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CHARACTERISATION OF MATERIALS THROUGH X-RAY MAPPING

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ABSTRACT

Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), wavelength dispersive spectroscopy (WDS) and the combination of these techniques through x-ray mapping (XRM) have become excellent tool for characterising the distribution of elements and phases in materials. Quantitative x-ray mapping (QXRM) enables reliable quantitative results that can be an order of magnitude better than traditional analysis and is also far superior to regions of interest x-ray maps (ROIM) where low levels of an element or elemental overlaps are present.

With the development of faster computers, improved electronics, multi-detector systems and more powerful software, XRM can be performed with an EDS spectrum and/or WDS data collected at each pixel point of the SEM image. This allows full characterisation of a material at a latter stage off-line from the instrument. To obtain a better understanding of a material's chemical and microstructural properties a number of post-processing methods, such as elemental mapping, pseudo colouring, ratio mapping, scatter diagram creation, rotational scatter diagrams and phase mapping should be employed.

Keywords: X-ray mapping, pseudo colouring, quantitative analysis

1. INTRODUCTION

Characterisation is an essential aspect of materials research and of quality control in materials production. Characterisation of materials frequently involves the determination of point-to-point variation in composition, structure and microstructure, so that a variety of imaging and analysis techniques come into play. Understanding the distribution of elements and phases in structures is critical to optimising the performance of all materials. Subtle changes in composition have been studied for many years to determine the properties of many materials and aid in the production of these materials.

Scanning electron microscopy (SEM) micrographs prepared with the back scattered electron signal (BSE) can provide direct information on compositional heterogeneity through the mechanism of atomic number contrast. BSE images are quite useful for characterising microstructures, but the compositional information that they contain is non-specific. The BSE image contains no information to identify the elements present or the concentration levels. A BSE image with energy dispersive X-ray spectrometry (EDS) analysis is an established technique for the analysis of the chemical composition of materials in a SEM.

More recently, x-ray mapping (XRM) is becoming important in understanding the elemental distributions in materials. XRM is the collection of characteristic x-rays as a function of the position of the scanning electron beam on the specimen. This analytical technique provides a high magnification image related to the distribution and relative abundance of elements within a given specimen. This capability makes XRM particularly useful for: (i) identifying the location of individual elements and (ii) mapping the spatial distribution of specific elements and phases within a sample (material surface).

Currently, x-ray mapping is an extremely useful problem solving tool. However, the two major problems for energy dispersive spectroscopy are interpretation of results under non ideal conditions (strong overlap and small peak size relative to background), and the time required to obtain a good quality map (4 to 12 hours). Most mapping is relegated to out-of-hours (overnight) mapping. With the development of high count rate detectors and multi-detector systems, the time required to acquire XRM decreases. With a single EDS detector at 20kcps output, a reasonably good 256x256 quantitative map can be obtained in around 1 hour for major elements (>10wt% evenly distributed) and minor elements (>1wt% localised). It is now possible to quantitatively map using multi-detectors and combined detectors such as WDS-EDS, hence not only reducing mapping time but also improving the ability to map trace elements very accurately [1].

If utmost care is taken with collecting and processing x-rays maps, then further processing such as scatter diagram creation, chemical imaging, ratio mapping and phase mapping can be performed. In this paper we will be discussing region of interest mapping (ROIM), quantitative x-ray mapping (QXRM), full-spectrum x-ray mapping, and the use of scatter plot diagrams for examining compositional maps and reconstructing the

spatial distribution of a phase in a chemical image of the specimen.

2. TYPES OF X-RAY MAPPING (XRM)

There are many types of x-ray maps, which include 1) dot mapping, 2) regions of interest (ROI) mapping, 3) background subtracted and overlap corrected mapping, 4) quantitative mapping and 5) full spectrum mapping (or spectrum mapping). An understanding of these different types of x-ray mappings as well as subsequent limitations, are required before correct interpretation of the results can be made.

2.1 X-ray Dot Mapping

X-ray dot mapping is two dimensional scanning, which involves taking the output of the single channel analyser (SCA) and using it to modulate the brightness of the CRT during normal electron raster scanning. Each x-ray photon detected appears as a dot on the CRT, with regions of high concentration characterised by a high dot density [1, 2]. The limitations with this technique is that it is qualitative only and gives no quantitative information, lacks background correction, is slow and gives poor contrast sensitivity at high concentration levels. Today, this type of mapping is rarely performed due to the greater advantages of the other types of x-ray mapping.

