Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for "Critical Factors of the 3D Microstructural Formation in Hybrid Conductive Adhesive Materials by X-ray Nano-tomography"

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Appendix 1 - Experimental Details

Preparation of the conductive adhesive tracks was accomplished by first mechanically mixing a typical thermoset type of adhesive test vehicle with a loading between 78-85 wt% of silver-plated copper to form a uniform paste. The composition is then applied onto a substrate to form conductive traces or electronic circuitry. Usual methods of applying the composition to a substrate include dispensing by stencil, screen, rotogravure or flexo printing, with screen printing being generally used for this application. The thermoset adhesive filled with Ag-Cu was then cured for 30 min at 170ºC under nitrogen and let cool down for 1h before testing.

The set thermoset adhesive filled with Ag-Cu was then cut into a sharp wedge-shaped sample and mounted onto a stainless steel pin with epoxy to allow x-ray nano-tomography measurement. A FIB cross-sectioning was performed using a FEI Strata DB-235 dual-beam FIB/SEM system. SEM analysis and X-ray mapping was performed using FEI Quanta 200 Field-Emission SEM equipped with Oxford Instruments X-MaxN 80 mm^2 Silicon Drift EDS Detector to reveal the morphology and chemical information at a cross-section of the Ag-Cu hybrid filler sample.

X-ray nano-tomography of the Ag-Cu hybrid materials was carried out using transmission x-ray microscopy at the beamline X8C, National Synchrotron Light Source [12]. An x-ray energy of 8 keV was used with the field of view of 40 x 40 μm^2. A CCD camera was used to collect the images with binning 2x2. A total of 1441 projections were collected on a conductive adhesive material sample with Ag-Cu hybrid micro-fillers, over a 180° angular range. The 3D reconstruction was performed by a standard filtered back-projection algorithm to recover the linear absorption coefficient distribution in 3D.

Image segmentation was carried out to separate the Ag, Cu and background phases from the gray-scaled reconstruction images into three distinctive levels. Watershed threshold segmentation method was applied to the dataset using commercial software Avizo Fire (v7.0, VSG). The detailed 3D morphological analysis was then performed on the segmented images to quantify the 3D morphological parameters.

To determine the size of the Cu particles and the thickness of the Ag coating, an algorithm developed by Holzer *et al* was used [1] and implemented in a customized Matlab program (R2012, Mathworks) developed in house at Brookhaven National Laboratory. The segmented images were analyzed to calculate the size distribution of both the Ag and Cu coating. In addition, the average and standard deviation of the Ag coating thickness were calculated from the Ag thickness distribution to determine the overall quality of the Ag coating.

A method based on the Region Growth method was used to measure the Ag coverage in freeware FIJI. This algorithm consists of various steps. First, the Cu phase was dilated by one voxel. Then, the original copper particles was subtracted from the dilate Cu and the surface of the Cu is obtained. Consequently, the Ag particles are added to the Cu surface obtained. The overlapped region was where Cu covered by Ag. As for the last step, the ratio of the Ag area over Cu area was calculated. The illustration of region growth algorithm used to obtain the coverage is shown in Appendix 2.

