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Review of the development and application of phase change thermal storage

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Abstract: *Although the research on phase change thermal storage technology has onlyafewdecadesofhistory,ithasbeenwidelyusedandhasbecomeanewtechnology that is increasingly valued. Phase change thermal storage has a wide application prospect in the fields of solar energy utilization, power "peak-shifting and valley- filling", waste heat and waste heat recycling, as well as energy saving in industrial and civil buildings and air conditioners. In this paper, the characteristics, advantages and disadvantages as well as applications of phase change thermal storage are roughly introduced.*
Keywords: *phase change thermal storage*

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I. Introduction of phase change heat storage and the reasons for its rise

1.1 Compared with other forms of thermal storage, the characteristics of phase change thermal storage

1.1.1 Characteristics and advantages of phase change thermalstorage

Phase change thermal storage is the use of phase change materials to absorb or release heat when the phase change occurs to achieve energy storage, and the heat storage density of phase change thermal storage is 5~10 times or even higher than that of sensible thermal storage. The high performance heat storage capacity is 4 times higherthanthatofthesamevolumeofwater;theperformancewillnotbedegradeddue to the deformation of the material caused by repeated changes of state; it is an environmentally friendly material that is not harmful to living creatures, and has no metal corrosion and high stability; various heat saving capacities can be achieved by controlling its manufacturing process. The effect is poor. The common phase change processes are mainly solid-liquid and solid-solid phasechanges.

1.1.2 Characteristics of sensible heat storage and its disadvantages compared with phase change heatstorage

Thermal storage is the storage of thermal energy by the rise or fall of the temperature of the thermal storage material. This heat storage method is simple in principle, mature in technology, abundant in material sources and low in cost, so it is widely used in chemical, metallurgical and thermal energy storage and conversion fields. The use of ceramic particles, water, oil and other heat capacity for thermal storage, the heat has been high temperature or low temperature transformation of thermalenergystoragetobeused,suchassolidsensibleheatstorageofironmakinghot airfurnace,heatstorageheatexchanger,thermalstorageburner,etc.,theusualsensible heat storage method is simple, low cost, but compared with the phase change thermal storage, its stored heat is small, its exothermic can not be constant temperature drawbacks.

1.1.3 Characteristics of chemical reaction heat storage and its disadvantages compared with phase change heatstorage

Chemical reaction heat storage is the use of reversible chemical reactions for energystoragethroughtheconversionofthermalenergytochemicalheat.Itundergoes a reversible reaction when heated or cooled and absorbs or exerts heat externally, respectively, so that the thermal energy can be stored. Its main advantage is that the heatstorageislarge,noinsulatedstoragetankisneeded,andtheheatcanbestoredfor alongtimeifthereactionprocesscanbecontrolledbycatalystsorreactants.However, the chemical stability ispoor.

1.2 Classification of phase change thermal storagematerials

1.2.1 Low-temperature phase change thermal storagematerials

Thephasechangethermalstoragematerialsthataregenerallyusedattemperatures below 100°C are called low and medium temperature phase change thermal storage materials. Low-temperature phase change thermal storage materials are mainly inorganic and organic two types of inorganic phase change materials. Organic phase change materials mainly include paraffin wax, fatty acid and other types. Paraffin waxes are mainly made from a mixture of straight chain alkanes of different lengths. MostofthefattyacidscanbeextractedfromplantsandanimalsandtheirrawmaterialsareRenewable and environmentally friendly, which is a hot research topic in recent years. Other organic solid-solid phase change

materials, such as high-density polyethylene, polyol, etc., are also available. When the phase change of this material occurs, the volume change is small, the subcooling degree is light, no corrosion, high thermal efficiency, is a very promising phase changematerials.

1.2.2 Medium temperature phase change thermal storagematerials

Herethedefinitionofthemediumtemperaturerangeisbasedonasimplefact:90 ~ 550 ℃ temperature range, enough for other equipment or applications to provide thermalpowerhigh-temperatureheatsource,550℃hightemperaturerangecanalso provide thermal power source, but the difference between the two is: the former is relatively low efficiency, volume and mass is relatively large, the requirements of all aspectsarerelativelylow,suitableforlarge-scaleapplications,mainlyforground-based civilianareas;thelatterButthelattercanachievehigherefficiency,relativelycompact operation equipment, relatively light mass, mainly for applications inspace.

