State of the Art of CHF Enhancement using Graphene Oxide

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1. Introduction

Graphene Oxide (GO) is chemically modified graphene, which is different from graphite with its structural difference and their molecular structure. Graphene oxide is a fragment of graphene with carboxyl functional group which has electrical polarity. Because of its characteristic, GO has a benefit of good solubility with water base solutions. Researchers can deposit graphene oxide on a heater surface by boiling of GO nanofluid (mixture of distilled water and graphene oxide nanoparticles) with electrically direct heating. Also, in this coating process, rough graphene structure is formed on the heater surface. Through the process of heating graphene oxide nanofluid with electrically direct heating, the functional groups like carboxyl functional group which has oxygen are degraded from its graphene body. This is reduction process of GO. This reduction process changes the characteristic of graphene oxide and affination between water and GO nanoparticle. This chemically inherent GO characteristic makes variation of CHF values using different GO nanofluids in pool boiling experiments [1, 2, 3, 4, 5].

The CHF enhancement mechanism using GO nanofluid is not clearly defined. A number of studies of pool boiling with graphene oxide argue that the mechanisms of CHF enhancement with GO are surface wettability, hydrodynamic instability, thermal activity [5], microlayer dryout model, and so on. But they cannot fully explain how GO enhances the CHF.

This paper is a review of CHF enhancement meachsnim using GO nanofluids. We analyze and compare CHF value, porosity, permeability ,and Scattering Electron Microscope (SEM) images to validate Liter-Kaviany CHF mechanism.

2. Reduction of Graphene Oxide

GO has a structure of graphene plate with functional group like carboxyl, hydroxyl and aldehyde [6, 7, 8]. Simply, GO is oxidized (combined with oxygen) grapheme. There are many ways to reduce GO (detach oxygen from graphene plate). There are three kinds of reduction method; adding deoxidizing agent, using heat to cut the bond between carbon and oxygen, and electrochemical reduction. Most of pool boiling experiments use direct joule heating using wire and plate heater surfaces. This heating method can reduce GO with electrochemical method and heating method.

At the beginning of reduction of graphene oxide, hydrophilic functional groups are separated from graphene. And then, dispersed reduced GO starts to attract to each other and make cluster of graphene (Reduced Grapheme Oxide; RGO) [6, 7, 8]. Bright brown GO solution turns into immiscible liquid with black clustered graphene while GO are clustered. Fig. 1 shows graphene oxide nanofluid and reduced graphene nanofluids.

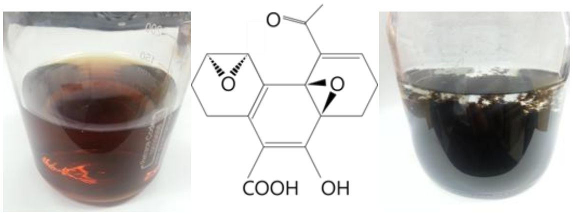


Fig. 1. GO and RGO fluids

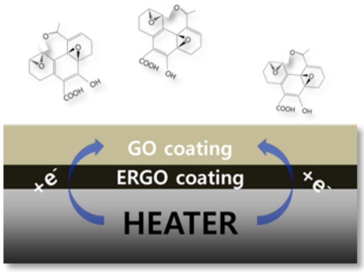


Fig. 2. Reduction of Graphene oxide on heater surface

2. CHF enhancement with Graphene Oxide

Until now, the study of CHF enhancement has been conducted widely. But the studies using GO nanofluids are limited. Wire and plate heaters were studied using GO nanofluids and the concentration of GO nanofluids was in ranges from 0.0001 vol.% to 0.001 vol.%. In the case of wire pool boiling experiments, the diameter of heaters was in the range from 0.1 mm to 0.5 mm.

