

Electronic Supplementary Information (ESI) for:
Tuning the ligament/channel size of nanoporous copper by
temperature control

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Advantages of ball milling method over conventional metallurgy techniques:

Compared to normal solidification (to obtain bulk samples) and rapid solidification (to get ribbons), ball milling (or mechanical alloying) has some advantages.¹ Firstly, the size of milled powders ranges from several hundred nm to several microns, much smaller than bulk samples or ribbons (normally above 30 microns in thickness, several mm in width and several cm in length). Because the dealloying reaction evolves from the surface into the inner part of samples, thus the dealloying of these bulk or ribbon-like samples normally takes much long time (several hours to even several days!!). During this long-term dealloying, significant coarsening may take place and it is also difficult to control the structural formation of nanoporous metals. In contrast, the milled powders have smaller size, the dealloying consumes much shorter time (normally less than 1 hour), and one can easily control the dealloying process to obtain nanoporous metals with homogeneous structures. Secondly, the ball milling method can provide powder-like samples which possess slightly higher specific surface areas for the similar ligament/channel sizes compared to ribbon-like or bulk samples. The higher specific surface areas are beneficial to their catalytic, electrocatalytic and sensing applications. Thirdly, ball milling can provide maximum flexibility in alloy design because some alloys (especially refractory metals, like W, Mo) cannot be easily produced by the melting method. In contrary, the ball milling method can produce almost all the alloys with different compositions.

Detailed derivative process of equation (2):

The analytical description of surface diffusion can be estimated by the following expression for the time dependence of the ligament/channel radius $r(t)$ ^{2,3}

$$\frac{d(r(t)^4)}{dt} = \frac{2\gamma a^4 D_s}{kT} \quad (\text{S1})$$

where a represents the lattice parameter, γ is the surface energy, k is the Boltzmann constant ($1.3806 \times 10^{-23} \text{ J K}^{-1}$), t is the dealloying duration and T is the temperature. Integration of equation 1 between r_0 and r for $t = 0$ and $t = t$, leads to:

$$r(t) = \left[r_0^4 + \frac{2\gamma a^4 D_s t}{kT} \right]^{\frac{1}{4}} \quad (\text{S2})$$

According to the model of Sieradzki *et al.*,⁴ there is a built-in length scale, ξ^{perc} , which is associated with clusters comprising interconnected atoms of the less noble species. For a binary alloy, ξ^{perc} can be obtained through the equation $\xi^{\text{perc}} = a_{nn}(1 + p)/(1 - p)$ where a_{nn} is the nearest-neighbor spacing and p is the mole fraction of the less noble element.⁴ The initial pore size (diameter), d_0 , can be approximately given by $2\xi^{\text{perc}}$.⁵ Theoretical estimates based on curvature effects in alloy dissolution suggested the average ligament diameter of ~ 2.0 nm during the initial stages of the dealloying process of Al_2CuMg .⁶ ($r_0 = \sim 1.0$ nm). The present ligament/channel sizes ($d(t)$) range from 17.9 ± 2.0 to 43.1 ± 4.2 nm (Table 1). Due to the tremendous margin between $[r(t)]^4$ and r_0^4 (namely, $[d(t)]^4$ and d_0^4), the r_0^4 term in equation (S2) can be ignored. Thus, the following equation can be obtained.

$$D_s = \frac{[d(t)]^4 kT}{32\gamma a^4} \quad (\text{S3})$$

References:

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Table S1. The ligament/channel size of NPC obtained by dealloying the mechanically alloyed $\text{Al}_{66.6}\text{Cu}_{33.4}$ powders in the NaOH solutions of 0.2, 2.0 and 5.0 M at 298 K for different durations, and corresponding surface diffusivity of Cu adatoms.

T , K	Concentration of NaOH, M	t , s	$d(t)$, nm	D_s , $\text{m}^2 \text{s}^{-1}$
298	0.2	3600	21.8 ± 2.3	4.7×10^{-19}
	2.0	2400	21.3 ± 2.7	6.5×10^{-19}
	5.0	1800	29.7 ± 2.9	3.3×10^{-18}

Figures:

