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Insights into the Formation of Bicontinuous, Porous CuZn nano/micro Particles by *in-situ* (S)TEM

Subhajit Kundu[1]* and K. Andre Mkhoyan[1]

[1.] Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, 55455 USA.

* Corresponding author: kundus@umn.edu

Porous materials are highly desirable for catalysis, sensing, actuation, energy storage [1]. In that regard, various synthetic methods like chemical/electrochemical dealloying, liquid metal dealloying and Vapor Phase Dealloying (VPD) have been studied [2]. Recently, VDP has gained a lot of attention due to its distinct advantage, over the other methods, in having no chemical waste, high material yield and lesser coarsening [3]. It exploits the difference in vapor pressure of the constituent elements in an alloy to form a porous structure. Zn, having higher vapor pressure at lower temperature than other metals, have been fairly used as sacrificial moiety in synthesis of porous materials [2, 4, 5]. However, all studies, till date, have been *ex-situ* and hence the developed understanding relied on the post mortem analysis of the synthesized product. Real-time visualization of the process would give complimentary insights into the phenomenon resulting in better predictability for future applications.

In this study, we performed *in-situ* TEM heating experiments to show the evolution of the γ-brass alloy micro/nano particles into bicontinuous, porous Cu-rich alloy exploiting the natural vacuum environment (~10^{-7} torr) of the electron microscope columns. TEM/STEM analysis was performed using a FEI F30 and aberration-corrected Titan G2 60-300 equipped with Super-X system for EDS analysis. In a typical experiment, dilute suspension of γ-brass powder was drop-casted onto chip-based TEM support membranes which were subsequently heated using Protochips Fusion TEM heating holder. The temperature of the sample was increased in steps of 200°C and the time evolution of the morphology was captured in BF-TEM mode (Figure 1). Initial pore formation is observed at ~400°C which grows with increasing temperature/time. Careful investigation reveals that multiple of such pores nucleate in particles which are bigger than the average pore size at the probed temperature/time. Electron diffraction from individual grains reveal single crystalline pattern matching closely with the face centred cubic phase of Cu indicating that the remnants are rich in Cu.

To gain further insights into the preferential evaporation of Zn, additional investigations were carried out in the STEM mode. Analysis of the samples, before heating, revealed that the starting γ-brass particles are extremely homogeneous in composition with an average content of 34% Cu and 66% Zn. However, analysis after the heating experiment shows a drastic variation of molar composition along the alloy particles. An averaged composition of 61% Cu and 39% Zn was observed for the porous region indicating a severe loss of Zn from the particle [6].

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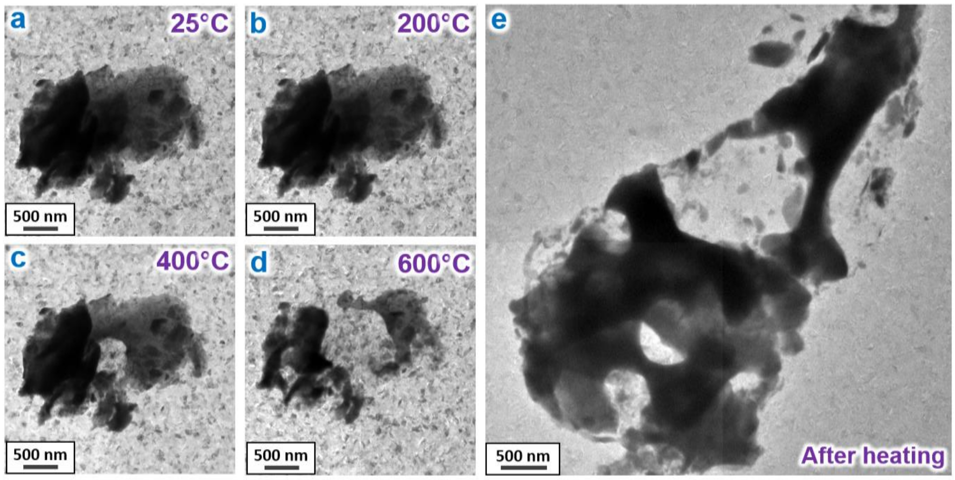

Figure 1. (a-d) BF-TEM images of a γ-brass particle at different temperature. (e) Imaging, after the heating experiment, reveals formation of multiple pores in particles which are larger than the average pore at that temperature/time.

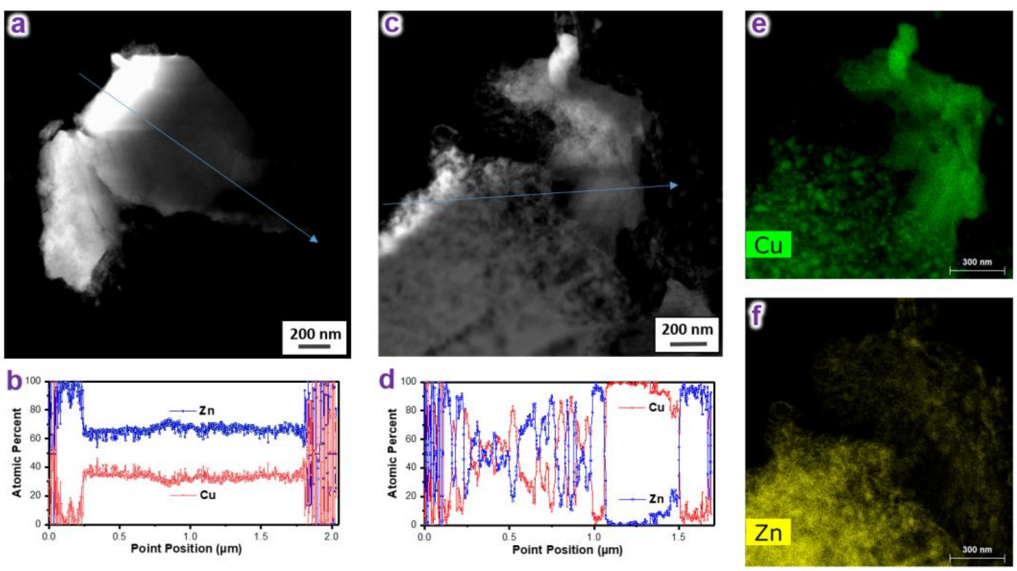

Figure 2. (a) ADF-STEM image showing a typical γ-brass particle before the heating experiment. (b) Quantified EDS line scan along the particle reveals a uniform molar concentration of Cu and Zn in the starting alloy. (c) Heating the alloy, results in formation of bicontinuous, porous morphology, as is evident from the ADF-STEM image. (d) Quantified EDS line scan shows an abrupt change in molar concentration of Cu and Zn at the final stage. (e & f) EDS maps of Cu-K and Zn-K, further, showing the distribution of the elements at the final stage.

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