English Translation

THE MEASUREMENTS OF PHYSICAL PROPERTIES

OF BORON CARBIDE PELLETS

AND

THE POSSIBLE RECOVERY OF BORON CARBIDE

POWDER FOR SINTERING FROM ITS PELLET

February 28, 1970

DENKI KAGAKU KOGYO CO., LTD.

Contents

List of Tables and Figures

1. Introduction

It is decided that pelleted boron carbide will be used for the control rod material of an experimental fast breeder reactor. The preparation of B_4C pellets was carried out, for the purpose of making preliminarily control rods for the experimental fast breeder reactor, and they were delivered to Power Reactor and Nuclear Fuel Development Corporation (PNC) in October, 1970. In this experiment B_4C pellets, prepared by a hot-press on the same conditions as those delivered to PNC, have been tested on their physical properties, in order to utilize the data obtained to prepare control rods for JEFR.

The experiment consists of;

(1) measurements of mechanical and thermal properties of natural B_4C pellets

(2) measurement of mechanical properties of enriched B_4C pellets

(3) a feasible recovery of sintering powder from B_4C pellet.

The experiment was commissioned by PNC to Denki Kagaku Kogyo Co., Ltd. and made at its Central Laboratory.

2. Samples and specimens for the experiment

Both natural and enriched B_4C powder used were the same as those for the pellet preparation, specimen for the measurements of physical properties being prepared by hot-pressing under the same conditions as in the case of the pellets preparation. The characteristics of B_4C powder used are shown in Table 1. However, the natural B_4C pellet specimens used for the thermal shock test were provided with those remained after the delivery to PNC.

3. Microphotographs of B_4C pellets

Both natural and enriched B_4C pellets were cut at the center of pellets hot-pressed, the cut section being polished, etched with phosphoric acid-potassium iodate solution, and its surface observed by optical microscope. The microphotographs are shown

- 1 -

in Photos 1 and 2.

There are only pores in both natural and enriched B_4C to be seen before the etching, and no difference to be observed between them. The grain boundary is observed clearly after the etching in the case of natural B_4C pellets, and the grain size agrees with the grain diameter approximately.

There is not any clear grain boundary on the etched surface of enriched B_4C as in the case of natural B_4C, and the surface of the grain itself is being etched. This was the same case as at a shorter etching time. The cause of easy etching is not clear, however, it is supposed to be one of causes that enriched B_4C contains more boron than theoretical equivalent (T.B with ^{10}B of 90 atm. % : 77.2%).

4. The measurements of mechanical properties of B_4C pellets

Both natural and enriched B_4C were measured on the compression strength, the bending strength, the Young's modulas and the Poisson's ratio.

4.1 The compression strength

4.1.1 The method of the measurement

The specimen of 10 mmϕ x 10 mmh was prepared by a hot-press, and used for the measurement of the compression strength. A measuring apparatus, "Shimazu" universal tester Type RH-30, was used to press at a rate of 10 ton per 70 sec.

As the results of a preliminary test, it was found that there was the smallest variation in the measured values when a stainless steel plate of 1 mm thick was placed between the specimen and the pressing part at the time of the measurement. Therefore the measurement was carried out by placing stainless steel plates both on top of and under bottom of the specimen.

4.1.2 The results of the measurement

The results of the measurement on the compression strength of both natural and enriched, hot-pressed specimens are listed in Table 2 as below. The results of the compression strength in average were 26.27 ton/cm^2 for natural

B_4C and 25.40 ton/cm^2 for enriched B_4C, respectively.

4.2 The bending strength

4.2.1 The method of the measurement

The specimen used for the measurement was of the dimension of 45 x 12 x 6 mm, as shown in Fig. 3, piano wire was placed on top of and under bottom of the specimen and the load was put using the same apparatus as for the measurement of the compression strength to obtain the breaking load. The bending strength was calculated by the following equation from the breaking load.

$$\text{The Bending Strength (kg/cm}^2) = \frac{3pl}{2bt^2}$$

where

      p : breaking strength (kg)

      b : width of the specimen (mm)

      t : thickness of the specimen (mm)

      l : distance between fulcrums (mm)

4.2.2 The results of the measurement

The results of the measurement are shown in Table 3. The bending strength (in average) for natural B_4C was 2980 kg/cm^2, smaller than that of enriched B_4C, 5430 kg/cm^2 in comparison.

4.3 The Young's modulas and the Poisson's ratio

4.3.1 The method of the measurement (The strain-gauge method).

The method of the measurement is outlined as in Fig. 6. Two dimentional gauges were pasted on top of and under bottom of the specimen, and the Young's modulas and the Poisson's ratio were calculated from the relationship between the load P and the strain. The load P was increased by 10 kg to 100 Kg in the measurement. The measurement was made twice top and back, and averaged. As the Young's modulas (E) can be obtained from the stress σ / the strain ε , a stress-strain curve is plotted to determine the gradient, tan θ_1 , from a longitudinal

- 3 -

stress (ε_1) and a stress (σ), that is, the Young's modulas. As the Poisson's ratio is obtainable by the transverse contraction / longitudinal elongation, the gradient, tan θ_2 , of the transverse strain (ε_2) against the stress (σ) is got from the stress-strain curve, and then tan θ_1 / tan θ_2 using tan θ_2 obtained above, that is the Poisson's ratio. The stress σ is obtainable by the following equation

$$\sigma = \frac{3pl}{bt^2}$$

where

      p : the load (kg)

      l : the distance between fulcrum (19 mm
                                          in this case)

      b : the width of the specimen (mm)

      t : the thickness of the specimen (mm)

4.3.2 The results of the measurement

The description of the specimen measured are shown in Table 4, and the stress-strain curves obtained in Figs. 5 and 6. The Young's modulas and the Poisson's ratio, calculated from the stress-strain curves, are shown in Table 5.

As is seen in Table 5, each value of the Young's modulas and the Poisson's ratio was the same in both natural and enriched B_4C.

5. The measurements of thermal properties of natural B_4C pellets

Natural B_4C pellets only were tested and measured in terms of the coefficient of thermal expansion, the thermal conductivity, the specific heat and the resistibility to thermal shock.

5.1 The coefficient of thermal expansion

5.1.1 The method of the measurement

The measurement apparatus used was a measuring apparatus of thermal expansion and contraction, Type G.E.W of Gakei Electric Work Co., Ltd. The thermal expansion of the specimen can be measured using this apparatus, by heating it in the electrical-heating furnace and measuring the expansion

of it by a telescope in the outside of the furnace. The description is shown in Fig. 7. The measurements were carried out, heating two pieces of the specimen to 1,000°C at the rate of 3.4°C per min. The relative density (R.D) of the specimens measured were 98.33% for the specimen A and 99.37% for the specimen B.

5.1.2 The results of the measurement

As shown in Fig. 8, there was no difference in the two measurements and the expansion of 0.46% was obtained in the range from 60°C to 1,000°C. This corresponds to the coefficient of the thermal expansion of 4.89×10^{-6} 1/°C.

5.2 The thermal conductivity

5.2.1 The method of the measurement

The measuring apparatus of Type SS.T.C-18, manufactured by Shibayama Science Co., was used. The outline of this apparatus is sketched in Fig. 9. The principle of the measurement by the apparatus is as follows: Using two kinds of liquid whose boiling points (10 - 20°C) are different, contact a steady flow of vapour to the heating plate P_2 by heating solution A with higher boiling point, and then solution B is heated to boil by the heat transferred to the specimen S. The vapor of B is then cooled by a cooler K_2 and received into a receiver V. When B is 1 ml and the time required to evaporate t is measured, the thermal conductivity will be calculated by the following equation:

$$\lambda = \frac{Q}{t(TA-TB)} \frac{1}{C} \quad ,$$

where

λ : the thermal conductivity (Kcal/m.Hr.°C)

Q : the heat of evaporation of 1 ml of solution with lower b.p. (Kcal/ml)

t : the time required to evaporate 1 ml of solution with lower b.p. (ml/Hr)

T_A-T_B : the temperature difference between solutions with lower and higher boiling points.

1 : the thickness of the specimen

C : the section of the specimen

In practice, as there is a contact resistance at surfaces of P_1 and P_2, the relationship, l/t, between the thickness of the specimen, l, and the time required to condense 1 ml of a solution of lower boiling point, t, was obtained by changing l in order to make a correction due to the contact resistance. The thermal conductivity was calculated from such values as those corrected. Three kinds of the specimen with different thickness and used for the measurement are shown in Table 6.

There are three sets of the combination of solutions with lower and higher boiling points, used in the measurement, as follows:

1) System of acetone-benzene

2) System of toluene-monochlorobenzene

3) System of bromobenzene-o-dichlorobenzene

5.2.2 The results of the measurement

The measurement was made nine times in all:

After the specimen was placed in the apparatus and set in place, the time was measured three times until 1 ml of condensate with lower boiling point had been obtained, then after resetting the specimen in place the time was measured thrice once again.

The average of the nine measurements and the thickness of the specimen was plotted in a graph, the gradient, l/t, being obtained by the least square method to calculate the thermal conductivity .

The measured data are shown in Tables 8 and 9, and the graph of l/t in Fig. 10. From obtaining l/t from the Fig. 10, the thermal conductivity was calculated as shown in Table 10.

