

## Understanding reduction alloying of core-shell nanoparticles through in-situ powder x-ray diffraction

Robert J. Koch,<sup>1</sup> Guangfang Li,<sup>2</sup> Hui Wang,<sup>2</sup> and Scott T. Misture<sup>1</sup>

<sup>1</sup>Kazuo Inamori School of Engineering, Alfred University, 2 Pine Street, Alfred, NY 14802

<sup>2</sup>Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208

It has been shown in various metallic systems that chemical stability can be tremendously enhanced by alloying with a chemically more inert noble metal. For example, Au-Ag alloy nanoparticles with Au content above the parting limit are remarkably more resistive to oxidative dealloying, chalcogenation, and galvanic replacement corrosion than their monometallic Ag and Au-Ag heterostructured counterparts. The same trend is found in Au-Cu alloy nanoparticles: Au-Cu alloy nanoparticles with Cu atomic fractions below the parting limit (~67% Cu) are resistive to dealloying in the presence of a chemical etchant, while those with Cu content above the parting limit tend to form spongy nanoframes in the presence of a chemical etchant.

The nature of this compositional based stability is not yet clear. To establish a deeper understanding of this system, this study focuses on the formation of  $\text{Au}_x\text{Cu}_{1-x}$  random alloy nanoparticles through reduction alloying of Au-Cu<sub>2</sub>O core-shell nanoparticles. In-situ powder x-ray diffraction was used to track the reaction establish a pathway for the formation of  $\text{Au}_x\text{Cu}_{1-x}$  random alloys as a function of Cu/Au ratio (Cu/Au = 1/3, 1, and 3). It was found that, independently of composition, the reaction occurs through a complex and concurrent process of reduction, multi-phase nucleation and transformation, and multi-step alloying. Through line-profile analysis, phase formation, relative Cu content, average crystal domain size, and stacking defect content are tracked for each phase as a function of temperature. Careful analysis of the line profiles provides new insight into the complex diffusional processes that occur in-situ, as well as demonstrating that these systems change on cooling. In addition, the study has shown the mechanisms by which the nanostructures of the spongy nanoframe precursor particles are formed, and we find that in all but the Au rich phase, weak, highly broadened intermetallic peaks remained even after cooling. This partial ordering provides some explanation of the reduced stability of the Cu-rich compositions.