Measurement of Thermalphysical Properties of Thermal Storage Materials With an Adiabatic Water Bath Calorimeter

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Abstract: An adiabatic water bath calorimeter was constructed to measure specific heat and fusion heat of materials. Models and experimental method were provided to calibrate parameters and accuracy of the calorimeter. Heat capacity, stirring power and heat release of the calorimeter were calibrated by experiments. Specific heats of copper and water at three temperatures, and fusion heats of ice and paraffin were measured by the calorimeter. Results given by the calorimeter go well with reference values. The calorimeter provides a convenient method and accurate experimental results for measurement of thermalphysical properties of thermal energy storage materials.

Key words: water bath, calorimeter, thermalphysical properties, accuracy, calibration

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绝热式水浴量热计对蓄能材料性能参数的测量

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[摘要] 设计了一套绝热式水浴量热计, 用于对蓄能材料的比热容和相变潜热进行测量. 提出了标定量热计热容、散热量和搅拌器功率等参数的数学模型, 通过实验对这些参数进行了标定. 使用量热计对水和铜在 3个温度下的比热容, 以及冰和石蜡的相变潜热进行了测量, 测量结果与这些参数的参考值很好地吻合. 绝热式水浴量热计可以方便而准确地对蓄能材料的性能参数进行测量.

[关键词] 水浴, 量热计, 热物理参数, 精度, 标定

As a result of extensive research in thermal energy storage, more and more thermal energy storage materials are explored for various thermal energy storage usages. Specific heat and fusion heat are important parameters for evaluating performance and application fields of a thermal energy storage material. Measurement of these thermalphysical properties is a preliminary work for the study of a thermal energy storage material.

Various methods can be used to measure specific heat and fusion heat of a material, such as the blending method, the adiabatic method, the comparison method, the pulse method and the DSC method. Each of these methods can be used only within proper range of temperature and to appropriate materials. The adiabatic water bath calorimeter has the merits of simple configuration and high accuracy. It can be used to measure thermalphysical properties of a material within the temperature of 0℃ – 100℃, while the material has no chemical and physical reaction with water.

Water bath calorimeter can be divided into single bath method[1,2], twin bath method[3,4] and temperature history method[5-7]. The single bath calorimeter needs to calibrate heat capacity and heat release of the calorimeter, and power of the bath stirrer. Li Xiaoyan et al.[1] used this kind of calorimeter to measure the specific heat and fusion heat of a mixture composed of caprylic acid and capric acid. Heat capacity and heat release of the cal-

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orimeter were calibrated simultaneously. No stirrer was used in their calorimeter, so the water bath couldn't get a uniform temperature field. Hiroyuki Kumano et al.[2] measured fusion heat of ice in various aqueous solutions with a single bath calorimeter equipped with a magnetic stirrer. But heat release of the calorimeter and power of the stirrer were not considered in their models.

A single bath calorimeter was constructed in this study. Models to calculate the thermal physical properties of materials and parameters of the calorimeter were provided. The parameters of the calorimeter such as heat capacity, heat release and stirring power were calibrated. Thermal properties of some materials were experimentally measured.

1 Experimental method

An adiabatic single bath calorimeter, which is shown in Fig. 1, was constructed to measure thermal properties of materials. Fixed mass water (1 000.00 g) was placed in the Dewar vessel. The material was immerged in the water. The stirring system was used to get a thermal equilibrium in the water and between the water and the material. The water was heated to an appropriate temperature. The temperature field in the Dewar vessel was homogenized by the stirrer after heating. In the case of fusion taking place in the measured material, the following equation describes the thermal balance of this process:

$$C_b(t_2-t_1)+mc_{ps}(t_f-t_1)+mc_{pl}(t_2-t_f)+mL=P_h\Delta\tau_h+P_s\Delta\tau_s-\Phi\Delta\tau_h. \quad (1)$$

