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Development of a novel thermal storage molten-salt filled with nanoparticles for concentration solar plants

Dongxiao Niu, Yan Lu, Di Wu*

North China Electric Power University, No.2, Beinong Road, Huilongguan, Changping District, 102206 Beijing, China

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Solar thermal power generation technology is the most feasible technology to compete with fossil fuels in the economy, and is considered to be one of the most promising candidates for providing a major share of the clean and renewable energy needed in the future. The appropriate heat transfer fluid and storage medium is a key technological issue for the future success of solar thermal technologies. Molten salt is one of the best heat transfer and thermal storage fluid for both parabolic trough and tower solar thermal power system. It is very important that molten salt heat transfer mechanisms are understood and can be predicted with accuracy. But studies on molten salts heat transfer are rare.

This study will lay a foundation for the application of carbon nanotubes in molten salt which can remarkably improve the stability and capacity of thermal storage. Preliminary experiments found that adding nanoparticles provided an anomalous enhancement to the specific heat capacity of molten salt. According to the experiments, multi-walled carbon nanotubes and Au nanoparticles both can enhance the specific heat capacity of molten salt by a factor approaching 100%.

In this paper, the interface thermal resistance theory is used to explain the phenomenon of the significantly improved heat capacity, then investigate the factors which affect the mechanism of specific heat capacity enhancement, such as the concentration, the size, the attributes, the stability of the nanoparticles, and dispersion behavior of the nanoparticles in the eutectic composition. The microstructure was confirmed by scanning electron microscope (SEM) and transmission electron microscope (TEM).

***Key words*:** Molten Salt, Nanoparticles, Concentration Solar Plants, Interfacial Thermal Resistance

INTRODUCTION

Solar thermal techniques are especially promising since these platforms can provide uninterrupted power supply during off peak times. Solar thermal power plants rely on high temperature thermal storage facilities and require the storage medium to have high heat capacity and thermal conductivity. Hence, there is a need to find better performing thermal-energy storage technologies and materials that are cost effective. It should be noted that novel materials (such as nano-material additives) can become cost-effective if they can increase the operating range of the storage facilities to a higher range of temperatures. High-temperature molten salt acting as the heat storage medium has the following advantages:

(1) The heat transfer coefficient of the molten salt is twice that of other organic heat carriers, making the thermal stability of the molten salt relatively high.

(2) The upper temperature limit of the molten salt which is put into practical applications is at present 600ºC.

Therefore, in order to improve the operating parameters and efficiency of solar concentrating systems and reduce the cost of electricity, approaches to enlarge the thermal capacity, enhance the heat transfer characteristics and increase the

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* To whom all correspondence should be sent. E-mail: woodncepu@163.com

thermal stability higher of molten salt, are urgently needed. Many related research works have shown that nanoparticles can enhanced heat transfer characteristics, most of these research works focus on how to improve the thermal conductivity. This paper sets out to study the change in specific heat capacity in molten salt after mixing it with nanoparticles, as well as to find the main factors causing this change. Chiefly, the motivation of this study was to synthesize novel nanomaterials for TES in CSP applications. The experiments preliminarily validate that, nanoparticles strongly enhance the heat capacity of molten salt. Moreover, much to our surprise, endothermic and exothermic characteristics of molten salt change significantly after mixing in multi-walled carbon nanotubes during a certain temperature period.

THEORETICAL ANALYSIS

There are few related research works about the mechanisms by which nanoparticles improve the specific heat.

Three independent thermal transport mechanisms were proposed to explain the unusual enhancement of the specific heat capacity:(1) Mode I: enhanced specific heat capacity through nanoparticles due to higher specific surface energy (compared with the bulk material); (2) Mode II: additional thermal storage mechanisms due to interfacial interactions between nanoparticles and the adhering liquid molecules due to the extremely high specific surface area of the nanoparticles; and (3) Mode III: the existence of a semi-solid liquid layer adhering to the nanoparticles, which are likely to have enhanced specific heat capacity due to the smaller inter-molecular spacing similar to the nanoparticle lattice structure on the surface.

However, the three theoretical models are not fully proved by theory and experiments research is still at the speculation stage. The objective of the study is to explore the effect of the addition of nanoparticles on the specific heat capacity of eutectic salt. And the influence factor and mechanical of the synthesis protocol on the specific heat capacity of the nanomaterials is also explored in this study.

