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The influence of chemistry and various fabrication parameters on the properties of tungsten heavy metals

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The aim of this project is to improve tungsten heavy metals, particularly with regard to their ductility, porosity and density.

The emphasis of the two-year program is to investigate the influence of the heavy metal composition (W content, binder composition) and the chemical purity of raw materials on the properties of heavy metals. In addition, particular attention is given to the influence of the fabrication conditions

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INTRODUCTION
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The aim of this project is to improve tungsten heavy metals,
particularly with regard to their ductility, porosity and density.

The emphasis of the two-year program is to investigate the
influence of the heavy metal composition (W content, binder
composition) and the chemical purity of raw materials on the
properties of heavy metals. In addition, particular attention
is given to the influence of the fabrication conditions on
the quality of the product.

A wide range of extremely varied parameter influencing the
properties of W is conceivable, some are discussed in the
literature (1-7), shortly summarized in the following:

a) Composition:

Increasing the W content increases primarily the density, but
also the hardness, the tensile strength and the E-module.
However, it reduces the ductility.

To achieve a good ductility, the binder should have a hardness
and deformation properties similar to those of W grains.
The most common binders are the Ni-Cu types with various
ratios of alloying metals. The addition of Co to the Ni-Fe
binders has proven advantageous. Binders containing Mo have
also been tested. Marked improvements in the finished alloy
can be achieved by adding even slight amounts of various
elements.

Another important but as yet hardly investigated factor in
the properties of heavy metals is the role of the binding
forces between the W grains and the matrix alloy. The binding
forces are linked with the wetting between the liquid binder
and the W grains which is important during sintering and is
also a function of interface energies.

b) Structure:

The general mechanical properties, especially the ductility, are strongly affected by the structure of the tungsten heavy metals. The optimum for good ductility is a fine grained product in which the individual grains are evenly distributed in the matrix and completely surrounded by binder with a minimum of bridging.

However through Ostwald ripening and coalescence during sintering, a pronounced coarsening of the W powder grains occurs. Thus, in general, measures which inhibit grain growth also tend to improve ductility. Little is presently known about the action of various additives which influence grain growth so that the purity of the W powder assumes a particular importance.

c) Purity of starting materials:

Since even slight amounts of additional elements in the W powder or the binder can have a considerable influence on grain growth, to obtain reproducible results it is necessary to begin with materials having the highest possible purity, or at least with those having exactly known and controllable impurities. Only in this way can the type and amount of additives be correctly selected.

d) Fabrication conditions:

Even though the sintering conditions (temperature and duration), above all because of their influence on the sintered density and on the W grain sizes, play the major role in determining the products' properties, further parameters are also of great importance.

A thoroughly mixed sinter charge from a fine grained starting material is essential for a product with desirable properties.

The compaction pressure on the green compacts is an other important factor: green compacts with a maximum density and a minimum of pressing faults are necessary to obtain a minimum residual porosity in the final products.

The compactibility of the sinter charges is a function of various factors. Measures to improve the compactibility of the powder mixtures, for example the use of coarser starting powders, can result in undesirable sintering behavior and thus in a product with inferior properties. It should be mentioned here that the rate of cooling the freshly sintered samples also influences the final properties.

e) Sintering atmosphere:

According to the literature, the sintering atmosphere could also influence the properties of the sintered products. Above all the influence of H_2 is stressed, although it is still unexplained. The usual practice today is to sinter in an atmosphere containing at least some H_2.

f) Heat treatment:

It is also known that the thermal handling of the sintered heavy metals can strongly influence their properties. For certain compositions of the heavy metal samples, such a treatment can cause favorable structural changes.

The present work has, at least partially, to take into account all these areas. During the first year the investigations have been concentrated on the compactibility of a broad range of powder mixtures an on the influence of the sintering conditions on the properties of the heavy metal products.

The majority of the tests were made on samples with a uniform composition of 90 wt % W, 6.7 wt % Ni and 3.3 wt % Fe, the composition commonly in use today. Usually a uniform standardized

W powder was used, for individual tests W powders with other grain sizes and different chemical purities were also checked.

1. Starting materials:

The W powders used in this work are supplied by an Austrian
tungsten manufacturer. Powders with varying grain size and
with different chemical purities have been made available
to us (see table 1).

T A B L E 1

Mean grain sizes and chemical compositions of the W powders.

Powder	mean grain size in μm	impurity levels in ppm									
		Al	Ca	Fe	Mo	Na	Ni	O	P	Si	C
230/78	0.74	10	7	15	492	36	17	1370	28	28	70
197/77	0.75	16	7	14	20	26	19	1180	22	40	40
234/78	0.84	16	76	18	24	20	23	1220	24	44	31
503/79	3.05	10	10	12	20	26	10	240	21	20	20
434/78	3.13	10	10	12	20	22	10	260	28	20	24
429/78	3.16	10	10	10	20	24	10	260	30	20	15
412/78	14.00	10	10	26	20	12	12	260	15	20	6

The specifications on chemical purities and mean grain sizes
are given by the manufacturer. Grain sizes were determined
with the Fisher subsieve sizer. These grain size distributions
are in good agreement with those determined by standard
sedimentation methods (original readout sheets are attached).

The powders with an average grain size near 0.8 μm have high
impurity levels, especially of O_2. The powders having mean
grain sizes near 3 and 14 μm generally have the lowest impurity
levels.

Our sintering tests so far have been made primarily with
powders 434/78 and 503/79, both of which are   available

in quantity. The two powders are from separate lots but
were made using the same starting materials under the same
conditions. Their chemical purities and grain size distri-
butions are thus quite similar.

SEM photographs also show quite similar grain sizes and
shapes. Grain sizes in both powders fall within a relatively
narrow range. Pictures with lower magnification show that
very fine powder particles are nearly absent (Fig.1a and
1b). However as can be seen in the highly magnified shots,
most of the grains are composed of agglomerates from finer
particles (Fig. 2a, 2b). This is especially clear in Fig. 3b,
which shows a further enlargement of the surface of the
particle from 2b. For both W powders, in addition to the
agglomerates (5b) single particles which are larger and
denser can be observed (4a, 4b).

Powder 503/79			Powder 434/78	
Fig. 1a	1800 x		1b	2000 x
2a	1800 x		2b	3500 x
4a	9000 x		3b	10,000 x
			4b	10,000 x
			5b	10,000 x

The manufacturer will also supply us with W powders having
carefully selected types and amounts of "impurity" level
(doping additives). The first shipments have already arrived.
These powders are to be used mainly for testing the role
of impurities in grain growth during sintering and their
influence on heavy metal properties.

Ni and Fe powders for the binder are supplied by the BASF
company and are of carbonyl powder quality, with mean grain
sizes near 15 μm. The powders were sifted in our laboratories
prior to use to remove the few grains >30 μm. The elimination
of the coarser fraction proved to be very important for
obtaining uniform heavy metal sinter compacts. The O_2 content

of the Ni powder is 910 ppm, of the Fe 2020 ppm. Besides the usual camphor as pressing lubricant, a neutral wax (HV-wax from Hoechst) was also tested.
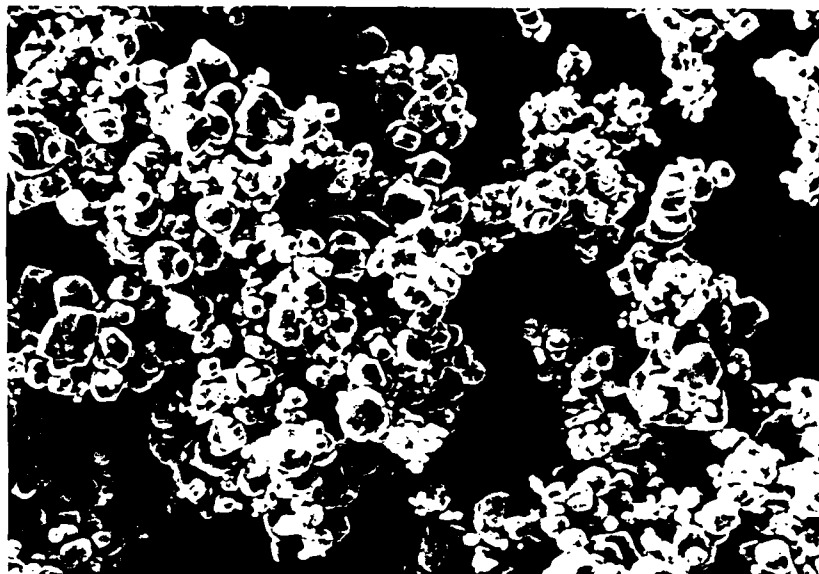
Fig.1a   Powder 503/79   1800 x
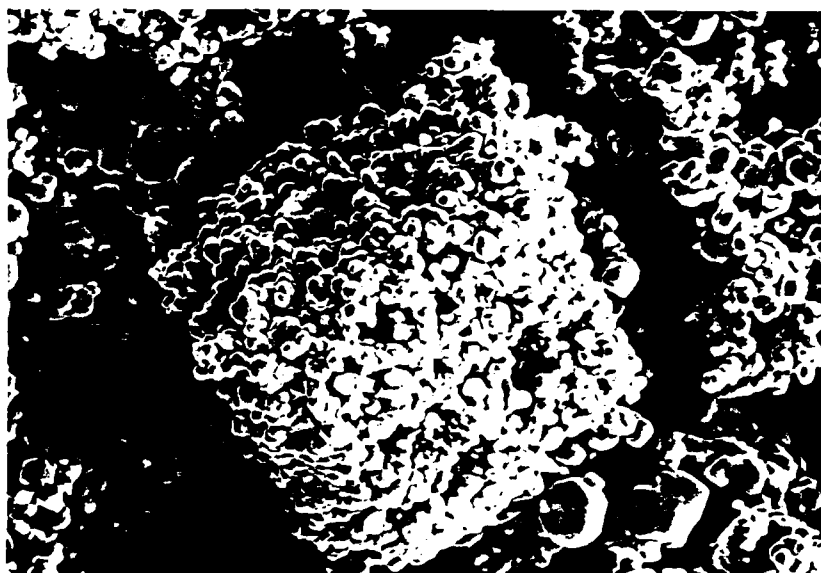

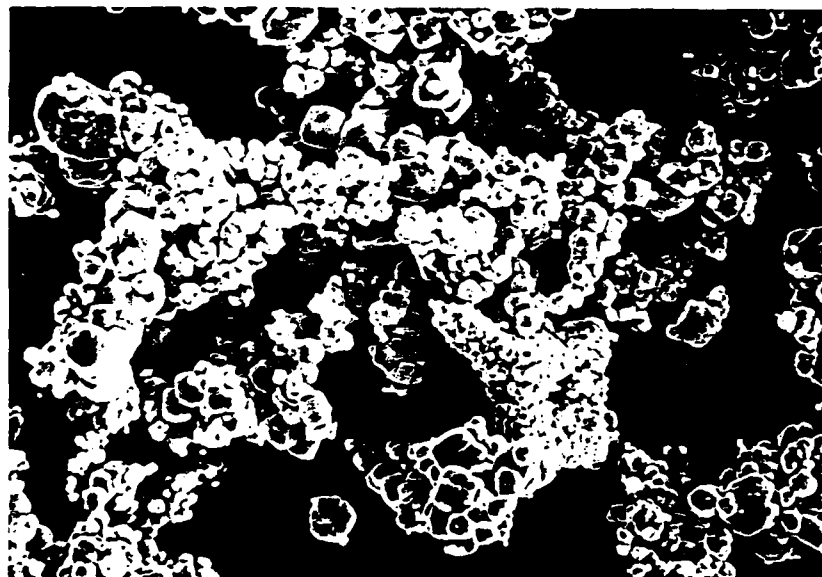Fig.2a   Powder 503/79   1800 x

Fig.4a   Powder 503/79   9000 x

Fig.1b   Powder 434/78   2000 x
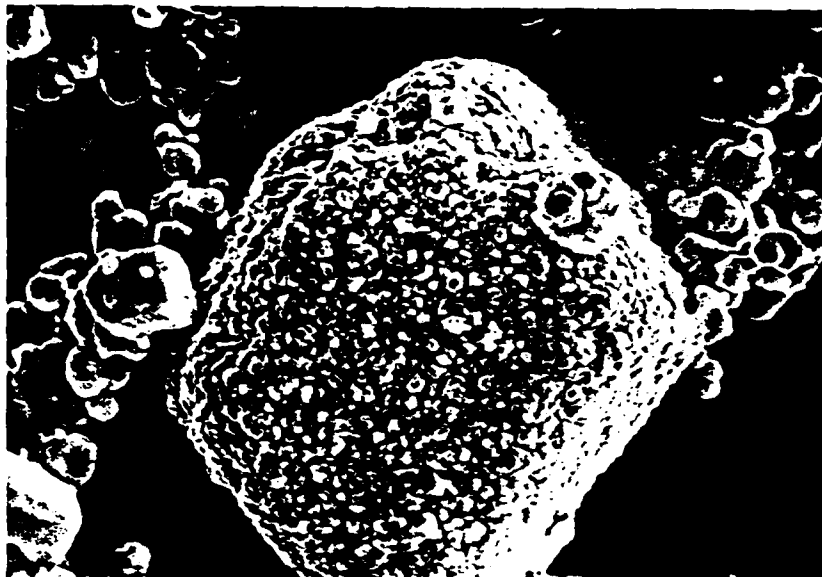
Fig.2b   Powder 434/78   3500 x
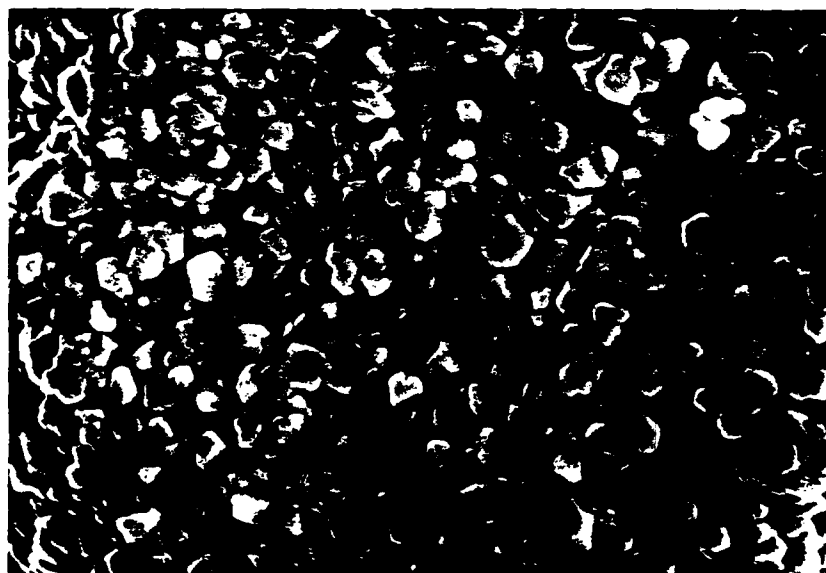

Fig.3b   Powder 434/78   10000 x

Fig.4b   Powder 434/78   10000 x

Fig.5b   Powder 434/78   10000 x

2. Pressing behavior:

Uniform powder mixtures of 90 wt % W, 6.7 wt % Ni and 3.3 wt % Fe were prepared using various mixing or ball milling procedures. The attainable green densities have been measured after compaction with different pressures. Various amounts of different pressing lubricants have also been tested.

2.1. Blending of the powders and granulation:

Some powder charges were wet mixed with cyclohexane for 3^{hr} in a rotation mixer, others were wet ball milled with cyclohexane for 3^{hr} in a laboratory attritor. Pressing lubricant, either 0.7 or 1 % camphor or HV-wax, was added to each sample before blending.

Following the mixing or milling process the cyclohexane was partially evaporated. The still slightly damp powder was then forced through a 0.8 mm mesh sieve for granulation and then thoroughly dried.

2.2. Bulk and tap densities of the powder charges:

The bulk and tap densities of the carefully dried powder charges were determined by standard methods. For the bulk density the powder was poured into a calibrated beaker and then weighed. For the tap density the powder was poured into a beaker being lightly shaken to help it settle and then weighed. The results are summarized in Tab.2.

T A B L E   2

Treatment and densities for the various powder charges.
Composition: 90 wt % W, 6.7 wt % Ni, 3.3 wt % Fe.

Charge	W powder	Blending treatment	Pressing lubricant	bulk density g/cm³	tap density g/cm³
1	230/78	mixed, granulated	1%camphor	2.45	3.63
2	197/78	-"-	-"-	2.37	3.45
3	234/78	-"-	-"-	2.80	4.09
4	234/78	attritormilled	-"-	2.72	3.96
5	429/78	mixed	-"-	3.72	5.28
6	429/78	mixed, granulated	-"-	3.52	5.20
7	429/78	-"-	0.7%HV-wax	4.22	5.83
8	429/78	-"-	1 % HV-wax	4.17	5.74
9	429/78	attritormilled	1% camphor	3.71	5.42
10	412/78	mixed	-"-	4.36	5.77
11	412/78	mixed, granulated	-"-	4.71	5.83
12	412/78	-"-	0.7% -"-	4.80	5.91
13	412/78	-"-	1 % HV-wax	5.15	6.07
14	434/78	-"-	1% camphor	3.50	5.18
15	434/78	attritor, granulated	-"-	3.58	5.21
16	434/78[+]	mixed, granulated	-"-	3.72	5.45
17	503/79	-"-	-"-	3.52	5.20

[+]Fraction <1 μm sifted off and removed.

The bulk and tap densities are primarily a function of the
grain size of the starting W powder. Finer powders result
in decidedly lower bulk and tap densities. The mixing or
ball milling methods have only a minor influence. Attritormilled
products have slightly higher densities. Granulating the
charges lowers the bulk and tap densities somewhat. A further
influence is exerted by the type and amount of pressing
lubricant. Distinctly lower powder densities are observed

for charges with camphor than for those with HV-wax. Charges
with greater amounts of pressing lubricant and medium W
powder grain sizes have lower bulk and tap densities, while
those with coarser W powders have higher densities.

2.3. Compactibility:

For the compactibility tests a 150 ton capacity hydraulic
press with a pressing die for standard tensile strength bars
was used. The pressing die (see Fig.6,7) is of a quality
corresponding to that normally found in the Pm industry.
The die as well as the upper and lower punches are exactly
guided in the pressing frame. Thus a uniform filling of the
powder sample and nearly frictionless pressing are possible.
The powder is pressed simultaneously from above and from
below so that the neutral - that is, the section where the
powder particles do not move relative to the die wall - lies
exactly in the middle of the pressed sample, a bar 5-6 mm
thick.

The green densities for the various pressed samples were
determined by the Hg displacement method developed in our
institute. The method gives reproducible results and, as
opposed to the usual determination in water, requires no
pretreatment to seal the pores since Hg neither wets the
green compacts nor does it penetrate into the pores.

