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QUANTITATIVE IMAGING OF LITHIUM IN ALUMINUM-LITHIUM ALLOYS

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Abstract

The detection and quantification of Li on a sub-micron scale is a challenging microanalysis problem, but essential to the interpretation of the microstructure of Al-Li base alloys. Recent developments in data collection and analysis have permitted quantitative elemental images of Li to be obtained with a spatial resolution of < 100 nm through the technique of scanning ion microscopy (SIM) which gives quantitative images of the Li distribution in bulk specimens. Alternatively, electron energy-loss spectrometry (EELS) of thin (electron-transparent) specimens in a transmission electron microscope (TEM) offers a spatial resolution of < 100 nm. In the case of EELS, Li can be quantified either through the detection of the ionization of Li atoms or through the measurement of changes in the free electron density of Al due to the presence of Li. However, EELS is limited by the need to prepare extremely thin specimens. SIM is more difficult to quantify than EELS but offers rapid data acquisition and relatively easy specimen preparation. SIM can easily be applied to multi-element commercial alloys and composites, and both techniques can be applied to elemental imaging of other light elements commonly found in Al alloys and metal-matrix composites such as Mg, C and O.

Introduction

Light element microanalysis is difficult to carry out because the traditional technique of x-ray microanalysis is extremely limited when seeking elements below Na in the periodic table and cannot detect elements below Be. For the aluminum alloy metallurgist, therefore, x-ray analysis of Li is impossible and study of other elements of interest such as C and O are particularly difficult. Therefore, non-traditional techniques are required, but if these techniques are to be useful, they must exhibit high spatial resolution and/or high analytical sensitivity combined with quantification. For microanalysis of all the elements, including the light elements, the best approach, in the opinion of the authors, is to combine microanalysis with digital imaging in the form of compositional images or maps (e.g. see Lyman [1]). Microanalysis in this form is also a microscopy technique, since high magnification elemental images are produced. This is a crucial advantage of mapping since it facilitates a one-to-one comparison between any composition variations in the specimen and the defect structure, or whatever other features are imaged by the accompanying microscopy techniques. Compositional imaging of the light elements, particularly Li, is the theme of this paper, and will be illustrated with two different techniques.

The technique used for compositional mapping depends on the form of the specimen, i.e. bulk (non-transparent to the radiation) or thin (transparent). The former has the advantage of relatively simple preparation from the parent sample and, consequently, relatively few artifacts. In addition, the sampling statistics are good since a large area of the specimen (many μm^2) is imaged and the

minimum mass fraction is generally ~10-1000 ppm. The price to pay is relatively poor spatial resolution (typically not much less than a micrometer). Thin specimens generally offer high spatial resolution (a few nanometers) and good minimum detectable mass (a few hundred atoms). But thin specimen preparation and the need for a pristine surface are problems which often limit the quality of the microanalytical data.

Microanalysis in the materials sciences aims to relate composition variations to the properties of the material, often revealed through the defects imaged in the microscope. Within this framework, high resolution is not the only criterion for good microanalysis. For example, mechanical properties could just as easily be controlled by the chemistry of micron-sized inclusions (e.g. short-transverse toughness) as by nanometer-level Gibbsian segregation (e.g. temper embrittlement). So the best approach is to exercise all the necessary techniques to span the spectrum of low-resolution, high-sensitivity bulk microanalysis to high resolution, specimen-preparation limited thin-foil techniques. This paper discusses two techniques which span this range of analytical requirements.

Compositional Imaging of Bulk Specimens

Principles of Scanning Imaging/Mapping

More than thirty-five years ago Cosslett and Duncumb [2] introduced the idea of x-ray dot mapping using wavelength-dispersive spectrometry (WDS) in the electron-probe microanalyzer (EPMA). This concept was a development of the basic SEM image-forming system. In dot-mapping, the scanning beam on the CRT display is modulated in intensity by the strength of the characteristic x-ray signal detected from a given element in the specimen which is being scanned synchronously by a high energy electron beam. The x-ray mapping technique developed slowly but with the advent of x-ray energy-dispersive spectrometry (EDS) in the early 1970s, qualitative multi-element mapping became common. Now with digital beam control and the associated computer technology, quantitative EDS and WDS mapping are a reality (Newbury [3]). Light element mapping of this kind is also possible, but generally more difficult to quantify because of problems such as strong x-ray absorption as already described. However, the concept of Cosslett and Duncumb formed the basis for all subsequent scanning imaging processes, in particular, the scanning ion microscope (SIM), which creates images from ions separated through a secondary ion mass spectrometer (SIMS) in a manner which is described below.

