Surface grown copper nanowires for improved cooling efficiency

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Abstract: The interactions between heat sink surfaces and coolant play important roles in cooling methods. This study relies upon controlled nanostructuring of heat sink surfaces that produces orders of magnitude increases in surface area, excites local vortexes and improves the phase change mechanisms to enhance cooling efficiency. A scalable, economical and environmentally benign technique to grow copper nanowires with a strong/conductive base-anchorage on the surface of copper and related materials is described. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were used to monitor the reduction and morphology of the nanowires. Transmission electron microscopy (TEM), electron diffraction (ED) and X-ray diffraction (XRD) were employed to understand the structure of the as-grown copper hydroxide nanowires and reduced copper nanowires. The convective heat transfer of nanostructured surfaces was measured in the laboratory and compared to a theoretical treatment of the nanowire array effects on convective heat transfer. The various surface treatments tested showed heat transfer increases of up to 93% in good agreement with a theoretical analysis.

Keywords: Nanoscale heat transfer; heat sink surface cooling; copper nanowire

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PUBLIC INTEREST STATEMENT
Heat removal is a key technological roadblock in electronic and other applications. Trends toward more compact electronic devices demand still higher levels of heat removal, challenging the limits of today’s thermal management technologies. Our approach relies upon increasing the surface area of heat sinks through introduction of nanoscale features, i.e., nanostructuring. This article discusses a simple, cost-competitive, scalable, economical and environmentally benign technique to produce such nanostructuring and demonstrated that improvements in heat transfer efficiency as high as 93% can be achieved.
1. Introduction
Heat removal is a key technological roadblock in electronic and other applications. The concentration of power in increasingly compact electronic devices, demands removal of growing levels of heat flux, of the order of megawatts per square meter. This is challenging the limits of today’s thermal management technologies (Ekstrand, Ma, Zhang, & Liu, 2005). Forced convection or phase change phenomena are emerging as the prevalent methods of heat dissipation. The interactions between heat sink surfaces and the fluid (coolant) play important roles in heat dissipation via convection and phase change (Dharmendra, Suresh, Kumar, & Yang, 2016; Dietz & Joshi, 2008; Morshed, Yang, Ali, Khan, & Li, 2012). Alternative means of improving heat transfer efficiency in active cooling systems include roughening of convective surfaces, adding fins, inducing swirl flow, use of porous media, using electric vibration devices and introducing solids as part of the heat transfer working fluid (Kim, Choi, Shim, Kim, & Cho, 2016; Mori, Aznam, & Okuyama, 2015; Rothenow, Hamett, & Ganic, 1985; Sheikholeslami, Gorji-Bandpy, & Ganji, 2015). These techniques are generally more costly and difficult to implement when compared with nanostructuring of heat sink surfaces. For example, measures such as 2D and 3D roughening or introduction of micro-fins require the use of expensive electrode discharge machining (EDM) processes (Ahmed, Ismail, Sulaeman, & Hasan, 2016; Baxi & Wong, 2000; Zahiruddin & Kunieda, 2016).

Nanostructuring of heat sink surfaces has drawn extensive attention as an effective method to enhance the heat dissipation capacity of heat sinks. Such nanostructured surfaces can produce orders of magnitude increases in surface area, and can also excite local vortices and improve the phase change mechanisms that greatly benefit heat dissipation efficiency (Betz, Jenkins, & Attinger, 2013; Dietz & Joshi, 2008; Ekstrand et al., 2005; Fan et al., 2007; Hu, Shenogin, Keblinski, & Raravikar, 2007; Morshed et al., 2012; Zhong et al., 2006). Carbon nanotubes have played pioneering roles in exploring the potential benefits of nanomaterials in different fields of application, including convective heat dissipation (Haq, Nadeem, Khan, & Noor, 2015). Multiwalled carbon nanotube arrays tend to be closely spaced and the somewhat tangled nature of nanotubes limits the effectiveness of the interactions of nanotubes with the coolant fluid. Therefore, the orders of magnitude increases in the exposed surface area have not translated into significant gains in heat transfer efficiency (Dietz & Joshi, 2008). To overcome this setback, patterned growth of multiple-nanotube “fins” was introduced (Ekstrand et al., 2005; Hu et al., 2007), and was observed to yield a 200% gain in the efficiency of heat dissipation via forced convection with water (Ekstrand et al., 2005; Tullius, Tullius, & Bayazitoglu, 2012). However, these efforts on nanostructuring, have not realized the full potential of hot-surface nanostructuring because: (i) the high surface density of nanotubes within the fin inhibits effective interactions between the enormous surface area of the nanotubes and the coolant; (ii) the non-optimal arrangement of the fins prevents the coolant from contacting the hot surface and the lower parts of the fins; (iii) high flow rates force bending of the nanotube fins, thereby decreasing their effective contact with the coolant and compromising their ability to generate vortices in the flow (Hu et al., 2007). Further, the growth processes of carbon nanotubes are costly and difficult to scale-up.

Nanostructuring of heat sink surfaces has also benefited the boiling heat transfer coefficient and the critical heat flux in phase-change cooling schemes (Ujereh, Fisher, & Mudawar, 2007). In a pioneering work on the effects of nanowire on phase-change heat dissipation (Li et al., 2008), important gains in boiling performance resulted from nanostructuring of copper surfaces. Striking differences were observed in the dynamics of bubble nucleation and release with introduction of copper nanowires, including reduced bubble diameters, increased bubble release frequencies and an approximately 30-fold increase in the density of active bubble nucleation sites. The fact that nanostructured surfaces induced stable nucleation of bubbles at low superheated temperatures was attributed to a synergistic coupling effect between the nanoscale gas cavities (or nanobubbles) formed within the nanowire interstices and the micro-scale defects (voids) formed on nanowire array surfaces. In this coupled system, interconnected nanoscale gas cavities stabilize (or feed) bubble nucleation at micro-scale defect sites, and the stability of bubble nucleation is ensured by features which are orders of magnitude smaller than the cavity-mouth opening (Li et al., 2008).
Some active cooling configurations, including flow through porous media, introduction of geometric features for generating disturbed or swirling flows or jet impingement, can improve fluid interactions with (nanostructured) surfaces by inducing flow at an angle with respect to the surface (Bournonville, Grandotto, Pascal-Ribot, Spitz, & Escourbiac, 2009; Leung, Wong, & Probert, 2001; Vijiapurapu & Cui, 2007). Various processing techniques have been developed for fabrication of nanowires and nanotubes. Among these, many are based on high-temperature processes such as vapor-liquid-solid (VLS) growth (Dingman, Rath, Markowitz, Gibbons, & Buhro, 2000; Pan, Dai, Ma, & Wang, 2002), laser ablation (Morales & Lieber, 1998; Zhang et al., 1998), chemical vapor deposition (Nigro, Malandrino, & Fragalà, 2001) and vapor-solid reaction (Whittingham, Marshall, Mitrevski, & Jones, 2004). Other methods exploit the confined spaces of hard templates; examples include alumina (Cao, Xu, Sang, Sheng, & Tie, 2001), track-etching polycarbonate membranes (Jirage, Hulteen, & Martin, 1997), silica (Huang, Choudrey, & Yang, 2000), mica (Sun, Searson, & Chien, 2000) and soft templating methods such as liquid crystals (L. Huang et al., 2002), reverse micelles (Qi, Ma, Cheng, & Zhao, 1997) and surfactant templates (Murphy & Jana, 2002). One problem with template-guided synthesis is that nanowires are prone to aggregation when the template is etched away (Sapp, Lakshmi, & Martin, 1999). In general, control of the size and morphology of nanowires/nanotubes is a challenging issue due to difficulties in controlling the nucleation and growth processes of nanostructures (Xia et al., 2003).

