REMARKS ON THE SIZE DISTRIBUTION FUNCTION OF ULTRAFINE METAL PARTICLES

Gerda-Hanne Comsa

REMARKS ON THE SIZE DISTRIBUTION FUNCTION OF ULTRAFINE METAL PARTICLES

Gerda-Hanne COMSA

Institut für Chemie 2, Kernforschungsanlage, Jülich
D-5170 Jülich, Postfach 1913, West-Germany

Résumé. — On montre les résultats d'une analyse détaillée concernant les distributions de taille des petites particules métalliques préparées par évaporation et condensation en gaz inerte (GET). En tenant compte des deux mécanismes de croissance par lesquels les particules sont produites (c'est-à-dire croissance par absorption d'atomes et croissance par coalescence) les formes réelles des distributions de taille (du type *normal* jusqu'au type *logarithmico-normal*) sont interprétées comme étant le résultat d'une superposition des deux distributions de taille contrairement asymétriques. L'une d'elles — produite par la croissance par coalescence — est en accord avec la référence [1] de type logarithmico-normal. L'autre — produite par la croissance par absorption d'atomes — est qualitativement similaire à la distribution de taille prévue pour la croissance des particules sur un substrat par le mécanisme de transport d'atomes contrôlé par une réaction d'interface.

Abstract. — The results of an detailed analysis of experimental size distributions of particle samples prepared by the gas evaporation technique (GET) are reported. By considering both growth processes involved in the particle preparation by GET (i.e. growth by absorption of metal atoms and growth by coalescence), the shapes of the observed size distributions (from normal-like to log-normal) are interpreted as the result of the superposition of two oppositely skew bell shaped size distributions. The one — due to coalescence — is according to reference [1] of log-normal type. The other — due to absorption growth — is assumed to be qualitatively similar to the size distribution predicted for particle growth on a substrate by interface reaction controlled atom transport.

Introduction. — Recently it was shown [1] that the size distributions of assemblies of small metallic crystallites grown by a coalescence process are log-normal, i.e. that the logarithms of the crystallite sizes are normally distributed. In the quoted paper it was stated that the size distribution of ultrafine metal particles prepared by the gas evaporation technique (GET) can be ascribed entirely to a mechanism of growth by coalescence. By using the *true* log-normal size distribution function when checking the log-normality of experimental size distributions it was implicitely assumed that coalescence growth is an unlimited growth process.

In particle preparation by means of the GET, however, coalescence is not the only growth process [2, 3]. Once nucleation centers exist in the metal vapor, growth takes place first by the addition of metal atoms to the nuclei. Particles grown by this *absorption growth* process may collide with each other and thereby coalesce. Thus, absorption growth is later on accompanied by coalescence growth.

Starting from the fact that the absorption growth is the first and a non-negligible growth process in GET, the following conclusions concerning the particle size distributions will be drawn :

1. The observed size distributions should be in general the result of the superposition of two kinds of size distributions, the one brought about by absorption growth, the other due to coalescence growth. As a function of the actual experimental conditions the one or the other of the growth processes may be predominant and thus may predominantly influence the size distribution. In this paper an analysis of experimental size distributions is given to illustrate this fact.

2. On account of the pre-existence of the absorption growth process in the GET, coalescence is not a true unlimited growth process. Consequences of the limited character of coalescence growth for the graphical determination of mean size and dispersion in size will be discussed in accordance to a paper by Irani [4].

*

Size histograms of small metal particles prepared by evaporation and condensation of metals in an inert gas atmosphere at pressures between 10^{-1} and 10^{2} torr show generally more or less skew bell shapes with the tail towards larger sizes. By acting upon the preparation conditions (nature, pressure and purity of the inert gas, temperature at which the evaporation is carried out, temperature of the collector, position of the collector relative to the vapor source, nature and amount of evaporated metal) the larger size tail in the histograms can to

