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In-situ HAADF-STEM observation of phase transformation in microencapsulated Al-Cu-Si alloy

Dr Melbert Jeem[1], Dr Norihito Sakaguchi[1], Dr Takahiro Nomura[1]
[1]Faculty of Engineering, Hokkaido University, Sapporo, Japan

Background incl. aims

The increasing relevance of latent heat storage through phase change materials (PCMs) in advanced thermal energy storage technologies is underscored by challenges such as deformation during thermal cycling. This issue is typically mitigated by encapsulating PCMs to create microencapsulated PCMs (MEPCMs) with high thermal conductivity, rigid structures, and improved durability.1 Despite these enhancements, hysteresis during solidification remains a concern. Recent innovations include a core-shell structure of Sn@α-Al2O3 MEPCM that lowers the energy barrier for nucleation, effectively reducing hysteresis through the formation of localized Sn nanoparticles on an α-Al2O3 nanoparticle.2 Expanding on this, we used an Al-Cu-Si alloy for a similar MEPCM structure, achieving notable hysteresis suppression. Unlike Sn, Al-Cu-Si does not volatilize, avoiding the formation of oxide byproducts over repeated thermal cycles. These MEPCMs were calcined at 1000°C in an O2 atmosphere, developing a dense α-Al2O3 shell. However, no localized nanoparticles were detected, prompting further in-situ HAADF-STEM studies to explore hysteresis mechanisms in Al-Cu-Si@α-Al2O3 MEPCM.

Methods

Al-Cu-Si alloy (m.p. = 529 °C, ϕ ≈ 38 µm, 99.95% purity, Hikari Materials Industry Co., Ltd, Japan) was encapsulated with α-Al2O3 nanoparticles (ϕ ≈ 100-200 nm, 99.99% purity, Kojundo Chemical Laboratory Co., Ltd., Japan) using a dry synthesis method, as described in our previous study.2 The encapsulation was facilitated by a rapidly spinning rotor equipped with blades, which promoted the adherence of α-Al2O3 nanoparticles to the Al-Cu-Si microparticles. Sintering at 1000°C for 6 hours in an O2 atmosphere helped form a dense α-Al2O3 shell. For in-situ S/TEM sample preparation, a 6 × 6 µm lamella of the MEPCM was processed using FIB milling (JEM-9320 FIB, JEOL) followed by a standard lift-off procedure. A lamella of the raw Al-Cu-Si alloy was also prepared for comparative analysis. The lamella was placed on a MEMS-based microheater (FEI) with a silicon nitride heating element capable of reaching temperatures up to 1000 °C (Fig. 1). The lamella was positioned over the electron-transmissible window, and the holey film was removed by FIB milling to eliminate non-sample-derived Si X-rays. To secure and enable heating of the lamella, a 300 nm thick tungsten (W) film was deposited at the contact area between the lamella and the heating pad using FIB. S/TEM observations were performed using a Titan3 G2 60-300 (FEI) double aberration-corrected microscope, operated at 300 kV. In-situ heating observation involved acquiring a series of HAADF images with a convergence angle of 17.9 mrad. The camera length was set to 115 mm for a HAADF collection range of 51–200 mrad. The series were taken with a pixel size of 512 × 512 and a dwell time of 2 µs/pixel, resulting in an image frame rate of 787 ms/frame. The probe current was set to 44 pA. The MEMS microheater's temperature was controlled using a closed-loop feedback system to prevent temperature undershoot or overshoot, starting from room temperature and increasing to a maximum of 500 °C at a rate of 5 °C min-1, similar to the heating rates used in differential scanning calorimetry (DSC) for latent heat measurements. A series of HAADF images were taken during each temperature ramp. The temperature was maintained at each 100 °C increment until no further changes were observed, and EDX analyses were performed at each stage. The FEI heating holder's slight curvature over the microheater's window slightly compromised EDX signal counts for the 4-quadrant Super-X windowless detectors. EDX maps were acquired with a resolution of 256 × 256 pixels, a dwell time of 20 µs, and a total of 250 – 350 frames per map.

Results

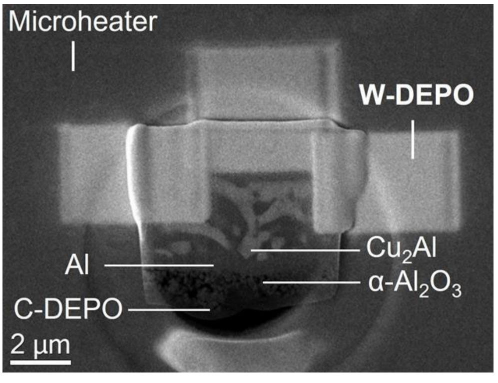
The target observation area focused on the core-shell interface structure consisting of α-Al2O3 and the Al-Cu-Si alloy. Compared to the raw Al-Cu-Si, the calcined MEPCM exhibits coarsening of intermetallic Cu2Al and Si. In-situ heating observation of the raw substrate revealed initial dendritic Si structures becoming denser and increasingly aligned with the Cu2Al structure during heating from 100 to 500 °C. This suggests a possible higher melting temperature for Cu-Si formations, which remain solid even at the eutectic melting point of 529 °C. This compound is confirmed in the MEPCM calcined at 1000 °C, where it appears as dispersed nanoparticles in the primary Al matrix. During the temperature ramp from 100 to 300 °C, the applied voltage increased linearly while a notable increase in current is observed, likely due to the thermal lattice expansion of Cu2Al, which leads to fluctuations in electrical conductivity. This was validated by rigid registration of the acquired frames, confirming an approximate size increase of 100 nm in Cu2Al.

This behavior persists until 300 °C. Thereafter, during the ramp to 400 °C, the current value nearly stabilizes, indicating that the Cu2Al phase is reaching its thermal stability limit and beginning to dissolve into the Al matrix. A continued ramp to 500 °C results in complete phase dissolution. This dissolution involves the diffusion of Cu and Al atoms out of the Cu2Al phase and into the surrounding matrix, driven by the gradient in chemical potential caused by temperature changes and the concentration gradients of Cu and Al in the different phases. Interestingly, during the complete phase dissolution, some phases from the Cu2Al adhere to the α-Al2O3 surface. Although α-Al2O3 acts as an inert barrier, surface defects and partial charges may provide sites for adsorption or chemical interactions. If the lattice constants of the dissolute phases are close enough to those of the α-Al2O3, epitaxial growth or nucleation could occur. Atomic resolution HAADF observations in the area where adhesion occurred confirm the presence of seed crystals.

Conclusions

The in-situ HAADF-STEM observations have provided valuable insights into the thermal expansion and dissolution behaviors of Cu2Al within Al-Cu-Si@α-Al2O3 MEPCM during heating. A critical observation from this study is the adhesion of dissolute phases from Cu2Al to the α-Al2O3 surface during phase transformation. This adhesion suggests a potential for epitaxial growth or nucleation at the interface, which could effectively induce nucleation in the Al-Cu-Si alloy during solidification, thereby suppressing hysteresis.

Graphic:



Keywords:

In-situ, MEMS, HAADF, PCM, alloy

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