Silicon nitride-nickel compatibility: the effects of environment

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The effect of gaseous environment on the high temperature stability of nickel-coated silicon nitride whiskers has been investigated. Under vacuum conditions above 900°C, the nickel coatings broke up to form spheroidal particles, which subsequently became faceted (activation energy = 26 kcal/mol) and wetted the whiskers (activation energy = 74 kcal/mol) In addition, at 1100°C, whisker disintegration occurred rapidly due to the formation of a nickel silicide reaction product. Under similar conditions in a nitrogen atmosphere the whiskers remained coherent and in an argon atmosphere the whiskers developed side growths. These results are correlated with variations in the nitrogen and oxygen partial pressures between the various conditions.

1. Introduction

In a previous investigation [1] it was demonstrated that a reaction occurs at elevated temperatures between silicon nitride whiskers and pure nickel. As such a reaction provides an obvious limitation to the potential application of a silicon nitride whisker-nickel matrix composite, a more comprehensive study of silicon nitride-nickel compatibility was initiated. In this paper the particular effect of environment on the high temperature stability of individual nickel coated silicon nitride whiskers is reported. It was found that the reaction and whisker disintegration which occurred in the 950 to 1100°C range under vacuum could be inhibited in different ways in a nitrogen or argon atmosphere. Some possible correlations between these results and the variation in oxygen and nitrogen partial pressures between the three conditions are discussed.

2. Experimental procedure

The whiskers, containing approximately 90% of the α phase of Si_3N_4, were supplied in the form of mats by the Ministry of Defence ERDE. A nickel coating of 100 to 200Å was deposited on the whisker mat through evaporation in a vacuum chamber. Samples of the nickel coated whiskers were then prepared for electron microscope examinations using the "replication-transmission" technique developed by Andrews [1]. In addition some nickel coated whiskers

were heat treated prior to examination according to the following schedules:
(1) At 900 to 1100°C, for times up to 17 h, in 10^{-5} torr vacuum.
(2) At 1100°C, for times up to 17 h, in high purity nitrogen.
(3) At 1100°C, for times up to 17 h, in high purity argon.

3. Results

3.1. In vacuum

Uncoated silicon nitride whiskers did not exhibit any changes of morphology in the temperature range investigated, as demonstrated for example in Fig. 1.

The nickel coating was deposited as a continuous film, but on heating the whiskers above 800°C, the film broke up to give a series of spheroidal particles. Fig. 2 shows the structure obtained after an anneal at 900°C for 65 min. It can be seen that there is a range of particle diameters from approximately 0.01 to 0.3 µm and that some of the particles are adhering to the whiskers, although it should be emphasized that a greater number of particles had become detached from the whiskers during the replication process. An anneal at a higher temperature (950°C) for 15 min, produced a similar nickel particle distribution, although some of the particles had developed a faceted rather than a spheroidal form, as shown in Fig. 3. With longer times at 950°C there was an increase both

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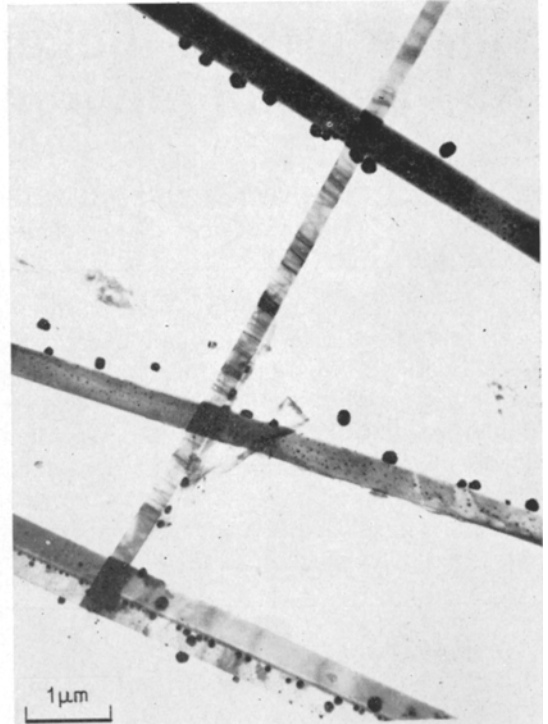*Figure 1* Silicon nitride whiskers after 17 h at 1100°C in vacuum.