To overcome this obstacle, an approach is proposed that employs a simple method of growing metal nanowires with the desired spacing, diameter and length on heat sink surfaces, which can excite local turbulence to enhance the interaction of coolant with the high surface area of nanowires. Additionally, by proper geometry and spacing of nanowires, the generated vortexes provide effective interaction of the fluid with nanowire surfaces, and enhance the mixing of fluid for effective heat transfer. Moreover, with proper arrangement of nanowires a large fraction of their surface area occurs outside the stagnant (viscous) sublayers within the flow boundary layer. Nanowires protruding above the viscous sublayer and exciting vortexes further benefit convective heat transfer efficiency.

This study employs simple, low-cost and scalable techniques to introduce copper nanowires with controlled diameter, spacing and length upon copper heat sink surfaces exposed to the coolant. Copper is particularly attractive since it has high thermal conductivity, and is relatively cheap. The nanowire growth mechanisms produce strong metallic bonds between the nanowires and the metal surface, ensuring their stability under high flow rates. The versatility of this approach enables adjustment of the metal nanowire geometry and spacing to match the fluid dynamic and structural requirements for effective interaction of the large nanowire surface area with the coolant. The key improvement involved processing of nanowires to substantially reduce the porosity and give increased grain size, resulting in enhanced thermal conductivity. This study aims to achieve significant gains in the efficiency of heat dissipation by forced convection or phase change through controlled nanostructuring of the heat sink surfaces. The significant rise in the exposed surface area results from the growth of nanowires on heat sink surfaces. Depending on the nanowire diameter, length and spacing, orders of magnitude gain in heat transfer efficiency are expected as the enormous surface area of the nanowires can effectively interact with the coolant.

Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS) were used to characterize and monitor the growth of the nanowires and their morphology. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and electron diffraction (ED) methods were also utilized for better understanding of structural changes in copper hydroxide nanowires grown directly on TEM grids. The effects of nanowire arrays on convective heat transfer were investigated in the laboratory. Finally, based on classical heat transfer models for fully developed turbulent pipe flow, preliminary analyses are performed on the overall heat transfer by convection in pipes with and without nanowires.

2. Materials and methods
Analytical grade sodium hydroxide, ammonium persulfate (NH₄)₂S₂O₈, APS) and acetone were purchased from Sigma-Aldrich. Solutions were prepared by dissolving NaOH (10 mol/l) and APS (1.0 mol/l)
in deionized (DI) water, and stored in brown glass bottles. The copper alloy CuCrZr sheets and tubes (12.6 mm outside diameter and 6 or 9 mm inside diameter) were purchased from NSRW.

2.1. Characterization

2.1.1. Field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy

The FESEM technique was implemented using a JEOL 6400V field-emission microscope (Japan Electron Optics Laboratories) with a LaB6 emitter (Noran EDS). This microscope is equipped with an EDS system. For SEM imaging, a thin film of osmium was sputtered on the sample surface to prevent charging.

2.1.2. Transmission electron microscopy, X-ray diffraction and electron diffraction

TEM techniques were implemented using a JEOL 2200FS 200 kV field emission transmission electron microscope with an accelerating voltage of 200 kV. This TEM offered the ability to perform electron energy loss spectroscopy, ED, including selected area electron diffraction (SAED) and EDS.

2.1.3. X-ray diffraction

XRD patterns were recorded on a (Japan Rigaku D/max-gB) X-ray diffractometer with Cu Ka radiation ($\lambda = 1.54178 \, \text{Å}$), operated at 40 kV and 80 mA. In XRD, peaks in the diffraction patterns form due to XRD from crystalline planes.

2.2. Growth of nanowire arrays

A low-temperature, solution-based and environmentally benign favorable method was developed to fabricate aligned Cu(OH)$_2$ nanowire arrays on a copper surface, without using templates and surfactants. The method involves etching of copper from the heat sink surface and redeposition as copper hydroxide or copper oxide nanostructures. A subsequent heat treatment step in hydrogen reduced the Cu(OH)$_2$ or copper oxide into Cu nanowire arrays, with retention of the original nanostructure.

Different variations of the nanowire growth process produced either copper hydroxide or copper oxide nanostructures. By fine-tuning the growth conditions, different morphologies of the nanoscale features were realized. These morphologies include nanowires, nanoribbons, nanotubes and nanoparticles. The copper hydroxide or copper oxide nanomaterials were reduced to copper nanomaterials by heating in a hydrogen environment while retaining the original nanoscale morphology. The original copper hydroxide or copper oxide nanostructures formed were phase-pure single crystals, which were converted into polycrystalline copper by the reduction process. The nanowire growth and reduction steps are schematically depicted in Figure 1. The primary process developed in this study comprises three steps: (i) surface cleaning via sonication to remove any adhered impurities (and to introduce atomic-scale defects); (ii) nanowire growth using an etching solution of sodium hydroxide and APS; and (iii) gas-phase reduction through heating in hydrogen.

2.2.1. Surface preparation and nanowire growth

The surface upon which nanowires was to be grown (e.g., interior pipe surfaces) was subjected to different treatments in order to determine the effects on the nanowire growth process. The treated

![Figure 1. Schematic depiction of the growth and reduction processes of nanowires.](image)
surfaces considered included: (A) reamed; (B) reamed and milled; (C) reamed and honed; (D) designed cross-section; (E) just drilled without any surface finish and (F) sand-blasted. Just prior to nanowire growth, the surfaces were cleaned through sonication in acetone for 15 min, followed by washing with deionized (DI) water. Two procedures were used for nanowire growth, as described below.