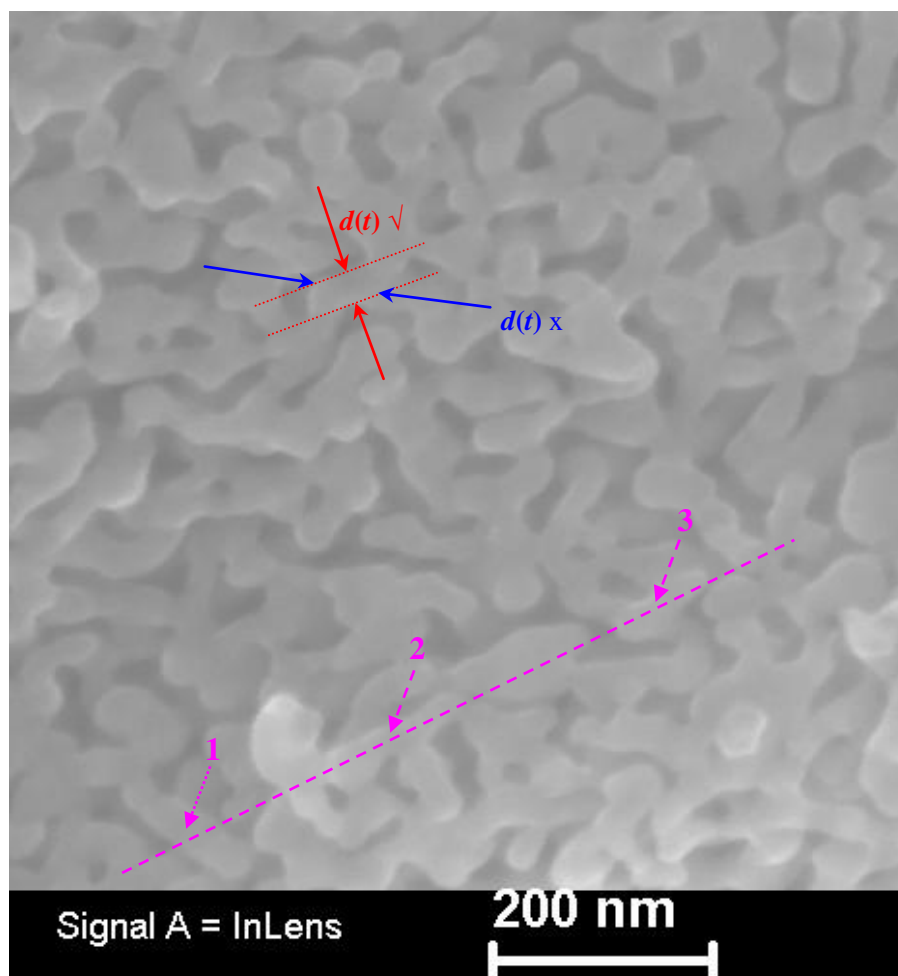


Fig. S1. A schematic illustration denoting how to determine the ligament size ($d(t)$). Here, we made measurements across the shortest distance of each ligament/channel and then took an average. The red arrows show the correct way to get the shortest distance of each ligament, but the blue arrows give a wrong way. In addition, the intercept method which is normally used to evaluate the grain size is not appropriate for determining the ligament/channel size because ligaments are actually interconnecting nanowires. For example, if we draw a straight line in the SEM image (dashed pink line), we can get a correct $d(t)$ value for ligament 1 (denoted by dotted pink arrow), but wrong values for ligament 2 and 3 (denoted by dashed pink arrows). For ligament 1, we get the shortest distance (diameter). For ligament 2 and 3, however, the values will be obtained along the length direction of nanowires.

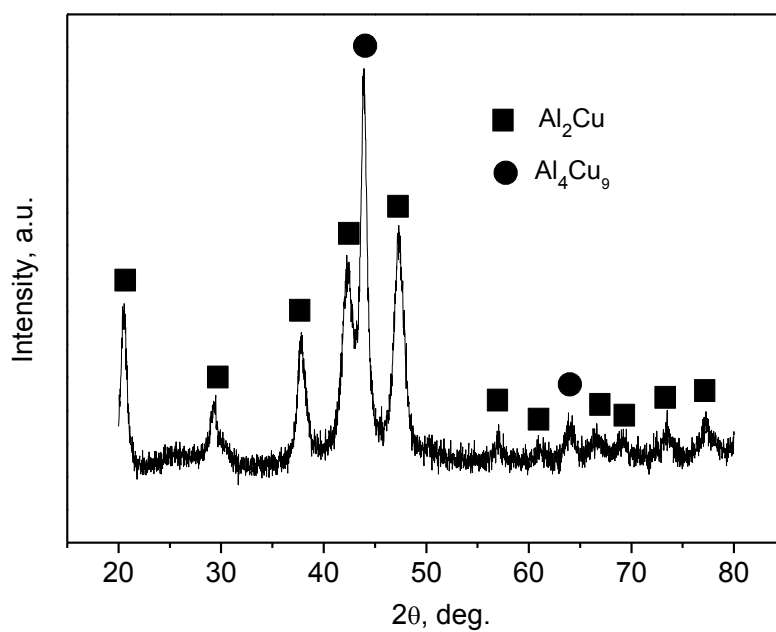


Fig. S2. XRD pattern of the as-milled Al_{66.6}Cu_{33.4} precursor powders after milling time of 60 h.

