 DOI 10.1002/mawe.201200949

Highly heat conductive open-porous aluminium fibre based parts for advanced heat transfer applications

Hoch wärmeleitfähige offenporöse Aluminiumfaser-Strukturen für Wärmeübertragungsanwendungen mit speziellen Anforderungen

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Due to their oxygen affinity, aluminium alloys are difficult-to-sinter materials. Either mechanical destruction or the action of a liquid phase can be used to break oxide layers and thus achieve the desired diffusion bonds between the individual particles. In the present work, a liquid phase sintering approach is used in conjunction with high-purity particulates and controlled processing conditions in order to obtain high-purity, high-porosity (up to 90 %) parts with an exclusively open porosity. Appropriate sinter conditions were determined with the help of thermodynamic calculations using the PANDAT software package. Bonding of the sintered fibre structures to tubes, sheets and other massive structures may be achieved by co-sintering or brazing. The resulting metallic contacts allow for excellent heat transfer between the fibre structure and heat-carrying fluids. These advantageous properties may be exploited in applications such as adsorption cooling devices or very fast phase-change material (PCM) heat-storage devices. The present study reports on the manufacturing of such PCM-aluminium fibre compounds and their performance measured on a PCM storage demonstrator run in a laboratory environment.

Keywords: Aluminium / liquid phase sintering / phase change material / heat storage / heat transfer / cellular metal / porosity / metal fibre

Aluminium-Legierungen sind bedingt durch die hohe Sauerstoff-Affinität des Aluminiums nur schwer sinterbar. Die störenden Oxidschichten auf den Pulverteilchen können mechanisch oder durch das Vorhandensein einer flüssigen Phase aufgebrochen werden. In der vorliegenden Arbeit wird letzterer Weg in Verbindung mit der Verwendung hochreiner Partikulate beschritten, um hochporöse (bis zu 90 %) Bauteile mit einer ausschließlich offenen Porenstruktur zu erhalten. Geeignete Sinterbedingungen wurden durch thermodynamische Berechnungen mit dem Programmpaket PANDAT ermittelt. Die stoffschlüssige Anbindung dieser Strukturen an Rohre, Bleche oder andere massive Strukturen kann schon während des Sinterns oder durch anschließendes Löten erfolgen. Die resultierenden metallischen Kontakte sorgen für einen sehr guten Wärmeübergang zwischen der Faserstruktur und einem Wärmeträger-Medium. Diese vorteilhaften Eigenschaften lassen sich für Adsorptions-Kältemaschinen oder sehr schnelle Phasenwechselmaterial-Wärmespeicher (PCM-Speicher) nutzen. Die vorliegende Arbeit berichtet über die Herstellung von PCM-Aluminiumfaser-Verbunden und zeigt Testergebnisse, die an solchen PCM-Speicherdemonstratoren unter Laborbedingungen erhalten wurden.

Schlüsselwörter: Aluminium / Flüssigphasen-Sintern / Phasenwechsel-Material / Wärmespeicherung / Wärmeübertragung / Zellulares Metall / Porosität / Metallfaser

1 Introduction

Up to date, it has been difficult to build PCM storage devices with fast charging and discharging performance due to the fact that phase change materials (PCM) usually suffer from a very low heat to conductivity of less than 1 W/(m K). It is therefore necessary to combine the PCM with a highly conductive matrix which, on the other hand, should not consume too much of the storage volume. Sintered metal fibre structures made from aluminium alloys seem to be a well suited matrix for this purpose. They can provide a reasonable compromise between heat conductivity and structural porosity, especially when their strongly anisotropic characteristics are exploited. Additionally, their manufacturing process ensures that no closed cavities are contained in the structures, this way making sure that the available storage volume will be used to the fullest.