The results of the compactibility tests are summarized in
Tab.3. Pressing faults, mainly as cracks in the green compact
perpendicular to the direction of the pressure, are noted
as appropriate. The charge numbers correspond to those in
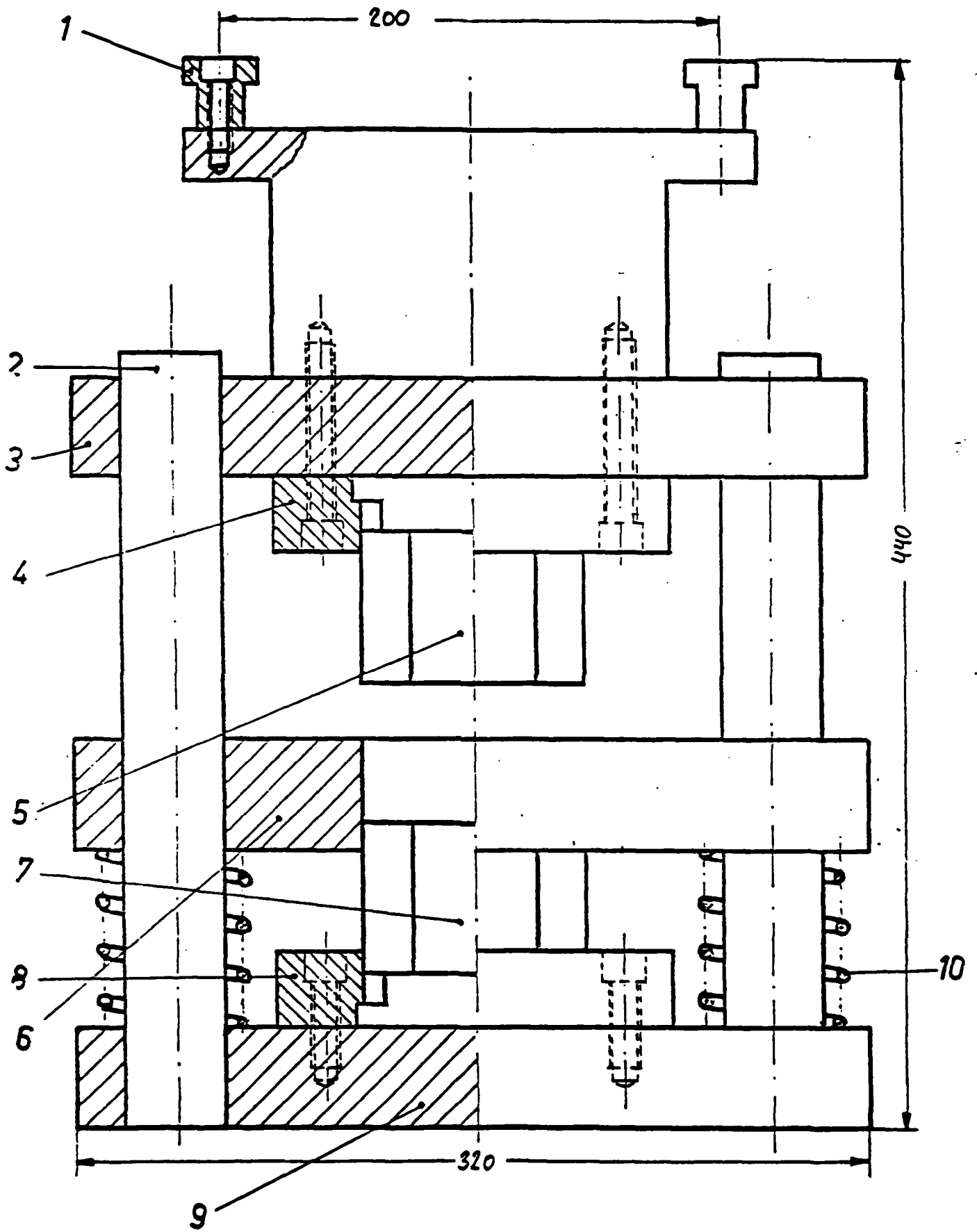Tab.2.

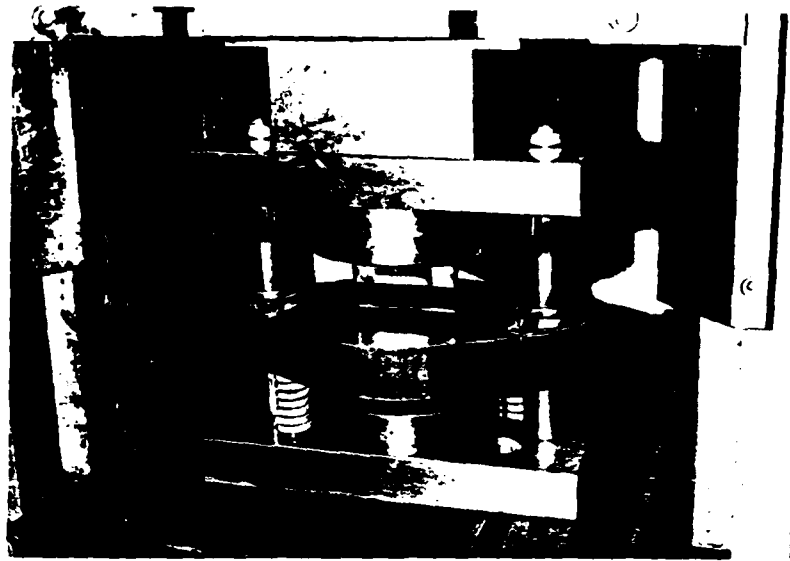Fig.6 Pressing tool with a pressing frame for standard tensile
strength bars.

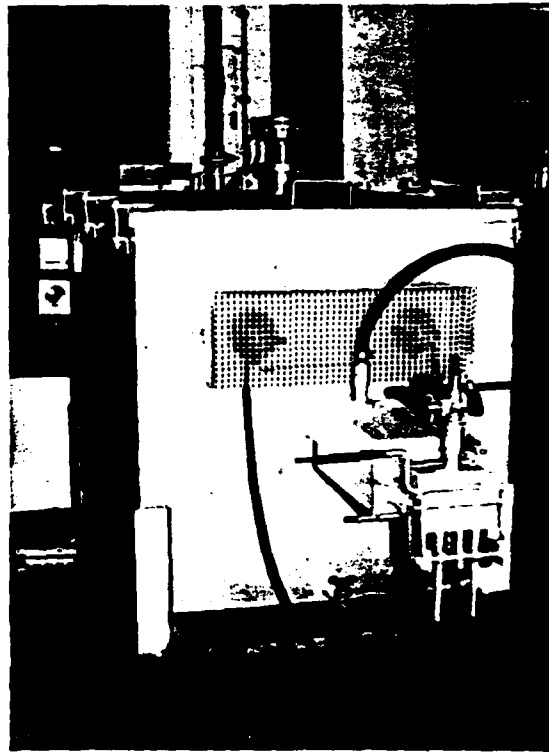Fig.7 Pressing tool for standard tensile
strength bars.

Fig.10 Sintering furnace for temperatures up
to 1600°C.

T A B L E 3

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Green densities for different applied pressures.

Charge	Green density (g/cm^3) at pressures (ton/cm^2) of						
	1.8	2.2	2.7	3.4	4.0	4.7	5.35
1	crumbling of the green compacts at all pressures						
2				-"-			
3				-"-			
4				-"-			
5	9.31	9.63	10.12	10.25^+	10.70	$-^+$	$-^+$
6	9.58	9.87	10.24	10.57	10.98	11.38	11.62^+
7	crumbling						
8	9.43	9.86	-	10.71	$-^+$	$-^+$	$-^+$
9	9.48	9.74	10.12	-	10.78^+	$-^+$	$-^+$
10	9.96	10.26	11.12	11.69	12.02	$-^+$	$-^+$
11	10.41	10.92	11.35	11.81	12.25	12.56	12.81
12	10.35	10.53	10.95	11.51	11.81	12.18	12.50^+
13	10.91	11.29	11.72	12.22^+	12.55^+	$-^+$	$-^+$
14	9.34	9.65	10.15	10.53	10.73	11.06	11.38
15	9.34	9.65	10.15	10.53	10.73	11.06	11.38
16	9.52	9.90	10.38	10.78	11.02	11.36	11.55
17	9.30	9.66	10.14	10.48	10.75	11.10	11.38

$^+$ Compression cracks perpendicular to direction of pressure

Charges with very fine W powders (1-4) could not be compacted. The resulting green compacts crumbled even as they were expelled from the die. Powders with grain sizes near 3 or 14 μm can be pressed quite well though at higher pressures the appearance of more compression cracks were observed. The compactibility is improved and the densities are increased as W powders of larger grain sizes are used.
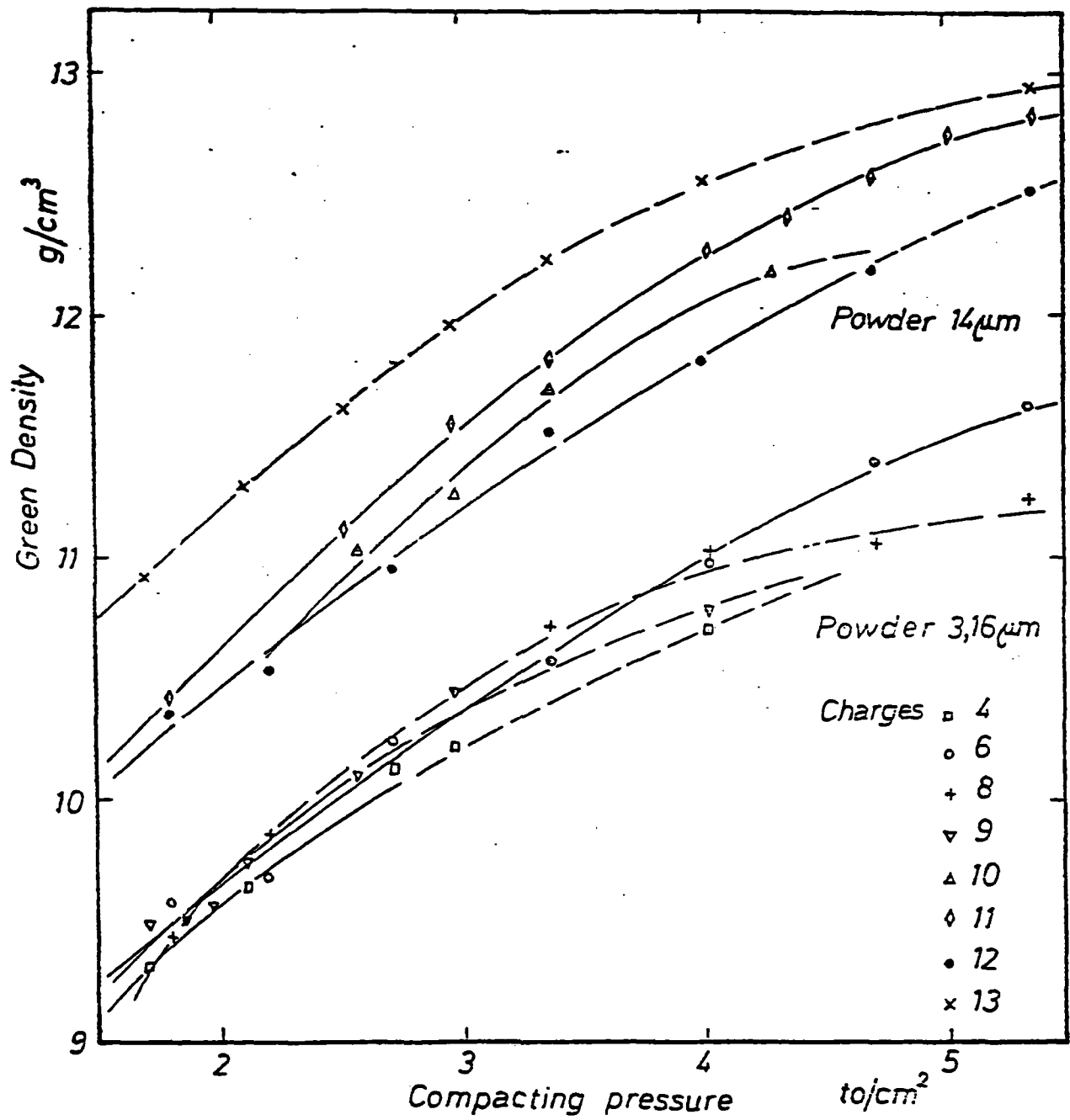
Fig.8 : Green densities of the charges 4 – 13 as a
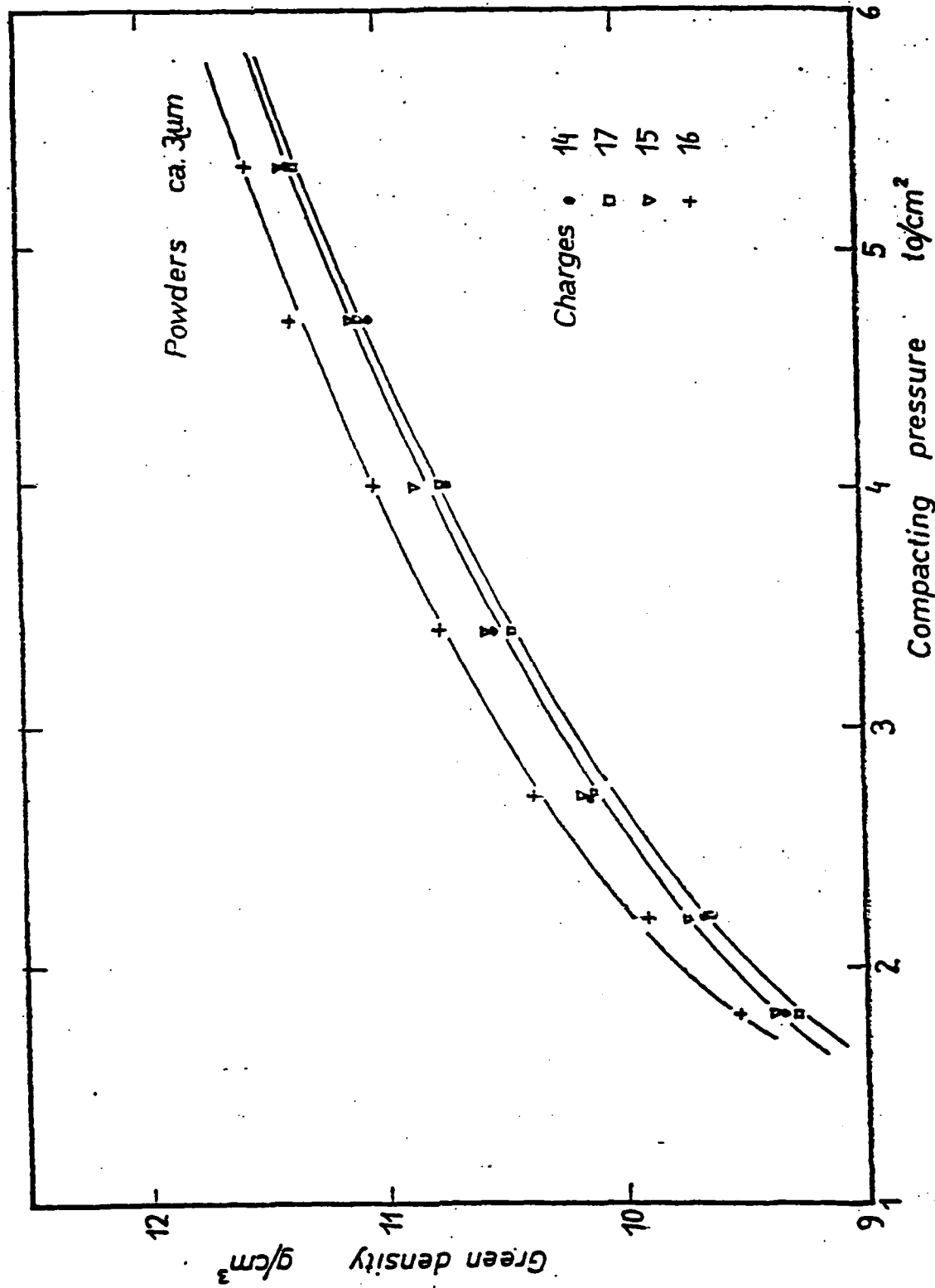function of compaction pressure.

Fig.9 : Green densities of the charges 14 - 17 as a function of compaction pressure.

As can be seen from the values in Tab.3, charges with W grain sizes near 14 μm have markedly higher green densities than those near 3 μm. The removal of the superfine fraction (<1 μm) by air classification from a 3 μm powder (2 % of the sample) resulted in noticeably improved compactibility- compare Fig.8 and 9. However, for industrial purposes the removal of the superfines is hardly practical because of the involved and costly procedure.

As further can be seen from Tab. 3, with Hv-wax instead of camphor as a pressing lubricant, higher green densities are obtained. However, samples with HV-wax tend to have more compression cracks. More lubricant (1 % rather than 0.7 %) appears to reduce this tendency toward cracking.

The blending treatment seems to be an important factor in obtaining higher green densities and inhibiting compression cracks. Attritormilled products are slightly less compactible. The granulation treatment proved to be advantageous when done properly: recent tests have shown that thorough drying of the granulated samples is essential for good results. Even at higher pressures no compression cracks appeared in the well dried samples, while those with even slight amounts of residual cyclohexane showed a pronounced tendency toward compression cracks. Using thoroughly dried granulated samples, the most recent tests (Charges 14-17) all produced flawless green compacts.

The dependence of the green densities on the pressure is shown in Fig. 8 and 9 (Charge numbers as in Tab. 2 & 3). Solid lines indicate flawless green compacts, broken lines the appearance of compression cracks.

2.4. Summary of the compaction tests:

The pressing behaviour of heavy metal charges is determined by a variety of factors. Above all the grain size of the

W powder is important. Fine W powders, which generally
have higher O_2 contents, are unsuitable for compacting and
cause severe compression cracks. The poorer compactibility
of the finest powders might be linked at least partially
with the greater amounts of O_2 present. A correlation exists
between grain size and O_2 content.(due to oxygen pickup)

Though with increasing grain size not only the compactibility
is improved, but also higher green densities are obtained,
for the fabrication of heavy metals coarser W powders are
not generally used as the sintered compacts should have the
finest structure possible. This can best be obtained by
starting with a finer W powder.

Higher pressures increase the tendency towards compression
cracks, however, it appears that appropriate pretreatment
of the powder charges -- intensive blending, granulation
and careful drying of the granulate -- can result in sound
green compacts. The higher green densities obtainable with
greater pressures would be of technical interest as the
denser green compacts shrink less during the liquid phase
sintering, tend to distort less, and thus can be made within
narrower tolerance limits. Highest pressures are however
not commonly applied industrially, 3.5 ton/cm^2 generally
being regard as the upper limit. The benefits of greater
green densities at higher pressures are outweighed by the
accompanying decrease in tool life.

In our tests various measures were taken to improve green
densities at constant pressure. The results show that natural
wax is better than camphor for increasing green densities
but poorer in regard to inhibiting compression cracks.
Granulation causes a slight reduction in pressed densities,
but very decidely inhibits the formation of compression
cracks. Attritormilled powder charges exhibit a somewhat

poorer compactibility but the effect of the ball milling treatment is not strong.

