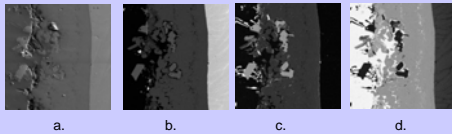


Ken Moran <sup>1,2</sup> and Richard Wuhrer <sup>1</sup><sup>1</sup> Microstructural Analysis Unit, University of Technology Sydney and <sup>2</sup> Moran Scientific Pty Ltd, Goulburn**Introduction**

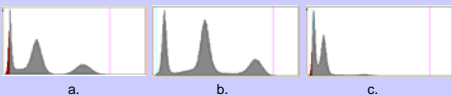
X-Ray Mapping (XRM) and more importantly quantitative x-ray mapping (QXRM) are powerful characterization techniques aiding in the understanding of the spatial distribution of elements in materials. However, much of the quantitative information is extremely complex and as such is enormously difficult to reproduce as a single image. What is required is a method that can select quantitative concentration data and to be able to show where this concentration data exists on a spatial distribution. A simple intuitive method to accomplish this is through the use of two and three dimensional (2D and 3D) scatter (or correlation) diagrams, which are generated from the x-ray maps (Figure 1). Simple two dimensional scatter plots are where pixel frequency versus element concentration profiles are plotted against each other for selected elements within the sample. It is also possible to create two dimensional ternary scatter plots and more complicated three dimension (3D) rotational diagrams and 3D data cubes.



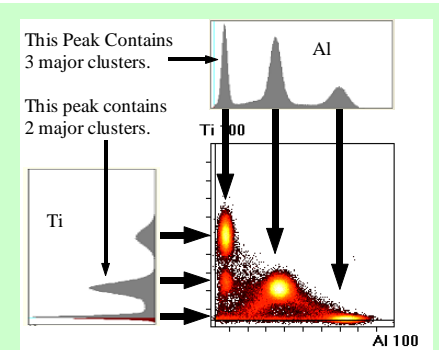
**Figure 1:** Titanium alloy bonded to an aluminium alloy by the vacuum casting method. a) SE image of the interface between the two alloys and elemental x-ray maps of b) titanium, c) silicon and d) aluminium. Maps collected at 20keV, 512x512 pixel, 100msec/pixel and 7kcps. Width of field (WOF) = 288 microns.

**Generation of Scatter Diagrams**

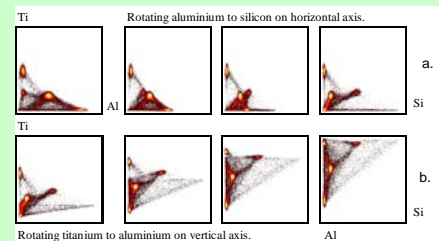
Figure 1 displays the SE image and x-ray maps from a simple three element system. The generation of 2D scatter diagrams is best understood by considering the information given in the intensity distribution histogram from each individual element (Figure 2). The 2D scatter diagram may be considered as an intensity distribution histogram where two of the linear intensity histograms (distributions) are plotted in relation to each other for each pixel in the image. Figure 3 shows this in a diagrammatic form. The 2D intensity histogram is actually created by plotting the concentration of each element for every pixel in the image. The two dimensional scatter diagrams are given an extra dimension by thermally colouring the intensity of points on the diagrams. This dimension indicates the number of points in the image with this concentration (Figure 3). Figure 4 shows a rotational sequence for the three element system.



**Figure 2:** Intensity histograms for each of the respective elements produced from the x-ray maps shown in Figure 1. a) titanium, b) aluminium and c) silicon. Areas marked red are negative values of concentration.



**Figure 3:** Scatter diagram generated from the titanium distribution plotted against the aluminium distribution. The intensity distributions are from Figure 2.



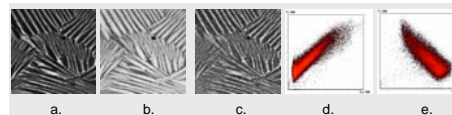
**Figure 4:** Rotating two dimensional scatter diagrams. a) aluminium rotating to silicon in the horizontal axis and b) titanium rotating to aluminium in the vertical axis.

**Properties of scatter diagrams**

There are a number of very important aspects of scatter diagrams as well as many considerations necessary to be taken into account for correct interpretation of scatter diagrams. Of particular interest are:

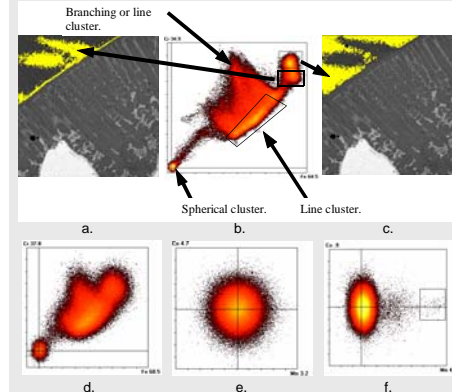
- (i) Individual clusters (or nodes) in each scatter diagram, the type or shape of the clusters (spherical clustering, oval clustering and linear clusters), and zoning.
- (ii) Branches and links between clusters in each scatter diagram and how these features correlate the chemical distribution of elements both in and around the phase region.
- (iii) Minor element distributions and the effect of the statistics of clusters and averaging.