some extend be reduced. In special conditions even size distributions may be obtained which at first glance resemble a gaussian distribution function. An example of such gaussian looking size histograms are those given in figures 14 and 15 of reference [2*b*] for aluminium particle samples with mean size between 50 and 400 Å. As the aim of the just quoted work was to study the influence of the collector location upon the mean size and the dispersion in size, care was taken to avoid the deposition of large amounts of particles on the electron-microscope grids. On the other hand, highly skew size distributions, which fit well the log-normal behaviour, see e.g. figure 1 in reference [1], are brought about by quite different experimental conditions, i.e. when large amounts of particle powder are collected at great distances between evaporation source and collector. A typical example for the most frequently encountered *intermediate* size histogram shapes (which look neither normally-like nor log-normally-like) is shown in figure 1. It belongs to a vanadium particle sample of 65 Å mean size which was prepared in a low-pressure helium atmosphere and deposited onto a cooled collector surface [3, 5]. Also shown in figure 1 are the calculated number densities corresponding either to a normal or to a log-normal distribution function with the same mean size and the same dispersion in size as the experimental distribution.

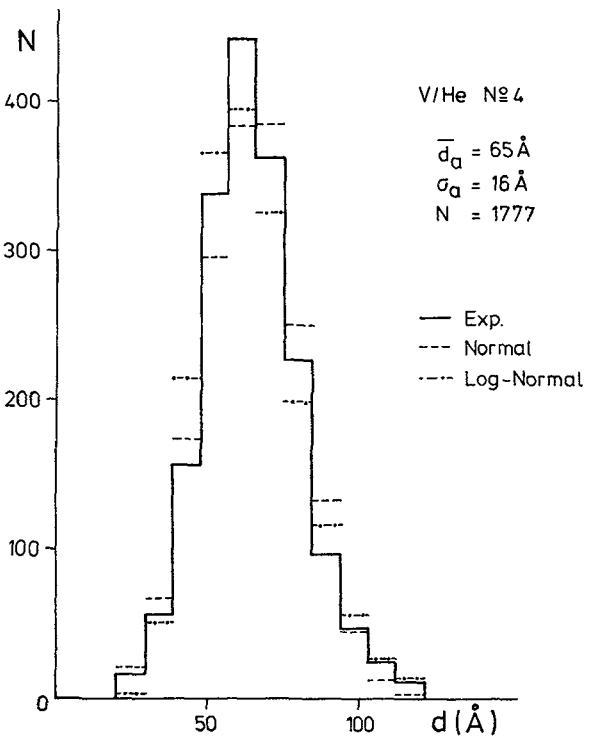

FIG. 1. — Size distribution histogram of a vanadium particle sample. (Full line : experimental size distribution. Dashed line : calculated number densities of the normal size distribution having the same arithmetic mean diameter, $\bar{d}_a$, and standard deviation, σ_a, as the experimental distribution. Dash-dotted line : calculated number densities of the log-normal size distribution having the same geometric mean diameter, $\bar{d}_g$, and standard deviation, σ_g, as the experimental distribution.)

Although real size distributions can never be truly gaussian (because this would imply the existence of negative sizes) the notion of normal distribution is used here to describe more or less symmetrically shaped size histograms. This is often implicitely assumed in the small metal particle literature when size distributions are characterized by the arithmetic mean and its standard deviation. A brief description of some general features of the normal and the log-normal size distribution functions is given in table I.

TABLE I

Characteristic Features of Normal and Log-normal Distributions

Experimental data ($n_1 \chi_1$, $n_2 \chi_2$, ... $n_n \chi_n$)	Normally distributed χ_i-values	Log-normally distributed χ_i-values (≡ normally distributed ln χ_i-values)
Distribution function	$f_n(\chi) = \frac{1}{\sqrt{2\pi}\,\sigma_a} \exp\left[-\frac{(\chi - \bar{\chi}_a)^2}{2\sigma_a^2}\right]$	$f_l(\chi) = \frac{1}{\sqrt{2\pi}\ln\sigma_g} \exp\left[-\frac{(\ln\chi - \ln\bar{\chi}_g)^2}{2\ln^2\sigma_g}\right]$
Mean value	$\bar{\chi}_a = \frac{\sum n_i \chi_i}{\sum n_i} = \frac{\sum n_i \chi_i}{N}$ $\bar{\chi}_a \equiv$ arithmetic mean	$\ln\bar{\chi}_g = \overline{\ln\chi} = \frac{\sum n_i \ln\chi_i}{N}$ $\bar{\chi}_g = (n_1\chi_1 . n_2\chi_2 \ldots n_n\chi_n)^{1/N}$ ≡ geometric mean
Standard deviation	$\sigma_a = \sqrt{\frac{\sum n_i (\chi_i - \bar{\chi}_a)^2}{N}}$ $\sigma_a \equiv$ arithmetic standard deviation	$\ln\sigma_g = \sqrt{\frac{\sum n_i (\ln\chi_i - \ln\bar{\chi}_g)^2}{N}}$ $\sigma_g \equiv$ geometric standard deviation
Degree of dispersion	$V = \frac{\sigma_a}{\bar{\chi}_a}$	$V \equiv \sigma_g$
Cumulative plots on probability paper	Straight line on linear probability paper	Straight line on logarithmic probability paper