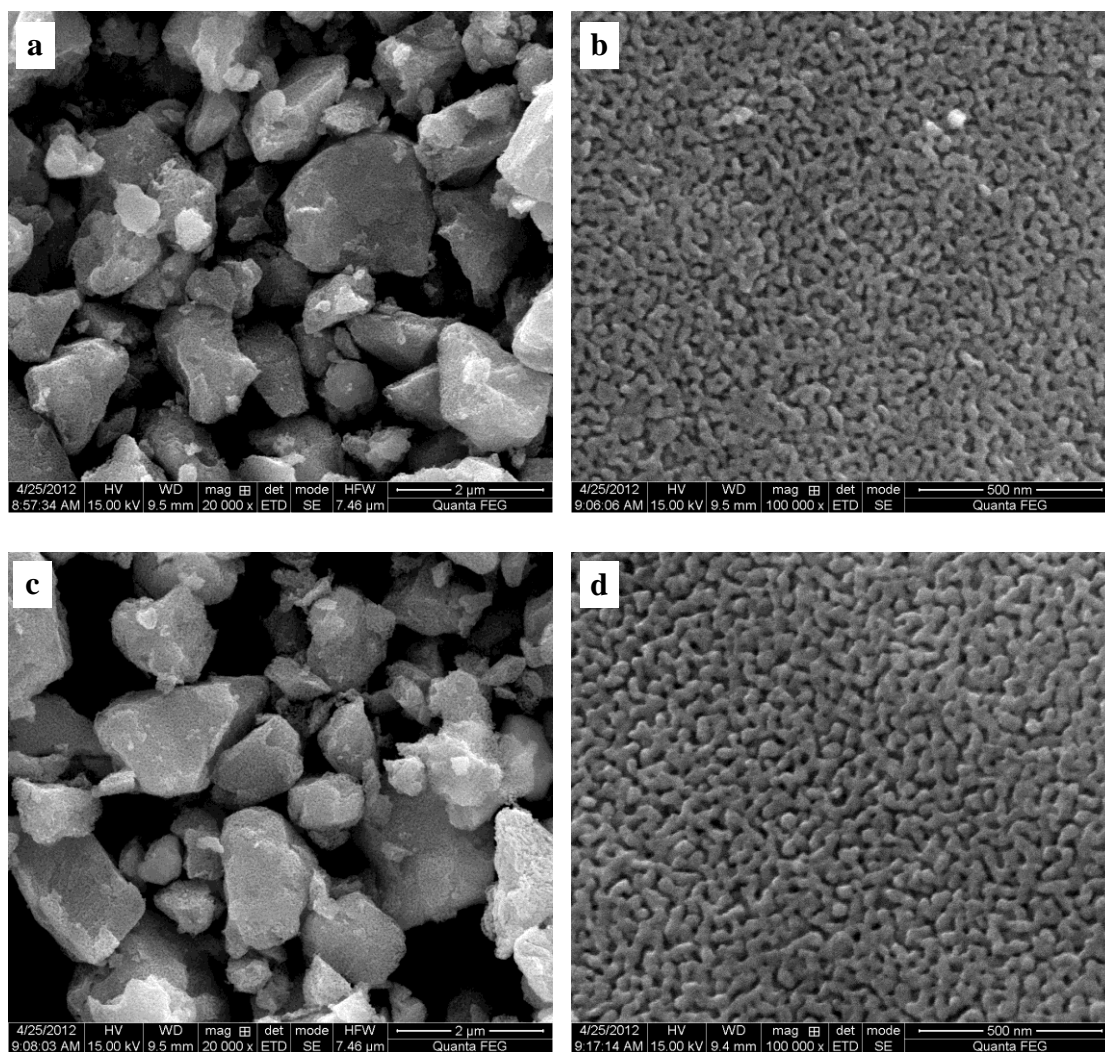


Fig. S3. SEM images showing the microstructure of NPC fabricated by dealloying the mechanically alloyed $\text{Al}_{66.6}\text{Cu}_{33.4}$ powders in the (a,b) 0.2 M and (c,d) 5.0 M NaOH solutions at 298 K.

