THERMAL CONDUCTIVITY AND THERMAL MECHANISM OF ALUMINUM NANOPARTICLES/OCTADECANE COMPOSITE PHASE CHANGE MATERIALS FROM MOLECULAR DYNAMICS SIMULATIONS AND EXPERIMENTAL STUDY

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In this paper, the physical model and simulations of the octadecane in the paraffin and composite materials with different mass fraction of aluminum nanoparticles is established by molecular dynamics method and an analysis of the microscopic mechanism of thermal conductivity was given, in this paper, composite phase change materials were produced by the two-step method of combining chemical dispersion and physical dispersion, the thermal conductivities of composite phase change materials were measured with transient thermal probe method.In the end, a comparison was made among experimental data, theory calculation value and numerical simulation value.Results show that, the thermal conductivities of composite phase change materials increase constantly, along with the content of aluminum nanoparticles increase. Besides, the coefficient of thermal conductivity of composite phase change materials in solid is greater than that in the liquid. Error still exists between the experimental data and the simulation value.

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Keyword: Composite phase change materials, Thermal conductivity, Nanoparticles, Molecular dynamics simulation，experiment

1. Introduction

Solar energy as a kind of green renewable energy, has a lot of advantages as inexhaustible and pollution-free, but it also has some characteristics of intermittent and unstable. Solar power systems usually have storage devices, so the study of heat storage materials becomes very necessary.As a kind of typical phase change thermal storage materials, paraffin is characterized by large phase change latent heat, and no super-cooling, good stability and low price, besides, the phase temperature of octadecane belonging to paraffin is about 28℃, which is especially applicable to serve as the heat storage material[1,2] of chimney power plant system with vertical heat collector. But paraffin has a disadvantage of low thermal conductivity, to improve the storage/exothermic capacity of paraffin in the heat storage system, domestic and foreign experts have conducted a number of studies, mainly includes the following two aspects: first, structural design on the thermal storage devices for a better heat transfer, such as the use of fins, cellular structure, porous media and other structures to enhance heat transfer[3-6]. Second, to increase the thermal conductivity of heat storage material, for instance, adding some metal powder, wire-netting , graphite, carbon fibers into paraffin or combining it with different phase change materials to improve the heat transfer performance[7-11].

In this paper, by the methods of combining molecular dynamics simulation and

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experiment, the thermal conductivities of the octadecane and aluminum nanoparticles / octadecane composite phase change materials were calculated, and a further study of the thermal property of it .At the same time, the mechanism that nanoparticles could enhance thermal properties of paraffin matrix was explored by the view of the microscopic molecular motion. The results obtained by the two methods were compared and analyzed.

2. Numerical Simulation

2.1 Build physical models

The octadecane molecule is a straight-chain alkane consisted of C, H atoms, the molecular formula is C18H38, molecular mass is 254.502, Melting point is about 301 k, boiling point is about 589 ℃， In order to simplify the model,the bond angles of C-C-H, H-C-H, C-C-C are 109°, the dihedral angles are 0°[12].The model of individual octadecane molecule was built by the software named Material Studio,as shown in Figure. 1,the white balls represent hydrogen atoms, the dark gray balls represent carbon atoms and the sticks between two atoms represent C - C keys or C - H keys.

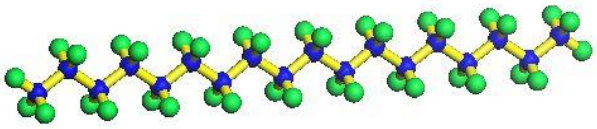
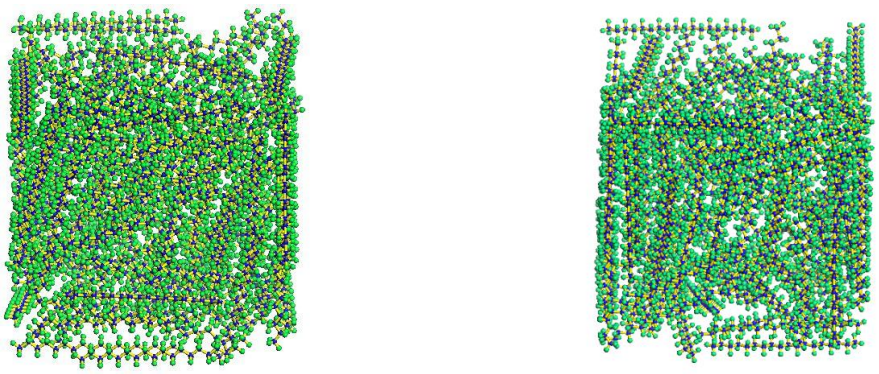


