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STATISTICAL ANALYSIS OF ATOM PROBE DATA

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ABSTRACT—This paper gives some suggestions and caveats on how to estimate the confidence limits on data obtained from atom-probe experiments. There are four sections covering autocorrelation, the use of contingency tables, estimation of ordering parameters and testing for clustering. This paper certainly does not exhaust the possibilities for statistical tests which may be applied to atom probe data, but demonstrates some useful techniques, which as far as the authors are aware have not been used before.

I-INTRODUCTION

A general approach to the statistical analysis of data should consist /1-2/, first, of the postulation of a null hypothesis and an alternative hypothesis. The null hypothesis is the assumption that the data has been obtained from a random distribution, and the alternative hypothesis is that there is in fact a pattern to the data. An appropriate experiment should then be designed and performed, followed by a statistical test based on the null hypothesis. The confidence limits (usually given as a percentage) for the rejection of the null hypothesis and the acceptance of the alternative hypothesis then depend on the assessment by the experimenter of whether it would be worse to reject a true null hypothesis (a type I error) or a true alternative hypothesis (a type II error).

The following studies show the application of various statistical tests. Two of the most important aspects of the process of interpreting data will not, and indeed cannot, be discussed in general terms. They are the design of an experiment which is free from systematic errors and the interpretation of the results in the context of the physical consequences of the acceptance of the null hypothesis; these rely on the skill and experience of the experimenter.

II-AUTOCORRELATION ANALYSIS

The autocorrelation function can be a powerful tool for examining regular modulations in composition. The interpretation of some of the features that might be expected in an autocorrelation plot have been discussed by Piller and Wendt /3/ (although their estimations of the errors of values are not always precisely calculated; for example, their estimation of the maximum value of $R(k)$, their equation 5, is independent of the number of samples taken which is plainly unrealistic). However, this kind of interpretation of an autocorrelation is beyond the scope of this paper. The first step that has to be made is to ensure that one is not trying to interpret a plot that is merely a set of random points, and this is the problem which we will tackle.

The discrete autocorrelation function is often defined as

$$R(k) = \frac{N}{N-k} \left(\sum_{i=1}^{N-k} (C_i - C_0)(C_{i+k} - C_0) / \sum_{i=1}^N (C_i - C_0)^2 \right)$$

where C_i is the composition of the i th block of data and C_0 is the average composition. It is worth pointing out that the precise formulation is

$$R(k) = \frac{\sum_{i=1}^{N-k} (C_i - C'_0)(C_{i+k} - C''_0)}{\left(\sum_{i=1}^{N-k} (C_i - C'_0)^2 \cdot \sum_{i=k}^N (C_i - C''_0)^2 \right)^{\frac{1}{2}}}$$

This is a far more cumbersome equation (since it requires the calculation of two means, C'_0 and C''_0 over the appropriate ranges and a new normalizing factor for every k),^o yet, is nevertheless the precise expression of the product-moment correlation coefficient of a scatter of points about their centroid. However, the value of the first expression is its ease of computation, and it is this expression which we will consider in the rest of the paper.

The first, somewhat surprising, result that we can obtain is that the average value of the $R(k)$'s is not zero as one might expect but $-1/(N-1)$ where N is the number of composition blocks. The derivation of this is simple. Writing $x_i = C_i - C_0$ and

$$s = \sum_{i=1}^N (C_i - C_0)^2$$

The mean value m of all the $R(k)$'s, including $k=0$, is

$$m = \frac{1}{s} \sum_{k=0}^{N-1} \sum_{i=1}^N x_i x_{i+k}$$

The summation in both i and k is taken to N (with the assumption that the composition of the $(i+N)$ th block is the same as the i th block) in order to eliminate the need for the $1/(N-k)$ scaling factor, but this does not affect the result.

