Computer Aided Phase Determination by Electron Probe Microanalysis

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Abstract

A measuring procedure and a computer program have been developed for energy dispersive microanalysis to study segregation properties of various bulk, polished samples (alloys and ceramics). A few hundred sampling points were selected at random or regularly forming a grid pattern on the surface of the sample. Energy dispersive spectra were stored and ZAF corrected, and the obtained concentrations were evaluated statistically. An IBM AT compatible computer was used to calculate concentration distribution functions of the elements present in the sample. In addition to the usual statistical values, several types of concentration distribution functions were calculated. The method was tested on an Al-Mn standard sample used for spark excited optical spectroscopy and on refractory bricks. The advantages of this method as compared to concentration mapping are discussed.

Introduction

The practical application of bulk materials requires, if possible, studies on complex specimens obtained from bulk structures. Often, the aim is to find correlation between the macroscopic and microscopic properties of materials. The microanalytical results should characterize the specimen as accurately as possible. The reliability of data can be improved by statistical methods.

The aim of this work is to present a procedure within the electron probe microanalysis (EPMA) by which the composition of the whole specimen is characterized by statistical methods helping to find the different phases or segregations. The procedure is to some extent similar to image analysis, deriving characteristic results for the whole sample from a series of microscopical measurements.

From the very beginning, the electron probe microanalyzers have been capable of photographing two-dimensional distribution of intensities of characteristic X-rays from a specimen under study. Highly developed EPMA equipments could display the concentration distribution (instead of the intensity) of elements present in the specimen (Aiba, 1986; Statham, 1988). This made it considerably easier to find foreign phases or precipitates in the sample. We have, however, followed another line of thought, based on information from the literature (Butler, 1987; Gungor, 1989; Howell and Bee, 1989; Stefaniay et al., 1983; O'Brien et al., 1989; Altan et al., 1990; Lange and Hirlinger, 1985): instead of determining the two-dimensional distribution of concentrations on the real plane surface of the sample (the so-called quantitative elemental mapping), we selected a large number of points of analyses on statistical bases, carried out concentration determination (ZAF correction procedure) by points, and determined concentration probability distribution functions and plotted the concentration of element pairs in a rectangular coordinate system, on an abstract plane. In the latter case, particular phases manifest themselves as agglomerations of data points in the plot and the composition of the phase in question can be determined from the position on the graph.

The practical need of finding the composition of alloys on a microscopic scale motivated some researchers to develop similar methods for the determination of phases and of segregations. The quantitative methods of composition mapping (Aiba, 1986; Statham, 1988) eliminate the most serious drawbacks of intensity mapping. In order to obtain data for a regular map, the acquisition time at one point is very short and the precision is limited by statistical factors. However, if we dispense with surface mapping, we can choose the location and duration of analyses more freely.

The examples we followed can be categorized as follows:

- spot analysis (Butler, 1987; Gungor, 1989; Howell and Bee, 1989; Stefaniay et al., 1983);

- area scan analysis (O'Brien et al., 1989; Altan et al., 1990; Lange and Hirlinger, 1985).

Spot analysis is carried out at some hundred points distributed at random. (Of course, the specimen should satisfy the requirements of the quantitative analysis). This method is easily adoptable both on energy (EDS) and wavelength (WDS) dispersive spectrometers. The analyzed points in Stefaniay's measurement lie on a zigzag line determined by a random number generator. Butler (1987), Gungor (1989), and Howell and Bee (1989) analyzed points lying on a square grid. According to Hilliard and Chan (1961), the measurements are statistically independent if the mesh size of the grid is sufficiently large.

In the area scan analysis, series of spectra are acquired in picture mode while successively increasing the magnification. This method cannot be adopted on WDS instruments, and the treatment of data is less straightforward than in the first method.

Experimental Procedure

A Philips 505 scanning electron microscope (SEM), a Link AN10000 energy dispersive X-ray analyzer with beam positioning facility and an IBM AT compatible computer were used.

The use of an energy dispersive analyzer is justified by the fact that the intended application of the method cannot be realized economically on a wavelength dispersive spectrometer because of the number of elements present in the sample. In our practice, the parallel acquisition of spectra and the ease of use of the EDS system proved more advantageous than the accuracy and speed of WDS instruments.

Our work consisted of:
- sample preparation,
- data acquisition,
- composition calculation, and
- statistical evaluation of concentrations.