Figure 2 Nickel coated whiskers after 65 min at 900°C in vacuum.
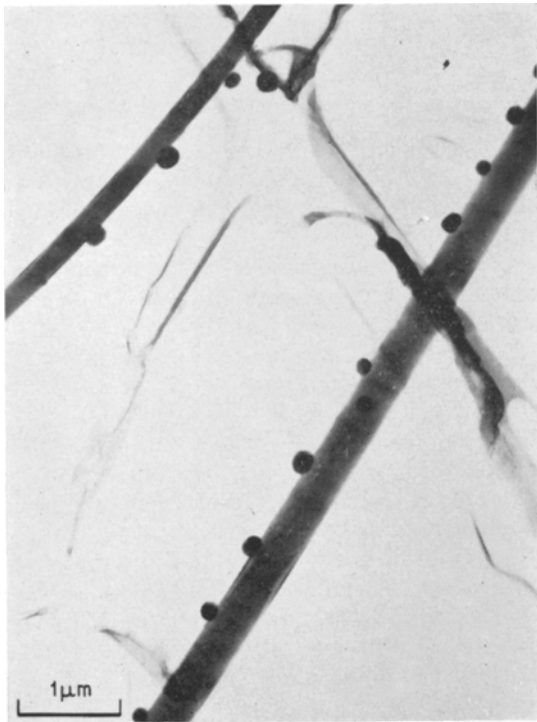

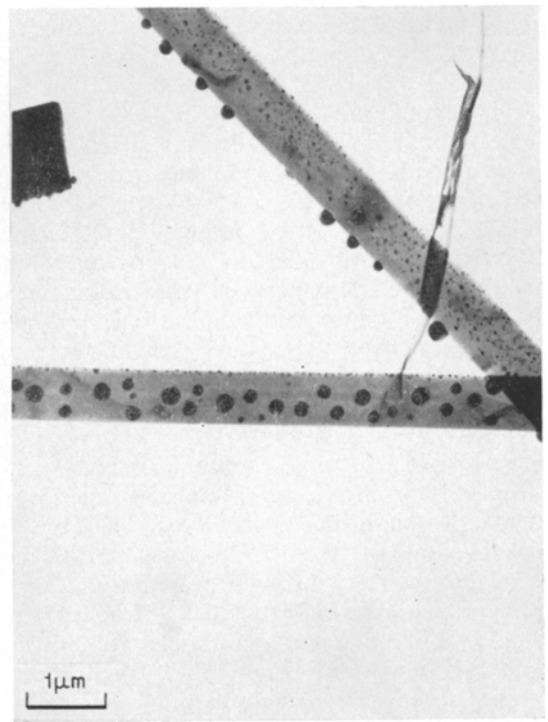*Figure 3* Nickel coated whiskers after 15 min at 950°C in vacuum.

Figure 4 Nickel coated whiskers after 30 min at 950°C in vacuum.

in the size of the particles and the average number of adherent particles per unit area of whisker, as illustrated in Fig. 4 (950°C/30 min). An increase was also noted in the contact area between the particle and whisker, particularly for times at 950°C, greater than 4 h (Fig. 5). This transition was also noted after anneals at 1000°C (as shown in Figs. 6 and 7) and 1050°C (as shown in Figs. 8 and 9), but after shorter times of approximately 90 and 30 min respectively. In addition some examples of "tailed" spheroids (Fig. 9) were noted at the higher temperature.

After an anneal at 1100°C for 15 min (Fig. 10) a distribution of regular platelets was obtained, with all the platelets firmly adhering to the whisker. Fig. 10 also demonstrates that at this temperature some of the platelets melted producing holes in the whiskers.

The nature of the platelets was investigated by selected area diffraction. Extra smaller rings were detected after the 1100°C treatment which were consistent with the larger interplanar spacings expected from a nickel silicide compound as compared with pure nickel. The measurements obtained are shown in Table I, together with the predicted values for the possible forms of nickel silicide.

3.2. In nitrogen

The platelet formation and melting noted at 1100°C under vacuum was not repeated with similar temperature anneals under a high purity nitrogen atmosphere. After 15 min a few spheroidal particles were noted on the whiskers (Fig. 11) while most of the particles were detached by the replication process. This situation persisted for times up to 17 h and the whiskers remained generally coherent, although there was evidence for some general irregularity and pitting of the whisker surface.

