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C.J. DALZELL

Department of Mathematics and Statistics, Memorial University of Newfoundland, St. John's, Newfoundland, A1C 5S7, Canada

Abstract - The atom probe was used to study the microstructure of samples of Fe-Cr (32 at%) aged for different periods. The data were expected to reveal evidence of spinodal decomposition, with the wavelength of the sinusoidal fluctuations increasing with aging time. This paper discusses a statistical model for the data. A two- stage hierarchical model is used, in which the first stage models the spinodal decomposition, and the second stage models the sampling fluctuations introduced by the atom probe. Through estimating the parameters of the model, it is possible to smooth the data and obtain an estimate of the period of the sinusoidal fluctuations. This estimate can be used as a basis of comparison between different specimens. Devising statistical analyses that exploit information about the instrument and the alloy can yield more precise answers than exploratory methods based on the correlogram or the spectrum.

A statistical analysis of atom probe data must take into account the purpose of the experiment under consideration. During the preliminary stages of investigating an alloy, an exploratory method may be sufficient. Such methods include plotting and smoothing the sequence of outcomes, and studying the sample spectrum and correlogram. However, the main strength of statistical theory is revealed in more focused experiments where we are interested in testing an hypothesis or estimating some quantity of physical interest. This paper presents an example of how one might estimate the spinodal microstructure of a binary alloy using atom probe data.

Five samples of iron chromium (Cr 32 at%) were aged for different times (193, 669, 5000, 10000 hours; 2 samples at 5000) at a constant temperature of 470 C, and examined in the atom probe. See Brenner et al. [1] for a description of the experiment and the results. The alloy was expected to show the development of a spinodal decomposition with the wavelength of the spinodal fluctuations increasing with aging time, and it was hoped that the atom probe would confirm this expectation.

The task of the statistician is to detect a spinodal microstructure, if it is present, and to provide some analytical means of comparing the different samples. Since theory predicts longer wavelengths for longer aging periods, the comparison can reasonably be based upon estimates of the wavelength. Finding those estimates should be one goal of the statistical analysis.

The data provided by the atom probe are the mass to charge ratios of the ions of Fe and Cr, in the order of their removal from the specimen, together with the location of the planar boundaries in the sequence. Since we have no further information regarding the original distribution of the ions in the specimen, we can use as data, the sequence $(Y_1, \ldots, Y_n)$ of proportions of Cr on each successive plane removed by the probe.

A descriptive method, such as plotting the data or computing the correlogram, is clearly not adequate to the more precise task of estimation and comparison required here, although these methods can be helpful in conjunction with estimation. An alternative approach is to posit a probabilistic model for the data, specified up to certain unkown parameters, which can be estimated from the data.

Briefly, a probability model is given by a probability density function that weights the possible outcomes of an experiment by their likelihood of occurring. The general form of this function can often be determined from theoretical considerations up to a small number of parameters. Were the parameters known, the probability of the outcomes could be computed. One way of estimating these parameters is to reverse the argument: for a given outcome of the experiment, choose the parameters that maximize the likelihood of getting what you actually got.

In a sensible model, the parameters should have physical significance so as to be used as summary statistics for each specimen and form a basis of comparison between these. In modelling the spinodal decomposition thought to obtain in FeCr, it is natural to include as parameters, the overall concentration of Cr in the alloy, μ, some measure of the amplitude of the concentration fluctuations, σ^2, and the wavelength of the fluctuations, λ.

In addition to these parameters, the data can be thought to depend on the concentration profile of Cr in the specimen. That is, we can say that the expected concentration of Cr on the jth plane is θ_j, say, or

$$E[Y_j \mid \theta_j] = \theta_j, \quad j = 1, \ldots, n.$$

The n values $(\theta_1, \ldots, \theta_n)$ form the concentration profile over that portion of the specimen. Although these values govern the distribution of the observed Cr proportions, as do regular parameters, they differ from these in that they are themselves subject to variation from one specimen to the next. The sort of sequences $(\theta_1, \ldots, \theta_n)$ that are likely for an alloy is determined by the microstructure. The θ's are termed "hyperparameters". In this example, they represent the theoretical profile of chromium concentration as this has evolved through a spinodal decomposition.

A model for the data can be constructed in two stages:

Stage 1. Conditional on the concentration profile, set $(Y_1, \ldots, Y_n)$ to be multivariate normal with mean vector $(\theta_1, \ldots, \theta_n)$, and variance matrix $\tau^2 I$, where I is the identity matrix.

