SEM/EDS Techniques for Analyzing NdFeB Magnet Material in the Automotive Industry

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Key Words

NORAN System 7 X-ray Microanalysis System, NORAN Analytical Software (NSS), COMPASS Phase Mapping, Heterogeneous Materials, Neodymium Magnet, Permanent Magnets, Point Analysis, SEM/EDS

Introduction

Permanent magnets are very important materials for the automotive industry. Typical automobiles today use a large number of magnets in motors and sensors throughout a car. These are used for drive motors, power steering, power windows, starters, generators, power seats, fuel sensors and more.

For the most part, these magnets are comprised of Nd, Fe and B. However, additions of small amounts of other elements change the magnetic properties of the material as well as the corrosion properties and improve utility at higher temperature.

As part of incoming inspection, automobile companies need to confirm that the correct grade of material was supplied or whether the supplied material satisfied the requirements of the grade. In some cases it may be important to investigate failures.

The nature of the material makes this a difficult analysis. NdFeB magnets are formed by sintering a mixture of the powdered constituents at certain temperatures and pressures. The result is a dominant matrix populated by at least two other phases. The exact composition depends on the grade of the material. Heterogeneous structures like this are difficult to analyze.

To obtain the average composition with high precision, the typical procedure would be to use X-Ray Fluorescence (XRF) technology, Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) or similar technique. In order to use these analytical methods one must first homogenize the sample. For XRF the sample is milled and blended and pressed into a pellet or dissolved in a flux to form a disk.
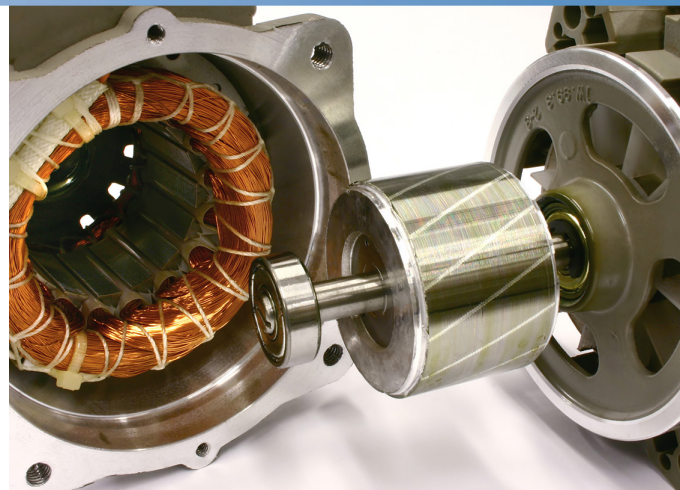
For most other technologies the sample is first put into solution by digestion in an acid or other solvents. These techniques produce a very high precision analytical result describing the average composition of the material but lacking in any structure information. This is critically important as it is the size, distribution and composition of the phases which, in part, determine the magnetic properties of the material.

Although heterogeneous materials cannot easily be quantified they may be characterized. It is straightforward to inspect the material and analyze anomalies. Also, it may be possible to know that two materials are either very similar or different even if the materials cannot be quantitatively described. Finally, it is possible to measure the microstructure in a reproducible manner. Following are descriptions of the possible measurements that can be employed.

A tool well suited for this kind of analysis is a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Spectrometer (EDS). The SEM uses a fine electron beam to probe the sample. The EDS is able to identify the elements present wherever the electron beam impinges on the sample. The electron beam can be
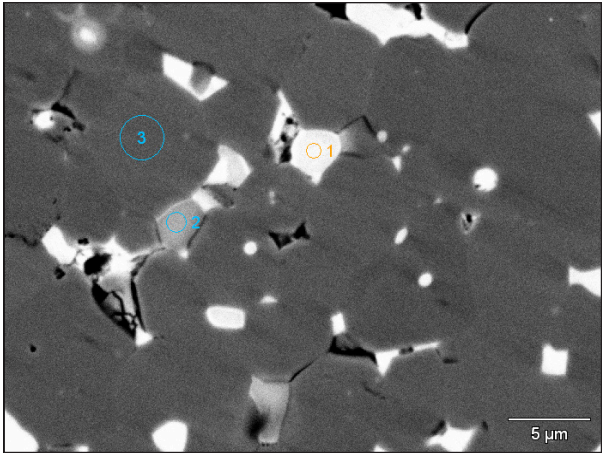
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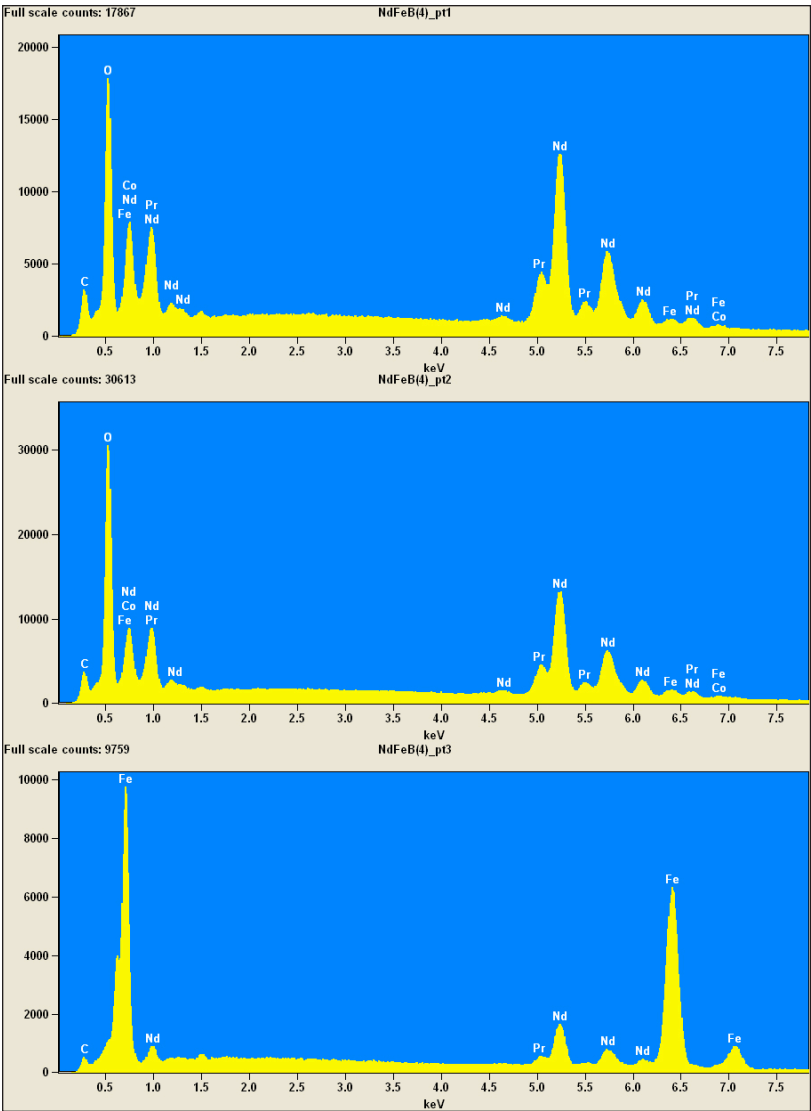Figure 1: Point and Shoot regions selected for analysis

