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SILICON CARBIDE MIRRORS AT THE DARESBURY SRS

by

M.M. KELLY and J.B. WEST, Daresbury Laboratory

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Science & Engineering Research Council
Daresbury Laboratory
Daresbury, Warrington WA4 4AD

INTRODUCTION

This story begins late in 1979, when a material was being sought which could withstand the high x-ray flux anticipated from the SRS and still maintain good optical figure. At that time copper mirrors were being used at other facilities to cope with this problem. Copper, however, is far from ideal as an optical material. It needs to be coated to maintain reflectivity in the far UV. Early work by Rehn and Choyke(1,2) had established that silicon carbide (SiC) has a high reflectivity in the VUV down to the silicon 2p edge at ~ 110 Å, but only small pieces could be obtained at that time. Thus our priority was to obtain large pieces of SiC (~ 750 × 50 mm) sufficiently homogeneous to permit optical polishing and shaped to the required optical figure.

This report describes our progress in this respect. We have included background information on the materials being used and information on their optical performance. Despite the failures encountered along the way, in our view SiC is still the most suitable material. We are confident that we shall succeed in producing mirrors of good optical quality that will survive the hostile conditions to which they are subjected at the SRS.

SILICON CARBIDE: ITS VARIOUS FORMS AND PROPERTIES

Prior to 1979 the only SiC mirrors available were a few centimetres square. At the SRS, where mirrors are generally a few metres from the source, much larger mirrors are required to collect a useful amount of light. This led us into the technology of producing SiC, most of the expertise in this country residing with the British Ceramic Research Association (BCRA) and British Nuclear Fuels Limited (BNFL). Before going into detail on our work with them, it is worth summarising the properties of SiC and explaining why it is the best material for our purpose.

Mirrors are needed which maintain dimensional stability and surface figure when subjected to synchrotron radiation. Glasses tend to contract and craze, crystalline materials become porous and metals distort(3-6). The ideal mirror material for synchrotron radiation applications must have good thermal stability, must be highly polishable and reflective over a broad spectral range.

A good figure of merit for thermal stability is the ratio K/α (where K is thermal conductivity and α is thermal expansion coefficient). The various types of SiC have high thermal figures of merit for thermal stability and great elastic stiffness for dimensional stability. Table 1 lists the thermal and mechanical properties of various polycrystalline forms of SiC, some of which, notably CVD and Refel, have proved to be polishable to a very smooth finish and surface figure(7). Measurement of the reflectivities of polished SiC samples have shown them to be more reflective in the vacuum UV region at normal incidence than any other material known(8,9). Figure 11 compares the reflectivities of various potential mirror and coating materials(8-15). SiC mirrors can be used uncoated in VUV beamlines, but require a metallic overcoat to enhance reflectivity at longer wavelengths and below the Si $L_{II,III}$ edge. As grazing incidence soft x-ray reflectors, the various polytypes of SiC are comparable to carbon, Au or Pt(16,17). The chemical stability and abrasion resistance of SiC are important when cleaning and recoating of mirrors is required. Vacuum outgassing rates of CVD(18), and of hot pressed and Refel SiC(19), indicate that these materials are compatible with the UHV environment of the SRS.

MANUFACTURE OF SILICON CARBIDE

Hot pressed SiC discs up to 200 mm in diameter are produced by the BCRA, by pressing fine SiC powder inductively heated in a graphite die. The round, flat blanks are then cut to size and diamond ground to the required surface figure prior to polishing. Grinding a concave surface was found to cut through a porous layer exposing denser material in the central region. This caused differential polishing problems. An attempt was made to press the required curvature into the blank using a graphite die with a machined convex surface. This method produced a homogeneous surface, which facilitated polishing. However, the blank still required diamond grinding prior to polishing, because the surface was very rough due to partial adhesion to the die. Hot pressed SiC has about 3% porosity. The polished surface of the first hot pressed SiC mirror was traced using a talystep and found to contain about 4% porosity, the pits being on average 400 Å deep and 5 µm in diameter. The areas between the pits were smooth (± 20 Å). In 1980 the BCRA provided us with three hot pressed SiC mirrors, two spherical and one cylindrical which were installed as premirrors in ports 12, 13 and 6 in 1981.

Reaction bonded SiC (Refel or KT) is produced by isostatic pressing fine SiC and graphite powder mixtures which are then siliconised in a furnace. Molten Si permeates through the bulk material, reacting with the carbon to produce self-bonded SiC. Large blanks (up to 750 mm long) are produced by extrusion prior to siliconising, rather than by isostatic pressing. Both Refel (BNFL) and KT (Carborundum Co.) contain about 10% free Si and no porosity. These materials can be diamond ground then polished to the required optical figure and surface finish. The free Si polishes at a different rate to the bulk SiC giving similar polishing problems to those encountered with the areas of differing density in the hot pressed material. A final surface finish comparable to that of the hot pressed material (± 20 Å) can be achieved but without pitting of the surface. Six large Refel premirror blanks (up to 711 × 50 × 15 mm) have been manufactured by BNFL. These were diamond ground, then polished to a flat, cylindrical or spherical figure, prior to installation in the VUV beamlines on the SRS in 1983.

