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Full Length Article

Wettability of eutectic $NaLiCO_3$ salt on magnesium oxide substrates at 778 K

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ABSTRACT

We investigated the wetting behavior of a eutectic carbonate salt of $NaLiCO_3$ on MgO substrates at an elevated temperature of 778 K by measuring contact angle with a sessile drop method. Both sintered and non-sintered MgO were prepared and used as the substrates. The sintered substrates were obtained by sintering compacted MgO powders at 500–1300 °C. For comparison purposes, a single crystal MgO substrate was also used in the work. The different sintering temperatures provided MgO substrates with different structures, allowing their effects on salt penetration and hence wettability and surface energy to be investigated. A scanning electron microscope equipped with energy dispersive spectrometry and an atomic force microscope were used to observe the morphology and structures of the MgO substrates as well as the salt penetration. The results showed a good wettability of the carbonate salt on both the sintered and non-sintered MgO substrates and the wettability depended strongly on the structure of the substrates. The non-sintered MgO substrate has a loose surface particle packing with large pores and crevices, leading to significant salt infiltration, and the corresponding contact angle was measured to be ~25°. The contact angle of the salt on the sintered MgO substrates increased with an increase in the sintering temperature of the MgO substrate, and the contact angle of the salt on the single crystal substrate was the highest at ~40°. The effect of the sintering temperature for making the MgO substrate could be linked to the surface energy, and the linkage is validated by the AFM measurements of the adhesion forces of the MgO substrates.

1. Introduction

Surface wetting and its alternation play an important role in numerous industrial applications. One of such applications is related to the storage of thermal energy using composite phase change materials (CPCMs) [1–4], which have a wide range of applications including peak shaving of power grids, effective use of curtailed wind energy, solar thermal power generation, and space heating using distributed domestic storage heaters and centralized district heating networks, to name but a few. A CPCM often consists of a phase change material (PCM) and a shape stabilization material (SSM) [5,6]. A thermal conductivity enhancer (TCE) may also be needed in the formulation if heat transfer becomes a constraint [5–7]. Such materials can be fabricated by using the following three methods: (a) physical mixing of milled PCM, SSM and TCE, followed by shaping and finally sintering; (b) physical mixing of milled SSM and TCE, then shaping and sintering, followed by vacuum infiltration of PCM at liquid state; (c) shaping and sintering SSM, followed by vacuum infiltration of liquid PCM containing TCE [8–10]. In all these methods, the wettability of liquid PCM on both SSM and TCE at elevated temperatures can play a very important role in the determination of structure, density, mechanical properties, and thermal properties of the composites. However, little has been found in the literature on this area, which forms the major motivation for this work.

Numerous PCMs exist, which can be divided into two categories of organic and inorganic materials. Examples include fatty acids and paraffin waxes, which are organic and mainly for low temperature applications, and carbonate, nitrate and sulphate salts, which are inorganic and mainly for medium to high temperature applications [5,9]. There are many materials that could be used as SSMs, including diatomite, magnesium oxide, expanded graphite and silicates, to name but a few [11,12]. This work focuses on the use of MgO as SSM and eutectic $NaLiCO_3$ salt as PCM for the composite.

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The rationales behind the choice lie in the high surface energy of MgO towards the carbonate salt and high energy density of the PCM. The main objective is to investigate the wettability of the eutectic carbonate salt of $NaLiCO_3$ on MgO substrates through the measurements of contact angle. The influences of two factors on the contact angle were studied: (a) penetration of carbonate salt into MgO substrate, which may change the contact angle dynamically, and (b) surface tension changes due to different fabrication temperatures of the substrates, for which little information can be found in the literature. Scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS) and atomic force microscopy (AFM) were used in the study.

2. Experimental method

2.1. Preparation of eutectic carbonate salt samples and MgO substrates

The salt samples used in this study were made with eutectic carbonate salt ($NaLiCO_3$), which were in a cylindrical (rod) shape and had a mass of approximately 50 mg. The eutectic carbonate salt contained 50 wt% Li_2CO_3 and 50 wt% Na_2CO_3. The samples were made by thoroughly mixing the two salts followed by shaping in a cylindrical mould with a diameter of 4 mm. MgO substrates used were either a sintered or a non-sintered cylindrical plate with 13 mm diameter and 4 mm thickness. The sintered MgO plates were sintered at different temperature from 500 °C to 1300 °C to examine the effect of salt infiltration into MgO substrates (substrates sintered at different temperatures give different porosities). For comparison purpose, a 10 mm × 10 mm single crystal MgO (100) plate (Sigma-Aldrich Co. LLC, UK) was purchased, which had a purity of 99.9% and a relative density over 96%. Such a single crystal MgO plate could be made by sintering at ~3000 °C. One flat surfaces of the plates was polished to give a mirror finish using various grades of SiC abrasive papers and three grades of diamond pastes (with particle diameters of 6, 3 and 1 μm) to an average surface roughness of 400–500 nm as measured by a surface profilometer (KLA Tencor MicroXAM 2, USA) over a length of 150 μm at a speed of 20 μm/s. The substrates were carefully cleaned in acetone using an ultrasonic machine before wettability experiments.

