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Thermal expansion models for polycrystalline salt-ceramics

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Abstract

This paper describes a method for the estimation of the thermal expansion in polycrystalline hybrid systems. These new materials have been developed for use in high temperature thermal storage applications. A simple crystallite model is compared with the complex model specified by Hashin and Shapery. After describing and validating the models, the calculated expansions are compared with measurements on the following different hybrid systems:

- MgO/Na_2SO_4, Na_2SO_4-fraction 10–45%
- SiO_2/Na_2SO_4, Na_2SO_4-fraction 20–50%

The results show that all measurements are within the calculated second order boundaries. A good estimation is also given by the simple crystallite model. The maximum deviation between calculated values and measurements at 800°C is less than 10%. This model can also be applied for SiO_2 as a carrier component.

Keywords: Thermal expansion; Polycrystalline materials; Salt ceramic; Composite; Hybrid system

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1. Introduction

Due to the shortage of raw materials, it is essential that ways to reduce the consumption of primary energy are found. The storage of process heat at high temperatures is one of these possibilities. Such storage is utilized in for example blast furnaces. At present, oxide ceramics are used as the storage materials. The energy density and thereby the efficiency of these materials is reduced by a high pore fraction. In order to raise the efficiency, new composite materials with higher specific heat capacities as well as higher mechanical and thermal stabilities have been developed.

These composites consist of a solid ceramic matrix as a carrier material and a salt used as a phase-change material inside the pores. In addition to a higher specific heat, the melting enthalpy of the salt can also be used for storing heat. Another positive effect is the temperature constancy at the melting point of the phase-change material. The utilization of heat storage is thereby improved and the conditions for charging and discharging are attained later. Consequently more heat can be stored [1, 2, 3].

A problem, however, is the differing thermal expansions of the composite materials which could

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lead to storage internal stresses within the composite. The researched thermal expansion of the composites is an important indicator for the thermal stability of the composite.

The carrier materials used are MgO and SiO_2. The phase-change material is a salt (Na_2SO_4, melting temperature 885°C) with a fraction of between 10 and 50%. A detailed description of the materials is given in [1]. The thermal expansions of the different composites have been determined by measurements and estimated by using both known and newly developed models. The samples used were provided by the German Aerospace Research Institute (DLR).

2. Production and structure of the hybrid materials

Our samples were made of technically pure powders which were pressed in the cold state, dried, sintered and subsequently annealed at 1000°C.

Figure 1 shows a 60x enlargement of the hybrid system with a Na_2SO_4-fraction of 40%. The pores are equidistant; the pore size is approximately equal to the size of the SiO_2 crystallites.

3. Models for the calculation of thermal expansion

3.1. Crystallite model

None of the components in the hybrid material shows a characteristic lattice structure. The solidus therefore consists of single crystallites. Each of these crystallites has its own free expansion. Calculating the expansion coefficient α of a solid, the volume fraction v_n and the expansion coefficient α_n must be considered for each of the components $(1, 2, \ldots n)$, whereby the pores are treated as a special component.

$$\alpha = v_1\alpha_1 + v_2\alpha_2 + \ldots + v_n\alpha_n + v_{pore}\alpha_{pore} \quad (1)$$

For real composites however, it is supposed that contact between the components will predominantly cause additional influence on the stress-strain state of the composite and so hence lead to the expansion characteristics.

3.2. Complex models

3.2.1. Literature

Models for the expansion characteristics of salt-ceramic hybrid materials are not to be found in

