General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

NASA TECHNICAL MEMORANDUM NASA TM-77094

CHARACTERIZATION OF CERAMIC POWDERS BY AN X-RAY MEASURING METHOD

G. Ziegler

(NASA-TM-77094) CHARACTERIZATION OF CERAMIC POWDERS BY AN X-RAY MEASURING METHOD (National Aeronautics and Space Administration) 15 p HC A02/MF A01 CSCL 11B N84-18398
Unclas
G3/27 11806

Translation of "Charakterisierung keramischer Pulver durch ein röntgenographisches Messverfahren", Keramische Zeitschrift, Vol. 33, No. 5, 1981, pp. 287-290.

MAR 1984
RECEIVED
NASA STI FACILITY
ACCESS DEPT.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 JULY 1983

STANDARD TITLE PAGE

1. Report No. NASA TM-77094	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle CHARACTERIZATION OF CERAMIC POWDERS BY AN X-RAY MEASURING METHOD		5. Report Date JULY 1983
		6. Performing Organization Code
7. Author(s) B. Ziegler		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 "Charakterisierung keramischer Pulver durch ein rontgenographisches Messverfahren", Keramische Zeitschrift, Vol. 33, No. 5, 1981, pp. 287-290.

16. Abstract

X-ray line broadening analysis gives quantitative data on structural changes of ceramic powders after different processing steps. Various Al_2O_3 powders were investigated and the following points are discussed on the basis of these results: X-ray line broadening analysis, structural changes during grinding, structural changes during annealing, influence of structural properties on sintering behavior and application of line broadening analysis to quality control of powders.

ORIGINAL PAGE IS
OF POOR QUALITY

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 15	22. Price

CHARACTERIZATION OF CERAMIC POWDERS BY AN X-RAY MEASURING METHOD

G. Ziegler

Abstract: X-ray line broadening analysis gives quantitative data on structural changes of ceramic powders after different processing steps. Various Al_2O_3 powders were investigated and the following points are discussed on the basis of these results: X-ray line broadening analysis, structural changes during grinding, structural changes during annealing, influence of structural properties on sintering behavior and application of line broadening analysis to quality control of powders. /287*

Definition of the Problem and Setting the Objective

From the point of view of the user, there are still several problems with ceramic and special ceramic materials with high requirements for quality. They include:

- improvement of the reproducibility of the properties
- increase in the absolute values of the mechanical, and of certain physical properties such as the transparency [1].
- reduction in the variability of the mechanical properties in particular
- the controlled establishment of certain mechanical and physical characteristics.

How can these problems be solved?

The properties of the sintered structures are determined by the structure and by the chemical composition of the starting material. The structure can be influenced to a large extent by the process parameters (e. g., sintering temperature, holding time, pressure, atmosphere, etc) and by the powder properties. The process parameters can be checked and optimized relatively simply. In order to solve the problems outlined, there remains principally the optimization of the powder characteristics with respect to improved reproducibility and increased satisfaction on sintering.

---

* Numbers in margin indicate foreign pagination.

Three main questions arise in discussion of this subject:

1. How can the powder properties be optimized?
2. How can the methods of characterization be improved?
3. How can the firing control be optimized for specified powder properties?

Improvement of the powder properties requires optimization of the manufacturing process and refinement of the preparation methods. Point 2 assumes improved characterization of the powder in the raw material and during the individual processing steps. On question 3 it should be noted that in the early stage of sintering there are fine structural changes that can significantly affect the entire sintering process and, therefore, the properties of the final product. These structural changes can be checked and optimized by controlling the sintering process. For that reason it is necessary to measure the changes of powder properties up to the actual liquefaction process, and to investigate the fundamental relations between the individual powder properties and the structure of the sintered body.

