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DEPOSITION OF PYROLYTIC SILICON CARBIDE ON DISCS IN A FLUIDIZED BED

by

E. ERBEN and H. HAUSNER

1973

Joint Nuclear Research Centre
Ispra Establishment - Italy

Materials Division

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ABSTRACT

The chemical vapour deposition of pyrolytic silicon carbide on discs in a fluidized bed has been investigated. The influence of the deposition conditions on density, microstructure, crystallite size and chemical composition of the material was determined. Besides temperature the deposition rate had a strong influence on the structural appearance.

KEYWORDS

SILICON CARBIDES
COATING
PLATES
FLUIDIZED BED

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1. INTRODUCTION.

The purpose of this study was to prepare pyrolytic silicon carbide for diffusion studies of solid fission products like cesium, strontium and barium and to examine the influence of the deposition conditions on the characteristics of pyrolytic silicon carbide. It is well known that the retention behaviour of pyrolytic silicon carbide with regard to the fission products mentioned above is much better than that of pyrolytic carbon. With the general trend in the development of high temperature reactors (HTR) to go to higher fuel temperatures the problem of fission product retention becomes more and more important. Although several investigators (1,2,3,4) have produced pyrolytic silicon carbide on particles we concentrated our work mainly on disc coating because this geometry was more convenient for the diffusion studies.

2. EXPERIMENTAL.

2.1. Fluidized bed.

All samples were prepared in a fluidized bed (DRAGON type) with an internal reaction tube of 40 mm Ø. In Fig.1 a schematic diagram and in Fig. 2 a frontal view of the equipment is shown.

2.2. Materials.

Graphite and silicon carbide discs were used as support material. The graphite discs have been obtained from Ringsdorff with a diameter of 6 and 9 mm and a thickness of 1 mm. Two different types of silicon carbide discs were used. Hot pressed silicon carbide discs with a diameter of 6 mm, a

thickness of 1 mm and 50% th.density and pyrolytic silicon carbide discs prepared under static conditions with a diameter of 6 mm, a thickness of 1 to 1.5 mm and > 99% th. density. The fluidizing medium was graphite grit between 1.2 to 1.6 mm Ø. The coating source was trichlormethylsilane (Schuchardt) with a purity of more than 99%. The carrier gas was a mixture of argon and hydrogen.

2.3. Deposition conditions.

The two main parameters which were changed are the deposition temperature ranging from 1400 to 1800°C and the linear deposition rate ranging from 0.5 to 8.8 µm/min. Different trichlormethylsilane concentrations were obtained by changing the temperature of the silane bubbler (12 to 24°C ± 0.1°C) and by the hydrogen flow through the bubbler. The trichlormethylsilane concentration was calculated from the measured amount of trichlormethylsilane which had been used during the run. Deposition temperatures in the furnace were measured with radiation pyrometer. The partial radiation pyrometer was used for temperature measurements on the outside of the reaction tube, the accuracy of the measurements was ± 1% (1400 to 1800°C). The bed temperature was measured directly with a total radiation pyrometer with an accuracy of ± 3% in the range mentioned above. The different linear deposition rates were achieved by variation of the amount of the fluidizing medium or by variation of the trichlormethylsilane flux. All experimental conditions are summarized in Table 1.

3. CHARACTERIZATION.

3.1. Density.

Density was determined in a density column (Davenpart, London). Mixtures of aethylalcohol and bromoform in the range 2.8 to 3.3 g/cm^3 at 23°C were used. The specimens were fragments of coatings. The main problem in this case was to remove completely the graphite support without introducing errors. The samples were heated in air for 8 hours and 24 hours at 700 and 800°C; it was tried furthermore to remove the carbon with olium-HNO_3 mixtures and samples were treated 30 minutes with HF after the heat treatment in order to remove eventually existing oxide films. In Table 2 the densities measured after the different treatments are shown. The highest density can be measured after treating the samples in air at 700°C for 8 hrs.

3.2. Microstructure.

Metallographic examination has been one of the most useful tools for this study. All samples were prepared by the metallographic technique described in details by Herold et al.(5). After mounting in copper powder and grinding with 320 or 400 grit paper the specimens with a supporting disc of graphite have been etched with CrO_3-solution in order to remove partially the graphite support. The sample was reimpregnated with Araldite and was ground on metal mesh with 15 µm and with 6-8 µm diamond paste. After ultrasonic cleaning the polishing on metal mesh with 3 µm and 1 µm was continued. The polished samples were etched with CrO_3-solution (10-20% CrO_3 in aqueous solution with small additions of HF; the voltage applied was 25 V and the current between 0.2 and 1 A/cm^2).

TABLE 1 : Experimental coating conditions.

No	Input			Output			Dep.temp	Total gas	Silane conc.		Bed surface	Layer thickn.	Dep. Rate	
	Weight [g]	Vol. [cm^3]	H/D*	Weight [g]	Vol. [cm^3]	H/D	[°C]	[l/min]	[Vol.%]	[Mol/h]	[cm^2]	[µm]	[µm/min]	[g.SiC/cm^2h]
47	50	59	1.17	60	66	1.31	1400	25	2	1.4	1000	46.5	1.16	$1.62 \cdot 10^{-2}$
48	50	62	1.23	83	71	1.41	1600	25	2	1.4	1000	49.5	1.24	$2.0 \cdot 10^{-2}$
49	50	59	1.17	80	72	1.43	1800	25	2	1.4	1000	26.8	0.77	
54	40	48.5	0.964	66	61	1.21	1400	25	2.4	1.6	800	102	3.0	$3.2 \cdot 10^{-2}$
53	40	47	0.932	78	62	1.23	1600	25	2.6	1.7	800	86.5	2.5	$3.6 \cdot 10^{-2}$
55	40	47	0.932	73	64	1.27	1800	25			800	48.5	1.4	$1.5 \cdot 10^{-2}$
52	30	35	0.695	49	46	0.913	1400	25	2.3	1.9	600	114.5	3.5	$4.15 \cdot 10^{-2}$
50	30	35	0.695	74	54	1.07	1600	25	3	2.0	600	157.5	3.9	$6.2 \cdot 10^{-2}$
51	30	37	0.725	60	51	1.01	1800	25	2.3	1.6	600	98.5	3.0	$3.85 \cdot 10^{-2}$
60	20	26	0.515	34	33	0.654	1400	25	2.8	2.0	400	120.5	6.0	$7.2 \cdot 10^{-2}$
58	20	25	0.496	40	36	0.715	1600	25	2.9	2.0	400	175.4	8.8	$12.8 \cdot 10^{-2}$
61	20	26	0.515	39.9	37	0.735	1800	25	2.9	2.0	400	145	7.25	$6 \cdot 10^{-2}$
59	30	37	0.735	65	50	0.991	1650	25	3.0	2.2	600	144.7	4.8	$7.15 \cdot 10^{-2}$
57	60	72	1.43	100	83	1.65	1650	25	1.9	1.3	600	34	0.68	$1.12 \cdot 10^{-2}$
61	20	26	0.515	19.9	11	1.243	1800		2.9	2.6		145	7.25	$6 \cdot 10^{-2}$
76	30	29	0.575	44.5	37	0.735	1600		4.8	1.29	600	57.2	2.3	$4.4 \cdot 10^{-2}$
77	30	33	0.654	45.8	40	0.793	1600		3.4	0.92	600	75	2.1	$4 \cdot 10^{-2}$
78	30	33	0.654	53.3	47	0.932	1600		10.9	3.22	600	81.6	5.4	$10.5 \cdot 10^{-2}$

* Bed geometry height/diameter

TABLE 2 : Density measurements after different preparation of samples.

	Heated 8h at 700°C	Heated 8h at 700°C 8h at 800°C	Heated 8h at 800°C	C-removed with olium + HNO_3 (*)	8h at 800°C 30min. in HF	24h at 700°C	24h at 800°C	Coating thickness /um
Density g/cm^3	3.193	3.182						30
	3.194	3.185	3.189	3.193	3.199	3.185	3.172	200
	3.187	3.130	3.137	3.139	3.163	3.138	3.037	140
	3.178	3.156	3.135	3.123	3.159	3.137	3.156	156
	3.191	3.149						
	3.188	3.152						
	3.187	3.184						
	3.185	-	3.149			3,182		

(*) Olium-HNO_3 2:1 15 min.

3.3. Surface examination.

The surface of the as deposited pyrolytic silicon carbide and fracture surface were examined with a scanning electron microscope, type Jeon.

