



High temperature thermal storage materials with high energy density and conductivity



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ABSTRACT

A metastable miscibility gap in the C–Al binary phase diagram has been exploited to produce macroscopically solid phase-change enhanced thermal energy storage materials. With 50% by volume of Al or Al–12.7%Si dispersed in a graphite matrix, the materials have thermal conductivity of ~150 W/m K, energy densities of 0.9 and 1.1 MJ/L for $\Delta T = 100$ °C and energy storage/delivery temperatures centred around 660 °C and 577 °C respectively. These characteristics are matched to both direct-steam and fluid-mediated concentrated solar thermal power systems using conventional Rankine cycle steam turbine-generator technology. Powder metallurgy processing combined with a low-temperature binder ensures a non-percolating inverse microstructure in which the phase change Al or Al–Si particles are securely encapsulated, thereby overcoming the usual containment problems associated with metallic phase change materials. The graphite and binder system used have been shown to be stable upon short-term thermal cycling or holding at the maximum expected operating temperature.

1. Introduction

The majority of energy consumed in modern societies is heat-based. Nearly half is utilised as thermal energy (heating, cooking and high temperature industrial processing); and most of the remainder passes through a thermal energy stage on its way to the consumer (fossil fuel electricity generation, transportation etc.). The management of thermal energy resources and the development of thermal energy storage (TES) is therefore of paramount importance in developing sustainable energy systems. Stored heat may be used for: space heating; as an off-peak load for conventional electricity generation; to provide a power block with a steady operating point (e.g. to fix a turbine inlet temperature in a Steam Rankine Cycle); for load levelling using industrial or commercial waste heat; and time-shifting of retail solar PV electrical energy. In addition to these small-medium scale applications, thermal storage is of paramount importance in the growing Concentrated Solar Thermal (CST) electricity generation industry (Pelay et al., 2017).

Materials for TES applications have been widely reviewed (Kenisarin, 2010; Laing et al., 2012; Rathod and Bannerjee, 2013; Tian and Zhao, 2013; Kuravi et al., 2013; Khan et al., 2016; Alva et al., 2017). Most of the materials studied suffer from one or more of: relatively low and variable operating temperature; very low thermal conductivity; and modest energy density. Phase change materials (PCM)

offer high energy density and a variety of operating temperatures, however the most commonly studied are still hampered by low thermal conductivity (Khan et al., 2016). This causes the melting and freezing processes to proceed at very low rates making the availability of the stored energy low. Consequently, there has been increased interest in metallic PCM due to their improved thermal conductivity. The major drawback of metallic PCM are their tendency to react with their containment vessel and the associated health risk of large quantities of molten metal escaping.

A new class of thermal energy storage material based on Miscibility Gap Alloys (MGA) was recently introduced by Sugo et al. (2013) and Kisi et al. (2013). These new materials do not require elaborate and costly heat transfer infrastructure, pumping, parasitic heating losses, conductivity enhancement or other secondary infrastructure. Instead, MGA combine the very high thermal conductivity of metals with the advantages of phase-change materials within an outwardly solid form. Miscibility gap thermal energy storage alloys are two-phase combinations. One phase is a highly thermally conductive, thermodynamically stable matrix, usually a metal or semi-metal. The matrix encapsulates a high volume fraction of a lower melting temperature phase (also usually a metal) in a finely distributed non-percolating microstructure.¹ Once this microstructure is established, energy is stored in the MGA as both the latent heat of melting of the encapsulated phase and sensible

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¹ Percolation in this case refers to a continuous path of connected lower melting temperature particles which would allow them to drain from the storage material at high temperature.

heat in the whole alloy. Many potential systems² have been identified with phase change temperatures ranging from 150 °C to 1410 °C. Of particular interest are systems, which have operating temperatures in the range 400–750 °C and can therefore be matched to solar concentrators and conventional steam turbine electricity generation within the concentrated solar power industry (CSP). The ability to store thermal energy in this manner has multiple advantages including a narrower band of operating temperature (say ± 50 °C) around the melting temperature of the active phase. This is valuable for controlling steam quality and maintaining turbine efficiency.

Macroscopically, at all stages of operation, an MGA TES material remains solid – only the encapsulated particles melt and solidify during thermal cycling. At the desired operating temperature, the two phases within an MGA are required to be immiscible and to not react to form compounds so that the microstructure, once formed, does not degrade over time or with thermal cycling. As the desired microstructure is the inverse of that which naturally forms if immiscible metals are solidified from the fully liquid state, powder metallurgy techniques are utilized to manufacture MGA storage materials (Sugo et al., 2013).

Early studies of MGA focused on model systems such as Al-Sn and Fe-Cu for experimental convenience, (Sugo et al., 2013) however these are rather costly. Later work has been directed at systems such as C-Zn, Fe-Mg, C-Mg and C-Cu (Reed et al., 2017) that are not only cheaper, but also provide substantial energy density. The introduction of graphitic carbon as a matrix phase has certain advantages. Graphite can be considered as a 2-dimensional metal with exceptional thermal (and electrical) conductivity within the basal plane of the crystals (up to 2000 W/m K) and rather poorer conduction in the transverse direction (< 10 W/m K). The macroscopic average thermal conduction depends on the manufacturing method used however it is typically in the range 80–200 W/m K and therefore rather well suited to MGA fabrication. Commercial graphite is produced by mixing graphite or other carbonaceous powder with a tar pitch binder, initial firing at 1200 °C and then sintering at very high temperatures (2000–3000 °C). This is an unsuitable procedure for MGA production due to the effect of these extreme temperatures on the embedded metal particles. Instead, a low temperature binder based on sodium silicate has been developed and its optimization and characteristics continues to be explored in more depth (Copus et al., 2017). The binder has been successfully tested on the C-Zn system which has an operating range centred around the melting temperature of zinc, 420 °C. Although the C-Zn system has a relatively high energy density, it has a moderate operating temperature range and higher temperature systems are sought for application as the primary storage in high temperature steam turbine-generator based CSP plants such as power towers.

