JOURNAL OF MATERIALS SCIENCE 6 (1971) 1486–1492

On the Tensile Strength of Ribbon-like SiC Whiskers

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An investigation is made of the correlation between surface defects and the tensile strength of ribbon-like SiC whiskers grown by lanthanum stimulation. Based upon this investigation a model is developed leading to a relation between dimensions and strength of these whiskers. With the aid of the model the influence of etching on the defects of basal and side faces and the average tensile strengths of whiskers characterised by dimensions and etching time are predicted.

1. Introduction

In the past years, whiskers of materials with high Young's modulus, e.g. of Al_2O_3 [1] and SiC [2, 3], have been developed, for the reinforcement of ductile matrices. Unidirectionally whisker reinforced materials have in general shown lower tensile strengths than was expected by simple application of the "corrected rule of mixtures" [4]. Probably this is not only due to misalignment and unsuitable handling of the whiskers but also to their great spread in tensile strength.

It was shown by Rosen [5] and Zweben and Rosen [6] that to obtain high composite tensile strength, in addition to a high average tensile strength of the whiskers, a small spread of the tensile strength is needed.

Whether improvement of the tensile strength of whiskers of a given kind can be obtained by sorting, after treatment, or by changes in growth conditions, is determined by the distribution and nature of the failure causing defects. A size dependence of the tensile strength, as found for glass fibres by Griffith [7], was observed for whiskers by Gyulai [8], Brenner [9], Regester *et al* [10] and Bayer and Cooper [11]. The last named authors improved the average tensile strength in batches of Al_2O_3 whiskers by chemical polishing [12].

When the tensile strength of the ribbon-like SiC whiskers developed by Knippenberg and Verspui [3] is plotted versus the outer surface area of the whiskers between the grips of the tensile testing machine a large scatter and sometimes no clear dependence of the tensile strength on the outer surface area is observed [13]. In order to get more insight into these phenomena a typical batch of these whiskers was more closely investigated. The irregularly tapered whiskers have an approximately rectangular cross-section of 12×70 μm^2 and an average length of 20 mm. The crystals are of a hexagonal structure (6H) [17] and are dominantly grown in the [100] direction [13].

2. Measurement and Observations

Measurements were performed on groups of whiskers before and after etching for different periods (4 min, 4 h, 50 h) with HF (1:4) + 5% concentrated H_2SO_4. The tensile strength measurements were performed with the aid of the apparatus described before [13, 16]; the dimensions of the cross-sections of the whiskers were determined microscopically. Eighty specimens were measured for each group of whiskers. The gauge length varied randomly from 0.5 to 4 mm. In view of this relatively small gauge length the tapering of the whiskers did not hamper the measurements. The tensile strengths of the whiskers, taken into account in the calculation (see section 3) fell between 6×10^7 and 942×10^7 N/m². Therefore the strength histogram corresponding to a particular group, covers strength values from 0 to 950×10^7 Nm/²; it consists of ten intervals. An example of the strength histogram of a group is given in fig. 6. A few whiskers had tensile strengths greater than 950×10^7 N/m² (up to 2240×10^7 N/m²).

By means of dark and bright field microscopy and with the aid of an interference contrast

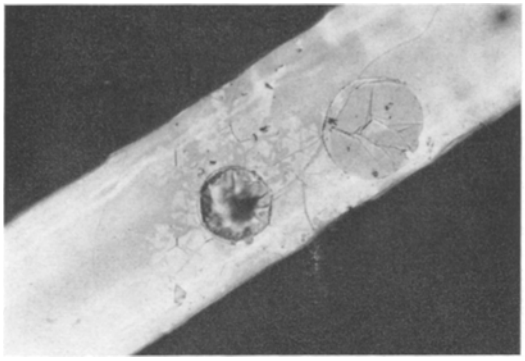

Figure 1 Impurity specks on a basal face (× 550).

