

THE INFLUENCE OF IMPURITIES IN TUNGSTEN AND MATRIX  
COMPOSITION ON THE TUN..(U) TECHNISCHE UNIV VIENNA  
(AUSTRIA) INST FUER CHEMISCHE TECHNOLO.. B LUX ET AL.  
OCT 82 DAJA37-80-C-0008 F/G 11/6

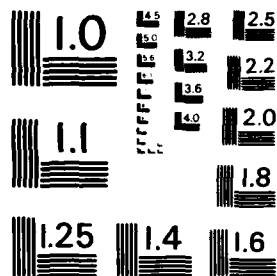
112

UNCLASSIFIED

OCT 82 DAJA37-80-C-0008

LUX E-1 A  
F/G 11/6

NI



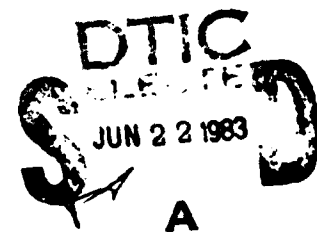
MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS - 1963 - A

ADA 1 29652

14

The Influence of Impurities in  
Tungsten and Matrix Composition  
on the Tungsten-Matrix Interfacial  
Properties of Heavy Metal Alloys

DTIC FILE COPY



This document has been approved  
for public release and sale; its  
distribution is unlimited.

06 22 016

Contract No. DAJA - 80 - C - 0008

The Influence of Impurities in  
Tungsten and Matrix Composition  
on the Tungsten-Matrix Interfacial  
Properties of Heavy Metal Alloys

Final Technical Report

covering the period

November 1979 - November 1982

SECRET  
JUN 22 1983  
A

B.Lux, W.J.Huppmann, G.Jangg, H.Danninger, W.Pisan  
Institut für Chemische Technologie Anorganischer Stoffe  
TU Vienna

This document is not to be  
for public release  
distribution is restricted

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

R&amp;D 2751-MS

| REPORT DOCUMENTATION PAGE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                       | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM                 |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|-------------------------------------------------------------|
| 1. REPORT NUMBER                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER                               |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | AD-A129652            |                                                             |
| 4. TITLE (and Subtitle)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                       | 5. TYPE OF REPORT & PERIOD COVERED                          |
| The Influence of Impurities in Tungsten and Matrix Composition on the Tungsten-Matrix Interfacial Properties of Heavy Metal Alloys                                                                                                                                                                                                                                                                                                                                                                                                         |                       | Final Technical Report<br>Nov 79 - Nov 82                   |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                       | 6. PERFORMING ORG. REPORT NUMBER                            |
| 7. AUTHOR(s)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                       | 8. CONTRACT OR GRANT NUMBER(s)                              |
| B. Lux, W.J. Huppmann, G. Jangg, H. Danninger, W. Pisan                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                       | 37<br>DAJA-80-C-0008                                        |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                       | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
| Institut für Chemische Technologie anorganischer<br>Technische Universität Wien<br>Getreidemarkt 9, A-1060 Vienna                                                                                                                                                                                                                                                                                                                                                                                                                          |                       | 6.11.02A<br>1T16 1102BH57-04                                |
| 11. CONTROLLING OFFICE NAME AND ADDRESS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                       | 12. REPORT DATE                                             |
| USARDCG-UK<br>Box 65<br>FPO New York 09510                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                       | October 1982                                                |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                       | 13. NUMBER OF PAGES                                         |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                       | 135                                                         |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                       | 15. SECURITY CLASS. (of this report)                        |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                       | Unclassified                                                |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                       | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE                  |
| 16. DISTRIBUTION STATEMENT (of this Report)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                       |                                                             |
| Approved for public release; distribution unlimited                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                       |                                                             |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                       |                                                             |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                       |                                                             |
| 18. SUPPLEMENTARY NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                       |                                                             |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                       |                                                             |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                       |                                                             |
| Tungsten heavy metals, liquid phase sintering, starting W powders, pore formation by impurities, influence of the sintering cycle, sintering time.                                                                                                                                                                                                                                                                                                                                                                                         |                       |                                                             |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                       |                                                             |
| The mechanical properties of tungsten heavy metals are strongly influenced by the quality of the starting materials, especially the powders. Powders that are too coarse result in highly porous heavy metals, regardless of the sintering conditions, as, due to insufficient distribution of the binder melt, liquid phase sintering occurs only locally. A second, although different, type of porosity is caused by traces of alkaline metals or rare earths, the pores in this case being formed during liquid phase sintering. These |                       |                                                             |

DD FORM 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

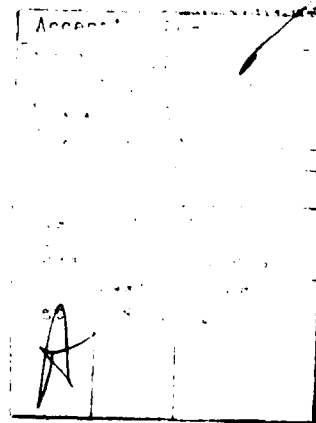
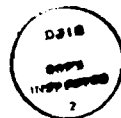
UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. (continued)

elements apparently promote reduction of oxide traces and Ostwald ripening of the resulting micropores. The influence of most other impurities is less pronounced but could be identified by statistical evaluation.

Another important parameter is the sintering cycle. An optimal sintering cycle affords sufficient pre-reduction before liquid phase sintering and yields a fine, homogeneous microstructure. Too short a time for liquid phase sintering results in inhomogeneous material with insufficient ductility. Too long a sintering time results in grain coarsening and in considerable microporosity, which is apparently caused by the same mechanism as with alkaline metals, i.e. reduction of oxide traces, though at a much slower rate.



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

## 1. Introduction

The two-phase alloys commonly known as "Tungsten Heavy Metals" are a successful combination of the heavy and strong but relatively brittle bcc W grains and a highly ductile fcc Ni-Fe-W binder. High density - almost that of pure W - and strength combined with excellent ductility are the principal advantages of these alloys. Depending on binder content, densities ranging from 17,1 (with 10% binder) to 18,5 (with 3% binder) are attained; a further increase in W content does not yield a corresponding increase in density as the resulting material is porous (1). The tensile strength is usually between 950 and 1000 N/mm<sup>2</sup>, and, most important of all, the elongation ranges from < 5% for 97% W to > 20% for 90% W. However, the properties, especially the ductility, depend very much on several parameters, the most important of which are:

- a) formation of the appropriate microstructure during the sintering process, which is influenced mainly by the sintering parameters temperature and time
- b) absence of certain impurities which appear to cause strong embrittlement of the heavy metals by lowering the interphase strength between W grains and binder or by causing pore formation.

The sensitivity of the heavy metals towards those parameters is probably responsible for certain difficulties encountered in the reproducibility of the properties; slight changes in the sintering parameters or starting materials can cause considerable deterioration of the mechanical properties, esp. of the ductility.

The first group of problems is mainly a function of furnace control, esp. furnace temperature and temperature distribution within the sintering boats and even within the samples. The problems encountered with impurities, however, are more difficult to identify, as there are several sources for detrimental elements:

- 1) Impurities contained in the starting powders W, Ni, Fe. As both Ni and Fe of "carbonyl quality" are used, they are relatively pure. Further their amount in the heavy metals is much lower than that of W, so that the impurities contained in the W powders are of much greater importance.
- 2) Impurities brought into the material during blending and compaction. In this stage contamination can be easily avoided by proper precautions.
- 3) Residues from cracked pressing lubricant not removed during de-waxing. By using suitable pressing lubricants and carefully optimizing the de-waxing stage of the sintering cycle, at least with smaller samples the pressing lubricant can be completely removed.
- 4) Impurities from the sintering atmosphere absorbed by the heavy metals during sintering.

Earlier experiments (2,3) had shown that the most pronounced deterioration of the mechanical properties is caused by oxygen. During storage, the surface of the powders - W, Ni and Fe - are inadvertently oxidized. During liquid phase sintering the oxides are to some extent reduced by  $H_2$ , and the resulting  $H_2O$  tends to form pores and blisters which weaken the material; remaining oxygen is concentrated at the phase boundaries where it weakens interphase strength and causes the material to fail at very low degrees of deformation ( $< 2\%$ ). This contamination, however, can easily be identified by SEM investigation of the fracture surfaces; it is characterized by intergranular fracture and esp. by W spheres from which the binder has completely peeled off without leaving any traces. Careful prereluction of the compacts at temperatures  $> 1000^\circ C$  before liquid phase sintering, however, is sufficient to obtain reasonably oxygen-free material.

Further test proved that heavy metals are also sensitive to hydrogen embrittlement: due to the strong influence of the temperature on the solubility of hydrogen both in W and Ni-Fe, rapid cooling may trap hydrogen in the heavy metals. Heat treatment in vacuum or even slow cooling permits the surplus hydrogen to escape, more than doubling the elongation.

Formation of brittle intermetallic phases by slow cooling, as described by several authors (4,5), was not observed. The decrease in ductility through rapid cooling was more pronounced the higher the temperature from which the samples were quenched; below 800°C no detrimental effect was observed (6; see also 7).

First experiments with intentionally doped W powders had shown that Na in particular promotes formation of pores and often even externally visible blisters which considerably weaken the material. Certain impurities, e.g. Al can also be harmful, while many other dopants investigated had no effect on the properties (1,3,6). With this in mind, the extension of the work to include new dopants, and in particular combinations of various additives was regarded to be of principal importance. The excellent reproducibility attained with the developed sintering cycle would enable identification of even slight effects from the doping additives. However, further investigation of the sintering process was also interesting, because it was hoped that more detailed knowledge could lead to better explanations for several as yet unclear effects which had been observed.

## 2. Starting materials

All W powders investigated were specially prepared and supplied to us by an Austrian tungsten manufacturer. In accordance with the intentions of the program, W powders with various doping additives were produced. The elements selected for doping were mainly those present in varying quantities in the usual industrial W powder grades.

All dopants were added to the tungstate solution before precipitation of APT, thus ensuring homogeneous distribution. The reduction parameters - temperature, humidity of the hydrogen atmosphere - were selected for powders of  $\sim 3 \mu\text{m}$  average grain size, as usually used for the production of W heavy metals. Due to the promoting effect of several elements on grain growth during  $\text{H}_2$  reduction e.g. Na, Li (8,9) the powders containing those elements were considerably coarser with grain sizes up to  $>20 \mu\text{m}$ , as shown both by Fisher SSS and sedimentation (see attached sheets). The chemical compositions of the powders as supplied by the manufacturer are shown in Tab. 1. The purity of the W powders themselves is very satisfactory, the impurity level generally being lower than 20 ppm and in some cases even  $< 10$  ppm. By comparing the amount of dopant added before reduction to the real content in the W powder as analyzed after reduction, the evaporation of some elements during reduction is clearly shown (9).

The compacting and sintering behaviour of the W powders is also influenced considerably by parameters not identified by Fisher SSS or sedimentation, e.g. grain shape and tendency to form agglomerates. Therefore all powders were also investigated by SEM; representative photos are shown in Fig. 1-37.

Besides the differences in grain size and grain size distribution as shown by Fisher SSS and the sedimentation sheets, the differences in grain shape are noteworthy. In some cases clear-facetted crystals are observed (e.g. with the powders containing Li and Na) while other final materials are roughly irregular or even almost spherical (e.g. the powders doped with Al or K). The powders containing Al also exhibit surface contaminants which were shown by EEDS to consist of  $\text{Al}_2\text{O}_3$ .

Regarding the agglomerates, almost all powders contain certain amount of agglomerates, although they are of the rather different form. The powders containing alkaline metals in particular exhibit very dense, compact agglomerates; as shown

Table 1: Chemical Analysis of the W-powders (contents in ppm)

|      | Additive                       | C  | O <sub>2</sub> | P  | Al  | Ca  | Co  | Cr  | Cu  | Fe  | K   | Mg  | Mo  | Na  | Ni  | Si  | V   |
|------|--------------------------------|----|----------------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 503  |                                | 20 | 240            | 21 | <10 | <10 |     |     |     | 12  |     |     | <20 | 26  | <10 | <20 |     |
| E 2  | 250 Na                         | 7  | 130            | 42 | <10 | <10 |     |     |     | <10 |     |     | <20 | 20  | <10 | <20 |     |
| E 5  | 250 Li                         | 4  | 630            | 44 | <10 | <10 |     |     |     | <10 |     |     | <20 | <10 | <10 | <20 |     |
| E 8  | 188 Ca                         | 15 | 280            | 43 | <10 | 220 |     |     |     | <10 |     |     | <20 | <10 | <10 | <20 |     |
| E 11 | 250 B                          | 24 | 760            | 48 | <10 | <10 |     |     |     | <10 |     |     | <20 | 22  | <10 | <20 |     |
| E 14 | 250 Al                         | 17 | 470            | 37 | 288 | <10 |     |     |     | <10 |     |     | <20 | 22  | <10 | <20 |     |
| E 17 | 100 Si                         | 11 | 470            | 24 | <10 | 12  | <10 | <20 | <10 | 12  | 14  | <10 | <20 | 48  | <10 | 96  | <25 |
| E 21 | 140 Na, 100 P                  | 24 | 310            | 93 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | 24  | <10 | <20 | <25 |
| E 24 | 100 As, Sb, Bi                 | 15 | 640            | 31 | <10 | 12  | <10 | <20 | <10 | 24  | <10 | <10 | <20 | 26  | 12  | <20 | <25 |
| E 27 | 100 U                          | 11 | 450            | 29 | <10 | 16  | <10 | <20 | <10 | <10 | <10 | <10 | <20 | 18  | <10 | <20 | <25 |
| E 30 | 188 Na, 106 Al<br>113 U, 500 F | 14 | 220            | 52 | 64  | <10 |     |     |     | 12  |     |     | <20 | 48  | <10 | <20 |     |
| E 33 |                                | 11 | 310            | 49 | <10 | <10 |     |     |     | <10 |     |     | <20 | 14  | <10 | <20 |     |
| E 36 | 100 Na                         | 13 | 240            | 30 | <10 | 12  | <10 | <20 | <10 | <10 | 14  | <10 | <20 | 22  | <10 | <20 | <25 |
| E 39 | 50 Na                          | 6  | 270            | 23 | <10 | 16  | <10 | <20 | <10 | <10 | 10  | <10 | <20 | 22  | <10 | <20 | <25 |
| E 45 | 100 Li                         | 4  | 530            | 36 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | <10 | <10 | <20 |     |

Table 1 (continued)

|      | Addition          | grain size (um) |    | C   | O | P  | Al  | Ca  | Co  | Cr  | Cu  | Fe  | K   | Mg  | Mo  | Na  | Ni  | Si  | V   | Dopant      |
|------|-------------------|-----------------|----|-----|---|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------------|
| 640  |                   | 3,00            | 20 | 240 |   |    | 23  |     |     |     |     | 16  |     |     | 60  | 18  | <10 | <20 |     |             |
| E 48 | 200 Na            | 25,10           | 7  | 30  |   | 16 | <10 | <10 | <10 | <20 | <10 | 16  | 16  | <10 | <20 | <10 | <10 | <20 | <25 | 10 Na       |
| E 51 | 200 Li            | 40,00           | 22 | 450 |   | 51 | <10 | <10 | <10 | <20 | <10 | 12  | 30  | <10 | <20 | <10 | <10 | <20 | <25 | 193 Li      |
| E 56 | 200 Al            | 11,95           | 12 | 200 |   | 31 | <10 | <10 | <10 | <20 | <10 | 16  | 20  | <10 | <20 | <10 | <10 | <20 | <25 | 116 Al      |
| E 61 | Impure Blue Oxide | 18,00           | 8  | 200 |   | 47 | 116 | <10 | <10 | <20 | <10 | 20  | 16  | <10 | <20 | 12  | <10 | <20 | <25 | 20 F        |
| E 53 | 200 K             | 4,58            | 2  | 160 |   | 33 | <10 | <10 | <10 | <20 | <10 | 14  | <10 | <10 | <20 | <10 | <10 | <20 | <25 | 10 K        |
| E 67 | 100 K             | 4,90            | 10 | 140 |   | 30 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | <10 | <10 | <20 | <25 | 10 K        |
| E 1  | 50 K              | 3,95            | 10 | 180 |   | 31 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | <10 | <10 | <20 | <25 | 10 K        |
| E 7  | 200 Na, 120 Si    | 5,80            | 17 | 330 |   | 28 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | 64  | <10 | 100 | <25 | 64Na, 100Si |
| E 83 | 100 Na, 80 F      | 5,20            | 5  | 140 |   | 31 | <10 | <10 | <10 | <20 | <10 | 12  | <10 | <10 | <20 | 20  | <10 | <20 | <25 | 20Na, 20F   |
| E 87 | 150 Mg            | 3,01            | 9  | 310 |   | 29 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | 200 | <20 | 16  | <10 | <20 | <25 | 200 Mg      |
| E 91 | 200 Ba            | 3,35            | 8  | 250 |   | 28 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | <10 | <10 | <20 | <25 |             |
| E 95 |                   |                 |    |     |   |    |     |     |     |     |     |     |     |     |     |     |     |     |     |             |
| E 99 | 100 Zn            | 3,75            | 11 | 200 |   | 25 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | 14  | <10 | <20 | <25 |             |
| E103 | 100 Cu            | 3,19            | 24 | 290 |   | 29 | <10 | <10 | <10 | <20 | 132 | <10 | <10 | <10 | <20 | 14  | <10 | <20 | <25 | 132 Cu      |
| E107 | 100 Ni            | 3,18            | 6  | 210 |   | 27 | <10 | <10 | <10 | <20 | <10 | 12  | <10 | <10 | <20 | 12  | 152 | <20 | <25 | 152 Si      |
| E111 | Rare Earths 84 Ce | 3,40            | 19 | 230 |   | 29 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | 10  | <10 | <20 | <25 |             |
| E115 | 100 P             | 3,13            | 19 | 250 |   | 83 | <10 | <10 | <10 | <20 | <10 | <10 | <10 | <10 | <20 | 14  | <10 | <20 | <25 | 83 P        |

these agglomerates formed during reduction when small particles were cemented together by molten tungsten bronzes; the high strength and density of these objects is thus hardly surprising. On the other hand Al is particularly effective in inhibiting the agglomerates or at least in making them less compact since it inhibits in the formation of tungsten bronzes (10,11). The amount of agglomerates, their size and their strength are not only of academic interest. They may cause incorrect results for grain size measurements in that abnormally large sizes would be measured, while for liquid phase sintering, esp. for the solution-reprecipitation mechanism, the radius of the individual grain determines the tendency to be dissolved in the binder. In Ref. (1) three powders were shown to be much finer than indicated by Fisher SSS; measuring the grain size by means of SEM photos revealed a grain size just under 1  $\mu\text{m}$  rather than the 3  $\mu\text{m}$  measured by both Fisher SSS and sedimentation.

For the binder elements Ni and Fe powders of "carbonyl quality" with average grain size of  $\sim 5 \mu\text{m}$  were used; to avoid binder inhomogeneities in the heavy metals, particles  $> 45 \mu\text{m}$  were screened off. Without this separation step a considerably increased scatter in the measured values, particularly in those for elongation, had been observed.

### 3. Investigation of the sintering process

As stated above, the formation of the appropriate microstructure is of decisive importance for the properties of W heavy metals. Due to various grain growth mechanisms, e.g. solution, reprecipitation and coalescence (12,13), both grain size and grain shape change considerably during sintering; thus the sintering time is probably one of the most important parameters for the microstructure. The investigation of the changes in the microstructure during sintering and of the effects on the mechanical properties was regarded as necessary in order to set a standard against

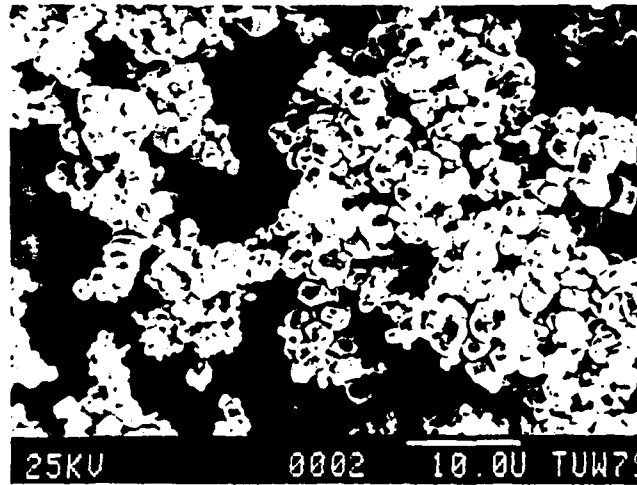


Fig.1  
undoped standard  
powder 503/79

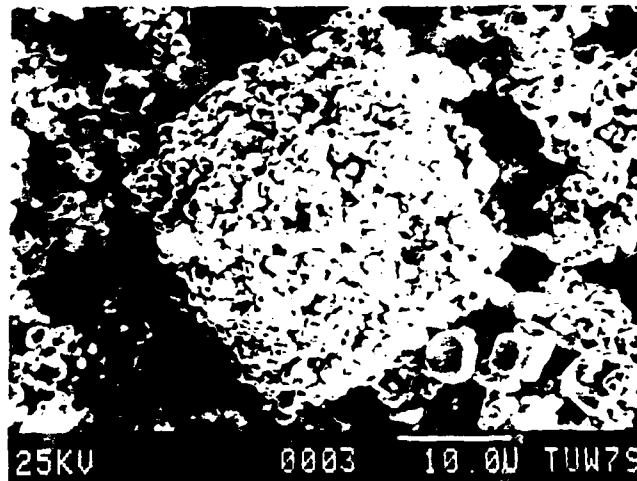


Fig.2  
W503/79  
typical agglom-  
merate



Fig.3  
W503/79  
grain shape of  
the standard  
powder

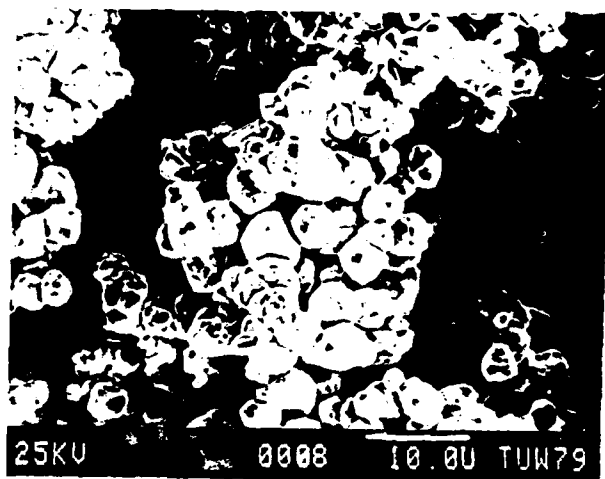


Fig.4  
E2W  
(W powder doped  
with 250ppm Na)



Fig.5  
E5W  
(250ppm Li)

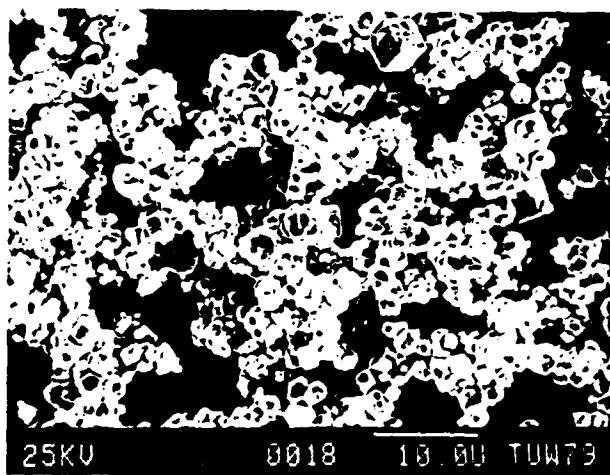


Fig.6  
E8W  
(188ppm Ca)



Fig.7  
E11W  
(W powder doped  
with 250ppm B)

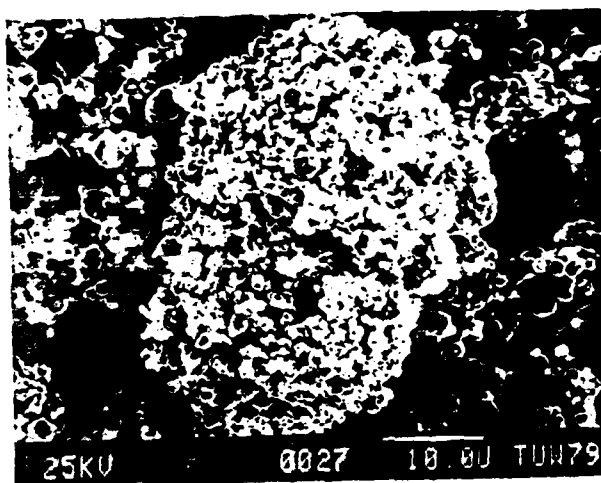


Fig.8  
E14W  
(Dopant 250ppm Al)

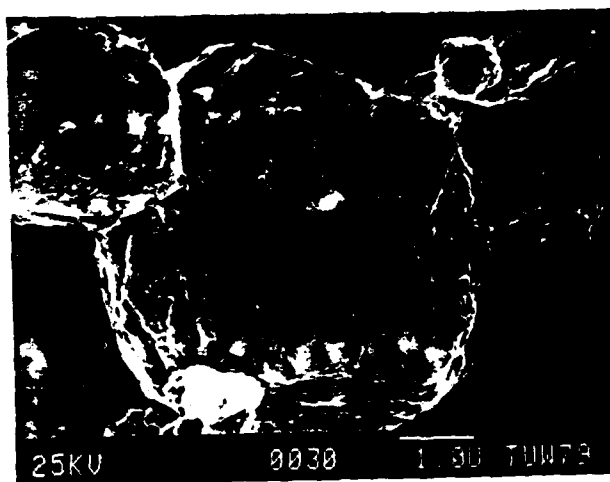


Fig.9  
E14W  
grains covered  
with small  
 $\text{Al}_2\text{O}_3$  particles

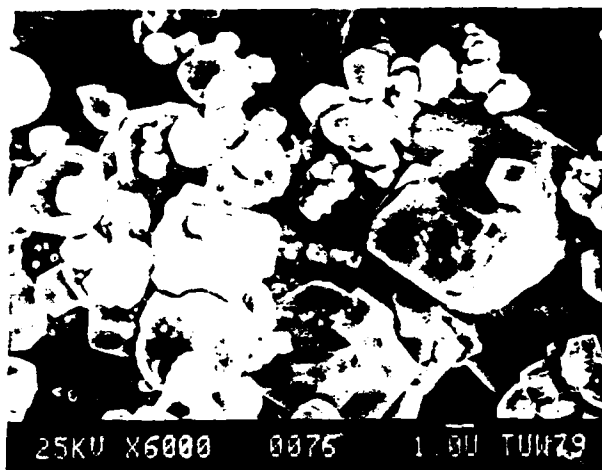


Fig.10  
E17W  
W powder doped  
with 100ppm Si

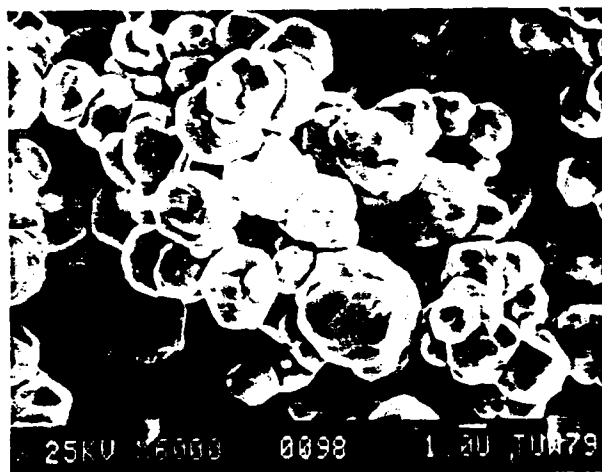


Fig.11  
E 21W  
(doped with  
140ppm Na, 100  
ppm P)

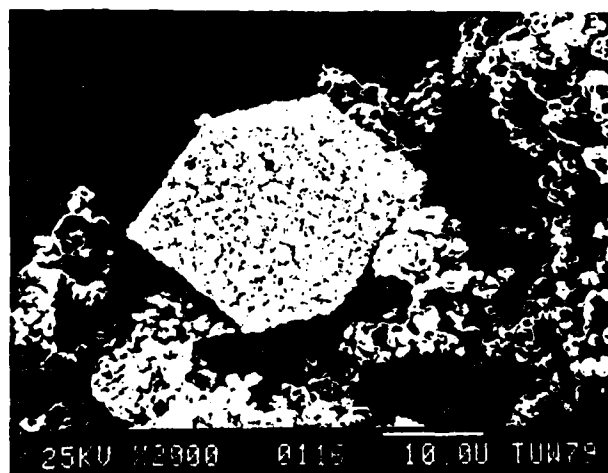


Fig.12  
E24W  
doped with As,Sb,  
Bi (100ppm each)  
characteristic  
pseudomorphous  
structure)

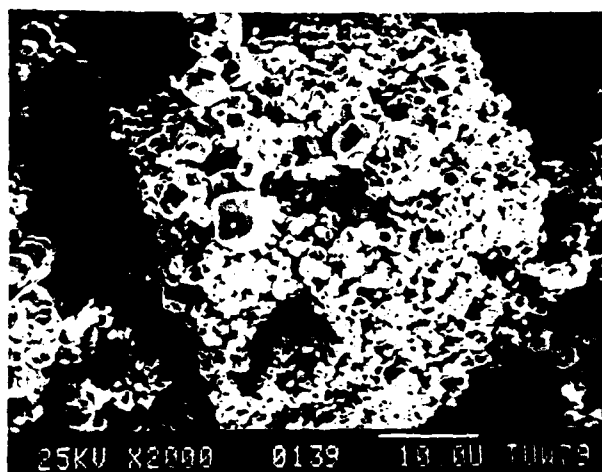


Fig.13

E27W

W powder doped  
with 100ppm U

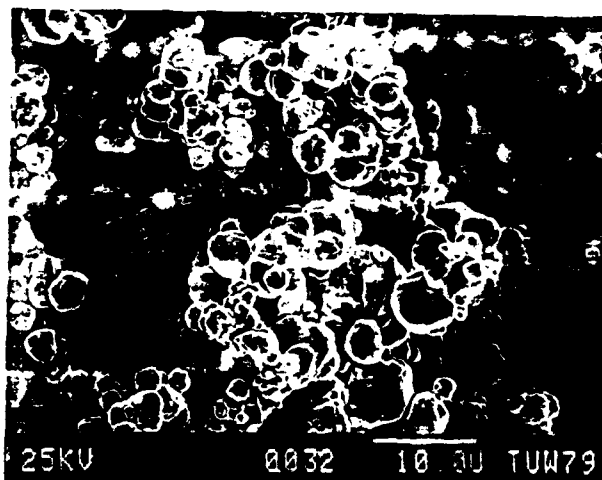


Fig.14

E30W

W powder prepared  
from impure blue  
oxide

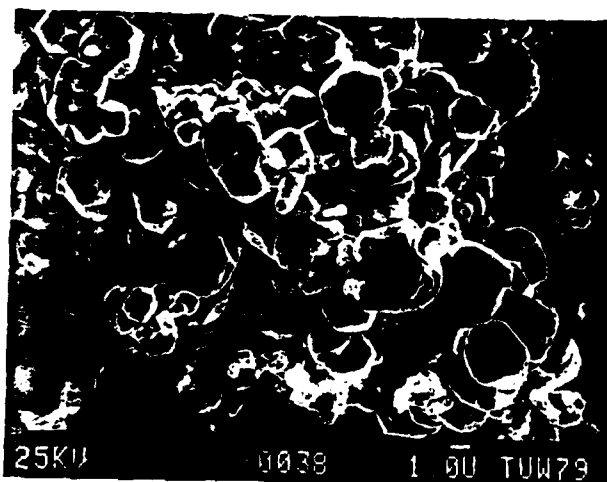


Fig.15

E33W

undoped W powder

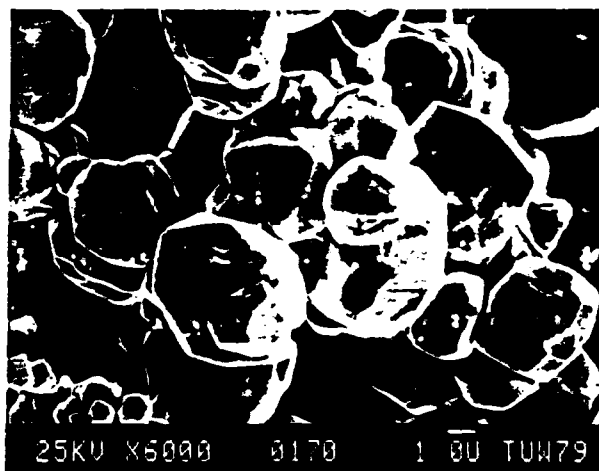


Fig.16

E36W

W powder doped  
with 100ppm Na

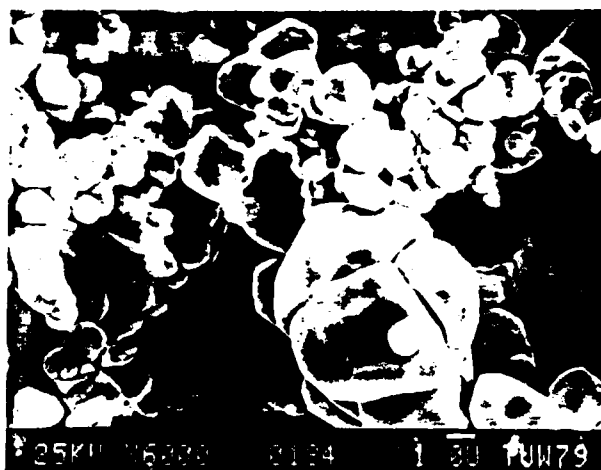


Fig.17

E39W

Dopant 50ppm Na

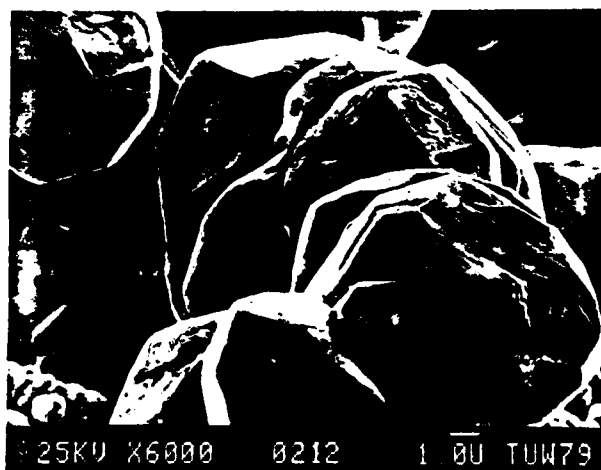


Fig.18

E45W

W powder doped  
with 100ppm Li;  
very coarse powder

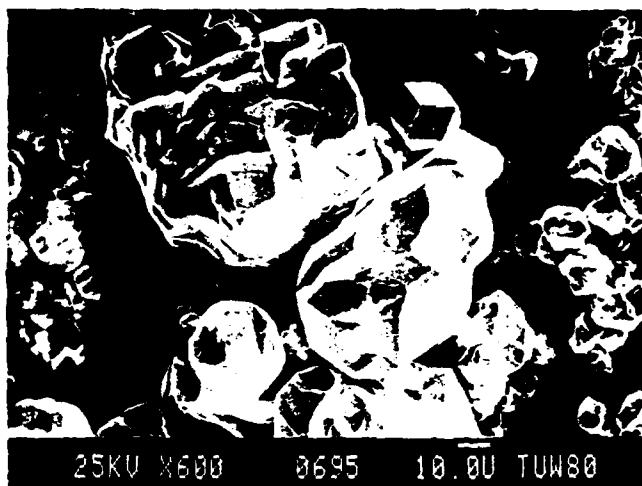


Fig.19  
E48W  
W powder doped  
with 200ppm Na;  
coarse powder



Fig.20  
E51W  
W powder doped  
with 200ppm Li;  
extremely coarse  
powder



Fig.21  
E56W  
doped with 200ppm  
Al; surface con-  
taminated with  
 $Al_2O_3$

