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STUDY AND APPLICATION OF SILICON NITRIDE AS A HIGH TEMPERATURE MATERIAL

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A.M.L. Report No. A/75(S)
January, 1959

ADMIRALTY MATERIALS LABORATORY

Metallurgical Division

STUDY AND APPLICATION OF SILICON NITRIDE AS A HIGH TEMPERATURE MATERIAL

by

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SUMMARY

The need for an engineering material with good mechanical properties and stability for service in gas turbines at temperatures of the order of 1200°C has led to the study and development of silicon nitride for this purpose. This material, although brittle at room temperature, has excellent oxidation resistance, comparatively good thermal shock resistance, and adequate creep strength at the temperatures involved if stiffened with a very fine dispersion of silicon carbide which may be incorporated during the reaction sintering production process.

Methods for producing the material in suitable form, and in the best physical state for engineering designs, have been evolved, and the properties of the material have been fully explored by laboratory evaluation and field trials.

If the characteristics of the material are taken into account during its application, it will provide a much needed and valuable contribution to the presently available high temperature materials. Its usefulness promises to extend far beyond the applications originally envisaged. Some of these fields of application are described and others suggested.

(Sgd.) T. C. J. OVENSTON
Superintendent, A.M.L.

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STUDY AND APPLICATION OF SILICON NITRIDE AS A HIGH TEMPERATURE MATERIAL

1. INTRODUCTION

Advances in gas turbine and rocket design are now demanding engineering materials with good mechanical properties at temperatures in excess of 1000°C, a figure which is generally considered to approach the upper limit of high temperature alloy development. Some hope is still entertained that molybdenum- or niobium-based alloys can be developed with sufficient self- or surface-induced resistance to high temperature oxidation in order that their good creep properties may be exploited at such temperatures. Considerable effort has also been spent in an endeavour to produce mixtures of ceramics and metals (cermets) in order that the refractoriness of the one, and the ductility of the other, may be combined to produce a ductile material with good creep strength and oxidation resistance at these high temperatures. A summary of the properties of a number of high temperature materials developed in the United States of America since World War II is given in B.J.S.M. (Navy Staff Report) Sci Ad 34/52, which also provides information on a number of intermetallic and refractory compounds.

So far, no material had yet been found which satisfied all conditions liable to be encountered in service at these temperature levels. Where stability, oxidation resistance and creep strength of the refractory type compounds were found to be adequate, the results were invariably invalidated by lack of resistance to thermal shock. An experimental programme was therefore commenced in 1956 which was aimed at finding material which would satisfy all conditions demanded by gas turbine nozzle guide vanes operating at temperatures of the order of 1200°C.

A number of intermetallic compounds and cermets were prepared, but while some of these had good oxidation resistance at 1200°C, they were invariably brittle at room temperature, and all of them had poor resistance to thermal shock except silicon nitride. Details of this preliminary work are given in A.M.L. Report No. A/74(S). It was decided to accept the room temperature brittleness of silicon nitride and to concentrate upon its further study and development. Workers at the British Ceramic Research Association had also found that silicon nitride has good oxidation resistance, and a low coefficient of thermal expansion, with consequent high resistance to thermal shock, and have reported other properties.(1, 2, 3)

Preliminary thermal shock tests were conducted on silicon nitride by plunging samples repeatedly heated to 1000°C into cold water. The material stood up to these tests without sign of failure, and this was sufficiently encouraging to warrant further development. An attempt was then made to produce samples of the highest possible density and in the optimum physical condition, and to evaluate their physical and mechanical properties. Subsequently, the creep strength of pure silicon nitride at 1200°C was found to be inadequate, and effort was then directed towards improving this without sacrificing the other good high temperature properties.

2. THE NITRIDING OF SILICON

The nitriding of silicon is brought about by heating the element in an atmosphere of nitrogen for a period of time, at temperatures above 1200°C. If lump silicon is used, the reaction is confined to the surface, and only a thin layer of nitride is formed in the manner shown in Fig. 1. It may be seen that this layer apparently consists of two distinct phases which exhibit free-growing hexagonal forms. These two phases are probably α and β hexagonal silicon nitride which have slightly different lattice dimensions. Identification of the two separate phases, and agreement on the precise conditions under which they are formed, has been the subject of several recent papers(4, 5, 6). The α phase is claimed to be produced by nitriding at temperatures between 1200° and 1400°C, while the β phase is formed by nitriding at temperatures

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/above ...

above 1450°C. A transformation of α to β is said to take place when the former is heated above 1550°C. This transformation does not appear to take place easily in the presence of uncombined silicon at temperatures below 1450°C.

When compacted powder is used, the enormous increase in specific surface enables the nitriding process to be taken to completion in a reasonable time, the weight gain corresponding closely to the formula Si_3N_4. The nitriding process appears to be associated with the diffusion of nitrogen into the silicon powder and at temperatures over 1200°C results in the growth of an interpenetrating matte of Si_3N_4 crystals from adjacent silicon particles. This matte fills the pores of the powder compact, thereby imparting mechanical strength, and as it is micro-porous it permits the continuous diffusion of nitrogen to the interior. The rate of the reaction is temperature dependent, as can be seen from Fig. 2, which gives the rate of nitrogen absorption for a 200-mesh powder compact at 1250, 1350 and 1450°C over periods of time. Apart from the obvious significance of particle size and packing coefficient, these rates are influenced also by the shape of the compact, as may be seen from the two tests at 1350°C on samples having different areal dimensions per unit mass.

It may be seen from Fig. 2 that nitriding is complete in a comparatively short time at 1450°C, whereas many hours are required at lower temperatures. As the highest of these temperatures is above the melting point of silicon (1420°C) a preliminary reaction-sintering operation at temperatures between 1250 and 1350°C is necessary so that the collapse of the powder into a molten pool may be avoided. This operation produces a rigid network which retains the uncombined silicon and thus permits a gas-solid-liquid reaction at temperatures above the melting point of silicon, the nitrogen being transported to the central areas through the now intercommunicating silicon nitride matte. The fairly rapid reaction which takes place at 1450°C results in the conversion of all the remaining silicon to a consolidated form of silicon nitride having a much greater hardness and density than that of the matte produced by solid-state reaction at the lower temperature. The relative hardnesses of the silicon nitride matte, the consolidated silicon nitride, and the uncombined silicon, may be observed by microhardness tests; this subject is discussed in detail later. Various stages in the nitriding of silicon, which has been termed a 'reaction-sintering process', are illustrated in Fig. 3(a)-(e). Prolonged reaction-sintering at temperatures below the melting point of silicon also results in the production of a skeleton of consolidated silicon nitride, as shown in Fig. 3(d). It can thus be seen that various times of reaction-sintering at temperatures below and above the melting point of silicon will result in quite different internal structures in the resulting silicon nitride. A very long reaction-sintering below 1400°C will produce an extremely dense matte and ultimately a hard skeleton of silicon nitride crystals, whereas a short two-stage reaction-sintering process at 1350°C and 1450°C will produce a softer matrix of the silicon nitride matte in which are dispersed islands of hard, consolidated silicon nitride. The density of the fully sintered material will be the same in each case.

The prolonged reaction-sintering times required for the complete nitriding of compacts of silicon powder at temperatures below its melting point are unrealistic for production purposes. The following convenient reaction-sintering schedule was devised, therefore, and adopted for subsequent studies of the properties of silicon nitride.

Stage I. Nitriding of the compacted powder is carried out below the melting point of silicon at a temperature of 1250°C for periods up to 16 hours. This produces an intercommunicating silicon nitride network but the reaction rate gets progressively slower as the silicon nitride matte thickens.

Stage II. Nitriding is then continued above the melting point of silicon at a temperature of approximately 1450°C for three or four hours in order to convert all remaining silicon completely to nitride.

The surface of nitrided silicon powder is invariably covered with a white wool-like substance as shown in Fig. 4. At higher magnifications this may be resolved into numerous single-crystal whiskers of silicon nitride (Fig.5).

It is .../

It is pictured that the matte between silicon particles in the body of partially reacted powder is an inter-penetrating mass of these single crystals which eventually merge with prolonged nitriding at temperatures above 1300°C.

When sectioned, silicon nitride has a mottled grey appearance, and if oxygen is present during the nitriding operation another phase, which is possibly white silicon oxynitride(4), is found to be present. Unreacted silicon may be identified as glittering particles on a fractured surface, or as islands of a bright phase in polished microsections. The structure and constitution of the material is described in more detail later.

The silicon used for this investigation contained about 2% impurity which was mainly iron and oxygen. Analysis by the Bragg Laboratory, Sheffield, of silicon nitride produced by nitriding this grade of silicon powder gave the following figures:-

Total Silicon	59.35%
Nitrogen	39.2%
Iron	.9%
Aluminium	.05%
Oxygen	.4%

It was therefore concluded that, apart from a small amount of iron oxide, the silicon nitride was reasonably pure (Si_3N_4 theoretically contains 60.24% of silicon and 39.76% of nitrogen).

Commercial nitrogen was used in the first experiments, any oxygen present as impurity being removed by passing the gas over copper gauze heated at 600°C. Moisture was removed by passing the gas through a calcium chloride tower and finally over phosphorus pentoxide. Purer nitrogen (White Spot) was substituted for commercial nitrogen for later experiments, thus enabling the purification train to be simplified, the gas being passed over phosphorus pentoxide only, to remove traces of moisture.

3. EQUIPMENT FOR THE NITRIDING OF SILICON

The equipment used for the production of the silicon nitride is shown diagrammatically in Fig. 6 and photographically in Fig. 7. It consists essentially of a non-porous refractory reaction tube (re-crystallised alumina or mullite), closed at one end, which is located in the centre of a cluster of crusilite resistance heating elements which are capable of raising the temperature of the central portion of the reaction tube to 1500°C. A temperature control system is arranged so that a hot zone about 5" long can be maintained to within ± 5°C for long periods. The open end of the reaction tube (which for the work described in this report was 3" in diameter) was sealed with a water-cooled 'O' ring vacuum end-cap provided with ports to accommodate thermocouple sheaths and gas entry and discharge. A stainless steel heat barrier was provided between the hot zone and the end caps.

Provision was made for the evacuation of the furnace tube prior to the introduction of the nitrogen atmosphere, which was then maintained in the reaction tube at a positive pressure of around 6" Hg. The silicon powder was held either in alumina boats or as powder compresses supported upon grooved alumina or silicon nitride tiles. Heating and cooling cycles were protracted in order to reduce furnace component deterioration to a minimum.

4. THE PRODUCTION OF SHAPES

In order for silicon nitride to be useful as an engineering constructional material it was necessary to produce it in suitable shapes and in the best possible physical and mechanical condition. Nitriding of loose silicon powder supported in a refractory boat gave it some mechanical strength, as may be seen from Fig. 8, but the resulting product is very porous and must still be handled with care.

In order .../

In order to improve its mechanical properties it was necessary to compact the powder before nitriding, by means of a suitable pressing operation. There is an optimum degree of powder consolidation beyond which homogeneous reaction-sintering becomes difficult and prolonged, and other production difficulties arise.

The compacting of silicon powder to a suitable shape is most conveniently done by cold-pressing in a suitable die set. Simple cylindrical or rectangular dies of the type illustrated in Fig. 9 give the most easily controllable means of providing even powder packing during the pressing operation. The angular nature of the hard non-ductile fine silicon powder particles, illustrated in Fig. 10, explains its resistance to flow under die pressure, which makes the use of deep and intricate die shapes impracticable. Some assistance can be given to flow by mixing into the powder a suitable lubricant before loading the die. This lubrication also gives an additional 'green' strength to a cold pressed shape. It is also an advantage to distribute and partially consolidate the powder in an assembled die by light vibration before applying pressure. This expels some of the occluded air and helps to ensure a uniform density before the load is applied. Dies should be designed to allow the ready removal of the 'green' pressing which at this stage is extremely delicate and therefore prone to damage by handling. If possible, the 'green' pressing should be extruded directly on to its firing tile so that it may be put into the reaction chamber without further handling.

In earlier experiments, 10% cetyl alcohol in methylated spirits was used as a binder and lubricant for obtaining 'green' shapes, and satisfactory results were produced by using 2-3 ml of this solution with every 10 g of 200-mesh silicon powder. The cetyl alcohol was driven off in the early stages of nitriding, leaving some free carbon in the furnace tube. When it was desired to produce very pure silicon nitride, however, the use of this lubricant was considered undesirable.

Powder pressings made without the aid of a binder are very weak and difficult to handle, but it has been found that moisture can be employed as both binder and lubricant in the production of satisfactory 'green' pressings which may be handled from the die to the tile, the moisture then being removed slowly by air or oven drying. The optimum quantity of water to be used is a function of the particle size of the silicon powder, but about 3 ml per 10 g of 200-mesh material has been found to give satisfactory results.