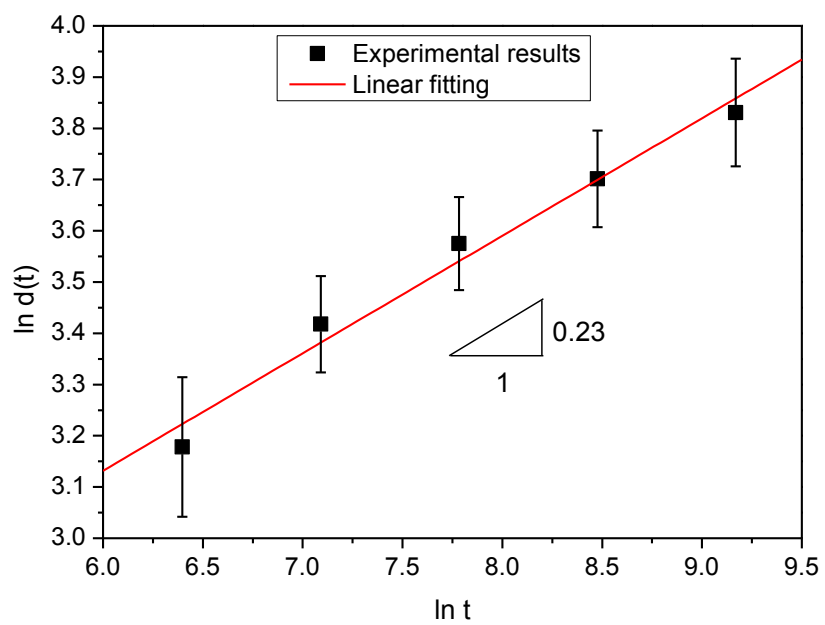


Fig. S4. Measurement of the coarsening exponent n by plotting $\ln[d(t)]$ versus $\ln t$.

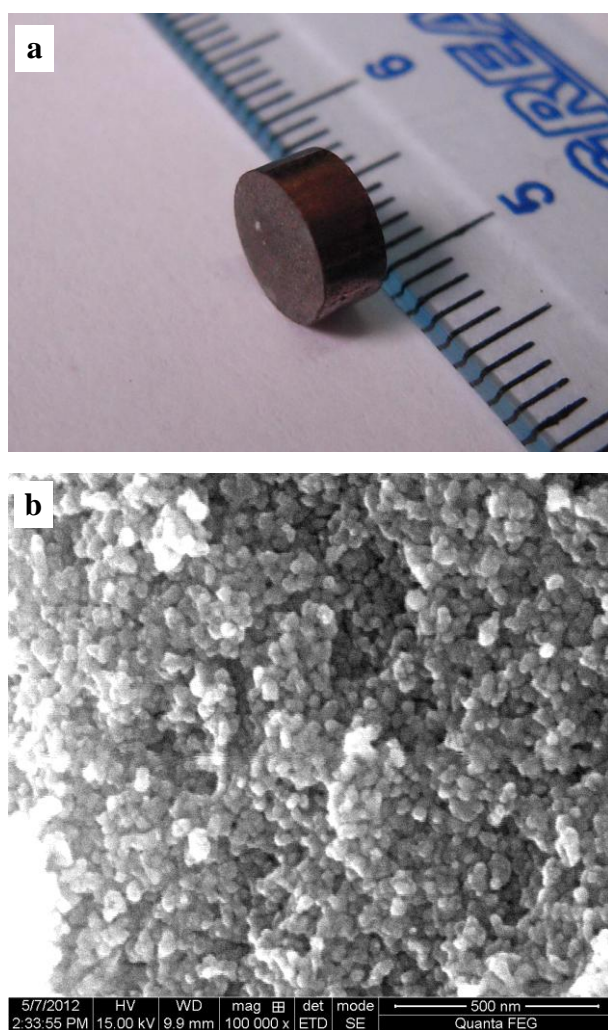


Fig. S5. (a) Macrograph of bulk NPC sample (columnar, 6 mm in diameter and 2.5 mm in height) fabricated through the dealloying method (in the 2.0 M NaOH solution at 323 K) and subsequent cold-pressing technique. (b) SEM image showing the section-view microstructure of the bulk NPC sample. Obviously, bulk NPC samples with good mechanical integrity and strength can be obtained from NPC powders through the simple cold-pressing process. The cold-pressing process has some influences on the porosity and sizes of nanopores, but the nanoporous structure can still be observed and the porosity was calculated to be ~40%. Moreover, through adjusting the parameters such as the applied pressure, one can tune the porosity of these bulk NPC samples.