Theoretical assessment of systematic errors in volume fraction determinations by microscopy methods

Edgar Dutra Zanotto

Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, 13565-905, São Carlos-SP, Brazil

A set of equations were derived to estimate systematic errors in experimental determinations of volume fractions transformed by microscopy methods. For reactions that occur by continuous nucleation and growth, the experimental values of volume fractions transformed may be subjected to significant errors when the largest grain size of the distribution is close to the microscope resolution limit. For transformations occurring from a fixed number of nuclei, the systematic errors are smaller than those observed in the continuous nucleation case, but can still be significant when reflection methods are used. Transmission methods lead to smaller errors than reflection techniques.

In several problems of phase transformations, such as in nanomaterials synthesis, rapid-solidification studies of metallic alloys, glass-ceramic development, and crystallization research in general, the final grain size can be very small. That fact may render the accurate quantification of important microstructural parameters, such as the number of second phase particles per unit volume, crystal size distributions, and volume fractions transformed, quite difficult.

To estimate those microstructural parameters from two-dimensional planar cuts (the specimen cross sections), one often uses microscopy methods, associated with stereological procedures. In most situations one neglects the possible stereological errors and only takes into account the statistical errors due to the limited number of measurements.

In a previous paper it was demonstrated that the average number of crystals per unit volume can be heavily underestimated if the microscopes used have a limited resolution power; i.e., no particles whose sizes are below the resolution limit (ϵ) can be detected.[1] The problem is amplified when the measurements are carried out by reflected light optical microscopy (RLOM) or scanning electron microscopy (SEM), due to the fact that even particles that are larger than ϵ may show circular cuts smaller than ϵ in the examined cross section. With transmitted light optical microscopy (TLOM) or TEM the problem is minimized, but can also be relevant in some situations because a fraction of particles may be smaller than the resolution limit.

Thus, the following question arises: What would be the typical *errors* in the experimental values of volume fractions transformed for typical cases of phase transformations? In this communication a theoretical assessment of those errors is provided, and demonstrates that the volume fractions transformed can be significantly underestimated in some situations.

For phase transformations proceeding by simultaneous nucleation and growth of a second phase (homogeneous nucleation), a uniform size distribution of particles, with diameters ranging from the critical nucleus size (a few Angstroms) to some maximum size, result. The largest particle size depends on the material chosen as well as on the synthesis conditions and heat treatment employed. The typical grain size varies from a few microns down to nanometer size.

The fractional surface area, x_s, of circular particles in a cross section can be calculated by the following expression:

$$x_s = A_c/A_t = 2\pi \int_{r^*}^{r_m} n_s(r)\,dr , \qquad (1)$$

where $n_s(r) = N(r)/A_t$ is defined as the number of particles of radius r per unit area of the specimen cross section, which originated from a uniform size distribution, i.e., from the real crystal size distribution in the specimen volume, from the critical size r^* to r_m, the radius of the largest particle of the distribution.

If a portion of the particles is below the resolution limit, the undetectable crystallized area fraction on the sample cross section, A_u/A_c, is given by:

$$A_u/A_c = \int_{r^*}^{\epsilon/2} n_s(r)r\,dr \Big/ \int_{r^*}^{r_m} n_s(r)r\,dr . \qquad (2)$$

It is well documented in stereology texts that the fractional area in the specimen cross section should be equal to the volume fraction for a random ensemble of particles in a continuous matrix. Thus, one may use Eq. (2) to determine the magnitude of some typical errors in volume fraction measurements.

The frequency distribution function, $n_s(r)$, was derived by Toshev and Gutzow[2] and is given by:

$$n_s(\sigma) = 2\sigma \ln\{[1 + (1 - \sigma^2)^{1/2}]/\sigma\}, \qquad (3)$$

where $\sigma = r/r_m$. Therefore, the undetectable fractional area A_u/A_c (or undetectable volume fraction) can be calculated by substituting Eq. (3) into (2). Thus

$$A_u = 2r_m^2 \int_{\sigma^*}^{\sigma_\epsilon} \sigma^2 \ln\{[1 + (1 - \sigma^2)^{1/2}]/\sigma\} d\sigma, \qquad (4)$$

where $\sigma^* = r^*/r_m$ and $\sigma_\epsilon = \epsilon/2r_m$. One may assume that $r^* \sim 0$ (indeed, the critical nucleus size is several orders of magnitude smaller than the usual microscopic crystals). A_c may be calculated by integrating the above expression from 0 to 1, which gives a value of 0.262. Equation (4) was then solved numerically and divided by $2 \times 0.262 r_m^2$. The resulting values of A_u/A_c are plotted in Fig. 1 (SEM/RLOM-homo). Hence, the A_u/A_c ratio, i.e., the experimental underestimation of volume fraction transformed, decreases with increasing crystal size.