Secondary Ion Mass Spectrometry (SIMS) and Scanning Ion Microscopy (SIM)

Ion microscopy in general is based on the principles of SIMS (e.g., Benninghoven et al. [4], Czanderna and Hercules [5]) and has traditionally been the broad-beam, analog form which gives image resolutions of the same order as the EPMA (~1 μm) (see Figure 1). These images are quantified on the basis of a working curve [6] relating the SIMS signal from a specific ion species (Li^+) to the known content of that species in a standard specimen. New liquid metal (e.g. Ga) ion sources produce high brightness, small diameter ion beams that are capable of putting reasonable imaging currents into <50 nm probes. Under these circumstances, it is possible to produce SIM digital images and the results presented here were obtained with the University of Chicago Scanning Ion Microprobe (UC SIM) described by Levi-Setti et al. [7]. The SIM images are formed by different ion species, with a spatial resolution of <100 nm. There are specific advantages and disadvantages of SIM/SIMS with regard to mapping of light elements, Li in particular. A comparison of the SIM technique with the more common EPMA technique has been given recently by Newbury et al. [8] and relevant points are:-

A. SIMS is sensitive to most elements and isotopes, in some cases to the ppb level. As with most analytical techniques, high spatial resolution and sensitivity are mutually exclusive. SIMS is very sensitive to light elements such as B, O and C, which are rather difficult to detect and quantify in