In this study, multi-walled carbon nanotubes are selected as the main object of study, Au nanoparticles are also selected for comparison.

First of all, when the state of mixture of salt and nanoparticle is unclear, we have to analyse the simple mixing state in which the salt and nanoparticles are separated exist in molten state. The state is considered whether it can anomalous enhance the specific heat capacity of eutectic.

A simple mixing rule (Equation 1) was used to estimate the property values of the mixture (nanomaterials), as follows:

$$C_{p,t} = \frac{m_{np}C_{p,np} + m_b C_{p,b}}{m_{np} + m_b} \tag{1}$$

Where C_P is specific heat and m is mass of the sample. Subscripts t, np, b denote property values of the mixture (nanomaterial), the nanoparticles, and a pure solvent material (eutectic). This equation is frequently used in the nano-fluids literature.

The specific heat capacity of the eutectic is easy to determine, but the specific heat capacity at constant pressure of nanoparticles is difficult to calculate quantitatively.

The Debye theory is used to calculate the specific heat capacity of carbon nanotubes. The Debye theory assumes that a crystal is an isotropic continuous elastic medium where the thermal motion of atoms is sent in the form of elastic waves, Each elastic wave vibration mode is equivalent to an harmonic oscillator, the energy is quantized, and specifies a maximum elastic wave frequency ω_D, called the Debye frequency. Since the Debye temperature for carbon nanotube is expected to be 2500K as high as that for diamond, the quantum effect for the heat capacity is very important even at room temperature.

The degrees of freedom in a crystal which is composed of N atoms is $3N$, therefore there can only be $3N$ vibration modes, so:

$$\int_0^{\omega_D} g(\omega)d\omega = 3N \tag{2}$$

Substitution into the state density of elastic wave:

$$g(\omega) = \frac{3V\omega^2}{2\pi^2 v_s^3} \tag{3}$$

The Debye frequency values can be determined:

$$\omega_D = \left(\frac{6N\pi^2 v_s^3}{V}\right)^{\frac{1}{3}} = \left(6\pi^2 n\right)^{\frac{1}{3}} v_s \tag{4}$$

n is the number of atoms per unit volume.

The Debye crystal vibration theory is the basis of traditional crystal molar heat capacity theory, which is suitable for the calculation of molar volume heat capacity for macro crystalline materials $C_V(T)$. Through the relation between $C_V(T)$ and $C_P(T)$, $C_P(T)$ can be calculated. The $C_V(T)$ formula in the Debye model theory is :

$$C_V(T) = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \tag{5}$$

Where $C_V(T)$ is the Moore constant volume heat capacity of the material, with units of $J/(mol\ K)$; T is the thermodynamic temperature, with units of K ; θ_D is Debye temperature of material, with units of K ; R is the molar gas constant, which equals to 8.314 $J/(mol\ K)$.

In order to conveniently calculate $C_p(T)$, a semi-empirical relation from the literature is used.

Where T_m is the melting point of carbon nanotubes, with units of K; $A_0$is a universal constant, equal to 3.9 x 10^{-3} $mol\ K/J$。

This is the modified Nernst-Lindrmann equation, which is a widely used semi-empirical formula. The formula is used to calculate the $C_p(T)$ of carbon nanotubes. The melting point of carbon nanotubes T_m is substituted into formula (6):

$$C_P(T) = C_V(T)\left(1 + 3RA_0 \frac{T}{T_m}\right) \tag{6}$$

The simulation curve shows that in the work temperature segment, carbon nanotubes are not enough to improve the value of the heat capacity of nanomaterial reached 100%. It can be concluded that the nanoparticles and the salt do not form an independent simple mix in the eutectic compound but form a composite structure, which can anomalously enhance the specific heat capacity of the eutectic.

