Quantifying the Composition and Size of Bimetallic Clusters

Aaron C. Johnston-Peck[1]

[1.] Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD USA

The ability to determine the number and type of atoms in a cluster is useful in the pursuit to establish structure-property relationships. Au and AuAg clusters were characterized using scanning transmission electron microscopy. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images normalized to the incident beam intensity can be used for quantitative analysis [1]. A simple method to interpret the image intensity is to assume the scattering cross section of the cluster (σ_C) is the equal to the linear combination of the scattering cross section (σ_{atom}) of a single isolated atom; therefore, the number of atoms in a cluster (n) becomes $\sigma_C = n\ \sigma_{atom}$ [2]. For clusters containing multiple elements this relationship becomes $\sigma_C = n \sum \sigma_{atom,i}\, \chi_i$, where χ is the atomic percent of each respective element.

Using multislice calculations simulated datasets were generated from which the scattering cross sections of clusters were normalized by the scattering cross section of single atoms thereby probing the validity and limits of this linear model. Relevant sample and microscope parameters were systemically adjusted. Clusters with an octahedron geometry were stimulated. Varying sizes, compositions, orientations, and degrees of disorder (thermal and static) were considered. Differing lens aberrations as well as convergence and collection angles were also tested. Examples of these results are shown in Figure 1. It was found that the linear model can provide accurate quantification of size (n) but only under specific conditions. This linear model becomes inaccurate when microscope and sample conditions promote electron channeling. Therefore, it is best suited for small clusters, those that are oriented away from a crystallographic zone axis or are disordered. Such conditions were present in the materials analyzed and it is expected that the method of image analysis is not the dominate factor in determining the accuracy of the quantification but other experimental constraints such as noise or sample instability.

Au and AuAg clusters were synthesized using wet chemistry techniques using a procedure designed to produce clusters containing nominally 25 atoms. A single image is adequate to quantify the number of atoms in a single element cluster. An example HAADF image of Au clusters is shown in Figure 2. When analyzing bimetallic (or one containing multiple elements) clusters a data set comprised of a single image is underdetermined and no longer contains sufficient information to quantify both the total number of atoms and the fraction of each element. To address this limitation sampling of the cluster scattering distribution was increased. This was performed by: (1) acquiring multiple HAADF images using different camera lengths thereby changing the collection angles; (2) using 4D-STEM to acquire the scattering distribution at each point of the raster. By using these approaches AuAg clusters were quantified to determine both number of atoms and composition. Discussion on the limitations and sources of errors in these approaches will be presented.

References:

[1] JM LeBeau and S Stemmer, Ultramicroscopy **108** (2008), p. 1653
[2] A Singhal, JC Yang, JM Gibson Ultramicroscopy **67** (1997), p. 191