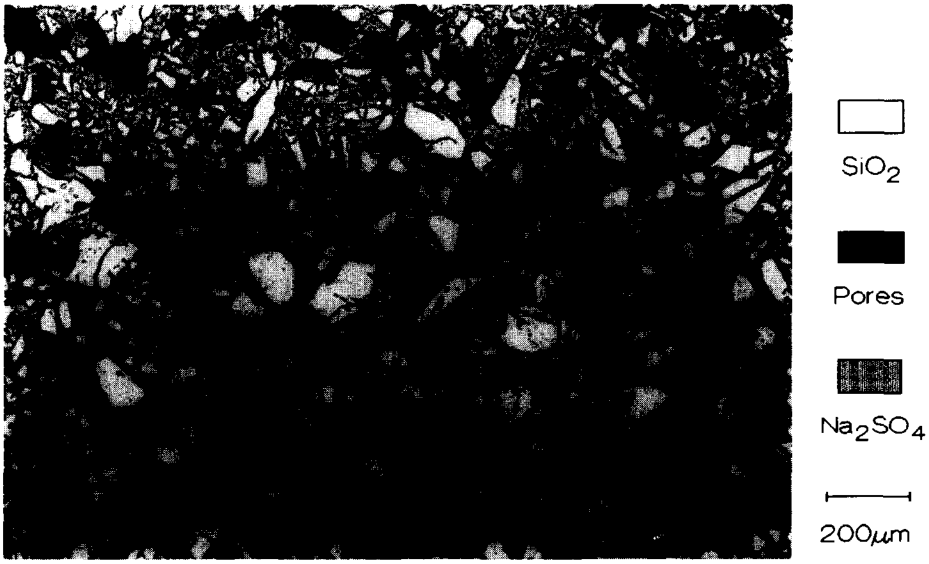


Fig. 1. Structure of a SiO_2/Na_2SO_4-composite with a Na_2SO_4-fraction of 40% after production.

literature. Unidirectional fibre-reinforced composites however, have been investigated both theoretically and experimentally.

Transverse to the fibre direction, fibre-reinforced composites have a similar structure as the hybrid materials investigated. By studying different models, Bowles and Tompkins [4] recognized in 1989 that only the model of Hashin and Rosen [5] showed similar results to the respective measurements. This model was based on the assumption that it was possible to determine the stress and strain conditions in a solid provided the sum of the local thermal elasticities were in equilibrium in the static solid. Thus the effective macroscopic linear expansion could be calculated following consideration of:

— isotropic components and the composite

— all mechanical and thermal properties do not depend on the temperature

— linear elasticity only.

From these, Hashin derived a relationship between the thermal expansion coefficient α^* of a composite consisting of 2 components (1,2) and the thermal and mechanical properties of its components.

$$\alpha^* = \bar{\alpha} + \frac{(\alpha_1 - \alpha_2)}{\left(\frac{1}{K_1} - \frac{1}{K_2}\right)}\left[\frac{1}{K^*} - \left(\overline{\frac{1}{K}}\right)\right] \tag{2}$$

where

$$\left(\overline{\frac{1}{K}}\right) = \frac{v_1}{K_1} + \frac{v_2}{K_2} \tag{3}$$

$\alpha_{1,2}$: thermal expansion coefficient of component 1 and 2 respectively

$v_{1,2}$: relative volume fraction of component 1 and 2 respectively

$K_{1,2}$: bulk modulus of component 1 and 2 respectively

$\bar{\alpha}$: volume-averaged thermal expansion coefficient

$\bar{K}$: volume-averaged bulk modulus

α^*: effective macroscopic thermal expansion coefficient of the composite

K^*: effective macroscopic bulk modulus of the composite

The bulk modulus K^* is the only unknown quantity in Eqn. 2. There are different modes for its estimation:

3.2.2. *First order models*

The components inside the composite can be arranged in two different ways (Fig. 2): When arranged *in series* the stress σ in each of the components is constant. Thus the bulk modulus of the composite is

$$K^* = \frac{1}{\frac{v_1}{K_1} + \frac{v_2}{K_2}} \tag{4}$$

In a *parallel* arrangement however, the same strain ε is caused in each component. Each of the components has a different state of stress. The bulk modulus is

$$K^* = v_1 K_1 + v_2 K_2 \tag{5}$$

The difference between upper and lower expansion coefficient α^* of the composite consequently depends on the difference between the bulk moduli.

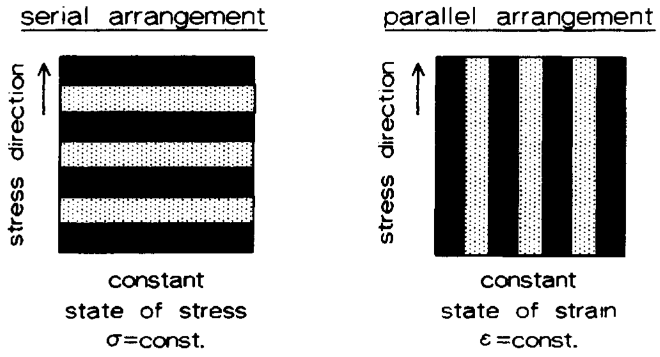


Fig. 2. Extrene arrangements for the components inside a composite.