2.2 Regions of Interest (ROI) maps

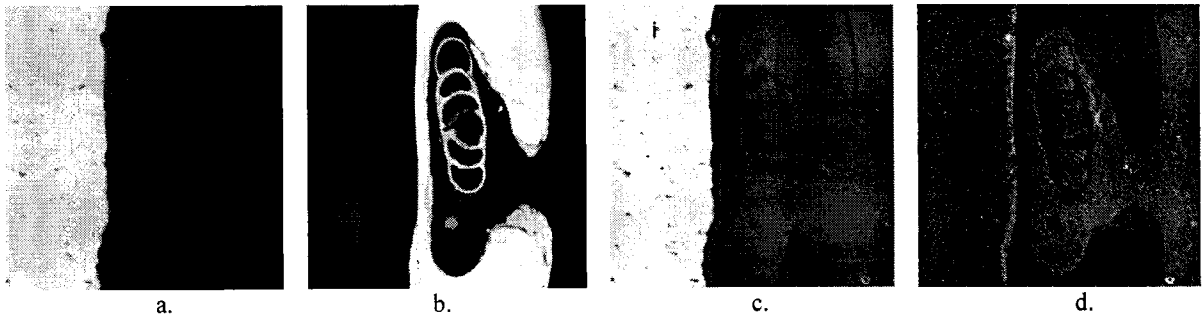
Regions of interest mapping (ROIM), is where you set up a number of channels or an energy range where a elemental line exists to see the distribution of the element you are interested in. ROIs are assigned to a single channel analyser (SCA) and a different colour is assigned for different elements. X-ray maps are usually collected using raw counts from the elemental peaks of interest, however traditional region of interest mapping (ROIM) does not always provide a completely accurate description of the material phases or elemental distribution. The integrated peak counts are only partially related to the true composition of the material and in fact may not be related at all. Indeed, using ROIM may introduce errors and misleading results.

Figure 1 shows a comparison between RIOM and QXRM for a barnacle attached to an aluminium hull plate. Figures 1a and 1b show the intensity x-ray map for aluminium and calcium, where the aluminium is on the left hand side of the image and is represented as region (i). Region (ii) is the barnacle and region (iii) is the resin that that has been used to mount and polish the sample. Often from a visual point of view the chlorine ROI map (Figure 1c), looks better than the chlorine QXR map (Figure 1d), and is consequently used for presentation. The reason is that the intensity map has more x-ray counts, as the background has not been removed, giving improved counting statistics and thus making the image look better (smoother). It is obvious that the ROIM for chlorine (Figure 1c) is incorrect and actually inverted. The ROIM of chlorine (Figure 1c), shows the magnesium plus aluminium sum peak as well as the tail edge of the aluminium sum peak in region (i), which occurs at the energy for chlorine and region (ii) is brighter than it should be because the background has not been subtracted. For a true spatial elemental distribution we require background subtraction, overlap correction and inter-element correction. Thus the quantitative map (Figure 1d) shows the correct spatial element distribution. The ROIM is very problematic when looking at moderate to low levels of elements.

The accuracy of ROIM is dependent on what elements are present in the material. If the elements are present in reasonable amounts and have no overlaps with other elements then the ROIM would be near to correct. However, great care must be taken for other artefacts [3], such as escape peaks and sum peaks that can occur on the EDS spectrum.

2.3 Background subtracted and overlap corrected maps

As the name implies, these maps involve background subtraction and overlap removal. This is required to accurately understand the elemental distributions in the material, especially where overlapping peaks exist. Background subtracted and overlap corrected maps are more accurate than ROI maps. These maps reflect true elemental distribution, except in cases of severe absorption.



a. b. c. d.

Figure 1: A barnacle attached to an aluminium plate which has been set in a resin, sectioned and polished. a) RIOM for aluminium, b) RIOM for calcium c) RIOM for chlorine and d) QXRM for chlorine. Region (i) is the aluminium plate with <0.02 wt% Cl (less than the EDS detection limit), region (ii) is the barnacle with ~0.03 wt% Cl and region (iii) is the resin with ~1.3 wt% Cl (HWOF=260um).

