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ON THE STATISTICAL ANALYSIS OF ATOM PROBE DATA

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ABSTRACT - The statistical techniques that have been applied for presenting and analyzing atom probe data are critiqued. These techniques include raw data analysis, character plots, ladder diagrams, frequency distributions of composition profiles, Markov chains, contingency tables, cross correlations, power spectrum, and autocorrelations. A comparison of the suitability of the individual techniques for specific metallurgical applications is also presented.

INTRODUCTION

The atom probe is accepted as a basic tool for metallurgical research. All experimental atom probe data must be statistically analyzed to establish physical parameters. These parameters can then be compared with those obtained from other experiments and used to explain physical properties. The purpose of statistical analysis is first to determine the limits of confidence on the estimate of the deviation and second to parameterize the deviation. Apparently sophisticated techniques can sometimes obscure rather than expose more information and the usefulness of the simple techniques should not be underestimated. A summary of some effects which have been studied using an atom probe indicating the relevant statistical methods is given in Table 1. These statistical methods should be available for the user during the experiment to assure the validity of the data.

In the following sections, the techniques will be grouped by applications. It is assumed that possible systematic errors have been minimized by using appropriate experimental conditions such as standing voltage and pulse fraction, specimen temperature, evaporation rate, and vacuum conditions. These conditions should ensure there is a) no preferential evaporation or retention, b) no pile-up of ions at the detector, and, c) no hydride formation. It is also assumed that the effective probe aperture is adjusted during the experiment to ensure a constant area of analysis. The effects of local magnification will be discussed elsewhere. It should also be cautioned that 1) adjacent atoms detected in an atom probe experiment are not necessarily neighbors in the specimen, 2) the detection efficiency of atoms is always less than 100%, and 3) the time series may not be stationary, especially in materials where there are marked inhomogeneities in composition from one region to another.

Table 1. Summary of statistical techniques and their applications in atom probe analyses.
( x = suitable, ? = questionable )

<table>
<thead>
<tr>
<th>Technique</th>
<th>Clustering</th>
<th>Cosegregation</th>
<th>Interfaces</th>
<th>Particle Size</th>
<th>Modulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Data Analysis</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Character Plots</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ladder Diagram</td>
<td>?</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filtering</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Contingency Tables</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cross Correlations</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Markov Chains</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Frequency Distributions</td>
<td>x</td>
<td>x</td>
<td></td>
<td>?</td>
<td>x</td>
</tr>
<tr>
<td>Power Spectrum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Autocorrelations</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
RAW DATA: character plots, ladder diagrams, and composition profiles

First, information may be obtained by considering the data as a time series or by accumulating a given number of the ions which were detected sequentially into blocks.

Perhaps the simplest way to examine the data is to list the atoms in the order in which they are detected; i.e., a character plot. Usually, the number of elements plotted in a row is chosen to be approximately equal to the number of ions detected per atomic plane, so that the number of rows gives an approximate depth scale. This technique is generally used to detect clustering or to examine particles. However, this visual aid should be treated with care since it is very easy to see clusters or particles when none is present. If we are looking for an element B with volume fraction \( p \) distributed randomly in a solution of A, then the most likely separation of two sequential B atoms is zero. The mean separation is \( p/(1-p) \) with a standard deviation of \( \sqrt{p(1-p)} \) (i.e., larger than the mean). The human eye is very good at recognizing patterns and may pick them out from a completely random distribution. Further analysis is prudent in this case.

The ladder diagram is another useful visual aid for the examination of raw data. Displacements parallel to the x-axis represent the detection of one type of element and those parallel to the y-axis another. Additional elements can be superimposed on the plot. This display is particularly suitable for examining ordering or the composition at interfaces or surfaces. An estimate of the error on a composition obtained from the slope can be made in the same way as for a block of atoms (see below), except that it must be remembered that the block may not have been chosen at random but selected and the null hypothesis should allow for this.

If a large number of ions is detected in a single experiment it may be more sensible to divide the data into blocks and analyze the compositions of the blocks. The block size may be chosen to be either a fixed number of atoms or contain the atoms from one atomic layer determined by the observation of the evaporation of planes of atoms at a crystallographic pole. If \( n \) atoms are included in a block and \( N \) of them identified as B atoms, and the sample is drawn from a population with an assumed binomial distribution, the unbiased estimator of the mean composition, \( C \), of the block is \( N/n \) and the estimate of the standard error of this estimate is \( \sqrt{C(1-C)/n} \). Variations of the composition may be obvious. Smoothing of these composition profiles can assist in reducing the noise arising from the relatively small number of atoms in an individual block. A moving average using a cubic or quintic polynomial filter is generally suitable for this purpose since the spatial information is not seriously degraded.