The need for solar thermal utilization and building energy efficiency and other fields makes low-temperature range thermal storage materials have a wide range of application prospects; in high-temperature industrial furnace thermal storage chamber, industrial heating system waste heat recovery devices and applications in space to promote the rapid development of high-temperature phase change thermal storage technology. Therefore, considerable research has been done on refrigeration, low- temperature and high-temperature phase change thermal storage materials (PCM) at home and abroad, but medium-temperature PCM is less used.

However, the development of related fields has created a lot of space for the application of medium temperature PCM. For example, the Stirling engine developed by Abdullah et al [8] can operate as long as there is a high temperature heat source above 70°C, and even a temperature difference as low as 8°C has been reported [9]. Including trough solar thermal power plants, organic Rankine cycle combined heat storagetechnology,mobileheatstoragetechnology,etc.fortheapplicationofmedium- temperature PCM to create the "need" and technical conditions. The application of distributed energy systems is an important development direction for the energy industry in the 21st century. However, when the user's demand fluctuates greatly and coldandheatcannotbetakenintoaccountatthesametime,itoftenfailstoachievethe expected goal; or when there are multiple application possibilities in the future time period, and it is uncertain whether it will be used for power generation, high- temperature heat source for various industries, dehumidification of rotors, heating or cooling, medium-temperature storage technology can be applied to store relatively high-quality heat source heat first to provide a capacity buffer to ensure the future regulation of In the absence of a medium-temperature thermal storage system, the advantages of a distributed energy system with high total thermal efficiency may not berealized.Sincemedium-temperaturePCMisusuallyusedasthermalstoragematerial for thermodynamic high-temperature heat sources, which is in great demand, and the costofthermalstoragematerialgenerallyaccountsforalargeproportionofthecostof TES systems, "abundant production, low cost, and easy manufacturing" is bound tobe an important selection principle. Although there are many types of materials suitable for medium temperature PCM, the focus of research and development should be different for each type.

1.2.3 High temperature phase change thermal storagematerials

Thethermalpropertiesofhigh-temperaturephasechangematerialsinclude:latent heat of phase change, thermal conductivity, specific heat capacity, expansion coefficient,phasechangetemperatureandotherimportantpropertiesthatdirectlyaffect the heat storage density, heat absorption and discharge rate of the material, the measurement of the thermal properties of phase change materials is particularly important for the study of phase change materials. Such as the study of molten salt, as solarenergyhasintermittentandcannotbeastablesupplyofdefects,cannotmeetthe requirementsofindustriallarge-scalecontinuousenergysupply,mustdeveloplow-cost heat transfer heat storage medium, the development of high-efficiency heat storage technology,inordertoeffectivelysolvetheproblemofsolarenergyconversion,storage and transport. The study of the design and preparation theory and transmission mechanism of high-efficiency heat storage and heat transfer media is not only related to the efficiency of heat absorption, storage and heat transfer, but also directly affects the reliability and stability of system operation. In the literature [4], a new type of molten salt high-temperature ramped layer hybrid heat storage system (>200°C) is proposed, which improves the heat storage capacity per unit volume and simplifies the injection and discharge structure of molten salt liquid compared with the existing heat storage system. It can be applied to heat storage in production processes (such as chemical, metallurgical, thermodynamic, nuclear industry and other thermal energy storage and conversion fields) and also in the field of renewable energy utilization, which has important theoretical significance and practicalvalue.

High-temperature phase change materials are usually corrosive at high temperatures and often require encapsulation. Microencapsulated phase change materials have many advantages that have prompted this research. The potential applications of microencapsulated phase change materials in different thermal control areas will be limited by their cost, but for space applications, thermal control performance far outweighs their cost. Some researchers believe that phase change material microencapsulation technology will be a milestone in

space technology.

