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TWO NEW CHLORIDE EUTECTIC MIXTURES AND THEIR THERMO-PHYSICAL PROPERTIES FOR HIGH TEMPERATURE THERMAL ENERGY STORAGE

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ABSTRACT

Considered as promising candidates of composing eutectic chloride molten salts for high temperature energy storage and transfer, NaCl-KCl-$CaCl_2$ and NaCl-$CaCl_2$ systems are formulated into proper to satisfy the property requirement for heat storage and transfer. The thermal properties of the eutectic molten salts liquid such as melting points, specific heat capacity, density, viscosity and thermal stability were measured by DSC, Archimedes, rotation and mass loss curves under isothermal conditions methods. The results shown out, with appropriate operating temperature, lager heat capacity, acceptable viscosity and good thermal stability, NaCl-KCl-$CaCl_2$ and NaCl-$CaCl_2$ systems are the excellent high temperature heat storage and transfer materials under 850℃.

Keywords: Chloride eutectic molten salts, thermo-physical properties, thermal stability

1. INTRODUCTION

With the rapidly development of industry society, energy and environment have become urgent problems to be solved. In the key scientific issues of transformative technology, energy storage is one of the important research directions and heat storage is an indispensable key link in the process of energy storage. Among various heat transfer and heat storage materials, molten salts are attractive to be thermal energy storage medium due to their low vapor pressure, wide operating temperature range, low viscosity and good thermal stability [1-3]. The binary molten salt Solar Salt[4-6] and the ternary nitrate Hitec salt [7-8] are widely used in all over the world. However, nitrate salts currently used in industry are unstable in higher temperatures over 500 ℃ , which would generate a series of nitrogen oxides NOx [9] that cause environmental pollution. And the heat transfer efficiency of nitrate salts will be affected. Therefore, it is necessary to

develop new types of high-temperature molten salts heat storage materials.

Molten chloride salts have good application prospects as a solar heat transfer and heat storage medium because of its wide source, low cost, large latent heat of phase change, wide temperature range and high heat storage density[10]. In order to find a suitable high heat storage temperature heat transfer material, we have been explored two kinds of molten salt materials NaCl-KCl-$CaCl_2$ and NaCl-$CaCl_2$ in this paper, and the eutectic point, melting enthalpy and heat capacity, density, viscosity of the two molten salt materials are measured ,and thermal stability experiments are carried out to determine the optimum operating temperature range of these molten salts, in order to examine whether the above two molten salts are suitable for high temperature heat transfer and heat storage medium.

2. EXPERIMENTS

Weighed NaCl (AR), $CaCl_2$(AR) and KCl(AR) respectively after drying for 24 hours to prepare NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ mixture then ground and mixed thoroughly. The mixtures were placed in a muffle furnace respectively and heated to 600℃ and held 3 hours to form a uniform liquid and then cooled to natural temperature. The solidified salt mixtures were ground and vacuum sealed and kept in desiccators.

STA 449 F5 Synchronous Thermal Analyzer (Germany NETZSCH companies) was used to determine the eutectic point of the above two salt mixtures. The measurement accuracy of STA 449 F5 Synchronous Thermal Analyzer was $\pm 2\%$. About 8-10mg samples were put into platinum crucible with a reference empty one. The measurements were conducted in purified nitrogen atmosphere with a flow rate of 40ml/min and at a heating rate of 20k/min to 90℃ and held for 10 minutes in order to remove water from the sample, And then 10k/min to 600℃.

Subsequently, the thermal-physical properties of the two eutectic molten salt mixtures were measured. The heat capacity was obtained by DSC curve using the sapphire standard material comparison method; Density was determined by molten salt density comprehensive test instrument which was designed base on the Archimedes theory; Viscosity was measured from high temperature rotational viscometer; The measurement accuracy of density and viscosity were both under 2%.Weighed 50g of the two different eutectic molten salt mixtures were put in alumina crucibles respectively in a muffle furnace ,held in different temperatures for 20 hours, and took mixtures out of every 4 hours, weighed by Sartorius.

