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Tutorial Review

X-ray Mapping in Electron-Beam Instruments

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Abstract: This review traces the development of X-ray mapping from its beginning 50 years ago through current analysis procedures that can reveal otherwise obscure elemental distributions and associations. X-ray mapping or compositional imaging of elemental distributions is one of the major capabilities of electron beam microanalysis because it frees the operator from the necessity of making decisions about which image features contain elements of interest. Elements in unexpected locations, or in unexpected association with other elements, may be found easily without operator bias as to where to locate the electron probe for data collection. X-ray mapping in the SEM or EPMA may be applied to bulk specimens at a spatial resolution of about 1 μm. X-ray mapping of thin specimens in the TEM or STEM may be accomplished at a spatial resolution ranging from 2 to 100 nm, depending on specimen thickness and the microscope. Although mapping has traditionally been considered a qualitative technique, recent developments demonstrate the quantitative capabilities of X-ray mapping techniques. Moreover, the long-desired ability to collect and store an entire spectrum at every pixel is now a reality, and methods for mining these data are rapidly being developed.

Key words: X-ray mapping, compositional imaging, X-ray spectrometry, EDS, WDS, concentration–concentration histograms, spectrum imaging, position-tagged spectrometry, principal component analysis, multivariate statistical analysis

Introduction

Production of images showing elemental distributions on a fine scale is an important contribution of electron microscopy to scientific investigations. X-ray maps are formed by collecting characteristic X rays from elements in the specimen as a focused electron beam is scanned in a raster across the specimen. In the 50 years since the first compositional image was obtained in an electron-beam instrument (Cosslett & Duncumb, 1956), there has been extraordinary progress. For the first 25 years, qualitative analog dot maps were used to form X-ray maps of elemental distributions. Computer control of the electron beam and computer storage of digital images dramatically changed X-ray mapping to the point that digital methods are standard in all commercial systems.

This article reviews X-ray mapping in the scanning electron microscope (SEM), the electron probe microanalyzer (EPMA), and the type of analytical transmission electron microscope (AEM) based on the scanning transmission electron microscope (STEM). Electrons are ideal for generating X-ray compositional images because they can be focused to a small probe, they can be deflected to form a scanned beam raster, and they can excite atoms in the specimen to produce characteristic X-ray signals. All other beams that might be used to excite an element-specific signal suffer from specimen preparation difficulties, poor spatial resolution, or quantification problems. Other compositional imaging methods are compared with electron beam methods in Table 1. Two important analytical parameters are listed in the table for each method: the spatial resolution of analysis and the elemental detection limit, the smallest amount of an element that can be detected in a matrix. For Table 1 these parameters have been estimated for the mapping mode of analysis where the values are about an order of magnitude worse than the ultimate capabilities of each instrument. X-ray mapping remains the most convenient and popular method for producing compositional images.

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Analog versus Digital Maps

Early Work

Castaing (1951) built the first practical EPMA in which an electron beam excited characteristic X rays that were detected with an X-ray spectrometer; however, that instru-

Table 1. X-ray Mapping Methods Compared with Other Methods for Determining the Distribution of Elements in Solids

	Method name[a]	Input beam	Output signal	Lateral resolution	Detection limit[b]	Remarks
X-ray mapping methods	SEM/EDS	Electrons	X rays	~1 μm[c]	1 wt%	Routine specimen preparation, rapid
	EPMA/WDS	Electrons	X rays	~1 μm	0.1 wt%	Quantitative X-ray maps
	AEM/EDS	Electrons	X rays	~2–5 nm	1 wt%	Normal thickness TEM specimens
Other methods	AEM/PEELS	Electrons	Electrons	~1 nm	0.1 wt%	Very thin TEM specimens required
	SAM/AES	Electrons	Electrons	~50 nm	1 at%	Surface analysis, depth profiles
	SIMS	Ions	Ions	1 μm	100 ppb	Depth profiles, best element sensitivity
	PIXE	H^+, He^{++}	X rays	2 μm	0.01 wt%	Analytical sensitivity
	Atom probe	Atom extraction voltage	Ions	Atomic	One atom	Sharp needle specimen required
	Micro IR	Infrared light	Infrared light	10 μm	N/A	Molecular spectroscopy