2.4 QUANTITATIVE X-RAY MAPPING (QXRM)

Quantitative maps involve converting the background and overlap corrected maps to weight percents by some correction technique, such as phi-rho-z ($\phi\rho z$) or ZAF (atomic number, absorption and fluorescence correction). Figure 2 shows ROIM, QXRM and WDS maps for a hard facing material bonded to a steel substrate. The elements manganese, silicon and molybdenum were deliberately chosen due to there difficulty in mapping these elements in this sample. As can be seen, the quantification of the data is critical for accurate elemental mapping. Figures 2a-c are the ROI maps and show lovely features as well as a smooth looking maps however, it is not until the maps are quantified (Figures 2d-f) that the true elemental distribution is revealed. Furthermore, the WDS maps (Figures 2g and 2h) show even further subtle changes that the EDS detector cannot reveal due to the poorer detection limits.

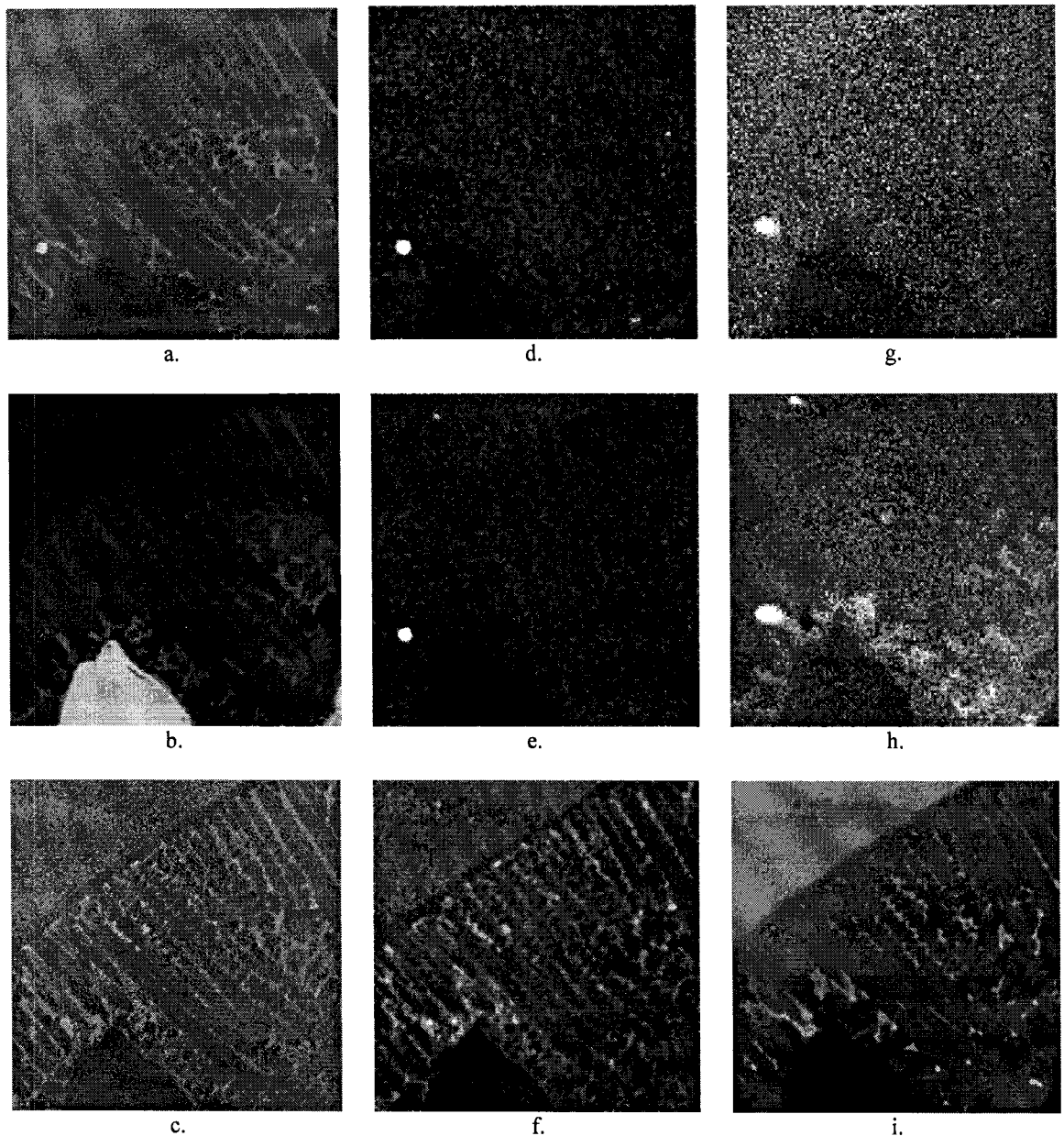


Figure 2: Hard facing material bonded to a steel substrate. The steel substrate is the upper left hand side of image. a-c) EDS region of interest x-ray maps for Mn, Si and Mo, d-f) Quantitative x-ray maps for Mn (~1wt%), Si (~1wt%) and Mo (~2wt%), g-h) WDS x-ray maps for Mn and Si and i) Pseudo colouring map of three elements (Cr-red, Fe-green and Ni-blue). Maps collected at 20kV (HWOF=100um). Wt% values are average matrix values.

Traditional QXRM requires that all the elements of interest be known before the mapping proceeds so that they could be extracted from the full spectrum at each pixel during mapping. One of the limitations of quantitative mapping is that there could be other elements present, that were initially neglected, and thus a complete new map would be required for any new elements to be ascertained. This constriction was due to the memory needed to retain the full spectrum at each pixel (approx 500Mb compared with 20Mb). With present computer technology this is no longer a limiting factor.

