool boiling heat transfer experiments for PF-5060 and PF-5050 as working fluids. Wong and Leong [155] developed and tested 3-D printed porous lattice, fabricated by selective laser melting (SLM), for boiling performance. They reported 2.81 times enhancement in HTC as compared to the plain surface. In a similar study, Zhang et al. [156] tested 3-D printed grid structure manufactured by SLM technique. The CHF was reported to be enhanced by 3 times.

Deng et al. [157,158] used solid-state sintering method to develop porous structures with re-entrant cavities (PS-RC). Omega-shaped porous copper powder coating, shown in Figure 15 and Table 4, and solid structure of the same shape and material were prepared for comparison of nucleate boiling heat transfer. They demonstrated significantly improved results for both wall superheat and boiling heat transfer for ethanol and water tests for porous structures. The enhancement was reported due to increase in nucleation sites, overall surface area and enhancement in liquid replenishment.

Hybrid copper nanowires (CuNWs) and microgrooves were fabricated and tested for NBHT by Chen and Li [146]. First, 70 nm diameter of CuNWs were fabricated in three different heights of 5 μ m, 15 μ m, 25 μ m on plain Cu substrate via anodic aluminum oxide templates. Second,

microgrooves with different mesh pitches were fabricated to study the modulated wavelength effect on pool boiling CHF. Thirdly, hybrid of these CuNWs and micro-groves were fabricated to obtain two-tier structures. As compared to untreated flat Cu surface, the two-tier structures resulted in maximum CHF enhancement of 119.3%, followed by microgrooves by 110.5% and CuNWs by 68.6%. Mori et al. [159] proposed coating of hybrid porous cellulose beads and TiO2 nanofluid for the enhanced NBHT performance on a curved surface. The study reported 2 times enhancement of CHF. Zhou et al. [160] coated micro-pin-fins topped with nanoparticles, and reported enhanced boiling performance for FC-72 as working fluid. Cao et al. [161] performed a similar study by coating FeMn oxide nanoparticles on silicon micro-pin-fin configuration and reported enhanced CHF and HTC results. Figure 16 represents, the comparative analysis of CHF enhancement using micro-scale coating, among referenced articles.



Figure 13. Schematic of multi-level modulated wicks with liquid/vapor flow, wick geometries and hydrodynamic instability wavelengths studied by [152]: (Design A) plain surface; (Design B) monolayer; (Design C) columnar posts; (Design D) mushroom posts wicks [152].



Figure 14. Cu foam for boiling heat transfer enhancement by [153].



(a)



(b)



(c)



Figure 15. Re-entrant cavities with porous coating: (a) geometric dimensions; (b) cross-section of coating; (c) top view of coating; (d) profile of the surface [157,158].

S. No	Substrate	Coated Material	Geometry	Coating Technique	CHF	Ref.
1	Tin	Metallic copper foam	V shaped grooved metallic foam with porosity of 0.95 and thickness 2 and 4 mm.	Binding by Welding	Enhancement of CHF 1.5 times and HTC 3 times.	[162]
2	Porous structure of cu particles	Cu particles of 250 μm to 400 μm	Uniform Thick porous structures and pillars porous structures	Sintering	CHF 450 W/Cm ² , 3 times higher to corresponding plain surface. And HTC 3 times higher	[163]
3	Al And Cu	ZnO	ZnO Nanostructured on Substrate	Micro Reactor-Assisted-Nanomaterial- Deposition (MAND)	CHF: 82.5 W/Cm2, 3.5 Times Enhancement	[164]

