

Quantitative Composition Measurements of Atomic Columns Using STEM; Application to L1₂ Precipitates

C Ophus¹, A Gautam¹, E Marquis², U Dahmen¹ and V Radmilovic¹

¹ National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA

² Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI

Accurately determining the local composition of extremely tiny structures is an ongoing area of intense research in materials science. Determining the positions of light elements, in particular Li, with atomic accuracy is becoming increasingly crucial as research into energy savings leads towards more efficient batteries, lighter structural materials and more effective catalysts. In this study, we demonstrate a simple technique to measure mean column composition in a crystal from a high angular annular dark field (HAADF) micrograph taken with a scanning-transmission electron microscope (STEM) using adjacent columns as a local calibration.

Imaging lithium and other light elements have traditionally proven difficult to accomplish in transmission electron microscopy (TEM). High resolution, high sensitivity and (relatively) thick samples are required to image a column of pure Li [i,ii]. In a HAADF micrograph, resolving light elements is even more difficult. This is because on a low-index crystallographic zone axis the scattering intensity I at high angles depends on the atomic charge z in a column of N atoms as

$$I \propto (Nz)^\beta \quad (1)$$

Where β is a constant between 1.6 and 2 [iii]. This dependence naturally suggests the usefulness of comparing the intensity ratios of adjacent columns. Indeed, other authors have used “column ratio mapping” to analyze structural boundaries [iv]. The column intensity ratios can also be used to determine column composition. Consider two columns with mean charges z_1 and z_2 having respective intensities of I_1 and I_2 . Using Equation (1) we can solve for the ratio of a charges as a function of the intensities ratios:

$$\frac{z_2}{z_1} = \left(\frac{I_2}{I_1} \right)^\beta \quad (2)$$

To show the usefulness of this technique, we have applied it to core-shell precipitates in an AlLiSc alloy. More information on the preparation and characterization of this alloy is given in [v]. A HAADF micrograph showing the precipitate morphology is shown in Figure 1(a). The entire precipitate has a contiguous L1₂ structure, coherent with the surrounding fcc aluminum matrix. Each unit cell contains three columns of pure Al, and a fourth column of Li, Sc or a mix of Li and Sc. The overall composition of the precipitates has been determined with atom probe tomography (APT). A 3D map of Li and Sc positions is given in Figures 1(b) and (c). A representative composition profile is plotted in Figure 1(d). We see that the precipitate shell is pure Al₃Li, where as the shell has a composition of Al₃(Li,Sc). Knowing the composition of the core and the ordering on the LiSc sublattice is critical in understanding the kinetic formation of these precipitates as well as their mechanical properties. However, the APT data does not provide accurate *local* compositions; only mean values.

To measure the local column composition, we use intensity ratios taken from HAADF micrographs of the precipitate cores. Each (Li,Sc) column has a mean atomic charge of $3(1-x_{Sc}) + 21x_{Sc}$ per atom, where x_{Sc} is the fraction of Sc present in the column. The Al columns have a charge of 13 per atom. Substituting these two charges into Equation (2) and solving for the composition gives

$$x_{Sc} = \frac{13}{18} \left(\frac{I_{LiSc}}{I_{Al}} \right)^{1/\beta} - \frac{1}{6} \quad (3)$$

The intensity of each (Li,Sc) column is compared against the mean intensity of the eight surrounding Al columns. Because the TEM foils are very flat, each column will have a thickness very close to that of its neighbors. Equation

(3) will therefore be approximately valid for any film thickness, since only local Al columns are used for the calibration. The value of β is determined for our experiments from multislice simulations [iii]. Figure 2(a) shows a series of column intensities measured from a HAADF similar to Figure 1(a). We then solve for the composition of each (Li,Sc) column, shown in Figure 2(b). The mean measured composition of 15.5 at.% Sc agrees very well with the mean value measured with APT, shown in Figure 1(d). This technique is thus very promising for interpreting HAADF results [vi].