Because of the high spatial resolution of the maps, we can very easily choose methods that allow for the averaging of large numbers of image points. This allows high quality analyses to be carried out on spectra that have statistically significant peaks of elements present in low concentration. Quantitative x-ray mapping enables us to achieve this as well as giving us a means to verify the results by post processing to determine actual analyses of spatially distinct areas of the sample from the stored data. In other words, QXRM enables reliable analyses, which are extracted from the maps, that can be an order of magnitude better than traditional spot or area analyses.

2.5 Full Spectrum maps or Spectrum mapping

Advances in computer processing speeds, and media capacity, has made acquisition of full-spectrum x-ray mapping (FSXRM), whether using energy dispersive spectroscopy (EDS) or wavelength dispersive spectroscopy (WDS), a very popular characterisation tool for determining the elemental distribution in materials. Full spectrum mapping saves a spectrum for each pixel of an image. Spectrum mapping was designed as a full data collection package allowing the user to acquire data and recall all information at a later time. This form of mapping allows the user, at whim, to create new maps (QXRM or ROIM), line scans or line profiles, and analyse spectra from the saved data without having to reload the sample or redo the acquisition.

Through FSXRM, ordinary spectra can be created off-line from the entire image area, selected matrix regions, lines, and individual points. Full quantitative analysis can then be performed on the spectrum using the standard EDS analysis software. Elemental intensity maps can be built from the saved data and the element lists can be changed to create new maps in addition to those collected initially. Quantitative maps can be created during post processing using the data saved with the spectral maps. Each pixel's corresponding spectrum is recalled for a complete ZAF corrected quantitative analysis, which is then converted into a series of quantitative maps. All of this post processing can be performed using the calibration data saved with the FSXRM or calibration data created from the FSXRM itself. High quality quantitative analysis may also be performed due to the longer acquisition time for a spectrum that has been obtained from the addition of many hundreds or even thousands of individual spectra, as shown in Figure 3.