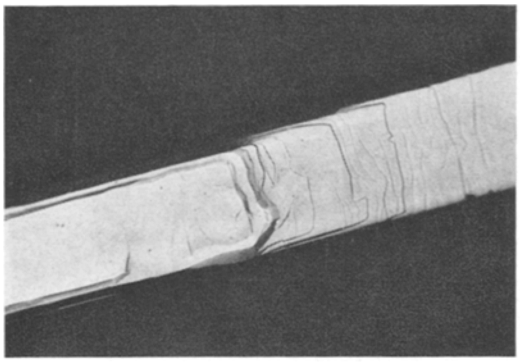

Figure 2 Small growth steps and a large step on a basal face (× 280).

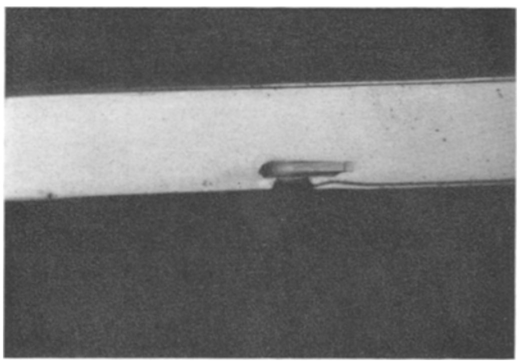

Figure 3 Grown-in crack on a side face (× 280).

technique several types of defects were observed at the outer surfaces of the whiskers. For the basal faces:

impurity specks (fig. 1)
steps divided into
small growth steps (fig. 2) (step height about 0.05 to 0.3 μm) and
large steps (fig. 2) (step height about 1 to 3 μm)
twin ridges.

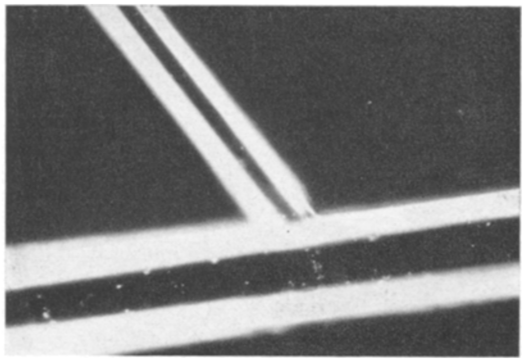

Figure 4 Branch on a side face (× 280).

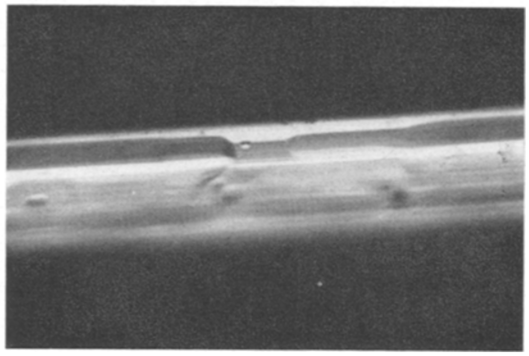

Figure 5 Ridge on a side face (× 960).

For the side faces:

impurity specks
grown-in cracks (fig. 3)
branches (fig. 4), and
ridges (perhaps a location where a branch starts to grow out, fig. 5).

For the different types of defects the stress concentration factor and the reduced tensile

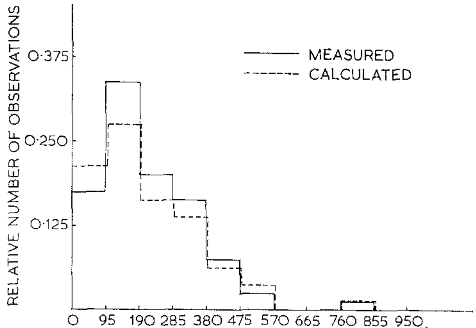

Figure 6 Measured and calculated tensile strength histogram for a group of eighty whiskers etched for 4 min.

strength due to such a defect when it is exclusively present, was estimated. The latter will be further called the reduced tensile strength due to the defect. For the unetched whiskers, the respective reduced tensile strengths, due to the defects were estimated with the usual approximations for the stress distribution around the end of a notch, in a stressed elastic body [14, 15]; e.g. for a growth step the reduced tensile strength will be in general:

$$\sigma_r = \sigma_{th} \cdot \sqrt{\frac{\rho}{d}} \qquad (1)$$

in which σ_r = reduced tensile strength, σ_{th} = theoretical tensile strength, ρ = radius of curvature at the foot of the step, d = step height, and for a grown-in crack:

$$\sigma_r = \sigma_{th} \Big/ \left(1 + 2\sqrt{\frac{d}{\rho}}\right) \qquad (2)$$