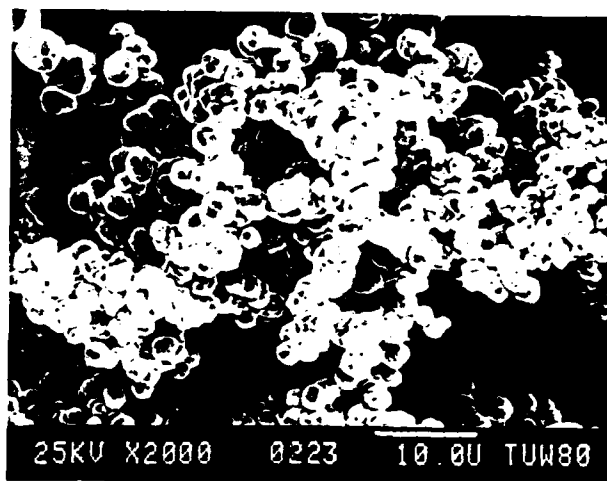


Fig.22  
E63W  
W powder doped  
with 200ppm K

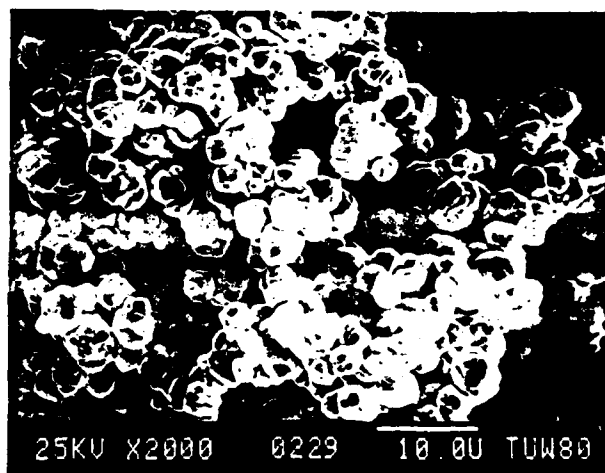


Fig.23  
E67W  
doped with  
100ppm K

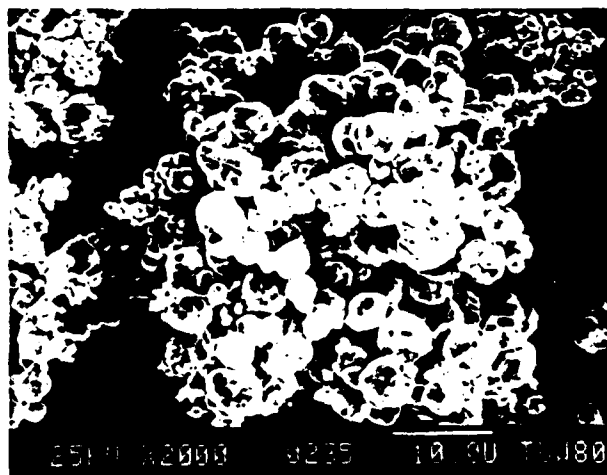


Fig.24  
E71W  
doped with  
50ppm K

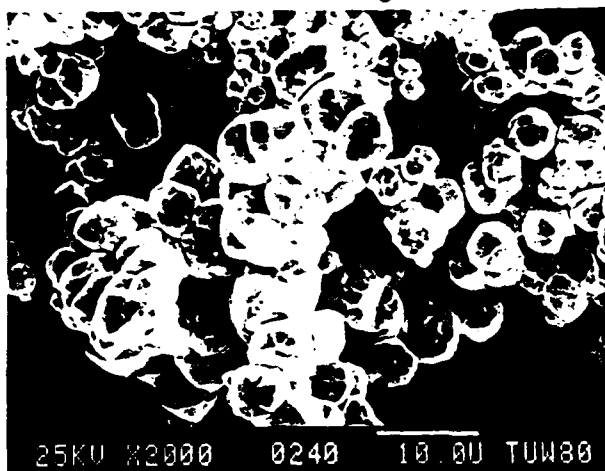


Fig.25  
E79W  
W powder doped  
with 200ppm Na,  
120ppm Si

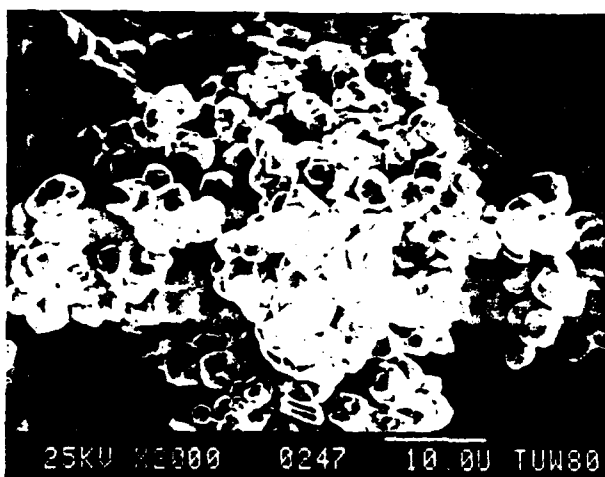


Fig.26  
E83W  
doped with 100ppm  
Na, 80ppm F

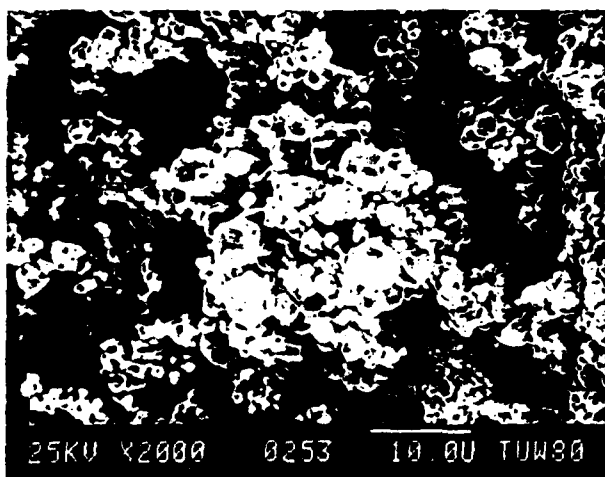


Fig.27  
E87W  
doped with  
150ppm Mg

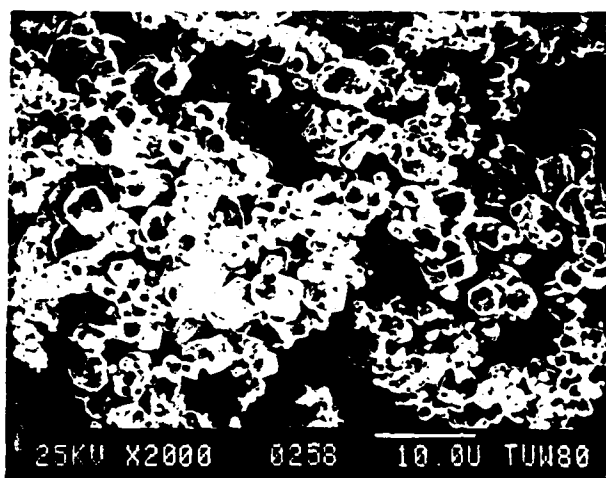


Fig.28  
E91W  
W powder doped  
with 200ppm Ba

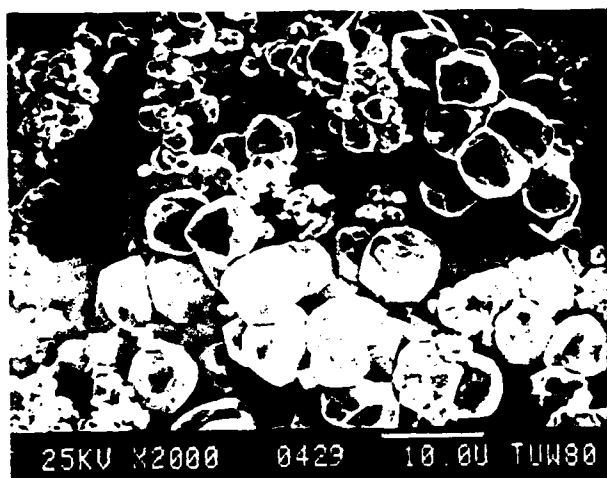


Fig.29  
E95W  
doped with  
100ppm Sn

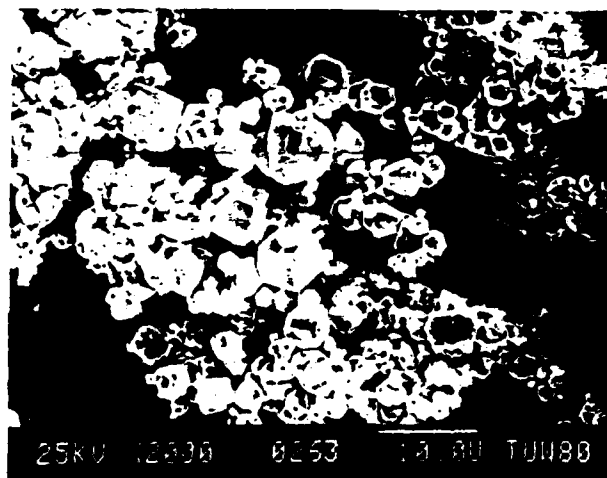


Fig.30  
E99W  
doped with  
100ppm Zn

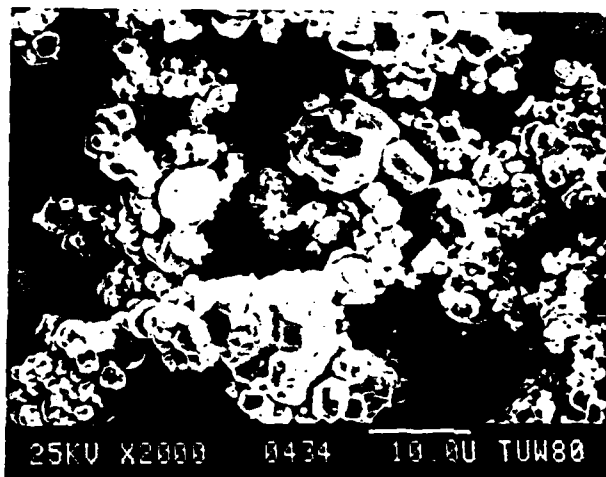


Fig.31  
E103W  
W powder doped  
with 100ppm Cu

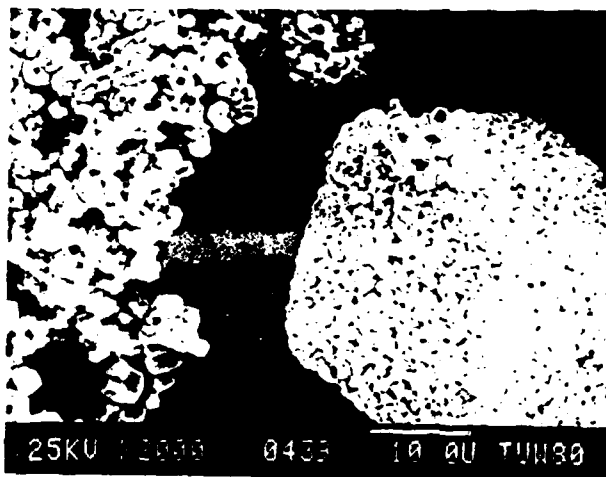


Fig.32  
E107W  
doped with 100ppm  
Ni; very dense  
agglomerates

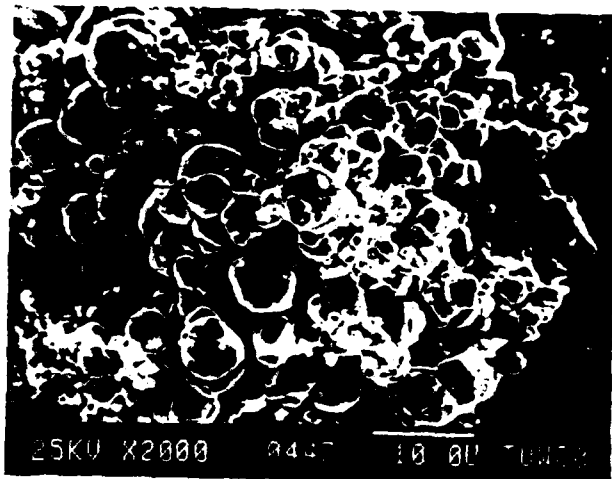


Fig.33  
E111W  
doped with rare  
earths

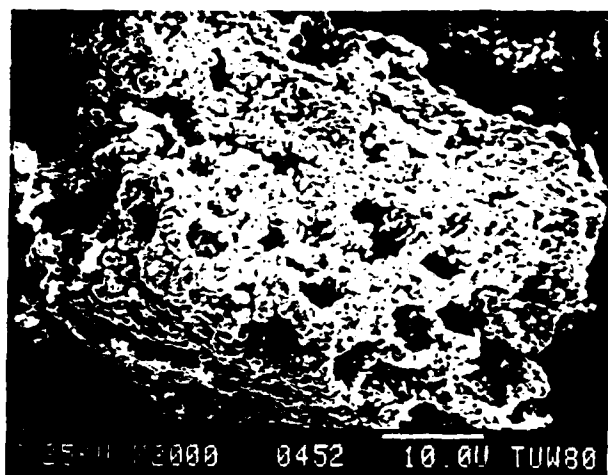


Fig.34  
E115W  
W powder doped  
with 100ppm P

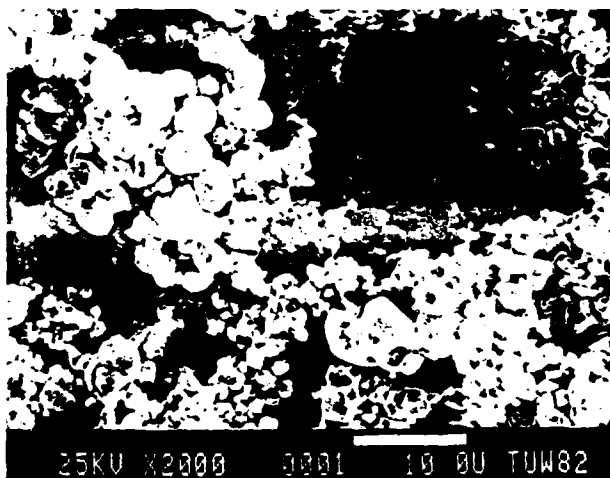


Fig.35a  
W640/81  
standard W powder  
(undoped)

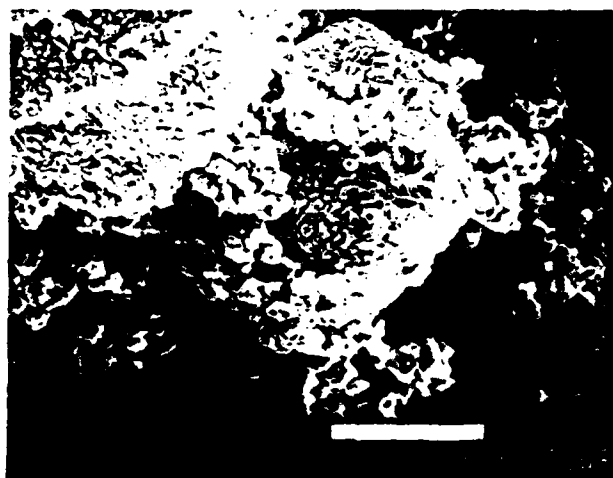


Fig.35b  
W640/81  
typical  
agglomerates

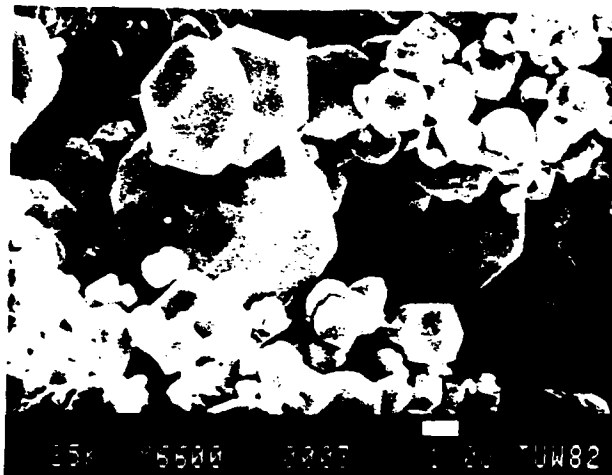


Fig.35c  
W640/81  
standard powder;  
shape of indi-  
vidual grains

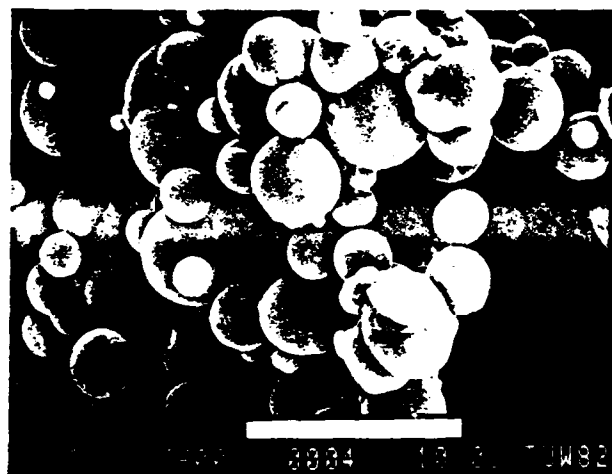


Fig.36  
Carbonyl Fe

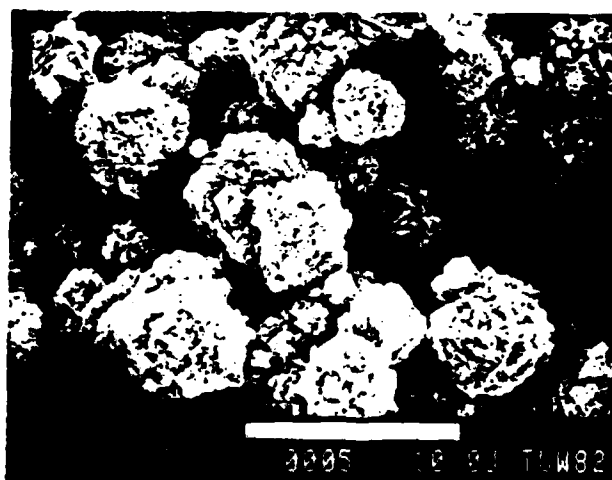


Fig.37  
Carbonyl Ni

which the experiments with doped powders could be correctly compared and evaluated. It was thought possible that the doping elements in the W powder would influence not only the properties of the heavy metals but also the sintering process; sufficient knowledge about the sintering process thus might make it possible to identify and explain special effects caused by the dopants.

### 3.1 Experimental procedures

The experiments were carried out with heavy metals of the standard composition 90 wt% W - 6,7 wt% Ni - 3,3 wt% Fe and 1% camphor as pressing lubricant; the W powder used was the standard powder W 640/81 of  $\sim 3 \mu\text{m}$  average grain size. The Ni and Fe powders were the 'Carbonyl powders' - average grain size  $5 \mu\text{m}$  - described in the last chapter. After 3 hrs mixing in cyclohexane the solvent was partially evaporated and the still somewhat damp powder was granulated through a 0,8 mm mesh sieve and then dried. The granulate was compacted in a pressing tool for standard tensile strength bars (MPIF standard 10-63). The excellent flow characteristics of the granulate resulting in uniform filling of the die so that pressing faults were completely avoided. The tensile strength bars were sintered in a high temperature furnace with an Mo heat conducting coil at a temperature of  $1475^{\circ}\text{C}$ ; the sintering atmosphere was technical hydrogen with a flow rate of 2 l/min. As mentioned above, a pre-reduction treatment to reduce any oxides in the powders as well as slow cooling after liquid phase sintering are necessary to avoid embrittlement of the heavy metals. Fig.38 shows the temperature-time diagram for the sintering cycle. Pre-reduction was carried out by slowly heating the samples from  $500^{\circ}\text{C}$  to  $1400^{\circ}\text{C}$  and then keeping them at  $1400^{\circ}\text{C}$  for 1 hr. After a short rest in a somewhat cooler zone of the furnace to enable the heating zone to reach sintering temperature the samples were liquid phase sintered for the desired length of time and then the furnace was simply switched off, the samples cooling down to  $500^{\circ}\text{C}$  within 14 hrs. The short inter-cooling was regarded necessary for exact control of the sintering time; it does not affect the mechanical properties of the heavy metals.

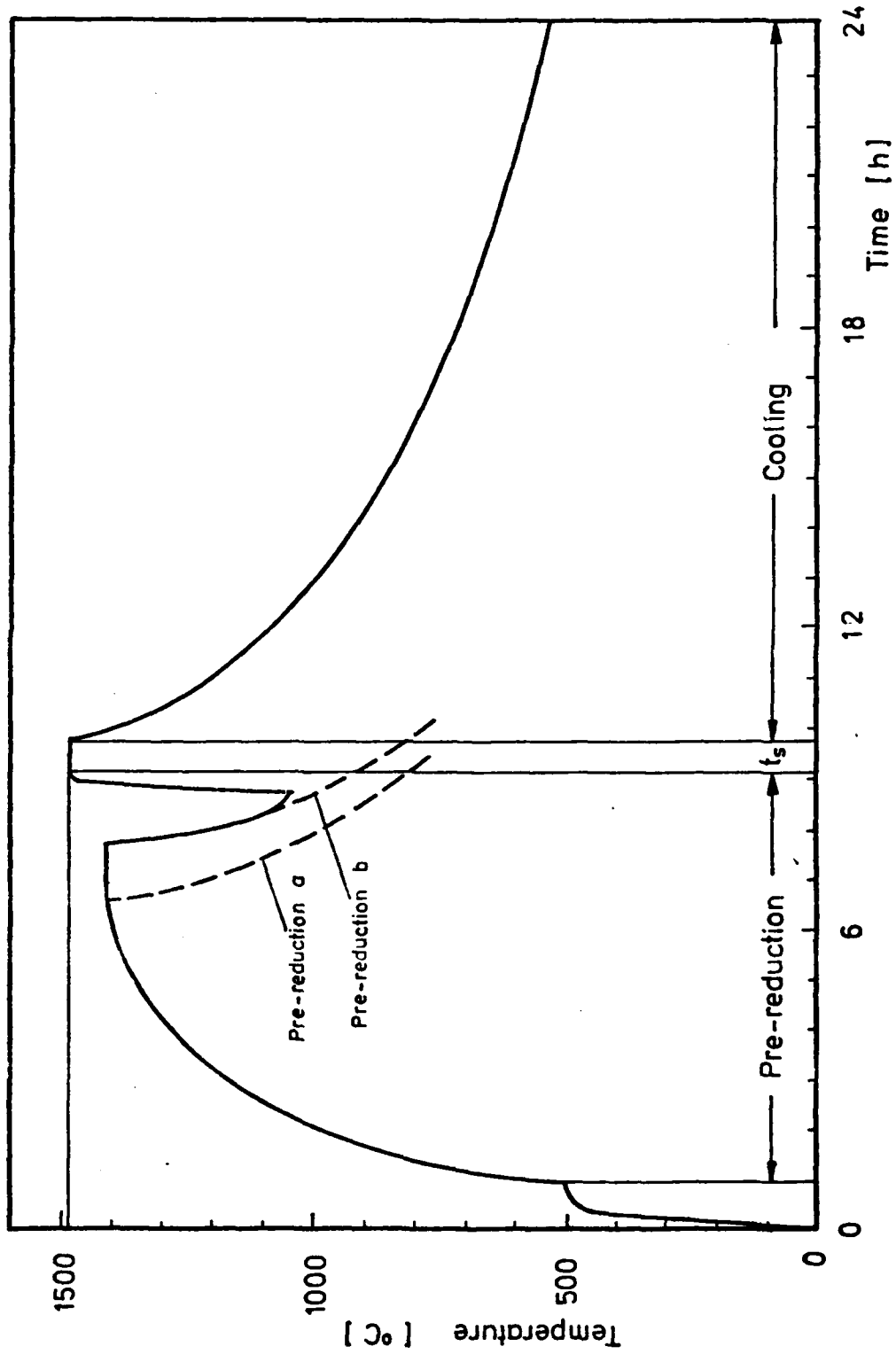


Fig.38: Standard sintering cycle for heavy metals containing 90%W

While the sintering temperature was held constant at  $1475 \pm 5^{\circ}\text{C}$ , the sintering time was varied from 1-120 min. To control the state of the material before liquid phase sintering, samples in different states of pre-reduction (a,b in Fig.38) were also investigated. The mechanical properties of the samples thus produced are shown in Table 2.

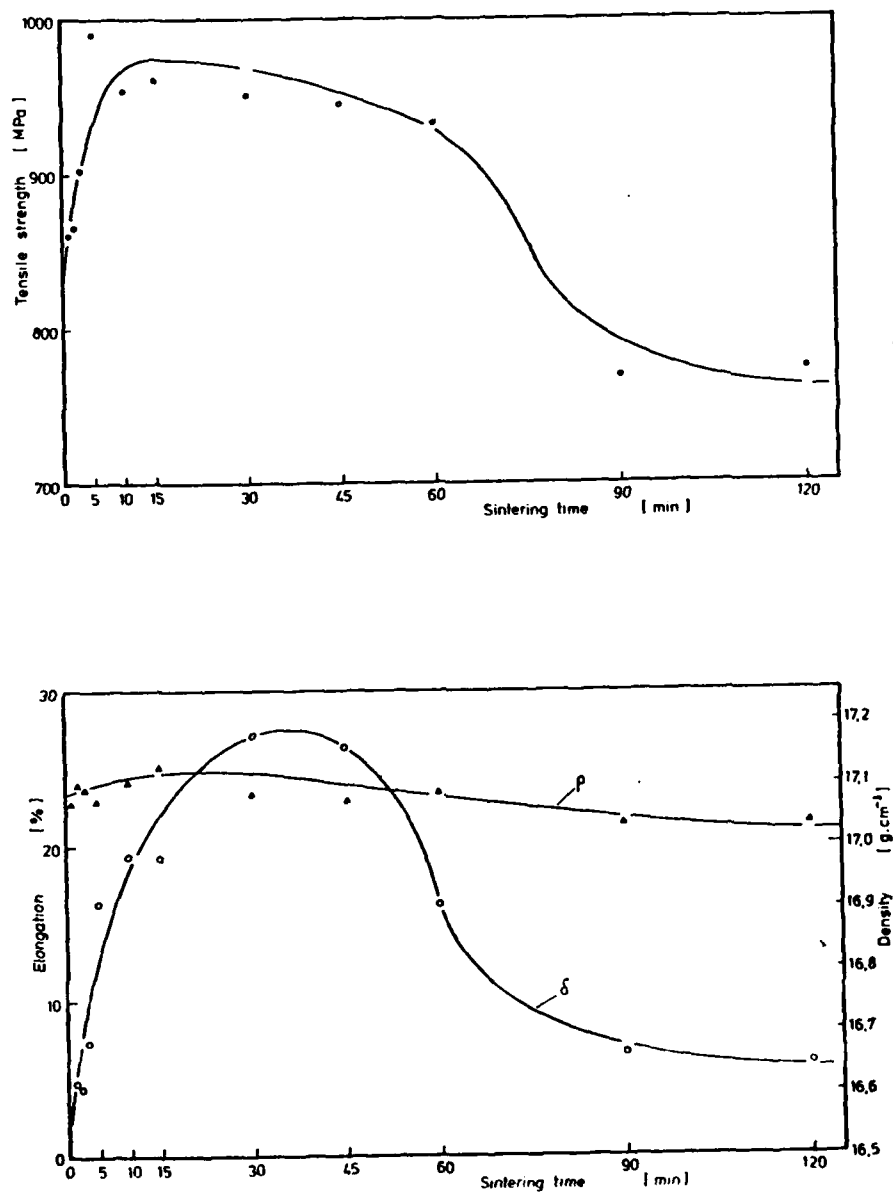
### 3.2 Experimental results

Surprisingly, even after short pre-reduction and before reaching liquid phase sintering very high density was attained and the porosity was already below 3%. After extended prereduction (b in Fig.38) practically full density was achieved. Apparently, at those temperatures solid state sintering is very rapid. The binder materials probably act as promoters for the sintering of W (14), the driving force being the saturation of W with the binder materials (15). During liquid phase sintering there are almost no changes in density; only after very long sintering times (>60 min) could a slight decrease in density be measured. This may be attributable to the formation of pores, as already described for longer sintering times by Churn and Yoon (16).

The high density of pre-reduced samples also explains their quite good tensile strength; in accordance with the increase in density, extended pre-reduction also increases tensile strength. Although the density is equal to that of liquid phase sintered material, the tensile strength is still considerably lower. The stress-strain diagrams show that with these samples only elastic deformation occurs, the tensile strength being identical to the yield strength, and the samples are not strengthened further by work hardening. After melting of the liquid phase the tensile strength increases rapidly, the maximum value being attained after only 5 min where it remains nearly constant up to 60 min. This is followed by rapid decreases at 90 and 120 min, an effect attributable to the above mentioned pores.

Table 2: Mechanical properties of W heavy metals  
(90%W - 6,7% Ni - 3,3% Fe) sintered at 1475°C  
for different lengths of time. Average values  
from 4 samples

| Sintering<br>time (min)                           | Density<br>(g/cm <sup>3</sup> ) | Tensile strength<br>(MPa) | Elongation<br>(%) | Mean grain<br>size (μm) |
|---------------------------------------------------|---------------------------------|---------------------------|-------------------|-------------------------|
| 0                                                 | 16,652                          | 725                       | 0                 | -                       |
| 0<br>pre-reduction<br>extended by<br>1h at 1400°C | 17,057                          | 833                       | 0                 | -                       |
| 1                                                 | 17,073                          | 861                       | 4,8               | 7,0                     |
| 2                                                 | 17,104                          | 867                       | 4,5               | -                       |
| 3                                                 | 17,084                          | 904                       | 7,3               | 10,6                    |
| 5                                                 | 17,060                          | 990                       | 16,3              | 13,8                    |
| 10                                                | 17,109                          | 954                       | 19,4              | 16,2                    |
| 15                                                | 17,125                          | 961                       | 19,2              | 16,9                    |
| 30                                                | 17,080                          | 954                       | 27,3              | 18,6                    |
| 45                                                | 17,069                          | 946                       | 26,4              | 25,2                    |
| 60                                                | 17,082                          | 933                       | 16,5              | 23,3                    |
| 90                                                | 17,0313                         | 769                       | 6,6               | 31,0                    |
| 120                                               | 17,039                          | 774                       | 5,9               | 35,0                    |



**Fig.39/40:** Mechanical properties of W heavy metals (90%W - 6,7%Ni - 3,3%Fe) as a function of the sintering time ( Sintering temp. 1475°C )

The elongation showed a behaviour similar to that of the tensile strength: the prerduced samples were extremely brittle with unmeasurable low elongation, but after only 1-2 min of liquid phase sintering the samples showed a measurable ductility. The elongation increases much slower with longer sintering times than the tensile strength does, the maximum values being attained at 30-45 min. The elongation also drops sharply after 60 min to a rather low level; apparently the pores formed at the time act as crack initiators and cause the material to fail even at very low degrees of deformation.

The scatter of the individual values of  $\sigma_B$  and  $\delta$  also indicates the quality of the heavy metals. With the tensile strength, an interesting trend was observed: the higher the value, the lower the absolute scatter. The absolute scatter of the elongation values, however, remains largely constant over the entire range of sintering time. Broad scatter of the tensile strength values would thus indicate some defect in the sintering process, as the tensile strength is not as sensitive to the external parameters as is the elongation.

SEM investigations of the fracture surface revealed a fundamental change both in structure of the heavy metal and in fracture behaviour: The samples which were merely pre-reduced or sintered for very short times (Fig. 41,42,43) exhibited angular W grains with entire surfaces formed by sintering necks or pore surfaces. The binder is concentrated in a few spots separated by large areas of pure W and numerous pores mostly at the junctions of several grains are visible. It is also evident, however, that even during prereluction rapid grain growth occurs: Comparing Fig.41 (usual prereluction) and Fig.42 (prereluction extended for 1 h), both the different grain sizes and grain shapes are evident. In Fig.41 the grains are still separated by many pores, and their shape is partially polyhedral, partially irregular; but after treatment at 1400°C, the grains have grown together and are almost entirely

polyhedral to fill up all possible pores (an observation which is also confirmed by the remarkable increase in density, see Tab.2). Apparently the tendency of the fine W grains to sinter together is very marked during solid state sintering also; a grain size similar to that in Fig.42 is obtained after only 5-10 minutes of liquid phase sintering. Maybe this pre-treatment could offer an advantage by removing the very fine W grains responsible for the extremely rapid grain growth in the first moments of sintering.

During the sintering process, the binder becomes more evenly distributed; after only 3 min. the binder concentrations have disappeared (Fig.44). Simultaneously, the W grains become more spherical in shape, and the percentage of the W surface covered by sintering necks decreases significantly. After 5-10 min., the typical microstructure of heavy metals has formed, and accordingly high elongations are obtained. Some transgranular fractures can be observed even after 3 min. sintering time, but this type of fractures becomes predominant. at 30 min. At shorter sintering times the fracture tends to run through the binder and across the sintering necks. The highly ductile samples (Fig.46, 47) exhibit the typical features of a satisfactory heavy metal: mainly transgranular fracture, considerable binder deformation and only rather few and small sintering necks in the fracture surface. At longer sintering times, pore formation begins to cause serious problems (Fig.48). Although the fracture surface apart from the pores appears to be sound (Fig.49) with numerous transgranular fractures, the larger pores formed at that stage sufficiently weaken the microstructure and cause it to fail prematurely.

Churn and Yoon (16) offer two explanations for this pore formation: either coalescence of small pores or generation of  $H_2O$  by reduction of small amounts of oxides. In our opinion the two processes work together and cannot be separated. It had been observed earlier that heavy metals with high oxygen contents

result in extremely porous samples when sintered without pre-reduction (3), apparently due to the generation of  $H_2O$  in the samples during liquid phase sintering. But even in carefully pre-reduced samples some oxygen remains, at least in oxides of Na, Li etc. (elements which incidentally, also lead to pore formation, see 1,3) as oxygen trapped in the W grains and set free during the solution/precipitation process. Due to its rather high solubility in the Ni-Fe binder, oxygen can be transported in the binder but inadvertently reacts with hydrogen, which is also dissolved in the binder to form  $H_2O$ . The  $H_2O$  is much less soluble and tends to form bubbles. At first these bubbles are small and most of them will disappear again. During the sintering process, however, Ostwald ripening of the pores occurs, and soon larger, stable pores are formed. Such pore growth processes are well known from annealing of Al in humid atmosphere, where hydrogen blisters grow in a quite similar manner (17, 18). As indicated by the dihedral angles between binder and W grains, the pores are further stabilized by deterioration of wetting, as, due to the oxygen equilibrium between pore atmosphere and W surface, small amounts of oxides are formed on the W grains and in turn inhibit wetting of the grains by the binder, thus causing the binder to retreat from this area. In Fig.48 the high dihedral angles are clearly visible, as are the sintering necks, which indicate that the pores are not completely empty but simply areas without binder and filled only with W grains. The spherical shape of the W grains indicates that there must have been binder in this area, as the usual grain growth processes have taken place and only afterwards has the binder been driven away. Fortunately such pore formation is characteristic of sintering times not recommendable for technical applications for other reasons, as well such as grain coarsening.

### 3.3 Metallographic investigations

To evaluate the microstructure of the samples, metallographic sections of the differently sintered samples were prepared and etched in  $\text{CuSO}_4/\text{NH}_3$  solutions. Photos taken from these sections are shown in Fig.50-55. As clearly visible, grain growth starts very rapidly at the beginning of liquid phase sintering; along with it the typical microstructure of heavy metals is formed. After 1 min. the W grains are still angular and are mostly sintered together, and the binder is concentrated in a few places, as already shown by the respective SEM photos. After 3 min., the grains have grown and rounded considerably; they are still sintered together in many places, but the binder is already more evenly distributed and begins to surround all W grains. After 10 min., further grain growth has occurred but the microstructure is still not homogeneous and numerous large sintering necks are present. These are probably responsible for the still unsatisfactory elongation because of the separation under stress and formation of microcracks. After 30 min. sintering time the microstructure is finally rather homogeneous; the sintering necks are generally small, and most W grains are almost completely surrounded by binder. At 60 min. considerable grain coarsening is evident; while at 30 min. many grains are  $<20\text{ }\mu\text{m}$  in diameter, here most grains are  $\sim 30\text{ }\mu\text{m}$ , although there are still some small ones. Even after 120 min. the small grains have not completely disappeared, but the grains  $>50\text{ }\mu\text{m}$  predominate, and there are very long, pronounced sintering necks because of the extreme grain shape accommodation.

The average grains sizes were determined by counting and measuring the individual grains on the photos. In Fig.56 the resulting apparent average grains size is given as a function of the sintering time. The rapid grain growth at the beginning of the liquid phase sintering process is clearly discernible,

but then the rate of growth follows an almost straight line. A comparison of this with observations in the literature (12) concerning the rate of grain growth and the final grain size

indicates that even a time of 120 min. is still rather short relative to the entire process. Earlier investigations (2) have shown that after 15 hrs. of sintering a grain size of  $>100\text{ }\mu\text{m}$  is attained. Since the relative differences between real (3-dimensional) and apparent (2-dimensional) grain size should always be the same, the real diagram would be quite similar, with only slightly increased absolute values.

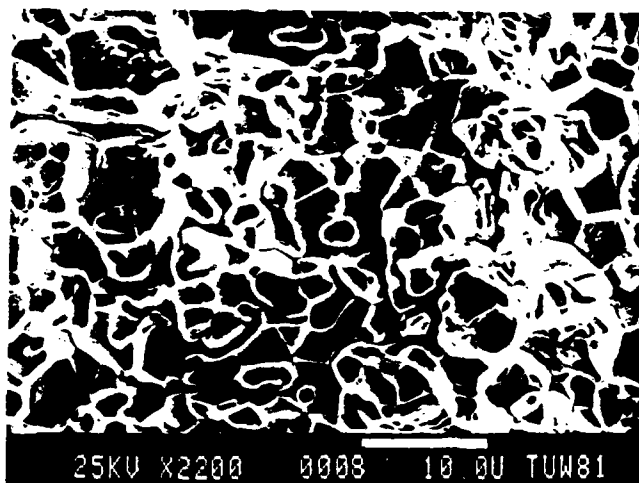


Fig.41  
Fracture surface of  
pre-reduced heavy metal  
(90%W; pre-reduction  
a) in Fig.38)

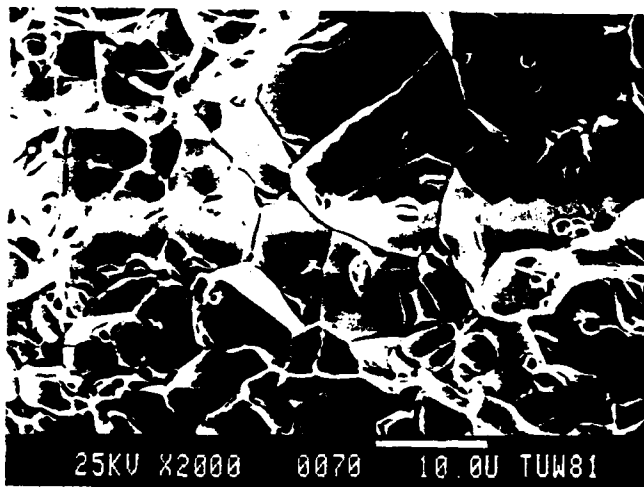


Fig.42  
Pre-reduction extended  
for 1 hr at 1400°C  
(Pre-red. b) in Fig.38)

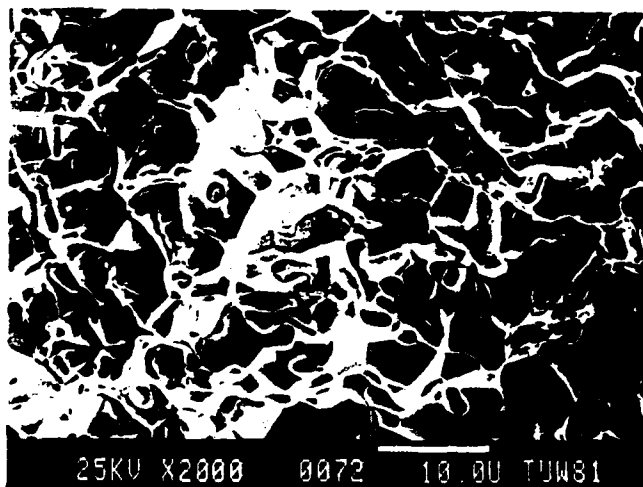


Fig.43  
Heavy metal liquid-  
phase sintered 1 min  
at 1475°C

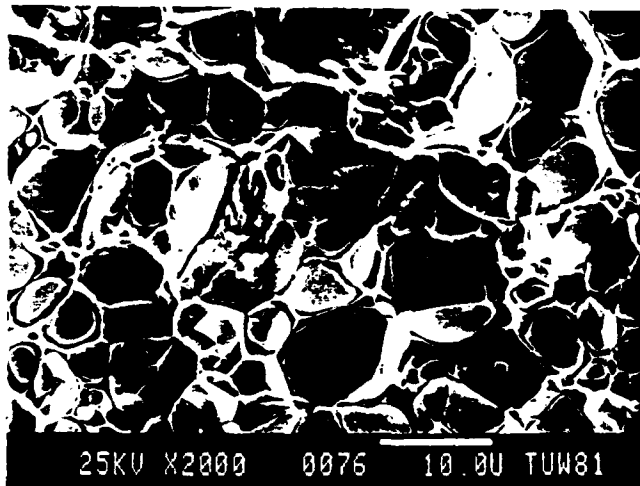


Fig.44

W heavy metal (90%W)  
liquid phase sintered  
3 min at 1475°C.  
Marked rounding of the  
W grains

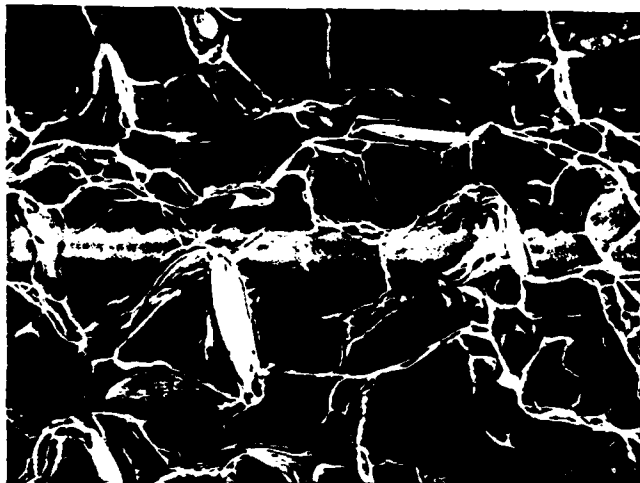


Fig.45

Sintered 5 min at  
1475°C. 2000x

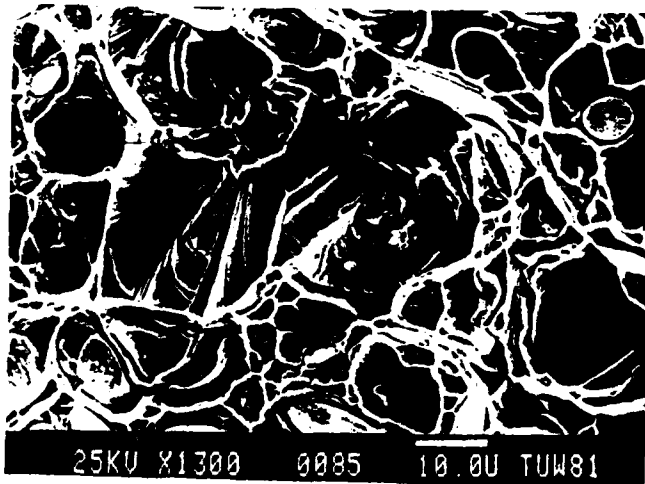


Fig.46

Sintered 30 min at  
1475°C.

