Destruction of Silicon Nitride Whiskers by Reaction with Metals at High Temperatures

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A preliminary study has been made of the reaction, at elevated temperatures, between whiskers of silicon nitride and pure metals (aluminium and nickel). The subject is important in the context of composite materials using refractory whiskers as a reinforcing component. The method involves reacting the whiskers with a thin, evaporated layer of the metal concerned and observing the results under the electron microscope. The effects of reaction are described and may be explained in terms of either crystallographic etching or recrystallisation of the whisker, though the former appears the more likely. The results do not necessarily reflect the behaviour of bulk composites made from the same constituents.

1. Introduction

The nearly ideal strength properties of "whiskers" (filamentous single crystals) of various materials can only be exploited by incorporating them in a supporting matrix of some kind, to provide a structural solid. The principle of fibre reinforcement has been put to good use in composites of glass fibre and polymeric resins, and it is a logical step to hope that whiskers, especially those of refractory solids, might be employed to reinforce metals, giving greater stiffness and resistance to high-temperature creep [1].

Outstanding among the problems which must be overcome if such materials are to find useful application is that of reaction between the matrix and the whisker during manufacture of the composite and during "ageing" at elevated temperatures. Destruction of the whiskers under such conditions is observed with a wide range of matrix and whisker materials, and, since the composites are designed for high-temperature applications, this phenomenon presents a serious barrier to progress. However, relatively little is known about the phenomenon, and there is some uncertainty as to whether the destructive process is a straightforward chemical reaction or a physical recrystallisation of the whisker to a morphologically more stable form. The work described below was undertaken as a preliminary attempt to elucidate the mechanism of destruction. The whiskers were those of α-silicon nitride, and the metals were aluminium and nickel.

2. Experimental

2.1. Reacting the Whiskers with Metal

The whiskers, containing approximately 90% of the α-phase of Si_3N_4, were supplied by the Ministry of Aviation, ERDE, in the form of as-grown mats resembling cotton-wool. Whisker diameters ranged from 0.1 to 2 μm. In order to limit the extent of reaction, the whiskers were not incorporated into a metallic matrix but were surface-metallised with a thin, evaporated film of the metal concerned. To achieve this, the whisker mat was placed in a vacuum chamber and a known quantity of metal evaporated onto its surface from a tungsten filament at a distance of 10 cm. The film thickness obtained could then be calculated and was of the order of 100 to 200 Å in the experiments reported below. The evaporated metal penetrated into the mat a distance of several mm, as judged by the dark

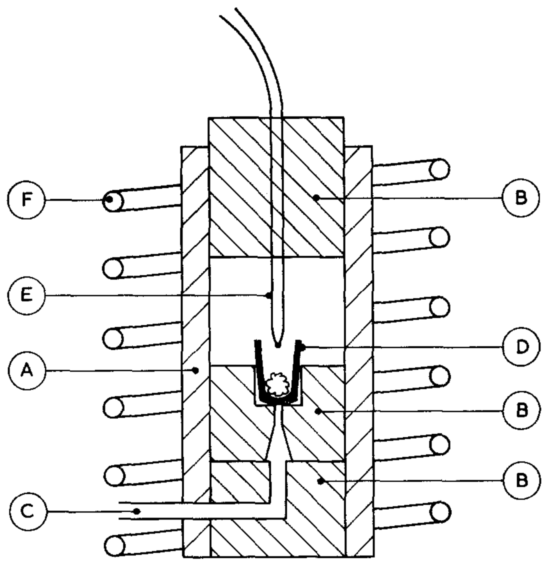

Figure 1 Heat-treatment furnace for coated whiskers: A, steel cylinder; B, carbon plugs; C, argon stream; D, alumina crucible; E, thermocouple; F, radio-frequency coil.

stain produced, but, of course, the coating was in general on one side only of a given whisker.