In some cases, e.g. branches, the radius of curvature could be measured directly. In the case of steps, the radius of curvature was estimated from multiple interference patterns. In the case of the impurity spots, the shape of the surface damage (visible after an etch treatment), was taken to be the relevant notch-form. Of ten examples of each type of defect, the reduced tensile strength was determined. The number of defects of each type per unit area was counted both for basal and side faces. For certain types of defects (impurity specks, steps, grown-in cracks, ridges), a more or less constant concentration was observed. For other types (twin ridges, branches) this was not evident. The results are shown in figs. 7 and 8 where the counted number of defects per unit area, of the respective types of defects, are plotted against their calculated reduced tensile strengths, In view of the difficulty of determining the relevant radius of curvature of the notches, the values of the reduced tensile strengths plotted for the defects must be looked upon as a rather rough approximation.Therefore this microscopic defect analysis was only made for the unetched whiskers. Generation of new defects by prolonged etching or the shielding properties of a surface layer before etching, could only be found by a calculative analysis based upon the observations and measurements discussed in this section.

Bulk initiated cracks, with tensile strengths corresponding to the lowest strength interval (fig. 6), were not observed. For high tensile strengths bulk initiated cracks may occur.

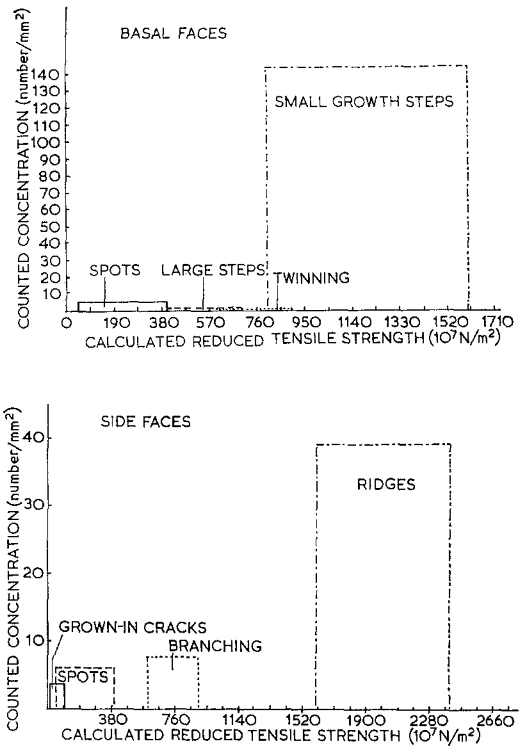

Figure 7-8 **Counted concentration of the various defects on the basal or side faces in their respective reduced tensile strength ranges.**

3. Elaboration of the Measurements

When, of each defect enumerated, the reduced tensile strength was determined, the block functions in figs. 7 and 8, will in general have the form of probability curves. The sum curve of the respective probability curves will tend to be a more or less smooth function of the reduced tensile strength. Based upon figs. 7 and 8 it is assumed that this sum curve can be represented by equation 3:

$$n = D\,.\,(\sigma_r - \sigma_0)^m \qquad (3)$$

in which n = concentration of defects for a certain reduced tensile strength interval, σ_r = reduced tensile strength of the interval, σ_0 = reduced tensile strength corresponding to the empty interval below the lowest tensile strength interval (fig. 6), and m, D are constants.