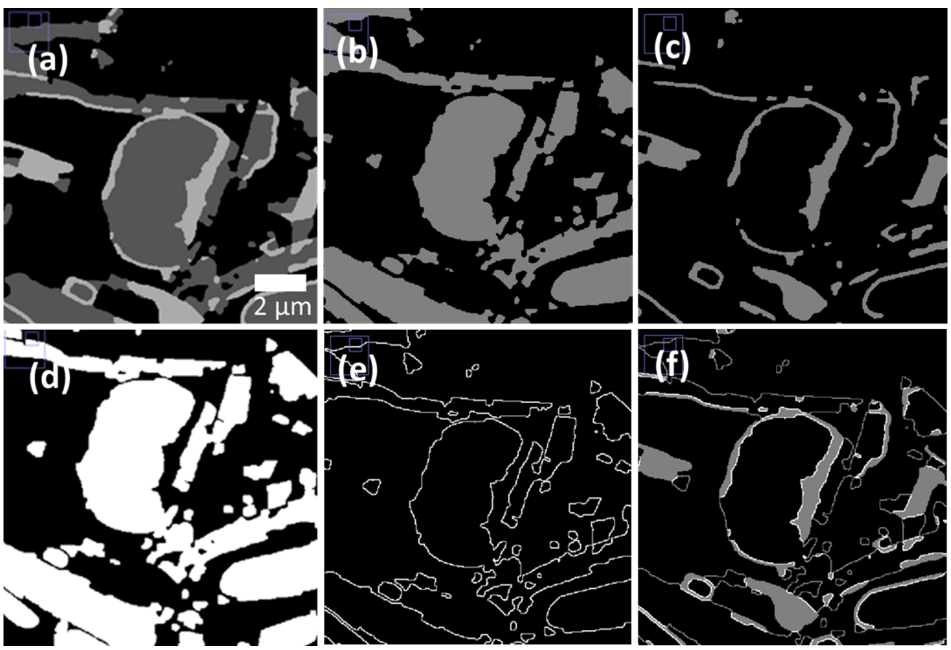
2,339 individual particles comprising the sample were first separated using *Avizo Fire.* Their surface area, volume, shape factor and surface coverage are quantified. Particle volumes were determined by voxel counting, whereas the surface coverage (C) for each individual particle was determined by the same region-growth algorithm described previously. The shape factor (S) is a critical new factor proposed in this work and was defined as the product of specific area surface area (S_v) and particle radius (r, approximated by sphere). Because the particles in an ICA sample consist of both sphere shape and disk shape, this shape factor S can effectively represent both shapes. The detailed mathematical derivation can be found in the supporting information (Appendix 3). The specific area S_v is defined as the ratio between the surface area and the volume of each particle. The surface area can be measured using a surface mesh approximation. The particle radius r approximated by sphere was calculated to obtain the equivalent sphere radius that will result in the same volume in a sphere as in the calculated particle (whether it is sphere or disk shape). As a result of the definition, ball-shaped particles exhibit $S = 3$, which is independent of the particle size. The shape factor for the disk-shaped particles will depend on their radius-to-thickness ratio (a). For a disk with a thickness of t and a radius of $R = a\ t$, the shape factor will be:

$$S = \frac{2(a+1)}{\sqrt[3]{\frac{4a}{3}}} \qquad (S.\ Equation\ 1)$$

For instance, a disk/cylinder particle with $R = t\ (a=1)$ will result in $S = 3.636$. For a disk with a larger radius-to-thickness ratio, the shape factor will also increase. As an example, a disk with $R = 20\ t\ (a=20)$ will give $S = 14.058$.

To examine the particle segregation, Ag coverage and volume fraction were quantified in $N \times N \times N$ independently cropped volumes with N = 4 -6, which correspond to cubes with length (l = 40 μm/N) ranging from 6.7 – 10.0 μm. This range was chosen to result in enough sub-volumes that yield statically significance while having the sub-volume size significantly greater than the average particle size of Cu in order to accurately sample the volume.

Appendix 2 – Measurement of surface coverage by region growth algorithm



Supplemental Figure 1 - use of Region Growth algorithm to obtain the Ag coating coverage on Cu. (a) Segmented image, (b) Cu phase, (c) Ag phase, (d) Image after dilating Cu by one voxel, (e) Cu surface: subtracting Cu from the dilated Cu, and (f) identifying Cu surface covered with Ag phase by doing a voxel counting on the overlap voxels of dilated Cu and Ag

Appendix 3– Mathematical relationship between the shape factor and the geometrical factors in spherical and disk-shape particles

Considering the case I & II below together, we demonstrate here that we can use one single geometric 'shape factor *S'*, defined as the specific area (S_v, surface area divided by volume) times the ball-shape equivalent radius r_e, to quantify the shape of any given particles.

Case I. Ball shape

Provided a ball with a radius of r, its surface area $A = 4\pi r^2$, volume $V = 4/3\ \pi r^3$. The specific area $S_v = A/V = 4\pi r^2 /(4/3\ \pi r)^3 = 3/r$

Therefore the shape factor $S = Sv \times r = 3$ is a constant for the ball shape, independent from the radius.