3.3. In argon

Completely different morphological changes were noted under an argon atmosphere at 1100°C to those noted under either vacuum or nitrogen. After a short time (15 min) at 1100°C under high purity argon, side growths developed on the original whiskers which displaced the nickel particles away from the whisker (Fig. 12).
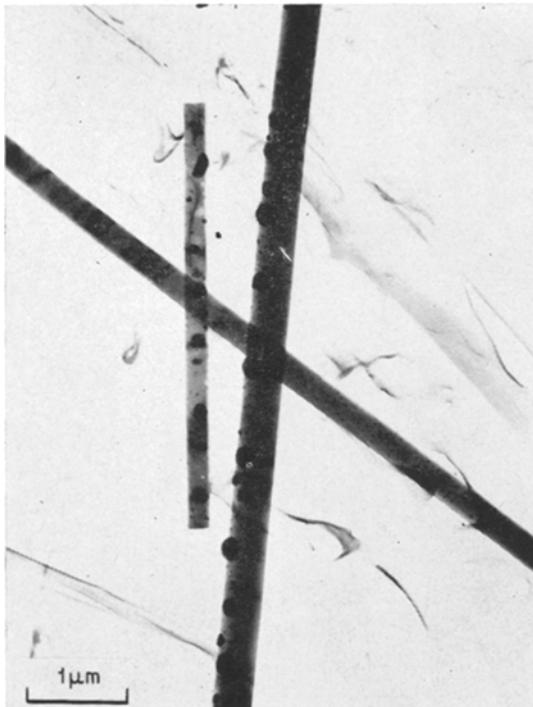

Figure 5 Nickel coated whiskers after 4 h at 950°C in vacuum.

Figure 6 Nickel coated whiskers after 30 min at 1000°C in vacuum.

TABLE I A comparison of predicted and measured ring radii (cm) for various heat-treatments.

(a) Predicted

Compound	Chemical formula								
Nickel silicide	Ni_3Si_2	0.52	0.81	0.82	0.83	0.84	0.85	0.86	0.94
β Nickel silicide	Ni_3Si	0.67	0.82	0.94	1.15	1.33	1.42	1.48	1.63
δ Nickel silicide	Ni_2Si	0.50	0.60	0.72	0.83	0.89	1.20	1.43	1.51
	Ni_3Si_2	0.81	0.83	0.84	0.86	0.95	1.33	1.57	1.60
	$NiSi_2$	0.57	0.83	0.87	1.01	1.22	1.33	1.50	1.59
Nickel silicon	Ni_3Si	0.47	0.66	0.82	0.94	1.34	1.56	1.63	1.88
γ Nickel silicon	Ni_5Si_2	0.84	0.86	1.20	1.36	1.47	1.48	1.53	1.60
η Nickel silicon	$NiSi$	0.58	0.84	0.86	0.94	1.32	1.38	1.41	1.60
θ Nickel silicon	Ni_2Si	0.50	0.60	0.84	0.87	1.20	1.48	1.50	1.60
Nickel	Ni	0.81	0.94	1.32	1.56	1.63	1.88	2.04	2.09

(b) Measured

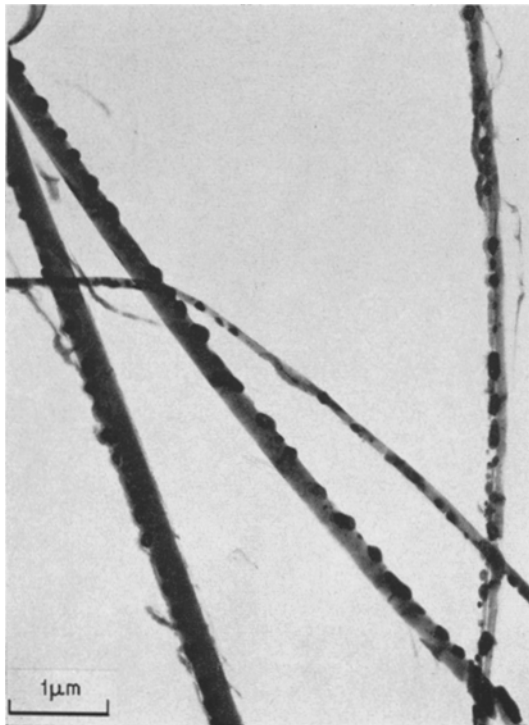| Heat treatment °C									
950		0.80	0.94	1.30	1.52	1.95	2.04	2.15	
1000		0.80	0.91	1.29	1.49	1.95	2.00	—	
1100		0.58	0.68	0.79	0.89	1.00	1.23	1.43	

