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STATISTICAL ANALYSIS OF ATOM-PROBE DATA (I) : DERIVATION OF SOME FINE-SCALE FEATURES FROM FREQUENCY DISTRIBUTIONS FOR FINELY DISPERSED SYSTEMS

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Abstract : A statistical model has been developed in order to predict the concentration histograms which are used in atom-probe analyses. This method allows theoretical distributions to be calculated for finely dispersed systems containing spherical particles. Some statistical methods are proposed for the interpretation of experimental histograms.

I - INTRODUCTION

Because of its high spatial resolution, the atom-probe is a particularly suitable instrument for the investigation of early stages of decomposition in materials. Two experimental modes are usually used : the selected area analysis and the random area investigation.

In the first mode, Field Ion images allows precipitates to be located and individually analysed. This requires however, the occurrence of a well visible contrast between phases. This contrast is often obtained for high tip temperatures which can produce artefacts. Preferential evaporation effects indeed, are known to be more pronounced at high temperature and lead to biased compositions.

In the opposite way, continuous random area analyses are much less tedious and have the advantage to provide more quantitative data. Provided that a sufficient number of precipitates is detected in profiles, the size as well as the number density of particles or the volume fraction can be easily deduced from composition profiles. This requires however, statistical methods to be developed like autocorrelation analysis [1], [2]. Such methods are highly desirable for materials which contains very small precipitates or clusters. When the particle size is of the same order of magnitude as the analysis area, the phase composition as well as the volume fraction may be difficult to be determined.

An elegant method consists in analysing the concentration signal with the help of a frequency distribution. Such concentration histograms have been often used for spinodally decomposed materials [3] or alloys containing fine clusters [4]. The aim of the present paper is to describe a theoretical approach connected with the statistical model we described last year [5], [6]. This method allows theoretical distributions to be built for finely dispersed materials which contain small spherical particles. We will try to derive the phase composition as well as the volume fraction from the features of such concentration histograms.

II - THEORETICAL CONCENTRATION HISTOGRAMS FOR A FINELY DISPERSED MATERIAL

Let us consider a binary alloy AB which contains B rich spherical particles the diameter of which is Φ . The investigation of this material may be interpreted as an analysis along a cylinder whose diameter is Φ_a . We will try to calculate the basic law which governs the number of B atoms which are detected per desorbed layer. Our intention is to derive the theoretical concentration histogram which is expected for a given configuration. The basic set of parameters is the phase composition (C_p , C_m), the particle size (Φ), the volume fraction (F_v or the number density N_v) and the spatial resolution (Φ_a).

The main hypotheses of this model are the following :

- Particles are homogeneously distributed in the matrix and every precipitate has the same diameter.

- Both phases are chemically disordered so that the statistical dispersion of concentrations may be represented by binomial distributions.

- The number density of particles is low enough in order to ensure that the mean distance between particles, as measured in concentration profiles, is lower than the particle diameter :

$$N_v \ll 4/\pi \cdot (\Phi + \Phi_a)^2 \cdot \Phi$$

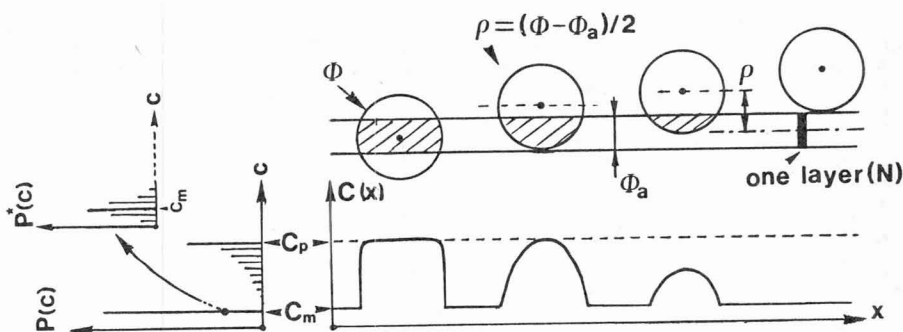


Figure 1 : Theoretical concentration profile related to the analysis of spherical particles along a cylinder. $P(c)$ is the ideal concentration histogram which would be observed for a "pure" concentration profile. The Dirac peak related to matrix leads to a simple binomial distribution $P^*(c)$ when statistical fluctuations due to sampling are taken into account.