Chemical vapour deposited (CVD) SiC is by far the best mirror material for synchrotron radiation applications$^{(20,21)}$. This is produced by deposition from methyltrichlorosilane (CH_3SiCl_3) in the presence of hydrogen, on to a hot pressed SiC, Refel or graphite substrate$^{(22,23)}$. CVD SiC has better thermal properties even than hot pressed and reaction bonded SiC, combined with excellent polishability. A large composite CVD SiC mirror (150 × 75 ×10 mm) has been produced by Deposita and Composites Inc. using a KT reaction bonded SiC substrate (fig.1). There was sufficient thickness (> 1 mm) of the CVD layer to allow grinding to a spherical figure, radius of curvature R = 7.8 m. The Toshiba Ceramic Co. has produced larger CVD mirrors using graphite as a substrate, but the deposit is too thin to allow anything other than a flat figure. These have been used as premirrors in the Photon Factory, Japan, using a second reflection as the focusing element in the beamline.

A small hot pressed/CVD SiC composite (25 × 25 × 10 mm) produced by

the BCRA is to be used by Astron Developments Ltd. to investigate the feasibility of etching diffraction gratings in the CVD material. Some work along these lines has already been carried out at the National Physical Laboratory. SiC gratings would be extremely hardy compared to those made of silica.

On fig.2 are shown electron micrographs of the various forms of SiC; these were used for the measurements presented in ref.$^{(8)}$.

THE PERFORMANCE OF MIRRORS IN THE SRS

Thermal degradation of mirrors has been a problem in the VUV beamlines and is especially severe in lines 12 and 13. The infra-red mirror in port 13 was seen to glow red hot in the beam and finally fracture (figs.3 and 4). The hot pressed mirrors in ports 12 and 13 were mechanically clamped onto cooled copper backplates in a UHV environment. This meant that the cooling mechanism was primarily radiative, since there were effectively only three points of contact between mirror and cooling plate for removal of heat by conduction. Cold spots developed in the mirror at these efficiently cooled points, so that large thermal gradients were set up. These, combined with mechanical stresses induced in the material by the clamping mechanism, led to catastrophic fracture of the two mirrors. An electroless nickel-coated OFHC copper mirror similarly mounted and subjected to the same conditions became very badly distorted, completely losing its optical figure (see fig.5). An evaporated aluminium overcoat on this type of mirror has been found to suffer a mysterious form of radiation damage over the whole of the exposed area, resulting in a non-reflecting matt surface (fig.6). A similar effect was observed in gold coatings on glass mirrors, but only along the median plane where heating effects would dominate (fig.7). A beryllium mirror in use in the synchrotron radiation monitor was found to be severely radiation damaged through to the back face (figs.8 and 9). The photographs show these mirrors after exposure to synchrotron radiation. Figure 12 shows an alternative method of coping with heat loading; a slot has been cut through the centre of the synchrotron light monitor mirror allowing the hottest part of the beam to pass through. This has some disadvantages for the optical system that follows, in that the centre of the image is always missing.

Provision of SiC mirrors and the R & D programme on the mirror testing facility on port 10 are providing solutions to these problems. The ultimate aim of the mirror development programme is to provide properly cooled SiC mirrors. Methods of providing a good thermal contact between SiC and metals are being investigated in collaboration with Harwell and Culham Laboratories. Brazing might be used to join Refel SiC mirrors to water-cooled structures, preferably made of molybdenum rather than copper, to match the expansion coefficient. Various potential braze alloys have been tested for their wetting abilities and 10% copper/10% tin/80% titanium braze alloy has been recommended for fabrication trials. Refel SiC mirrors brazed directly onto molybdenum cooling pipes will be subjected to irradiation in the mirror test port. Another technique being tried is to "float" the SiC mirror on a thin film of liquid gallium, which is a liquid metal with an extremely low ($\sim 10^{-8}$ torr) vapour pressure at 30°C. It has been shown that gallium wets both SiC and copper, so this technique looks promising. The distance from the tangent point to the mirror test chamber is 3.5 metres, comparable to that in HA12; thus direct evaluation can be made of the performance of any cooling arrangement for the premirror in port 12, under working conditions. The results obtained on port 10 will be the subject of a separate technical memorandum.

SUMMARY OF SiC VUV OPTICS AT THE SRS

We are now sufficiently confident of the quality and optical performance of SiC that the first pre-mirrors for the stations on line 3 and 6, where horizontal deflections are involved, have been made in SiC and installed (fig.10). The temporary mirrors placed in these positions, made of float glass, have suffered severe deterioration (figs.7 and 10) and, in two cases, fracture rendering them useless. However, an early SiC hot pressed mirror in port 6 has now been exposed to synchrotron radiation for ~ 6 months and suffered no visible deterioration. This mirror, at a grazing angle of 20° and the worst case on these two lines from the heat loading point of view, is due to be replaced with the superior Refel type. The only other first pre-mirrors which have not suffered damage are those giving a vertical deflection and at grazing angles ~ 0.5°. In this case the heat load is spread over a much greater area, both because of the small grazing angle and vertical deflection. Second premirrors, or in some cases diffraction gratings, all use vertical deflection or dispersion, and for this fused silica has been found to be suitable.