5.2.3 The consideration

The thermal conductivity of B_4C are 21.3 Kcal/m.Hr.$^{\circ}$C at 196°C, 12.7 Kcal/m.Hr.$^{\circ}$C at 104.2°C according to the report by Robert E. Brocklehurst,[1] and the measured values in this test are smaller than those by him. Especially the measured values at 121°C and 167°C are smaller than those by Robert E. Brocklehurst. It is necessary to confirm this fact

Note 1)   ASD-TDR-63-597

- 6 -

further by the other method of the measurement in parallel with the method at this time.

5.3 The specific heat

5.3.1 The method of the measurement

The measuring apparatus used is "Differential Scanning Calorimeter", manufactured by Perkin-Elmer Corp. The apparatus employs sapphire as a standard sample. The specific heat of the sample is obtained in comparing the heat contents of both samples of the standard and for the measurement, required for heating at the same rate. The measurable amount of the sample are 50 - 10 mg, and a broken piece of hot-pressed boron carbide was used as the sample. The measurement was carried out at four temperature steps of 97°c, 197°C, 277°C and 447°C.

5.3.2 The results of measurement

The measurement was run twice, and the results were listed in Table 11.

5.3.3 The consideration

In general, the relation between specific heat Cp and temperature are approximately represented by an equation of the second order of temperature as follows:

$$Cp = a + bT + cT^2 \text{ (cal/g. }^{o}K) \text{ ----------- (1)}$$

The results of the measurement shown in Table 11 are reduced to the following equation of the second order in terms of temperature (^{o}K).

$$Cp = 0.278 - 0.0000178T + 0.000000433T^2 \text{ ---------- (2)}$$
Cp in cal/g. ^{o}C
T in ^{o}K

The equation (2) and the measured values are shown in Fig. 10. The specific heat of boron carbide by Brocklehurst stated above are reported as 0.37 at $500^{o}C$ and 0.50 (cal/g.^{o}C) at $1,000^{o}C$. The present values are a little higher than them. It is understood that the different conditions in the porosity,

- 7 -

the composition and the hot-pressing of the sample resulted
in the different measured values.

5.4 The thermal shock test

5.4.1 The test procedure

The sample of natural B_4C, $15\phi \times 25$ h (mm) in size,
immersed into molten lead, subjected to the repetition of
heating and cooling, and observed concerning the situation
of cracking in the pellet sample. Lead of 2 kg in weight
was placed in an alumina crucible of 80 mm in inner dia-
meter and 70 mm high and heated to melt by an electrical
furnace with heating element of nicrome wiring (Fig. 11).
A set of two crucibles was placed side by side and molten
lead in them was held at 500°C and 370°C.
B_4C pellet wound by iron wire (2 mmϕ) was put into molten
lead held at 370°C for more than two minutes, and then
moved quickly into another molten lead held at 500°C to
heat rapidly. After it was held at 500°C for more than two
minutes, it was quickly moved back into the former molten
lead held at 370°C to cool rapidly. The cycle of 370°C
500°C ⟶ 370°C was repeated five times for each heat treat-
ment, and then it was cooled and examined on the presence
of crack. In a similar way, it was treated in the cycle of
370°C ⟶ 800°C ⟶ 370°C, but in this case it was examined
on the presence of crack after each cycle.

5.4.2 The test results

The test results are shown in Table 12. As it is, in the
case of 370°C ⟶ 800°C (temperature difference : 430°C), it
cracked after one cycle or two. On the other hand, in the
case of 370° ⟶ 500° (temperature difference : 130°C), one
of the samples cracked after 45 - 50 cycles, but the other
one of the samples stood intact even after 75 cycles.

5.4.3 The consideration

When B_4C pellet of $15\phi \times 25$ h mm was subjected to the treat-
ment of rapid heating and cooling in molten lead, it broke
after one cycle or two in the case of 430°C of temperature
difference, while it could stand intact for rapid heating

and cooling in less than 50 cycles in the case of 130°C of temperature difference.

On the assumption that B₄C pellets are used for control rods in a fast breader reactor, it is supposed that they are subjected to the thermal shock much less than in this test, because of a stainless steel cladding tube which covers them. It is the subject for a future study whether B₄C pellets can stand for whatever extent of heating and cooling when they are cladded with stainless steel tube.

6. Conclusion

The results of the measurements in this experiment are summarized and listed in Table 13.

7. A feasibility test of recovering B₄C powder for sintering from B₄C pellets fragment.

B₄C pellets was crushed into powder and it was tested, whether, once again, it could be suitable for the material for hot-pressing.

7.1 The test method

Two pieces of natural B₄C pellet of 50 mmø x 50 mmh were taken for sample, and crushed following to the flow sheet shown in Fig. 14.

The specifications of the crushers used are shown in Table 14 as follows:

A hydrochloric acid treatment was applied to remove iron entered in the crushing process. The sample obtained from the ball mill crushing was put into a glass beaker of 3 litre, and with the addition of 2 litre of 10% hydrochloric acid, it was heated for 5 hours to the extent of gentle boiling. Then it was filtered in suction through Buchner's funnel, rinsed with pure water until cl' diminished, and dried at 100 – 110°C. B₄C powder thus obtained was hot-pressed as before and its physical properties was measured.

7.2 The results of test

7.2.1 Material balance

The weight balance, after crushing according to the flow sheet shown in Table 14, is indicated in Table 15 as follows: 418.2g of product, crushed and dried, was obtained from 490.1 g of pellet, it corresponding to 85.3% of yield. When 18.3g of over 125 μ fine (coarse) particles after stamp-milled is subtracted as a return material, the yield becomes 88.8%, as 418.2g was got from 471.8g.

Most of the loss was caused by scattering at the time of crushing with the stamp mill and the loss amounted to 7.8%. In the closed crushing more than 95% of yield product in the form of crushed powder would be attainable, because the loss due to scattering becomes negligible.

7.2.2 Grain size and composition of granular product

The size distribution and chemical composition of the granular product obtained by crushing are shown in Table 15 along with B_4C powder used for the preparation of the pellets. The crushed product was finer than B_4C powder used for the preparation of the pellets, it being half in average grain diameter. The chemical composition shows a greater total boron (T.B) in the case of the crushed product, but it is difficult to say that there are actually some difference between them from the viewpoint of the precision in analysis. As to impurities in very small quantity according to the spectrometry, the crushed product contains less calcium and magnesium, but as much of other ingredients as the starting material of B_4C powder.

7.2.3 Hot-pressing of the crushed product

The pellets of 15 mmϕ x 25 mmh were prepared for trial by hot-pressing the crushed product as the starting material. The description of the hot-pressed article is shown in Table 16, and there is not any difference to be observed in the removal from the mold and the surface conditions as well, when they were compared with those in the case of the former B_4C as the starting material.

The microphotographs of the surface of the hot-pressed

pellets after polishing are shown in Fig. 16. The grain
boundary becomes so much smaller in the case of the crushed
product because of smaller grain size, but there is no dif-
ference in other respects.

7.3 Consideration

The preparation of normal B_4C powder for hot-pressing is carried
out in the process of crushing of B_4C ingot-pulverizing by ball
mill — acid treatment — classification by the elutriation.
In this test, the hot-pressed B_4C pellets were crushed to regain
B_4C powder for hot-pressing, and B_4C powder recovered was as
satisfactory as that from crushing ingot.
B_4C has a great hardness and is likely to be contaminated with
impurities in the crushing process, however, it matters little
by all means, because iron (value) entered can be removed by
the acid treatment of the crushed product, if a crusher made of
iron family is used.

Appendix: A hot-press test on enriched boron carbide powder
with the addition of carbon black

Enriched boron carbide supplied by PNC contained more boron
than the theoretical ratio B/C as B_4C, and a reaction
between B_4C and the carbon die at the time of hot-pressing
was observed.
On this account, it was difficult to remove the hot-pressed
article from the die and also its surface did not look
smooth. Therefore, a test was carried out to find out how
the reactivity with the die and the shape and quality
would be when carbon black as a source of carbon was added
to enriched boron carbide containing more boron.

1. The method of test

Enriched boron carbide supplied by PNC had T.B. of 80.42 wt% and
T.C. of 19.88 wt. %, and 1.0 g of carbon black was added to 32.4g
of enriched boron carbide so as to obtain 77.09 wt% of theoretical
boron content in it ([10]B : 90 atm%). The composite material was

thoroughly mixed with a kneader, and the starting material for hot-pressing was made of it. Under the same conditions for enriched B₄C pellets delivered to PNC, the enriched B₄C powder with addition of carbon black was hot-pressed, and the reactivity with the carbon die and the shape and quality of the hot-pressed sample were studied. The shape of the sample was in the form of a cylindrical pellet of 15 mm∅ x 20 mmh.

2. Test results

As shown in Table 17, the density of the sample obtained by hot-pressing are 98.7 and 99.5%, the same values as those of the theoretical density. When carbon black was not added, the hot-pressed pellets could not be so readily removed from the die due to adhesion to it. However, in the case of addition of carbon black, they were as ready to remove from the die as those of natural B₄C and of much smoother surface conditions as shown in Fig. 17 than those with no addition of carbon black.

The surface condition, when it was polished and etched with a potassium iodate - phosphoric acid solution, showed, as shown in Fig. 18, a grain boundary near to that in the case of natural B₄C. Without addition of carbon black, it tended to be likely etched in other place than the grain boundary in the same procedure of etching (Fig. 2), but it was not the case with the addition of carbon black.