Table I Summary of studies on enhancing CHF with graphene oxide nanofluid

	concentration	*Heater type*	*Heater geometry*	*CHF enhancement*	*Used mechanisms*	*note*
SD. Park[1]	0.001 vol.%	Wire	Dia = 0.5 mm	279 %	Thermal activity, Hydrodynamic instability(λ)	
SD. Park[4]	0.0001 vol.%	Wire	Dia = 0.49 mm	187 %	Micro layer dryout	Tilted heater effect
HS. Ahn[17]	0.0005 wt.%	Wire	Dia = 0.1 mm Dia = 0.2 mm	120 % ~320%	Hydrodynamic instability(λ)	Two-side coating effect
HS. Ahn[18]	0.0001 wt.% (0.000056 vol.%)	Plate	25 mm x 20 mm	200 %	Porosity, Thermal activity	
	0.0005 wt.% (0.000028 vol.%)		25 mm x 20 mm	162 %		
	0.001 wt.% (0.00056 vol.%)		25 mm x 20 mm	150 %		
SB. Moon[20]	0.001 vol.%	Wire	Dia = 0.5 mm	167 %	Wettability & other factor	Coating time

Commonly, in the case of pool boiling experiment, the critical heat flux can be predicted by Zuber CHF correlation [9].

$$q_{CHF(zuber)} = \frac{\pi}{24} h_{lg} \rho_g^{0.5} [\sigma g(\rho_l - \rho_g)]^{1/4} \text{ ---- } (1)$$

But the model did not consider any heater surface characteristics so that vapor jets are fixed even though the different heater surfaces are considered.

Table I. is the summary of studies on enhancing CHF with graphene oxide nanofluid. Park et al. [1] used 0.001 vol.% GO nanofluid and the CHF was enhanced ~ 279 % using 0.5 mm diameter wire surface. To investigate CHF enhancement mechanisms, contact angle and capillary height were measured and compared with Al_2O_3 nanofluid. The deposition layer of GO surface was confirmed by SEM image and the coating surface was compared to the Al_2O_3 experiment. The GO coating surface showed regular structure, which could be called as 'self-assembly'. This result is different from Al_2O_3 result, which has irregular structure. The measurement result of contact angle and capillary height did not enchanced compared to the bare wire. The CHF enhancement mechanism, described by surface wettability CHF model, could not explain the result of GO nanofluid.

To analyze CHF enhancement, they discussed about the property of graphene, which delivers heat conduction effectively. Thermal activity was introduced to explain CHF enhancement. Not only using thermal activity, hydrodynamic instability was also described to explain CHF enhancement. Rather than surface wettability, the change of wavelength agreed with CHF enhancement mechanism.

Park, et al [3], suggested GO nanofluid as a coolant of ERVC (External reactor vessel cooling) for IVR (in-vessel retention) of nuclear power plant to cool down corium. So they considered various heater angles. Horizontal, 30°, 60°, and vertical heater's CHF values were also demonstrated using high-speed images. As results, CHF enhanced ~187 % in horizontal and ~142 % in vertical heater using GO nanofluid.

Ahn, et al [4] used 0.1 mm and 0.2 mm wire heaters in pool boiling experiments. One notable result is that the coating layer and structure was different for each side of wire (anode & cathode, Fig. 2). GO which has carboxyl functional group is negatively charged and is dragged to anode because of electric field around wire heater during pool boiling. This phenomenon made thicker coating layer in the anode side. Also, CHF is occurred in cathode side because of immature coating layer on cathode side. If the wire was coated regularly with GO, CHF could be enhanced up to 320 %. They used thermal activity to explain how CHF is enhanced. After Coating surface test, in the position of anode, the wettability did not enhanced. And also they found coating tendency has Taylor-wavelength.

Ahn, et al [5], used plate heater and reduced graphene oxide (reduced with hydrazine) from 0.0001 to 0.001 wt.% nanofluid. They used 25 mm x 20 mm silicon oxide surface coated with platinum heater to charge the electricity for boiling experiments. They found that the CHF enhancement was degraded when high concentration GO nanofluid was used. However, onset of nucleate boiling was triggered at lower heat flux when the concentration of GO was increased. Also, the structures of RGO coting were divided into three groups; BGL (Base graphene layer), SGF (Self Assembled foam like graphene structure) and TGL (Thickly aggregated graphene layer). In the case of SFG and TGL, they have hydrophobic characteristics.