It is only on lines 12 and 13 that problems have arisen even with SiC, and integrally cooled copper mirrors have been installed here. Once a satisfactory technique for cooling SiC has been established, from work on the test port, they may be replaced by SiC. Table 2 shows all the SiC mirrors presently installed or awaiting installation at the SRS, together with their optical parameters and heat loadings.

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TABLE 1

Thermal and mechanical properties of polycrystalline forms of silicon carbide.

Type of SiC	REFEL	REFEL 'S' GRADE	HOT PRESSED	CHEMICAL VAPOUR DEPOSITED
Thermal Conductivity (K) W cm^{-1} K^{-1} (25°C)	2.0	1.6	0.7	2.5
Thermal expansion coefficient (α) $\times 10^{-6}$ K^{-1}	4.3	4.3	4.8	3.0
Figure of merit (K/α) $\times 10^{5}$ W cm^{-1}	4.65	3.72	1.46	8.3
Modulus of rupture psi $\times 10^{3}$	76	40	55	76
Youngs modulus psi $\times 10^{6}$	60	58	64	65

TABLE 2

	Spectrometer	Mirror size (H × V × T) mm	Distance from tangent point (metres)	Distance to focus (metres)	Optical figure	Heat loading grazing angle of incidence
(Port 3)						
3.1	1 metre Seya-Namioka	336 × 50 × 15	8	2	cylindrical R = 17.91 m	120 watts 4.3 watts/sq.cm 10° (H)
3.2	5 metre McPherson	590 × 60 × 15	10.5	-	plane	80 watts 1.26 watts /sq.cm 5° (H)
3.3	T.G.M.	711 × 40 × 15	6.5	3.25	cylindrical R = 47.29 m	160 watts 3.3 watts/sq.cm 5° (H)
(Port 6)						
6.1	Mykake-type grazing incidence	560 × 50 × 10	7.0	3.5	cylindrical R = 49.95 m	160 watts 3.3 watts/sq.cm 5.7° (H)
6.2	T.G.M.	214 × 50 × 10	7.0	3.5	cylindrical R = 13.64 m	160 watts 11.2 watts/sq.cm 20° (H)
(Port 12)						
12.1	80 cm Czerny-Turner	150 × 75 × 10	3.1	- 7.1 (HF) 25 (VF)	spherical R = 7.8 m	400 watts 126 watts/sqcm 45° (V)
(Port 13)						
13.1	IR Fourier transform	100 × 150 × 10	1.27	- 2.4 (HF) -19.2 (VF)	spherical R = 3.85 m	1232 watts 670 watts/sq.cm 45° (V)
13.2	0.5 metre Seya Namioka	100 × 150 × 10	1.27	As above	shared mirror with 13.1	As above
Synchrotron light monitor		135 × 35 × 7	3.1	-	plane; slot cut from centre 70 × 7 mm	Through slot

Notes: HxVxT = horizontal size × vertical size × thickness
HF = horizontal focus; VF = vertical focus;
H = horizontally deflecting; V = vertically deflecting.

FIGURE CAPTIONS

Fig.1 Silicon carbide in the CVD form on a slab of the KT material; it is shown prior to grinding and polishing.

Fig.2 Scanning electron micrographs of SiC samples: (a) CVD [625]; (b) CVD [650]; (c) hot pressed [653]; (d) REFEL [650]; (e) CVD [650]. Figures in square brackets are magnifications. (e) Shows polishing streaks on an inferior slab of the CVD material similar to (b). Full details are contained in reference 8 .

Fig.3 The fractured SiC mirror on IR13, the main crack being along the median plane of the SRS.

Fig.4 A similar view of the HA12 SiC mirror, which was aluminium coated.

Fig.5 The copper mirror, cooled only by contact, used on IR13. The temperature on the surface has been sufficient to melt the nickel coating and the small forces exerted by the clamps were sufficient to distort it.

Fig.6 The copper mirror used on HA12, which was coated with electroless nickel and then aluminium. Only the areas exposed to synchrotron radiation have suffered adversely indicating that heating affects alone were not the cause of this problem.

Fig.7 The gold coated float glass mirror used on 6.1 efter ~ 100 hours exposure to SRS energies < 1.8 GeV. The deterioriation along the median plane is clearly visible.

Fig.8 The Be flat used on the synchrotron light monitor (front surface).

Fig.9 As fig.8, but rear surface.

Fig.10 The Refel silicon carbide flat to be installed in 3.3 is shown in the background; reflected in it, from the foreground, is a float glass mirror also used after ~ 10 hours exposure at 2 GeV. It is cracked along the median plane up to the region where the major vertical fracture is visible.

Fig.11 Normal incidence reflectivities of various materials in the range 200-1800 Å.

(1) CVD SiC$^{(8)}$
(2) CVD SiC$^{(10)}$
(3) Au$^{(11)}$
(4) Pt$^{(12)}$
(5) Pt$^{(13)}$
(6) Single crystal SiC$^{(14)}$
(7) Os$^{(15)}$

Fig.12 Variation on a theme: the slotted SiC mirror, before polishing, to be fitted to the synchrotron light monitor.

