Acta Materialia 107 (2016) 254–260

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Energy storage materials with oxide-encapsulated inclusions of low melting metal

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ARTICLE INFO

Article history:
Received 11 July 2015
Received in revised form
26 January 2016
Accepted 31 January 2016
Available online xxx

Keywords:
Metal composite
High thermal conductivity
Phase change materials

ABSTRACT

A composite energy storage material (ESM) with inclusions of a low-melting point metal encapsulated in protective metal oxide shells is prepared and characterized. ESM precursor is a metal matrix composite with metal oxide inclusions. Controlled redox reaction between the matrix and inclusions yields a composite with inclusions of an oxide encapsulated, easy to melt metal. Al/Bi_2O_3 nanocomposite thermites served as precursors for ESM with Al matrix and Bi inclusions encapsulated with Al_2O_3. Thermal and mechanical properties of the ESM were compared to those of reference binary Al/Bi and ternary Al/Bi/Al_2O_3 materials. The material containing encapsulated Bi inclusions stored energy by melting and solidifying Bi inclusions repeatedly. The inclusions did not drift upon heating; composite structure remained largely intact upon thermal cycling. Conversely, the structure of reference materials with similar compositions but without encapsulated Bi inclusions was not preserved upon thermal cycling. Molten Bi tended to separate from Al and form coarse network of inclusions. Upon cycling, Bi accumulated on surface of the material. Difference in mobility between encapsulated and non-encapsulated Bi inclusions caused differences in the mechanical properties of the composites. Materials with encapsulated Bi inclusions were much stronger and capable of retaining their structure and strength despite thermal cycling.

1. Introduction

Metal based energy storage materials (ESM) have advantages of high thermal conductivity, potentially high strength, and others [1]. The main issue is that the metal that melts upon heating (and thus serves as an energy storage medium) needs to be contained in order for the material to be used in repetitive heating cycles. Containment of liquid metals is difficult; often bulk containers are used [2], which limit significantly the types of structures that can be manufactured using the ESM. Using couples of metals that do not form intermetallics, such as Ag/Bi was reported recently [3]; however, such systems are limited and even if no intermetallics are formed, inclusions of an easily melting metal (Bi) are expected to migrate and coalesce after thermal cycling.

Composite materials can be readily prepared, in which a low-melting point metal is dispersed in a metal or ceramic matrix with a higher melting point. However, without encapsulation of the low-melting point metal inclusions, the material becomes structurally weak when the low-melting metal is liquid, and therefore deteriorates rapidly. Repeated heating may additionally cause formation of alloys and other compounds, altering the melting point of inclusions and thus affecting their energy storage capacity. Further, repeated melting may cause redistribution of non-encapsulated material within the structure, causing loss of uniformity. Finally, the strength of the composite material containing low-melting point inclusions would be reduced dramatically when the inclusions melt. The above negative effects can be circumvented if inclusions of the low-melting point material are encapsulated in a matrix that is thermally stable and mechanically sound.

In the structures described here, the energy storing medium (an easy to melt metal or alloy) is enclosed in nano-scale inclusions or layers surrounded by protective metal oxide. Such structures are stable in time and are not destroyed by repeated melting and solidification of the encapsulated inclusions.

2. Technical approach

The ESM is made using a precursor material, a nanocomposite

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http://dx.doi.org/10.1016/j.actamat.2016.01.074
1359-6454/

thermite powder prepared by arrested reactive milling [4]. Alternatively, it may be a nanocomposite layered structure prepared by vacuum deposition. The preparation of the energy storage material by milling and its structure are illustrated schematically in Fig. 1. Starting materials for the milling are regular powders, one of which is a metal, such as aluminum, and another is a readily reducible metal oxide. For ESM, the reduced oxide should yield an easily melting metal; examples include oxides of bismuth, indium, tin, and others. After milling, a fully dense composite is prepared with the metal matrix and oxide inclusions. Typically, the dimensions of inclusions are close to 100 nm [5]. Using a highly heat conductive aluminum as the metal matrix ensures the capability to reduce nearly all metal oxides. Other metal fuels that can be used with many oxides include magnesium, zirconium, and titanium. Different metal/oxide combinations can be used to prepare the ESM capable of storing energy at different temperatures and having tunable thermal conductivity and heat capacity.

To prepare the energy storage material, the nanocomposite material prepared by milling is heated up slowly so that the redox reaction between the metal matrix and oxide inclusions occurs. The heating should be well controlled so that the reaction occurs heterogeneously and the structure of the composite material is retained. For example, maintaining the temperature below the melting point of the metal matrix will help stabilize the structure. As a result of the redox reaction, each oxide inclusion is reduced to its respective metal surrounded by a layer of the product oxide. For the example of aluminum matrix and bismuth oxide inclusions, the product will be bismuth metal inclusions encapsulated in aluminum oxide. The encapsulated bismuth inclusions will be inside a metal matrix for fuel rich compositions. For compositions close to stoichiometry, the matrix will be primarily made of the formed oxide. For tin oxide inclusions in aluminum matrix, the product will be tin inclusions encapsulated in aluminum oxide. Once produced, such encapsulated metal inclusions can be heated above the melting point of the encapsulated metal, e.g., Bi. The metal will remain within the protective oxide shell (e.g., Al_2O_3 shell) and will be capable of melting and solidifying repeatedly, without changing the overall material structure or morphology. The continuity and structure of the matrix will be unaffected by melting of encapsulated inclusions. Thus, the desired energy storage material is produced.

Properties of the nanocomposite energy storage material derived from energetic nanocomposites can be adjusted by changing the original metal/oxide ratio: compositions closer to the stoichiometry of the redox reaction will produce more metal (e.g. Bi), as well as more product oxide (e.g. alumina). The resulting energy storage material has therefore a higher energy storage capacity, and it is mechanically stronger. Its bulk thermal conductivity will be lower, however. More metal-rich energetic composites will result in energy storage materials with less product metal (lower energy storage capacity), less product oxide (lower mechanical strength), and more residual metal (higher thermal conductivity). This gives the opportunity to tailor the material to specific applications.

3. Experimental and instrumentation techniques

3.1. Material synthesis

Bismuth inclusions serve as melting energy-storing medium in the materials described here. Selecting bismuth is justified by earlier studies of ESM [3,6]. Starting materials used to prepare fuel rich Al/Bi_2O_3 nanocomposite were elemental aluminum powder, −325 mesh (<45 μm), 99.5% pure, from Atlantic Equipment Engineers and fine powder of bismuth oxide, 99% pure, from Skylighter, Inc. The powders were mixed to produce two different compositions, with 6 and 12 mol of Al per mole of Bi_2O_3, designated respectively as $6Al/Bi_2O_3$ and $12Al/Bi_2O_3$. The blended powders were ball-milled under inert argon gas environment using a shaker mill (SPEX Certiprep, 8000 series) with two 50 mL flat-ended steel vials cooled by room-temperature air jets. Case-hardened carbon steel balls 3/8″-diameter, were used as a milling media. Ball to powder mass ratio (BPR) was fixed at 10. During milling, 3 mL of hexane was used as the process control agent (PCA). Milling time was set to 45 min.

Nanocomposite powders, consisting of fully dense individual particles obtained by ball milling [7,8], were used to prepare two types of ESM samples. For thermal analysis, the powders were pressed into 1/8-inch diameter pellets with a uniaxial die at a force of 1000 lbs using a Carver automatic pellet press in room air. Although not quantified, pervious experience shows negligible amount of air may have been trapped inside during pelletizing at these conditions [9]. The pellets were heated in a furnace of a thermal analyzer (Netzsch STA409 PG) in argon to obtain bismuth inclusions encapsulated in aluminum oxide. The pellets were heated to 550 °C and 300 °C and were held at the maximum temperature for 6 and 64 h, respectively. For mechanical testing, ¼-inch pellets were prepared using the same pellet press and annealed at 300 °C for 5 days using an Omegalux LMF-3550 box furnace under inert argon gas environment. Any air trapped within

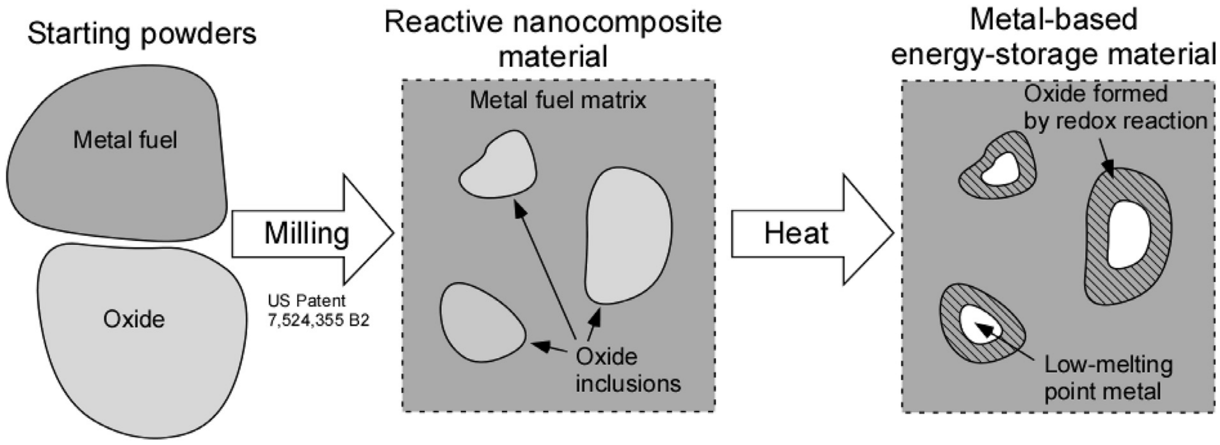

Fig. 1. Schematic diagram showing preparation of the metal-based energy storage material and its structure.