S. No	Substrate	Coated Material	Geometry Coating Technique		CHF	Ref.
4	Silicon	Cu and Si	Nanowires on Cu and Electroplating and Etching W Si Substrate		CHF: 192 And W/Cm2, Enhanced By 100%.	[43]
5	Copper	Cu Particles	Porous coating of Cu particles on Cu Substrate	Brazing	CHF: 2.1-fold	[165]
6	Cu	Cu Particles	Micro-porous coating	Sintering	CHF: 4.5 Times Higher	[53]
7	Cu	Cu Particles	Hierarchical micro-porous structures	-	CHF Enhancement: 412%	[166]
8	Si	Diamond Particles	Diamond Based Micro-Porous coating on Si Heater	Diamond-Omega Bond-Acetone (DOA) Coating	47 W/Cm ² , up to 60% Enhancement.	[167]
9	Cu	Alumina	Porous alumina coating in a mini channel	Spray pyrolysis coatings	28.3% enhancement in heat flux	[168]
11	Cu Chip	-	Porous Layers on micro-channelsFins Top	Two step electrodeposition process	Up-to 3250 KW/m ²	[169]
12	Cu	Al ₂ O ₃ -TiO ₂	Nanostructured porous surface	Facile hot-dip galvanizing/dealloying process	CHF and HTC increased by 52.39% and 44.11%.	[138]
13	Cu	Porous graphite	Porous surface with pores ranges from 1 to 100 μm.	-	Enhanced HTC by 57% and CHF 15%	[170]
14	Cu	Porous coating	Porous coating on copper fin top	Electrodeposition	Maximum CHF enhancement of 270%	[7]
15	Stainless steel foil	micro-cavities	Multi-scale micro-cavities (0.2 to 10 µm)	Laser-processed	HTC increased by 3.7 factor	[171]
16	Cu	Cu micro particles	Micro-nano bi-porous surface	Hydrogen bubble template deposition method	HTC increased by 4.8 times	[172]
17	Si	Boron nitride	Film coating	Spray coating	Maximum HTC enhancement of 160%	[173]
18	Cu tube	Ag particles	Porous coating	Powder flame spraying technique	Maximum HTC increased by 2 times	[174]

Table 4. Cont.



 Cu particles [165]
 Cu particles [52]
 ZnO [163]
 Diamond [166]
 Al2O3-TiO2 [137]
 Cu foam [161]
 Alumina [167]

Figure 16. Maximum enhancement of CHF by modification of the substrate with porous coatings. Refer to Table 4, for detailed conditions of the studies listed on the *X*-axis. On *Y*-axis, "m" represents coated modified surface and "un" represents the uncoated flat surface.

3.4. Carbon Based Nanoparticles Coatings

Carbon Nano Tubes (CNTs) and Graphene (Gr) have one of the highest thermal conductivity [175–178]. Although lower wettability shifts nucleate boiling towards lower performance region of film boiling, the significant thermal conductivity of these materials overcome this effect and improve overall heat transfer performance [179,180]. CNT, graphene oxide (GO) and carbon nano fibers (CNF) are widely reported in the literature for NBHT performance enhancement [181].

Different researchers have studied the effect of single wall and multiwall CNTs for boiling heat transfer for both pool boiling [182–184] and for flow boiling [185,186] and obtained improved results. Seo et al. [187] used stainless steel as a substrate for single-walled CNT and reported 55% increase in CHF. In the case of CNT on a metal substrate, CNTs acts as hydrophobic dots to increase nucleation points. Bubbles appear to generate on top of these CNT coatings, while the untreated flat metal surface in their surrounding act as a hydrophilic region and helps in delaying film formation [188].

Both direct coatings of CNT on the substrate and its hybrid with other modification methods have been tested by various researchers. Launay et al. [189] developed a hybrid micro-nano scale surface by growing nano-scale CNT's on base surface with pin fins and micro-channels. Chemical vapor deposition (CVD) was used for the growing CNTs on the substrate surface. This combination of micro and nanostructures led to a significant performance increase of up to 100% enhancement on heat flux. This study also compared different silicon surfaces such as smooth, etched, untreated and fully coated with CNTs and 3D microstructures. Results showed the highest performance for 3D microstructure surfaces for boiling heat transfer using PF5060 and deionized water. Park et al. [190] applied spray coating of oxidized MWCNT and Gr coating, as shown in Figure 17. The contact angle on the substrate was noted to decrease with increasing spray coating time. The decrease in contact angle resulted in an increase in CHF, and maximum HTC appeared at 21.7° and 19.8° for Gr and MWCNTs respectively.