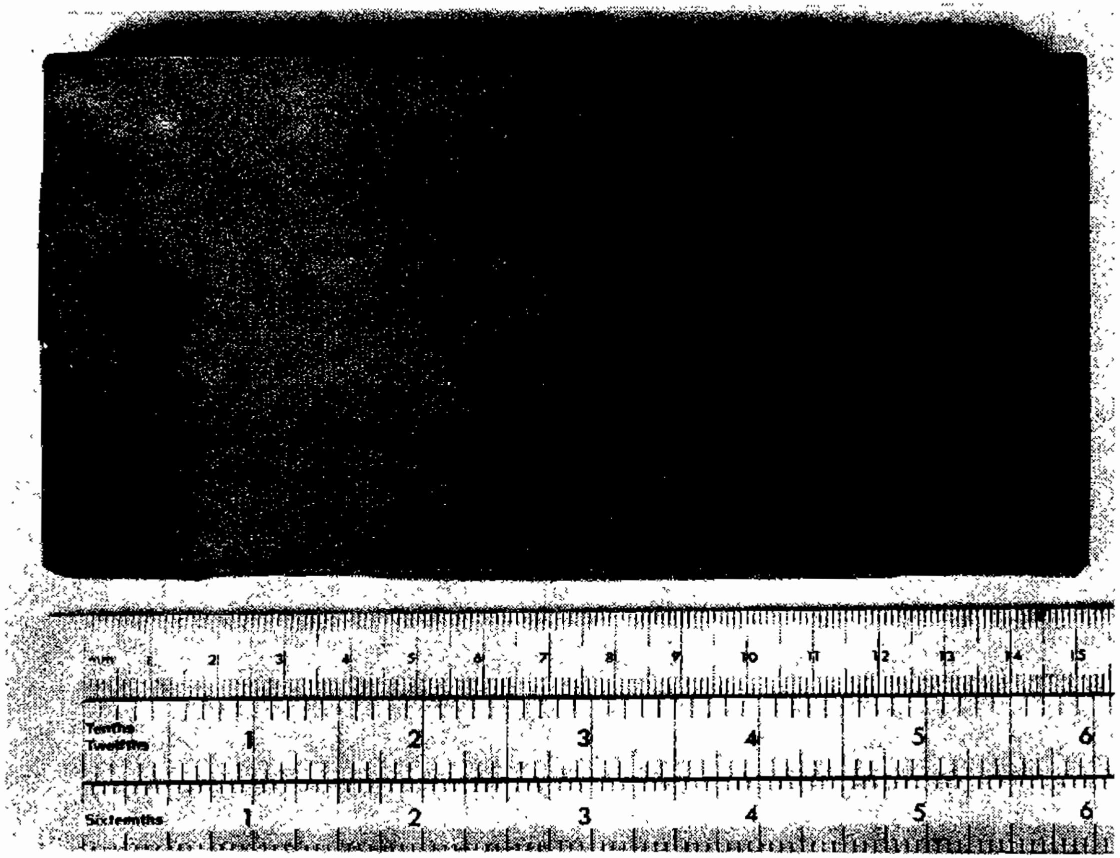
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Fig.1

