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Characterization of silicon nitride single crystals and polycrystalline reaction sintered silicon nitride by microhardness measurements

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Identification of α- and β-phases of Si_3N_4 single crystals grown from Si melt could be made with the help of Vickers microhardness measurements. The effect of chemical additives, e.g. metallic Fe and BaF_2, on the microhardness of Si_3N_4 was also determined. Different constants involved in the empirical Meyer relationship between load and indentation diameters could be correlated with the porosity and microhardness of Si_3N_4 single crystals and polycrystalline, reaction sintered Si_3N_4.

1. Introduction

For a long time microhardness measurements have been frequently utilized to characterize silicon nitride [1–4]. Parr *et al.* [1] investigated the effect of nitridation of silicon at various temperatures and characterized the resulting silicon nitride by microhardness measurements. Pratt [2] reported that the α- and β-phases of reaction sintered silicon nitride can also be distinguished by their microhardness properties, and in fact, α-Si_3N_4 was found to be harder than β-Si_3N_4 in the polycrystalline matte. But Noakes and Pratt [4] later reported that both the α- and β-phases of polycrystalline Si_3N_4 have identical Vickers microhardness values. Coe *et al.* [5] reported that an inverse relationship exists between hardness and strength of hot-pressed Si_3N_4. They further reported that an inverse relationship also exists between hardness and grain size of Si_3N_4. Niihara and Hirai [6] studied the microhardness anisotropy in different crystallographic faces of α-Si_3N_4 single crystals grown by the chemical vapour deposition (CVD) method. Hardness and wear behaviour of Si_3N_4 ceramics, with special reference to surface deformation behaviour, have been studied by Page *et al.* [7].

In the present paper an attempt has been made to identify α- and β-phases of Si_3N_4 single crystals grown from melt with the help of Vickers microhardness measurements. In addition, an attempt has been made to correlate the constants involved in the empirical relationship between load and indentation diameter with the porosity and microhardness of Si_3N_4 single crystals and polycrystalline Si_3N_4. The empirical relationship was first described by Meyer [8].

2. Experimental procedure

2.1. Preparation of Si_3N_4

β-Si_3N_4 single crystals (of size $\sim 60\,\mu m \parallel c$-axis and $\sim 30\,\mu m \perp c$-axis) were grown at 1450° C from silicon melt (of purity 99.99%) and specially pure nitrogen, with or without 0.1 wt% and 1.0 wt% Fe. Details of the experimental procedures have been reported elsewhere [9]. α-Si_3N_4 single crystals could be grown along with β-Si_3N_4 single crystals provided that the silicon melt contained 1.0 wt% Fe.

Polycrystalline α-Si_3N_4 was made by nitriding commercial silicon (particle size <200 mesh) at 1350° C, while $\alpha + \beta$-Si_3N_4 were made together by nitriding silicon first at 1350° C and then at 1450° C [10, 11]. Prior to nitriding the silicon bars were pressed either uniaxially [2 tsi ($3.09 \times 10^7\,N\,m^{-2}$) or 8 tsi ($1.24 \times 10^8\,N\,m^{-2}$)] or isostatically [16 tsi ($2.47 \times 10^8\,N\,m^{-2}$)]. Most of the polycrystalline Si_3N_4 samples were fully converted during the nitriding process but only a few had unconverted silicon in Si_3N_4. The α- and β-phases of Si_3N_4 were identified by X-ray analysis.

2.2. Measurement of microhardness

Small samples of Si_3N_4 were mounted in resin, ground and finally polished with diamond paste. The Vickers microhardness was measured with a Leitz Miniload Hardness Tester. Care was taken to make indentation only on that region of polycrystalline Si_3N_4 which had minimum number of visible pores. For the Si_3N_4 having unconverted silicon, indentation was made on a region free from unconverted silicon.

Microhardness measurements in order to identify the microhardness anisotropy could not be made on individual crystallographic faces because of the small sizes of single crystals. Therefore, the reported microhardness values should be considered as the average of values for different crystallographic faces.

2.3. Determination of porosity

The porosity of polycrystalline Si_3N_4 was measured using an Hg-porosimeter. The porosity of single crystals was assumed to be zero.