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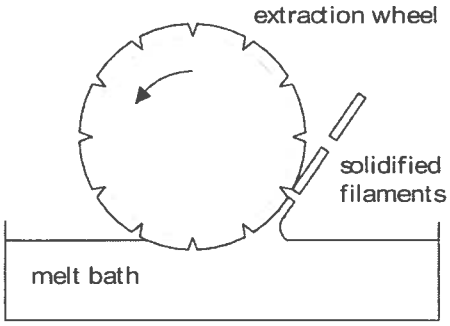

Figure 1. Schematic drawing of the crucible melt extraction process.

One important prerequisite for the manufacturing of sintered aluminium fibre structures is the availability of aluminium alloy fibres with appropriate composition and clean surface. This can be accomplished by utilising the crucible melt extraction (CME) process, by which it is possible to manufacture short fibres from almost any fusible material [1], *Figure 1*. To this end, a rotating wheel with a notched surface is placed over a melt pool. The rotating extraction device is water cooled and thus generates a high solidification rate. As a result, homogenous distribution of the alloying elements, small grain sizes, reduced segregation and extended solubility, as well as the formation of metastable phases is achieved. The melt extracted fibres typically show a sickle or kidney shaped cross-section.

Fraunhofer IFAM Dresden has improved the crucible melt extraction process to produce fibres of a mean equivalent diameter from 50 µm to 250 µm in batch sizes of one to several kilograms. The fibre length can be set from 3 mm to 25 mm with a deviation of approximately ± 15 %. The current state-of-the-art CME facility is shown in *Figure 2*. It allows for the extraction of fibres under vacuum or protective atmosphere (argon, nitrogen) with a pressure of up to 10 bar for improved secondary cooling.

Plates, rings, and cylinders can be manufactured from the fibres by depositing them on a suitable sintering substrate, followed by sintering and machining to the desired dimensions, *Figure 3*. The preferred cutting method is laser cutting which is suitable for cutting plates of up to 10 mm thickness. The porosity of the fibre structures can be set to anywhere between 50 and 90 % and is completely interconnected, allowing for free through-flow of fluids which is important for complete filling of the PCM storage devices. The pore size usually lies between 10 and 250 µm, depending on the porosity and the fibre diameter. The small pore size minimizes the distance that the heat has to travel within the badly conducting PCM, thus maximising the expected performance of such storage devices.

2 Design of sintering conditions for aluminium fibres

The attempted application of aluminum fibre structures as heat exchanger requires good heat conductivity of the base material and good interconnections between single fibres and supporting structures. The first steps towards sintered fibre structures were therefore carried out with the system Al-Cu-Zn as it seemed to be

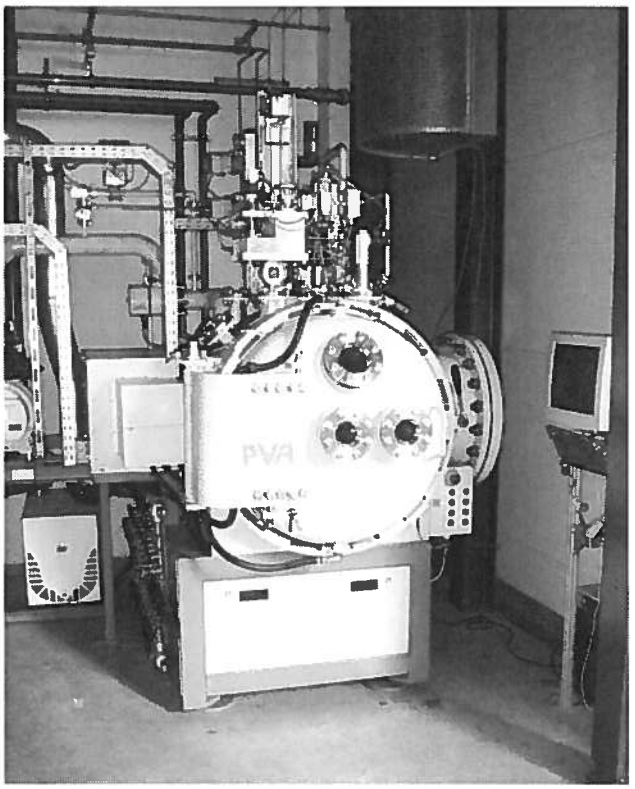

Figure 2. 10 bar crucible melt extraction facility.