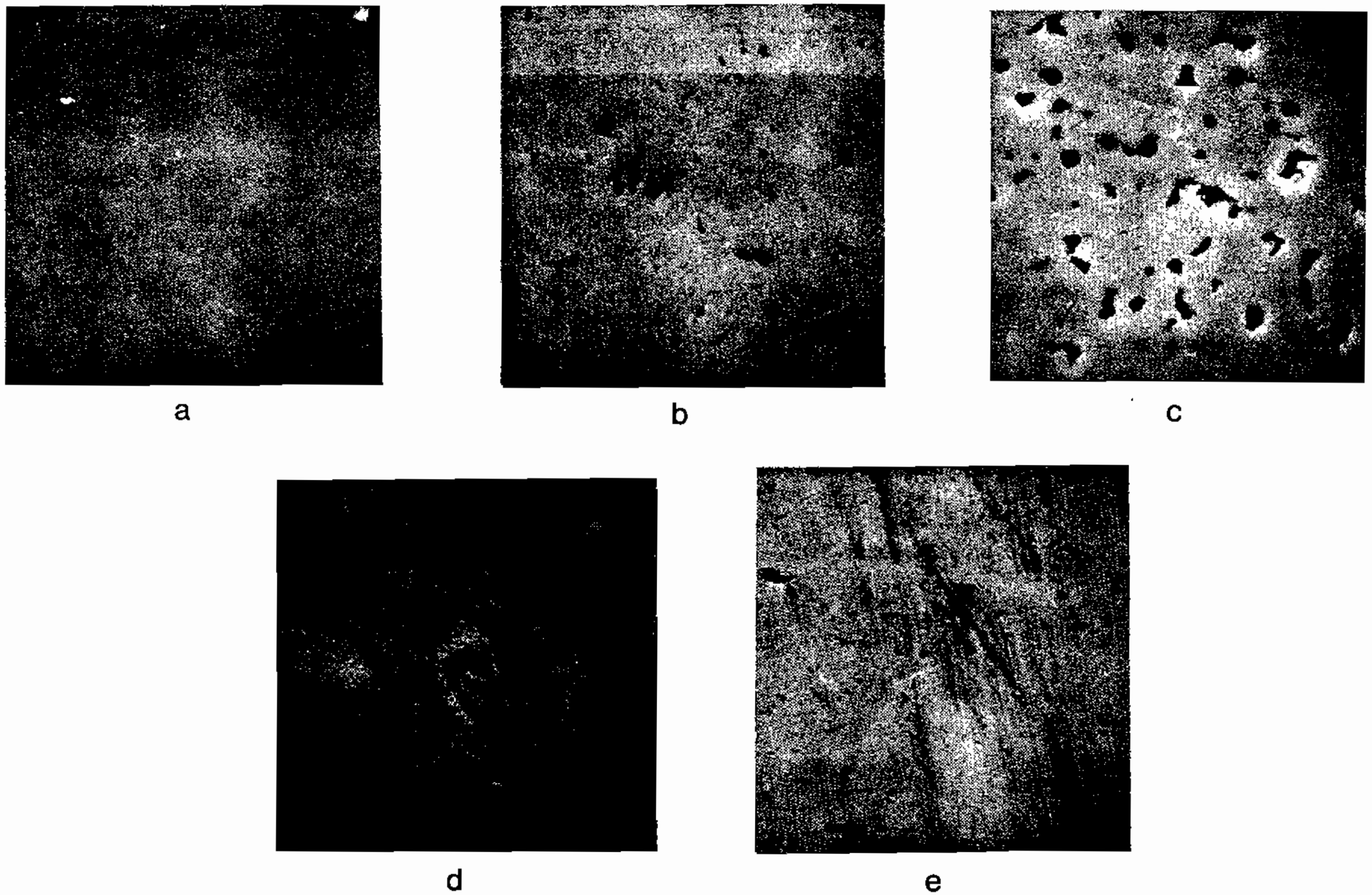


Fig. 2

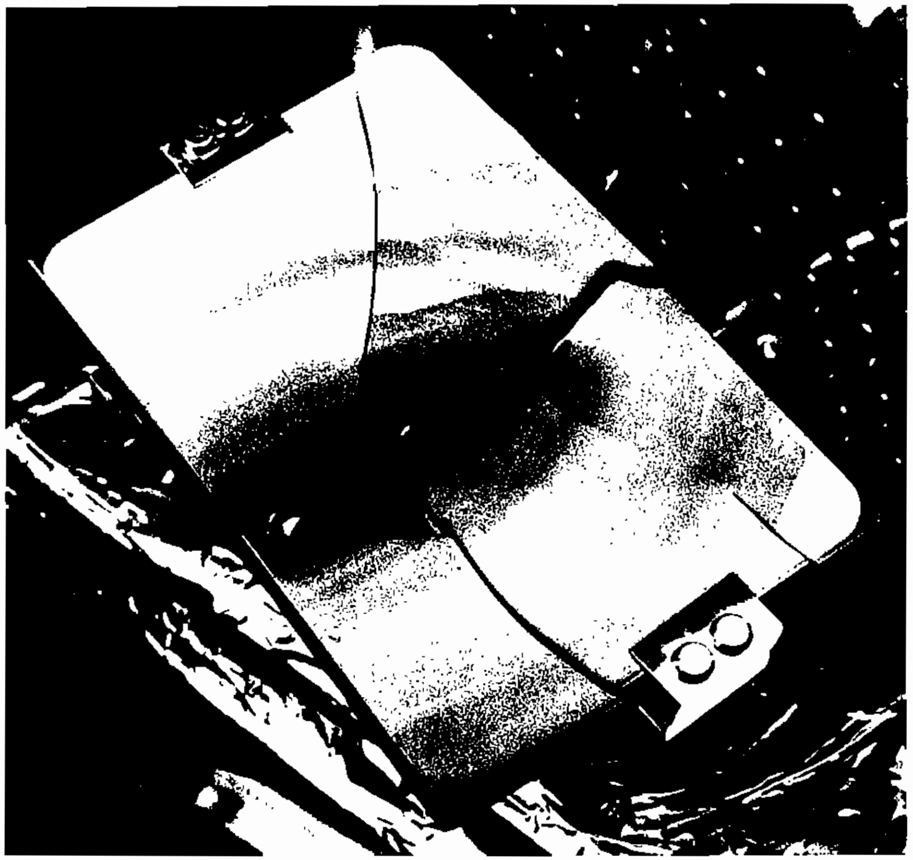
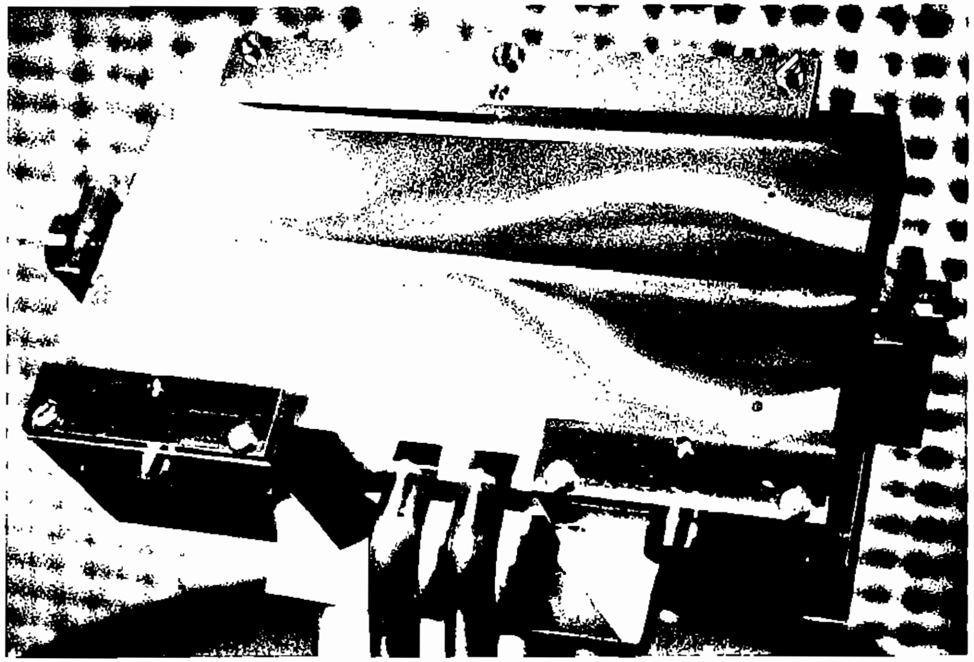


