PREPARATION AND CHARACTERIZATION OF COPPER OXIDE NANOPARTICLES AND DETERMINATION OF ENHANCEMENT IN CRITICAL HEAT FLUX

by

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The main focus of the present work is to prepare the CuO nanoparticles by economical sol-gel method and further to prepare the CuO nanofluid with base fluid as deionised water. The size of nanoparticles is determined by Debye-Scherer formula and size of the particles is conformed 20.4054 nm.

Critical heat flux characteristics of nanofluid were investigated with different weight concentrations of CuO nanoparticles. The experimental work revealed an increase in critical heat flux value just about 57.26%. Surface roughness of heater surface is measured for all weight concentrations of nanofluid which shows increase in R_a value up to some extent is a cause to enhance critical heat flux.

Key words: nanoparticles, nanofluid, critical heat flux, enhancement, de-ionised water

Introduction

Copper oxide nanoparticles are synthesized by aqueous precipitation method using CuCl₂ as a precursor and NaOH as stabilizing agent. This gives large scale production of nanoparticles. In the last decade, the developments of nanosize materials of metal and metal oxide particles are intensively pursued because of their prominence in different fields of applications. In all the transition metal oxides, CuO nanoparticles are used for the applications of magnetic storage devices, solar energy transfer, sensors and super capacitors, chemical plants, *etc.*

In general there are number of metal oxides are available in nature but some of the metal oxides are most useful in accordance with their applications in day to day life in science and technology. In the periodic table transition metals are large in number and have number of applications in different fields. Among the oxides of transition metals, CuO nanoparticles are of special interest because of their efficiency as nanofluid in heat transfer application. For example it has been reported that addition of CuO improves the thermal conductivity of water [1, 2]. The CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photo thermal applications.

Some transition metal oxides like ZnO, TiO_2 , Fe_3O_4 , *etc.* proved as potential candidates for so many applications. In the same way CuO is also one of the useful metal oxides and which has so many applications in various fields. The uniqueness of CuO nanoparticles is even though,

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they are metallic in bulk but they behave like semiconductors when they are in nanosize. Semiconducting materials have been particularly interesting because of their great practical importance in electronic and optoelectronic devices, such as electrochemical cell, gas sensors, magnetic storage devices, field emitters, high-tc super conductors, nanofluid and catalysts, etc. Due to the potentiality of CuO, it acts as a catalyst, whereas all metal oxides are not useful for the catalytic activity. In the fabrication of super capacitors also CuO is very useful and in nanorange it has the wide band gap nearly equal to ZnO. The favourable band gap of CuO around 2.6 eV makes it useful for solar energy conversion and it can be used as solar cell window material. The CuO nanoparticles act as a good catalyst in some of the chemical reactions. The CuO nanoparticles were prepared by sol-gel method. In this method CuCl₂·2H₂O (0.2 M) is added with acetic acid and heated to 100 °C with continuous stirring. To control the pH of the previous solution, NaOH is added to the solution till pH reached desired value. The colour of the solution changed from sky blue to black with precipitation. The black precipitation was washed 3-4 times with distilled water. Finally the solution was centrifuged and dried in air for one day. The CuO nanoparticles were characterized by studying their structure with X-ray diffraction (XRD) and composition by energy dispersive X-ray analysis. The size of the nanoparticles is estimated by XRD and transmission electron microscopy (TEM).

These nanoparticles are used to prepare nanofluid with base fluid as de-ionised water and experiment is conducted to determine critical heat flux (CHF) at different weight percent concentration in which maximum enhancement in CHF at 1.5 weight percent of CuO nanofluid observed 57.26%.

Preparation of CuO nanoparticles

Nanoparticles are prepared by using economical sol-gel method and characterization is done to finalize the size and purity of prepared nanoparticles.

Sol-gel method of synthesis

There are various techniques to prepare nanocrystals *e. g.* sputtering, laser ablation, cluster deposition, sol-gel method, *etc.* In the present work the synthesis of CuO is preferred by sol-gel route because this method is easy and economical [3, 4]. The sol-gel process involves the formation of colloidal suspension (sol) and gelatine of the sol to form a network in continuous liquid phase (gel). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive legends.

