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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　ZHU Shilei

学 位 論 文 題 名

Micro and Nano Scale Structure Design of Sn-Based Phase Change Materials for Thermal Energy Storage

(熱エネルギー貯蔵のための Sn 系相変化材料のマイクロおよびナノスケール構造設計)

Phase change materials (PCMs) are the materials that use phase transition process to achieve certain designed functions. In terms of thermal energy storage (TES), PCMs can be used to store and release thermal energy at a constant temperature through reversible phase transition. This feature makes them suitable storage medium in TES and the heat sink in thermal management of electronic devices. Compared to the common PCMs, like organic compounds and inorganic salts, metals exhibit high volumetric TES density which is helpful for a compact system, and high thermal conductivity which enable the fast charge and discharge of thermal energy. However, the metal PCMs should be encapsulated to avoid corrosion to container, morphology changes and deterioration of micro and nano scale metal PCMs. This thesis focuses on the nanostructure design of micro and nano scale Sn-based PCMs on the purpose of encapsulation of metal PCMs for long-term cyclic stability and morphology control.

In Chapter 1, the research background and objectives of this research are introduced.

In Chapter 2, silica was selected as the material of the protection shell for Sn PCM. A facile method was proposed for preparing a silica (SiO_2)-based material containing Sn nanoparticles (NPs) distributed inside for enhancing the thermal cyclic stability of the inserted Sn NPs. Absorption of a Sn precursor into a mesoporous SiO_2 matrix resulted in confinement of the Sn precursor in a mesoporous SiO_2 matrix. Hydrogen thermal reduction of the above composite yielded Sn nanoparticles with a diameter of ca. 30 nm uniformly distributed inside porous SiO_2 (p-SiO_2) spheres : Sn NPs @ p-SiO_2. The transformation of the porous SiO_2 structure for supporting Sn NPs revealed that the process was closely related to the transformation of the amorphous hydrolyzed Sn precursor into Sn oxides followed by, probably, the rearrangement of the SiO_2 matrix via its interaction with the melting Sn. This led to the formation of stable Sn NPs @ p-SiO_2. The SiO_2 matrix effectively prevented the coalescence of the Sn NPs, and the obtained product exhibited negligible changes in melting behavior during the second to 100th cycle of a freeze-melt cycle test.

In Chapter 3, alumina with higher thermal conductivity compared to silica was selected as the

material of the protection shell. In this part, for the first time, alumina-encapsulated metallic Sn-based PCMs, named Sn @ Al_2O_3, were successfully fabricated with tunable size (60 nm-2 μm) and core-shell structure by a facile process from low-cost chemicals. The robust fabrication process consists of a surfactant-free solvothermal synthesis of SnO_2 spheres, boehmite treatment on SnO_2 spheres, calcination in the air, and the final hydrogen reduction to transform SnO_2 to metallic Sn. The boehmite treatment, in which the penetration of aluminum species into SnO_2 spheres played an important role, was found to be responsible for the unique structure formation of final Sn @ Al_2O_3. The understanding of structure formation mechanism gives the possibilities of a new facile way for the synthesis of metal NPs and particle-distributed nanostructures. The obtained Sn @ Al_2O_3 particles not only have high PCM content (92.37 wt %) but also show a stable thermal behavior and morphology during 100 melt-freeze cycles in the air atmosphere, exhibiting the potential of fast thermal energy storage within the range of 100-300° C.

In Chapter 4, the formation of SnO_2 @ SiO_2 hollow nanostructures was demonstrated, for the first time, by diffusion of liquid state Sn cores in Sn @ SiO_2 core-shell NPs and further interaction with SiO_2 with real-time observation via in situ transmission electron microscopy (TEM). Based on the in-situ results, a designed transformation of nanoparticle structure from core-shell Sn @ SiO_2 to yolk-shell Sn @ SiO_2 and hollow SnO_2 @ SiO_2 is demonstrated, showing the controllable structure from starting core-shell Sn @ SiO_2 NPs via liquid state Sn diffusion in SiO_2 shell and further fixing of Sn by interaction with the dangling bond of SiO_2. The proposed approach expands the toolbox for the design and preparation of yolk-shell and hollow nanostructure, thus provides us a new strategy in fabrication of more complicated nanostructures, which can not only be applied in PCMs design but also in catalyst, batteries, etc.

Finally, Chapter 5 is a summary of all the results obtained in each chapter and prospectives for future research in the above areas.