Reversing the order of summation gives

$$m = \frac{1}{s} \sum_{i=1}^N x_i \sum_{k=0}^{N-1} x_{i+k}$$

which is zero since

$$\sum_{k=0}^{N-1} x_{i+k} = \sum_{k=0}^{N-1} (C_{i+k} - C_0) = N(C_0 - C_0) = 0$$

However, the value of $R(0)$ is 1 and therefore the mean, m , of the other values is $m = (0 - R(0))/(N-1) = -1/(N-1)$. From this we can derive just as simply that the variance of the distribution is $\text{var}(m) = 1/(N-k)$. Fig. 1 shows the autocorrelation of a set of random data from an Alnico 8 alloy. The graph has been extended to $k=N$ in order to demonstrate the increase in the standard deviation as the amount of data in the calculation becomes smaller, whereas the mean stays constant at $-1/(N-1)$. In reality there is little meaning to an autocorrelation extended beyond $k=N/4$.

We now need to decide whether an autocorrelation is random or not. Fig. 2 shows the autocorrelation between iron and aluminium from alternate (200) planes in the ordered Fe-Co phase in Alnico 8 /4/ and is clearly non-random. Comparing the theoretical and the observed means is clearly not a very sensible test since the observed mean is very close to the theoretical value despite obvious ordering. One method of testing for randomness would be to compare chain lengths of consecutive $R(k)$'s with values above $-1/(N-1)$ using a binomial model, in an analogous way to that discussed for chains of B atoms in section 4. However, it seems that the standard deviation of the results is a sensitive test for randomness of the data. If we weight the variance of $R(k)$ by $1/(N-k)$, then the expectation of the average of weighted variances will be $1/N$. If we now think of the standard deviation as a parameter just like any other we might have measured, then the value we have

calculated will have an error associated with it just like any other would. The standard deviation of the standard deviation is an estimate of this error, and is given by

$$\text{standard deviation of standard deviation} = s / \{2(n-1)\}^{\frac{1}{2}}$$

providing the distribution which has been sampled is a normal distribution. This condition is satisfied according to the central limit theorem providing N is greater than 120. (The central limit theorem states that if you take the average of enough values then the value of the average will have a normal distribution).

We now have a way of testing for randomness. If the standard deviation we measured came from a random population of standard deviations then that random population would have a Student's t distribution. The limits within which the actual standard deviation lies can therefore be estimated. This is best illustrated with an example. The standard deviation of the graph of fig. 2 is $s = 0.152$. From our null hypothesis that the $R(k)$'s are random the standard deviation of this standard deviation is $s = 0.152 / (17.2) = 0.0088$. Our alternative hypothesis is that the standard deviation is significantly larger than the theoretical value and therefore we perform a one-tailed test (if we had said that the value could be bigger or smaller a two tailed test would have been appropriate). We will reject the null hypothesis if the theoretical value lies outside the range in which 97.5% of the values based on the measured value should lie. There are $N-1=149$ degrees of freedom and our estimate of the standard deviation is therefore 0.152 with an error of $1.97 \times 0.0088 = 0.017$. The theoretical value is a long way outside this, and therefore we accept the alternative hypothesis. The deviation from a random distribution in fig. 2 was obvious without a test. However, fig. 3 shows an autocorrelation of carbon composition in a Fe-Ni-C alloy which is known to undergo a spinodal decomposition /5/. There is no obvious trend to this data. However, the frequency distribution of C compositions deviates significantly from what one would expect from a binomial distribution, and if we test the standard deviation of the autocorrelation it is found that it too indicates that the carbon distribution is non-random.

The measurement of the standard deviation of the points on an autocorrelation therefore seems to be a sensitive test of an autocorrelation function for atom probe experiments. Marking the expected standard deviation on a graph as in figs. 2 and 3 also helps to estimate where significant peaks in the graph lie.