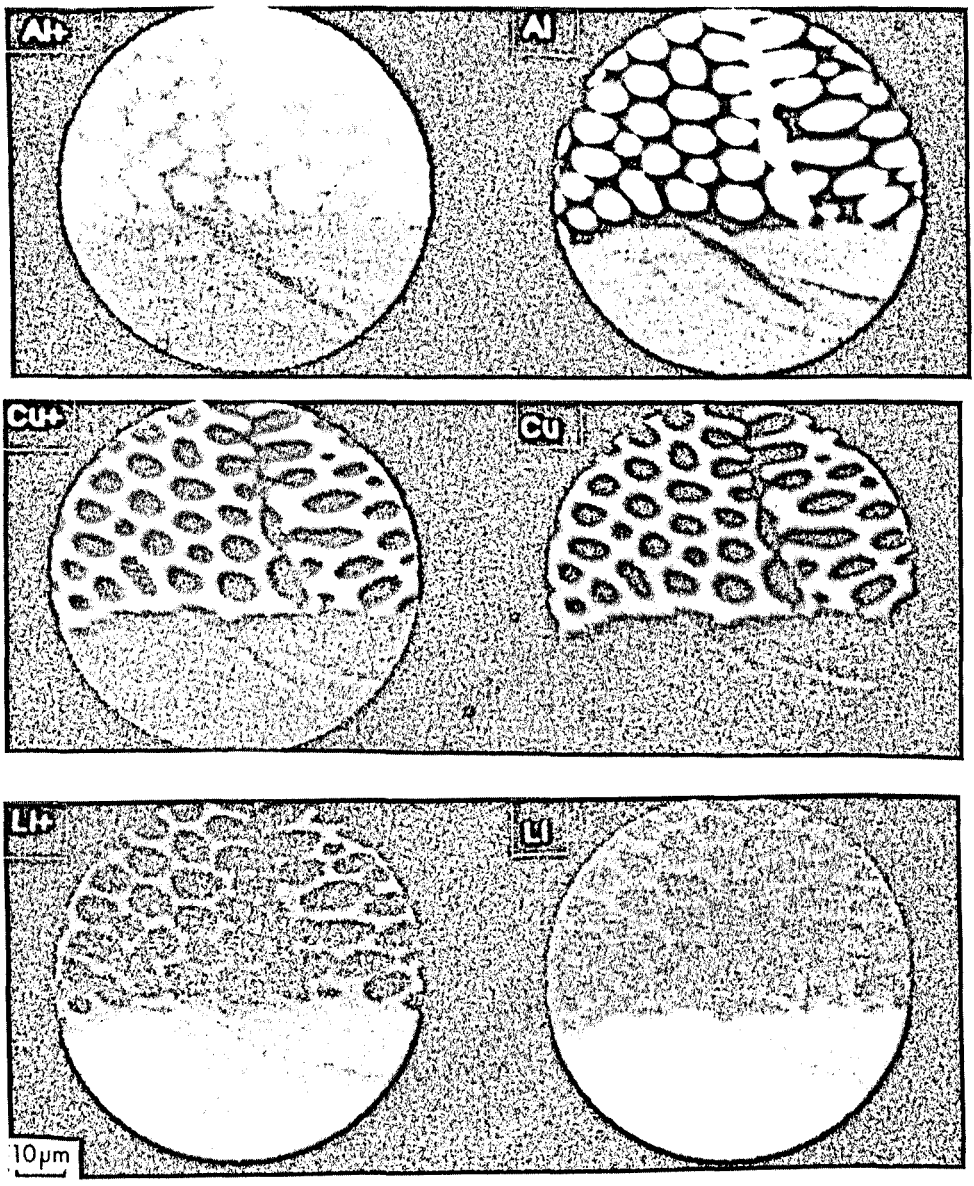

Figure 1. Analog SIMS images showing the distribution of Al, Cu and Li in a ternary Al-Li-Cu alloy containing the Al-rich T2 phase (Al_6Li_3Cu) and a eutectic mixture of the Cu-rich T1 phase (Al_2CuLi) and the Al-Li-Cu solid-solution. In each case the LH image is the direct ion image and the RH image is a quantitative map. Full scale is 150 μm in all images (from Soni et al., [6] reproduced courtesy of VCH Publishers, Inc., Deerfield Beach, FL.)

EPMA or are undetectable (e.g. Li). In fact the Li signal is one of the most intense generated in a SIM/SIMS. But absolute quantification of component concentrations can be difficult with SIMS. It is not uncommon to have $\pm 5\%$ error in quantification data, even after extensive attempts to calibrate the measurements.

B. The signals recorded with SIMS are usually significantly higher than those obtained with EPMA. The signal-to-noise ratio for SIMS is typically 10^3-10^5, compared with the equivalent peak to background ratio of 10^2-10^3 for EPMA. For comparison, the time required to accumulate a statistically significant 512 x 512 map of a single element is on the order of minutes with SIM, but can be up to several hours with EPMA.

C. Polished specimens often contain topographic surface relief at interfaces. This relief may disturb the absorption correction in EPMA. With care, one can study such samples with SIM because the ion signal is not as strongly influenced by surface roughness.

D. The lateral resolution in SIM images can approach the probe size if there is a large concentration of the species of interest, or if the species has a large ionization probability. The spatial resolution of SIM maps acquired with the UC SIM is routinely <100 nm. The ion signal originates from the top two monolayers of the sample. Consequently, only a small microvolume ($\sim 50^3$ nm^3) is sampled for each image element. The depth profiling capabilities of SIMS are well documented in Benninghoven et al. [6]. EPMA, on the other hand, samples the material composition to a depth of several micrometers, (depending on the beam energy and the average specimen composition) and laterally within ~1 μm^2.

E. In a SIM, the sample can be sputtered *in situ* with the ion beam, prior to analysis. This permits the recognition and elimination of polishing-induced artifacts. On the negative side, fragile structures can be difficult to study because of the destructive nature of SIMS.