3.4. Crystallite size.

The crystallite size has been measured by X-ray techniques. It is well known that the crystallite size is usually obtained by applying the Scherrer equation

$$\mathcal{E} = \frac{\lambda}{\beta \cos \theta}$$

where $\mathcal{E}$ is the crystallite size, λ is the wave length used and θ is the Bragg angle and β the pure diffraction broadening. In order to obtain β two main corrections are to be made. One is for the experimental factors (as optics of the system used, etc..) and the other is the correction due to the presence of the second strong wave in the X-rays. The first was done using a well-crystallized substance with infinite crystallite size and the second was accomplished by the use of Fouriers series. Then the pure broadening was obtained by following Scherrer i.c. substracting from the specimen broadening the instrumental broadening.

3.5. Layer thickness measurements.

The layer thickness has been measured with a normal caliper by microradiography and by metallography. The microradiography is generally used for the nondestructive thickness measurements of different layers of a coated particle. The specimens are placed on an aluminium plate and radiographed. The image thus produced on a photographic plate is

caused by the different absorption behaviour of the radiographed material (density) and projected at a fixed magnification onto a screen. The coating thickness is measured directly with calibrated paper (6). For comparison the layer thickness was measured in a metallographic section.

3.6. Chemical analysis.

Most of the various analytical methods for the determination of free silicon and silica in pyrolytic silicon carbide require several grams of material. Since the coatings to be analyzed are limited in their dimensions only small quantities of material are available and the sensitivity of the analytical methods had to be improved. Free silicon has been determined in two different ways. The first is based on a hydrogen determination after a treatment with alkaline solutions. The second method utilizes a selective acid attack of SiO_2 and SiO_2 + Si and a subsequent colorimetric analysis. Silica has been determined by a colorimetric method. A control of the total oxygen content by vacuum hot extraction or by neutron activation analysis has been realized.

3.7. Heat treatments.

In connection with the removal of the graphite support at 700 resp. 800°C the integrity of the SiC-coating on the graphite support could be investigated. The graphite burned out in case the silicon carbide coating was defect.

4. DISCUSSION OF RESULTS.

4.1. Density.

The measured densities do not show a dependance on the linear deposition rate in the range 1600 to 1800°C; at 1400°C a certain influence can be observed (Fig. 3 and Fig. 4). The density in function of the deposition temperature shows for deposition rates from 0.7 to 8.8 µm/min a strong increase between 1400 and 1600°C whereas from 1600 to 1800°C the densities are almost constant (Fig. 5). The linear deposition rate in function of the deposition temperature for initial bed surface areas between 400 and 1000 cm^2 are shown in Fig.6. There are probably not sufficient measured points to draw definite conclusions.

4.2. Microstructure.

The influence of deposition temperature and deposition rates are as follows :
At 1400°C and at deposition rates between 0.75 and 6 µm/min all deposits are laminar as shown in Fig. 7 and Fig. 8.
At 1600°C and at deposition rates between 0.56 and 2 µm/min relatively coarse globular structures are obtained (Fig. 9, 10 and 11). A change in the structure occurs at a deposition rate > 3 µm/min. A fine globular structure (Fig. 12) is formed. At higher deposition rates the structure becomes again coarser, porous inclusions can be seen (Fig. 13 and 14). At 1800°C and at all deposition rates large globular grains (Fig. 15 and Fig. 16) are present.

4.3. Surface examination.

The surface examination of the as deposited pyrolytic silicon carbide shows for the deposition temperature of

1600°C a change in the surface structure between a deposition rate of 2.5 and 4.1 µm/min (Figs. 17-26).
The fracture behaviour of the pyrolytic silicon carbide (1600°C) with deposition rates of 0.68 resp. 7.7 µm/min is shown in fig. 27 to Fig. 31. The fracture structure of deposits made with low deposition rates seems to be coarser than those with high deposition rates.

4.4. Crystallite size.

The dependance of the crystallite size on deposition temperature is indicated below.

Temperature [°C]	Deposition rate [µm/min]	Crystallite size [µm]
1400	1.16	0.09
	3.5	0.09
	6.0	0.04
1600	0.68	8.0
	1.24	8.0
	2.5	1.2
	3.9	0.3
	5.44	0.4
	8.8	0.14
1800	0.77	8.0
	1.24	1.2
	3.0	0.5

The crystallite size varies significantly at deposition temperatures between 1600 and 1800°C with the deposition rate. At these temperatures the crystallite size is large at low deposition rates whereas with increasing deposition rates the crystallite size becomes smaller.

4.5. Layer thickness measurements.

A comparison of some mean values obtained by different methods are given in Table 3. Difficulties to obtain exact values by metallography were caused by the large hardness difference between graphite and silicon carbide.

Table 3 : Comparison of layer thickness measured by different methods.

Layer thickness	Mechanical Method	Radiography	Metallograph. Method
/um	97	100	72
	66	65	52
	43	41	30
	25	24	16

4.6. Chemical analysis.

Table 4 shows some typical values for the concentrations of free silicon and SiO_2.

Table 4 : Free silicon and SiO_2 in pyrolytic silicon carbide.

Sample No.	Free silicon [wt%]	SiO_2 [wt%]
47	24.1	5
48	0.38	0.25
50	0.41	0.1
53	0.1	0.14

The free silicon content is very high at the deposition temperature of 1400°C.

4.7. Heat treatments.

In general samples with a layer thickness lower than 80 µm failed during the treatment whereas those with a layer thickness larger than 80 µm resisted. The colour of pyrolytic silicon carbide was black for SiC deposited at 1400°C, yellow-grey for those at 1600°C and completely yellow for SiC deposited at 1800°C.

5. CONCLUSIONS.

In the preparation of pyrolytic silicon carbide under non-static conditions a strong dependance of the structure on the deposition temperature and the deposition rate can be observed. At a deposition temperature of 1400°C the structure is general laminar, very strong laminations are observed at deposition rates >3 µm/min. At 1600°C and for deposition rates between 0.68 to 2.5 µm/min a relatively coarse structure exists; for deposition rates from 3.0 to 8.8 µm/min the structure changes towards a fine grained structure. For deposition temperature of 1800°C and a deposition rate from 1 to 3.0 µm/min the structure is coarse, at deposition rates >3.0 µm/min the effect is enhanced.

6. ACKNOWLEDGEMENT.

We acknowledge the assistance of Mr. Bottelier during the experiment work and Mr. Looman for the density measurements, Mr. Ruedl for the SEM studies, Mr. Herold for the metallography, Mr. Tassone for the grain size determination and Mr. Serrini for the chemical analytical determinations.

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Metallurgia Italiana n°4, 1972, p. 129.

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Fig. 24 - The outer surface of the layer examined by SEM, 1600°C, 4.1 µm/min, 1000x

Fig. 25 - The outer surface of the layer examined by SEM, 1600°C, 7.7 µm/min, 300x

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Fig. 27 - The fracture surface examined by SEM, 1600°C, 0.68 µm/min, 300x

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Fig. 29 - The fracture surface examined by SEM, 1600°C, 0.68 µm/min, 3000x