One consequence of the above discussion is that the optimum signal to noise ratio is not obtained when the size of the composition blocks is chosen to be one atomic plane in size, but when it is one atom in size (i.e. N is a maximum). Although it would be meaningless to describe a modulation wavelength to this accuracy, averaging to the nearest number of atomic planes should be done after the autocorrelation and not before. In many cases it is impractical to choose a block of one atom size because of the computation time which would be required and any real autocorrelation will be a compromise between optimising the signal to noise and having realistic computation times. It is also possible to improve the signal to noise ratio if additional information from a depth profile is included (obtained from counting the atomic layers evaporated from a crystallographic pole).

It is also possible to take a 'moving average'. For this the composition is taken over N atoms, but the atom which is considered to mark the start of the block is only n atoms further on from the atom used to start the preceding block where n is smaller than N. This is the discrete implementation of a low pass filter and the autocorrelation function will tend to the autocorrelation of the filter function as the number of random samples tends to infinity.

III-CONTINGENCY TABLES

Table 1a is a contingency table of the correlation between Cu and Ni in data taken from an iron alloy with 1.1 at% Cu and 1.4 at% Ni after aging for 10 mins at 825 K from a homogeneous state. The solubility of copper in iron at 825 K is 750 ppm and some small b.c.c. particles can be detected in the alloy after this aging treatment.

The data from the atom probe experiment was considered in blocks of 50 atoms. The number in the top left of the table gives the number of blocks containing no copper or nickel the second number in the first row, those blocks containing one nickel and no copper and so on. Table 1b is the values that would be expected if there was no correlation between the Cu and Ni. They are obtained by multiplying the number at the end of the row with the number at the bottom of the column and dividing by the total squared (i.e. $1082.0 = (1915 \times 1299) / (2299 \times 2299)$). The value of chi-squared calculated from this is table is 20.23 with 6 degrees of freedom (the number of degrees of freedom is the (number of columns-1) multiplied by the (number of rows-1) i.e. 2×3). This value is significant at the 0.3% level and indicates that there is an association between Cu and Ni after this aging time.

The correlation between copper and nickel could also be found using a cross-correlation (similar to an autocorrelation). However, we have found that contingency tables are easier to calculate, simpler to interpret and more sensitive.

IV-ORDERING IN ALLOYS

Once again the problem we first consider is how can we determine whether or not data is random. Although a so called ladder diagram can provide a striking demonstration of ordering (see /4/ for an example), it is of limited use for statistical purposes. As was shown in section 2 an autocorrelation function can be used to test for ordering, but the most appropriate way to examine the data is by considering it as a Markov chain (a Markov chain is one in which the outcome of a trial depends on the preceding trial, for instance, in a coin tossing experiment the probability of throwing a sequence of 2 heads on the 4th trial is conditional on a head being thrown on the 3rd trial). If the atomic fraction of an element B, in an alloy is p , then, if the data is random, the probability of any atom being of type B is p independent of what its neighbours are. The probability of getting a chain of n B atoms is therefore p^n . By comparing the observed numbers of chain lengths with the expected number it is possible to estimate the significance of a result. It is possible to count chains in different ways. If we were looking for chains of 3 B atoms, then a string of atoms

ABBBBABBABBBBBA

could either be considered to contain 1 chain (if we say the chain must be 3 atoms preceded and terminated by A atoms) or 6 chains (if we counted every set of 3 consecutive atoms irrespective of the starting and finishing atom and could include an atom in more than one chain). In fact the most useful way to count them is to say that there are 3 chains distributed as

A/BBB/(1)BA/BBB/(2)A/BBB/(3)BBA

so we have counted any chain of 3 B atoms irrespective of the atoms that terminate the chain but have only allowed any atom to be included in one chain at most. This is the most sensible way to count chains since it is possible to define a simple recurrence relationship for the probabilities of success on any trial. If the mean waiting time for the first chain of r atoms to occur is m , then the expected number, $E(n)$, of chains of length r from a total of N atoms is $E(n) = N/m$. Furthermore, if the variance in the waiting time for the first chain of length r is s , then $E(n)$, has an approximately normal distribution with variance $\text{var}(n)$ given by $\text{var}(n) = Ns^2/m^2$.

