Spectral Image Analysis: Getting The Most From All That Data

P.G. Kotula, M.R. Keenan, and R. Loehman
Sandia National Laboratories

How do you comprehensively analyze the chemistry of a microstructure with an SEM equipped with an energy-dispersive x-ray spectrometer (EDXS)? Prior to the 1990's there would have been perhaps two distinct and commercially available solutions to this problem. Firstly, you could have collected a number of point spectra each with a large number of counts and individually analyzed each one. The positive aspect of this, in principle, is that for each point the elemental correlations are maintained (e.g., a given point contains Al and O). The potential problem is that the region of the point analysis in question is not representative of the microstructure as a whole or subtle differences between different points could be missed. Additionally, point analyses are quite subjective and prone to missing potentially important regions of the microstructure. In other words, how many point analyses are necessary to fully characterize the microstructure, where do you acquire them from, and how closely do you compare them to each other or other prior analyses?

Secondly, you could have collected x-ray maps for a pre-determined group of elements. The positive aspect of this is that, in principle for a given element, spatial correlations are maintained across the microstructure. The potential problem is that the intensity in a given map could come from the pathological overlap of a peak from an unexpected element or from bremsstrahlung. Additionally, correlations between the maps for different elements are not maintained, elements present but not expected are not mapped for, and minor elements' maps have insufficient intensity to be distinguished from noise. Clearly, some combination of point analyses and mapping would have been required to analyze the chemistry of a microstructure at the expense of time and a still-significant possibility of missing something important.

In the 1990's with the advent of faster computers equipped with more memory, commercial systems became available that could combine the best of both point analyses and mapping by acquiring complete x-ray spectra for a 2D array of points, otherwise known as spectral images [1]. In principle then, with proper sampling (i.e., matching the pixel spacing to some fraction of the x-ray generation volume), all of the information about the chemistry of a microstructure (within signal-to-noise and spatial-resolution limitations) is contained in the spectral image data set. A typical spectral image might contain anywhere from about four thousand (e.g., 64x64 pixels) to one million (1024x1024 pixels) 1024-channel (or more) spectra. It is clear that it is impractical to analyze each individual spectrum manually and the software packages available prior to the work described in this paper (and elsewhere [2]) either allow mapping after-the-fact or some sort of manually assisted aggregation of raw spectra using the x-ray maps as guides [1]. Both of these methods offer only a marginal improvement over more conventional methods described above; they are subjective and may miss important details about the microchemistry of a specimen. The problem is comprehensively and efficiently handling spectral images that range from tens of megabytes to almost ten gigabytes in size.

In the present work, we describe the results of the application of our new automated, fast, robust, and commercially available [3] statistical analysis method [2] to an x-ray spectral image of a braze. The software typically takes less than two minutes for the full analysis of a spectral image on a standard personal computer. The software works by statistically comparing every energy channel with all the others in its spectrum as well as all the other spectra [2]. The solution is output in the form of component image/spectrum pairs. The component image tells us where and how much of the spectral feature from the respective component spectrum is in the microstructure. For a given chemical component (typically a chemical phase) automatically identified by the software, the correlations of different x-ray lines from the elements present in the component

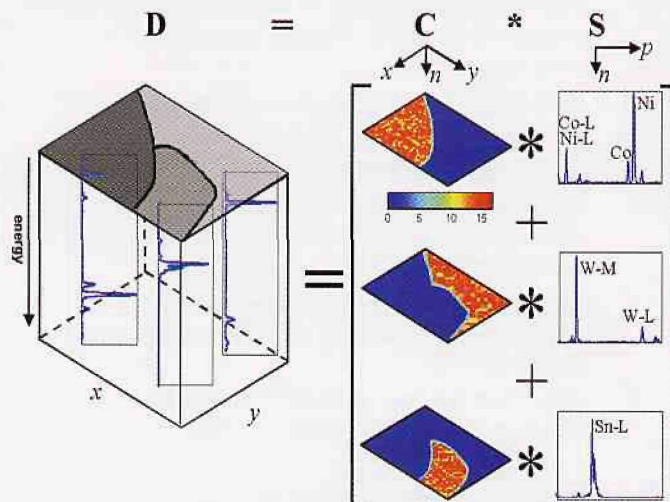

Figure 1. Schematic of the transformation of a large raw spectral image data cube to a much more compact and still physically meaningful solution with automated x-ray spectral image analysis.