Fig. 30 - The fracture surface examined by SEM, 1600°C, 7.7 µm/min, 300x

Fig. 31 - The fracture surface examined by SEM, 1600°C, 7.7 µm/min, 1000x

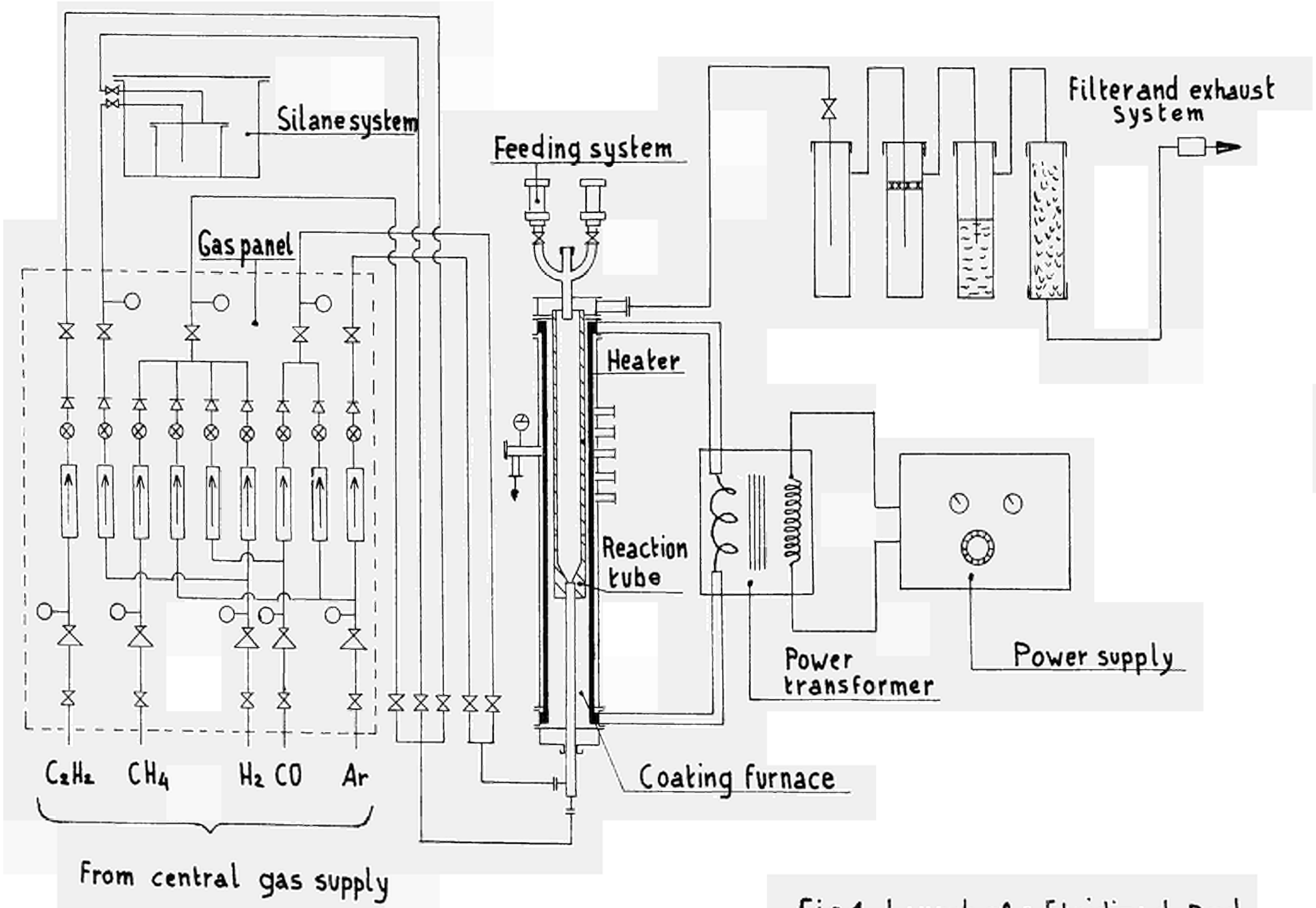

Fig.1 Layout of a Fluidized-Bed Coater and associated equipment

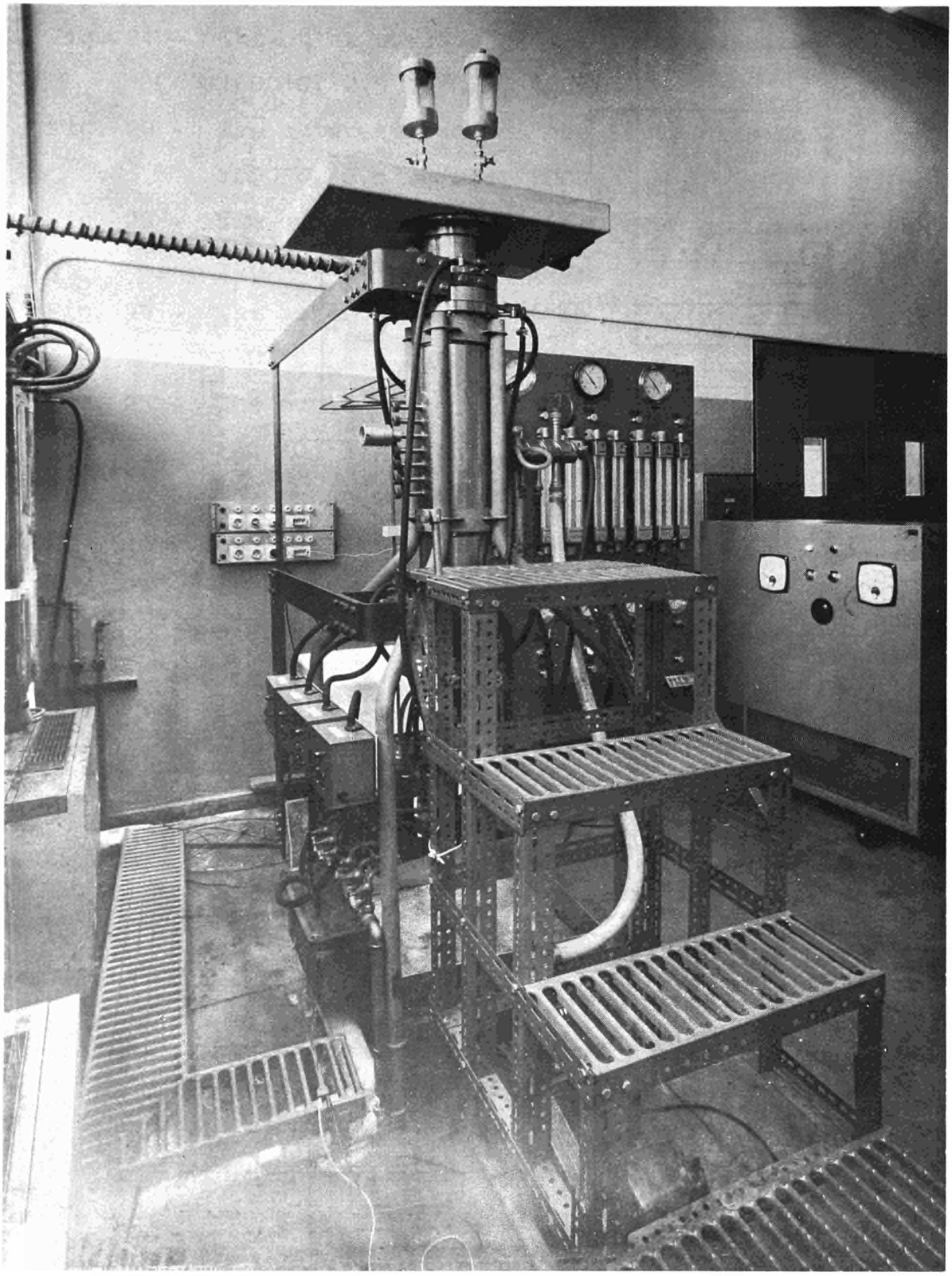

Fig.2 Frontal view of the equipment

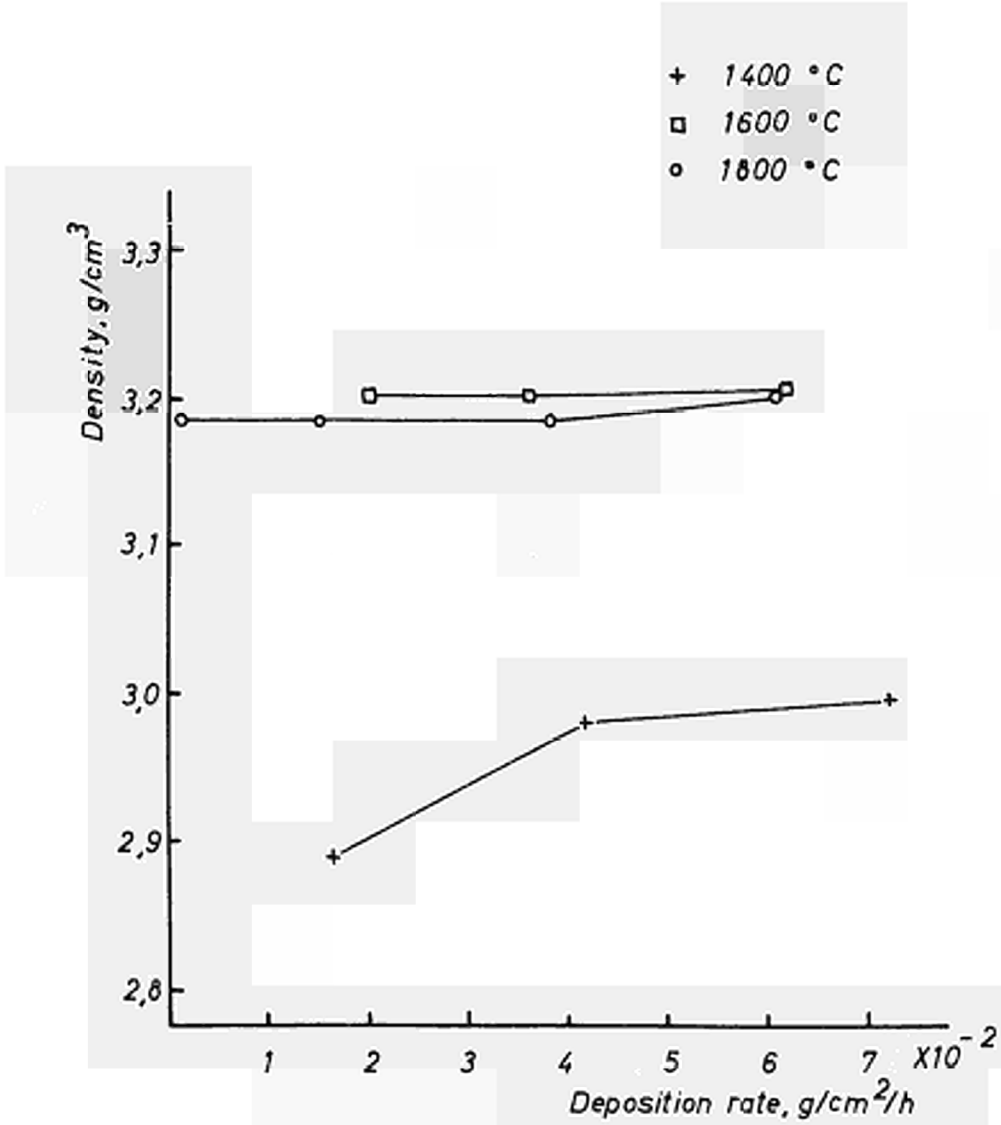

