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HREM and HAADF Imaging of Al_3(Sc, Zr) Core/Shell Structure

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Core-shell particle structures have received considerable recent attention because it has been demonstrated that the core properties can be significantly altered by the shell [1,2]. The majority of research in this field has concentrated on free standing particle systems with or without ordering in two or three dimensions [1,2]. Recent work on Al-Sc-Zr alloys [3] has shown that a core-shell structure may also be responsible for the modification of properties in a precipitate-hardened alloy system. It was demonstrated that the precipitates contained Sc and Zr, but that the distribution of Zr was not homogeneous. Instead, a Zr rich shell surrounded an Al_3Sc core. In this report we use the compositional sensitivity of *Z*-contrast imaging to show that the addition of Zr to an Al-Sc alloy leads to formation of a complex Al_3(Sc,Zr) core/shell structure.

The microstructure of an Al-Sc-Zr alloy has been investigated by a combination of conventional high-resolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive spectroscopy (EDS). The HRTEM micrograph in Figure 1A illustrates that the core of the precipitate exhibits contrast very similar to that of the matrix, although superlattice reflections were confirmed for most particles investigated. This is consistent with the results of Marquis and Seidman [4]. High-resolution Z-contrast images (Figures 1B and 2A) show that the highest contrast occurs at the Al_3(Sc,Zr)/Al matrix interface and that the contrast in the core is substantially higher that in the surrounding Al-rich matrix. It is also apparent that the precipitate is ordered, since only every other {002} plane is occupied by the heavy Sc or Zr solute atoms in the $L1_2$ structure, resulting in a fringe periodicity of 0.405nm (Fig. 1B). Since the HAADF-STEM images in Figs. 1B and 2A are obtained using collection angles between 60 and 100 mrad, the observed contrast can simply be interpreted in terms of differences in atomic number, i.e. the difference in Sc and Zr concentration in the core and shell of Al_3(Sc,Zr) precipitates. Employing the simple correlation $\sigma \sim Z^\beta$, where σ is intensity, Z the atomic number and β a constant, and using the surrounding Al matrix as an internal standard, it is possible to estimate the Sc and Zr content in the core and shell of this precipitate as shown in the table below.

Intensity-Experimental [arb. units]		Atomic number	Composition
Al	85	13	Al
Al_3(Sc,Zr) core	135	17	$Al_3(Sc_{.94}Zr_{.06})$ core
Al_3(Sc,Zr) shell	170	19.5	$Al_3(Sc_{.03}Zr_{.97})$ shell

These results are in fairly good agreement with our spot EDS analysis of 5.5% Sc and 18.3%Zr in the shell and 0.54%Sc and 18.2%Zr [at. %], indicating rapid initial formation of a Sc rich Al_3(Sc,Zr) core followed by formation of a Zr rich Al_3(Zr,Sc) shell. The Zr rich shell acts as a diffusion barrier and consequently modifies the growth rate of the Sc rich core [5].

References

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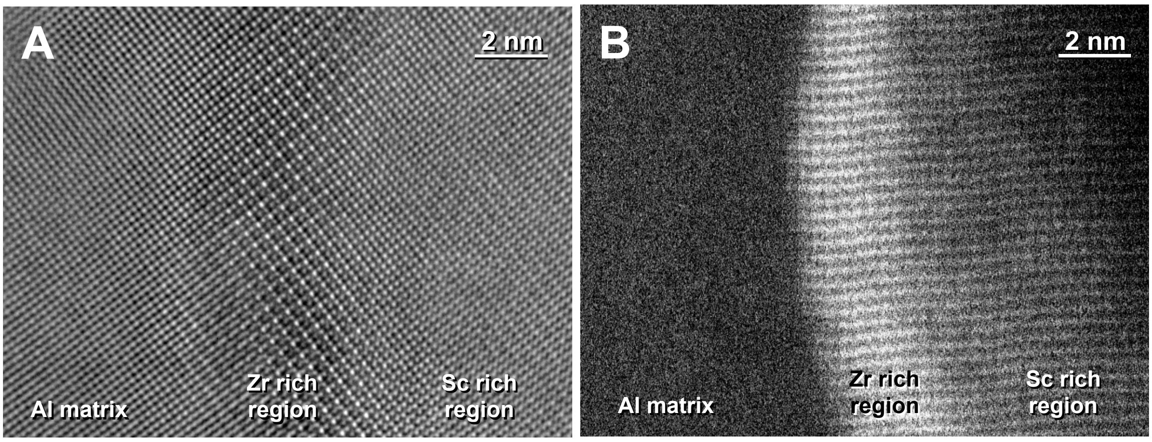

FIG. 1. (A) High resolution electron micrograph of cubic $Al_3(Sc,Zr)$ and (B) HAADF-STEM image obtained from a similar particle. Z-contrast appears as bright shell in (B), indicating Zr segregation.