Density and length of CNT's are important parameters for its performance in nucleate boiling. Ahn et al. [191,192] used CVD technique to coat CNTs on the silicon surface. They coated two different heights of 25 µm (Type A) and 9 µm (Type B). The results were reported for pool boiling experiments in nucleate and film boiling regimes using PF-5060 as working fluid. CHF of CNTs coated surfaces resulted in 25–28% enhancement as compared to the untreated surface. While in film boiling regime Type-A CNTs showed 57% higher heat flux and Type B showed no change as compared to the untreated surface. Another similar study was conducted by Bertossi et al. [188] for 3 µm to the 10 µm length of CNTs. Nucleation points were observed to generate on the top of CNTs due to their hydrophobic nature. The results showed that the higher the length the higher is the heat transfer coefficient and up to 100% increase was reported in HTC. Ujereh et al. [193] tested Different CNTs arrays and densities, on Cu and Si substrate for pool boiling performance. Iron was used as a catalyst for the growth of CNTs in plasma enhanced chemical vapor deposition (PECVD) system. The results showed that CNT coated Si substrate had high CHF and high heat transfer coefficient as compared to the uncoated CNT surface of Si substrate. Efforts were made for the enhancement of the performance by changing the density: the best performance was always achieved for the full dense surface. Cu surface gave better enhancement in performance as compared to the Si substrate because Si surface was comparatively smoother and hence had fewer nucleation points. A trend is expected to be followed in the direction of nanostructures on micro-surfaces modification through CNT's.

Similar to CNT, Gr has received much attention in heat transfer applications because of its unique properties [194]. Jaikumar et al. [195] investigated the boiling performance of GO and Gr coating on Cu substrate by dip coating. The study described an increase in performance with increase in thickness of the coating. They reported 47% and 42% of enhancement in HTC and CHF. In their follow up study, Jaikumar et al. [119] presented combined effect of GO with porous copper particles and reported increase in CHF and HTC values. Rishi et al. [196] compared GO and composite GO-Cu for boiling heat transfer performance. The study reported enhanced performance for composite GO-Cu coating as compared to GO coating.

Hybrid CNT and Gr nano-structures were investigated by Kumar et al. [197] for NBHT. Heterostructures of Gr/CNT were grown on Cu substrate using PECVD technique. This study reported 155% enhancement in HTC, 40% increase in CHF and 62% reduction in boiling superheat. In another study, Sadaghiani et al. [198] investigated the NBHT performance of CVD-grown 3D foamlike Gr-coated silicon hybrid surface. They investigated the effect of porous structures and foam thickness. Thickness levels from 8 nm to 55 nm were considered for testing, and maximum enhancement results of CHF and HTC were reported for 13 nm.

In Table 5, some of the studies in this field are summarized. However, it is worth noting that researchers used different experimental fluids, experimental conditions, and substrate materials; thus these studies cannot be compared, but the trend of the performance enhancement can be noted. Figure 18 represents, the comparative analysis of CHF enhancement using carbon based nanoparticles coating, among referenced articles in this study.





Figure 17. Spray coating of oxidized MWCNT and graphene coating for boiling heat transfer [190].

Figure 18. The maximum enhancement of CHF by modification of the substrate with CNT and graphene. Refer to Table 5, for detailed conditions of the studies listed on the *X*-axis. On *Y*-axis, "m" represents coated modified surface and "un" represents the uncoated untreated surface.

Table 5. Carbon nanotubes (CNT) and Graphene coating for boiling heat transfer enhancement.	

