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DETERMINATION OF PARTICULATE SIZES IN CERAMIC POWDERS BY ELECTRON MICROSCOPY

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Translation of "Elektronenmikroskopische Teilchengröesse-analyse von Keramischen Pulvern." Berichte der Deutschen Keramischen Gesellschaft, Vol.55, No. 2, 1978, pp. 76-78.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, DC 20546 APRIL 1983

STANDARD TITLE PAGE

1. Report No. NASA TM-77056	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle: DETERMINATION OF PARTICULATE SIZES IN CERAMIC POWDERS BY ELECTRON MICROSCOPY.		5. Report Date: APRIL 1983 6. Performing Organization Code
7. Author(s): Alfons Stiegelschmitt and Gerhard Tomandl		8. Performing Organization Report No. 10. Work Unit No.
9. Performing Organization Name and Address: SCITRAN, Box 5456, Santa Barbara, CA 93108		11. Contract or Grant No. NASw- 3542 13. Type of Report and Period Covered: Translation
12. Sponsoring Agency Name and Address: National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes: Translation of "Elektronenmikroskopische Teilchengröesse-analyse von Keramischen Pulvern." Berichte der Deutschen Keramischen Gesellschaft, Vol. 55, No. 2, 1978, pp. 76-78.

16. Abstract:

Ceramic powders of small particulate size can be characterized by electron microscopy. The usual methods of powder preparation were tested and compared with the method of N. Thaulow and E. White (1972). The data are analyzed in two ways.

17. Key Words (Selected by Author(s))	18. Distribution Statement: Unclassified - Unlimited		
19. Security Classif. (of this report): Unclassified	20. Security Classif. (of this page): Unclassified	21. No. of Pages: 9	22. Price

DETERMINATION OF PARTICULATE SIZES IN CERAMIC POWDERS BY ELECTRON MICROSCOPY

Alfons Stiegelschmitt and Gerhard Tomandl*

The development in the area of oxide ceramic leads to the use of increasingly /76** fine powders. To characterize these powders, the standard methods such as sieve analysis or sedimentation methods are suitable only to a limited extent. In the MSA centrifuge method (1), which supplements the sedimentation method up to particle sizes of 0.1 μm just as in all centrifuge methods, because of different error effects no absolute particle diameters are obtained so that only comparative measurements are possible. Other methods such as for example, determination of the specific area according to BET do not give any distribution function, but only an "integral" individual value. There are two methods by means of which very fine powders can be characterized well by a distribution function, specifically the calculation of the crystallite size distribution from x-ray line expansion (2) and the evaluation of electron microscopy images (3) which gives a particle size distribution.

The terms "particle" and "crystallite" require a more complete definition: with image-forming systems particles are corpuscles recognizable with image-forming systems as a unit which can be structurized in itself, that is they can consist of individual components, the crystallites. Crystallites are coherently scattering areas, that is areas of uniform crystallographic orientation. Generally in ceramic powders the individual particles are polycrystalline. This concerns also the powders investigated in this study.

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**Numbers in margin indicate foreign pagination.

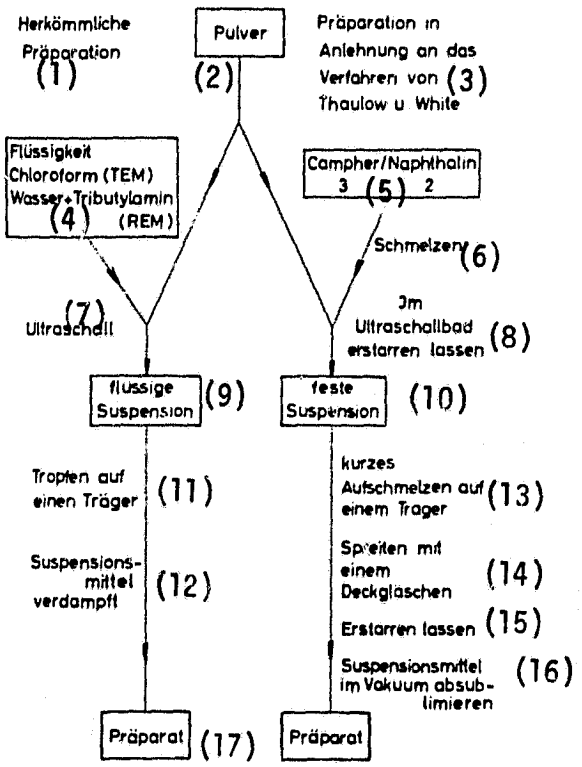
This study concerns the electron microscopy method and specifically individually the method of preparation of the REM (raster electron microscope) and the TEM (transmission electron microscope) as well as the corresponding image evaluation.

