Analytical transmission electron microscopy in the third dimension

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Abstract

For researchers in metallurgy, energy storage or functional nanomaterials, where elemental distribution is crucial to performance, full characterization is more difficult by decreasing feature sizes and increasingly complex architectures. Two-dimensional imaging and analytical techniques often cannot characterize nanostructures completely. A new three-dimensional (3D) tomography technique for STEM XEDS, namely ChemiSTEM™ Technology [1], reveals the true microstructure of materials offering high X-ray collection efficiency via its windowless detector design, and fast XEDS mapping with tilt response at all angles. ChemiSTEM features the X-FEG and Super X, containing four symmetric detectors for 3D chemical imaging at 0 degree tilt, with significant EDX signal collected under all tilt conditions. The EDS signal of STEM XEDS image tilt series can be processed like normal z-contrast images, because of the monotonic relationship between the EDS signal and the thickness of the TEM foil. Four symmetrically arranged silicon drift detectors (SDD) provide extreme high output count rates (300 kcps) required for acquisition of EDX maps of thick samples, especially on 3 mm disk samples for 3D tomography studies. Examples of 3D chemical mapping using XEDS are given on (InGa)N Nanopyramid LEDs, Ni based super alloy material for turbine blades, dielectric transistor, and catalytic particles. In lithium ion batteries, the elemental segregation of manganese and nickel, which is responsible for the aging of electrode materials made from lithium-nickel-manganese oxide layered nanoparticles was analyzed in 3D XEDS mapping [2].

1. Introduction

As the feature sizes in material science continues to decrease to the nanometer regime, 3D chemical information is required to improve the function of many materials. STEM tomography is a well established technique in material science to provide 3D structural information, but is failing to provide the necessary chemical information [3-7]. A combination of STEM tomography with XEDS mapping solves the problem. Atomic level chemical measurements [8, 9] benefit from the high brightness of the X-FEG and the reduced probe size, of course supported by the Cs corrected optics in the STEM. And Super X is the only solution that can deliver 3D, nanoscale structural and compositional information on regular 3 mm disk samples.
It is well known that the performance of lithium ion batteries degrades over time. Understanding this behavior requires an understanding of the chemical composition changes that take place during the battery's use. One application example is presented which is showing the advantage of 3D chemical data analyses over the 2D data generation resulting in a better interpretation due to faster acquisition and higher quality data.
ChemiSTEM analysis is used for superalloy material studies enabling the design and development of a jet turbine fan blade by helping to characterize the physical and chemical properties in a S/TEM. To our knowledge, researchers developing new alloys are focused on reducing the weight, and improving oxidation and corrosion resistance while maintaining the strength of the alloy. Furthermore with the increasing demand for the use of superalloys in turbine blades for power generation, another focus of alloy design is to reduce their cost. CMSX-4 superalloy [13], a heat resistant material, was especially designed for gas turbine blades in jet aircraft engines and stationary turbines generating electricity and investigated for the elemental distribution of the different components.

2. Experimental data

Chemical analysis in TEM has been initiated by extracting a site specific thin lamella from a superalloy material using FIB lift out technique on the FEI Helios SDB [10]. Available on FEI's Tecnai Osiris™, Talos™ and Titan™ G2 S/TEM and Titan™ Themis™ S/TEM, ChemiSTEM features Super X, a symmetric four detector design that allows 3D chemical imaging at 0 degree tilt, with significant EDX signal collected under all tilt conditions. A signal under all tilt conditions is mandatory to acquire 3D EDS maps. An example is the sub-set of Ni elemental maps acquired from a Li ion battery cathode material in the tilt range of ∓70 degrees, see Figure 1. Fast mapping electronics are capable of 100,000 spectra/second in EDX spectrum imaging. On Titan Themis, atomic chemical EDS maps can be measured with 500 spc/ sec. High speed processing provides the extreme high output count rates (300 kcps) required for acquisition of EDX maps of thick samples, especially on regular 3 mm disk samples for 3D studies. The experimental parameters for the studies of the Li battery specimen are described elsewhere [2]. The EDS tomography experiments of the Ni-based superalloy were acquired on the microscope at 200 kV acceleration voltage with a probe current of ~1.05nA in STEM mode at a nominal magnification of 56000 x. The total pixels 512 x 512 pix^2 with a pixel size of 3.60 nm result in a total image size of 1.84 um with an exposure time of 15 seconds. The dwell time for the EDS mapping is 50 usec. The reconstruction was performed with the software Xplore3D, mode: simultenous iterative reconstruction technique (SIRT) and visualized with the software Avizo Fire 7.0.