Table 1   Characteristic of B$_4$C powder

Kind \ Item	Natural B$_4$C	Enriched B$_4$C	Remarks
Chemical analysis			
T. B.	78.19±0.21wt%	80.42±0.21wt%	10$_B$ in enriched B$_4$C
T. C.	22.10±0.34	19.88±0.34	: 89.61±0.02 atm%
Impurities			
Si	–	460 p.p.m.	
Fe	1100 p.p.m.	* 244	* By atomic absorption
Ti	18	–	method; others by
Co	8	* <10	colonimetric method.
Cu	47	* < 5	
Mn	14	* < 5	
Mg	–	* 24	
Ca	–	* 320	
Ni	–	* <25	
Al	–	* <50	
Na	2	–	
Cl+F	80	–	
Free B	0.09wt%	0.10wt%	
Density	2.50g/cc	2.368g/cc	Pycrometric method
Grain size			Sedimentation balance
– 2μ	7wt%	6wt%	
2 ~ 6	56	37	
6 ~ 10	32	30	
10 ~ 14	5	16	
+ 14	–	11	
total	100	100	
Average grain diameter	5.4μ	6.5μ	
X-ray diffraction	Nothing was observed except B$_4$C	Nothing was observed except B$_4$C	

Table 2   Results of compression measurement

| Specimen No. | Description | | | Breaking load | Compression Strength |
	R.D. %	Diameter mm	Height mm		
Natural B₄C 1	98.9	10.00	10.20	16.18 ton	20.61 ton/cm²
2	97.3	10.00	10.15	21.77	27.70
3	97.7	10.00	9.95	19.32	24.61
4	97.4	10.00	10.15	25.23	32.14
5	98.0	10.00	10.25	12.72 *	—
Average					26.27
σ					4.24
Enriched B₄C 1	98.4	10.06	10.39	20.96	26.40
2	97.7	10.00	10.15	20.38	25.96
3	98.3	9.99	10.17	18.71	23.89
4	98.2	9.99	10.11	18.64	23.75
5	97.9	9.99	10.05	21.13	26.99
Average					25.40
σ					1.25

Table 3   Results of bending strength measurement

| Specimen No. | Description | | | Breaking load | Bending Strength |
	R.D.	Width mm	Thickness mm		
	%			kg	kg/cm^2
Natural B$_4$C 1	98.6	12.50	5.80	256	2.740
2	98.3	12.45	5.40	245	3.040
3	98.6	12.45	5.60	243	2,800
4	98.1	12.45	5.70	299	3,320
Average					2,980
σ					228
Enriched B$_4$C 1	98.4	12.45	5.85	454	4,790
2	97.9	12.45	5.90	492	5,100
3	98.0	12.45	5.85	605	6,390
Average					5,430
σ					693

Table 4   Specimen for measurement

Kind	Width (b)	Thickness (t)	Density	R. D.
Natural B_4C 1	12.50^{mm}	5.80^{mm}	$2.47^{g/cc}$	$98.1^{\%}$
2	12.45	5.60	2.49	98.6
Enriched B_4C 1	12.45	5.85	2.33	98.4
2	12.45	5.85	2.32	98.0

Table 5   Results of measurement

Kind No.	$\tan \theta_1$	$\tan \theta_2$	Young's modulas ($\tan \theta_1$)	Poisson's ratio ($\tan \theta_1 / \tan \theta_2$)
	$\times 10^4$	$\times 10^5$	$\times 10^4 kg/cm^2$	
Natural B_4C 1	4.66	3.22	4.65	0.163
	4.63	2.49		
2	4.67	3.39	4.53	0.135
	4.38	3.33		
Average			4.59	0.149
σ			0.12	0.021
Enriched B_4C 1	4.50	2.63	4.58	0.165
	4.66	2.92		
2	4.42	3.21	4.40	0.140
	4.37	3.07		
Average			4.49	0.153
σ			0.11	0.016

Table 6   Description of measuring specimen
for coefficient of thermal expansion

Specimen	Thickness mm	Diameter mm	Cross section cm^2	Density g/cc	R.D. %
A	1.552	18.05	2.56	2.52	100.0
B	5.762	18.05	2.56	2.52	99.4
C	11.460	18.10	2.57	2.49	99.0

Table 7   Results of measurement in the system
of acetone-benzene

Average boiling point   68.2^{o}C

Difference of boiling point   23.8^{o}C

Evaporation heat of acetone   97.7 cal/ml

Specimen	Time required for 1 ml of condensate acetone			
	1st run	2nd run	3rd run	Average
	sec	sec	sec	
A	22.5	21.4	23.2	sec
	23.0	22.5	23.1	22.7
	23.2	22.5	23.2	
B	33.7	32.8	31.5	
	34.1	32.5	31.8	32.7
	33.1	33.0	32.0	
C	57.5	52.6	56.8	
	56.2	51.6	57.8	55.5
	56.6	52.8	57.8	

Table 8   System of toluene-monochlorobenzene

Average boiling point   121.4 °C

Difference of boiling point   21.2 °C

Evaporation heat of toluene   75.7 cal/ml

Specimen	Time required for 1 ml of toluene condensate			
	1st run	2nd run	3rd run	Average
	sec	sec	sec	sec
A	44.4	41.8	44.2	
	43.4	41.2	44.0	43.6
		39.6	42.3	
B	58.0	55.4	57.2	
	59.0	57.8	59.8	57.6
			56.4	
C	112.4	108.9		
	111.4	109.7		110.8
		110.3		

Table 9   System of bromobenzene - 0 - dichlorobenzene

Average boiling point   167.7 $^{\circ}$C

Difference of boiling point   21.2 $^{\circ}$C

Evaporation heat of bromobenzene   88.6 cal/ml

Specimen	Time required for 1 ml bromobenzene condensate			
	1st run	2nd run	3rd run	Average
	sec	sec		
A	56.7	64.6		
	57.8	67.3		61.8
	58.2			
B	115.7	112.2	109.5	
	105.5	102.8	108.7	108.4
	104.7			
C	187.8	192.2	169.9	
	181.8	176.1	169.2	180.1
	183.1	174.9	171.2	

Table 10   Thermal conductivity of B$_4$C

Average temperature	l / t	Thermal conductivity
$^{\circ}$C	m/Hr	Kcal/m.Hr.C
68.2	1.075	17.23
121.4	0.519	7.24
167.3	0.301	4.52

Table 11   Results of specific heat measurement

Measurement temperature	1st run	2nd run	Average
	cal/ C.g	cal/ C.g	cal/ C.g
97 °C (370° K)	0.325	0.328	0.327
197 °C (470° K)	0.358	0.397	0.378
277 °C (550° K)	0.435	0.344	0.390
477 °C (750° K)	0.475	0.544	0.510

Table 12   Test results of thermal shock

Specimen		Test temperature	Presence of crack
No.	R.D.		
1	98.76%	370±10 ↔ 500±10	No change until 45th run, cracked at 50th run
2	98.65	"	No change until 75th run
3	98.39	360±10 ↔ 790±10	Broken at 2nd run
4	99.13	370±10 ↔ 800±10	Broken at 3rd run
5	98.69	380±10 ↔ 780±10	Broken at 1st run
6	98.80	370±10 ↔ 790±10	Cracked at 2nd run
7	98.61	360±10 ↔ 790±20	Cracked at 2nd run
8	98.53	380±10 ↔ 770±10	Cracked at 1st run

Table 13   Summary of test results

Item		Natural B_4C	Enriched B_4C
Compression strength	ton/cm^2	26.27	25.40
Bending strength	ton/cm^2	2.98	5.43
Young's modulas	kg/mm^2	4.59×10^4	4.49×10^4
Poisson's ratio	-	0.149	0.153
Coefficient of thermal expansion (60 ~ 1000°C)	$1/°C$	4.89×10^{-6}	
Thermal conductivity 68°C	$Kcal/m.Hr.°C$	17.23	
121°C		7.24	
167°C		4.52	
Specific heat 97°C	$ca./gr. °C$	0.327	
197°C		0.378	
277°C		0.390	
477°C		0.510	

Table 14   Specifications of crushers

Stamp mill	Diameter of mortar 14 cm Weight of pestle 7 Kg
Ball mill	Inside diameter-19 cm. Length-18 cm.Made of iron. Number of rotation -90 r.p.m. Size of iron ball-10~40 mmφ.Weight of iron ball used -7.9 Kg

Table 15   Grain size and composition of
            crushed product

	Crushed product	Starting material
Distribution of grain		
– 2 μ	36.0 wt %	7 wt %
2 ~ 6	49.5 "	56 "
6 ~ 10	13.0 "	32 "
+ 10	1.5 "	5 "
total	100.0 "	100 "
Average diameter of grain	2.7 μ	5.4 μ
Chemical composition		
T.B	78.37 wt %	78.19 wt %
T.C	21.7 "	22.1 "
Spectrometry		
Fe	++	++
Ca	+	++
Mg	+	++
Al	±	+
Si	++	++
Cu	+	+

(Note) Spectrometry   ++ Presented enough

+ Presented slightly

± Ambiguous

Table 16   Results of hot-pressing with crushed product

No.	B$_4$C powder	Weight of pellet	Diameter	Height	Density	R.D.
1	11.1 g	11.01 g	15.10mm	24.70	2.49	98.7 %
2	"	10.98 "	15.10 "	24.50	2.51	99.3 "
3	"	10.93 "	15.10 "	24.45	2.50	99.2 "
4	"	10.97 "	15.10 "	24.45	2.51	99.3 "