Fig. 1 The molecular model of octadecane

In this paper, the octadecane molecular models were filled to a cubic box by the software named Packmol. By the international definition of relative atomic mass which 1/12 of atomic mass in carbon isotope 12C is as the standard of quality, the number of the molecules in 4 nm cubic crystal cell when the octadecane is in solid state (the density of 777 kg/m3) can be calculated as:

$$n = \frac{777 \times (4 \times 10^{-9})^3}{1.66 \times 10^{-27} \times 254.50} \approx 1\,1\,7 \tag{1}$$

The physical model of the solid octadecane cubic unit cell was built by Packmol according to the calculated number of the molecules, as shown in Figure. 2(a). Because the eighteen alkanes volume expansion rate was 7.77%, physical model of liquid octadecane cubic unit cell is shown in Figure. 2 (b). The edge length of the cubic unit cell is about 4.1nm.



(a) solid (b) liquid

Fig. 2 The cubic crystal cell of octadecane

Aluminum: Aluminum is a kind of silver-white metal with light quality, excellent thermal and electrical conductivity, and whose specific gravity is only 27, melting point is about 933K, and boiling point is about 2600K. Then, using the same method, the aluminum nanoparticle model is created by Material Studio software which is shown in Figure 3. As a kind of metal crystal, aluminum has a face-centered cubic lattice structure which is short for FCC, as shown in Figure. 4.

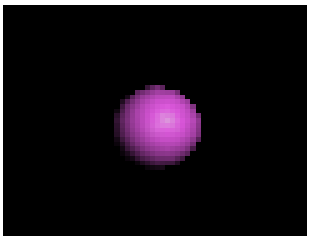


Fig. 3 Aluminum Nanoparticles

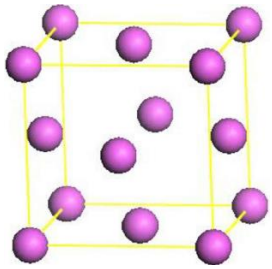


Fig. 4 Face centered cubic

There is respectively an atom on eight corners of the unit cell, who works as a vertex to constitute a cube, and on the center of six face center of the cube, there is respectively an atom. The coordination number of the FCC structure is 12, the density is 0.74, and the atomic radius is 24a where a represents the lattice constant.

According to the octadecane cubic unit cell model established above, the calculated radius of Al nanoclusters of which the mass fraction is 1%, 2%, 3%, 4%, 5% were approximately 0.35nm, 0.45nm, 0.51nm, 0.57nm, 0.62nm. In this paper, the Al nanoclusters calculated above were created by Material Studio. Spherical Al nanocluster model created by Material Studio of which the radius is 0.62nm (5% wt) is shown in Figure. 5 :

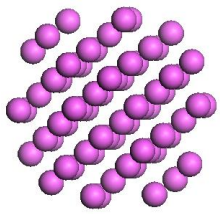
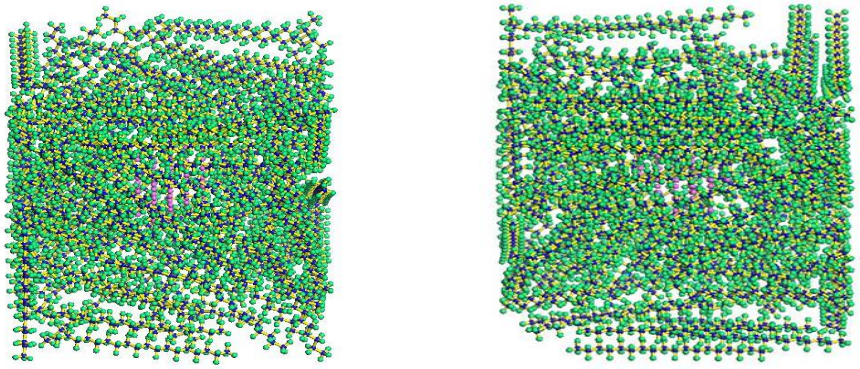