Sample preparation, and pre-investigation

10 x 10 mm samples were embedded in epoxy resin of 1 inch (2.54 cm) diameter, and polished to 1 micrometer finish by MgO. Before the analysis, we studied the samples by the SEM to determine the average

correlation length of microstructure in order to avoid the errors caused by the concentration correlations.

Data acquisition

The data acquisition was controlled by a computer program. A cobalt spectrum was taken to standardize the line intensities and control the energy calibration. Then 30-64 spectra were acquired on samples to be analyzed and stored. This procedure was repeated several times to get more than two hundred spectra. Three types of data acquisition procedures were developed: "manual", "automatic" and "precipitation". The first two types of measurements were done on points located on a square point grid. The grid spacing was comparatively large to the correlation length of concentration changes, determined by SEM investigation. Despite the regularity of measurement points, the results are statistically independent if the step size between two measured points is larger than the correlation length (Gungor, 1989; Hilliard and Chan, 1961). In the "manual" procedure, the manual setting of the stage gave great flexibility in the choice of the grid spacing. The "automatic" procedure used to work on a 8 by 8 point grid with the grid spacing set by the choice of magnification. In the third procedure, the beam was moved to different precipitations by cursor keys, to determine the composition of the second phase particles. In this case, the measured composition was not characteristic of the whole sample, but only of the second phase. In all cases, the spectra were acquired at 40 second livetime at a count rate of about 3000/second, resulting in 100,000 counts in the full spectrum.

Composition determination

The stored spectra were evaluated off line. This has the advantage that at any time we could re-evaluate the spectra, if, for example, a new element had to be incorporated in the analysis. In our EDS system, the ZAF correction procedure runs fast, typically less than 30 seconds for each spectrum, nearly independently of the number of analyzed elements. The concentrations were stored, and finally transferred to an IBM compatible computer.

Statistical evaluation

A menu-driven evaluation-program was written in Turbo-BASIC language with a menu structure similar to that of the LINK system. The structure of the program is described below:

The file operations module contains the usual data handling routines such as load, store, merge data files, and data transfer and conversion from the EDS system. The data file contains sample name and description, and chemical symbols and atomic weights of the analyzed elements. This header is followed by the fitting indexes and element concentrations for every point measurement.

The data preparation routine converts the data into ready-to-display form. There are two data conversion procedures, one for normalization of data to 100 mass per cent, and one for conversion to atomic per cent. Another routine processes composition thresholds. A

routine calculates some basic statistical parameters, such as mean values and standard deviations of element concentration distributions, and element correlation factors.

The display routine displays the results on the monitor or prints them on the printer in text and graphics. There are routines for listing point analysis data and for statistical data printout. The graphical output routine plots the probability density functions (PDF) and cumulative distribution functions (CDF) of the element concentration distributions and a special concentration "map". The diagram parameters are automatically set, but it is possible to override the automatic routine. We called the three types of diagrams "PDF", "CDF" and "MAP". On "PDF" diagrams, the PDF is plotted versus the concentration of the sample. It has its highest value at the concentration value which is the most probable in the sample. It is the most suitable mode in the visual evaluation of the measurements, giving peaks at the probable concentrations. The "CDF" diagram is used mostly for theoretical evaluations for example for fitting to the Scheil equation (Gungor, 1989). The "MAP" diagram plots one element concentration versus another element concentration in the rectangular coordinate system. This type of representation is similar to some types of phase diagrams: in concentration-areas of probable phases there are more data points.

The "PDF" and "CDF" display routines give the possibility to fit theoretical distribution functions to the measured data. We used Gaussian functions to fit phase compositions and three parameter Weibull functions to detect the minimal concentrations occurring in solid solutions (Harlow, 1989; Stefaniay *et al.*, 1983).

Investigation of Al-Mn standard samples

We investigated the homogeneity of the alloying elements in an Al-Mn standard for spark excited optical spectroscopy. The sample was previously analyzed carefully by different analytical laboratories. The mean composition is shown in Table 1, together with our measured values.

Table 1. Composition of Al-Mn standard

	Mn m%	Fe m%	Mg m%	Si m%	Ti m%
Certified	1.9	0.9	0.05	0.3	0.04
EDS	1.9	1.1	0	0.25	0

Previous optical spectroscopy analysis proved the homogeneity of this sample. Figure 1 shows a typical backscattered electron image of the standard sample, revealing eutectic phases of about 10 μm in size. The probable composition is Al_6Mn. Therefore the sample can be homogeneous for spark excited optical spectroscopy purposes, where the spark diameter is several mm, but it is obvious that the sample is not homogeneous on EPMA scale, where the spot size is a few μm.