3. Results and discussion

Table I lists sample nature, indentation diameter and Vickers microhardness at loads of 100 g, 200 g, 300 g and 500 g, for α- and β-Si_3N_4 single crystals with or without Fe-additive, and α- and $\alpha + \beta$-polycrystalline Si_3N_4 with or without BaF_2-additive. Si_3N_4 single crystals, polycrystalline Si_3N_4 and Si_3N_4 having unconverted silicon have been designated by SC, PC and UN respectively. The porosities of samples were found to be as follows: Samples 1–6, 0%; Samples 7–9, 12%; Sample 10, 18.5%; Samples 11–15, 25%; Samples 16–17, 27%. Each indentation diameter is the average of 15 observations. Standard deviation in per cent for indentation diameters have been indicated in parenthesis. The ratio of minimum to maximum loads, used for making the indentations, was kept at 1:5 following the suggestion of Dunegan [3] that it should be kept within 1:10. Loads lesser than 100 g were not used to avoid error in measurement due to the smallness of the resulting indentation diameter. Loads larger than 500 g were not used to avoid cracking around indentation. Table I shows that the Vickers microhardness (VMH) decreases with increasing load for Si_3N_4 single crystals and polycrystalline Si_3N_4 as expected for hard and brittle ceramic materials [3, 4].

3.1. Identification of α- and β-Si_3N_4 single crystals

The α- and β-phases of Si_3N_4 have a light grey and deep grey colour respectively [3], and consequently the two phases could be distinguished and the indentation could be made selectively on either of the two phases of Si_3N_4. Samples 1–3 show that α-Si_3N_4 single crystals have a higher VMH than β-Si_3N_4.

Fig. 1 shows a typical α- and β-Si_3N_4 single crystal with an indentation made at 100 g load. It can be easily seen that α-Si_3N_4 has smaller indentation diameter than β-Si_3N_4 indicating that the former is harder than the latter. It may be pointed out that this difference in microhardness cannot be due to differences in crystallographic orientation since both of the single crystals have similar types of orientation, as is evident from Fig. 1. Samples 7 and 10 show that polycrystalline α-Si_3N_4 has a higher VMH than polycrystalline $\alpha + \beta$-Si_3N_4 indicating that polycrystalline α-Si_3N_4 is harder than polycrystalline β-Si_3N_4. It may be noticed that Sample 10 has higher porosity than Sample 7. Present authors also performed VMH measurements on the α- and β-phases of Si_3N_4 in the two-stage polycrystalline samples, as performed by Pratt [4]. A consistent difference in the VMH for α- and β-phases could not be achieved, however, because of the dissimilar distribution of pores in the α- and β-phases. Because the β-phase is formed from the melt it normally has a lesser number of pores than the α-phase. Hence, perhaps, the

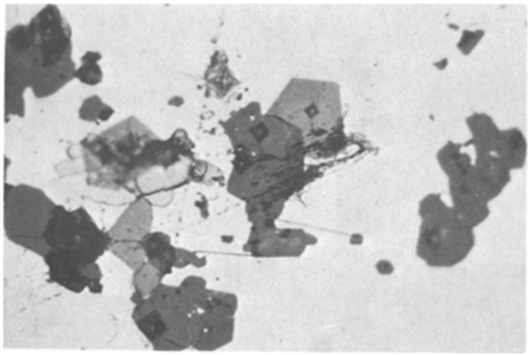

Figure 1 Optical micrograph of α- and β-Si_3N_4 single crystals with Vickers indentation at a load of 100 g. Light colour: α-Si_3N_4, deep colour: β-Si_3N_4, (× 280).