are displayed in its component spectrum. Additionally, all of the similar regions in the spectrum image will show up in the respective component image. Thus, the software efficiently solves the problem of comprehensive microanalysis and as a result reduces the amount of data necessary to describe the relevant chemical information in the sample to a manageable amount. If the raw data consists of 16384 x-ray spectra, the solution will typically consist of a handful of component images and spectra that are more than two orders of magnitude more compact. This greatly simplifies the job of interpreting the data and thereby the microchemistry of your sample. Figure 1 is a schematic of the decomposition of a raw spectral image data set (D) with three chemical components (chemical phases in this case). It is assumed that any raw spectrum for a given pixel can be reconstructed by summing the products of pure-component image intensities (C) and pure-component spectra (S) for that pixel (i.e., linear approximation). The color scale under the component image gives the amplitude or intensity of the associated spectrum in the microstructure.

To demonstrate the efficacy of the present automated x-ray spectral image analysis technique, a braze joint was analyzed. Specifically, the interface between alumina and copper-silver with 2wt.% Hf was examined. Point analyses failed to locate any Hf in the microstructure so an x-ray spectral image was acquired from a 20 x 20 µm region along the interface. The data were acquired in a JEOL 5900-LV SEM with W-filament, operated at 15kV. A Thermo NORAN Vantage (Digital Imaging with Spectral Imaging) was used to collect the spectral image at 128 by 128 pixels by 1024 energy channels (~160nm/pixel). The total spectral image acquisition time was about ten minutes or

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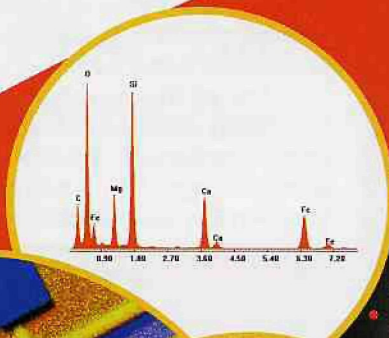

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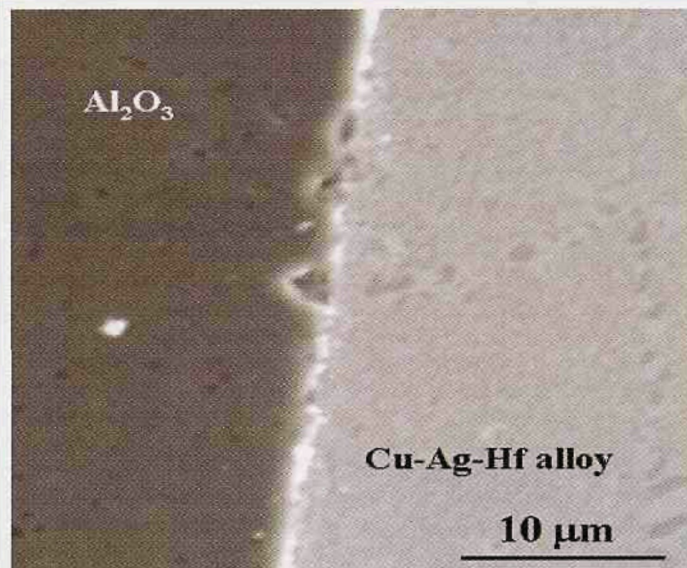

Figure 2. SEM image of the region of the braze joint from which the x-ray spectral image was acquired.

35 msec dwell time per pixel (i.e., individual spectrum). This resulted in an average of 300 total x-ray counts per spectrum in the spectral image. Spectra this noisy pose no difficulty to the automated analysis software because the entire collection of noisy spectra is analyzed together and the solution will statistically aggregate all the similar spectra. Figure 2 is an SEM image from the same location as the spectral image. The Cu-Ag eutectic structure (right-hand side of image) is very fine grained and there is no evidence from conventional SEM imaging of a phase at the alumina/Cu-Ag interface. Figure 3 shows the result of the automated x-ray spectral image analysis of the braze joint which clearly indicates that Hf is segregating to the alumina/Cu-Ag interface. The entire calculation took less than 2 minutes on a standard personal computer. Dark red in the component images corresponds to the maximum amplitude of the spectral shape in the pure component and spectral intensities are in normalized units. The arrows in Fig. 3 point along the interface