The coated whiskers were placed in an alumina crucible which was in turn placed within a steel cylinder sealed at each end by carbon plungers (fig. 1). Through one plunger, a continuous stream of argon could be passed, providing a positive pressure within the cylinder and preventing the entrance of oxygen. Through the other plunger was passed a thermocouple probe penetrating to a position close to the whisker mat. The steel cylinder was insulated with asbestos paper and placed within the heating coil of a radio-frequency heating unit dissipating from 0 to 2 kW. The desired temperature of reaction was attained as rapidly as possible and held by manual control of the power output. The reaction conditions used in the preliminary experiments described here were as follows:

	1	2	3
Metal	Al	Al	Ni
Coating thickness (approximate, Å)	100	200	200
Reaction temperature (° C)	560	630	1000
Time at reaction temperature (min)	15	30	15
Heating/cooling time (min)	10/10	12/12	30/30

2.2. Study of the Whiskers in the Electron Microscope

It was desired to examine the whiskers in the electron microscope both before and after reaction, in order to follow the progress of the reaction between the metallic surface coating and the silicon nitride. It is not difficult to detach whiskers from the mat and deposit them on a specimen grid, but the thickest of them are then only seen in silhouette. Ideally, one requires both whiskers and replicas of their surfaces in the same microscope specimen, and this was achieved by the following procedure.

The upper surface of the whisker mat was touched lightly on the sticky surface of a piece of "selotape", leaving a thin layer of whiskers adhering to the tape. In the case of metallised whiskers, the surface of interest was buried in the adhesive of the tape. A 20% solution of gelatine in warm water was flooded over the adhering whiskers and left to solidify, effectively embedding the whiskers except for such surfaces as were held by the adhesive tape. When the gelatine was hard, the selotape was stripped off under benzene, and the gelatine wafer washed in clean benzene to remove all traces of the adhesive. The whiskers were now embedded in the gelatine but with their (metallised) surfaces exposed.

A 20% solution of polystyrene in benzene was used next, to make a first-stage replica of the gelatine surface containing the exposed whiskers. The polystyrene, once hardened, stripped easily from the gelatine, and could be used as the basis for a second-stage replica of evaporated carbon which was then shadowed with gold-palladium alloy. Finally, the polystyrene was dissolved away in benzene, and the carbon replicas, after washing in one or two changes of the solvent, were collected for examination in the electron microscope.

It was found that, in addition to replicating whisker surfaces as planned, the polystyrene abstracted some whiskers from the gelatine, and these were transferred intact to the carbon replica. In this way both whole whiskers and replicas were present on the final specimen.

3. Results

3.1. Unreacted Whiskers

The unmetallised whiskers seen in silhouette in the electron microscope appear to be smooth-sided and uniform in width. The thinner ones are transparent to the electron beam, exhibit clear extinction contours and spot diffraction patterns. Replicas of uncoated whiskers reveal considerably more detail of their surface (fig. 2).

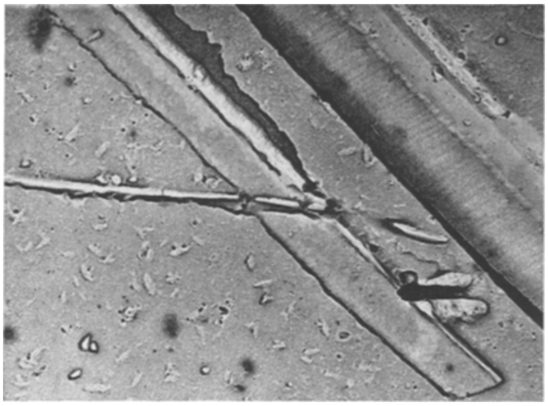

Figure 2 Replicas of whisker surfaces showing striations (× 11 500).

The whiskers appear to be polygonal in cross-section, and replicas invariably reveal two or more facets of the surface. These facets differ considerably in smoothness, and striations running perpendicular (or at a large angle) to the whisker axis are frequently found. These striations may signify the presence of monomolecular steps. Larger steps are also found running parallel to the striations. Other facets have been observed which appear to be encrusted with rows of nodules some 300 Å in diameter.