Fig. 2 shows the PDF diagram of this sample. The data with a higher manganese concentration than 4%
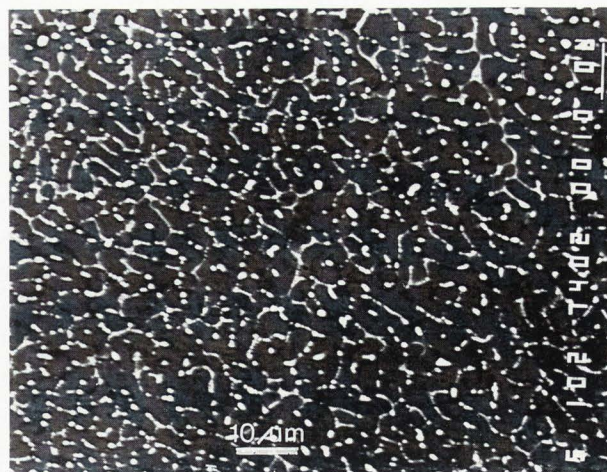

Fig. 1. Backscattered electron image of the standard for spark excited optical spectroscopy.
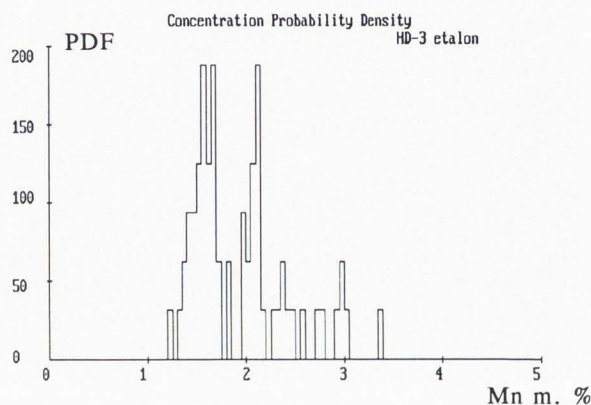

Fig. 2. PDF of Mn in the standard for spark excited optical spectroscopy.

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are excluded from this graph using the threshold function of the program. In this way, the figure shows only the analysis data arising from points lying on solid solution. The distribution is wider than 2%, also the concentration deviations in the "homogeneous' alpha phase are larger than the concentration itself. This is a surprising result for an analytical standard sample! But it should be remembered that this sample is made for optical spectroscopical purposes. It is obvious that the characteristic length of composition deviations is an important parameter for all analytical standards. Standards can prove satisfactory in one analytical technique and unsatisfactory in another technique (Liebich, private communication).

Investigation of ceramics samples

In ceramics, composition variations are larger than in most types of alloys, nevertheless the micro-scale composition in ceramics is no less important than in
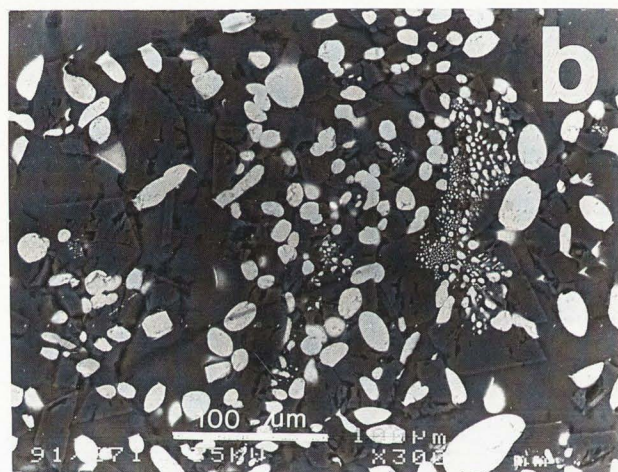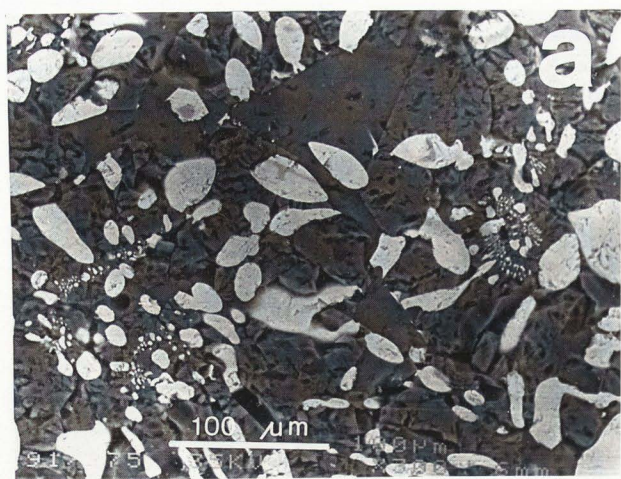
Fig. 3. Backscattered electron image of ZIRKOSIT A and ZIRKOSIT B bricks.