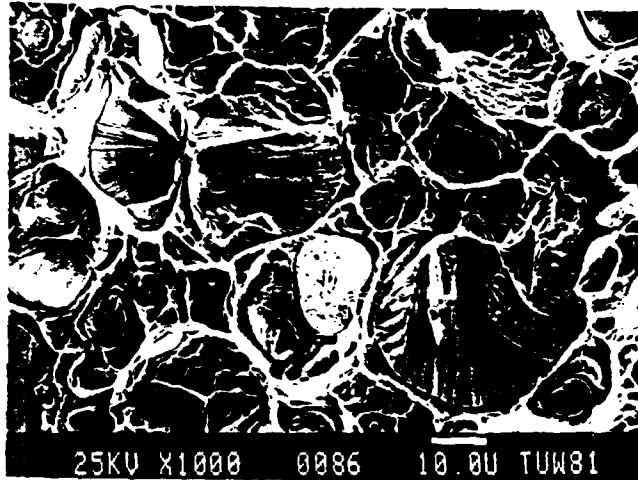


Fig.47

W heavy metal (90%W)  
liquid phase sintered  
45 min at 1475°C

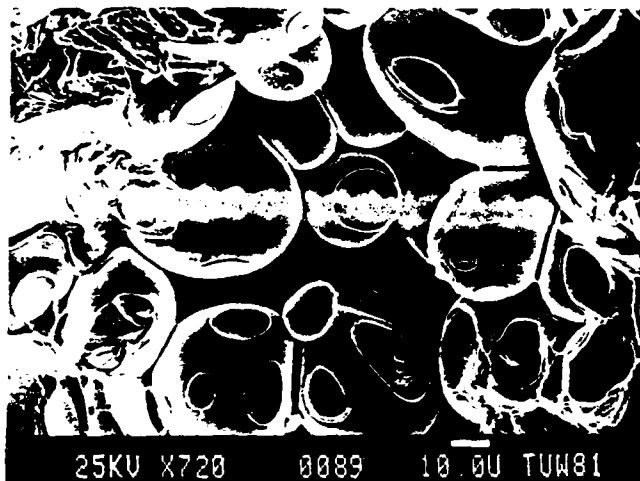


Fig.48

Sintered 90 min at  
1475°C. Pore

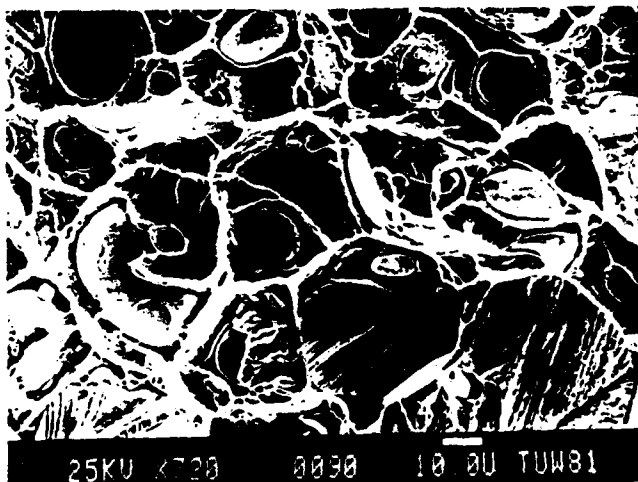


Fig.49

Same sample as on  
Fig.48; apparently  
sound structure  
except of the pores

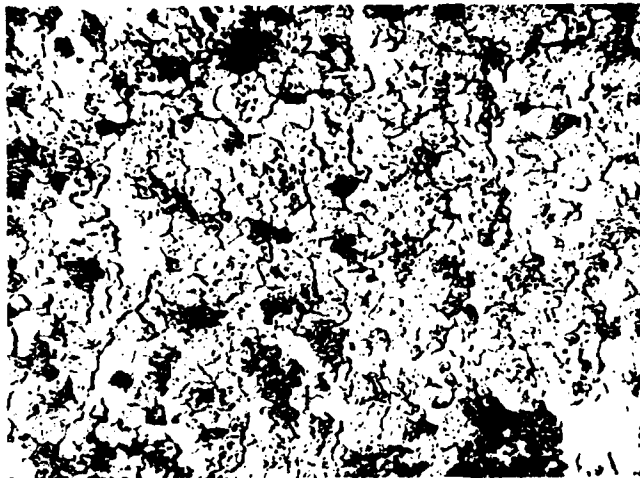


Fig.50  
W heavy metal (90%W)  
sintered 1 min at  
1475°C. Etched 2 min  
in  $\text{CuSO}_4/\text{NH}_3$ .  
500x

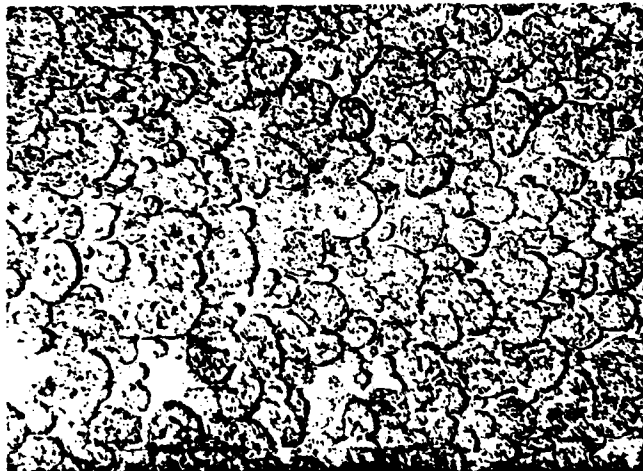


Fig.51  
Sintered 3 min at  
1475°C.  
500x

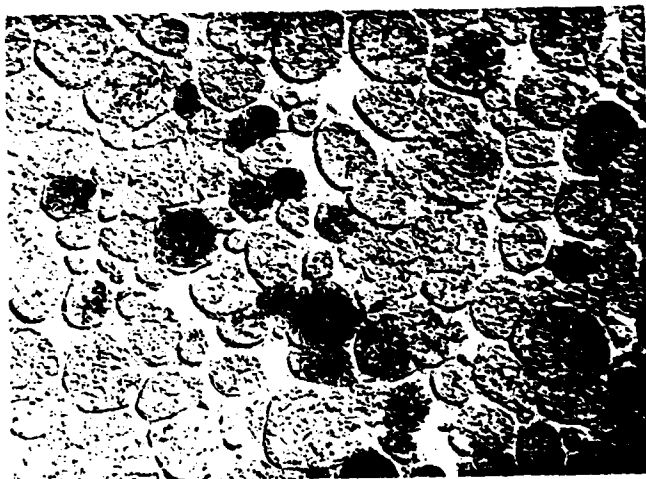


Fig.52  
Sintered 10 min at  
1475°C.  
500x

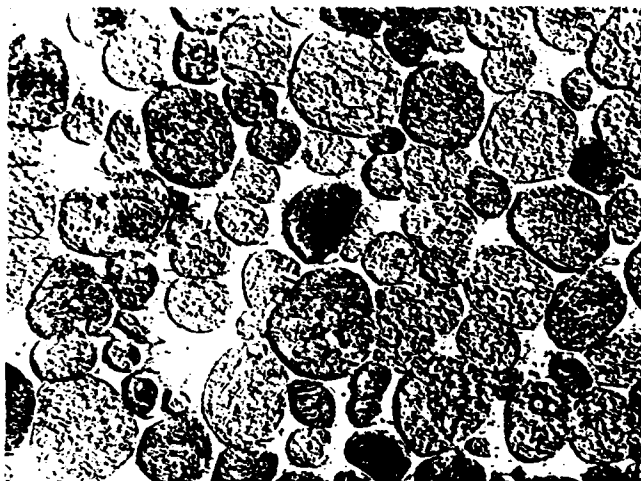


Fig.53  
W heavy metal (90%W)  
sintered 30 min at  
1475°C.  
500x

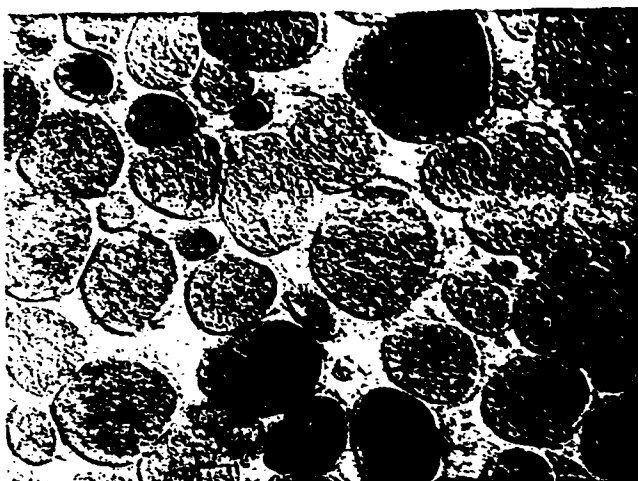


Fig.54  
Sintered 60 min at  
1475°C.  
500x

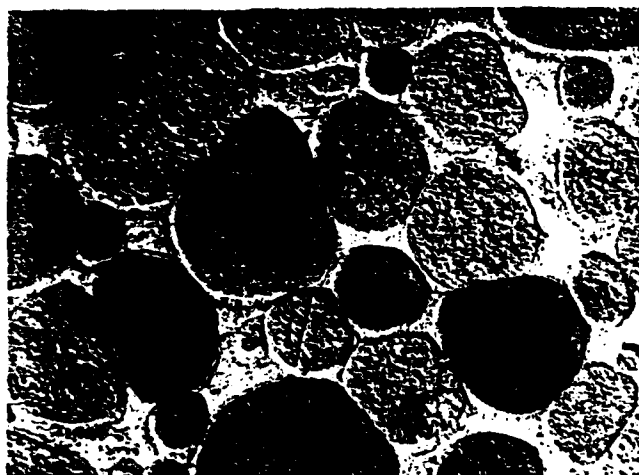
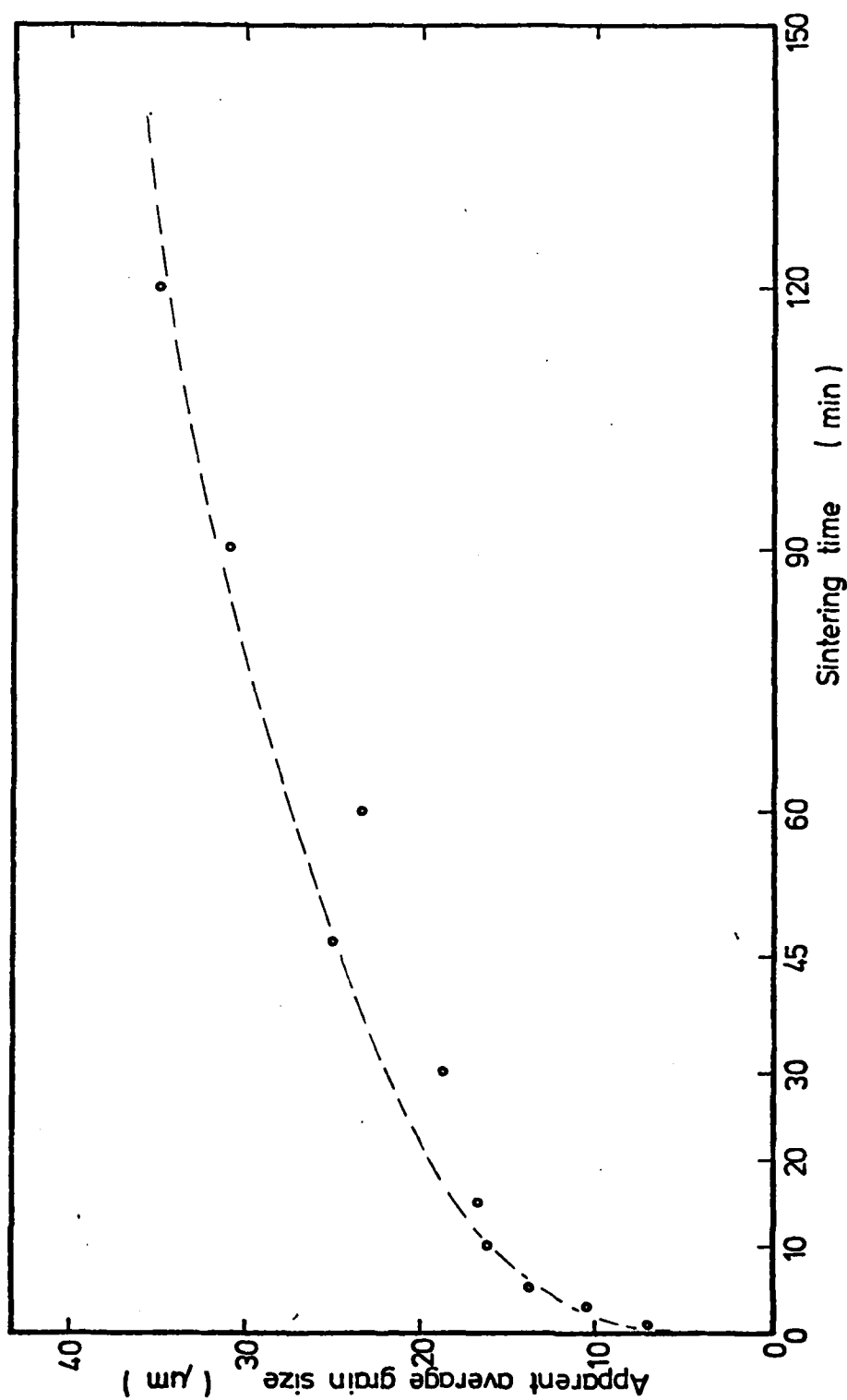


Fig.55  
Sintered 120 min  
at 1475°C.  
500x



**Fig.56:** Grain growth of heavy metals (90%W - 6,7%Ni - 3,3%Fe) during liquid phase sintering ( 2-dimensional grain size measured on metallographic sections )

#### 4. Heavy metals prepared from doped W powders

Heavy metals containing 90 and 96% W were prepared from the doped W powders described in Chapter 2. As had been shown by earlier experiments (1,3) due to the higher W content, the effect of the doping elements could be expected to be more pronounced in the samples containing 96% W. As stated above, the elements selected for doping were those most probable to be encountered in commercial W powders, and thus most probable to cause difficulties when shifting from one W powder to another. The final goal was, of course, to identify those elements whose presence must be investigated and analyzed before a powder is to be used for heavy metal sintering.

##### 4.1 90% W content

The samples containing 90% W were prepared as described in chapter 3; the standard composition of 90% W - 6,7% Ni - 3,3% Fe was maintained, and after addition of 1% camphor as pressing lubricant the powders were wet mixed, granulated and compacted; the green compacts were sintered following the cycle shown in Fig.38, the sintering being performed uniformly at  $1475 \pm 5^{\circ}\text{C}$  for 30 min. As described also in earlier reports (1,3) together with each batch of 4-5 doped samples an equal number of bars prepared from the standard powder W 640/81 was sintered for comparison purposes to indicate any effects of small changes in the sintering parameters. They were arranged in the sintering boat following the pattern shown in Fig.57

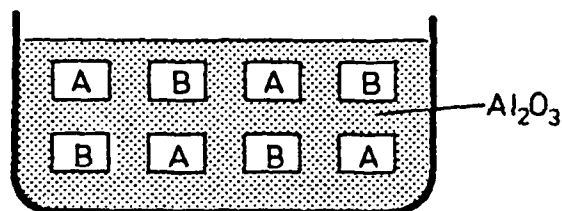


Fig.57: Arrangement of doped and undoped test bars in the sintering boat

The large number of parallel samples of each powder - at least 10 - enabled statistical evaluation of the results using the Weibull statistics (19,20) which allows calculation of the probability of fracture at a given stress.

The theoretical background, as also described in (1) is the following:

The probability of fracture (P) is influenced by the sample volume (V), tensile strength ( $\sigma$ ) and a parameter indicating the homogeneity of the material (m), according to the equation

$$P = 1 - 1/\exp. \frac{V}{V_0} \cdot \left(\frac{\sigma}{\sigma_0}\right)^m \quad (V_0, \sigma_0 \text{ refer to standard sample})$$

The equation is then transformed and  $\sigma_{50}$  inserted

$$\lg \lg \frac{1}{1-P} - \lg \lg 2 = m \cdot (\lg \sigma - \lg \sigma_{50})$$

For a given number N of samples, the P values depend only on the sample number n (from 1 to N). The graphic evaluation is carried out by taking the left side of the equation for the x-values and the right for y-values.

$$x = \lg \lg \frac{1}{1-P} \quad \text{with} \quad P_n = \frac{n}{N+1}$$

$$x = \lg \lg \frac{N+1}{N+1-n}$$

$$y = \lg \sigma$$

$$s_w = 1/m$$

This is the equation of a straight line

$$y - y_{50} = s_w \cdot (x - x_{50})$$

The slope of this straight line indicates the scatter of the individual values; the broader the scatter, the more pronounced the slope and the greater the probability of fracture at stresses considerably below the average tensile strength.

The mechanical properties of heavy metals prepared from those doped W powders not covered by (3), i.e. the powders E48 - E115 are listed in the following tables and diagrams.

Powder E 48 (200 ppm Na)

Table 3: Mechanical properties of the samples prepared from E 48 and of the reference sample from W 640/81

| E 48                        |                  |              | W 640                       |                  |              |
|-----------------------------|------------------|--------------|-----------------------------|------------------|--------------|
| $\rho$ (g/cm <sup>3</sup> ) | $\sigma_b$ (MPa) | $\delta$ (%) | $\rho$ (g/cm <sup>3</sup> ) | $\sigma_b$ (MPa) | $\delta$ (%) |
| 16,8635                     | 894              | 6,0          | 17,0933                     | 946              | 25,0         |
| 16,9559                     | 796              | 10,0         | 17,0850                     | 956              | 20,4         |
| 16,6594                     | 755              | 8,8          | 17,0779                     | 946              | 21,6         |
| 16,5630                     | 772              | 12,0         | 17,0320                     | 964              | 24,0         |
| 16,7392                     | 778              | 6,0          |                             |                  |              |
| 17,0900                     | 853              | 10,4 x)      | 17,0660                     | 956              | 22,4 x)      |
| 17,0757                     | 709              | 8,0 x)       | 17,0283                     | 911              | 20,0 x)      |
| 17,1235                     | 738              | 5,2 x)       | 17,0480                     | 928              | 25,6 x)      |
| 17,1128                     | 764              | 5,2 x)       | 17,0375                     | 918              | 16,0 x)      |
| 17,1118                     | 787              | 6,0 x)       |                             |                  |              |
| 17,1390                     | 726              | 4,8 x)       |                             |                  |              |

x) sintered at 1510°C

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 48  | 16,948 $\pm$ 0,210 | 775 $\pm$ 46 | 7,5 $\pm$ 2,5  |
| W 640 | 17,058 $\pm$ 0,025 | 939 $\pm$ 18 | 21,9 $\pm$ 3,1 |

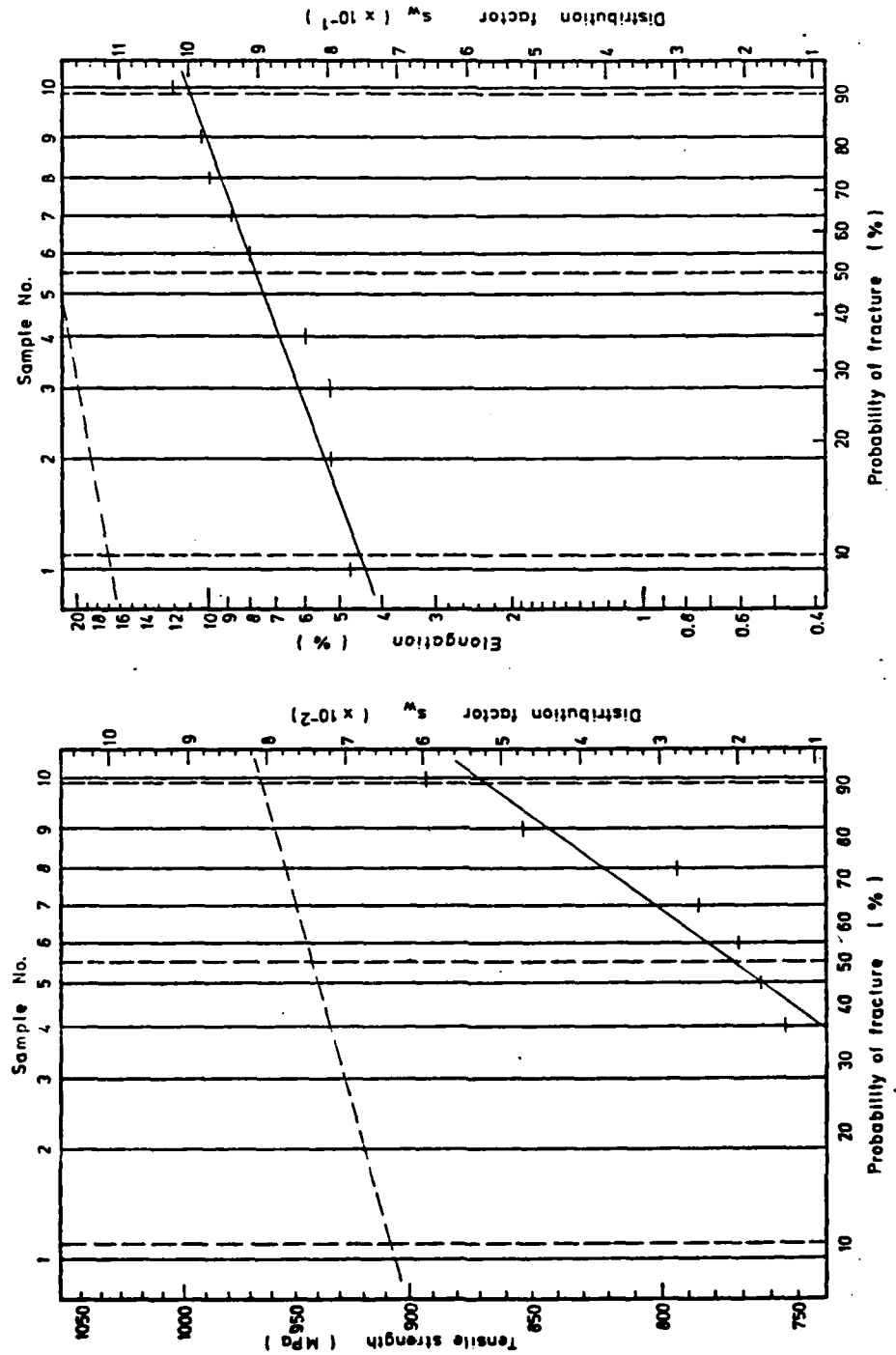


Fig.58: Weibull-diagrams for E48W (—) and W640/81 (---)

Powder E 51

Table 4: Mechanical properties of the samples prepared from E 51 and of the references sample from W 640/81

| E 51    |          |          | W 640   |          |          |
|---------|----------|----------|---------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$  | $\sigma$ | $\delta$ |
| 15,3712 | 602      | 3,0      | 17,0864 | 960      | 20,0     |
| 15,4735 | 559      | 3,2      | 17,0514 | 945      | 18,4     |
| 15,7986 | 612      | 4,0      | 17,0494 | 953      | 27,4     |
| 15,7558 | 663      | 4,4      | 17,1148 | 941      | 22,8     |
| 15,7474 | 564      | 2,8      |         |          |          |
| 15,6246 | 615      | 4,0      | 17,0510 | 955      | 23,6     |
| 15,9797 | 599      | 3,2      | 17,0532 | 960      | 24,0     |
| 15,8924 | 596      | 4,0      | 17,0621 | 946      | 22,6     |
| 15,9900 | 555      | 2,4      | 17,0739 | 979      | 24,0     |
| 15,4951 | 547      | 3,0      |         |          |          |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 51  | 15,713 $\pm$ 0,215 | 591 $\pm$ 36 | 3,4 $\pm$ 0,7  |
| W 640 | 17,068 $\pm$ 0,023 | 954 $\pm$ 12 | 22,8 $\pm$ 2,7 |

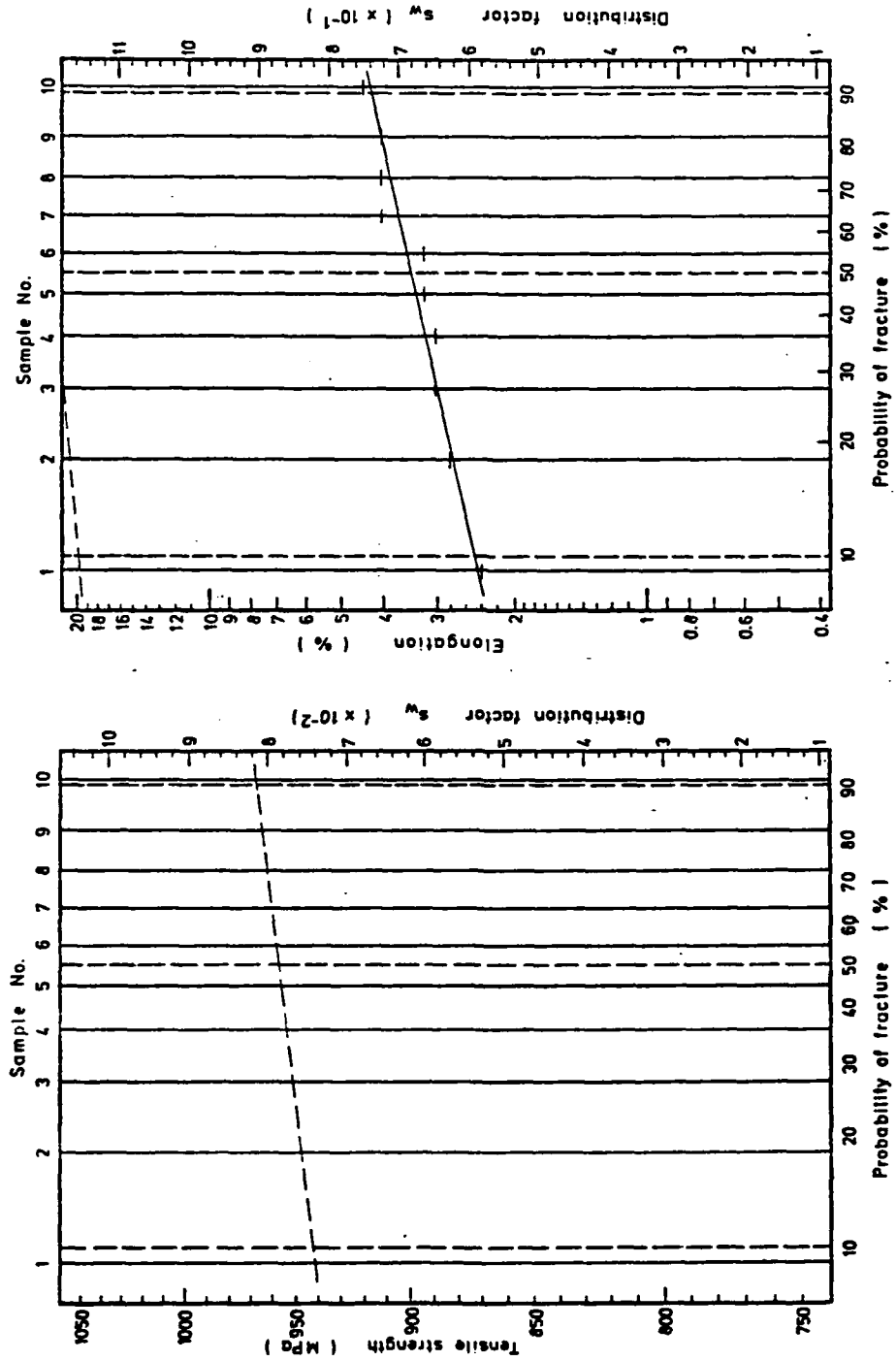


Fig.59: Weibull-diagrams for E51W (—) and W640/81 (---)

Powder E 56

Table 5: Mechanical properties of the samples prepared from  
E 56 and of the reference sample from W 640/81

| E 56                        |                  |              | W 640/81                    |                  |              |
|-----------------------------|------------------|--------------|-----------------------------|------------------|--------------|
| $\rho$ (g/cm <sup>3</sup> ) | $\sigma_b$ (MPa) | $\delta$ (%) | $\rho$ (g/cm <sup>3</sup> ) | $\sigma_b$ (MPa) | $\delta$ (%) |
| 16,9905                     | 933              | 16,4         | 17,0758                     | 941              | 24,0         |
| 16,9906                     | 907              | 14,8         | 17,0753                     | 963              | 22,8         |
| 17,0012                     | 947              | 22,8         | 17,0319                     | 975              | 25,0         |
| 16,9756                     | 902              | 10,8         | 17,0340                     | 987              | 22,6         |
| 17,0241                     | 923              | 17,2         | 17,0428                     | 966              | 28,0         |
| 17,0201                     | 936              | 22,4         | 17,0506                     | 959              | 25,0         |
| 17,0077                     | 950              | 20,3         | 17,0749                     | 960              | 20,4         |
| 17,0004                     | 864              | 18,4         | 17,0859                     | 965              | 26,0         |
| 17,0083                     | 909              | 18,0         | 17,0942                     | 946              | 23,2         |
| 17,0044                     | 944              | 20,8         |                             |                  |              |
| 17,0358                     | 908              | 21,0         |                             |                  |              |

Mean values  $\pm$  standard deviations

|       |                     |              |                |
|-------|---------------------|--------------|----------------|
| E 56  | 17,0053 $\pm$ 0,017 | 920 $\pm$ 25 | 18,4 $\pm$ 3,6 |
| E 640 | 17,0628 $\pm$ 0,023 | 962 $\pm$ 14 | 24,1 $\pm$ 2,2 |

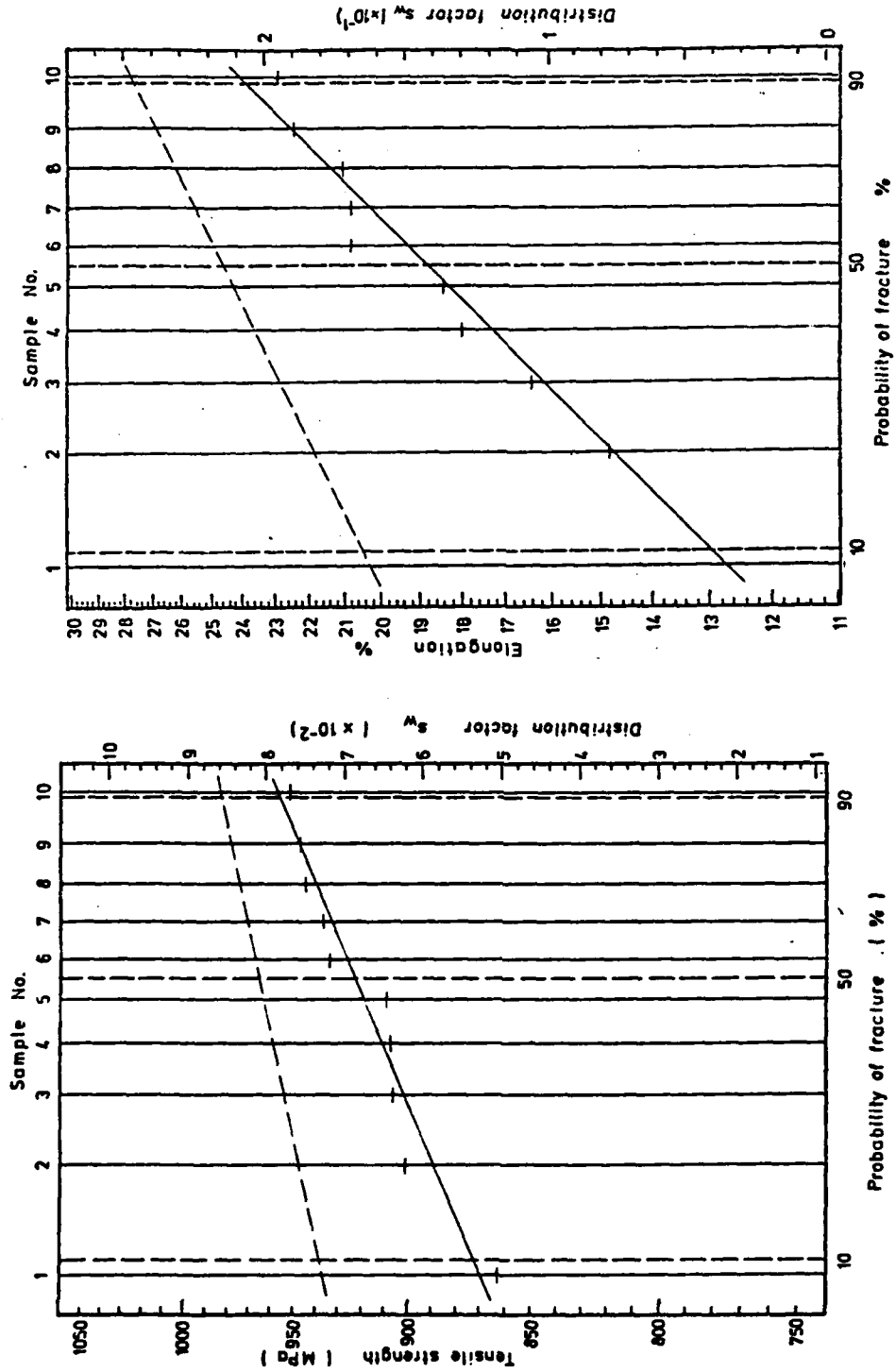


Fig. 60: Weibull-diagrams for E56W (—) and W640/81 (---)

Powder E 61

Table 6: Mechanical properties of the samples prepared from  
E 61 and of the reference sample from W 640/81

| E 61    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 16,9651 | 947      | 16,8     | 17,0749  | 960      | 20,4     |
| 16,9846 | 845      | 8,4      | 17,0859  | 956      | 26,0     |
| 16,9971 | 931      | 14,4     | 17,0942  | 946      | 23,2     |
| 17,0088 | 898      | 10,6     | 17,0319  | 975      | 25,0     |
| 17,0067 | 805      | 5,2      | 17,0340  | 987      | 22,6     |
| 17,0157 | 936      | 18,0     | 17,0428  | 966      | 28,0     |
| 17,0204 | 930      | 14,8     | 17,0506  | 959      | 25,0     |
| 16,4855 | 911      | 12,0     | 17,0131  | 957      | 20,8     |
| 16,4651 | 854      | 8,8      | 17,0728  | 953      | 23,0     |
| 16,7564 | 905      | 12,0     | 17,0486  | 963      | 22,8     |

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 61  | 16,870 $\pm$ 0,222 | 896 $\pm$ 47 | 12,1 $\pm$ 4,0 |
| W 640 | 17,055 $\pm$ 0,026 | 963 $\pm$ 11 | 23,7 $\pm$ 2,3 |

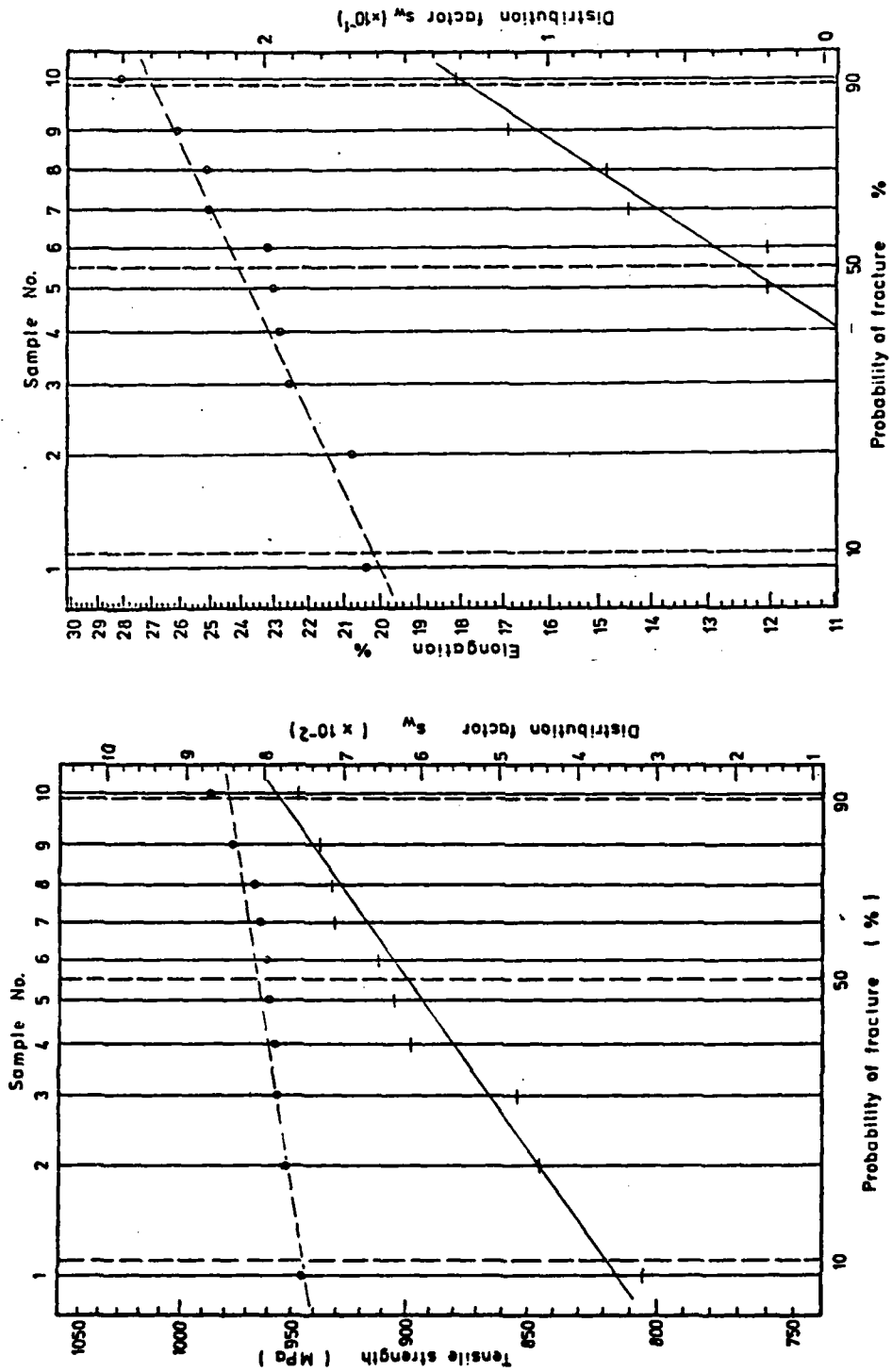


Fig. 61: Weibull-diagrams for E61W (—) and W64O/81 (---)

Powder E 63

Table 7: Mechanical properties of the samples prepared from E 63 and of the reference sample from W 640/81

| E 63    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,1004 | 969      | 19,2     | 17,0410  | 949      | 18,8     |
| 17,0986 | 925      | 15,2     | 17,0324  | 939      | 25,4     |
| 17,1029 | 900      | 11,8     | 17,0515  | 907      | 16,6     |
| 17,0476 | 925      | 13,4     | 17,0795  | 919      | 19,2     |
| 17,0245 | 919      | 15,4     | 17,0270  | 939      | 21,4     |
| 17,0310 | 928      | 13,4     | 17,0125  | 949      | 19,6     |
| 17,0194 | 929      | 15,6     | 17,0229  | 930      | 22,0     |
| 17,0005 | 924      | 16,0     | 17,0314  | 918      | 20,4     |
| 17,0172 | 926      | 18,0     | 17,0231  | 923      | 19,0     |
| 17,1025 | 952      | 16,0     | 17,0602  | 950      | 20,8     |
| 17,0929 | 963      | 16,8     | 17,0553  | 963      | 23,2     |
| 17,0936 | 927      | 12,8     | 17,0444  | 942      | 19,8     |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 63  | 17,061 $\pm$ 0,041 | 932 $\pm$ 19 | 15,3 $\pm$ 2,2 |
| W 640 | 17,040 $\pm$ 0,019 | 935 $\pm$ 16 | 20,5 $\pm$ 2,3 |

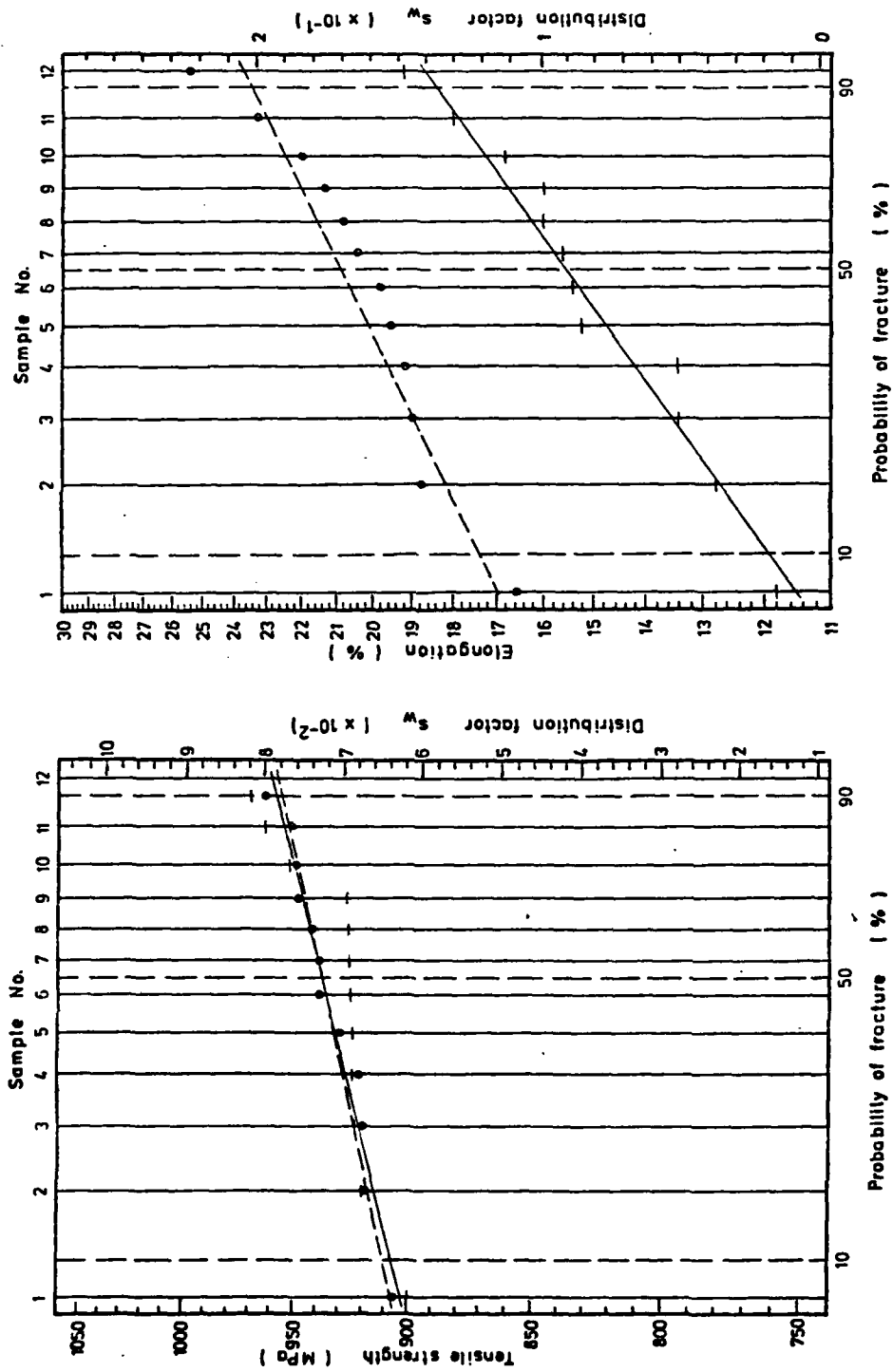


Fig. 62: Weibull-diagrams for E63W (—) and W640/81 (---)

Powder E 67

Table 8: Mechanical properties of the samples prepared from E 67 and of the reference sample from W 640/81

| E 67    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,0243 | 951      | 14,4     | 17,0131  | 957      | 20,8     |
| 17,0679 | 920      | 19,2     | 17,0118  | 917      | 20,8     |
| 17,0610 | 961      | 23,2     | 17,0131  | 938      | 24,0     |
| 17,0618 | 975      | 18,0     | 17,0905  | 939      | 24,6     |
| 17,1072 | 958      | 20,0     | 17,0903  | 947      | 24,6     |
| 17,0634 | 901      | 12,8     | 17,0986  | 952      | 25,2     |
| 17,0244 | 932      | 19,4     | 17,0765  | 962      | 23,6     |
| 17,0646 | 969      | 23,2     | 17,0357  | 947      | 21,0     |
| 16,9990 | 905      | 18,4     | 17,0614  | 945      | 20,0     |
| 17,0966 | 914      | 10,8     | 17,0384  | 955      | 20,6     |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 71  | 17,057 $\pm$ 0,033 | 938 $\pm$ 27 | 17,9 $\pm$ 4,1 |
| W 640 | 17,053 $\pm$ 0,035 | 946 $\pm$ 13 | 22,1 $\pm$ 2,0 |

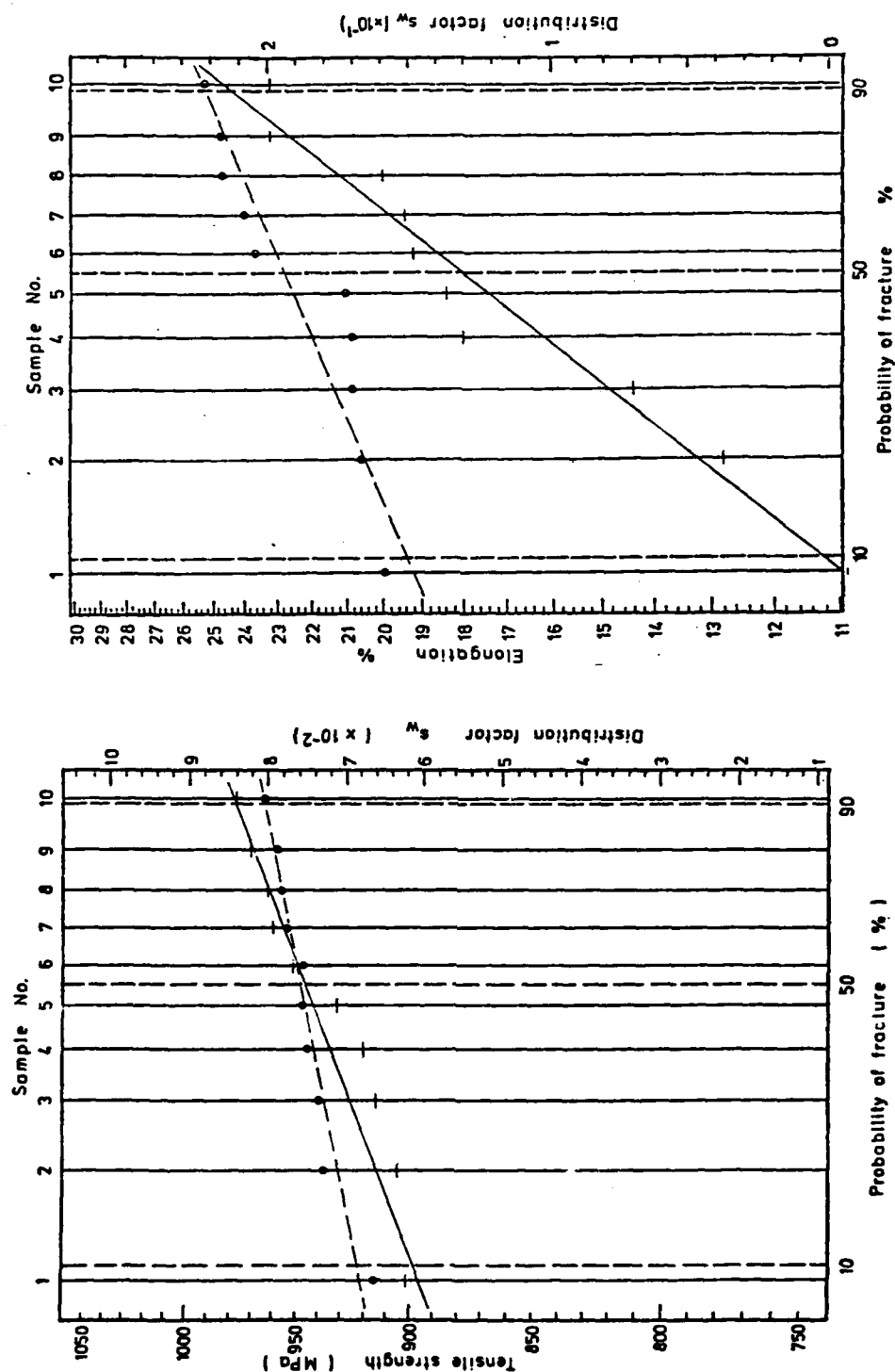


Fig. 63: Weibull-diagrams for E67W (—) and W640/81 (---)