(1) $(Y_1, \ldots, Y_n \mid \Theta)$ is $MN(\Theta, \tau^2 I)$.

Stage 2. $\Theta = (\theta_1, \ldots, \theta_n)$ has some probability density, g, depending on μ, σ^2 and λ.

(2) Θ is $g(\mu, \sigma^2, \lambda)$.

Combining the models from equations (1) and (2) yields a density for the data in the parameters τ^2, σ^2, μ and λ, which can then be estimated from the data.

This procedure is known as hierarchical modelling. Note that all information concerning the microstructure is contained in stage 2, while stage 1 describes the variation in a particular sample given a theoretical concentration profile. In this example, the density for Θ was taken to be multivariate normal with constant mean μ and variance matrix Σ.

(2a) Θ is $MN(\mu, \Sigma)$ where $\Sigma = [\sigma_{ij}]$

$$\text{and } \sigma_{ij} = \operatorname{cov}(\theta_i, \theta_j) = \frac{\sigma^2}{2} \sin\left(\frac{2\pi(i-j)}{\lambda}\right) \cdot \frac{\lambda}{2\pi(i-j)} .$$

The derivation of this model is given in [2], and it is based on a simulation formula for spinodal decomposition by J.W. Cahn [3]. Readers unfamiliar with the multivariate normal distribution should consult [4], or any standard work on multivariate statistics. The normal distribution is very widely used in statistics, since it is tractable, and often a reasonable choice.

When both stages of an hierarchical model are multivariate normal, the global model is also multivariate normal [5], with the useful consequence that the entire structure of the model is given through the variance matrix. The model could be adapted to other alloys and different microstructures simply by specifying a different structure for Σ.

There is a connection between the hierarchical model given here and the correlogram or spectrum of the series of observed proportions $(Y_1, \ldots, Y_n)$. If the model is correct, then the sample correlogram is estimating the entries of Σ, standardized by the variance.

$$\rho_k = \sigma_{ij}/(\sigma_{ii}\sigma_{jj})^{1/2} \quad \text{when } k = |i - j|.$$

ρ_k is the correlation at lag k, which is estimated by the value of the sample correlogram at lag k. Furthermore, the eigenvalues of Σ are approximately the spectrum of the series evaluated at the frequencies $2\pi i/n$, i =1, .., q where n = 2q + 1. The eigenvectors are approximately proportional to vectors of the form $[\cos(2\pi ij/n)]_j$ and $[\sin(2\pi ij/n)]_j$.

Spectral decomposition expresses a series as a weighted sum of sine and cosine functions, with the squared weights estimated by the spectrum. Knowing Σ enables us to reverse this process, and estimate the concentration profile given the spectrum. The estimate is obtained by a weighted least squares regression of the data onto the vectors with jth entry $\cos(\frac{2\pi ij}{n})$ and $\sin(\frac{2\pi ij}{n})$, j = 1, .., n and i = 1, .., q, with weights given by the spectrum.

For the spinodal model, the spectrum has a very simple form. It gives 0 weight to all frequencies greater than $2\pi/\lambda$, and equal weight to the lower frequencies. The concentration profile is estimated by means of a simple least squares fit of the model:

$$\theta_j = \alpha + \sum_{i=1}^{k} \beta_i \cos(\tfrac{2\pi ij}{n}) + \sum_{i=1}^{k} \gamma_i \sin(\tfrac{2\pi ij}{n}) \text{ , where k is the}$$

greatest integer less than n/λ. In practice, λ is replaced by its estimate.

Figure 1 shows a portion of the data for the specimen aged 10,000 hours together with its estimated concentration profile. The wavelength parameter was estimated to be 17.49.

Concluding Results: The model fit rather poorly for the series aged for the shorter times, with some improvement for the longest series, that aged 10,000 hours. What data there was did not reveal a marked increase in wavelength with aging time. For the series aged 669 hours, λ was estimated to be 2, which implies that the data should be modelled as random noise. The apparent lack of structure for this series may have been due to the very small plane sizes that were observed. The estimated wavelengths are shown in table 1.

Table 1.

Series	aging time (hrs)	λ (estimated)
1	10,000	17.485
2	5,000	17.875
3	5,000	23.682
4	669	2.000
5	193	14.200

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Fig. 1 Data and estimated concentration profile for a portion of Fe-Cr (32 at%) aged 10,000 hours.