



# Novel form-stable phase change material composite for high-efficiency room temperature control



Andrey A. Chernousov\*, Ben Y.B. Chan

The Hong Kong University of Science and Technology, Department of Civil and Environmental Engineering, Clear Water Bay Road, Hong Kong, Hong Kong SAR

## ARTICLE INFO

### Keywords:

Phase change composite  
Thermal energy storage  
Form-stability  
Energy efficiency  
Porous aluminium composite  
Smart buildings

## ABSTRACT

Phase change material (PCM) driven thermal energy storage (TES) systems are showing promise for cooling energy saving in residential and office buildings. State-of-the-art TES for interior items such as tiles and furnishings require the material matrix to transfer heat rapidly between the adjacent PCM and the indoors. TES developers offer a large number of PCM composites, in which, however, the high thermal conductivity counterbalances the PCM volume capacity and material form-stability above the PCM melting point. Herein, we report a novel aluminium matrix with open ultrathin (mainly, below 150 nm) pores and the developed surface area ( $\sim 7 \text{ m}^2 \text{ g}^{-1}$ ) that solves the dilemma. The porous (22–46 vol%) aluminium matrix results from the compacted aluminium nanoflakes reactively (1 min at 873K in  $\text{N}_2$ ) sintered with the aid of oxidation of the nanoflake protector, stearic acid. The preparation method leads to partial transformation of the pores and an increase of the specific surface area. In the PCM fraction range, the prepared composite has the thermal conductivity in the range of 10–60  $\text{W m}^{-1}\text{K}^{-1}$ . The effects of the PCM volume fraction on the thermal conductivity and specific heat capacity are described. As an example, we have considered an affordable organic PCM such as coconut oil that can readily cling to the  $\text{Al}_2\text{O}_3$ -filmed surface of the material pores through the hydroxyl functionalities. With the use of vacuum infiltration, heated (373 K) coconut oil deeply penetrates the matrix pores. The PCM composite has shown the excellent form stability in terms of the coconut oil mass loss (below 1.5 wt%) at an elevated temperature of 318 K for over 1000 h.

Applied internally, this kind of TES composite can rapidly and efficiently transfer a considerable amount of heat energy within a large building area and regulate the indoor temperature.

## 1. Introduction

Latent thermal energy storage (TES) facilities containing phase change material (PCM) have been the subject of much interest in dealing with cooling energy saving in modern residential and office buildings [1,2]. This interest is also boosted by the rapidly growing TES market, projected to reach USD 6.2 billion by 2022 [3].

The saving principle of TES facilities with PCM is that the indoor air temperature can be counterbalanced with the phase changes (melting or freezing) occurring in the TES active component, either absorbing or releasing excessive heat energy. Currently, the voluminous-sized TES tanks operate centrally as outdoor installations, while the newly developed TES composites have promise be fitted indoors, as smart interior tiling and furnishing, and automatically stabilise the changing room temperature. Such smart interior systems could provide high energy efficiency, basically governed by the thermal conductivity ( $k$ ,  $\text{W m}^{-1} \text{K}^{-1}$ ) and heat exchange area ( $A_p$ ,  $\text{m}^2 \text{g}^{-1}$ ) between the composite matrix and the PCM media.

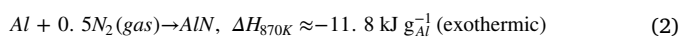
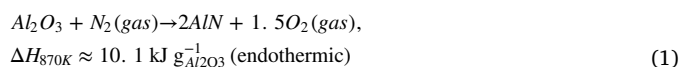
Commercial ceramic tiles are conductive (2–4  $\text{W m}^{-1} \text{K}^{-1}$ , [4]), but unsuited for TES due to low porosity, below 5% [5]. A higher PCM capacity ( $\approx 17 \text{ vol}\%$ ), as in porous porcelain ceramics, comes with even lower thermal conductivity ( $k \approx 1.2 \text{ W m}^{-1} \text{K}^{-1}$ ) where adverse epoxy lamination prevents PCM leakage through the relatively thick pores,  $t_p = 30\text{--}100 \mu\text{m}$  [6]. Because of the inadequate pore thickness, the PCM leakage problem is also of concern in the prospective TES matrixes, such as sintered copper microfibers ( $k \approx 53 \text{ W m}^{-1} \text{K}^{-1}$ , 50 vol% [7]), hot compacted carbon microfibers with Indium (5–40  $\text{W m}^{-1} \text{K}^{-1}$ , 21 vol% [8]) and traditional open-cell aluminium [9]. However, porous aluminium materials are more conductive ( $\approx 60 \text{ W m}^{-1}\text{K}^{-1}$ ) with a porosity of 50%, and are easily procurable at present [10]. An extensive review of advanced heat exchanger materials comparing the material density, strength, cost, thermal conductivity and machinability, recommended the use of aluminium, among the other conventional metals and ceramics [11]. Aluminium has an  $\text{Al}_2\text{O}_3$ -filmed surface that can readily incorporate and durably store a monolayer of saturated fatty acid [12–14] which is the basis of popular organic PCMs. This phenomenon