These results are in good agreement with those reported in the literature. Although nothing *seems to be reported on* pressing behaviour of heavy metal charges, A. R. Poster (9) does give a detailed discussion on the pressing of pure W powders.

According to Poster, the pressing behaviour is primarily a function of the grain size and shape, with the grain size distribution being also of importance. He too notes that finer grade powders are more difficult to compact than the coarser grades. For the same compaction pressure higher green densities are obtained from coarser grades, and at the same time the tendency towards compression cracks decreases. The influence of the grain size is-as in pure W- most pronounced in the $0.8 - 4.4 \mu m$ range. With grain sizes above $8 \mu m$ the influence become much less significant. Rounded grains result in better green densities, but the green compacts have a lower strength.

3. Sintering behavior:

To determine the optimum sintering parameters standard
tensile strength bars 5-6 mm thick were used. All specimens
were pressed from charges with the uniform composition
90 wt % W, 6.7 wt % Ni and 3.3 wt % Fe. The green compacts
were all sintered in a H_2 atmosphere. W powders 434/78 and
503/79 with mean grain size near 3 μm were used for the charges.
The following optimal preparation procedure, as determined
by the previously described test series, was used:

The starting metal powder with 1% camphor added as pressing
lubricant was wet mixed with cyclohexane for 3^h in a pug
mill. Most of the cyclohexane was then evaporated and the
damp powder granulated, then carefully dried. All samples
were compacted at 5.15 to/cm^2. In every case sound green
compacts were obtained.

3.1. Sintering furnace and sintering process:

The sintering furnace, constructed in our laboratories, is
a muffle oven (Fig. 10) with a Mo heat conducting coil which
permits temperatures up to 1600°C. Because of the Mo coil
the furnace must be operated in a reducing atmosphere. For
all tests technical H_2 (no special purification, dew point
~15°C) was used. The furnace temperature could be maintained
at better than $\pm$5°C over extended length of time.

The furnace is equipped with a shutter arrangement that
allows the green compacts to be shoved into the heated
furnace through the different zones. The green compacts are
transported in Mo boats coated with Al_2O_3 to prevent
sintering joins. By slowly pushing the samples in the ap-
propriate zones, the sintering temperature can be reached
at whatever speed might be desirable, and the compacts can
be held at some particular temperature for any length of
time necessary. In general the samples were held 20 min at
400°C to remove the pressing lubricant, afterwards they were

brought up to sintering temperature at different rates and
were held for different length of time at different sintering
temperatures. Cooling could be accomplished quickly by
moving the samples directly from the hot zone to the cool
zone. The slowest cooling rates were achieved by leaving
the samples in the heated zone but turning the furnace off
and letting them cool down as the furnace did. Fig. 11 shows
schematically the time/temperature diagram (cycle 1) used
for sintering the first samples.

For rapid heating the samples were shoved directly from the
lubricant bake out zone into the high temperature zone, in
which they reached sintering temperature within 2-3 min.

As the tests described below showed, it proved to be advan-
tageous to leave the samples for at least 30 min in the
temperature range 800 to 1000°C so they could be rapidly
brought up to the sintering temperature. The sintering point
is easily recognizable for the heavy metal samples: the
initially light, shiny samples suddenly appear dark. Known
in the literature as the "Silberblick" effect, this is due
to the liquid phase that forms at the sintering temperature.
It fills the pores of the green compact making the surface
smooth and less radiant. The exact temperature of the bars
during sintering was checked with an optical pyrometer. It
agreed well with the temperature registered by the furnace
regulator.

After the liquid phase appeared the samples were held for
the desired length of time at sintering temperature, then
cooled. During a quench cooling process, the specimens were
pushed out of the heating zone into the cooling chamber as
already described above. In the case of slow cooling the
furnace was switched off without removal of the specimens.
The temperature in the furnace first decreases relativly
rapidly and after just a few minutes the eutetic melts freeze.
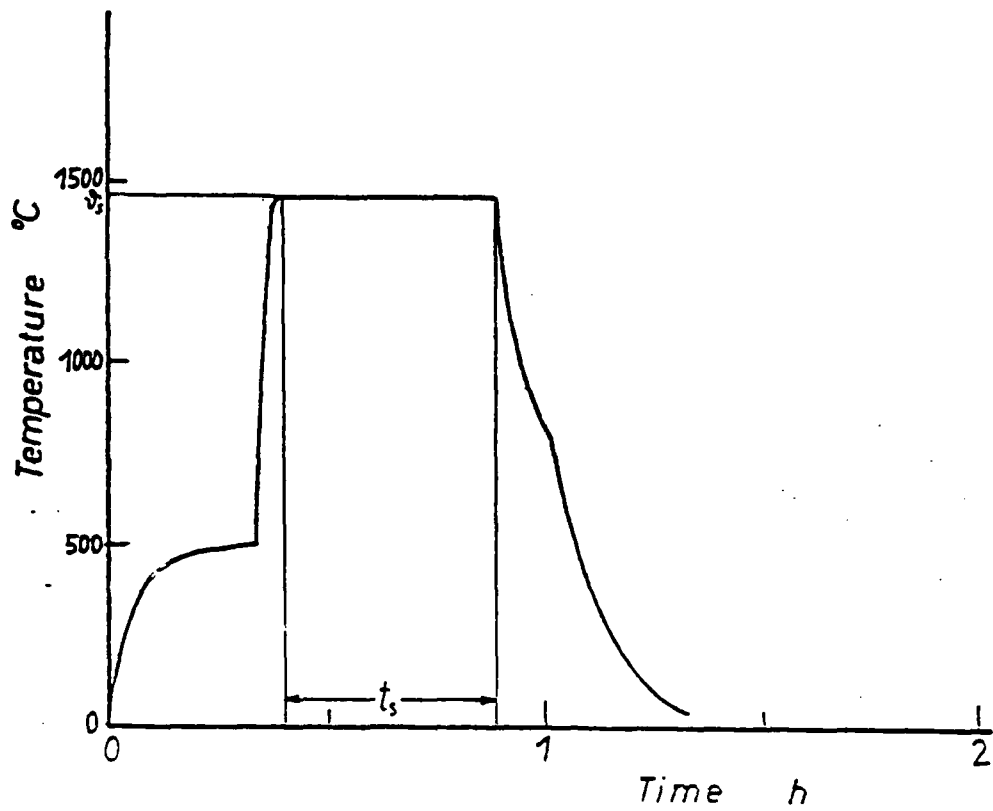
Fig.11   Temperature / time diagram for sintering
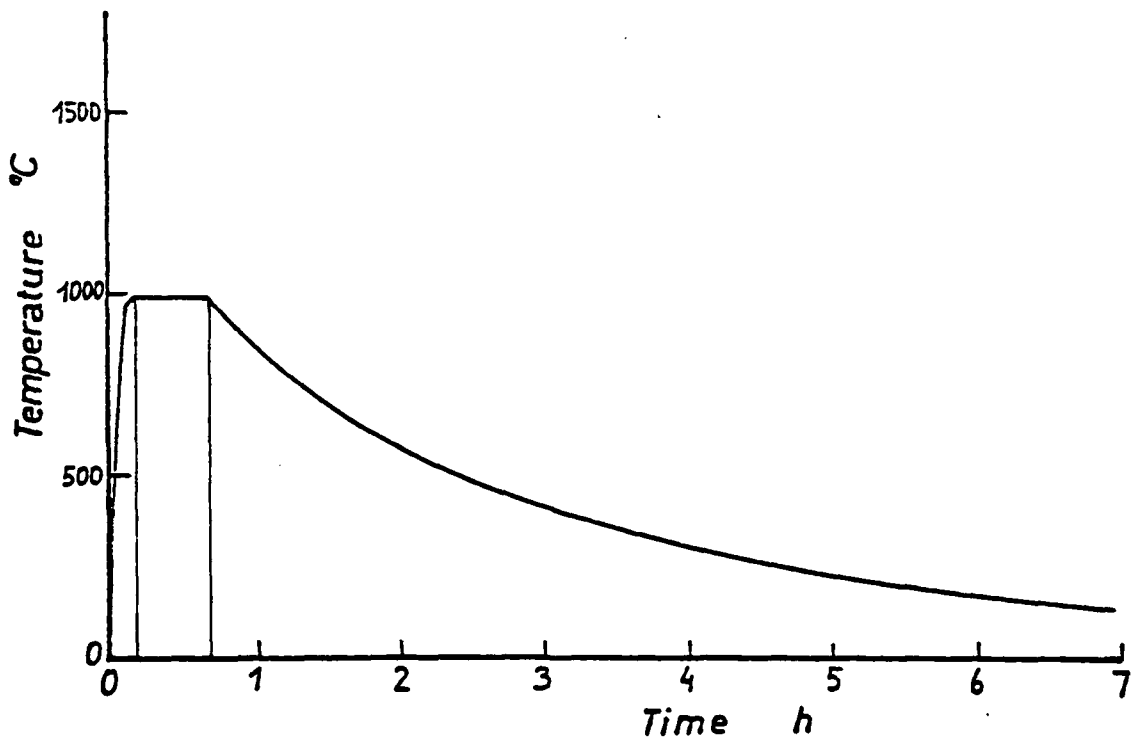   cycle 1.

Fig.13   Temperature / time diagram for the heat
         treatment.

About 30 min later the temperature is 1200°C. From this
point on the temperature falls more slowly -- the 1200 - 800°C
range, where interesting precipitates might be expected,
is transversed in 4-5^{hr}. The samples shich were slowly
cooled were removed from the furnace only after the tem-
perature had dropped below 400°C.

. . .

3.2. Examination of the properties of the sintered compacts:

With only a few exceptions where the sintering temperature
was too high, the samples retained their original shape and
were neither distorted nor deformed. However they had visibly
shrunk. Initially the Hg displacement method mentioned above
was used to determine the sinter compact densities. When
this method was compared with the water displacement method
though, it was seen that the Hg values were uniformly 0.1 g/cm^3
below those measured in water. For the sintered W specimens
the Hg values were also somewhat less reproducible. These
differences are due to the fact that Hg does not wet the
surface of the compacts, leaving residual surface pores un-
filled, and in some cases small air bubbles trapped on the
surface.

However, for determining the densities of green compacts
which are extremely porous, the Hg method gives reliable
results because there mercury's inability to wet the surface
and fill the pores is an advantage.

The sinter compacts were then checked for hardness (Hv 62.5)
tensile strength and ductility.

3.3. Results of the sintering tests:

3.3.1. Preliminary tests:

The first tests were made with sinter charges from different
W powders but with a uniform composition of 90 wt % W, 6.7 wt % Ni
and 3.3 wt % Fe. The green compacts from these charges were

compacted at different pressures, then sintered at temperatures between 1430 and 1460°C for different lengths of time. In these initial tests the samples were always heated rapidly after lubricant bake out to the full sintering temperature, and after sintering then were cooled quickly. These test results are summarized in Tab. 4. For the numbers of sinter charges used as well as the W powder type and preparation method, refer to Tab. 2.

T A B L E 4

Densities and hardnesses of different sintered W-Ni-Fe powder mixtures.

Charge	sint. temp °C	sint. time min.	compaction pressure for green compact to/cm²	sint. density g/cm³	residual porosity	hardness $Hv_{62.5}$
5	1460	30	1.71	16.89	1.43	292
			2.11	16.93	1.21	292
			2.71	16.92	1.23	294
			2.97	16.94	1.29	295
			4.02	16.95	1.10	299
9	1460	30	1.71	16.90	1.37	292
			1.97	16.90	1.37	295
			2.11	16.92	1.23	318
			2.56	16.93	1.19	321
			2.97	16.98	0.92	321
13	1430	30	2.11	12.84	25.1	114
			2.52	12.98	24.3	115
			2.97	13.13	23.4	124
			3.37	13.40	21.8	141
		60	1.71	13.07	23.7	124
			2.11	13.11	23.5	133
			2.52	13.25	22.6	137
			2.97	13.88	19.0	142

Charge	sint. temp °C	sint. time min.	compaction pressure for green compact to/cm²	sint. density g/cm³	residual porosity	hardness Hv$_{62.5}$
		90	3.37	14.27	16.7	182
	1440	30	5.35	15.57	9.1	276
	1460	30	5.35	16.98	8.8	282
11	1460	15	1.80	16.72	2.39	295
			2.20	16.78	2.08	304
			2.97	16.73	2.35	303
			4.02	16.85	1.68	308
			4.70	16.88	1.57	310
			5.02	16.86	1.58	311
		30	2.20	16.92	1.30	293
			2.52	16.92	1.24	293
			2.70	16.96	1.04	298
			3.37	16.95	1.10	297
			4.02	16.96	0.99	300
			4.28	16.96	1.00	298
			5.35	16.98	0.92	302
			5.80	16.98	0.88	301
		45	1.80	16.98	0.92	290
			3.37	16.98	0.89	292
			4.02	16.99	0.85	293
			4.70	16.98	0.88	292
		60	2.52	16.98	0.91	287
			3.37	16.98	0.92	288
			4.02	16.99	0.84	289
			5.35	16.99	0.85	291
		900	3.37	17.07	0.38	271

These tests showed that temperatures of 1430 and 1440°C
are insufficient. The liquid phase appears first at 1450°C.
At 1460°C nearly nonporous sinter compacts are obtained. At
sufficient sintering temperature the sinter compacts appear
shiny and silvery, below that they are still grey. The sintering
temperature of 1460°C seems to be rather too close to the

minimum necessary for liquid phase formation, later tests
were thus done at 1470°C (see below).

From the sintered specimens listed in Tab. 4 no useful
tensile data could be obtained. The compacts were so brittle
that some of them broke even before they could be fully
mounted between the claps of the tensile tester. Even when
it was possible to mount a compact in one piece, no measurable
elongation (values <0.1 %) and thus no meaningful ultimate
tensile strength values could be obtained.

Photographs of microsections (Fig. 12a-12d) from various
sintered samples in these series show that at 1460°C nearly
nonporous sinter compacts are obtained. In the micrographs
the grain coarsening of the W compacts during longer
sintering is clearly visible. In the sinter charges from
the 14 μm powder the grains are obviously larger after 60 min
sintering time than after only 30 min. The microphotograph
of the charge sintered for 900 min shows very coarse W grains.
The charges containing W powders with mean grain sizes
of 3.14 μm show a pronounced grain growth. Here the W grains
have, after only 30 min sintering time, reached an average
size >10 μm.

As described above only sinter compacts with very unsatisfactory
properties could be obtained in these preliminary runs. The
ductility was particularly poor. To find the causes of these
dissatifying results, further investigations into the in-
fluences of various parameters on the properties of the
sinter compacts were necessary.

3.3.2. Influence of a postsintering heat treatment:

Charges from W powder 434/78 (mean grain size 3.13 μm) with
1 % camphor pressing lubricant were mixed in the pug mill
or attritor milled, then uniformly granulated and pressed
with 5.15 ton/cm^2. All samples were held at 400°C for 20 min
to remove the pressing lubricant, then rapidly brought to
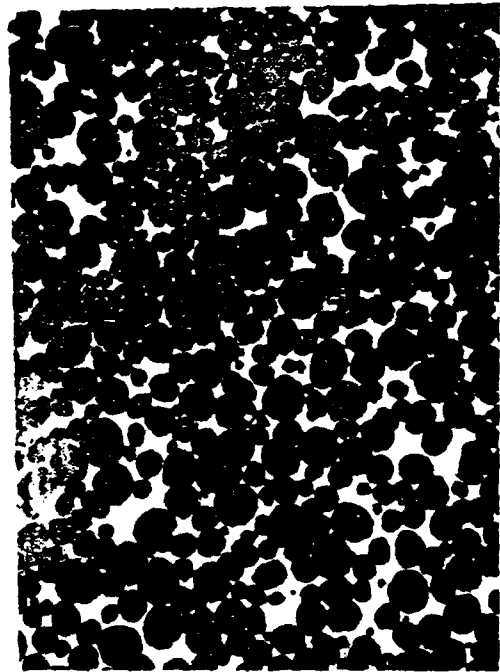the sintering temperature of 1470°C where they were held

a : 14 μm, 15 min.

b : 14 μm, 60 min.

c : 14 μm, 900 min.
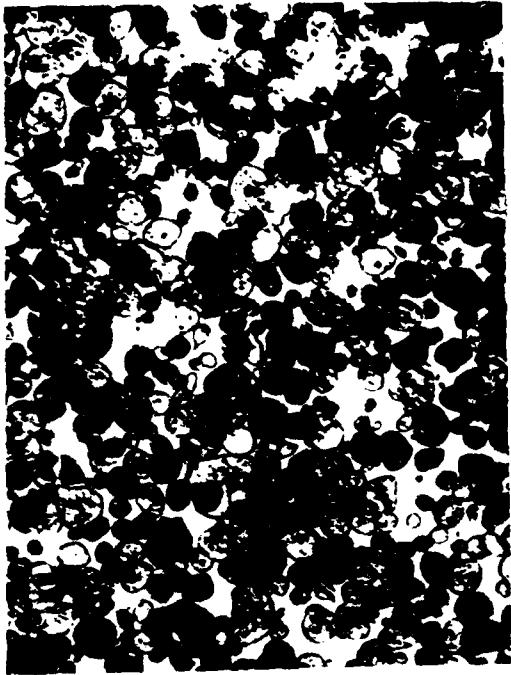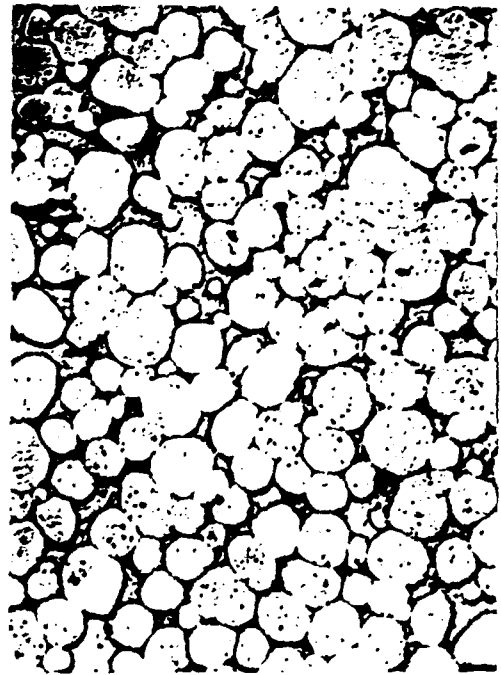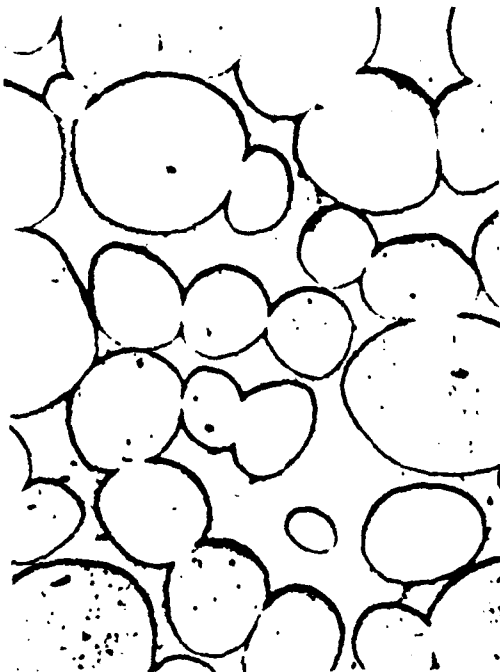
d : 3,16 μm, 30 min.