For chains of length r of the type defined above it can be shown /6/ that

$$m = (1 - p^r) / (q \cdot p^{r-1})$$

and

$$s = 1/(q \cdot p^{r-1})^2 - (2r + 1)/(q \cdot p^{r-1}) - p/q^2$$

where $q=1-p$. It is possible therefore to test whether or not data is random by

examining the the number of long strings and comparing it with the expected value. If an alloy is ordered we would expect to see far more long strings.

If we have determined that a material is ordered then we want to estimate the degree of order. The ordering parameter, L , of a binary alloy may defined as $L=(1 - p)/(1 - x)$ where p is the probability of an atom B occupying a B atom site and x is the atomic fraction of B atoms in an alloy. It is possible to estimate p from an atom probe experiment. The best way to do this is to observe planes collapsing and then count the number of B atoms on the planes. The probability p is then simply obtained by dividing this number by the total number of atoms collected. If this cannot be done then it is possible to obtain an approximate value of p by taking composition averages over groups of n atoms where n is much smaller than the number of atoms per plane. This will then produce peaks in the frequency distribution of the compositions at np and also nq where q is the probability of a B atom being on a 'wrong' site. The results of a computer experiment are shown in fig. 4 from which it can be seen that quite good results can be obtained from fairly small data chains, however this should be used with care.

V-MONTE CARLO CALCULATIONS

A Monte-Carlo computer calculation has been used to simulate the nucleation and growth of particles of an element B in solution in an element A after it has been quenched from a very high temperature to below the miscibility gap. The calculation considers nearest neighbour interactions. It calculates the change in energy if two atoms changed places. If the energy of the new configuration is lower than that of the initial one then it exchanges the atoms. If the energy is increased then it 'gambles'. It generates a random number between 0 and 1 and if that number is smaller than $\exp(-E/kT)$ (where E is the increase in energy k is Boltzmann's constant and T is the temperature) it keeps the new configuration and rejects it if the number is larger.

Atom probe experiments have been performed on these crystals, in order to try to determine the optimum conditions for investigating the earliest stages of nucleation. From a large number of experiment the following general points have been observed.

a) The detector efficiency is important and should be as high as possible. If the same volume is probed using detectors with efficiency 1 and 0.5, the first can reveal the decomposition after a time up to eight times shorter than the second.

b) The probe hole diameter must not be too small (too few atoms will be detected to give any meaningful results) or too large (the sequence that the atoms are detected no longer represents their relative positions very well) However, similar results are obtained for diameters of between 3 and 6 atoms. This is not therefore a critical parameter.

c) The best way to test for nucleation is by the measurement of the variance of the mean waiting times between adjacent solute atoms (the mean waiting time itself is not very sensitive to decomposition).

VI-CONCLUSIONS

A few applications of statistical tests have been discussed. We have found all these tests useful in assessing our experiments and in explaining our results to specialists from other fields.

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OBSERVED					EXPECTED				
Cu\Ni	0	1	>=2	Total	Cu\Ni	0	1	>=2	Total
0	1101	591	223	1915	0	1082.0	597.3	235.8	1915
1	156	87	35	278	1	157.1	86.7	34.2	278
2	17	19	9	45	2	25.4	14.0	5.5	45
>=3	25	20	16	61	>=3	34.5	19.0	7.5	61
Total	1299	717	283	2299	Total	1299	717	283	2299

Table 1. Contingency table, for an underaged Fe-Cu-Ni alloy containing copper precipitates, showing frequencies of copper and nickel ions in samples of 50 ions. The calculated level of significance of 0.003 indicates that the copper and nickel are associated.