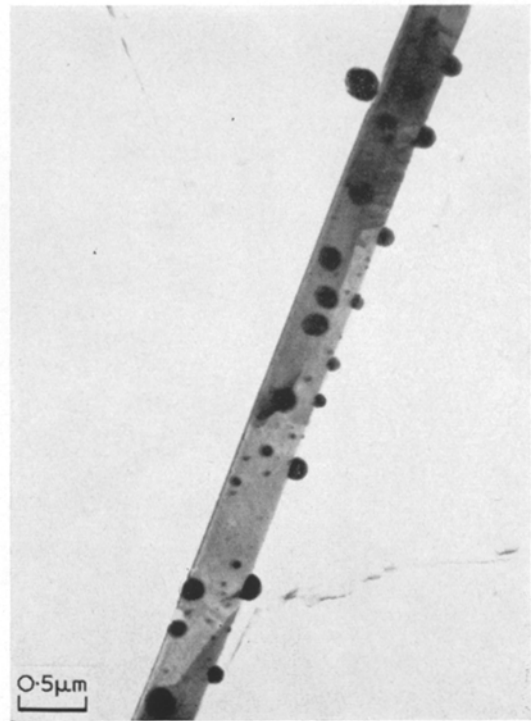*Figure 7* Nickel coated whiskers after 90 min at 1000°C in vacuum.

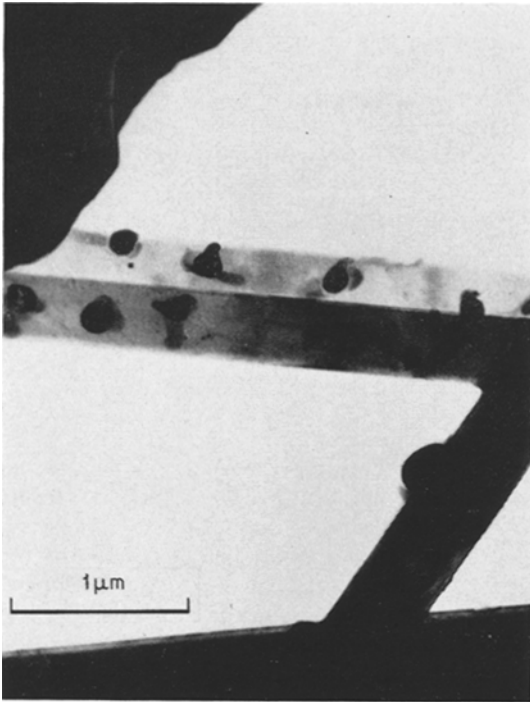*Figure 8* Nickel coated whiskers after 15 min at 1050°C in vacuum.

Figure 9 Nickel coated whiskers after 30 min at 1050°C in vacuum.

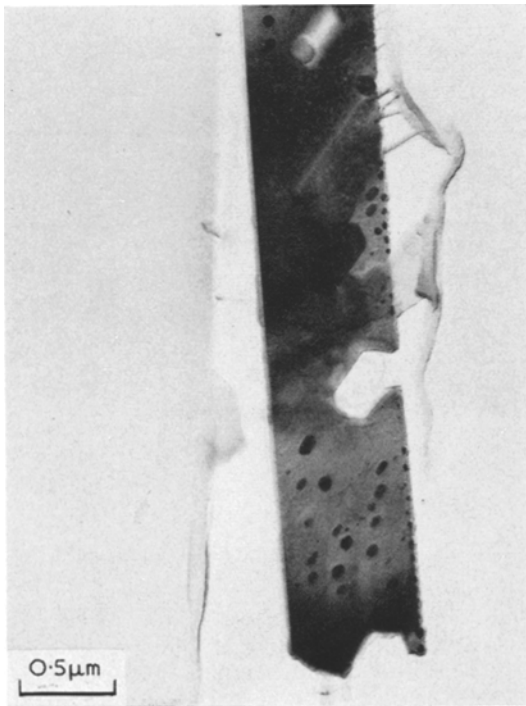Figure 11 Nickel coated whiskers after 17 h at 1100°C in nitrogen.