Powder E 71

Table 9: Mechanical properties of the samples prepared from E 71 and of the reference sample from W 640/81

| E 71                  |                        |              | W 640/81              |                        |              |
|-----------------------|------------------------|--------------|-----------------------|------------------------|--------------|
| $\rho(\text{g/cm}^3)$ | $\sigma_p(\text{MPa})$ | $\delta(\%)$ | $\rho(\text{g/cm}^3)$ | $\sigma_p(\text{MPa})$ | $\delta(\%)$ |
| 17,0741               | 964                    | 23,2         | 17,0765               | 962                    | 23,6         |
| 17,0408               | 932                    | 19,2         | 17,0440               | 945                    | 21,0         |
| 17,0179               | 949                    | 23,2         | 17,0250               | 953                    | 26,8         |
| 17,0323               | 971                    | 27,6         | 17,0400               | 928                    | (16,8)       |
| 17,0302               | 954                    | 27,6         | 17,0212               | 951                    | 23,6         |

One sintering batch omitted because of faulty temperature control

|         |     |      |         |     |      |
|---------|-----|------|---------|-----|------|
| 17,0391 | 954 | 24,2 | 17,0413 | 949 | 23,8 |
|---------|-----|------|---------|-----|------|

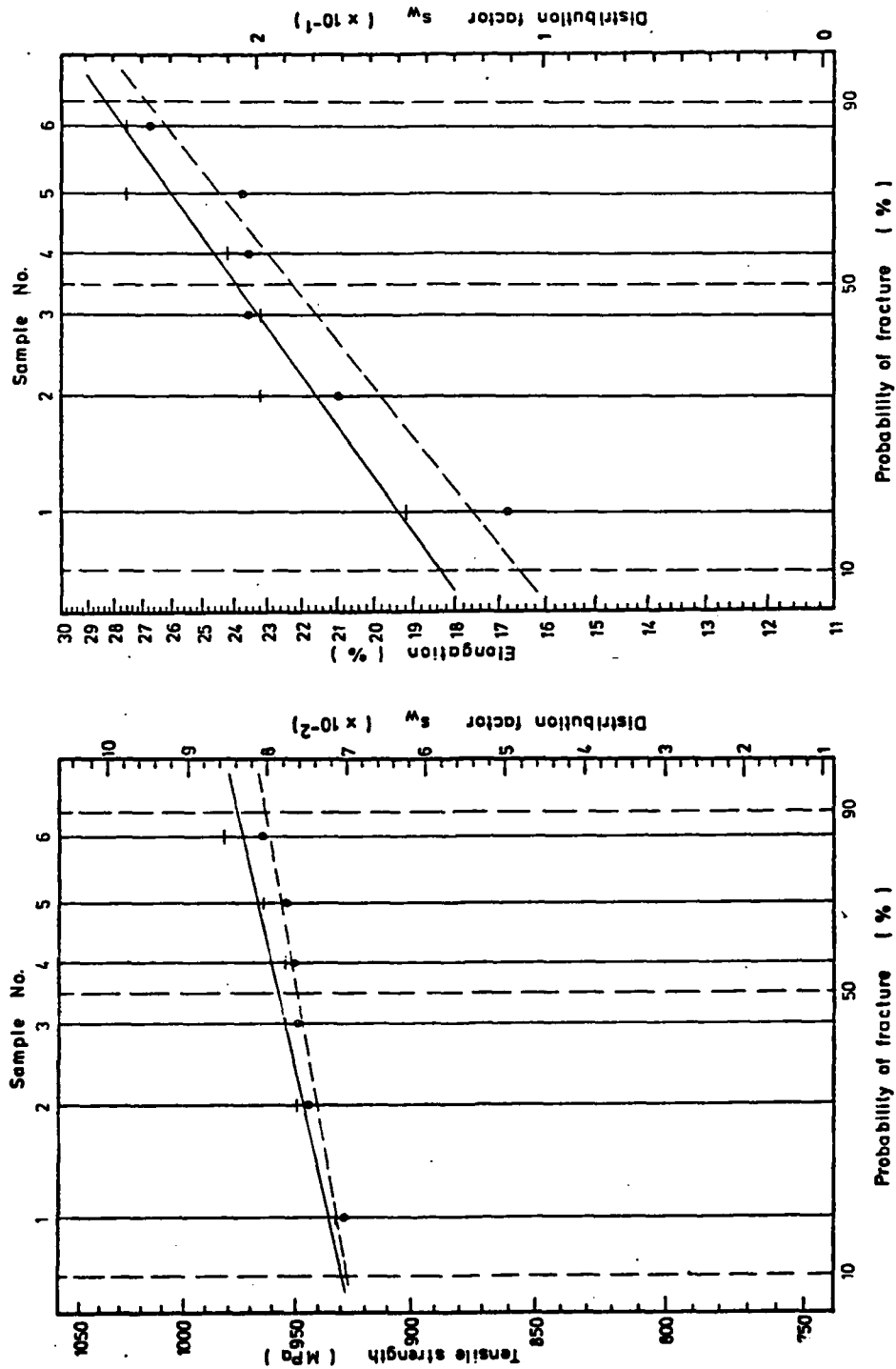


Fig.64: Weibull-diagrams for E71W (—) and W640/81 (---)

Powder E 79

Table 10: Mechanical properties of the samples prepared from  
E 79 and of the reference sample from W 640/81

| E 79    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,0915 | 814      | 5,4      | 17,044   | 961      | 22,0     |
| 17,0884 | 860      | 8,8      | 17,0615  | 924      | 20,0     |
| 17,1125 | 964      | 17,8     | 17,0467  | 926      | 16,6     |
| 17,1129 | 914      | 12,0     | 17,0771  | 944      | 20,8     |
| 17,090  | 846      | 7,6      | 17,0827  | 956      | 22,0     |
| 17,083  | 872      | 8,4      | 17,040   | 947      | 22,6     |
| 17,097  | 944      | 12,4     | 17,067   | 939      | 19,2     |
| 17,099  | 829      | 6,4      | 17,024   | 942      | 16,8     |
| 17,099  | 894      | 13,6     | 17,049   | 960      | 22,8     |
| 17,081  | 965      | 22,0     | 17,044   | 947      | 21,6     |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 79  | 17,095 $\pm$ 0,011 | 890 $\pm$ 55 | 11,4 $\pm$ 5,3 |
| W 640 | 17,053 $\pm$ 0,018 | 945 $\pm$ 13 | 20,4 $\pm$ 2,3 |

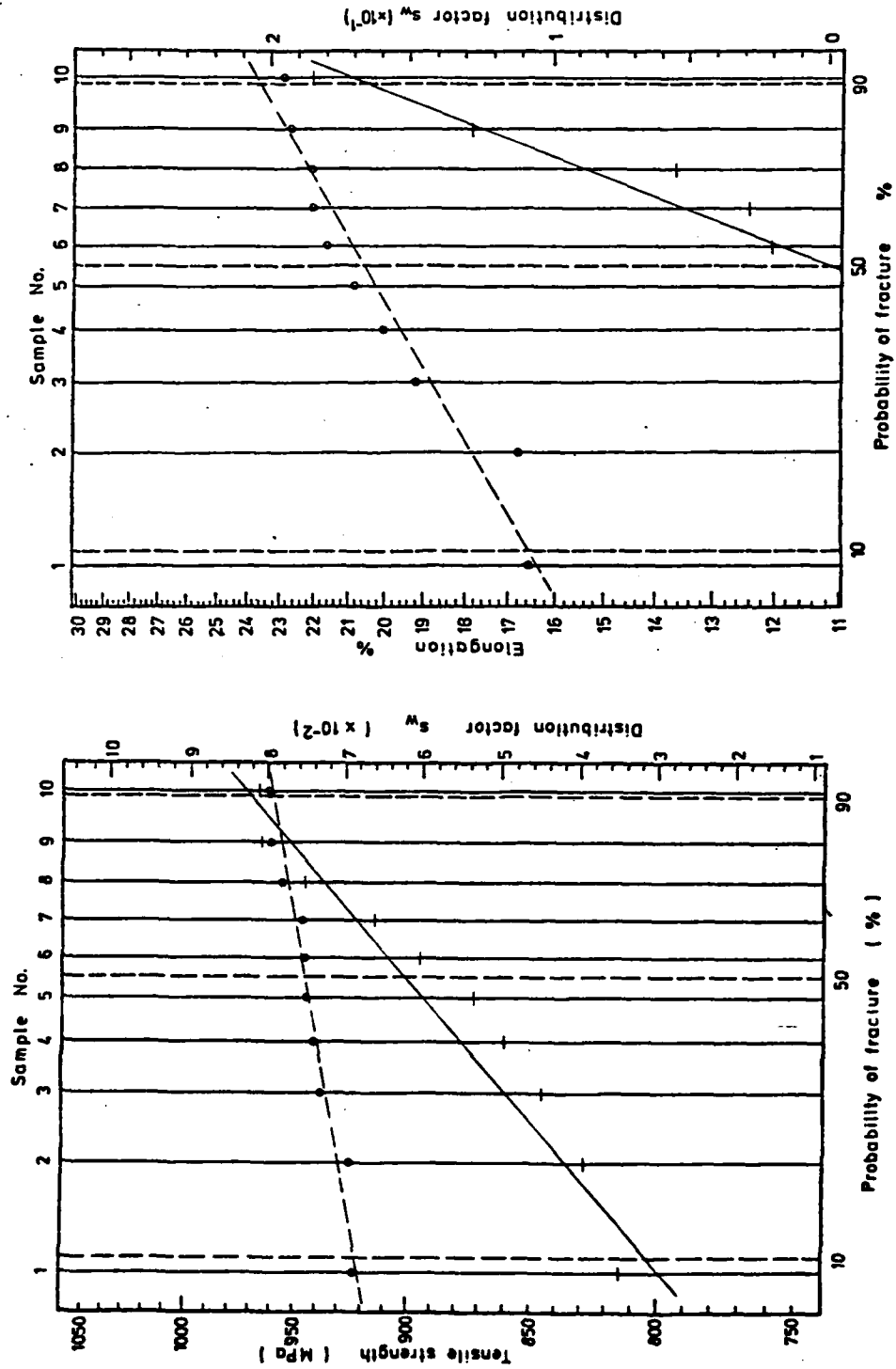


Fig.65: Weibull-diagrams for E79W (—) and W640/81 (---)

Powder E 83

Table 11: Mechanical properties of the samples prepared from  
E 83 and of the reference sample from W 640/81

| E 83   |          |          | W 640/81 |          |          |
|--------|----------|----------|----------|----------|----------|
| $\rho$ | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,037 | 1024     | 22,6     | 17,062   | 998      | 27,4     |
| 17,088 | 995      | 13,6     | 17,086   | 1000     | 28,2     |
| 17,095 | 997      | 22,8     | 17,088   | 976      | 25,6     |
| 17,080 | 999      | 26,2     | 17,046   | 976      | 24,0     |
| 17,088 | 984      | 30,0     | 17,075   | 975      | 27,2     |
| 17,067 | 961      | 18,4     | 17,080   | 994      | 28,8     |
| 17,067 | 952      | 22,4     | 17,080   | 964      | 29,2     |
|        |          |          | 17,088   | 957      | 32,2     |
| 17,049 | 956      | 23,4     | 17,081   | 959      | 24,0     |
| 17,038 | 940      | 25,6     | 17,074   | 979      | 24,0     |
| 17,078 | 987      | 28,0     | 17,100   | 977      | 26,4     |
|        |          |          | 17,091   | 997      | 28,0     |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 83  | 17,067 $\pm$ 0,020 | 974 $\pm$ 29 | 23,3 $\pm$ 4,7 |
| W 640 | 17,079 $\pm$ 0,014 | 979 $\pm$ 15 | 27,1 $\pm$ 2,5 |

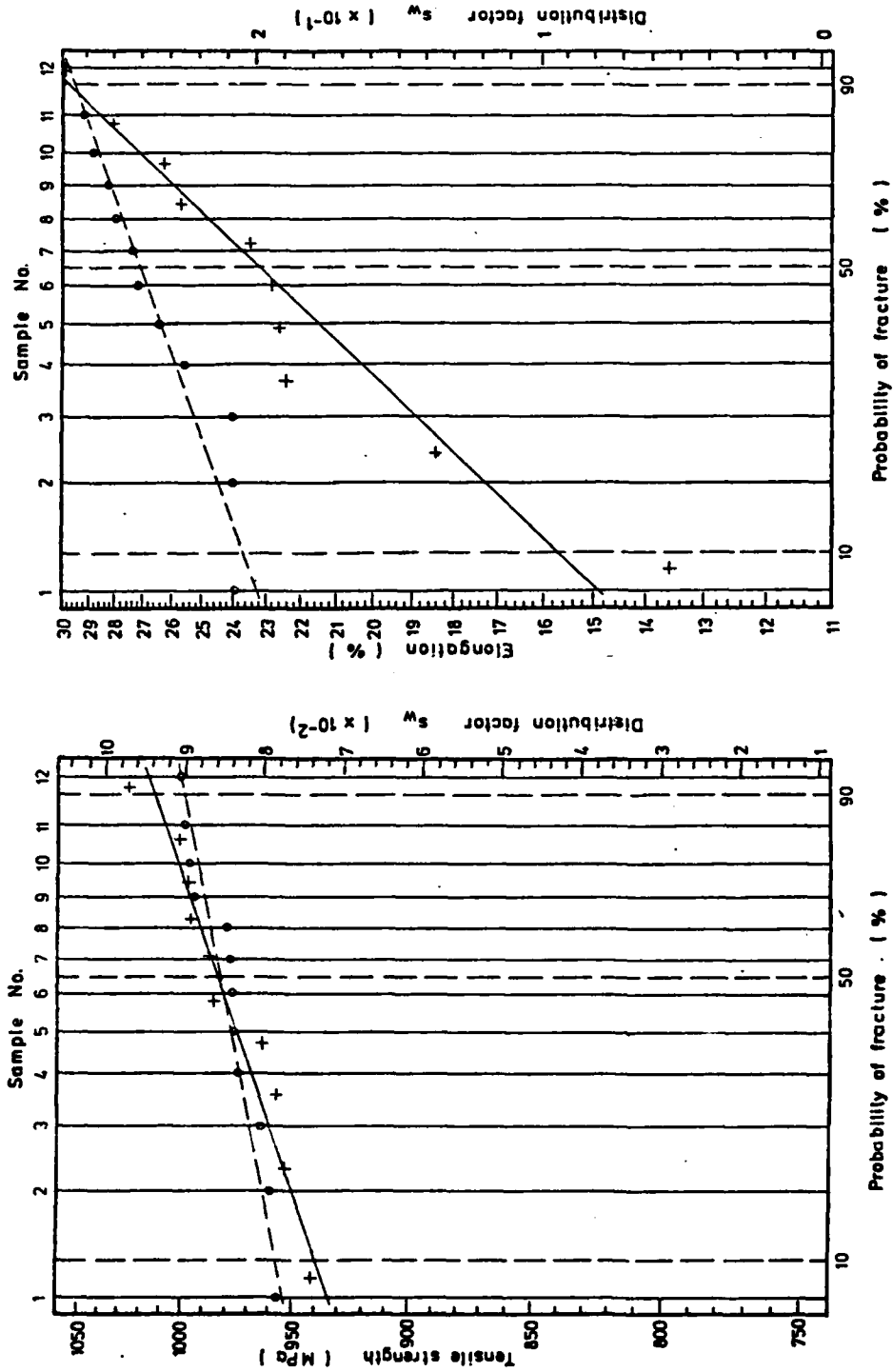


Fig.66: Weibull-diagrams for E83W (—) and W640/81 (---)

Powder E 87

Table 12: Mechanical properties of the samples prepared from  
E 87 and of the reference sample from W 640/81

| E 87    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,001  | 957      | 20,8     | 17,020   | 959      | 27,6     |
| 16,994  | 968      | 26,5     | 17,026   | 969      | 28,0     |
| 17,043  | 963      | 24,0     | 17,030   | 973      | 23,6     |
| 17,024  | 953      | 24,0     | 17,042   | 971      | 29,6     |
| 17,050  | 923      | 18,8     | 17,044   | 961      | 22,0     |
| 17,043  | 933      | 23,2     | 17,051   | 955      | 23,6     |
|         |          |          | 17,072   | 971      | 22,8     |
|         |          |          | 17,060   | 937      | 19,6     |
| 17,048  | 933      | 8,0      | 17,039   | 930      | 16,0     |
| 17,039  | 930      | 16,0     | 17,080   | 928      | 14,8     |
| 17,072  | 938      | 18,8     |          |          |          |
| 17,063  | 935      | 24,0     |          |          |          |
|         |          |          |          |          |          |
| 17,0377 | 943      | 20,4     | 17,0467  | 955      | 22,8     |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 87  | 17,037 $\pm$ 0,025 | 943 $\pm$ 16 | 20,4 $\pm$ 5,4 |
| W 640 | 17,046 $\pm$ 0,019 | 955 $\pm$ 18 | 22,8 $\pm$ 4,9 |

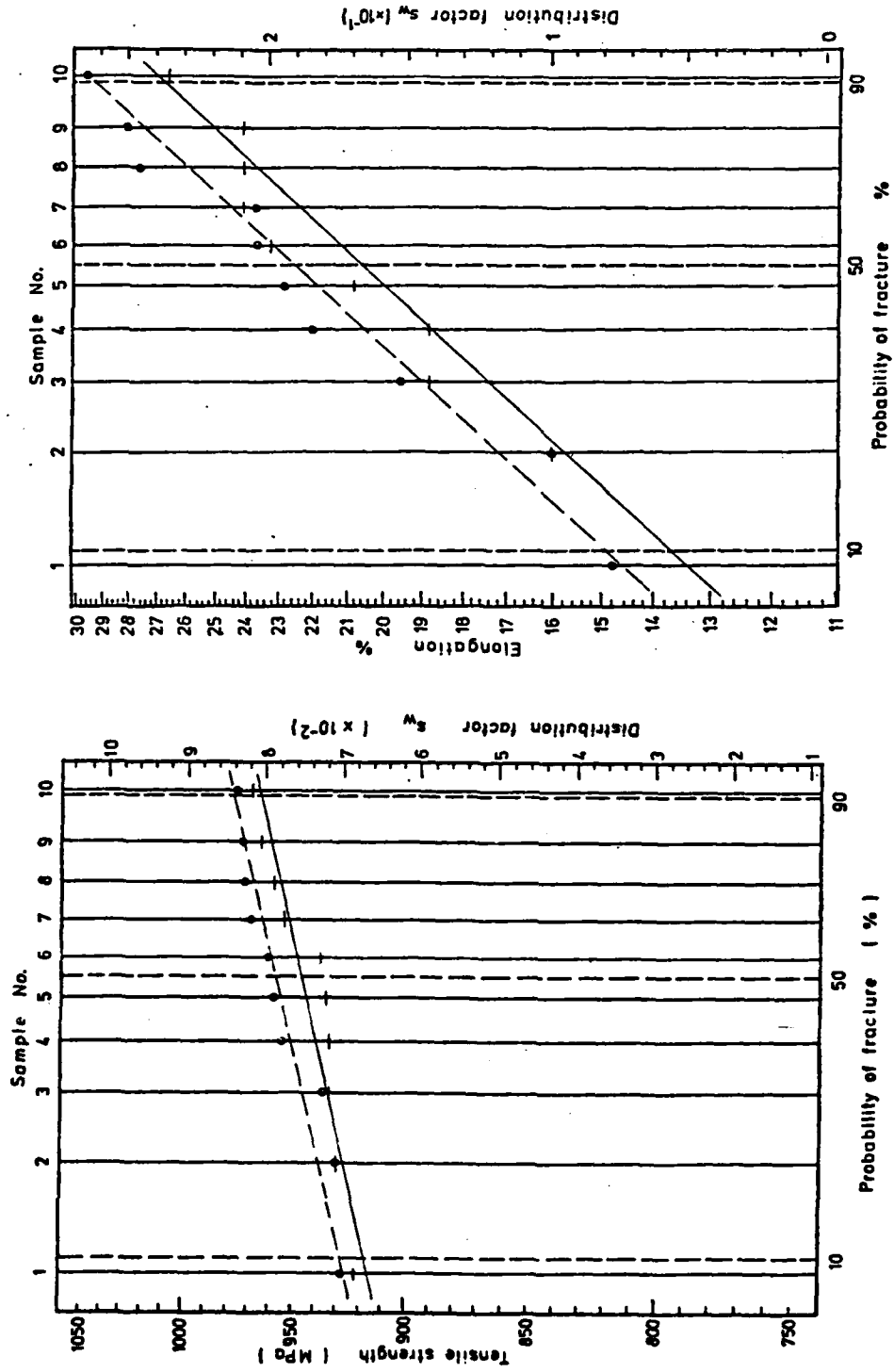


Fig.67: Weibull-diagrams for E87W (—) and W640/81 (---)

Powder E 91

Table 13: Mechanical properties of the samples prepared from  
E 91 and of the reference sample from W 640/81

| E 91    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,034  | 836      | 7,6      | 17,036   | 945      | 26,8     |
| 17,045  | 893      | 9,6      | 17,055   | 941      | 24,4     |
| 17,003  | 912      | 17,2     | 17,032   | 962      | 29,6     |
| 17,012  | 942      | 15,4     | 17,053   | 949      | 28,8     |
| 16,921  | 941      | 18,8     | 17,079   | 942      | 27,2     |
| 16,987  | 950      | 24,8     | 17,072   | 954      | 27,6     |
| 17,005  | 968      | 16,0     | 17,002   | 958      | 28,8     |
| 17,017  | 977      | 16,0     | 17,034   | 940      | 27,2     |
| 17,0030 | 927      | 15,7     | 17,0454  | 949      | 27,6     |
| 16,7200 | 794      | 9,2      | 17,0640  | 950      | 29,0     |
| 16,9035 | 855      | 11,6     | 17,0769  | 938      | 22,8     |
| 17,0429 | 891      | 11,6     | 17,0904  | 964      | 24,0     |
| 17,0848 | 911      | 14,6     | 17,0744  | 956      | 22,4     |
| 17,0865 | 969      | 12,8     | 17,0591  | 964      | 28,0     |
| 17,0741 | 938      | 10,0     |          |          |          |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 91  | $16,996 \pm 0,092$ | $913 \pm 52$ | $14,1 \pm 4,4$ |
| W 640 | $17,055 \pm 0,024$ | $950 \pm 9$  | $26,7 \pm 2,4$ |

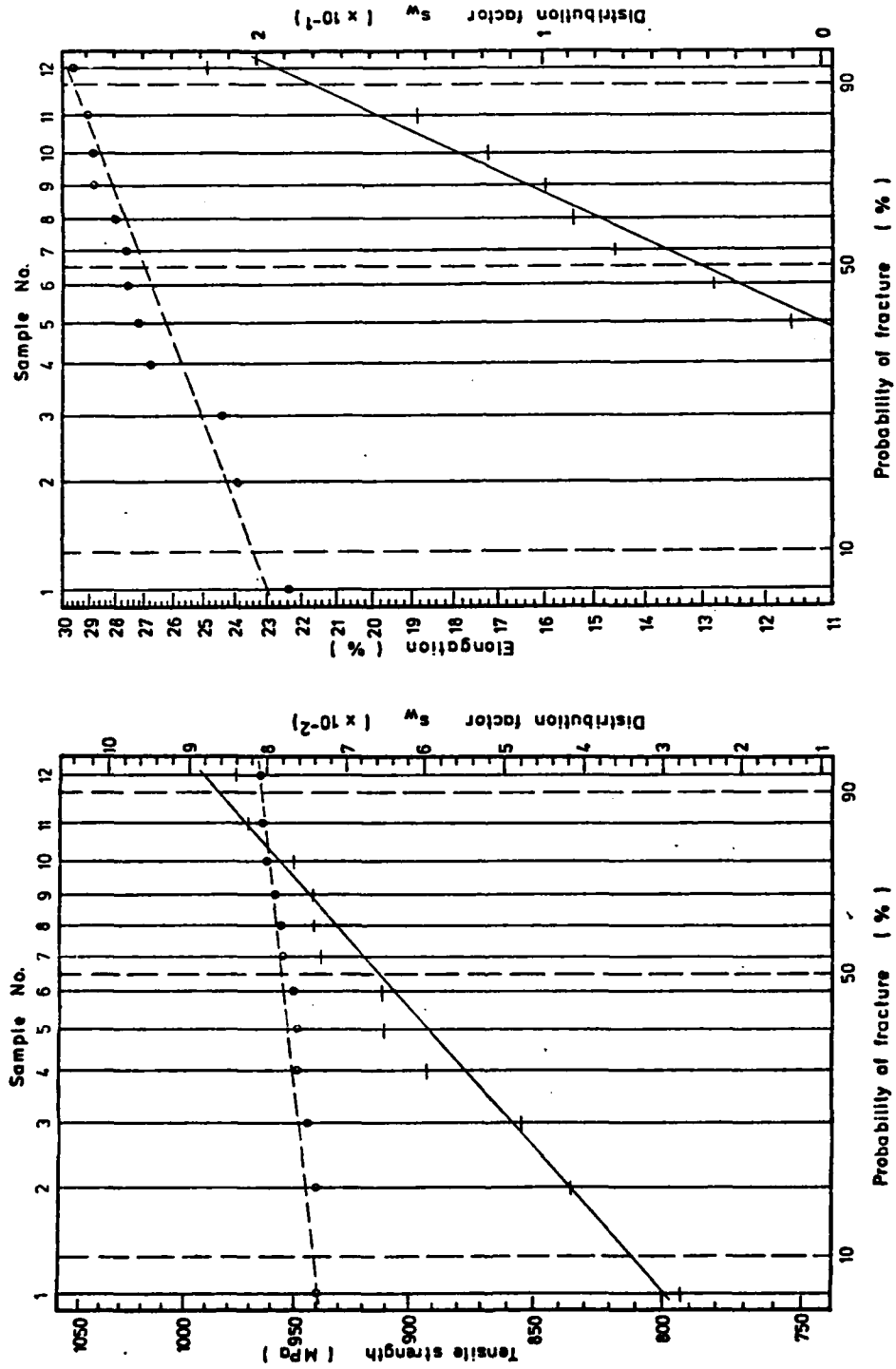


Fig. 68: Weibull-diagrams for E91W (—) and W640/81 (---)

Powder E 95

Table 14: Mechanical properties of the samples prepared from E 95 and of the reference sample from W 640/81

| E 95    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\xi$   | $\sigma$ | $\delta$ | $\xi$    | $\sigma$ | $\delta$ |
| 17,0797 | 942      | 15,6     | 17,0680  | 945      | 15,8     |
| 17,0807 | 964      | 15,2     | 17,0239  | 967      | 19,8     |
|         |          |          | 17,0672  | 958      | 18,0     |
| 17,0875 | 956      | 16,6     | 17,0583  | 961      | 22,2     |
| 17,1048 | 976      | 21,8     | 17,0654  | 967      | 22,2     |
| 17,0841 | 950      | 14,2     |          |          |          |
| 17,1018 | 1023     | 19,2     | 17,0262  | 973      | 21,6     |
| 17,0747 | 952      | 12,6     | 17,0673  | 990      | 21,6     |
|         |          |          | 17,0843  | 965      | 18,2     |
| 17,1141 | 990      | 23,2     | 17,1166  | 992      | 21,6     |
| 17,1061 | 945      | 13,0     | 17,1054  | 994      | 18,4     |
| 17,0985 | 1001     | 20,2     | 17,0723  | 961      | 19,4     |
| 17,1221 | 1014     | 20,2     | 17,1190  | 960      | 16,8     |
| 17,1253 | 963      | 28,2     | 17,1190  | 976      | 25,2     |
| 17,1224 | 963      | 15,6     | 17,0973  | 994      | 25,6     |
|         |          |          | 17,1024  | 1014     | 19,6     |
| 17,0829 | 997      | 18,2     | 17,0998  | 987      | 26,6     |
| 17,0977 | 1001     | 18,8     | 17,0639  | 878      | 9,4      |
|         |          |          | 17,0613  | 976      | 18,8     |
|         |          |          | 17,0694  | 988      | 22,4     |
|         |          |          | 17,0772  | 989      | 23,6     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 95  | 17,0989 $\pm$ 0,0169 | 976 $\pm$ 26 | 17,5 $\pm$ 3,2 |
| W 640 | 17,0851 $\pm$ 0,0412 | 979 $\pm$ 19 | 20,3 $\pm$ 3,8 |

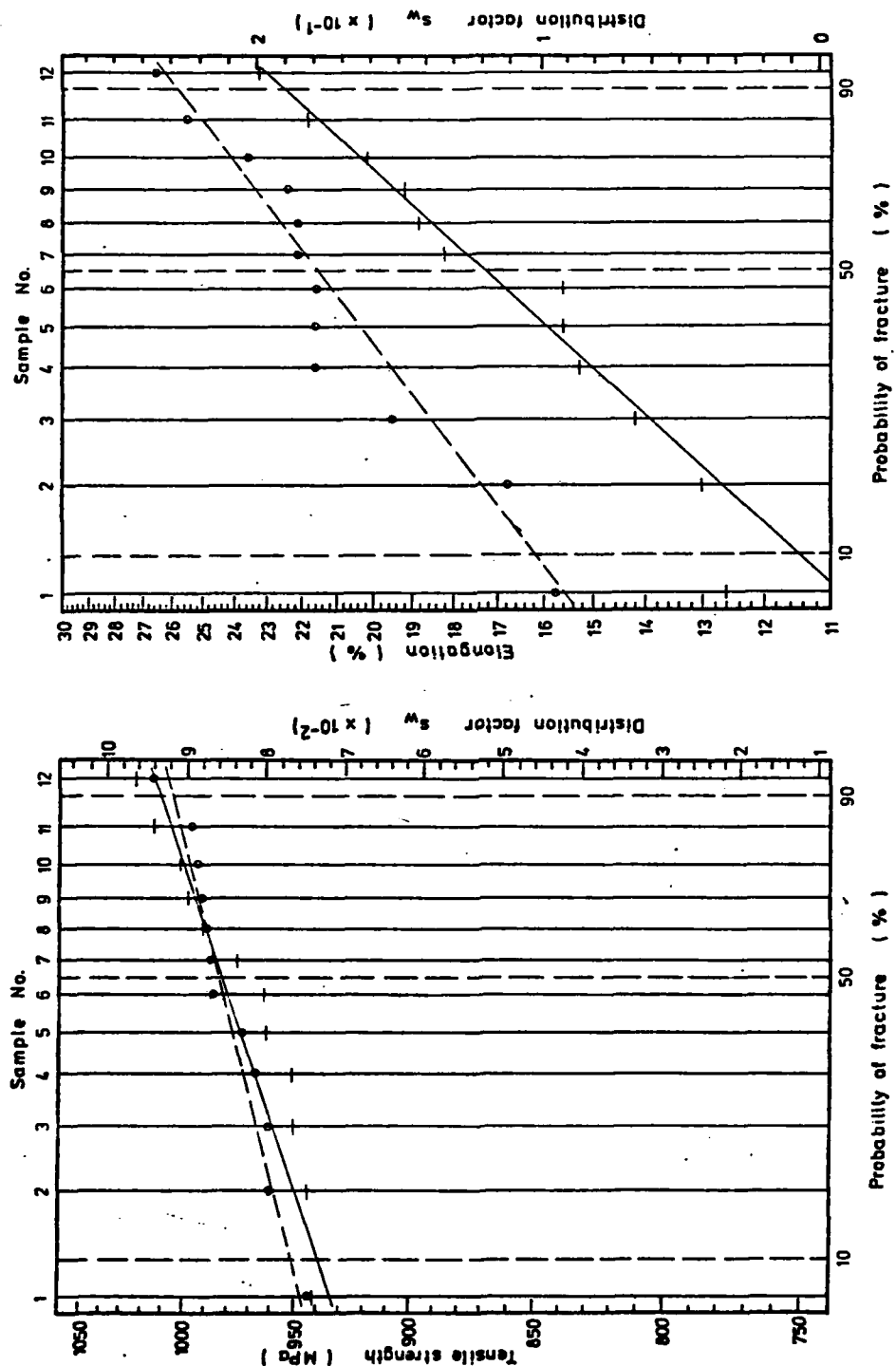


Fig. 69: Weibull-diagrams for E95W (—) and W64O/81 (---)

Powder E 99

Table 15: Mechanical properties of the samples prepared from E 99 and of the reference sample from W 640/81

| E 99    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,0860 | 956      | 26,8     | 17,0640  | 950      | 29,0     |
| 17,0945 | 960      | 21,2     | 17,0739  | 938      | 22,8     |
| 17,0668 | 939      | 21,6     | 17,0251  | 933      | 22,8     |
| 17,0609 | 942      | 18,8     | 17,0418  | 926      | 22,0     |
| 17,0980 | 937      | 21,0     |          |          |          |
| 17,0972 | 960      | 28,0     | 17,0795  | 947      | 23,6     |
| 17,0232 | 909      | 12,0     | 17,0602  | 931      | 26,0     |
| 17,0360 | 949      | 21,8     | 17,0178  | 948      | 22,2     |
| 17,0656 | 918      | 13,4     | 17,0322  | 944      | 20,0     |
| 17,0614 | 948      | 22,8     | 17,0257  | 943      | 22,2     |
| 17,0520 | 948      | 17,2     | 17,0384  | 932      | 20,0     |
| 17,0657 | 944      | 16,6     | 17,0742  | 952      | 21,2     |
| 17,0819 | 970      | 23,4     | 17,0544  | 943      | 23,2     |

Mean values  $\pm$  standard deviations

|       |                     |              |                |
|-------|---------------------|--------------|----------------|
| E 99  | 17,0684 $\pm$ 0,023 | 944 $\pm$ 17 | 20,3 $\pm$ 4,7 |
| W 640 | 17,049 $\pm$ 0,021  | 940 $\pm$ 8  | 22,9 $\pm$ 2,5 |

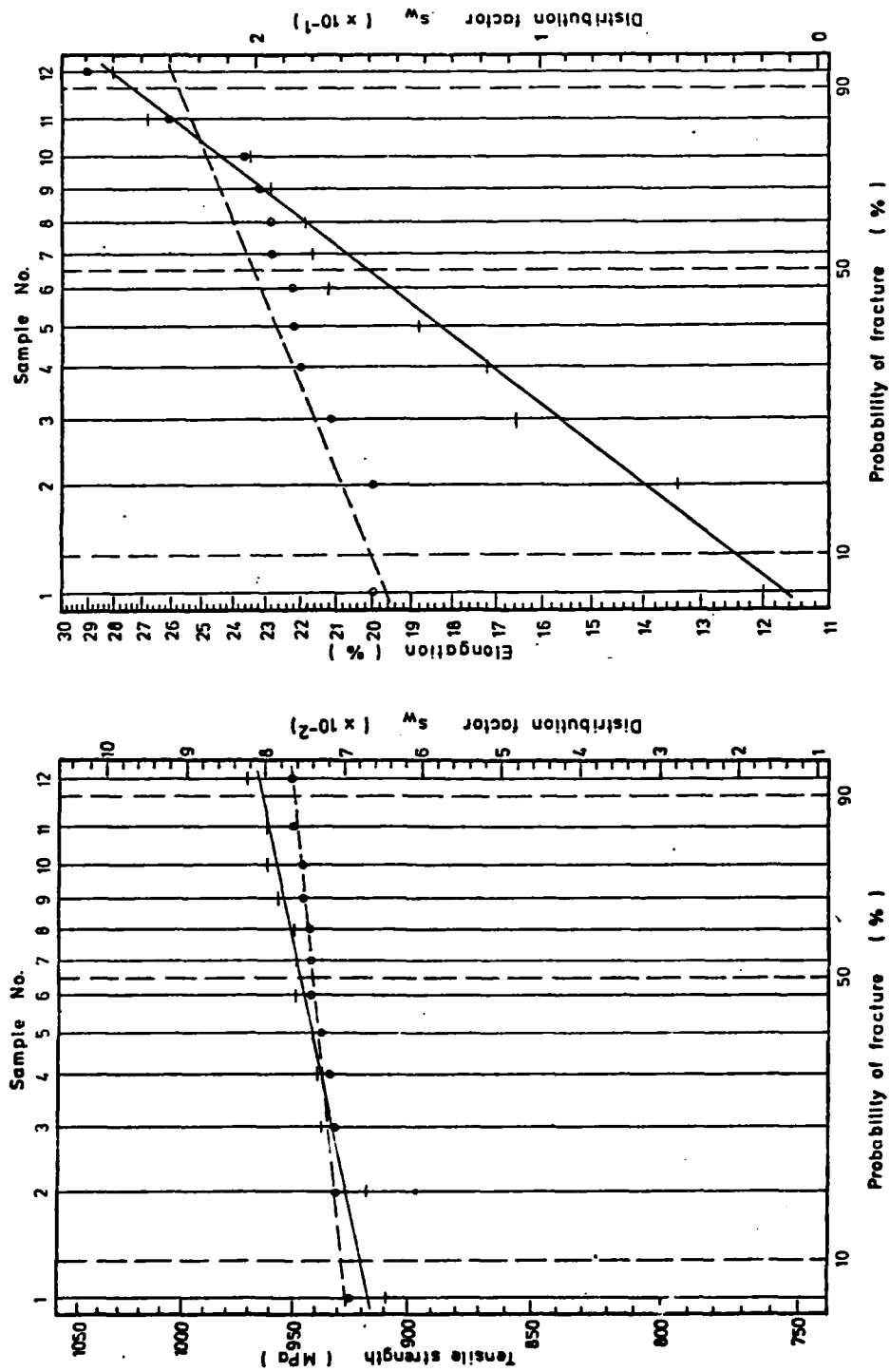


Fig.70: Weibull-diagrams for E99W (—) and W640/81 (---)

Powder E 103

Table 16: Mechanical properties of the samples prepared from E 103 and of the reference sample from W 640/81

| E 103                       |                  |              | 640/81                      |                  |              |
|-----------------------------|------------------|--------------|-----------------------------|------------------|--------------|
| $\rho$ (g/cm <sup>3</sup> ) | $\sigma_f$ (MPa) | $\delta$ (%) | $\rho$ (g/cm <sup>3</sup> ) | $\sigma_f$ (MPa) | $\delta$ (%) |
| 17,0711                     | 856              | 9,2          | 17,0642                     | 914              | 18,0         |
| 17,0658                     | 860              | 8,8          | 17,0454                     | 906              | 19,6         |
| 17,0462                     | 879              | 12,0         | 17,0358                     | 917              | 16,0         |
| 17,0594                     | 883              | 12,0         | 17,0766                     | 972              | 23,0         |
| 17,0349                     | 895              | 16,0         | 17,0239                     | 967              | 19,8         |
| 17,0807                     | 956              | 21,0         | 17,0583                     | 961              | 22,2         |
| 17,0662                     | 941              | 17,6         | 17,0262                     | 973              | 21,6         |
| 17,0879                     | 918              | 14,8         | 17,1166                     | 992              | 21,6         |
| 17,0858                     | 897              | 12,0         | 17,0723                     | 961              | 19,4         |
| 17,0930                     | 960              | 20,8         | 17,0694                     | 988              | 22,4         |
| 17,0654                     | 871              | 10,8         | 17,0772                     | 989              | 23,6         |
| 17,1061                     | 928              | 16,8         |                             |                  |              |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 103 | 17,072 $\pm$ 0,020 | 904 $\pm$ 36 | 14,3 $\pm$ 4,2 |
| W 640 | 17,061 $\pm$ 0,027 | 958 $\pm$ 31 | 21,5 $\pm$ 3,6 |

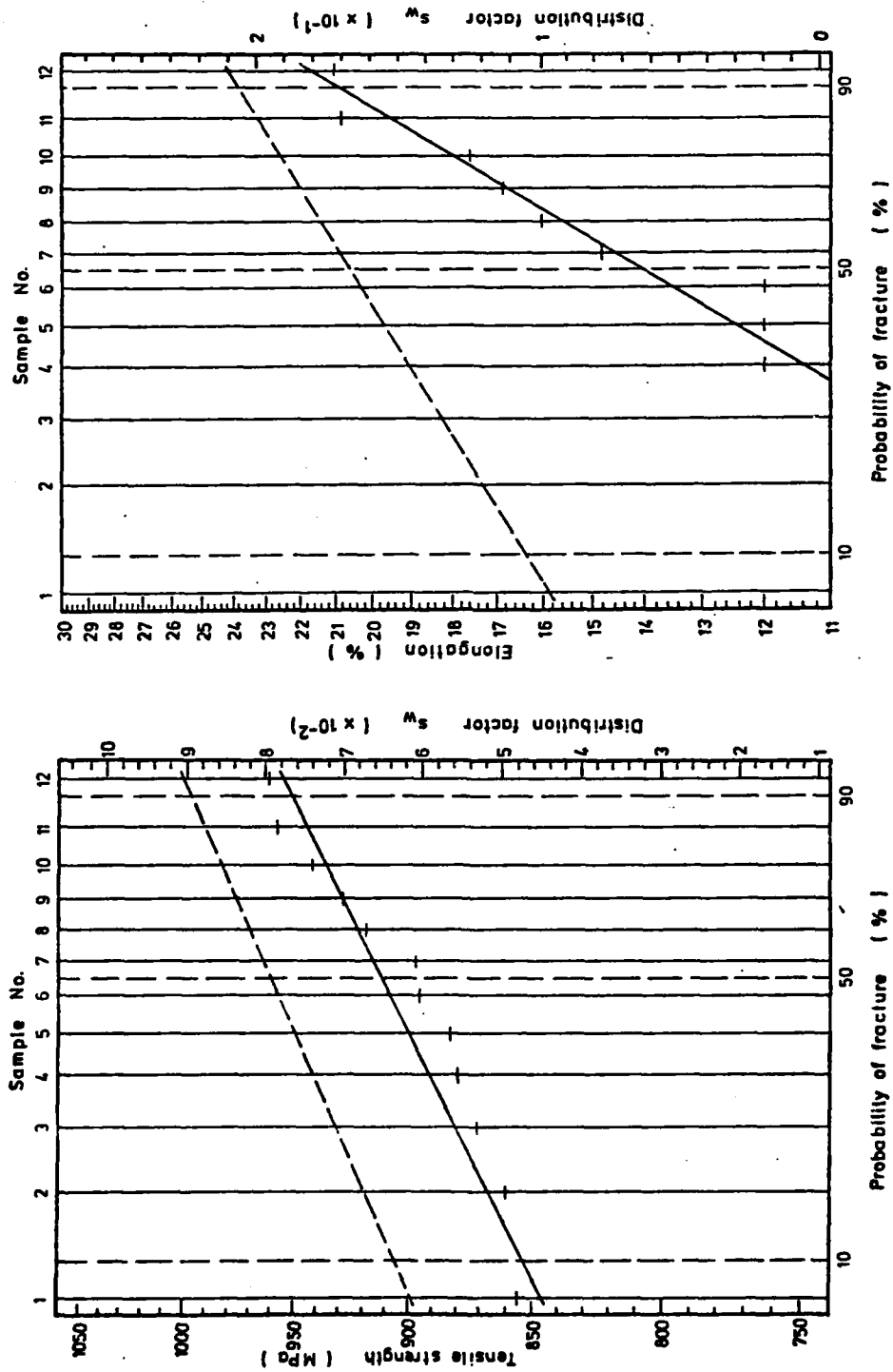


Fig.71: Weibull-diagrams for E103W (—) and W640/81 (---)