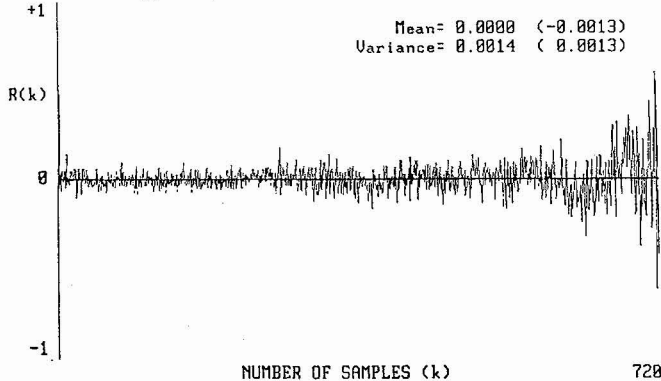


Figure 1. Autocorrelation analysis of iron and nickel taken from the homogeneous iron-rich phase in Alnico 8. The sample size was 1 atom and the total number of samples was 721. The numbers in brackets are the values which would be expected from a random distribution based on the theory given in the text.

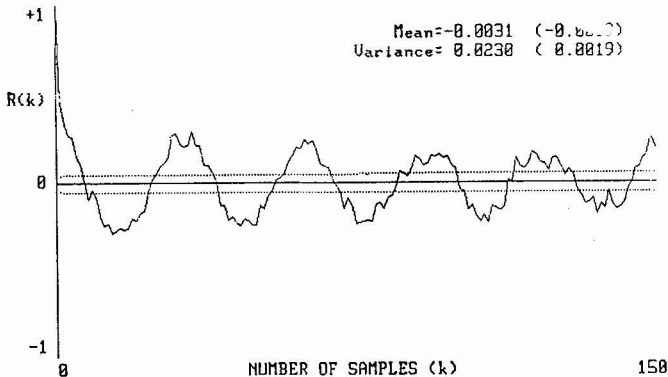


Figure 2. Autocorrelation analysis of iron and aluminium taken from the a (200) plane in the ordered iron-rich phase in Alnico 8. The sample size is 1.

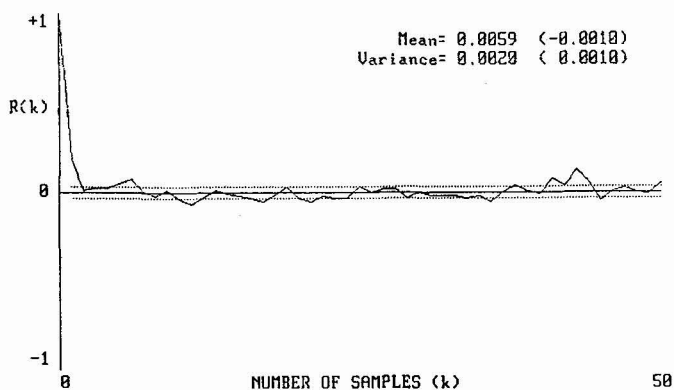


Figure 3. Autocorrelation analysis of carbon in an as quenched Fe-Ni-C alloy which is known to undergo a spinodal decomposition. The initial stages of the decomposition may already be detected in the autocorrelation. The sample size is 1.

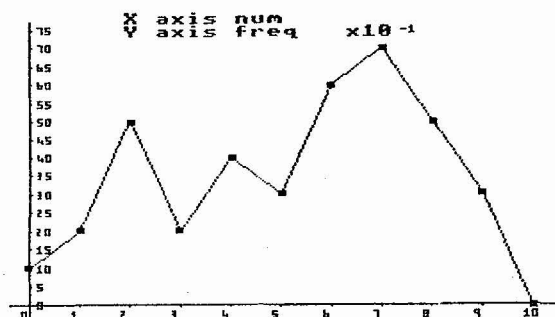


Figure 4. Frequency distribution of B atoms in blocks of ten atoms, from a computer simulation. Four atomic planes of 94 atoms were studied. The probability of finding an B atom on a B lattice site was 0.7 and the probability on a 'wrong' lattice site was 0.25.