Figure 2: Spectra from each of the three analysis regions indicated in Figure 1

focused very tightly such that features much less than one micron across can be inspected. Moreover, little sample preparation is required beyond polishing the sample to a flat surface. For magnets, one additional requirement is that they be demagnetized.

In cases where a fracture has occurred, the fracture face may be inspected in the SEM directly, with no polishing or grinding, to attempt to identify any foreign inclusions that may have caused the fracture.

Point Analysis

One of the simplest EDS techniques is to visually inspect a sample and direct the electron beam to conduct an analysis at a specific point. In this technique an image is captured from the electron microscope then the analyst points at regions in the image to be analyzed. The computer directs the electron beam to those areas and conducts the analysis. The result is one or more elemental analyses as well as an image documenting their locations and the appearance of the sample.

Figure 1 shows a typical field of view. The scale marker indicates the length of 5 microns in the image. This is a backscattered electron image (BSE). In this image the brighter areas indicate higher average atomic number. The visible inclusions range from about five microns across to sub-micron.

Note in the figure that three areas are highlighted. The spectra for these three areas are shown in Figure 2. In this example one measurement was made of the matrix, one of a dark grey inclusion and one of a bright white particle. (See reference[1] for more information about X-ray spectra and how to read them.)

- The matrix consists largely of Nd and Fe
- The bright particles consist of Nd, Pr, and O
- The dark particles also consist of Nd, Pr, and O but with more O than the bright particles

Figure 3 shows the visual comparison of the spectra from the two kinds of inclusions seen in the sample.

The approximate composition of each area may be calculated. This data is presented in Table 1. In a simple analysis the accuracy is about two or three percent. With care this can be greatly improved. It is important to be aware that these analyses represent just the tiny points indicated in the image, and do not represent the whole sample.

Table 1: Quantitative estimates of compositions at the four analyzed regions indicated in Figure 1

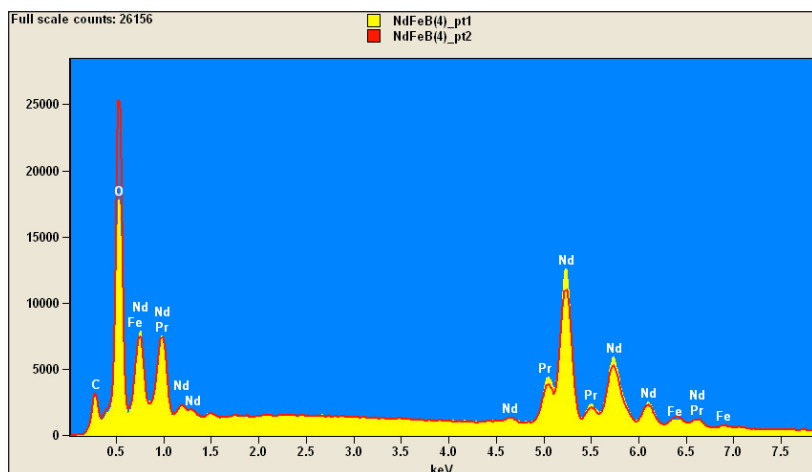|	O-K	Fe-K	Pr-L	Nd-L
NdFeB(4)_pt1	15.5	2.1	17.4	65.0
NdFeB(4)_pt2	22.0	3.4	15.5	59.1
NdFeB(4)_pt3		75.2	4.5	20.3

Figure 3. Comparison of spectra from the bright (pt 1) and grey (pt 2) inclusions seen in Figure 1. Even without numerically analyzing them, comparisons provide a way for contrasting the compositions of multiple features.

In special cases where the peaks are difficult to separate by EDS a different spectrometer can be mounted on the SEM and used together with the EDS detector. The Wavelength Dispersive Spectrometer (WDS) is an excellent complement to EDS as it provides much higher peak resolution which in turn provides for much greater certainty and precision when performing quantitative analysis of trace elements.[2]

Point analysis is well suited to quickly characterizing features which can be selected by eye. This can easily be used to check the composition of the matrix and other known features as well as the composition of anomalies that appear in the field of view.

