1. Introduction

The information of the distribution of precipitate particles in 3-dimensions is essential to understand the kinetics of phase transformations and properties of materials. This is particularly relevant to the development of the technique of microstructure control by inclusions. In common practice the microstructure is observed on the plane of polish and a stereological treatment is applied to determine the particle number, morphology and size distribution in the specimen volume.1–9) One such treatment is the Schwartz-Saltykov analysis.4,10–12) In this treatment particles are assumed to be spherical. The size of particles is measured on the plane of polish and the number of particles in the predetermined size groups is counted. The distribution of precipitate particles in the specimen volume are then estimated from the probability of sectioning the particles by randomly oriented and randomly positioned planes.

A number of problems arise in applying this analysis to actual microstructures. First, the maximum particle size, one of the key parameters in the analysis, can not be determined easily. Usually, the observed maximum particle size is assumed to be the actual maximum particle size. Secondly, the morphology of particles is irregular. Even if the particle shape can be classified in a single morphology, e.g. oblate ellipsoid, the aspect ratio varies widely in one specimen. Thirdly, particles are not formed uniformly. In the areas of high particle density the impingement of particles may occur extensively.

In this report the influence of these complexities in actual microstructures on the determination of particle numbers in 3-dimensions is studied by computer simulation. Spherical or ellipsoidal particles were generated in a volume of fixed dimensions. The total number of particles per unit volume was calculated from the number and the size distribution of sections on a random plane, and compared with the number in the volume to discuss how various assumptions and model parameter values affect the results.

2. Simulation Method

2.1. Outline of Schwartz–Saltykov Diameter Analysis

Consider a cubic volume (the length of the side is $L$) in which $N$ spherical particles are contained as illustrated in Fig. 1. First, all particles are assumed to have the same diameter $D$ (mono-dispersed system). Circular sections on a random test plane are divided into $k$ groups according to their diameter. If the diameter lies between $2r_i$ and $2r_{i+1}$, where $2r_i=i\Delta$, $\Delta=D/k$ is the width of the size group and $k$ is the number of groups, the section is included in the $i$-th group. The probability of a section belonging to the $i$-th
group is given by,

\[ P_i = \frac{2}{D} (h_i - h_{i-1}) = \frac{1}{k} \left\{ \sqrt{k^2 - (i-1)^2} - \sqrt{k^2 - i^2} \right\} \]

......................(1)

where \( h_i \) is the distance from the center of a sphere to the test plane which yields a section of radius \( r_i \). The number of sections of the \( i \)-th group per unit area is given by,

\[ (N_A)_k = P_i D N_V \] ..........................(2)

from which the particle volume density \( N_V (=N/L^3) \) can be calculated if \((N_A)_k\) is measured.

In case that particles of different radii are randomly mixed (poly-dispersed system), the probability of a sphere of size \( j \) being cut and yielding a circular section of size \( i \) is given by,

\[ P_{ij} = \frac{1}{j} \left\{ \sqrt{j^2 - (i-1)^2} - \sqrt{j^2 - i^2} \right\} \] ..........................(3)

The number of sections of size \( i \) per unit area from spheres of size \( j \) is written as,

\[ (N_A)_j = P_{ij} D_j (N_V) \] ..........................(4)

where \((N_A)_j\) is the number of spheres of size \( j \) per unit volume. Since all spheres of diameter \( D = 2r \approx 2r_i \) can yield the sections of size \( i \), the number of sections of size \( i \) on the test plane is given by,

\[ (N_A)_k = (N_A)_j + (N_A)_{j+1} + \cdots + (N_A)_k \] ..........................(5)

and the total number of sections is calculated from the equation,

\[ N_A = \sum_{j=1}^{k} (N_A)_j = \sum_{j=1}^{k} \sum_{i=1}^{k} P_{ij} D_j (N_V) \] ..........................(6)

Since a section of size \( k \) comes only from a sphere of size \( k \), i.e. \((N_A)_k = (N_A)_{k,k}\),

\[ (N_V)_k = \frac{(N_A)_k}{P_{k,k} D_k} \] ..........................(7)

The \((N_A)_{k-1,k}\) is calculated from,

\[ (N_A)_{k-1,k} = \frac{P_{k-1,k} D_k (N_V)_k}{P_{k,k}} \] ..........................(8)

From Eqs. (4) and (5) with \( i = k - 1 \) the \((N_V)_{k-1}\) is calculated as,

\[ (N_V)_{k-1} = \frac{(N_A)_{k-1,k} - 1}{P_{k-1,k} D_{k-1}} \]

\[ = \frac{1}{\Delta(k-1)P_{k-1,k}D_{k-1} - 1} \]

\[ \times \left\{ (N_A)_{k-1} - \frac{P_{k-1,k}}{P_{k,k}} (N_A)_k \right\} \] ..........................(9)