The most significant drawback to SIMS is that quantitative concentration information cannot be readily extracted from the raw SIMS data. This difficulty is exacerbated when analyzing materials at high spatial resolution. The secondary ion signal is affected by well known and notorious matrix effects, and secondary ionization probabilities for a compound are not known *a priori*. Surface chemical effects, such as the enhancement of SIMS signals due to the presence of oxygen or alkalis, complicate the quantification even if calibration standards similar in composition to the material under study are available. But correct calibration standards often cannot be chosen until the phases are identified. Nevertheless, relative concentrations and gradients across a surface can be very accurately determined with SIMS (to within $\sim \pm 1\%$). These relative concentration data provide valuable clues about material composition. Figure 2 shows digital SIM maps of various elements in an Al-Li metal matrix composite. Note the ease with which Li can be mapped, since the Li^{7+} ion is one of the most easily ionized species. The maps are not quantitative, but with due care and the generation of suitable working curves, quantification of Li can be achieved (Chabala et al. [9]).

Compositional Imaging of Thin Specimens

Principles of Thin Specimen Microanalysis

Thin specimen microanalysis is carried out in the scanning/transmission electron microscope (S)TEM, often termed an analytical electron microscope (AEM). Possible signals for analysis include x-rays, Auger electrons and energy-loss electrons. As already discussed, the x-ray signal is not very useful for light elements and useless for Li. Even though current x-ray energy-dispersive spectrometer (EDS) systems can detect Be K_α x-rays (E = 110 eV), the x-ray signal is very weak because of a) the poor fluorescence yield ($<10^{-4}$ for Be) b) the reduced interaction volume in a thin specimen and c) the increased absorption of the low energy characteristic x-rays in both the specimen and the detector. WDS is not yet an option in the TEM although compact spectrometers for AEMs are under development (Goldstein et al. [10]). The Auger signal is a possible source of light element surface analysis, but a pristine surface is required and this means