The aqueous solution of $CuCl_2 \cdot 2H_2O(0.2 \text{ M})$ is prepared in cleaned round bottom flask. To previous aqueous solution was added 1 ml of glacial acetic acid and heated to 100 °C with constant stirring and then 8 M NaOH is added to previous heated solution till pH reaches to 7. The colour of the solution turned from green to black immediately and the large amount of black precipitate is formed immediately. The entire process is depicted in figs. 1(a) and 1(b). The precipitate is centrifuged and washed 3-4 times with de-ionised water. The obtained precipitate was dried in air for 24 hours. This powder is further used for the characterization of CuO nanoparticles. The chemical reaction is:

 $CuCl_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaCl$ $Cu(OH)_2 \text{ decomposes into CuO on heating:}$ $Cu(OH)_2 \longrightarrow CuO + H_2O$

Structure and micro-structure of CuO nanoparticles

The structural and micro-structural properties of the CuO nanoparticles prepared by sol-gel method are:

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Structure analysis CuO of nanoparticles

Figure 2 shows the XRD pattern of prepared CuO nanoparticles. All the peaks in diffraction pattern shows monoclinic structure of CuO, and the peaks. The average grain size calculated by using Debay-Scherrer formula is approximately 20.4054 nm are comparable with JCPDS file No. [72-0269]. The lattice parameters were calculated from XRD data are: a = 0.4529 nm, b = 0.343 nm, and c = 0.507 nm. The average grain size calculated by using Debay-Scherrer formula is approximately 20.4054 nm. Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where β is full width at half maxima of the peak in XRD pattern and θ – the angle of the peak, wavelength of X-rays. Elastic strain is also calculated from XRD results. The strain results

suggested that if the particle size is less than 20 nm than they have more strain and greater than 20 nm particles have less strain. It clearly shows that the smaller particles have high strain and bigger particles have less strain. These values are in agreement with the literature values [3]. Morphology index was calculated from XRD full width at half maxima values and it is found that if the size of the particle increases, then the morphology index is also increases.



Figure 2. The XRD pattern of CuO nanoparticle

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Figure 3. The SEM images of CuO nanoparticles

Scanning electron microscopy examination

Scanning electron microscopy (SEM) micrographs of the synthesized CuO are shown in the fig. 3. From the figure it is quite evident that there is no definite morphology in the sample. It seems that the particles were agglomerated and form a cluster. As the particle size calculated from the XRD is in nanorange and not getting any exact information about the surface morphology of the sample from the SEM

micrograph. The morphology observed in the sample not showing any hard grains which gives the idea that size of the particle is small and further needs to be characterized by TEM to obtained exact morphology and size of the particles as shown in figs. 4 and 5. Select-area electron diffraction (SAED) image of the particles is shown in fig. 5.



Figure 4. The TEM image of CuO nanoparticles



Figure 5. The SAED of prepared CuO nanoparticles (for color image see journal web site)

Nanofluid preparation (CuO)

In the experiment, nanofluid is prepared by using two-step method, dispersing nanoparticles in to the base fluid afterward magnetic stirring continuously for four to five hours. De-ionised water is used as base fluid and CuO nanoparticles are used without using any additives. The CuO nanoparticles are prepared in the laboratory by sol-gel method. It is observed that surfactants could be used to stabilize the nanoparticles suspension, but it may have influence on the rheological behaviour of the fluid and boiling heat transfer [5]. Das *et al.* [6] noted that nanoparticles dispersed without surfactant did not change the surface tension of the base fluid.

In the present experiment, surfactants are not used and ultrasonic excitation was performed for four hours just before the experiment. A glass beaker of 500 ml capacity is used for the preparation of nanofluid. Magnetic stirrer made by Maneto Company, Model # 08849-00, rating 150 B & 230 V AC supply is used. A magnetic needle of 10×10 mm used to stirrer the solution. Mercury thermometer is used for temperature measurement. The CONTECH 0.1 mg weighing balance is used. Kshirsagar, J., *et al.*: Preparation and Characterization of Copper Oxide Nanoparticles ... THERMAL SCIENCE: Year 2017, Vol. 21, No. 1A, pp. 233-242

Determination of enhancement in CHF

The NiCr wire having 0.321 mm diameter is used as heater surface. The length of the heater is 110 mm. For benchmarking the experiment the Zuber's correlation is used initially for de-ionised water, average CHF for ten experiments is found to be 1.2 MW/m^2 , (refer figure 7).

Theoretical determination of CHF

Methodology and correlation used are presented.