3.2.3. Second order models

Taking the component shear moduli G_1 of component 1 and G_2 of component 2 in account, Shapery [6] derived the following equation to calculate a lower boundary for the bulk modulus K^* of a composite:

$$K^* = K_1 + \frac{v_2}{\frac{1}{K_2 - K_1} + \frac{v_1}{K_1 + (4/3)G_1}} \tag{6}$$

The upper boundary can be obtained by substituting for indices 1 and 2 relating to component 1 and component 2. Hence it is possible to obtain two boundary values which are closer to each other than those from the first order model.

3.2.4. Influence of pores

Size, geometry and distribution of pores all have an influence on the thermal expansion of a material. Large pores cause boundary effects which change the thermoelastic stresses inside the composite. Ondracek [7] used the following empirical equation which shows how the bulk modulus depends on the relative pore fraction ($0\% \leq v_{Pores} \leq 50\%$).

$$K^*_{Pores} \approx K^*(1 - 1.21 \cdot (v_{Pores})^{0.666}) \tag{7}$$

v_{Pores}: relative volume fraction of pores
K^*: effective macroscopic bulk modulus of the composite, *without* consideration of pore influence
K^*_{Pores}: effective macroscopic bulk modulus of the composite, *with* consideration of pore influence

This equation is apparent for spherical pores. For elliptical pores, Ondracek applied a different equation [7].

3.3. Validation of the model of Hashin and Shapery

In order to validate the model of Hashin [5] and Shapery [6] copper/lead-alloy [8] was used. At a lead-fraction of between 36 and 87% by weight, a miscibility gap exists in the melt; the load is uniformly distributed throughout the copper. At the solidification point of copper a structure is formed in which the liquid lead is distributed. At a temperature less than 327°C the lead solidifies as well. Information on the bulk modulus and thermal expansion of the two pure materials is given in the literature [9, 10].

Figure 3 shows the relative linear expansion of two components, copper and lead, as well as the expansion of a copper-lead alloy, containing 50% of

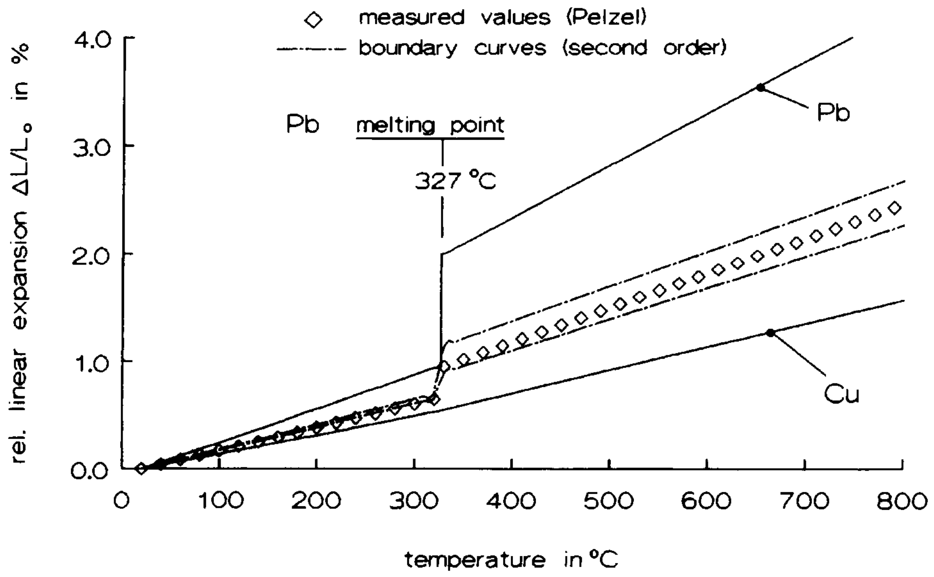


Fig. 3. Relative linear thermal expansion of a copper-lead alloy with a lead-fraction of 50% of weight.

weight of lead. In addition to this, the two boundary curves which have been calculated using the described second order model of Hashin [5] and Shapery [6] are plotted on this diagram. In the investigated temperature range between 20°C and 800°C, the measured values remained within the calculated boundary curves.