One major point in the further development of high-quality ceramic and special ceramic materials is, then, the characterization of powders as supplied and the characterization of the changes of the powder properties after various processing steps and in the early stage of the sintering process. The goal of this work is to make a contribution to this problem by applying an X-ray measuring process. The powder characterization is usually accomplished by study methods using powder metallurgy, morphology, chemistry, X-rays, and electron microscopy [2-4]. As is well known, the important characteristics of the powders are the specific surface, the mean size and the distribution of the primary particles (see Nomenclature [5]), the geometry and surface structure of the particles, agglomerate and aggregate formations, as well as the purity and the phase composition. In the near future, also, surface analytical methods (Auger and X-ray photoelectron spectroscopy (ESCA)) may play major roles in making determinations of the chemistry of the thin surface layers. As practice shows, the study methods listed are often not

sufficient. One reason for that is that diffusion and recrystallization processes occur during sincering. These processes can be strongly affected by lattice defects. It follows that, along with the procedures already mentioned, characterization of ceramic powders should be supplemented by methods that give information about changes of the crystalline state. This can be done by the method of X-ray line width analysis, which /288

- makes possible qualitative and quantitative determinations of the crystallite size and the lattice distortions,
- indicates the lattice defects in the material, and
- determines the energy content of the powder due to the small crystallite size and to lattice defects.

In this contribution, we show what determinations can be provided by the process of X-ray line width analysis in quality control of raw materials and in processing ceramic powders after various process steps. Various consequences of the following points are discussed using Al_2O_3 as an example:

1. X-ray line width analysis as a supplemental method for characterizing ceramic powders. The fundamentals of the method are considered here, although only insofar as necessary for understanding and application of the process in practice. For detailed information about the individual process steps the reader is referred to the original literature.

2. Structural changes on grinding. This point also considers the effect of the properties of the initial powder on the mechanical activation by the grinding process.

3. Structural changes on annealing. The effect of the mechanical and chemical activation on the change of crystallite size and on the lattice distortions in annealing are discussed here.

4. Influence of the structural properties on the liquefaction and sintering behavior.

5. Consequences for the characterization of ceramic powders.

On the basis of the results of points 1 to 4, we present here an evaluation of the process of line width analysis with respect to simple and rapid routine characterization of ceramic powders.

X-ray Line Width Analysis For Determination of Crystallite Size and Lattice Distortions

Crystallites are defined as monocrystalline lattice regions which have essentially no inhomogeneous lattice distortions, and which therefore contain no crystallite boundaries or similar strong lattice distortions (Figure 1a). Primary particles visible with optical systems usually consist of several crystallites. By lattice distortions we mean the mean relative deviation of the lattice plane distances from their mean, due to the incorporation of lattice defects (Figure 1b). With this process it is possible to demonstrate the lattice defects that disturb the coherence of the lattice and which lead to a local distortion of the lattice. Using X-ray measurements, and especially by analysis of the shape of the interference lines, it is possible to measure these structural properties of ceramic materials.

The process for determining structural properties is based on the fact that the X-ray interference lines are broadened if the crystallite size in a crystalline material goes below a certain limiting value, and if the lattice distances are dispersed about their mean (Figure 2). The broadening is greater the smaller the crystallite size and the greater the stress in the lattice. Information about the crystallite size and the lattice distortions can be obtained both by quantitative evaluation of the widths of the interference lines -- half-peak widths (HWB) or integral widths (B) (Figure 2) -- and also by evaluation of the entire line profile. In this work we describe the process of line width analysis made possible from the mean crystallite size and by the average lattice distortions. The basis for separating the contributions of crystallite size and lattice distortions to the total line width broadening is the different dependence of the two broadening effects on the

