Quantifying Ordering Phenomena Through High-Resolution Electron Microscopy, Spectroscopy, and Simulation

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Advances in aberration corrected scanning transmission electron microscopy (STEM) have allowed researchers to investigate structure-property relationships at the atomic scale [1–4]. In many systems, ordering phenomena at the atomic level can have a dramatic impact on the structural, electronic, and magnetic properties of the material. By combining experiment, simulation, and data processing, these ordering phenomena can be studied in a quantitative way, opening the door for new insights into the structure-property relationships of a wide variety of material systems. Experimentally, high angle annular dark field (HAADF) STEM and energy dispersive X-ray spectroscopy (EDX) are two very powerful techniques for probing compositional variations at the Ångstrom scale. In order to fully understand and quantify these techniques, image simulation and ionization calculations using the quantum excitation of phonons model can be used [5,6].

For the first time, using a double aberration corrected FEI Themis™ with a Super-X™ XEDS detector compositional mapping of a Ni-based superalloy (commercially available HL-11) was collected at atomic resolution across a stacking fault, as seen in Figure . Individual spectra in the atomic resolution XEDS maps exhibit low signal-to-noise, usually having very few counts per channel. Based on previous characterization of the fault structure determining structural periodicity[4], the data was summed over a repeating unit cell of the fault structure along the [110] projection, resulting in almost an order of magnitude increase in the peak maxima of the XEDS spectra and even larger increase in integrated peak counts. These modified 3D data cubes were then fed into the Bruker Esprit software package and quantified using experimentally determined Cliff-Lorimer k-factors from a solutionized sample of the same material. By preprocessing these data before quantification, the error in the quantification was significantly reduced, allowing for site-specific determination of solute segregation in and around the fault structure in this Ni-based superalloy, leading to the determination of a novel high temperature strengthening mechanism.

In addition to using spectroscopy to quantify compositional variations at the Ångstrom scale, there have been many reports of using HAADF-STEM images to quantitatively understand ordering phenomena [7–9]. Double perovskite thin films with the general formula $A_2BB'O_6$ have been studied extensively for their interesting electronic and magnetic properties [10–12]. These properties, however, can be highly dependent on the degree of cation ordering, especially B and B′ atoms due to superexchange between them across bridging O atoms [10]. A structural characterization of Sr_2CrReO_6 (SCRO) films was performed using HAADF-STEM imaging and diffraction leading to the identification of highly prevalent antiphase domains. To further confirm these findings images and diffraction patterns were simulated for SCRO models with antiphase domains present.

Extending the use of simulation, the effects of atomic-scale ordering on HAADF-STEM image intensity were characterized. The results of these simulations indicate that the commonly held $\sim Z^{1.8}$ dependence of intensity in HAADF imaging is also sensitive to variations in atomic ordering along the column parallel to the beam. We report that columns of the same mean square atomic number can exhibit

intensities that are upwards of ±20% difference, as seen in Figure 2. These findings are further explained through an in-depth analysis of probe channeling and variations in thickness, as well as different mean square atomic numbers.

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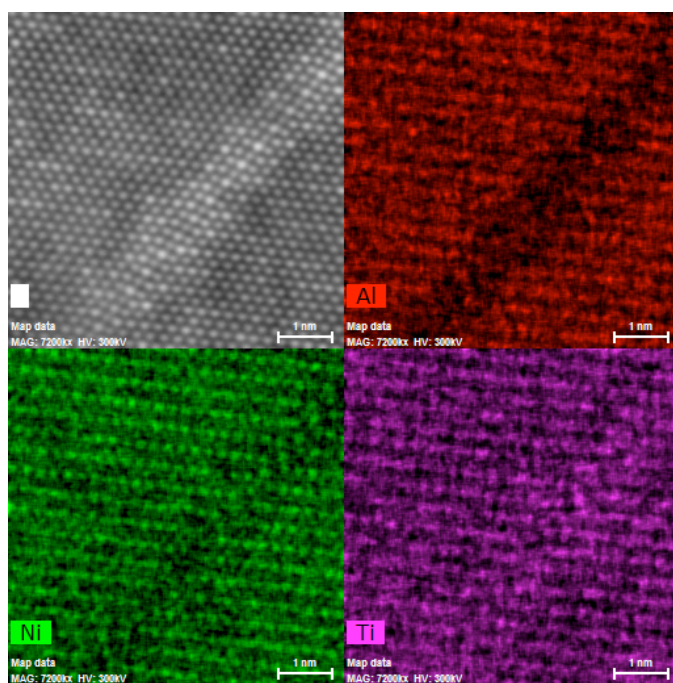
Figure 1: Atomic resolution intensity maps of a fault in HL-11 Ni-based superalloy. HAADF-STEM image shows increased contrast and ordering (top left); Al (red); Ni (green); Ti (magenta); scale bar is 1nm
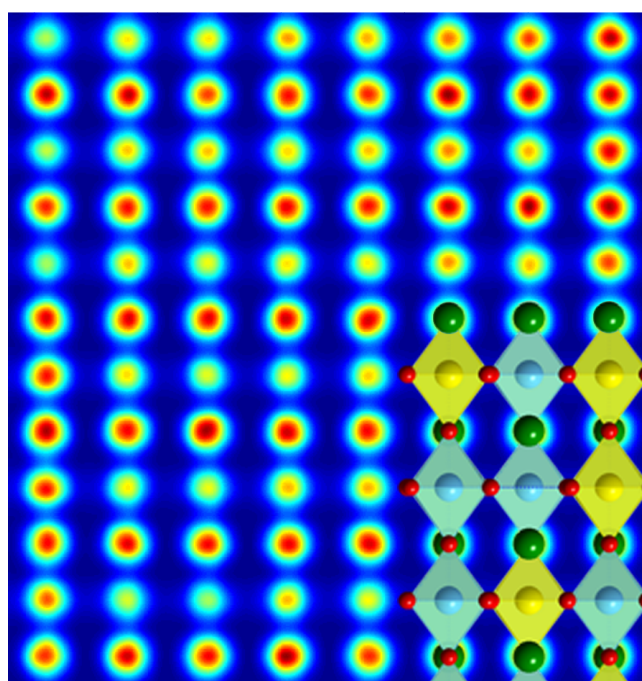

Figure 2: HAADF-STEM image simulation showing variation on the Cr/Re columns (blue and yellow octahedra, respectively) for a model with a constant mean atomic number ($Cr_{0.8}Re_{0.2}$)