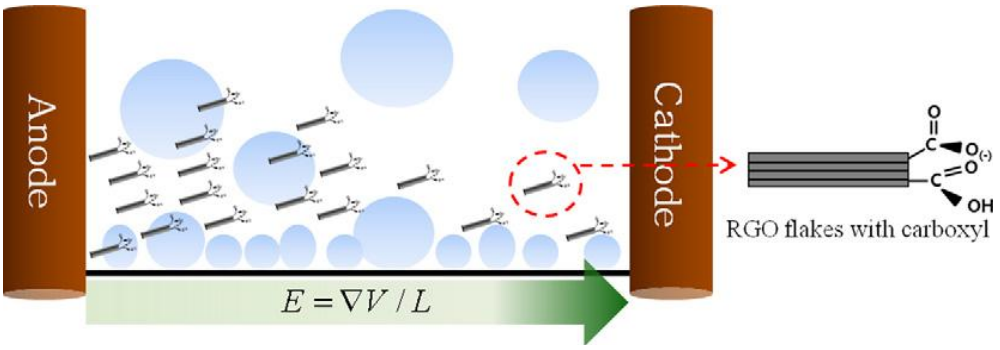


Fig. 3. electrophoresis of the RGO coating during pool boiling [17]

Regrading boiling heat transfer, SFG and TGL has advantage in boiling heat transfer. They explained how RGO flake was aligned and how coating layer interacted with water and explain wettability of RGO coating by carboxyl group activation. They analyze CHF enhancement with porosity structure and good heat transfer property of graphene..

Moon, et al [2] demonstrated pool boiling experiment using 0.5 mm Ni-Cr wire. Boiling curve was obtained with 167 % CHF enhancement. In this research, the electrochemical reduction of GO was main focus by describing surface coating and advance contact angle and receding contact angle for various heat flux points (=elapsed time). As result, GO coated on the surface and floating in the fluid is reduced as boiling time was increased. And the biggest amounts of reduction were occurred at CHF region. To find out the tendency of reduction process, contact angle was measured for various coating time steps. Contact angle is related to the characteristic of infinity between GO and water because oxygen-carbon bonds in GO interacted with water. Enhanced CHF value of 167 % was not explained by wettability. They concluded other facts should be considered to explain the change of CHF instead of surface wettability aspect.

Difference of CHF enhancement between Ahn's [4] experiment of once-side-coated wire experiment and Park's and Moon's wire experiment can be explained by the geometrical difference. Relatively, Ahn's [4] wire was much thinner and much longer than Park and Moon. This long and thin wire makes more different coating tendency between anode and cathode. But, in Park's and Moon's experiment, thick and short wire did not make big difference coating structure between anode and cathode.

4. Heater Surface SEM images

Nanofluids boiling experiment changed the surface morphology, so observations of coating surface are needed. SEM and TEM techniques are commonly used to investigate the surface characteristics.

Fig. 3 is SEM images obtained from references, which used GO nanofluid in pool boiling. Fig. 3(A) is Park's coating surface SEM image. The porous structure could be found and the size of pore was estimated as 2 μm.

Fig. 3(B) and (C) are Ahn's plate pool boiling coating surface images. The pore size of coating layer can be estimated in Fig.3 (B) and coating surface thickness was measured using Fig. 3(C). In the case of 0.0005 wt.% concentration, pore size was measured in 2 μm and coating thickness was measured in 10 μm. In the case of 0.001 wt.%, pore size was increased with 5 μm and thickness was also increased with 45 μm. .

