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In Situ TEM Heating Study of Cu and Ag Nanoparticle Interaction

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Nanoparticles (NPs) possess unique properties in comparison to their bulk counterparts. For example, the melting point of metallic NPs is typically lower than that of the material in bulk due to their high surface area to volume ratio. The phenomenon of melting temperature suppression has led to new applications such as new joining techniques that bond at lower processing temperatures but remain viable at higher temperatures [1]. However, further development and optimization of such techniques requires detailed knowledge of the controlling interactions between metallic NPs. Several recent studies have used *in situ* transmission electron microcopy (TEM) to study interactions amongst single NP types at elevated temperatures [2, 3]. However, no work to date has been reported on *in situ* TEM heating studies of dissimilar NPs.

In this work, we have studied the reaction processes and associated atomic mechanisms of Cu and Ag NP interactions via *in situ* TEM heating experiments using the Protochips Aduro^{TM} *in situ* heating stage, which is capable of extremely fast heating and cooling rates (1000^{o}C/s). These experiments were performed in an aberration-corrected scanning TEM (AC-STEM) (FEI Titan^{TM} G2 80-200) equipped with SuperX energy-dispersive X-ray spectroscopy (EDS) (i.e., quadruple windowless silicon drift EDS detectors), which was used to follow the compositional change throughout the Cu-Ag NP interaction. Experimental results were coupled with atomic-scale molecular dynamic (MD) modeling to further elucidate the reaction mechanism.

Figure 1a shows the Cu-Ag NPs deposited on a carbon film prior to heating. The as-prepared Cu and Ag NPs have sizes of about 15 nm and 6 nm, respectively. Our results show that thermal heating at a temperature as low as 300^{o}C (well below the respective melting temperatures) can induce significant interaction between Cu and Ag NPs. An example is shown in Figure 1b where thermal annealing by a heat pulse of 60s at 300^{o}C, without simultaneous electron beam exposure, has led to changes in particle size and morphology, and formation of a Cu/Ag interface in some particles. In contrast, areas that were exposed to the electron beam during the same heat pulse showed no visible changes (Figure 1c). This discrepancy is believed to be due to the formation of a graphitic shell on the NPs under electron beam exposure [4]. The effect, however, makes it difficult to observe the initial stage of the interaction, which is critical for alloy formation.

The resulting microstructure of the interaction at 300^{o}C was studied by STEM-EDS spectral imaging. Figure 2 shows the result of EDS mapping. The Cu/Ag interface reveals a sharp transition from Cu to Ag, as expected due to limited mutual solubility. However, the Cu atoms appear to surround the Ag particles (Figure 2d), forming a Cu-shell and Ag-core structure. Further work is underway to understand the phenomena [5].

References:

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[5] Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the US Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

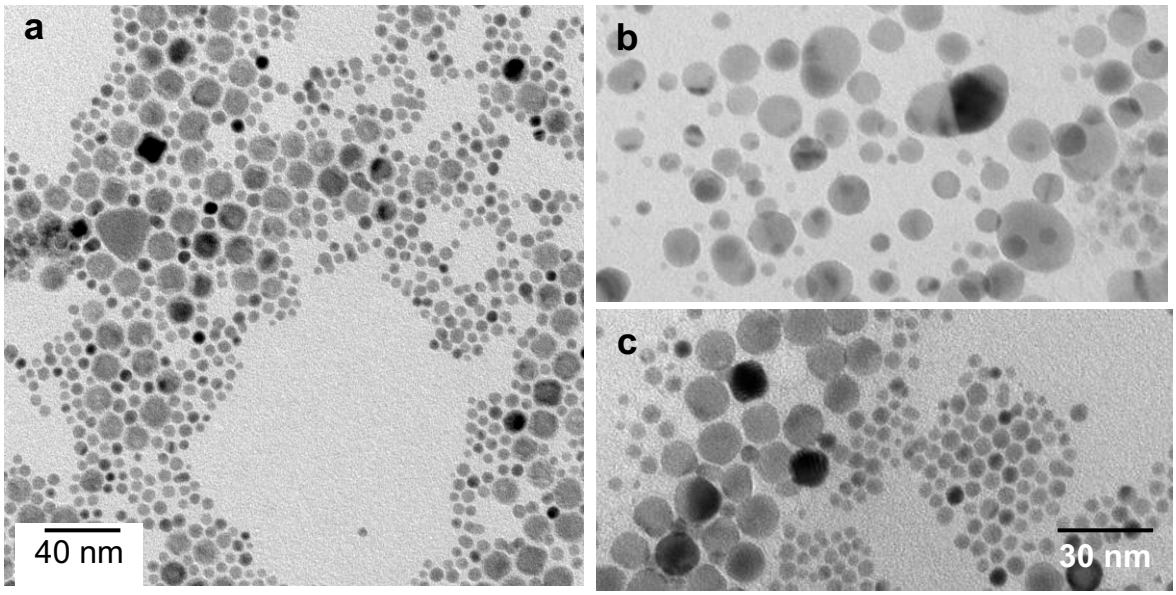

Figure 1: TEM micrographs showing (a) mixture of Ag-Cu NPs deposited on carbon film before heating; (b) an area after 60 second, 300°C heating without electron beam exposure during the heating; and (c) an area after 60 second, 300°C heating but with electron beam on during the heating.

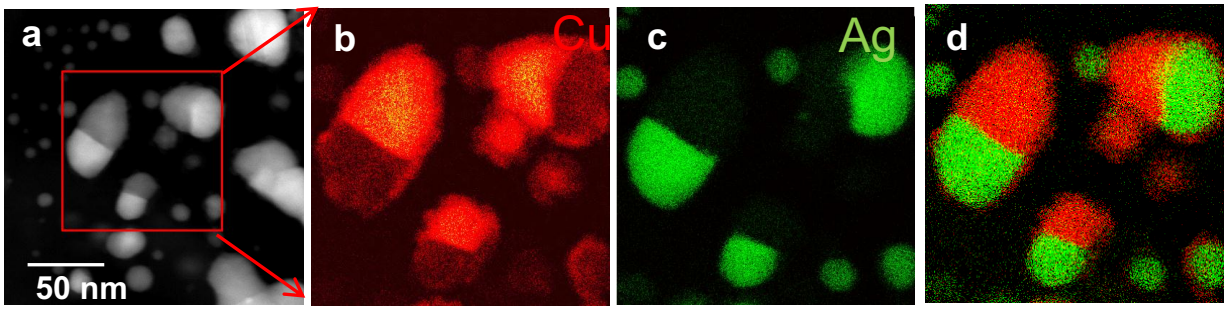

Figure 2: (a) HAADF imaging showing an area used for EDS compositional map; (b) EDS map of Cu (K_α) and (c) EDS map of Ag (L_α and L_β), and (d) composite map of Cu and Ag.

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