Procedure I: An aqueous solution was prepared in a 60-ml glass bottle by mixing 7.5 ml of NaOH solution (10 mol/L), 1.5 ml of APS solution (1 mol/L) and 21 ml of deionized (DI) water. The copper substrate, which had been ultrasonically cleaned in acetone and rinsed with distilled water, was immersed in the solution before adding the APS solution. The copper substrate was left in the solution (after adding the APS solution) at room temperature and ambient pressure. The surface color of the copper substrate was observed to turn light-blue after a few minutes, with the initially colorless solution gradually turning blue. In about 30 min, a light-blue film covered the copper surface. After about half an hour to two hours, the copper substrate was taken out of the solution, rinsed with distilled water and ethanol several times, and dried in air.

Procedure II: Different variations of this method were considered. In a typical approach, an aqueous alkaline solution was prepared in a 50-ml glass bottle by mixing 7.5 ml of NaOH solution (10 mol/L) with 19.5 ml of DI water. The copper substrate, after cleaning via ultrasonication in acetone and then in DI water, was immersed in the solution. Subsequently, 3 ml of APS solution (1 mol/L) was added. The immersed copper substrate was stored in a low-temperature bath with its temperature fixed at 0°C. After a reaction time of 6 to 15 h, the surface color of the copper substrate turned deep-blue, and then a few black spots started to appear. The copper substrate was removed from the solution at this stage, washed with DI water and then dried in air. The grown copper hydroxide (or copper oxide) nanowires were heated in a hydrogen environment to produce copper nanowires. Different periods of heating in hydrogen were evaluated for identifying the preferred reduction condition. In some cases, pre-heating was used to convert the copper hydroxide to copper oxide nanowires.

2.2.2. Post-reduction heat treatment of nanowires
Reduction of copper hydroxide into copper nanowires was found to produce porous nanowires (with reduced thermal conductivity). Post-heating treatment (annealing) was, thus, necessary to improve the structure and properties of the nanowires. Annealing can reduce voids by various diffusion phenomena, and can also remove crystalline defects. Annealing is generally accomplished at temperatures greater than half the melting point on the absolute temperature scale. For example, bulk copper melts at 1083°C; hence, annealing of bulk copper is generally performed at temperatures greater than 405°C (678°K or 761°F). In order to accelerate the process, it is common to anneal bulk copper at about 700 to 800°C. Nanostructures of copper generally have lower melt points than bulk copper; their annealing would, thus, occur at somewhat lower temperatures than bulk copper. Annealing needs to be performed in an inert environment or under hydrogen in order to prevent possible oxidation of nanostructures during annealing. After some trial-and-adjustment steps for identifying a viable anneal temperature and duration, we selected exposure to 350°C for 1 h (in vacuum) as the preferred condition for annealing the reduced copper nanowire structures.

Melting of crystalline materials is characterized by the loss of crystalline order followed by a transformation into liquid phase. The melting behavior of nanoscaled features can be quite different from that of bulk materials (Alcoutlabi & McKenna, 2005; Chushak & Bartell, 2001; Dippel et al., 2001; Jackson & McKenna, 1990; Shijin, Shaoqing, & Hengqiang, 2001; Wang, Petroski, Green, & El-Sayed, 1998). Melting of nanostructures reportedly starts with an enhanced surface diffusion. With reduced dimensions, the surface-to-volume ratio increases along with the surface curvature, which makes surface-atoms more prone to detachment from their positions and to surface-diffusion as adatoms. This process can cause pronounced shape change (Link, Wang, & El-Sayed, 2000; Wang et al., 1998) at relatively low temperatures when compared with the melting point of bulk material. Surface-diffusion is followed by partial melting of the nanostructure, mainly within a thin layer close to the surface (called “surface melting” or “pre-melting”) (Lewis, Jensen, & Barrat, 1997). Pre-melting of nanomaterials generally occurs at lower temperatures than the bulk
material melting point, with actual values depending on parameters such as the size (Dippel et al., 2001; Wang, Wang, Chen, & Zhao, 2003) and morphology (Wang et al., 2002) of the nanostructure, impurities, defects (Link et al., 2000), strain (Wang et al., 1998) and crystallographic orientation at the surface (Dippel et al., 2001; Wang et al., 1998). Similar to pre-melting, the interior melting of a nanomaterial can take place at temperatures lower than the bulk material melt point. While copper nanorods produced by a solution-based chemical synthesis melted at temperatures close to the bulk material melt point of 1083°C (Lisiecki, Sack-Kongehl, Weiss, Urban, & Pileni, 2000), some Cu nanorods with 20 nm diameter and 1 µm length exhibited a pre-melt at temperatures close to 450°C, causing shape-change and producing shorter nanorods with increased diameter.

3. Results and discussion

3.1. Scanning electron microscopy of copper hydroxide nanowires

Figure 2 shows scanning electron microscope images (at different magnifications) of the as-grown copper hydroxide nanowires on copper pipe surfaces. The nanowires were observed to have diameters of 200 to 500 nm, and form reasonably aligned arrays that were nearly perpendicular to the pipe surface. Attempts were made to use profilometry techniques to assess the surface roughness; the results, however, were not reliable due to the conformable nature of the nanowire array. Therefore, based on an examination of SEM images (Figure 2b), it is estimated that the average nanowire length (array thickness) was about 30 to 50 µm.

3.2. Reduction of copper hydroxide to copper nanowires

The grown copper hydroxide nanowires were subjected to different sequences of heating in ambient condition and vacuum, always culminating with exposure to hydrogen (or vacuum with bleeding hydrogen) at elevated temperatures for reduction of nanowires to copper. Initial heating in ambient condition (or in vacuum) was used in some cases to convert copper hydroxide to copper oxide prior to exposure to hydrogen for reduction of copper oxide to copper. Figure 3 shows SEM images of copper nanowire arrays subjected to different heating/reduction conditions. The original morphology of the nanowire arrays was largely preserved after reduction to copper (Figure 3a-e); the nanowire diameters seemed to have shrunk in the process (as confirmed by TEM microscopy, vide infra).

EDS elemental analyses (Table 1) indicated that the most thorough reduction to copper (with minimum remaining oxygen content) was achieved through heating in the presence of hydrogen to 120°C for 3 h and then to 200°C for 2 h. SEM images of these copper nanowires are shown in Figure 3c. Figure 4a and 4b show the EDS spectra of copper hydroxide nanowires and copper nanowires after reduction using this preferred condition.