Fig. 5 Nanoclusters of aluminum

Finally, the physical model of Al nanoparticles/octadecane composite phase change materials is obtain by adding Al nanocluster to octadecane cubic unit cell using Packmol. The physical model of the composite phase change material of which the Al nanoparticles mass fraction is 5% is shown in Figure. 6:



(a) solid (b) liquid

Fig. 6 The physical model of Al nanoparticles/octadecane composite phase change material

2.2 Parameter setting

The numerical simulation of thermal conductivity was studied by NEMD method, selecting micro-canonical ensemble (NVE); initial speed was assigned in accordance with Maxwell - Boltzmann distribution function, The velocity distribution function of each particle is the product of the velocity [Vx, Vy, Vz] distribution function in three directions:

$$\mathrm{f}_v(v_x, v_y, v_z)z = f_v(v_x) f_v(v_y) f_v(v_z)$$

The widely used Lennard—Jones、Morse pair potential model whose potential function is fitted through the first principles is adopted in this simulation.

As for octodecane, the AIREBO potential function was selected for calculation, and the expression of potential function is as follows:

$$E = \frac{1}{2}\sum_{\mathrm{i}} \sum_{j \neq i} \left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i,j} \sum_{I \neq i,j,k} E_{kijI}^{TORSION} \right]$$

As for the Al particle region, the EAM potential function was selected for numerical simulation, and the expression is as follows:

$$E_{\mathrm{i}} = F_\alpha \left(\sum_{j \neq i} \rho_\beta (r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta} (r_{ij})$$

The role of non-bonding between Al nanoparticles and octadecane was described by Lennard-Jones potential function, the expression of potential function are as follows:

$$E = 4\varepsilon \left[\left(\frac{\sigma}{\mathrm{r}} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

For Al, C, H atoms in the model, the parameters[13] of Lennard - Jones potential function as shown in the following Table. 1:

LJ potential parameters between Al atoms and C atoms were calculated by

Loveniz-Berthelot mixing rule[14] , the same case also exists between Al atoms and H atoms, its calculation formula is as follows:

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

The Lennard Jones potential function parameters of Al-C, Al-H after calculation are shown in Table. 1:

Tab. 1 Parameter Lennard-Jones potential function[15]

	σ / Å	ε /ev
Al—Al	2.85	0.5
C—C	3.37	0.0024
H—H	2.928	0.00318
Al—C	3.11	0.03464
Al—H	2.89	0.03987

The cut-off radius r_{cut} for the Lennard-Jones potential function was assigned for 3.2; the periodic boundary condition was selected as the boundary condition; the equations of motion were solved with the Velocity-Verlet algorithm[16-19].

2.3 The analysis of simulation results

The model of liquid and solid phase change materials were created by Material Studio and Packmol, the established molecular models were simulated for thermal conductivity by the software named lammps. In the simulation, the integration step process is assigned for 0.1fs, the total number of time steps N = 2000000; the phase transition temperature for simulation of the material in liquid model was assigned for 320K, the phase transition temperature for simulation of the material model in solid is assigned for 290K.

