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Thermophysical properties of the composite ceramic-salt system (SiO_2 /Na_2SO_4)

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ABSTRACT

A composite ceramic-salt packed bed configuration is being developed for high-temperature thermal storage. The range of application is industrial waste heat recovery and utilization, off peak utilization reserve and solar thermal power systems application.

The thermophysical properties of the hybrid system SiO_2 /Na_2SO_4 have been investigated in the range from room temperature to temperatures above the melting point of the salt, 884°C. The Na_2SO_4 fraction in the composite materials was variied between 20 % and 50 %.

The following properties were measured:

- the specific enthalpy
- the coefficient of thermal expansion
- the thermal diffusivity.

The measurement of the thermal expansion was performed with a commercial difference dilatometer; the specific enthalpy was measured by drop calorimetry and the thermal diffusivity with a laser flash device. The measured values are correlated to the base properties of the different SiO_2 crystalline modifications. Special attention has been paid to phase change behaviour.

INTRODUCTION

Commonly used high temperature heat storages consist of solid matter using gas as heat carrier. Typical storage materials are various oxid ceramics based on alumina, magnesia and silica, which can be used up to a temperature of 1500°C depending on the desired application.

High temperature thermal storages being available at present have been optimized with respect to the quality of heat exchange, whereas the aspect of the

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optimization of heat storage capacity is regarded as less important. The storage cycle periods lie below 90 minutes. The application of high temperature storages in industry is economical only in exeptional cases like regenerators in ceramics industry or steel production. A new field of application could be the storage of solar energy provided that the cycle period can be extended to several hours.

The use of phase change materials came out to improve the storage capacity and the cycle periods of solid matter storages, but technical problems arose fron the deterioration of heat transfer rates. These problems could be overcome by using salt-ceramic hybrid materials (Petry and Claar, 1989). These materials consist of an inherently stable ceramic matrix in the pores of which up to 50% of a certain kind of salt is homogenly embedded; this salt gives an additional amount of latent heat to be stored when the melting temperature is reached. The melted salt stays in the ceramic matrix due to capillary forces.

In 1988 a research program was started with the aim to develop and optimize hybrid materials and to investigate thermophysical properties in a laboratory scale as well as under working conditions. Participants of the project are the German Aerospace Research Institute (DLR), a producer of high temperature ceramics (Didier Co.) and Stuttgart University (ITW). In the present contribution an investigation of thermophysical properties of composite materials will be reported. The samples were provided by DLR.

MATERIALS

The first problem to solve is the choice of appropriate combinations of ceramics and phase change materials for the high temperature range between 700°C and 1000°C. A series of preliminary experiments including repeated thermal cycling was carried out with different combinations of ceramics (alumina, magnesia, silica) and salts (carbonates and sulfates) to check the thermal, chemical and mechanical stability. The use of silica and Na_2SO_4 came out to be the most promising basic materials. Since the thermal behaviour of either is somewhat complicated, a brief description shall facilitate the discussion of the measurements.

Na_2SO_4

At normal pressure (p = 1 bar) five modifications of Na_2SO_4 can be observed:

$$\alpha\text{-}Na_2SO_4 \overset{\sim 200^\circ}{\rightleftharpoons} \beta\text{-}Na_2SO_4 \overset{240^\circ}{\rightleftharpoons} \gamma\text{-}Na_2SO_4 \overset{575^\circ}{\rightleftharpoons} \delta\text{-}Na_2SO_4 \qquad (1)$$

The modification δ-Na_2SO_4 is stable up to the melting point at 884°C. Values for the heat of fusion are reported to be in the range 147.3 to 179.1 J/g. In the presence of SiO_2, a decomposition of Na_2SO_4 to Na_2SiO_3 is observed, but this reaction starts above 1000°C. Along with the α-β- transition and the β-γ-transition length changes of -0.305% and 0.63% are observed respectively (Gmelin, 1958). Values for the thermal conductivity are not available.