Owing to the non-ductile characteristics of silicon powder, it was found that the maximum die pressure was limited by the necessity for avoiding the subsequent occurrence of internal cracks in planes of maximum shear stress. Such internal cracking, which inevitably appears at excessive die pressures, persists throughout the entire reaction-sintering process, and is still present in the final product as fissures, the surfaces of which are covered with a white layer. This layer is possibly silicon oxynitride formed by entrapped oxygen escaping along the preferential paths presented by the cracks during the early stages of nitriding. The maximum pressure which may be applied at any particular pressing in order to avoid internal fissures must be determined beforehand by examination of the surface and fracture appearance of sacrificial pressings. Internal fissures are readily identified, as may be seen from Fig. 11. Care must be taken to avoid local distortion and cracking while the 'green' pressing is being removed from the die. Using water as the binder and lubricant it is possible to produce 'green' shapes, free from cracks, with loads up to 4 t.s.i. on 200-mesh silicon and up to 2 t.s.i. on 400-mesh silicon in a simple rectangular die. Loads as low as 1 t.s.i. resulted in cracks when silicon powder was pressed in the same die without the addition of an internal lubricant.

It is nevertheless possible to produce 'green' powder pressings to the geometrical form finally required provided this is comparatively simple, and examples of such shapes, produced and fired without any machining operation whatsoever, are given in Fig. 12 (a and b).

Reaction-sintered silicon nitride is difficult to machine; it is sufficiently hard to cause undesirably heavy wear on orthodox machine tools, though it may be machined by diamond-impregnated grinding wheels. A more satisfactory method for producing intricate shapes consists of producing a simple stock silicon powder pressing and then sintering it in nitrogen at a temperature of 1200°C for an hour or so to produce a loosely sintered product which has a texture somewhat similar to that of soft chalk. The extent of reaction-sintering at this stage is a compromise between that required to give the material sufficient mechanical strength to be gripped in a machine, and too much hardness, which would cause gross wear of machine tools. After this loosely sintered material has been machined to the finished dimensions, it is replaced in the reaction chamber and nitrided in the usual manner. Dimensional changes observed after complete reaction-sintering amount to about 0.01% shrinkage and may therefore be considered insignificant for most practical purposes. By this method it is possible to produce intricate shapes to close tolerances, and examples of these are shown in Fig. 13 to 16.

5. ATTEMPTS TO IMPROVE THE DENSITY OF REACTION-SINTERED SILICON NITRIDE

The true density of silicon nitride is 3.2, that of the loosely sintered powder 1.5, and that of the cold-pressed sintered material between 2.0 and 2.5. The difference between the theoretical and apparent values arises from the micro-porosity which remains after the firing operation. Too great a densification of the powder in the cold-pressing stage resists the formation of silicon nitride in the central areas during the standard nitriding process and can be offset only by prolonging unduly the reaction-sintering operation. However, it was reasonable to suppose that any increase in density, with corresponding reduction in micro-porosity, would result in an improvement in the mechanical properties of the material. The following attempts were therefore made to see if the average density of 2.2 could be improved upon.

(a) The die pressure was increased up to 16 t.s.i. by employing hydraulic pressure on the outside of a rubber sac containing silicon powder, in the manner illustrated in Fig. 17. After a prolonged reaction-sintering operation, silicon nitride having an average density of 2.5 was obtained on small specimens.

(b) An increasing fineness of powder particle size was employed with the standard pressing technique to achieve a better packing coefficient, but without any marked beneficial effect.

(c) Mixed particle sizes were employed in an effort to improve the packing coefficient, but this showed little improvement.

(d) Several mixtures of 200-mesh silicon nitride and silicon powder of the same fineness were cold pressed to 3½ t.s.i. in a standard die set and the 'green' pressings nitrided in the usual manner. No increase in density was obtained and subsequent mechanical properties were found to be below those normally expected from straight nitriding of the silicon powder.

(e) Densification of reaction-sintered silicon nitride was attempted by heating the top of a block of the material in an inert atmosphere for 4 hours at about 1700°C. A reduction in cross sectional area took place, as can be seen from Fig. 18, but as the density of the reduced areas remained unaltered, reduction was assumed to have resulted from partial sublimation.

(f) Attempts were made to hot-press loose silicon nitride powder in a silicon nitride die under a pressure of 1½ t.s.i. for 10 minutes at 1400°C in an atmosphere of nitrogen. Although some compacting took place the resulting product had little mechanical strength.

(g)/...

(g) Following a suggestion by Abbey(7) for increasing the rate of reaction, 2% calcium fluoride was incorporated in the 'green' powder pressing as a possible catalyst to see if this would also improve densification. Its influence on a number of variations of the standard reaction-sintering procedure was studied, but in no case did it influence densification materially, and its presence had an adverse effect on stability and oxidation resistance.

6. PROPERTIES OF SILICON NITRIDE

The chemical and physical properties of silicon nitride have been the subject of wide interest for some years, although the structure of its crystal forms has been established only comparatively recently. Little or no information was hitherto available on the mechanical properties of this material.

(a) Chemical and Physical Properties

Its dimensional stability and oxidation resistance when subjected to temperatures up to 1400°C are excellent. The changes in weight of a number of silicon nitride samples held at 1200°C for 100 hours is shown graphically in Fig. 19. After a small initial gain in weight which takes place within the first five hours there is no further change. The inferior oxidation resistance of the partially nitrided sample containing 30% free silicon confirms that the initial gain is probably due to the oxidation of a small amount of unreacted silicon in surface layers to silica.

Silicon nitride is not wetted by any of the common metals and therefore it has not yet been found possible to overcome its porosity by infiltration methods. It is not attacked at room temperature by gases containing sulphur or chlorine, and it is resistant to attack by most acids. It is more resistant to hydrofluoric acid than silica but can be decomposed by this acid, or by potassium hydroxide at temperatures around 400°C. It is attacked by sodium chloride and vanadium pentoxide at temperatures of about 1000°C.

The apparent density of reaction-sintered silicon powder compacts is around 2.2, which is about two-thirds of the true density of silicon nitride (3.2).

The coefficient of linear expansion of silicon nitride is low, and is recorded as 2.5×10^{-6} over the range 20°C-1000°C(3). Thermal conductivity at an apparent density of 2.2 is given as 0.0037 c.g.s.(3) and electrical resistivity when dry is about 1.4×10^{7} ohm-cm. (as measured on several samples at A.M.L.).

(b) Mechanical Properties

(i) Young's Modulus. An average value for Young's Modulus for silicon nitride with a density of 2.2 is 4,000 tons/sq.inch at room temperature and approximately the same value at 1000°C.

(ii) Transverse Rupture Strength The transverse rupture strength of reaction-sintered silicon nitride compacts was measured on a three-point loaded beam at room temperature and at 1200°C on a number of samples with different bulk densities. The results, which are given in Table I, compare favourably with those already published by Vassiliou(1) and Collins and Gerby(8).

Table I/...

TABLE I

Transverse Rupture Strength of a Number of Samples of Silicon Nitride of Varying Density and Composition

	Pressing Pressure (t.s.i.)	Bulk Density	Transverse Rupture Strength at 1200°C (t.s.i.)	Transverse Rupture Strength at Room Temp. (t.s.i.)
Silicon Nitride	16*	2.5	13.0	9.79
	4	2.25	7.12	6.87
	2	2.10	6.85	5.29
	2/	2.10	7.40	6.85
	1	1.90	4.34	4.87
	Loose Powder	1.50	0.4	0.4
Silicon Nitride + 10% SiC	2	2.2	5.65	7.37
Silicon Nitride + 5% SiC	2	2.2	6.97	5.21
Silicon Nitride + 5% Carbon	2	2.2	5.47	5.03

*Special hydrostatic pressing, remainder of pressings carried out in steel dies.

/After prolonged first stage nitriding at 1350°C.

It can be seen that material with a density of 2.2 has a rupture strength of around 7.0 t.s.i. at room temperature and slightly higher value at 1200°C. Prolonged first stage nitriding at 1350°C resulted in the slight improvement given in Table I. The best result was obtained with hydrostatically pressed powder which after nitriding had a density of 2.5 with a strength of 10.0 t.s.i. at room temperature, rising to 13.0 t.s.i. at 1200°C.

(iii) Thermal Shock resistance. As a result of its low coefficient of expansion, the thermal shock resistance of silicon nitride was expected to be unusually good for a material of the ceramic type. Comparison with other materials was made using the fluidised bed testing technique developed by the National Gas Turbine Establishment. This test, in which special test pieces are submitted to repeated sharp thermal stress gradients, consists of the rapid transference of a wedge-sectioned disc specimen (illustrated in Figs. 12a and 12b) from a hot to a cold fluidised zircon sand bed, and vice versa.

By arranging for the cross-section of the taper disc specimen to be comparable with that of the trailing edge of a gas turbine blade, and by adjusting the temperature difference between the hot and cold beds to as much as 1000°C, it is possible to make this test very representative of service conditions in gas turbines presented by sudden "hot starts" or "blow-outs". Results so far obtained, both at A.M.L. and under more closely controlled conditions at N.G.T.E., indicate that it is possible to subject small taper disc specimens of silicon nitride to as many as 50 cycles of rapid heating and cooling before radial cracks begin to appear at the edges. (Thermal shock tests have yet to be carried out on large taper disc test pieces made from silicon nitride, produced by the improved techniques as described later in the report.) Present indications are that in terms of thermal shock resistance silicon nitride is one of the best materials of its class, and under some conditions approaches the thermal shock life to be expected from metals. For more details of the N.G.T.E. work, and for the comparative thermal shock resistance of other refractory materials under this type of test, reference should be made to individual N.G.T.E. reports(9).

(iv) Creep Strength. The creep strength of silicon nitride was evaluated on a beam specimen which was held at a temperature of 1200°C and subjected to 4-point loading in the equipment illustrated in Figs. 20 and 21. Tests were carried out under loads of 1½ t.s.i. for periods up to 400 hours on a beam specimen of average density of 2.1, having a rectangular cross section of the dimensions given in Fig. 20. Total deflection and creep rates for these tests are shown graphically in Fig. 22 in which a comparison with Nimonic 80 at 3 t.s.i. and 800°C is provided.

It was generally considered from these results that the creep resistance of pure silicon nitride at 1200°C was disappointing, particularly on material of average production density. It was therefore decided to investigate the effect of a fine dispersion of a hard stable compound which could be incorporated during the reaction-sintering process. Compounds employed separately were silica, alumina, molybdenum disulphide, silicon carbide and carbon. The greatest improvement in creep strength was obtained with a 5% addition of silicon carbide. It was subsequently found that the fineness of the dispersion was important, and the best results obtained to date have been with a 5% or 10% addition of silicon carbide powder having a very fine, mixed particle size, the largest particles being no greater than 400 B.S. mesh. Some of the best results obtained may be seen from the creep curves given in Fig. 22. These indicate that a dispersion of silicon carbide in silicon nitride reduces the primary creep, and gives a low secondary creep rate, so that after 300 hours the total deformation is only one quarter of that of pure silicon nitride of the same density. It is not yet known whether this creep stiffening is attributable to a critical dispersion of silicon carbide throughout the silicon nitride crystals, to a certain degree of solid solution hardening, or to the physical influence of the silicon carbide particles during the nitriding operation.

Indications are that the improvement in creep strength is associated with the fineness of the particles of the silicon carbide. In an effort therefore to reduce the silicon carbide particle size even further, silicon powder was intimately mixed with colloidal graphite before proceeding with the nitriding operation, in the hope that fine silicon carbide would be produced during the nitriding operation. Creep tests carried out on silicon nitride formed from silicon powder pressings originally containing 5-10% carbon are also given in Fig. 22, from which it may be seen that although some improvement has been effected it is still less than that achieved with the addition of fine silicon carbide.

As might be expected, density is an important factor in the creep strength of silicon nitride, as may be seen from the creep curves, obtained on material with three widely varying densities, given in Fig. 22a. The creep strength of silicon nitride prepared from hydrostatically pressed powder is about the same as that of material of a lower density, but containing a dispersion of silicon carbide.

The combined .../

The combined effect of hydrostatic pressing and incorporating a dispersion of silicon carbide is also shown in Fig. 22a, but this curve represents a single result only.

7. SURFACE TREATMENT

The inherent porosity of silicon nitride, with or without silicon carbide additions, could be a serious disadvantage in certain applications. The possibility of developing a glaze which would be closely adherent and which would effectively seal the surface pores was therefore investigated. It was realised that such a glaze would have to have a coefficient of thermal expansion similar to that of the parent material, and, if possible, should be self-healing in the event of local rupture. Silica appeared to be the obvious choice, but the formation of a surface glaze merely by dusting the surface of the silicon nitride with fine silica powder and then heating, was found to be unsuccessful. It had been observed, however, that a fine machined surface of silicon nitride tended to become partially self-glazed after prolonged heating at 1200°C in air when in the presence of alumina.

The phase equilibrium diagram for silica and alumina, reproduced in Fig. 23, indicates a low melting point eutectic at 5% Al_2O_3. The melting point of this eutectic is further lowered in the presence of iron oxide. This was further suggested by the fact that, during attempts at self-glazing, the most promising results were obtained at temperatures above 1500°C when the operation was carried out on alumina tiles, using silicon nitride containing iron as an impurity. Examples of areas glazed with iron-contaminated silica, on a silicon nitride nozzle guide vane, are shown in Fig. 24.