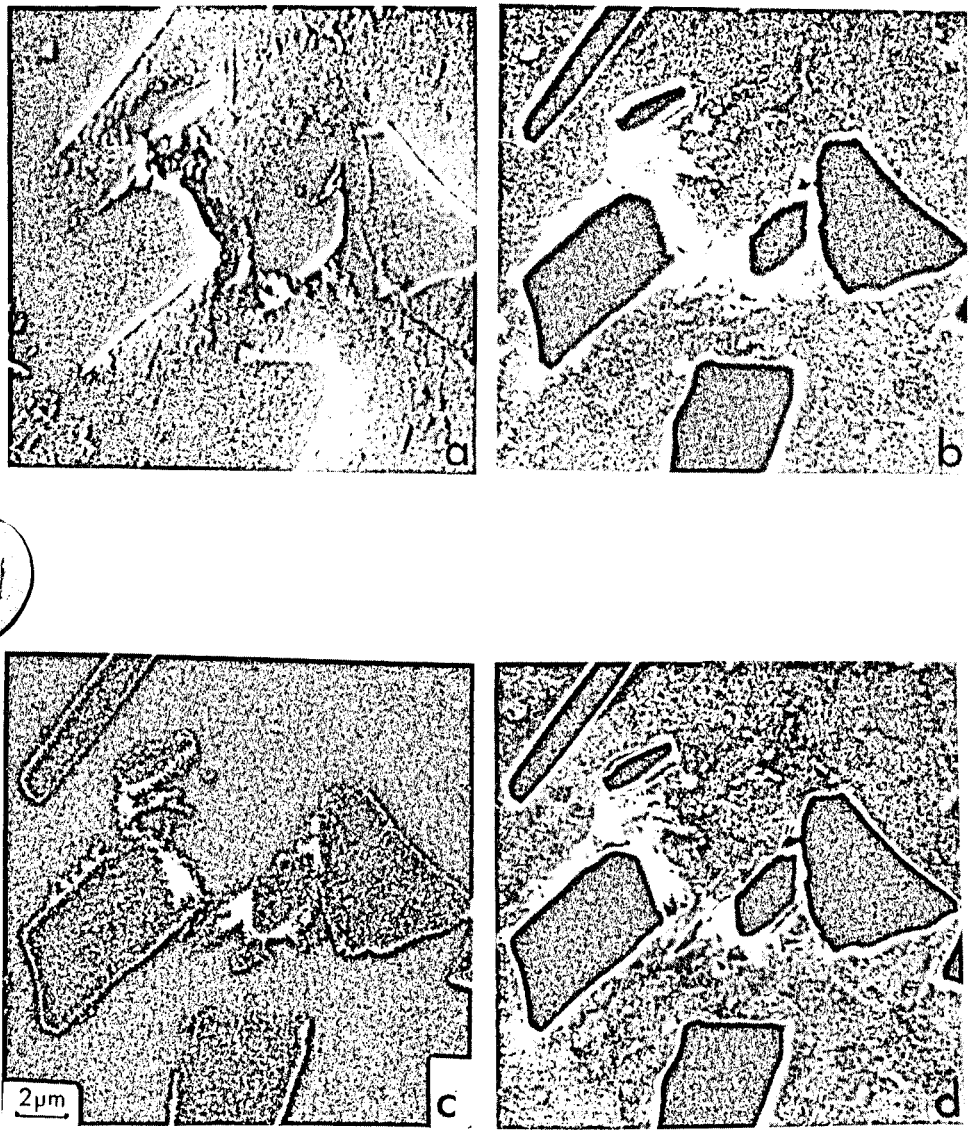

Figure 2. Digital SIM images of an Al-Li-SiC composite: (a) the total ion-induced secondary ion image revealing the topography of the polished composite which was sputter cleaned with Ar ions before imaging: (b) Al^+ (c) Si^+ and (d) Li^+ images. All images are 20 μm full scale and displayed with a logarithmic gray scale (specimen courtesy E. J. Lavernia, U. Cal. Irvine).

that only UHV AEMs are useful. Some progress in interfacing Auger systems to AEMs is being made by several investigators, (e.g., Hembree [11]). Currently the best option for light element thin specimen microanalysis and the only option of Li is to detect and image the energy-loss electrons using electron energy-loss spectrometry (EELS). The EELS spectrum contains a wealth of information beyond the simple elemental ionization edges, (which are especially well suited to for light element detection). For example, in addition to compositional information, the low-loss plasmon spectrum contains thickness, dielectric constant, interband transition and bonding data. The ionization-loss edges also contain fine structure that reflects both the local atomic bonding and the atomic environment surrounding the ionized atom and, as described below, all of this information can be translated into images.

Any kind of microanalysis in the AEM usually involves selecting a region of interest, positioning the beam on that region and gathering a spectrum for sufficient time to permit either immediate qualitative analysis or subsequent quantitative analysis. However, a single point analysis, or indeed several analyses, provides very poor sampling of the chemistry of the chosen region. A biased selection of the points of analysis and a pre-selection of the suspected elements present in the region are almost inevitable. In most analyses, there is only one opportunity to collect the data. So the analyst confines the search to certain elements and, particularly in the case of EELS, selects the appropriate portion of the spectrum to collect. If subsequent analysis of the spectrum indicates the presence of an unforeseen element, or the quantification process is unsatisfactory because of insufficient counts, then it is often difficult or impossible to find the exact analysis region again. The experiment has to be re-done on a different specimen or a different area of the same specimen. Even if the original region is found, the analysis point may have been damaged by the prior electron exposure, covered by contamination or oxidized during storage. To some extent these limitations are overcome by elemental mapping, but this method is often qualitative (e.g. dot mapping) and the maps are usually confined to one or two elemental distributions. Hgowever, all these problems can be overcome using the technique called spectrum imaging (Jeanguillaume and Colliex [12], Hunt and Williams [13]).

EELS Spectrum Imaging

Spectrum imaging is the acquisition of a full EELS spectrum at every pixel in a STEM image of the specimen. With this process a complete record of all the detected beam-specimen interactions is stored at each point in the image. Sophisticated software allows the stored spectra to be accessed rapidly and sectioned in 'spectrum space' so that any feature in the spectrum may be mapped. As a result of this approach no information is lost and all the data can be processed in batches after the acquisition so (S)TEM time is only spent gathering, not processing, data. It is possible to return to the stored data at any time to check for unforeseen features in the spectrum. A parallel-collection (PEELS) spectrometer is essential for spectrum imaging because a serial (SEELS) system is too slow: e.g. A 128 x 128 image has 16,384 pixels. A SEELS system recording a 60 s spectrum at each pixel requires over 11 days to collect a spectrum image. A PEELS system recording the spectrum in 0.2 s requires only 54 mins. A large data storage capability (10 Mb - 1 Gb) is essential because a 128 x 128 (pixel) x 1024 (channel) spectrum image contains 16.8 Mb of data. A 512 x 512 x 1024 spectrum image contains 269 Mb. A field-emission gun (FEG) STEM to maximize the count rate at each pixel makes spectrum imaging much more efficient because an FEG is 10^3 times brighter than the best thermionic source and spectrum acquisition times are reduced proportionately. Suitable software is required to retrieve and analyze the requisite fraction of this enormous amount of data in a reasonable time.