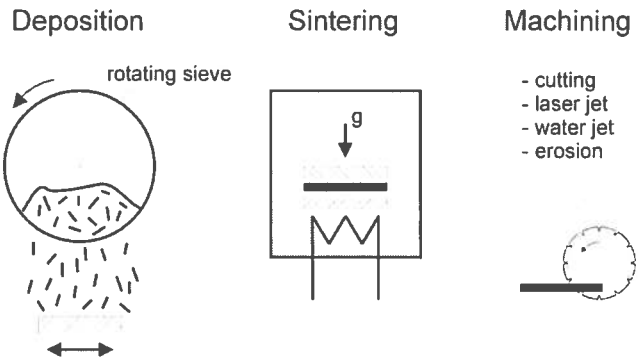

Figure 3. Manufacturing of sintered fibre structures.

a promising candidate for successful liquid phase sintering [2]. In order to find optimum sintering conditions for pre-alloyed fibres, thermodynamic calculations were carried out with the software package PANDAT at the Technical University of Clausthal, Germany [3, 4].

As a result of this work, a calculated partial phase diagram with constant content of Cu and increasing Zn content is presented in *Figure 4*. The first phase precipitating from the liquid is (Al) followed by θ-Al_2Cu. At temperatures above 350 °C the phase diagram does not change significantly with varying Zn content. Below 350 °C there are differences for low Zn contents, however, due to the rapid cooling during fibre manufacturing it can be assumed that a solid state reaction at lower temperatures is very unlikely. For that reason, these differences were not taken into consideration for further discussion.

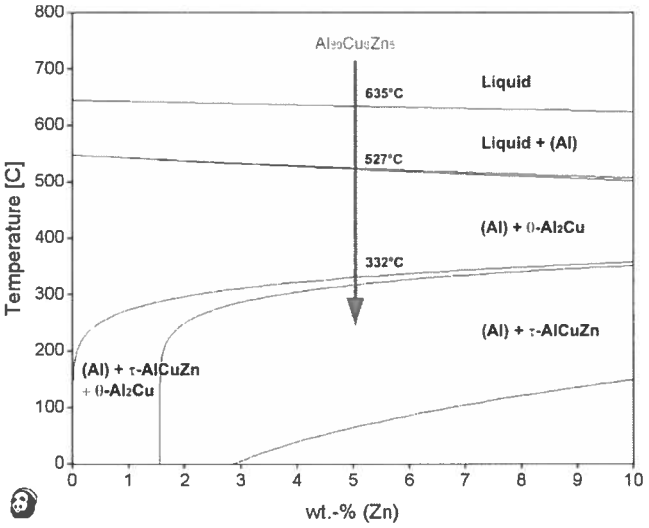

Figure 4. Calculated partial Al-Cu-Zn phase diagram for a constant content of 6 wt.-% Cu.

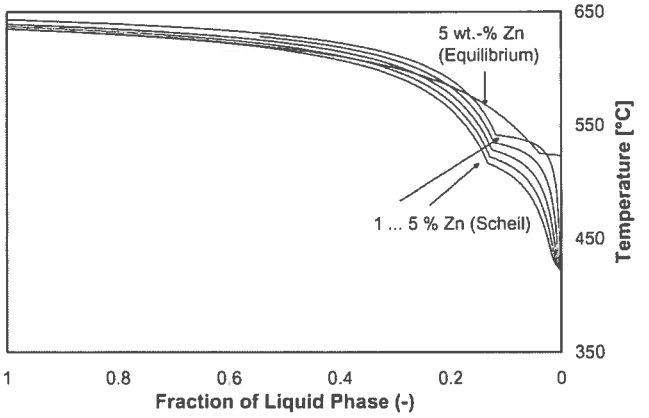

Figure 5. Solidification curves in dependence of Zn content and solidification model.