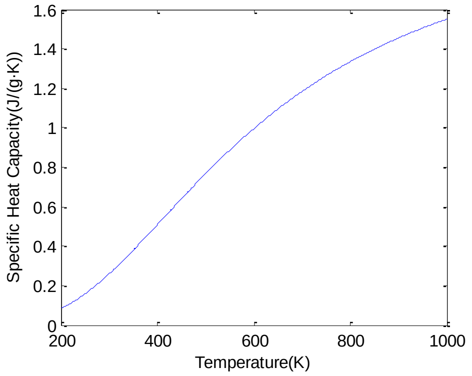

Fig 1. The variation of specific heat capacity with temperature for carbon nanotubes by simulation

By research, it can found that the influencing factors of carbon nanotubes/molten salt composite material thermodynamics performance mainly include: the degree of carbon nanotubes dispersion, carbon nanotube content percentage by mass, morphology and diameter of carbon nanotubes, carbon nanotube/molten salt two-phase interface thermal resistance.

Of these factors, the interface thermal resistance is regarded as the most important one. Interface thermal resistance causes the blockage of heat flow because of the difference of two phase phonon spectra, and the weakness of interface interaction. Interfacial thermal resistance has an intensity rejection effect to the heat transfer between nanoparticles and salt molecules, which makes the heat conduction rate slow, thus greatly enhancing the heat capacity. Phonon heat conduction is the main mechanism in multi-walled carbon nanotubes. However, in molten salt/multi-walled carbon nanotube composite materials, the phonon heat conduction between the multi-walled carbon nanotubes have to through salt molecules.

The impact of heat capacity caused by dispersion, mass percentage, morphology and diameter are all contributed by the interfacial thermal resistance, it will be analysed below.

EXPERIMENTAL ANALYSIS

Experimental procedure

In this paper, the molten salt samples are nitrate salts. Nitrate salts were selected for Solar Two use because of their favorable properties compared with other candidates. In particular, these nitrate salts have low corrosion rates with common piping materials, are thermally stable in the upper temperature range required by steam Ranking cycles, have very low vapor pressures, are widely available, and are relatively inexpensive.

The general protocol for preparing the nanofluid eutectic is as follows: 600mg of Sodium nitrate, 400mg of Potassium nitrate were mixed and heated to a molten state. After cooling, the mixture is ground to powder and called the molten salt. 5mg multi-walled carbon nanotubes and 50mg gum arabic (GA) is dissolved in 20ml of Ultrapure water. After ultrasonically vibrating the water solution for one hour by an ultra sonicator (PS-20, Shenzhen Yida Corporation), 495mg of the new salt is added. This water solution, which now contains 1% of eutectic nanofluid, was ultrasonicated again for one hour to obtain a homogeneous dispersion of the nanofluid. This is the reference group called the nanofluid. The water solution was then rapidly evaporated in a drying oven, which was maintained at 100℃. A portion of the dry sample was put into a differential scanning calorimetry (DSC) measurements to test the heat capacity. The temperature was then ramped up to 500℃ at 20℃/min.

What is more, to discover the reasons that result in the enhancement of specific heat capacity of nanofluid, six groups of comparative experiments were designed. Each of them altered one property that had a great impact on nanoparticles, such as the size, the mass percentage and so on to explore the reasons that result in the enhancement of nanofluid's heat capacity. The experimental group is listed as follow:

Sample A: 1.5% concentration of multi-walled carbon nanotubes in nanofluid.

Sample B: 0.5% concentration of multi-walled carbon nanotubes in nanofluid.

Sample C: half an hour ultrasonication time.

Sample D: 50°C evaporating temperature.

Sample E: $10\mu L$ gold particle (Ted pella)of 5nm diameter to substitute the multi-walled carbon nanotubes.

Sample F: 10 μL gold particle (Ted pella) of 10nm diameter to substitute the multi-walled carbon nanotubes.

Results and data analyses

According to the data obtained from six sets of comparative experiments, curves that reflect the specific heat capacity coefficient of the comparative groups under ambient conditions were obtained. As is shown in the graphs, nanoparticles enhance the specific heat capacity of a water solution significantly, but not to the same level. Properties of nanoparticles, volume fraction, particle diameter and suspension stability of the nanofluid are important factors that influence the thermal conductivity of nanofluid. The impact of various factors are analysed as follow:

Adding nanoparticles to the in pure eutectic.