In systems where the scale of a second phase is of the same order of magnitude as the area of analysis, the composition that is measured may not be representative of the true composition due to simultaneous sampling of the particle and the surrounding matrix. The resolution limit of the atom probe in detecting particles from atom probe composition profiles has been discussed by Blavette and Chambrelan. However, this simple model incorrectly states that the fraction of particles resolved drops to zero when the diameter of the area of analysis is equal to or greater than the particle size. Instead, this point marks the cutoff where the true composition cannot be measured.

These simple techniques are convenient ways of presenting data obtained from an atom probe experiment. The technique which is most appropriate is determined by the scale over which composition fluctuations are expected to occur. In many cases, deviations from a random distribution can be clearly revealed by these simple methods.

FREQUENCY DISTRIBUTIONS AND MARKOV CHAIN ANALYSIS

These two techniques are comparable because they both reveal deviations from a random distribution of solute, but do not provide direct information about the scale over which this occurs.

The frequency distribution is obtained by plotting the total number of composition blocks with a given number of atoms of an element, B, against that number of atoms. Each atom in a block is assumed to be drawn from a population such that it has a probability \( p \) of being a B atom. This probability can be estimated from the total data obtained in the experiment or from analysis using another technique. The frequency distribution of block sizes is expected to have a binomial distribution and the distribution \( \chi^2 = (\hat{e}_n - e)\hat{e}_n \) (where \( \hat{e}_n \) is the observed frequency of blocks of a given B content and \( e \) is the expected number) is expected to follow that of the chi-squared variable. It is simple therefore to test this null hypothesis.

A number of authors have discussed treating the sequence of data as a Markov chain. A series of events may be considered as a Markov chain if the outcome of each event is dependent only on the previous event. The earliest and most scholarly treatment of the application of Markov chains theory to measure clustering parameters from the data obtained from atom probe data is that of Johnson and Klots. They derive the maximum likelihood function for a short range ordering parameter \( \theta \), where \( \theta p \) is the probability of a B atom being detected if the previous atom in the chain is a B atom and \( p \) is
the atomic fraction of the element B. For a large sample they show that $\theta$ is estimated by

$$L_n(\theta) = n_BB/\theta - n_{BB}p/(1-\theta p) + n_{AB}p^2/(1 - 2p + \theta p^2) = 0$$

where $n_{AA} + n_{BB} + n_{AB} = n - 1$, and

$$n_{BB} = \sum x_i(1-x_{i+1}), \quad n_{AB} = \sum x_i(1-x_{i+1}), \quad n_{AA} = \Sigma (1-x_i)(1-x_{i+1}), \quad \text{and} \quad x_i = 0 \text{ or } 1 \text{ as the atom is type A or B}. \quad \text{The variance of this parameter is}$$

$$r^2 = \theta (1 - \theta p) (1 - 2p + \theta p^2) / p^2 (1 - 2p + \theta p)$$

It has subsequently been pointed out that the sequence of the detected ions is not usually directly related to their spatial location since the analyzed area is usually larger than one atom in size.\textsuperscript{[14]} Tsong et al. also attempted to apply a Markov analysis to atom probe experiments.\textsuperscript{[12]} An objection to their analysis is that their Markov event is not defined and, furthermore, it is not even possible to conceive of any event the probability of whose occurrence is zero if the atoms are distributed completely randomly as Tsong et al. suggest. Moreover, their estimate of the error in the parameter which is used to test for clustering is that it is just a fraction $1/\sqrt{n}$ of the observed value. No justification is given for this and it seems unlikely that a more rigorous analysis would produce such a convenient result. The value of Tsong et al.'s analysis is therefore limited.

Neither approach therefore provides a feasible method for estimating a cluster parameter. However, the method of Johnson and Klotz does provide a method for answering the simpler question of whether or not clustering has occurred, since if the parameter deviates significantly from random it must be as a consequence of some clustering. Hetherington et al.\textsuperscript{[13]} and Hetherington and Miller\textsuperscript{[14]} have also suggested that the variance of the separation of adjacent B atoms is a suitable method for testing of clustering, and that computer simulation may provide a method of deriving an estimate of the clustering from experimental data. The standard deviation of the separations in a large sample will approximate to

$$\sigma = q/p \quad \text{with a standard error of} \quad (1 + 6q + q^2) q / p^4 \quad \text{where} \ q = 1 - p$$