ORIGINAL PAGE IS
OF POOR QUALITY

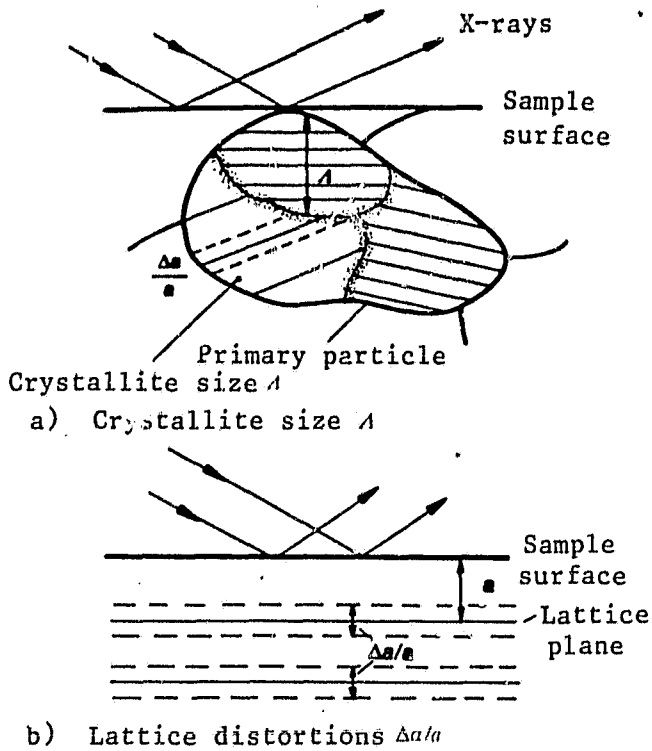
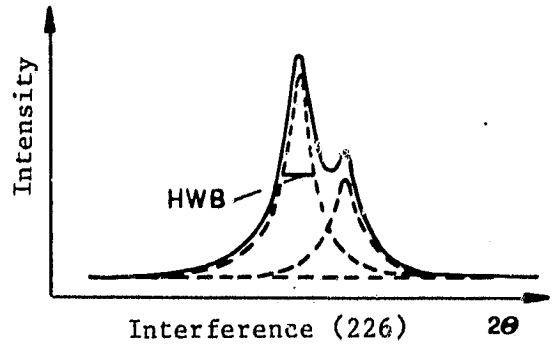


Figure 1. Schematic representation of the crystallite size and the lattice distortions.

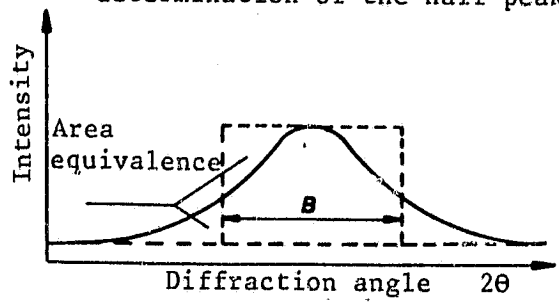
diffraction angle θ of the X-rays (Table 1). The broadening due to small crystallites is inversely proportional to cos θ, while the broadening from lattice distortions is proportional to tan θ. Therefore, it is possible to make quantitative statements about both the mean crystallite size and the mean lattice distortions by measuring several interference lines of the material being studied as functions of the diffraction angle θ. That means that in order to determine crystallite size and lattice distortions several -- at least two -- X-ray interference lines must be measured. The process assumes some corrections so as to obtain only the broadening due to the crystalline state of the the sample. The fundamental equations for the process and the corrections needed for application of the process are shown in Table 1.

ORIGINAL PAGE IS
OF POOR QUALITY



Starting powder with low activation

a) starting powder with low activation
- separation of the $K\alpha_1/K\alpha_2$ doublet
- determination of the half-peak width (HWB)



Strongly mechanically activated powder

b) Strongly mechanically activated powder
- Determination of the integral width (B) evaluated in this work

Figure 2. Evaluation of the measured line profile. Effect of the activation on the width of the interference line [226].

ORIGINAL PAGE IS
OF POOR QUALITY

TABLE 1. FUNDAMENTALS OF THE MEASURING PROCESS OF LINE WIDTH ANALYSIS FOR QUANTITATIVE DETERMINATION OF CRYSTALLITE SIZE AND LATTICE DISTORTIONS

Fundamentals of the method:

$$\beta_T = \frac{K \cdot \lambda}{\Lambda \cdot \cos\Theta}; \qquad \beta_V = 4\frac{\Delta a}{a}\tan\Theta;$$

Corrections:
- separation of the $K\alpha_1/K\alpha_2$ doublet
- splitting of the line broadening by geometric influences (natural spectral line width included)

Determination of the true broadening β determined by the crystalline state of the material.