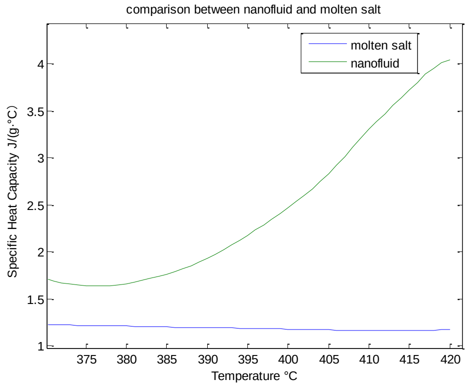

Fig 2. The variation of specific heat capacity with temperature for the pure eutectic and the nanofluid in liquid phase.

It shows that the heat capacity of the pure molten salt eutectic is about 1.25 $J/(g\ K)$, which is the same as given in the literature. In the 370~420°C high temperature work section, the specific heat capacity of sample nanofluid has been improved nearly 100% by adding 1% of multi-walled carbon nanotubes compared to that of the pure molten salt. What is more, the specific heat capacity is increasing by temperature. When the temperature is 420℃, the specific heat capacity is about 4.2 *J/(g K)*, which is nearly 332% of pure molten salt. The mechanism and influence factors will discuss below.

volume fraction.

The sample nanofluids in Fig 3 and 4 are the same as the one in Fig 2, but they choose the different work temperature. Fig 2 is 370-420ºC, and Fig 3 and 4 is 365-410ºC, this is mainly determined by the stability of thermal analysis base line in DSC graphic. The specific heat capacity of sample A and B are both less than nanofluid. The value of sample A is approach to the pure molten salt and has a small enhancement which is 1-1.5 *J/(g K)*. Sample B has a similar variation tendency with nanofluid which has an obvious enhancement effect. But the value of sample B is smaller than nanofluid all the time. So the two conditions of volume fraction have different mechanisms.

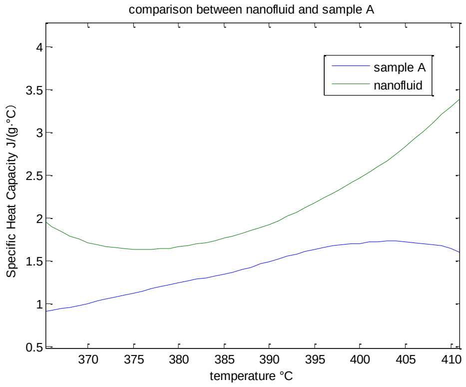

Fig 3. The variation of specific heat capacity with temperature for sample A and the nanofluid in liquid phase.

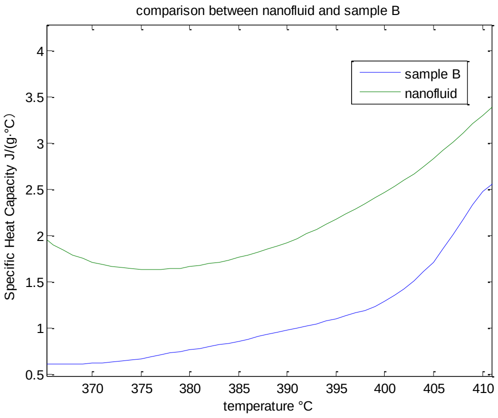

Fig 4. The variation of specific heat capacity with temperature for sample B and the nanofluid in liquid phase.

There are two mechanisms of heat transfer in the composite structure:(1) nanotube-molten salt heat transfer; (2) nanotube -nanotube heat transfer. They are respectively restricted to the interfacial thermal resistance and thermal contact resistance. The concentration of carbon nanotubes is low, interfacial thermal resistance is the main influence factor of composite materials ; The concentration is high, nanotube-nanotube heat transfer is remarkably improved, the interfacial thermal is weakend which causes a reduction of specific heat capacity.

It can be seen that the concentration of carbon nanotubes does not have a linear relationship with specific heat capacity, but there is an ideal concentration range for nanomaterial. Too high or too low a concentration are both a disadvantage for the formation of the interfacial thermal resistance .

suspension stability of nanofluid

Fig 5 and 6 shows the specific heat capacity of sample C and D is not enhanced but has a large reduction which are both less than 1 *J/(g K)*. Moisture and shortage of ultrasonic sonication all lead to the agglomeration of carbon nanotubes, which are then unable to form the effective interfacial thermal resistance. It caused the salt molecules absorb more heat in the same temperature region that leads to the reduction of specific heat capacity.