3.3. Transmission electron microscopy, X-ray diffraction and electron diffraction

TEM and ED techniques were employed to improve our understanding of the structure of the as-grown copper hydroxide nanowires and the reduced copper nanowires. TEM analyses were
Figure 3. Scanning electron microscope images of copper nanowire arrays after different heat treatment processes culminating with heating under exposure to hydrogen, (a) 120°C for 3 h and 200°C for 2 h in vacuum with hydrogen bleeding, (b) 120°C for 3 h and 180°C for 2 h under vacuum followed by 200°C for 1 h in hydrogen, (c) 120°C for 3 h and 200°C for 2 h in vacuum with hydrogen bleeding, (d) 400°C for 1 h under vacuum with hydrogen bleeding, (e) 100°C for 2.5 h at ambient pressure followed by 400°C for 1 h in hydrogen.
Table 1. EDS elemental analyses of reduced copper nanowires

| Reduction Condition | Weight Percentage After Reduction |
|---------------------|----------------------------------|
|                     | Cu | Oxygen |
| As-grown Cu(OH)$_2$ nanowires | 53.5 | 46.5 |
| (1) 200°C for 1 h in H$_2$ | 59.4 | 40.6 |
| (2) 120°C for 3 h and 180°C for 2 h in vacuum followed by 200°C for 1 h in H$_2$ | 73.4 | 26.6 |
| (3) 100°C for 1.5 h in ambient condition followed by 200°C for 1 h in H$_2$ | 77.1 | 22.9 |
| (4) 200°C for 2 h in H$_2$ | 88.7 | 11.3 |
| (5) 120°C for 3 h and 200°C for 2 h in H$_2$ | 95.9 | 4.1 |
| (6) 400°C for 1 h in H$_2$ | 85.8 | 14.2 |
| (7) 100°C for 1.5 h in ambient condition followed by 400°C for 1 h in H$_2$ | 86.3 | 13.7 |

Figure 4. EDS spectra of (a) as-grown copper hydroxide nanowires, and (b) copper nanowires after the preferred reduction condition (120°C for 3 h and 200°C for 2 h in H$_2$; corresponding to reduction condition 5 in Table 1).
undertaken on copper hydroxide nanowires grown directly on TEM grids (and subsequently reduced to copper using hydrogen reduction condition (5) in Table 1). Figure 5 shows high-resolution TEM images and ED patterns for as-grown and reduced nanowires. The copper hydroxide nanowires exhibited a dense (solid) and ordered structure, with smooth sides that ended in a flat tip. The observed diameters were consistent with those found by SEM for copper hydroxide nanowires grown on copper tubes (in the 200–500 nm range). The reduced copper nanowires (Figure 5, right) are both shrunken and considerably less smooth than the parent copper hydroxide nanowires. ED (insets to Figure 5) shows that the copper crystallites are significantly smaller than for the copper hydroxide: as the electron beam impinges on a number of crystallites giving a number of sets of diffraction spots. Higher resolution TEM images (Figure 6) confirm the decrease in crystallite size between the copper hydroxide and copper. The TEM image of the as-grown copper (Figure 6 right) indicates that during the reduction process the growth of smaller copper crystallites has also resulted in significant porosity. Such porosity of the copper nanowires would be predicted to lower their thermal conductivity and, thus, their contribution toward heat transfer.

SEM and TEM give detailed information about only small regions of a sample, and so to characterize the composition and phase-purity of the as-grown copper hydroxide nanowires and the reduced copper nanowires as a whole XRD was carried out. Figure 7 presents the XRD patterns of the nanowire arrays. The XRD pattern of Figure 7a can be assigned to the orthorhombic phase of copper(II) hydroxide (Oswald, Reller, Schmalle, & Dubler, 1990; Von Jaggi & Oswald, 1961) based on the observation of six diffraction peaks. The other five observed peaks are from the underlying copper (JCPDS Card 04–0836). After reduction of the nanowires (Figure 7b), the disappearance of the peaks at 23.6°, 33.9°, 35.9°, 38.1°, 39.6° and 53.2° (2θ) positions is consistent with the conversion of copper(II) hydroxide to metallic copper.

3.4. Improvement of the reduced copper nanowire structure via annealing

The void formation observed during reduction of copper hydroxide into copper nanowires is expected to adversely influence the thermal conductivity of the resulting copper nanowires. Further, smaller crystallites will give more grain boundaries that would also be expected to also reduce the thermal conductivity. Annealing is, thus, desirable to improve the microstructure of the nanowires. After some trial-and-adjustment steps for identifying a viable anneal temperature and duration, we selected exposure to 350°C for 1 h (in vacuum) as the preferred condition for annealing the reduced copper nanowire structures. The improvement in structure can be seen in the TEM images in Figure 8. The TEM images show the original solid and ordered structure of the grown copper hydroxide nanowires (Figure 8a), the porous structure of reduced copper nanowires (Figure 8b) and the improved structure with substantially reduced porosity achieved after annealing of the copper nanowires (Figure 8c).
Figure 6. High-resolution TEM images (at different magnifications) of as-grown copper hydroxide nanowire (left) and reduced copper nanowire (right).

(a) As-grown copper hydroxide nanowires
(b) Reduced copper nanowires
Higher resolution images of the copper nanowires (Figure 9a) confirm the formation of a crystalline structure without noticeable voids after proper annealing of the reduced copper nanowires. The ED patterns shown in Figure 9b for different locations of nanowires illustrates an improved crystalline structure exhibiting a combination of single- and poly-crystalline features (probably due to grain growth during annealing).

3.5. Impact of growth conditions on nanostructure morphology

The reaction that accounts for the Cu(OH)$_2$ nanowire growth is essentially an oxidation process:

$$\text{Cu} + 4 \cdot \text{NaOH} \cdot (\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow \text{Cu(OH)}_2 + 2 \cdot \text{Na}_2\text{SO}_4 + 2 \cdot \text{NH}_3 \uparrow + 2 \cdot \text{H}_2\text{O}$$