3. RESULTS AND DISCUSSION

3.1. Determination of molten salts' lowest eutectic point

Compositions and eutectic temperature of eutectic point of the above two molten salt materials were finally determined by measuring mixtures of lots of different compositions of binary NaCl-$CaCl_2$ and ternary NaCl-KCl-$CaCl_2$, and the results are shown in Table 1. The DSC curve under the eutectic composition is shown in Figure 1. The eutectic points and the latent heats of melting of NaCl-$CaCl_2$ and ternary NaCl-KCl-$CaCl_2$ are 499.2℃,133J/g and 503.8℃,169J/g respectively, the large value of the latent heats of melting which were considerable for thermal energy storage.

Table 1: Compositions and melting point of two eutectic molten salts of NaCl-CaCl2 and NaCl-KCl-$CaCl_2$

Salt component	Composition (mol%)	melting point of eutectic salts
NaCl- $CaCl_2$	49.0-51.0	499.2℃
NaCl- $CaCl_2$ - KCl	41.7-52.2-6.1	503.8℃

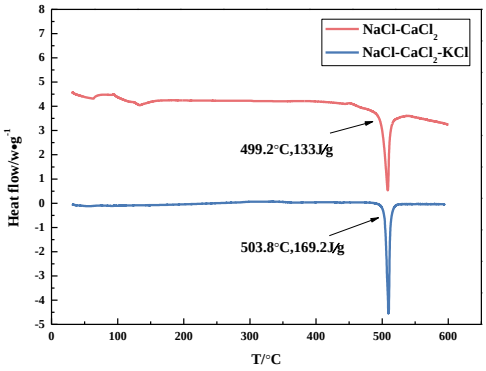

Fig. 1. DSC curves of NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$

3.2. Heat capacity

The heat capacity of NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ systems between 550 and 650 °C are shown in Fig. 2. The heat capacity of the two systems are relatively large, which are prospective materials as heat transfer and storage medium. At the same temperature, the value of heat capacity of NaCl-KCl-$CaCl_2$ system is higher than NaCl-$CaCl_2$; And the heat capacity of the two systems increases with the increase of temperature, this phenomenon indicates that the above two systems are very suitable to apply into the heat transfer and storage process[10] .

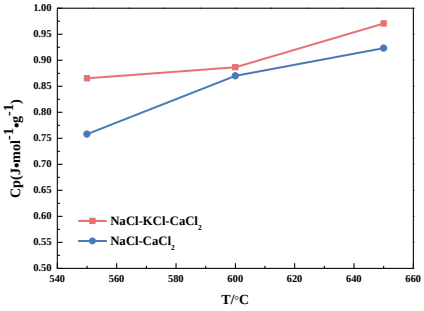

Fig. 2. Heat capacity of NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$

3.3. Density

The density of NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ as function of temperature was plotted in Fig.3, It is observed that the density of NaCl-KCl-$CaCl_2$ and NaCl-$CaCl_2$ linearly decreases from 1.98g/cm^3 to 1.94g/cm^3 and from 1.96g/cm^3 to 1.93g/cm^3 with increasing temperature between 515℃ and 600 ℃ respectively, which could be satisfactorily expressed by the equations 3-3-1 and 3-3-2;The density of the two salts did not change much with temperature and the values are also close at the same temperature.

$$\rho(\mathrm{g}\cdot cm^{-3}) = 2.20483 - 0.000441\mathrm{T}(℃)$$
$$R^2 = 0.98246 \qquad (3\text{-}3\text{-}1)$$
$$\rho(\mathrm{g}\cdot cm^{-3}) = 2.17124 - 0.000402\mathrm{T}(℃)$$
$$R^2 = 0.99351 \qquad (3\text{-}3\text{-}2)$$

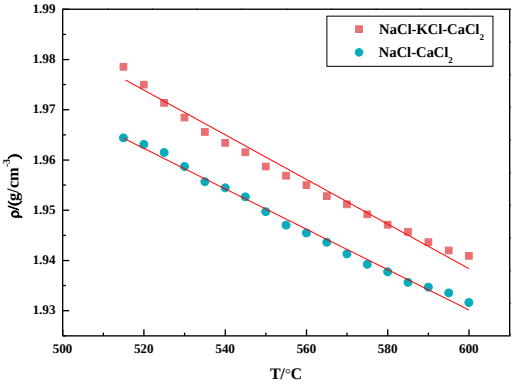

Fig. 3. Densities of NaCl- $CaCl_2$ and NaCl-KCl-$CaCl_2$ as function of temperature