Separation of the broadening influences from crystallite size and lattice distortions:

$$\frac{\beta \cdot \cos\Theta}{\lambda} = \frac{1}{\Lambda} + 4\frac{\Delta a}{a}\cdot\frac{\sin\Theta}{\lambda}$$

β_T	Line broadening due to small crystallites
β_V	Line broadening due to lattice distortions
β	True line width due to the crystalline state of the materials
Λ	Mean crystallite size
$\frac{\Delta\alpha}{\alpha}$	Mean lattice distortions
K	Crystallite form factor
λ	Wavelength of the X-rays used
Θ	Bragg diffraction angle

TABLE 2. PROCEDURE FOR THE QUANTITATIVE DETERMINATION OF CRYSTALLITE SIZE AND LATTICE DISTORTIONS IN Al_2O_3 POWDERS.

Recording of the line profile	(014),(113),(116)
Interferences evaluated	(300),(226),(416)
Separation of the $K\alpha_1$-$K\alpha_2$ doublet	according to Rachinger [6]
Determination of the	integral width B
Measurement of the apparatus broadening b	annealed Al_2O_3 sample
Determination of the true integral β width after removal of the apparatus broadening	$\beta = B - \frac{b^2}{B}$
Separation of the broadening effects of crystallite size and lattice distortions	$\frac{\beta \cdot \cos\Theta}{\lambda} = \frac{1}{\Lambda} + 4\frac{\Delta a}{a}\cdot\frac{\sin\Theta}{\lambda}$
Recording conditions:	- Cu $K\alpha$ radiation - X-ray diffractometer - Stepping mechanism - Diaphragmed sample size <3 mm

B	Measured, still uncorrected integral width of the material studied
b	Integral width of a stress-free comparison sample with the same crystallites for separation of the apparatus broadening (annealing at temperatures >1400°C)
β	Corrected integral width of the material studied after separation of the apparatus broadening. Otherwise, see Table 1.

ORIGINAL PAGE IS
OF POOR QUALITY

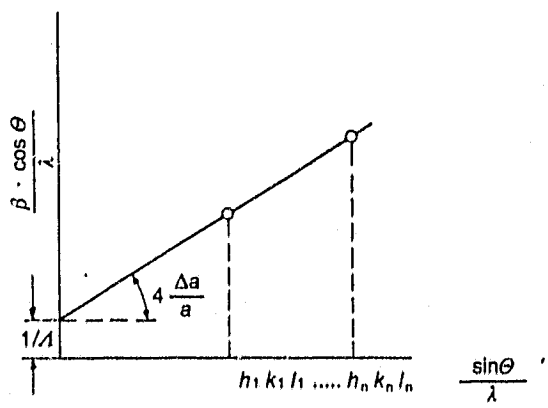


Figure 3. Quantitative determination of the crystallite size and lattice distortions by the Hall-Williamson method [7,8] according to Table 2.

The evaluation procedure explained in Table 2 has proved good for measurements on Al_2O_3 and on various other ceramic and metallic materials [3]. This table summarizes the individual steps of the process for characterization of Al_2O_3 powder interference lines and the recording conditions. The procedure of line width analysis includes essentially three procedural steps:

1. Recording of the line profiles of various interference lines. Measurements on Al_2O_3 have shown that the evaluation of several interference lines $h_n k_n l_n$ is necessary for high accuracy.

2. Determination of the true line width caused only by the crystalline state of the material being studied.
   After splitting up the $K\alpha_1$-$K\alpha_2$ doublet it is necessary to eliminate the broadening effects of the apparatus (See Table 1). This is done by recording the line profile, under the same measuring conditions, using an annealed, stress-free Al_2O_3 sample with large crystallites. From the line widths of this comparison sample, which are broadened only by the instrument geometry, and the measured line widths of the powder being studied, the true line widths determined by the crystalline state of the powder can be determined [3].