Fig.3 SiC density as a function of deposition rate for different deposition temperatures

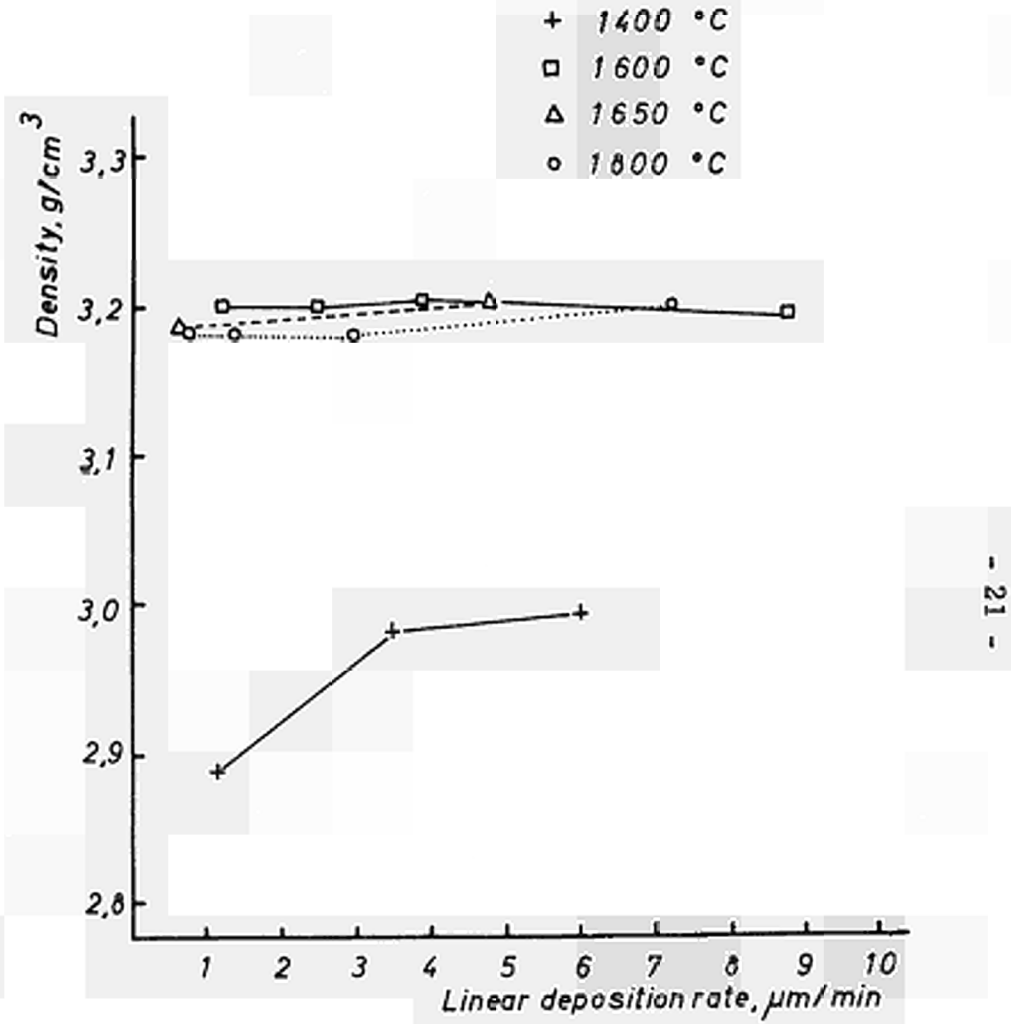

Fig.4 SiC density as a function of linear deposition rate for different deposition temperatures

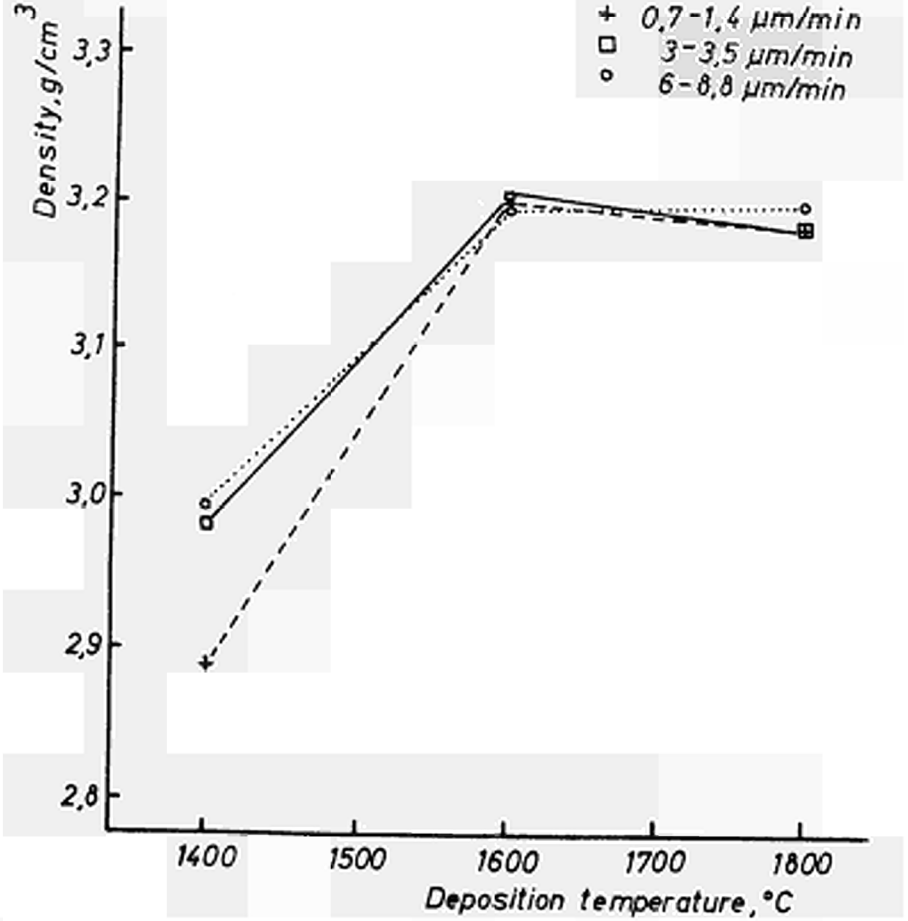

Fig.5 SiC density as a function of deposition temperature for different deposition rates