Mapping

A more sophisticated analysis technique is called Spectral Imaging (SI). In this case the field of view is selected by the analyst then the computer rasters the electron beam in a grid pattern across the sample. At each node in the grid a spectrum is measured and stored. The result is a two dimensional array of spectra that describe the elemental composition of this area.

For a fuller discussion of this technology and what it provides see the following reference.[3] For the purposes of this discussion only two features of SI will be used.

The main purpose of mapping is to reveal the distribution of an element in the field of view. Because the technique analyzes a large area it does not depend on the analyst locating a feature by eye for inspection. Every part of the sample is analyzed. Figure 4 shows an image of the area mapped and Figure 5 shows the spectrum acquired from the entire field of view. This shows the elements that may be found in this region.

This spectrum reveals the presence of Nd, Pr, Fe, Nb, Co, O, C, and a trace of Dy.

Figure 6 shows maps of the discovered elements except for Dy which is present at too low a level to map easily in this particular sample and C which is likely merely a contaminant. These are processed maps in which background information and peak interference overlaps have been removed.
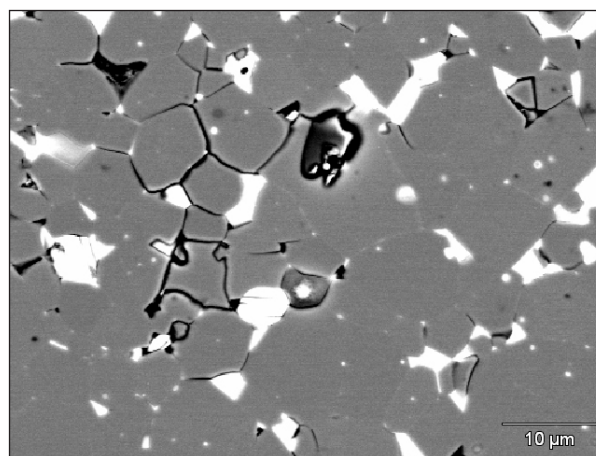

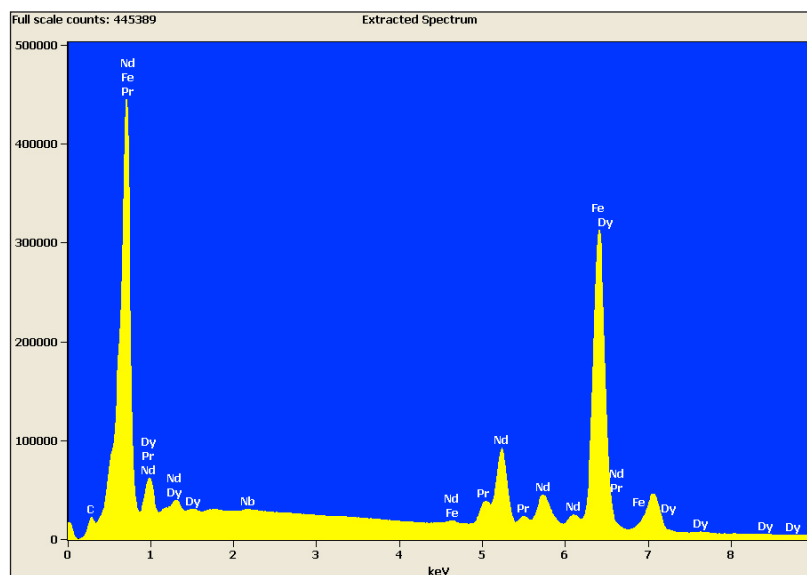Figure 4: Greyscale image of area mapped with Spectral Imaging

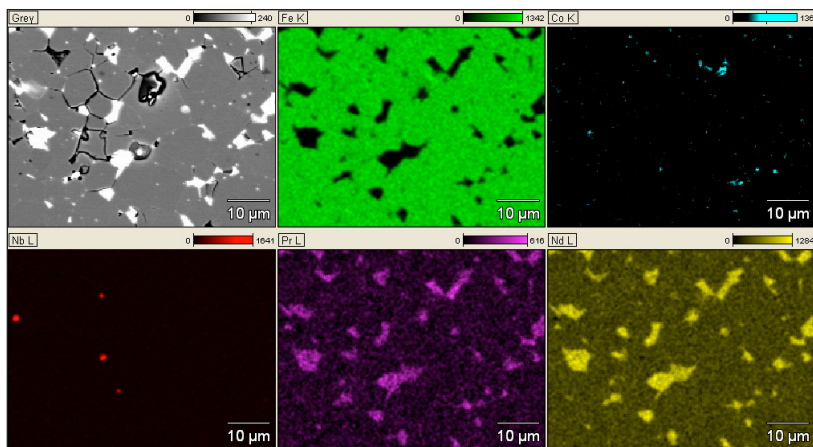Figure 5: Gross spectrum from full field of view of Figure 4