Fig.3



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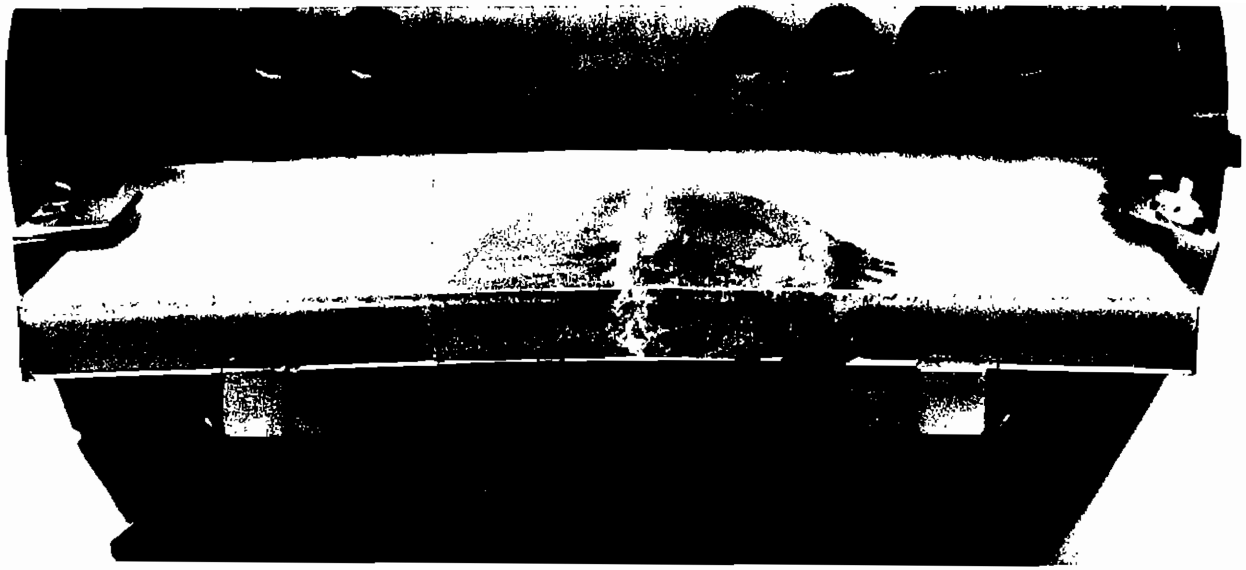