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alloys. Mechanical and chemical properties are determined by the amount, distribution and crystalline state of small second phase precipitations (Lange and Hirlinger, 1985; Jang and Moon, 1990).

We investigated two types of ZIRKOSIT refractory bricks. These are heat resistant materials composed of Al_2O_3, ZrO_2 and SiO_2. Figure 3 shows the backscattered electron image of two samples of ZIRKOSIT, termed as "good" (A) and "bad" (B). The difference in microstructure is not obvious for these two samples. The microanalysis results are given in Table 2 (mean concentrations of oxides in mol percent; oxygen concentration is given in a separate column in atomic percent):

Table 2. Composition of ZIRKOSIT bricks.

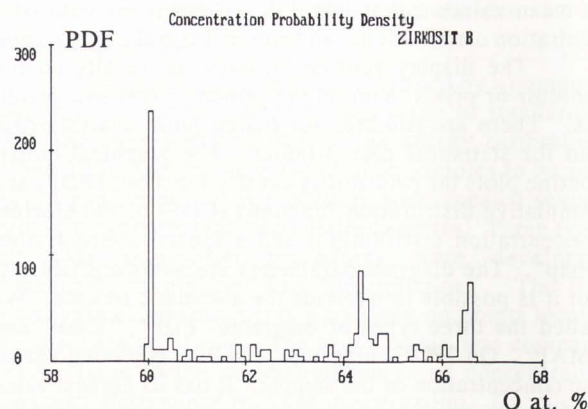|	Al_2O_3 mol%	SiO_2 mol%	ZrO_2 mol%	Na_2O mol%	O at%
Sample A	65.0	17.4	15.9	0.91	62.1
Sample B	46.2	25.8	25.6	1.4	62.7

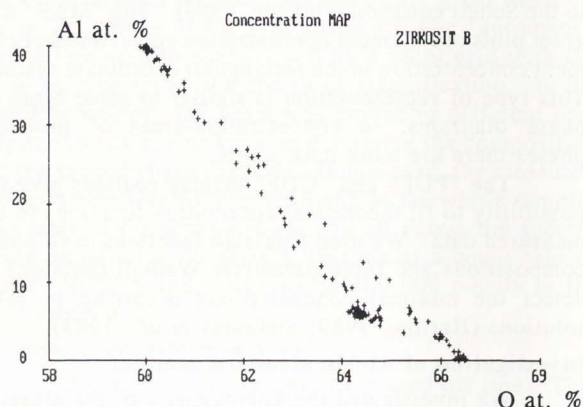**Fig. 4**. PDF of oxygen in ZIRKOSIT B brick.

Fig. 5. MAP concentration distribution of aluminum versus oxygen in ZIRKOSIT B brick.

The major difference in the composition is the excess aluminum oxide in sample "A". The concentration PDF of oxygen (Fig. 4) shows 3 peaks corresponding to the oxygen content of three oxide types in the sample: at 60 at% in Al_2O_3, at 66 at% in ZrO_2, and at 64 at% in the SiO_2 containing silicate (silicon is present in the form of aluminum-silicate containing about 5% of aluminum).

The same effect on a "MAP" concentration distribution function shows the Al content of the silicate phase (Fig. 5). The three phases in this figure occupy three separate areas, and the points between them indicate the phases dissolved in each other. In Figure 6 "MAP" concentration distribution function for silicon and oxygen gives the answer to the question: why brick "B" is of inferior quality as compared, to brick "A"? There are no measurement points between the silicate (at about 64 at% oxygen and 28 at% silicon) and ZrO_2 (at 66 at% oxygen on this axis) phases and nearly no points between the Al_2O_3 and ZrO_2 (both on the "X" axis) phases. The

points between the Al_2O_3 and silicate phases prove that these phases are dissolved in each other to a greater extent than the ZrO_2. Thus the matrix is more homogeneous in the sample with lower ZrO_2 content resulting in higher toughness.