Fig. 12 a – d Metallographic sections of samples sintered
at 1460°C for different length of time. Sintering
durations and average W grain sizes (14 or
3,16 μm) are noted.

Magnification : 250 x

for different length of time and then cooled.

For one charge the superfines ($<1\,\mu$m) were sifted off prior to mixing and granulating. The superfine fraction accounted for only a few percent of the total, but we hoped thereby to obtain sinter compacts with better properties.

The finished sinter compacts were reheated to 1000°C, held there for 30 min, then slowly cooled in the furnace (see Fig. 13).

The mechanical properties of these sinter compacts were measured and are summarized in Tab. 5.

T A B L E 5

Mechanical properties of the heat treated sinter compacts (rapid heating and cooling prior to and following sintering at 1470°C)

Heat treatment: reheating to 1000°C, holding for 30 min, then cooling slowly.

sint. temp. °C	sint. time min	HV$_{62.5}$	density g/cm^3	tensile strength N/mm^2	elongation % gauge length 25mm
Sinter charge--mixed and granulated					
1470	15	299	17.10	705	0.4
	30	305	17.06	700	0.7
	60	297	17.06	674	1.1
	120	292	17.06	668	0.8
Sinter charge--superfines sifted off, powder blended and granulated					
1470	15	292	17.07	736	2.0
	30	296	17.07	742	2.5
	60	298	17.05	711	1.3
	120	294	17.03	668	1.5

sint. temp. °C	sint. time min	HV$_{62.5}$	density g/cm^3	tensile strength N/mm^2	elongation % gauge length 25 mm
Sinter charge--attritor milled and granulated				
1470	15	297	17.06	633	0.7
	30	293	17.06	646	0.7
	60	293	17.03	624	0.8
	120	289	17.03	642	0.7

As can be seen from these results the subsequent heat treatment brought no definite improvement in the ductility. Tests in which randomly chosen specimens were reheated to 1200-1300°C, or only to 800-1000°C, and then slowly cooled (6-8^{hr} until the temperature falls below 400°C) gave no better results. Thus, the brittleness of the sinter compacts is apparently not due to an unfavourable cooling rate.

Further, tests showed that sifting off the superfines from the W powders brought no measurable improvement. Similarly the pretreatment--mixing or milling--had no appreciable effect on the hardness or the sintered density. It is noteworthy that the sintered density in all three cases decreased slightly with extended sintering time. Attritormilled sinter charges result in sinter compacts with measurably lower tensile strength. The ductility was in all cases poor, only those charges where the superfines were sifted off showed better ductilities.

3.3.3. Influence of the lubricant removal conditions:

The possibility that the brittleness of the compacts might be due to residual C was considered. If the temperatures were increased too rapidly for the pressing lubricant to be fired out, traces of C could remain. To check this, green compacts from 90 wt % W powder 434/78 were mixed, granulated, pressed (5.15 ton/cm^2) and fired out with extreme care:

over a period of 8^{hr} they were brought from room temperature
to 800°C, then rapidly raised to the sintering temperature
of 1470°C where they were held 30 min. Some sinter compacts
were cooled quickly, some slowly in the furnace. The mechanical
properties of the products from this test series are given
in Tab. 6.

T A B L E   6

Mechanical properties of the sinter compacts made from green
compacts with the pressing lubricant carefully removed.

Sintering temperature: 1470°C, sintering time: 30 min

	Density g/cm^3	Tensile strength N/mm^2	elongation % gauge length 25 mm
lubricant baked out slowly, cooled rapidly after sintering	17.09	493	0.2
slow bake out, cooled slowly after sintering	17.07	668	0.4
rapid bake out, cooled slowly after sintering	17.07	749	3.0

The careful removal of the lubricant from the green compacts
also brought no improvement in the ductility, nor did the
speed with which the compacts were cooled down from the
sintering temperature appear to have a noticable effect on
the ductility. Contrary to the case described in Tab. 5
where the rapidly cooled sinter compacts received a subsequent
heat treatment, in the tests here the sinter compacts were
not reheated but were simply cooled very slowly. This
measure however brought no improvement in the properties of
the final products.

C analyses of various sinter compacts, with lubricant both
rapidly and slowly fired out, showed very slight C contents
all in the range of 16-53 ppm (analyses courtesy of the
manufacturer of the W powders). No correlation between the
C contents and the ductilities of the sinter compacts could
be found. Thus the possibility of too much residual C causing
the low ductilities could be excluded.

3.3.4. Alloying additives in the binder:

Attemps were made to improve ductilities by adding different
metals to the Ni-Fe binder. The amount of additive was always
0.2 wt % of the binder fraction, which is 0.02 wt % relative
to the whole sample. Binder additives in the form of fine
powders (30 μm) from Co, Cr, Mo, V, and Cu were tested. To
obtain a uniform and thorough blending of all components,
all samples were wet ground for 15 min in the attritor, then
granulated, dried, and pressed 5.15 ton/cm^2 to standard
tensile strength bars. The lubricant was fired out for
20 min at 400°C, then the compacts were rapidly brought up
to the sintering temperature and rapidly cooled after
sintering. All sinter compacts were subsequently heat
treated (30 min at 1000°C followed by slow cooling).

As can be seen from the values in Tab. 7, in certain cases
improvements were realized.

T A B L E 7

Mechanical properties of green compacts with different metallic doping additives.

Each sample was attritormilled for 15 min, granulated, compacted at 5.15ton/cm^2, rapidly heated to sintering temperature (1470°C), sintered, cooled rapidly.
Subsequent heat treatment: reheating to 1000°C, after 30 min slowly cooling.

sint.temp. o°C	sintering time min.	density g/cm^3	tensile strength N/mm^2	elongation % gauge length 25mm
Charge with 0.02 % Co				
1470	15	17.06	754	1.5
	30	17.05	726	1.4
	60	17.06	680	1.0
	120	17.04	674	1.6
Charge with 0.02 % Cr				
1470	15	17.07	903	10.1
	30	17.05	888	11.1
	60	17.03	792	11.4
	120	17.03	814	6.1
Charge with 0.02 % Mo				
1470	15	17.06	794	1.3
	30	17.07	733	1.4
	60	17.06	743	3.3
	120	17.05	692	1.7
Charge with 0.02 % V				
1470	15	17.08	936	9.8
	30	17.06	923	10.2
	60	17.07	956	13.1
	120	17.05	892	10.0
Charge with 0.02 % Cu				
1470	15	17.01	822	1.1
	30	17.07	762	1.4
	60	17.06	704	0.8
	120	17.06	742	1.3

While additions of Co, Mo and Cu brought no appreciable
improvement in the properties of the sinter compacts,
additions of Cr and V gave surprisingly positive results
in the ductility. Elongation values up to 10 % were obtained.
The tensile strength of the compacts with Cr and V are
also much better than those of others (Tab. 7). Recent tests
reconfirm our experience that prolonged sintering causes
a slight decrese in the density and the tensile strength.
Longer sintering times are, as also noted in the literature,
unsuitable for the fabrication of W heavy metals.

Tests have shown that the originally surprising effect of
the Cr and V additives is due to their deoxidizing abilities--
of all the doping additives only these two bind oxygen
better than the basic starting materials W, Ni and Fe.

Further tests were made to investigate the possibility
that the low ductilities previously obtained were due to
residual O_2, that is, to insufficient deoxidation of the
starting materials.

3.3.5. Effect of the residual oxygen:

Residual oxygen can affect the ductility of the heavy metal
compacts in several different ways. It is known from the
literature that oxygen levels of even several hundred ppm
can cause embrittlement in Mo. A negative effect on W is
known too. Residual oxygen can according to the results
reported below also affect the binding forces between the
W grains and the binder phase in the heavy metal.

The starting powders all have rather high oxygen contents,
generally in the form of thin oxide layers on the grain sur-
faces. Analyses showed oxygen levels between 250 and 300 ppm.
The Ni and Fe powders had much higher oxygen levels. However
since the compacts are sintered under H_2 and the oxides of
all three elements are easily reduced, the oxygen is
usually removed.

It is conceivable that too rapidly heating the green
compacts leaves the deoxidation incomplete. The first liquid
phases, which are near the surface, could trap the H_2O al-
ready formed inside and prevent further H_2 from penetrating
into the compact.

Therefore tests were made in which the compacts were slowly
heated, particularly in the 800-1000°C range where rapid
reduction occurs. Here the compacts are still porous and a
thorough deoxidation is possible. W powder 503/79 (mean grain
size 3.05 μm, O_2 level 260 ppm) was used in the usual
(90 wt % W) proportion. 1 % camphor was added to the charge
which was wet mixed in the pug mill, granulated, dried and
compacted at 5.15 ton/cm^2. The green compacts were placed in
the cold furnace in H_2 and slowly heated. Sufficient time
was thus available for baking out the pressing lubricant.
The furnace required 9^{hr} to reach the sintering temperature,
going from 800 to 1000°C took over 2^{hr}. Thus enough time
was available for reducing the Oxygen level through reaction
with H_2 before sintering occured. The temperature/time
profile for these tests, "Cycle 2", is given in Fig. 14.
When furnace temperature reached about 1400°C the samples were
temporarily held in a cooler zone until the exact temperature
for sintering was reached in the furnace. Then the compacts
were returned to the sintering zone for the specific length
of time desired.

These sinter compacts have better ductilities (Table 8)
than earlier ones similarly prepared but rapidly heated
(compare Tab. 5). The rate at which these compacts were cooled
also affected the ductilities: slowly cooling the compacts
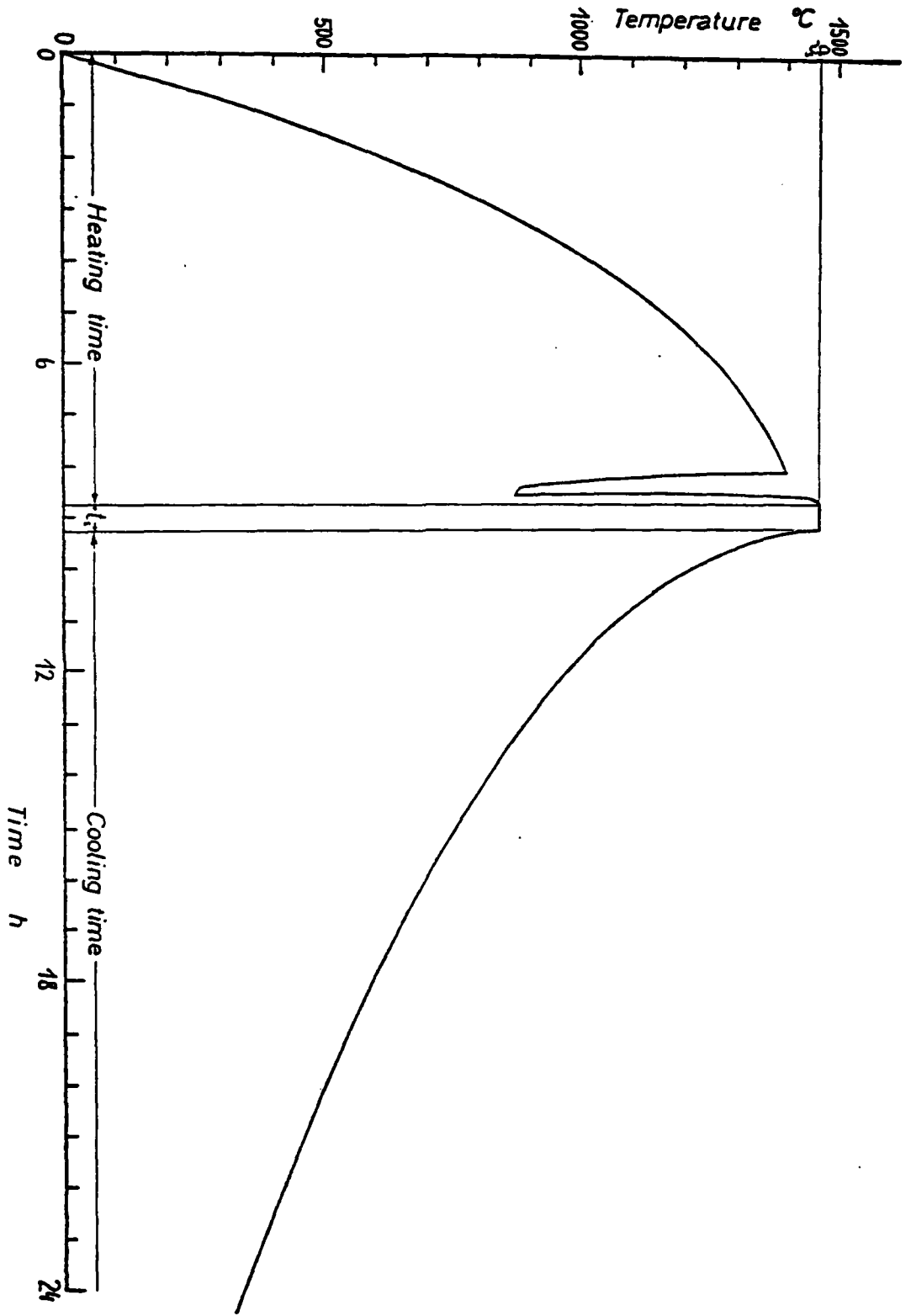about doubled the ductilities.

FIG. 14 Temperature / time diagram for sintering cycle 2.

T A B L E 8

Mechanical properties of samples slowly heated to sintering temperature.

(W powder 503/79, 90 wt % W, 6.7 wt % Ni, 3.3 wt % Fe, 1 % camphor, wet ground in a pug mill, granulated, compacted with 5.15 to/cm^2, sintered at 1470°C for 30 min)

	density g/cm^2	Hv$_{62.5}$	tensile strength N/mm^2	elongation % gauge length 25 mm
rapidly cooled	17.05	306	858	11.3
slowly cooled	17.06	315	998	22.4

From this same charge further green compacts were made (5.15 to/cm^2) and sintered at different temperatures for different length of time to determine the optimal conditions. All samples were slowly heated to sintering temperature and slowly cooled after sintering (sintering cycle 2 in Fig. 14).

T A B L E 9

Mechanical properties of compacts sintered with different times and temperatures but slowly heated and cooled.

Preparation of green compacts as in Tab.8. Each value in Tab. 9 is the average of measurements made on 5 individual samples.