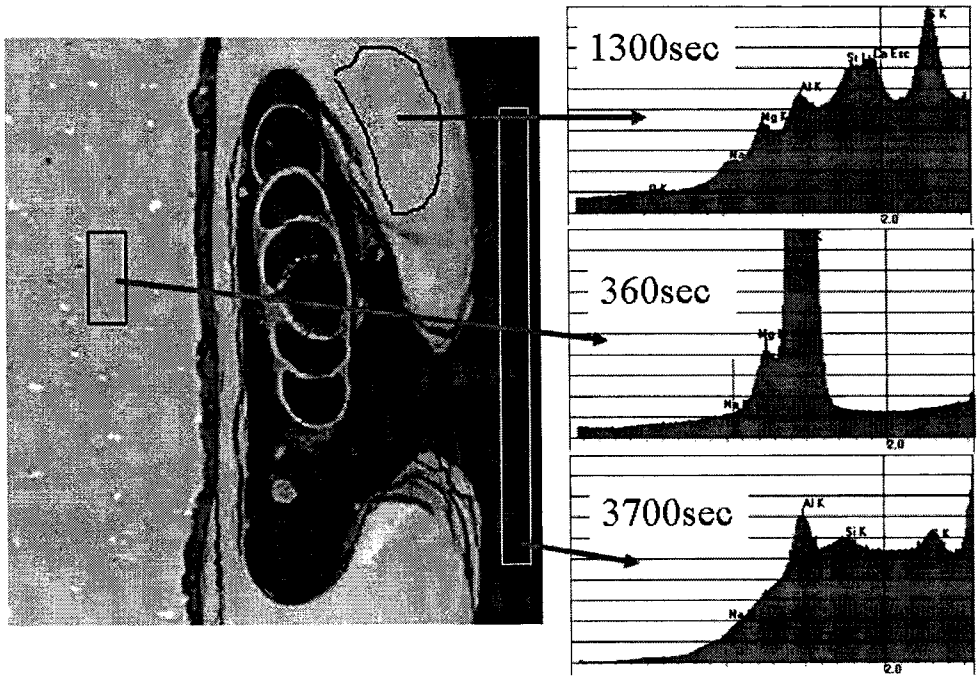


Figure 3: Spectra extracted from a full spectrum map of a barnacle sample attached to an aluminium hull. Arrows show regions from where the spectra were obtained. The composition of the elements shown on the barnacle spectrum (1300 second spectra) to be Na 0.3wt%, Mg 0.4wt%, Al 0.3wt%, Cl 0.03wt%, Sr 0.3wt% and S 0.6wt%. BSE image, HWOF=260μm, 200msec/pixel, 512x512, collected over 15hrs at 50kcps and 165eV resolution.

3. POST PROCESSING OF X-RAY MAPS AND CHEMICAL IMAGING

Once an x-ray map (XRM) has been collected a number of analytical software methods can be used to process the data and determine further information about the microstructure and properties of the material. However, much of the quantitative information is extremely complex and as such is enormously difficult to reproduce as a single image. What is required is a method that can select multiple quantitative concentration criteria and be able to show where this concentration data exists on a spatial distribution. Through the use of two and three dimensional (2D and 3D) scatter (or correlation) diagrams the x-ray images can be presented as singular or combinations of elements [2, 4, 5] (phases to be displayed singularly or superimposed over backscattered or secondary electron information). Where, scatter diagrams are pixel frequency versus element concentration profiles plotted against each other in two dimensions for selected elements within the sample, Figures 4e-g.