Calculations were also carried out for alloy compositions in the range of Al93-X Cu6 ZnX (X = 1 ... 5) based on solidification from the liquid state with blocked diffusion in the solid state (Scheil model). The results show significant differences with regard to the solidification temperatures and should yield a better representation of the conditions during sintering than the equilibrium calculations. *Figure 5* shows the results of these calculations.

Solidification temperatures decrease from 643 °C (1 wt.-% Zn) down to 635 °C (5 wt.-% Zn). The solidification is generally broader with higher content of Zn. The precipitation temperature of θ-Al_2Cu is also shifted to lower temperatures, which is clearly visible at the kinks of the curves in Figure 5. Differences between Scheil model and equilibrium are explained by the development of the liquid phase fraction and the resulting temperature of complete solidification. With the Scheil model, solidification in all alloys is finished at about 382 °C, whereas the equilibrium calculation for 5 wt.-% Zn predicts that the solidification is finished much earlier at 523 °C. The results are summarized in *Table 1*.

Table 1. Calculated amounts of liquid phase in dependence of zinc content and temperature.

Zinc Content	Solidification Model	Liquidus Temperature	Liquid Fraction		
			0.2	0.15	0.1
	(wt.-%)	(°C)	(°C)	(°C)	(°C)
1	Scheil	643	590	568	540
2	Scheil	641	584	559	532
3	Scheil	639	578	551	524
4	Scheil	637	571	543	516
5	Scheil	635	565	534	508
5	Equlibr.	635	584	572	555

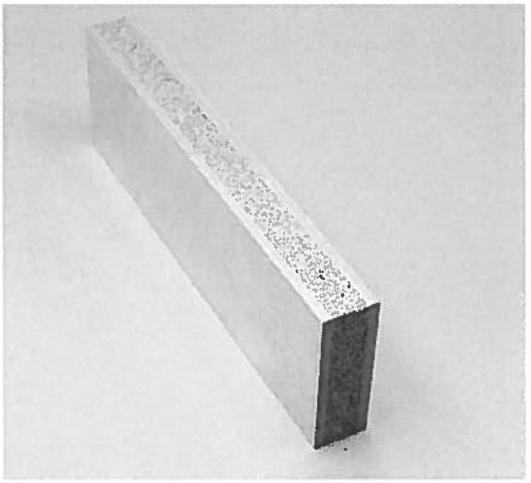

Figure 6. Sintered aluminum fibre core sandwich.

According to the calculations, an increasing content of Zn gives rise to higher amounts of liquid phase at lower temperatures. Additionally, the dependence of the amount of liquid phase on temperature is less pronounced. Hence, the alloy composition was chosen as Al89Cu6Zn5 for further experiments. In order to obtain a sufficiently high amount of liquid phase during sintering, the sintering temperature was set to 565 °C, corresponding to a calculated value of 20 % liquid phase for the given composition.

Melt extraction was then used to produce short Al89Cu6Zn5 fibres with a mean circular cross section equivalent diameter of 154 µm and a mean length of 9.5 mm. The fibres were deposited homogeneously onto an Al 99.9 cover sheet with thickness 2 mm via the rotating sieve drum technology. Another cover sheet was placed onto the fibre deposit and sintering was carried out at 565 °C. The resulting samples were cut to the desired dimension of 30 mm × 100 mm by wire-electro discharge machining, *Figure 6*. The thickness of the sintered fibre core was 7 mm.

The nature of the inter-fibre and cover plate-fibre bonds was investigated by metallography. *Figure 7* illustrates that there is an excellent metallurgical bond in all cases. The dark phase corresponds to the solidified liquid phase and consists mainly of Al_2Cu. Based on these promising results, a patent for such structures was filed [5].