In presence of humidity the orthorhombal anhydrid Na_2SO_4 -T (thenardite) is built at any temperature between room temperature and 240°C from α-Na_2SO_4:

$$\alpha\text{-}Na_2SO_4 \longrightarrow Na_2SO_4\text{-T (thenardite)} \xrightarrow{240^\circ} \gamma\text{-}Na_2SO_4 \qquad (2)$$

This Na_2SO_4-T remains stable up to 240°C, where the transition to γ-Na_2SO_4 occurs.

SiO_2

At room temperature SiO_2 exists in different states, namely the amorphous quartz-glass and the three cristalline forms quartz, tridymite and cristobalite. Each of the cristalline forms can be divided into two modifications (Hollemann and Wiberg, 1985):

$$\begin{array}{lcl} \alpha\text{-quartz (trigonal)} & \overset{575^\circ}{\rightleftharpoons} & \beta\text{-quartz (hexagonal)} \\ \alpha\text{-cristobalite (tetragonal)} & \overset{270^\circ}{\rightleftharpoons} & \beta\text{-cristobalite (cubic)} \\ \alpha\text{-Tridymit (rhombisch)} & \overset{117^\circ}{\rightleftharpoons} & \beta\text{-Tridymit (hexagonal)} \end{array} \qquad (3)$$

A transformation of quartz to β-cristobalite is observed at a temperature of about 1050°C to 1100°C. The β-cristobalite phase can be obtained in a stable form by subcooling and by addition of mineralizers. A transformation of quartz or cristobalite to tridymite is only possible in the presence of special mineralizers like Na_2WO_4.

The changes of length connected with α-β modification changes are 0.266% for quartz, 0.12% for cristobalite and 0.12% for tridymite.

Hybride materials

Our samples are made of technically pure powder which was cold pressed, dried, sintered and finally annealed at 1000°C. The different materials are basic ceramic (technical grade SiO_2), the 20-50% Na_2SO_4-salt (purum p.a.>99%, 100μm grain size) and further additives as chemical binders and water in minor quantity (<2%). Main influence on the thermal and mechanical stability of the composites is caused by particle size of the main components, the particle size distribution of the ceramic, type and quantity of the binder and the tempering and burning process (Tamme, 1990). X-ray diffractometry was used to investigate the structure of the ceramic matrix, which revealed qualitatively the dominating modifications (quartz, tridymite and cristobalite). The investigated samples consisted mainly of christobalite, but it was not possible to quantify the fraction of different modifications.

MEASUREMENT DEVICES

The most important properties for the design of thermal storages are heat capacity, thermal dilatation and thermal diffusivity.

Calorimetry

The specific enthalpy of the above mentioned composite materials was measured with a drop calorimeter. A sample (a cylinder of 5 mm diameter and 5 mm length) tempered at room temperature is dropped into a heated measuring crucible which is completly enclosed by a thermoelectric pile. During the heating up of the sample the resulting heat flow is measured by the thermopile. The enthalpy difference between room temperature and the final sample temperature is determined by an integration of the measured heat flow. The measurements were carried out in an atmosphere of slowly flowing argon. The device has been checked with pure MgO. The results agree with literature data within 4% up to 1000°C.

Dilatometry

For the measurement of linear expansion a difference dilatometer is used; therby the dilatation of of a certain sample is measured and compared with a reference sample, cancelling out apparative expansion factors.

The measurements were carried out under vacuum conditions ($p < 0{,}05\,\mathrm{mbar}$) with a temperature transient smaller than 2K/min. The samples (cylinders of the same size as those used for calorimetry) are mounted horizontally. For checking the device we made a reference measurement with pure MgO. The results agree with literaure data within 2% up to 1000°C.

Laserflash

Compared to available measurement methods for the thermal conductivity, the laser flash method, which yields the thermal diffusivity, has the advantage of small size of the used samples and a remarkable save in measuring time, especially at high temperatures. Furthermore diffusivity data meet our needs for storage simulations, since for the calculation of the transient behaviour the thermal diffusivity $a = \lambda/\rho c_p$ is the main input variable.