Solarenergyisahugetreasuretroveofenergy,withcleanandnon-polluting,easy toaccess,especiallyinsomehighlandareassuchasChina'sYunnan,QinghaiandTibet, solar radiation intensity, and other energy shortages, so the use of solar energy will be morecommon.Butthesolarradiationthatreachestheearth'ssurface,energydensityis very low, and by geography, day and night and seasonal factors, as well as cloudy and sunny clouds and rain and other random factors, its radiation intensity is constantly changing, with significant thinness, intermittency and instability. In order to maintain a stable and uninterrupted operation of the heating or power supply installation, it is necessary to store solar energy in thermal storage, and then release it when the solar energyisinsufficient,soastomeettheneedsofcontinuousandstablesupplyofenergy for production and living. Almost all solar energy installations used forheating, supplying hot water, heat for production processes, etc. need to store thermal energy. Even in outer space, spacecraft operating in Earth orbit are characterized by discontinuitiesinthereceptionofsolarenergyduetotheshadingoftheEarth,sospace power generation systems also require thermal storage systems to maintain continuous and stable operation. Solar thermal storage technologies include both low-temperature and high-temperature. Water is the commonly used storage medium for low-temperature solar thermal storage systems, and paraffin wax and inorganic hydrated salts are also commonly used; high-temperature solar thermal storage systems mostly use high-temperature molten salts, mixed salts, metals or alloys as storage media. In addition,energystoragetechnologycanalsobeusedforheatingbuildings.Insummer, when the sun is shining strongly, solar heaters are used to heat water and store it in undergroundaquifersorwell-insulatedcavities,wherethestoredhotwatercanbeused to heat the building when wintercomes.

Solar high temperature thermal power generation will play an increasingly important role in the future energy field. Whether for tower thermal power generation, trough thermal power generation or dish thermal power generation systems, high temperature thermal storage is an important technology, which is of great significance for improving system power generation efficiency, reducing power generation costs, and improving system power generation stability and reliability. In practice, different thermal storage methods should be selected according to different thermal power generation methods, different temperatures, different storage capacities and economic requirements.Nomatterwhatthermalstoragemethodischosen,itshouldbeconsidered frombothtechnicalfeasibilityandeconomiccost.Solidthermalstoragematerialsusing concreteorfoundryceramicsasmediumaregainingimportanceduetolowinvestment costsandsimpleoperation,andareexpectedtobeusedonalargescaleintank-type solar thermal power generation systems in desert areas. Double-tank thermal storage systemwithmoltensaltasmediumhaslowtechnicalrisk,easytorealizelarge-capacity thermalstorage,andcanrealizecontinuousandstablepowergeneration,whichismore suitablefortower-typesolarthermalpowergenerationsystem.Slanttemperaturelayer singletankthermalstoragesystemhasrelativelyhightechnicalrisk,butitsinvestment costcanbereduced,andisalsoakeydirectionforfutureresearch.Directsteampower generationsystemsarealsothemostpromisingmethodtoreduceinvestmentcosts,but they place very high demands on the pressure resistance of the heat transfer system. Steam accumulator technology needs to be further investigated to make it possible to store heat for long periods of time. High-temperature phase change and chemical reaction heat storage technologies are still in the experimental or pilot stage, and more suitable phase change materials, thermochemical reactions and devices need to be found. Each thermal storage method does not exist independently, and sometimes a hybrid thermal storage system can be formed by combining different thermal storage methods in one system depending on the design needs.[10]

1.3 Current applications of phase change thermal storagematerials

1.3.1 Application of low-temperature phase changematerials

(1) Carbon fiber thermally conductive low temperature composite phase change materials for electric heating[2].