Metallographic cross-sections of a large number (approx. 500) of fibres are used in order to determine the specific surface area

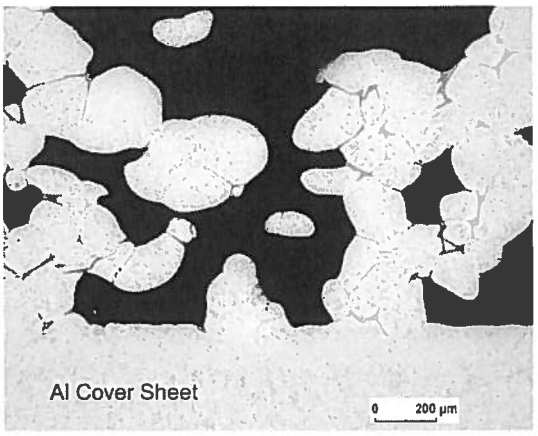

Figure 7. Cross-section of aluminium fibre core sandwich.

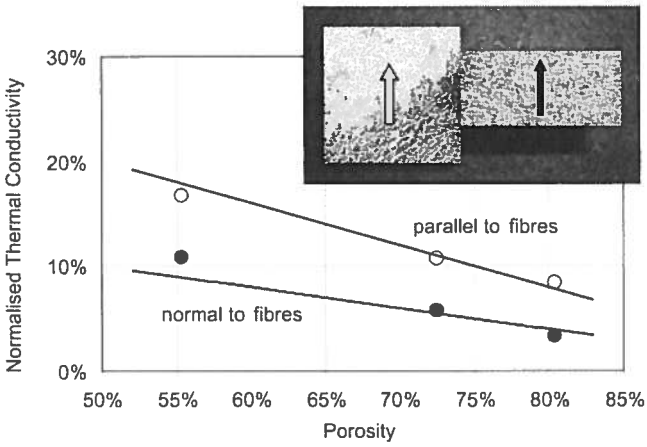

Figure 8. Normalised heat conductivity of aluminium fibre structures versus porosity.

of the fibres. Depending on such measurements, the volume specific area of sintered fibre structures can be calculated. Accordingly, their area density can be adjusted anywhere between 2,500 and 50,000 m^2/m^3 by changing the fibre diameter and the fibre core density.

3 Heat conductivity of sintered aluminium fibre structures

The heat conductivity of sintered fibre structures is usually characterised by a pronounced anisotropic behaviour. Comparison of the thermal conductivity parallel to the main fibre orientation with the corresponding value normal to that orientation yields a factor of two and higher. This strong anisotropy has to be considered when choosing a qualified measurement method for the effective heat conductivity. Among the different measurement techniques available at Fraunhofer IFAM Dresden, a simple steady-state plate method proved best for fibre structures.

In order to measure the heat conductivity, prismatic fibre samples were prepared with varying porosity and fibre orientation with respect to the measurement direction. During every test procedure, the sample is positioned together with a reference sample (stainless steel with known heat conductivity) between

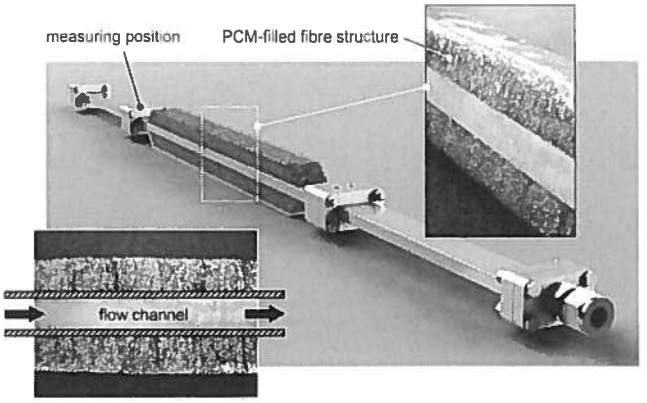

Figure 9. Prototype high-power latent heat storage device with connecting tubings.

an electric heater and a cooling plate. The resulting steady-state temperature differences at the fibre and reference sample surfaces are used to calculate the unknown effective heat conductivity of the fibre structure from Fourier's Law. In *Figure 8*, results of selected measurements are shown as normalised heat conductivity in dependence of the porosity of the structure. The normalised heat conductivity is the effective heat conductivity of the fibre structure in relation to the bulk material's heat conductivity which amounts to approx. 200 W/(mK).