sintering temperature °C	sint. time min	density g/cm^3	Hv$_{62.5}$	tensile strength N/mm^2	elongation % gauge length 25 mm
1430	30	16.29	293	627	0.2
	60	16.48	298	624	0.4
	90	17.00	302	816	0.6
1460	30	17.10	306	994	24.7
	60	17.10	305	985	25.3
	90	17.09	301	924	17.2
1490	30	17.11	308	950	20.5
	60	17.07	303	988	27.7
	90	17.08	297	898	18.3
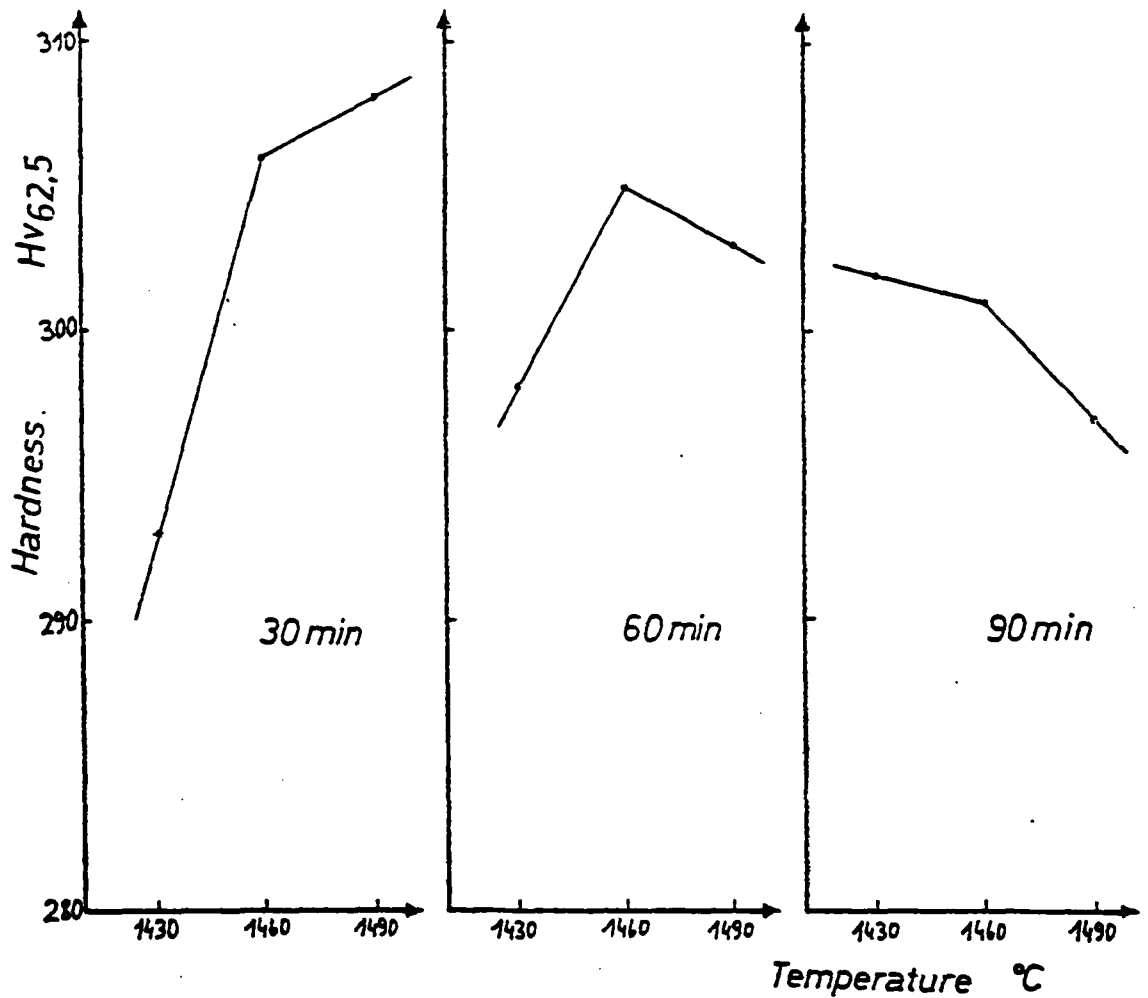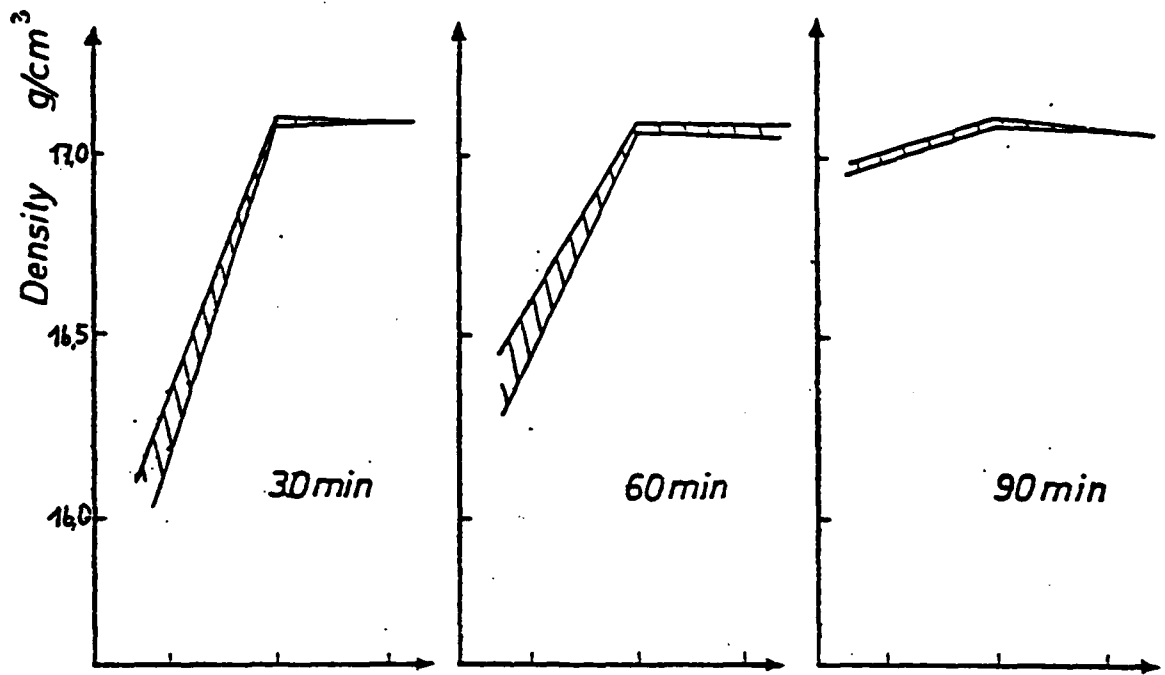
Fig.15a Density and hardness of slowly heated and cooled
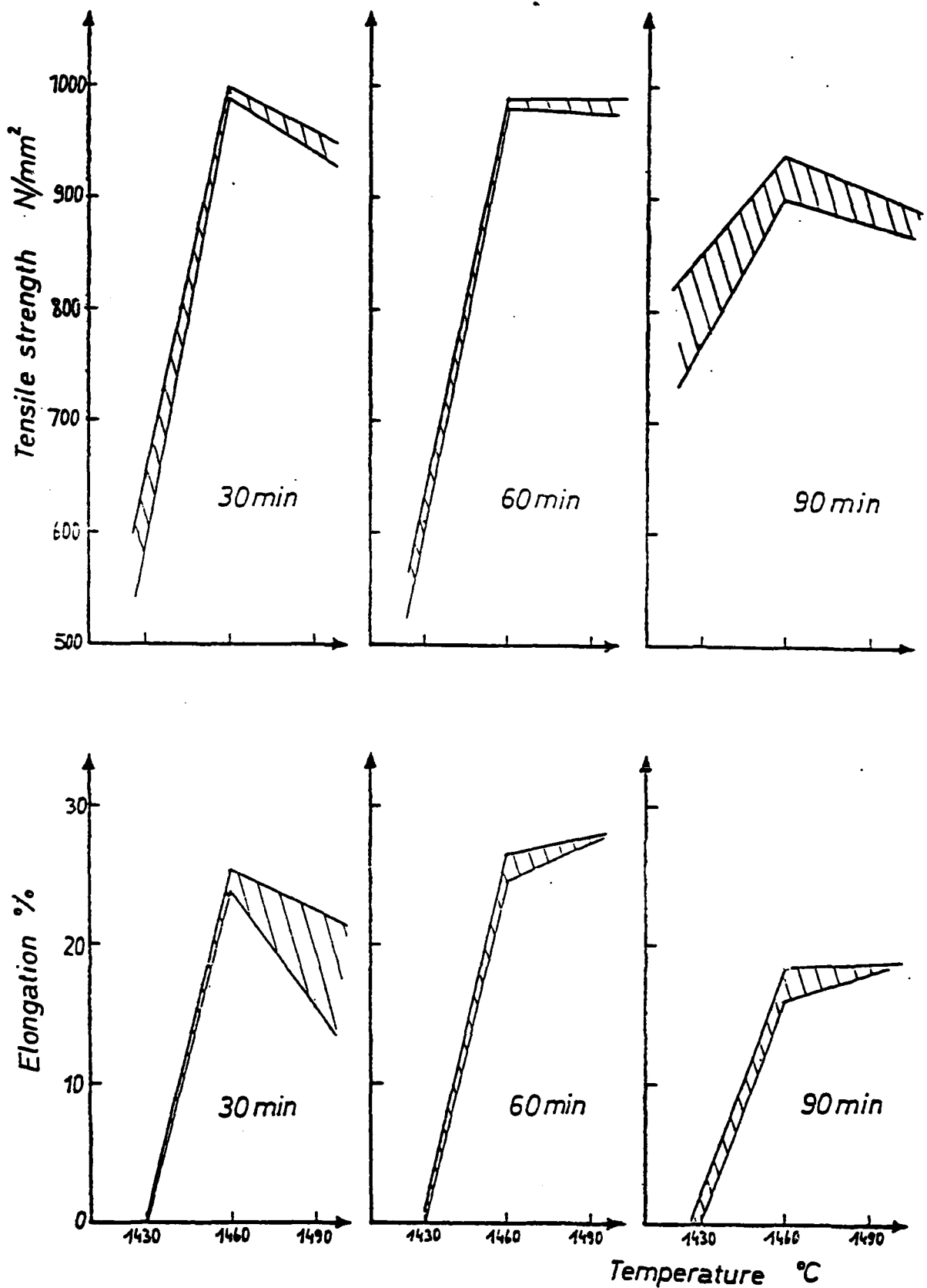samples as a function of sintering temperature
and time.

Fig.15b Tensile strength and elongation of slowly heated
and cooled samples as a function of sintering
temperature and time.

The individual results of the five samples tested for each of the values in Tab. 9 are shown in Fig. 15a and 15b. The narrow spread for each set of values is apparent.

The better ductilities obtained by slowly heating the samples were assumed to be due to the better deoxidation thereby possible. However, comparative Oxygen analyses, made by the manufacturer of the W powders, showed no correlation between level of residual Oxygen and ductility.

T A B L E   1 0
- - - - - - - - -

Oxygen levels in various sintered samples.

| Charge basis | blending treatment | sintering conditions | | | | elong. % | O_2 ppm |
		heating	temp. °C	time min	cooling		
434/78	mixed, granulated	rapid	1470	30	rapid+HT	0.7	54
434/78	-"-	rapid	1470	30	slow	0.4	57
434/78	attritormilled +0.02 Cr	rapid	1470	30	rapid+HT	11.1	85
503/78	mixed, granulated	slow	1470	30	rapid	11.3	53
503/78	-"-	slow	1470	30	slow	22.4	85
503/79	-"-	slow	1460	30	slow	24.7	51

As shown in Tab.9 1430°C is apparently insufficient for sintering, nonporous sintered samples are first obtained at 1460°C. Although their ductilities are relatively poor, the still porous specimens "sintered" below 1460°C have surprisingly high tensile strength.

As can be seen in Fig. 15a and 15b, sintering at 1460-1470°C for 30-60 min appears optimal. The final density is reached quickly at a sufficient sintering temperature and remains practically constant with increased time or temperature. Especially the hardness, and, to a lesser extend the tensile

strength, decrease as the sintering time is extended.
The best ductilities are obtained by sintering for 60 min,
after which they too decrease.

Increasing sintering temperatures for a constant sintering
time cause decreases in hardness and tensile strength, only
the ductility benefits somewhat. As can further be seen from
Tab. 9, for well sintered samples a direct correlation
between tensile strength and ductility appears to exist
samples with higher tensile strengths also have better
ductilities.

This rather unusual positive correlation between tensile
strength and ductility, and their worsening with increased
sintering intensity (time and temperature), had also been
observed in some of our earlier work (12). This phenomenon
is due to grain coarsening that progresses with the
sintering intensity. The finer structures have better
tensile strengths and ductilities.

3.3.5. Metallographic investigations:

Metallographic sections of differently prepared samples
reveal their structural differences. While very regular
structural features (Fig. 16a) are seen for the samples
which were slowly heated to the sintering temperature,
intermediate layers between the W grains and the binder
phase can be observed for the rapidly heated samples (Fig.16b).
These layers are in the form of rings, apparently indicating
a poor contact between grain and binder. Scanning electron
microscope (SEM) studies confirmed this (see below). In
the rapidly heated samples impurities or precipitates on
the grain boundaries of the bridged grains are visible
(Fig. 16c). SEM photographs (shown below) confirm the low
strength of these bridges. These visible boundary lines
could, as Huppmann(9) presumed, be thin layers of the
binder phase which due to coalescence passed through one
of the adjoining grains.

In parts of the rapidly heated but slowly cooled or sub-
sequently heat treated samples, lamellar precipitates in
the binder phase can also be observed (Fig.16d). In both
the rapidly cooled and the slowly heated/slowly cooled
samples no lamellar precipitates were found.

For a series of samples prepared under otherwise constant
conditions (slowly heating, sintering at 1470°C, slowly
cooling) but sintered for different lengths of time, the
photographs clearly show the grain coarsening (Fig. 17a-17d).

The grains of the 3 μm starting powders show clearly,
even after very short sintering times (samples cooled shortly
after appearance of liquid phases--"Silberblick" effect--
for 2 min sintering time). uniform grains of about 15 μm.
With extended sintering the grains continue to grow but
not at the same rate (Tab. 11).

T A B L E   1 1

Grain sizes (see text below) of the W grains in samples
with different sintering times.

W powder	initial grain size um	sintering cycle	sint. temp. °C	sint. time min	final average grain size μm
434/78	3.13	1	1470	2	14.8
				30	20.2
				60	23.6
				900	60.3
503/79	3.05	2	1460	2	14.6
				30	19.1
				60	23.2
				90	24.2
			1490	30	20.1
				60	23.4
				90	25.9
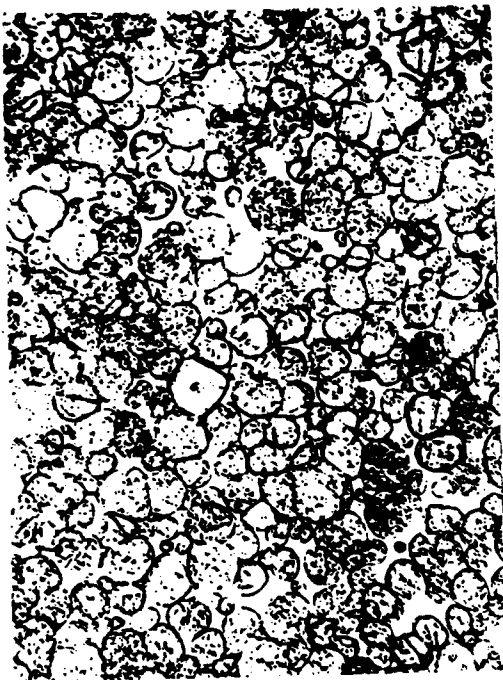
Fig.16a Metallographic section
         of a slowly heated and
         cooled sample. 200 x
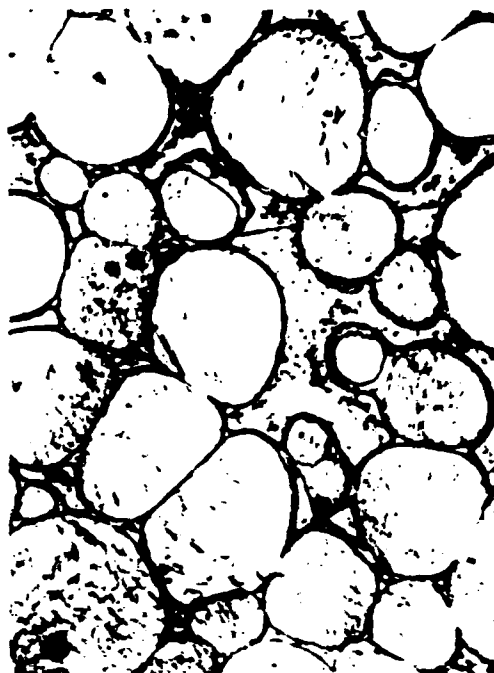
Fig.16b Metallographic section
         of a rapidly heated and
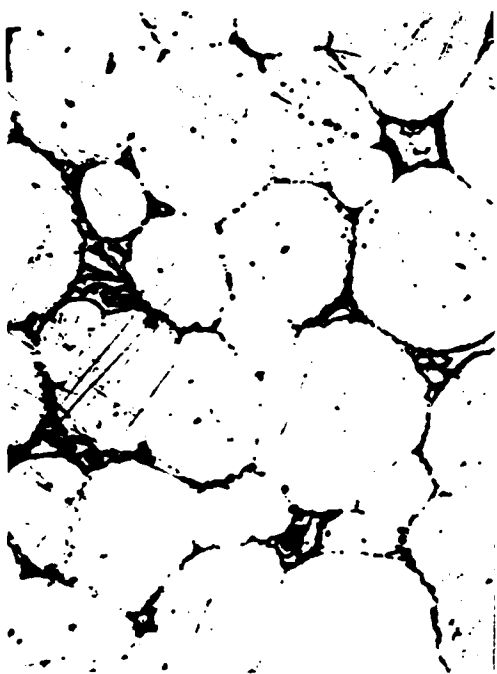   cooled sample. 1000 x

Fig.16c As Fig.16b
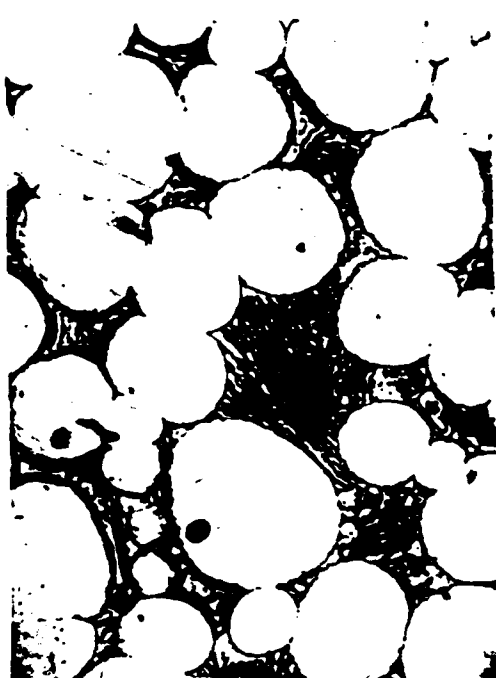
Fig.16d Metallographic section
         of a rapidly heated and
         cooled sample afterwards
         subjected to heat treatment.
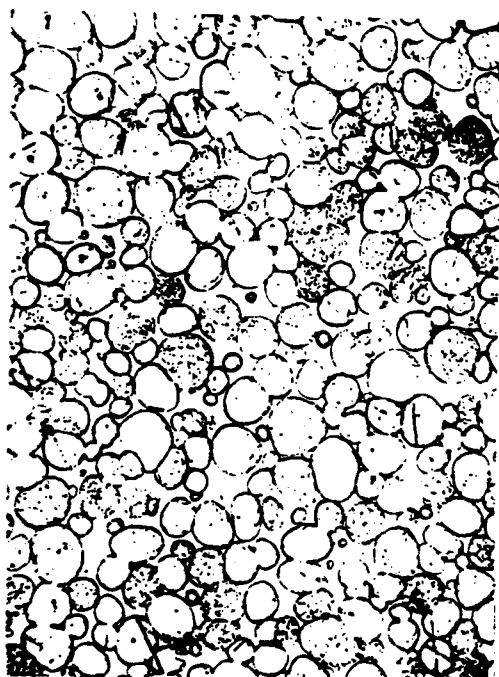   1000 x

Fig.17a 1470°C 2 min

Fig.17b 1470°C 30 min

Fig.17c 1470°C 60 min

Fig.17d 1470°C 900 min

Fig.17   Metallographic sections of slowly heated and cooled
         samples prepared from powder 434/78 and sintered
         for different length of time.   200 x

The grain sizes were determined from sample sections etched with a $CuSO_4$ solution. For each specimen the W grains in 9 parallel 0.6 mm strips were counted and, taking into consideration the area due to binder, the average grain size was calculated. Since cut grains tend to appear smaller than they really are, the values from this method are only relative, but still quite suitable for comparisons.

The rate of heating before sintering does not seem to affect grain growth during sintering. At higher sintering temperatures a slightly faster rate of grain growth is observable. Later investigations will explore methods to slow or stop the undesirable grain growth with doping additives.

3.3.6. Effect of the cooling rate:

As already mentioned, the rate of cooling the specimens after sintering also has significant effect on the ductility. If the specimens have a high ductility, the cooling rate influences the structural development in the binder phase and thus its hardness. According to Holtz (3) good ductilities in heavy metals are achieved when the W grains and the binder have comparable hardnesses, while poor ductilities are observed for strongly dissimilar hardnesses. To test this theory the microhardnesses of the W grains and the binder phases in sintered specimens having various ductilities were measured (Tab. 12).

T A B L E   1 2

Microhardness values for W grains and binder phases from differently prepared sintered specimens.
(uniform sintering temperature of 1470°C and time of 30 min)

W Powder	sintering treatment	heat treatment	microhardness W grain	binder	elongation % gauge length 25 mm
429/78	cycle 1	-	319	212	0.4
434/78	-"-	-	312	198	0.2
434/78	-"-	30min 1000°C	338	270	3.2
434/78 + 0.02 Cr	-"-	30min 1000°C	335	275	13.2
503/79	cycle 2	-	310	267	25.1
503/79	-"-	-	319	270	27.6

"Cycle 1" corresponds to a rapid heating and rapid cooling of the sample (see Fig. 11), "Cycle 2" to slow heating and cooling (see Fig. 14).

As can be seen from Table 12, binder hardness for samples which were slowly cooled or which underwent a heat treatment is greater, but the W grain hardness is not appreciably affected by the postsintering treatment. Thus, the slow cooling rate improved ductilities by lessening the difference between grain hardness and binder hardness.

The most important influence though seems to be the slow heating, by which, as previously discussed, through deoxidation occurs. Otherwise similarly handled samples (rapid heating, subsequent heat treatment), but one with and one without Cr additive in the binder, showed distinctly different ductilities for essentially the same difference in hardness between W grains and binder.