E 107

Table 17: Mechanical properties of the samples prepared from  
E 107 and of the reference sample from W 640/81

| E 107   |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,1054 | 913      | 12,0     | 17,1082  | 987      | 24,0     |
| 17,0563 | 970      | 20,0     | 17,0833  | 1000     | 27,6     |
| 17,0851 | 970      | 17,6     | 17,0772  | 976      | 22,8     |
| 17,0946 | 945      | 17,2     |          |          |          |
| 17,0924 | 930      | 14,4     | 17,0392  | 951      | 19,2     |
| 17,0946 | 950      | 16,2     | 17,0850  | 956      | 20,4     |
| 17,0697 | 960      | 20,0     | 17,0778  | 946      | 24,0     |
| 17,0750 | 855      | 6,8      | 17,0660  | 911      | 20,2     |
| 17,0920 | 899      | 11,6     | 17,0683  | 952      | 22,4     |
| 17,1014 | 916      | 14,6     | 17,0553  | 963      | 20,8     |
| 17,0984 | 780      | 4,8      | 17,0975  | 942      | 19,8     |

Mean values  $\pm$  standard deviations

|       |                    |              |                |
|-------|--------------------|--------------|----------------|
| E 107 | 17,088 $\pm$ 0,015 | 917 $\pm$ 57 | 14,1 $\pm$ 4,9 |
| W 640 | 17,081 $\pm$ 0,015 | 959 $\pm$ 25 | 22.1 $\pm$ 2,6 |

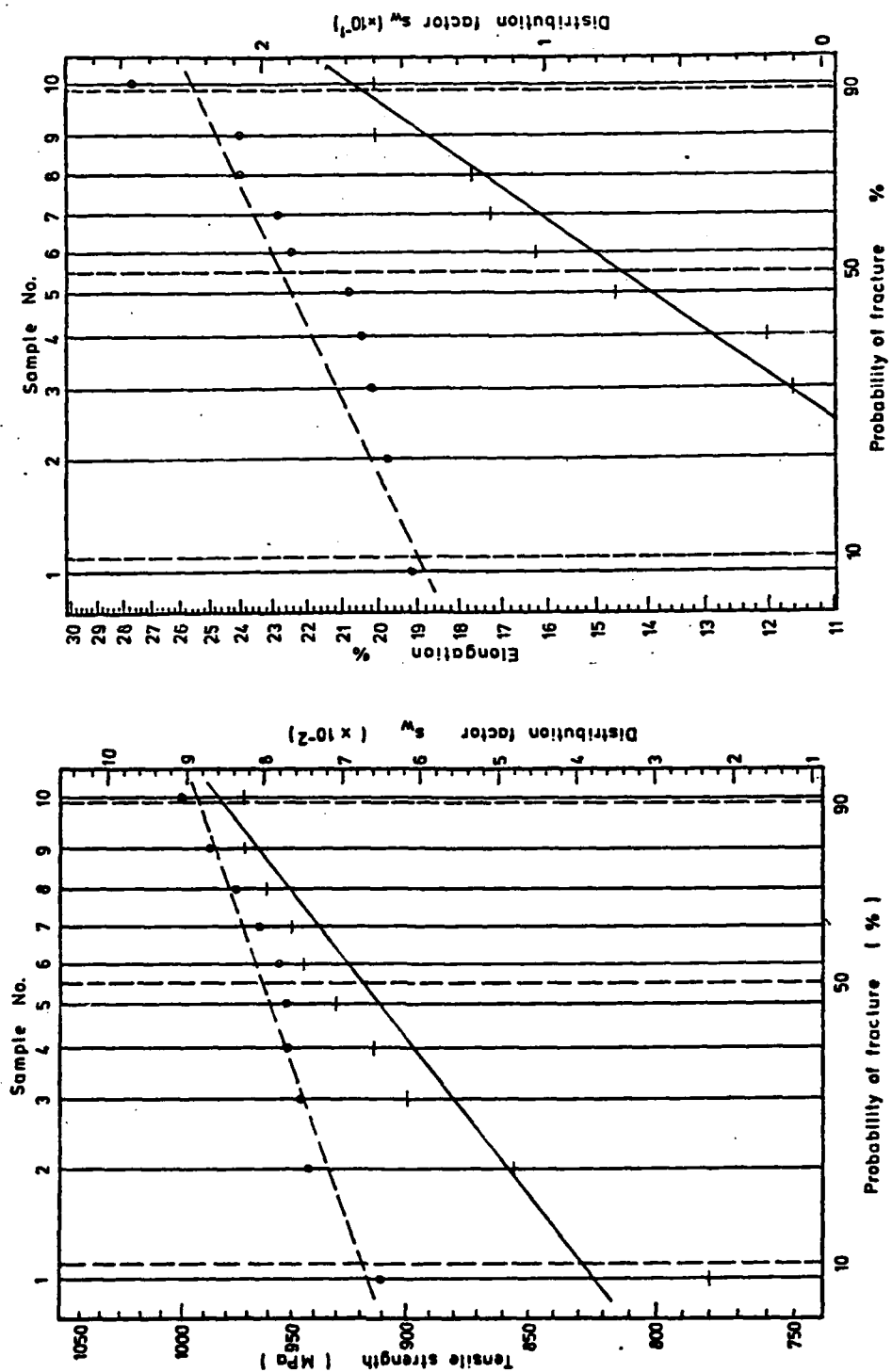


Fig.72: Weibull-diagrams for E107W (—) and W640/81 (---)

Powder E 111

Table 18: Mechanical properties of the samples prepared from E 111 and of the reference sample from W 640/81

| E 111   |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 15,5661 | 753      | 14,4     | 17,0680  | 945      | 15,8     |
| 15,4417 | 757      | 12,0     | 17,0239  | 967      | 19,8     |
|         |          |          | 17,0672  | 958      | 18,0     |
| 17,4555 | 867      | 14,6     | 17,0583  | 961      | 22,2     |
| 16,5128 | 856      | 17,4     | 17,0654  | 967      | 22,2     |
| 16,4943 | 857      | 13,6     |          |          |          |
| 16,3354 | 855      | 12,4     | 17,0262  | 973      | 21,6     |
| 16,3362 | 860      | 12,2     | 17,0873  | 990      | 21,6     |
|         |          |          | 17,0843  | 965      | 18,2     |
| 16,9206 | 958      | 17,2     | 17,1166  | 992      | 21,5     |
| 16,9733 | 965      | 10,2     | 17,1054  | 994      | 18,4     |
|         |          |          | 17,0723  | 961      | 19,4     |
| 16,7759 | 957      | 26,6     | 17,0998  | 987      | 26,6     |
| 16,3555 | 936      | 13,8     | 17,0639  | 878      | 9,4      |
| 16,5980 | 942      | 14,0     | 17,0613  | 976      | 18,8     |
|         |          |          | 17,0694  | 988      | 22,4     |
|         |          |          | 17,0772  | 989      | 23,6     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 111 | 16,3971 $\pm$ 0,4699 | 880 $\pm$ 74 | 14,0 $\pm$ 2,2 |
| W 640 | 17,0704 $\pm$ 0,0244 | 974 $\pm$ 15 | 20,7 $\pm$ 2,7 |

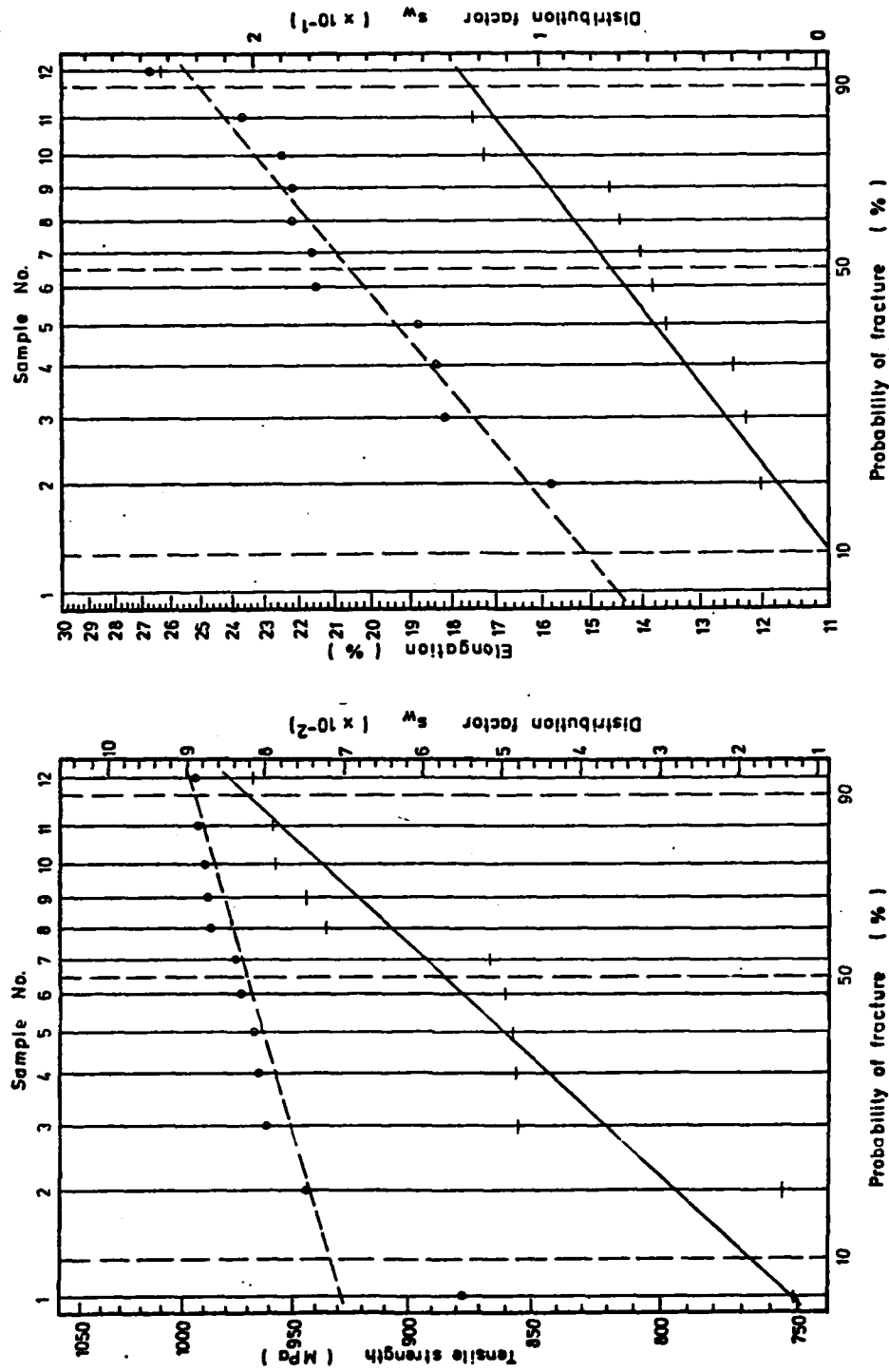


Fig. 73: Weibull-diagrams for E111W (—) and W640/81 (---)

Powder E 115

Table 19: Mechanical properties of the samples prepared from E 115 and of the reference samples from W 640/81

| E 115   |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,0530 | 971      | 17,0     | 17,0680  | 945      | 15,8     |
| 17,0900 | 992      | 28,0     | 17,0239  | 967      | 19,8     |
| 17,0625 | 978      | 27,6     | 17,0672  | 958      | 18,0     |
| 17,0242 | 989      | 15,4     | 17,0583  | 961      | 22,2     |
| 17,0710 | 985      | 26,0     | 17,0654  | 967      | 22,2     |
| 17,1010 | 977      | 21,8     | 17,0262  | 973      | 21,6     |
| 17,1162 | 1004     | 26,6     | 17,0673  | 990      | 21,6     |
| 17,0375 | 944      | 23,8     | 17,0843  | 965      | 18,2     |
| 17,1058 | 992      | 27,0     | 17,1666  | 992      | 21,6     |
| 17,1254 | 938      | 25,6     | 17,1054  | 994      | 18,4     |
|         |          |          | 17,0723  | 961      | 19,4     |
| 17,1052 | 992      | 27,6     | 17,1190  | 960      | 16,8     |
| 17,1226 | 977      | 26,4     | 17,1190  | 975      | 25,2     |
| 17,1184 | 996      | 26,8     | 17,0973  | 994      | 25,6     |
|         |          |          | 17,1024  | 1014     | 19,6     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 115 | 17,0925 $\pm$ 0,0329 | 984 $\pm$ 15 | 24,6 $\pm$ 4,1 |
| W 640 | 17,0795 $\pm$ 0,0306 | 974 $\pm$ 19 | 20,4 $\pm$ 2,8 |

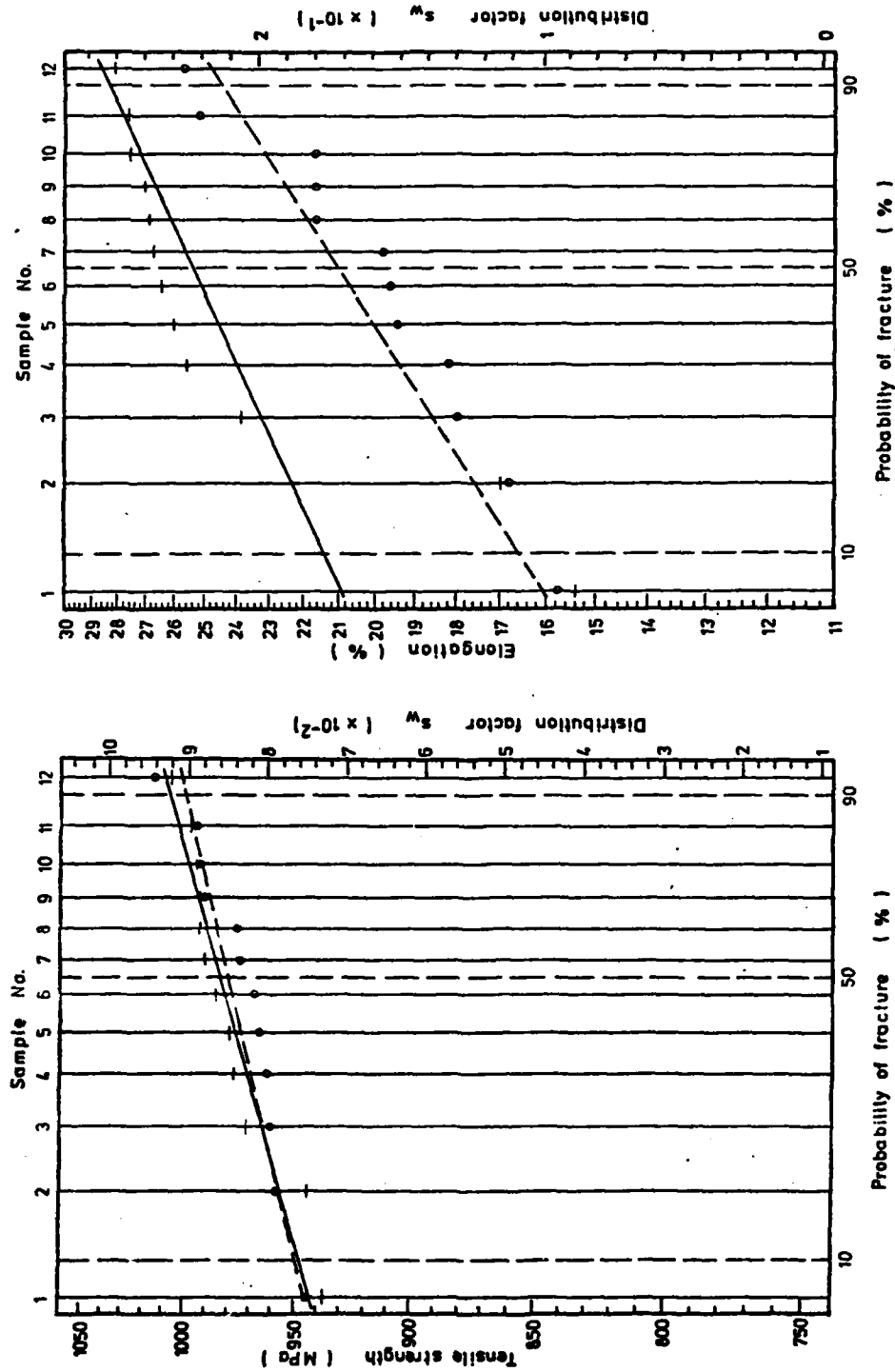


Fig.74: Weibull-diagrams for E115W (—) and W640/81 (---)

Regarding the results as a whole, except for those heavy metals roughly equal in quality to those prepared from standard powder, there are two groups of heavy metals with unsatisfactory mechanical properties, esp. elongation: the first group contains those heavy metals with low sintering density due not to pores or blisters but to overall unsatisfactory sintering. Even from their external appearance it can be seen that they are not properly sintered: they do not look metallic but rather dull grey, as if they had not been liquid phase sintered; also they had shrunk very little, much less than the properly sintered samples. Specimens in this group were those heavy metals prepared from E 48(Na) and E 51(Li), the coarser powders with grain sizes  $>20 \mu\text{m}$ . Both tensile strength and elongation here are correlated to the grain size, E 51(Li), the coarser one, being inferior in both respects. SEM investigations (Fig.76, 77) showed that those samples are only partially sintered and contain large areas where no liquid phase sintering at all had taken place. This is evident from the irregular shape of the W grains as compared to the spherical W grains in the pore on Fig.48, where pore formation had taken place during liquid phase sintering. It must be assumed, therefore, that the starting powder size is of great importance for the heavy metals. Based on the knowledge about the process of liquid phase sintering described in chapter 3 it may be assumed that the capillary driving force that distributes the binder melt homogeneously within the material is too low if the particles are too large in diameter and thus the W skeleton is not uniformly filled with binder. In those places where enough binder is present to fill the pore space, normal liquid phase sintering leads to the usual sound microstructure (Fig.76, right side of the photo) while in the places without binder only solid state sintering occurs, which leads to a structure similar to that of sintered W that may be strong but is necessarily brittle. Generally, with these materials the importance of the correct microstructure even before liquid phase sintering is clearly shown (21,22).

If W grains have not sintered together closely as shown in Fig.41 and 42, even long sintering time at high temperature does not yield fully dense products.

The other group of heavy metals with unsatisfactory properties contains those that have been properly sintered but have formed pores and, in extreme cases, blisters during liquid phase sintering. The latter is the case with E111, containing rare earths. The samples produced from this powder contain small pores, as also observed with heavy metals sintered for a long time, i.e. areas where most of the binder has been driven off (Fig.78). Further, there are verly large pores, with diameters  $>100\text{ }\mu\text{m}$  (Fig.79), which are really empty spaces apparently formed by considerable internal pressure. Similar pores have been observed with the samples prepared from E36 and E39 (see Fig.50 in (1)). For E111, however, those large pores were not in the center but rather near the surface; thus the internal structure was not weakened so much and the mechanical properties were not quite as bad as might be expected from the porosity.

There are also several other powders resulting in porous heavy metals, although the pores are not as spectacular as those in E111. Instead they are mostly small ones similar to those in Fig.48 and 78. Again the powders doped with Na show a strong tendency to form pores: E61 prepared from "impure blue oxide" which contains considerable amount of Na, and E79, doped with Na and Si, exhibited numerous pores in the fracture surfaces (Fig.80, 81). As typical for this class of heavy metals, the fracture surfaces, except for the pore look rather sound, exhibiting transgranular fracture of the W grains and generally good interphase strength between W grains and binder (Fig.82, 83). In contrast to E79 (Na,Si) the powder E83 (Na,F) resulted in quite satisfactory materials, with elongations well above 20%. It may be assumed that the higher Na content of the former powder is responsible for its different behaviour,

although experiences with the furnace lining indicate that  $\text{SiO}_2$  in which form Si is still present after reduction is probably reduced to a considerable degree at sintering temperature and the resulting  $\text{H}_2\text{O}$  causes pore formation.

With K, which was added to W powders in 3 different concentrations, a certain tendency to form pores was observed for those powders doped with 500 and 100 ppm K (Fig.84) while with 50 ppm the resulting bars were even somewhat better than the reference bars prepared from W 640/81. As the analysis sheets for all three powders showed K contents  $< 10 \text{ um}$ , the difference in sintering behaviour remains inexplicable unless it is assumed that - unmeasurable - differences in K content below 10 ppm are responsible for this phenomenon.

Slight pore formation was also observed for E91, containing 200 ppm Ba, and E107, doped with Ni, although the pores in these cases are rather small and not conspicuous (Fig.85, 86). They do, however, have a considerable effect on the ductility, esp. regarding the scatter of the individual values. Generally, the characteristic difference between the samples prepared from E48 and E51 and the other porous ones regarding the elongation is the scatter of the individual values: the former exhibit consistently low elongation, as their microstructure is unable to withstand higher degrees of deformation. The latter are characterized by a very broad spread in the elongation values, often with values  $< 10\%$  and  $> 20\%$  being measured in the same sintering batch. As their basic structure is ductile, the probability of fracture at a given degree of deformation depends on the - largely statistical - distribution of the pores within the material.

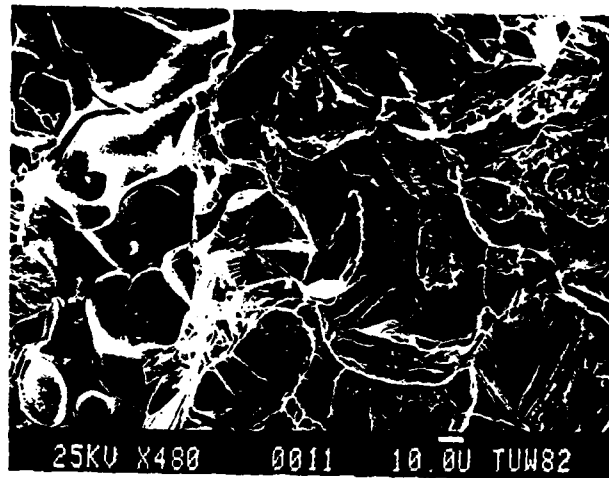


Fig.76  
Heavy metal (90%W)  
prepared from  
E51W; insufficient  
densification

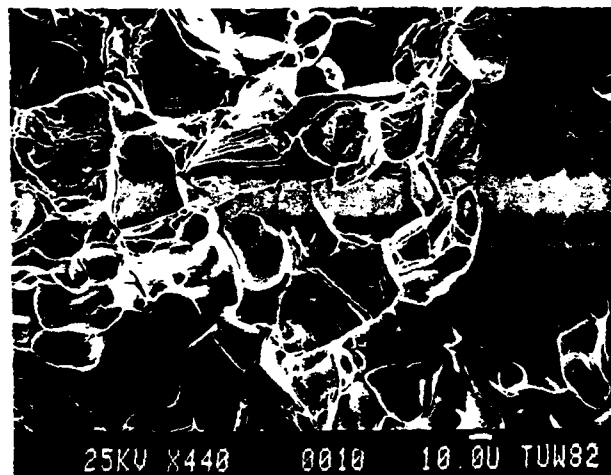


Fig.77  
as Fig.76

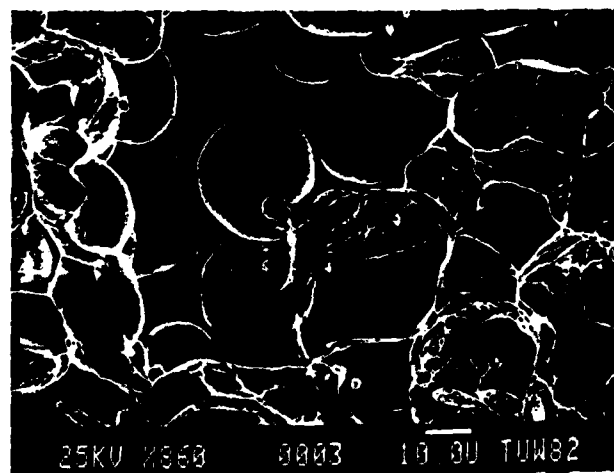


Fig.78  
Heavy metal doped  
with rare earths  
(E111W); pore  
formation during  
sintering

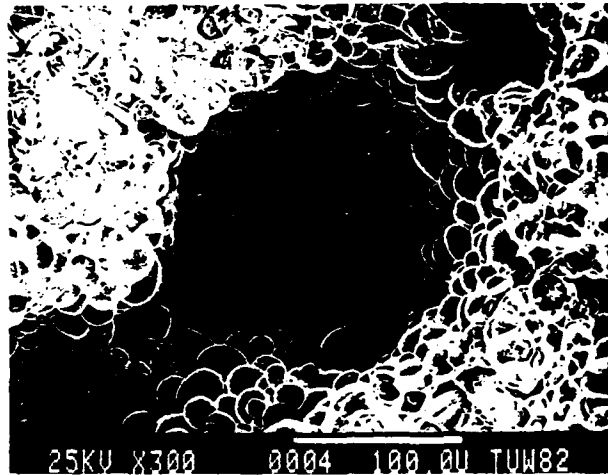


Fig.79  
As Fig.78; large  
pore directly  
beneath the  
surface

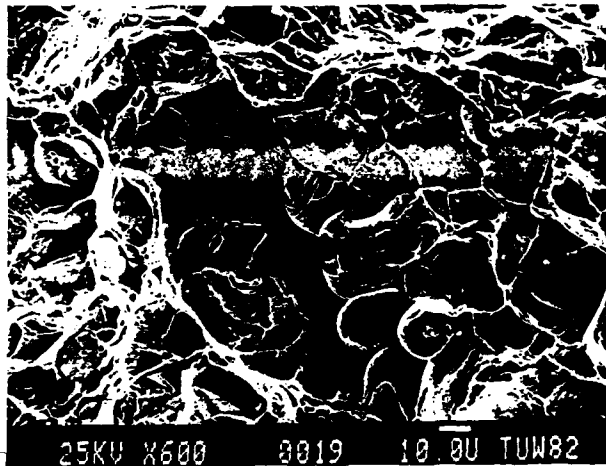


Fig.80  
Heavy metal  
sintered from  
E61W (containing  
impurities from  
blue oxide)

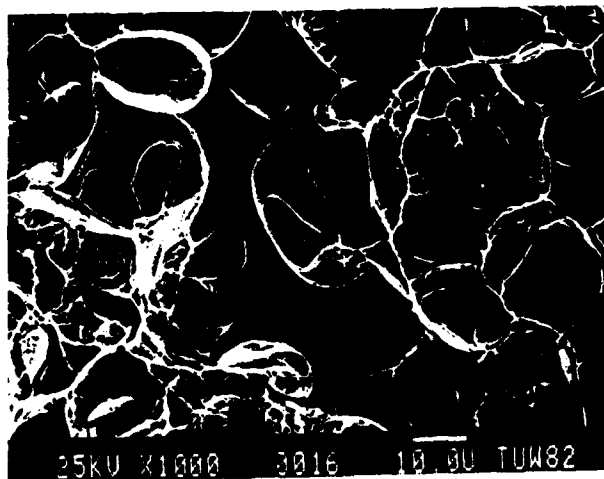


Fig.81  
Heavy metal doped  
with Na, Si (E79W)

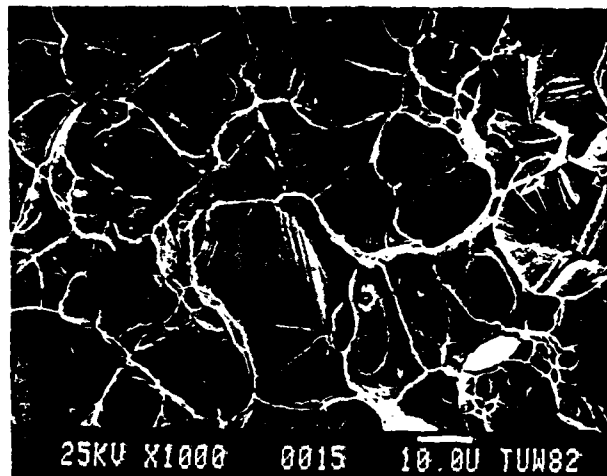


Fig.82  
Same surface as  
on Fig.81; only  
local porosity

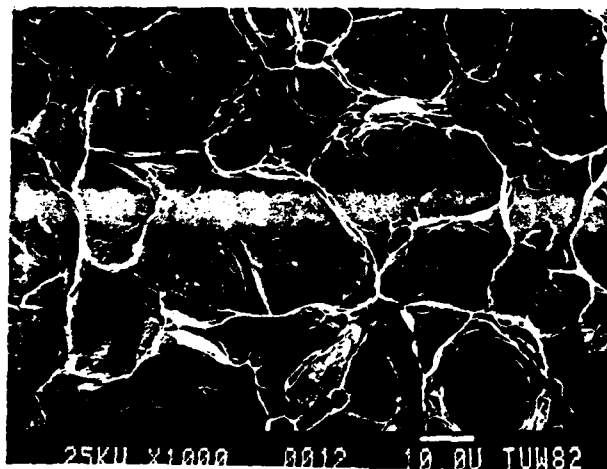


Fig.83  
Same surface as  
on Fig.80; sound  
dtructure

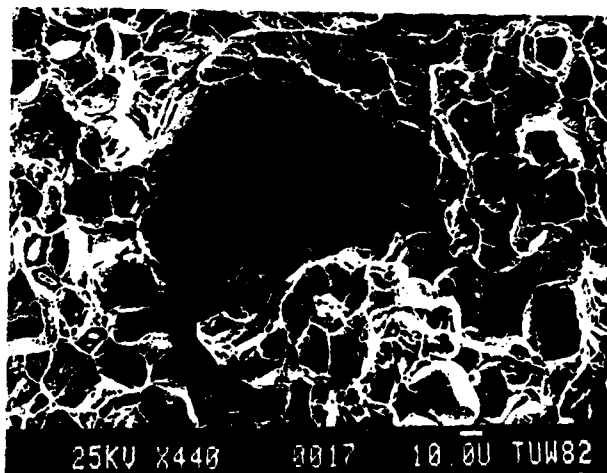


Fig.84  
Heavy metal (90%W)  
prepared from  
E63W; some iso-  
lated pores

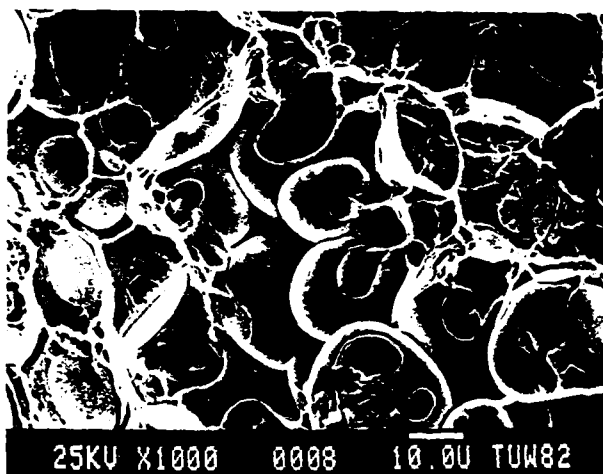


Fig.85  
Heavy metal (90%W)  
prepared from  
E91W

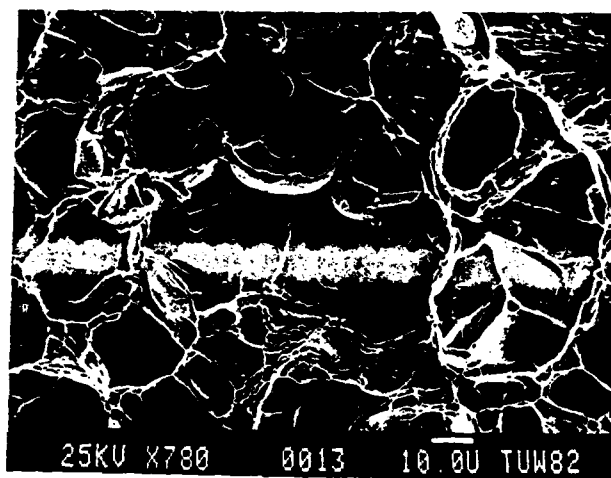


Fig.86  
Heavy metal pre-  
pared from  
E107W

#### 4.2 96% W content

The samples with high W content were prepared in quite the same manner as those containing 90% W. Due to the very effective granulation treatment, no problems were encountered during compaction even with this high W content and no pressing faults were observed. Beginning with E 48(Na), however, the sintering cycle was modified. Investigations had shown that, unlike the 90% W samples, the 96% W test bars were still porous after pre-reduction, and it was thought that inter-cooling as shown in Fig.38 might cause re-oxidation which would worsen the properties. Thus the samples were held for 1h at 1400°C and then slowly heated up to sintering temperature. As already described in (1) the optimum sintering temperature for these samples was found to be considerably higher than with the 90% W bars, 1570-1580°C was selected for optimum ductility. The temperature/time diagram for the modified sintering cycle is shown in Fig.87. As described in 4.1. reference samples prepared from W 640/81 were sintered together with the doped samples to set a standard against which the doped powders could be evaluated. The experimental results and Weibull diagrams are shown on the following pages.

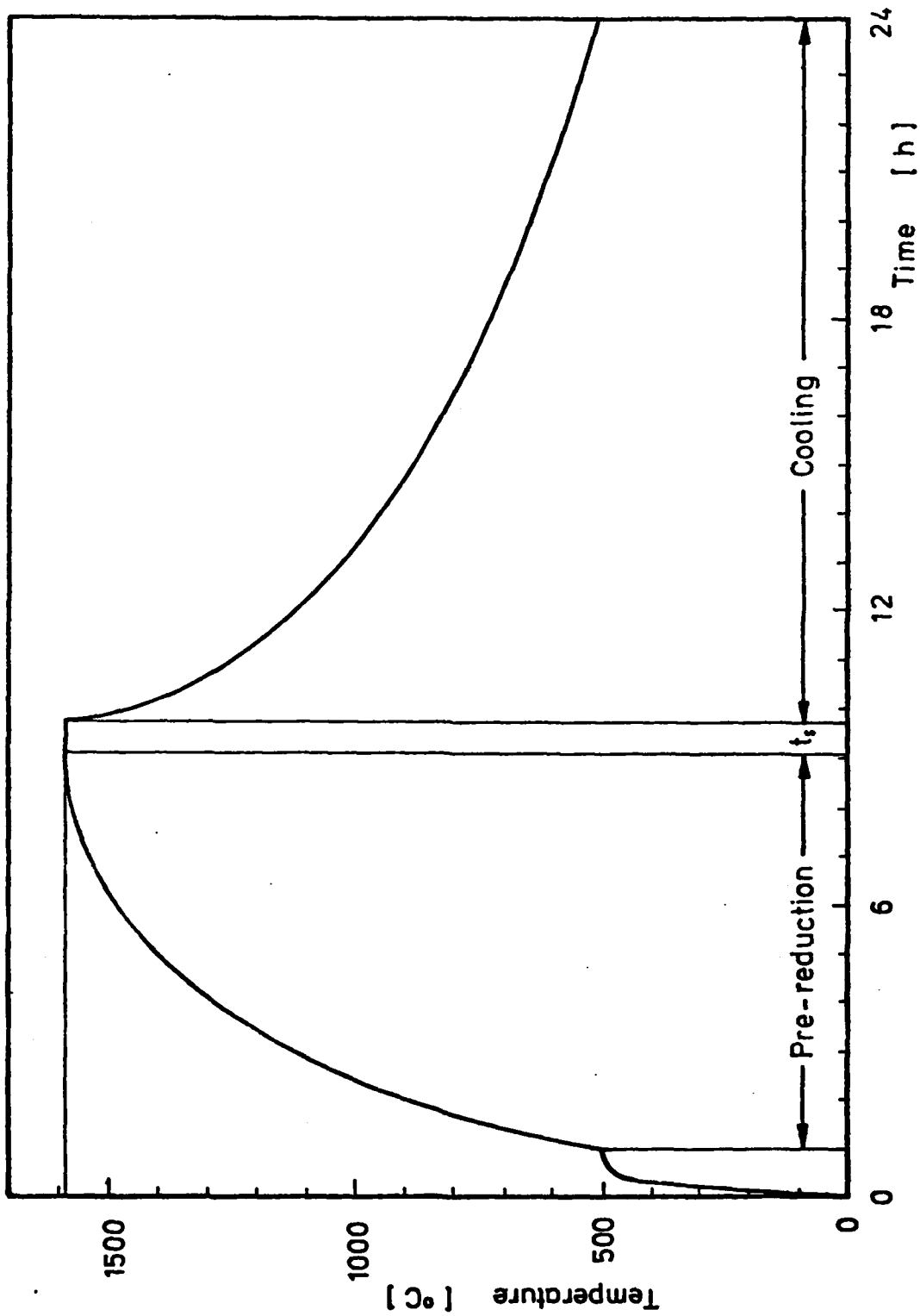


Fig.87: Standard sintering cycle for heavy metals containing 96%W.