Our experience suggests that both of these techniques are more sensitive to clustering or phase decomposition than the autocorrelation function, with of course the disadvantage that no information about the scale is given. The frequency distribution of a TiAl alloy in which clustering of the Al has occurred is shown in Fig. 1. The observed distribution deviates from the expected distribution with a level of significance of 10%. The value of the parameter $\theta$ which is used by Johnson and Klotz is 12.1 (with an estimated standard error of 0.13), which deviates from the value of 1 expected from a random distribution and the standard deviation of the separation of neighboring Al atoms is 417 (with a standard error of 4.1) which also deviates with a high level of significance from the value of 216 expected from a random distribution. As might be expected, combining the data into blocks destroys some information and the levels of significance of the deviation are therefore lower. The Markov chain analyses are therefore more sensitive, although, it may be easier to interpret the frequency distribution (for example, Hetherington and Miller\textsuperscript{[14]} have estimated the amplitude of the spinodal from the frequency distribution using a maximum likelihood method). These techniques are useful in the detecting the early stages of phase decomposition of an alloy.

### CONTINGENCY TABLES AND CROSS-CORRELATION

Techniques based on analysis of contingency tables and cross-correlation are used for evaluating the co-segregation of elements.

Once again the data is divided into composition blocks. The rows of the contingency table presented in Table 2 represent the number of Cu atoms and the columns represent the number of Ni atoms in a block where the matrix consists of Fe atoms.\textsuperscript{[13]} The expected value from a null hypothesis, that there is no correlation, can be easily calculated\textsuperscript{[10-13]} from this table and a Chi-squared test may be performed. The division of atoms into composition blocks must be considered with care. If a fixed block size of N atoms is chosen, then there will still be a correlation between the number of atoms in the rows and columns (e.g. B and C in a matrix of A) even if the elements are randomly distributed since if there are n atoms of type B, there are only N-n atoms left which could possibly be C atoms. This drawback does not apply if the block size is chosen to be N atoms of type A and B, and the number of C atoms within this block is added to this. The total number of atoms in a block is therefore variable and equal to N plus the number of C atoms. Even if the B and C compositions are not found to differ significantly from a random distribution using the tests described above, it is still possible that this test will show cosegregation of B and C.
The cross-correlation R(k) function for pairs of terms k units apart is given by:

$$R(k) = \frac{1}{n-k} \sum_{i=1}^{n-k} \left\{ \frac{C_i - \bar{C}}{\sqrt{n}} \cdot \frac{D_{i+k} - \bar{D}}{\sqrt{n}} \right\}.$$ 

where $C_i$ and $D_i$ are the compositions of the ith measurements for the two species, $\bar{C}$ and $\bar{D}$ are the mean of the measurements, and n is the number of measurements.

The interpretation of this function is not simple.[15] The only condition under which the R(k)'s are independent and normally distributed is if the A and B compositions of each block are independent and normally distributed. In an atom probe experiment the variable block size as discussed above must be used to ensure this independence. The cross-correlation function correlates two compositions as they vary with distance through the specimen. A metallurgist is likely to be most interested in the value of cross-correlation at k=0 since a non-zero value is indicative of cosegregation. The contingency table examines the correlation at this point in much greater detail. In most applications, contingency tables provide a clearer examination of cosegregation.

**POWER SPECTRUM AND AUTOCORRELATION**

These two techniques both provide information about the spatial variation of the composition. Mathematically the two contain equivalent information; the autocorrelation function being the Fourier transform of the power spectrum.

The power spectrum has been used only sparingly to obtain spatial information about a phase separation.[16] The power spectra obtained from simulated APFIM experiments of evenly spaced and randomly spaced identically sized particles are shown in Figs. 2(a) and 2(b), respectively. It is fairly easy to interpret the former. However, even for the idealized case of randomly spaced particles it is not simple to interpret the spectrum. If an alloy which was in the early stages of a spinodal decomposition were examined, one might expect to see a peak in the spectrum corresponding to the wavelength of the spinodal.

The serial correlation or autocorrelation coefficient $r_k$ between pairs of terms k units apart is given[8] by

$$r_k = \frac{1}{n-k} \sum_{i=1}^{n-k} \left\{ \frac{C_i - \frac{1}{n-k} \sum_{i=1}^{n-k} C_i}{\sqrt{n-k}} \cdot \frac{C_{i+k} - \frac{1}{n-k} \sum_{i=1}^{n-k} C_{i+k}}{\sqrt{n-k}} \right\}.$$ 

where $C_i$, $C_{i+k}$ are the composition of the ith and i+kth measurements, and n is the number of measurements. This form of the autocorrelation function is preferred over the generally applied formula in analysis of atom probe composition profiles since it is less sensitive to small sample sizes.