Figure 6: Maps showing elemental distributions in a region of the sample
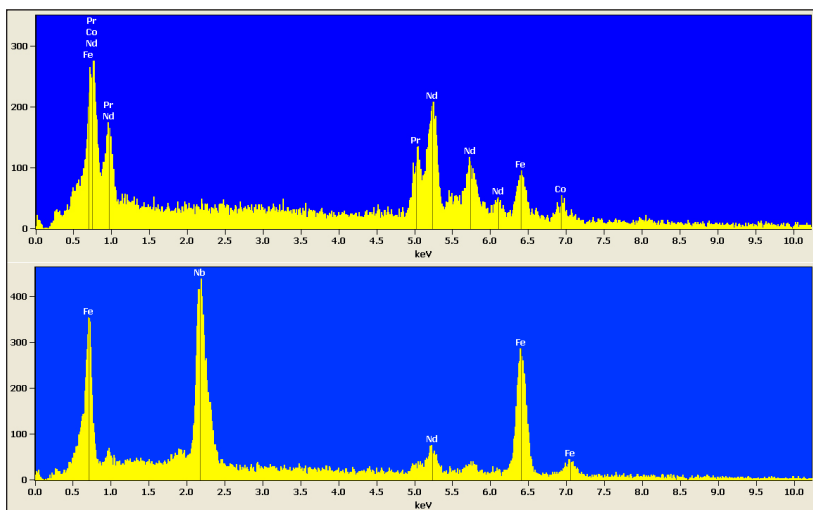

Figure 7: Extracted spectra from Nb and Co rich regions. Note that Co is just at the trace level.

Maps reveal the size and shape of the inclusions containing each element. These maps clearly show that the Nb and Co are located in just a few areas, while Fe and Nd are abundant throughout the map.

Because a full spectrum is stored at each point in the map it is easy to extract a spectrum from a feature to confirm the composition. Figure 7 shows the spectra extracted from Nb and Co rich regions confirming the correctness of those identifications.

Displays of Net Counts values for specific elements requires knowing that one should look for those elements. Another technique parses the Spectral Imaging data set automatically and can find elements that weren't expected to be present.

Available exclusively on the Thermo Scientific™ NORAN™ System 7 X-ray microanalysis system, COMPASS™ uses principal component analysis (PCA), a powerful algorithm[4] that finds element groupings in the field of view then produces a map of the abundance of that set of elements across the field of view.

For a simple example consider a sample that has three kinds of magnesium silicates – olivine, pyroxene and serpentine. All contain Mg and Si but in different ratios. Simple mapping would show maps for Mg and Si. COMPASS PCA would identify each ratio as a different component and produce a map showing the distribution for each component.

COMPASS phase mapping groups together nodes in the map with similar values and flags it as a unique phase. The software then calculates the percent area of that phase in the image and collects all of the individual spectra from each point in the phase and sums them into one spectrum. This reveals a map that shows the composition of the phase.

Figure 8 shows the COMPASS PCA results calculated from the same map data shown above. The components look like spectra but actually mathematically derived shapes.
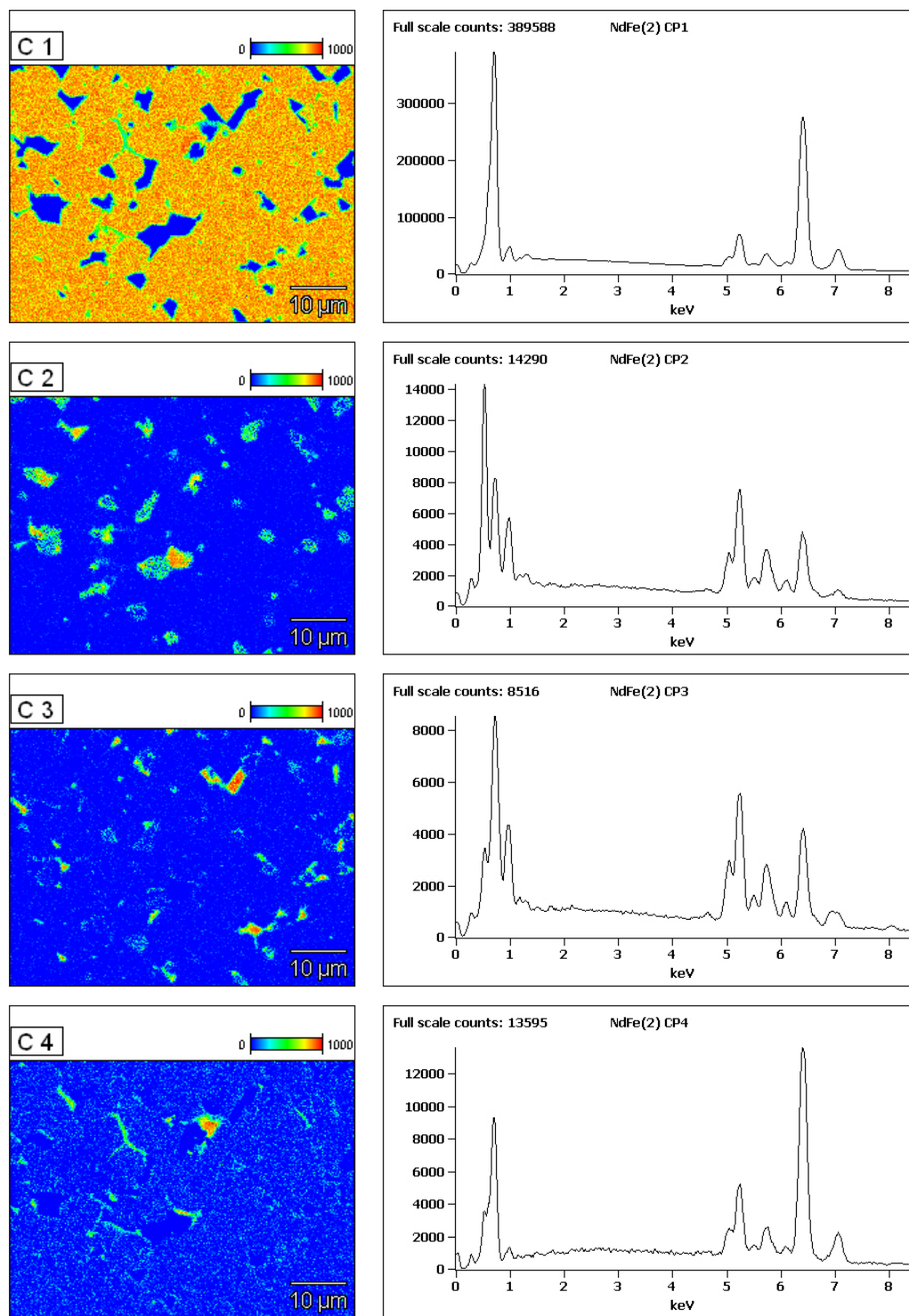
Figure 8: COMPASS PCA components and distributions