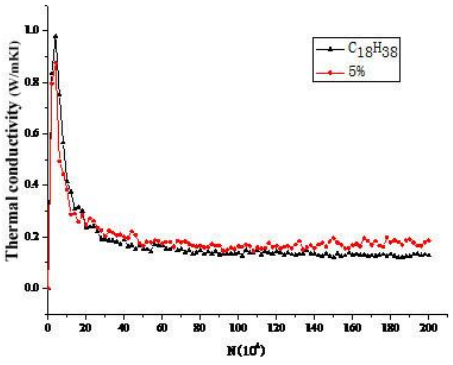


Fig. 7 Time history of the liquid PCM thermal conductivity

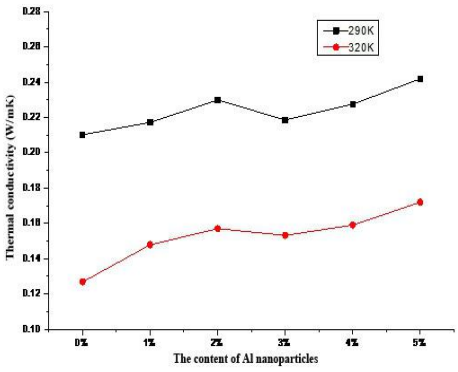


Fig. 8 Thermal conductivity of composite materials with different copper content

Figure. 7 shows the relationship between the thermal conductivity and the number of steps with the octadecane and 5% wt Al nanoparticles / paraffin composite phase change material at a temperature of 320K (liquid). The figure shows that the first 1000000 steps is used to balance the

cell internal energy, there is a high temperature gradient in which the thermal conductivity of the phase change material has not reached a stable value; after 1000000 steps, the system is beginning to stabilize, the thermal conductivity can be counted with the last 1000000 steps. At 290K(solid), the graph showing time history of the solid PCM thermal conductivity which was obtain by simulations is similar to Graph.1-5,and not be described herein.

Figure. 8 shows the thermal conductivity of the phase change material obtained by simulating: it can be seen that the thermal conductivity coefficients of composite phase change material in liquid state is less than the thermal conductivity coefficients in solid state. In liquid state: thermal conductivity coefficient of octadecane is 0.1268W / mK, when the content of the Al nanoparticles reaches 1% wt, the coefficient of thermal conductivity of composite phase change materials is 0.1479 W/mK, with the most obvious increase by about 17%, when the content of the Al nanoparticles reaches between 1% wt and 4% wt, thermal conductivity：increases gently; When the content of the Al nanoparticles reaches 5% wt, the thermal conductivity has a greater gradient compared with the previous period. In solid state: the thermal conductivity coefficient of octadecane is 0.2103W / mK, with the addition of Al nanoparticles, the thermal conductivity increases not significantly with an increase of thermal conductivity less than 10% in the content of 1%; when the phase change materials are in the solid, the rate of increase of the thermal conductivity is less than which in liquid. The reason for this case might be explained as follows: in the solid state, the model structure is compact and the space motion of Al nanoparticles is confined.

3.Experiment

3.1 experimental materials

The aluminum nanoparticles used in this experiment is produced by Xuzhou Czech innovative materials technology co., LTD, whose purity is 99.9% and particle size is 40nm. The PCM (phase-change material) is the octadecane produced by Sinopharm chemical reagent co., LTD, the melting point of which is 27.0-29.0℃, and the dispersing agent is oleic acid.

3.2 preparation of sample

The uniform and well dispersed composite phase change materials were prepared by the combination of chemical dispersion and physical dispersion. At first, the Al nanoparticles and oleic acid dispersant with certain quality were weighed whose mass ratio is 1:1, and then put them into melting octadecane liquid, use ultrasonic to vibrate for 5 minutes under melting state. Using this method, the composite phase change materials with mass fraction of Al were produced, they are 1%, 2%, 3%, 4% and 5%.

3.3 Fourier infrared spectrum

Figure. 9 and Figure 10 shown that the complex relationship between octadecane and aluminum nano-particles is a physical complex relationship.