In Figure 5, results from an investigation of a slag material revealed complete dendritic growth of the magnesium rich phase, giving a substantial overlap between the dendritic growths and the calcium rich matrix. The scatter diagrams demonstrate direct calcium and titanium correlation (Figure 5d) while titanium and magnesium show anti-correlation (Figure 5e).

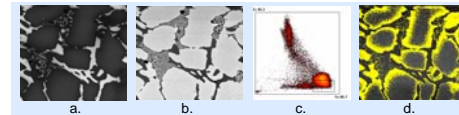


**Figure 5:** Slag material. a) Calcium x-ray map, b) magnesium x-ray map, c) titanium x-ray map, d) titanium-calcium scatter diagram and e) titanium-magnesium scatter diagram. Maps collected at 20kV (WOF=330um). Map collected at 256x256, 120msec/pixel and 2.5kcps.

The spread of the points in each cluster may represent true concentration variations, artefacts or a measure of the statistical distribution of the intensity data at each pixel in the image. The position of the cluster gives the relevant concentration of the two elements in the correlation. However, there is often other information within an individual cluster. For example, zoning within a phase can be determined by plotting sections of the cluster, as shown in Figure 6a-c and Figure 7. By selecting the lower section of the cluster (Figure 7c) a zoning region can be highlighted (Figure 7d).



**Figure 6:** Hard facing material bonded to a steel substrate. a) BSE image with low chrome region superimposed over image (the overlays are on the steel substrate and represent 24wt% Cr), b) scatter diagram for chromium and iron showing many of the different cluster types after averaging, c) BSE image with high chrome region superimposed over image and represent 28wt% Cr, d) chromium and iron original scatter diagram for Figure 6b prior to averaging, e) cobalt-manganese raw scatter diagram revealing a spherical cluster about zero point (the crosshairs represent 0% for each element) and the size is due to poor counting statistics, and f) scatter diagram that has had the data averaged to improve statistics, which allows small localized phases to be located. This appears to distort the manganese axis, which is actually due to different axis scale. The main cluster is now shifted to the right of the crosshairs. The manganese axis consists of at least two un-separated gaussian peaks centering on 0.2% and 0.4% manganese (quantitation determined from grouping multiple pixels on the image). The main cluster is still approximately spherical, if the x-axis is set to the same axis scale. The square to the right of Figure 6f has been identified as a small localized phase enriched in manganese. Maps collected at 20keV, 512x512 pixel, 200msec/pixel and 7kcps (WOF=100um).

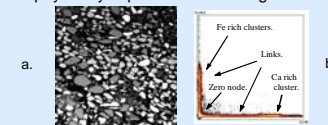


**Figure 7:** Example of zoning from a high chromium cast iron. a) Chromium x-ray map, b) iron x-ray map, c) quantitative Cr-Fe scatter diagram showing area of cluster selected and d) zoning image created by selecting a cluster of points and then superimposing these points on the SEM image. Maps collected at 20keV, 256x256 pixel, 4700msec/point and 2.5kcps (WOF = 155um).

The presence of *spherical clustering* usually means that the concentration range and statistical error for both elements is the same or similar. Figure 6e shows a scatter diagram for a sample which has cobalt and manganese present with similar composition. This scatter diagram reveals a spherical cluster about the zero composition point. This spherical cluster exists as a single cluster even though we know that multiple phases exist within this cluster (Figure 6f).

The occurrence of *oval and linear clustering* on the scatter diagrams means that there may be a narrow to broad range respectively of concentrations (solid solution), or a mixture of spherical, oval or linear clusters plus boundaries. Figure 6b scatter diagram reveals not only oval clustering (with the upper region selected) but also a mixture of linear clustering and branching. Branching is a link with a node at one end only, and is often referring to compositional variations of the same phase or separate phases of similar solid solution. Whereas, linking is the connection between two clusters, and is distinct from the correlation or anti-correlation of two elements (branching or oval clustering).

*Axis cluster (also linear clustering)* normally means that there is little or no association between the two elements. The example shown in Figure 8 reveals at least two linear clusters along the length of the scatter diagrams axes linked to a spherical cluster at the origin. There is no linking between the axis clusters, which are not at the origin, as they are physically separated in the image.



**Figure 8:** Welding flux material. a) BSE image of particles and b) iron-calcium scatter diagram. Maps collected at 20keV, 512x512 pixel, 550msec/pixel and 2.5kcps (WOF=2.25mm).

**Conclusion**

The use of scatter diagrams is a very powerful and useful technique for transforming x-ray maps from spatial to concentration dimensions and consequently allows more thorough examination of elemental and phase distributions in materials. The other important functions of scatter diagrams are being able to 1) group these points for analysis, 2) display points as overlay on the image and 3) select points on the image to display on the scatter diagrams.