S. No	Material	Geometry	Experimental Working Fluid	Manufacturing Techniques	Heat Transfer Enhancement Compared To Untreated Surface	Ref.
1	CNT	CNT growth on microchannel	Pf5060 and deionized water	CVD	100%	[189]
2	MWCNT	9 μm and 25 μm height and nano diameter	Pf-5060	CVD	25–28%	[191,192]
3	CNT, Aln, Sic On Cu	Porous Cu–CNT–AlN and Cu–CNT–SiC composite coatings	R134a	By mechanical alloying and cold gas dynamic spraying	Heat transfer enhancement ratio: 2.83 times and 2.52 times respectively.	[199]
4	CNT	Si surfaces coated with CNT	FC-72	PECVD	CHF By 1.5 times and HTC by 400%	[200]
5	CNT and Cu particles	CNT and sintered Cu particles coated on Cu substrate	Deionized water, segregated hydrofluoroether, Hfe-7300	Sintering (for cu particles)	Max. CHF enhancement by 45%	[201]
6	MWCNTs	MWCNT On Si And Cu Substrate	FC-72	PECVD	CHF 18.1 W/Cm2, up-to 0.75%	[193]
8	CNT	CNT forest of 3 to 10 µm.	Water	CVD	Up-To 100% CHF enhancement	[188]
9	SWCNT on stainless steel substrate	296, 613,845 and 1432 nm with roughness up to 9.76 nm	Deionized water	SWCNT film adhesion	55% Increase in CHF but HTC decreased a little (due to roughness decreased).	[187]
10	Cu And graphene	Electrodeposited Graphene On Cu	-	graphene solution (electrochemically obtained) coated on a copper chip	HTC Increased By 82%	[202]
11	Graphene, Sic layers	Graphene, Sic, deposited On Indium Tin Oxide (ITO) surface	FC-72	Graphene: Rta Sic: PECVD	Up-to 90%	[203]
12	Indium tin oxide (ITO)	Untreated surface, deposition of graphene layer on ito and deposition silicon carbide (SiC) particles on ITO	FC-72	-	Enhancement with respect to untreated ITO: graphene layer 9% and Sic: 42%	[204]
13	CNT	CNT on Cu substrate	De-mineralized water	HFCVD	CHF enhancement by 38%	[182]
14	GO	Film on Cu substrate	distilled water	Dip coating	Enhancement in HTC and CHF by 47% and 42%, respectively.	[195]
15	Reduced GO	Coating on Ni-wire	Water-rGO	NBHT	HEC enhancement up-to 245%	[205]

4. Conclusions and Future Recommendations

This paper presents a comprehensive and critical review of nano-coating techniques for nucleate boiling heat transfer (NBHT) along with an integrated discussion on their physics and related key parameters necessary for enhanced heat transfer characteristics. In addition, it critically analyses the enhancement abilities of pool boiling through these nanocoating techniques along with their limitations that commonly arise from their durability and cost-effectiveness. The physics behind NBHT is not completely understood and still needs further research. However, the review of related literature verifies that surface modification is one of the main variables for NBHT. Microand nano-scale manufacturing technologies offer a wide range of surface coating, enhancement and modification possibilities within industrially applicable boundaries of high productivity, cost-effectiveness, reliability, and durability. Hence, the advancements in manufacturing technologies in these directions have made heat transfer enhancement by surface modification an emerging field in heat transfer research.

As a summary of the critical literature review on nano-coatings and techniques on NBHT, the following conclusions and recommendations can be made.

- Despite the significant improvements in nucleate pool boiling heat transfer performance mainly through newly developed micro-nano coating materials and techniques, industrial application is still not practical. Emphasis should be given to durability and cost improvements of these nano-coatings, which are the main constraints for their industrial and practical implementations.
- Research should be conducted in order to identify the root cause of the physical mechanism of failure of these nano-coated surfaces, and to how to overcome them.
- Novel manufacturing techniques need to be studied to ensure the cost-effectiveness of nano-coatings and surfaces.
- Hybridization of different techniques should be applied to study the possibilities of enhanced heat transfer results such as a combination of nanoparticles on the microstructured porous coating, and the hybrid of microporous and hydrophilic coatings.
- Surfaces developed at lab scale for NBHT need to be applied and tested under their practical applications. In addition, applications of such passive performance enhanced surfaces need to be explored to make their use more attractive for other applications such as water harvesting, self-cleaning in remote areas, aerospace applications, and heat tubes.
- Although highly efficient methods have been reported in the literature, there is a lack of techno-economic studies for these techniques. Likewise, further studies also need to be carried out on corrosion, erosion and adhesion aspects of these nano-coating materials and techniques for NBHT application.
- A standardized lifetime test needs to be developed for performance assessment to make an easy comparison of these nano-coatings techniques and materials.

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