Figure 9 shows the phases calculated from the results. The spectrum for each phase is shown as well.

The proprietary method is very useful as no prior knowledge about the sample is required before applying it to the map. No judgements are required from the analyst so every operator gets the same results. This makes it an excellent tool for screening incoming material. Note that in the results COMPASS PCA automatically isolated the Nb and Co rich areas even though they were minor constituents. COMPASS PCA is very good at finding features that are different from the matrix, even if they comprise a very small fraction of the field of view.
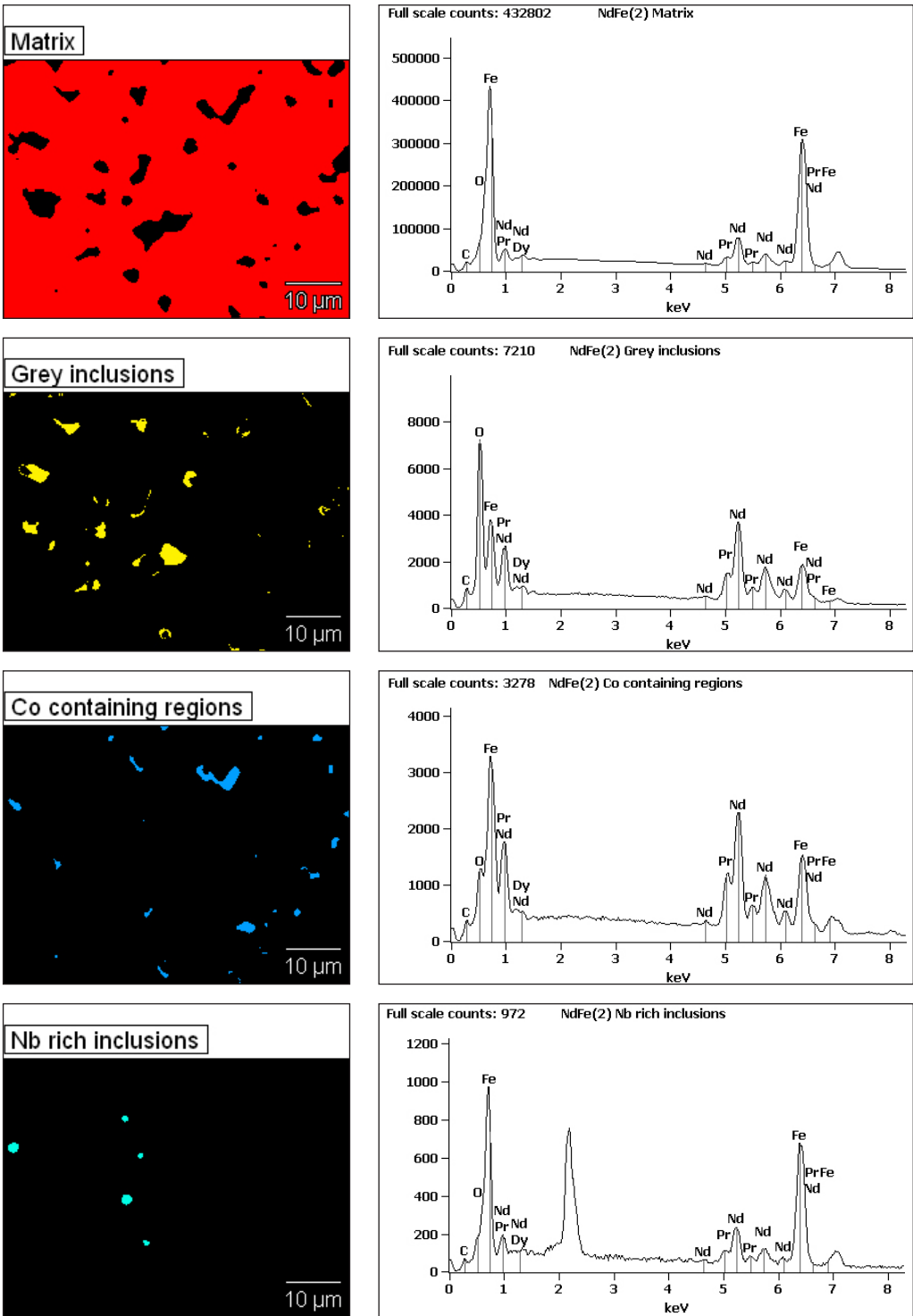

Figure 9: Phase distributions

A second sample was examined with Spectral Imaging. The image is shown in Figure 10 and the maps are shown in Figure 11. In this case it was suspected that P and S might be present. They appear to exist at three points in this field of view.

Figure 12 shows the spectrum extracted from the SI data set. Because the particle was so small in this image the spectrum was quite weak. To improve the confidence of the identification Point and Shoot was used. Figure 12 also shows this image and the spectrum acquired from a point indicated by the map as containing P and S. As the spectrum shows the identification was correct. In this way mapping and point analysis complement each other. SI helps in the rapid identification of where something might be located while Point and Shoot excels at a confident identification of the sample at a specific area.