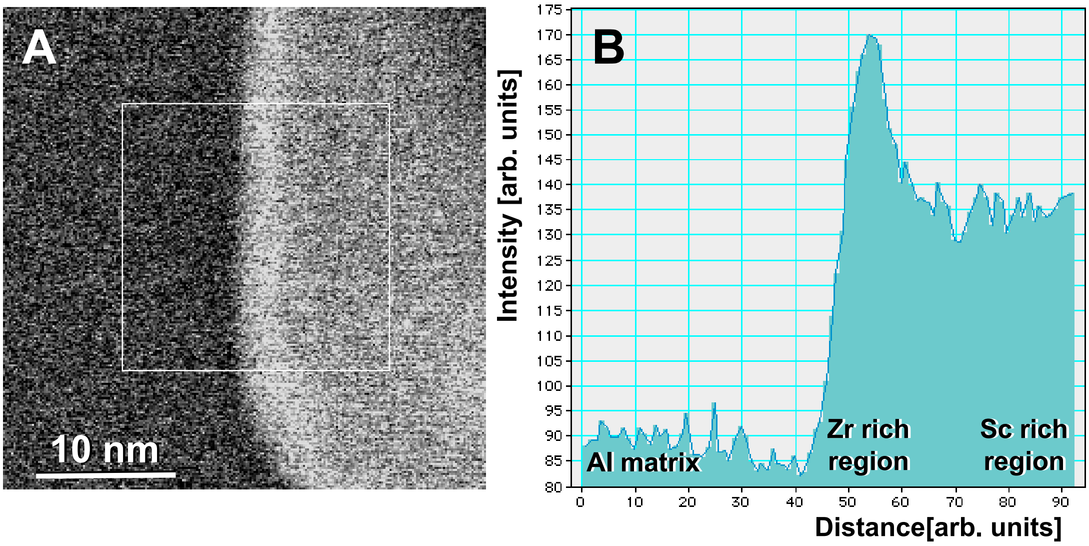

FIG. 2. (A) HAADF-STEM images and (B) Integrated Z contrast profile from the region indicated in (A). The tail in the shell intensity profile probably indicates a diffuse interface due interdiffusion of Zr and Sc across the core/shell interface.

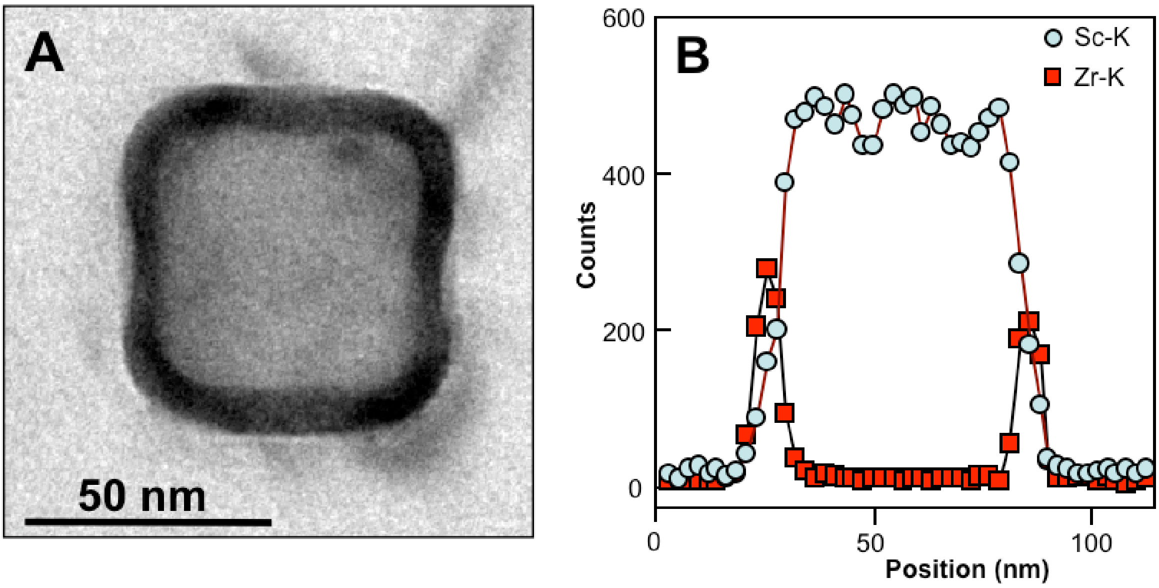

FIG. 3. Bright field image (A) and composition profile (B) measured across the particle in (A).