4. Thermal expansion of hybrid materials

4.1. Measurement devices

A difference dilatometer was used for the measurements; the dilatation of a given sample was measured and compared with a reference sample so as to cancel out instrumentation effects. The measurements were carried out under atmospheric conditions. The temperature gradient was less than 2K/min. The samples (of 5mm diameter and 5mm length) were mounted horizontally. Pure sapphire and MgO were used to verify the apparatus. The results up to 1000°C agreed with literature values to within 2%.

4.2. Comparison of calculated and measured values

For the two-component system MgO/Na_2SO_4 it is possible to calculate the thermal expansion between 20°C and 800°C using the model of Hashin [5] and Shapery [6] as well as the crystallite model described above. No experimentally validated values for the thermal expansion of Na_2SO_4 exist in the range above 800°C. The calculated expansion values for temperatures above 800°C were therefore extrapolated, without taking the melting point of the salt at 884°C into consideration.

The large difference between the bulk modulus values for MgO and Na_2SO_4 resulted in a large difference between the lower and the upper boundary curves and hence a greater uncertainty.

4.3. MgO/Na_2SO_4-composite

In order to calculate the thermal expansion using the model of Hashin [5] and Shapery [6] it was necessary to know the densities and bulk moduli of the various components [11, 12]. By means of the Grüneisen-relation [13], it was possible to calculate the bulk modulus $K(\vartheta)$ for MgO and Na_2SO_4 using Eqn. 8.

$$K(\vartheta) = \gamma_G(\vartheta)\rho_0 \frac{c_p(\vartheta)}{[1 + \int \beta(\vartheta)\,d\vartheta]\,\beta(\vartheta)} \tag{8}$$

where ρ_0 is density at room temperature, $\beta(\vartheta)$ is the volume expansion coefficient, $\gamma_G(\vartheta)$ is the Grüneisen-factor and $c_p(\vartheta)$ the specific heat capacity

Figure 4a and 4b show the relative linear expansions for composites with Na_2SO_4 weight-fraction of 20% and 30% respectively.

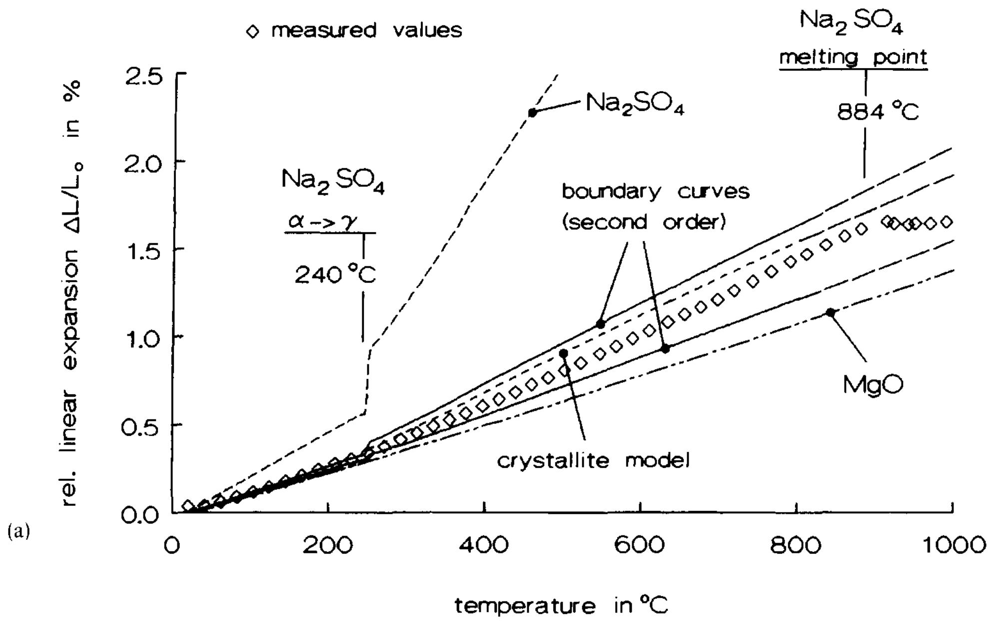
The linear expansion of the composite with the Na_2SO_4-fraction of 20% (Fig. 4a) remained in the middle between the two boundary curves. Using the crystallite model, there were only small deviations from the measured expansion observed.

The composite with a Na_2SO_4-fraction of 30% (Fig. 4b) showed a constantly increasing expansion gradient between 600°C and the melting point of salt. Neither model conformed to this qualitative shape of the curve. However the results of the measurement remained between the calculated boundary curves.