The measurements were carried out with a comercially available laser flash device consisting of a vacuum chamber containing the sample, a laser and a pyrometer. The pressure in the high vacuum chamber was about 10^{-6}mbar during the measurements, the temperature can be chosen between room temperature and 1500°C. A problem arose from the transparency of the investigated materials (SiO_2 and Na_2SO_4) for infrared radiation, which could be overcome by coating the sample surface with graphite.

RESULTS

The examined samples consist of mixtures of 20/80, 40/60, and 50/50 wt% Na_2SO_4 and different modifications of SiO_2. The X-ray analysis shows very intensive peaks indicating a cristobalite structure, whereas quartz and tridymite peaks can hardly be observed.

The first property being discussed is the specific enthalpy. The use of a drop calorimeter allows the determination of the absolute value of the specific enthalpy and the enthalpy change on transitions very exactly. Our device is restricted to the temperature range above 500°C.

Fig. 1a shows measured specific enthalpy values of Na_2SO_4, the cristobalite and the quartz phase of SiO_2 and of a 50/50-sample. The measured values above and below the melting point are interpolated linearly.

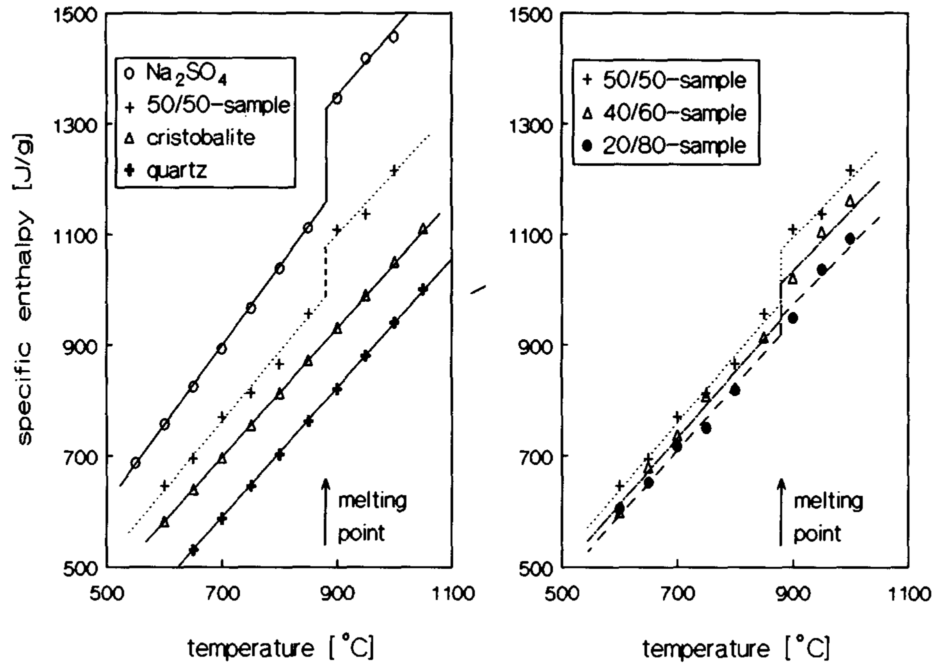

Fig. 1 a: Specififc enthalpy of a 50/50-sample in comparison with the pure materials

Fig. 1 b: Specififc enthalpy of 50/50-, 40/60- and 20/80-samples

An examination of the calorimetric measurements shows that a simple weight fraction mixture rule can be applied, which is reasonable since we don't expect chemical reactions between SiO_2 and Na_2SO_4. Assuming the cristobalite fraction to be 80% of the ceramic matrix material, we obtain calculated enthalpy values which fit the measurements of 20/80-, 40/60- and 50/50-samples shown in Fig. 1b within the scatter of the data.

Fig.2 a,b show the linear thermal expansion and the thermal diffusivity of a 50/50-sample in comparison with the pure materials Na_2SO_4, cristobalite and quartz. For the diffusivity measurements a quartz sample was not available.