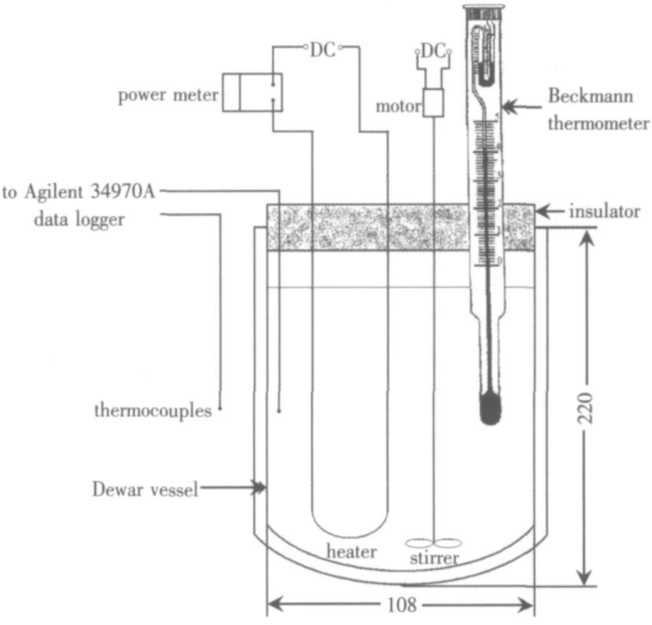

Fig.1 Schematic diagram of the single bath calorimeter

Temperatures of the water and the surroundings were measured by K type thermocouples. The temperatures were used to calculate heat release of the calorimeter. The thermocouples were connected to Agilent 34 970A data logger. The accuracy of the data logger system was ±0.1℃. The temperature increase of the bath, i.e. (t_2-t_1) in Eq. (1), was measured by Beckmann thermometer. With a 20 times reading glass, the accuracy of Beckmann thermometer was ±0.001℃. An electric stopwatch with an accuracy of ±0.01 s was used to measure heating time, stirring time and heat release time. A D26/1-W type power meter with accuracy of ±0.5% was employed to determine the heating power of the heater. The accuracy of the balance used to measure the mass of the water and measured material was ±0.01 g.

2 Results and discussions

2.1 Parameters of the calorimeter

Heat capacity, heat release and stirring power of the calorimeter should be calibrated by experiments preliminary. The mass of water in the Dewar vessel was fixed to 1 000.00 g at each experiment. First, the fixed mass water at room temperature was put into the vessel. The water was heated to get a slight temperature increase (about 1℃). Because the temperature difference between the bath and the surroundings was small, heat release of the bath can be neglected in this case. The stirrer was electrified a short time (20s) at the end of heating just for the homogenization of the temperature field in the bath. This process can be denoted by the following equation:

$$C_b(t_2-t_1)=P_h\Delta\tau_h+P_s\Delta\tau_s, \quad (2)$$

Then the calorimeter was charged with water at room temperature again. With the stirrer electrified for long

time (3600s), the water would be heated by stirring power. The water was still heated to get a slight temperature increase. The voltage of stirrer motor was kept at constant, so the stirring power was the same at each experiment. This heating process can be expressed as Eq. (3).

$$C_b(t_2 - t_1)' = P_s \Delta\tau', \tag{3}$$

Heat capacity of the calorimeter and stirring power of the stirrer can be obtained by an iterative calculation with Eq. (2) and Eq. (3). At the beginning of the iterative process, the stirring power in Eq. (2) was set to 0 J/kg. Table 1 shows the results of the calculation. These experiments were performed 5 times. Table 1 also shows standard deviation of these parameters. Heat capacity of the calorimeter was extrapolated to 0℃ for convenience. The heat capacity is mostly affected by the temperature of water, so it should be calibrated when temperature of the water deviates from 0℃.

Table 1 Experimental results of heat capacity and stirring power

Parameter	Value	Standard deviation
C_b/(J/kg at 0℃)	5 594.67	5.83
p_s/W	0.249	0.002

* Standard deviation $E_s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(E - \bar{E})^2}$.

The water was heated to about 90℃ to measure heat release of the calorimeter. The temperature of the water decreased gradually because of heat release. The temperatures of the water and the surroundings were logged by the thermocouples. The temperature decrement of the water was still acquired by Beckmann thermometer. Heat release of the calorimeter can be obtained by the follow.

$$\Phi = C_b(t_1 - t_2). \tag{4}$$

Heat release calculated by Eq. (4) was at a mean temperature difference which could be obtained by the thermocouples. Heat release at various mean temperature differences could be achieved. The heat release and mean temperature difference can be related as Eq. (5).

$$\Phi = f(\Delta t). \tag{5}$$

Fig. 2 is the experimental results of heat release of the calorimeter and the related heat release curve. Eq. (6) is related heat release function. Heat release in Eq. (1) can be calculated by Eq. (6) with a measured mean temperature difference.

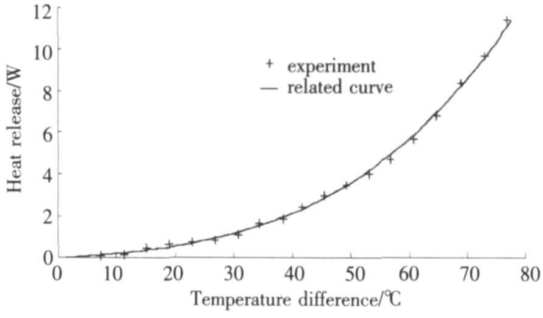

Fig.2 Experimental results and related curve of heat release of the calorimeter

$$\Phi = (2.125 \times 10^{-5}\Delta t^2 - 6.296 \times 10^{-5}\Delta t + 1.792 \times 10^{-2})\Delta t. \tag{6}$$

2.2 Results of measurement of specific heat

The calorimeter was used to water and copper respectively as examples for measurement of specific heats of liquid and solid. When there is no phase change taking place in the measured material, the specific heat can be calculated by Eq. (7).

$$C_b(t_2 - t_1) + mc_p(t_2 - t_1) = P_h\Delta\tau_h + P_s\Delta\tau_s - \Phi\Delta\tau_h. \tag{7}$$

Specific heats of water and copper were measured at different temperatures. Table 2 shows the experimental results. Reference values of these specific heats are also shown in Table 2. It can be found from the table that the calorimeter can give satisfying results of specific heat of liquid and solid materials.