The techniques of transmitted light optical microscopy, TLOM, and transmission electron microscopy, TEM, are seldom used for the determination of volume fractions transformed, due to experimental difficulties with sample preparation. However, it is instructive to derive equations that allow the evaluation of systematic errors in these types of measurements to compare with those of RLOM and SEM. By analogy with the previous
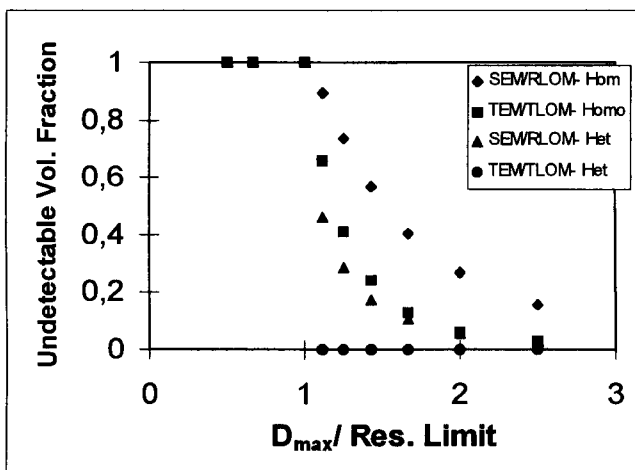

FIG. 1. The undetectable volume fraction as a function of the ratio between the diameter of largest crystal size of the distribution and the resolution limit of the microscope. (a) Homo = simultaneous nucleation and growth. (b) Het. = instantaneous growth from a constant number of sites. TEM/TLOM refers to transmission methods and SEM/RLOM refers to reflection techniques.

case, one may write:

$$V_u/V_c = \int_0^{\epsilon/2} n_v(r)r^2\, dr / \int_0^{r_m} n_v(r)r^2\, dr, \qquad (5)$$

where V_u/V_c is the fractional undetectable volume fraction. However, in this case, there are no stereological problems because the real size distribution in the specimen volume is probed by the microscope. Thus, the number of particles per unit volume, $n_v(r)$, is equal to $I_v t$, where t is treatment time and $n_v(r)$ is simply given by:

$$n_v(r) = (I_v/U)r_m, \qquad (6)$$

where I_v and U are the volume nucleation and growth rates (which are constant for a given temperature) and $r_m = Ut$. Thus, a constant distribution of particle sizes is predicted.

By substituting Eq. (6) into (5) and solving, one has the fractional undetectable volume fraction:

$$V_u/V_c = (\epsilon/2r_m)^4 = (\sigma_\epsilon)^4. \qquad (7)$$

When the transformation occurs rapidly from pre-existing nuclei, such as in typical cases of heterogeneous nucleation, a monodispersed particle distribution results in the sample volume. In that case, the cumulative fraction of circles in a cross section having radii equal or less than r, is equal to $1 - (1 - \sigma^2)^{1/2}$.[2] The frequency distribution function is given by its derivative, $\sigma/(1 - \sigma^2)^{1/2}$. Thus, using the reduced parameter $\sigma = r/r_m$ and $n_s(\sigma) = \sigma/(1 - \sigma^2)^{1/2}$ in Eq. (2), the undetectable fractional area transformed is given by the ratio A_u/A_c, where:

$$A_u = r_m^2 \int_0^{\sigma_\epsilon} [\sigma^2/(1 - \sigma^2)^{1/2}] d\sigma, \qquad (8)$$

and A_c is calculated by integrating the above expression from 0 to 1, which gives a value of 0.785. The analytical solution of the integral in Eq. (8) is:

$$A_u(\sigma) = -1/2[\sigma(1 - \sigma^2)^{1/2} - a\sin(\sigma)]. \qquad (9)$$

In the case of a monodispersed system of particles in the specimen volume, the particles will not be detected by TLOM or TEM only if the resolution limit of the microscope employed is insufficient, i.e., if $r_m \leq \epsilon/2$.

The undetected volume fractions transformed are shown in Fig. 1 as a function of the largest crystal diameter of the distribution. They were calculated by Eq. (4) divided by $2 \times 0.262 r_m^2$ for experimental determinations by RLOM or SEM, by Eq. (7) for experimental determinations by TLOM or TEM, and by Eq. (8) divided by $0.785 r_m^2$ for experimental determinations by

RLOM or SEM, respectively. Clearly the volume fraction transformed can be significantly underestimated if the *diameter of the largest crystal* is not larger than *twice* the resolution limit. However, the undetectable volume fraction decreases very quickly with increasing crystal size. For instance, if d_m is *three* times the resolution limit, the fraction lost when using any microscopy method ($\sim 1\%$) is negligible when compared to the typical statistical errors in that type of measurement ($10-20\%$).

When using microscopy methods to study microstructural developments of reactions occurring by *simultaneous* nucleation and growth, the volume fraction transformed may be severely underestimated. This fact is observed when the diameter of the largest crystal is not larger than twice the resolution limit of the microscope used in the experiment. However, such a situation can be intuitively detected by any experienced researcher. Obviously, in that case, a better microscope should be used.

Summarizing, one should be aware of the possible systematic errors when working in limiting conditions, i.e., when $d_m \leq 2\epsilon$. The inaccuracy is minimized when transmission methods, TLOM or TEM, are used instead of reflection techniques such as RLOM or SEM. Phase transformations proceeding from a fixed number of sites lead to smaller errors than those occurring in continuous nucleation and growth type of transformations.

ACKNOWLEDGMENTS

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