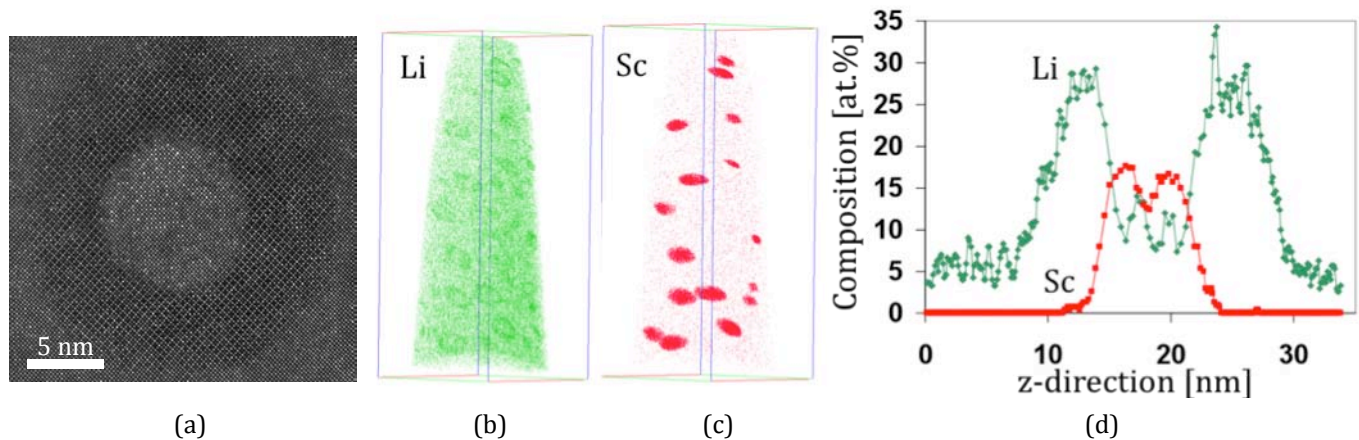


Figure 1 – (a) HAADF micrograph of a core-shell L12 precipitate in an AlLiSc alloy. 3D map of (b) Li and (c) Sc positions recorded by APT. (d) Z-direction line profile of mean Li and Sc compositions recorded from a single particle in (b) and (c).

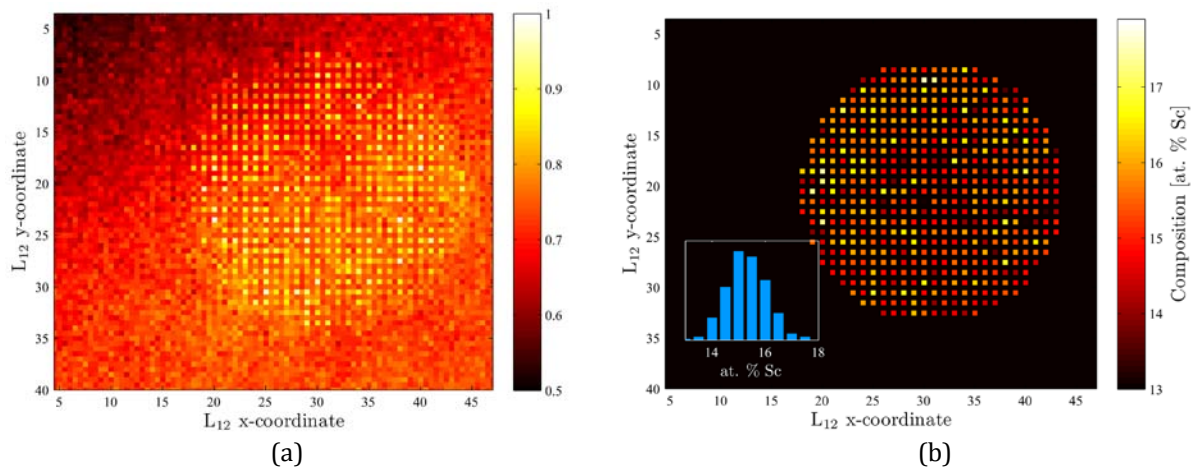


Figure 2 – (a) Peak intensities of a precipitate core measured from a HAADF similar to Figure 1(a). (b) Compositions of the Li-Sc columns in a precipitate core, with histogram inset.

References

- [i] Y Shao-Horn, L Croguenne, C Delmas, EC Nelson and MA O-Keefe, *Nat Mat* 2 (2003) 464.
- [ii] MD Rossell, R Erni, M Asta, V Radmilovic and U Dahmen, *Phys Rev B* 80 (2009) 024110.
- [iii] EJ Kirland, *Advanced Computing in Electron Microscopy*, Plenum, New York 1998.
- [iv] PD Robb and AJ Craven, *Ultramic* 109 (2008) 61.
- [v] V Radmilovic, C Ophus, E Marquis et al., *manuscript submitted to Nat Mat*.
- [vi] This research was supported by the US Department of Energy under Contracts # DE-AC02-05CH11231 and DE-FG02-06ER46282 (MA). CO would like to acknowledge the NSERC Canada for funding.