To quickly evaluate a relatively large area SI can be extended with the Analysis Automation option which integrates NORAN analytical software (NSS) software with the stage motors of the electron microscope. In this way an analyst can setup an analysis to collect maps from a grid of areas, move that data to another workstation and then process it offline to search for anomalies. In this way product can be screened in a routine manner and when anomalies are discovered they can be brought to the attention of a senior engineer.
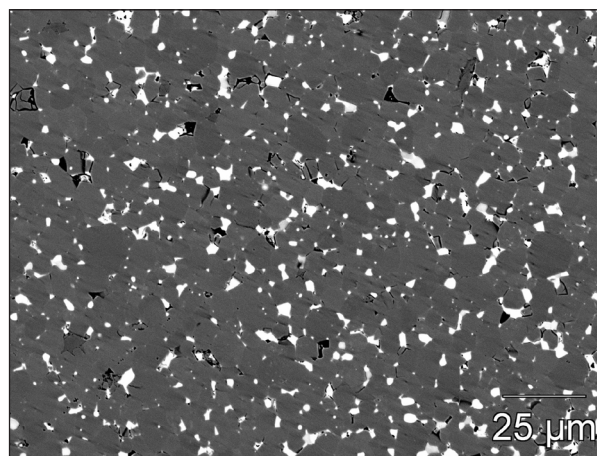

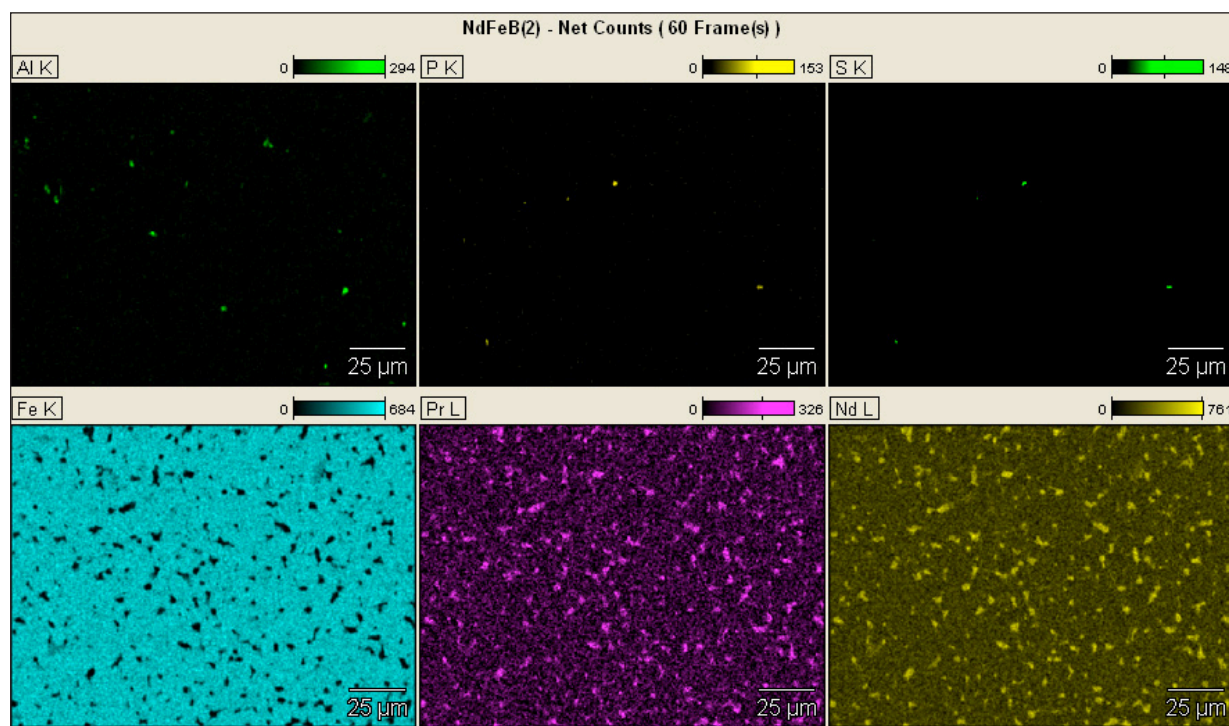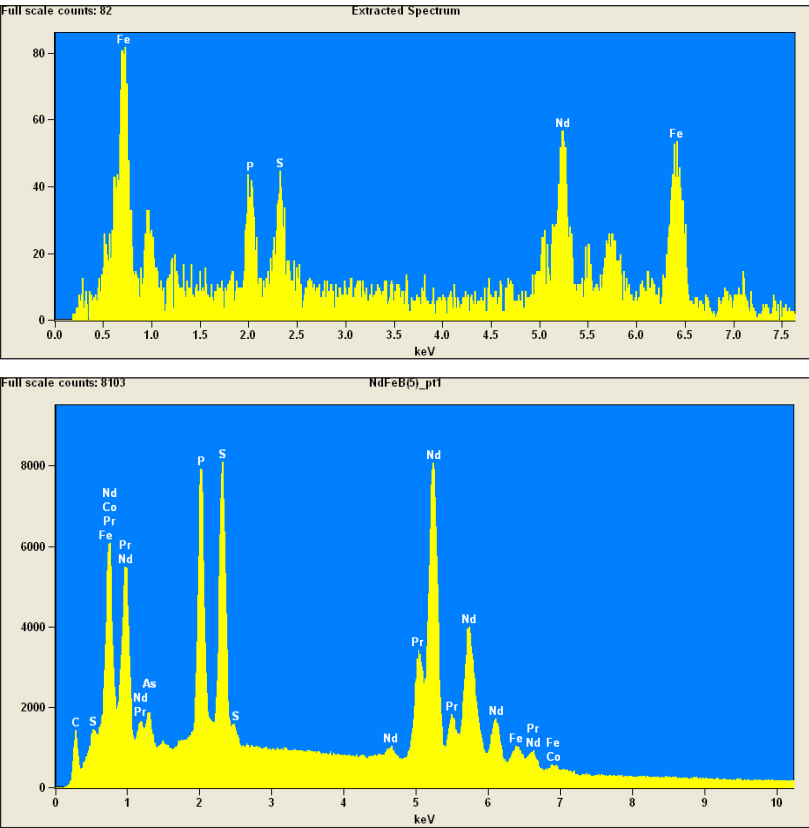Figure 10: Image of area mapped in second example