\* Corresponding author.

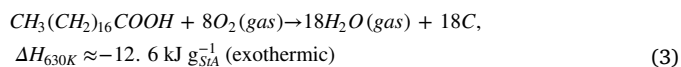
E-mail address: [chernous@ust.hk](mailto:chernous@ust.hk) (A.A. Chernousov).

adapted to the extremely thin pore channels ( $t_p < 1 \mu\text{m}$ ) in the aluminium matrix could mitigate or even avoid the PCM leakage issues.

Porous aluminium with passageways of 200–500 nm can be prepared by the novel and mass production approach, flake powder metallurgy, transforming aluminium nanoflakes into the bulk material [15,16]. The nanoflakes are prepared via ball milling of spherical Al microparticles ( $< 10 \mu\text{m}$ ) by using stearic acid ( $\sim 1 \text{ wt}\%$ ), which is then evaporated during annealing (1 h at 673 K in Ar). However, Zhang and co-workers have considered complete densification of the compacted flakes through energy-intensive sintering (2 h at 903 K in Ar) and extrusion (at 673 K in Ar) stages, resulting in a loss of the pores [15,16]. Partial bonding of the compacted nanoflakes in an industrial nitrogen atmosphere, however, could allow both the desired structure and affordable production of TES material. Furthermore, a nitrogen atmosphere is the only choice when sintering fine ( $\sim 1 \mu\text{m}$ ) aluminium particles covered with a relatively large amount of aluminium oxide [17–19]. For this purpose, the protective oxide film is usually reduced (Eq. (1)) by using additives such as Sn, Mg or Al itself, decreasing the oxygen pressure in the compact pores below a threshold level,  $p_{\text{O}_2}(\text{thr}) \sim 10^{-33}$  Pa at 870 K, to  $\sim 10^{-51}$  Pa at 870 K (see the thermodynamic calculation I. in the Supporting Information). It further leads to spontaneous nitriding (Eq. (2)) of the unshielded aluminium particles and the release of a great deal of heat, sufficient to sinter the particles.



However, the nitriding process is fleeting and destructive for the pore channels. That is why controllable partial bonding in the described conditions should be carried out within a short period of time. Moreover, the stearic acid (StA) covering the aluminium nanoflakes can be an efficient deoxidizer. StA distinctly ( $p_{\text{vap},630\text{K}} \approx 70 \text{ kPa}$ , [20]) evaporates above 630 K and its oxidation effect (Eq. (3)) can facilitate partial disruption of the native alumina skin and sintering of the nanoflakes upon reaching 870 K, when the heating rate is high enough.



In fact, StA oxidation can decrease the oxygen pressure to the range of  $10^{-49}$  to  $10^{-41}$  Pa (620–780 K, see the thermodynamic calculation II. in the Supporting Information), low enough to cause am- $\text{Al}_2\text{O}_3$  to undergo thermodynamical instability, leading to decomposition.

To the best of our knowledge, the sintering process and porosity control in such an Al nanoflake compact are unexplored, while the breakthrough method needs thorough study.

The porous aluminium matrix mainly addresses an organic class of PCM based on saturated fatty acids (SFAs) or their various compositions. In this connection, coconut oil (CtO) seems qualified (SFAs  $\approx 94\%$ ) to be reliably held by the Al matrix developed surface. On the other hand, the high cost of petroleum based PCMs makes coconut oil and its derivatives the only viable option for green building construction in developing tropical regions. As of now, such bio-based PCMs are already being encapsulated in highly porous silica [21], vermiculite [22], bentonite [23] and compacted nano graphite [24,25], as admixtures for energy saving concrete.

In this study, we attempted to describe the preparation and key characteristics of a novel aluminium composite matrix to broaden the existing list of TES materials.