Table 17   Test results of hot-pressing with the addition of carbon black

No.	Weight of powder	Weight of pellet	Diameter	Length	Density	R.D.
1	8.35 g	8.27 g	15.05mm	19.80mm	2.34g/cc	98.7 %
2	"	8.24	15.05	19.65	2.36	99.5
3	"	8.29	15.05	19.75	2.36	99.5
4	"	8.28	15.05	19.70	2.36	99.5

Before etohing (x 270)   After etching (x 540)

Fig. 1 Microphotographs of Natural B_4C pellet
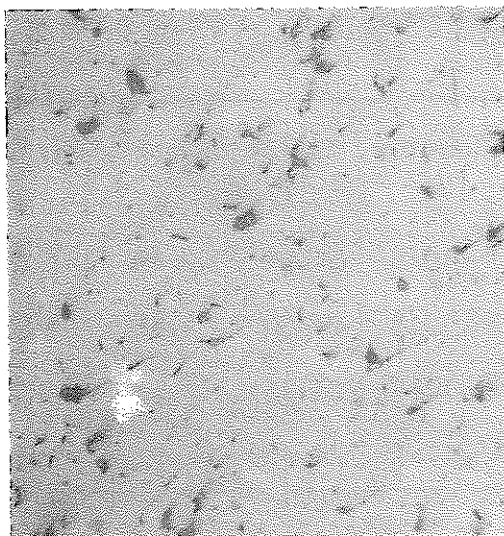
Before etching (x 270)   After etching (x 540)
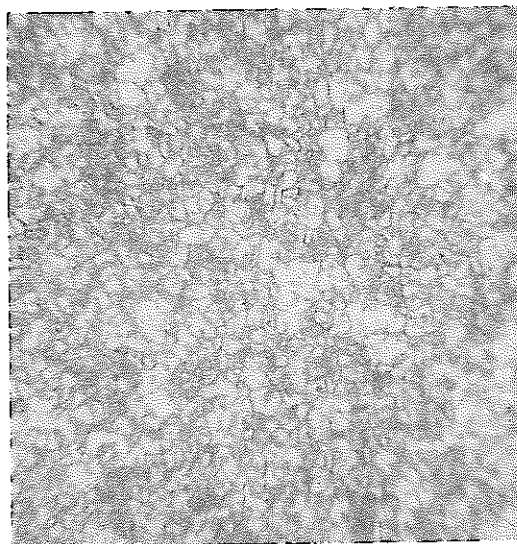
Fig. 2 Microphotographs of enriched B_4C pellet
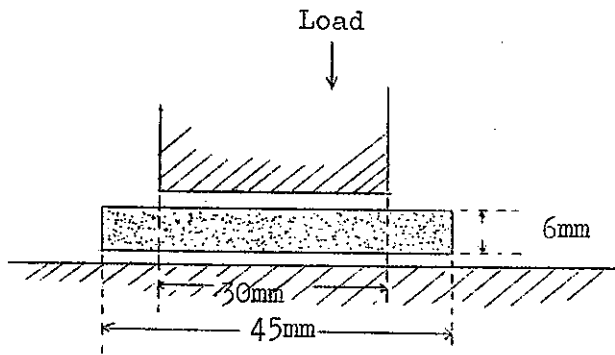
Fig. 3 Measurement of bending strength
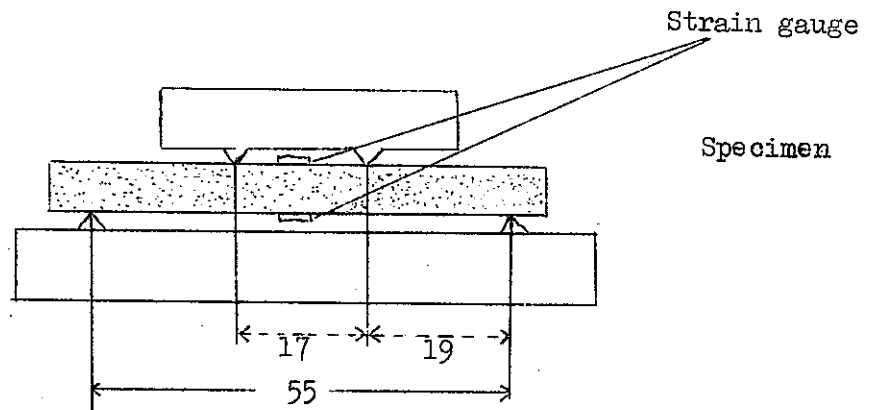
Fig. 4 Method of measurement

σ (k g / ㎜²)

15

10

5

ε₂

ε₁

No.1 ---
No.2 ——

0   100   200   300

$\varepsilon_1, \varepsilon_2 \times 10^{-6}$ ( )
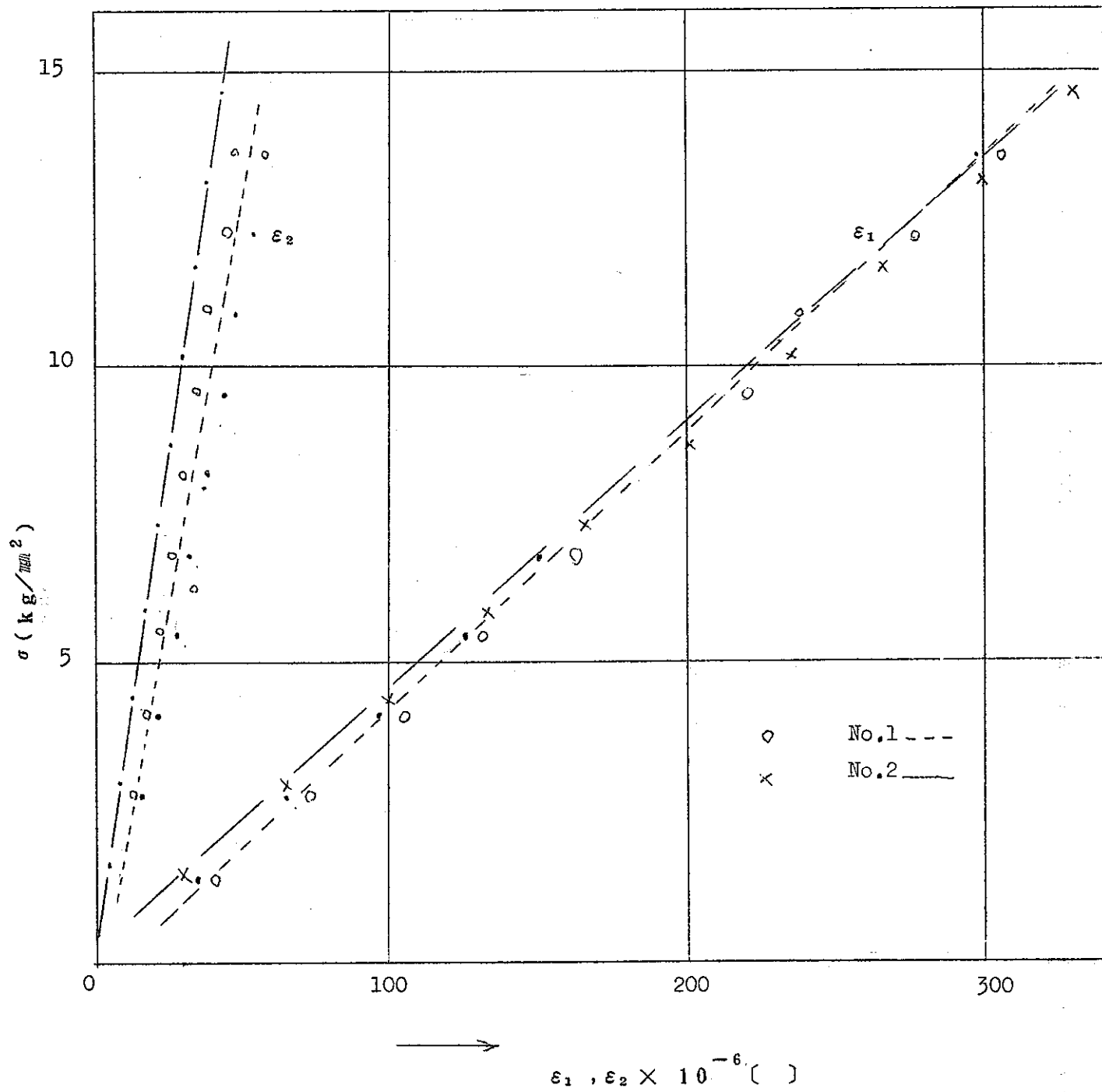
Fig. 5 Stress-strain curve for natural B₄C