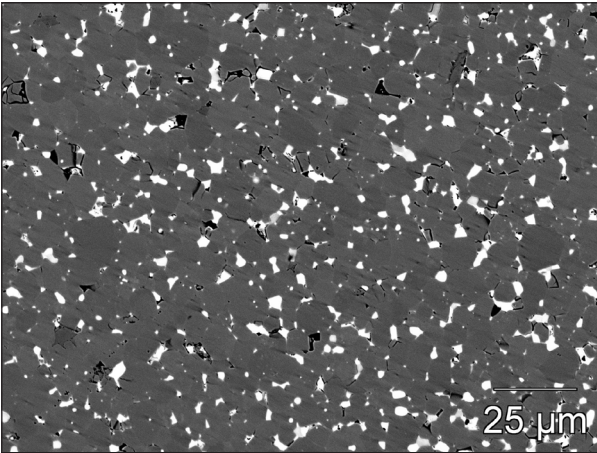Figure 11: Elemental maps of area shown in Figure 11. Note the presence of P and S.

Figure 12: The spectrum (top left) was extracted from the map at one of the spots in Figure 11 indicating the presence of P and S. To improve the precision of the identification Point and Shoot was used at the location indicated by the map. This enlarged image is shown below. The spectrum (bottom left) was acquired from Point 1 in the image. It shows with greater confidence the identification of P and S in this sample at this point.

Match

Another technology that can be brought to bear is the Match algorithm. Most analytical techniques attempt to characterize a sample by measuring the abundance of each element in the sample. This works well for simple, homogeneous samples. However, there is no standard way of analyzing a heterogeneous sample.

However, a remarkable feature of EDS is that if the same material is measured under the same instrument conditions the same spectrum will be obtained (except for small, statistical fluctuations). Due to the physics of X-ray generation nothing else matters. This is true even for complex, heterogeneous samples.

Match takes advantage of this repeatability by attempting to identify materials by numerically comparing a spectrum from a material with a set of spectra taken from known samples. Rather than trying to identify the elements in each spectrum and measure their abundance it simply looks at the shapes of the spectra and finds the most similar shapes among the candidate spectra. This makes it well suited to answering the question "Is material A reasonably similar to material B?" even when the materials are complex.

This requires some small effort to setup the methodology and sample preparation for particular materials as improper sampling would bias the result. Once the method has been established for a particular material it can be employed with little operator input.

To setup a test several spectra were taken from a NdFeB sample – some from the matrix and some from the bright areas with slightly different composition.

In the first example, a spectrum was taken from a different area of the matrix. The results are shown in Figure 13. A better match is indicated by a smaller Chi-squared value. As expected, the two other matrix spectra are show very low chi-square values.
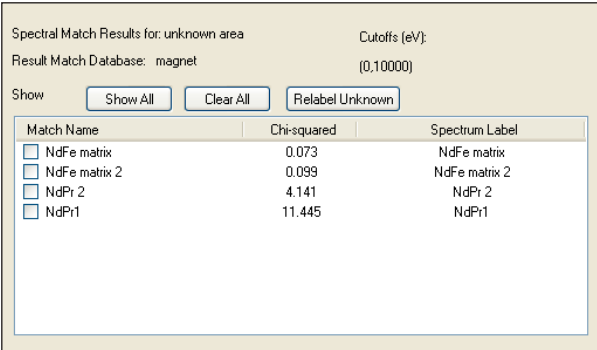

Figure 13. Match results for unknown from the matrix

A second spectrum was acquired from a bright particle. The result is shown in Figure 14. This is a good match for the first type of bright.

Once it has been setup Match is a very fast way to identify materials, even those with complex compositions.

Match also can be extended with Analysis Automation such that a large number of areas across a sample can be atomically measured and processed. With complex samples a distribution of results from a large number of measurements is often more helpful to characterize a sample.

Feature Sizing and Chemical Typing (FSCT)

Finally, Feature Sizing and Chemical Typing can be used to count the different visible features in a field of view and measure their sizes, shapes and elemental compositions. Most often this is used with Analysis Automation to measure features over a large number of fields. The result is a table of numbers characterizing hundreds, if not thousands of features in a material. Histograms are calculated for measurements such as area, diameter and perimeter, enabling the analyst to quantitatively view the nature of the sample.

With modern EDS detectors and SEMS the measurement of each feature may require from about 0.5s to 5s depending on the nature of the feature and the desired precision. Setting up a method for a particular sample type may require some investment of effort after which the application of the method is simple and routine and mostly automated.