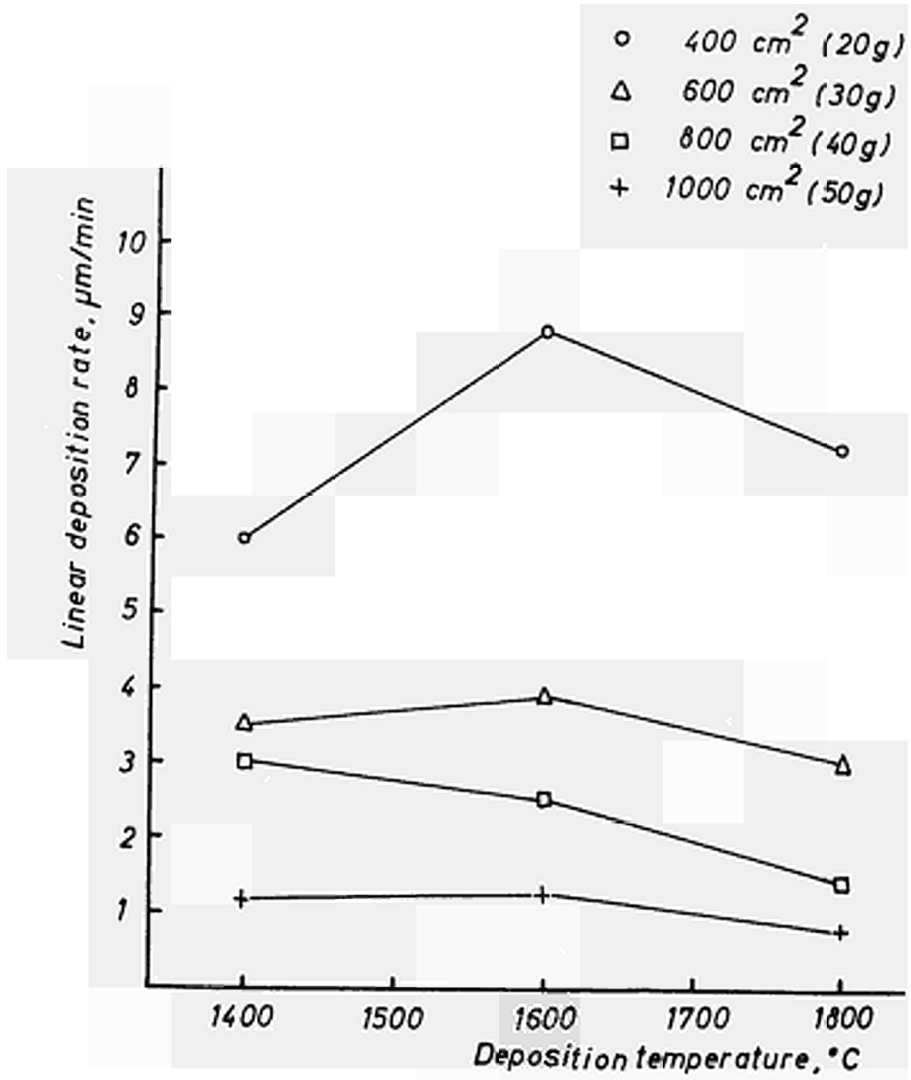

Fig.6 Linear deposition rate as a function of deposition temperature for different surface areas