4.3.1. Accuracy of the models

For a Na_2SO_4-fraction of 10%, the deviation between the crystallite model and the values measured between 300°C and 1000°C was less than 6% and for a saltfraction of 20% less then 10%. If the salt-fraction was higher, the increasing expansion gradient caused a greater deviation towards the virtually linear shape of the crystallite model. The composite with a salt-fraction of 30% showed a deviation of between 10 and 20% within the temperature range 340–650°C. At temperatures lower than 340°C and higher than 650°C, the deviation was less than 10%. A composite with a salt-fraction of 45% showed a deviation of 10 to 20% between 250°C and 650°C; outside this temperature range the deviation was less than 10%.

The maximal linear expansion is of great interest for evaluating a new material. Table 1 shows the percentage deviation of the crystallite model from the measured linear expansion at 800°C. The maximal deviation from the mean from the model of Hashin [5] and Shapery [6] is also given.



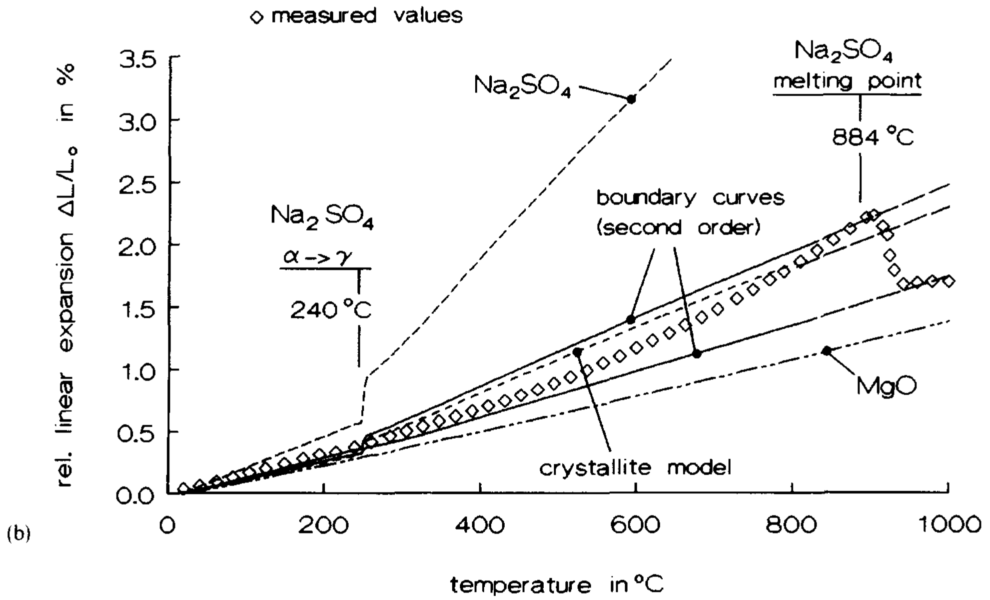


Fig. 4. Relative linear expansion of a MgO/Na_2SO_4-composite with a Na_2SO_4-fraction of a) 20% Na_2SO_4 b) 30% Na_2SO_4 for comparing measured and calculated values.

Hence an estimation of the linear expansions of MgO/Na_2SO_4-composites with salt-fractions of between 10 and 45% by weight are possible by using the model of Hashin [5] and Shapery [6] as well as by using the crystallite model. The qualitative expansion shape at a Na_2SO_4-fraction of 30% and

Table 1
Relative linear expansion $\Delta l/l_0$ for MgO/Na_2SO_4-composites with different Na_2SO_4-fractions at 800°C-deviations between measured and calculated values

Na_2SO_4-fraction [weight-%]	Measured value $\Delta l/l_0$ [%]	Hashin and Shapery 2. order			Crystallite model	
		$\Delta l/l_0$ lower boundary [%]	$\Delta l/l_0$ upper boundary [%]	Uncertainty from mean	$\Delta l/l_0$ calculated value [%]	Deviation from measured value
10	1.1116	1.11	1.348	± 9.7%	1.151	+3.1%
20	1.45	1.217	1.641	±14.9%	1.546	+6.2%
30	1.827	1.351	1.937	±17.8%	1.841	−0.76%
45	1.893	1.502	2.415	±23.3%	1.866	−1.4%

above, cannot be reproduced by either of the two models.