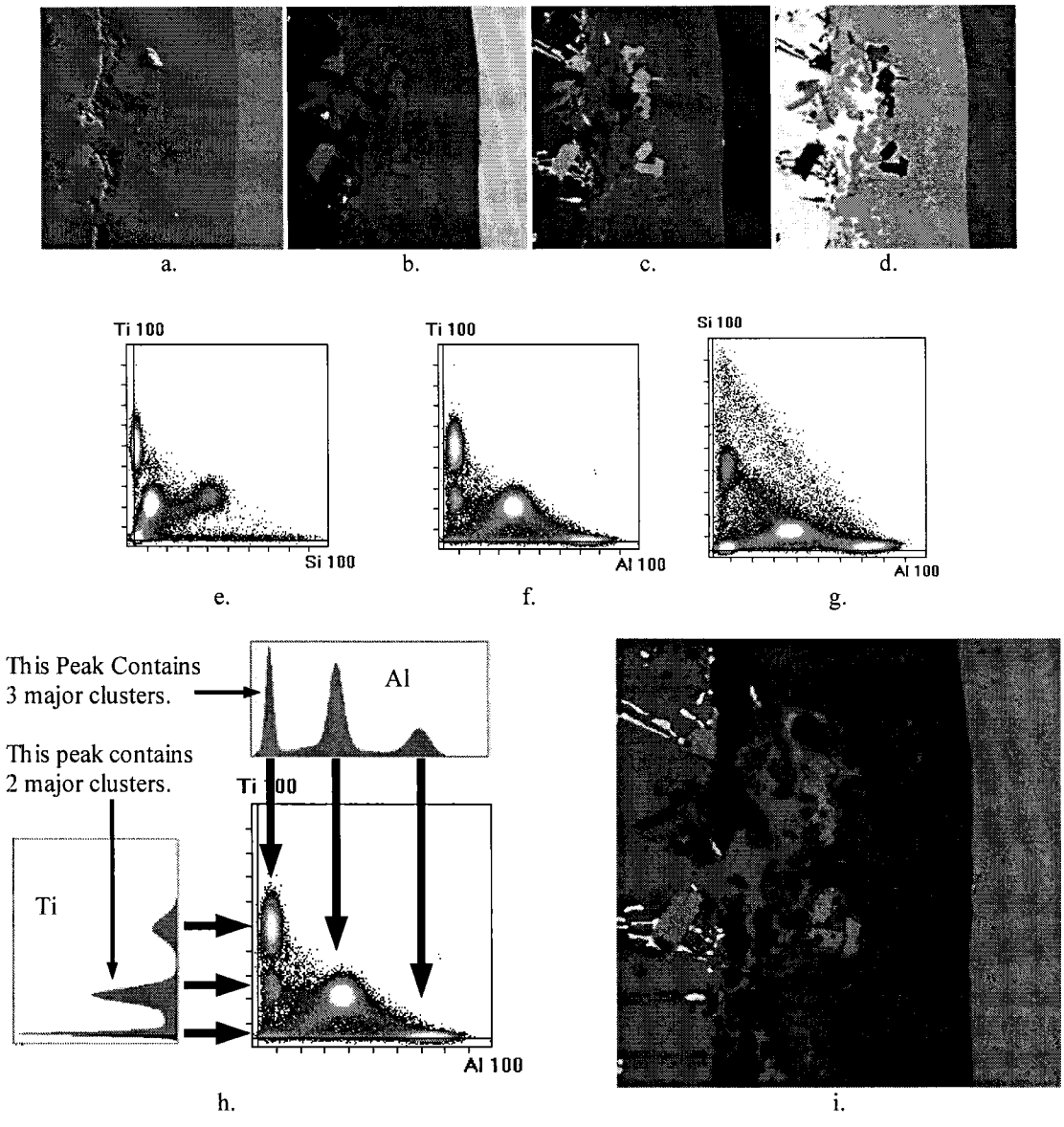


Figure 4: Titanium alloy bonded to an aluminium alloy by the vacuum casting method [6]. a) SE image of the interface between the two alloys and elemental x-ray maps of b) titanium, c) silicon and d) aluminium. The complete set of scatter diagrams showing 5 different clusters from the bond interface region: e) titanium versus silicon, f) titanium versus aluminium, g) silicon versus aluminium, h) scatter diagram generated from the titanium distribution plotted against the aluminium distribution (The aluminium intensity distribution shows three major intensity peaks, of which the left hand peak consists of three major clusters. Similarly, in the titanium intensity distribution, the middle peak contains two major clusters) and i) pseudo colour map for the elements (Ti-red, Al-blue and Si-green). Maps collected at 20keV, 512x512 pixel, 100msec/pixel and 7kcps. Width of field (WOF) = 288 microns.

The generation of scatter diagrams is accomplished by considering the information given in the linear intensity distribution histogram from each individual element (Figure 4h). The histograms are created from the data contained within each corresponding elemental x-ray map (Figures 4b-d). From this information, a two-dimensional scatter diagram is produced (Figures 4e-g). The clusters observed in the scatter diagrams correspond to different phases and boundaries within the material. The contributing pixels to each cluster can be used to reconstruct the spatial distribution of its associated phase or boundary in a chemical image of the specimen.

The larger cluster in Figure 4f is a titanium-aluminium intermediate phase, which occupies a corresponding area on the image as shown in Figure 4i (blue-purple colour).