When copper surfaces are exposed to an alkaline oxidant solution, a blue film of Cu(OH)$_2$ gradually grows on the copper surface. The reaction is accompanied by the evolution of gas bubbles with a pungent ammoniacal odor, indicating the formation of ammonia. Control experiments with less basic solutions (pH 8–10), performed under similar conditions, did not produce Cu(OH)$_2$ nanowires. Under exposure to an alkaline oxidant solution, Cu ions from the copper surface get etched by the strong alkaline condition (pH > 14), and enter the solution phase. Within a few minutes of addition of APS the blue color appears on the surface, and grows more intense with time until a stable level of intensity is reached. The hydroxide ion of these solutions is approximately 3 M. The solubility product for dissolution of Cu(OH)$_2$ in water is $2.2 \times 10^{-20}$, so for [OH$^-$] = 3 M this gives [Cu$^{2+}$] = $2 \times 10^{-21}$ M at equilibrium. Precipitation of Cu(OH)$_2$ is potentially in competition with the formation of copper-ammonia coordination complexes. The equilibrium constant for formation of the copper ammonia complex, Cu(NH$_3$)$_4^{2+}$ is $1.7 \times 10^{13}$. The APS concentration is 0.1 M so complete conversion to ammonia and a homogeneous solution would give an ammonia concentration of 0.1 M, which...
could give the maximum concentration of Cu(NH$_3$)$_4^{2+}$ as $2 \times 10^{-25}$ M. It is reasonable to expect that there would be a concentration gradient of the ammonia formed which would result in a higher ammonia concentration close to the surface (and so larger Cu(NH$_3$)$_4^{2+}$ concentration). However, there would be an opposing gradient for the APS which would be depleted close to the surface. It, therefore, seems very unlikely that Cu(NH$_3$)$_4^{2+}$ plays a major role under these conditions; consistent with the observation of the blue-green color of copper(II) hydroxide. For the lower pH conditions, e.g., pH of 8, the copper ion concentration at which precipitation occurs is significantly higher: $2 \times 10^{-8}$ M. Under these conditions complete reaction of APS to produce 0.1 M ammonia concentrations would be sufficient to give effectively stoichiometric formation of the Cu-ammonia complex. This is consistent with our observations at lower pH that no nanowires form.

The nanowires are formed at the high pH conditions used, and so further discussion will focus on these conditions. When the concentration of copper becomes high enough in the solution phase ($> 2 \times 10^{-21}$ M), copper ions deposit back onto nucleation sites on the surface (such as atomic dislocations) as copper hydroxide. These sites become the nucleation points for further growth into nanowires. Eventually, this growth process stops due to self-limitations. The nanostructure growth process and shape are very much dependent on the growth conditions, including temperature, concentration of solutes and time of exposure to the alkaline oxidant solution. While we have established the desired growth conditions for achieving nanowire arrays, diverse morphologies can be produced by changing the growth conditions (Figure 10).

Given the role of surface defects as nucleation sites for nanowire growth, the surface finish is another factor influencing the nature of nanostructures. Figure 11 presents SEM images of different features grown on copper surfaces with different commercially available finishes. These

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**Figure 10.** Scanning electron microscope images of different nanostructures obtained on copper surfaces depending on reaction conditions (a) at 70°C for 24 h, (b) at room temperature for 48 h, (c) at 60°C for 4 h, and (d) 1 h of sonication during growth.
images highlight the significant effects of surface finish on the growth process. In the mirror-finish sample, the polished surface embodies fewer defects which diminish the nanowire growth. Past investigations of nanowire growth at elevated temperatures have also noted that nanowire growth initiates at surface atomic dislocations (Xu, Woo, & Shi, 2004).

It has been noted that, as in crystallization, nanowire growth via different routes (from vapor, liquid or solid) involves the two fundamental steps of nucleation and growth (Xia et al., 2003). As the concentration of the building blocks (atoms, ions or molecules) increases to a sufficiently high level, they aggregate into small clusters through homogeneous nucleation. With a continuous supply of such building blocks, these nuclei can serve as seeds for further growth to form larger structures. It is generally accepted that
the formation of a perfect crystal structure requires a reversible pathway between the building blocks on the solid surface and those in the fluid phase. These conditions allow the building blocks to easily assume their correct positions while developing the long-range-ordered, crystalline lattice. The mechanisms involved in the formation of Cu(OH)$_2$ nanowires require further investigation. However, nanowires appear to be produced from a highly non-equilibrium reaction system, in which different growth rates of the crystal faces determine the ultimate morphology of nanomaterials (Wen, Zhang, & Yang, 2002). The growth of Cu(OH)$_2$ nanowires along the [100] direction can be understood on the basis of the assembly of oblate $\rightarrow$ Cu(OH)$_2$Cu$<_<$ chains in the plane (001), oriented along [100]. According to the Bravais-Friedel-Donnay-Harker law, the growth rate of orthorhombic Cu(OH)$_2$ crystals is normally proportional to $1/d_{hkl}$. Hence, the growth of Cu(OH)$_2$ along [100] is much faster than those along other directions, leading to the formation of nanowires and similar (e.g., ribbon-like) nanostructures.

3.6. Morphology changes during conversion of copper (II) hydroxide to copper
Based on the differences in density, the reduction of copper hydroxide nanowires to copper nanowires would be expected to produce a 75% decrease in volume. A significant decrease in nanowire diameter and no apparent change in length is observed. The formation of porous, polycrystalline copper nanowires upon reduction of solid, single-crystal copper hydroxide nanowires may be analogous to void formation in the Kirkendall effect (Yin et al., 2004), where pores form because of the difference in diffusion rates of two components in a diffusion couple. This phenomenon, referred to as Kirkendall Effect (Smigelskas & Kirkendall, 1947), was the first experimental proof that atomic diffusion occurs through vacancy exchange, not direct interchange of atoms. The net directional flow of matter is balanced by an opposite flow of vacancies, which can condense into pores or annihilate at dislocations. During the reaction process, hydrogen gas diffuses to embrace the Cu(OH)$_2$ nanowires, and reacts with Cu(OH)$_2$ to form thin layers of Cu$_2$O/CuO and finally Cu on the Cu(OH)$_2$ nanowire surface. The by-product H$_2$O can exit the Cu layers through outward diffusion. Past investigations (Yin et al., 2004) indicate that placing solid nanocrystals containing one reactant in a comparatively dilute solution creates an additional asymmetry that may favor the creation of hollow structures. The relatively large change in the concentration of core material between the core and the solution provides a greater driving force for the outward diffusion of the core material. The surface free energy may also influence the formation of these hollow structures. Removal of water molecules is also a factor in void formation during reduction. A decrease in nanowire diameter is observed during reduction (Figure 12), which points at some diffusion phenomena occurring to compensate for lost atoms; this is, however, not enough to avoid development of a porous (reduced) copper nanowire structure.