The heat storage and discharge rate can be adjusted by using active/passive heat releasetomeettheheatingloaddemandofdifferentrooms.Theheatstorageefficiency oftheexperimentaldevicecanreach67%,whichcanrealizepeakandvalleyreduction. According to Beijing's time-sharing tariff policy, this low-temperature phase change heat storage heater can save 52.98% of the operating cost compared with ordinary electric heaters. Under the operating condition of heat storage at night and heat release atday,thetemperaturefluctuationoftheroomheatedbythisphasechangeheatstorage heater is small and has better thermal comfort. Taking paraffin wax as heat storage material compared with ordinary water as an example [5] 60L of water can store 3.5kWh of energy. While changing to phase change thermal storage material for heat storage,60Lofparaffinwaxcanstore3.6kWhofenergy.Althoughtheyhavethesame amount of heat storage after the completion of heat storage, but the same heat source, the water is relying on the temperature rise to store heat, as the heat storage proceeds, the smaller the temperature difference with the heat source, the lower

the heat storage efficiency;andthecompositephasechangeheatstoragematerialheatstorage

completion is relying on phase change heat absorption, phase change temperature change is small, as the heat storage proceeds, the temperature difference with the heat source is relatively large, so the heat storage capacity per unit time is stronger, and the heat flow density is larger. The storage temperature is also 80℃, the storage time of paraffin heat storage box is 10h, the exothermic time is 14h, the storage time of water heat storage box is 3.5h, the exothermic time is 3.5h. It shows that the paraffin heat storage box can meet the demand of heat storage in the valley electricity time and exothermic in the peak electricity time. In addition, the heat storage capacity of the paraffinheatstoragetankismuchlargerthanthatofthewatertank,andthetemperature changes smoothly during the exothermic process, so that the problem of large fluctuations in the temperature of the water tank is alleviated. In practice, the use of phase change heat accumulator can greatly reduce the size of the tank, reduce engineering costs and reduce the spaceoccupied.

(2) Composite fatty acid phase change thermal storage materials in the insulation box, packaging meal box application[6]

The results showed that when the heat-conducting enhanced composite phase change thermal storage material was applied to the EPS thermal insulation box, the thermal insulation time of the box with the addition of nano/micron heat-conducting composite phase change thermal storage material increased by 2 h compared with the control group. Microcapsules, when applied to the temperature control container of foodandbeveragepackaging,thetimerequiredforthetemperaturetodropfrom100℃ to 60℃ was 1h, while the temperature could be maintained at 40℃60℃ for about 3h and above 36℃ for 6.5h, which could meet the basic heat preservation needs of the lunch box. It can be seen that the heat-conducting enhanced phase change materials playanimportantroleintemperaturecontrolduringtheshort-rangetemperaturecontrol of the insulationcontainer.

1.3.2 Application of medium-temperature phase change thermal storagematerials

(1) Waste heat utilization of industrial processes[16].

Thewasteheatofindustrialprocessexistsbothcontinuousandintermittentwaste heat. For continuous waste heat, it is usually recovered by means of preheating raw materialsorair,whileintermittentwasteheatisnotwellutilizedduetothediscontinuity ofitsgenerationprocess.Forexample,somefurnacesinthenon-ferrousmetalindustry and silicate industry have a certain periodicity in the production process, which makes wasteheatrecoverydifficult,therefore,thethermalefficiencyofsuchfurnacesis usually less than 30%. One of the outstanding advantages of phase change heat storage is that it can store the excess heat in the production process and provide a stable heat source when needed. It is especially suitable for intermittent industrial heating processes or occasions with multiple heating equipment that do not work simultaneously, and the use of heat storage systems can save 15% to 45% of energy by using phase change heat storage technology. According to the different working temperatures and heat storage media of the heating system, the phase change heat storagesystemappliedtoindustrialheatingcanbedividedintothreeforms:heatstorage heatexchanger,heatstoragechambertypeheatstoragesystemandsensibleheat/latent heat composite heat storage system. The heat storage heat exchanger is suitable for intermittent industrial heating process, which is a kind of heat storage device and heat exchangedevicecombinedintoonephasechangeheatstorageheatexchangedevice.It takes the form of shell and tube or plate heat exchanger structure, one side of the heat exchangerfilledwithphasechangematerial,theothersideisusedasachannelforheat transfer fluid. When the intermittent heating equipment operation, the flue gas flow through the fluid channel of the heat exchanger type heat storage system, the heat will be transferred to the other side of the phase change medium so that the solid-liquid phase change, the waste heat of the heating equipment in the form of latent heat stored inthephasechangemedium.Whentheintermittentheatingequipmentworksfromnew, thecombustionairflowsthroughtheheatexchangechannelofthe heatstoragesystem, and the phase change material on the other side for heat exchange, and the heat stored in the phase change material is transferred to the heated fluid to achieve the purpose of preheating. One feature of the phase change heat storage heat exchange device is that it can be manufactured as a stand-alone device, and when used as a waste heat utilization device for industrial heating equipment, there is no need to modify the heating equipment itself, and it can be easily used by simply modifying the piping of the equipment. Heat storage chamber type heat storage system in the industrial heating equipment waste heat utilization system, the traditional heat storage usually uses refractory materials as the absorption of waste heat storage materials, because the absorption of heat is only dependent on the refractory material of the apparent heat capacity change, this heat storage chamber has a large volume, expensive, thermal inertia and output power gradually declining disadvantages, in the field of industrial heating is difficult to popularize the application. Phase change heat storage system is a newtypeofwasteheatutilizationsystemthatcanreplacethetraditionalheat accumulator. It mainly uses the latent heat absorption and release of material in the processofsolid-liquidstatechangetorealizethestorageandoutputofheatenergy.The phase change heat storage system has the characteristics of large heat storage, small volume, small thermal inertia and stable output. Compared with