- 26 -
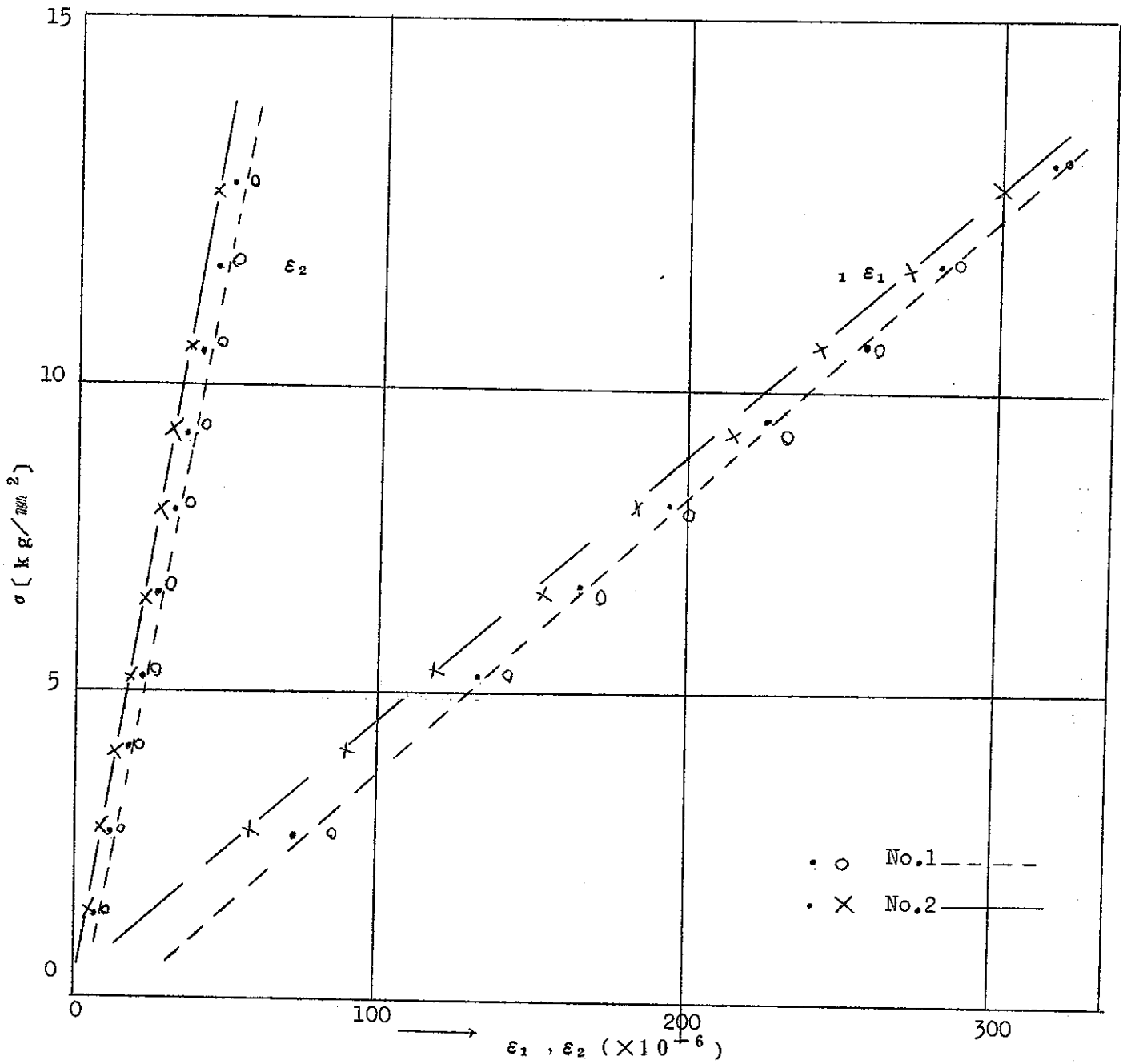
Fig. 6 Stress-strain curve for enriched B₄C
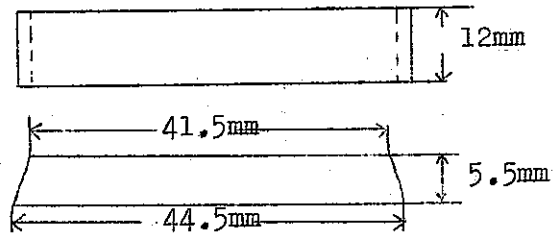
Fig. 7 Measuring specimen for thermal expansion test

Fig. 8 Thermal expansion curve for natural B_4C

Coefficient of thermal expansion

Temperature ^oC

A : Higher boiling point solution

B : Lower boiling point solution

S : Specimen

P_1, P_2 : Heating plate of silver

K_1, K_2 : Cooler

V : Receiver for condensate
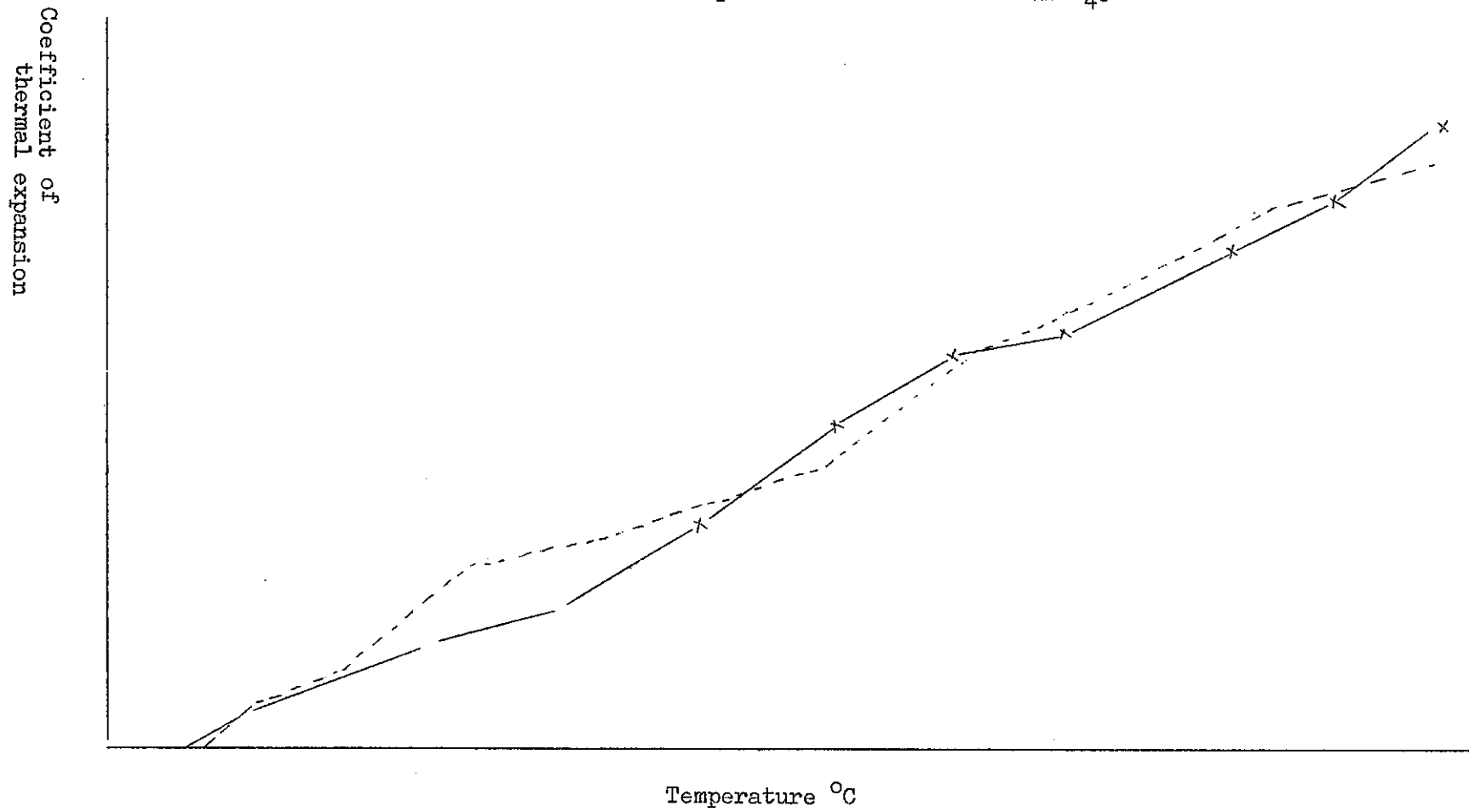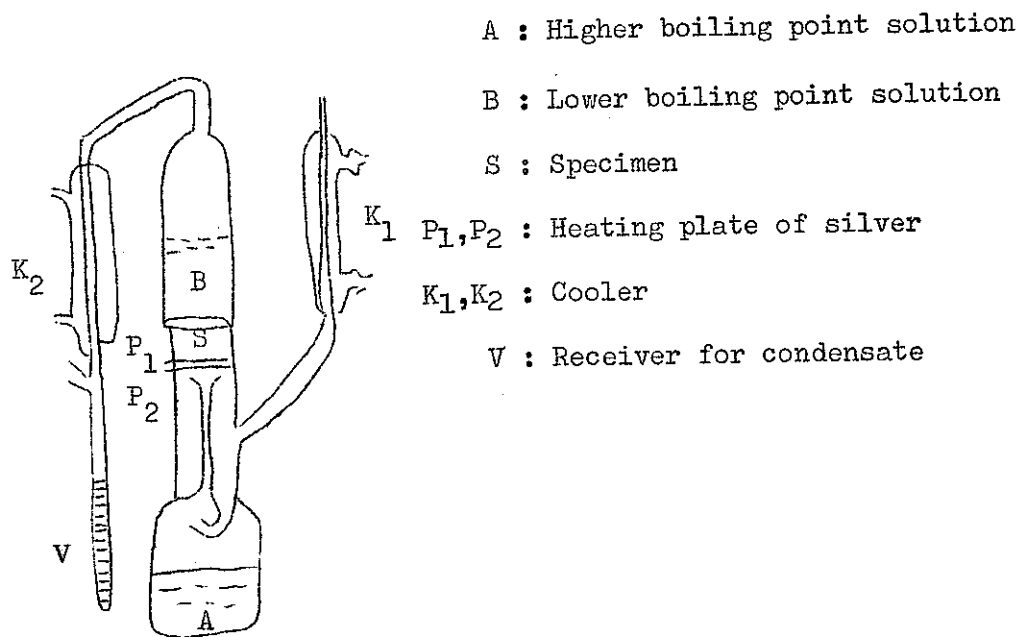
Fig. 9 Outline of measuring apparatus