3.7. Evaluation of convective heat transfer
The effect of nanowire arrays on convective heat transfer was investigated using the test setup shown in Figure 13. This active cooling test setup uses nitrogen gas as the coolant. The inlet gas
pressure was 2 MPa, and the flow rate was 1050 SLPH. The incoming gas was heated to 30°C, and the copper pipe was heated to 100°C. The outlet gas temperature was measured using a thermocouple, with the gas temperature rise during flow within the pipe reflecting the convective transfer of heat from the pipe interior surfaces to the gas. The test setup was instrumented with thermocouples, pressure transducers and flow meters, all of which were connected to a computer-based data acquisition system for monitoring of the system parameters throughout the test period. After the pipe was heated to 100°C, gas flow was initiated, and data were collected over a period of 2.5 h, allowing the system to reach equilibrium.

Two internal pipe diameters (6 and 9 mm) were considered in the heat transfer test program. Three samples were tested for each (surface finish) condition, and the average values (and ranges) are reported. Table 2 summarizes the percent increase in outlet temperature rise (reflecting enhanced convective heat transfer) resulting from the introduction of copper nanowires on 6 and 9 mm diameter copper pipes, respectively. Different surface finishes and nanowire structures were considered. While the gains in cooling efficiency with introduction of the porous/polycrystalline nanowires (Figure 9b) were limited to 32% and 21% in the case of 6 and 9 mm diameter copper pipes (with proper surface finishes), respectively, these percentage gains in cooling efficiency almost tripled when solid/more crystalline copper nanowires were used instead of porous/polycrystalline ones. The sensitivity of cooling efficiency to the surface finish used prior to nanowire growth reflects mostly the effects of surface finish on nanowire morphology. The surface roughness (prior to nanowire growth) varied from 0.2 to 0.8 μm, depending on the surface finish. Without nanowire growth, different surface finishes did not produce significant differences in cooling efficiency.

The nanowire diameter, length and spacing considered in cooling efficiency tests varied within a narrow range in cooling efficiency tests. Figure 12b presents a scanning microscope image of a nanowire array which was representative of those used in the cooling efficiency tests. With a diameter of about 100 nm, average length of about 50 μm, and a spacing that is a few times the diameter, these nanowires produce about two orders of magnitude gain in surface area. The fact that the gains in cooling efficiency realized by introduction of these nanowires approach 100% (compared to 10,000% rise in surface area) indicates that: (i) the nanowire spacing is not adequate to effectively excite vortexes that can enhance the fluid interactions with the enormous surface area of the nanowires and (ii) the length of the nanowires (about 50 μm) is less than the boundary layer thickness (estimated at 100 μm in our tests); the nanowire surface area thus occurs largely within the stagnant region of fluid where convective heat transfer is limited. It should be noted that the nanowire length exceeds the viscous sublayer thickness (estimated at 10 μm in our tests).
where the fluid is particularly stagnant. Tailoring of the nanowire spacing, length and diameter thus promises to improve the interactions of nanowire surfaces with the fluid; with orders of magnitude rise in surface area upon introduction of nanowires, such improved interactions promise to bring about significant gains in heat transfer efficiency.

3.8. Theoretical treatment of the nanowire array effects on convective heat transfer

Among the various modes of heat transfer (conduction, free and forced convection, and radiation), forced convection is the mode commonly used for heat removal in fusion reactors and electronic devices as well as industrial/residential heat exchangers and commercial nuclear reactors. The heat transfer characteristics may also be enhanced by changing the properties of the fluid used for forced convection, including its density, conductivity and Prandtl number. It is worth mentioning that laminar and turbulent flows involve well-defined and random flow conditions, respectively. Turbulent flow is preferred in our approach because turbulence produces a mixing action within the fluid, and magnifies the fluid interactions with (nanowire) surfaces; these effects benefit the efficiency of active cooling.

Growth of conductive nanowires of relatively high aspect ratio and surface density upon the interior walls exposed to flowing fluid substantially increases the apparent heat transfer surface area. Copper nanowires can also excite small-scale fluid turbulence close to the wall; thus, increasing the overall heat transfer between the surface and the fluid.

The interaction between (nanostructured) surfaces and fluid in turbulent flow is very complex, and involves exchange of both heat and momentum between the turbulent eddies, and also heat exchange between the wall and eddies at various length and time scales. The structures of velocity and temperature fields directly influence the nanowire effects on heat transfer. Naturally, smaller turbulent eddies are expected to interact more with nanowires. Therefore, by tailoring the size and

---

Table 2. Heat transfer test data for pipes with 6 and 9 mm internal diameter

| Surface Finish Prior to Nanowire Growth | Nanowire Structure | Inlet Pressure, psi | Outlet Pressure, psi | Flow Rate, SLPH | Temperature Rise (% Increase)* |
|----------------------------------------|--------------------|--------------------|----------------------|----------------|-------------------------------|
| Reamed                                 | Porous/polycrystalline | 291                | 291                  | 1030           | 34.1 ± 1.0 (32%)              |
| Reamed & milled                        | Porous/polycrystalline | 291                | 291                  | 1048           | 30.8 ± 1.2 (20%)              |
| Reamed & horned                        | Porous/polycrystalline | 293                | 293                  | 1030           | 32.5 ± 2.5 (26%)              |
| Reamed                                 | Solid/crystalline   | 291                | 291                  | 1035           | 49.9 ± 1.4 (93%)              |
| Reamed                                 | Porous/polycrystalline | 291                | 291                  | 1035           | 36.7 (17%)                    |
| Reamed & milled                        | Porous/polycrystalline | 291                | 291                  | 1072           | 34.9 (8%)                     |
| Reamed & horned                        | Porous/polycrystalline | 292                | 292                  | 1072           | 38.1 (21%)                    |
| Just drilled                           | Porous/polycrystalline | 290                | 290                  | 1052           | 37.2 (18%)                    |
| Sand blasted                           | Porous/polycrystalline | 291                | 291                  | 1066           | 35.3 (12%)                    |
| Reamed                                 | Solid/crystalline   | 291                | 291                  | 1040           | 48.3 (54%)                    |

*Versus condition prior to nanowire growth
structure of the turbulent vorticity field one can intensify the heat exchange between nanowires and the flowing fluid.

The benefits to heat transfer resulting from nanowire growth on cooling surfaces can be largely attributed to the rise in surface area and the enhanced near-wall fluid/turbulence interactions with the surface. Based on classical heat transfer models for fully developed turbulent pipe flow, we have performed preliminary analyses of the overall heat transfer by convection in pipes with and without nanowires. These preliminary calculations simply (and conservatively) view nanowire growth as a means of surface roughening, neglecting any interactions of the fluid with the large peripheral surface area of the nanowires. Even this conservative approach predicts significant gains in heat transfer efficiency with introduction of nanowires on hot surfaces.

