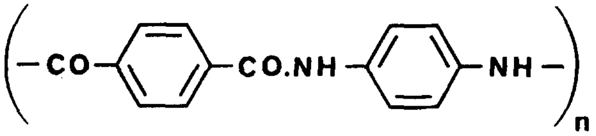

Figure 1 Poly (*p*-phenylene terephthalamide).

isomeric esters were not detected, nor any monofunctional acid ester from acids which might have been used to control the molecular weight of the polymer.

The hydrolysate, after removal of the precipitate, was neutralized with sodium hydroxide containing sodium metabisulphite (0.2 g). Sodium acetate (2.5 g) and acetic anhydride (1 ml) were then added, successively. The precipitated acetyl derivative was collected, washed with water and dried in a vacuum. An infra-red spectrum showed the material to be diacetyl *p*-phenylene diamine. GLC on a OV 210 column confirmed this identification and showed no impurities. From 0.490 g of Kelvar, 0.309 g of the diacetyl derivative was obtained corresponding to 78% of theoretical yield. However, this method does not give quantitative recovery of the diamine. When *p*-phenylene diamine was acetylated under the same conditions only 90% was recovered. Thus at least 85% of the diamine in Kevlar can be considered to be *p*-phenylene diamine.

An ultra-violet spectrum of the hydrolysate was not like that expected for *p*-phenylene diamine; however, if this amine is treated with 90% sulphuric acid at 190° C the spectrum obtained is very similar. This absorption is probably due to a highly absorbing oxidation product. The hydrolysate was investigated further by thin layer chromatography on silica gel using mixtures of chloroform, ethanol and aqueous ammonia (s.g. 0.88) as eluants. Other amines such as *m*-phenylene diamine, *p*-aminophenol and *p*-aminobenzoic acid were not detected.

Thus this analysis of Kevlar 49 fibre is consistent with its being solely a condensation polymer from terephthalic acid and *p*-phenylene diamine, confirming the conclusions derived from instrumental analysis of Gan and co-workers [3]. The suggestion by Brown and Ennis [4] that there are *p*-aminobenzoic acid derived groups in the polymer is not supported by the present work.

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Hardness anisotropy of α-Si_3N_4 single crystal

High hardness of silicon nitride (Si_3N_4) is exceedingly attractive in both cold and hot tribological applications [1, 2]. However, the hardness of Si_3N_4 varies widely depending upon the fabrication methods such as reaction sintering, hot pressing and chemical vapour depositing techniques [3–9]. This might be attributed not only to improper techniques and incipient cracking around an indenter in hardness measurements, but also to the composition, density (porosity), inclusions and microstructure of samples measured. To know the real hardness characteristic of Si_3N_4, the effect of crystallographic orientation on the hardness of α-Si_3N_4 single crystals has been examined.

Single crystals of α-Si_3N_4 for hardness measurements were needle-like crystals along the $[0\,0\,0\,1]$ or $[2\,\bar{1}\,\bar{1}\,0]$ directions (up to 15 mm long, 1.5 mm^2 in cross-section) and pyramidal crystals with large $(1\,1\,\bar{2}\,0)$ or $(1\,0\,\bar{1}\,0)$ planes (up to 3.5 mm^2 area), which were prepared by pyrolysis of a NH_3 and H_2-carried $SiCl_4$ mixture on a heated graphite

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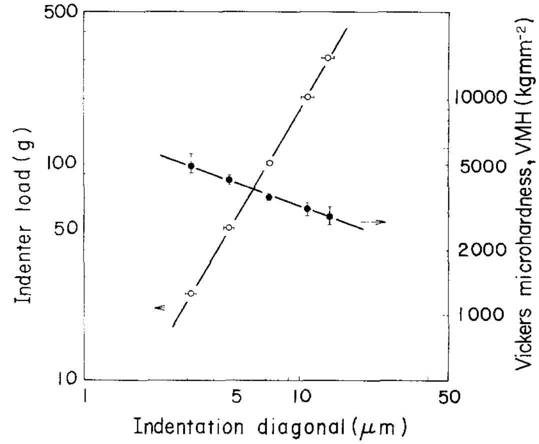

Figure 1 Relationship between Vickers microhardness (VMH) and indenter load on the $(10\bar{1}0)$ plane of α-Si_3N_4 single crystals.

substrate. The preparation conditions were as follows: the substrate temperature, 1500 to 1700° C; the total gas pressure, 10 to 50 Torr; the flow rates of NH_3, $SiCl_4$ and H_2, 60, 0.8 (in liquid) and 700 $cm^3 min^{-1}$, respectively. The detailed process is the same as that reported previously [10, 11]. The single crystals were embedded in resin so as to make the (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ planes parallel to the resin surface, followed by polishing with a fine diamond paste (0.25 μm). After confirming the crystallographic orientation by X-ray diffraction, both Vickers microhardness (VMH) and Knoop microhardness (KMH) tests were carried out using an AKASHI diamond hardness tester (Model: MVK, Type: D). Indenter loads of 25 to 300 g were used to establish the Meyer lines [12]. Usually, a load of 100 g was employed to minimize the errors resulting from small indentations and crack formation. Other experimental conditions were similar to those reported previously [9]. For the KMH measurements, the long axis of indentations was adjusted to be parallel and perpendicular to the $[10\bar{1}0]$ and $[11\bar{2}0]$ directions on the (0001) plane and to the c-axis on the $(10\bar{1}0)$ and $(11\bar{2}0)$ planes.