None of the calculated number densities (Fig. 1) fit the experimental density levels, and it is difficult to decide, whether the normal or the log-normal assumption is closer to the experimental distribution. The same conclusion results, when the experimental data are plotted in the cumulative manner on linear probability paper (Fig. 2) and on log-probability paper (Fig. 3). Such cumulative plots should be straight lines, when the assumption of normality respectively of log-normality is correct [6]. However, in the given case, both plots (Figs 2 and 3) show deviations from the straight line behaviour. The only difference is, that in figure 2 (normal) the deviations occur at the larger diameter end of the distribution, whereas in figure 3 (log-normal) the non-concordance is on the smaller diameter side. From the analysis of a great number of experimental size distributions, this result seems to be typical for size distributions with *intermediate* shape.

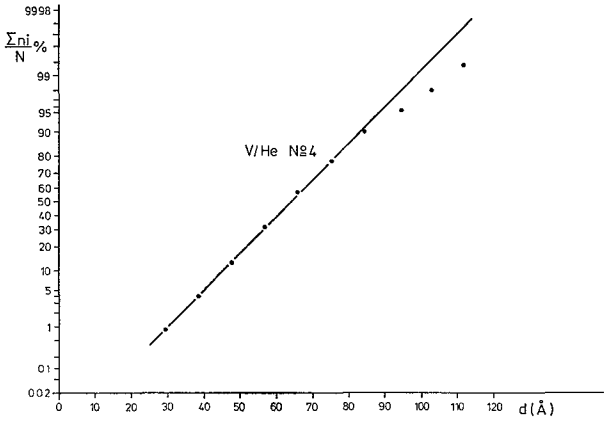

FIG. 2. — Linear probability plot of the size distribution shown in figure 1. (On the ordinate : percentage of particles with diameters smaller than d.)

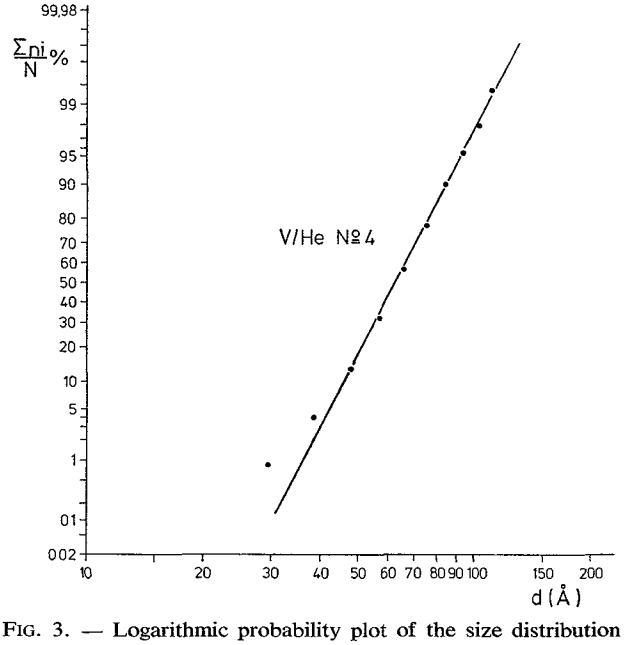

FIG. 3. — Logarithmic probability plot of the size distribution shown in figure 1. (On the ordinate : percentage of particles with diameters smaller than d.)