## 2. Experimental section

### 2.1. Materials

The aluminium nanoflake powder (Sigma-Aldrich) was used in an

**Table 1**  
The chemical substance information of the CtO.

Component acid	Percentage	
	(wt%)	(vol%)
Caprylic (C8:0)	6.7	6.4
Capric (C10:0)	5.8	5.7
Lauric (C12:0)	50.8	50.9
Myristic (C14:0)	19.6	19.9
Palmitic (C16:0)	8.2	8.4
Stearic (C18:0)	2.7	2.6
Oleic (C18:1)	5.0	4.9
Linolenic (C18:2)	1.2	1.1

as-received form and without further purification. According to the manufacturer, it is relatively pure aluminium protected by a StA film ( $\approx 0.3 \text{ wt}\%$ ). The PCM was produced by the Peter Paul Philippine Corporation and contains about 94% of saturated fatty acids. Table 1 shows the CtO composition provided by the manufacturer. The density of the coconut oil was measured as the ratio of the mass to volume, resulting in a value of about  $0.904 \text{ g cm}^{-3}$ .

### 2.2. TES composite fabrication

Fig. 1 schematically represents the compaction, heat treatment and PCM infiltration processes, successively transforming the loose aluminium nanoflake powder into the compact, partially sintered matrix and PCM composite, respectively.

The cold isostatic pressing route was used to compress the aluminium powder into small scale (SS) and large scale (LS) cylindrical compacts of the respective diameters,  $\varnothing 12.7 \text{ mm}$  and  $\varnothing 28.8 \text{ mm}$ , and thicknesses, 2.9–3.2 mm and 5.6–8.8 mm. The powder compression was carried out in the pressure range from 60 to 310 MPa. The powder showed a good compactability above 60 MPa, avoiding disintegration of the compacts. The compacts were exposed to rapid ( $40 \text{ K min}^{-1}$ ) heating and annealing at about 873 K ( $\sim 0.9T_{\text{melt}}$ ) in industrial grade (99.95%,  $\sim 50 \text{ ppm H}_2\text{O}$ ,  $\sim 50 \text{ ppm O}_2$ ) flowing nitrogen. Further in the text and formulae, subscript 1 refers to the powder compacts (e.g. SS<sub>1</sub>, LS<sub>1</sub>  $\phi_{E1}$ ) and subscript 2 refers to the partially sintered compacts (e.g. SS<sub>2</sub>, LS<sub>2</sub>,  $\phi_{E2}$ ). Before heat treatment of the samples in large tube ( $\varnothing 70 \text{ mm}$ ) conditions (ROHT 75/300/18, Thermconcept Dr Fischer GmbH & Co), chemical interactions between the nanoflakes (loose or compacted form,  $\approx 8 \text{ mg}$ ) and the atmosphere were analysed using differential thermal analysis (DTA) (SETSYS-1750, Setaram Instrumentation). It enabled the annealing time to be optimised for achieving partial sintering in the powder compacts. Also, a K-type thermocouple was used to calibrate the heating zone temperature in the tube furnace. In the infiltration stage, we evacuated the annealed samples to an air pressure of 20 kPa, using the scheme detailed in [24]. The coconut oil infiltrate was heated up to 373 K to make it less viscous ( $\eta_{303\text{K}}/\eta_{373\text{K}} \approx 8$ , [26]). It respectively enhances the infiltration rate  $l^2/\tau$  of coconut oil penetrating under its own capillary pressure:  $l^2/\tau = t_p \gamma \cos \theta / 4\eta$  (Washburn's equation, [27]), where  $\tau$  is the time for a liquid of dynamic viscosity  $\eta$  and surface tension  $\gamma$  to penetrate a distance  $l$  in a  $t_p$  thick pore having a wetting angle  $\theta$  with the liquid. The infiltration time took 30 min, after which the removed specimens were cooled down to 298 K and the surface was cleaned of coconut oil.

### 2.3. Material structure characterization

The surface morphology and composition of the Al nanoflake powder was characterised by scanning electron microscopy (SEM) (JEOL 6700F) and transmission electron microscopy (TEM) (JEOL 2010). The Brunauer Emmett Teller (BET) method (SA 3100, Beckman Coulter), with the ten-point analysis, was used to determine

متن کامل مقاله

دریافت فوری ←

**ISI**Articles

مرجع مقالات تخصصی ایران

- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان دانلود رایگان ۲ صفحه اول هر مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات