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

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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/Bi₂O₃ nanocomposite thermites served as precursors for ESM with Al matrix and Bi inclusions encapsulated with Al₂O₃. Thermal and mechanical properties of the ESM were compared to those of reference binary Al/Bi and ternary Al/Bi/Al₂O₃ 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.

Keywords: metal composite; high thermal conductivity; phase change materials

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

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4 structures are stable in time and are not destroyed by repeated melting and solidification of the
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6 encapsulated inclusions.
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9 10 **2. Technical Approach**

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13 The ESM is made using a precursor material, a nanocomposite thermite powder prepared by
14 arrested reactive milling [4]. Alternatively, it may be a nanocomposite layered structure
15 prepared by vacuum deposition. The preparation of the energy storage material by milling and
16 its structure are illustrated schematically in Fig. 1. Starting materials for the milling are regular
17 powders, one of which is a metal, such as aluminum, and another is a readily reducible metal
18 oxide. For ESM, the reduced oxide should yield an easily melting metal; examples include
19 oxides of bismuth, indium, tin, and others. After milling, a fully dense composite is prepared
20 with the metal matrix and oxide inclusions. Typically, the dimensions of inclusions are close to
21 100 nm [5]. Using a highly heat conductive aluminum as the metal matrix ensures the capability
22 to reduce nearly all metal oxides. Other metal fuels that can be used with many oxides include
23 magnesium, zirconium, and titanium. Different metal/oxide combinations can be used to prepare
24 the ESM capable of storing energy at different temperatures and having tunable thermal
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45 To prepare the energy storage material, the nanocomposite material prepared by milling is heated
46 up slowly so that the redox reaction between the metal matrix and oxide inclusions occurs. The
47 heating should be well controlled so that the reaction occurs heterogeneously and the structure of
48 the composite material is retained. For example, maintaining the temperature below the melting
49 point of the metal matrix will help stabilize the structure. As a result of the redox reaction, each
50 oxide inclusion is reduced to its respective metal surrounded by a layer of the product oxide. For
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4 the example of aluminum matrix and bismuth oxide inclusions, the product will be bismuth
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6 metal inclusions encapsulated in aluminum oxide. The encapsulated bismuth inclusions will be
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8 inside a metal matrix for fuel rich compositions. For compositions close to stoichiometry, the
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10 matrix will be primarily made of the formed oxide. For tin oxide inclusions in aluminum matrix,
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12 the product will be tin inclusions encapsulated in aluminum oxide. Once produced, such
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14 encapsulated metal inclusions can be heated above the melting point of the encapsulated metal,
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16 e.g., Bi. The metal will remain within the protective oxide shell (e.g., Al_2O_3 shell) and will be
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18 capable of melting and solidifying repeatedly, without changing the overall material structure or
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20 morphology. The continuity and structure of the matrix will be unaffected by melting of
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22 encapsulated inclusions. Thus, the desired energy storage material is produced.
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29 Properties of the nanocomposite energy storage material derived from energetic nanocomposites
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31 can be adjusted by changing the original metal/oxide ratio: compositions closer to the
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33 stoichiometry of the redox reaction will produce more metal (e.g. Bi), as well as more product
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35 oxide (e.g. alumina). The resulting energy storage material has therefore a higher energy storage
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37 capacity, and it is mechanically stronger. Its bulk thermal conductivity will be lower, however.
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39 More metal-rich energetic composites will result in energy storage materials with less product
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41 metal (lower energy storage capacity), less product oxide (lower mechanical strength), and more
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43 residual metal (higher thermal conductivity). This gives the opportunity to tailor the material to
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45 specific applications.
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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/Bi₂O₃ 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 moles of Al per mole of Bi₂O₃, designated respectively as 6Al/Bi₂O₃ and 12Al/Bi₂O₃.