The principle of the computer aided calculus of concentration histograms is the following. The basic parameters being chosen, the first stage consists in computing the local concentration profile (Figure 1). This is carried out for a given position (ρ) of the particle with respect to the analysis cylinder. This calculation is confined to the enriched region that is for $|x| < x_\ell$ (Figure 2).

$$x_\ell(\rho) = \sqrt{(\Phi/2)^2 - (\rho - \Phi_a/2)^2}$$

It is clear that for $|x| > x_\ell$, $C(x) = C_m$. In the vicinity of a particle ($|x| < x_\ell$), the theoretical profile $C_p(x)$ simply writes :

$$C_p(x) = C_m + (C_p - C_m) \cdot \frac{S(\rho, x)}{\pi \phi_a^2/4}$$

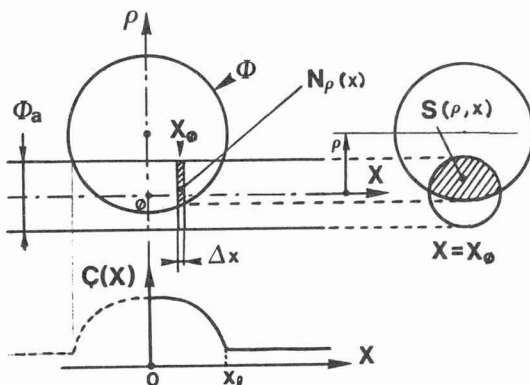


Figure 2 : Principle of the construction of theoretical profiles.

$S(\rho, x)$ is the common area between the analysis cylinder and a particle located at a given distance ρ with respect to the cylinder axis. This area depends on both parameters ρ and x and may be calculated from elemental geometrical considerations. C_p and C_m are the precipitate and matrix composition respectively.

For a given value of the sphere position (ρ), the partial profile is computed for increasing abscissa (x) up to x_f with a step equal to Δx (a "layer"). The "depth resolution" (Δx) is calculated from the number of collected ions per layer (N) which is chosen for the construction of histograms :

$$\Delta x \cdot \pi \phi_a^2/4 = N \cdot V_{at}/Q$$

Q is the detection efficiency and V_{at} the mean atomic volume of the material.

As the profile $C_p(x)$ is known, it is now possible to determine the number of layers which contain a given number (n) of B atoms. This operation leads to the construction of a partial concentration histogram $P(\rho, n)$ which depends on the position of the sphere (ρ). The probability to find a layer containing n B atoms $P(\rho_j, n)$ for a given position ρ_j of the particle is the sum of binomial distributions the parameter of which is the composition (C_{ij}) of various layers :

$$P(\rho_j, n) = \frac{1}{i_M} \sum_{i=0}^{i_M} \frac{N!}{(N-n)!n!} (C_{ij})^n (1 - C_{ij})^{N-n}$$

C_{ij} is the composition $C_p(x)$ for $x_i = i\Delta x$ and $\rho_j = j\Delta\rho$.
 $i_M = x_f(\rho_j)/\Delta x$ is a function of the sphere position (ρ_j).

In order to obtain the overall distribution of concentrations, all this procedure is repeated a hundred times between $\rho = 0$ and $\rho = (\phi + \phi_a)/2$. Before summing the various elementary histograms, one must take into account the "statistical weight" of various configurations (ρ). The probability to find a particle at a given distance ρ within $\Delta\rho$ is proportional to the elementary volume $\Delta v = 2\pi\rho \Delta\rho$. Thus the statistical weight is :

$$W(\rho) = \frac{2\pi\rho \Delta\rho}{\pi (\phi + \phi_a)^2/4} \quad \text{with} \quad \Delta\rho = \frac{(\phi + \phi_a)/2}{100}$$

So that the overall distribution writes :

$$P(n) = \sum_{j=1}^{100} W(\rho_j) P(\rho_j, n)$$

Up to now, only those layers which intersect particles have been taken into account. In terms of analysed depth, these enriched layers correspond to the linear fraction (F_ℓ). The matrix layers which contain a constant concentration (C_m) lead to a simple binomial distribution ($B(n, C_m)$). The statistical weight of this distribution is $1 - F_\ell$ while that of enriched regions is F_ℓ . The final distribution related to the ideal concentration profile is the weighted summation of these two contributions :

$$P^*(n) = (1 - F_\ell) B(n, C_m) + F_\ell P(n)$$

$$\text{with } B(n, C_m) = \frac{N!}{(N-n)!n!} \cdot (C_m)^n (1 - C_m)^{N-n}$$

The linear fraction F_ℓ is proportional to the volume fraction of precipitates and may be written as a function of the reduced spatial resolution η (6).

$$F_\ell = F_v (1 + 3\pi \eta/4 + 3\eta^2/2)$$

$$\text{with } \eta = \phi_p/\phi$$

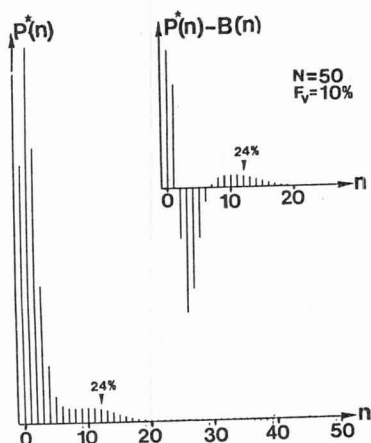


Figure 3 : A typical concentration histogram $P^*(n)$ and the corresponding differential distribution ($P^*(n) - B(n)$). Particles have a composition close to 24 % while that of matrix is 2.8 %, $F_v = 10$ %.