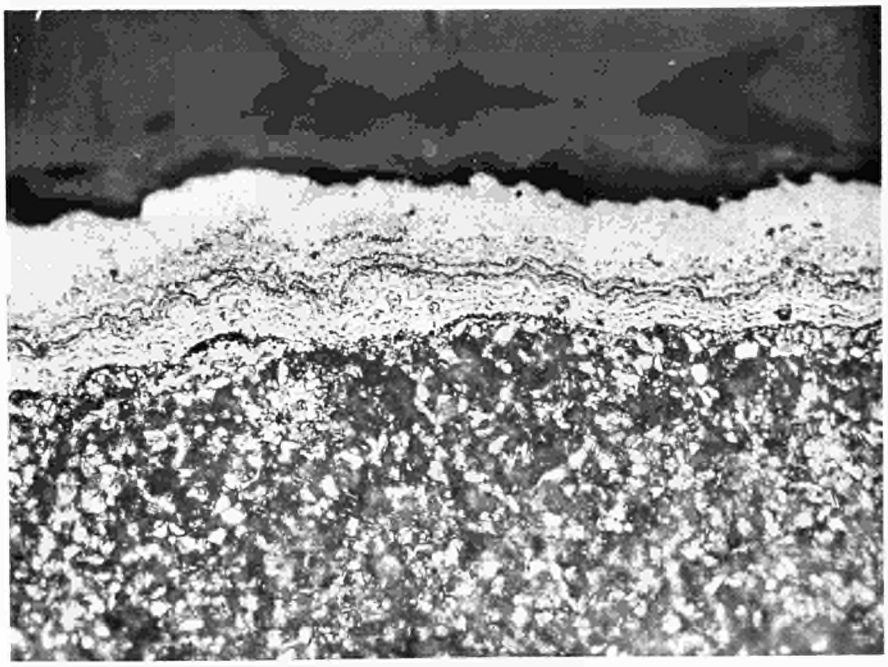

Fig.7 Metallographic section, deposited at 1400°C with 0,75µm/min, 400x

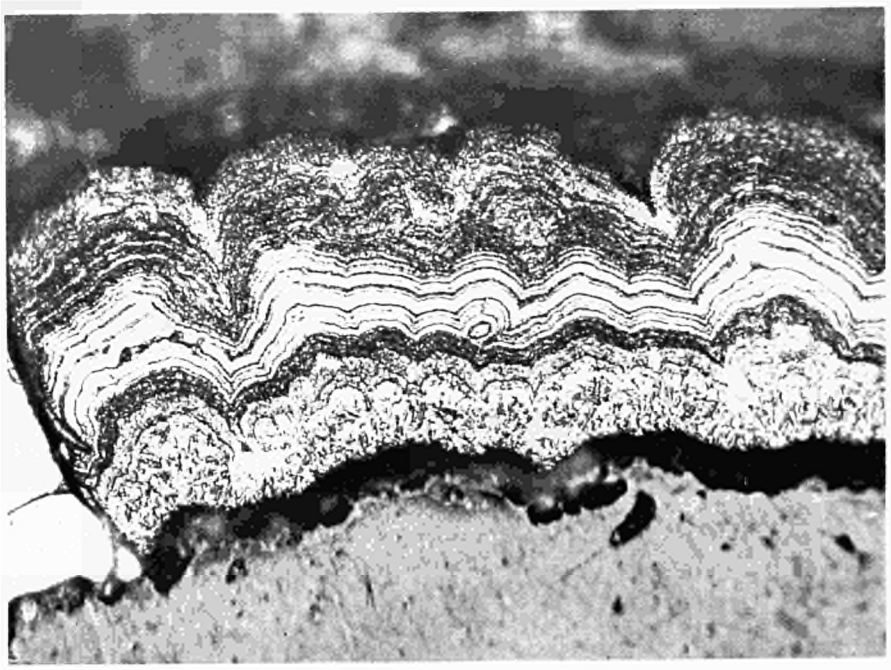

Fig.8 Metallographic section, deposited at 1400°C with 6µm/min; 400x

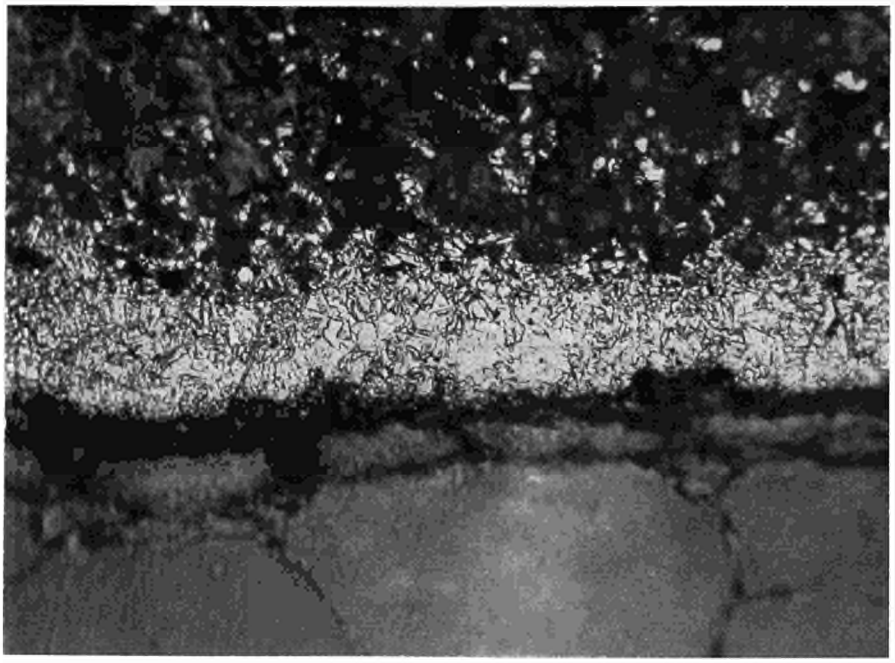

Fig.9 Metallographic section, deposited at 1600°C with 0,56µm/min, 400x

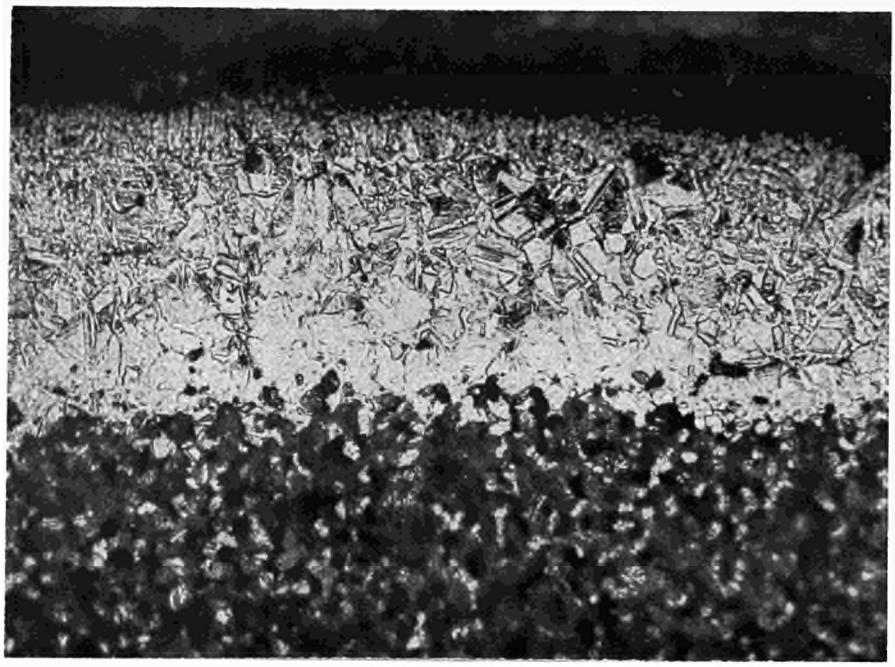

Fig.10 Metallographic section, deposited at 1600°C with 0,93µm/min, 400x

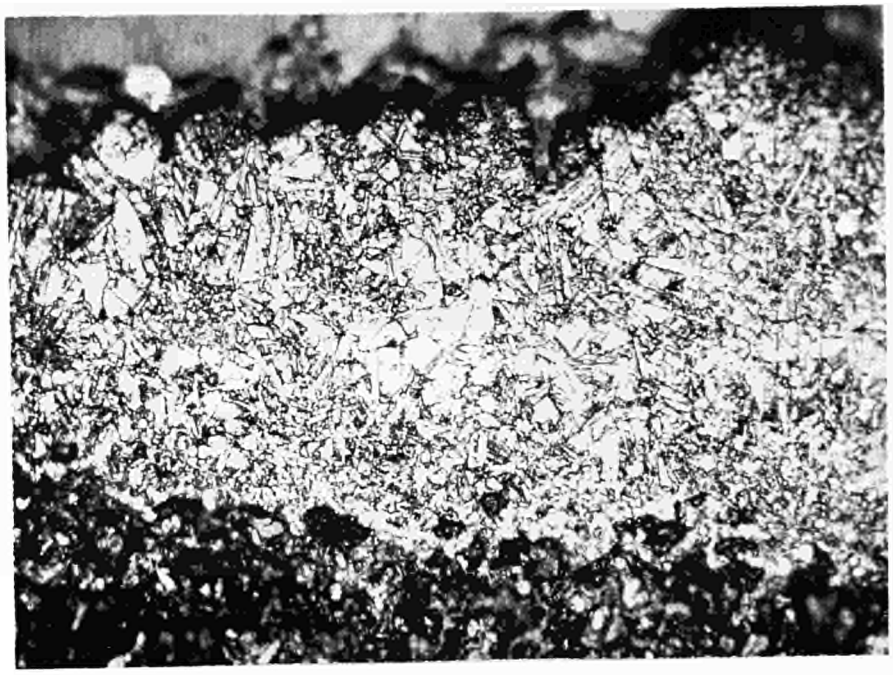

Fig.11 Metallographic section, deposited at 1600°C with 2µm/min, 400x

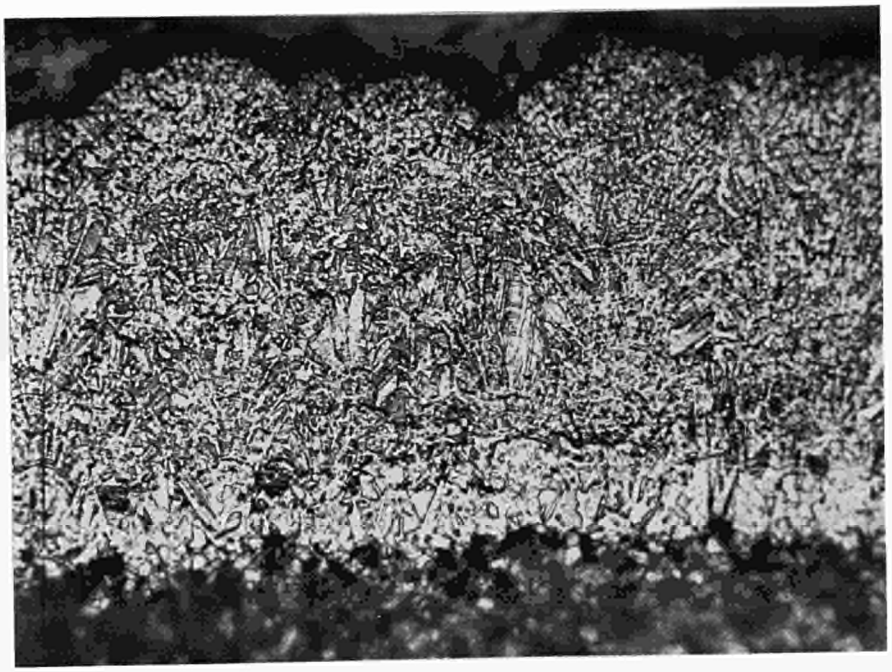

Fig.12 Metallographic section, deposited at 1600°C with 3,23µm/min, 400x

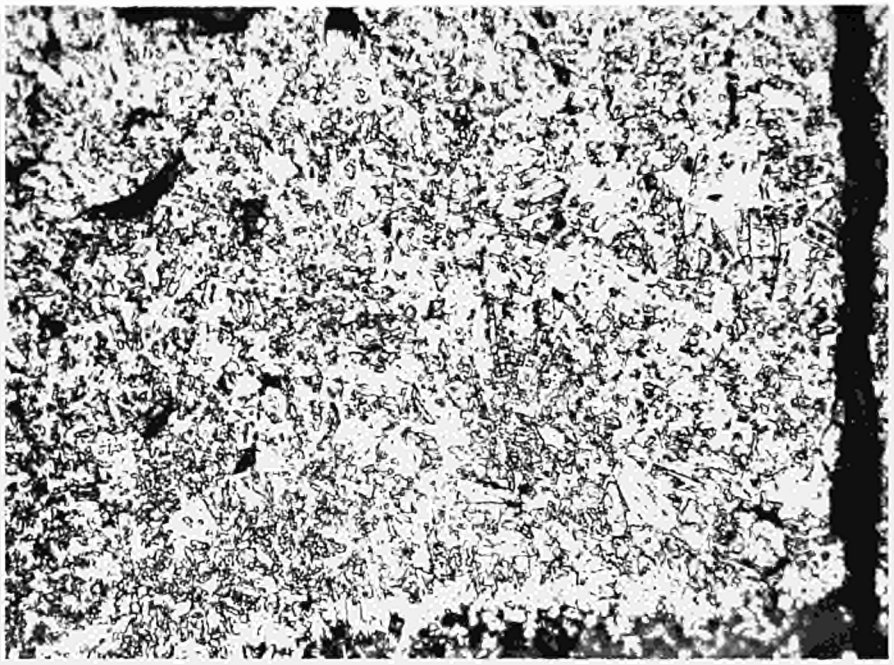

Fig.13 Metallographic section, deposited at 1600°C with 7,7μm/min, 400x

