Supplementary Information

A. Determination of NPG Network from Cu Iso-concentration Surfaces

Demarcating the NPG in the APT data is complicated by evaporation field differences between the NPG and Cu-fill. This gives rise to density variations and overlap between Cu atoms and atoms from the surfaces of the NPG. As the compositions of the ligaments are known to be variable, the dividing surface between the Cu-fill and NPG is defined using Cu iso-concentration surfaces. In calculating these surfaces, the APT data is binned into 0.75 x 0.75 x 0.75 nm^3 voxels, with concentrations in these voxels calculated over a delocalization distance of 1.5 x 1.5 x 0.75 nm (given in x,y,z coordinates, where z is along the long axis of the tip). The dividing surface separates the APT data into two parts: i) the AgAuPt-rich NPG phase and ii) the Cu-rich fill phase.

The dividing surface is calculated for Cu concentrations between 10 at.% and 80 at.%. Below and above these respective thresholds, volumes begin to be significantly affected by minor composition fluctuations, and the APT volume is no longer accurately separated into the two major phases. As shown in Figure S1a, the NPG is well-demarcated by the Cu iso-concentration surfaces, with little variation for different concentration values. To find the surface that best represents the original NPG microstructure, results are compared with the known nominal density of each phase. For every Cu composition value, the volume of each phase is calculated, then the measured density of the phase is calculated using the relevant ions contained within (i.e. Ag+Au+Pt for the NPG phase, Cu for the Cu-fill phase). To account for artifacts caused by ions overlapping with those of the other phase, a so-called "corrected" density is also calculated, which includes ions present in the other phase (i.e. Ag+Au+Pt in the Cu-fill phase are added to the NPG phase, and vice versa). The resulting densities are compared to nominal values, based on the lattice parameters of the two materials and the detection efficiency of the LEAP 4000X HR, calculated as 21.6 atoms/nm^3 for the NPG phase, and 30.6 atoms/nm^3 for the Cu-fill phase.
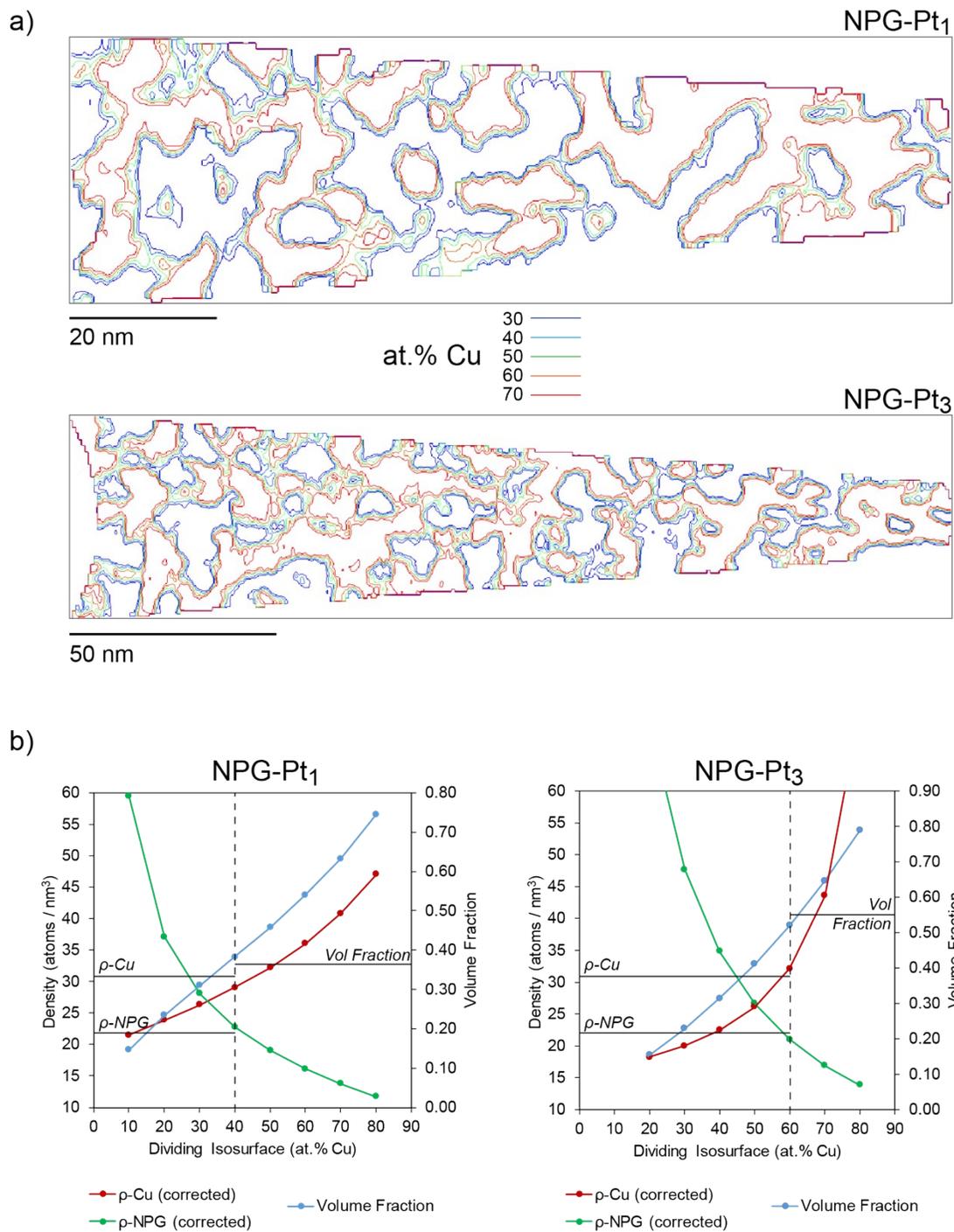
Figure S1. Determination of appropriate dividing surface for NPG-Pt$_1$ and NPG-Pt$_3$ based on Cu iso-concentration, and nominal density of the two phases (corrected for overlapping ions).