TABLE I The variation of indentation size with Si_3N_4 sample and load. Si_3N_4 single crystals, polycrystalline Si_3N_4 and Si_3N_4 containing unconverted silicon has been designated by SC, PC and UN, respectively

Sample	Nature of Si_3N_4	100 g load		200 g load		300 g load		500 g load	
		Indentation diagonal (μm)	VMH_{100} (kg mm^{-2})	Indentation diagonal (μm)	VMH_{200} (kg mm^{-2})	Indentation diagonal (μm)	VMH_{300} (kg mm^{-2})	Indentation diagonal (μm)	VMH_{500} (kg mm^{-2})
1	α-SC	6.4 (5.6)*	4527	9.9 (2.7)	3784	n.d.	n.d.	n.d.	n.d.
2	β-SC	7.2 (5.6)	3577	11.2 (5.8)	2957	15.2 (6.6)	2408	21.6 (2.0)	1987
3	β-SC	7.3 (6.0)	3480	11.0 (5.6)	3065	14.5 (6.6)	2646	21.5 (4.9)	2006
4	β-SC + 0.1% Fe	8.3 (6.3)	2692	13.9 (3.6)	1920	18.7 (5.5)	1591	26.0 (3.7)	1372
5	β-SC + 0.1% Fe	8.5 (6.5)	2567	13.7 (6.5)	1976	16.9 (7.2)	1948	24.0 (6.3)	1610
6	β-SC + 1.0% Fe	8.5 (3.4)	2567	13.9 (6.8)	1920	17.0 (6.9)	1925	23.7 (5.3)	1651
7	α + β-PC + F	7.8 (8.3)	3048	13.3 (7.5)	2097	17.7 (8.5)	1776	25.1 (8.4)	1472
8	α + β-PC + F-UN	7.8 (8.3)	3048	14.6 (7.5)	1740	18.4 (8.5)	1643	28.1 (8.4)	1174
9	α + β-PC	9.1 (9.2)	2239	15.0 (10.4)	1648	20.0 (5.0)	1390	29.9 (7.8)	1037
10	α-PC	7.0 (4.7)	3784	11.8 (6.1)	2664	15.6 (3.1)	2286	23.0 (6.0)	1755
11	α + β-PC	8.0 (6.9)	2898	22.4 (12.1)	739	27.9 (10.4)	715	41.3 (9.9)	543
12	α + β-PC	8.2 (7.6)	2758	21.5 (13.5)	805	27.8 (12.5)	720	42.8 (8.4)	504
13	α + β-PC	8.1 (7.1)	2826	16.6 (13.1)	1346	22.0 (12.1)	1149	30.1 (9.1)	1027
14	α + β-PC	8.4 (9.0)	2628	18.7 (13.5)	1061	26.9 (12.4)	768	36.3 (10.3)	704
15	α + β-PC	8.8 (10.2)	2395	21.4 (12.1)	810	28.0 (12.0)	710	42.9 (12.0)	504
16	α-PC	9.4 (10.8)	2099	24.3 (10.5)	628	32.1 (12.8)	540	45.0 (7.0)	458
17	α-PC UN	9.3 (9.0)	2144	22.9 (10.3)	707	28.9 (9.0)	666	38.1 (8.0)	638

n.d.: not determined.

F: BaF_2.

*Bracketed terms indicate standard deviation in %.

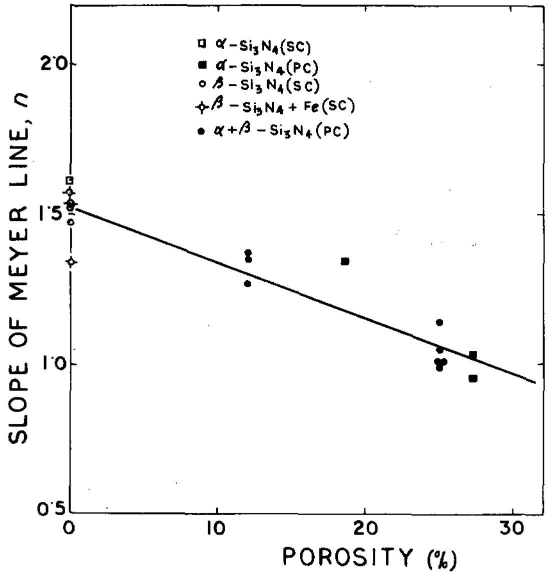

Figure 2 Relation between the slope of the Meyer line, n, and porosity (%) of Si_3N_4.

increased VMH of α-Si_3N_4 has been accentuated in such samples by the comparatively higher porosity of that phase and, consequently, the VMH of α-Si_3N_4 has been found to be lower than that of β-Si_3N_4. The only value obtainable in the existing literature of theVMH of α-Si_3N_4 single crystals grown by the CVD method is 3343 kg mm^{-2} at load of 100 g, which is the average of the values for the three crystallographic faces [7]. This is somewhat low in comparison with the VMH values obtained in the present work.