4.4. SiO_2/Na_2SO_4-composite

It is not possible to calculate the linear expansion of the SiO_2/Na_2SO_4-composite by means of the model of Hashin [5] and Shapery [6] because the carrier material SiO_2 exists in 3 different modifications, which in turn comprise 3 different components (quartz, cristobalite, tridymite) themselves [14].

It is however possible to compare the measurements using the simple crystallite model described above. As an example, Fig. 5 shows a composite with a Na_2SO_4-fraction of 50%. X-ray diffrac-

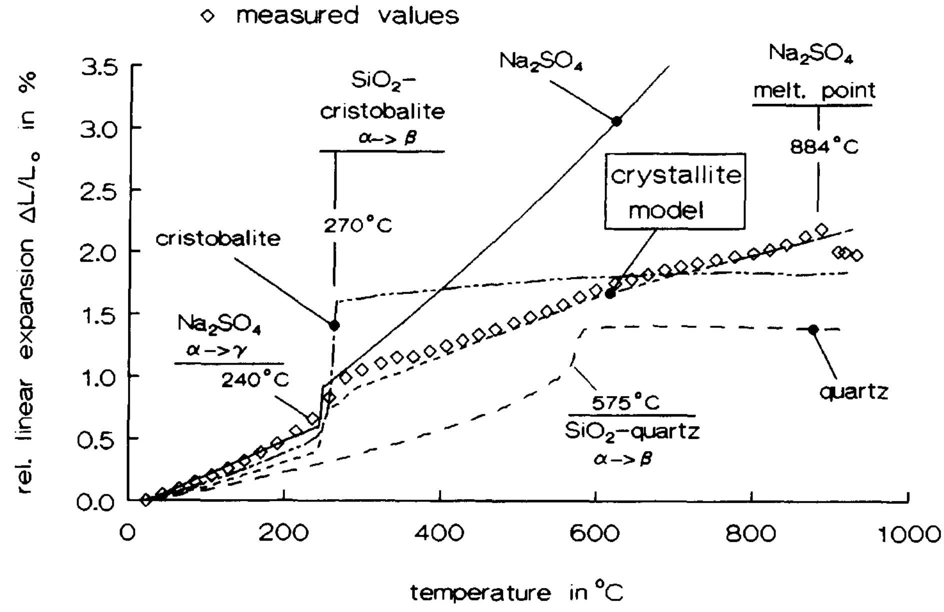


Fig. 5. Relative linear expansion of a SiO_2/Na_2SO_4-composite with a Na_2SO_4-fraction of 50%-compared measured and calculated values.

tometry shows a high cristobalite fraction. A cristobalite-fraction of 70% was assumed for the calculation.

Above the α-β-transition of cristobalite and the thenardite to γ-Na_2SO_4 transformation at about 250°C, a conformity between the measured thermal expansion and the expansion calculated by using the crystallite model was seen. The maximal deviation within the whole temperature range was -12% and the deviation at 800°C was -5%.

With regard to a lower salt-fraction of 20%, the maximal deviation was -9% within the temperature range above 250°C and the deviation at 800°C was -2.5%.

The crystallite model allows an estimation of the thermal expansion of SiO_2/Na_2SO_4-composites. The qualitative expansion shape can also be reproduced in contrast to the MgO/Na_2SO_4-composites which is probably due to the higher heterogeneity of SiO_2/Na_2SO_4-composites.

5. SUMMARY

Now composite materials have been developed to improve heat storage at high temperatures. Various possibilities of finding models for the prediction of the thermal expansion of composite materials have been investigated for the hybrid systems MgO/Na_2SO_4 and SiO_2/Na_2SO_4, with a Na_2SO_4 fraction of between 10 and 50%. The following conclusions can be drawn:

- the thermal and mechanical stability is guaranteed for all composites.
- the used models have been validated by copper-lead alloys.
- an estimation of the thermal linear expansion of MgO/Na_2SO_4 composite by using the model of Hashin and Shapery was possible. The crystallite model, which is easier to handle, can be used. The deviations towards the measured values was less than 7% for all Na_2SO_4-fractions near the melting point.
- the crystallite model also allows an estimation for the SiO_2/Na_2SO_4-system. The deviation towards the measured values was less than 7% for all Na_2SO_4-fractions near the melting point.

Acknowledgments

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