### 3.9. Theoretical modelling and analysis

An important dimensionless parameter involved in convective heat transfer is the Reynolds number. For a hollow cooling channel or pipe, the value of the Reynolds number determines if the flow is laminar or turbulent (Zhong et al., 2006). In turbulent flow, the boundary layer thickness and the average size of vertical turbulent structures in pipe or channel flow decrease as the Reynolds number increases. Here, the Reynolds number is defined as:

$$R_e = \left( \frac{\rho_f}{\mu_f} \right) \cdot \frac{u_a}{D_h}$$

where, $\rho_f$ is the density of the fluid, $\mu_f$ is the dynamic viscosity of the fluid, $u_a$ is the average fluid speed and $D_h$ is the hydraulic diameter of the channel or the inner diameter of the pipe.

The boundary layer forms near the pipe wall surface because the fluid velocity in direct contact with the solid surface goes to zero due to viscous forces acting between the shearing fluid/wall layers. Since fluids deform easily, the wall friction physically forces a parabolic boundary layer profile. Moving away from the wall, flow begins to return to free-stream velocity. The distance from the wall to the location where flow velocity returns to 99% of the free-stream velocity is called the boundary layer thickness. The boundary layer thickness for the pipe flow conditions considered in our experimental work was calculated at about 100 $\mu$m. This thickness and the inner structure of the boundary layer are very important as far as the effect of nanowires on heat transfer in turbulent flows is concerned. The thermal boundary layer, which is related to the fluid momentum/velocity boundary layer, is more important in heat transfer. The relative thickness of the thermal boundary layer with respect to the momentum boundary layer depends on the boundary conditions for temperature and velocity, and on the ratio of viscosity to thermal diffusivity (the Prandtl number). Under normal operating conditions, the Prandtl number is close to 1 for both nitrogen and helium, indicating that the thermal and the momentum boundary layers are somewhat similar.

The Reynolds number in our experimental setup is close to 100,000; we calculated the friction factor from the Moody diagram using this Reynolds number. The friction factor is directly related to the pressure loss in fully developed pipe flow, and is very different in laminar and turbulent flows. Convective heat transfer is dependent upon the fluid mechanics and friction factor. Generally, the rate of heat transfer increases with increasing friction factor. With the Reynolds number and the friction factor known, semi-empirical correlations can be derived for convective heat transfer of fully developed turbulent pipe flow to calculate the convective heat transfer coefficient and the overall heat transfer between the surface and fluid. The Moody diagram indicates that the roughness of the pipe interior surface strongly influences the friction factor (and thus the rate of heat transfer). In a preliminary approach to the calculation of the nanowire effect on the rate of heat transfer, we made the conservative assumption that nanowire growth upon the interior pipe surfaces can be viewed as a means of roughening the pipe surface. This analysis is summarized below.

Our preliminary analysis of the pipe flow conditions considered in our experiments assumed a constant mass flow rate ($\frac{dm}{dt}$) along the pipe:
\[
\frac{dm}{dt} = \frac{dm_0}{dt} = \frac{dm_l}{dt} = \rho \cdot V \cdot A
\]

where, \( \rho \) is the fluid density, \( V \) is the fluid average velocity and \( A \) is the pipe cross-sectional area \((= \pi \cdot D^2/4)\). The mass flow rate in our experimental work was \(8.8 \times 10^{-3}\) kg/s, and the pipe diameter and areas were 6 mm and 28.3 mm\(^2\), respectively. Pipes of 9 mm diameter were also considered in our experimental work.

Example values of pressure and temperature at \(x = 0\) \((P_0\) and \(T_0)\) were 2025 kPa \((294\) psi\) and 300 K, respectively, in our laboratory studies. The values \((at\ x = 0)\) of fluid density \((\rho_0)\), volumetric flow rate \((V_0)\) and Reynolds number \((Re_0)\) can be calculated as follows:

\[
\rho_0 = \frac{P_0}{R \cdot T_0} = \frac{2025}{0.297 \times 300} = 22.7\text{kg/m}^3
\]

\[
V_0 = \left(\frac{dm}{dt}\right) / (\rho_0 \cdot A) = \left(8.8 \times 10^{-3}\right) / \left(22.7 \times 28.3 \times 10^{-6}\right) = 13.7\text{m/s}
\]

\[
Re_0 = \frac{\rho_0 \cdot V_0 \cdot D}{\mu_0} = 22.7 \times 13.7 \times 6 \times 10^{-3} / \left(1.78 \times 10^{-5}\right) = 104,900 \gg 3000,\text{indicating turbulent flow.}
\]

In the above equations, \(R\) is the gas constant \((8.314/28 = 0.297\) J per Kelvin, and \(\mu_0\) is the fluid viscosity. The Moody diagram yields \((\text{with Reynolds number of 104,900 and smooth pipe})\) a friction factor \((f)\) of 0.018.

The friction factor can be used to calculate the Nusselt number \((Nu_0)\), which relates to the convective heat transfer coefficient \((h)\) as follows:

\[
Nu_0 = \left[\frac{\left(\frac{f}{8}\right) \cdot (Re_0 - 1000) \cdot Pr}{1 + 12.7 \cdot \left(\frac{f}{8}\right) \cdot 0.5 \cdot \left(\frac{Pr}{1000} - 1\right)\right]} \cdot \left[\frac{0.02}{8} \cdot (104911 - 1000) \cdot (0.716)\right] = 184
\]

In the above equation, \(Pr\) is the Prandtl number \((0.716)\). The convective heat transfer coefficient \((h)\) can be derived using the Nusselt number as follows:

\[
h = Nu_0 \cdot K / D = 184 \cdot \frac{25.9 \times 10^{-3}}{6 \times 10^{-3}} = 794\text{W/m}^2\cdot\text{K}
\]

In the above equation, \(K\) is the thermal conductivity of the fluid \((nitrogen\ in\ our\ experiments)\). The interaction of nanowires \((grown\ upon\ the\ interior\ pipe\ surfaces)\) with turbulent flow is a complex phenomenon. As a rough, conservative assumption, we neglected the beneficial complexities produced by the high surface area and protruding \((slender)\) geometry of the nanowires and their ability to form small Eddies \((see\ Figures\ 1\ and\ 2)\), which effectively interact with the magnified surface area of the nanowires. Our preliminary approach, which views nanowires simply as increased surface roughness, is expected to yield the lower limit of gains in convective heat transfer coefficient resulting from nanowire growth upon the interior pipe surfaces. In order to implement this approach, we need to define a relative roughness for use in the Moody diagram.