3.4. Viscosity

The measured viscosity values of NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ were given in Fig. 4,

the viscosity of the two molten salts increases with increasing temperature; At the same temperature, the viscosity of NaCl-KCl-$CaCl_2$ is larger than that of NaCl-$CaCl_2$; NaCl-$CaCl_2$ is more suitable for heat transfer in the pipeline than NaCl-KCl-$CaCl_2$. In the temperature range of 520-600 ℃, the viscosity of liquid NaCl-KCl-$CaCl_2$ gradually decreased from 6.534cp to 5.527cp, and the fitting result was as in Formula 3-4-1; the viscosity of liquid NaCl-$CaCl_2$ decreased from 4.426cp to 3.331cp, the fitting result is as shown in formula 3-4-2;

$$\mu(\mathrm{cp}) = 67.97221 - 0.20979\mathrm{T} + 0.000176T^2 \qquad R^2 = 0.99032 \qquad (3\text{-}4\text{-}1)$$

$$\mu(\mathrm{cp}) = 60.45986 - 0.1902\mathrm{T} + 0.000158T^2 \qquad R^2 = 0.99153 \qquad (3\text{-}4\text{-}2)$$

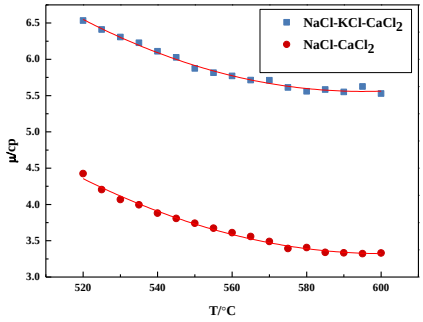

Fig. 4. Viscosities of NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ as function of temperature

3.5. Thermal stability

Thermal stability which determined the working temperature range of the molten salt can be stably used. The operating temperature range of the molten salt is also an important property for the industrial application of the molten salt material. In order to determine the working temperature range of molten salt, weight 50g of NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ into alumina crucible under isothermal conditions after 20h .the mass loss curves of NaCl-KCl-$CaCl_2$ and NaCl-$CaCl_2$ are shown in Figure 5 and Figure 6 respectively. The faster rate of mass loss in the higher the temperature. After 20 hours of incubation, the mass loss of the two materials was less than 1% at 800℃. The result shows the temperature range for stably used of the NaCl-KCl-$CaCl_2$ is 550-850℃. And the temperature range for stably used of the NaCl-$CaCl_2$ is 550-800℃.

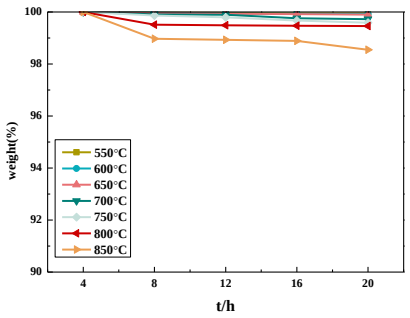

Fig. 5. Mass loss curves of NaCl-KCl-$CaCl_2$ under isothermal conditions

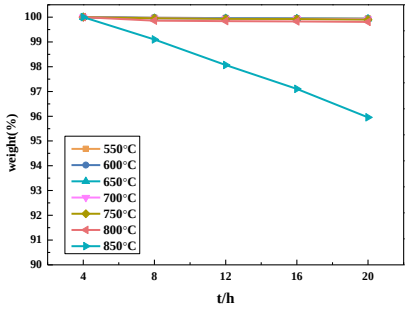

Fig. 6. Mass loss curves of NaCl-$CaCl_2$ under isothermal conditions

4. CONCLUSIONS

DSC technology was used to find the melting point of chloride salt mixtures. Besides, all of the relevant thermal-physical properties of NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ were determined. The heat capacity of the two chloride salt mixtures are considerable to apply into heat transfer and storage. The experimental density and viscosity all presented decreasing variation trend as function of temperature. The mass change

curves showed that NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ had a good thermal stability below 850 ℃ . So, appropriate operating temperature, lager heat capacity, acceptable viscosity and good thermal stability all indicated that NaCl-$CaCl_2$ and NaCl-KCl-$CaCl_2$ were suitable for high temperature heat transfer-thermal storage material.

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