The fact that neither the gaussian nor the log-normal distribution function is a good fit to *intermediate*-shaped size distributions may also be seen from figure 4. Here the relative degree of

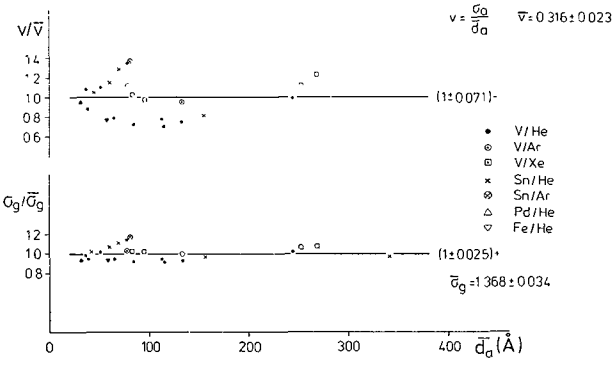

FIG. 4. — Relative degrees of dispersion of 24 experimental size distributions as a function of mean size. ($\bar{v}$ and $\bar{\sigma}_g$ are respectively the average values of the individual v- and σ_g-values. The geometric standard deviation was determined by means of its definition formula given in table I.)

dispersion (for the definition of the degree of dispersion see Table I) is given as a function of the mean particle diameter for 24 GET-particle samples of vanadium, tin, iron and palladium, by assuming either normal behaviour (upper curve) or log-normal behaviour (lower curve). For both cases, the values lie within a band around the average dispersion value, so that the degree of dispersion is practically independent of the mean particle size, regardless of the assumption made upon the nature of the distribution function. In reference [1] the constance of the geometric standard deviation (i.e. of the degree of dispersion) is discussed as a typical feature of log-normal distributions. In view of the above results, it seems that there is no univoque connection between the constance of the geometric standard deviation and log-normality.

Cumulative plots on probability papers are not a highly precise method to check the normal or log-normal behaviour of a given size distribution. Therefore, we decided to apply the χ^2-test [6] to the above mentioned 24 size distributions. In table II the results of this analysis are given as a function of the mean particle size. As a general remark one may say, that normality is highly improbable, log-normality is somewhat more probable and *intermediate* shapes are the most probable. In what regards log-normality, the probability is higher for larger mean sizes. By correlating log-normality with coalescence growth [1], one may conclude, that for samples with larger mean particle size the role of coalescence growth is more important than for samples with smaller mean size. The χ^2-test applied to two differently behaving metals, vanadium and tin, leads to the result, that log-normality is more

TABLE II

Results of the χ^2 (Chi-square)-test

Test conditions (*)	Number of analysed distributions		Number of normal distributions		Number of log-normal distributions	
	$\bar{d} \leq 80$ Å	$\bar{d} > 80$ Å	$\bar{d} \leq 80$ Å	$\bar{d} > 80$ Å	$\bar{d} \leq 80$ Å	$d > 80$ Å
$0.01 < W_{\chi^2} < 0.99$	12	12	—	1	2	5
$0.05 < W_{\chi^2} < 0.95$			—	1	1	4

(*) W_{χ^2} is the probability of the experimental χ^2-value.

probable in case of tin samples (Table III). This is in accordance with the electron-microscopic observation, that small tin particles show a much stronger tendency to coalesce than vanadium particles [7].

TABLE III

Comparison between the frequencies of log-normal size distributions for vanadium and tin particle samples

Test conditions (*)	Percentage of log-normal distributions (**)			
	Vanadium		Tin	
	$\bar{d} \leq 80$ Å	$\bar{d} > 80$ Å	$\bar{d} \leq 80$ Å	$\bar{d} > 80$ Å
$0.01 < W_{\chi^2} < 0.99$	0 %	40 %	25 %	50 %
$0.05 < W_{\chi^2} < 0.95$	0 %	30 %	0 %	50 %

(*) W_{χ^2} is the probability of the experimental χ^2-value.

(**) Related to the number of analysed distributions of the respective metal.