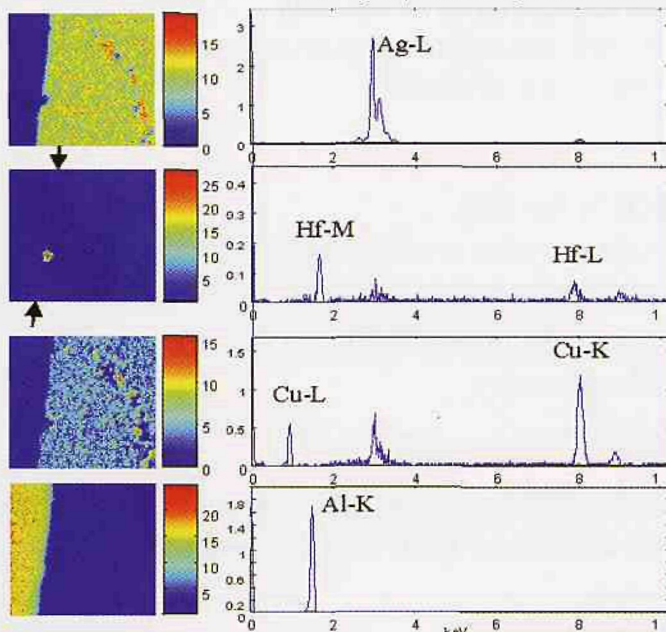

Figure 3. Example of automated x-ray spectral image analysis of the Hf-containing braze joint. Arrows on Hf image correspond to interface position.

and there is, in addition to the Hf in the particle, a subtle concentration of Hf along the interface. In addition to Hf, alumina, Cu and Ag are also identified as distinct chemical components in the microstructure. There is no a priori knowledge that goes into this solution. The software does not know, for example, that Hf has both L- and M-x-ray lines or that Ag has a family of L-x-ray lines with specific respective intensities. It is interesting to note that in the Hf particle the raw spectra had a maximum of 6 counts full-scale in the Hf-M x-ray line yet the automated software recognized that this was statistically significant. Additionally, there were only about 50 spectra containing Hf out of 16384 total x-ray spectra in the spectral image. This amounts to a successful solution to the needle-in-the-haystack problem. In fact, we have demonstrated

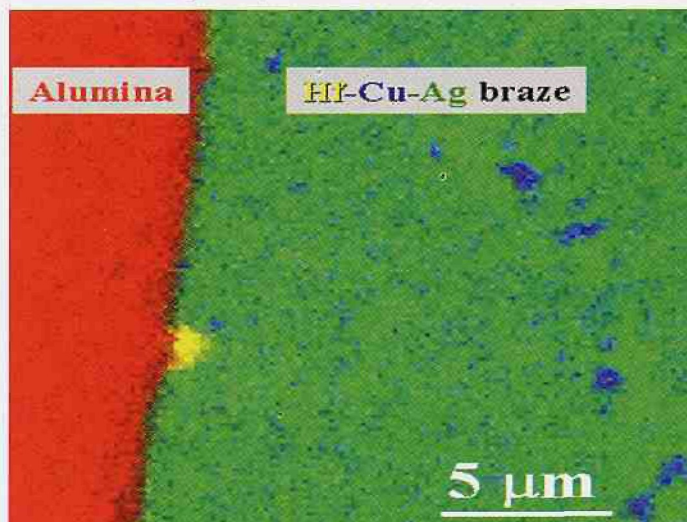

Figure 4. RGB Composite of the pure-component images from Fig. 3. Red is alumina, green is silver, blue is copper and yellow is Hf.

that one pixel of something spectrally distinct can usually be detected in a spectral image as long as it has at least 50 counts per 1024-channel spectrum [2]. Finally, to see how all the chemical components found in the automated analysis spatially relate to each other, a RGB composite image was constructed (Figure 4) from the pure component images. The pure component images were converted to 8-bits/channel (i.e., 0-255 gray-levels) and added together in the correct proportions to produce the color image shown in Figure 4. The Hf-particle is clearly at the alumina/Cu-Ag interface.