In the poly-dispersed system \( \Delta \) is defined by \( \Delta = D_k / k \), where \( D_k \) is the maximum particle size. Hereafter, \( D_k \) is denoted as \( D_{\text{max}} \). All \((N_A)_j\)'s are calculated in a similar way. It is seen that they are expressed by a linear combination of the \((N_A)_j\) terms. Hence, the total number of particles per unit volume is written as,

\[ N_V = \sum_{j=1}^{k} (N_A)_j = \frac{1}{\Delta} \sum_{i=1}^{k} \alpha_i (N_A)_i \] ..........................(10)

where the coefficient \( \alpha_i \) can be calculated successively from \( P_{ij} \). In Table 1 the \( \alpha_i \) values for \( k = 15 \) are shown. It is seen that \( \alpha_i \) diminishes with increasing \( i \), indicating that sections of larger radii contribute less to \( N_V \).

In case of non-spherical particles the size and the shape of sections vary not only with the distance of the test plane from the center of a particle, but also with the orientation of the particle relative to the test plane. In this study the influence of irregular particle morphology on estimation of a particle number is discussed assuming that particles are an ellipsoid of revolution.

A prolate ellipsoid has three principal axes \( a, b \) and \( c \), and the aspect ratio is defined as \( q = c/a \) (\( >1 \)). The size of elliptical sections is measured along the minor axis \( b^2 \), as illustrated in Fig. 2. The number of sections of size \( i \) from particles of size \( j \) oriented by the angle \( \theta \) from the normal of the test plane is given by,

\[ (N_A)_j, (\theta) = \kappa(\theta) P_{ij} A_j (N_A)_j \] ..........................(11)

where \( A_j \) is the (full) length of the minor axis of an ellipsoid of size \( j \). The distance from the center of a prolate ellipsoid to the test plane which yields a section of size \( i \), is greater than for a sphere by the factor,

\[ \kappa(q, \theta) = \sqrt{1 + (q^2 - 1) \cos^2 \theta} \] ..........................(12)

If all particles have the same orientation, e.g. vertical, to the test plane \((\theta = 0^\circ)\), the number of sections is \( q \) times as large as that of spheres. If particles are randomly oriented,
2.2. Calculation of the Size of Sections on the Test Plane

2.2.1. Spherical Particles

In the first step $N$ particles are generated randomly and their sizes were increased at a prescribed rate to simulate microstructural evolution during heat treatment. A horizontal test plane at $z=zh$ intersects the $n$-th particle if the radius at time $t$, $r_n(t)$, and the position of the center $(x_n, y_n, z_n)$ satisfy the inequality, $r_n(t) > |z_0-z_n|$. It produces a circle of radius,

$$r_n(t)^2 = (z_0-z_n)^2$$

Then, the size group of the section is determined and $N_v$ is calculated from Eq. (10).

Two modes of nucleation were assumed. They are continuous nucleation and instantaneous nucleation (or site saturation) modes. These are considered to be relevant in ferrite transformation in iron alloys.\cite{13, 14, 15, 16} For simplicity, the growth is assumed to occur at a constant rate, i.e., proportional to holding time.

As precipitate particles grow, they begin to impinge with each other. In case that precipitates formed in a local area, e.g., at grain boundaries, have an orientation close to each other, boundaries between the particles are not clearly etched. Practically, these particles are often counted as one large particle and their contribution to the size of the particles was recorded as a cluster of two particles.* If one cluster had the same radii, the particles were regarded as impinging and recorded as a cluster of larger size. This procedure was repeated until no cluster had a particle in common with the other clusters. In each cluster lines were drawn through the centers of all pairs of sections and the longest one was taken to be the cluster size, as illustrated in Fig. 4.

2.2.2. Ellipsoidal Particles

As shown in Fig. 2, in the $(x', y', z')$ coordinates a prolate ellipsoid of the aspect ratio $q$ is expressed by the equation,

$$x'^2 + y'^2 + z'^2 = a(t)^2$$

where $a(t)$ is the length of the minor axis of the particle at time $t$. The rotation from the $(x, y, z)$ to the $(x', y', z')$ coordinate system is expressed by the matrix,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos \theta \cos \phi & \cos \theta \sin \phi & -\sin \theta \\ -\sin \phi & \cos \phi & 0 \\ \sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

* It is possible that particles are impinging above or below the test plane, but not in it.

© 2000 ISIJ

1144
Those derived theoretically. This indicates that the procedures described above can measure the size of the sections correctly.

The figure indicates that if the average of b/a values is less than 0.5, the particles are an oblate ellipsoid.