It may be mentioned that β-Si_3N_4 has a slightly higher density than α-Si_3N_4 [12]; in spite of this, α-Si_3N_4 has been found to be harder than β-Si_3N_4. This is contrary to the normal behaviour of ceramic materials.

3.2. The effect of chemical additives on the hardness

Samples 2–6 show that β-Si_3N_4 samples grown with no Fe-additive exhibit a higher VMH value than those with an Fe-additive. The reason for choosing an Fe-additive is that it enhances and favours the growth of β-Si_3N_4 [13–15]. Samples 4–6 show that increase in the concentration of the Fe-additive from 0.1 wt% to 1.0 wt% does not further reduce the VMH values.

Samples 7–9 show that the addition of BaF_2 improves the VMH values of polycrystalline Si_3N_4. BaF_2 is added because it enhances the silicon–nitrogen reaction [11, 16]. Experience in this laboratory has shown that isostatically pressed silicon bars which were not fully nitrided, even after prolonged heating above 1420° C, could become so if 1 wt % BaF_2 was added to the mixture. It was also observed that the percentage of α-phase in BaF_2-containing polycrystalline Si_3N_4 was higher. Low temperature (< 1420° C) nitridation product of powdered silicon containing BaF_2 yielded more than 90 wt % of the α-phase. Addition of BaF_2 improves the VMH, probably due to an enhanced percentage of the α-phase being present in polycrystalline Si_3N_4.

Samples 7–8 and 16–17 show that unconverted silicon present in Si_3N_4 does not deteriorate the VHM of Si_3N_4.

3.3. Dependence of slope and intercept of Meyer line on porosity and microhardness

The Meyer line is defined by the linear relationship

$$\log P = n \log d + \log a, \qquad (1)$$

where P is the load, d is the indentation diameter, n is a constant that is the slope of the Meyer line and a is a constant. Meyer lines were drawn for the loads and indentation diameters listed in Table I. Thus n and $\log a$ could be found out from the slope and intercept of the Meyer line, respectively.

Plotting of the slope of the Meyer line, n, against porosity shows that n linearly decreases with increasing porosity (see Fig. 2). Hence, some estimation of the porosity of Si_3N_4 can be made from the slope of the Meyer line. This is an important observation because, until now, the slope of the Meyer line was not known to have any correlation with any physical property of Si_3N_4.

Vickers microhardness at a load of 100 g, VMH_{100}, is plotted against porosity in Fig. 3. In spite of the large scatter in VMH_{100} it can be observed that VMH_{100} for Si_3N_4 single crystals is higher than that of polycrystalline Si_3N_4, as expected. Moreover, VMH_{100} to some extent linearly decreased with porosity. The large scatter in VMH_{100} is due to the difference in VMH for the two phases α and β of Si_3N_4 and to the deterioration of VMH as a result of the influence of the Fe-additive (see Section 3.1).

Comparison of Figs 2 and 3 indicates that the scatter in data points in Fig. 2 is less than that in Fig. 3. Hence it can be pointed out that the slope of the Meyer line, n, can give a better indication of porosity of Si_3N_4 than the individual VMH