Automated x-ray spectral image analysis is a powerful tool for comprehensive microanalysis in the SEM. The algorithms developed in this work are compact and efficient, requiring only a few minutes to run on a standard desktop personal computer. In addition to the location and amounts of the major chemical constituents, the software can also find chemically distinct regions smaller than one pixel even in very noisy spectral image data sets. ■

Acknowledgements

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References

[1] R.B. Mott and JJ Friel, J. Microsc.-Oxford 193 (1999) 2.
[2] P.G. Kotula et al., Microsc. Microanal. In press (2002).
[3] The automated x-ray spectral image analysis software is currently available from Thermo NORAN under the COMPASS product name.

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COMPASS

FAREWELL, X-RAY MAPS

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The award-winning COMPASS statistical analysis tool evaluates spectra from each pixel location in a Thermo NORAN Spectral Imaging database. Looking for energy peak similarities, COMPASS sorts similar-appearing spectra into primary components and quickly generates pure component maps with single-pixel sensitivity.

While an excellent program for finding the spatial distributions of known materials, no other microanalytical tool is so adept at finding unknown components in needle-in-the-haystack applications and deconvoluting energy peaks that overlap. Because COMPASS finds components solely from Spectral Imaging data, user bias is completely removed from the analysis.

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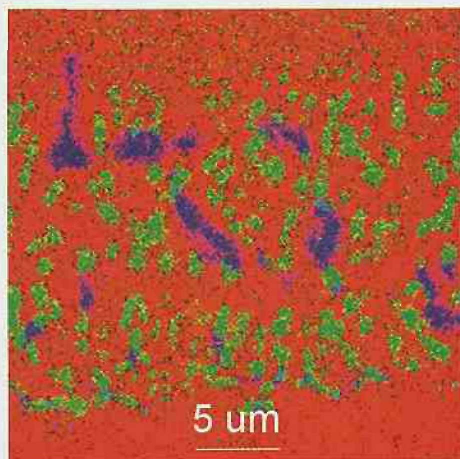
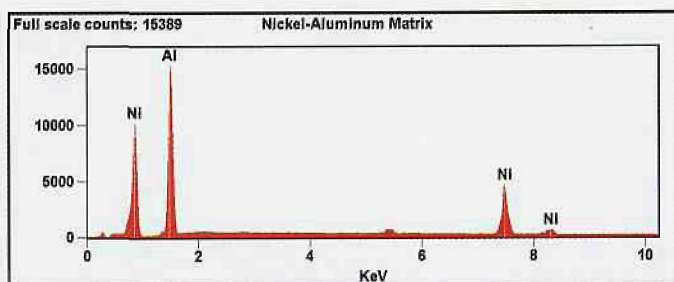
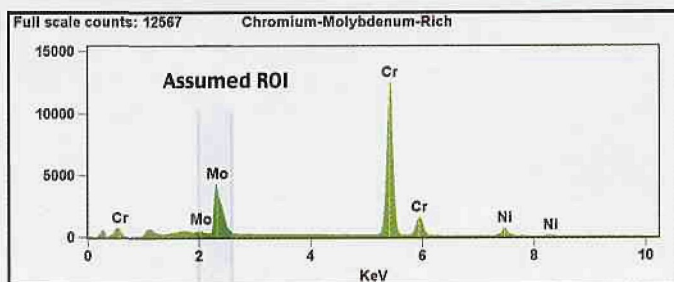


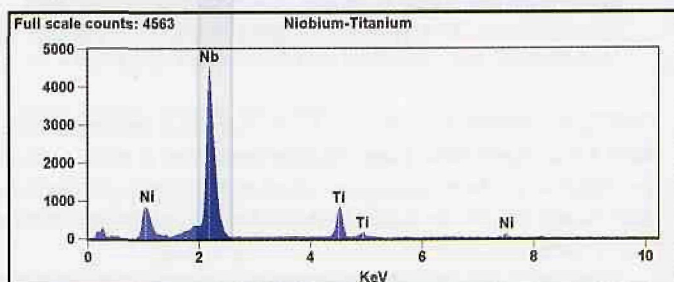
RGB overlay of COMPASS components (256 x 256 pixels) over a SEM image and corresponding spectra with coordinated RGB colors.

The red portions of the COMPASS overlay image show the sample's Nickel-Alumimum Matrix, while the green regions indicate a Chromium-Molybdenum Rich component, and the blue regions indicate a Niobium Rich component.

*With traditional x-ray mapping using ROIs, the Molybdenum and Niobium peaks cannot be separated, leading to an inaccurate analysis of the sample. COMPASS is able to deconvolute these true components and provide the **correct** answer.*







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