Fig. 10 Thickness of specimen (e) and condensate time (t)

Thickness of specimen (e)
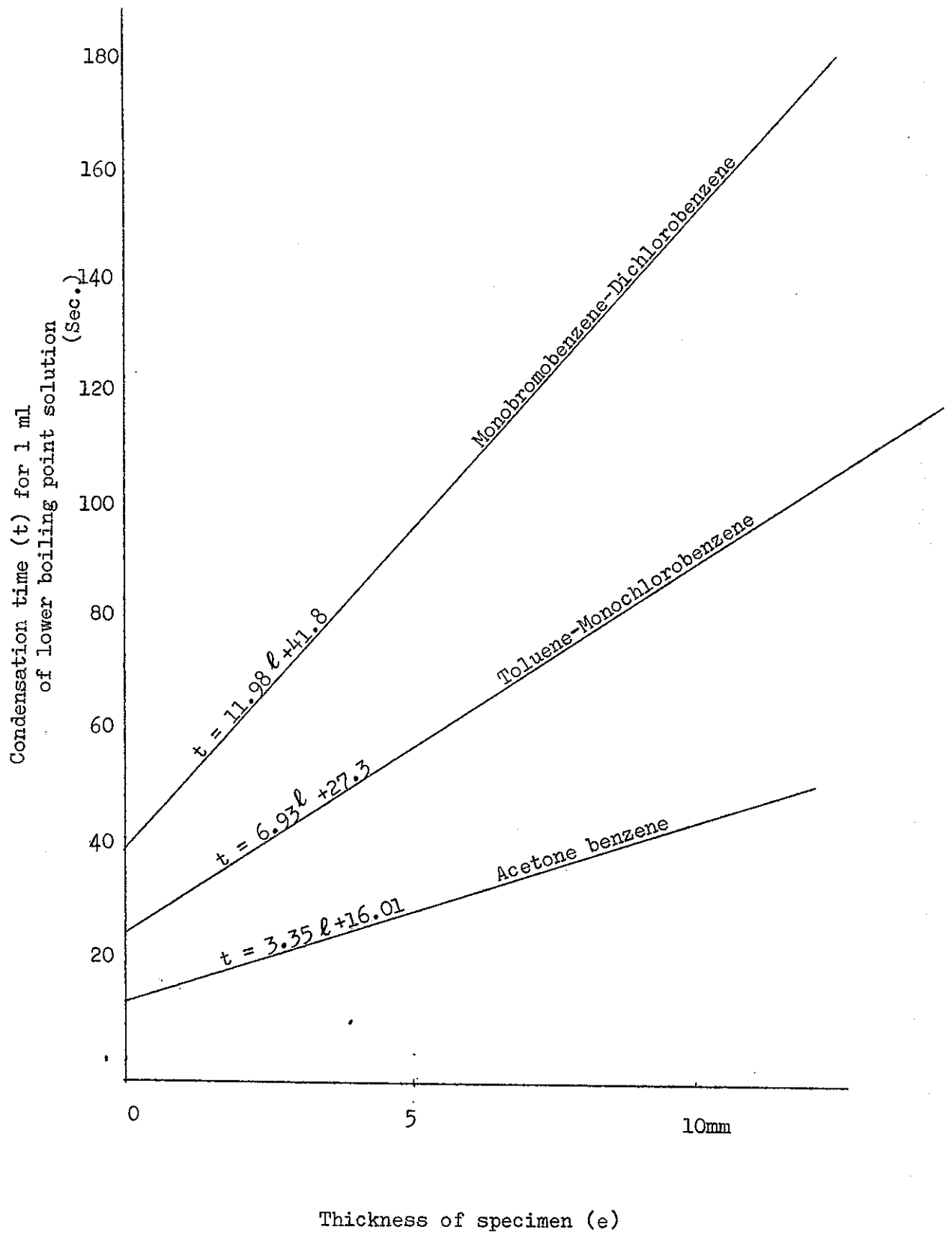
Fig. 10 Relationship between specific heat (Cp)
of B4C and temperature ($^\circ$K)