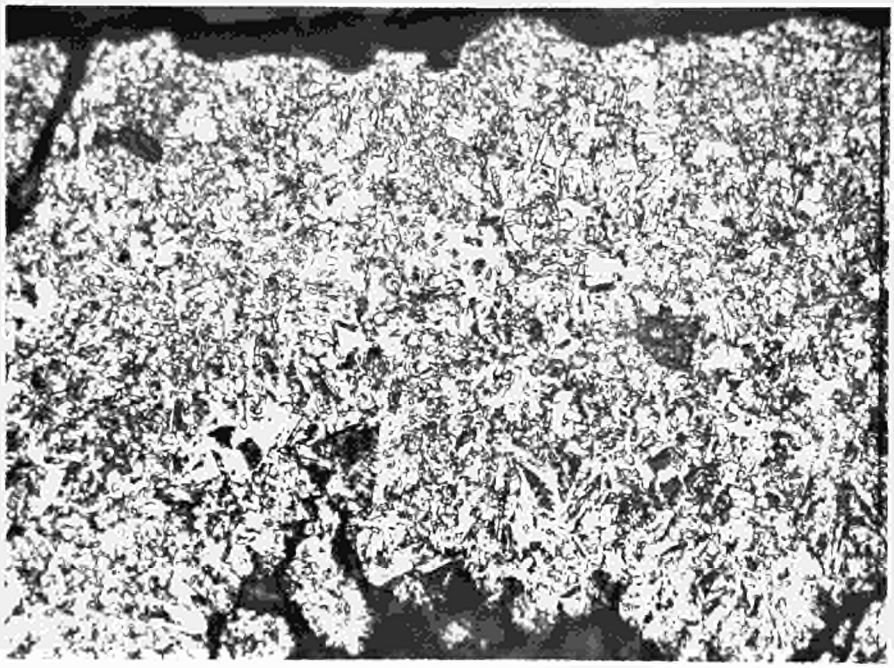

Fig.14 Metallographic section, deposited at 1600°C with 8,8μm/min, 400x

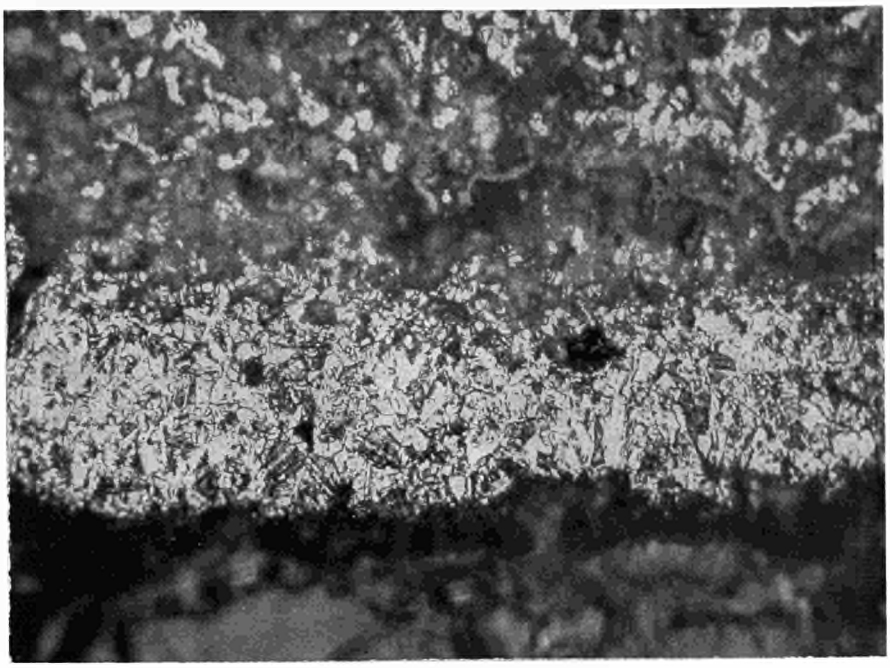

Fig.15 Metallographic section,deposited at 1800°C with 1,0µm/min, 400x

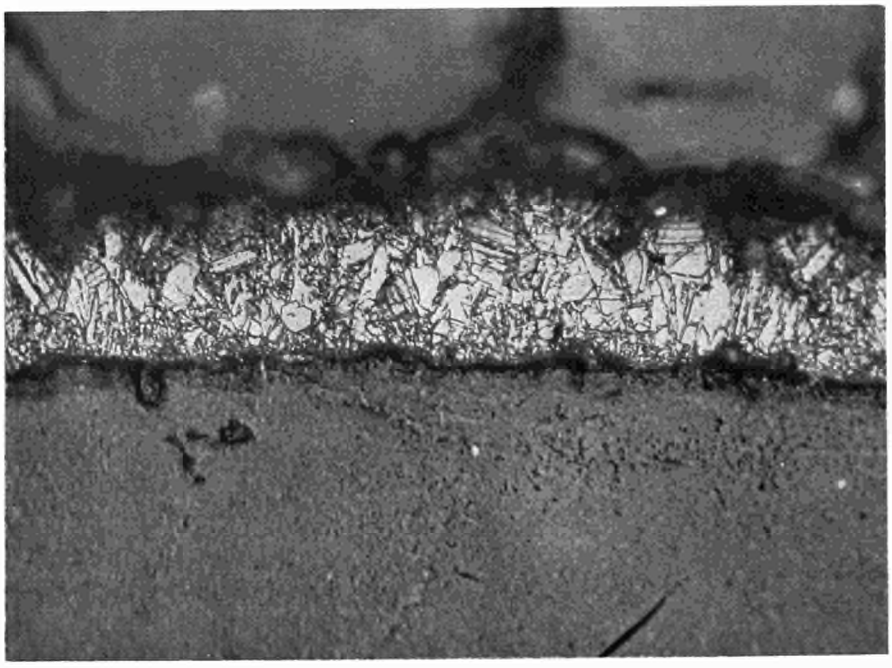

Fig.16 Metallographic section,deposited at 1800°C with 1,4µm/min, 400x

The outer surface of the layer examined by SEM

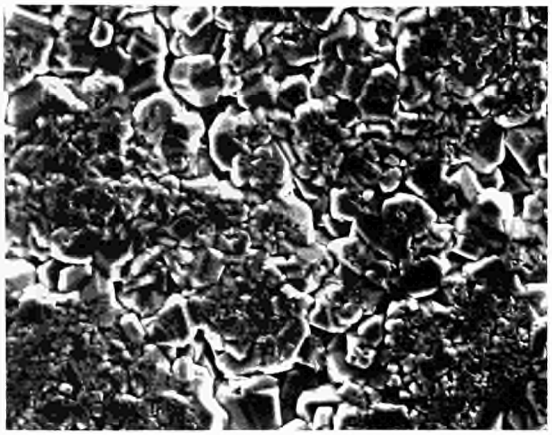

Fig.17 1600°C, 0,68µm/min, 300x

Fig.18 1600°C, 0,68µm/min, 1000x

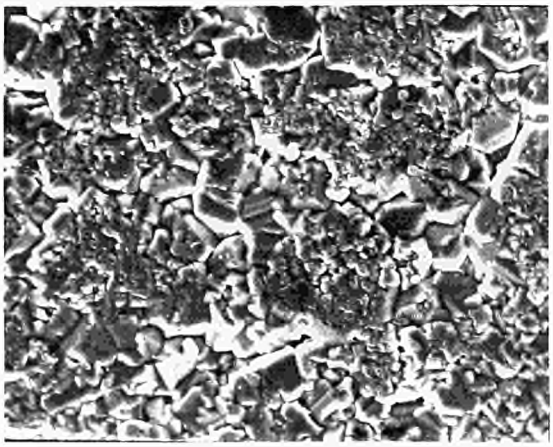

Fig.19 1600°C, 1,24µm/min, 300x

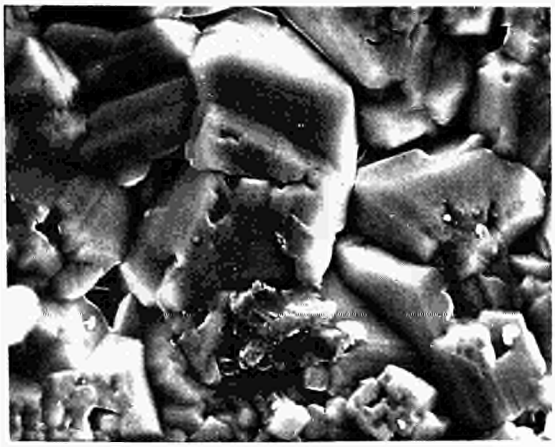

Fig.20 1600°C, 1,24 µm/min, 1000x

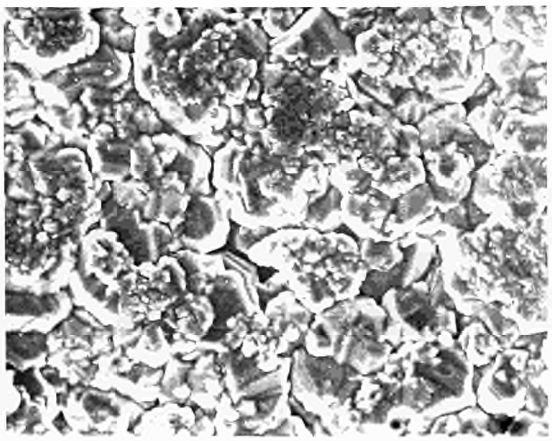

Fig.21 1600°C, 2,5µm/min, 300x

Fig.22 1600°C 2,5 µm/min, 1000x

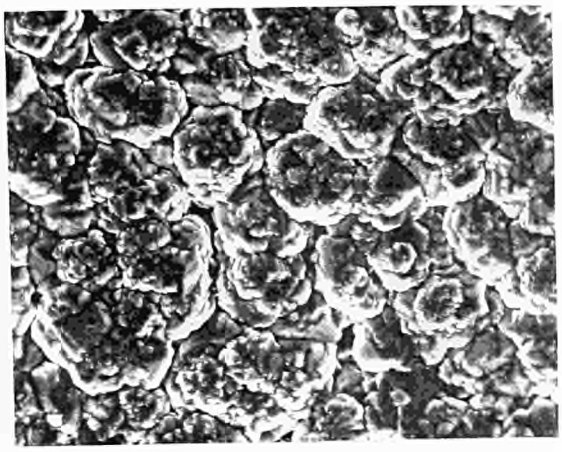