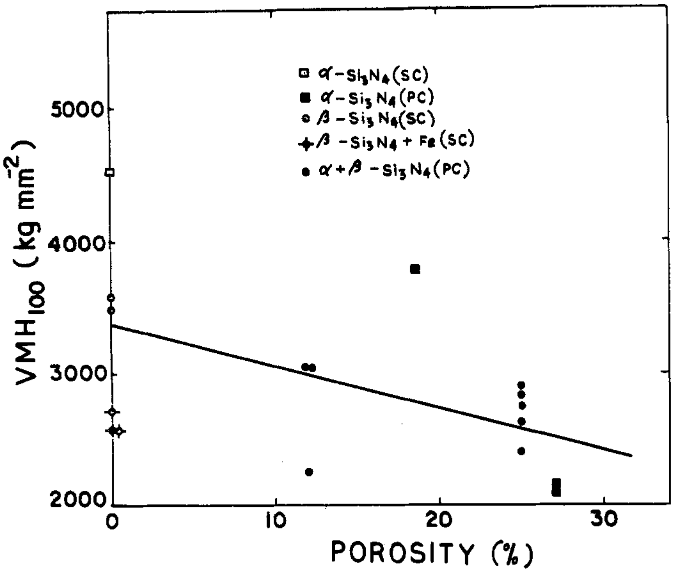

Figure 3 Relation between the Vickers microhardness at a load of 100 g (VMH_{100}) and porosity (%) of Si_3N_4.

value. This is so because the influence of the nature of the phase of Si_3N_4 and of the chemical additive is much more prominent in the VMH values than it is in the slope of the Meyer line.

Fig. 4 shows that slope of Meyer line, n, increases non-linearly with increasing VMH_{100} and, hence, n can given an indication of microhardness. A few values of VMH_{100} and corresponding n values from the existing literature [2, 6] have been introduced in Fig. 4. These data points from literature fit reasonably well within the present figure.

Fig. 5 depicts the intercept of the Meyer line, (log a), against VMH_{100}. It is observed that log a increases non-linearly with VMH_{100} and hence some evaluation of the VMH of Si_3N_4 can be made from the log a value.

It is observed from Table I that the standard deviation of the indentation diameters for the polycrystalline Si_3N_4 are on average two times larger than those for Si_3N_4 single crystals. This

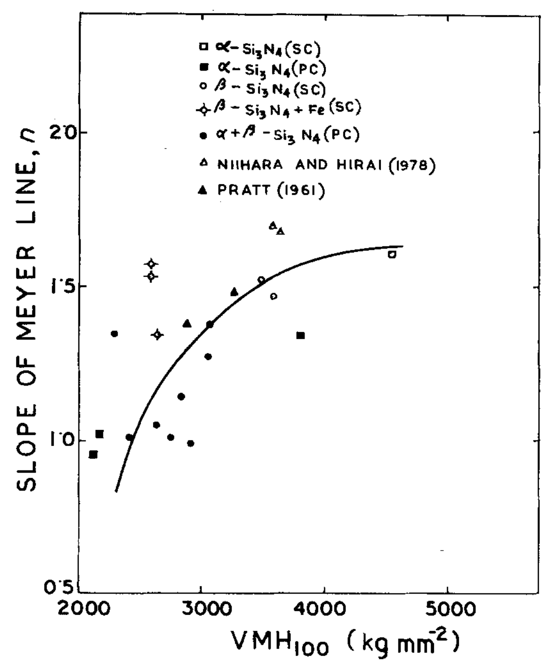

Figure 4 Relation between the slope of the Meyer line, n, and the Vickers microhardness at a load of 100 g (VMH_{100}).

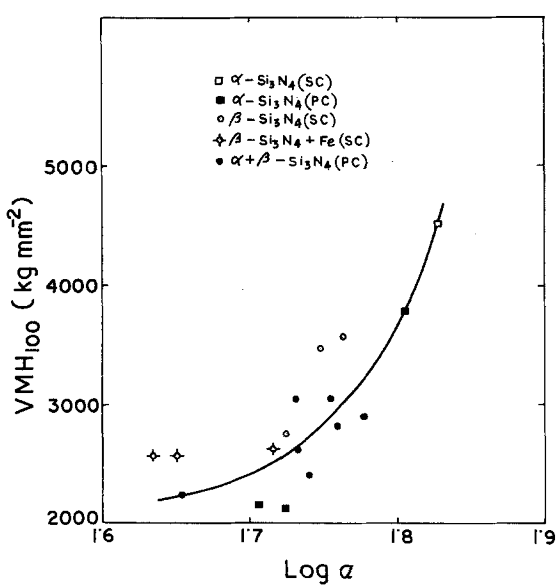

Figure 5 Relation between the intercept of the Meyer line (log a) and the Vickers microhardness at a load of 100 g (VMH_{100}).

clearly indicates that the indentation diameters are influenced by the different sizes of pores in polycrystalline Si_3N_4.

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