Alumel-Chromel T.C

B₄C pellet

Alumina Crusible

Molten Lead

Electric Furnace

Nicrom Wiring
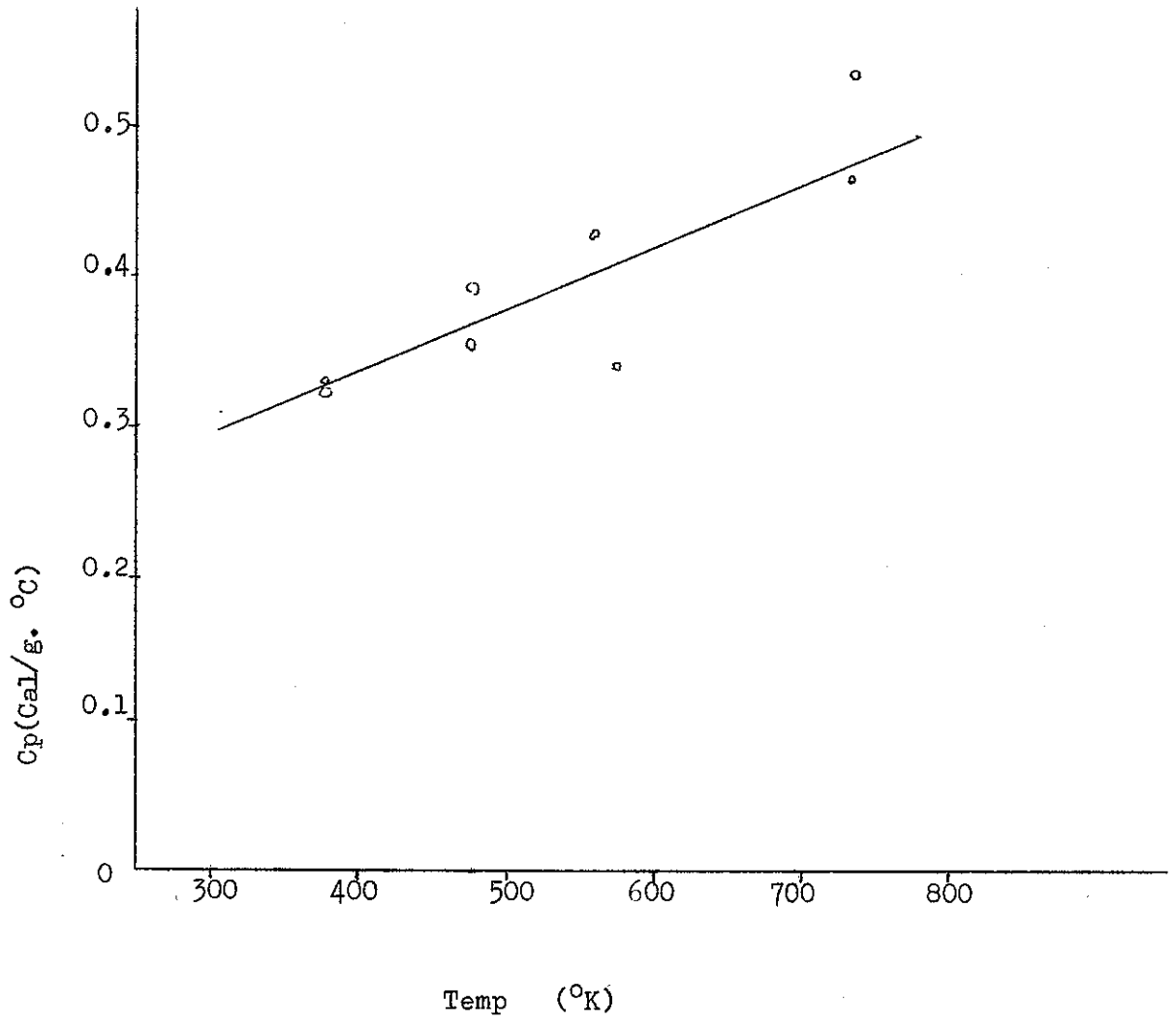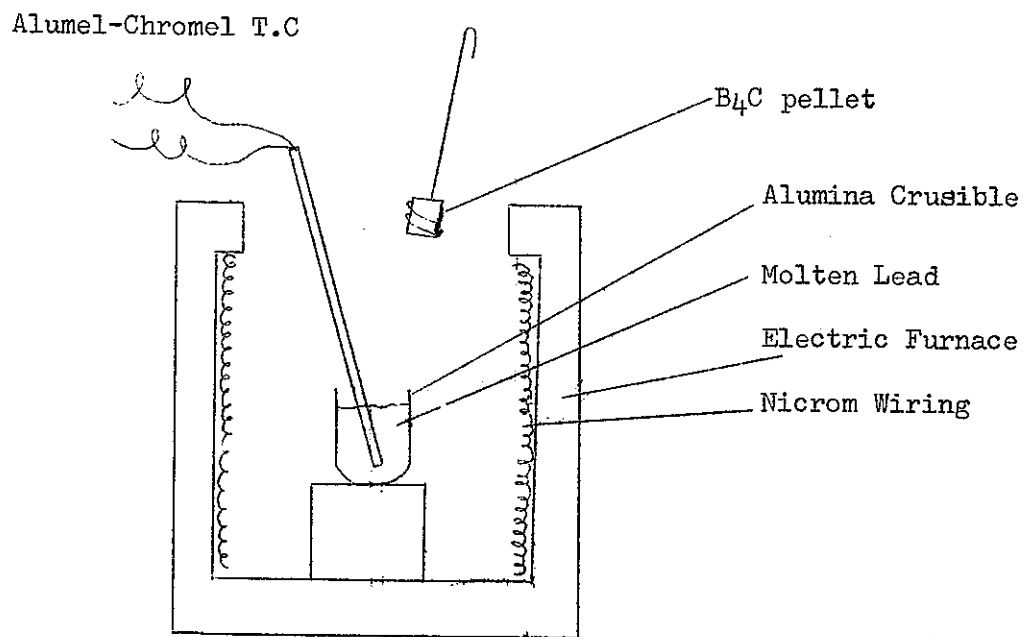
Fig. 11 Apparatus for measurement
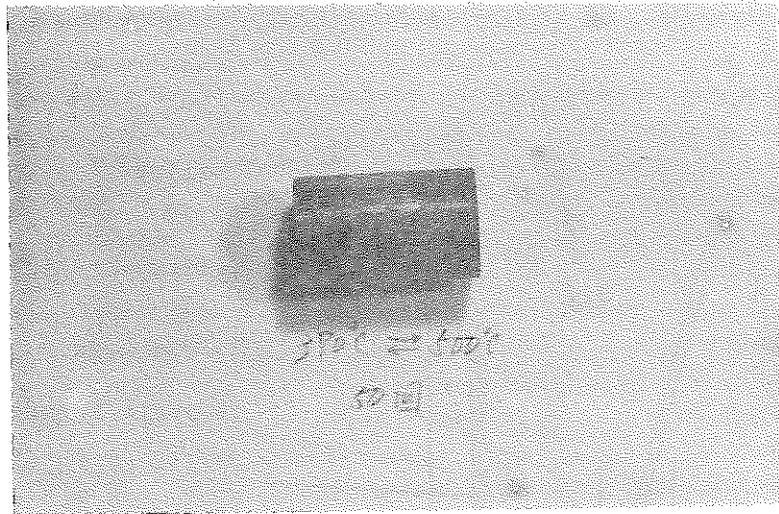
50th run
(a)
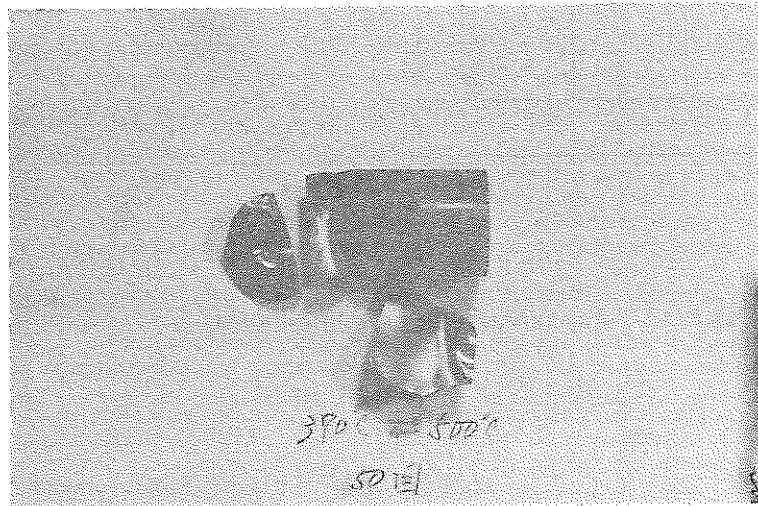
50th run
(b)
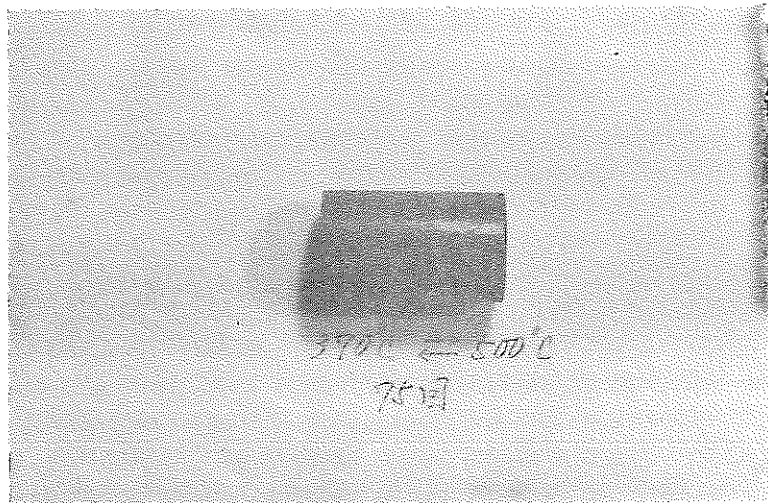
75th run
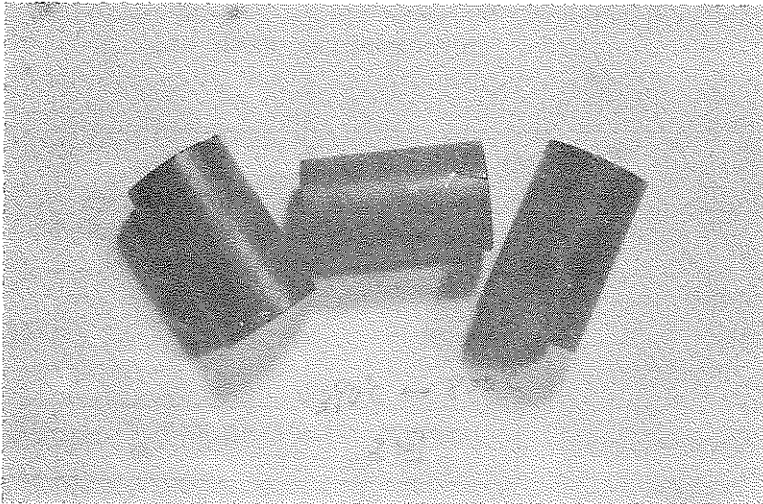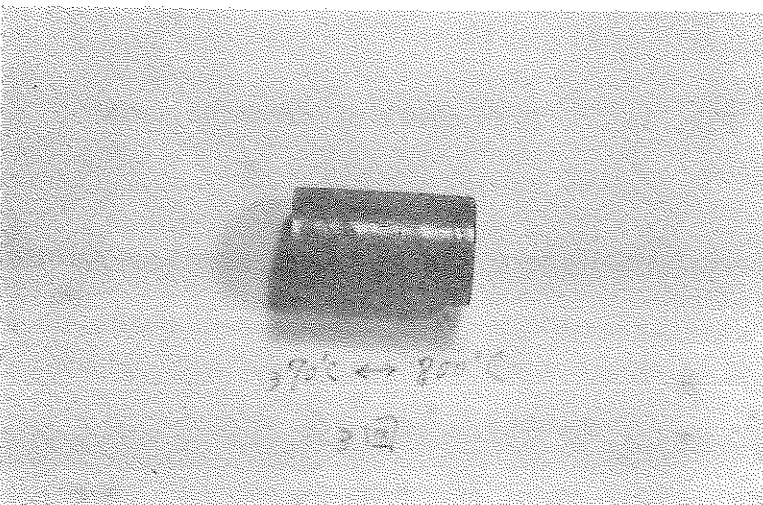(c)

Fig. 12 Thermal shock test specimen at 370 → 500 °C cycle
((a) and (b) are identical.)
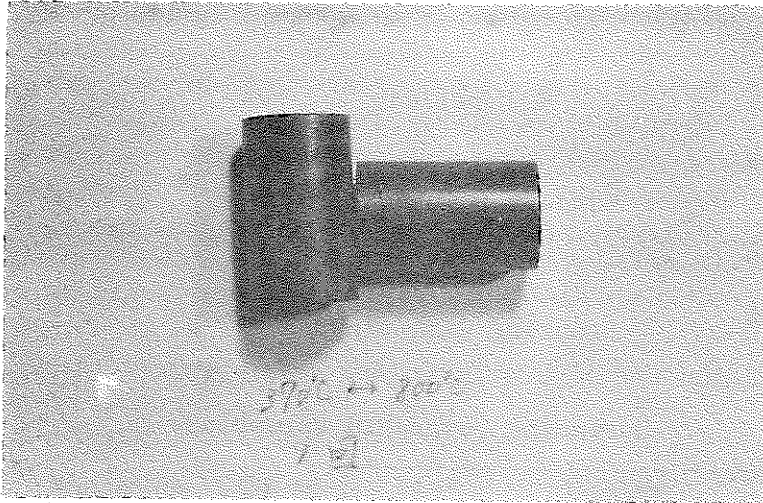
1st run

(a)

2nd run

(b)

3rd run

(c)

Fig. 13 Thermal shock test specimen at 370 °C → 800 °C cycle

B₄C pellet

↓

Hand-breaking to 100 mm
(with hammer)

↓

Crushing with stamp mill

↓

Screening (standard screening)

Over 125μ   Under 125μ
(retaining)