Fig.23 1600°C, 4, 1μm/min, 300x

Fig.24 1600°C, 4, 1μm/min, 1000x

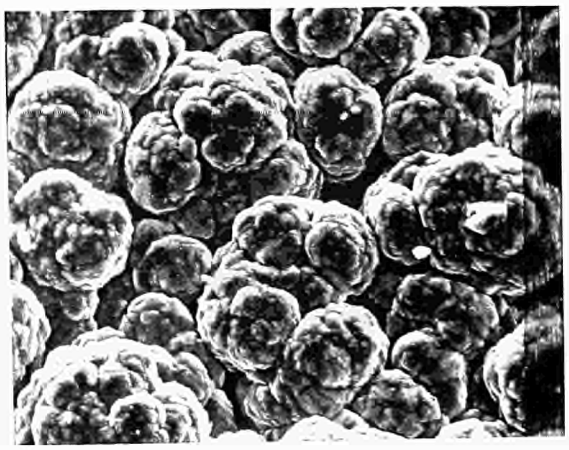

Fig.25 1600°C, 7, 7μm/min, 300x

Fig.26 1600°C, 7, 7μm/min, 1000x

The fracture surface examined by SEM

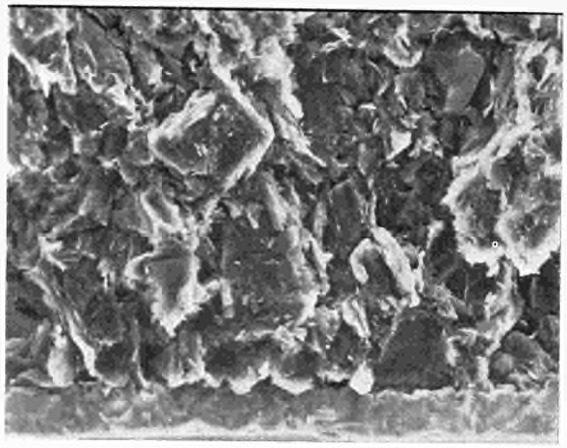

Fig.27 1600°C, 0,68μm/min, 300x

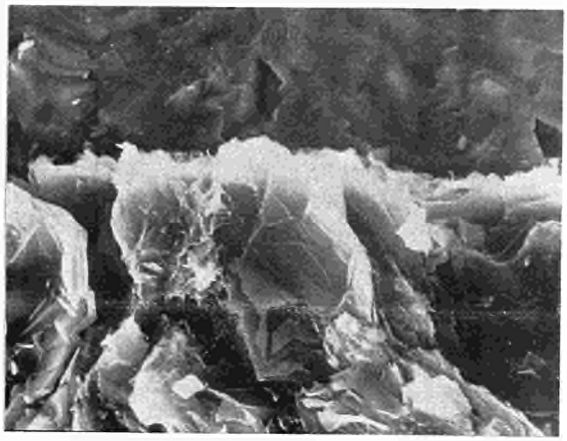

Fig.28 1600°C, 0,68μm/min, 1000X

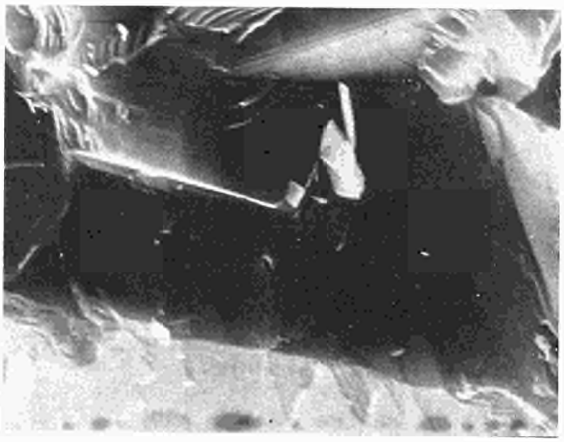

Fig.29 1600°C, 0,68μm/min, 3000x

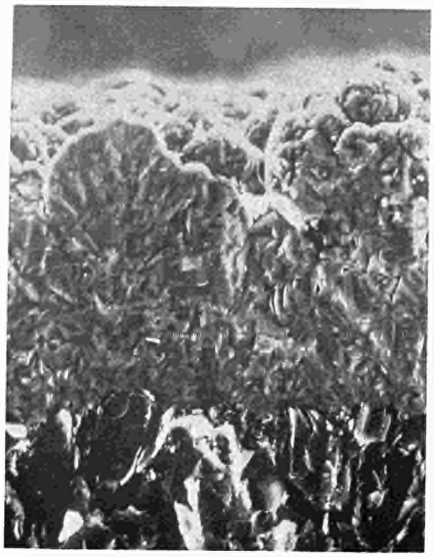

Fig.30 1600°C, 7,7μm/min, 300x

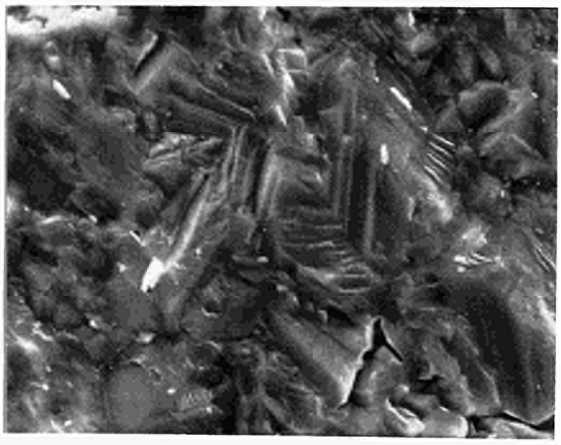

Fig.31 1600°C, 7,7μm/min, 1000x

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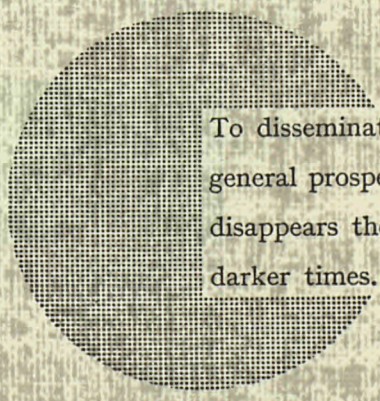

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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