It is concluded that although ZrO_2 increases the toughness of advanced alumina ceramics in highly dispersed form and in about 4 mol%, but in this sample the rough phase structure and high zirconium concentration together give worse mechanical characteristics at high temperature than the lower zirconium content.

Summary

We have presented a computer aided procedure for the electron probe microanalysis characterization of the specimen as a whole, which uses statistical methods for the evaluation of concentrations, obtained in a large number of point measurements.

An advantage over the conventional concentration mapping (or quantitative elemental mapping) is that the number of measurement points and their location can be selected more freely, consequently the duration of a single point measurement can be longer and the statistical errors are smaller than those of mapping.

Concentration density functions have been determined. Plotting the concentrations of element pairs in a two dimensional graph results in the agglomeration of concentration data points corresponding to the presence of different phases. This makes the procedure especially useful in the detection and determination of chemical composition of precipitates, segregations, and of second phases.

Acknowledgements

References

Aiba Y (1986) Application of EPMA to quality inspection of ceramics used for continuous casting of steel. JEOL News **24E** No. 3, 29-34.

Altan B, Misirli Z, Yorucu H (1990) The determination of the homogeneity mixtures. Z. Metalkde. **81**, 221-228.

Butler SA (1987) Segregation studies in low-alloy steels by energy-dispersive X-ray spectrometry. Scanning **9**, 205-214.

Gungor MN (1989) A statistical experimental technique for investigating microsegregation in cast alloys. Metallurgical Trans. **20A**, 2529-2533.

Harlow DG (1989) The effect of proof-testing on the Weibull distribution. J. Mater. Sci. **24**, 1467-1473.

Hilliard JE, Chan JW (1961) An evaluation of procedures in quantitative metallography for volume-fraction analysis. Trans AIME **221**, 344-352.
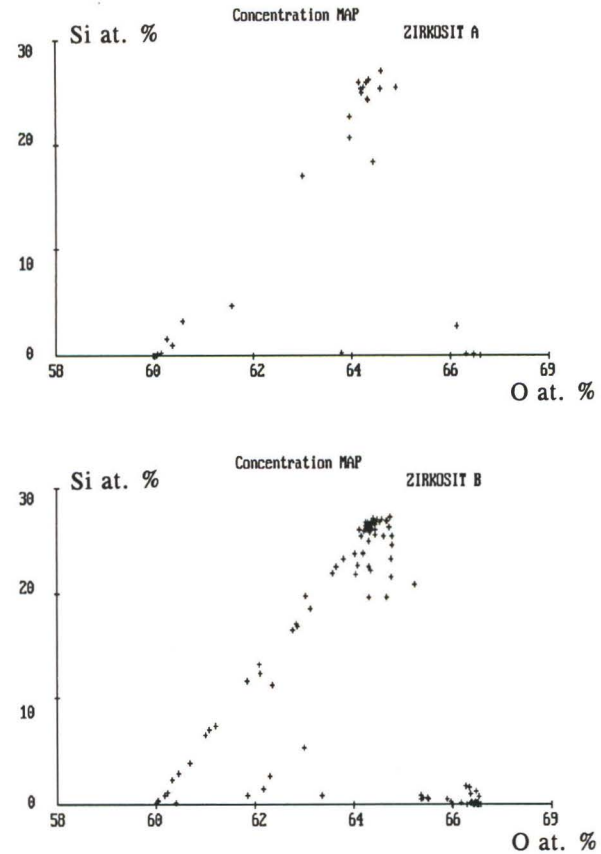
Howell PR, Bee JV (1989) A microanalytical study of the early stages of recrystallization in the nickel-base superalloy APK1. J. Mater. Sci. **24**, 1287-1290.

Jang HM, Moon JH (1990) Homogeneous fabrication and densification of zirconia-toughened alumina (ZTA) composite by the surface induced coating. J. Mater. Res. **5**, 615-622.

Lange FF, Hirlinger MM (1985) Phase distribution studies using energy dispersive X-ray spectral analysis. J. Mater. Sci. Letter **4**, 1437-1441.

O'Brien DM, Sharp RM, Stringer DJ (1989) EDS analysis of polyphase microstructures - with application Al-SiMg₂. Scanning **11**, 87-92.

Statham PJ (1988) Pitfalls and advances in quantitative elemental mapping. Scanning **10**, 245-252.