The dependence of the heat conductivity on porosity is clearly visible as well as the difference between the conductivity parallel and normal to the main fibre orientation. The solid curves correspond to numerical approximations using a superposition approach of the thermal resistances (parallel and serial combination of metal and fluid conductivity).

4 Performance of lab-scale thermal energy storage device

Phase change materials (PCM) usually suffer from a very low heat conductivity of less than 1 W/(m K) which results in a very slow charging and discharging behaviour. Sintered aluminium fibre structures can be used to significantly enhance the performance of phase change heat storage devices by filling them with PCM and coupling them with the heat-carrying fluid. Calculations based on the measured heat conductivity showed that the kinetics of charging and discharging can be changed by more than one order of magnitude depending on the porosity of the fibre structure. This allows for very fast devices that can be cycled within minutes. A first lab-scale device was built and tests showed very good agreement with the theoretical predictions.

The demonstrator consisted of fibre structures of porosity 85 % which were furnace brazed onto a rectangular channel, *Figure 9*. Prior to brazing, the fibre structure was cut into small pieces and mounted such that the preferential orientation of the fibres was parallel to the heat in- and outflow. The fibre structure was subsequently infiltrated with liquid PCM (paraffin mixture RT65 supplied by Rubitherm GmbH, Berlin, melting temperature 65 °C) and sealed with a transparent hose. Thermo oil was run through the channel and the inlet and outlet temperatures

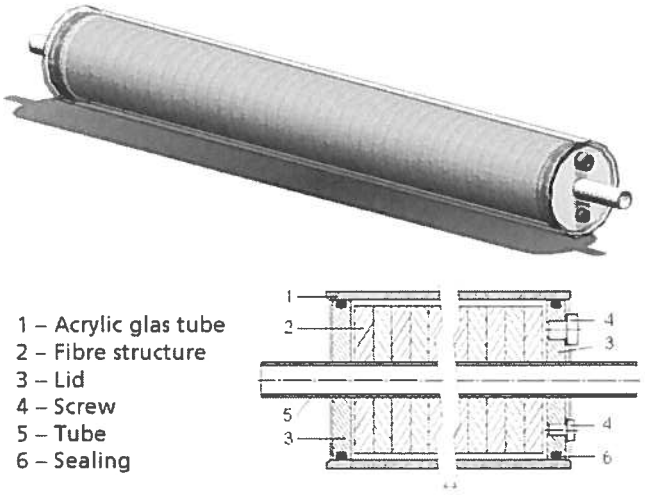

Figure 10. Technical drawing of basic latent heat storage module (Fraunhofer IFAM Dresden).

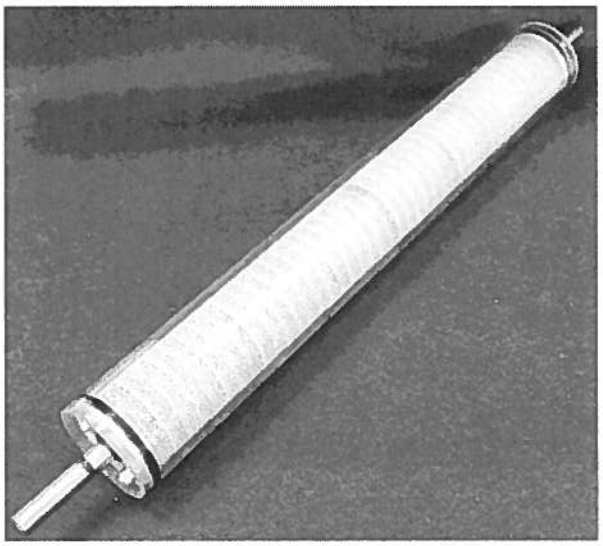

Figure 11. Fotograph of basic latent heat storage module prior to filling with phase change material (Fraunhofer IFAM Dresden).