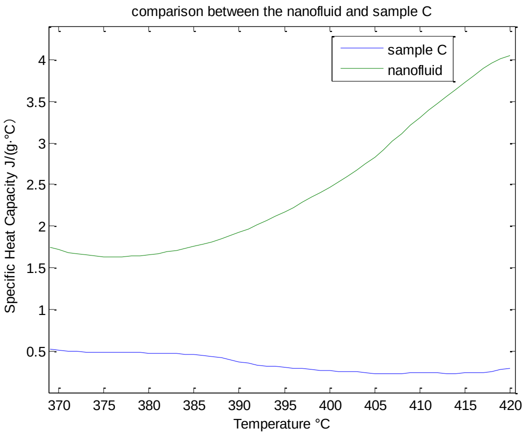

Fig 5. The variation of specific heat capacity with temperature for sample C and the nanofluid in liquid phase.

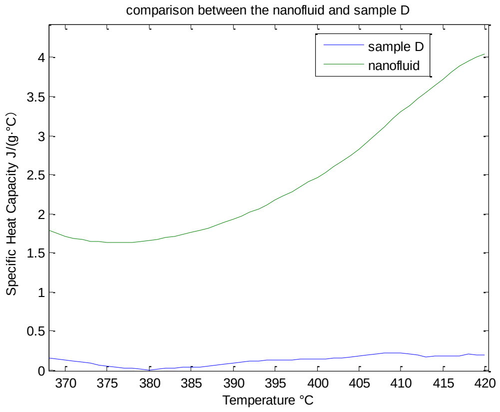

Fig 6. The variation of specific heat capacity with temperature for sample D and the nanofluid in liquid phase.

Properties of nanoparticles

Gold nanoparticles have stable physical and chemical properties which enhance the specific heat capacity of the solution. What is more, in a high-temperature section, the specific heat capacity of the eutectic composition is more stable and changes little.

Compared with multi-walled carbon nanotubes, nanometer gold particles have the shape of a ball, which makes the surface area large enough to scatter phonons. Therefore, the nanofluid containing gold nanopaticles has a very high interfacial thermal resistance, and the enhancement of the specific heat capacity is significant.

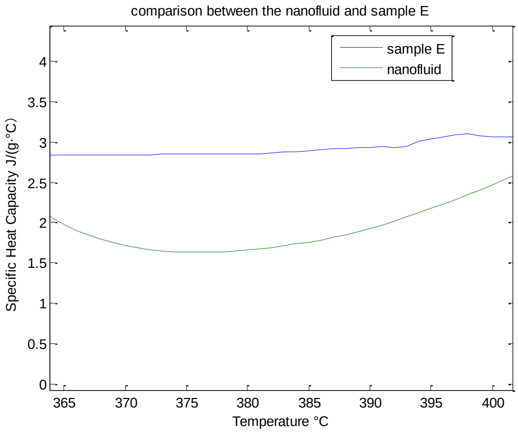

Fig 7. The variation of specific heat capacity with temperature for sample E and the nanofluid in liquid phase.

Fig 7 shows the comparison between sample E and sample nanofluid. In work temperature, sample E has the better effect of specific heat capacity enhancement than sample nanofluid, and the enhancement effect of sample E is more stable. Gold particles have the shape of a ball, which makes the surface area large enough to scatter phonons, due to many two-phase interfaces increased.Therefore, the nanofluid containing gold nanopaticles has a very high interfacial thermal resistance.

Particle diameter

Gold nanoparticles which have large particle size are less effective than smaller ones in enhancing the specific heat capacity of a nanofluid. According to the research, nanoparticles of large size can increase the density of low-frequency vibrational phonon modes, however, they reduce the interfacial thermal resistance and coupling loss of heat conduction from the interior of the nanoparticles to the surrounding salt molecules with phonons of different vibration frequencies. Therefore, nanoparticles of small size have the advantage in terms of improving heat capacity.

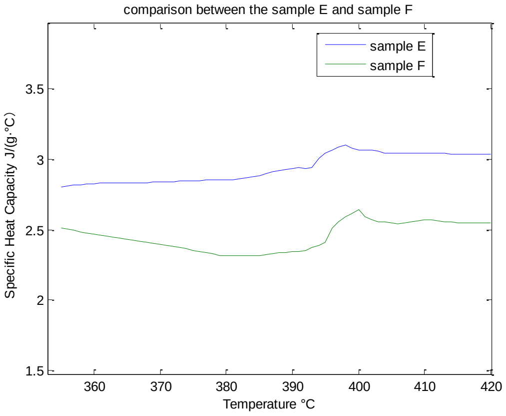

Fig 8. The variation of specific heat capacity with temperature for sample E and the sample F in liquid phase.