As mentioned in Section 2 of this report, silicon nitride, as removed from the reaction-sintering furnace, is invariably covered with a fine white dust or wool. It is essential to remove this fine dust by brushing, and if possible by burnishing, before a strongly adherent and even glaze can be applied. The surface-glazing operation is therefore best carried out by meticulously cleaning the surface of the parent material before applying a thin coating of a mixture of 5% fine alumina, 93% silicon powder and 2% ferric oxide, bound together with cetyl alcohol. The temperature of the article to be glazed should then be slowly raised to 1300-1500°C in an atmosphere of oxygen for a period of 3-4 hours and then allowed to fall slowly to ambient. A cross-section of the surface of silicon nitride glazed in this manner, illustrated in Fig. 25, shows the intimate attachment of the eutectic to the surface and its partial penetration into sub-surface cavities.

When oxynitride is formed as a result of the presence of oxygen as an impurity, it is identifiable under the microscope as a soft white compound. The presence, after nitriding, of this oxynitride on the surface of internal cracks which have been previously formed during the pressing operation, is thought to have been due to oxidation having taken place during nitriding as a result of entrapped oxygen escaping along preferential paths offered by the pressing cracks. It has been observed that when once lined with oxynitride, these cracks do not heal themselves during the nitriding process, nor is their presence on the surface masked by the glazing operation.

8. MICROSCOPY OF SILICON NITRIDE

An apparent variation in grain size of fully nitrided silicon may be seen from the surface appearance of the ground specimen illustrated in Fig. 26. Surfaces may be polished for metallographical examination at higher power, using the diamond-impregnated lap technique developed by the B.C.R.A.

The way in which silicon is converted to silicon nitride by different reaction-sintering schedules has already been discussed in Section 2, which deals with the nitriding of silicon. Unreacted silicon is readily identifiable as bright islands, and sometimes discrete particles, dispersed throughout the silicon nitride matte. The hardness value of the soft silicon nitride matte produced by reaction-sintering below the melting point of silicon, compared with unreacted silicon, may be readily seen in Fig. 27 from the relative microhardness

impressions/...

impressions made under a standard load on the Reichert microhardness indentor. Consolidated silicon nitride, formed by further nitriding at 1450°C, has a hardness similar to that of silicon. This may be seen from Fig. 28 which shows an intermediate stage during the final nitriding operation at 1450°C where free-growing crystals of Si_3N_4 converging from the silicon/matte interface are converting the remaining silicon to the consolidated form of silicon nitride. The hardness of this form is more than 1000 V.P.N. and lies between 7 and 9 on Moh's scale. Fig. 29 shows the structure when nitriding is finally complete, and gives the relative hardnesses of the matte and consolidated form. Very prolonged nitriding at 1250°C results in the appearance of islands of the consolidated Si_3N_4 in the matte. This has already been seen in Fig. 3(d) and its presence is shown again by the relative microhardness impressions given in Fig. 30.

The matte formed during the nitriding of silicon compacts produced by hydrostatic pressing at 16 t.s.i. is much denser following the standard nitriding procedure, as may be seen from the comparative hardness impressions shown in Fig. 31. Fine silicon carbide particles dispersed in the 'green' silicon powder pressing appear to be partly decomposed during the nitriding procedure, the unreacted material remaining dispersed throughout the matte in the manner shown in Fig. 32.

A combination of the silicon carbide addition and the hydrostatic pressing techniques produces a structure in which there is little difference in the hardness values of the matte and consolidated forms. This is illustrated in Fig. 33 which shows the hardness and dispersion of the silicon carbide particles and the greater homogeneity of the matte and consolidated silicon nitride as reflected by the uniformity of hardness values. Fig. 33 should be compared with Fig. 31 and 32 to see the separate effects of hydrostatic pressing and carbide additions. This development is fairly recent, and the resulting mechanical properties suggest that this is the most advanced form of the material yet produced for engineering purposes.

Preliminary experiments indicate that the transformation from α to β silicon nitride on heating above 1550°C is associated with softening, but this has yet to be confirmed. Experiments with age hardening treatments of the basic material and that containing silicon carbide are visualised.

9. FIELD TRIALS

The properties and characteristics of silicon nitride so far investigated aroused sufficient confidence for the material to be used in field trials. Various components were therefore prepared for full-scale trials in the test assemblies of other establishments. These included experimental gas turbine units at the Admiralty Engineering Laboratory, combustion chamber tests at P.A.M.E.T.R.A.D.A., and trials in a rocket efflux at R.A.E., Westcott.

(a) As Stator Blade Material

The initial use envisaged for silicon nitride was as a stator blade for water-cooled high-temperature gas turbines. Experimental nozzle guide vanes were prepared and incorporated in a turbo-blower unit installed at the A.E.L. The maximum operating temperature of this turbine, which employs diesel fuel, was 750°C. Although this temperature is much below that envisaged for silicon nitride, the equipment presented a useful opportunity to develop a technique for applying such a material to an engineering design.

It was necessary to allow adequate clearance during cold assembly owing to the difference between the coefficient of thermal expansion of silicon nitride stator blades and that of the heat-resistant steel housing in which they were located. An example of one of the nozzle guide vanes prepared for these trials has been illustrated in Fig. 13. The vanes were provided with lugs which fitted easily into slots cut in the shroud rings. Tolerances were arranged so that when the blades were under pressure they were in the precise position demanded by the stator assembly, in the manner shown in Fig. 34.

After .../

After 250 hours of intermittent service the nozzle vane ring was removed and the condition of the silicon nitride blades examined. These were found to be in perfect order, and covered with a light layer of combustion debris (Fig. 35).

Comparative gas bending trials on wafer specimens were carried out by P.A.M.E.T.R.A.D.A. in a special combustion chamber operating at temperatures of about 1200°C for periods of up to 200 hours. The sections of these wafers were such that a certain amount of bending due to creep took place, but there was no sign whatsoever of surface deterioration which might have been expected to result from reaction with fuel oil deposits or erosion by high velocity gas. In none of these trials was there evidence of cracking due to thermal shock.

The evaluation of silicon nitride as a material for gas turbine components is continuing, and there is no reason to suspect that it will not give entirely satisfactory service provided that adequate provision is made to guard against its room-temperature brittleness during assembly.

Design philosophy should not follow the conventional practice for metals and alloys, but should take into account the low coefficient of thermal expansion of this new engineering material. In particular, local stress concentrations which could arise from abrupt changes in section or from local pressure exerted as a result of the securing arrangements, should be avoided.

(b) As an Electrical Insulator

Owing to its good thermal shock resistance and high electrical resistivity, silicon nitride has a distinct use for electrical insulators which are expected to resist sudden violent changes in temperature such as are encountered on rocket-launching platforms. Trials are in hand at R.A.E., Westcott, in which a glazed specimen similar to that illustrated in Figs. 14 and 15 is being subjected to repeated blasts from the high temperature efflux of a rocket propellant. If successful, these trials will encourage the further application of this material for rocket throats.

(c) As Refractory Supports in Industrial Processes

In modern technology much use is made of crucibles, thermocouple sheaths, platforms and supports for advanced heat treatment, and containers for special purification and diffusion processes such as are employed in the semi-conductor field. Silicon nitride is an ideal material for such equipment due to its exceptional thermal shock resistance and complete inertness to molten metals.

(d) Other Possible Applications

Apart from its obvious use as an engineering material, silicon nitride has applications as a dielectric material.

Its thermal shock resistance, and its capacity to act as a carrier for other elements and compounds, suggests that it may also be of use as a medium for holding neutron-absorbing elements in nuclear reactor control rods. A dispersion of 2% boron nitride in silicon nitride has been produced for this purpose. Silicon nitride may also be used as a supporting vehicle for high temperature catalysts.

10. FUTURE WORK

Much work still remains to be done on this material from both production and evaluation aspects. In particular, a fuller understanding of the factors influencing the rate of nitriding, such as initial powder particle size, die pressures, higher final nitriding temperatures, and the use of ammonia instead of nitrogen, is required.

The hydrostatic pressing technique results in a much harder product, but its full influence on transverse rupture, creep strength, and thermal shock resistance

has yet/...

has yet to be determined. The combined effect of hydrostatic pressing and dispersion of silicon carbide needs further intensive study.

There are several other possible ways of increasing the density of the material towards its theoretical value, which deserve investigation. For instance, it may be possible to produce a network of silicon nitride, by a preliminary treatment, into which molten silicon can be filtered under vacuum. Such a network may provide the medium for nitrogen transport to the centre of the product during sabsequent nitriding, with the resultant production of a very dense material. The possibility of infiltration of other metals throughout the silicon nitride to impart greater room-temperature ductility is being explored, and rhenium is to be tried in this respect. The material shows promise as a good potential carrier for many other elements, any of which might influence its physical and mechanical properties substantially. The possible use of silicon nitride particles as a dispersant in high temperature cermets is also being borne in mind.

The physical examination of silicon nitride in its various forms and stages of production will be continued in order to explain some of its properties and throw more light on manufacturing techniques. The α-β transformation above 1550°C, and the influence of silicon carbide on the mechanical properties of silicon nitride, need further study.

Work is already in hand on a number of these matters, but it is expected that most of the available effort during the next twelve months will be devoted to the fabrication of specific components in silicon nitride in its present form for trials in test rigs and engines. This aspect of the work calls for considerable technological development; in particular, it is essential to be able to produce a wide variety of shapes in material of uniform density and completely free from cracks. A means for healing pressing cracks during the nitriding operation would greatly facilitate production and the complete removal of oxygen by outgassing 'green' compacts before nitriding is being considered in this respect. It may eventually be found that the best product is obtained by hydrostatic pressing and nitriding of bulk material followed by diamond-machining to the final shape, although this can only be achieved by prolonging the nitriding procedures. However, very recently, 'green' die-pressed shapes which had been encased and thoroughly evacuated in a rubber sac, and then hydrostatically pressed (without a preliminary nitriding operation as used in the method described at the end of Section 4), have been found to have good uniformity and adequate 'green' strength to permit light machining operations. This latest development shows much promise, not only for the production of sound bodies, but also to impart a high degree of mechanical strength in the end product. Exploration of the properties of silicon nitride at temperatures above 1200°C is in hand.

For many applications, where high density in the end product is of secondary importance, and perhaps even undesirable, it may be more convenient to produce the required shape by slip-casting methods. The use of deflocculating and mould release agents to facilitate this process, and perhaps also the extrusion process, has yet to be examined.

11. CONCLUSIONS

Silicon nitride appears to be a most interesting material for engineering applications. The experiments described show that it can be produced in a variety of conditions and in any shape required, and that it will give service up to at least 1200°C under fairly high stress intensities.

It is apparent that its transverse strength and creep strength are considerably influenced by the degree of densification that can be imposed during production, and that creep strength is further influenced by the presence of a critical dispersion of silicon carbide.

These properties, combined with good thermal shock resistance, commend it for development in small-scale production.

The engineering .../

The engineering design of silicon nitride shapes calls for special consideration of such factors as minimisation of stress concentrations, expansion tolerances and reasonable care in handling during assembly, although this latter point has not been an embarrassment in the field trials that are now proceeding.

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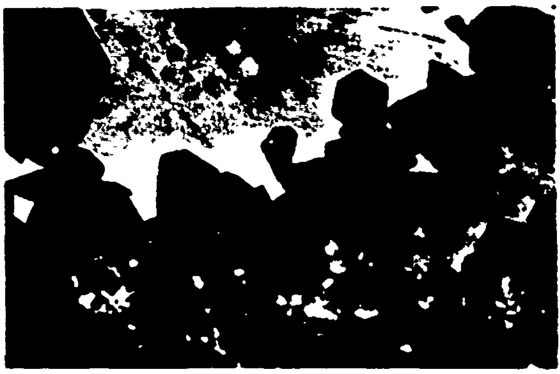


Fig. 1.

The formation of a skin of silicon nitride on the surface of lump silicon, by nitriding at 1350°C.

Surface

X 500

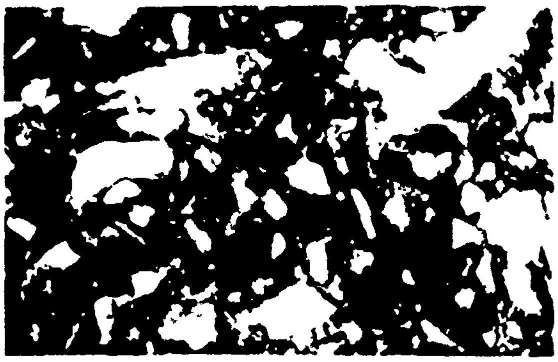


Fig. 3(a)

The first stages in the nitriding of Silicon Powder. The angular particles of silicon are loosely held together by Silicon Nitride produced by nitriding at 1250°C. for a few hours.