2.3 Results of measurement of fusion heat

Fusion heats of ice and paraffin were measured with the calorimeter. Ice has a fixed melting point, i.e. 0℃. Ice at temperature of -10.8℃ was prepared. The temperature of the water in the calorimeter was 1.3℃. Specific heats of ice and water were provided with reference values. The fusion heat of ice can be calculated by Eq. (1). The experimental result is shown in table 3 as well as the reference value.

Table 2　Specific heats of water and copper at some temperatures

Material	Temperature/℃	Experimental values	Specific heat capacity/J/(kgK) Reference values[8,9]	Relative error/%
Water	12.8	4 170.22	4 188.76	-0.44
	40.1	4 164.38	4 174.00	-0.23
	70.2	4 179.77	4 187.16	-0.18
Copper	12.1	374.35	378.80	-1.17
	40.7	382.27	385.24	-0.77
	69.5	378.47	391.72	3.38

Paraffin is a mixture of alkanes, whose fusion takes place within a range of temperature. The melting point and cloud point of paraffin are affected by the kind of alkanes which make up of the paraffin and components of the alkanes. Fusion heat of a paraffin provided by Daqing petrochemical Co. Ltd. was measured by the calorimeter experimentally. In each heating process during the experiment, the temperature increase of the bath was controlled to about 1℃. Specific heats of the paraffin can be obtained by Eq. (7). The experimental results are shown in Fig.3.

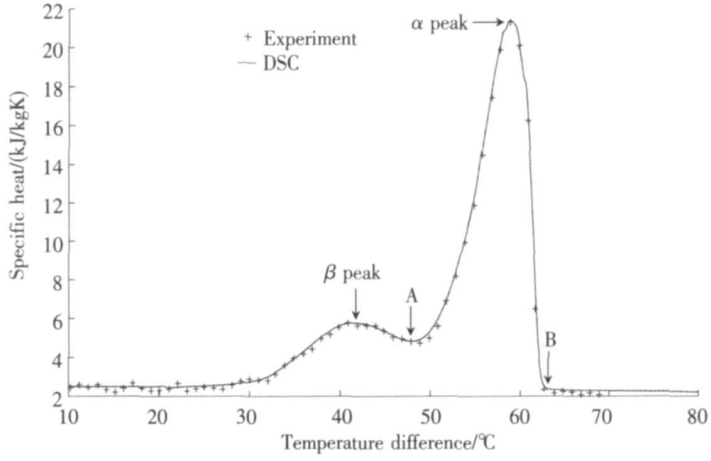

Fig.3　Experimental and DSC results of enthalpy of paraffin

Specific heats of the paraffin were also measured by a differential scanning calorimeter for comparison. The calorimeter was a Diamond DSC provided by PerkinElmer Inc. The scanning rate was 10℃/min. Fig.3 shows the scanning curve of the paraffin. It can be found from Fig.3 that there is two phase change process, i.e. α phase change and β phase change, during the heating process. Solid-liquid phase change takes place during α phase change. The fusion heat of paraffin is defined as the heat absorbed during this stage, namely the heat absorbed from A to B in Fig.3. The fusion heat of the paraffin can be obtained by an integral calculation of the DSC curve or sum of the experimental results. Table 3 displays the fusion heat of the paraffin measured by these methods.

Table 3　Fusion heats of ice and paraffin

Material	Fusion temperature/℃	Fusion heat/(J/kg)	Reference value[9]
Ice	0	333 322.93	333 269.28
Paraffin	47.93-63.13(DSC)	179 152.86(DSC)	
	47.84-62.71(experiment)	173 422.67(experiment)	

It can be found from Table 3 that the single adiabatic bath calorimeter can give a good result of fusion heat of ice. But there exits an obvious deviation between results of fusion heat of the paraffin measured by DSC and this experiment. The reason is that when the paraffin was melted, the liquid paraffin covered over the water. That leaded to the water couldn't vaporize freely. The heat release of the calorimeter was lower than that calculated by Eq. (6). So Eq. (7) gave lower values of specific heat of the paraffin with higher values of heat release.

3 Conclusion

An single adiabatic bath calorimeter was constructed. Models to calibrate parameters of the calorimeter and to calculate thermal properties of measured materials were provided. Heat capacity, heat release and stirring power of the calorimeter were calibrated by experiments. Specific heats of water and copper, and fusion heats of ice and paraffin were experimentally measured. The test measurements of water, copper and ice were in good agreement with the reference values. The experimental results of paraffin deviated from the DSC results somewhat. The calorimeter can give a satisfying results and a convenient method to measure thermaphysicall properties of thermal energy storage materials.

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