Once a spectrum image has been acquired and stored there are many ways to view the information. The simplest approaches are conventional methods such as a map of a specific edge intensity or a map of a specific plasmon shift. Alternatively, the image can be projected onto different image axes:- e.g. projection along the energy-loss axis giving a total (unfiltered) image, projected EELS spectra parallel to a line in the specimen or the total spectrum summed from the

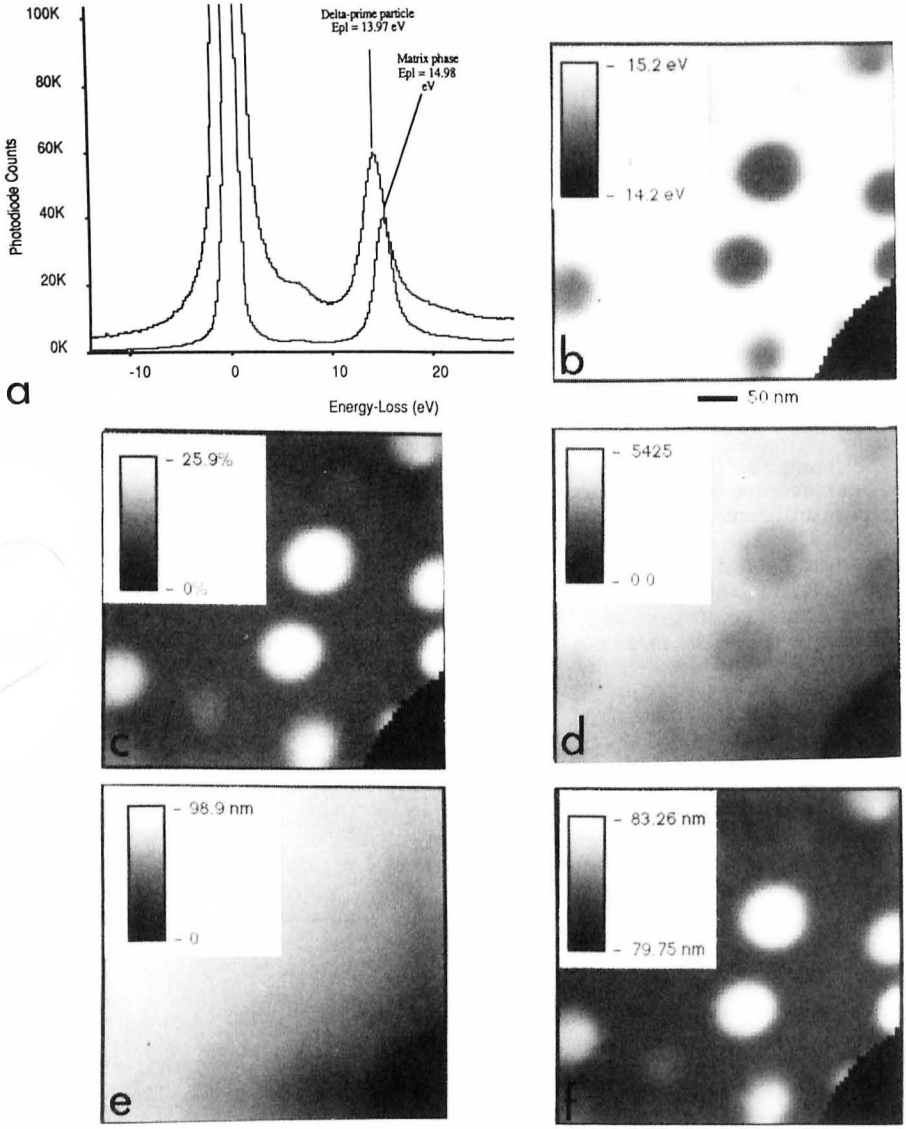

Figure 3 a) Two low-loss EELS spectra from an Al-10 at. % Li alloy showing the shift in the first plasmon peak with change in Li content between the α solid solution matrix (~5 at. % Li) and the δ' precipitates (~25 at. % Li); b) a spectrum image mapping the change in plasmon energy shift in a region of the specimen containing α and δ'; c) a spectrum image of the concentration of Li in the same region of the specimen; d) the absolute concentration of Al atoms in atoms/nm^2; e) the thickness of the specimen deduced from the plasmon-loss intensity and f) the inelastic mean-free path for 100 keV electrons. The gray scale look-up tables within figures b) - e) indicate the quantitative relationship between the image intensity and the characteristic that is being mapped.

whole specimen. Spectra at certain pixels in the image can be summed, such as those from a feature in the image that has a shape not amenable to analysis in spot or line mode. A specific edge can be imaged to determine the distribution of an element when its localization is not known *a priori* . Similarly, a specific edge can be sought when its presence was only suspected *a posteriori*. Finally, if the analysis routines prove unsatisfactory, then other routines can be applied to the original data without the need for further data acquisition. For example, if the data were acquired from an area that proved too thick for conventional linear least squares power-law background subtraction, then the same data could be deconvoluted to remove the multiple scattering contributions, or analyzed with the more robust first difference background subtraction procedure followed by multiple least squares fitting to standard spectra.