X 250

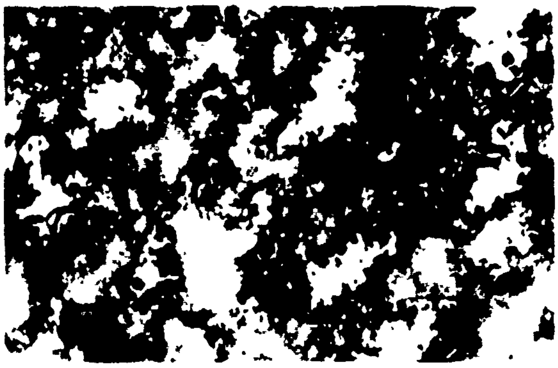


Fig. 3(b)

The appearance of semi-nitrided silicon. Partially reacted particles of silicon are dispersed in a porous matte of silicon nitride crystals after nitriding at 1250°C. for 16 hours.

X 250

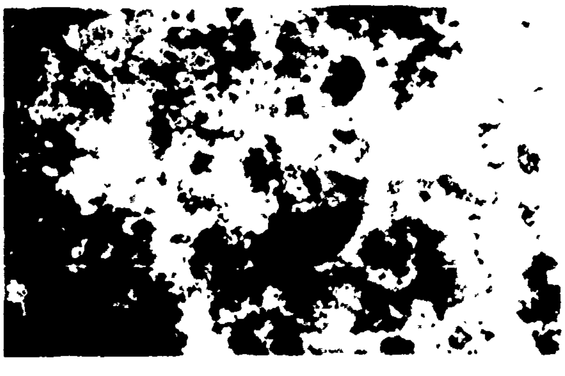


Fig. 3(c)

Fully nitrided silicon powder achieved by nitriding at 1250°C. for 16 hours, followed by a further 16 hours at 1450°C. Light areas are a porous silicon nitride matte and the darker grey zones are the hard, consolidated silicon nitride.

X 250

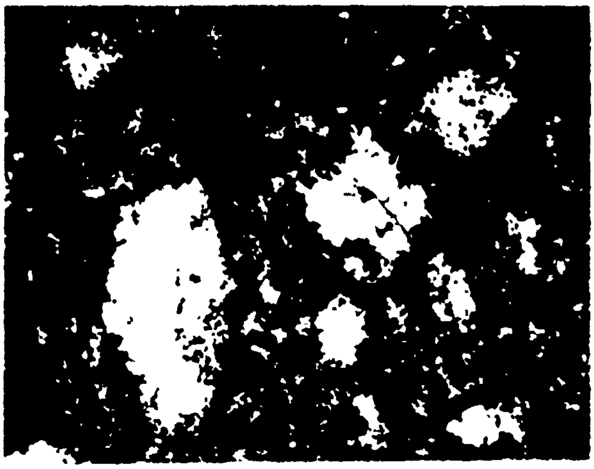


Fig. 3(d)

Semi-nitrided silicon powder after 150 hours at 1250°C. The partially reacted silicon particles are dispersed in a dense matte of silicon crystals which is beginning to develop a hard and dense skeleton.

X 500

Fig 3(e)

Evidence of free growing crystals of silicon nitride exhibiting hexagonal forms in silicon powder which has been partially nitrided at 1250 and 1450°C.

X 2000

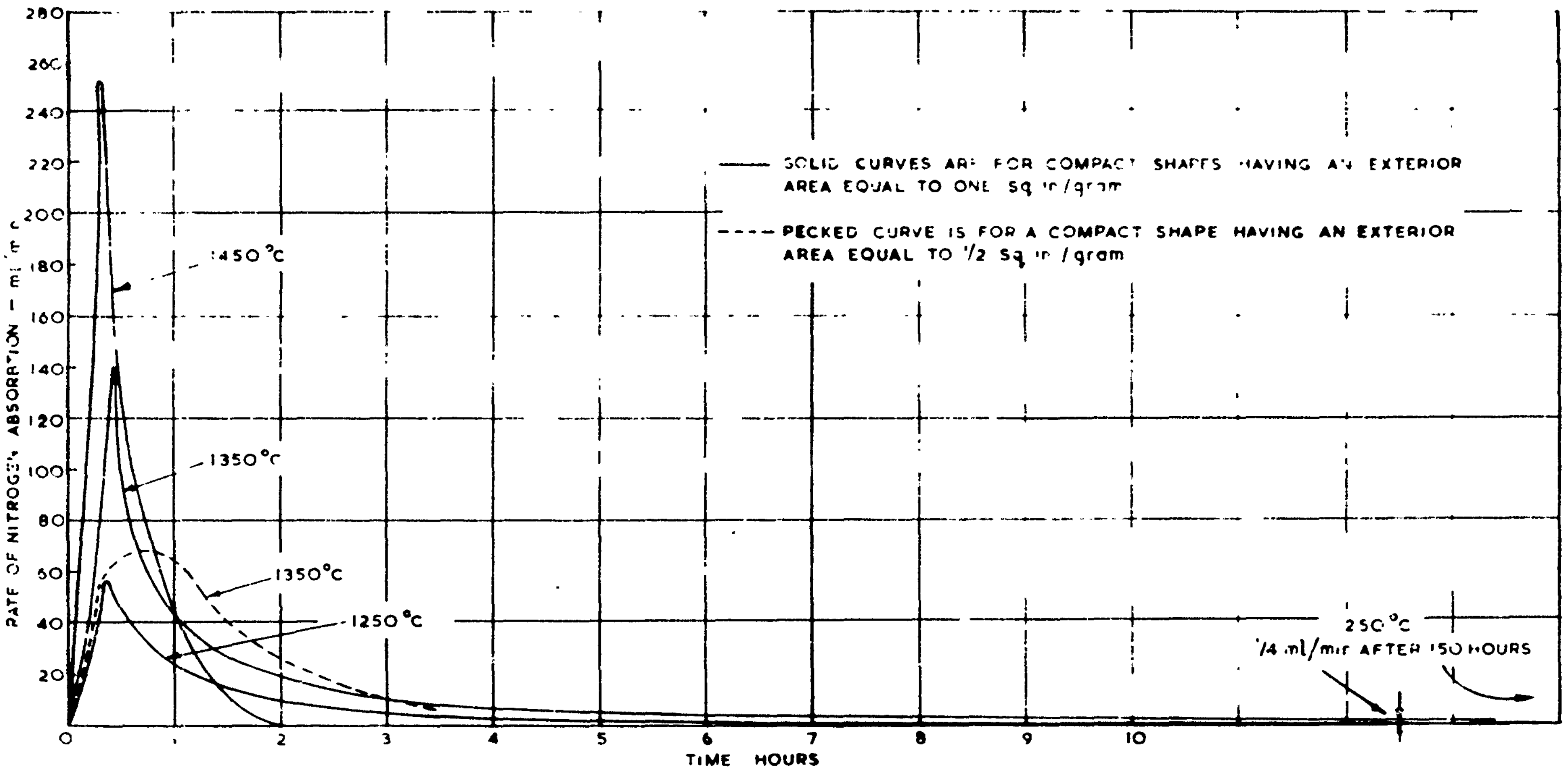
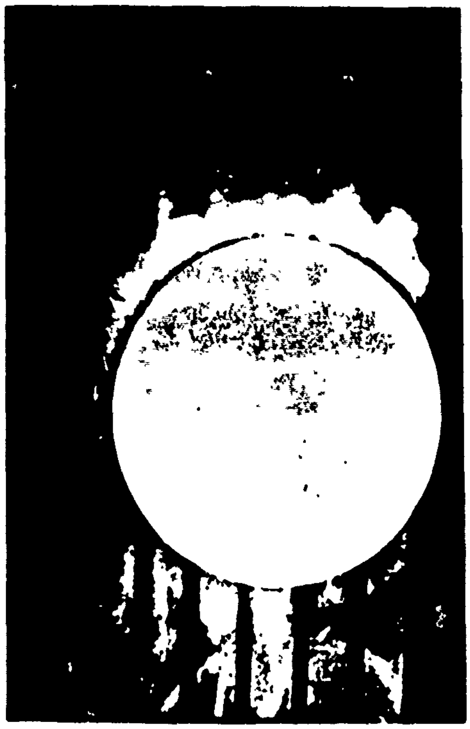
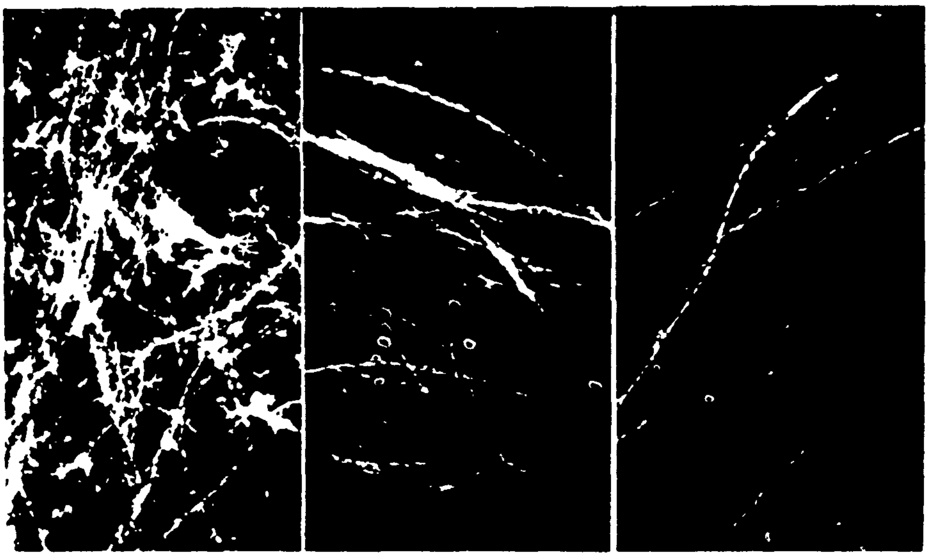


Fig 2 RATES OF REACTION OF SILICON POWDER COMPACTS WITH NITROGEN IN RESPECT TO TIME FOR A NUMBER OF TEMPERATURE LEVELS



X 2

Fig. 4. Silicon nitride wool which appears on the surface of fully-nitrided silicon powder pressings.



Common magnification X 60

Fig. [illegible]. Details of the silicon nitride wool shown in Fig. 4.