Pure quartz shows up to the α-β-transition a monotonuously increasing expansion coefficient; at the transition temperature (575°C) there is a sudden change of length caused by a variation of the lattice structure; above this temperature the expansion coefficient is quite constant.

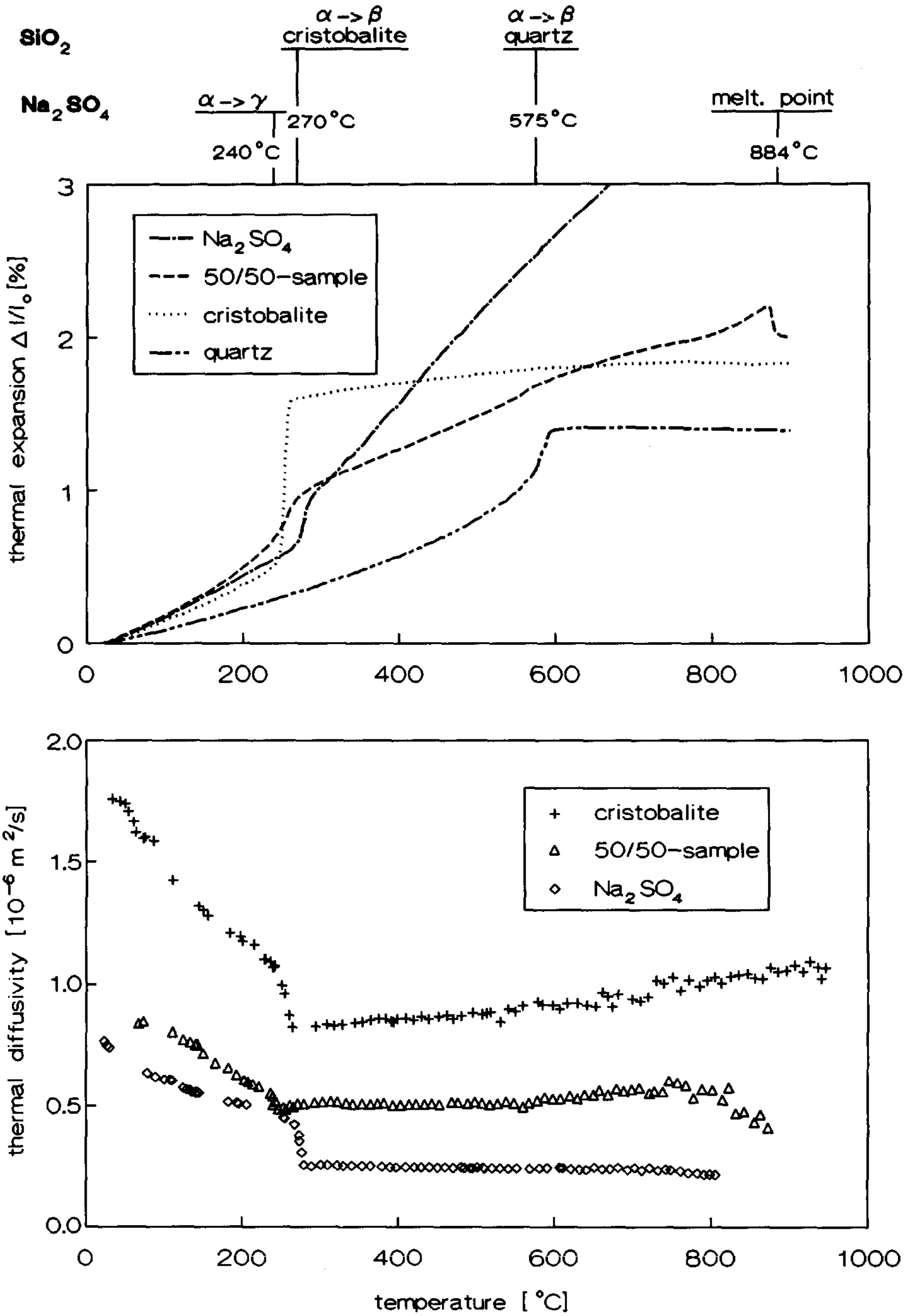

Fig. 2 a,b: Thermal expansion and thermal diffusivity of a 50/50-sample in comparison with pure materials