[a]SEM/EDS: scanning electron microscope/energy-dispersive spectrometer. EPMA/WDS: electron probe microanalyzer/wavelength-dispersive spectrometer. AEM/EDS: analytical transmission electron microscope/energy-dispersive spectrometer. AEM/PEELS: analytical transmission electron microscope/parallel collection electron energy loss spectrometer. SAM/AES: Scanning Auger microscope/Auger electron spectrometer. SIMS: secondary ion mass spectrometer. PIXE: proton induced X-ray emission.
[b]Detection limits for maps have been estimated to be 10× greater (worse) than single point analysis because of the limited dwell time per pixel.
[c]For low-voltage SEM/EDS the lateral spatial resolution can be as small as 0.1 μm.

ment could only analyze one specimen point at a time. Duncumb and Cosslett obtained the first X-ray "dot map" compositional image (Cosslett & Duncumb, 1956; Duncumb & Cosslett, 1957) by modifying an EPMA such that the electron beam could be scanned across the specimen surface to generate characteristic X-ray signals as a function of beam position (see Fig. 1). In this first X-ray map, the Cu K_α and Ag L_α signals were separated by the energy-dispersive properties of a gas proportional counter (about 1000 *eV* energy resolution). Because the detector was placed beneath the specimen and X rays were collected in transmission, dark lines appeared where X-ray absorption was the greatest. Soon after this initial demonstration, the wavelength-dispersive spectrometer (WDS) was employed to detect X rays for maps, extending the technique to more general commercial applications (Melford & Duncumb, 1958). A decade later the energy-dispersive X-ray spectrometer (EDS) became available for X-ray mapping in electron-beam instruments (Fitzgerald et al., 1968).

Analog Dot Maps

Because EDS and WDS systems can be attached to almost any SEM or EPMA, X-ray analog "dot maps" are possible on all such instruments, even those of old vintage. As the beam scans across the specimen in a continuous raster, a momentary bright flash is registered on the cathode ray tube (CRT) screen when an X ray enters the spectrometer within a preselected X-ray energy range. These flashes (dots) are captured directly on film by leaving the camera shutter open. The resulting image is one of dots built up on the film, and the relative concentration of the element is inferred by observing the clustering (areal density) of the dots. For guidelines on the setup of analog dot maps, the reader is referred to Goldstein et al. (1981). Because characteristic X-ray signals from the specimen are much weaker than emitted electron signals, analog X-ray maps are often acquired over several scan rasters (image frames), a process that may take up to an hour or longer for each element. A total of 250,000 counts (dots on the film) is considered the minimum exposure for a high quality dot map (Goldstein et al., 1992). An example of an analog dot map is shown in Figure 2. Although simple to acquire, dot maps have several disadvantages: They must be recorded (photographed) one element at a time upon acquisition, they lack discrete intensity levels, they lack a suitable method for background subtraction, and they are inherently qualitative (Newbury et al., 1990*a*). These difficulties can be resolved by collecting the X-ray map digitally.

Digital Intensity Maps

X-ray maps made with early digital mapping software showed only the presence or absence of the selected characteristic X ray for a digital array of pixels. In some early systems, there was only one intensity level at each pixel (see Fig. 3); however, element-specific phases were much easier to recognize compared with the analog dot map.

In true digital intensity maps the electron beam stops on an image pixel, and the number of counts collected from an element within a specified dwell time is recorded as a numerical value (Chambers, 1981; McCarthy et al., 1981; Newbury et al., 1990*a*, 1990*b*). The X-ray background may be subtracted in several ways, and the final image may be displayed at the microscope or stored to be photographed later. Figure 4 is an example of a digital map that clearly