Fig.5

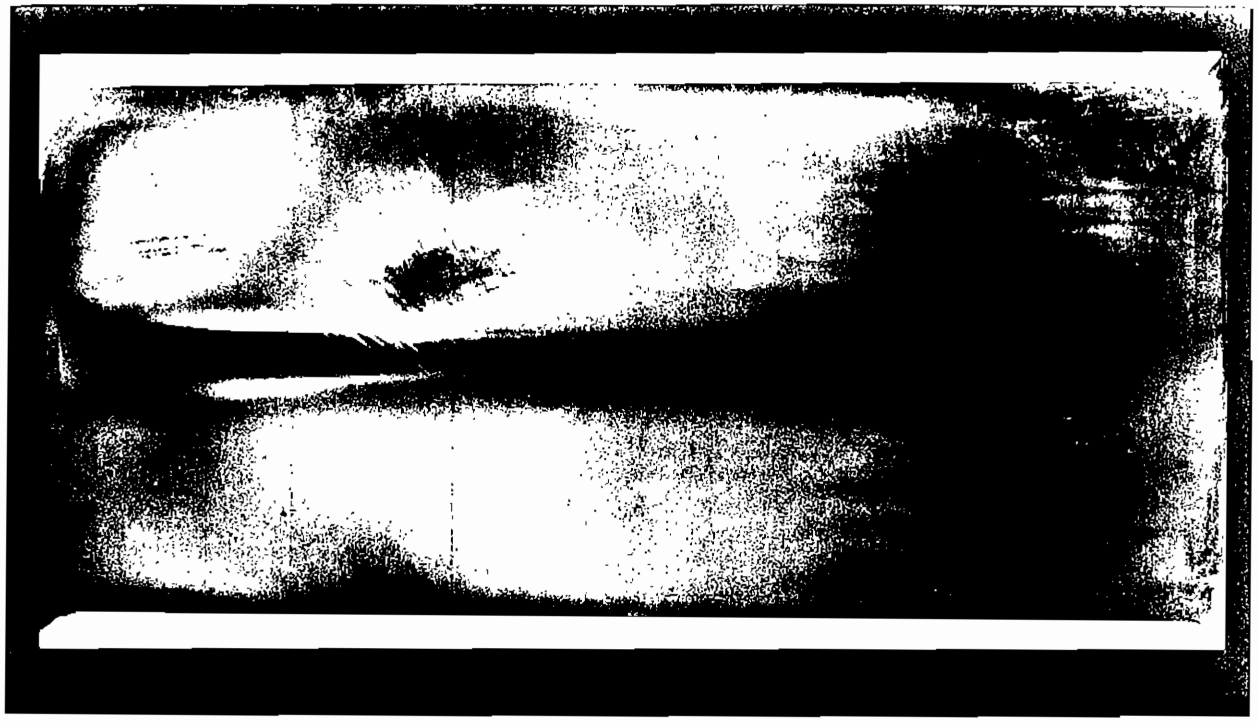

Fig.6

Fig.7

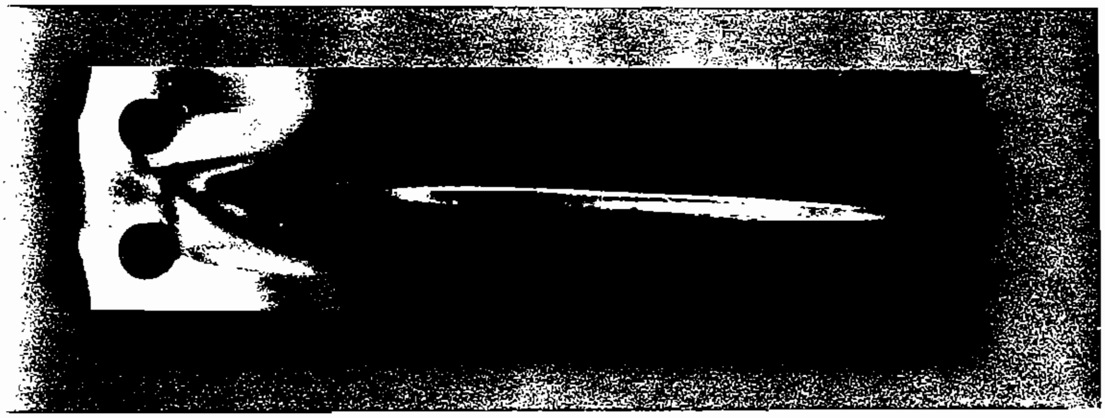

Fig.8

Fig.9

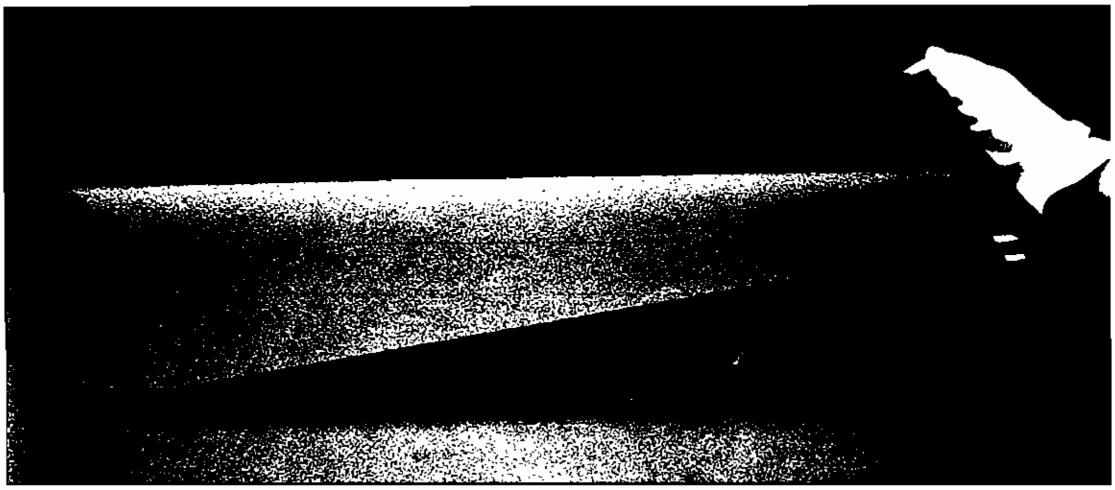