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, previous 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 hrs, respectively. For mechanical testing, 1/8-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 the pellet at the particle-particle interfaces, may react with the Al-rich surface of the particle to form Al_2O_3 during annealing under inert argon gas environment. However, this should only add additional barrier to prevent molten Bi migration and should not be in contact with the reduced Bi during the redox reaction, which occur inside the particle. From previous experience [9], pelletizing conditions described above, may only lead to 10 to 20% of porosity, which should not cause any differences to the finally formed ESM structure. For comparison, two additional composites were prepared. One reference material was used to observe the effect of encapsulation of Bi inclusions on its re-melting as a result of cycled heating. It consisted of a binary composite of Al and Bi with 6.5 moles of Al per mole of Bi: 6.5Al/Bi. It was also used to compare mechanical properties of different materials. The second material was used as a more appropriate reference for mechanical properties of the prepared material and included Al_2O_3 as well, which could cause dispersion strengthening. It consisted of a ternary Al, Al_2O_3 and Bi composite, with mole composition of 4Al/ Al_2O_3 /2Bi. The specific compositions 6.5Al/Bi and 4Al/ Al_2O_3 /2Bi were selected to fix the bismuth volume fraction of the Al/Bi and Al/ Al_2O_3 /Bi composites to mimic the expected bismuth volume fraction in the encapsulated ESM produced using 12Al/ Bi_2O_3 and 6Al/ Bi_2O_3 nanocomposite powders, respectively. Both reference composites were prepared using the same elemental aluminum as used to prepare Al/ Bi_2O_3 nanocomposite powders, elemental bismuth powder, 99.5% pure, - 325 mesh from Alfa Aesar, and α -aluminum oxide nano powder, 99.85% pure, APS 150 nm, from Inframat Advanced Materials. The blended Al/Bi, and Al/Bi/ Al_2O_3 powders used for different reference materials were ball milled using the same conditions as described above. The milling times were 45 minutes for 4Al/ Al_2O_3 /2Bi, and 60 minutes for 6.5Al/Bi. Pellets with diameters 1/8 and 1/4-inch were pressed for thermal analysis and mechanical tests, respectively.

3.2 Characterization Techniques

The particle and inclusion sizes, shapes, and morphology of both, as-prepared and reacted materials were characterized using back-scattered scanning electron microscopy (SEM) using a LEO 1530 Field Emission microscope. Since backscattered electrons are sensitive to the phase contrast between elements with different atomic weights, bismuth appears brighter than aluminum in the images.

Thermal stability and temperature-dependent phase changes were analyzed using differential scanning calorimetry (DSC). A Netzsch Simultaneous Thermal Analyzer STA409 PG with a DSC sample carrier and corundum sample crucibles was used to conduct the experiments in ultra-high purity argon (50 mL/min) environment at a heating rate of 10 °C/min.

The thermal stability and latent heat storage of the reacted materials (PCM) were analyzed in the DSC by cycling the annealed samples between 50 °C and 300 °C for 5 times. The thermal energy storage due to the melting of Bi, and the onset temperature of the melting peak was obtained for each cycle.

Using an Instron 5567 universal testing system equipped with a furnace, two different types of mechanical testing were conducted on the consolidated pellets. First, stress-strain curves were recorded at constant temperatures of 250 °C and 300 °C, selected to be respectively below and above the Bi melting point. These isothermal tests were performed for the annealed 12Al/Bi₂O₃ and 6.5Al/Bi pellets. A compressive stress-strain curve and strength at 5 % strain as function of temperature were obtained. In addition, creep tests at a constant load of 3kN were performed where the temperature was scanned from 200 to 300 °C. The strain as function of temperature was recorded; the test was performed for annealed 6Al/Bi₂O₃ and 4Al/Al₂O₃/2Bi. The

temperature was scanned by changing the furnace setpoint, which resulted in a nonlinear heating profile. The actual sample temperature was estimated from baseline creep tests, assuming initial and final stable states represent the respective temperature setpoints.