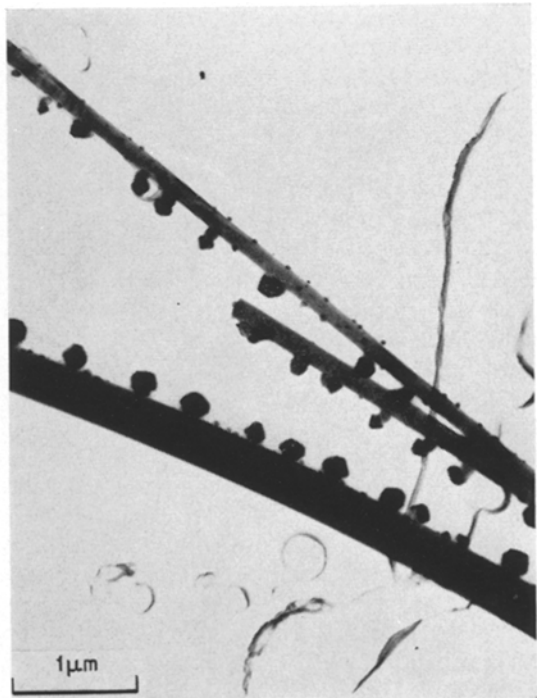Figure 10 Nickel silicide platelets after 15 min at 1100°C in vacuum.

Figure 12 Side growths after 15 min at 1100°C in argon.

Figure 13 Side growths after 17 h at 1100°C in argon.

The side growths increased in both length and width with further time at 1100°C and after 17 h ranged up to 5 and 0.5 μm respectively, as shown in Fig. 13. It can be seen that nickel particles, of about the original size, are still attached to a number of side growths.

4. Discussion

The results demonstrate clearly the effect of environment on the high-temperature structural-stability of nickel coated silicon nitride whiskers, as at 1100°C the whiskers, firstly, disintegrated under vacuum, secondly, remained essentially unchanged under nitrogen and, thirdly, developed side growths under argon. It was also shown that none of these changes occurred on uncoated whiskers. Further, a nickel-silicide reaction product was associated with the disintegration under vacuum but could not be detected under nitrogen or argon. Hence, it is concluded that the changes are all a consequence of the nickel coating, with a reaction between silicon nitride and nickel taking place under vacuum conditions to form a nickel silicide, as for example:

$$Si_3N_4 + 3Ni \rightarrow 3NiSi + 2N_2 \qquad (1)$$

As the progress of such a reaction will depend on the partial pressure of nitrogen (P_{N_2}), it is useful to determine the approximate level required under equilibrium conditions.

The free energy of the reaction in Equation 1 at 1373 K ($\Delta G°_{1373}$ is approximately 58 k cal/mol [2].

Also $\qquad \Delta G°_{1373} = - RT\ln K \qquad (2)$

with

$$K = \frac{(P_{SiNi})^3 (P_{N_2})^2}{(P_{Si_3N_4}) (P_{Ni})^3} \sim (P_{N_2})^2 \qquad (3)$$

Substituting in 2 and 3 we obtain

$$P_{N_2} \sim 2.5 \times 10^{-5} \text{ atm}$$

Hence, this estimate suggests that, under equilibrium conditions a nitrogen partial pressure $< 2.5 \times 10^{-5}$ atm is required for reaction (1) to proceed. Under experimental conditions the kinetics of the reaction will also be important and hence the critical value can only be regarded as approximate. However, with this reservation it can be seen from Table II, which lists the nitrogen partial pressure, that it is only under vacuum that the nitrogen partial pressure is sufficiently small for the reaction to proceed, in accordance with the experimental findings.

TABLE II Nitrogen partial pressures

Environment	Partial pressure of N_2 (atm)
Vacuum	$\sim 10^{-7} - 10^{-8}$
Nitrogen	~ 1
Argon	$\sim 3 - 5 \times 10^{-5}$

If the breakdown of silicon nitride, in the absence of nickel is also considered, we have

$$Si_3N_4 \rightarrow 3Si + 2N_2 \qquad (4)$$
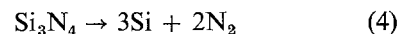
with

$$\Delta G_{1373} \sim 70 \text{ kcal/mol}$$

Then by a similar argument we obtain

$$P_{N_2} \sim 2.8 \times 10^{-6} \text{ atm}$$

This result suggests that direct breakdown of Si_3N_4 could occur in vacuum. Hence the fact that no breakdown was observed in the uncoated condition emphasizes that the critical nitrogen partial pressure also depends on kinetic factors.