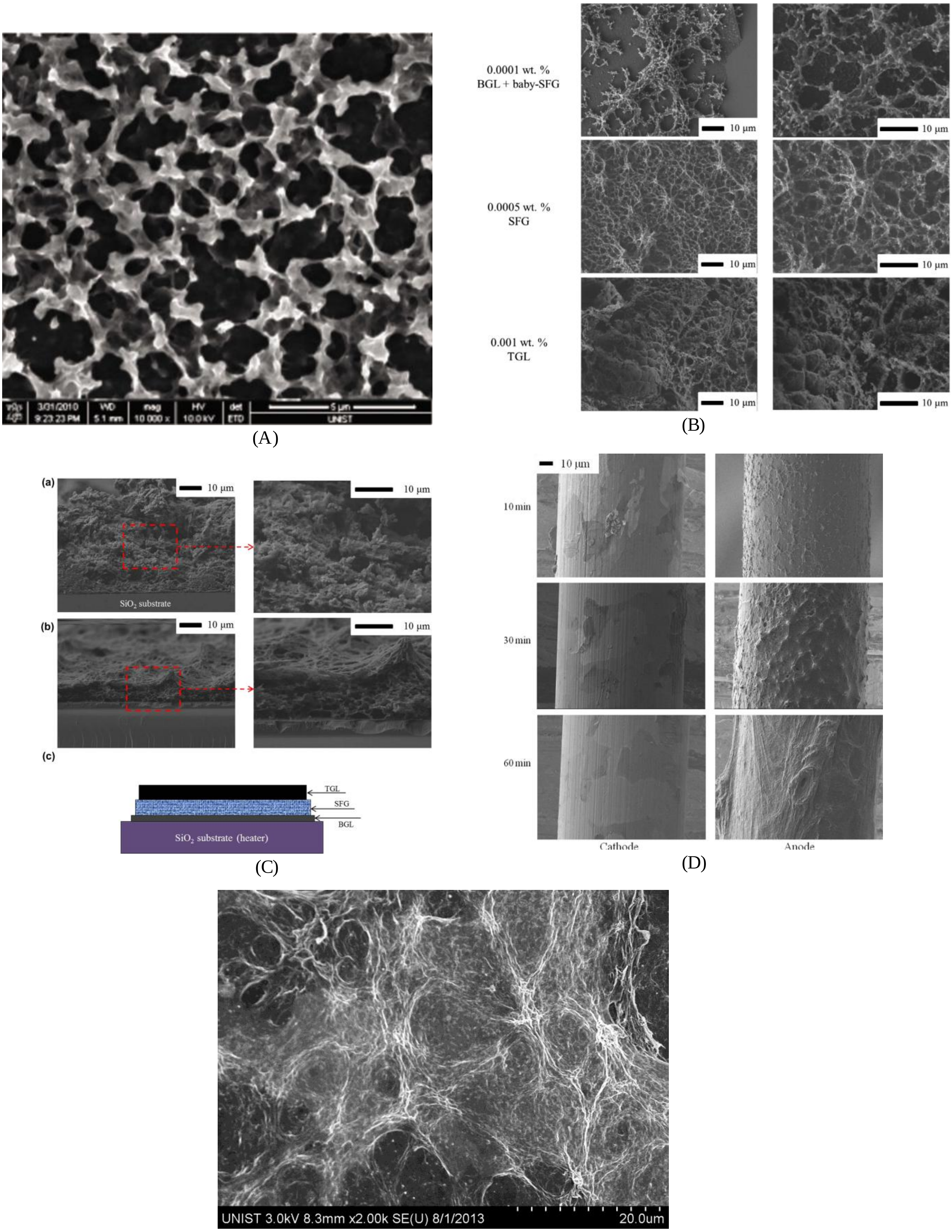
In the SEM image of Ahn's study Fig. 3(D), the different coating characteristics in cathode and anode were observed. Pore size was measured as 1 μm from SEM image.

In the SEM image of Moon's study Fig. 3(E), pore size was estimated as 2 μm. If the coating thickness of GO surface was assumed that coating thickness is proportional to GO concentration, the coating thickness can be estimated as 3.6 μm. Those coating thickness values will be considered in the next chapter.