1. Method of Preparation

Table 1 gives a survey of two different methods of preparation (specified for the REM). These methods can be applied in a somewhat modified form for the preparation in case of TEM.

For the ordinary methods of preparation the powder is suspended ultrasonically in a liquid. The suspension agent used should have good moistening properties. If water is used as a suspension agent, a dispersing agent must be added in low concentration. A strong agglomeration of the powder on the surface of the preparation is prevented by a rapid evaporation of the suspension agent (chloroform) or by an increase of the viscosity of the suspension (water) by dissolution of gelatin.

Table 1: Method of Preparation



Key: (1) ordinary preparation; (2) powder; (3) preparation based on the method of Thaulow and White; (4) liquid chloroform (TEM) water plus tributylamine (REM); (5) camphor-naphthaline; (6) melting; (7) ultrasound; (8) frozen in ultrasonic bath; (9) liquid suspension; (10) solid suspension; (11) applied in drops on a carrier; (12) suspension agent evaporated; (13) brief melting on a carrier; (14) spread with a cover glass; (15) allowed to freeze; (16) suspension agent sublimated in vacuum; (17) preparation.

In the new method (4) the powder is introduced in a melted camphor-naphthaline mixture and the suspension cooled in the ultrasonic bath. At about plus 30 degrees C, the suspension solidifies. A chip of this frozen suspension is melted briefly on a support (thin object carrier glass) spread with a cover glass and allowed to freeze on a refrigeration block. The suspension agent is removed from the surface of the preparation by sublimation under vacuum.

As compared with this method, the ordinary methods of preparation have serious drawbacks. In case of too high a solid concentration, the danger arises that large particles may deposit in spite of intensive ultrasonic effect. In the removal of the suspension with a pointed glass rod or with a platinum loop powder, residues can remain hanging. Another critical point is the behavior of the suspension of the carrier. The surface tension of the liquid leads to an enrichment of the particles and the edge of /77 the drop. Moreover, in the preparation for the REM, the powder particles can sink so far into the gelatin layer that they are lost to the evaluation. A "good" preparation section that is sufficiently covered must therefore be chosen (Figures 1 and 2). This causes doubts to arise as to how far such a preparation section is representative for the powder. As a whole, therefore the ordinary methods are only suitable for characterizing powders with great reservations.

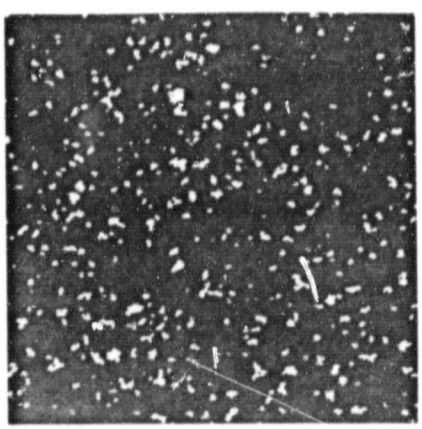


Figure 1: REM photo alumina CTB-7 (Giulini)