3. Results

FEI's ChemiSTEM Technology provides 3D chemical mapping with directly interpretable 3D structural and chemical compositional information, all crucial for materials scientists to better understand the properties of complex 3D nanostructures. Nowadays, sensitive detectors as the XEDS Super X enable the required signal strength for faster time to get high quality data. The time which was needed in the past for measuring static, two dimensional information can be the same but now providing an additional dimension in 3D. The advantage of rapid data acquisition is to expose the specimen area of interest minimal and beam sensitive samples can withstand the damage under the electron beam. The quality of data is improved by the X-FEG due to its stable long term (important for tomography) and short term (vital for ultrafast imaging and spectroscopy) emission current within a ≤ 1 % range.
The EDS signal of STEM XEDS image tilt series can be processed like normal z-contrast images, because of the monotonic relationship between the increasing EDS signal as a function of the thickness of the TEM foil. Total EDS signal behaves like Z-contrast, if you compare the intensities

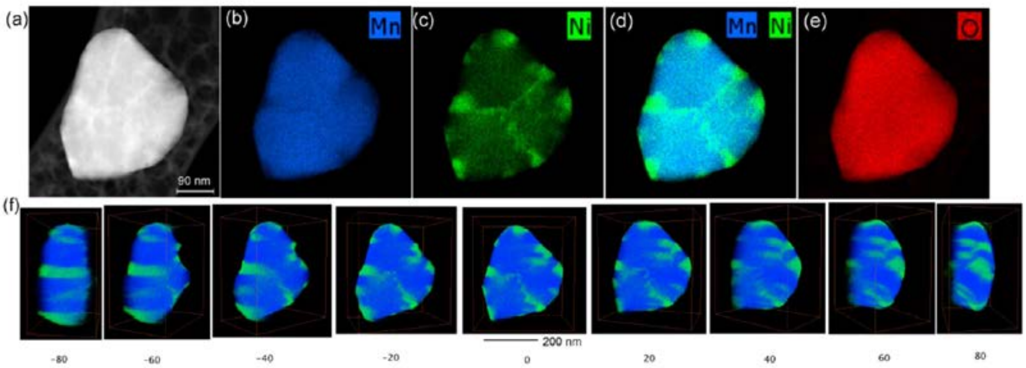

Figure 1 The STEM tomogram and corresponding elemental chemical maps, namely for Mn, Ni, Mn and Ni and O, were acquired from a Li ion battery cathode material [2]. The tilt series of +/- 70 degrees is presented.

and contrast of simultaneously acquired images corresponding to the HAADF signal and the total x-ray signal. The benefits of XEDS approach are that the majority of the elements is accessible via the XEDS signal (above Beryllium). On the one hand the signal increases monotonously with mass thickness while on the other hand the Peak-to-Background (P/B) ratio is independent and not varying with the sample thickness nor requiring a special sample geometry for investigation.

In the first application example, FEI's ChemiSTEM Technology was used to collect 2D and 3D chemical maps, see Figure 1, of a lithium ion battery [2, 11]. 3D EDX was applied to different parts in the battery to reveal the nanoscale chemical changes occurring during battery use. This technique has made it possible for the first time to observe the aging of electrode materials made from lithium-nickel-manganese oxide layered nanoparticles. What is now seen is that nickel segregation occurs, blocking the channels through which lithium normally travels during the charge-discharge cycle of the device.