Powder E 48

Table 20: Mechanical properties of the samples prepared from  
E 48 and of the reference samples from W 640/81

| E 48                        |                  |              | W 640/81                    |                  |              |
|-----------------------------|------------------|--------------|-----------------------------|------------------|--------------|
| $\rho$ (g/cm <sup>3</sup> ) | $\sigma_p$ (MPa) | $\delta$ (%) | $\rho$ (g/cm <sup>3</sup> ) | $\sigma_p$ (MPa) | $\delta$ (%) |
| 16,7525                     | 535              | 2,4          | 18,3325                     | 973              | 16,0         |
| 16,8901                     | 500              | 0            | 18,3093                     | 973              | 19,0         |
|                             |                  |              | 18,3262                     | 973              | 18,5         |
|                             |                  |              | 18,3001                     | 972              | 19,2         |
| 16,9636                     | 610              | 4,8          | 18,322                      | 975              | 19,2         |
| 16,9416                     | 576              | 4,0          | 18,3198                     | 965              | 20,6         |
|                             |                  |              | 18,3333                     | 979              | 15,2         |
| 16,5979                     | 452              | 0            | 18,3295                     | 953              | 20,4         |
| 16,7850                     | 544              | 2,0          | 18,3325                     | 967              | 19,6         |
|                             |                  |              | 18,3150                     | 959              | 17,6         |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 48  | 16,8218 $\pm$ 0,1381 | 536 $\pm$ 56 | 2,2 $\pm$ 2,0  |
| W 640 | 18,3220 $\pm$ 0,0111 | 969 $\pm$ 7  | 18,5 $\pm$ 1,8 |

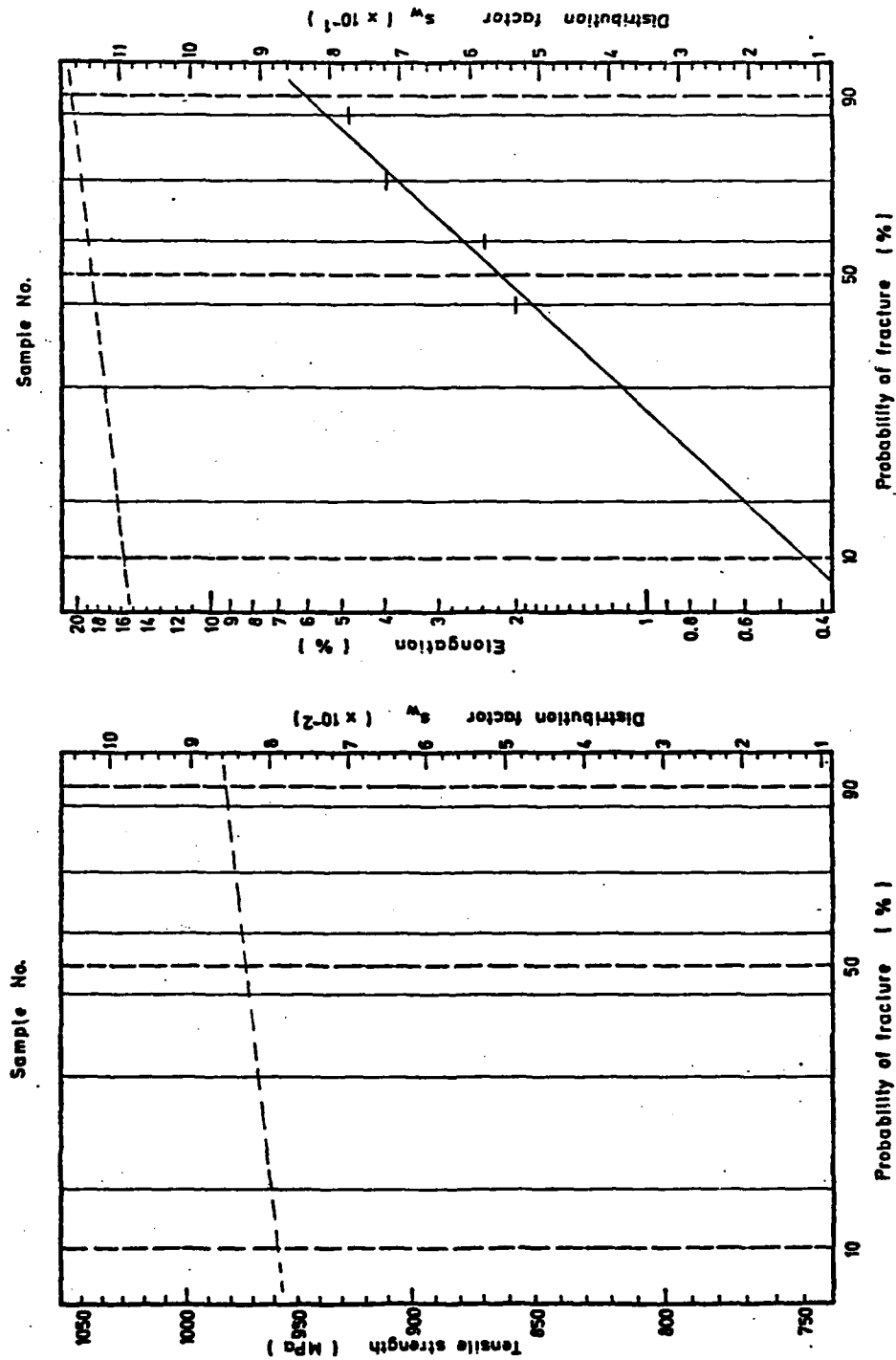


Fig. 88: Weibull-diagrams for E48W (—) and W640/81 (---)

Powder E 51

Table 21: Mechanical properties of the samples prepared from E 51 and of the reference samples from W 640/81

| E 51    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 16,8551 | 449      | <1       | 18,2722  | 989      | 16,0     |
| 16,8400 | 469      | <1       | 18,2550  | 989      | 17,6     |
| 16,8693 | 467      | <1       | 18,2728  | 979      | 19,2     |
|         |          |          | 18,2684  | 984      | 16,4     |
| 16,5932 | 456      | <1       | 18,2837  | 993      | 15,2     |
|         |          | <1       | 18,2774  | 981      | 14,0     |
|         |          | <1       | 18,2810  | 988      | 15,2     |

Mean values  $\pm$  standard deviations

|       |                      |             |                |
|-------|----------------------|-------------|----------------|
| E 51  | 16,7894 $\pm$ 0,1313 | 460 $\pm$ 9 | <1%            |
| W 640 | 18,2729 $\pm$ 0,0095 | 986 $\pm$ 5 | 16,2 $\pm$ 1,7 |

Powder E 56

Table 22: Mechanical properties of the samples prepared from  
E 56 and of the reference sample from W 640/81

| E 56    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 18,1157 | 857      | 8,4      | 18,3151  | 945      | 12,0     |
| 18,0280 | 860      | 8,4      | 18,3049  | 925      | 12,0     |
|         |          |          | 18,3172  | 950      | 9,8      |
| 17,9758 | 859      | 5,6      | 18,3543  | 972      | 13,6     |
| 18,2278 | 855      | 7,4      | 18,3458  | 972      | 11,2     |
|         |          |          | 18,3337  | 1004     | 20,2     |
|         |          |          | 18,3400  | 994      | 19,6     |
| 18,2368 | 865      | 7,6      | 18,3268  | 998      | 14,6     |
| 18,2403 | 818      | 5,2      | 18,3160  | 998      | 10,0     |
|         |          |          | 18,3215  | 1014     | 15,0     |
|         |          |          | 18,3049  | 1014     | 18,8     |
| 18,2940 | 865      | 7,2      | 18,3225  | 979      | 18,8     |
| 18,2934 | 855      | 7,0      | 18,3510  | 981      | 15,2     |
|         |          |          | 18,3205  | 980      | 19,0     |
|         |          |          | 18,2987  | 976      | 19,6     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 56  | 18,1765 $\pm$ 0,1218 | 855 $\pm$ 16 | 7,1 $\pm$ 1,2  |
| W 640 | 18,3249 $\pm$ 0,0170 | 981 $\pm$ 28 | 15,3 $\pm$ 3,8 |

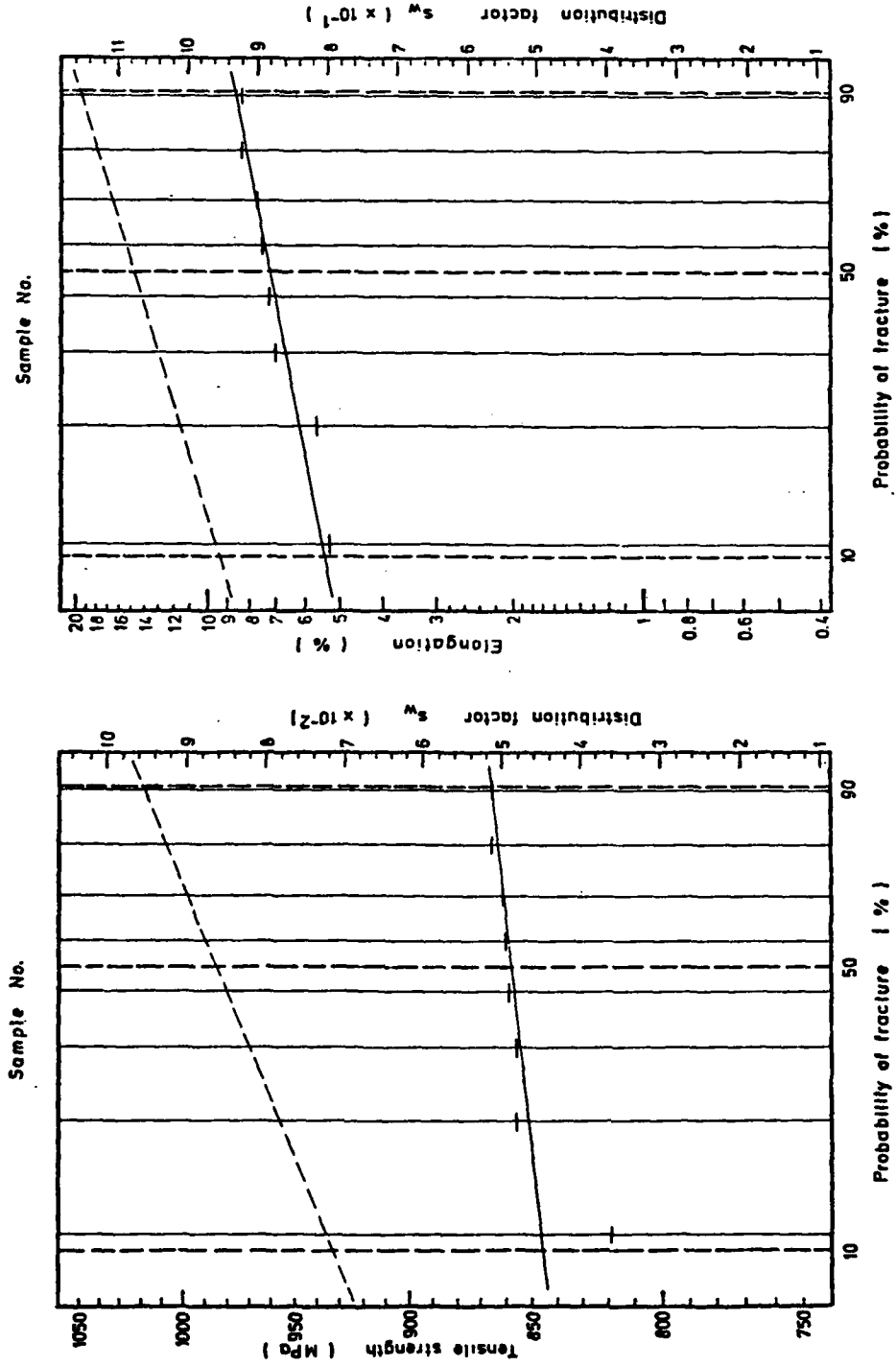


Fig.89 Weibull diagrams for E56W (—) and W640/81 (---)

Powder E 61

Table 23: Mechanical properties of the samples prepared from E 61 and of the reference sample from W 640/81

| E 61    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 16,8690 | 661      | 4,8      | 18,3325  | 973      | 16,0     |
| 17,0650 | 696      | 4,4      | 18,3093  | 973      | 19,0     |
|         |          |          | 18,3262  | 973      | 18,6     |
|         |          |          | 18,3001  | 972      | 19,2     |
| 17,1695 | 683      | 5,6      | 18,322   | 975      | 19,2     |
| 17,0846 | 687      | 5,8      | 18,3198  | 965      | 20,6     |
|         |          |          | 18,3333  | 975      | 15,2     |
| 17,0549 | 660      | 6,8      | 18,3295  | 958      | 20,4     |
| 17,1214 | 693      | 6,8      | 18,3325  | 967      | 19,6     |
|         |          |          | 18,3150  | 959      | 17,6     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 61  | 17,0607 $\pm$ 0,1029 | 680 $\pm$ 16 | 5,7 $\pm$ 1,0  |
| W 640 | 18,3220 $\pm$ 0,0111 | 969 $\pm$ 7  | 18,5 $\pm$ 1,8 |

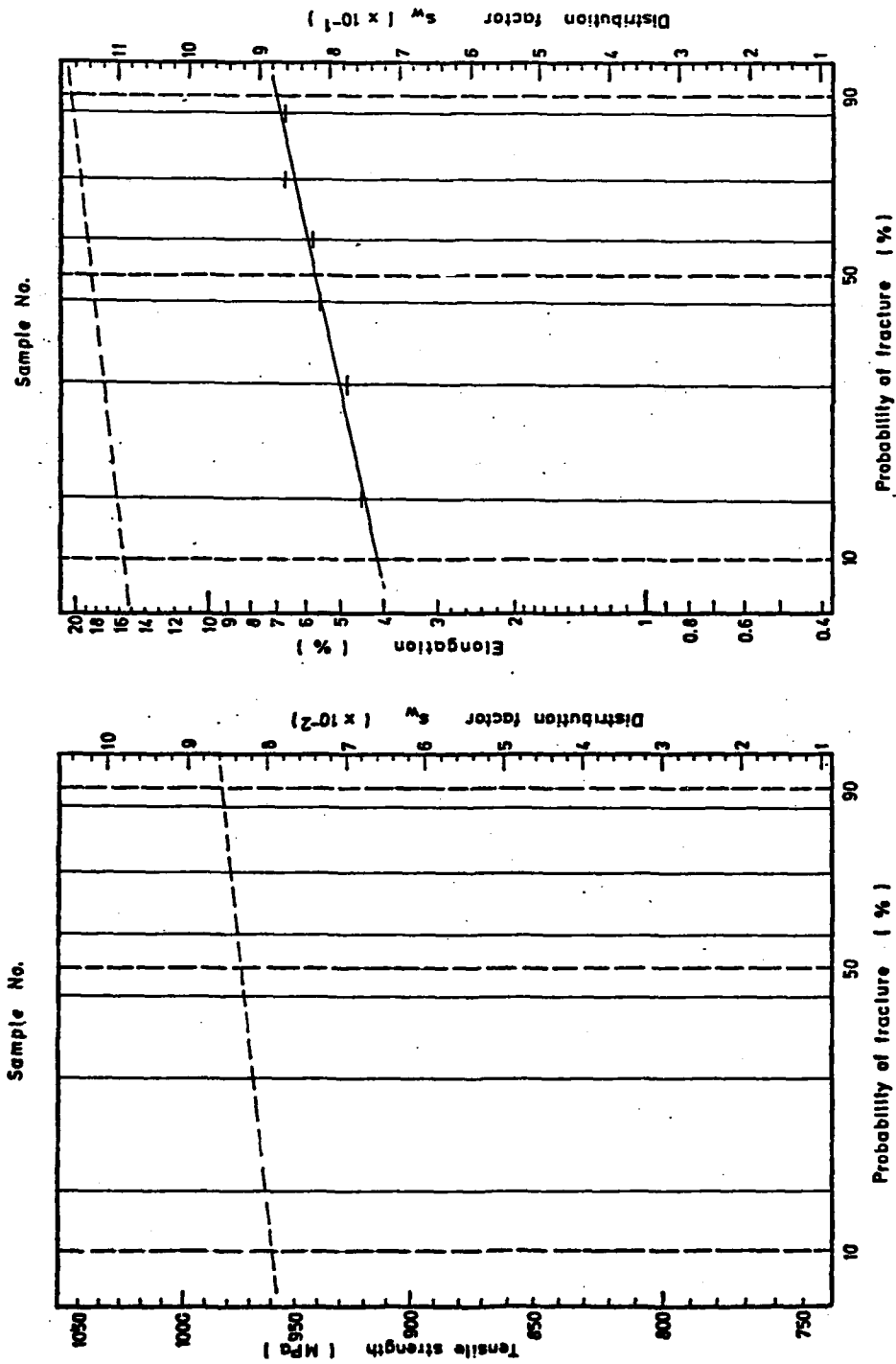


Fig.90: Weibull-diagrams for E61W (—) and W64O/81 (---)

Powder E 63

Table 24: Mechanical properties of the samples prepared from E 63 and of the reference sample from W 640/81

| E 63    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 18,3437 | 963      | 14,8     | 18,3092  | 963      | 16,0     |
| 18,3283 | 967      | 16,8     | 18,3211  | 957      | 19,6     |
|         |          |          | 18,3198  | 959      | 21,6     |
| 18,3266 | 963      | 20,0     | 18,3412  | 997      | 18,0     |
| 18,3336 | 937      | 16,8     | 18,3162  | 973      | 17,6     |
| 18,3141 | 969      | 16,2     |          |          |          |
| 18,3537 | 1000     | 17,6     | 18,3312  | 986      | 17,4     |
| 18,3704 | 1000     | 18,8     | 18,3175  | 966      | 20,8     |
| 18,3302 | 990      | 17,2     |          |          |          |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 63  | 18,3376 $\pm$ 0,0177 | 974 $\pm$ 22 | 17,3 $\pm$ 1,6 |
| W 640 | 18,3222 $\pm$ 0,0108 | 972 $\pm$ 15 | 18,7 $\pm$ 2,0 |

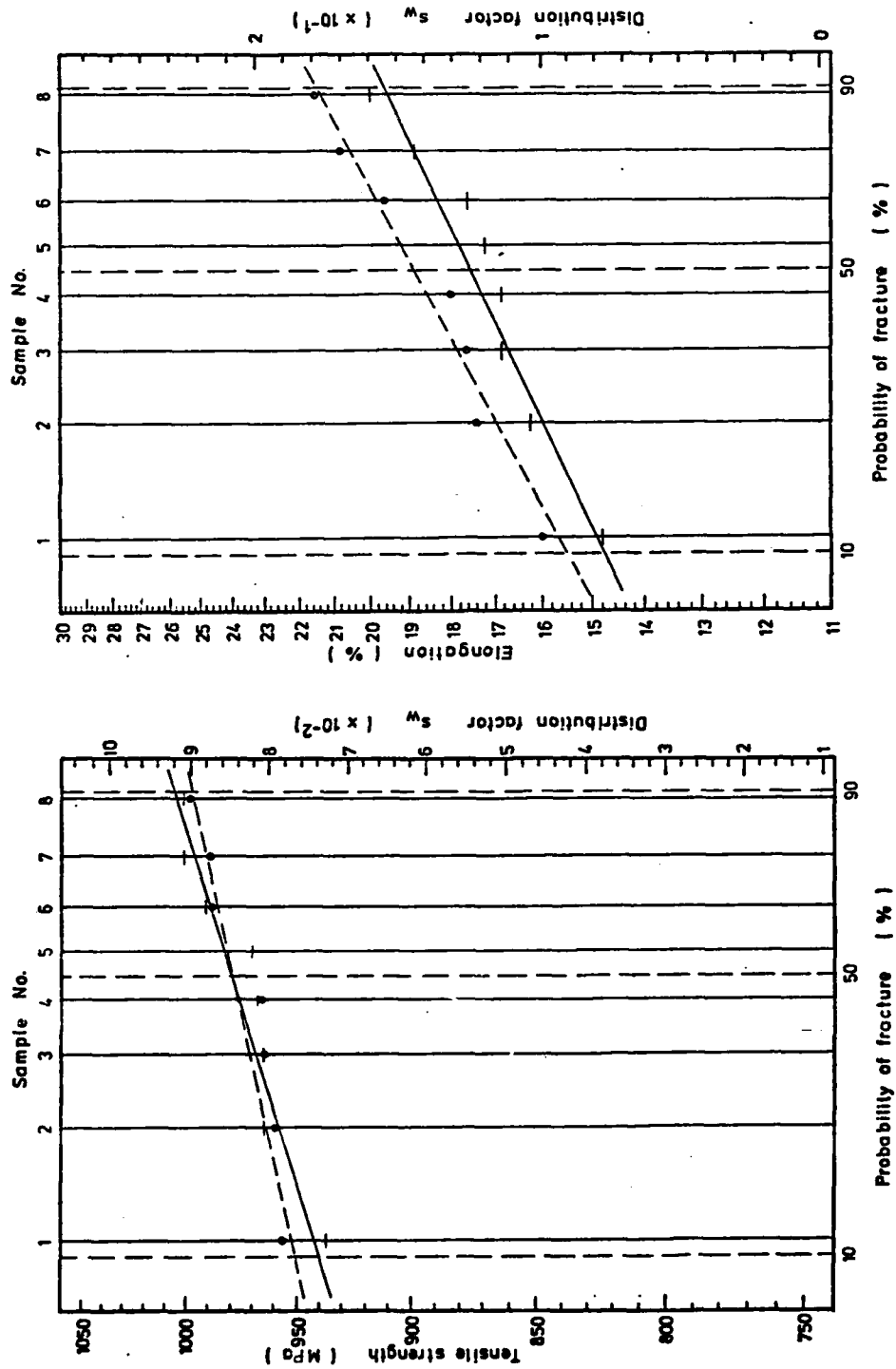


Fig.94: Weibull-diagrams for E63W (—) and W64O/81 (---)

Powder E 67

Table 25: Mechanical properties of the samples prepared from  
E 67 and of the reference sample from E 640/81

| E 67    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 18,3545 | 951      | 16,0     | 18,3082  | 963      | 16,0     |
| 18,3294 | 965      | 18,0     | 18,3211  | 957      | 19,6     |
|         |          |          | 18,3198  | 959      | 21,6     |
| 18,3388 | 987      | 20,0     | 18,3412  | 997      | 18,0     |
| 18,3119 | 952      | 12,6     | 18,3162  | 973      | 17,6     |
| 18,3519 | 967      | 14,0     |          |          |          |
| 18,3309 | 982      | 17,6     | 18,3312  | 986      | 17,4     |
| 18,3316 | 990      | 19,0     | 18,3175  | 966      | 20,8     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 67  | 18,3356 $\pm$ 0,0146 | 971 $\pm$ 16 | 16,7 $\pm$ 2,7 |
| W 640 | 18,3222 $\pm$ 0,0108 | 972 $\pm$ 15 | 18,7 $\pm$ 2,0 |

AD-A129 652

THE INFLUENCE OF IMPURITIES IN TUNGSTEN AND MATRIX  
COMPOSITION ON THE TUN..(U) TECHNISCHE UNIV VIENNA  
(AUSTRIA) INST FUER CHEMISCHE TECHNOLO.. B LUX ET AL.  
OCT 82 DAJA37-80-C-0008

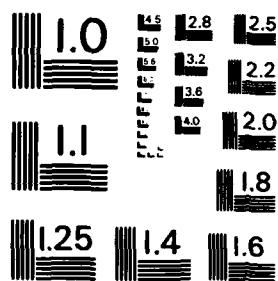
2/2

UNCLASSIFIED

F/G 11/6

NL

END  
7 8 9  
BT #



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS - 1963 - A

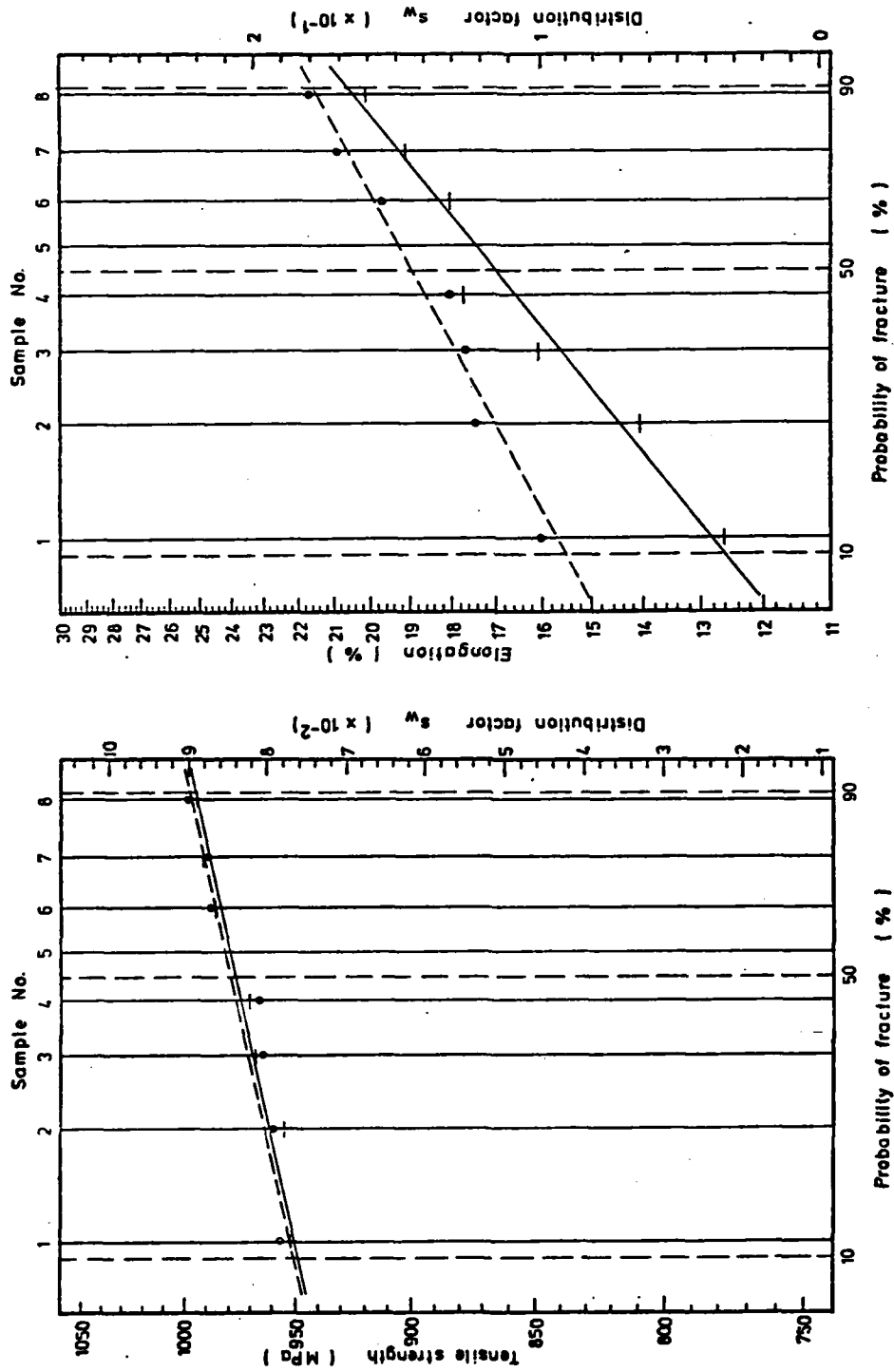


Fig. 92: Weibull-diagrams for I67W (—) and W64O/81 (---)

Powder E 71

Table 26: Mechanical properties of the samples prepared from E 71 and of the reference sample from E 640/81

| E 71    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 18,3595 | 974      | 19,2     | 18,3082  | 963      | 16,0     |
| 18,3414 | 984      | 18,0     | 18,3211  | 957      | 19,6     |
| 18,3352 | 816      | 6,0      | 18,3198  | 959      | 21,5     |
| 18,3197 | 979      | 20,0     | 18,3412  | 997      | 18,0     |
| 18,2330 | 985      | 18,2     | 18,3162  | 973      | 17,6     |
| 18,3445 | 995      | 16,0     | 18,3312  | 986      | 17,4     |
| 18,3289 | 997      | 21,6     | 18,3175  | 965      | 20,8     |
| 18,3167 | 973      | 13,6     |          |          |          |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 71  | 18,3335 $\pm$ 0,0147 | 986 $\pm$ 9  | 18,8 $\pm$ 1,9 |
| W 640 | 18,3222 $\pm$ 0,0108 | 972 $\pm$ 15 | 18,7 $\pm$ 2,0 |

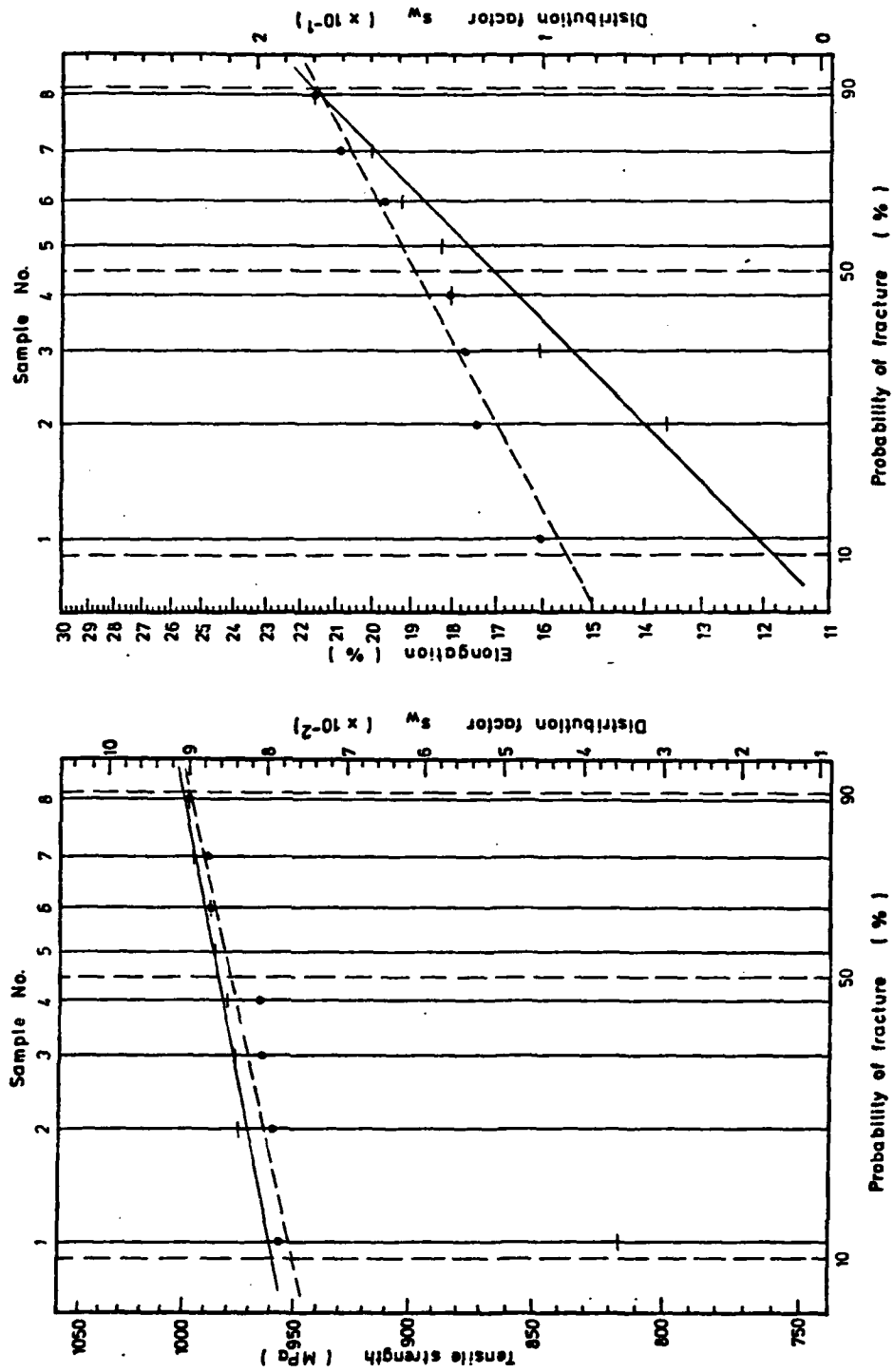


Fig.93: Weibull-diagrams for E71W (---) and W640/81 (—)

Powder E 79

Table 27: Mechanical properties of the samples prepared from  
E 79 and of the reference sample from E 640/81

| E 79    |          |          | 640/81  |          |          |
|---------|----------|----------|---------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$  | $\sigma$ | $\delta$ |
| 18,3113 | 857      | 6,80     | 18,3151 | 945      | 12,00    |
| 18,2824 | 932      | 8,80     | 18,3049 | 925      | 12,00    |
|         |          |          | 18,3172 | 950      | 9,8      |
| 18,2665 | 962      | 10,80    | 18,3543 | 972      | 13,6     |
| 18,3457 | 969      | 12,0     | 18,9458 | 972      | 11,2     |
|         |          |          | 18,3337 | 1004     | 20,2     |
|         |          |          | 18,3400 | 994      | 19,6     |
| 18,3263 | 973      | 16,8     | 18,3268 | 998      | 14,6     |
| 18,2870 | 919      | 10,8     | 18,3160 | 988      | 10,0     |
|         |          |          | 18,3215 | 1014     | 15,0     |
|         |          |          | 18,3049 | 1034     | 18,8     |
| 18,3282 | 70       | 20,0     | 18,3225 | 979      | 18,8     |
| 18,3025 | 972      | 19,2     | 18,3510 | 981      | 15,2     |
|         |          |          | 18,3205 | 980      | 19,0     |
|         |          |          | 18,2987 | 976      | 19,5     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 79  | 18,3062 $\pm$ 0,0267 | 944 $\pm$ 41 | 13,2 $\pm$ 4,9 |
| W 640 | 18,3249 $\pm$ 0,0170 | 981 $\pm$ 27 | 15,2 $\pm$ 3,7 |

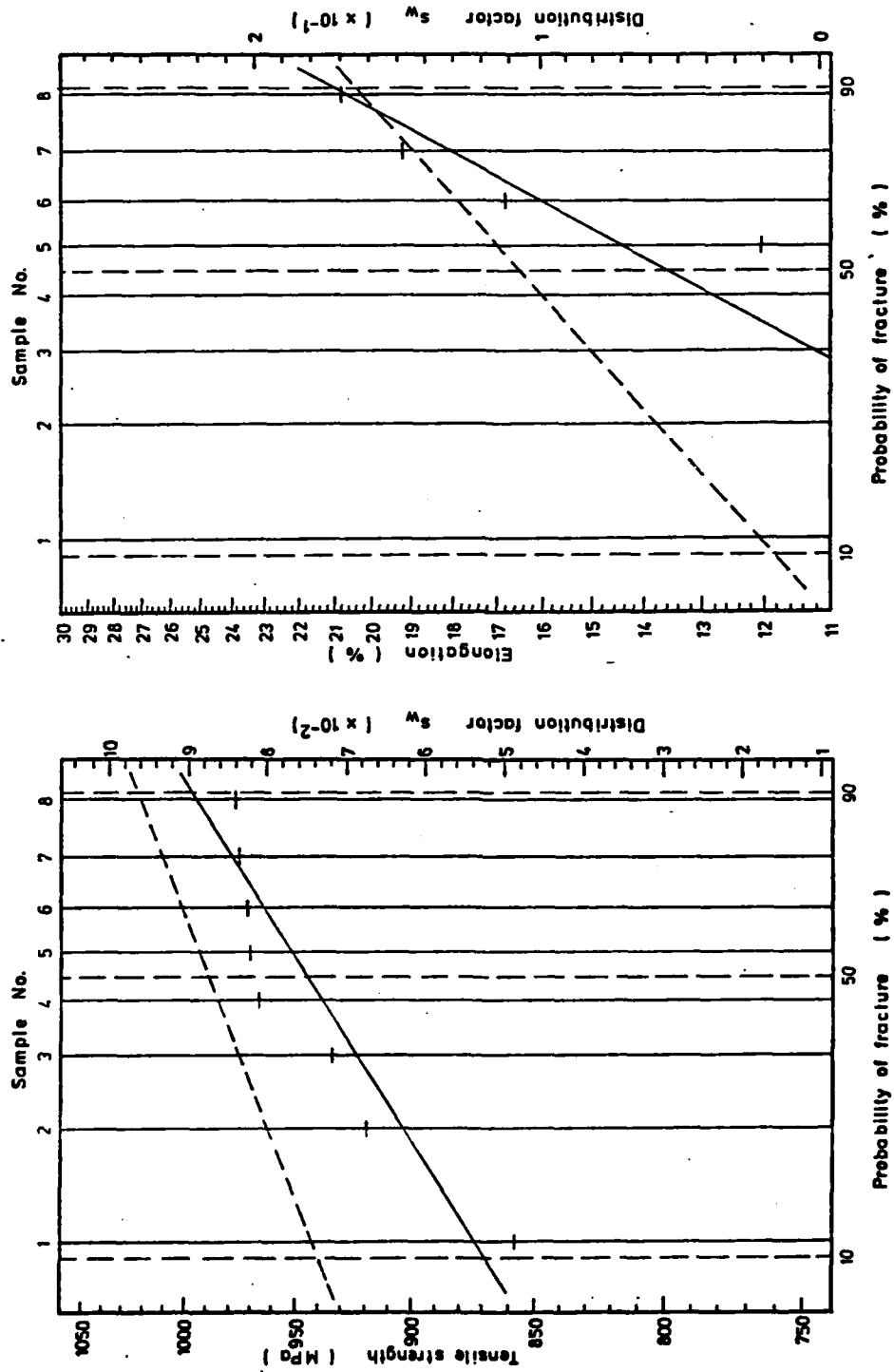


Fig. 94: Weibull-diagrams for E79W (—) and W640/81 (- - -)

Powder E 83

Table 28: Mechanical properties of the samples prepared from E 83 and of the reference sample from W 640/81

| E 83    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 18,3482 | 983      | 18,2     | 18,3325  | 973      | 16,0     |
| 18,3391 | 949      | 14,6     | 18,3093  | 973      | 19,0     |
|         |          |          | 18,3262  | 973      | 18,6     |
|         |          |          | 18,3001  | 972      | 19,2     |
| 18,3484 | 950      | 16,0     | 18,322   | 975      | 19,2     |
| 18,3396 | 947      | 18,8     | 18,3198  | 965      | 20,6     |
| 18,3402 | 959      | 16,0     | 18,3333  | 975      | 15,2     |
| 18,3069 | 960      | 19,0     | 18,3295  | 958      | 20,4     |
| 18,3267 | 971      | 15,6     | 18,3325  | 967      | 19,6     |
| 18,3270 | 944      | 17,0     | 18,3150  | 959      | 17,6     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 83  | 18,3345 $\pm$ 0,0138 | 958 $\pm$ 13 | 16,9 $\pm$ 1,5 |
| W 640 | 18,3220 $\pm$ 0,0111 | 969 $\pm$ 6  | 18,5 $\pm$ 1,8 |

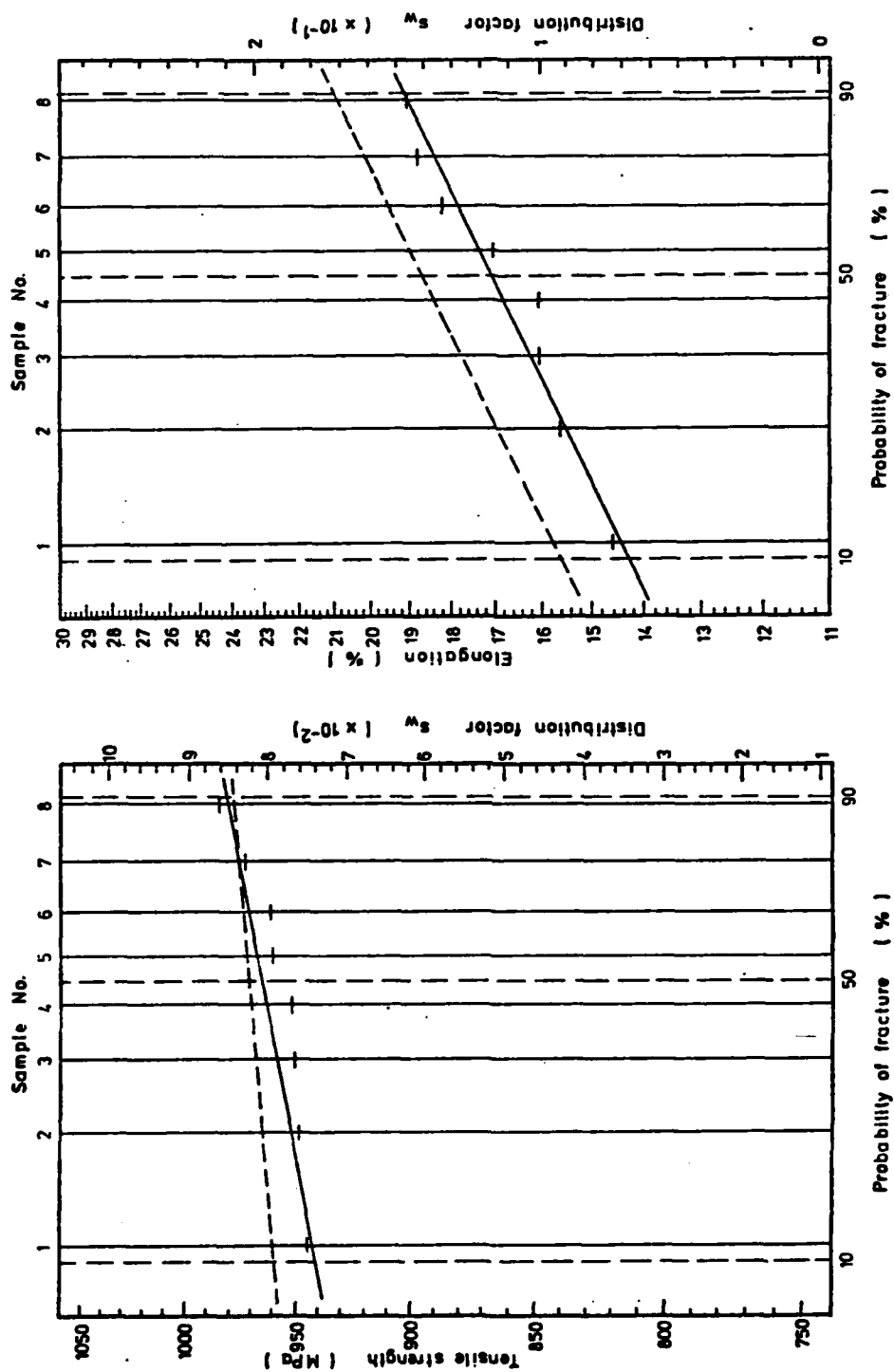


Fig. 95: Weibull-diagrams for E83W (—) and W640/81 (---)

Powder E 87

Table 29: Mechanical properties of the samples prepared from E 87 and of the reference samples from W 640/81

| E 87                        |                  |              | W 640/81                    |                  |              |
|-----------------------------|------------------|--------------|-----------------------------|------------------|--------------|
| $\rho$ (g/cm <sup>3</sup> ) | $\sigma_b$ (MPa) | $\delta$ (%) | $\rho$ (g/cm <sup>3</sup> ) | $\sigma_b$ (MPa) | $\delta$ (%) |
| 18,3058                     | 949              | 12,4         | 18,3194                     | 981              | 14,0         |
| 18,2940                     | 981              | 17,0         | 18,3363                     | 985              | 16,4         |
|                             |                  |              | 18,3288                     | 970              | 16,8         |
| 18,3084                     | 953              | 16,0         | 18,2933                     | 993              | 17,4         |
| 18,3151                     | 1009             | 14,8         | 18,3500                     | 1004             | 21,0         |
| 18,3077                     | 1001             | 17,4         |                             |                  |              |
| 18,3079                     | 971              | 12,6         | 18,3618                     | 977              | 20,0         |
| 18,3014                     | 961              | 13,4         |                             |                  |              |
| 18,3949                     | 972              | 13,6         |                             |                  |              |
| 18,3212                     | 927              | 14,2         | 18,2960                     | 941              | 14,6         |
| 18,2901                     | 932              | 12,8         | 18,3502                     | 948              | 19,0         |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 87  | 18,3147 $\pm$ 0,0296 | 970 $\pm$ 28 | 14,4 $\pm$ 1,8 |
| W 640 | 18,3295 $\pm$ 0,0253 | 975 $\pm$ 21 | 17,4 $\pm$ 2,5 |

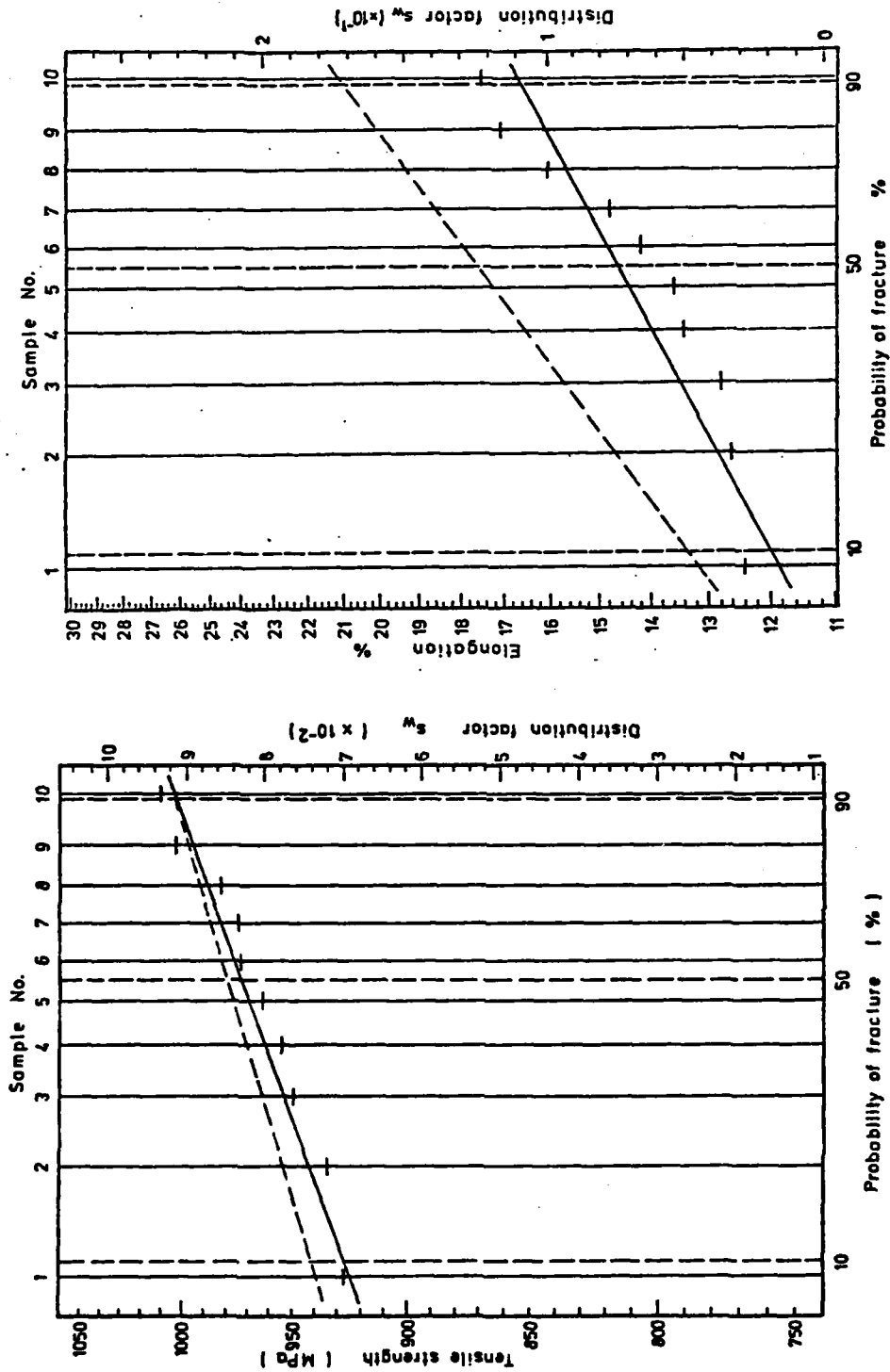


Fig. 96: Weibull-diagrams for E87W (—) and W64O/81 (---)