3.3.7. Wettability tests:

The hardness of the W grains is not, as was first thought,
a function of the deoxidation. Thus, an embrittlement of
the W grains cannot be the cause of the lower ductilities
found for samples which apparently still contained O_2. The
likelier cause is a lower adhesive strength between the
binder and the W grains due to poor wetting of the W grains
by the binder during sintering. The distinctly poorer
wettability of oxygen containing W grains is known from
Huppmann's investigations(8) in which rounded, very coarse
W grains were used.

To find possible differences in the wettability of W grains
in our powders, $5x5x60$ mm^3 bars of pure W were pressed from
the various powders. They were sintered for 1^{hr} at 1200°C so
that they were still quite porous. These sintered bars were
dipped vertically into liquid binder alloy at 1550°C. The
relative height to which the liquid binder rises in the W
bars should indicate the relative wettability of the W grains.
However, our bars were all thoroughly saturated. It appears
impossible, using our powders, to press bars sufficiently
long (>30 cm) to be used for this test and it had to be
discontinued.

From the preliminary test it is also evident that the
wettability seems to be more than sufficient in reducing
H_2 atmosphere under which W heavy metals are sintered. Our
tests had also included W bars sintered in a mixed H_2-N_2
atmosphere, in NH_3 and in Ar with traces of H_2, and all the
bars had been thoroughly saturated with the liquid binder.

The SEM photographs of fracture sections from the tensile
strength bars described below clearly indicate differences
in adhesion in the solid state though. It should be stressed
here that the relationship between the liquid phase wettability
and the solid state interface bonding strength for W and
the binder are not yet fully understood.

3.3.8. SEM micrographs of fracture surfaces of sintered bars:

The poor adhesion between binder and W grains is clearly
recognizable in samples with low ductilities, made by rapidly
heating the green compacts to the sintering temperature.
Fig. 18a and 18b show that the W grains and the binder
phase were literally torn apart where the bars fractured.
Good adhesion can be observed in very few places. As noted
above, a subsequent heat treatment for specimens so sintered
brings at best only a slight improvement in ductility. In
the SEM photo (Fig.18c) of such a sample, the W grains pro-
truding from the fracture surface are again visible, the
binder did not adhere to the W grains. There are only
slightly more signs of adhesion to be seen here than for
the rapidly cooled samples. The ductile yield for specimens
cooled slowly as well as for those subsequently heat treated
is, as would therefore be expected, correspondingly only
slightly higher.

Signs of a better adhesion between W grains and binder can
be recognized in Fig.18d, taken from the sintered compact
doped with 0.02 % Cr. This sample also has a much better
ductility.

In SEM photographs it can further be seen that W grains
which had sintered together can also be torn apart (see
Fig. 18d and 18e, an enlargement of such a W grain). In
these photos an apparent intermediate layer between the
grains is visible. The spots on the fracture surfaces in-
dicate inclusions or impurities (Fig. 18f).

The fracture surfaces of high ductility samples heated slowly
(sintering cycle 2) look entirely different. The binder
adhers well to the W grains so that they are not separated
when the bar breaks. Instead, the fracture goes through
the W grain (see Fig. 19a and enlargement in 19b).

Thus the better ductility observed for samples sintered according to Cycle 2 (slow heating) is due to better adhesion between the W grains and binder. It is quite probable that the improved adhesion arises from a better reduction of the green compact during the slow heating before sintering.

Fig. 18 SEM photographs of the fracture surfaces of tensile strength bars sintered as in Cycle 1.

a: W powder 434/78, sintered 30 min at 1470°C, cooled slowly. Ductility 0.4 %, 1500x.

b: As (a) but cooled rapidly from sintering temperature, ductility 0.1 %, 3000x.

c: As (a) but rapidly cooled then heat treated, ductility 0.7 %, 1500x.

d: Charge doped with 0.02 % Cr, rapidly cooled, ductility 11.1 %, 1500x.

e: As (a), ductility 3 %, 1500x.

f: As (b), ductility 0.2 %, 4000x.

g: Excerpt from (e), 3000x.

Fig. 19 SEM photographs of the fracture surfaces of tensile strength sintered as in Cycle 2.

a: W powder 503/79, sintered 30 min at 1490°C, slowly cooled, ductility 27.7 %, 1000x.

b: W powder 503/79, sintered 30 min at 1460°C, slowly cooled, ductility 24.7 %, 2000x.
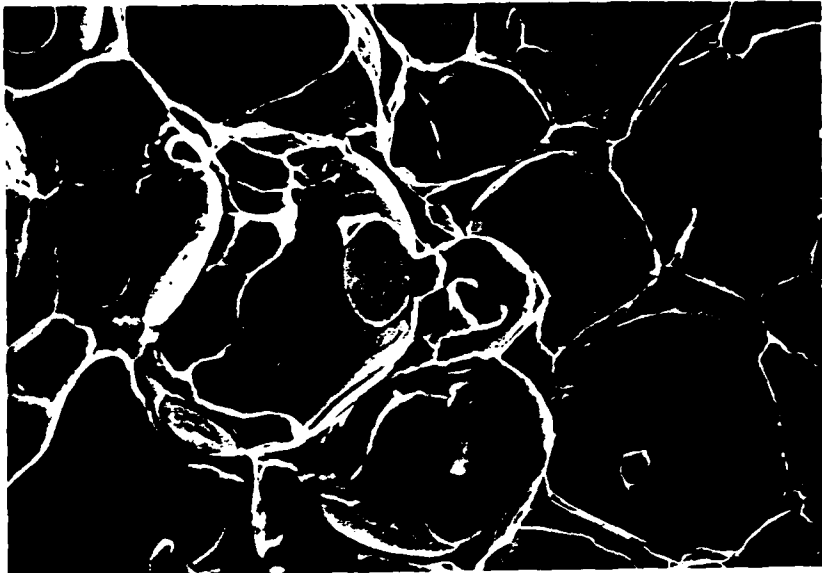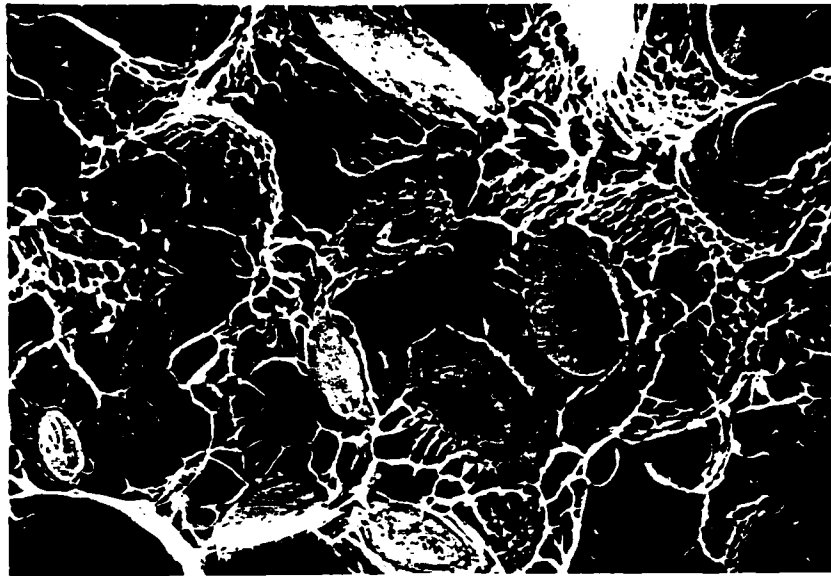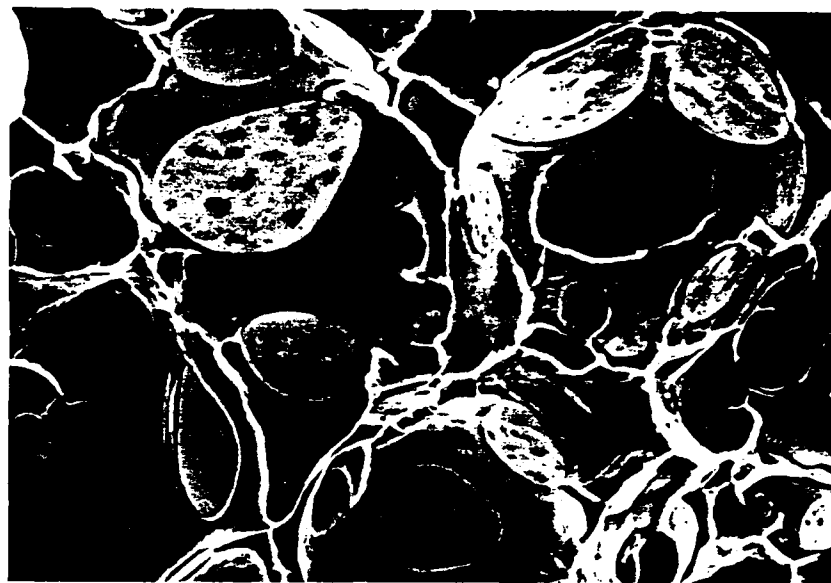
Fig.18a
1500 x
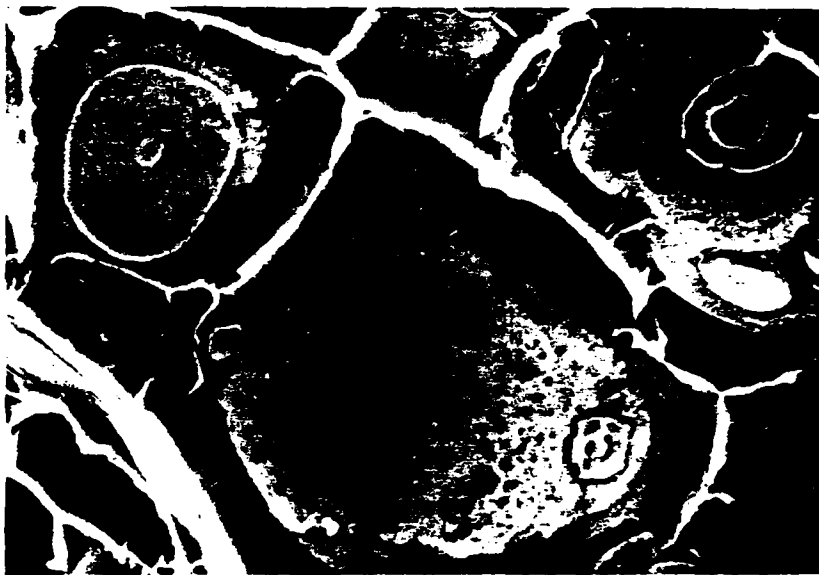
Fig.18b
3000 x
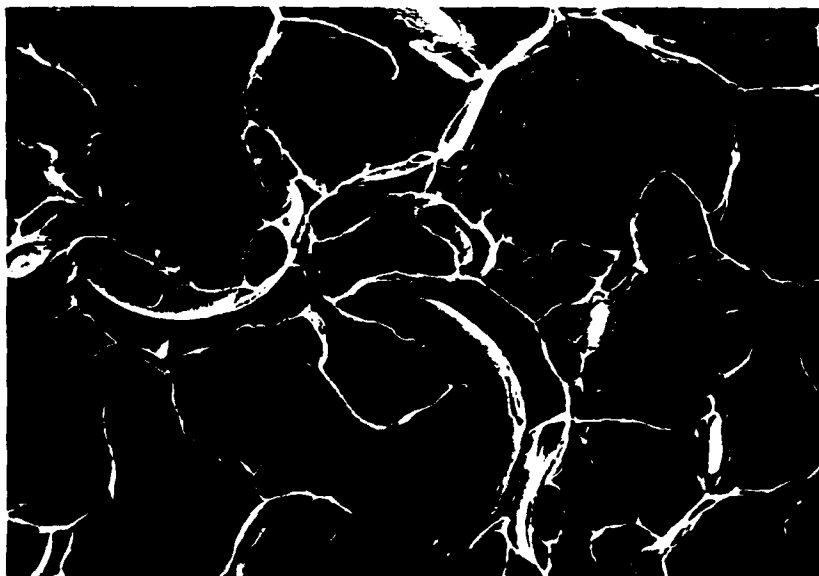
Fig.18c
1500 x

Fig.18d
1500 x

Fig.18e
1500 x

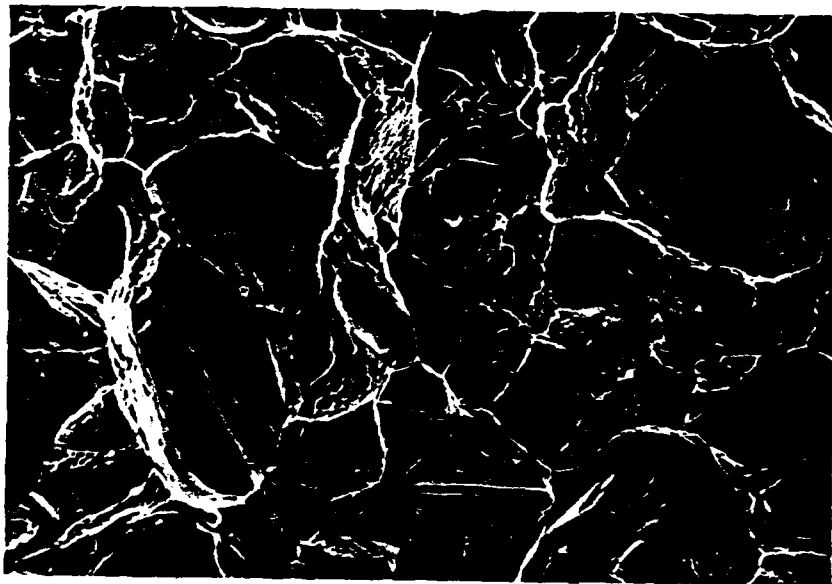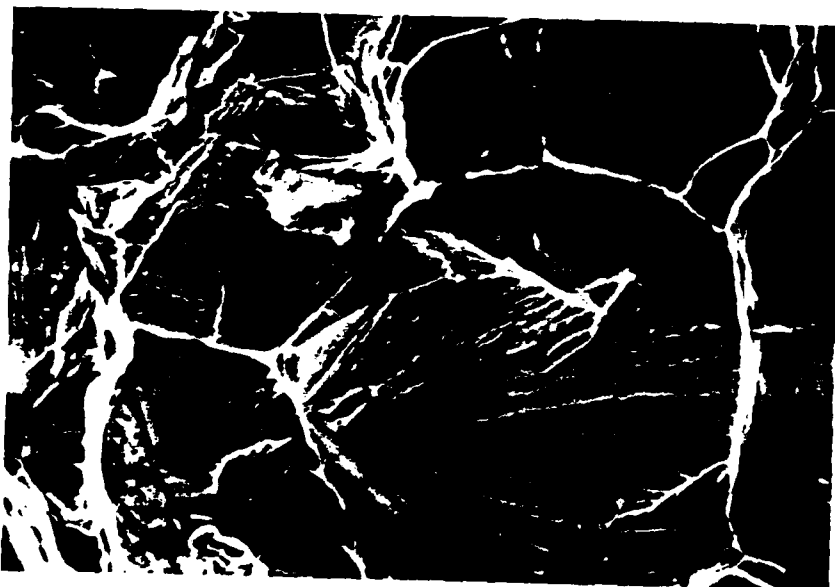
Fig.18f
4000 x

Fig.18g
3000 x

Fig.19a
1000 x

Fig.19b
2000 x

4. Heavy metals with higher W contents:

Especially high densities for W heavy metals can generally
be achieved by increasing the W content. Alternative measures
such as adding uranium (2) or other specifically heavy metals
to the binder have little effect because the binder accounts
for so little of the entire sample. According to Ariel, Barta
and Branton (10), increasing the W content for a given binder
composition increases the hardness slightly and decreases
the ducility, also slightly. Tensile strength is less affected
by the W content.

Our investigations included test with 95 and 97 wt % W charges
to determine their optimal sintering conditions and the final
mechanical properties. W powder 434/78 was used and the Ni:Fe
ratio in the binder was maintained at 2:1. The preparation
included the addition of 1 % camphor and ball milling with
cyclohexane followed by granulation.

4.1._Compactibility of_the_high W charges:_

The green densities obtained at different compaction pressures
are given in Tab. 13 and Fig. 20.

T A B L E 1 3

Green densities from charges with higher W contents at
different pressures.

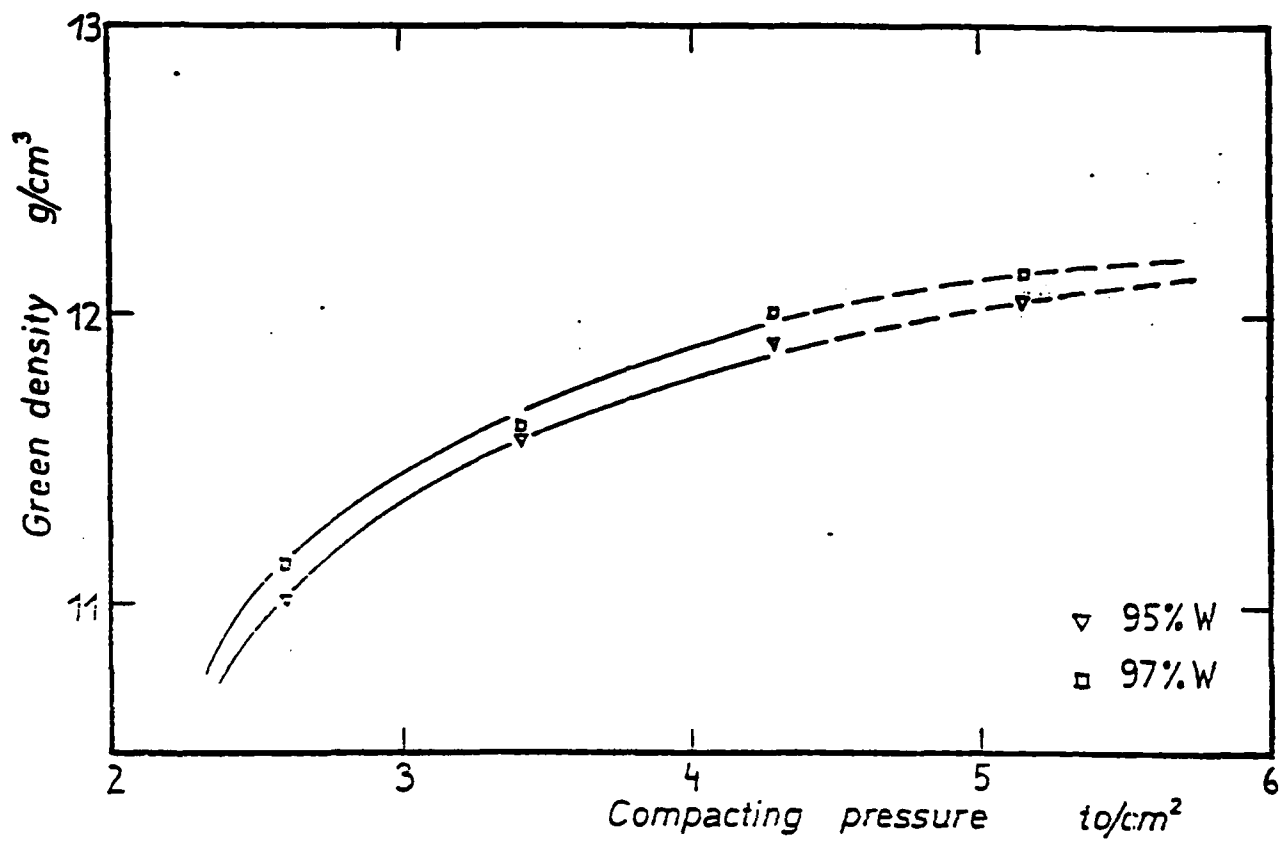| W content	density (g/cm^3) at a compaction pressure (to/cm^2) of			
	2.6	3.4	4.3	5.15
95 wt %	11.02	11.58	11.91	11.03[+]
97 wt %	11.14	11.61	12.01	12.13[+]

[+]compression cracks

Fig.20   Green density of heavy metals with higher
W - contents as a function of compacting
pressure.