4. Results and Discussion

4.1 Preparation of composite material with encapsulated bismuth inclusions

DSC traces for 1/8-inch diameter pellets of milled 12Al/Bi₂O₃, and 6.5Al/Bi composites are shown in Fig. 2. The samples were heated at 10 °C/min to 550 °C, well above the melting point of pure bismuth. For 12Al/Bi₂O₃ pellet, the DSC signal shows a broad exothermic peak overlapping with a weak endothermic peak near the melting point of pure bismuth metal. The exothermic reaction indicates reduction of Bi₂O₃ and oxidation of Al. By the time the Bi melting point is reached, a small amount of Bi has formed, causing a small endothermic peak overlapping with the broader exothermic peak. In contrast, as expected for the 6.5Al/Bi pellet, the DSC signal shows only an endothermic peak, indicating melting of Bi.

Backscattered electron SEM images of cross-sectioned pellets for as-milled and annealed 12Al/Bi₂O₃ and 6.5Al/Bi materials are shown in Fig. 3. Annealed materials were heated to 300 °C, held at that temperature for 64 hours, and then cycled between 200 and 300 °C for five times.

For as-milled 12Al/Bi₂O₃, light-colored micron- and nano-sized inclusions of Bi₂O₃ are embedded into a dark-grey Al matrix. After the material is annealed, it is observed that fine light-colored inclusions remain uniformly distributed in the material. Their dimensions remain close to those of the original Bi₂O₃ inclusions. The boundaries and shapes of inclusions change, but no coalescence or migration of inclusions within the sample are detected. The inclusions

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4 formed after annealing are mostly composed of Bi. Encapsulating Al_2O_3 cannot be distinguished
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6 from the Al matrix. Only amorphous Al_2O_3 is expected to form in samples exposed to 300 °C
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8 and 550 °C [10]. Such Al_2O_3 layers are nonporous, when formed in absence of an alumina-
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10 dissolving solvent [11] and thus should prevent migration of the Bi inclusions.
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15 For as-milled 6.5Al/Bi, the structure is very homogeneous and only nano-scaled inclusions of Bi
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17 are observed. After annealing, however, the structure changes substantially. Bismuth is
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19 redistributed to form a relatively coarse, interconnected web-like structure. Further, bismuth
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21 migrates to the surface of the sample pellet, forming a Bi-rich layer. This behavior is consistent
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23 with phase separation occurring in similar alloys upon heating [12]. The phase separation is due
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25 to a combination of the Marangoni and Stokes motions. No such redistribution was detected for
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27 the material prepared using 12Al/ Bi_2O_3 nanocomposite as precursor and producing encapsulated
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29 nano-sized Bi inclusions. It is expected that after continuing thermal cycling, the 6.5Al/Bi
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31 metal-metal composite will become mechanically weaker as more and more bismuth metal will
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33 concentrate at the outside of the pellet. The composite structure would further coarsen limiting
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35 practical usefulness of such material as ESM.
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42 **4.2 Energy storage performance**