A theoretical distribution is proposed in figure 3 for a volume fraction of 10 %, and particles the diameter of which is 4.5 nm ($C_p = 25$ %, $C_m = 2.8$ %). The size of the analysis cylinder is equal to 1.5 nm ($\eta = 1/3$) and $N = 50$ atoms/layer.

One easily sees on this figure the contribution of both phases. The matrix leads to a distribution which is close a Poisson law. As expected, the maximum is observed for $n = 1$ (C_m is close to 2 %) and the precipitate composition is located near $n = 12$ ($C_p = 25$ %). The concentration histogram related to particles, convolutes with the matrix one's. Because of the geometrical effects, this distribution shape cannot be as simple as for matrix. Smaller are particles, larger is the modification of the initial shape of the distribution. When the spatial resolution is too low, the presence of small particles or clusters is no more visible. The distribution is close to a simple binomial law.

A differential distribution is also proposed in figure 3. This histogram is the difference between the observed distribution $P^*(n)$ and a binomial law $B(n)$ centered on the nominal composition of the material. This representation has the advantage to enhance the deviations from the random state. The phase composition may also be estimated, provided that particles are not too small.

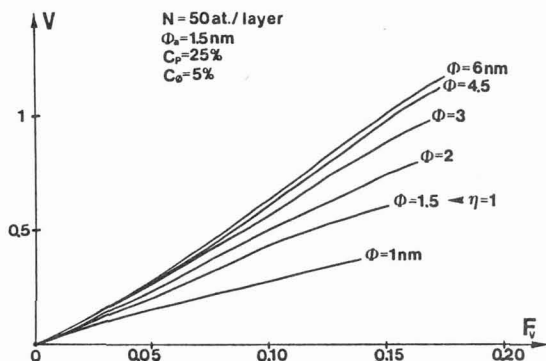


Figure 4 : The variation V as a function of the volume fraction for various values of the particle diameter ϕ .

ion is closely related to the volume fraction (Figure 4). This parameter called the variation (V), constitutes a measurement of the statistical distance between the "experimental" distribution and that which would be observed for a random solid solution.

$$V = \sum_{n=0}^N |P^*(n) - B(n)|$$

The variation is plotted versus the volume fraction for various particle sizes in figure 4. The particle composition (C_p) as well as the nominal concentration (C_n) were maintained constant in these calculus ($C_p = 25\%$, $C_n = 5\%$). For a given particle size, the volume fraction was increased by decreasing the matrix concentration and increasing the number density of particles. The graph clearly demonstrates that the variation (V) increases with the volume fraction (F_v). Moreover, the relationship between V and F_v depends on the particle size. Larger are the precipitates, higher is the variation. For very small clusters, V tends towards zero.

A differential histogram related to spherical γ' particles finely dispersed in a nickel base superalloy is proposed in figure 5. This distribution is given for Al atoms (see ref 6). The precipitate diameter is close to 7nm and the volume fraction is 10% ($C_p = 18\%$, $C_m = 1.52\%$, $C_\phi = 3.3\%$). A theoretical distribution has been computed from this set of data and is given for comparison. Both histograms are very close to each other. This good agreement shows that the predictions which are provided by our model are sensible.

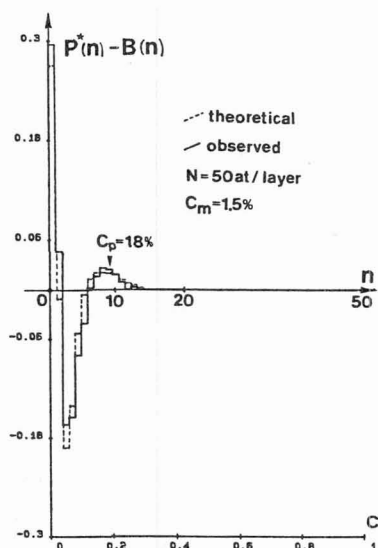


Figure 5 : An experimental histogram concentration related to a nickel base superalloy containing fine aluminium rich particles. The theoretical differential distribution $P^*(n) - B(n)$ is given for comparison.

III - CONCLUSION

The model we have proposed, provides a preliminary understanding of concentration histograms for finely dispersed systems. The ambition was initially to derive the volume fraction or the cluster composition from the features of these distributions. The introduction of differential distributions and the concept of variation have been shown to be valuable tools for this aim. However, when the number of desorbed layers is small, the value of the variation must be interpreted with prudence. For small deviations from randomness, this parameter may superestimate the actual statistical distance with respect to random state. Further development of this model is planned and should provide a new method for the study of clustering with the atom-probe.

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