Fig 8 shows the specific heat capacity of sample E and F have the same variation tendency and stability in work temperature. They all can enhance the specific heat capacity to 100%, and sample E is more effective than sample F, which can reach to 220%. According to the research, nanoparticle of large size can increases the density of low-frequency vibrational phonon modes, however, reduce the interfacial thermal resistance. Therefore, nanoparticles of small size have the advantage in terms of improving heat capacity.

CONCLUSIONS AND DISCUSSION

There are many reasons that contribute to the change of the specific heat capacity, like the degree of dispersion of nano particles, the mass percentage of nanoparticles or the morphology or type of nanoparticles. In this paper, a speculation is made that all those reasons mentioned above are effected through the two-phase interfacial thermal resistance of nanoparticles and molten salt, which in turn changes the value of the specific heat capacity. The improvement of interfacial thermal resistance of nanoparticles and salt molecules forms a good two-phase interface, so that lots of heat is absorbed by nanoparticles and the heat transfer speed of salt molecules is reduced. This causes the overall hybrid system to absorb or release heat with slower temperature fluctuations, resulting in a significant enhancement of specific heat capacity.

Transmission electron microscopy (TEM) and scanning electron microscope (SEM) are utilized to observe the microstructure of the samples which have finished the test on DSC. Compared with Fig.9, the images Fig.10 from the TEM show that multi-walled carbon nanotubes can still present a good dispersion in molten state, and formed a complex heat conduction network structure between salt molecules which can anomalously enhance the heat conduction between nanoparticles; Through the observation of SEM images, it can be found that the original salt eutectic has a smooth surface, however after adding nanoparticles, a lot of the punctation structures appear at the surface which is formed by gold-nanoparticles due to enhance the interfacial thermal resistance.

In this paper, specific heat capacity of molten salt is anomalously enhanced by adding nanoparticles, we explore the mechanism and impact factors of this phenomenon by theoretical analysis and experiments. We hope that it can attract the attention of other researchers to do further research in this field and to improve the theoretical and experimental research, our research group aims to explore this method for industrial applications.

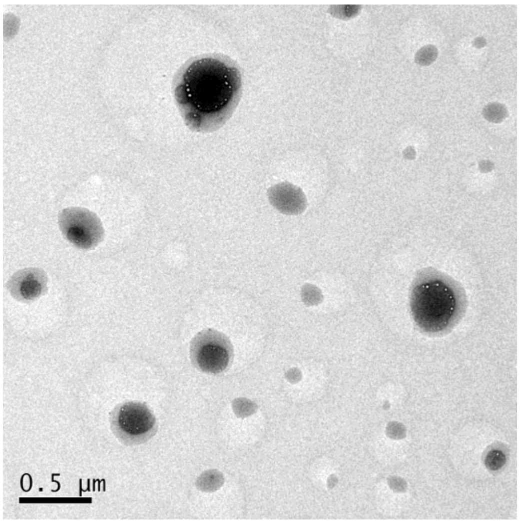

Fig 9. Transmission electron micrograph (TEM) of pure eutectic mixture after testing.

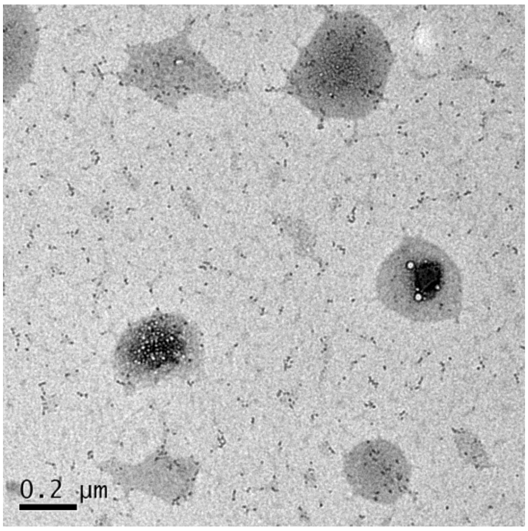

Fig 10. Transmission electron microscope (TEM) of nanofluid after testing. Multi-walled carbon nanotubes present good dispersion, and formed a complex heat conduction network structure.