3.1 Interpretations of Scatter Diagrams

As described in section 3 and Figure 4, scatter diagrams are element concentration profiles plotted against each other and also showing pixel frequency at each point. From these scatter diagrams we observe clusters, also referred to as nodes, which correspond to different chemical phases. We can also observe connection between clusters (linking) indicating the boundaries between phases within a material. Another type of cluster is branching, where there is a link with a node at only one end. This type of cluster is often referring to solid solutions (compositional variations) of the same phase or separate phases of similar chemistry. The contributing pixels to each cluster can be used to reconstruct the spatial distribution of its associated chemical phase or boundary in a chemical image of the specimen. In other words, from the scatter diagram you can select a cluster of points and then display these points redrawn on the electron image. The new image shows the selected analysis points superimposed on the electron image, which was collected while mapping, giving perfect correlation. The scatter diagrams may be derived from region of interest mapping (ROIM) or quantitative XRM (QXRM).

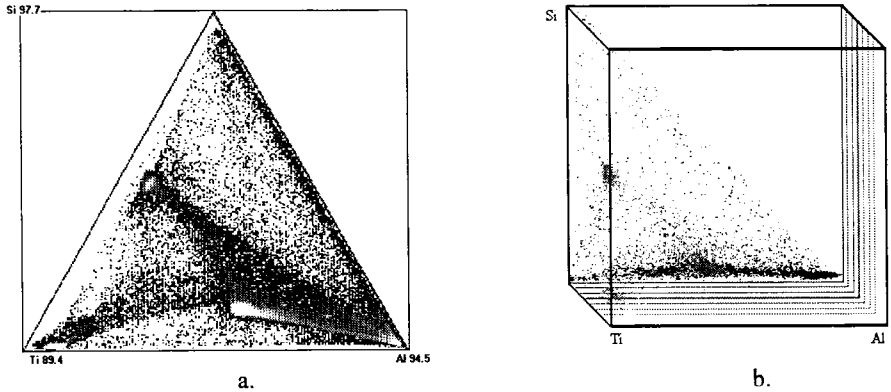
Selecting areas on the scatter diagrams and observing where the points lie on the image is a very important part of the phase identification process. These selected analysis points may then be summed for a more accurate analysis in total or by selecting strategic areas on the image. Selecting areas on the electron or x-ray image and showing where these points plot (retrace) on the scatter diagrams is also important in locating missing clusters.

3.2 Ternary and 3D Scatter Diagrams

It is also possible to create ternary scatter plots and 3D scatter diagrams. The advantage of ternary and 3D scatter diagrams is that correlations between related phases can be visualised in a single diagram (Figure 5). This helps provide more detail that could easily be missed in 2D diagrams. However, they can also be misleading, because some details may still be hidden. The way to solve this problem is to use rotating 3D scatter diagrams that can provide information and reveal facts about a sample that might otherwise have been overlooked. Furthermore, software needs to be developed that not only allows three elements to be selected and displayed, but also allows a fourth and fifth element and even a ratio of elements displayed in scatter diagrams.

3.3 Chemical Phase Mapping (CPM)

Through the use of scatter diagrams, the mapping of phases is possible through selecting the clusters and then displaying these similar concentration areas on the image. This is often referred to as phase mapping, but really it should be called chemical phase mapping (CPM), as phase mapping assumes knowledge of atomic positions and requires diffraction analysis. The XRM method that is being described uses chemistry through use of either EDS and/or WDS analysis. It is also important to recognise that all elements need to be mapped, as some phases are determined from very minor elemental variation and even elements that are difficult to analyse. If a full spectrum at each pixel is saved, this makes the process of looking for other elements much easier.



a. b.

Figure 5: a) Ternary scatter diagram and b) 3D scatter diagram which can be rotated for the results displayed in Figure 4.

Figure 6 shows the phase overlay superimposed on the secondary electron image, often referred to as composite image. The phases have been selected by using the scatter diagrams and by setting elemental chemistry criteria. This phase map has been created from the images shown in Figure 4. As can be seen, there are also areas on this phase map, which are grey in colour, representing phases that have not been identified.

It is best to use as many different methods as possible, such as pseudo colouring, ratio imaging and principal component analysis (PCA) to determine where the phases of interest are. For example, through using pseudo colouring, where a colour is assigned to a specific element, the colours of the elements can be rotated (changed), which can often reveal further information (and other phases) in the material. Indeed, the rotating of colours between elements can also show other features, such as hairline cracks, fine precipitates and small boundary interfaces that would be otherwise missed. Furthermore, any area that is black on the pseudo colour image indicates that another element is not represented by the three chosen to form the pseudo colour image, as shown in Figure 2i. Once a phase is determined, then the volumetric proportion of each phase in the sample can be calculated as well as the compositional range for each phase, Figure 7.