The cristobalite shows a similar elongation behaviour with a phase transition at 250°C and a slightly increasing expansion above the transition temperature. The thermal diffusivity data plotted in Fig. 2b indicate the transition by a steep decrease in the vicinity of 270°C. Above the transition point the diffusivity has a slight linear increase.

The expansion of Na_2SO_4 increases linearly up to a temperature of 260°C, which indicates a transition between thenardite and the γ-modification, since a α-β-transition should cause a shrinkage. The shift of the transition point from 240°C to 270°C is confirmed by the diffusivity data. It may be due to a lack of defects in the crystal structure. At higher temperatures there is no evidence for a further transition.

The 50/50-hybrid sample shows a first transition at about 250°C, affected by the α-β-transition of the cristobalite and the thenardite to γ-Na_2SO_4 transformation. The two effects can't be separated. The next interesting point of the curve lies at 575°C. Above this temperature the thermal expansion increases slower, while the thermal diffusivity begins to rise. Since the influence of the γ-δ-transformation of pure Na_2SO_4 is very weak, the 575°C-change of slope possibly indicates the presence of a certain amount of quartz. The melting point of Na_2SO_4 can be seen in the abrupt change of α at 880°C, where the sample suffers a shrinkage of 0.2%. Above the melting temperature the thermal expansion remains constant. The diffusivity begins to decrease at about 800°C.

In Fig.3a,b the thermal expansion and the thermal diffusivity of samples with a content of 20,40 and 50% Na_2SO_4 is shown. The elongation of the 20/80-sample below 240°C is larger than the expansion of the other samples. This indicates a certain amount of tridymite within this sample.

The most significant change of the thermal properties, caused by the α-β-transition of the cristobalite and the thenardite to γ-Na_2SO_4 transition, occurs in a temperature range between 240°C and 270°C.

The presence of quartz is indicated for all samples by a change of slope at 575°C. As expected, the final expansion of the measured materials depends directly on the portion of Na_2SO_4.

The thermal diffusivity of the hybrid material is deteriorated with an increasing amount of Na_2SO_4. It is reduced to about 75% of the pure ceramic by a content of 20% salt and saturates at roughly 50%, since the sample containing 40% does show a behaviour very similiar to the 50/50-sample.