The autocorrelation functions of idealized distributions are shown in Figs. 2(c) and 2(d). It is often stated that the first minimum, $k_0$, corresponds to the particle size and the first maximum, $k_1$, to the inter-particle separation. However, there are some caveats to which attention should be paid.[14] For a dispersion of identical size precipitates, $k_0$ indicates the particle size. However, if the particles have a range of sizes, $k_0$ is biased and gives a value larger than the mean particle size. This may be overcome by drawing a graphical extrapolated[17], however, this is an arbitrary procedure that often gives incorrect results. The position of the first minimum is a function of the mean size of particles AND the spread in particle sizes and this provides a complication in interpreting this value. The first maximum, $k_1$, is certainly related to the average spacing although a better estimate in high volume fraction materials is the difference between the second and first maxima $k_2-k_1$. However, the simulations of Alvensleben et al.[18] (although they do not draw attention to this) show that although it may be the average spacing between the observed particles, this is not necessarily the average spacing of the particles in the material and there may be a considerable error in this result. The orientation of modulations with respect to the cylinder of analysis, particularly in aligned microstructures, has to be accounted for in the accurate determination of the wavelength of the modulations. Piller and Wendt[17] interpret other values of the autocorrelation function. As has been pointed out in Hetherington et al.[12] these interpretations are rather optimistic.

The standard deviation of the autocorrelation coefficient (general formula) for each lag is $1/(n-k)^4$. 


Both Hetherington et al.\cite{18} and Alvensleben et al.\cite{18} have drawn attention to the estimation of the noise in an autocorrelation and that the mean of a set of lags obtained from random data is a biased estimator of the true mean. It should also be pointed out that, with a finite data set the cross-correlation between lags is not zero even if there is no correlation in the data. It is therefore possible that the second peak, \(k_2\), is just an artifact caused by the first peak and does not necessarily indicate a periodicity. This also draws attention to the care that should be taken in interpreting the data at large lags; it is regarded\cite{18} as good practice not to extend the autocorrelation beyond \(k=n/4\). In the absence of distance information, it is good practice to use the smallest possible block size.\cite{13,14} The block size should also be chosen to take account of the Nyquist limit to prevent aliasing.

Despite the apparent clarity of the information presented by the autocorrelation function, the interpretation of the peaks and troughs is not necessarily simple. Dalzell has taken a deeper approach to the problem.\cite{19} In order to interpret the data obtained from an alloy which has undergone spinodal decomposition, an analytical expression autocorrelation function was derived assuming the real compositions are those produced from spinodal decomposition obeying Cahn's equations. A maximum likelihood method was then used to fit the data to the analytical equation. This overcomes the problems in interpreting the autocorrelation mentioned above, but is neither convenient nor can be applied universally.

Although they contain the same information, the autocorrelation seems to provide a clearer representation of the data than the power spectrum, and is probably one of the most useful tools for the analysis of atom probe data since it provides spatial information about the deviations from a random distribution. Alvensleben et al., using computer simulations of atom probe experiments, have shown that it is relatively sensitive to small amplitude composition fluctuations.\cite{18}

CONCLUSIONS

The techniques discussed in this paper provide a framework in which data may be analyzed. It is usually simple to detect a non-random behavior in the material, however, it is far more difficult to deconvolute the actual distribution of the atoms. It should be noted that it is essential to have an understanding of the physical processes and helpful to have an estimate of the scale of the features being analyzed. The final words must however be to quote Disraeli's warning that there are lies, damned lies and statistics.

Acknowledgment


References

Fig. 1. Frequency distribution in a TiAl alloy which exhibits clustering.

Table 2. Contingency table for an underaged FeNiCu alloy containing copper clusters. Frequency of copper and nickel ions in 50 ion blocks. Copper and nickel are cosegregated (significance level 0.003).

<table>
<thead>
<tr>
<th>OBSERVED</th>
<th>EXPECTED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Ni</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1101</td>
</tr>
<tr>
<td>1</td>
<td>156</td>
</tr>
<tr>
<td>2</td>
<td>17</td>
</tr>
<tr>
<td>&gt;=3</td>
<td>25</td>
</tr>
<tr>
<td>Total</td>
<td>1299</td>
</tr>
</tbody>
</table>

Fig. 2. Power spectra and autocorrelations for a periodic and a random distribution of square particles.