Table II lists the summary of those surface coating thickness and pore size from references.

Table II. Coating pore size and thickness

	heater	*Concentration*	*d[μm]*	*D[μm]*
Park	Wire	0.001vol.%	2	3.6
Ahn	Wire	0.0005wt.%	1	1
Ahn	Plate	0.0001wt.%	2	10
		0.001wt.%	5	45
Moon	Wire	0.001vol.%	2	3.6



(A)

(B)

(C)

(D)

(E)

Fig. 4. SEM images from references. SD Park (A)[1], HS Ahn (B)[5], (C), HS Ahn (D)[4], Moon (E)[21]

5. Permeability and porosity effect on heater surface

Various mechanisms are considered to analyze CHF enhancement. There are hydrodynamic instability model, macro-layer dryout model, bubble interaction model, hot/dry spot model, and so on. Hydrodynamic model explains CHF with Zuber CHF correlation [9]. But, heater surface coating effect and liquid characteristic are not considered in the modeling. So there is limit to explain CHF enhancement with GO nanofluid or other coolants. Macrolayer dryout model [10] explains the CHF mechanism that CHF takes place when the heat flux is sufficient to boil the liquid film on heater surface before the mushroom shape vapor bubbles depart from surface. Bubble interaction model analyzes CHF mechanism with closed packed bubbles on heater surface. These closed packed bubbles interrupt liquid flow to the surface and make CHF. Bubble wait time, bubble departure time, and nucleation site density are key parameters of this model. On the other hand, hot/dry spot model determines the CHF when irreversible process was occurred at the dry patches due to the high heat flux. Surface wettability, modulation wavelength, and capillary force affect the CHF enhancement. Especially, porosity and permeability give driving force to liquid being supplied in the heater surfaces. Liter and Kaviany [11] modified Zuber's hydrodynamic instability model to explain vapor film formation on coating surface which blacks liquid to approach to the heater surface because of coating surface. Viscous-drag liquid chocking limit model (Fig. 5) explains that, when boiling occurs on the heater surface with liquid supplying through porous structure, CHF will be obtained when the ability of supplying liquid cannot satisfy the need of liquid to cover up the heater surface (bottom of coating) because of drag resistance between water and coating structure. CHF correlation about this capillary limit is below.

$$\frac{q_{CHF,c}}{0.53\left(\rho_l \sigma h_{lv}/\mu_l\right)\left(\left(K\varphi_s\right)^{1/2}/D\right)} = 1-\frac{C_E}{0.53}\frac{D}{\sqrt{\varphi_s}}\frac{q^2}{\rho_l \sigma {h_{lv}}^2} \quad \text{-------------(2)}$$

μ_l is viscosity of liquid, K is permeability of surface wick structure, C_E is Ergun coefficient, D is flow distance of liquid, and, φ_s is porosity of coating structure. As parameter of nanofluid coating, flow distance is coating thickness. And Cormen-Kozeny model calculates K and C_E with below equation

$$K=\frac{\varphi_s d^2}{\left[180\left(1-\varphi_s\right)^2\right]} \quad \text{---------------(3)}$$

$$C_E=\left(0.018/{\varphi_s}^3\right)^{1/2} \quad \text{---------------(4)}$$

Here, d is characteristic length which is determined by pore size of surface

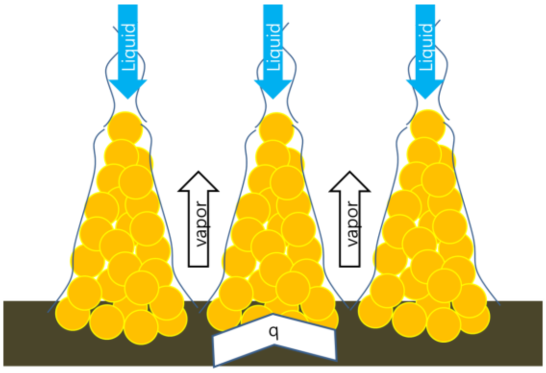


Fig. 5. Viscous-drag liquid-choking limit

Coating thickness is determined by nanofluid concentration and boiling time (taken time from nucleate boiling to CHF) and pore size can be measured by SEM observation. To evaluate predicted CHF with equation (2), the porosity property is needed. Because the porosity data were not measured in each reference, SEM images were compared with calculated porosity. Table III lists the summary of pore size, porosity, and permeability based on calculation.