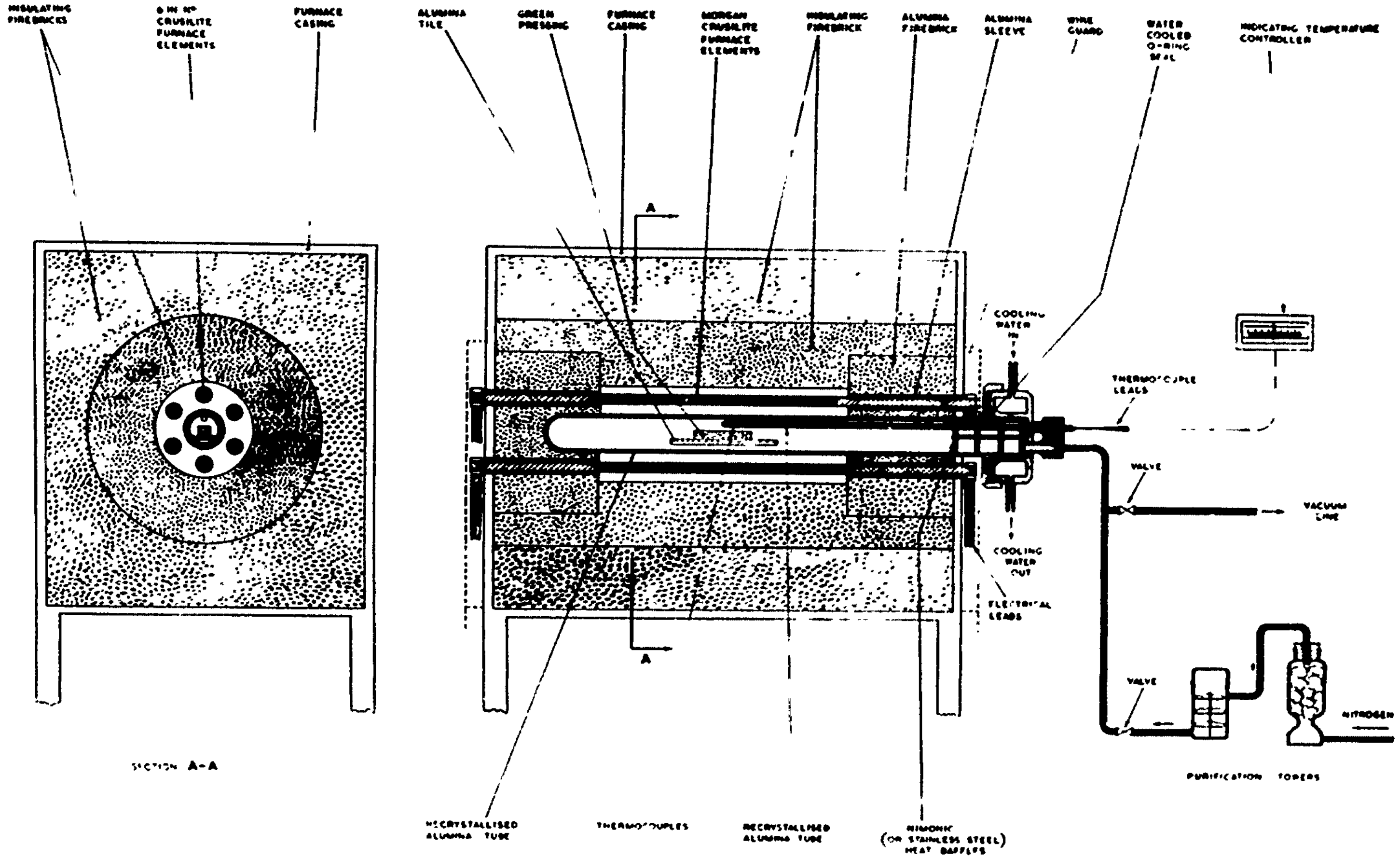


Fig 6 NITRIDING FURNACE

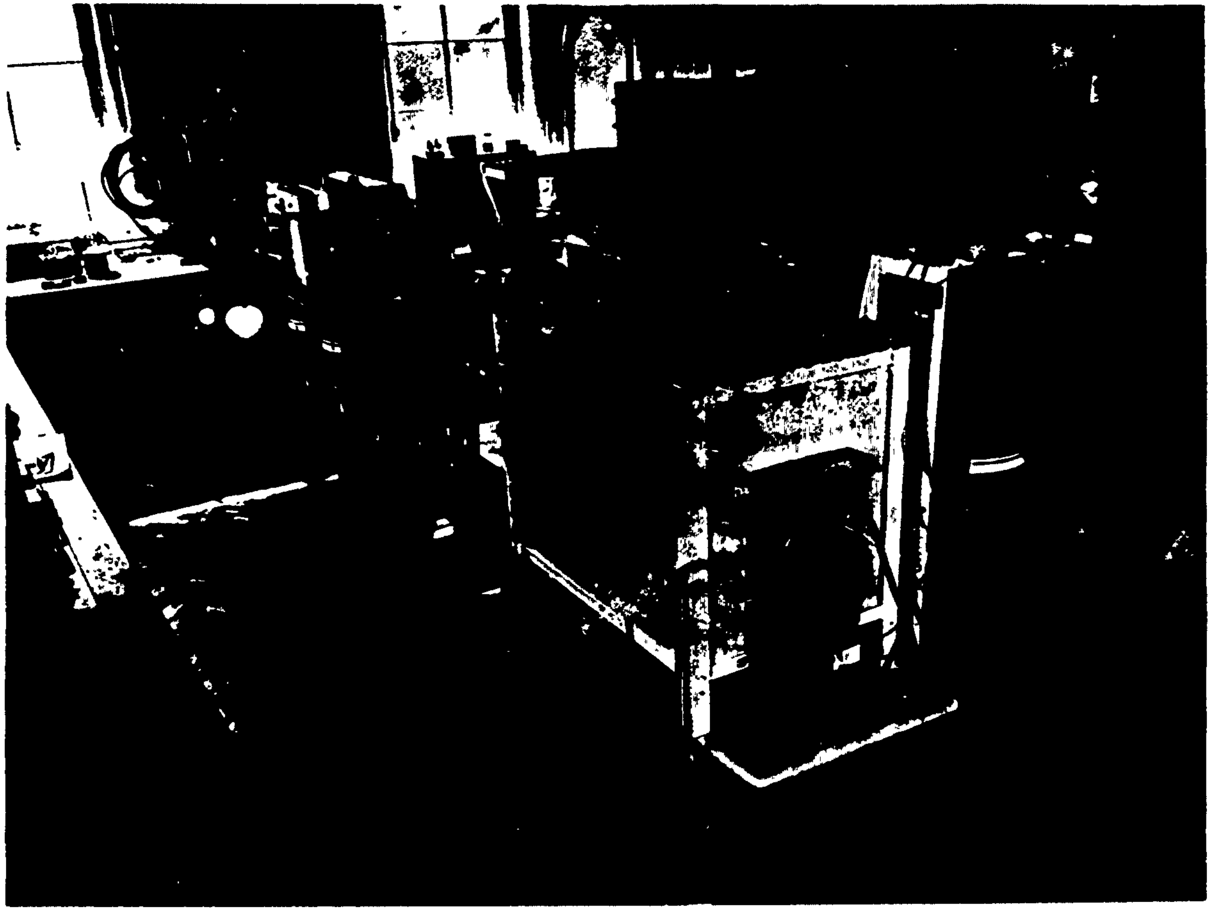


Fig. 7. Pilot plant equipment for the production of silicon nitride shapes.

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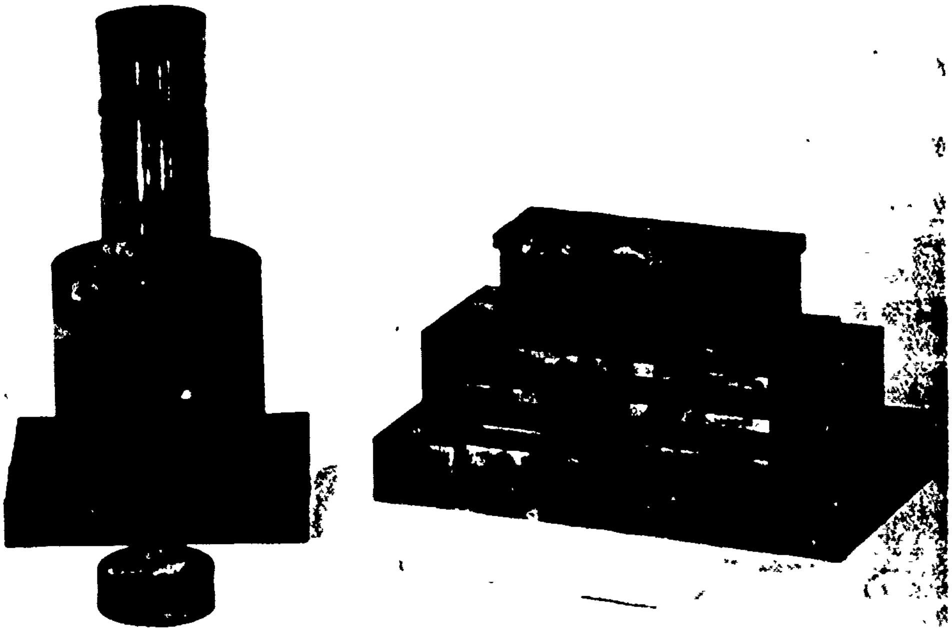


[illegible]

Fig. 11. Actual size.
Cracks produced in 'green' silicon powder compacts as a result of using too high die pressure.

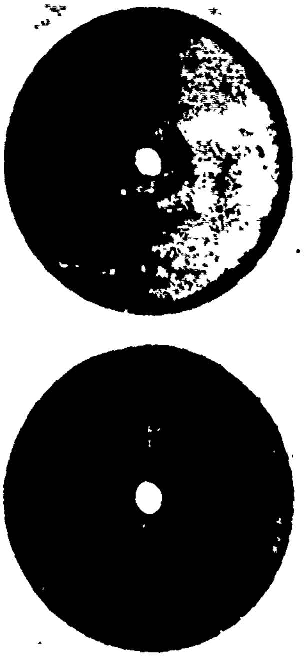
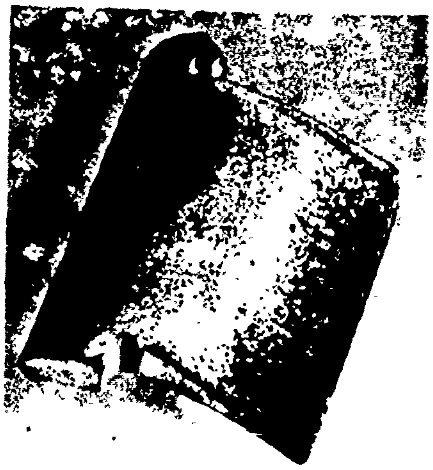


Fig. 12 Act[illegible] size
[illegible]

Fig. 13 Actual size.



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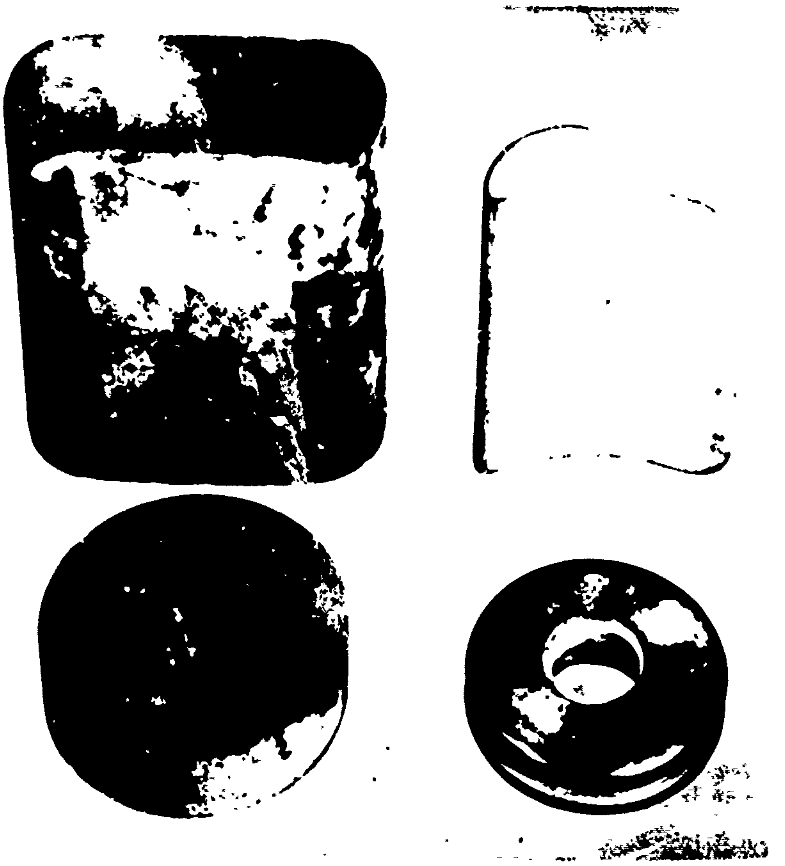

Fig. 14. Actual size.
Examples of turbine nozzles and high temperature insulators made by reaction sintering finished size components machined from loosely sintered blocks.

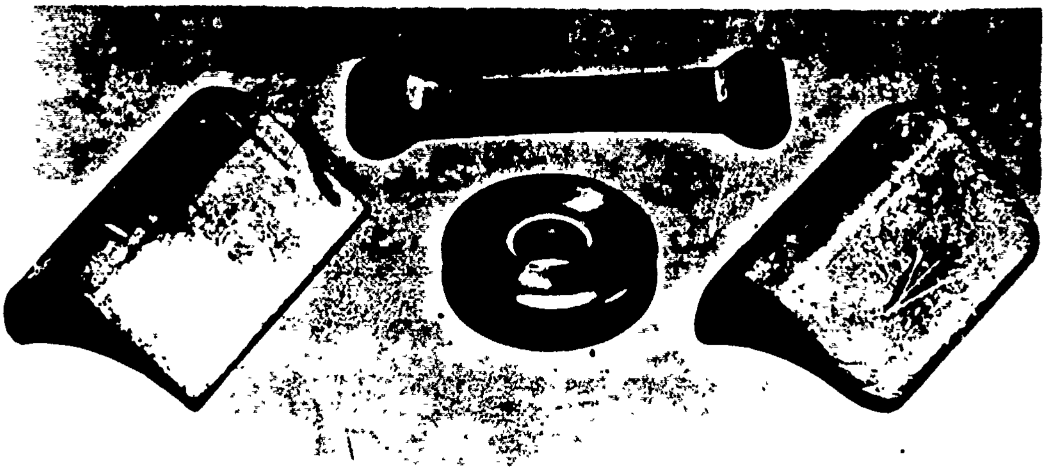

Fig. 15. Actual size.
Variety of shapes in silicon nitride.