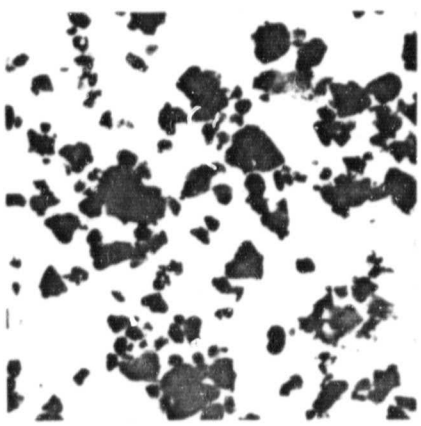


Figure 2: TEM photo alumina IV (Chemag)

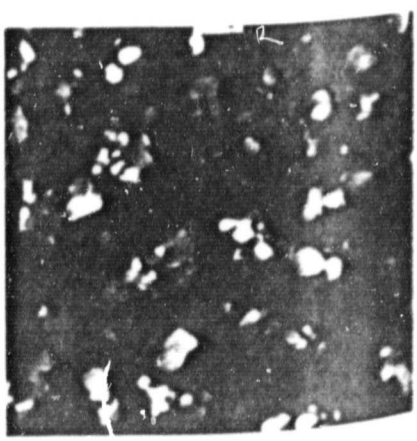


Figure 3: REM photo alumina CTB-7 camphor-naphthaline preparation. Lower edge of the picture 300 µm.

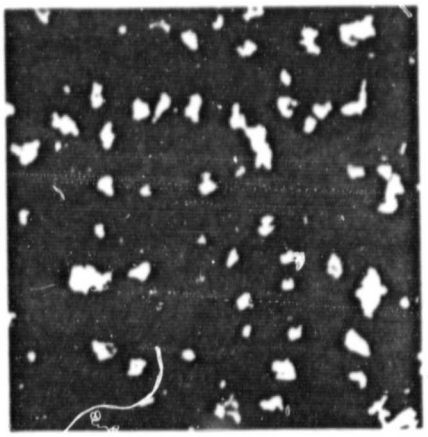


Figure 4: REM photo alumina CTB-7 camphor-naphthaline preparation lower edge of the figure 90 µm.

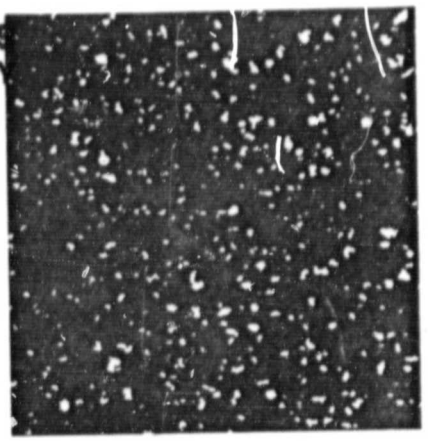


Figure 5: PFM photo of $BaTiO_3$. Lower edge of photo 300 µm.

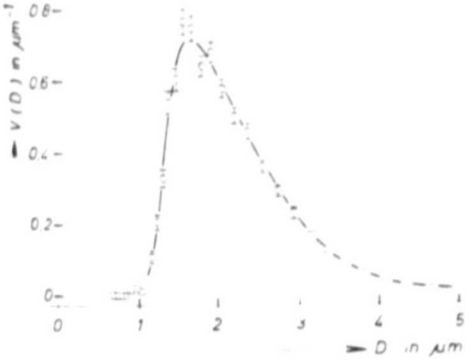


Figure 6: Alumina CTB-7, KuDV. 6000 particles counted.

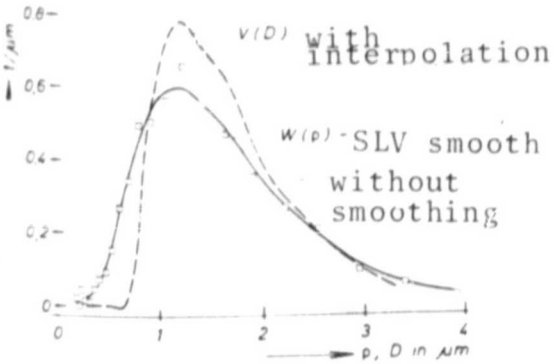


Figure 7: Alumina CTB-7. Comparison of W(ρ) and V(D) standardized to 1.