2.2. Experimental apparatus and measurement methods

A high temperature drop shape analyzer (Krüss, DSAHT17-2, Germany) was used to investigate the wetting behavior of eutectic carbonate salt on MgO substrates. The device is based on the sessile drop method; see Fig. 1 for a schematic illustration and an image of the experimental apparatus.

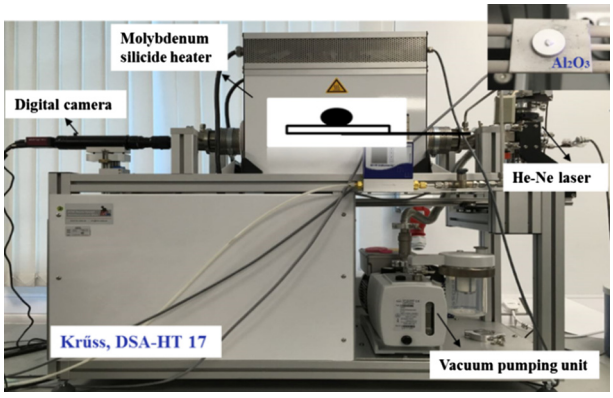

Fig. 1. A schematic illustration and a photograph of the sessile drop test apparatus.

The analyzer consists of a molybdenum reflector installed in a sealed chamber, a molybdenum silicide heater, an aluminum oxide supporting tube and a sample holding platform. It uses a type B thermocouple to measure, monitor and control the temperature through a programmable controller. There is a vacuum pumping unit with a rotary pump and a turbo molecular pump to control the pressure and atmosphere of the sealed chamber. The analyzer is equipped with a high-resolution digital camera providing an angular resolution of 0.1 degree and installed with an analysis software package.

A scanning electron microscope (SEM) with EDS (TM3030, HITACHI, Japan) was used for microstructural observations of the interface between the salt and the substrate. The surface morphology and roughness of the substrates were observed with an atomic force microscope (AFM, NanoWizard III NanoScience, Germany). In a typical experiment, a cylindrical sample was placed on an MgO substrate. The sample-substrate set was then carefully transferred to the holding platform, which upon adjusted to give a horizontal orientation before inserted into the center of the chamber. The chamber was then sealed followed by purging the chamber with a high purity nitrogen stream while being heated up to a pre-set temperature (505 °C, 778 K in this work) at a heating rate of 10 K/min. When the sample reached the measurement temperature, the N_2 gas flow was cut off and the digital camera was started to capture the image of the salt sample. The drop analysis software was then used to obtain the contact angle, the sample height and the contact diameter. Each experiment was repeated at least twice to study the repeatability. At end of experiments, the chamber was cooled down and the sample was then taken out for further analyses using the SEM-EDS and AFM.

3. Results and discussion

3.1. Surface roughness of substrates

It is well known that, for a given substrate material and a liquid, the wettability of the liquid on the surface is affected by surface roughness. Wenzel [13,14] studied such an effect and obtained the following relationship:

$$\cos\theta_R = A_R \cos\theta_i \quad (1)$$

where θ_R and θ_i represent respectively the contact angle on rough and smooth surfaces; and the A_R is the ratio of the true area of the rough surface to that of the smooth surface. The Wenzel model indicates that the contact angle of a liquid on a rough surface scales linearly to the surface ratio. Fig. 2 shows the AFM images of different MgO substrates (polished) from which the 3D surface roughness parameters can be calculated and the data are listed in Table 1.

The roughness parameters shown in Table 1 are the average roughness (R_a), the root-mean-square roughness (R_q), the valley depth or maximum height (R_z), the core roughness depth (R_k), and the kurtosis of the roughness (R_{ku}). One can see that all the polished MgO substrates have an average surface roughness of 430–510 nm (first row of Table 1) and therefore the surface roughness is excluded as a variable in the subsequent analyses and discussion.

3.2. Contact angle and drop dimension measurements

Fig. 3 shows the time evolution of the contact angle (θ) and the droplet diameter (D) and height (H) of the eutectic carbonate salt on the non-sintered MgO substrate at a measurement temperature of 505 °C (778 K). It can be seen that the contact angle and drop dimension change with time, and the change can be divided into three stages: an initial stage (a), a spreading stage (b), and a steady state stage (c). The initial stage could be regarded as the equilibrium stage since the contact angel and the droplet dimension are