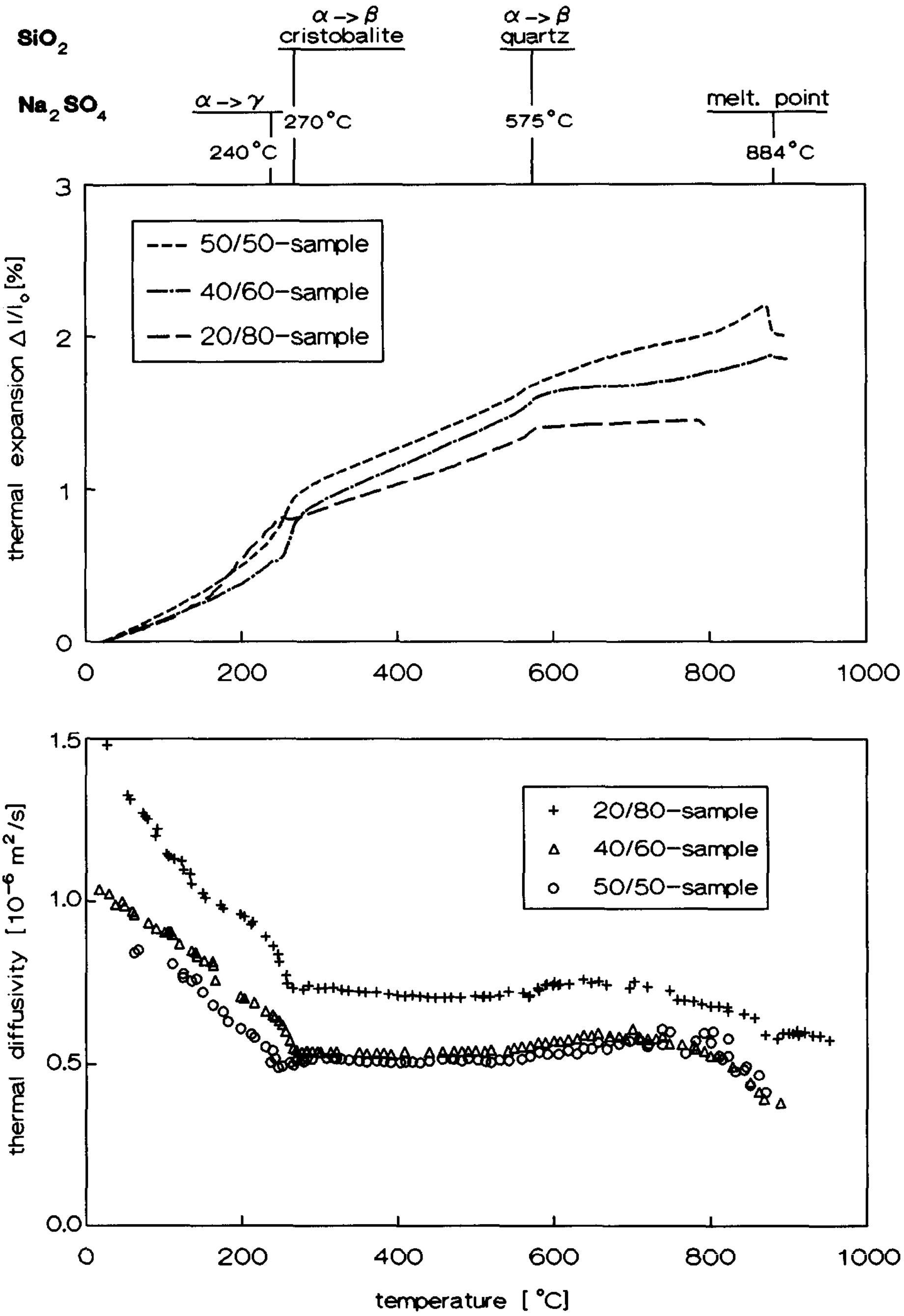

Fig. 3 a,b: Thermal expansion and thermal diffusivity of samples with different weight fractions of Na_2SO_4 (20,40,50 %)

CONCLUSIONS

In the range between room temperature and temperatures above the melting point of the salt the thermophysical properties of the hybrid system SiO_2/Na_2SO_4 have been investigated. It was the aim of the discussion to show the possibility of the prediction of the thermophysical behaviour of the hybrid material from the knowledge of the pure substances data.

- The specific enthalpy can be calculated by a simple mixture rule. Since the fraction of different SiO_2-phases can't be determined quantitatively, the cristobalite phase was assumed to build 80% or more of the ceramic fraction. Values calculated with this assumption lie within the uncertainty of measurement.
- The linear thermal expansion shows the main characteristics of either Na_2SO_4, quarzit and cristobalite, especially the different phase transitions were observed. It was not possible to quantify the thermal behaviour. The measured samples are mechanically stable even after repeatedly thermal cycling and at temperatures above the melting point of Na_2SO_4, showing that the pore fraction of the ceramic matrix is high enough to allow an elongation of the salt without crack-building.
- The thermal diffusivity of the hybrid material lies between the values for the basic materials, showing a remmarkable deterioration along with the increase of the amount of salt.

Further investigations shall focus on the preparation of samples with a large tridymite fraction, since it has the lowest expansion going along with the α-β-phase transition, and on the improvement of the thermal diffusivity.

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