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45 DSC traces for both ESM prepared using 12Al/ Bi_2O_3 and for reference 6.5Al/Bi samples are
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47 shown in Fig. 4. For each material, two samples were used in experiments: annealed at 550 and
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49 300 °C for 6 and 64 hrs, respectively. For clarity, the traces for materials annealed at different
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51 temperatures are shifted vertically relative to each other. For both 12Al/ Bi_2O_3 , and 6.5Al/Bi, an
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53 endothermic peak is observed near the pure Bi melting point. The peak onset temperatures and
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4 respective integrated heat effects are listed in Table 1. In addition, the heat effects estimated
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11 prepared using 12Al/Bi₂O₃. For this material, the peak comprises two closely overlapping
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13 endothermic events, particularly well seen for the sample annealed at 300 °C. The double peak
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15 may indicate dissolution of very small amount of aluminum in bismuth. The Bi-rich part of the
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17 Al-Bi phase diagram is not well quantified and the eutectic composition contains more than 99
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19 at-% of Bi [13]. Eutectic melting occurs at 270 °C, very close to the melting point of pure Bi,
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21 271.442 °C. If the amount of dissolved Al is less than that of the eutectic composition, the
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23 melting peak is expected to split into two closely located peaks, similar to what is observed in
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25 Fig. 4(A). However, if the amount of dissolved Al exceeds that of the eutectic composition, only
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27 the eutectic melting peak should be detectable in the present experiments. The liquidus line for
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29 the remaining, Al-rich solution will be at a much higher temperature, which was not reached in
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31 the present DSC tests. Because of the dissolved aluminum, the enthalpy of melting may exceed
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33 the melting enthalpy of pure Bi, as observed in Fig. 4(B).
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42 The melting peak onset temperatures are slightly lower for the ESM with encapsulated Bi
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44 inclusions compared to those for the binary Al/Bi material. It likely is associated with reduced
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46 dimensions of the Bi inclusions, so that the effect of melting point depression for nano-sized
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48 bismuth domains becomes noticeable [3, 6].
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53 The enthalpy of melting is consistently greater for the samples annealed at a higher temperature
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55 for both ESM with encapsulated Bi inclusions and for the reference material. For the ESM
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57 prepared using a nanocomposite thermite, the effect is most likely caused by a more complete
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reduction of Bi_2O_3 at elevated temperatures. Conversely, for the reference metal-metal composite, the effect is likely caused by a more significant dissolution of aluminum in the molten bismuth upon its heating to higher temperatures.

4.3 Mechanical Testing

Traces of stress as a function of strain for the isothermal mechanical loading tests are shown in Fig. 5 for annealed $12\text{Al}/\text{Bi}_2\text{O}_3$ and $6.5\text{Al}/\text{Bi}$ samples. Compressive stress-strain curves were recorded at 250°C and 300°C , below and above the Bi melting point of 271.442°C , respectively. Both materials deform elastically initially, until the yield strength is reached, after which plastic deformation starts. The ESM with encapsulated Bi inclusions prepared using a nanocomposite thermite is generally stronger than the metal composite. Both materials show a reduction in yield strength above the Bi melting point. At 5 % strain, the softening of the encapsulated composite amounts to a 15.6 % reduction in strength, while the strength of the metal composite decreases by 31.3 %. This suggests that the encapsulation of Bi in the molten state results in a material that is mechanically more sound, and less likely to deteriorate at prolonged or repeated exposure to temperatures above the melting point.

Strain measured in creep tests, when the samples were loaded with a constant force of 3 kN and heated up to 300°C is shown in Fig. 6. The results are shown for the ESM prepared using nanocomposite thermite $6\text{Al}/\text{Bi}_2\text{O}_3$ and for reference ternary composite material $4\text{Al}/\text{Al}_2\text{O}_3/2\text{Bi}$ annealed preliminarily at 300°C for 120 hrs. It is observed that the reference ternary material begins deforming at about 230°C as the Bi component starts to soften. Near the melting point of Bi, dramatic deformation occurs. Conversely, the ESM containing encapsulated Bi inclusions does not show an appreciable deformation in the entire temperature range considered.

SEM images of mechanically tested samples are shown in Fig 7 for the encapsulated materials prepared from 12Al/Bi₂O₃ and 6Al/Bi₂O₃ and the non-encapsulated materials, 6.5Al/Bi and 4Al/Al₂O₃/2Bi. For both materials containing encapsulated Bi shown in Figs. 7A and C, the bright Bi inclusions appear to be roughly equiaxial and uniformly dispersed in the darker Al-rich matrix. As in Fig. 3, it is difficult to detect Al₂O₃. For the material with greater Bi concentration (Fig. 7C), the Bi inclusions are greater in size and occupy a greater fraction of the material's volume. For both materials containing non-encapsulated Bi, bright Bi inclusions form interconnected networks. It is interesting to compare structures shown in Fig 7C and 7D, which have similar concentrations of Al, Bi, and Al₂O₃. Clear morphological differences between the two materials are observed. In Fig 7D, crystalline Al₂O₃ particles are visible. Such particles are well separated from one another and are surrounded by interconnected Bi metal matrix. In contrast, the Al₂O₃ is hard to detect in Fig 7C; however, multiple separated Bi inclusions are observed instead. Most of the Bi inclusions have well-defined boundaries surrounded by a darker phase, which is expected to be Al₂O₃ and Al.