3. Quantitative determination of the crystallite size and the lattice distortions by separating the two broadening effects.
   In this work, determination of crystallite size and lattice distortions is accomplished by the Hall-Williamson relation [7,8]. (Figure 3). In this process, evaluation of the line widths of various interference lines leads to a plot of $\beta \cdot \cos\theta / \lambda = f(\sin\theta / \lambda)$. With the assumption that the crystallite size and lattice distortions are independent of the measured lattice direction, this plot yields a straight line. The slope of the linear relation leads to statements about the mean lattice distortions perpendicular to the reflection planes. The reciprocal of the intersection at the ordinate gives the mean crystallite size perpendicular to the reflecting lattice planes. Lattice distortion and crystallite size distributions are approximated by Cauchy functions in the Hall-Williamson evaluation

ORIGINAL PAGE IS
OF POOR QUALITY

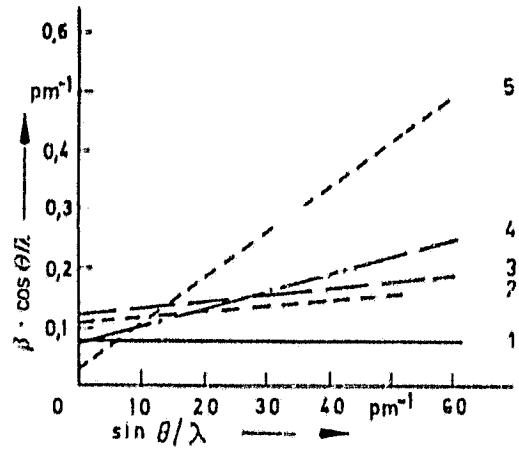


Figure 4. Line width analysis of various Al_2O_3 powders as supplied. Quantitative evaluation:

Material	Crystallite size (μm)	Lattice distortions (%)
1	0,14	0
2	0,09	0,02
3	0,08	0,03
4	0,14	0,07
5	0,31	0,19

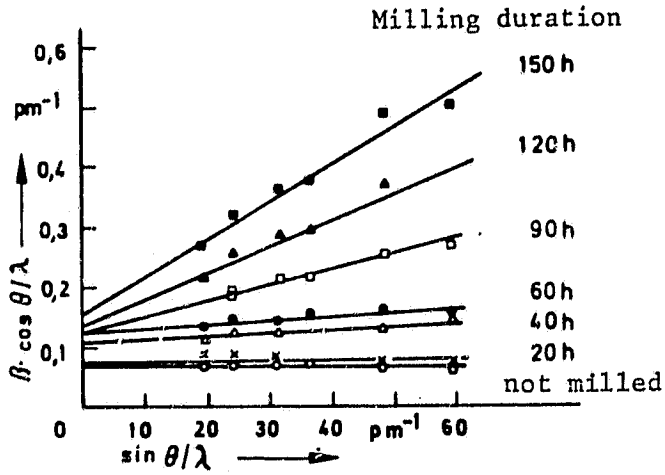


Figure 5. Line width analysis of an Al_2O_3 powder after different milling times.

method [7,8]. Variations can be compensated for well using this method.

This procedure is well known from metals [3]. With ceramic materials it has been used principally for characterizing oxide ceramics [3, 9-20] but can also be applied directly to other ceramic materials such as nitrides and carbides. G. Ziegler [3] has presented an evaluation of the measurement process and a summary of various evaluation procedures. Figures 4 to 6 show three examples that make clear the changes in crystallite size and lattice distortions from the courses of the lattice lines. Small values for the ordinate intersection indicate large crystallite size, and the increasing slopes of the lattice lines indicates an increase in the lattice distortions.

Example 1:

Characterization of various Al_2O_3 powders as supplied (Figure 4). The distinct changes in the course of the lattice lines indicate that there are substantial differences in crystallite size and lattice distortions in the individual powder charges. The quantitative data are summarized in Figure 4. The results of the variations between the individual powder charges can be taken from the further results in this report.

Example 2:

Changes in the structural properties of Al_2O_3 powders due to grinding (Figure 5).

The increase in the ordinate intersection and the slopes of the lattice lines with longer grinding duration show the increasing mechanical activation of these powders in the milling process (decreasing crystallite size, increasing lattice distortion).

Example 3:

Change in the lattice lines on annealing of a mechanically activated Al_2O_3 powder (Figure 6).