Whiskers which have been coated with metal, but not reacted at high temperature, are unchanged in appearance except that the evaporated layer of aluminium or nickel is sometimes clearly visible as a fine-grained polycrystalline film, of the kind normally obtained by evaporation onto a cold substrate. The grain size for aluminium was 70 to 100 Å and for nickel some 50 Å. There was no evidence of undue mobility of the metal atoms on the whisker surface, though, of course, this situation may alter as the temperature is raised.

3.2. Reaction between the Whiskers and Aluminium

After reaction at 560° C for 15 min, the whiskers with a 100 Å coating of aluminium were found to have suffered extensive attack, examples of which are given in figs. 3 and 4. A replica of a reacted whisker is shown in fig. 5. The reacted whiskers frequently appear to consist of a spiral arrangement of overlapping platelet crystals,

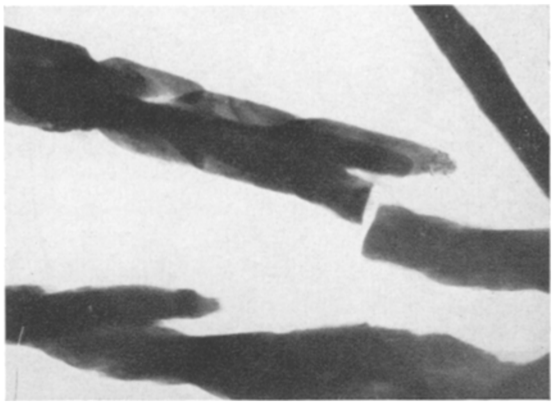

Figure 3 Si_3N_4 whiskers after reaction with aluminium at 560° C (× 17 500).

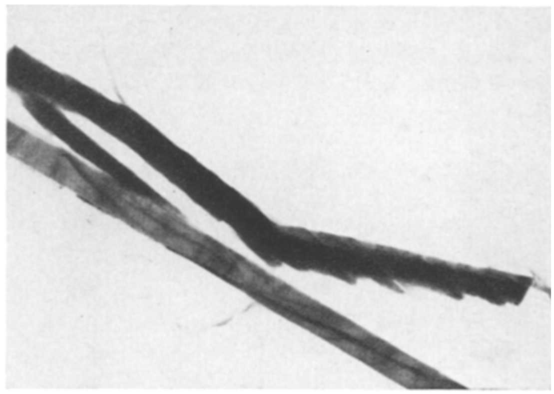

Figure 4 As fig. 3 (× 10 000).

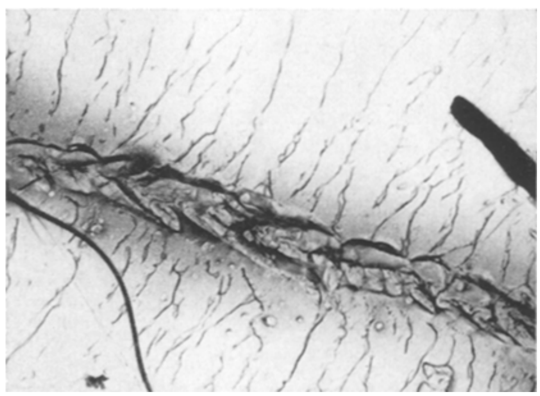

Figure 5 Replica of whisker reacted with aluminium at 560° C (× 4000).

the platelets being defined by two directions: one parallel to the whisker axis and the other at a well-defined angle of about 34° to this axis (measured angles vary from this figure upwards,

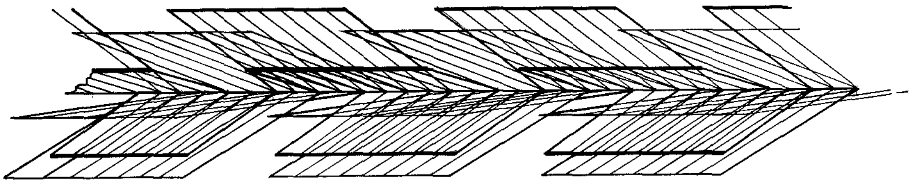

Figure 6 Spiral arrangement of platelets in reacted whisker sketched for comparison with fig. 3.

but this can be explained by the platelets not lying in the plane of the support film). This spiral arrangement is sketched in fig. 6.