One may summarize the above discussion by saying that, whenever the experimental conditions are such to strongly favour coalescence growth, the size distribution of GET-particle samples will show log-normal behaviour. Conditions which favour the contribution of coalescence growth to the overall growth mechanism in detriment to the contribution of the absorption growth are e.g. great distances between collector and vapor source (because in regions where practically no more metal vapor exists, growth may only occur *via* coalescence), collection of large amounts of particles (because coalescence may also occur on the collecting substrate), non-cooled collector surface [7] and/or no addition of oxidizing gases to the inert gas atmosphere in case of metals with strong tendency towards coalescence.

*

We have seen from tables II and III, that even in conditions less favourable for coalescence growth, the contribution of this growth process increases with increasing mean particle size. This means, that for finding out the influence of absorption growth upon the size distribution one should analyse the shape of size histograms belonging to samples with very small mean particle sizes (some tens of Angströms), prepared in conditions unfavourable to coalescence growth.

In the following the possible shape of the size distribution which would be brought about by absorption growth alone (supposing coalescence growth could be entirely suppressed) will be discussed. To this end, a comparison between the absorption growth in the GET and the mechanism of growth by atom transport in case of crystallites growing on a substrate seems to be useful.

Models of size distributions for crystalline particles grown by atom transport on substrates (i.e. grain growth in discontinuous films and particle growth in supported catalysts) were given by Chakraverty [8] and Wynblatt and Gjostein [9] respectively. The mechanism of growth constists in a series process : surface diffusion of atoms on the substrate and their attachment to the growing nuclei or particles. As either the first or the second of these processes may be rate determinant, two cases were analysed : growth controlled by surface diffusion and growth controlled by an interface reaction. For both cases the models yield skew size distribution functions with the tail towards smaller diameters, such that the peaks of these distributions are located at $d = 1.1\,\bar{d}$ (Ref. [9]), where $\bar{d}$ is the mean particle diameter. According to figure 8 in reference [9] the distribution function for interface reaction controlled growth has a somewhat larger range of existence and terminates less abruptly.

Particle growth by absorption of metallic vapor in case of GET may qualitatively be compared with particle growth on a substrate by interface reaction controlled atom transport. Similarity exists in what regards the rate controlling step, differences may arise from the existence or non-existence of a substrate. To what extent the missing substrate will modify the expression of the size distribution derived in reference [9] has to be analysed. Here we will assume, that no essential modifications should appear.

In case of small metal particle preparation by matrix techniques — where under careful conditions it is possible to get rid of coalescence [10] — size histograms have been reported (see Fig. 3 in ref. [10]), which are well fitted by the model distribution function for interface reaction controlled growth. In case of particle preparation by GET — where coalescence growth can never completely be ruled out (because it takes place also in regions where the absorption growth is important) — size distributions with large tails on the small diameter side have never been reported. However, the already quoted size histograms of reference [2b] with either a very faint skewness towards smaller sizes (Fig. 14 in ref. [2b]) or with practically symmetric shapes (Fig. 15 in ref. [2b]) may serve as good examples of size distributions brought about by the superposition of two kinds of size distribution : one due to absorption growth and having the tail on the small diameter side, the other due to coalescence growth and having the tail on the large diameter side. The results in this special case are histograms looking gaussian-like. For other experimental conditions, when coalescence growth is more important, the superposition may yield either to an *intermediate* shaped or to a log-normal distribution.

*

How important coalescence might ever be in the particle preparation by GET, it is always preceded by absorption growth. This means, that there is a lower limit size for coalescence growth. On the other hand, all size histograms terminate at a certain upper limit size which depends on the actual experimental conditions. Therefore, coalescence growth cannot be considered as an unlimited growth process. Irani [4] showed how one has to deal with log-normal size distributions, which are the result of a limited growth process. Instead of using the true log-normal distribution function (Table I), which ranges from $d = 0$ to $d = \infty$, one has to use a *modified* log-normal distribution function, which ranges from a minimum diameter, $d_{\min}$, to a maximum diameter, $d_{\max}$. The expression of the modified log-normal distribution function is :