Some advantages of spectrum imaging of light elements are illustrated in Figure 3 which shows how the low-energy plasmon loss peak in the EELS spectrum shifts as a result of differences in Li content and how it is possible to translate that shift into quantitative maps of the Li and Al distributions. There is also information about the specimen thickness and the inelastic mean-free path. Similar maps could be obtained using the ionization loss electrons, but the images would be noisier because of the lower cross section for ionization. However, the plasmon-loss images can only be interpreted when they are obtained from simple binary alloys, so their use is limited.

In summary, spectrum imaging permits formation of an image of the distribution of any feature in *any* spectrum (which gives EELS an advantage over EDS). Qualitative imaging is straightforward, but full quantitative imaging is only possible using sophisticated software and post-acquisition batch processing. It is possible to carry out searches for unsuspected elements, removing the possibility of having to try and re-acquire the spectral data. Direct comparison of different data reduction schemes is easily performed.

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References

1. Lyman, C. E., Microscopy: The Key Research Tool (The Bulletin of the Electron Microscopy Society of America), 22, (1992), 1.
2. Cosslett, V. E. and Duncumb P., Nature 177, (1956), 1172.
3. Newbury, D. E., Microscopy: The Key Research Tool (The Bulletin of the Electron Microscopy Society of America) 22, (1992), 11.
4. Benninghoven, A. et al., eds. Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects and Trends (New York, New York, USA: John Wiley, 1987).
5. Czanderna, A. W. and Hercules, D. M., eds. Ion Spectroscopies for Surface Analysis (New York, New York, USA: Plenum Press, 1991).
6. Soni, K. K. et al., Microbeam Analysis 2, (1993), 13.
7 Levi-Setti, R. et al., Surf. Sci. 246, (1991), 94.
8. Newbury, D. E. et al., Images of Materials, ed. D. B. Williams et al. (New York, New York, USA: Oxford University Press, 1991) 90.
9. Chabala, J. M. et al., Appl. Surf. Sci. 51, (1991), 185.
10. Goldstein, J. I. et al., Ultramicroscopy 28, (1989), 162.
11. Hembree G. G. et al., Proc XII Int. Cong. for EM, ed. L. D. Peachey and D. B. Williams (San Francisco, California, USA: San Francisco Press, 1990), 382.
12. Jeanguillaume, C. and Colliex, C., Ultramicroscopy 28, (1989), 252.
13. Hunt, J. A. and Williams, D. B., Ultramicroscopy 38, (1991), 47.