conventional thermal storage chamber, the volume of phase change thermal storage system can be reduced by 30%~50%.

1.3.3 Application of high-temperature phase change thermal storagematerials

(1) Al-Si-Cu ternary alloy phase change material[12].

The melting/solidification processes of Al-Si-Cu ternary alloy phase change materials in three different shapes of thermal storage cells were simulated and their thermal properties were analyzed and compared, and the following conclusions were drawn: combining the realistic factors of solar high-temperature phase change thermal storage and its own limitations, silicon element can increase the mass latent heat of aluminum-based phase change thermal storage materials, and copper element can increase the volume latent heat of aluminum-based phase change thermal storage materialsTheAl-SiandCuelementscanincreasethebulklatentheatofAl-basedphase change thermal storage materials. Compared with Al-Si and Al-Cu binary alloys, Al- Si-Cuternaryalloysshowcertainadvantagesinthermalconductivity,masslatentheat, volume latent heat and other thermal properties. Therefore, Al-Si-Cu ternary alloy phase change materials have wide application prospects in solar thermal power generation systems. The heat transfer performance of phase change thermal storage units with different structures is different, and comparing the square, hexagonal and circular structures, the thermal storage unit with circular structure has the best performance in the process of heat storage anddischarge.

(2) High temperature thermal reservoir[13]

A high temperature thermal store is an atmospheric pressure device filled with phase change energy storage materials and can exchange heat with the outside world. Itsrawmaterialsarecommonlyrecycledindustrialrawmaterials,andthewholeprocess ofheatstoragecycleisacontrolled,atmosphericpressurephysicalprocess.Asagreen and energy-saving heating technology, high-temperature thermal storage can meet the thermal energy storage and industrial needs in different spaces and under different objective conditions in an economically feasible way, providing heating and steam system solutions for customers. Take Jiangsu Power Grid Company as an example analysis.Theenterpriseadopts10kVpowersupply,thenatureofelectricity consumption is large industrial electricity, before using the heat bank: the original electric heating steam boiler system uses 1751kWh of electricity per day during peak hours, considering the efficiency of the electric boiler 98%, the annual running time is calculated according to 360 days, the peak electricity price is 1.1002 yuan/kWh, the annual running cost of the electric steam boiler is 1751kWh × 360 yuan/kWh ÷ 98% × 1.1002 = 707675 yuan. After the transformation: After adopting the high temperature phasechangeheatstoragesystem,theheatproducedbytheelectricsteamboilerduring the original peak hours is generated by the valley electricity instead, and the valley electricity price is 0.3200 yuan/kWh, considering the high temperature heat storage efficiency of 88% and the electric steam boiler efficiency of 98%, and the annual running time is calculated according to 360 days, the annual running cost of the high temperature phase change heat storage system is 1751kWh × 360 yuan/kWh ÷ 98% ÷ 88% × 0.3200 = 233,900 yuan. After changing to high-temperature phase change thermal storage system, the enterprise saves 473,775 yuan in annual operating cost, saving up to 66.95%, while achieving 360kW of peak electricity load transfer. The project has good economic benefits, short recovery period, zero pollution and zero emission, and is of positive significance for improving the grid load curve and promoting energy conservation and environmentalprotection.