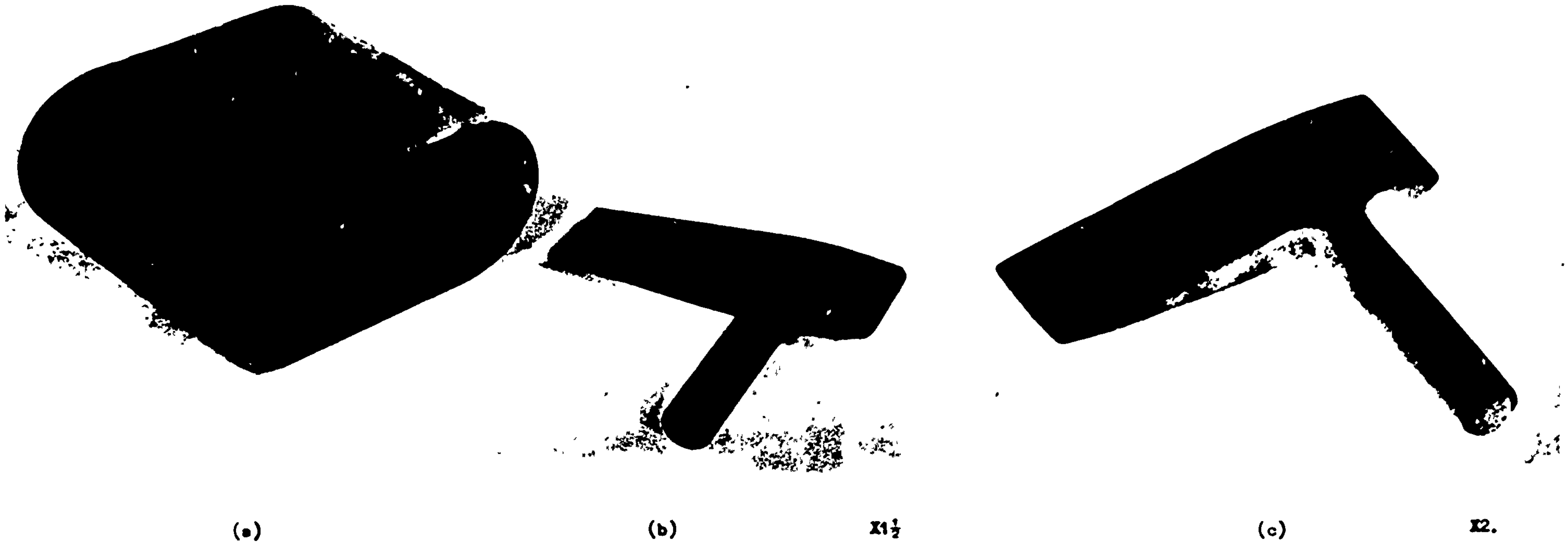

Fig. 16. Stages in the production of an intricate shape to close tolerances in silicon nitride.
(a) Loosely sintered block
(b) Shape machined by conventional methods to finished size.
(c) Final shape after nitriding, which is sound except for a pressing crack which may be seen at the lower end of the shaft.

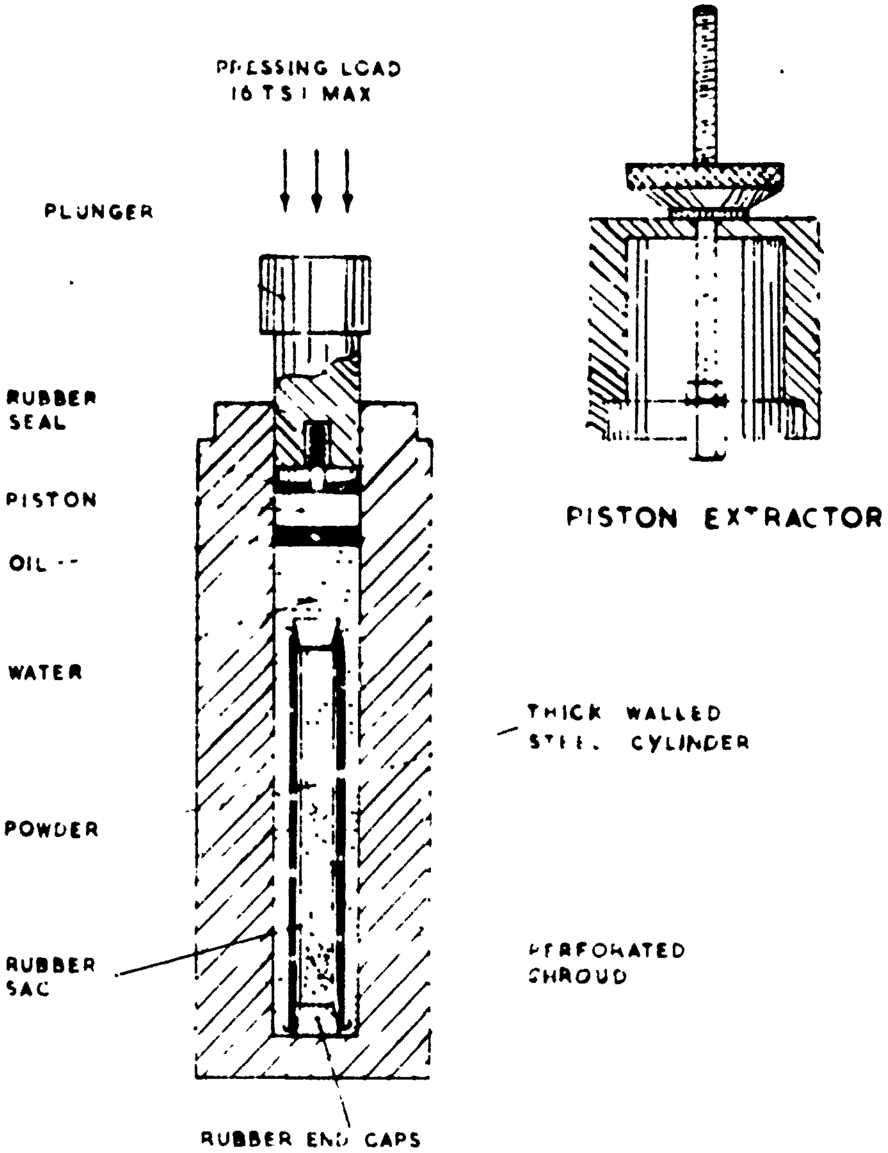

Fig 17 HYDROSTATIC PRESSING DIE & ASSOCIATED EQUIPMENT

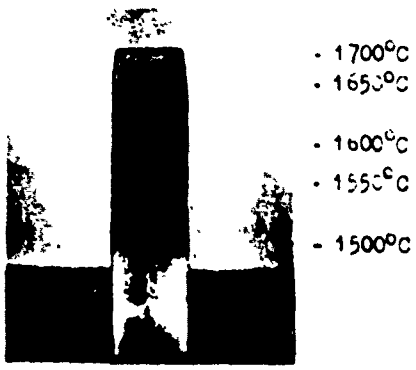

FIG. 18 Actual size

Reduction in cross sectional area of a block of silicon nitride heated in argon at a temperature which reached 1700°C at one end, but gradually decreased toward the other end.

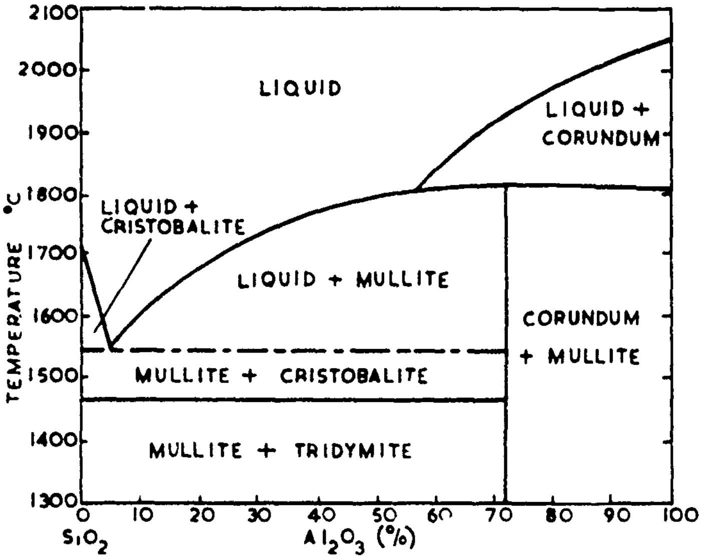

FIG. 23

Al_2O_3 - SiO_2 Phase diagram

N. L. Bowen and J.W. Greig, J.Amer.Ceram.Soc., 7(1924) 242.

(Iron oxide is said to lower the eutectic temperature)