As an example the region shown in Figure 15 was analyzed by FSCT. The discriminators were set to select the bright features. Fifty one particles were detected. Figure 16 shows the area measurements plotted as a histogram. Many other kinds of measurements are possible.

An X-ray spectrum was taken from each particle and stored in the analyzer. The software automatically sorted these spectra into five groups. Table 2 lists these categories. The analyst may create their own categories or they may modify the generated categories and apply them to the stored data and resort the data.

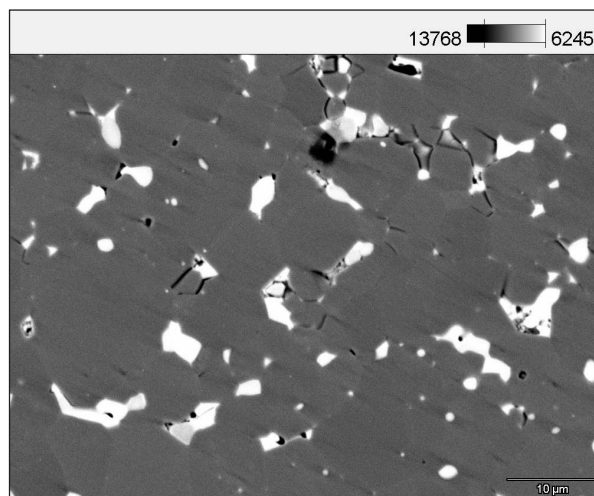Figure 14: Match results for unknown from a bright particle

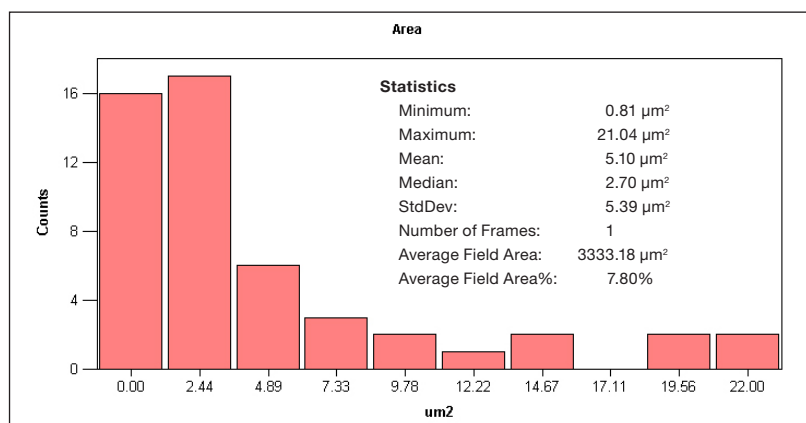Figure 15: Field of view used to generate features sizing data

Figure 16: Histogram plot of the measured areas of 51 particles in a sample of NdFeB magnet

Table 2: Categories automatically determined by software when spectra were acquired from particles. These mixed element categories consist of a center value and a range for each element. It is also possible to define categories as a single element and a minimum value.

	Fe	±	Pr	±	Nd	±	O	±
Learn 0	20	10	21	10	53	10		
Learn 1			19	10	66	10	9	10
Learn 2	34	10	18	10	46	10		
Learn 3	55	10	10	10	31	10		
Learn 4	8	10	21	10	55	10	14	10

Tables 3 and 4 are summaries of the particle results. Table 3 lists the area fractions of particles in each category and Table 4 summarizes the size ranges of each composition category.

Figure 17 shows part of the result table. The full table of results for all particles is available to the analyst as a spread sheet.

In case of complex samples it is possible to differentiate particles such that even particles within particles can be measured.

The value of this kind of measurement arises from the context of comparing it to similar analyses of known good samples. Then it is possible to see if particle sizes and shapes have changed. This is a powerful technique for discovering if incoming material has changed in the size, shape, and composition of the constituent features. Enormous numbers of particles may be sized and analyzed and the results summarized and categorized by the software.

Site License

An additional characteristic of this platform is that it includes a site license. With this the identical application software used to collect the data can be installed at an unlimited number of computers around the laboratory. This makes it possible to review data and generate reports while the SEM/EDS is busy collecting fresh data.

Summary

- NdFeB is a difficult material to analyze because it is a composite consisting of micron to submicron sized grains

- SEM/EDS provides multiple ways to analyze individual features down to dimensions less than one micron

- Point and Shoot provides for the analysis of individual features identified by the analyst

- SI Net Counts mapping shows the spatial distribution of elements chosen by the analyst in a field of view

- COMPASS phase mapping automatically parses a map into its constituent phases with little input from the operator beyond setting up the analytical conditions

- Match provides a simple, reliable method for identifying materials based on the similarity of their measured spectra to spectra from known materials

- Feature Sizing is a powerful technique that measures the sizes and shapes and compositions of the visible particles in a field of view

- Analysis Automation is an extension of the other features which allows these analyses to be automatically conducted at a large number of points across a sample

Table 3: Report summarizing the distribution of found particles among the composition categories

Chem Type	# Particles	% Particles	% Total Area
All Types	51	100	7.80
Learn 0	12	24	0.83
Learn 1	26	51	5.87
Learn 2	6	12	0.64
Learn 3	3	6	0.16
Learn 4	4	8	0.31

Table 4: Report summarizing the size distributions of found particles of the composition categories

Area Ranges	0.00–10.00	10.00–20.00	20.00–30.00	30.00–Max
All Types	44	5	2	0
Learn 0	12	0	0	0
Learn 1	20	4	2	0
Learn 2	5	1	0	0
Learn 3	3	0	0	0
Learn 4	4	0	0	0

Figure 17: Sample of the full table of results of particle measurements

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