If the chance of a whisker breaking due to a defect on the basal planes is called α, to a defect on the side planes β and to a defect in the bulk γ then

$$\alpha + \beta + \gamma = 1 \qquad (4)$$

In most tensile strength measurements the whisker fractured only once. When it is assumed that the defects are distributed at random (section 2), and that the whisker breaks by a defect distributed in a certain ratio over basal plane, side plane and bulk, then the probability relation (4) for a whisker of given dimensions and of a definite defect distribution can be rewritten:

$$2\,xyp + 2\,xzq + xyzr = 1 \qquad (5)$$

in which p = concentration of defects on the basal faces in the reduced tensile strength interval, corresponding with the measured tensile strength, q = *idem* on the side faces, r = *idem* in the bulk, and x, y, z = respectively length, width and thickness of the whisker between the grips of the tensile testing machine. Application of relation 3 to $p = n$, $q = n$ and $r = n$ respectively leads to

$$2\,Axy(\sigma_r - \sigma_0)^h + 2\,Bxz(\sigma_r - \sigma_0)^k + \\ + Cxyz(\sigma_r - \sigma_0)^l = 1 \qquad (6)$$

A, B, C and h, k, l are constants corresponding to D and m in relation 3.

For each group the values for the unknown factors A, B and C were calculated for the whiskers with tensile strengths in the range from 0 to 950 N/m² by means of a least squares method; taking the values -4, $-3\frac{3}{4}$ etc. through to $+4$ for h, and l. Meaningful solutions could only be obtained when the concentration of volume defects in the relevant reduced tensile strength range, was assumed to be zero. For each combination of A, B, h and k the sum of products of calculated concentration (relation 3) and sum of the surface areas of basal and side faces was calculated in each strength interval. For each interval the numbers obtained in this way (f) were also compared with the measured number (g). As fitting criterion, relation 7 was applied:

$$g - \sqrt{g} \leqslant f \leqslant g + \sqrt{g} \qquad (7)$$

The combination of A, B, h and k fulfilling relation 7 for every interval was selected. An example of a calculated histogram together with a measured histogram is given in fig. 6. The concentration of defects corresponding to a certain interval width and to a certain reduced strength could be found from relation 3. In figs. 9 and 10 the calculated concentration of defects is plotted against the reduced tensile strength due to the defects for unetched and etched whiskers, for an interval width of 95×10^7 N/m².

4. Results and Discussion

4.1. Influence of Etching

The values for A, B, h and k obtained with the procedure described in section 3 are listed for the different groups in table I.

In figs. 9 and 10 these results are presented graphically in plots giving the calculated

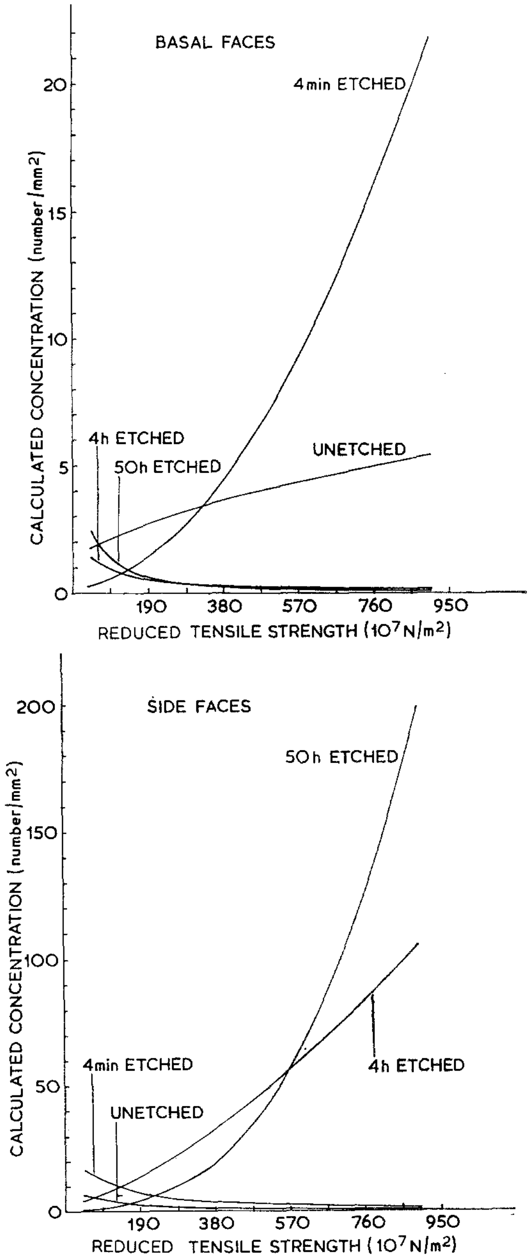

Figure 9-10 Calculated concentration of the various defects on the basal or side faces in their respective reduced tensile strength ranges according to fig. 6.