TABLE I Vickers microhardness at a 100 g load (VMH_{100}) and the Meyer exponent of α-Si_3N_4 single crystals

Plane	VMH_{100} ($kg\,mm^{-2}$)	Meyer exponent
(0001)	2825 ± 98	1.89
$(10\bar{1}0)$	3577 ± 145	1.70
$(11\bar{2}0)$	3627 ± 135	1.68

Fig. 1 shows the variation of VMH on the $(10\bar{1}0)$ plane with indenter load. With decreasing load, VMH increases obeying Meyer relation. Similar relations between VMH and loads are observed on the (0001) and $(11\bar{2}0)$ planes. Table I lists the values of VMH at a 100 g load (VMH_{100}) and the slope of the Meyer line on each plane. It is apparent from Table I that the basal plane (0001) exhibits lower VMH_{100} than that of the prismatic planes $(10\bar{1}0)$ and $(11\bar{2}0)$.

For the massive polycrystalline pyrolytic-Si_3N_4 oriented with the $(11\bar{2}0)$ and $(21\bar{3}0)$ planes parallel to the deposition surface, we observed that VMH_{100} on the deposition surface (3800 $kg\,mm^{-2}$) was higher than that on the cross-section (3100 $kg\,mm^{-2}$) [9]. This difference can be explained in terms of the anisotropy in the hardness between the basal and prismatic planes in a hexagonal α-Si_3N_4 crystal. Galasso *et al.* [8] obtained VMH = 2850 $kg\,mm^{-2}$ (unknown load) for the polycrystalline pyrolytic-Si_3N_4, which is lower than the above values probably because of the (0002) orientation of the sample used.

Typical Knoop indentations on the (0001) plane at a 100 g load are shown in Fig. 2, as obtained in the case of the long axis of an indenter parallel to the $[10\bar{1}0]$ direction. The occurrence of serious cracking is not observed around the indentations. The values of KMH_{100} measured for eight different orientations are summarized in Table II. KMH_{100} on the (0001) plane may indicate a periodic variation with a six-fold sym-

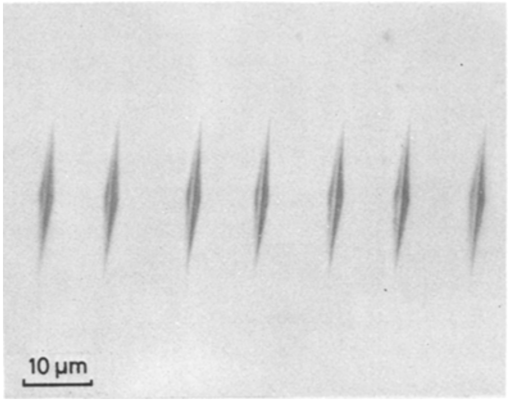

Figure 2 Optical micrograph of Knoop microhardness indentations at a 100 g load. The long axis is parallel to the $[10\bar{1}0]$ direction on the (0001) plane.

TABLE II Knoop microhardness at a 100 g load (KMH_{100}) of α-Si_3N_4 single crystals

Plane	Orientation of indenter's long axis	KMH_{100} (kg mm^{-2})
(0001)	$[10\bar{1}0]$	2787 ± 53
	$[11\bar{2}0]$	2625 ± 36
	$[1\bar{1}00]$	2793 ± 29
	$[1\bar{2}10]$	2588 ± 15
$(10\bar{1}0)$	$[0001]$	3486 ± 50
	$[1\bar{2}10]$	3151 ± 42
$(11\bar{2}0)$	$[0001]$	3476 ± 45
	$[1\bar{1}00]$	3237 ± 68

metry. In the case of the $(10\bar{1}0)$ and $(11\bar{2}0)$ planes, KMH_{100} in the c-axis direction is higher than that in the direction normal to the c-axis. Godfrey and Pitman [7] reported that KMH_{100} is 2569 kg mm^{-2} for the polycrystalline pyrolytic-Si_3N_4. This value is in reasonable agreement with the lowest hardness value on the (0001) plane in this work.

It is generally agreed that although brittle materials can hardly be deformed plastically in uniaxial loading and bending, a stress system containing a large amount of the hydrostatic component would induce plastic deformation. The normal hardness measurement involves such a stress system. The hardness anisotropy in the single crystal of α-Si_3N_4, therefore, is associated with the slip system on each plane, as discussed for the hard and brittle materials such as TiC, VC, NbC, TiB_2, ZrB_2, HfB_2 and SiC [13–17].

Evans and Sharp [18] reported that most of the observed dislocations in β-Si_3N_4 have a $[0001]$ Burgers vector and move primarily on a $(10\bar{1}0)$ slip plane with the $(11\bar{2}0)$ and $(12\bar{3}0)$ planes as secondary slip systems. Kossowsky [19] indicated that the most common Burgers vector for both α- and β-Si_3N_4 is $[0001]$. As shown in Table II, the hardness anisotropy of α-Si_3N_4 was largest on the $(10\bar{1}0)$ plane in this investigation. This result suggests that the primary slip system of α-Si_3N_4 might be also $(10\bar{1}0)$ $[0001]$, as is the case with β-Si_3N_4.

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