Distinctly higher green densities are obtained with 95 wt % W
than with 90 wt % (compare Tab. 3). A further increase to
97 wt % W has no appreciable effect, apparently because the
charges with so much W are so difficult to press.

Contrary to the green compacts with 90 wt % W, some of those
with 95 and 97 wt % W already had compression cracks when
compacted at 5.15 to/cm^2. As green densities are relatively
independent of compaction pressure, we used 4.3 to/cm^2 in
order to obtain sound green compacts .

4.2. Sintering the high W samples:

Preliminary tests showed that 1460-1470°C, although optimal
for sintering charges with 10 % binder, is apparently too
low for sintering the high W samples. At these temperatures
the sintered compacts had 1.5-2 % residual porosity, while
higher temperatures gave nonporous samples. Thus the high
W samples were sintered at 1490°C.

The green compacts were heated slowly (Cycle 2) and in general
cooled slowly, these conditions having been recognized by
then as being best. For comparison several samples were heated
slowly but cooled rapidly after sintering.

The mechanical properties of these sinter compacts are listed
in Tab. 14.

T A B L E   1 4

Mechanical properties of sintered specimens with higher
W contents.
Samples compacted at 4.3 to/cm^2, heated slowly, sintered
at 1490°C.

	sintering time min	cooling	density g/cm^3	HV$_{62.5}$	tensile strength N/mm^2	elongation % gauge length 25 mm
95 % W	15	slow	18.08	317	863	5.1
	30	slow	18.09	312	965	13.1
	30	rapid	18.08	308	906	7.2
	60	slow	18.07	312	898	8.7
	90	slow	18.12	305	851	5.0
	120	slow	18.13	302	876	6.9
97 % W	15	slow	18.46	293	873	2.0
	30	slow	18.52	316	898	4.2
	30	rapid	18.52	317	840	2.8
	60	slow	18.51	312	831	3.3
	90	slow	18.55	314	812	2.6
	120	slow	18.53	312	835	4.2

The values of the mechanical properties as a function of
sintering time are shown in Fig. 21a and 21b. As can be seen,
for obtaining good ductilities and high tensile strength, 30
min appears to be the best sintering time. The sintered
density increases slightly with extended sintering. Very
few pores remain, apparently because of the relatively small
proportion of binder, and these close with prolonged sintering.
However the gain in density is much less than the extensive
losses in tensile strength and ductility resulting from the
longer sintering. The hardness also decreases with increased
sintering time, due to the increased W grain coarsening
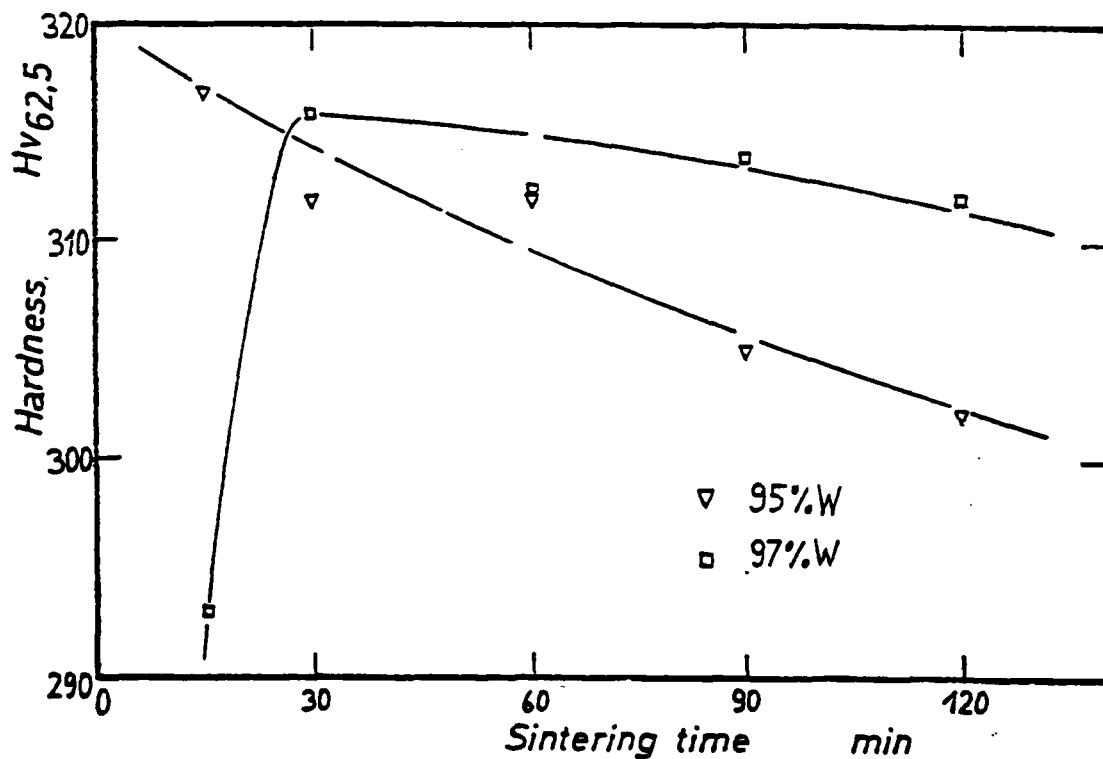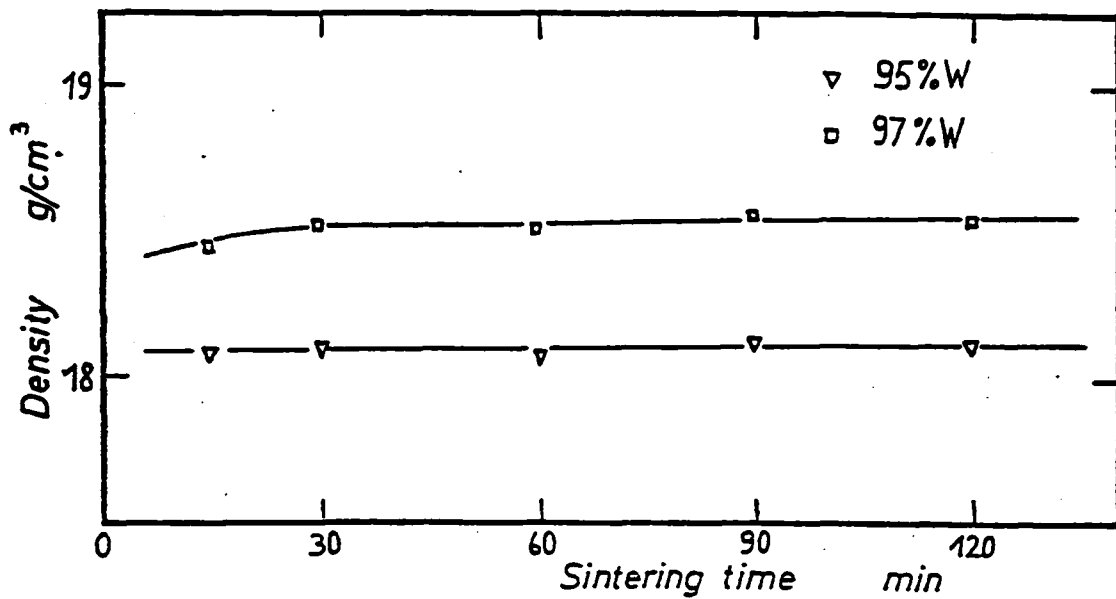which is observed again in these samples.

Fig.21a Heavy metals with higher W - contents sintered
at 1490°C :
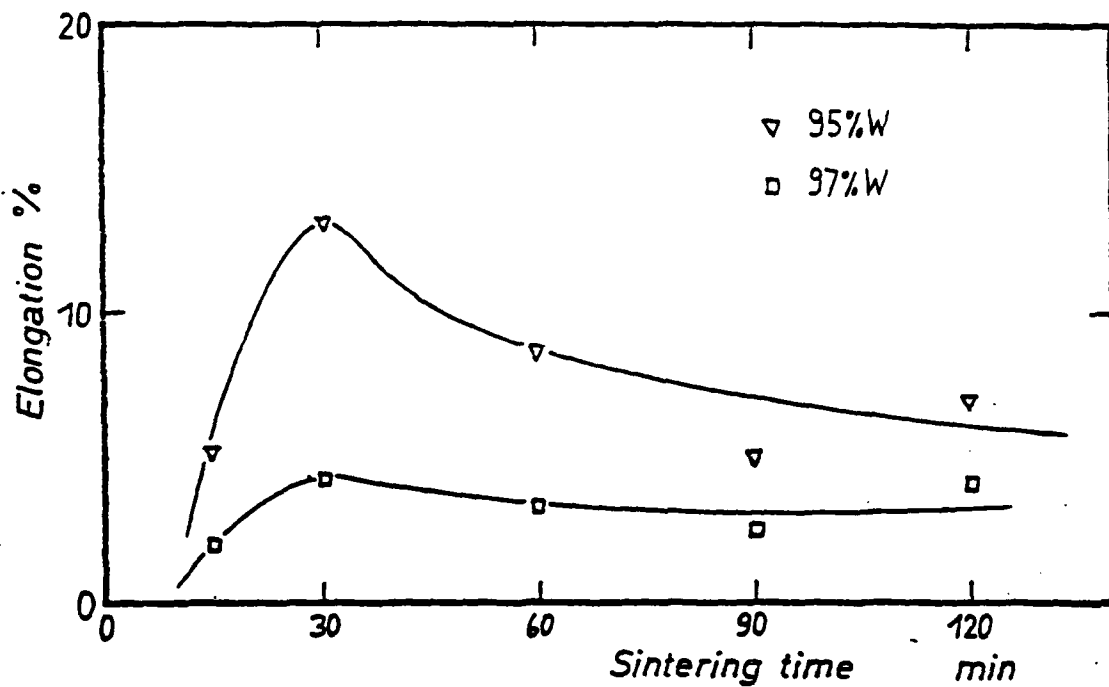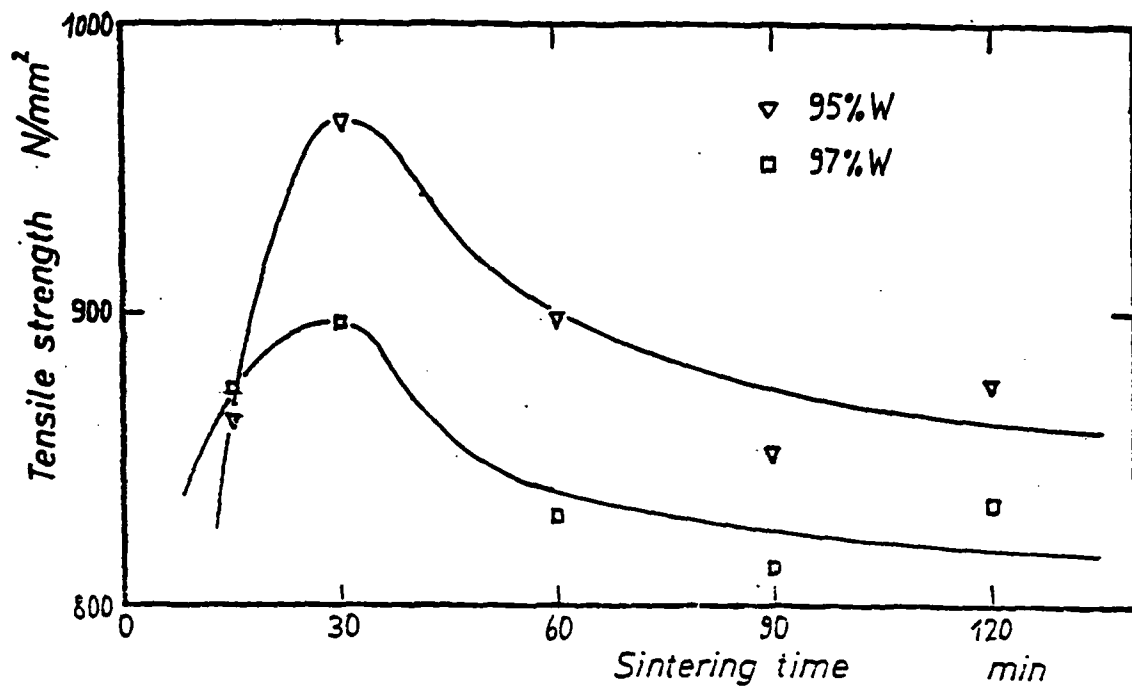Density and hardness as a function of sintering
time.

Fig.21b Tensile strength and elongation as a function of sintering time.

As a comparison between the values in Tab. 11 and Tab. 9 shows, the hardness increases with increasing W content, but not decidedly. While samples with 90 wt % W have HV = 300-305, samples with 95 wt % W have hardnesses around 310 and 97 wt % W, near 315.

As expected the tensile strength decreases with increasing W content, though not substantially. The W content has a greater influence on ductility. Samples with 90 wt % W have ductilities of 20-25 %, those with 95 % W just up to 13%, and with 97 % W only slightly over 4 %. The influence of the cooling rate is also apparent for the ductilities of the high W samples. Rapid cooling causes distinctly lower ductilities than slow cooling.

5. Summary:

The first goal of this project, to fabricate sintered heavy
metals with good tensile strengths and ductilities, has been
reached. With 90 wt % W and 10 % Ni-Fe binder in the ratio
2:1, sintered specimens with tensile strengths of 950-1000
N/mm^2, ductilities up to 27 % and densities near 17.10 g/cm^2
were achieved. With 95% W densities near 18.0 g/cm^3, tensile
strength over 900 N/mm^2 and ductilities up to 13 %, with
97 % W densities over 18.5 g/cm^3, tensile strengths up to
900 N/mm^2 and ductilities over 4 % were attained.

Extensive tests on the pressing behavior of the sinter
charges showed the best compactibility and the highest green
densities are attained by adding 1 % camphor to the powder
mixture and wet blending it with cyclohexane. This is then evaporated
till the powder is crumbly, the right consistency for granulation.
The granulate must then be thoroughly dried. Alternatives,
such as attritor ball milling the powder charge, using other
pressing lubricants, omitting the granulation, or incompletely
drying the granulate, worsen the compressibility. Powders
unfavorably prepared frequently have compression cracks
even at lower compaction pressures, while properly prepared
powders give sound green compacts at 5.15 To/cm^2.

Investigations of many sintering parameters have shown that
nonporous sintered specimens are possible only above 1460°C.
Enough eutetic melt for liquid phase sintering cannot form
below that. Higher W contents (95 and 97 wt %) require an
een higher sintering temperature. Further, 30 min was found
to be the optimum length of time for sintering. Longer
sintering causes too much grain coarsening which lowers the
final mechanical properties.

The deoxidation of the green compacts prior to sintering has
a substantial effect on the quality of the product. The
best deoxidation is achieved by slowly heating the green

compacts in H_2 up to the sintering temperature, with a
longer holding time in the 800-1000°C region. Poor pre-
reduction gives brittle sintered specimens with low
ductilities. Residual C, possibly from too rapidly baking
out the pressing lubricant, could not be established. Improved
ductilities through doping with reducing metals (Cr, V)
were realized, while doping with nonreducing metals (Co, Mo,
Cu) had little influence on the ductilities. The post sintering
treatment of the samples is also important, slow cooling
from the sintering temperature or a subsequent heat treat-
ment for rapidly cooled samples is necessary for favourable
structural development in the binder phase. Appropriate
postsintering heat treatment approximately doubles ductilities
as compared to simply cooling the samples rapidly.

During the slow cooling process the binder becomes much
harder. W grains and binder then have similar hardnesses
which, according to the literature is desirable for high
ductilities.

The decisive realization however appears to be that the
complete removal of oxygen prior to sintering necessary
for obtaining good quality heavy metals. Inferior batches
during production could be due to poor reduction of the
sintering specimens. This point will receive particular
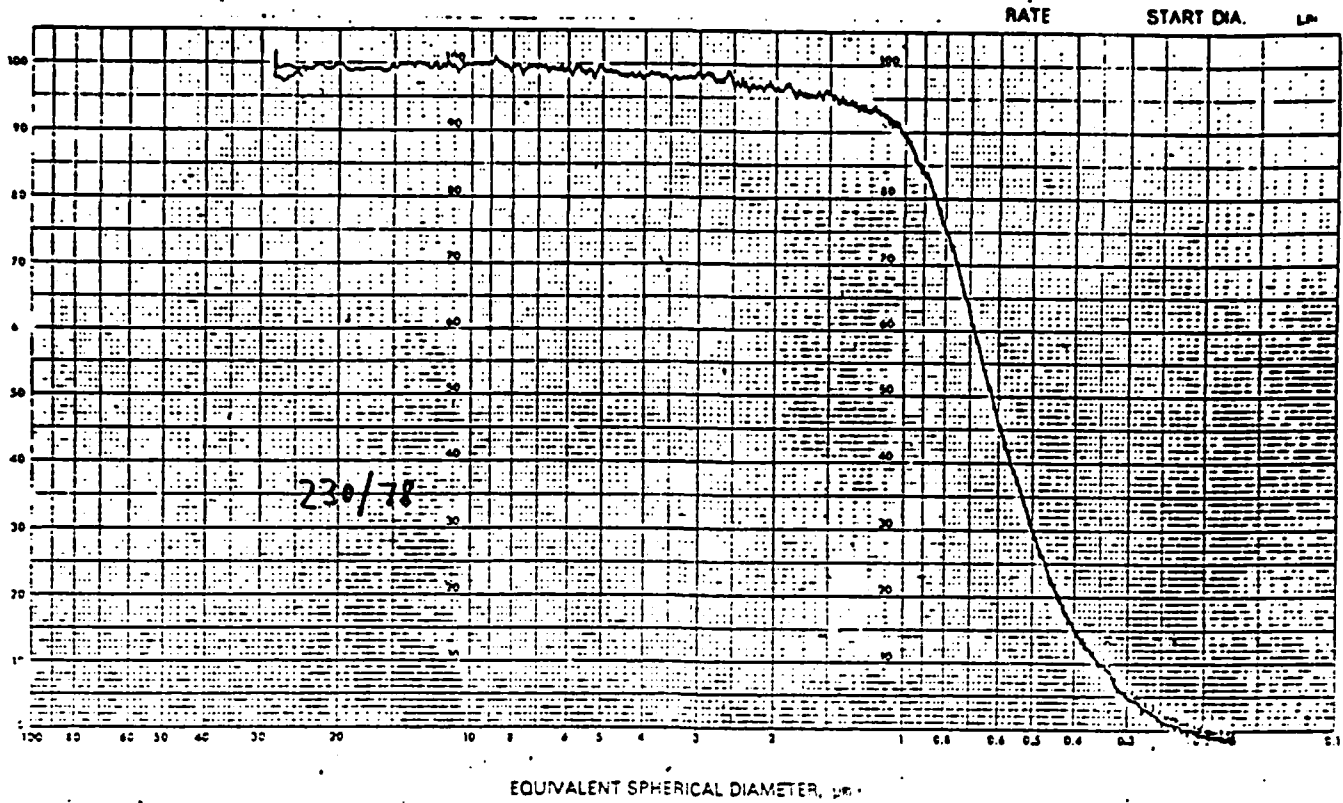attention in future studies.