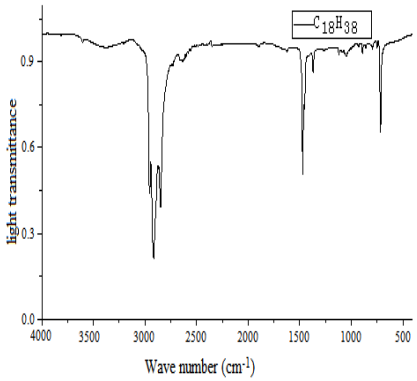


Fig. 9 C18H38 IR absorption spectra

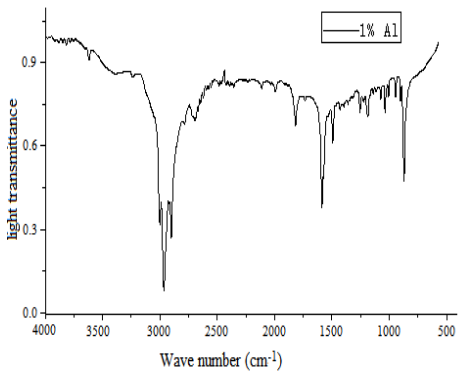


Fig. 10 IR absorption spectra of composite phase change materials

3.4 experimental apparatus and measuring method

The thermal conductivity of the composite phase change materials was measured by the method of transient thermal probe, and the measurement was carried out at room temperature. Before measuring the experimental materials, the sample materials is measured, and the results show that the thermal needle method can meet error requirement. Read the voltage value of each moment from software to get the law that the voltage change with time, then the slope can be got, and the current value was got from the ampere meter. Then substitute these parameters into formula (1):

$$\lambda_m = \left(\frac{I^3 R_{W0}{}^2 \beta}{8\pi L}\right) \Big/ \left(\frac{\mathrm{d}V_{out}}{d(\mathrm{Ln}\,\tau)}\right) = KI^3 \Big/ \left(\frac{dU}{d(Ln\tau)}\right) \quad (1)$$

The thermal conductivity of nanocomposite materials was calculated by formula (1), repeat the experiment for eight times, and take the average value as the final thermal conductivity of the composite phase change material.

3.5 Results and discussion

Thermal conductivity is measured with transient thermal probe method using transient thermal needle at 290K and 320K, the results is shown in Figure. 10.The phase change material is solid when the temperature is 290K and the phase change material is liquid when the temperature is 320K..

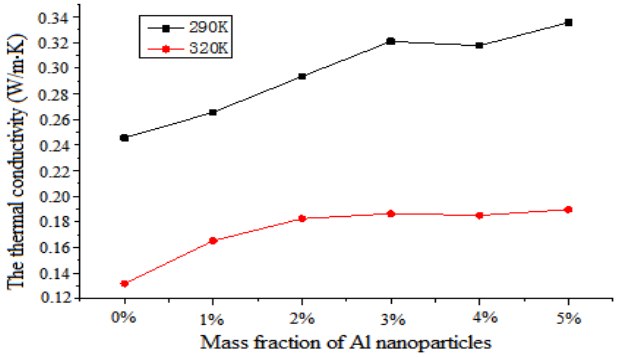


Fig. 11 Thermal conductivity of composite materials with different aluminum content

From the Figure. 11, it can be seen that the experimental values of the thermal conductivity increase with the addition of Al nanoparticles.But when the mass fraction of nano Al particles exceeds a certain range, the thermal conductivity of the composite phase change material increases slowly.When the phase change material is in liquid,the thermal conductivity increases most obviously when the content of Al nanoparticles is 1%wt and 2%wt.When the phase change material is in solid,the thermal conductivity increases most obviously when the content of Al nanoparticles is 1%wt-3%wt.The reason for this case might be explained as follows:

（1）Aluminum is a kind of metal material with a property of readily heat-conducting; as a kind of crystalline substance, the heat transfer is achieved by frequent collision between free electrons in the electron gas and atoms under the action of heat, with the energy transfered from the high temperature portion to the low temperature portion. As a kind of amorphous substance, the heat transfer in the octadecane is achieved by the thermal vibration of molecules arranged randomly and surrounding a fixed position, with energy transfered to the neighboring molecules all in one time. The heat transfer between the aluminum and octadecane is achieved by the fact that the aluminum lattices of which vibration energy is converted from most kinetic energy of the electron drift within the lattice collide the surrounding molecules.