5. Conclusions

Energy storage materials containing inclusions of an easy-to melt metal, Bi, encapsulated with protective Al₂O₃ in an aluminum matrix were prepared using nanocomposite Al/Bi₂O₃ thermite as a precursor material. The precursor material was slowly annealed to reduce Bi₂O₃ and form encapsulated Bi inclusions. The material is shown to be capable of storing energy by melting and solidifying Bi inclusions. The inclusions do not drift inside the material upon heating; prepared composite structure remains largely intact upon thermal cycling. Conversely, the structure of reference composite materials with similar bulk compositions but without encapsulated Bi inclusions is not preserved upon thermal cycling. Molten Bi tends to separate

from Al and form interconnected coarse network of inclusions. Upon cycling, Bi accumulates on surface of the material. Difference in mobility between encapsulated and non-encapsulated Bi inclusions causes dramatic differences in the mechanical properties of the resulting composites. Materials with encapsulated Bi inclusions are much stronger and capable of retaining their structure and strength despite thermal cycling expected for useful energy storage materials.

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

Figure 2. DSC signal of 12Al/Bi₂O₃ nanocomposite and 6.5Al/Bi metal-metal composite heated to 550 °C at 10°C/min.

Figure 3. Backscattered electron cross-sectional SEM image of (A) 12Al/Bi₂O₃ metal-metal oxide nanocomposite as milled (B) 12Al/Bi₂O₃ pellet annealed at 300 °C and held at isothermal for 64 h before cycled for 5 times (C) 6.5Al/Bi metal-metal composite as milled (D) 6.5Al/Bi pellet annealed at 300 °C and held at isothermal for 64 h before cycled for 5 times and evidence of Bi metal pooling to the outer surface is observed.

Figure 4. DSC signal of 12Al/Bi₂O₃ nanocomposite and 6.5Al/Bi metal-metal composite annealed at 550 °C and 300 °C for 6 hrs and 64 hrs, respectively, and heated a second time to 300 °C.

Figure 5. Stress-strain curves of 1/4-inch pellets of a 12Al/Bi₂O₃ metal-metal oxide nanocomposite, and a 6.5Al/Bi metal-metal composite.

Figure 6. Creep Test of 6Al/Bi₂O₃ and 4Al/Al₂O₃/2Bi.

Figure 7. Backscattered electron cross-sectional SEM image of samples annealed at 300 °C for 5 days before compression and creep tested using Instron (A) 12Al/Bi₂O₃ metal-metal oxide nanocomposite compression tested at 250 °C (B) 6.5Al/Bi metal-metal composite compression tested at 250 °C (C) 6Al/Bi₂O₃ metal-metal oxide nanocomposite creep tested from 200 – 300 °C at 3 kN. (D) 4Al/Al₂O₃/2Bi creep tested from 200 – 300 °C at 3kN.

Table 1. Peak onset temperature and energy stored for the prepared materials. For the measurements, annealed samples were cooled to 50 °C and re-heated to 300 °C, above the melting point of Bi.

Material	Annealing conditions	Peak onset, °C	Energy Stored, J/g	
			Actual	Expected
12Al/Bi₂O₃	550 °C for 6 hrs	256.9	26.40	27.5
	300 °C for 64 hrs	253.4	22.39	27.5
6.5Al/Bi	550 °C for 6 hrs	264.4	31.74	28.3
	300 °C for 64 hrs	264.2	29.40	28.3