Fig.10

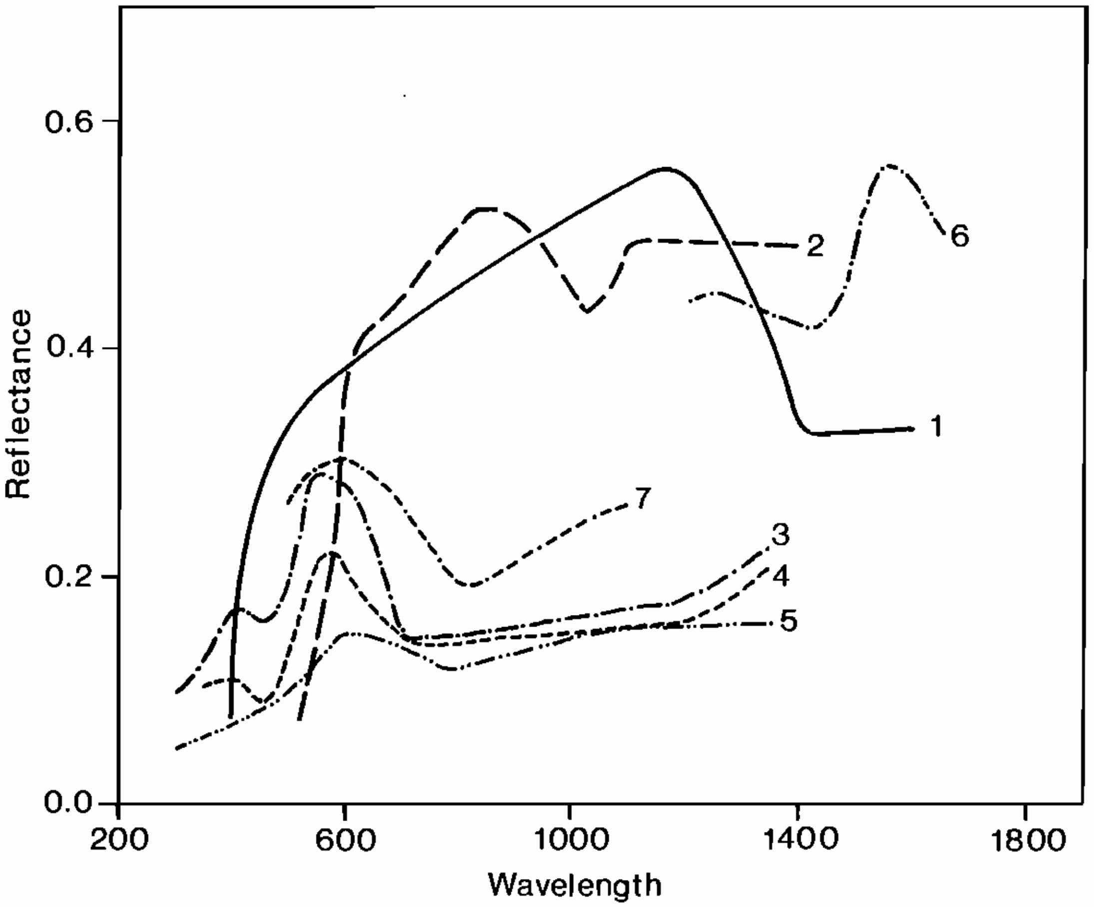

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Fig. 11

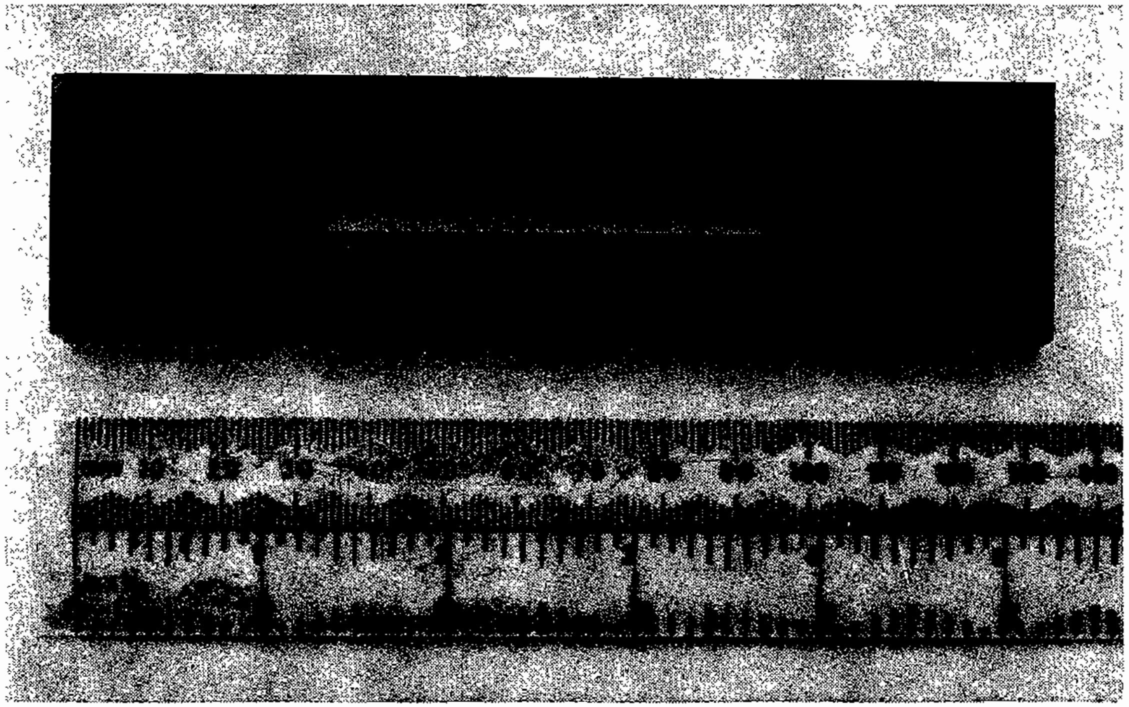

Fig. 12