3. Results and Discussion

3.1. Influence of Dmax on the Estimation of NV

In practice the largest particle size observed on the plane of polish is assumed to be Dmax, the maximum particle size in the volume. It is necessary to check how much error is involved if a wrong Dmax value was used. First, N=400 spherical particles of radius 2r=10 (mono-dispersed) and secondly, N=400 particles of diameter 2r=20 (poly-dispersed) were distributed randomly in a cubic volume of L=200. The average of estimated Nv values with six different random number sequences is shown in Fig. 6. The number of size groups is k=15. For simplicity the cubic volume is regarded as unit volume and thus, Nv=N. In the mono-dispersed system Nv is overestimated with Dmax less than 10. On the other hand, the calculated Nv is close to the actual particle number with Dmax up to ca. five times the size of particles. In the poly-dispersed system Nv is close to the actual particle number with Dmax greater than ~15 and up to ~60. Thus, it is not necessary to use Dmax exactly equal to the actual maximum particle size. Instead, it may be advantageous to assume a Dmax value 2–3 times larger than the observed maximum particle size for safety.

The distribution of (Nv) in the poly-dispersed system is shown in Fig. 7. Even if the total number density is evaluated correctly, (Nv)'s are considerably different from the actual distribution of the particle size, implying that (Nv) is fairly sensitive to (Nv). The difference between them was not reduced in the simulation with larger particle numbers.

3.2. Precipitate Nucleation Rate

Figure 8 shows the variation with time of Nv in the system of N=400 particles. The particles are nucleated at time t=0 (site saturation mode) and grow at a rate of ∆t=0.5 per unit time (time t is measured in an arbitrary unit). It is seen that the calculated Nv is nearly constant as expected, whereas the total number of sections on the test plane Ns increases. This indicates that the increase in the apparent number on the test plane does not necessarily mean the increase in the number of particles per unit volume.
Figure 9 shows the variation of $N_V$ with time in a system in which $\Delta N = 100$ particles are nucleated successively per unit time and grow at the same rate as in Fig. 8. The rate of increase in the particle number was determined to be $J_V = 102.8$ by least square method, close to the increasing rate of actual particle numbers. These figures show that the procedures described above can correctly estimate the particle density in the case of both constant and varying particle numbers.

### 3.3. Simulation Incorporating Particle Impingement

Figure 10 shows the variation of $N_V$ with time calculated with the same nucleation and the growth rate as in Figs. 8 and 9, incorporating particle impingement. The $N_V$ first increases with time, but turns to decrease at $t = 8$. If nucleation stops at $t = 8$, the amount of decrease becomes greater. Figure 11 shows the variation with time of the number of clusters of impinging particles, where $n$ is the number of sections contained in one cluster. Solid triangles are the sum of the clusters of various sizes to be observed on the test plane. Thus, the influence of particle impingement on the estimation of particle density is very large. The simulat-
Simulation results for prolate particles of $q=3$ are shown in Fig. 12b. The $N_V$ is again correctly evaluated by incorporating the shape factor ($=1.81$) as shown by solid symbols. A slightly smaller $N_V$ value at the earliest time ($t=0$) is probably because $D_{\text{max}}(=20)$ was too large compared to the particle size at that time ($2r=1$). If these particles were treated as spheres and the particle size was measured along the major axis, larger $N_V$ values were obtained as shown by open symbols. This is the result of two opposing effects; one is the increase in the $(N_{A,i})$ values of larger size groups ($D_{\text{max}}$ is fixed) which reduces $N_V$ according to Eq. (8). The other is the increase in $N_V$ due to the omission of the shape factor.

The shape factor of oblate particles is deviated at most only $\sim$20% from unity, whereas the shape factor of prolate particles increases rapidly with the aspect ratio (Fig. 3). Hence, the total number of particles $N_V$ may be overestimated when oblate and prolate ellipsoids are mixed.

4. Summary

Possible sources of error associated with the stereological analysis for the estimation of particle numbers per unit volume from measurements on polished specimen surfaces, i.e. Schwartz-Saltykov analysis, in real microstructures were studied by computer simulation. The following conclusions may be drawn,

1. As long as $D_{\text{max}}$ is less than 3–5 times the actual maximum particle size, $N_V$ can be correctly evaluated. A smaller $D_{\text{max}}$ than the actual maximum particle size may cause a significant amount of error. It is advisable to use $D_{\text{max}}$ a few times greater than the observed maximum particle size.

2. The temporal variation of particle numbers on the plane of observation can be significantly different from that of actual particle numbers in the specimen volume. That is, the apparent particle number on the specimen surface can increase solely due to growth of particles; it can decrease due to extensive impingement even if particles continue to be nucleated.

3. The number of oblate particles is slightly underestimated if the shape factor is omitted and particles are approximated as spheres. On the other hand, the number of prolate particles is overestimated, although the omission of the shape factor mitigates the error. The error becomes quite large with increasing the axial ratio of particles. As a result, when oblate and prolate particles are mixed, the total number tends to be overestimated.

The advantage and necessity of stereological analysis in the characterization of transformation behavior is emphasized.

Acknowledgement

The work was supported by Research Promotion Fund of the Iron and Steel Institute of Japan (1997–1999).

REFERENCES