The relative roughness is the ratio of average surface roughness to pipe diameter. The lengths of nanowires we have grown in our experimental work ranged from 10 to 50 \(\mu\)m. The relative roughness is, thus, \([10 + 50]/2\times6000\ = 0.005\). For the Reynolds number of 104,900 calculated earlier, with relative roughness of 0.005, the Moody diagram indicates a friction factor \((f)\) for the rough pipe of 0.032 \((compared\ to\ 0.018\ for\ smooth\ pipe)\). The Nusselt number \((Nu_0)\) and the heat transfer coefficient \((h)\) with this value of friction factor can be calculated as follows:

\[
Nu_0 = \left[\frac{\left(\frac{f}{8}\right) \cdot (Re_0 - 1000) \cdot Pr}{1 + 12.7 \cdot \left(\frac{f}{8}\right) \cdot 0.5 \cdot \left(\frac{Pr}{1000} - 1\right)\right]} \cdot \left[\frac{0.02}{8} \cdot (104911 - 1000) \cdot (0.716)\right] = 354
\]
\[
h = Nu_0 \cdot \frac{K}{D} = 354 \cdot \frac{25.9 \times 10^{-3}}{6 \times 10^{-3}} = 1528 \text{ W/m}^2 \cdot \text{K}
\]

The conservative view of nanowire growth as a means of increasing surface roughness, thus, projects an increase of the convective heat transfer coefficient \(h\) from 794 to 1528 W/m\(^2\).K (by 92%). Even this conservative estimate is observed to yield major gains in the heat transfer coefficient, which can be further increased by increasing the Reynolds number. It is worth re-emphasizing that the increased surface area and the interactions of nanowires with turbulent flow are expected to further enhance the nanowire benefits to convective heat transfer coefficient beyond those calculated here. The theoretically conservative prediction that the heat transfer efficiency can be almost doubled with introduction of nanowires in our experimental conditions compares well with our test results. This finding indicates that the nanowire spacing and geometry considered in our experiments limits the fluid access to the tremendous peripheral area of nanowires; the nanowire interactions with fluid are thus limited to their tip surface area (which is the assumption of our conservative theoretical analysis).

The Reynolds analogy (Burmeister, 1993) used above suggests that the convective heat transfer coefficient, \(h\), is proportional to the friction factor, \(f\), because shear generates resistance to flow as well as thermal resistance for fluids with Prandtl numbers close to one (which is the case in our experiments). Given the relatively low fluid velocity within the boundary layer near the pipe surface, convective heat transfer would benefit from protrusion of nanowire tips above the laminar sublayer into the turbulent boundary layer section of flow. One may argue that a useful parameter for characterizing heat transfer in pipes with nanowires grown upon their interior surfaces should be the ratio of nanowire length to the laminar sublayer thickness. The laminar (viscous) sublayer is the closest sublayer to the pipe wall in a turbulent boundary layer, where viscous effects are dominant. The laminar (viscous) sublayer thickness for our experimental conditions was calculated at about 10 μm. It is worth mentioning that increasing the Reynolds number reduces the boundary layer thickness; thus, enhancing the benefits of nanowires toward convective heat transfer. One should distinguish between the effects of nanowires on turbulent velocity fluctuations versus temperature fluctuations.

The preliminary theoretical analysis presented above is based on the highly conservative assumption that nanowires interact with the fluid only via their limited tip area (which is order of magnitude smaller than their peripheral area). The nanowire diameter, surface density and length can potentially be selected to enable effective interactions of their enormous (peripheral) surface area with the coolant by exciting local turbulence (vortices), and by ensuring that the nanowire length protrudes above of the viscous sublayer (or the boundary layer). The versatility of copper nanowire arrays in terms of surface density is particularly important because, within the narrow passages between nanowires, flow quickly becomes laminar or even stagnant near the nanowire surfaces. For a similar reason, the ability to increase the nanowire length above the laminar sublayer (near the pipe wall) can further enhance the gains in convective heat transfer with nanowire growth.

In summary, the gains in heat transfer efficiency associated with nanowire growth on actively cooled surfaces can be further improved through: (i) improving the nanowire structure and thermal conductivity; (ii) increasing the nanowire length, and tailoring the nanowire diameter and surface density; (iii) increasing the fluid velocity (mass flow rate); (iv) increasing the Prandtl number; (v) generating secondary and swirling flows and (vi) exciting small-scale turbulence near the surface. A higher fluid velocity will increase the Reynolds number and decrease the boundary layer thickness, thereby enhancing the interactions between nanowires and small-scale turbulence close to the surface. The Reynolds number can also be increased (at constant flow rate) by decreasing the pipe diameter; this step also increases the friction factor (and thus the heat transfer efficiency). Similar benefits can be realized by increasing the nanowire length, especially when it exceeds the viscous sublayer thickness in the boundary layer. Increasing the Prandtl number is another beneficial step which decreases the thermal boundary layer thickness, thus intensifying the exposure of nanowires to small-scale fluctuating temperature fields, and thereby benefiting heat...
transfer by increasing the interactions between nanowires and the fluid temperature field. Other means of increasing the fluid interactions with nanowires include extended surfaces, swirl tape, roughening and porous media heat exchangers, and exciting the near-wall small-scale turbulence by physically or acoustically perturbing the flow (Baxi & Wong, 2000). A viable combination of these steps promises to produce multifold gains in convective heat transfer associated with nanowire growth upon actively cooled surfaces.

4. Conclusions

Significant increases of up to 94% in heat transfer have been found by growing copper nanowire arrays on actively cooled surfaces. This increase was achieved by optimizing the process used to produce the nanowires and the preparation of the surface on which the nanowires were grown. Highly alkaline solutions are required to cause copper hydroxide to precipitate as nanowires. The growth of these nanowires is nucleated by defects at the copper surface, and so the morphology and density of the nanowires is sensitive to surface preparation of the copper. The initially grown copper hydroxide nanowires were reduced to yield porous copper nanowires with small crystallite grains. The best heat transfer increase realized with this nanowire coating was only 32%. Annealing of the nanowires to reduce the porosity and increase the grain size lead to close to a tripling of the heat transfer improvement. Based on a theoretical analysis the improvement is assigned to interactions of the enormous (peripheral) surface area of the nanowires with the coolant, and increased local turbulence caused by the nanowires. Further increases in efficiency are predicted if the nanowires protrude above of the viscous sublayer (or the boundary layer). Potentially controlling the surface density of the nanowires could also yield further improvement, as within the narrow passages between nanowires, fluid flow quickly becomes laminar or even stagnant near the nanowire surfaces.

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