The decrease in the ordinate intersection with increasing annealing temperature indicates continuous growth of the crystallites. The decrease in the slope shows the healing of lattice defects at higher temperatures.

ORIGINAL PAGE IS
OF POOR QUALITY

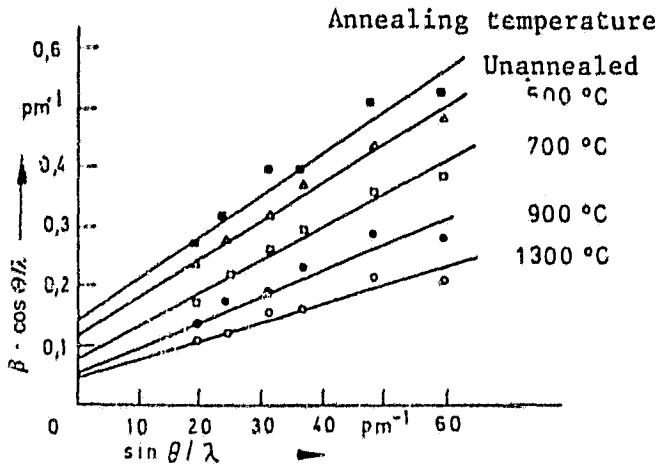


Figure 6. Line width analysis on a mechanically activated Al_2O_3 powder after annealing at different temperatures (annealing time 1 hour).

REFERENCES

[1] Patent application 80b, 8-03 (C04 b, 35-10). 2120802. Ziegler, G. Method for producing a transparent aluminum sinter body. AT 28.4. 71.

[2] Hausner, H. Science of Ceramics, Vol. 8 (1976), pp. 1-21.

[3] Ziegler, G. Powder Metallurgy Internat., Vol. 10, (1978) [2] pp. 70-73.

[4] Ziegler, G., Powder Metallurgy Internat. Vol. 10 (1978), [3], pp. 131-134.

[5] Leipold, W., Mortel, H. and Schuller, K.H. Ber Dt. Keram. Ges, Vol. 52, (1975), pp. 263-270.

[6] Rachinger, W.A., J. Sc. Instrum, Vol. 25, (1948), p. 254.

[7] Hall, W.H. Proc. Phys. Soc. Ser. A 62 (1949) pp. 741-743

[8] Williamson, G.K. and Hall, W.H. Acta Met 1 (1953), pp. 22-31.

[9] Prummer, R. and Ziegler, G. Ber. Dt. Keram. Ges, V91. 51, (1974) pp. 343-347.

[10] Prummer, R. and Ziegler, G. Powder Metallurgy Internat., Vol. 9, (1977) [1], pp. 11-14.

[11] Ziegler, G. Structural exchanges during grinding and sintering of aluminum oxide powders. Vortrag Tag Dt.Keram. Ges. Wiss. Ausschuss, Dusseldorf, 8.10, 1976

[12] Royen, P. and Tromel, M. Ber. Bunsengesellschaft fur physikalische Chemie 9/10 (1963) pp. 908-920.

[13] Royen, P., Tolksdorf, W., Granzer, F. and Schuster, H. Ber. Bunsengesellschaft fur physikalische Chemie, Vol. 67, (1963), pp. 1246-1252.

[14] Lewis, D. and Lindley, M.W. J. Amer. Ceram. Soc. Vol. 47, (1964) pp. 652-653

[15] Krauth, A. and Oel, H.J. Ber.Dt. Keram. Ges. Vol. 13, (1966), pp 1199-1206.

[16] Kneschke, G. and Schrader, R. Silikattechnik, Vol. 19, (1968) pp. 172-175.

[17] Kneschke, G. and Schrader, R. Ber.Dt.Keram.Ges. Vol. 46 (1969) pp. 398-401.

[18] Schrader, R. and Rump, H.; Z. f.anoran and allgem. Chemie, Vol. 350, (1967), pp. 137-141.

[19] Schrader, R., Arnold M. and Rump, H. ibid, pp. 120-129.

[20] Schrader, R., Rump, H. and Sanner, G. ibid, pp. 130-136