TABLE I The values for the constants *A, B, h* and *k* from relation 6 for unetched and etched whiskers.

	Unetched whiskers	Whiskers etched for		
		4 min	4 h	50 h
A	0.1750	$0.2415 \times 10^{+4}$	0.1279×10^{3}	0.2270×10^{4}
B	0.5990×10^{3}	$0.1572 \times 10^{+4}$	0.3598×10^{-2}	0.5224×10
h	$\frac{1}{2}$	2	-1	$-1\frac{1}{2}$
k	-1	-1	$\frac{3}{2}$	3

concentration of defects against the reduced tensile strength due to the defects for an interval width of 95×10^{7} N/m^2.

For the side faces (fig. 10) the calculated average curve for the unetched whiskers gives a total of eighteen defects/mm^2 in the strength range taken into account in the calculation. In this strength range the summed counted concentration is also eighteen defects/mm^2. The reduced tensile strength due to the ridges is higher than 950×10^{7} N/m^2 (fig. 8). The curve corresponding to 4 h etching gives a significant increase in the concentration of defects corresponding with the higher strength intervals. After prolonged etching (50 h) the number of defects of the highest intervals is even more increased. Probably the reason for this can be found in the formation of etch pits in the side faces. The dimension of these pits in the side faces (fig. 11) (2 μm) is about twice the dimension of the etch pits in the basal faces. The reduction of tensile strength by the etch pits in the basal faces therefore probably exceeds the reduction of the tensile strength in the region, which is taken into account.

For the basal faces, the calculated averaged curve for the whiskers etched for 4 min indicates such a total number of defects, that the small growths steps have to be appreciably effective. For the unetched whiskers, the averaged curve

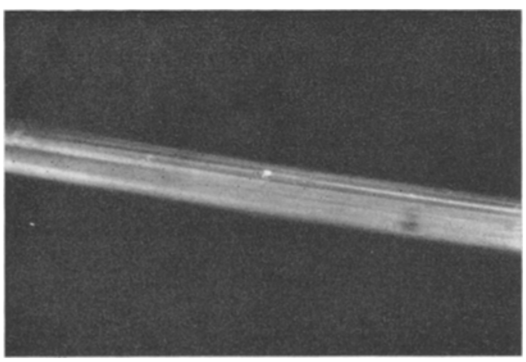

Figure 11 Etch pit on a side face ($\times$ 960).

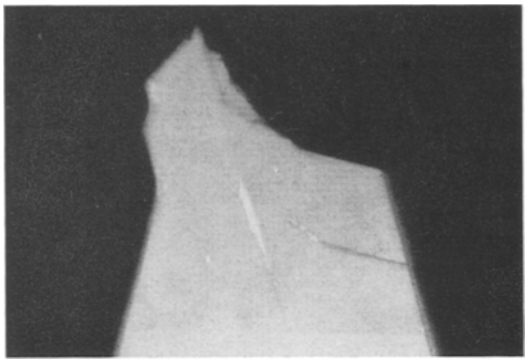

Figure 12 Reflection effects around a crack in the surface layer on a basal face ($\times$ 960).

indicates that a smaller part of the small growth steps contributes in the region taken into account in the calculation. After 4 h and 50 h of etching, the averaged curve gives about $\frac{5}{8}$ of the number of defects, without the small growth steps. The etch treatment of 4 min probably removes a surface layer, decreasing the radius of curvature of the steps, while after 4 and 50 h etching, the radius of curvature of the growth steps is increased by preferent etching at the foot of the step, bringing the steps again in an interval outside the strength range investigated. The probability for the presence of an SiO_2 layer being obtained during the preparation of the whiskers, with a thickness of about 0.2 μm, was supported by the chemical analysis of the solution obtained after treating the whiskers with HF (1:1) and concentrated HNO_3. Also the reflection effects, near the ends of broken unetched whiskers, observed around the cracks, suggest the presence of a loosened transparent surface layer (fig. 12).