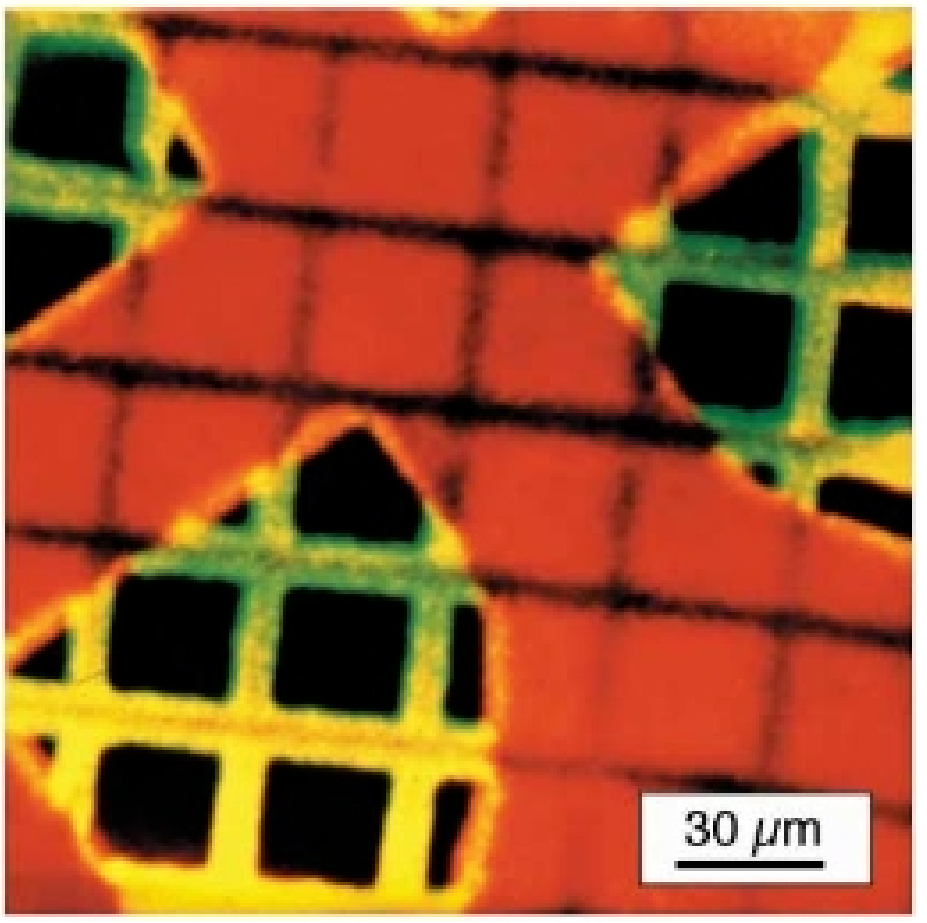

Figure 1. First use of a scanning electron beam instrument to record X-ray maps. The detector was a proportional counter mounted under the specimen. Separate maps were acquired for the Cu K_α line and the Ag L_α line. Separate element maps were converted to color and superimposed with red = Cu and green = Ag. (Courtesy of P. Duncumb.)

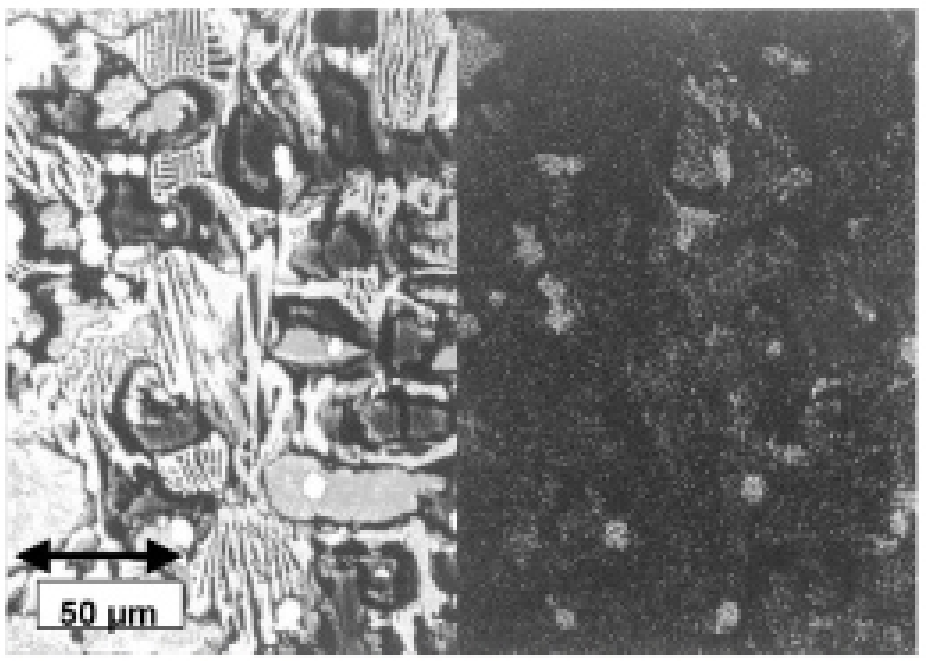

Figure 2. Analog "dot map" of niobium (right) in a tool steel shown with BSE image (left) for comparison. Note the presence of niobium in Nb-carbides.

shows aluminum present in two distinct concentrations (two phases). Digital image processing (Fiori, 1986*a*) and analysis (Russ, 1990) may be performed on stored maps to reveal stereological information about the specimen such as the volume fraction of a particular phase or chemical compound.