The ability to characterize superalloy material and their design with 2D and 3D chemical analysis using FEI's ChemiSTEM Technology was critical to understand and successfully optimize micro-structures of gas turbines. Partition of alloying elements within the γ/γ' microstructure of the Ni-based superalloy is extremely important and defines the mechanical properties of the superalloy at high temperatures [12]. The 3D chemical information revealed necessary information to improve their performance, life time and efficiency.
The first single crystal CMSX-4 nickel-base superalloy (Figure 2) features a very complex chemical composition containing Ni – 8.4 Co – 6.4 Cr – 6.5 Ta – 6.4 W – 5.68 Al – 2.8 Re – 1.04 Ti – 0.58 (in wt %). The microstructure of the single crystal superalloys consists of a high volume fraction of cuboidal γ' precipitates surrounded by γ matrix channels with nanometric width and different chemical composition. The γ' precipitates are an ordered Ni_3Al-base intermetallic phase (Pm m) with the lattice parameter $a_{\gamma'}$ = 0.35718 nm which is only slightly smaller than that of the Ni base 3 solid solution (Fm m), $a_{\gamma'}$ = 0.3524 nm. EDX microanalysis of the γ and γ' phases allowed identification of the chemical variation with nanometer resolution and enabled detection at the highest intensities even from elements with low concentrations.

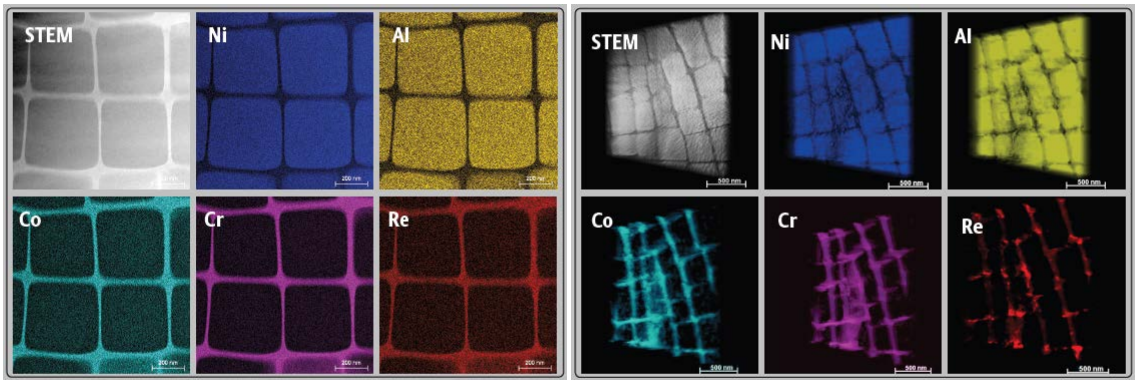

Figure 2 Comparison of 2D (left) and 3D (right) reconstructions of HAADF STEM and STEM XEDS intensities of Ni, Al, Co, Cr and Re. The 3D chemical mapping simply resolves the true structure of the material and reveals the 3D distribution of the individual elements through the the thickness of the TEM foil.