Powder E 91

Table 30: Mechanical properties of the samples prepared from  
E 91 and of the reference samples from W 640/81

| E 91    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 18,2939 | 980      | 14,2     | 18,3194  | 981      | 14,0     |
| 18,2630 | 974      | 14,8     | 18,3363  | 985      | 16,4     |
| 18,2160 | 943      | 12,0     | 18,3288  | 970      | 16,8     |
| 18,2959 | 986      | 15,8     | 18,2933  | 933      | 17,4     |
| 18,2491 | 983      | 16,2     | 18,3500  | 1004     | 21,0     |
| 18,2628 | 960      | 17,0     | 18,3618  | 977      | 20,0     |
| 18,2252 | 952      | 12,6     |          |          |          |
| 18,1745 | 954      | 12,2     |          |          |          |
| 18,2756 | 918      | 11,6     | 18,2960  | 941      | 14,6     |
| 18,2852 | 918      | 12,8     | 18,3502  | 948      | 19,0     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 91  | 18,2541 $\pm$ 0,0388 | 957 $\pm$ 25 | 13,9 $\pm$ 1,9 |
| W 640 | 18,3295 $\pm$ 0,0253 | 975 $\pm$ 21 | 17,4 $\pm$ 2,5 |

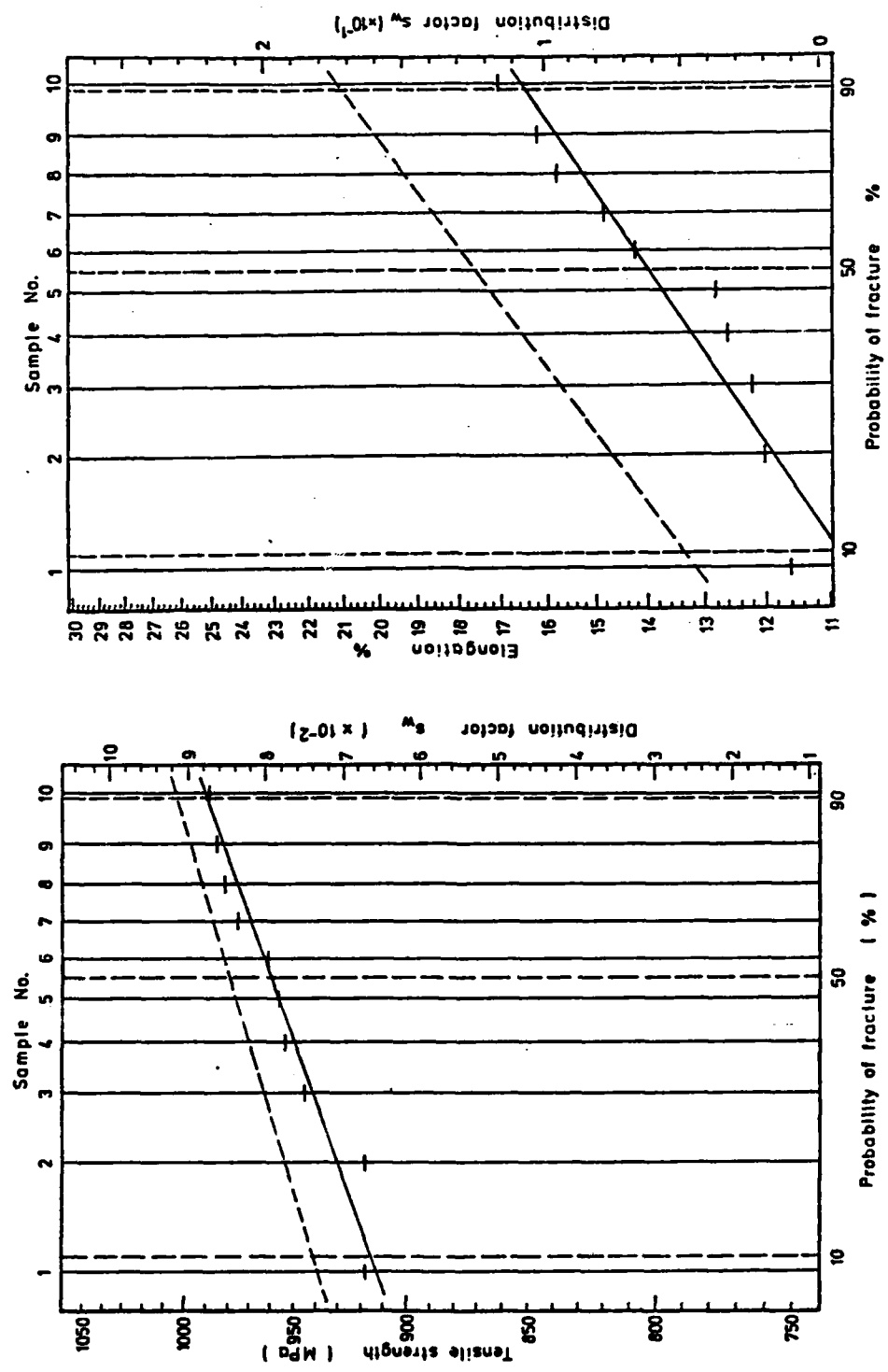


Fig. 97 Weibull-diagrams for E91W (—) and W640/81 (---)

Powder E 99

Table 31: Mechanical properties of the samples prepared from E 99 and of the reference samples from W 640/81

| E 99    |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\xi$   | $\sigma$ | $\delta$ | $\xi$    | $\sigma$ | $\delta$ |
| 18,3420 | 994      | 15,4     | 18,3194  | 981      | 14,0     |
| 18,3444 | 960      | 13,0     | 18,3363  | 985      | 16,4     |
|         |          |          | 18,3288  | 970      | 16,8     |
| 18,2975 | 978      | 14,0     | 18,2933  | 993      | 17,4     |
| 18,3334 | 991      | 12,0     | 18,3500  | 1004     | 21,0     |
| 18,3468 | 994      | 13,4     |          |          |          |
| 18,3255 | 1006     | 16,0     | 18,3618  | 977      | 20,0     |
| 18,3148 | 1000     | 14,8     |          |          |          |
| 18,3522 | 989      | 14,0     |          |          |          |
| 18,3565 | 924      | 13,1     | 18,2960  | 941      | 14,6     |
| 18,3450 | 938      | 15,4     | 18,3502  | 948      | 19,0     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 99  | 18,3358 $\pm$ 0,0184 | 977 $\pm$ 28 | 14,1 $\pm$ 1,3 |
| W 640 | 18,3295 $\pm$ 0,0253 | 975 $\pm$ 21 | 17,4 $\pm$ 2,5 |

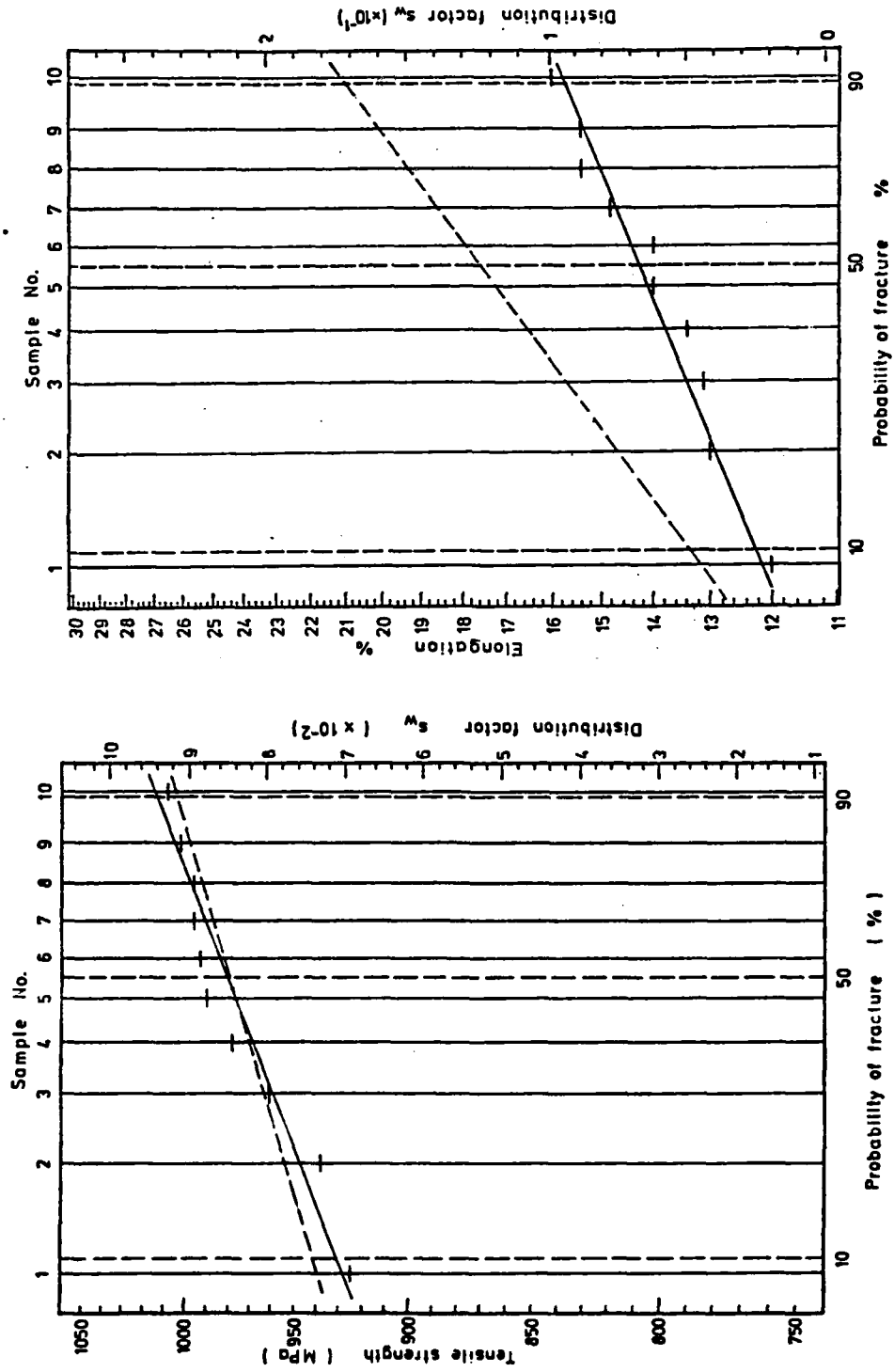


Fig. 98: Weibull-diagrams for E99W (—) and W64O/81 (---)

Powder E 103

Table 32: Mechanical properties of the samples prepared from  
E 103 and of the reference samples from W 640/81

| E 103   |                |          | W 640/81 |                |          |
|---------|----------------|----------|----------|----------------|----------|
| $\rho$  | $\bar{\sigma}$ | $\delta$ | $\rho$   | $\bar{\sigma}$ | $\delta$ |
| 18,3852 | 949            | 13,4     |          |                |          |
| 18,3615 | 961            | 12,4     |          |                |          |
| 18,3763 | 964            | 16,6     |          |                |          |
| 18,3759 | 956            | 13,4     |          |                |          |
| 18,3548 | 939            | 14,6     |          |                |          |
| 18,3435 | 996            | 21,2     | 18,3352  | 984            | 22,8     |
| 18,3490 | 983            | 21,0     | 18,3387  | 1023           | 18,2     |
| 18,3522 | 982            | 20,6     | 18,3308  | 969            | 21,8     |
|         |                |          | 18,3450  | 1003           | 20,6     |
|         |                |          | 18,3369  | 1001           | 22,2     |
| 18,3431 | 963            | 15,2     | 18,3323  | 1050           | 17,6     |
| 18,3474 | 956            | 12,2     | 18,3387  | 985            | 21,2     |
|         |                |          | 18,3403  | 989            | 19,0     |
|         |                |          | 18,3380  | 984            | 19,4     |
|         |                |          | 18,3294  | 988            | 19,2     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 103 | 18,3589 $\pm$ 0,0152 | 965 $\pm$ 17 | 16,4 $\pm$ 3,4 |
| W 640 | 18,3365 $\pm$ 0,0047 | 997 $\pm$ 24 | 20,2 $\pm$ 1,7 |

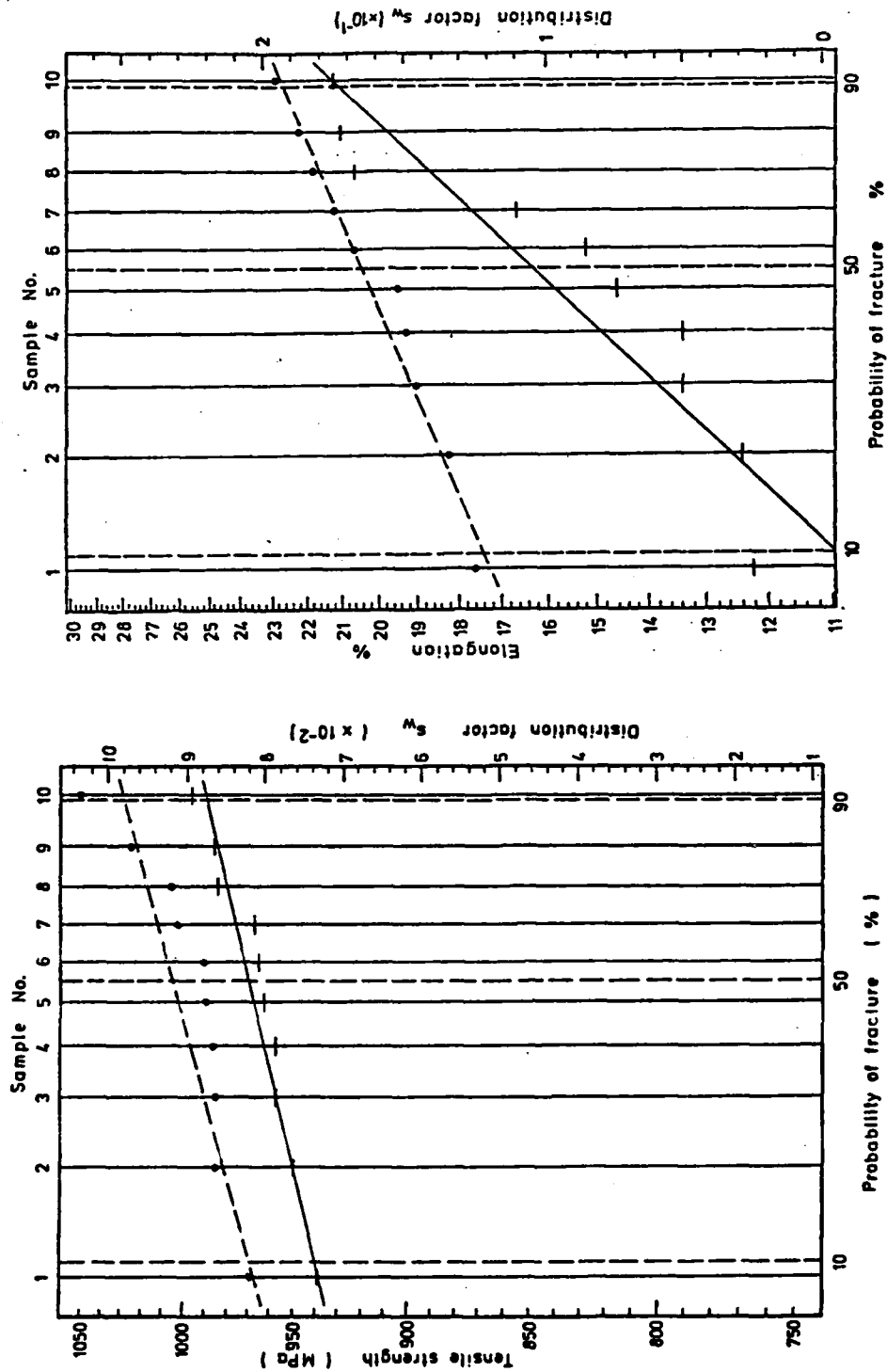


Fig. 99: Weibull-diagrams for E103W (—) and W640/81 (---)

Powder E 107

Table 33: Mechanical properties of the samples prepared from E 107 and of the reference samples from W 640/81

| E 107   |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\xi$   | $\sigma$ | $\delta$ | $\xi$    | $\sigma$ | $\delta$ |
| 18,3361 | 969      | 15,0     |          |          |          |
| 18,3541 | 967      | 17,2     |          |          |          |
| 18,3576 | 949      | 12,0     |          |          |          |
| 18,3398 | 965      | 16,4     |          |          |          |
| 18,3600 | 960      | 14,6     |          |          |          |
|         |          |          | 18,3352  | 984      | 22,8     |
| 18,3607 | 990      | 20,6     | 18,3387  | 1023     | 18,2     |
| 18,3374 | 986      | 18,8     | 18,3308  | 969      | 21,8     |
|         |          |          | 18,3450  | 1003     | 20,6     |
|         |          |          | 18,3369  | 1001     | 22,2     |
|         |          |          |          |          |          |
| 18,3564 | 981      | 14,4     | 18,3323  | 1050     | 17,6     |
| 18,3450 | 983      | 13,8     | 18,3387  | 985      | 21,2     |
| 18,3491 | 966      | 15,2     | 18,3403  | 989      | 19,0     |
|         |          |          | 18,3380  | 984      | 19,4     |
|         |          |          | 18,3294  | 988      | 19,2     |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 107 | 18,3496 $\pm$ 0,0095 | 971 $\pm$ 13 | 15,8 $\pm$ 2,5 |
| W 640 | 18,3365 $\pm$ 0,0047 | 998 $\pm$ 23 | 20,2 $\pm$ 1,3 |

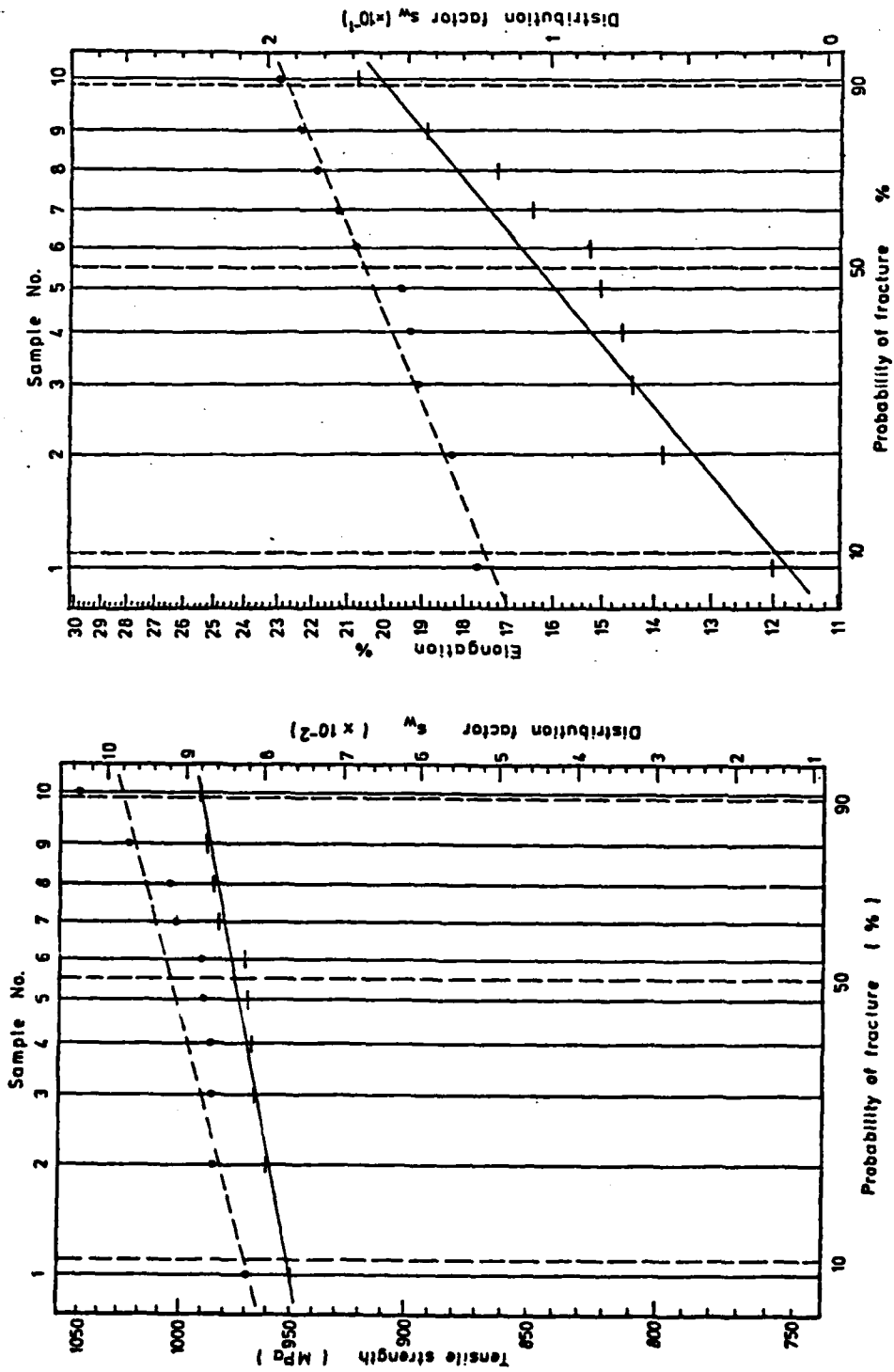


Fig. 100: Weibull-diagrams for E107W (—) and W640/81 (---)

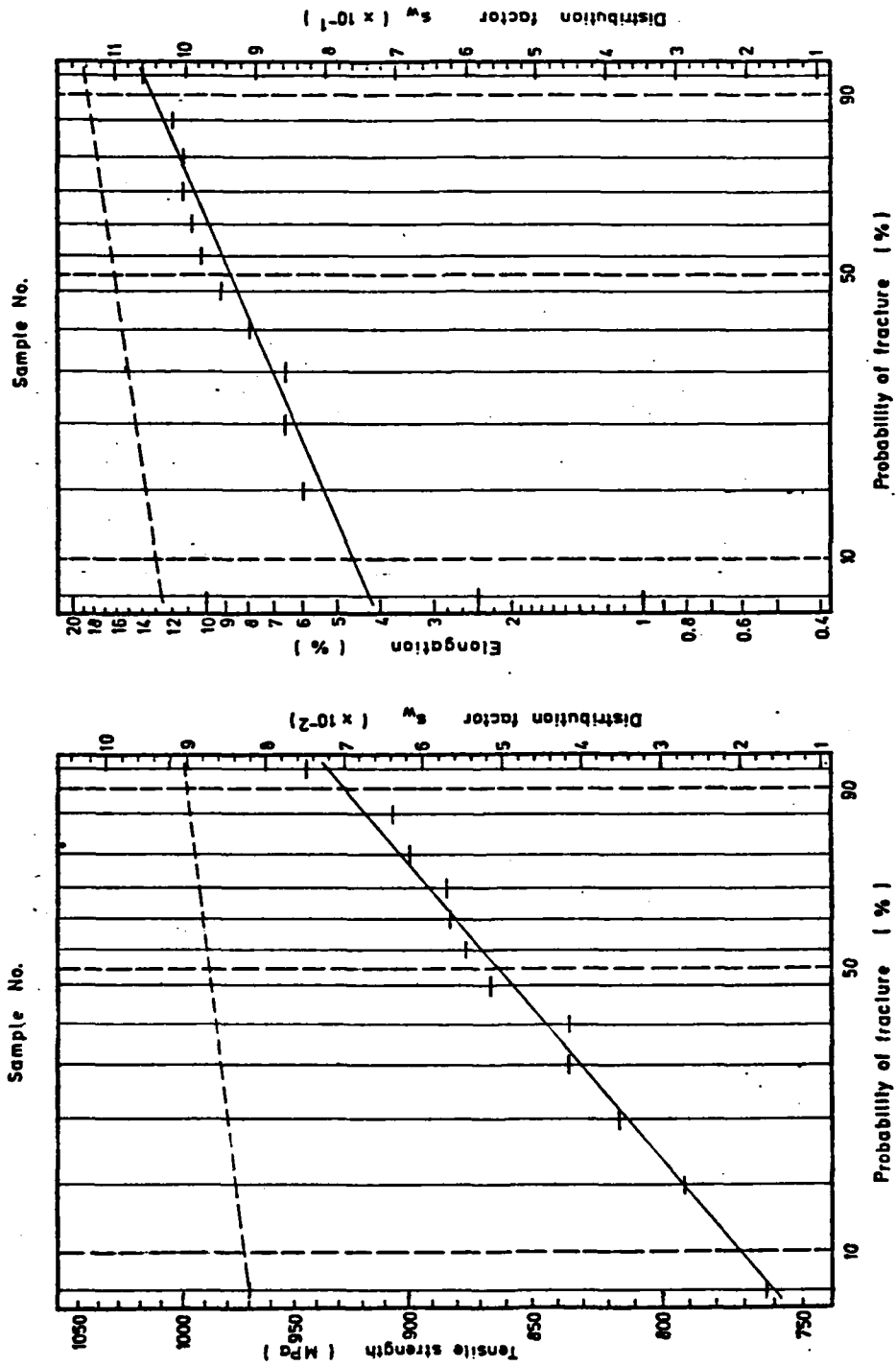
Powder E 111

Table 34: Mechanical properties of the samples prepared from  
E 111 and of the reference samples from W 640/81

| E 111   |          |          | W 640/81 |          |          |
|---------|----------|----------|----------|----------|----------|
| $\rho$  | $\sigma$ | $\delta$ | $\rho$   | $\sigma$ | $\delta$ |
| 17,3363 | 945      | 11,2     | 18,2722  | 989      | 16,0     |
| 17,2927 | 867      | 8,0      | 18,2550  | 989      | 17,5     |
| 17,2151 | 877      | 11,2     | 18,2728  | 979      | 19,2     |
|         |          |          | 18,2684  | 984      | 16,4     |
| 17,6825 | 882      | 10,8     | 18,2837  | 993      | 15,2     |
| 17,6632 | 883      | 10,2     | 18,2774  | 981      | 14,0     |
| 17,8032 | 908      | 14,0     | 18,2810  | 988      | 15,2     |
| 17,7224 | 900      | 12,0     |          |          |          |
| 17,7254 | 836      | 9,2      | 18,2234  | 970      | 14,4     |
| 17,7308 | 836      | 6,0      | 18,3261  | 979      | 12,4     |
| 17,8090 | 762      | 2,4      | 18,3207  | 970      | 17,6     |
| 17,7592 | 816      | 6,6      | 18,3180  | 1007     | 17,6     |
| 17,8816 | 791      | 6,6      |          |          |          |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 111 | 17,6351 $\pm$ 0,2227 | 853 $\pm$ 64 | 9,0 $\pm$ 3,2  |
| W 640 | 18,2817 $\pm$ 0,0305 | 984 $\pm$ 11 | 16,0 $\pm$ 2,1 |



Powder E 115

Table 35: Mechanical properties of the samples prepared from E 115 and of the reference samples from W 640/81

| E 115                 |                        |              | W 640/81              |                        |              |
|-----------------------|------------------------|--------------|-----------------------|------------------------|--------------|
| $\rho(\text{g/cm}^3)$ | $\sigma_b(\text{MPa})$ | $\delta(\%)$ | $\rho(\text{g/cm}^3)$ | $\sigma_b(\text{MPa})$ | $\delta(\%)$ |
| 18,2400               | 943                    | 10,4         | 18,3151               | 945                    | 12,0         |
| 18,3310               | 899                    | 8,8          | 18,3043               | 925                    | 12,0         |
| 18,3147               | 999                    | 15,0         | 18,3172               | 950                    | 9,8          |
| 18,3271               | 985                    | 14,6         | 18,3543               | 972                    | 13,6         |
| 18,3414               | 1025                   | 13,8         | 18,3458               | 972                    | 11,2         |
|                       |                        |              | 18,3337               | 1004                   | 20,2         |
|                       |                        |              | 18,3400               | 994                    | 19,6         |
| 18,3176               | 969                    | 19,0         | 18,3268               | 998                    | 14,6         |
| 18,3478               | 964                    | 17,6         | 18,3160               | 998                    | 10,0         |
|                       |                        |              | 18,3215               | 1014                   | 15,0         |
|                       |                        |              | 18,3049               | 1034                   | 18,8         |
| 18,3196               | 994                    | 19,0         | 18,3225               | 979                    | 18,8         |
| 18,3137               | 980                    | 20,0         | 18,3510               | 981                    | 15,2         |
|                       |                        |              | 18,3205               | 980                    | 19,0         |
|                       |                        |              | 18,2987               | 976                    | 19,6         |

Mean values  $\pm$  standard deviations

|       |                      |              |                |
|-------|----------------------|--------------|----------------|
| E 115 | $18,3170 \pm 0,0312$ | $973 \pm 36$ | $15,4 \pm 3,9$ |
| W 640 | $18,3249 \pm 0,0170$ | $981 \pm 28$ | $15,3 \pm 3,8$ |

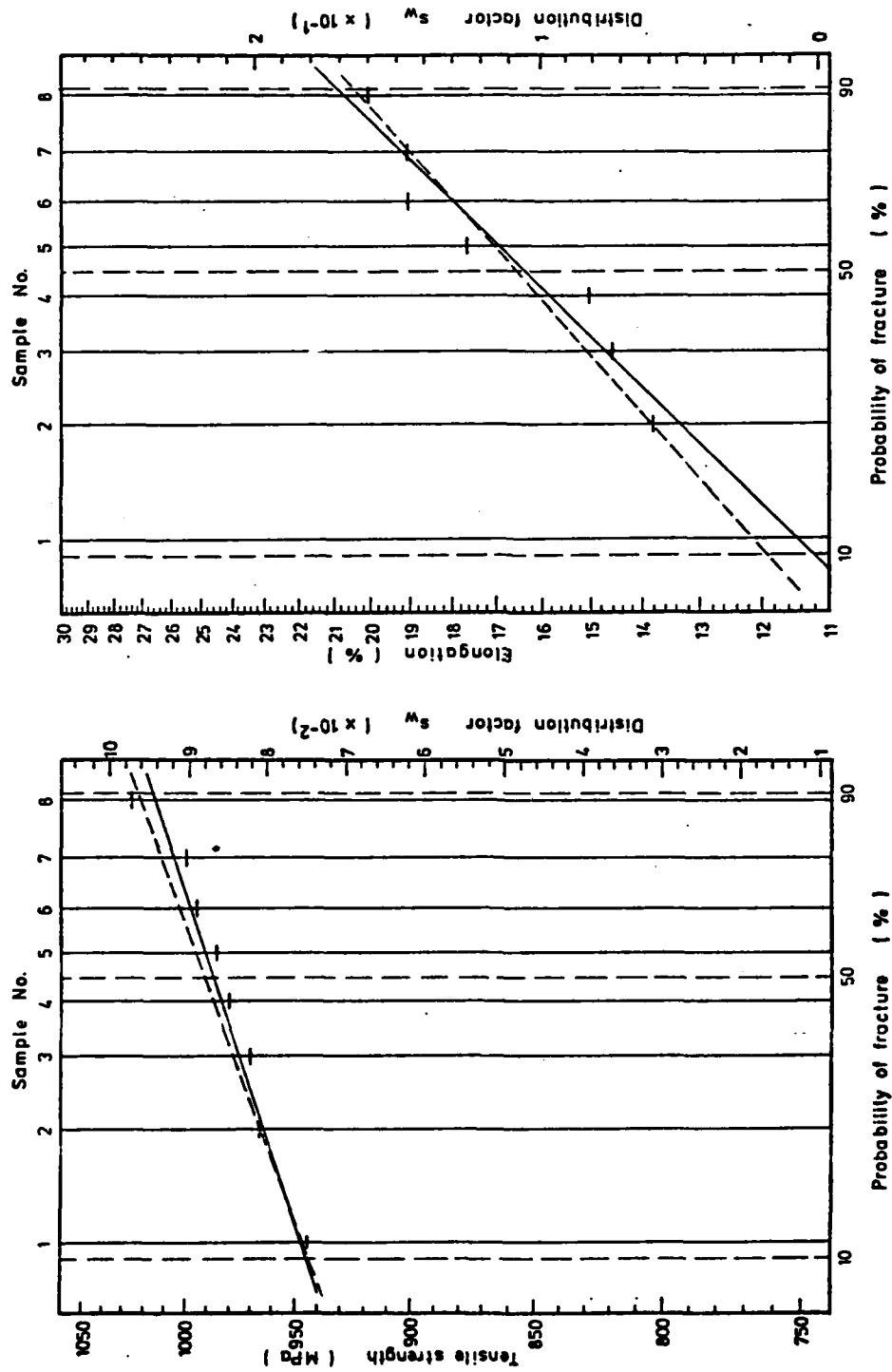


Fig.102: Weibull-diagrams for E115W (—) and W64O/81 (---)

As with the samples containing 90% W, the most conspicuous phenomenon is the quite unsatisfactory sintering of those samples prepared from coarse powders, resulting in high residual porosity and correspondingly low mechanical properties. For the 96% W samples, however, the powders resulting in insufficiently sintered bars were not only E48 and E51 but virtually all those with average grain sizes  $>10\text{ }\mu\text{m}$ . As the amount of binder melt here is much lower, W grains must be sintered more closely together before the binder melts in order to enable uniform distribution of the binder phase. Apparently powder  $>10\text{ }\mu\text{m}$  cannot meet these sintering requirements. For example, the residual porosity in samples prepared from E 51 was 7% for 96% W content as compared to 1,3 for 90% W.

The degree of porosity is shown clearly by SEM photos: With the extremely coarse E48 and E51 there are only a few grains on each photo which have sintered together properly. Most of the others are held together only by W-W grain boundaries which, as described in Chapter 3, are inherently weak and unable to withstand higher degrees of deformation (Fig.103, 104). There are even some areas where no liquid phase sintering seems to have occurred at all (Fig.105) and the structure looks like that of solid state sintered W. Comparison with Fig.41, depicting an only prereduced sample, shows the striking similarity; understandably, the mechanical properties are equally unsatisfactory.

E 61, with a starting powder size of  $\sim 18\text{ }\mu\text{m}$ , yielded somewhat better results, although the typical rounded shapes of W grains which had not undergone liquid phase sintering are visible in several places (Fig.106), and there are also many W-W grain boundaries in the fracture surface. E 56 with a medium grain size of  $\sim 12\text{ }\mu\text{m}$  resulted in largely sound compacts, as also indicated by its density value, although the SEM photo (Fig.107) reveals numerous large W-W grain boundaries indicating somewhat defective sintering. Fig.103-107,

arranged according to their elongation, closely resemble the sequence Fig.41-45, better ductility being associated with more satisfactory liquid phase sintering. In Fig. 108 the elongation of equally sintered 96% W samples is plotted against the starting powder size.

It is evident that the fine powders are closely grouped together, while all samples with elongations  $< 10\%$  have been prepared from coarse W powders ( $> 10 \mu\text{m}$ ). Even the extremely porous samples prepared from E111 are more ductile than the almost fully dense products from E56, an observation which also stresses the importance of proper liquid phase sintering, a factor apparently much more important than the particular purity of the starting powder.

The second type of pore formation observed with 90% W content, i.e. pore formation during liquid phase sintering, is not as pronounced with the 96% W samples.

This somewhat surprising result can be explained by the more efficient sintering cycle particularly the much higher temperature for sintering and pre-reduction. As pore closure occurs at considerably higher temperatures, the pre-reduction is more complete and leaves less oxide to be reduced during the liquid phase sintering. The only powder that exhibited really pronounced pore formation and blisters was E111, which behaved exactly as the sample with 90% W. Most of the large pores are situated near the surface rather than in the centre of the test bars. Most other powder also exhibited a few pores in the fracture surface, even those with very high ductility; the pores are quite different in size and shape and therefore also in their effect on the mechanical properties (compare Fig.109, 111). The basic structure however seems to be sound, as indicated by the fracture surface outside of the pores (Fig.110, 112); if there is even one pore in the whole test bar, it will probably be found in the fracture surface, as it is a weak point in the structure. Even in the fracture surface of a reference bar (Fig.113) that showed an elongation of 21,6%, a small pore is discernible in the

lower right corner of the photo. Pore closure or at least shrinkage might be achieved by hot isostatic pressing of the sintered samples, although this process is rather expensive and recommendable only for the highest standards.

Generally, with the modified sintering cycle the sintering of the heavy metals with high W content has reached a surprisingly high standard, Elongations >15% can be attained with satisfactory reproducibility. Heating the samples more slowly from 1400°C to sintering temperature brings a further increase in ductility as the slower heating apparently promotes reduction of the above mentioned oxides. If fine W powder (<5 um) is used for production, and if the sintering is performed following the optimum sintering cycle, the heavy metals are not very sensitive to the trace impurities, commonly present in commercial W powders.

In Fig.114 and 115 the tensile strength and elongation of the doped heavy metals, with both 90 and 96% W are compared to those of the standard samples. The powders E51, E48, E61 and E56 exhibit the lowest mechanical properties due to their insufficient sintering can effect which is particularly pronounced with 96% W. With 90% W there is a continuous increase in both tensile strength and elongation, while with 96% W the remaining powders are grouped closely together, only the porous E111 (rare earth) lying between the two groups. Although the tensile strength is relatively independent of the type of doped powders, the standard powder W640/81 has proved to be generally superior both for heavy metals with 90 and 96% W.