The well known Zuber's correlation is used for validation of the test set-up. Experimental values of q'' is compared with that as predicted by Zuber's correlation. The q'' is calculated using Zuber's correlation:

$$q'' = 0.149 \rho_{\rm g}^{0.5} h_{\rm fg} \Big[\sigma g \big(\rho_{\rm l} - \rho_{\rm v} \big) \Big]^{0.25}$$
⁽²⁾

Experimental determination of CHF with Ni-Cr wire

Figure 6 shows a schematic illustration of the experimental set-up. The pool boiling experiment set-up consists of 250 (length) mm \times 100 (width) mm \times 230 (height) mm rectangular vessel made up of acrylic sheet. The transparent acrylic sheets are used to construct set-up to facilitate visualisation of boiling process. The thickness of acrylic sheet is 0.6 mm. On top of the vessel 16 mm thick nylon sheet is used to cover test vessel. Rubber gasket is used for the alignment of Nylon sheet on test vessel. Two holes of 5 mm diameter, each are drilled at a distance of 55 mm from centre, for inserting and holding Cu electrodes. Another hole of 20 mm diameter is drilled at the centre of the nylon sheet to hold the condenser inlet, which collects the vapours generated in the test cell. The condenser is placed at the top of test cell. One 5 mm hole is drilled, and from this K-type thermocouple is inserted in the test cell to measure the bulk temperature of the fluid during experimentation. An arrangement is done to hold the preheater in the test cell on nylon sheet. This

preheater is used to heat bulk fluid in the test cell to saturation temperature. Vent is provided through the nylon sheet, so that atmospheric pressure always acts on the test cell. Two Cu electrodes of size 5 mm (diameter) \times 150 mm (length) are used for holding the test heater. The Ni-Cr wire of 0.321 mm diameter is used as heater surface. The length of the heater is 110 mm. The DC power supply with a capacity of 60 V, 20 A is used. The power supply has a pro-



Figure 6. Schematic diagram of pool boiling apparatus; 1 - Ni-Cr wire, 2 - Cu electrodes, 3 - thermocouple, 4 - condenser; 5 - preheater; 6 - stand



Figure 7. Variation in CHF with different weight concentration of CuO nanofluid

vision to increase the voltage with a step of 0.1 V. The Cu electrodes are connected to power supply with ten gauge Cu wire and Cu lugs to have minimum resistance. Two pipes of ¹/₄ inch diameter are used for circulation of cold water and hot water from the condenser, so that, the vapours form are converted to water and the volume of test cell remains unchanged. All data are collected by the data acquisition system.

During the experimentation, condition at breaking of wire due to CHF is noted and corresponding voltage and current are recorded. The CHF is calculated:

$$q'' = \frac{VI}{\pi DL} \tag{3}$$

Uncertainty in CHF

The main source of uncertainty of the applied voltage and current only due to contact resistance between the wire heater and electrodes connected with the clamps in addition to this uncertainty also associated with length and diameter of the Ni-Cr wire heater.

The uncertainty is computed by using the equation proposed by Holman [7]:

$$\frac{\Delta(q)}{q} = \sqrt{\left(\frac{\Delta V}{V}\right)^2 + \left(\frac{\Delta I}{I}\right)^2 + \left(\frac{\Delta D}{D}\right)^2 + \left(\frac{\Delta L}{L}\right)^2} = \sqrt{1.63^2 + 3.49^2 + 0.31^2 + 1.81^2} = 4.26\%$$
(4)

The uncertainty of the applied voltage and current are 1.63% and 3.49%, respectively. The uncertainty of diameter and length are 0.31% and 1.81%, respectively. From the previous analysis the maximum uncertainty for pool boiling is estimated 4.26%.

Results and discussions

Pool boiling experiment is carried out using CuO nanofluid and CHF is compared with de-ionised water. Significantly improvement in CHF is observed. Figure 8 shows CHF values at different weight concentration of CuO nanofluid. It is observed that CHF enhancement occurs for various concentrations of Cuo nanofluid.



Figure 8. The CHF at different weight concentration of CuO nanofluid

The CHF of nanofluid has been compared with pure water by various researchers. The CHF enhancement is nearly 73% for stain steel wire with Al_2O_3 , ZrO_2 , and SiO_2 nanofluid. Kim *et al.* [8] the enhancement in CHF is only due to increase of contact area by deposition of nanoparticles over the heating surface. The nanoparticles generate porous layer on the test section tube surface thus reducing the contact angle between the fluid and heater surface [8]. The existence of sorption layer enhance the trapping of liquid in nanoporous sorption layer and prevents the vapour blankets formation, so that the CHF increases with increasing the sorption layer thickness at lower particle concentration range.

After the particle concentration exceeds a certain value, the sorption layer thickness would not increase and therefore CHF not increased, fig. 9 shows the enhancement in CHF with concentration of nanoparticles compare with deionised water. It can be observed from fig. 10, that CHF of nanofluid is greater than de-ionised water.

Nanoparticles affect the surface characteristics and therefore influence the boiling heat transfer. The concentration increased surface deposition of the nanoparticles. Thickened and more micronized structures were formed on a heating surface. The similar phenomenon was also reported by Kim *et al.* [9].