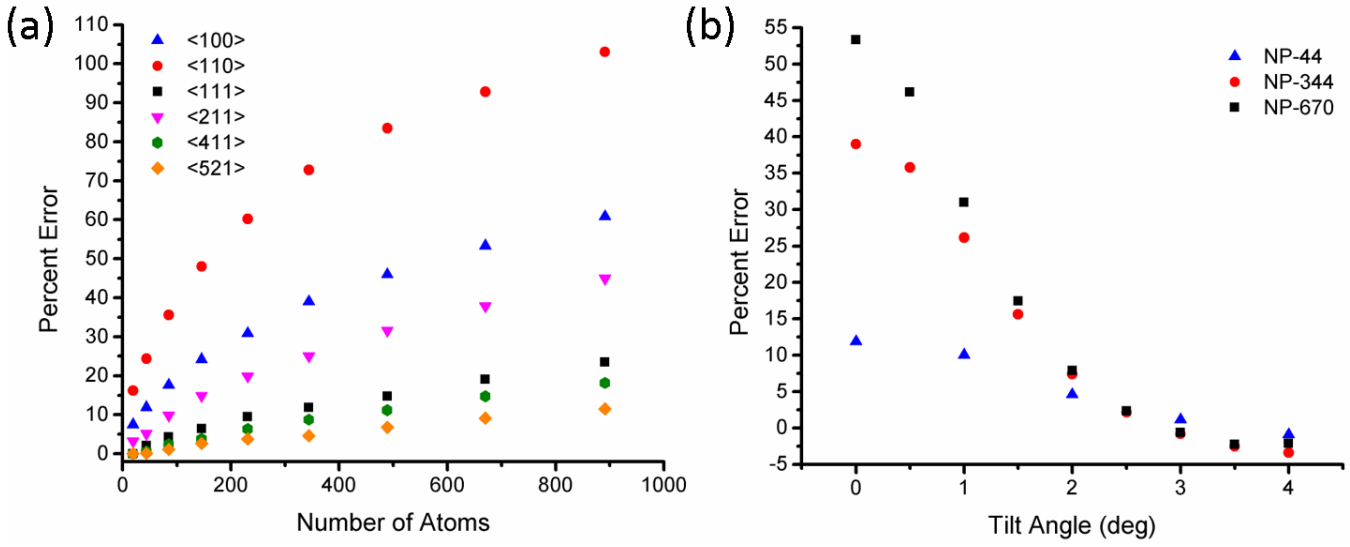

Figure 1. Simulated datasets were used to establish error in the linear model as a function of different parameters. Percent error as a function of number of the atoms in the cluster, several different orientations were considered (a). Percent error as <001> oriented clusters are tilted away from the zone axis, clusters containing 44, 344, or 670 atoms were simulated (b). Percent error is defined as the number of atoms calculated using the linear model versus the number of atoms in the supercell used for multislice calculations.

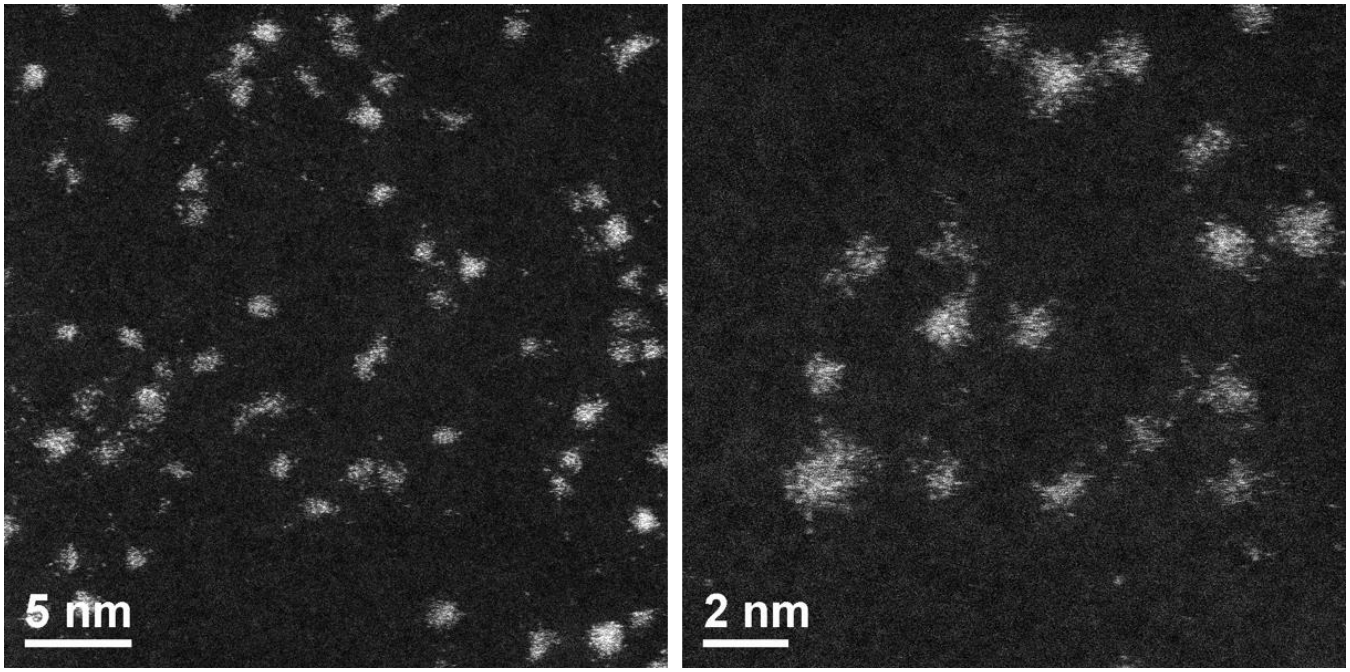

Figure 2. HAADF-STEM images of Au clusters.