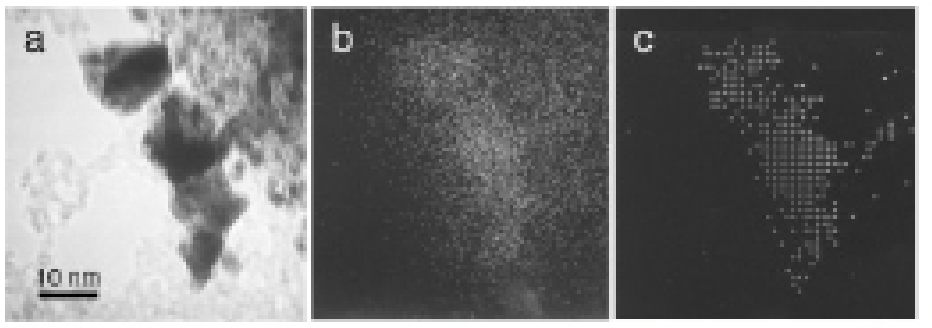

Figure 3. Comparison of analog dot map with digital map of palladium particle on carbon. a: STEM bright-field image of Pd particle. b: Conventional dot map of particle taken with Pd L_α X rays. c: Digital map taken with Pd L_α X rays of same area after subtracting one count of background X rays (Lyman, 1992). (Courtesy of the Microscopy Society of America.)

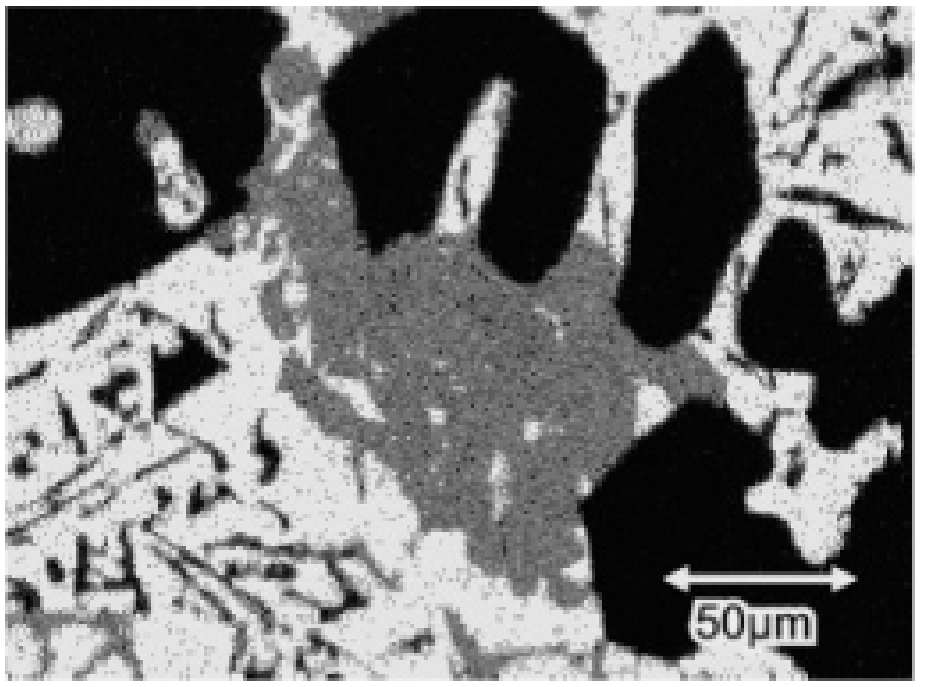

Figure 4. Digital X-ray map of Al in a corrosion-resistant alloy. Note that the relative X-ray intensity shows Al at two distinct concentration levels (two phases).

Because of the ability to display and store digital intensity levels and the flexibility of computer processing, digital X-ray map collection has completely displaced the analog method in modern systems (Marinenko et al., 1987; Goldstein et al., 1992). A disadvantage of digital maps, though, is that they are generally collected sequentially. That is, the beam dwells at each pixel for a specified time to collect X-ray counts, and then the beam steps to the next pixel. Usually, the map as a whole is not available until completion, which may take up to an hour or more, and in that time specimen drift, contamination, and electron-beam damage may invalidate the map. One advantage that analog "dot" maps had was that they allowed the user to do a survey scan of an area to check its suitability for collection of longer-term maps. Various schemes for "fast mapping" have been developed to collect digital maps more rapidly, so as to mimic the survey-scan capability of analog maps.