Case II. Disk shape

Provided a disk with a radius of R and a thickness $t = 1/a\ R$, its surface area $A = 2\pi R^2 + 2R\pi t = 2\pi R^2 + 2R\pi(1/a\ R) = 2\pi R^2(1+1/a)$, and volume $V = t\ \pi R^2 = 1/a\ \ \pi R^3$. The specific area $S_v = 2\pi R^2(1+1/a)/(\ 1/a\ \ \pi R^3) = 2(1+a)/R$

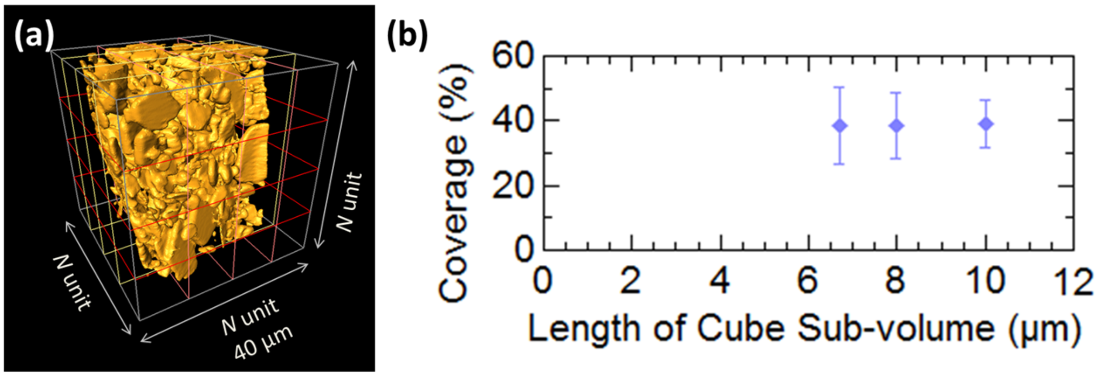
In order to set a united parameter for both ball and disk shapes, we can calculate the equivalent ball radius r_e for the disk, which results in the same volume:

$V = 1/a\ \ \pi R^3 = 4/3\ \pi r^3 \rightarrow R = (4a/3)^{1/3}\ r_e$

The disk specific area $S_v = 2(1+a)/\ [(4a/3)^{1/3}\ r_e]$

The shape factor S for disk shape is $S = S_v \times r_e = 2(1+a)\ /\ (4a/3)^{1/3}$. Note that for disk shape particles, the shape factor is also independent from their size, but only depends on their radius-to-thickness ratio, *a* here.

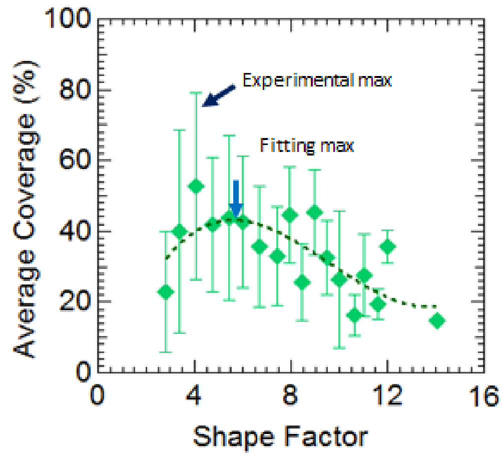
Appendix 4 – Quantification of particle segregation using sub-volume divisions



Supplemental Figure 2 - (a) illustration of the sub-volumes division from the original volume, (b) the average coverage and its standard deviation (shown as the error bars) vs. sub-volume length.

Appendix 5 - The relationship between the average coverage vs. the shape factor

The relationship between the average coverage vs. the shape factor is shown in the Supplemental Figure 3. It can be seen that the particles with shape factor = 4, close to a spherical shape, exhibit the highest average coverage experimentally. In the fitted average coverage v.s. shape factor curve, the maximum average corresponds to a shape factor of 5.59, where the radius-to-thickness ratio of a cylinderical particle is 3.8. Note that there is no significant difference in the average coverage for the shape factor 3.8-6.2, with an exception of the shape factor = 4. Based on this observation, we conclude that the ideal shape for this process would be a ball shape or a cylinder with low radius-to-thickness ratio. This findings can be directly applied to the manufactureing by focusing on further improving surface coverage with particles exhibiting small shape factors.



$$C_{avg} = 0.094S^3 - 2.71S^2 + 21.49S - 8.81$$

Supplemental Figure 3 - The relationship between the average coverage vs. the shape factor. C_{avg} is the average coverage, and S is the shape factor.

Reference

[1] B. Munch, L. Holzer, J. Am. Ceram. Soc. 2008, 91, 4059.