$$(d) = \frac{1}{\sqrt{2\,\pi} \ln \sigma_g} \exp\left[- \frac{\left(\ln \frac{(d - d_{\min})\,(d_{\max} - d_{\min})}{\bar{d}_g (d_{\max} - d)}\right)^2}{2 \ln^2 \sigma_g} \right]$$

where $\bar{d}_g$ and σ_g are the geometric mean diameter and the geometric standard deviation. Irani pointed out that this four-parameter distribution function may also lead to a straight line on log-probability paper, but in contrast to the true distribution function, it does not permit the correct determination of $\bar{d}_g$ and σ_g from the points in which this straight line passes the 50 % and 84 % levels. Thus it might be misleading to check the log-normality of a given size distribution simply by the straight line behaviour of the log-probability plots and then to use the straight line for the graphic determination of $\bar{d}_g$ and σ_g. To avoid errors in the $\bar{d}_g$ and σ_g determination it would therefore be safer to check first by means of the χ^2-test if the condition of unlimited growth is fulfilled

*

Conclusions. — Two growth processes are important in the preparation of small metal particles by the gas evaporation technique : growth by absorption of metal atoms and growth by coalescence of particles. The former process, which is a necessary condition for the onset of the second one, is finally accompanied by the latter. The observed size distributions should therefore reflect the influence of both growth processes.

The contribution of absorption growth to the overall size distribution is considered here as being qualitatively similar to the size distribution predicted for particle growth on a substrate by interface reaction controlled atom transport [9], which is a skew distribution with the tail towards smaller sizes. On the other hand, the contribution of coalescence growth consists in a log-normal size distribution [1], i.e. a skew distribution having the tail on the larger size end. Thus, the observed size distribution should be the result of the superposition of two oppositely skew size distributions. Depending on the actual experimental conditions, the contributions of absorption growth to the size distribution can be less or more overwhelmed by the influence of coalescence growth, so that normal-like or *intermediate* or even log-normal shapes should appear. This is in agreement with the observed size distributions of GET-particle samples.

Coalescence growth in case of GET is not a true unlimited growth process and therefore care has to be taken when log-probability plots are used for the graphical determination of the size characterizing parameters (mean size and dispersion in size) of a particle sample.

*

Acknowledgments. — The continuous support of this work by Dr. D. Heitkamp is gratefully acknowledged.

References

[1] GRANQVIST, C. G., BUHRMAN, R. A., *J. Appl. Phys.* **47** (1976) 2200.

[2] a) KIMOTO, K., KAMIYA, Y., NONOYAMA, M., UYEDA, R., *Japan J. Appl. Phys.* **2** (1963) 702 ;
KIMOTO, K., NISHIDA, I., *Japan J. Appl. Phys.* **6** (1967) 1047.
b) YATSUYA, S., KASUKABE, S., UYEDA, R., *Japan J. Appl. Phys.* **12** (1973) 1675.
c) WADA, N., *Japan J. Appl. Phys.* **6** (1967) 553, and **7** (1968) 1287.

[3] COMSA, G.-H., HENSEL, F., *Vak. Tech.* **24** (1975) 169.

[4] IRANI, R. R., *J. Phys. Chem.* **63** (1959) 1603 ; see also IRANI, R. R., CALLIS, C. F., « *Particle Size: Measurement, Interpretation and Application* » (Wiley, New York) 1963, p. 44.

[5] COMSA, G.-H., HEITKAMP, D., RÀDE, H. S., *Solid State Commun.* **20** (1976) 877.

[6] HERDAN, G., « *Small Particle Statistics* », II. Ed., Butterworth, London, 1960, p. 122.

[7] COMSA, G.-H., HENSEL, F., RINGELMANN, F., Proc. Sec. Internatl. Colloquium on Surface Physics and Chemistry, Brest, 27-30 Mai 1975, in Le Vide, Les Couches Minces, **30A** (1975) 130.

[8] CHAKRAVERTY, B. K., *J. Phys. Chem. Solids* **28** (1967) 2401 and 2413.

[9] WYNBLATT, P., GJOSTEIN, N. A., in Progress in Solid State Chemistry (Pergamon, New York) 1975, Vol. 9, p. 21.

[10] YEE, P., KNIGHT, W. D., *Phys. Rev. B* **11** (1975) 3261.