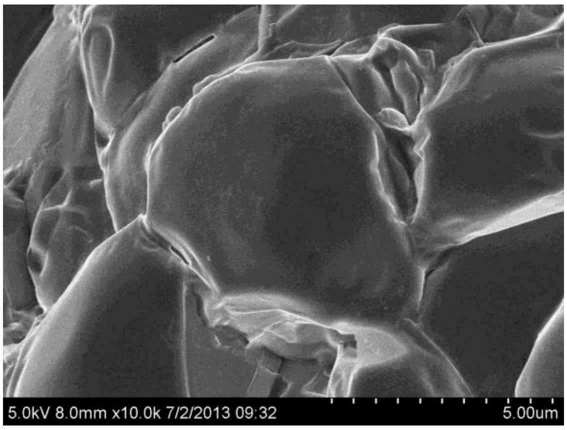

Fig 11. Scanning electron micrograph (SEM) of pure eutectic mixture after testing.

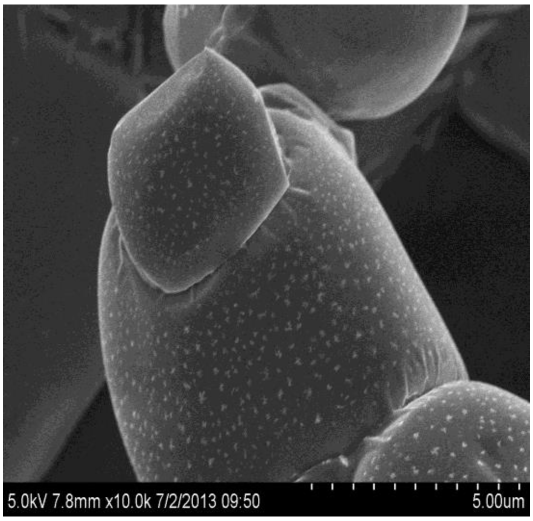

Fig 12. Scanning electron micrograph (SEM) of Sample F after testing. Special punctation structures are formed all over the nanomaterial (gold nanoparticle).

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РАЗРАБОТВАНЕ НА НОВА, ТОПЛО-СЪХРАНЯВАЩА СТОПИЛКА ЗА СОЛАРНИ ИНСТАЛАЦИИ, ЗАПЪЛНЕНА С НАНО-ЧАСТИЦИ

Донгсяо Ню, Ян Лу, Ди У*

Севернокитайски електротехнически университет, Хуилонггуан, район Чангпинг, Бейджин, Китай

(Резюме)

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Соларните термични станции са най-конкурентноспособните спрямо основаните на изкопаеми горива. Те се смятат за най-обещаващите из технологиите с чисти и възобновяеми енергийни източници в бъдеще. Подходящият флуид за топлообмена и за съхраняване на топлината е от ключово значение за успеха на соларните енерго-технологии. Солевите стопилки са най-добрите флуиди при параболичните и колонните соларни системи. От голямо значение е да се познават механизмите на топлообмена при тези стопилки. Такива изследвания са рядкост.

Настоящото изследвания поставя основата на приложението на въглеродни нанотръби в солеви стопилки, които могат значително да подобрят стабилността и капацитета на топлинното съхранение. Предварителни експерименти показаха, че добавянето на наночастици води до аномално повишаване на специфичния топлинен капацитет на солевата стопилка. Според тези експерименти многостенните въглеродни нанотръби и златните наночастици заедно може да повишат специфичния топлинен капацитет на солевата стопилка с близо 100%.

В настоящата работа е използвана теорията на междуфазното съпротивление за да се обясни явлението на значително повишения топлинен капацитет. След това са изследвани факторите, които влияят на механизма на повишения топлинен капацитет (концентрация, размери, състав, стабилност на наночастиците, дисперсионни отнасяния на наночастиците в евтектичния състав). Микроструктурата е потвърдена чрез сканираща електронна микроскопия (SEM) и трансмисионна микроскопия (TEM).