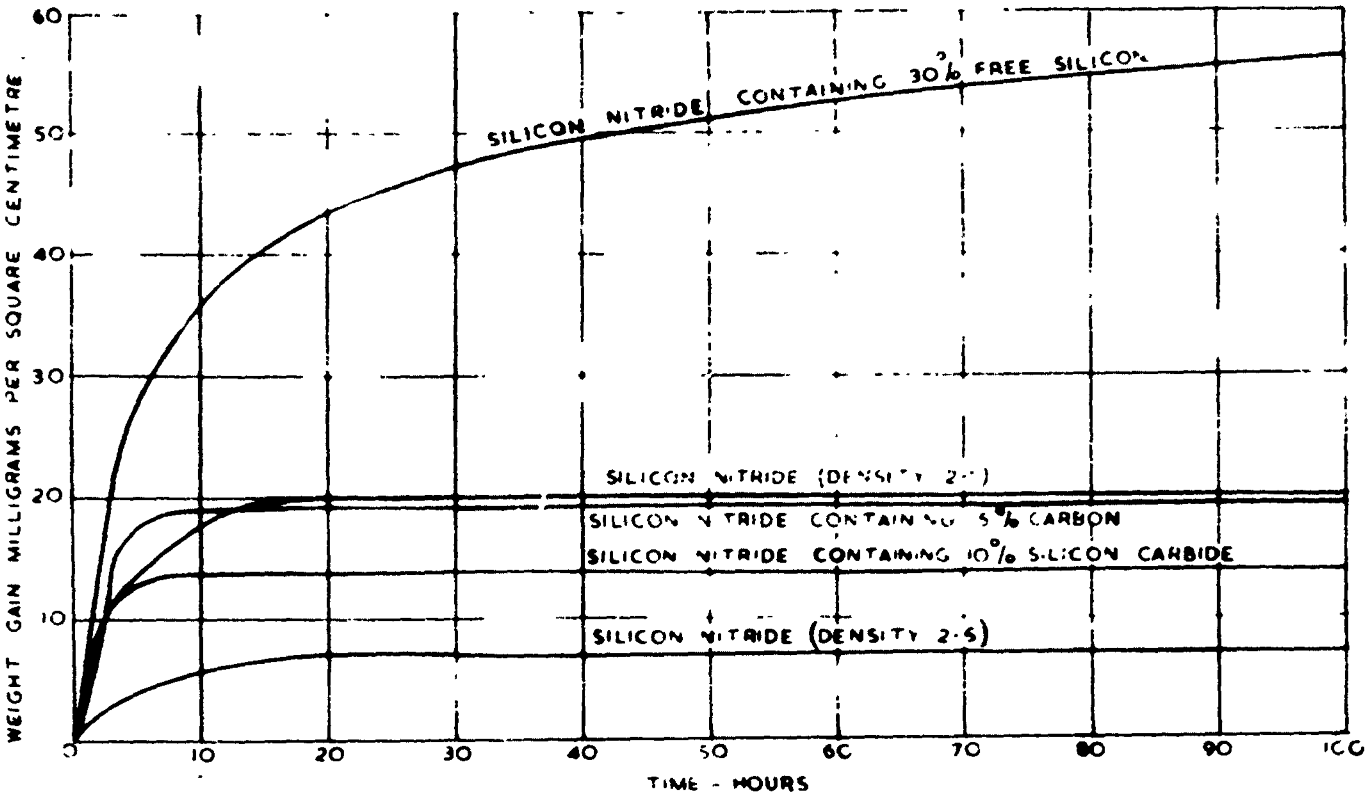

FIG. 19 OXIDATION RATES FOR PURE & COMBINED SILICON NITRIDE AT 1200°C IN AIR

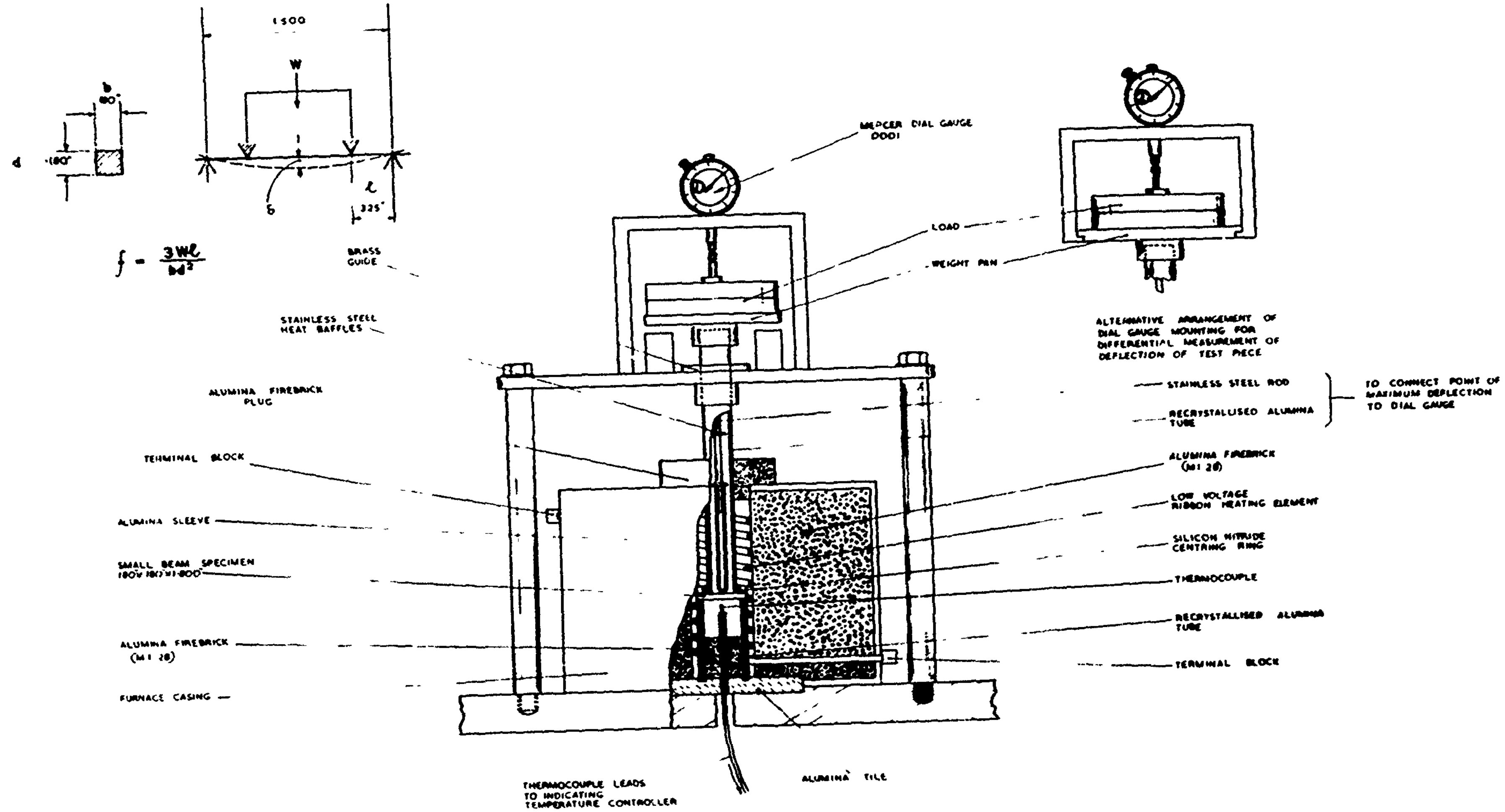

FIG. 20. SIMPLE HIGH TEMPERATURE CREEP APPARATUS FOR USE WITH CLOSE AMBIENT TEMPERATURE CONTROL

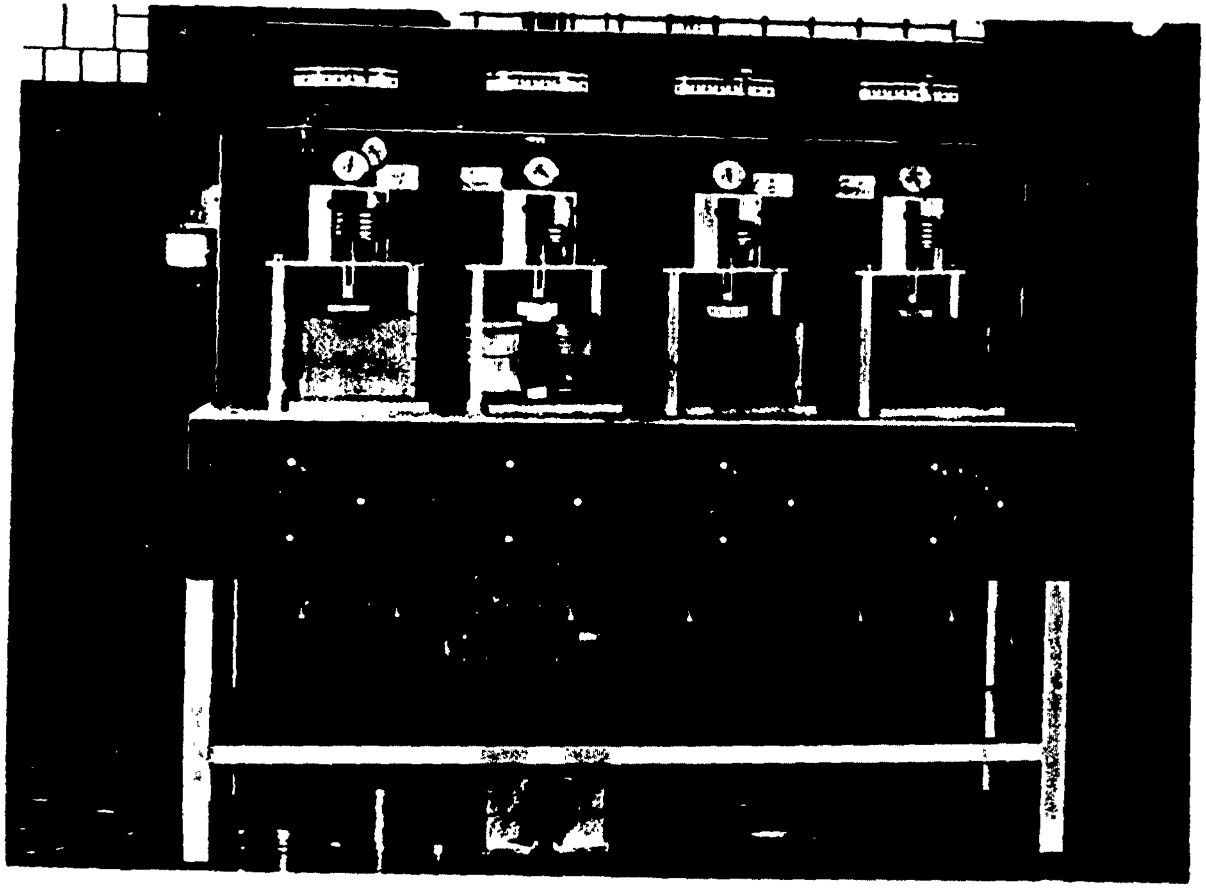

Fig. 21. General view of Creep Testing Equipment.

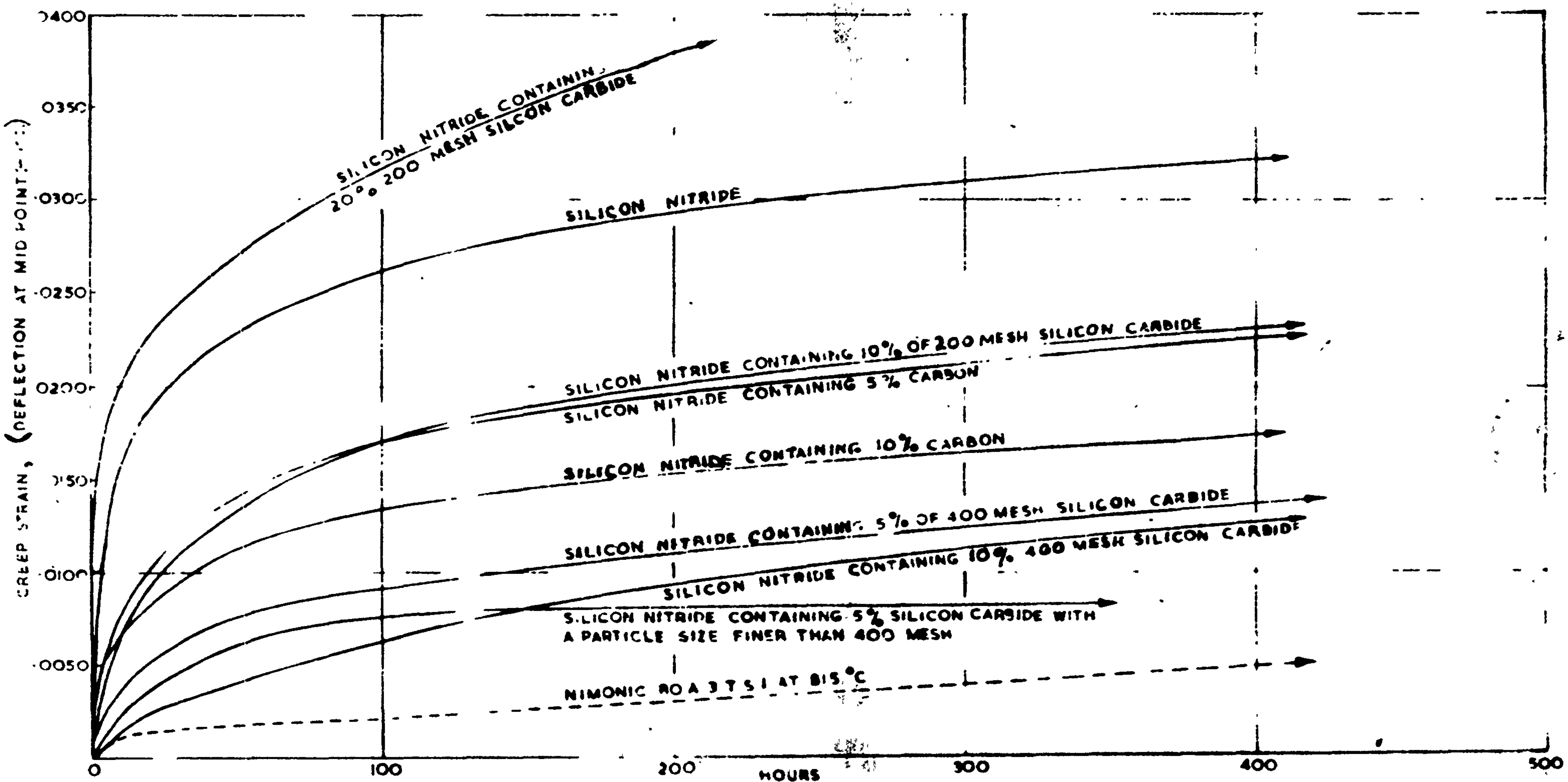

Fig. 22 COMPARATIVE CREEP CURVES OF SILICON NITRIDE (AVERAGE DENSITY 2·1) & SIMILAR MATERIAL CONTAINING DISPERSIONS OF SILICON CARBIDE OR CARBON, UNDER A BENDING LOAD OF 1½ T.S.I. AT 1200°C

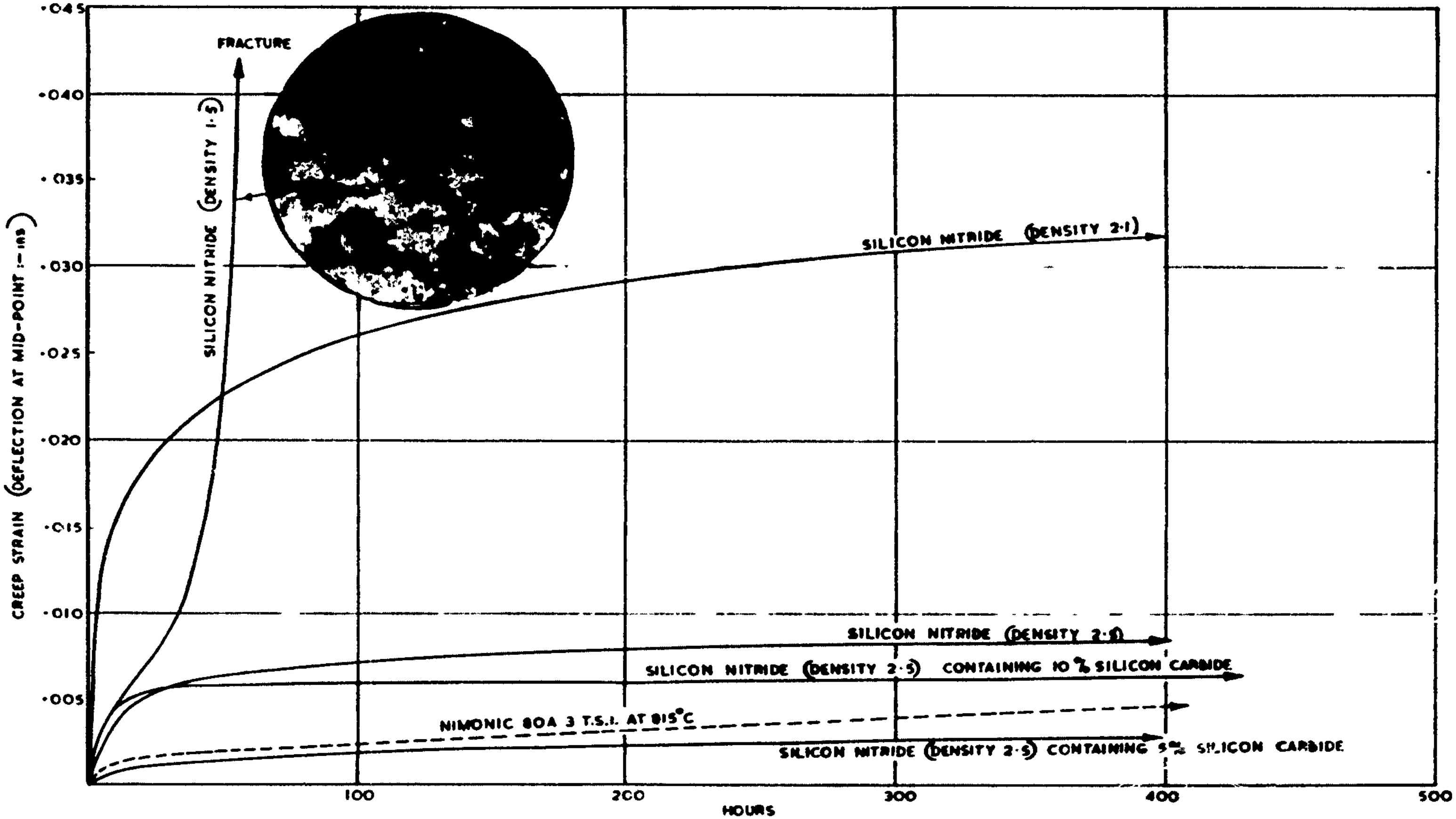

FIG. 22A. COMPARATIVE CREEP CURVES OF SILICON NITRIDE (WITH DENSITIES OF 1·5, 2·1 & 2·5) AND OF SILICON NITRIDE WITH A DENSITY OF 2·5 CONTAINING DISPERSIONS OF SILICON CARBIDE FINER THAN 400 MESH, UNDER A BENDING LOAD OF 1½ T.S.I. AT 1200°C.