（2）When the composite phase change material is in liquid state, a liquid layer of octadecane molecules adhere to the surface of Al nanoparticles with a large specific surface which has been greatly improved thermal conductivity, the adsorption layer plays a facilitating role to improve the thermal conductivity of the composite phase change materials. Because of the Small size effect, Al nanoparticles in the random thermal motion under the Brownian force carry the energy from the liquid at high temperatures to the cryogenic liquid with accelerating the energy transfer rate and increasing the thermal conductivity; In addition, the micro-convection generated by the random thermal motion improve the thermal conductivity in the heat transfer.

（3）With the increase of Al nanoparticles, the polymerization degree of nanoparticles intensify, limiting the motions in the Al nanoparticles solution. When Brown force and van der Waals forces are not large enough to against gravity of the polymerized nanoparticles, the sedimentation occurs with the effective nanoparticles content decreasing, while this phenomenon will lead to micro-convection weakened; ultimately, the increase rate of thermal conductivity decreases.

4. Comparative Analysis of Simulation Values and Experimental Values

Figure. 12 is a comparison graph of simulation values and experimental values of composite phase change material thermal conductivity. It can be seen that the results gained from the experimental study have the same trend with the results gained from the simulation research, both increase with the addition of Al nanoparticles.

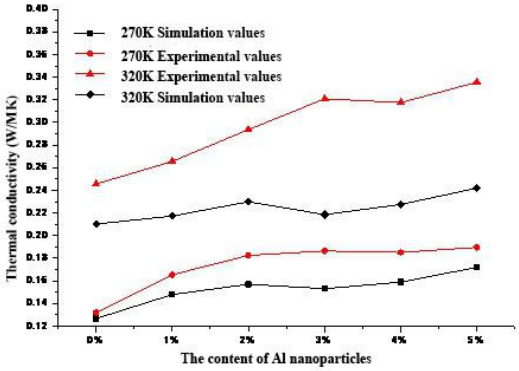


Fig. 12 Simulation and experimental values of composite phase change material thermal conductivity

When the phase change material is in liquid, simulation values are similar to the experimental values. The thermal conductivity increases most obviously when the content of Al nanoparticles is 1%wt.When the phase change material is in solid, the simulation values of thermal conductivity is smaller than the experimental values, with a large gap between them. There are three reasons for difference between the simulation values and experimental values of phase change material thermal conductivity might be explained as follows:

(1) There is a big gap between the actual materials size and molecular models created by the Material Studio、Packmol software(Especially for the molecular models of Al nanoparticles);

(2) Impact of micro-convection on the liquid phase change material is not be considered in the numerical calculation.

(3) Lennard-Jones potential function parameters setting.

5. Conclusion

In this paper, thermal conductivity of paraffin was enhanced by adding Al nanoparticles into octadecane matrix, the thermal conductivities of the octadecane and the composite phase change materials were calculated by the molecular dynamics simulation method, the conclusions comparing calculated values with experimental values are as follows:

(1)The thermal conductivity of composite phase change materials simulated in liquid state is less than that in solid state. In liquid state: the thermal conductivity of octadecane is 0.1268W/mK, when the content of Al nanoparticles comes to 1%,the thermal conductivity of the phase change material has rose by the most of about 17%. In solid state, the thermal conductivity coefficient of octadecane is 0.2103W / mK, with addition of Al nanoparticles, the thermal conductivity increases not significantly which less than 10% as the content of 1%.

(2) It can be seen by comparing values obtained by simulation and experimental: the experimental and the simulated values of the thermal conductivity both increase with the addition of Al nanoparticles.When the phase change material is in liquid, the simulation values are similar to the experimental values. The thermal conductivity rise most obviously when the content of Al nanoparticles is 1%wt.When the phase change materials exists in solid, the simulation values of thermal conductivity is smaller than the experimental values with a large gap between them. The deviation between simulation values and experimental values is due to the molecular model size,

the impact of micro-convection which can not be calculated, and the select of Lennard-Jones potential function parameters.

Acknowledgements

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