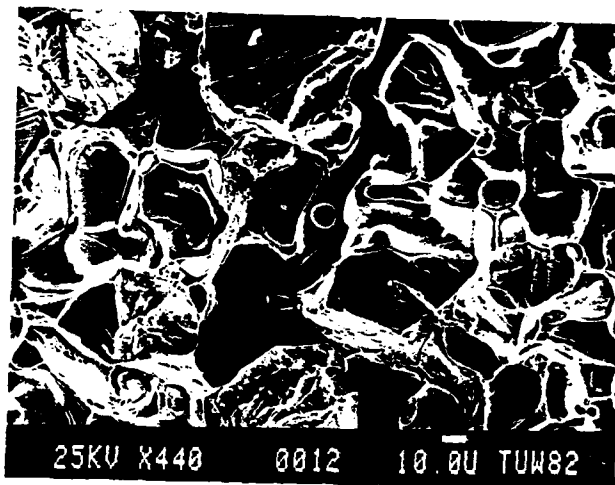


Fig.103

Heavy metal (96%W)  
sintered from  
E48W (200ppm Na);  
insufficient  
sintering

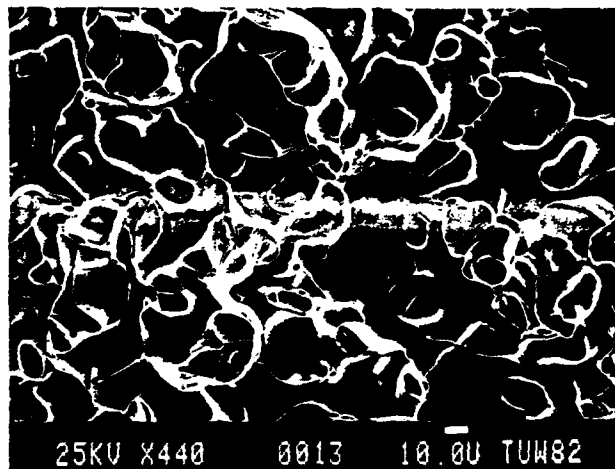


Fig.104

As Fig.10 ;  
only solid state  
sintering

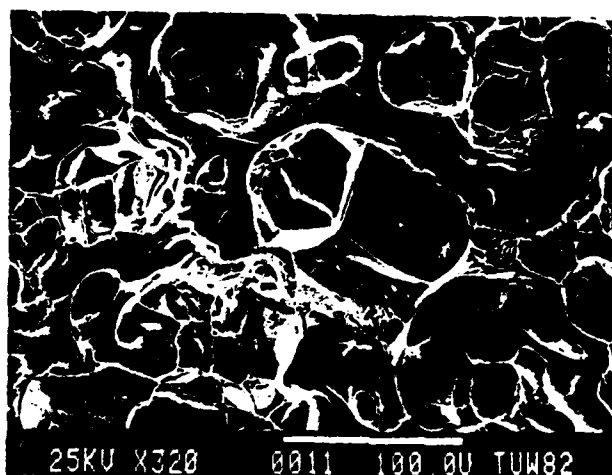


Fig.105

Heavy metal pre-  
pared from E51W;  
fracture surface  
similar to E48W  
material



Fig.106  
Heavy metal (96%W)  
sintered from  
E61W; inhomogeneous  
distribution of the  
binder

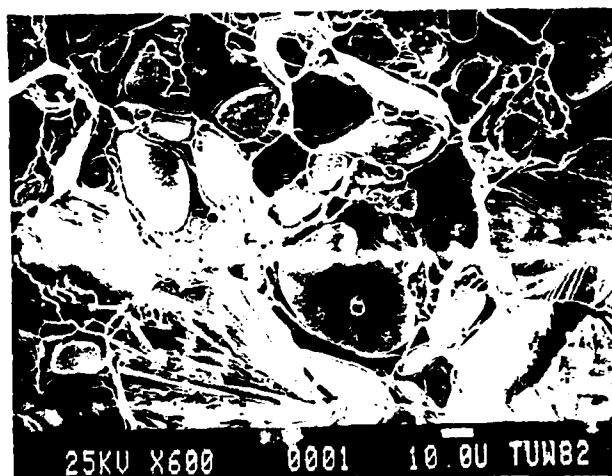


Fig.107  
Heavy metal pre-  
pared from E56W  
(doped with Al);  
intergranular  
fracture predomi-  
nant



Fig.109  
Heavy metal pre-  
pared from E71W  
(50ppm K); isolated  
pore

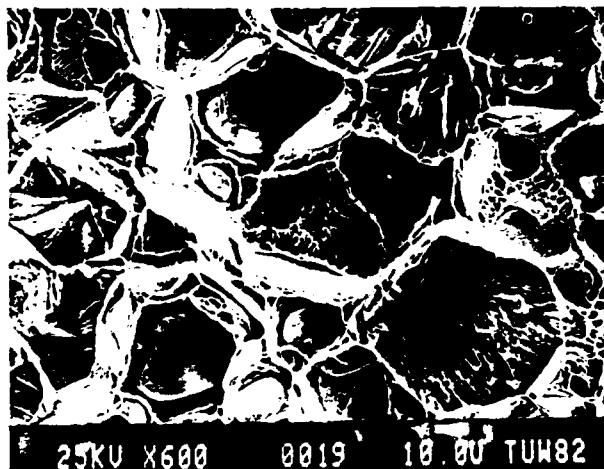


Fig.110  
Same surface as  
on Fig.115;  
no pores visible

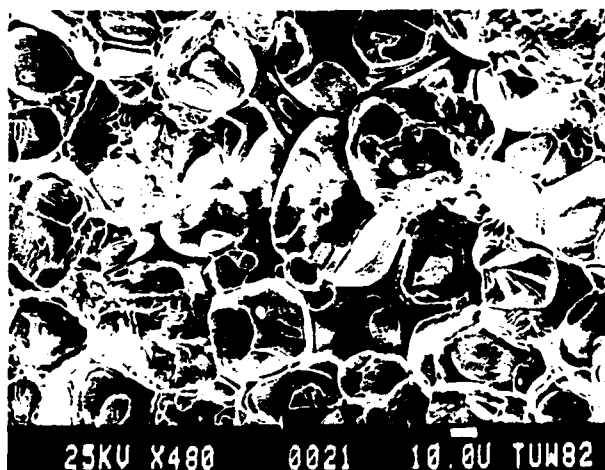


Fig.111  
Heavy metal pre-  
pared from 183W;  
small pore



Fig.112  
Same surface as  
on Fig.117;  
apparently satis-  
factory structure

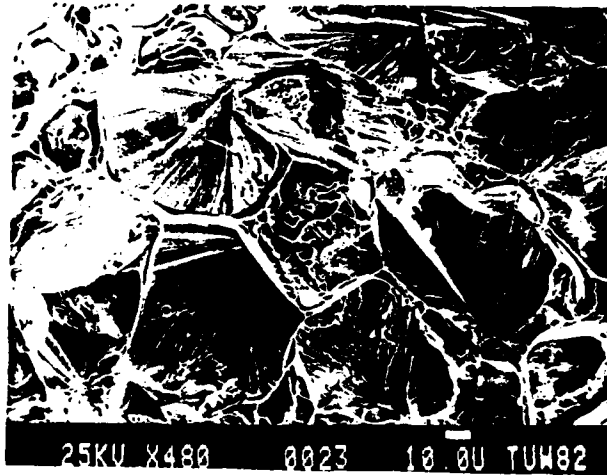


Fig.113  
Heavy metal (96%W)  
prepared from  
standard W powder  
W640/81; trans-  
granular fracture  
and excellent  
ductility

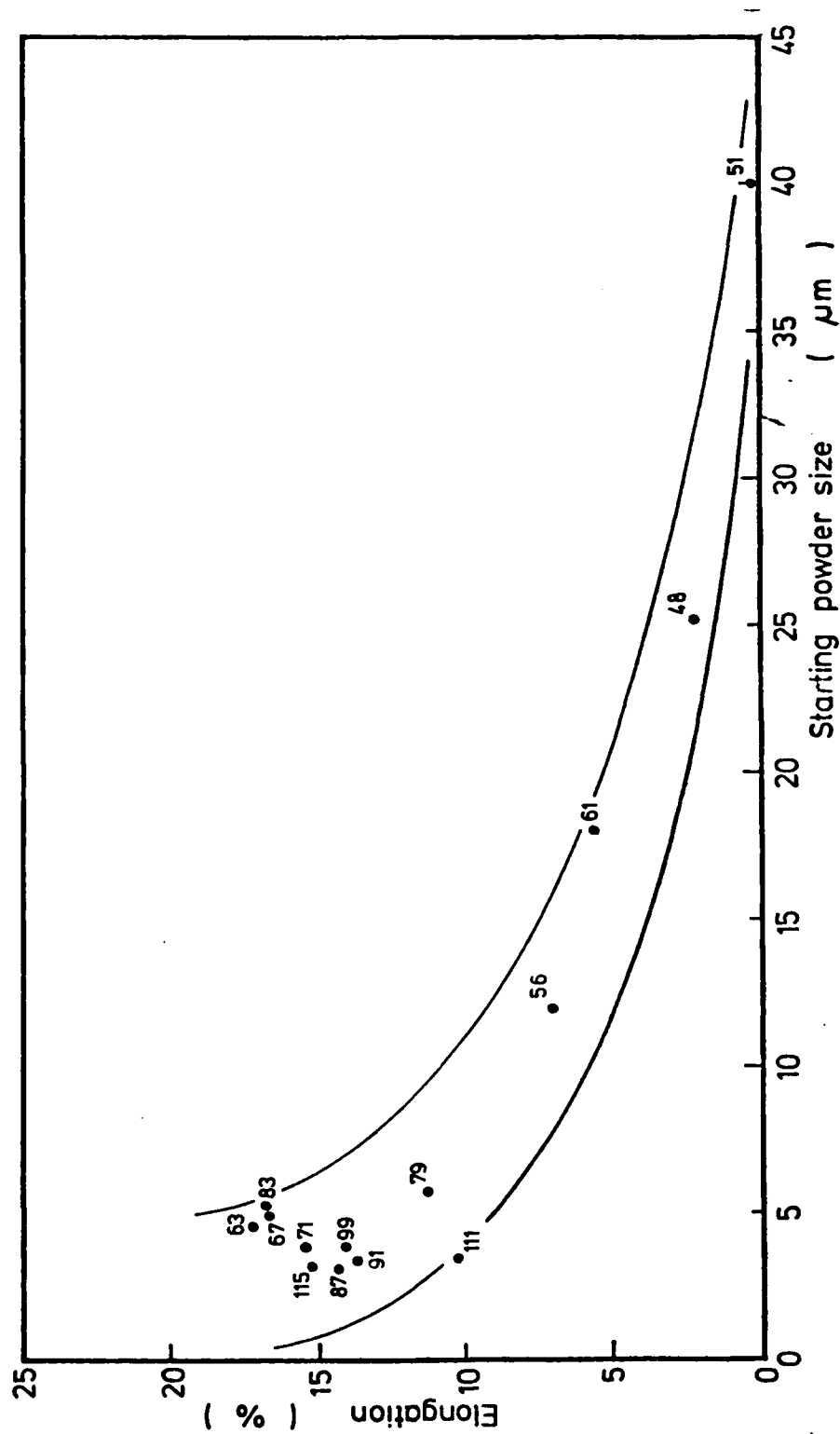


Fig.108: Influence of the starting W powder size on the ductility of heavy metals (96%W)

uniformly sintered 30 min at 1580°C.

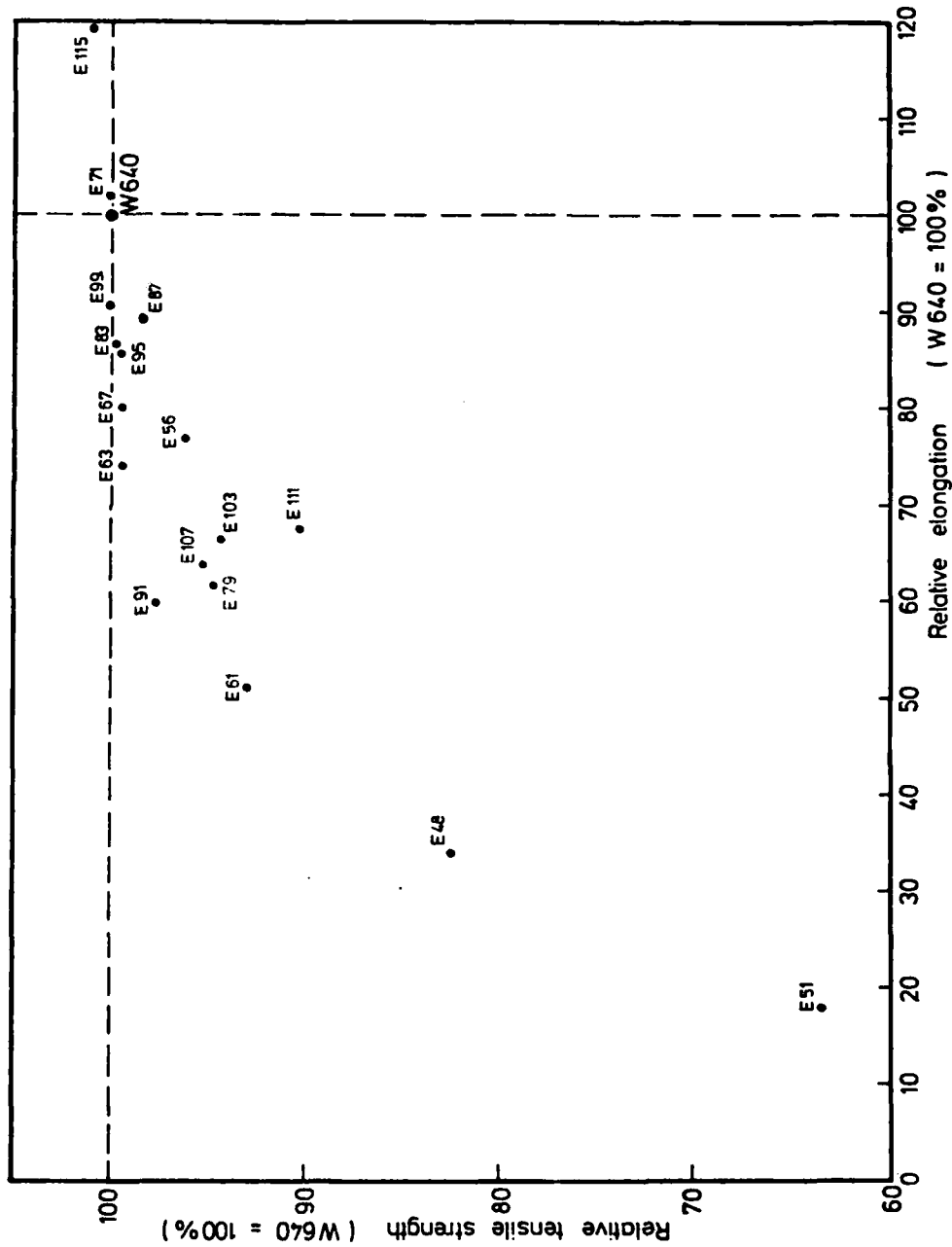


Fig. 114: Relative tensile strength and elongation of various " heavy metals  
( 903W -- 6,73Ni -- 3,39Fe )

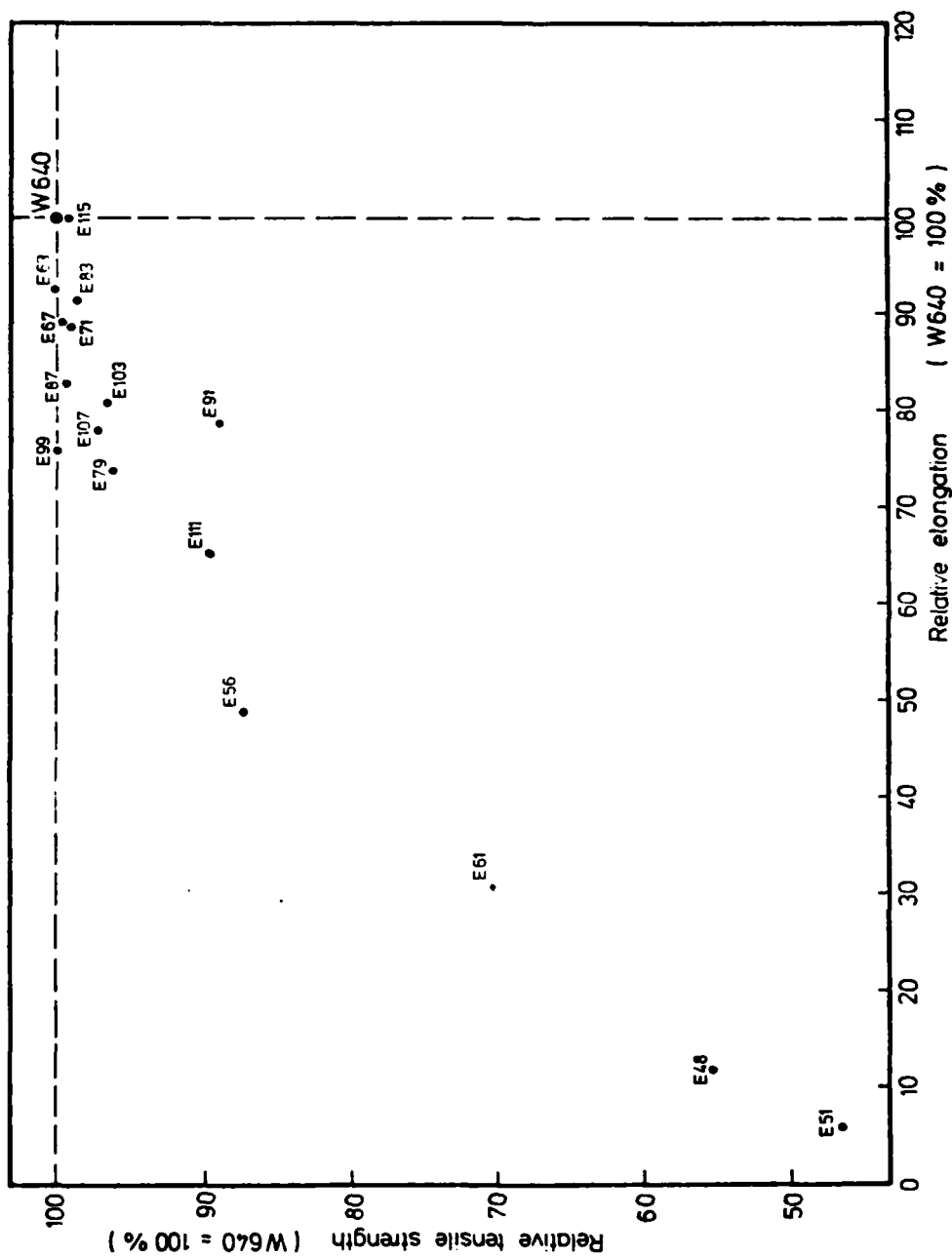


Fig. 115: Relative tensile strength and elongation of various heavy metals

( 96%W - 2,7%Ni - 1,3%Fe )

5. Heavy metals doped with carbon

From the production process, W and esp. the carbonyl powders Ni and Fe contain considerable amounts of carbon (219 ppm in Fe, 707 ppm in Ni), and furthermore, traces of pressing lubricant not removed during dewaxing may also contaminate the heavy metals. Therefore it was decided to investigate the effects of C addition on the heavy metals. By adding the carbon as very fine WC (0,7  $\mu$ m) and mixing the powders carefully, homogeneous distribution was expected. The C concentrations selected were 50, 100 and 500 ppm; to keep the effect of the carbon contained by Ni and Fe as low as possible, the experiments were carried out with samples containing 96% W. This type of heavy metals had been shown by earlier experiments to be more sensitive towards impurities than heavy metals with higher binder content. The results of the tests are shown in Tables 36-38.

**Table 36: Mechanical properties of W heavy metals (composition 96% W - 2,7% Ni - 1,3% Fe) doped with various amounts of C and sintered 30 min. at 1580°C.**

| $\rho$ (g/cm) | 50 ppm C         |              |               | 100 ppm C        |              |               | 500 ppm C        |              |               | reference samples (undoped) |              |     |
|---------------|------------------|--------------|---------------|------------------|--------------|---------------|------------------|--------------|---------------|-----------------------------|--------------|-----|
|               | $\sigma_B$ (MPa) | $\delta$ (%) | $\rho$ (g/cm) | $\sigma_B$ (MPa) | $\delta$ (%) | $\rho$ (g/cm) | $\sigma_B$ (MPa) | $\delta$ (%) | $\rho$ (g/cm) | $\sigma_B$ (MPa)            | $\delta$ (%) |     |
| 18,2998       | 994              | 19,2         | 18,3244       | 998              | 18,8         | 18,2960       | 990              | 14,0         | 18,3239       | 993                         | 23,0         |     |
| 18,2978       | 957              | 14,0         | 18,3170       | 1011             | 19,0         | 18,3352       | 985              | 13,6         | 18,2982       | 1007                        | 19,0         |     |
| 18,3158       | 1009             | 21,2         |               |                  |              |               |                  |              | 18,2993       | 988                         | 16,0         |     |
| 18,3019       | 998              | 13,8         | 18,3147       | 998              | 20,4         | 18,3244       | 988              | 22,8         | 18,3026       | 1018                        | 21,6         |     |
| 18,3197       | 966              | 16,2         | 18,3090       | 999              | 22,0         | 18,3336       | 969              | 14,4         | 18,3243       | 975                         | 16,8         |     |
| 18,3677       | 965              | 16,2         | 18,3421       | 986              | 21,6         | 18,3329       | 984              | 15,0         |               |                             |              | 125 |
| 18,3298       | 985              | 19,0         | 18,3220       | 994              | 20,8         | 18,3382       | 831              | 5,4          | 18,3125       | 984                         | 21,2         |     |
|               |                  |              |               |                  |              | 18,3262       | 927              | 10,8         | 18,3218       | 967                         | 16,2         |     |
|               |                  |              |               |                  |              |               |                  |              | 18,3223       | 964                         | 21,2         |     |
| 18,3690       | 969              | 22,2         | 18,3418       | 936              | 12,0         |               |                  |              |               |                             |              |     |
| 18,3418       | 966              | 14,8         | 18,3231       | 959              | 15,8         | 18,3539       | 976              | 17,8         | 18,3314       | 969                         | 20,2         |     |
| 18,3381       | 979              | 19,4         | 18,3486       | 979              | 15,0         | 18,3159       | 705              | 3,6          | 18,3021       | 944                         | 12,8         |     |
| 18,3375       | 984              | 18,4         | 18,3185       | 976              | 20,6         | 18,3495       | 964              | 18,8         | 18,3558       | 978                         | 18,2         |     |
| 18,3237       | 951              | 15,0         | 18,3065       | 967              | 19,2         | 18,3395       | 944              | 12,6         | 18,3310       | 972                         | 23,6         |     |
|               |                  |              | 18,3285       | 956              | 16,0         |               |                  |              |               |                             |              |     |

Table 36 continued

Mean values  $\pm$  standard deviation

|                       |                     |              |                |
|-----------------------|---------------------|--------------|----------------|
| 500 ppm C:            | $18,3314 \pm 0,016$ | $993 \pm 88$ | $13,5 \pm 5,6$ |
| 100 ppm C:            | $18,3243 \pm 0,013$ | $979 \pm 21$ | $18,2 \pm 3,0$ |
| 50 ppm C:             | $18,3278 \pm 0,022$ | $976 \pm 16$ | $17,4 \pm 2,7$ |
| standard<br>(undoped) | $18,3188 \pm 0,017$ | $980 \pm 20$ | $19,2 \pm 3,2$ |

As shown by the experiments, 50 and 100 ppm C do not cause a significant deterioration of the mechanical properties, neither of tensile strength nor , which is more important, elongation. The tensile strength values do not show any difference to those of standard samples, and the decrease in elongation is so small that it is really within the range of the natural scatter. Only in case of 500 ppm C both tensile strength and elongation are considerably lower, and esp. the scatter of the values is much higher, which indicates that the distribution of C within the samples is of critical importance. This hypothesis is supported by C analyses carried out with samples of different elongation; no significant correlation between elongation and C content could be found. For technological purposes, therefore, contamination of heavy metals with C due to insufficient dewaxing seems to be not extremely harmful, although care must be taken to avoid excessive C residue in the material.

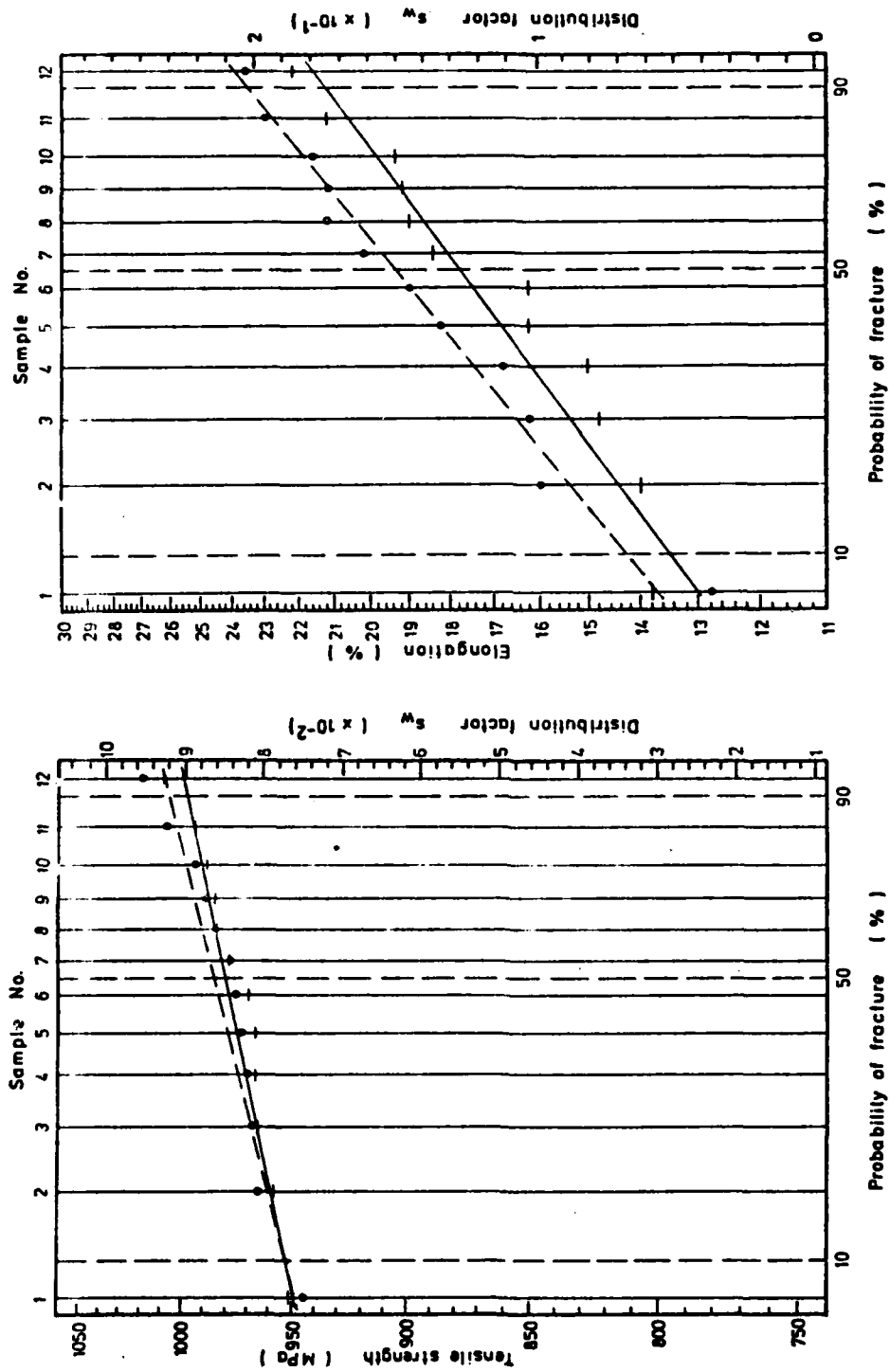


Fig.116: Weibull-diagrams for heavy metal doped with 50ppm C and undoped standard samples

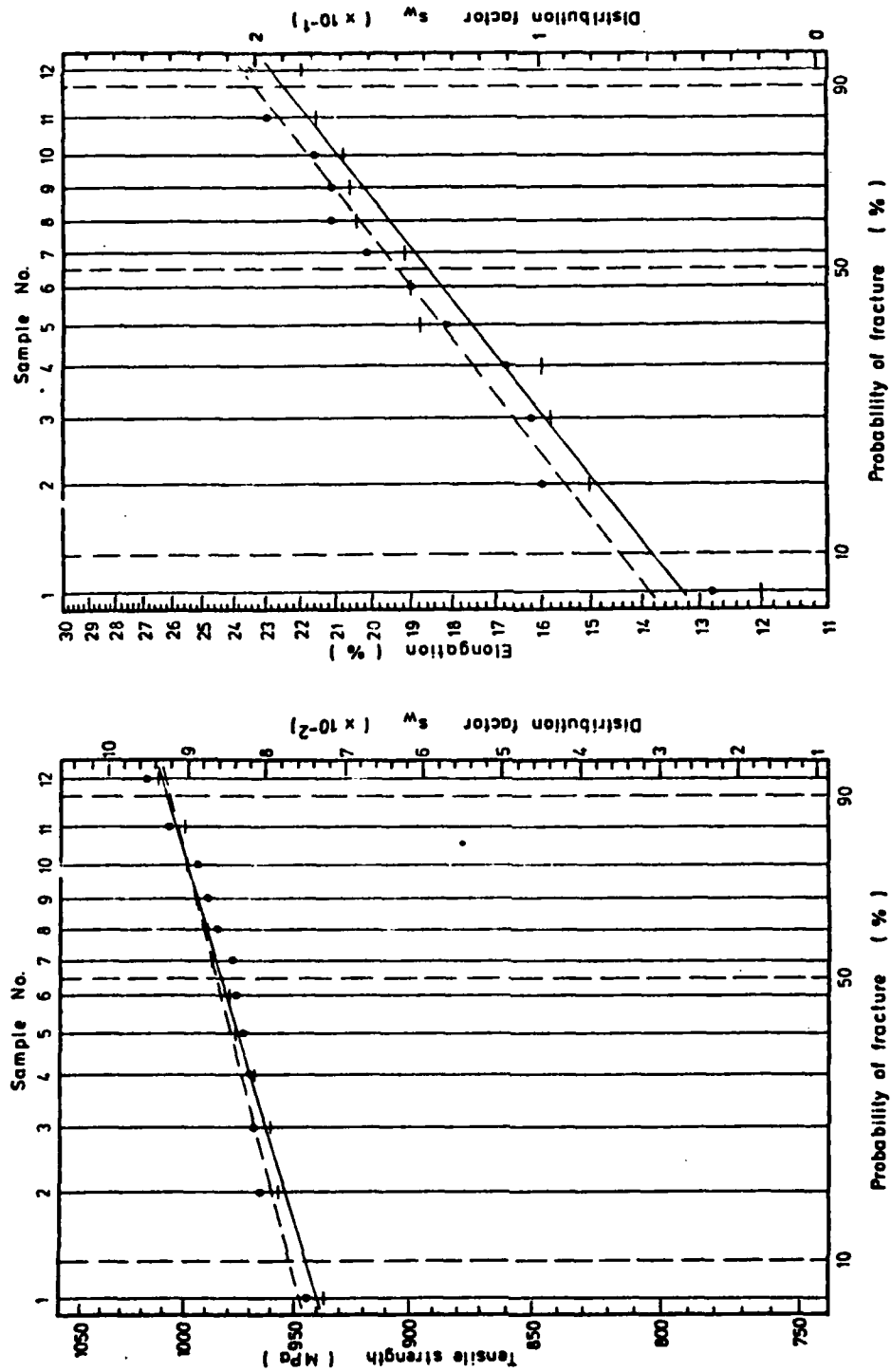


Fig. 117: Weibull-diagrams for heavy metal doped with 100ppm C and undoped standard samples

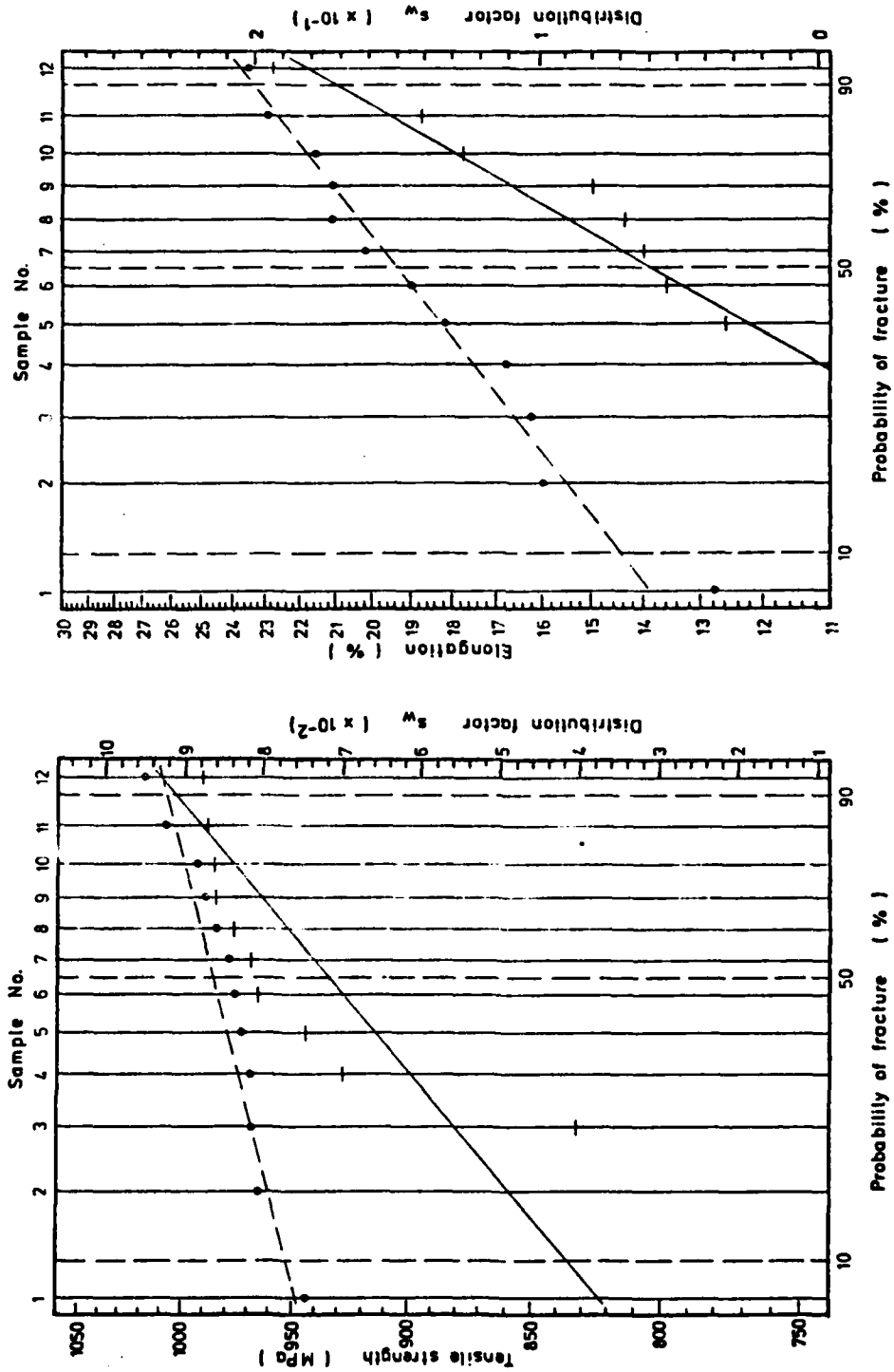
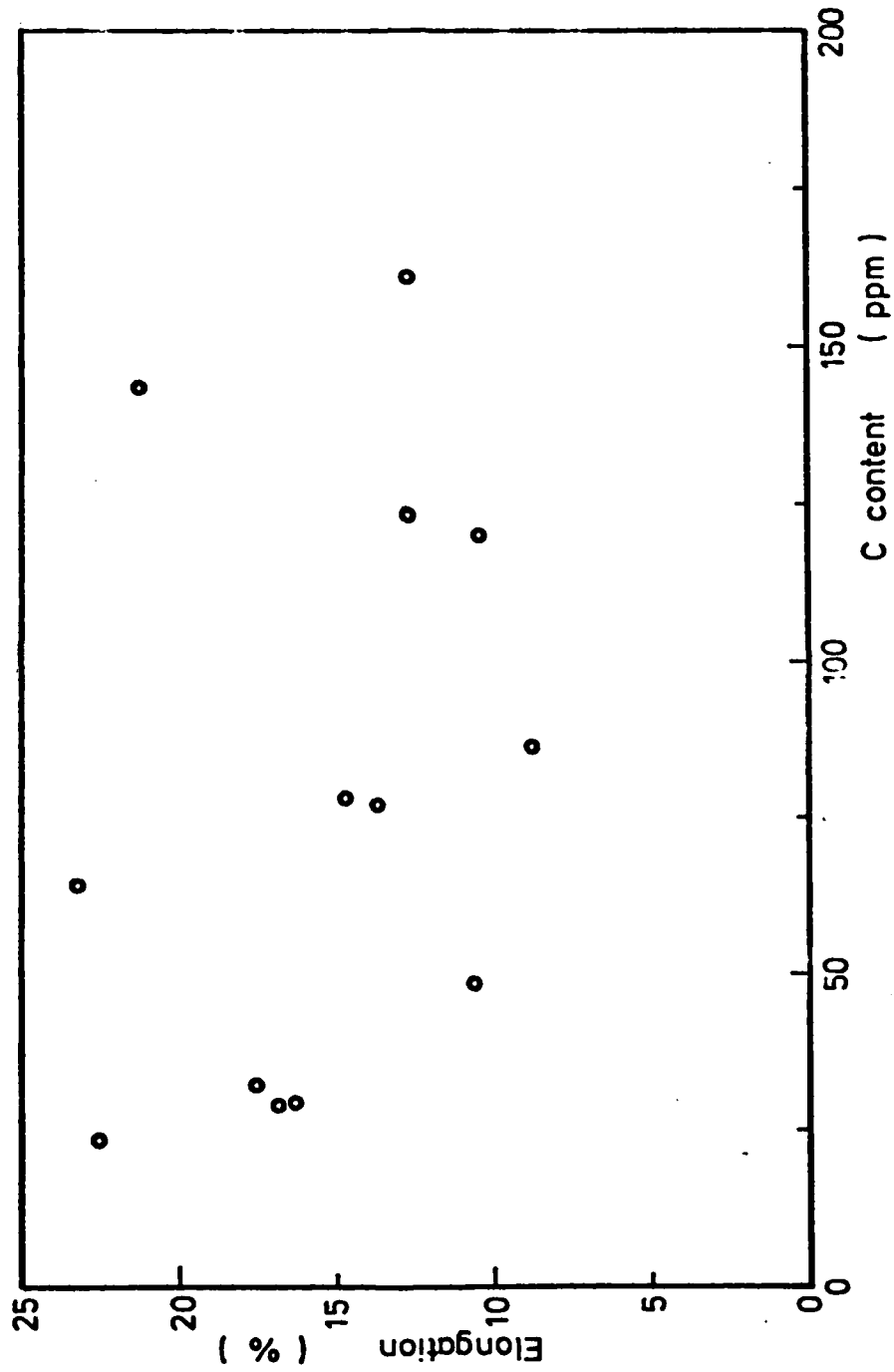


Fig.118: Weibull-diagrams for heavy metal doped with 500ppm C and undoped standard samples



**Fig.119:** Elongation of W heavy metals (96%W) plotted against the C content; evidently no correlation

## 6. Summary

The work carried out in the last year concentrated on the investigation of the effects of trace impurities in the starting W powder on the sintering behavior and the resulting properties of the heavy metals. To explain possible effects of the impurities on the sintering process, a thorough investigation of the sintering process with standard (undoped) samples was regarded necessary. These experiments were carried out by sintering heavy metals of uniform composition (90W, 6,7Ni, 3,3Fe) at constant temperature but for different length of time. It was shown that a fundamental change occurs in the microstructure of the heavy metals during sintering, which changes are necessary to obtain the mechanical properties desired. After prereduction (slow heating up to 1400°C), the samples are almost fully dense, and their tensile strength is surprisingly high, but as their microstructure is quite similar to that of pure W, the elongation is accordingly low. During liquid phase sintering the tensile strength improves rapidly; the elongation rises much slower, following the rounding of the grains and the homogeneous distribution of the binder. After 15 - 20 min. the typical microstructure of heavy metals has developed, with resulting high tensile strength and elongation. At longer sintering times however, the mechanical properties decrease sharply, as pores are formed in the structure, apparently by slow reduction of remaining oxides by hydrogen dissolved in the binder. The micropores grow through Ostwald-ripening until they are sufficiently large to weaken the structure and to cause failure at low degrees of deformation.

The investigations carried out with doped W powders were based on these results. Generally, it was shown that the least satisfactory materials were obtained when using coarse W powders ( $> 10 \mu\text{m}$ ). SEM-photos revealed that these samples had not sintered properly, the liquid phase sintering being confined to a few areas, while in other parts of the samples only solid

state sintering had occurred, the resulting microstructure being similar to that observed with only prereduced samples. Apparently the uniform distribution of the binder melt in the W skeleton is not afforded in these materials, the capillary forces being too low, as the pores left after prereduction are still too large to surge the binder melt into them. This phenomenon was more pronounced with samples containing 96% W than with those with 90% W, which is logical because of the much lower amount of binder available in the former type of heavy metals.

This type of porosity is quite different, and easily discernible, from that observed with heavy metals prepared from several other powders. In the latter case, pore formation occurs during liquid phase sintering, in areas that have already been filled with binder melt. This second type of porosity is similar to that observed with heavy metals sintered for too long times, indicating that reduction of oxides is responsible for the porosity in these cases, too. Pore formation was observed with powders containing several elements that form rather stable oxides (e.g. Na, Si, rare earths) which may be reduced to some extent during sintering, but most probably act as oxygen transporters and thus accelerate pore growth, pore formation thus being observed at fairly short sintering times at which the standard (undoped) samples are still pore-free. Surprisingly, this type of porosity is more pronounced in heavy metals containing 90% W than with 96% W. If the dopants themselves were reduced, the reverse would be expected, but as probably the reduction of W, Ni and Fe oxides is responsible for pore formation, this effect can easily be explained, because the more effective prereduction in case of 96% W (up to much higher temperatures) leaves less oxide to be reduced during liquid phase sintering.

The investigations carried out with carbon doped heavy metals showed that up to considerable C contents in the starting materials ( $\geq 100$  ppm) no deterioration of the mechanical properties occurs; apparently the carbon reacts with oxides

covering the powder particles already during prereduction and is thus largely removed as CO. Only with 500 ppm of C added, a marked decrease of tensile strength and elongation was observed, the wide scatter of the individual values indicating that the distribution of C rather than the overall content determines the resulting properties. Under technical conditions, however, C contamination of the heavy metals due to incomplete dewaxing is largely eliminated during prereduction, which explains the low sensibility of heavy metals towards changes of the dewaxing process observed in earlier investigations.

Conclusively it must be stated that both careful control of the sintering process and selection of the starting materials are of decisive importance for the production of heavy metals. Improper sintering may cause embrittlement by oxygen or hydrogen and/or pore formation in the material; selection of unsuitable starting W powders may result in insufficiently sintered or at least porous heavy metals, which both are unsatisfactory for most applications. Although the effects of several nonmetallic (e.g. O,H) and metallic impurities (Na,K,Al,...) have been shown to advantage, there is still a lot of investigation to be done to gain overall knowledge about the mechanisms through which the impurities influence the sintering behaviour and thus the properties of heavy metals.

Literature:

- 1) Contract No. DAJA-80-C-008, First Annual Report
- 2) Contract No. DAERO-78-G-086, First Annual Report
- 3) Contract No. DAERO-78-G-086, Final Technical Report
- 4) R.V.Edmonds, D.N.Jones: Met.Transactions AIME 10A(1979)289
- 5) L.Ekbom: Scand.J.Metallurgy 5(1976) 179
- 6) H.Danninger, G.Jangg, E.Lassner, B.Lux: high temp., high press.  
1981, vol.13, 541
- 7) R.V.Minakova, A.N.Pilyankevich, O.K.Theodorovich, I.N.Frantsevich  
Poroshkovaya Met. 6(66)(1968) 61
- 8) H.Mayer, E.Lassner, M.Schreiner, B.Lux: high temp., high press.  
1981, vol.13, 529
- 9) E.Lassner, H.Petters, B.Tiles: Planseeber.Pulvermet.23(1975)86
- 10) S.Jamazaki, I.Koseki, S.Ogura, R.Akijama: Planseeber.Pulvermet.  
22(1974)279
- 11) J.Neugebauer: Planseeber.Pulvermet. 23 (1975) 77
- 12) G.Petzow, W.J.Huppmann: Z.Metallkde. 67 (1976) 579
- 13) E.G.Zukas, P.S.Z.Rogers, R.S.Rogers: Z.Metallkde. 67 (1976) 591
- 14) C.Agte: Hutnicke Listy 8 (1953) 227
- 15) W.A.Kaysser, F.Puckert, G.Petzow: Powder Met.Int.12, No.4  
(1980) 188
- 16) K.S.Churn, D.N.Yoon: Powder Met. 1979, No.4, 175
- 17) H.Kostron: Z.Metallkde. 43 (1952) 269,373
- 18) S.N.Tiwari, J.Beek: Metal Sci. 1978 , 356
- 19) W.Weibull: Appl.Mech.Rev. 1952, 449
- 20) H.E.Exner: Materialprüf. 7 (1956) 357
- 21) W.A.Kaysser, O.J.Kwan, G.Petzow: Int.Powder Met.Conf.1982, Florenz
- 22) V.Smolej, S.Pejovnik, W.A.Kaysser: Powder Met.Int.14 (1982) 34

END

DATE  
FILMED

7 83

DT