6. Further Program :

Following the conclusion of the initial investigations, further work will be done to study the influence of doping additives on W grain growth during sintering. Heavy metals with different binder compositions will be made and the effect of different alloying elements, especially Cu, will be tested.

The influence of the sintering atmosphere on the heavy metal properties will be examined closely. Besides pure H_2, NH_3, N_2-H_2 mixtures, and Ar atmospheres, as soon as the vacuum furnace is finished it should be possible to sinter under vacuum.

Supplementary investigations, especially concerning the adhesion between the binder and the W grains, and perhaps attemps to improve wettability, are planned.

L i t e r a t u r e

1. E.C.Green, D.J.Jones,   Iron Steele Inst.; Spec.
   W.R.Wilkins   Rep. 58 (1956) 253
2. R.Kieffer, K.Sedlatschek   Planseeber. f. Pulvermet.
                                  5 (1957) 104
3. F. Holtz, R. Thyne   Rep. Armour Res. Found.;
                                  Chicago 1969
4. A.J.Davis, D.J.Jones   Engl. Pat. 1.172,754-56
                                  (1968)
5. E.I.Larsen, R.H.Krock   I. Electrochem. Soc. 108
                                  (1961) 284
6. R.H.Krock, L.A.Shepard   Trans. Met. Soc. AIME
                                  227 (1963) 1127
7. R.Minakova, A.Pilyankovich,   Poroshkovaya Met. 5 (1968)
   O.Teodorovich, I.Frantsevich   73
8. G.Petzow, W.J.Huppmann   Z. Metallk. 67 (1976) 571
9. A.R.Poster   Powder Met. 9 (1962) 301
10. E.Ariel, J.Barta, D.Brandon   Powder Met. Int. 5 (1970) 3
11. J.L.Chermant, M.Coster,   Prakt. Metallogr. Sonderb.
    P.Dujardin   8 (1978) 192
12. G.Jangg, R.Kieffer,   Planseeber. f. Pulvermet.
    B.Childeric, E.Ertl   22 (1974) 15

230/78

EQUIVALENT SPHERICAL DIAMETER, μm

m micromeritics
instrument corporation

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION _194/77 N.5 IV ... /5... ... ... KG ... 9,69 μ_   DATE _12.78_

Density _2.0.9_ g/cc   LIQUID _............._   Density _0.8999_ g/cc   Viscosity _6.947_ cp   BY _TB_

Preparation _.... ...._   TEMPERATURE _33_ °C

RATE _213_ START DIA. _21_ μm

197/77

CUMULATIVE MASS PERCENT

EQUIVALENT SPHERICAL DIAMETER, μm
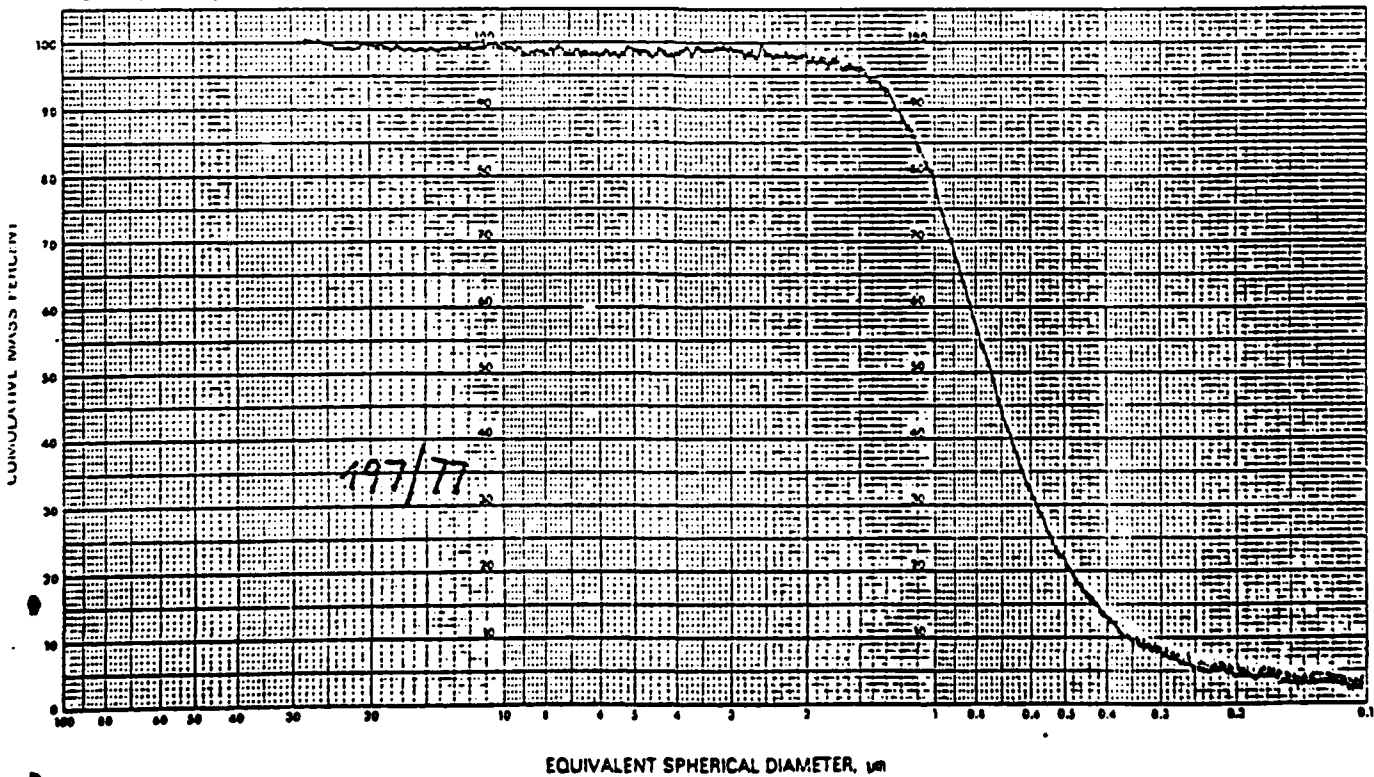
m micromeritics

Density _19,3_ g/cc   LIQUID _SEDISPERS E_   Density _0,1249_ g/cc   Viscosity _7,660_ cp   BY _RA_

Preparation _60' deagglomeviel L +45' US_

TEMPERATURE _30_ °C

RATE _192_   START DIA _72_ µm

CUMULATIVE MASS PERCENT

231/72

EQUIVALENT SPHERICAL DIAMETER µm
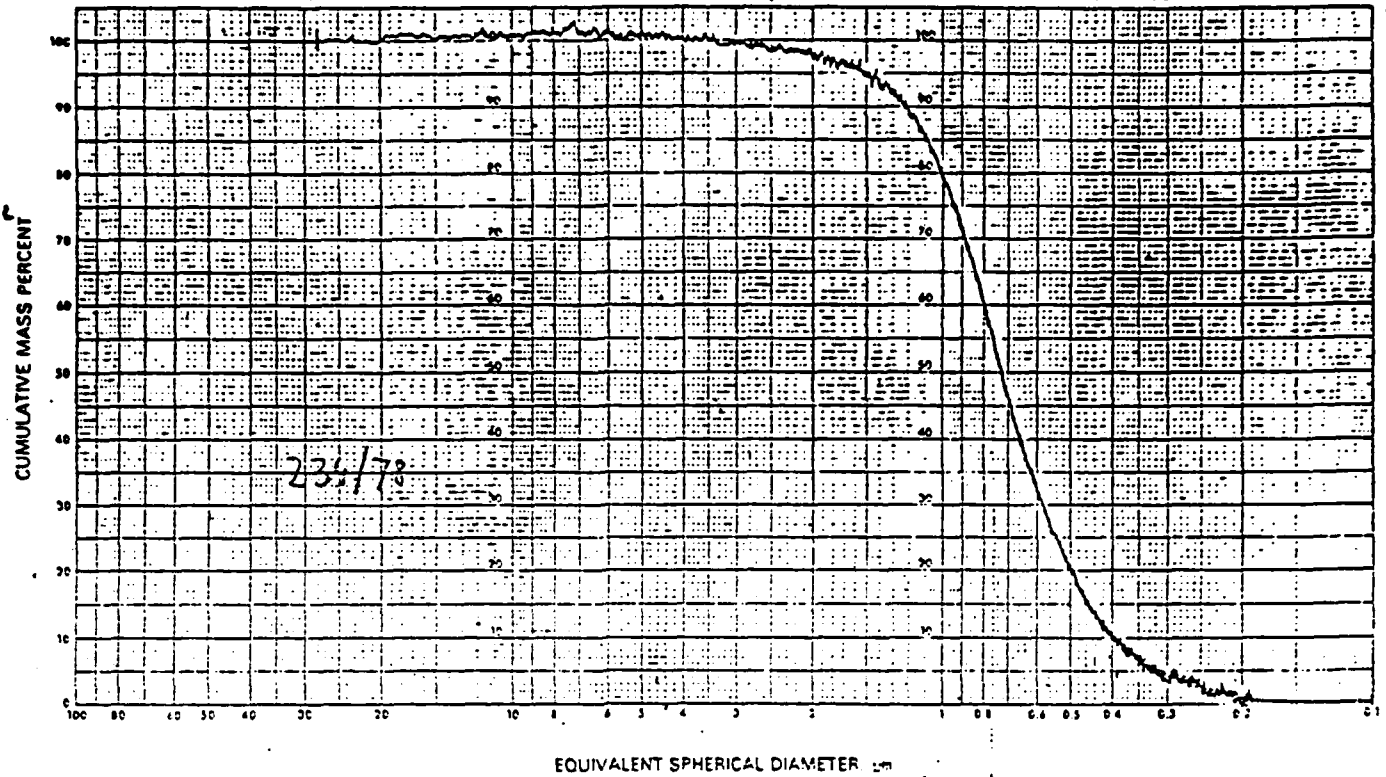
m micromeritics

SAMPLE IDENTIFICATION _429/70 WB_   /Fsss Kg= _3,16 µ_   DATE _78-11-07_

Density _19,3_ g/cc   LIQUID _SEDISPERSE A-13_   Density ____ g/cc   Viscosity ___ cp   BY _RA_

Preparation _60' deagglomeviel + 15' US_

TEMPERATURE _33_ °C

RATE _679_   START DIA _50_ µm
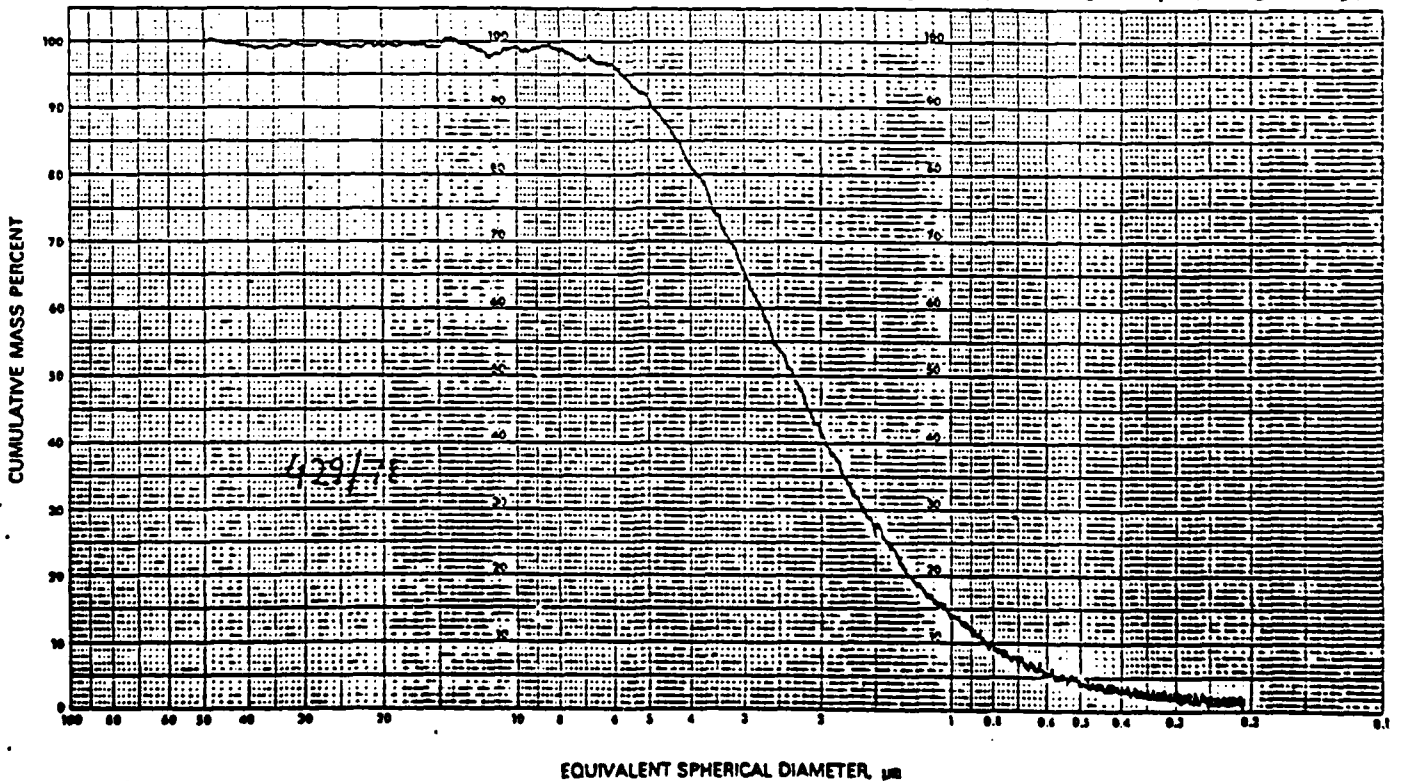
CUMULATIVE MASS PERCENT

429/70

EQUIVALENT SPHERICAL DIAMETER µm

EQUIVALENT SPHERICAL DIAMETER, μm
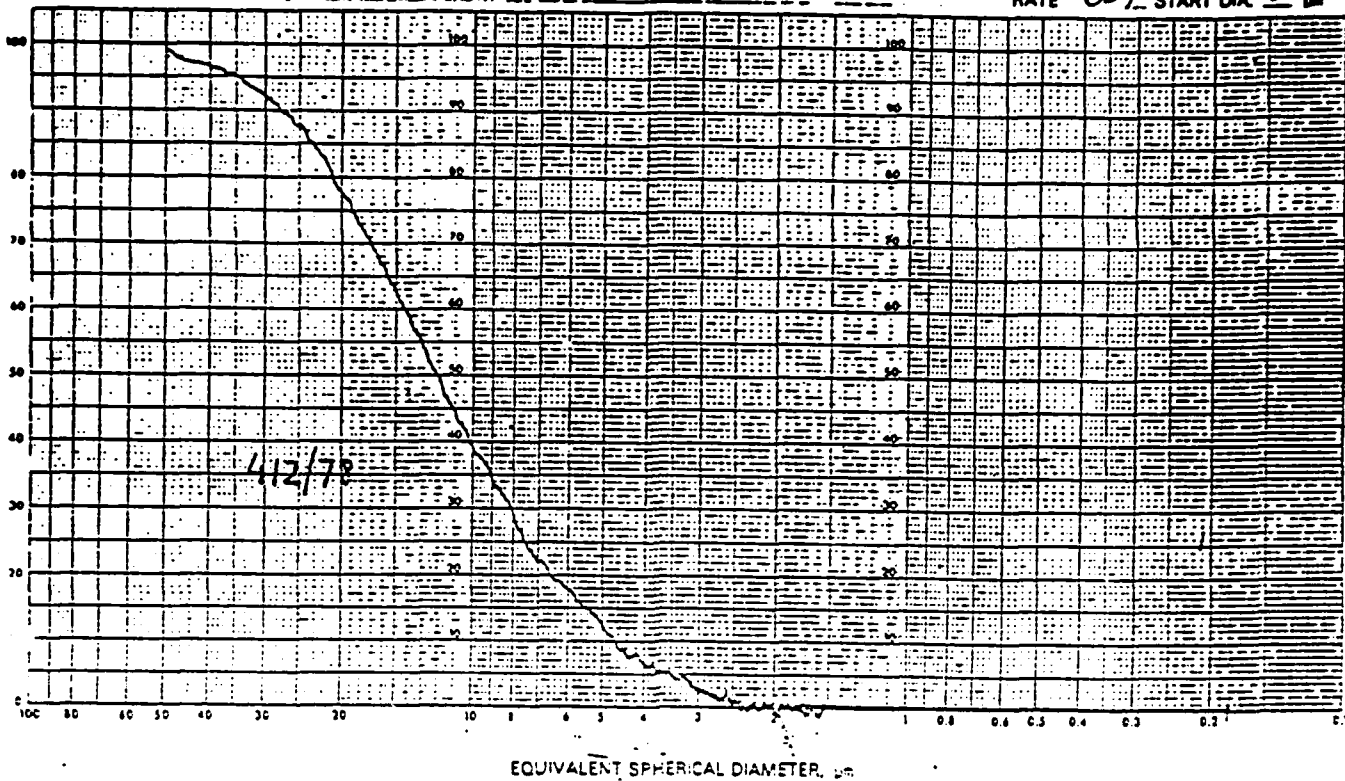
m   micromeritics

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION 503/79 WB. Ⓥ

Density 19,3 g/cc   LIQUID SEDISPERSE K-13 Density _____ g/cc   Viscosity _____ cp

Preparation ____ 60' deagglomeriert + 15' US _____

DATE 79-04-05

BY RH

TEMPERATURE 30 °C

RATE 59 % START DIA 50 μm

EQUIVALENT SPHERICAL DIAMETER, μm

m   micromeritics
instrument corporation

SAMPLE IDENTIFICATION 434/78 WB (V) / FSS KS=3,13,   DATE 78-11-27

Density 19,3 g/cc   LIQUID Spicerese n-13 Density ____ g/cc   Viscosity ____ cp   BY RA

Preparation   60' desaggtomavient + 15'US   TEMPERATURE 51 °C

                                                             RATE 617   START DIA 50 µm

ECUIVALENT SPHERICAL DIAMETER, µm