Stefaniay V, Sapsal V, Gillemot L, Dekany E, (1983) Investigation of the processes occurring during the homogenization of the alloy $AlMgSi_{0.5}$ by electron probe microanalysis. Aluminum **59**, 8-13.

Fig. 6. MAP concentration distribution of silicon versus oxygen in both types of ZIRKOSIT bricks.

See next page for Discussion with Reviewers

Discussion with Reviewers

K. Kiss: Could the author elaborate on the method used in his three dimensional Weibull statistical analysis to detect the "minimal concentrations occurring in solid solutions". What are the values of minimal? Was the much simpler two dimensional Weibull analysis attempted and found to be inapplicable?

Author: "Minimal" concentration in solid solutions may be rather high as in liquid solutions, for example, copper dissolves upto 100% of gold. In other systems, the solubility limit lies on a few tenths or hundredths of percent, for example Fe in Al, or in W. The minimal concentration occurring in solid solutions is affected also by segregation processes, which increase or decrease the local concentration. The measured concentration is also determined by the limited spatial resolution of electron beam microanalysis. The measured concentration distribution function is usually asymmetrically shaped and starts with a high slope at a defined concentration value.

The two dimensional Weibull distribution has its origin in the origin of the coordinate system, the two parameters determine only the shape of the function. The additional third parameter (or dimension) is a zero shift, in our case to the above discussed minimal concentration value.

K. Kiss: Is this program available to interested parties and if so is it free of charge (as often analysts will offer their programs to the scientific community free)? If it is not available free what is its price?

Author: The problem is rather a technical, not a commercial one: the data input is worked out for only one type of EDS system. For interested parties I am willing to transfer the program to other systems.

P. Statham: You claim that reduction of statistical error is a significant advantage of spending more time on fewer points than for conventional X-ray mapping. However, your "MAP" plots show large variations in concentration for each component, presumably much greater than variations expected due to statistics. In practice, if the total time of an experiment is fixed, how would you plan for the best compromise between the number of points analyzed and statistical precision at each point?

Author: As I stated above, the variations on "MAP"-s or the width of a peak in PDF is mostly determined by **a)** real differences in the sample; **b)** the limited spatial resolution; and **c)** the statistical error. To reach the detectability limit of 1 % in a dilute alloy containing 1 % alloying element by count rates of 3000/sec order you need about 1 second. For the relative accuracy of some ten percent you need some tens of seconds. On the other hand, if the sample has 1 % segregates in volume, 100 measurements are needed to detect one particle of the second phase. Consequently a few hundred measurements of a few tens of seconds of livetime are needed to properly investigate a dilute solution of 1 % order.

S.A. Butler: What is the estimated accuracy and precision of an individual analysis?

Author: The estimated accuracy according to the counting statistic was well under 1 % for every detected element. To determine the real precision is rather difficult, because of the spatial resolution. I estimate it, from the PDF diagrams, to be 1-2 %.

S.A. Butler: How was the oxygen content for ZIRKOSIT samples determined: by stoichiometry or by difference?

Author: By stoichiometry.

S.A. Butler: The only "MAPS" shown for ZIRKOSIT are of Al or Si against oxygen. Were the "clusters" not evident in "MAPS" of Al against Si, Si against Zr, etc.?

Author: Yes, they were. The "MAPS" containing oxygen were chosen only because on these diagrams the relation is more evident, partly because the oxygen concentration was determined by stoichiometry, partly because the oxygen is the "link" between the particular phases.

S.A. Butler: The basic technique used in the paper has been previously described by J.C. Russ and T.M. Hare ("Characterization of Heterogeneous Polycrystalline Materials", Microbeam Analysis, 1981, pp 186-189); i.e. the identification of individual phases present in polycrystalline materials by energy-dispersive x-ray analysis at a number of points arranged on a rectangular grid. The principal differences appear to be that Russ and Hare used (a) X-ray intensities rather than ZAF-corrected compositions, and (b) a more sophisticated process of cluster analysis in N-dimensional intensity space to identify the distinct phases.

The author also appears to be unaware of the paper by R.V. Heyman ("The Application of an Automated Microprobe Procedure for the Evaluation of Elemental Segregation in Alloys", Microbeam Analysis, 1984, pp 299-301). This paper refers to the use of multiple analyses at random points on the sample and the use of cumulative probability plots (c.f. your "CDF" plots).

Author: Thank you for your comments. The paper you mention are similar to mine, but they do not cover the entire topic that I discuss; especially the considerations connected to solid solutions are not discussed by them.