(3) Electric heating combined with phase change materials[14].

Electric heating combined with phase change thermal storage material is safe, reliable, easy to use, comfortable, pollution-free, clean and environmentally friendly, and occupies less land. Therefore, high-temperature phase change thermal storage electric heating system has a very good promotion prospect.

2. Development prospects and research status

2.1 Current problems to be solved for phase change thermal storagematerials

Phasechangethermalstoragematerialscanmakefulluseofsolarenergyresources and reduce building energy consumption, which is in line with the basic national conditions of energy conservation and emission reduction and the creation of green mountains in China. However, there are still some technical and application problems thatneedtobesolved:(1)thephysicalpropertiesofPCMs,suchasthevolumechange of the phase change material itself, fatigue strength and life, etc.; (2) economic, the price of phase change materials and packaging technology on the market is high, resultingintheoverallapplicationcostsarehigh;(3)regional,China'svastterritory, different performance parameters in different regions, the need to reconsider the phase change (4) environmental protection, quality of life is what the public wants, sound absorption and noise reduction, sterilization and moisture resistance, earthquake and pressureresistanceareallissuesthatneedtobeconsideredforphasechangematerials.

2.2 Difficulties in the current stage of research on phase change energy storage materials[5]

2.2.1 The durability of phase change energy storage materials, this problem is divided into three

maincategories.

(1) Degradation of thermophysical properties of phase change materials during cyclic phasechange.

(2) Phasechangeenergystoragematerialsaresubjecttoleakageandvolatilization duringlong-termrecycling.Thisyear'sresearchisalltowardthedevelopmentofphase change material containers that can resist high temperature, such as this year's experimentalstudyontheselectionofhightemperaturephasechangematerialAl-Si12 alloy and its compatibility with metal containers. (1) Al-Si12 is a high temperature phase change material with excellent performance, its latent heat is large, highthermal stability and good thermal conductivity; (2) temperature has a significant effect on the diffusion and permeation between Al-Si12 and metal materials, low temperature reactionisslow,hightemperaturereactionisfast;(3)whenthemetalcontainerisused inhightemperaturesolarthermalstoragesystem,themaximumheatingtemperatureof the phase change material should not exceed 650℃; small temperature change. It is conducivetothecontainermaterialresistancetothermalfatigue.Consideringthesafety of use, if the temperature cannot be strictly controlled, the metal container cannot be usedasaphasechangematerialcontainerinthehightemperaturesolarthermalstorage system.[11].

(3) The effect of the phase change material on the base material, the phase change process of the phase change material causes the base material to bedestroyed.

The price of phase change energy storage materials and phase change energy storage composites is high, which leads to the increase of energy storage cost. Energy storage performance of phase change energy storage materials: In order to make the energy storage body more compact, phase change energy storage compositesare requiredtohavehigherenergystorageperformance.Thecurrentenergystoragedensity of phase change energy storage composites is generally less than 120J/g, and their thermal conductivity is generallypoor.

3.Summary section

With the increasingly tight global energy situation, energy conservation and environmentalprotectionarereceivingmoreandmoreattentionfromcountriesaround theworld.However,duetothestrongtemporalandspatialnatureofenergysupplyand demand, there is an incongruity between energy supply and energy consumption in many energy utilization systems (such as solar energy systems, building air conditioningandheatingsystems,combinedcooling,heatingandpowersystems,waste heat and waste heat utilization systems, etc.), which causes unreasonable energy utilization and large amount of waste. Phase change energy storage materials, as the basis of energy storage technology, have been greatly developed at home and abroad, andfromtheaboveanalysis,phasechangethermalstoragematerialshavefar-reaching development prospects.

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