4.2. Dimension Effects

The probability ratio for the failure-causing defect occurring on basal or side face ($\alpha:\beta$) (see relations 4 and 5) and the corresponding average tensile strength is calculated for etched and unetched whiskers with given dimensions (table

TABLE II Probability ratio for the failure-causing defect on basal or side face ($\alpha:\beta$) and corresponding average tensile strength for unetched and etched whiskers with given dimensions x, y and z.

Dimensions mm			Probability ratio $\alpha:\beta$ for corresponding average tensile strength (10^7 N/m^2).			
x	y	z	Unetched whiskers	Whiskers etched for		
				4 min	4 h	50 h
2.7	0.100	0.016	9:5	5:8	7:3	3:5
			47.5	142.5	47.5	237.5
2.7	0.100	0.008	9:3	1:7	2:7	1:10
			47.5	47.5	237.5	427.5
2.7	0.050	0.016	8:2	5:5	2:8	1:14
			237.5	237.5	142.5	332.5
2.7	0.050	0.008	15:1	9:2	1:7	1:20
			332.5	332.5	237.5	427.5
1.3	0.100	0.016	24:1	5:2	1:7	1:21
			332.5	332.5	237.5	427.5
1.3	0.100	0.008	49:1	10:1	1:25	1:18
			427.5	332.5	522.5	522.5
1.3	0.050	0.016	23:1	10:1	1:28	1:35
			902.5	522.5	332.5	427.5
1.3	0.050	0.008	70:1	20:1	1:35	1:30
			902.5	522.5	522.5	522.5

II). Therefore the interval selected, where the sum of the products of surface area and concentration of basal and side faces, equalled one.

For the lower strength intervals, of the whiskers etched for 50 h, the fit according to relation 7 between the measured and calculated histogram, was not fulfilled, thus the calculated concentration of defects at the sidefaces, will deviate from the real number of defects per unit area. Therefore an inaccuracy in the calculated tensile strength is to be expected.

A dimension effect is most evident for the unetched whiskers and least evident for the whiskers etched for 50 h. The high values for the tensile strengths of small unetched whiskers, disappear after etch treatment for 4 min, similarly after prolonged etching (4 and 50 h) no high values occur (table II). An optimal etching time between 4 min and 4 h can be expected, which does not yet introduce etchpits but increases the radius of curvature of the steps, leading to high values of tensile strength in whiskers with small overall dimensions. For whiskers etched for 50 h, the dimension effect is less distinct. According to table II the tensile strength of the larger whiskers is increased. Taking into account the possibility of an inaccuracy for the lower strengths, it is not yet improbable that general prolonged etching decreases the spread in tensile strength and increases the mean tensile strength of the whiskers.

From the probability ratios given in table II it appears that the smaller unetched whiskers, break along defects of the basal faces (steps); the smaller prolonged etched whiskers break along defects of the side face (etch pits) whereas the larger whiskers break on side and basal faces as well (respectively grown-in cracks and spots).

5. Conclusions

1. HF (1:4) + 5% concentrated H_2SO_4 etches SiC crystals preferentially at sharp edges at the surfaces.
2. The ribbon-like SiC whiskers grown by La stimulation show a dimension effect of the tensile strength, which is most distinct in unetched whiskers, but becomes less clear on etching.
3. Prolonged etching decreases the spread in tensile strength and probably increases the average tensile strength of the whiskers.
4. Surface oxidation, during the preparation of the whiskers, decreases the stress concentration factor of some defects (e.g. steps).
5. Prolonged etching decreases the stress concentration factor of the existing defects, but generates etch pits.

Acknowledgements

The author wishes to thank Dr W. F. Knippenberg for stimulating discussions. He is indebted to Mrs N. van der Sande, and Mr R. van Leeuwen for performing the tensile strength measurements. Thanks are also due to Mr A. W. C. van Kemenade for his help with the computer programme.

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Amended version received 11 July and accepted 18 August 1971