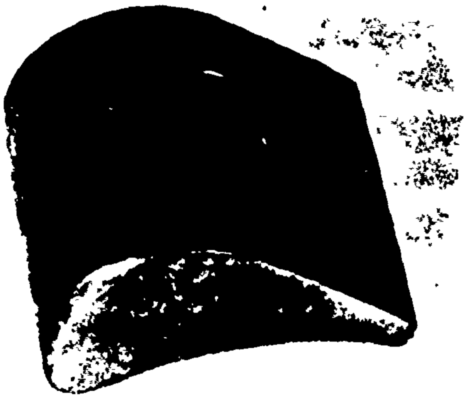

Fig. 24. Actual size.
Appearance of a surface-glazed component in silicon nitride after firing in air at 1500°C for 48 hours.

Fig. 25. X500
Cross section of the surface of glazed silicon nitride, showing the thickness, and the intimate attachment of the silica-alumina eutectic.

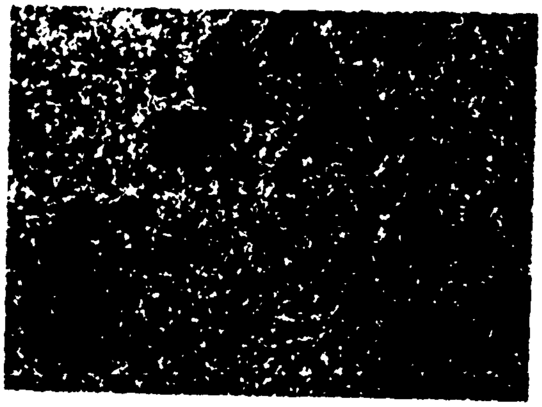

Fig. 26. X5
Variations of grain size in fully reacted silicon nitride

Fig. 27. X325
Partially nitrided silicon. Islands of unreacted silicon in a porous matte of silicon nitride produced by nitriding for 16 hours at 1350°C. Relative hardnesses are indicated by the size of the diamond impressions.

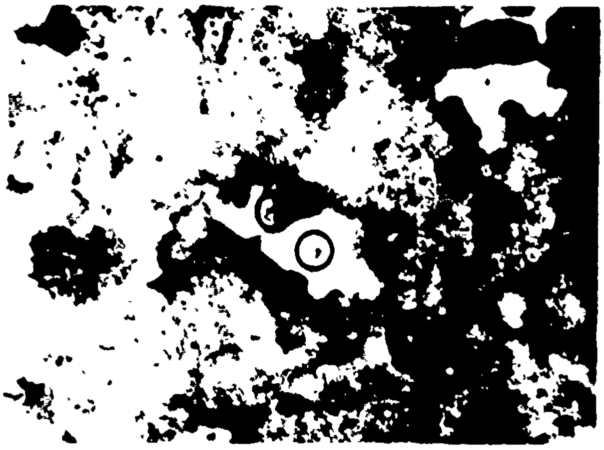

Fig. 28. X325
Partial conversion of the unreached silicon, shown above, to a consolidated form of silicon nitride by further nitriding at 1450°C. The hardness of the developing Si_3N_4 is approximately similar to that of the remaining Silicon.

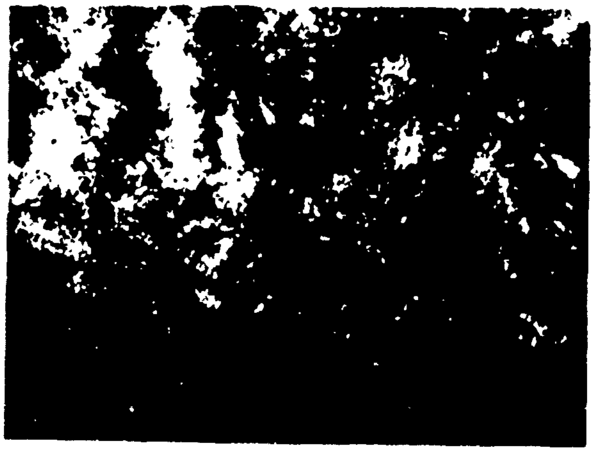

Fig. 29. X325
Fully nitrided silicon nitride after 16 hours at 1250°C. followed by a further 16 hours at 1450°C. The relative hardness of the matte and consolidated Silicon nitride is shown by the adjacent microhardness impressions.

Fig. 30. X325.
The production of islands of consolidated Silicon Nitride in the Silicon Nitride matte by prolonged nitriding (150 hours) at 1250°C. - as revealed by comparative microhardness impressions.

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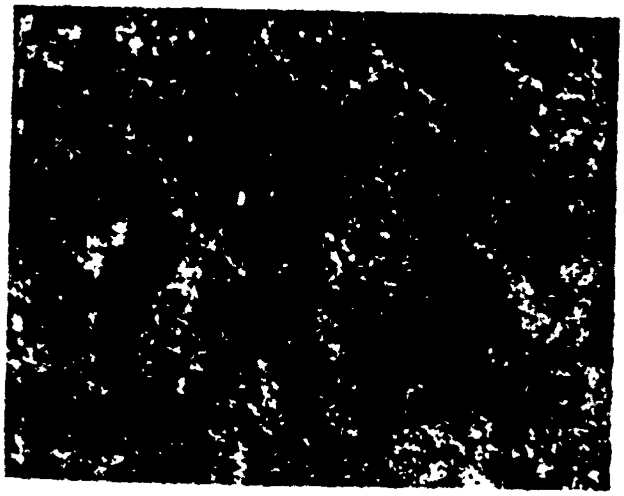

Fig. 31. X325.
Microhardness impressions showing the increased hardness of the Silicon Nitride matte associated with initial hydrostatic pressing of the Silicon powder.
The hardness of the consolidated Silicon Nitride remains unaltered.

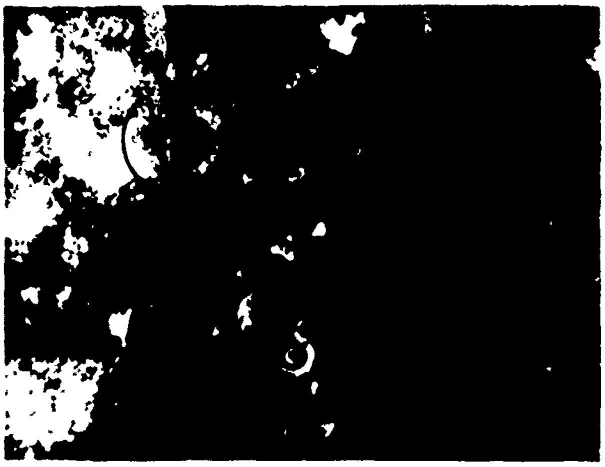

Fig. 32. X325.
Microstructure and comparative hardness values of Silicon Nitride containing a 5% dispersion of fine particles of Silicon Carbide. This material was produced by the standard die-pressing technique followed by nitriding at 1250°C. and 1450°C. Microhardness impressions are shown on the matte, the consolidated Silicon nitride, the unreacted Silicon and on one of the Silicon Carbide particles. The last mentioned gave the smallest impression under standard comparative loads.

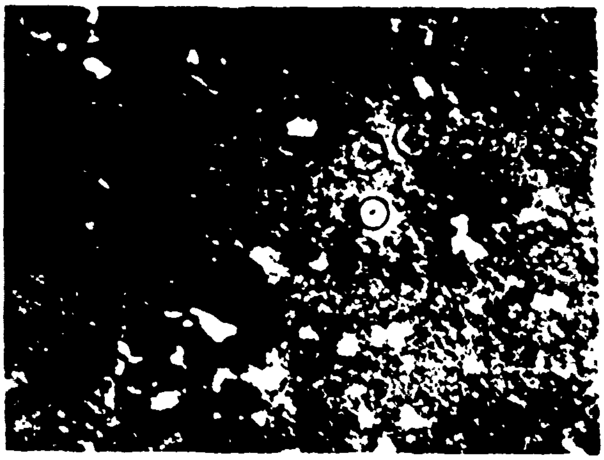

Fig. 33. X325.
Silicon Nitride containing a dispersion of Silicon Carbide similar to that shown in Fig. 32, but produced by the hydrostatic pressing technique. Microhardness impressions indicate that the matte of this material has a hardness similar to that of the consolidated Silicon Nitride and uncombined Silicon Carbide.

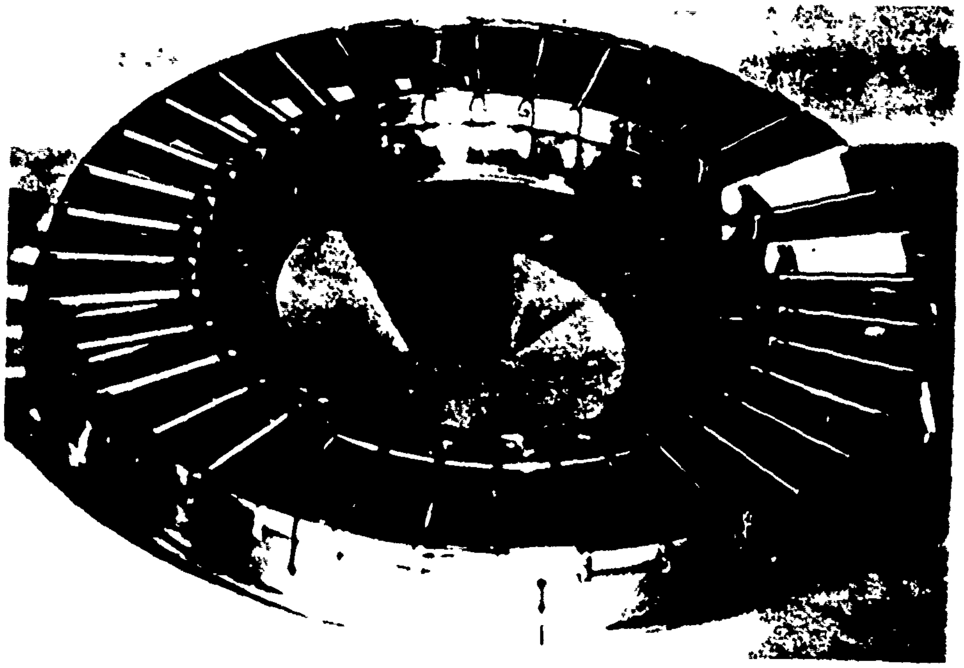

Fig. 34.
Gas turbine nozzle guide vane assembly showing the method of incorporating trial vanes produced in Silicon Nitride.

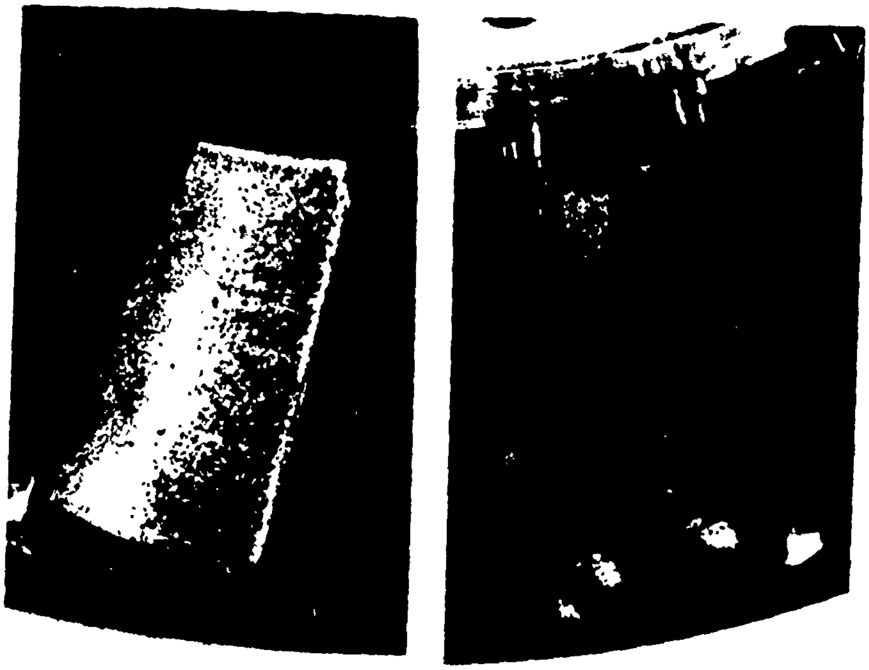

Fig. 35.
The condition of the face and flank of one of the above blades after 250 hours of service.

dstl

[illegible]
dstl [illegible]
[illegible]

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