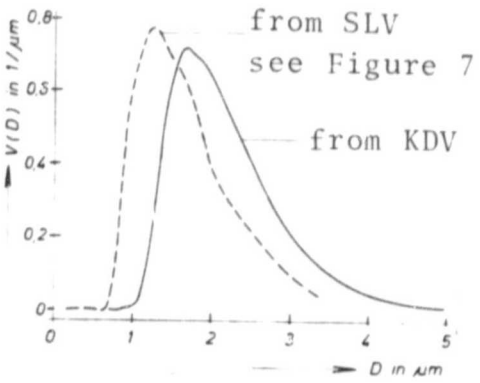


Figure 8: Alumina CTB-7. Comparison of V(D) from KDV and SLV standardized to 1.

These inconsistencies are avoided by the method of preparation with camphor-naphthalene. The only critical moment is the melting of the chip of the carrier to spread the suspension. To avoid the agglomeration the process stages, melting, spreading, solidification should be carried out as quickly as possible. With this method uniformly coated preparations are obtained (Figure 3), therefore it is possible to obtain from such a preparation a whole series of photos. An agglomeration of the /78
particles is prevented to a much greater extent than for the usual methods (Figure 4).

The method of preparation with camphor and naphthalene has also proven satisfactory for powders such as for example $BaTiO_3$ (Figure 5). Attempts to prepare copper powders by this means failed because of the lack of moistening properties. The camphor-naphthalene method proves to be very suitable for the preparation of ceramic powders. The time consumed for an individual preparation is about 30 minutes, but becomes correspondingly shorter when whole series of preparations are produced. The possibilities of errors are smaller by far than for the ordinary methods of preparation.

2. Evaluation of the Photos and Discussion of the Results

Two different methods were used for the evaluation.

a) The particle surface is measured. With the particle size counter TGZ 3, according to Endter circles of equal area are inscribed in the particles. Thus we obtain directly a KuDV (ball diameter distribution, Figure 6). It proved to be sufficient to count about 3,000 particles.

b) A line raster is placed over the photos and the section chord lengths are measured. The measurement can be conducted with an evaluation table (digitalization table). Here we obtain the coordination values of the intersections between particles and chords on punched tapes which are classified and processed with a computer program.

In this connection we have an SLF (chord length distribution). The latter may be converted in the following way into a KuDV:

$$V(D) = -\frac{k}{D}\int_{D}^{\infty} \frac{\varrho}{\sqrt{\varrho^2 - D^2}} \cdot \frac{dW(\varrho)}{d\varrho}\, d\varrho$$

ϱ =chord length, W(ϱ)=SLV, D=ball diameter, V(D)=KuDV, k=constant.

With this calculation procedure the SLV is differentiated. The curve must therefore be carefully smoothed digitally beforehand (Figure 7).

In a comparison of the ball diameter distributions obtained by the two methods, the following is found: the effective KuDV determined from the SLV is as compared with the KuDV determined with the Endter equipment shifted towards smaller diameters (Figure 8).

Strictly speaking,the indicated conversion formula applies specifically only to spherical particles. For the alumina investigated in this study (compare Figure 4), therefore we cannot expect a consistency of the two distribution functions. The corners and tips are included in the distribution, as though there was an additional fine component. Since corners and tips as well as small particles increase the sintering activity, the effective KuDV calculated from the SLV characterizes the powder better. Naturally because of the subsequent differentiation in the determination of the SLV, the statistics must be greater than in the case of measurements on the Endter equipment. The time taken for the method of evaluation of the image with the digitalization table is very great, if we wish to achieve satisfactory statistics. Therefore the SLV should be determined with an automatic image evaluation equipment.

3. Literature

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Received on January 23, 1978, revised editions February 3, 1978.