B. Checking Solute Distributions in the Bulk Metal

First nearest-neighbor (1NN) distributions were calculated in the bulk metal for NPG-Pt$_1$ and NPG-Pt$_3$, and compared with distributions for randomized data (see Figure S2). The matching distributions for each major element with the randomized data indicate that no clustering is present in the bulk metal below the dealloying front, and it is a random solid solution. Note that comparative 1NN analysis of the NPG layer is not meaningful, due to the effect of density variations across the ligaments arising from local magnification.
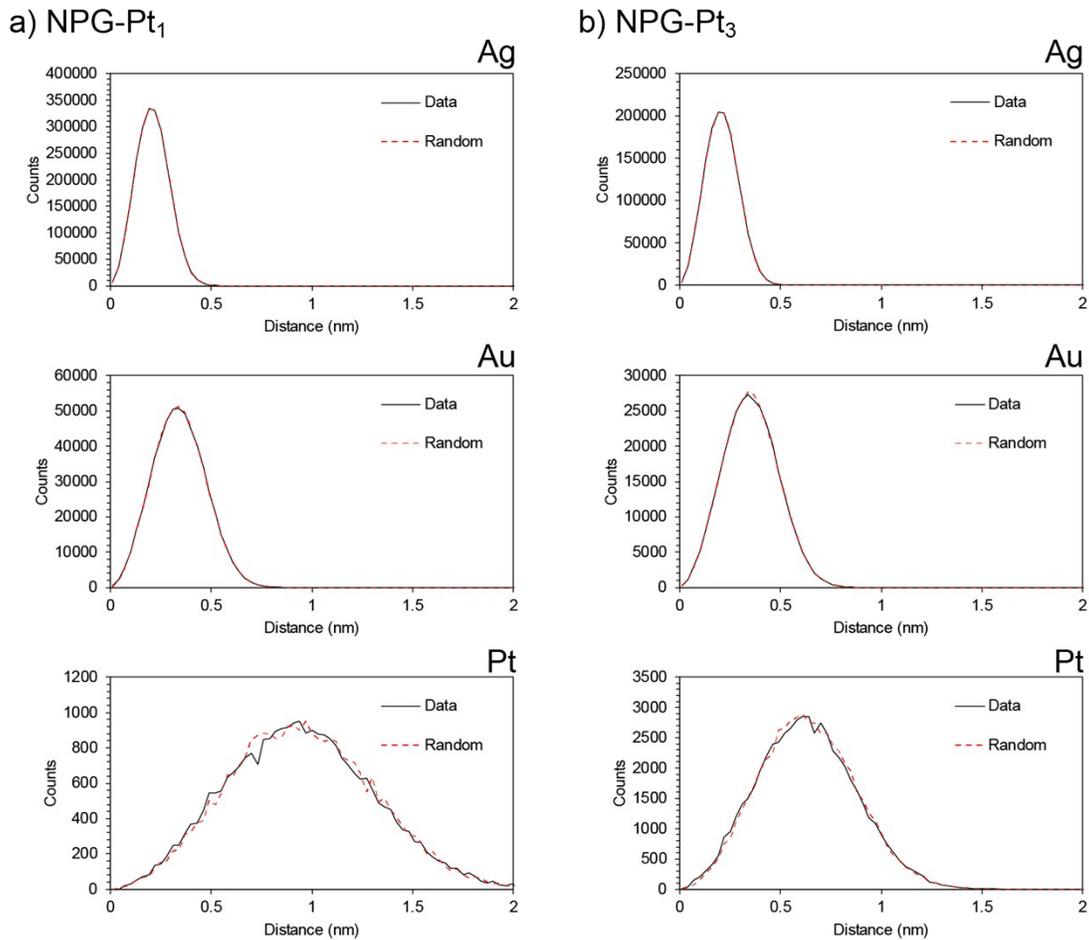

Figure S2. 1NN profiles of Ag, Au, and Pt atoms, taken from APT data of bulk metal for a) NPG-Pt$_1$, and b) NPG-Pt$_3$.