Two systems, C-Al and C-(Al,Si), were selected for investigation due to their very high energy density (Table 1) resulting from the large latent heat of fusion of Al and Si as well as the favourable melting temperatures of Al (660 °C) and Al-12.7 wt% Si (577 °C). Energy density in the table is given as the heat of fusion added to the sensible heat for $\Delta T = \pm 50$ °C around the melting temperature of the fusible phase although the total energy content is much higher. Unlike typical MGA systems, the C-Al system does not have a classic miscibility gap in the binary phase diagram (Massalski et al., 1990). Instead, there is an equilibrium carbide phase, Al_4C_3 , and only a metastable miscibility gap before equilibrium is established. The carbide is undesirable as a constituent of an MGA as it locks the Al into a very high melting temperature compound instead of allowing it to melt at the desired operating temperature, 660 °C. There are very few studies of the kinetics of Al_4C_3 formation and none were found describing the direct reaction of pressed powders in the C-Al system. Sharifi et al. (2012), describes the formation of Al- Al_4C_3 composites after prolonged high-energy milling of Al and C starting powders. Milling was conducted in a planetary mill

Table 1
Calculated thermal properties of candidate MGA thermal storage media for $\Delta T = 100$ °C.

System	Phase change (°C)	Heat of fusion (kJ/L)	Energy density ^a (MJ/L)	Thermal conductivity ^b (W/mK)
C-Zn	420	843	0.62	100
C-Al	660	1071	0.9	158
C-(Al-Si)	577	1516	1.1	158
Molten salt ^c	N/A	N/A	0.27	< 0.7

^a Energy density here includes ± 50 °C of sensible heat around the phase change temperature and ΔT of 100 °C for the molten salt.

^b Thermal conductivity was calculated using the Lattice Monte Carlo technique (Rawson et al.).

^c Sodium Nitrate (60%) and Potassium Nitrate (40%), ($NaNO_3 - KNO_3$).

under an argon atmosphere with 5 steel balls (20 mm) in a chromium steel vial (150 mm). Milling alone for up to 60 h did not form Al_4C_3 however the carbide did form when samples milled for 60 h were annealed at 500 °C and above for 1 h. This was no doubt influenced by the well-known effect of high energy milling on the rates of solid state reactions. Etter et al. (2007) investigated the infiltration of Al-Si alloy into porous graphite and found that Al_4C_3 was present if the infiltration was conducted at 750 °C whereas it was absent in eutectic (12.7 wt% Si) samples infiltrated and held at 670 °C. Lee et al. (1998) predicted on theoretical grounds that the addition of Si to the C-Al system can suppress carbide formation. Their theoretical and experimental results show that there is a threshold temperature, 620 °C, above which the concentration of Si to suppress carbide formation increases sharply from around 1% to 7%. Taking these previous results into consideration, it was considered that the C-Al and C-(Al,Si) systems may be strong candidates for high energy density, high conductivity thermal storage materials. This paper concerns the synthesis, characterisation and short term performance of these two prospective MGA systems.

2. Methodology

Samples weighing 10 g were manufactured from graphite powder (< 45 μm , Alloys International), Al powder (< 75 μm , Alloys International) and Al-12.7 wt% Si powder (< 90 μm , Oerlikon Metco). Powders were prepared at 50 vol.% (46 wt% Al) by hand mixing with 20 vol% of a solution of 2 wt% $NaSiO_4$ in distilled water. This was followed by cold uniaxial pressing at 175 MPa in a 19 mm diameter die to form green pellets which were approximately 10 mm in height, followed by binder dry-out at 80 °C for 48 h in an air-oven. Sample mass was recorded after 24 h and 48 h respectively and as these were the same, it was assumed that drying was complete. Sintering was conducted on the Al-foil wrapped samples in an argon atmosphere by heating at 5 °C/min to 700 °C (C-Al) or 650 °C (C-Al-Si) and holding for 1 h.

It was of interest to demonstrate, using thermal analysis, that the melting transitions are uncompromised by inclusion within the graphite matrix. Standard Differential Scanning Calorimeters (DSC) cannot be used to study MGA materials as the amount of sample is too small to give representative results (not much larger than one Al particle). To obtain the correct average response would require a DSC able to accommodate 10 g samples and no such instrument was available. Instead, Differential Thermal Analysis (DTA) was undertaken upon both the C-Al and C-Al-Si systems in order to understand their thermal behavior when heated to the desired operating temperature. This provided direct confirmation of PCM behavior when the encapsulated materials transitions from solid to liquid. On a standard DTA instrument the typically 50–100 mg sample size is not suitable when studying MGA as this would not provide a correct average response from the heterogeneous MGA microstructure; much larger samples are required. Therefore a purpose built DTA was constructed within which whole

² Excluding rare, expensive, radioactive or toxic metals.

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