The periodicity of "attack" along the whisker varies from about 0.5 to 1 μm, though this may be a function of whisker diameter.

More severe reaction conditions (630° C for 30 min with 200 Å coating of aluminium) resulted in complete disintegration of the Si_3N_4 whisker. Debris was observed in the form shown in fig. 7, and occasional crystal platelets were found lying free on the support film.

Figure 7 Disintegrated whisker after reaction with aluminium at 630° C (× 5000).

3.3. Reaction between the Whiskers and Nickel

In this case, only one reaction was carried out, namely, at 1000° C for 30 min, the nickel coating being some 200 Å thick. The whiskers were found to be encrusted with small "limpet" crystals obviously in the course of growth and varying in size from about 0.1 to 0.5 μm (fig. 8). These crystals, which clearly contain nickel, because of their general opacity to the electron beam, tend to be regularly spaced along the whisker and appear to be eating into the whisker at their point of contact. This is particularly evident in fig. 9, where limpet crystals have been displaced at the points arrowed, leaving deep pits in the whisker surface.

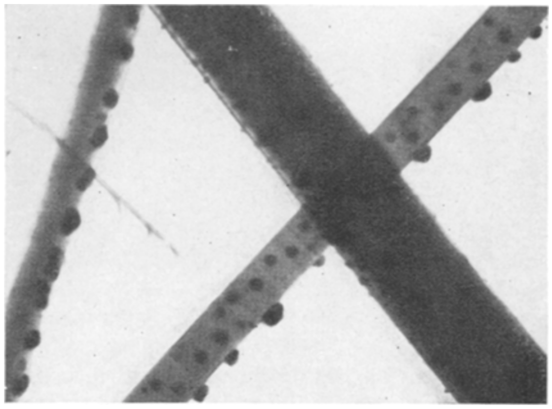

Figure 8 Whiskers encrusted with limpet crystals after reaction with nickel at 1000° C (× 6500).

Replicas of these same whiskers present further aspects of interest (fig. 10), being qualitatively similar to those resulting from attack by aluminium. Again, periodicity and a crystallographic directionality are found. It is not immediately obvious that the replicas do correspond to the whiskers of fig. 8, since in the replicas the surface protrusions often span the width of the whisker, whilst the limpet crystals

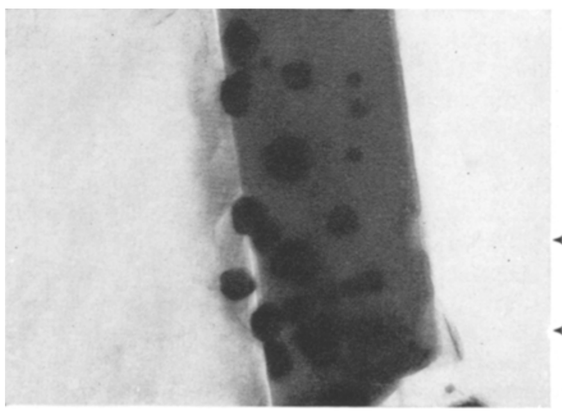

Figure 9 As fig. 8. Note pits in whisker where limpet crystals have become detached (× 10 000).

Figure 10 Replicas of whiskers after reaction with nickel at 1000° C (× 6500).

appear generally to be symmetrical bodies. It is possible that the limpet crystals are only part of more extended regions of attack, rather like the "head" of a comet whose "tail" contains no nickel and thus is electron-transparent. This suggestion is encouraged by such pictures as fig. 10, but clearly requires further investigation.

4. Discussion

The observations detailed above raise the following questions:

(a) Is whisker destruction the result of chemical reaction or simply recrystallisation of the silicon nitride?