The results show that CHF enhancement is definitely possible by using different nanofluid instead of de-ionised water for



Figure 9. Ratio of CHF to CHF of de-ionised water



Figure 10. Variation in percent of increase in CHF with surface roughness

cooling fluids. However, the surface coating of heater surface is depending on particles concentrations of the nanofluid, a layer build up which may increase or decrease surface roughness that will depend upon porosity and nanoparticles size.

The surface roughness measurement is taken when the test surface exposed to different weight concentration of nanofluid after pool boiling CHF tests made, known that CHF enhancement of nanofluid is closely related with the surface microstructure and enhanced surroundings from the deposition of nanoparticles. From the study it is also known that the change in surface roughness is not only depends on the concentration but also on some other factors *i. e.* change in time [10].

In tab. 1 different values of surface roughness are given after pool boiling experiment at various weight concentrations, it is observed that there exists a thin sorption layer on the surface formed by nanoparticles. The sorption layer on the Cu surface decreases active nucleation sites and the contact angle [11]. Less active nucleation sites and the contact angle would delay inception of boiling and generation of fewer bubbles at the given heat flux, the sorption layer increases the heat resistance between metal surface and nanofluid. The surface roughness of heater influences the boiling heat transfer coefficient as shown in fig. 11. The increased surface roughness gives better heat transfer at given wall superheat [12, 13]. Webb and Pais [14] also showed the enhancement of boiling heat transfer coefficient of refrigerants by increasing the surface roughness of heaters. This was confirmed through surface roughness tests conducted before and after the boiling experiment.

Surface roughness of test wire is carried out for all weight concentration nanofluid and compare with bare wire heater as shown in figs. 11-16. Porous layer forms on the surface of heater due to interaction of carrier nanofluid during the experiment.

Sr. No.	Wt. concentration of CuO nanofluid	$R_{\rm a}$ value [μ m] of bare heater surface of Ni-Cr wire	$R_{\rm a}$ value [µm] after pool boiling exp. on heater surface of Ni-Cr wire
1	De-ionised water	0.111	0.111
2	0.3%	0.111	0.116
3	0.6%	0.111	0.464
4	0.9%	0.111	0.611
5	1.2%	0.111	1.646
6	1.5%	0.111	1.194

Table 1. Surface roughness data

It is observed that surface roughness increases from 0.116 μ m to 1.646 μ m for weight concentration 0.3% to 1.2% and surface roughness decreases to 1.194 μ m for 1.5% weight concentration, as in figs. 11-16.

This can be suggested that nanoparticles up to certain concentration could enhance CHF through the surface of heater.



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Conclusions

It is observed from the structural analysis that the CuO nanoparticles are monoclinic in nature. Strain of the prepared CuO nanoparticles concluded that the strain for small particles have high strain and for large size of nanoparticles have low strain.

The SAED shows that the nanoparticles are pure well crystallized. The average size of the particle determined by Debay-Scherrer formula is 20.4054 nm. The SEM micrograph represents agglomeration of some CuO nanoparticles.

The CHF in the nanofluid are investigated with five weight concentrations of CuO in the nanofluid at 0.3%, 0.6%, 0.9%, 1.2% and 1.5%. Ni-Cr wire is used to generate heat flux. It is observed that CHF increases with increase in weight concentration of nanoparticles. The maximum enhancement was found 57.29% over de-ionised water as boiling fluid.

It is found that surface roughness of heater wire increases with increase in weight concentration of nanoparticles in nanofluid upto 1.2% of weight concentration. Further increase in weight concentration reduces surface roughness of heater wire. It is also observed that rate of enhancement of CHF reduces after acquiring maximum surface roughness of heater, thus it is conclude that surface roughness of heater plays vital role in enhancement of CHF.

Nomenclature

D	_	diameter of heater, [m]
g	_	acceleration due to gravity, [ms ⁻²]

- $h_{\rm fg}$ latent heat of vaporization, [kJkg⁻¹]
- current, [A]
- L length of heater, [m]
- $M\ -\ mole$

q'' R_a	_	critical heat flux, [MWm ⁻²] average roughness, [µm]	$\rho_{\rm v}$ – density of vapour, [kgm ⁻³] σ – surface tension, [Nm ⁻²]
V	_	voltage [V]	Subscripts
Gre	eek	symbols	fg – vaporization
β	_	full width half maxima of the peak, [rad]	1 – liquid
Δ	_	difference, [-]	v – vapour
θ	-	peak, [rad]	Acronyms
λ	_	X-ray wavelength of vapour jets, [m]	CUE antical bast flux
ρ	_	density, [kgm ⁻³]	CHF – critical neat nux
$ ho_{\mathrm{l}}$	-	density of liquid, [kgm ⁻³]	

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