Table III Calculated porosity and Permeability

	Heater	*Concentration*	*porosity*	*Permeability (x10^19)*
Park	Wire	0.001 vol.%	0.000846	188
Ahn	Wire	0.0005 wt.% 0.00028 vol.%	0.0002	11.00
Ahn	Plate	0.0005 wt.% 0.00028 vol.%	0.00137	305.3
		0.001 wt.% 0.00056 vol.%	0.00234	3265.264
Moon	Wire	0.001 vol.%	0.00051	113.449

In the CHF correlation of Liter and Kaviany, the important surface parameters are porosity, pore size, and coating thickness. In the reference, however, porosity was not measured. So the validation of Liter and Kaviany's model will be analyzed based on backward calculated porosity from CHF values and SEM images.

Basically, porosity of Ahn's plate pool boiling had the biggest porosity. In the same condition, porosity was bigger than other wire pool boiling experiments. Though twice bigger porosity and bigger than twice sized pore makes 10 times bigger permeability value was calculated. The increase of pore size can make decrease of CHF. This result is also obtained from heater coating thickness. Heater thickness was much bigger than those other plate experiments. Thicker coating layer blocks liquid supply into the coating layer and this made low CHF value.

In the results from studies of Moon and Park, the CHF values were different even though the same experimental condition was applied. the reason why the pore size and the coating thickness were the same but CHF is different, difference of porosity. This can be easily found out in difference between Fig 2(A) and (E). This implies that different coating surface could be formed using the GO nanofluids. This means that different coating structure can make different CHF value which follows Ahn's study: different GO nanofluid coating structure (BGL, SFG and TGL).

Thin coating thickness does not provide good permeability so the enhancement of CHF was less than the thicker coating layer..

6. Conclusion

It is well know that cooling a high temperature structure, nucleate boiling region has the biggest efficient in heat transfer. And the cooling limit is determined by critical heat flux. To enhance the CHF, many kinds of nanofluid [12, 13, 16, 15, 14, 17] were studied. Especially in GO nanofluid, it showed that the biggest CHF enhancement was obtained but the enhancement mechanism was not clear. The discrimination of GO compared to other nanoparticle is uncertainty attributed from reduction of GO. Because GO has polarity, different coating characteristics was obtained at the opposite electric sides.

In this paper, the study of CHF enhancement mechanism was conducted using Liter-Kaviany models instead of surface wettability in GO nanofluid. Surface porosity, capillarity, and permeability were considered. The following results were obtained.

1. With Ahn's plate pool boiling experiment, high porosity structure makes good permeability with CHF enhancement. But if the coating thickness is very thick, thickness resistance blocks liquid supply into the heater surface. This makes less CHF value.
2. In the same experiment condition, if porosity is big, CHF is more enhanced. Different pore size is made for different coating structure like Ahn's study.
3. If GO nanofluid is directly heated with electricity, coating is differently formed in the position of each anode and cathode. In this case, relatively thin and not sufficient coating is formed in cathode because this cannot supply the liquid onto surface. Because of this structural difference between cathode and anode, CHF is much bigger in uniformly coated wire (twice coating with changing cathode and anode).
4. In this research, porosity is calculated from Liter-Kaviany correlation. And this value and SEM images are compared to each other. With this comparison, tendency is well satisfied. So, Liter-Kaviany CHF correlation using permeability can explain the CHF enhancement tendency well.

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