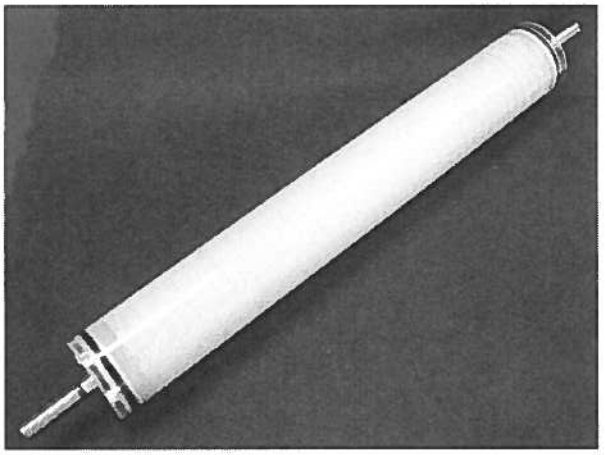

Figure 12. Fotograph of basic latent heat storage module after filling with phase change material (Fraunhofer IFAM Dresden).

were measured. An approximately constant fluid outlet temperature indicates the ongoing PCM phase transition and so the storage charging time can be detected by a simple temperature measurement.

Resulting from such measurements, the thermal power of the storage module was determined to 0.15 kW with a corresponding charging time of 3.5 minutes. In addition to the experimental investigations, analytical calculations were executed which allow the prediction of the time-dependent position of the phase boundary in a melting or freezing substance. The calculated heat flux for the present storage module using a composite of aluminium fibres and paraffin was 0.13 kW, corresponding to a charging time of 3.4 min, which is in excellent agreement with the measurement. The calculated charging time of a similar storage device with just pure paraffin and no added heat conductive fibre structure would amount to approximately 80 min. Therefore, it can be concluded that the implementation of the aluminium fibre structure enhances the thermal power output of the storage module by a factor of 22 with a capacity loss of only 15 % due to the metal fraction. This demonstrates that adding metal fibre structures to PCM is a powerful approach to tailor the thermal performance of latent heat storage devices with respect to variable boundary conditions.

5 Second-generation latent heat storage modules

In order to explore the full potential of sintered fibre-PCM compounds, a project was set up with partners from industry. One of the goals was to create basic latent heat storage modules which are easy to manufacture and can easily be combined into larger storage units. Basic considerations led to a design where sintered fibre discs are laser-cut from larger semi-finished aluminium fibre plates and stacked onto a tube. The final design is shown in *Figure 10*. Depending on the required heat conductivity, the fibre discs are either simply mechanically fixed or brazed onto the tubes. The net storage volume for the PCM amounts to roughly 0.9 l. *Figure 11* shows a basic storage unit prior to filling with the PCM, *Figure 12* after filling with mounted transparent housing. It turned out that 99 % of the theoretically available volume could be filled with liquid PCM, which demonstrates that solely open porosity is present in the sintered fibre structures. Extensive testing of such basic storage units is in progress.

6 Summary and outlook

It was demonstrated that aluminium fibre structures can be manufactured via liquid phase sintering, provided that the alloy composition and sintering conditions have been chosen carefully. Adding such metal fibre structures to PCM is a powerful approach to enhance and tailor the thermal performance of latent heat storage devices with respect to variable boundary conditions. Basic latent heat storage units can be manufactured in a cost-effective way and testing of such units is in progress.

Future work will concentrate on providing aluminium fibre structures made from aluminium silicon alloys. This system offers improved compatibility with commercially available brazes and will thus open up new opportunities with regard to the application of high-temperature phase change materials.

Acknowledgements

The authors would like to thank Carsten Liebert for the excellent work done on the construction and joining of the basic latent heat storage modules. We also gratefully acknowledge the financial support of the Fraunhofer Society for the initial development work on aluminium fibre structures (internal project THOKA) as well as that of the German Ministry for Research and Education (BMBF) in the "Innovative SME" programme (grant no. 01LY1019A). The latter is carried out in cooperation with WÄTAS GmbH and Rubitherm GmbH, both based in Germany.

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Received in final form: February 1st 2012 T 949