Phenomenologically, it was observed that the formation of nickel silicide was preceded by
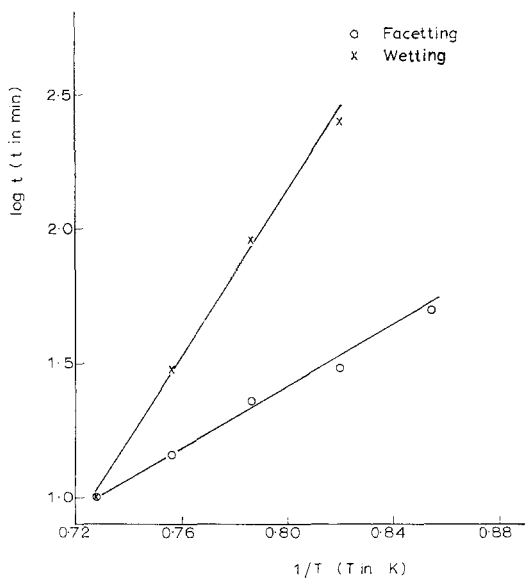
Figure 14 The effect of temperature on the time for nickel faceting and wetting on silicon nitride in vacuum.

three distinct stages. Firstly above 800°C the nickel coating broke up to form a series of spheroidal particles, in the manner that has also been noted for nickel coated carbon fibres [3] and nickel coated sapphire whiskers [4]. Secondly, the nickel particles developed facets, an event that took place rapidly in the 900 to 1100°C range. Substituting estimates of the time (*t*) required for faceting at the various temperatures (*T*) in the rate equation:—

$$\log \frac{1}{t} = \log k - \frac{Q}{RT} \qquad (5)$$

we obtain an activation energy (*Q*) = 26 kcal/mol, as shown plotted in Fig. 14. It is suggested that this represents the activation energy for self diffusion in the nickel particles. Thirdly, the whiskers were wetted by the nickel particles, for which from Equation (5) and Fig. 14 an activation energy of 74 kcal/mol is obtained. This value compares with the significantly larger activation energy of 110 kcal/mol [3] required for the diffusion of nickel into carbon fibres under similar experimental conditions.

Although the mechanism(s) producing the side growths on nickel coated whiskers under an argon atmosphere cannot yet be precisely identified, some of the necessary conditions can be defined. It was shown that the reaction required the presence of nickel as it did not occur on uncoated whiskers. In addition the nickel particles did not decrease significantly in size during the extension of the side growths, which suggests that the side growths did not contain nickel. Such a conclusion was supported by electron microprobe analysis which indicated the presence of silicon, but not nickel in the side growths. It was previously shown that the nitrogen partial pressure was sufficient to inhibit the formation of silicon nitride. In addition the oxygen partial pressure in the argon ($\sim 10^{-5}$ atm) is greater than that required for equilibrium oxidation of silicon ($\sim 3 \times 10^{-8}$ atm), although this level has been shown to depend critically on kinetic factors [5]. It has also been shown that oxidation of silicon nitride powder can result in an appreciable weight gain ($\sim 1.5\%$/h) [6], which could account for the magnitude of the side growths ($\sim 30\%$ in 17 h). Consequently it seems most likely that the effect is due to the oxidation of the whisker to form silica. The absence of localized depletion of the whiskers further suggests that it is a vapour phase reaction which is catalysed by nickel.

5. Summary

(1) Under vacuum, at temperatures above 900°C the following sequence takes place on nickel-coated silicon nitride whiskers. (a) The initially continuous coating breaks up to form a series of nickel spheroids. (b) The spheroids develop facets (activation energy = 26 kcal/mol). (c) The faceted spheroids wet the whisker surface (activation energy = 74 kcal/mol). (d) At 1100°C the nickel spheroids and silicon nitride whiskers react to form nickel silicide platelets which melt and separate from the whisker.

(2) Under nitrogen, at a temperature of 1100°C, the nickel coated silicon nitride whiskers remain coherent for times up to 17 h due to the high nitrogen partial pressure.

(3) Under argon, at a temperature of 1100°C, side growths develop continuously for times up to 17 h, possibly due to a vapour phase oxidation reaction catalysed by nickel.

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