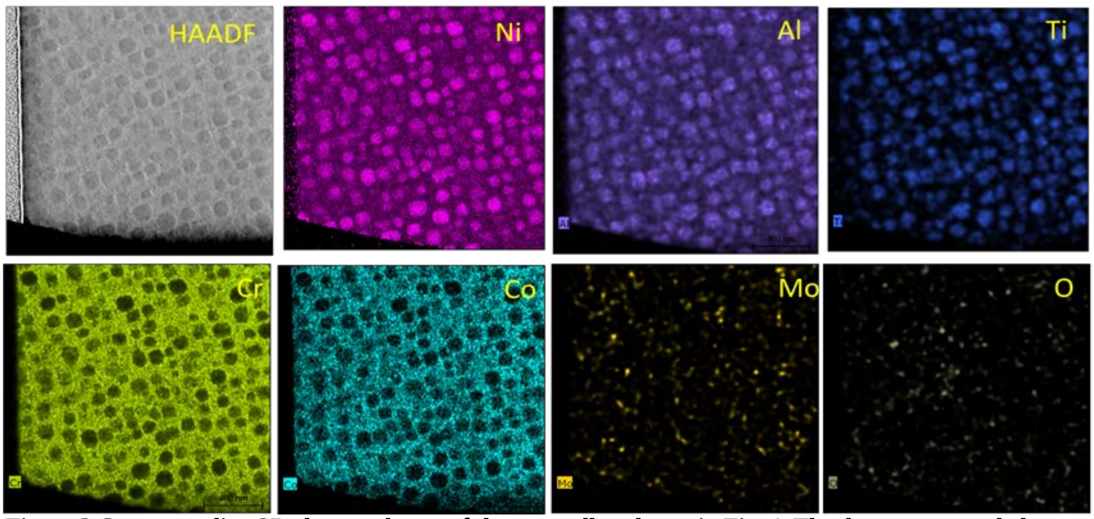

Figure 3 Corresponding 2D elemental map of the superalloy shown in Fig. 4. The data was recorded on a S/TEM with ChemiSTEM^{TM}.

The chemical composition of the other superalloy specimen is also very complex and contains Ni, Al, Ti, Cr, Co and Mo. The microstructure of single crystal superalloys consists of a higher volume fraction of cuboidal γ' precipitates, an ordered Ni_3Al-base intermetallic phase, surrounded by matrix channels with nanometric width [12]. XEDS microanalysis of the γ and γ' phases chemical composition is acquired with a few nanometer resolution on a superalloy heat treated to breaking point at 1150 °C. The results of STEM-EDX tomography (Figure 3) are compared to the 2D elemental maps (Figure 4) showing the advantage of this new technology in the accurate analysis of three dimensional elements distribution in a super alloy in both γ and γ' phases. There is no Oxygen observed on the surface indicating that no oxidation occurred. However, further investigations are necessary to accompaign the result quantitatively.

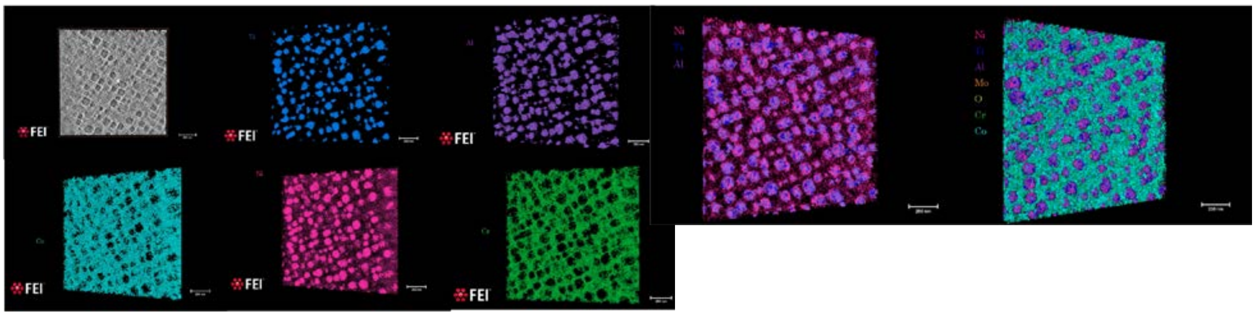

Figure 4 Corresponding 3D chemical tomograms to Figure 3 of the superalloy containing Ni, Al, Ti, Cr, Co and Mo. This comparison also depicts the superior chemical sensitivity of STEM XEDS tomography over conventional HAADF STEM tomography in a multi-component system resulting in the finding that there is no oxidation on the surface.

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