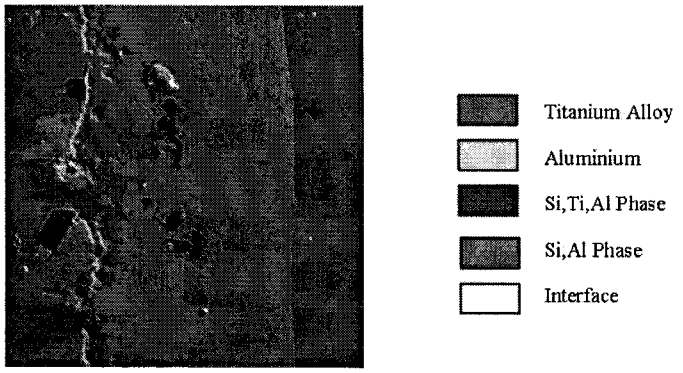
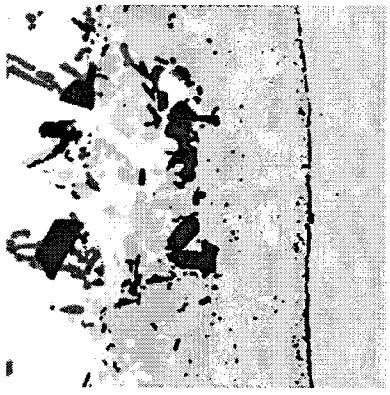
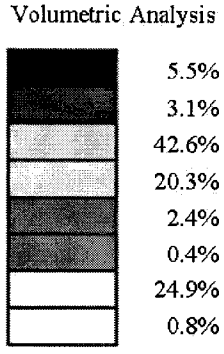


Figure 6: Phase overlay superimposed on the secondary electron image. The phases are selected by setting elemental chemistry criteria. These phases are then assigned a colour, where this colour is then modified by the electron image grey level information to produce the final image. Results are from sample shown in Figure 4. Maps collected at 20keV, 512x512 pixel, 100msec/pixel and 7kcps. Width of field (WOF) = 288 microns.



a.



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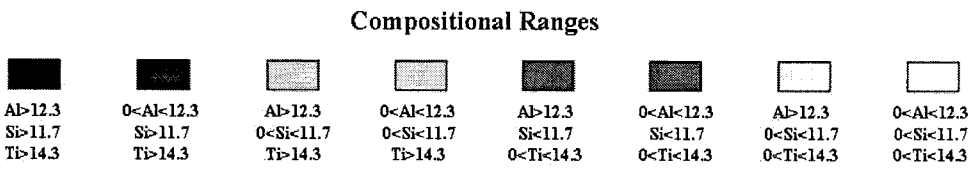

c.

Figure 7: a) Phase map without overlay, b) volumetric analysis and c) compositional ranges. Results are from sample shown in Figure 4. Maps collected at 20keV, 512x512 pixel, 100msec/pixel and 7kcps. Width of field (WOF) = 288 microns.

4. CONCLUSION

Interpretation of an image, whether an optical image, back-scattered electron image or a secondary electron image, is only qualitative. Combining the processes of imaging with spectroscopy (EDS or WDS) gives the capabilities for chemical analysis and chemical mapping on a microscopic scale. The subsequent production of elemental maps and chemical phase maps can make it quantitative.

Collecting the full spectrum x-ray map, even if it takes 8 to 36 hours to collect, is the easy part of the analysis. To completely characterise a sample, a number of post-processing methods, such as elemental mapping, pseudo colouring, ratio mapping, scatter diagram creation, rotational scatter diagrams and phase mapping should be employed. There is so much information that can be extracted from full spectrum mapping that it is easy to get lost in the process.

Materials characterisation is the determination of all aspects of material composition and structure relevant to properties under consideration. This classification is therefore very important to the study and control of both a materials property and its processing. Through the use of x-ray mapping and post-processing techniques (chemical imaging), a better understanding of a materials chemical properties and chemical phase information can be determined.

Acknowledgements

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