(b) If chemical attack is the cause, are the platelet crystals observed with aluminium the remnant of etched Si_3N_4, or are they new crystals of some reaction product? If simple etching is taking place, what determines its crystallographic form?

(c) What is the explanation of the periodicity of attack along the whisker?

The work reported here only provides partial answers to these questions, but some deductions can be made. Recrystallisation would supply no explanation of the observations on nickel-coated whiskers, since here the intact whiskers are observed with surface etching produced by localised attack. The limpet crystals may be simply nickel grains which have grown by migration of the evaporated material at high temperature, and which, subsequently, react with the whisker at their point of attachment. Against this, however, it may be argued that the volume of material in the limpet crystals attached to a given length of any whisker is found to exceed, by a factor of about 5, the volume of nickel initially present. Although the latter quantity is not very well defined, this does suggest that the limpet crystals are composed not of nickel but of some reaction product. The most likely possibility is nickel silicide, but until it is possible to obtain selected area diffraction pictures of isolated limpet crystals this question remains open.

Recrystallisation appears to be more likely in the reaction with aluminium, especially since the typical angle (34°) of the platelet crystals which constitute the "whisker" after reaction corresponds closely to the minimum angle between the *a* axis of the unit cell and the (10$\bar{1}$1) planes of α-Si_3N_4 [2]. However, since some of these whiskers grow in a direction parallel to (10$\bar{1}$1) (Cook, private communication), this observation could also be explained in terms of a preferential etching of the basal plane. In this connexion, it is interesting to note that the unit cell of α-Si_3N_4 contains six quite large "holes", disposed as indicated in fig. 11, which lead to a

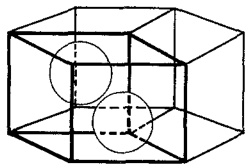

Figure 11 Sketch of unit cell of α— Si_3N_4 showing two of the six "holes" in the structure.

low atomic population on a plane parallel to, but intermediate between, the basal faces of the cell. It is possible that this plane represents an easy diffusion path and facilitates a basal-plane etch.

Whether or not recrystallisation occurs in the early stages, it seems clear from fig. 7 that complete disruption of the whisker does eventually take place. The debris seen in fig. 7 is more consistent with the idea of chemical reaction than with that of recrystallisation, since it is difficult to imagine the latter process resulting in such a fine array of microcrystals as to resemble a fused mass.

The periodicity of attack may be the result of a statistical effect, by which metal atoms are drawn from neighbouring "catchment areas" to feed the reaction (or recrystallisation) initiated at a distribution of points. Competition between near-by reaction foci will lead to the growth of some, at the expense of others, and result eventually in an apparent periodicity of etch. This suggestion could be tested by studying the effect of metal layer thickness, since increasing thickness should mean a smaller spacing between points of attack. For a whisker embedded in a continuous metal matrix, no periodicity should be obtained. If this thickness effect is not found, of course, it will be necessary to involve some structural peculiarity of the whisker to account for periodicity in the pattern of reaction.

5. Conclusion

The method described lends itself to a systematic study of the reactions which may occur between ceramic whiskers and metals at elevated temperatures. Apart from requiring only small quantities of material, an obvious advantage when "screening" scarce whisker material for compatibility with a given metal, the method provides control over a variety of variables, such as the extent of reaction, the atmosphere, and the temperature and duration of testing. It should therefore be possible to obtain information on the kinetics of the reaction, as well as its nature and ultimate result.

It must be stressed, however, that the results of the present experiments do not necessarily reflect the behaviour, at equivalent temperatures and reaction times, of bulk composites. Such parallel work as has been carried out (Cannell, private communication), using aluminium metal and Si_3N_4 whiskers, indicates that the whiskers can tolerate hot-pressing temperatures in contact with the metal in excess of those found to cause serious damage in the present work. This discrepancy may be due to the higher chemical activity and more intimate contact of an evaporated layer as compared with the pressed metallic powder.

Acknowledgement

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