↓

Dry crushing with ball mill of iron

↓

Wet crushing with ball mill of iron

↓

Hydrochloric acid treatment

↓

Drying

↓

Powder, starting material for
hot-pressing
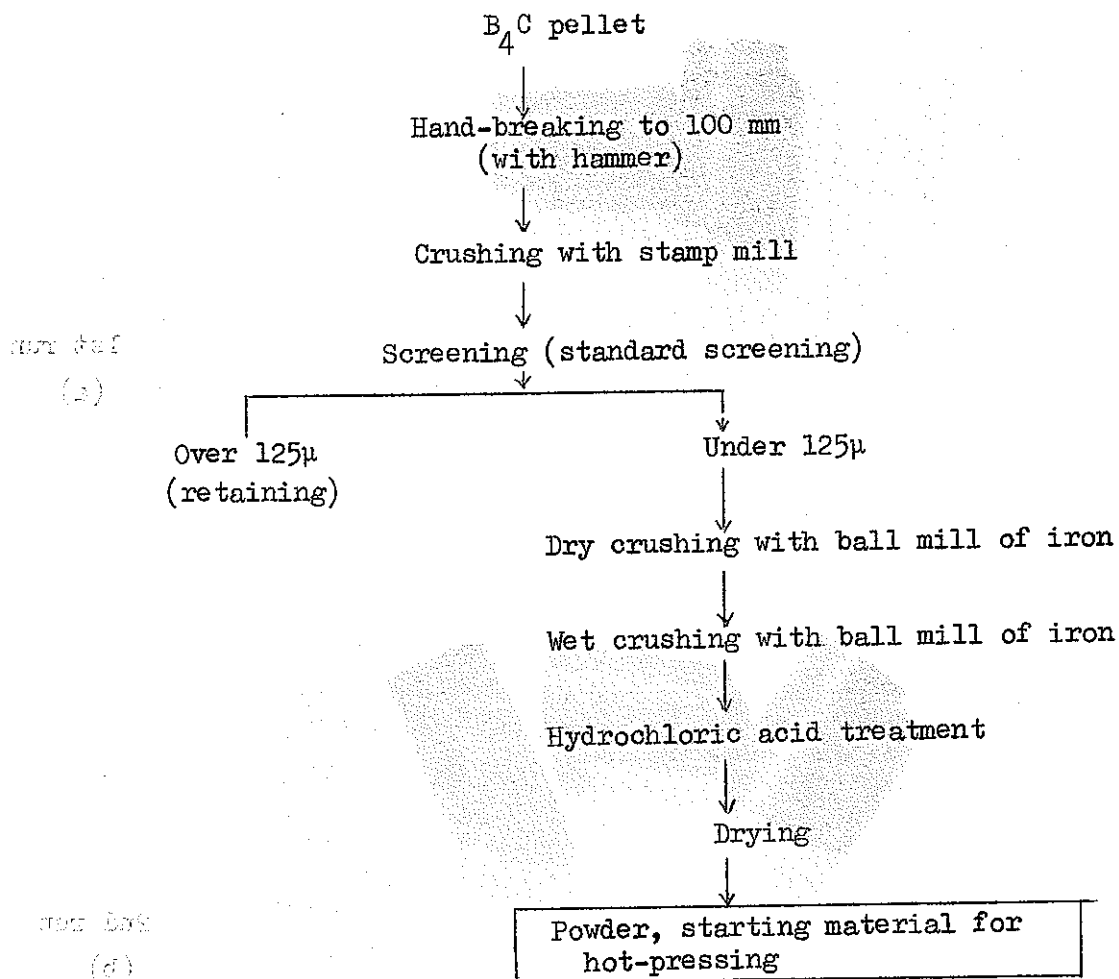
Fig. 14   Flow sheet of crushing test

Two pellets of 50∅ x 50h (mm)

490.1g

Stamping

Screening

Over 125μ   Under 125μ
18.3g   433.8g
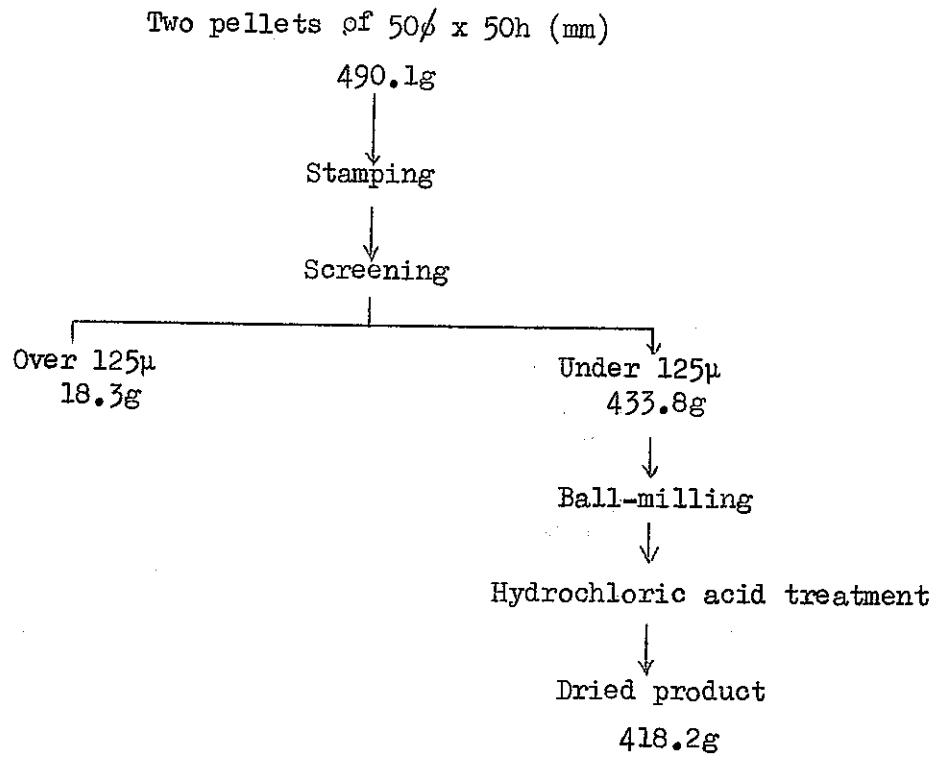
Ball-milling
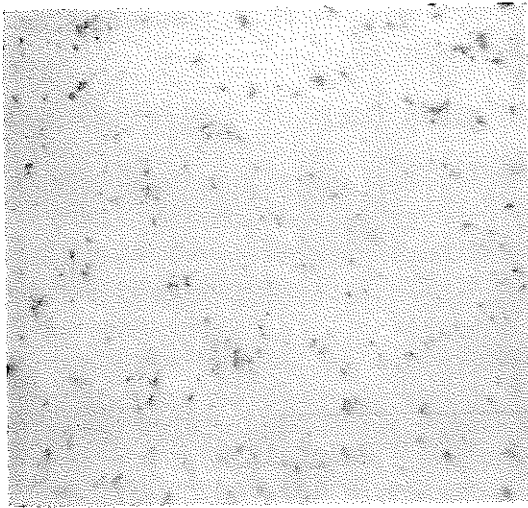
Hydrochloric acid treatment

Dried product
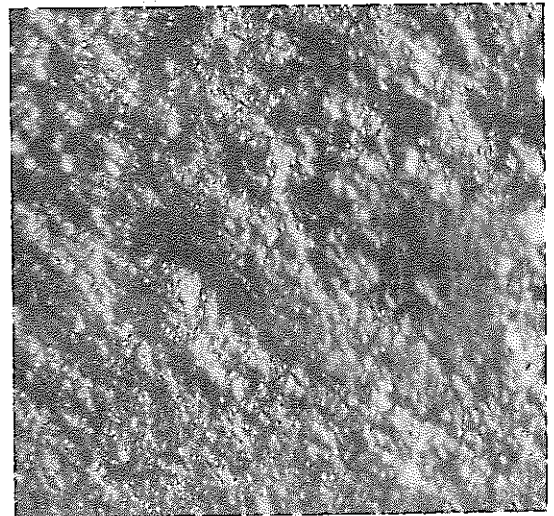418.2g

Fig. 15   Material balance for crushing test

Before
etching

After
etching

Fig. 16 Microphotographs of B_4C pellet in the case
of crushed product

$\begin{pmatrix}\text{With addition}\\\text{of carbon}\\\text{black}\end{pmatrix}$
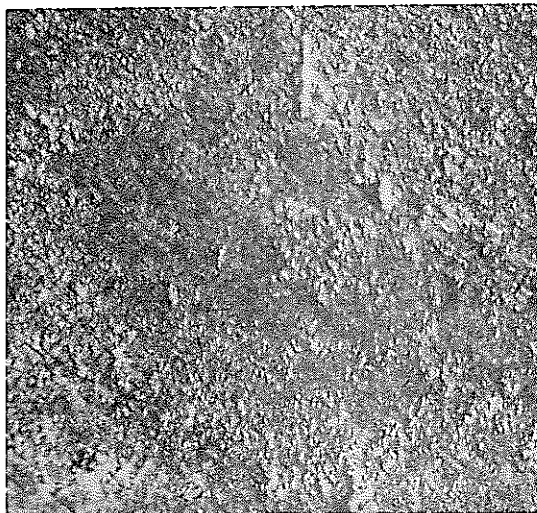
$\begin{pmatrix}\text{Without addition}\\\text{of carbon black}\end{pmatrix}$

Fig.17 Surface condition of hot-pressed pellet
with and without addition of carbon black