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# Stability of nickel coated sapphire whiskers

W. BONFIELD, A. J. MARKHAM
*Department of Materials, Queen Mary College, London, UK*

The effect of high temperature annealing (1100 to 1300° C) on the stability of nickel coated "purified" sapphire whiskers has been investigated. It was found that the initially coherent coating spheroidized to form a series of partially adherent nickel particles, which increased in size with continued time at temperature. The time for complete adhesion of the particles, which was established from the product of the number and volume of particles per unit area of surface, decreased from ~72 h at 1100°C to ~3 h at 1300°C, giving an activation energy of ~70 kcal/mol. In addition at 1300° C, after ~8 h, there was evidence for whisker breakdown from a sapphire-nickel reaction.

## 1. Introduction
Previous investigations [1, 2] of the temperature stability of "as-grown" sapphire whiskers have demonstrated that removal of the intrinsic second phase impurity is a necessary prerequisite for the prevention of whisker disintegration at temperatures above 1000° C.

Consequently, in considering sapphire whiskers as a potential reinforcement for a high temperature nickel based composite, attention must be directed exclusively to "purified" rather than "as-grown" whiskers, i.e. to the form capable of withstanding temperature excursions above 1000° C. In this paper the compatibility of individual "purified" sapphire whiskers with an evaporated pure nickel coating is discussed. The structural changes produced by anneals at 1100 to 1300° C for various times were determined and the conditions for adhesion and reaction between nickel and sapphire evaluated.

## 2. Experimental procedure
Sapphire whiskers obtained from Compagnie Thomson Houston (CTH) and Thermokinetic Fibers Inc (TFI) were treated in a 20% HF 20% $H_2SO_4$ solution for 120 h to reduce the impurity concentration to a low level [2] (Table I) and washed in distilled water to remove the reaction product. The "purified" whiskers were coated with a 500 Å thick nickel coating by evaporation in a vacuum chamber. Samples of the nickel-coated whiskers were annealed for various times at 1100, 1200 and 1300° C, in high-purity argon, and were then prepared for electron microscope examination using the "replication-transmission" technique described previously [1].

## 3. Results
A control sample of uncoated "purified" CTH and TFI whiskers did not exhibit any changes of morphology in the temperature range investigated, as demonstrated for example in Fig. 1 (after 17 h at 1300° C).

The nickel coating was deposited as a continuous film, but on heating both types of whiskers at 1100 to 1300° C, the film broke up

TABLE I Semi-quantitative spectrographic analyses of CTH and TFI whiskers.

| Element | CTH | | TFI | |
|---|---|---|---|---|
| | "As-grown" | "Purified" | "As-grown" | "Purified" |
| % | | | | |
| Si | 6 | 0.15 | 0.2 | 0.07 |
| Na + K | 1.7 | — | — | — |
| Ca | 0.2 | 0.01 | 0.01 | 0.02 |
| Fe | 0.12 | 0.35 | 0.01 | 0.07 |
| Mg | 0.15 | 0.06 | 0.01 | 0.04 |

to give a series of spheroidal particles. Fig. 2 shows the structure obtained after an anneal at 1100°C for 2 h. It can be seen that there is a range of particle diameters (average ~0.14 μm) and that many particles are adhering to the whiskers, although it should be emphasized that a greater number had become detached during the replication process. With longer times (4, 8, 17 and 72 h) at 1100°C there was an increase in the size of the particles and a decrease in the average number of adherent particles per unit area of surface, as illustrated in Fig. 3 (after 17 h) and Fig. 4 (after 72 h). It was only after a 72 h anneal that complete adhesion appeared established, as for all shorter times a significant number of particles were removed by replication (as shown in Fig. 5). An alternative, and perhaps more precise, measure of the extent of adhesion is given by the total volume of nickel (the sum of the particle volumes) per unit area of surface, which is represented in Table II as a percentage of the original volume of the nickel coating. It can be seen that this percentage increased with time and approached 100%, i.e. complete adhesion, only after 72 h. Some faceting of the initially spheroidal particles was noted after 8 h, but the effect was not significant until after a 72 h anneal. The results obtained were similar for both CTH and TFI whiskers, as shown in Table II.

An increase in nickel particle size with time for both CTH and TFI whiskers was also noted after anneals at 1200°C for times up to 17 h, but the number of particles per unit area initially increased before exhibiting a progressive decrease (Table II). At any given time the average particle diameter was larger than that measured after an 1100°C anneal, as can be seen by a comparison of Fig. 6 (1200°C/2 h) with Fig. 2 (1100°C/2 h). In addition the time required for faceting and complete adhesion, as observed by replication and also was calculated from the total volume of nickel per unit area of surface, was reduced to ~4 h.

Similar trends to those noted after 1200°C anneals were observed after 1300°C anneals for

TABLE II Variation of nickel particles on sapphire whiskers with time and temperature.

| Whisker type | Temperature (°C) | Time (h) | Average diameter (μm) | No. of particles per unit area ($\mu m^{-2}$) | Total volume of Ni per unit area/ original volume per unit area (%) |
|---|---|---|---|---|---|
| CTH | 1100 | 2 | 0.23 | 2.2 | 25 |
| | | 4 | 0.24 | 3.7 | 50 |
| | | 8 | 0.25 | 5.0 | 75 |
| | | 17 | 0.26 | 3.1 | 52 |
| | | 72 | 0.39 | 1.7 | 105 |
| | 1200 | 2 | 0.25 | 1.7 | 26 |
| | | 4 | 0.28 | 6.0 | 130 |
| | | 8 | 0.41 | 2.4 | 154 |
| | | 17 | 0.35 | 1.2 | 150 |
| | 1300 | 2 | 0.40 | 1.5 | 92 |
| | | 4 | 0.39 | 2.3 | 142 |
| | | 8 | 0.81 | 0.21 | 102 |
| | | 17 | 1.14 | 0.36 | 540 |
| TFI | 1100 | 2 | 0.14 | 7.0 | 21 |
| | | 4 | 0.21 | 3.7 | 30 |
| | | 8 | 0.20 | 4.9 | 40 |
| | | 17 | 0.30 | 2.7 | 74 |
| | | 72 | 0.43 | 1.3 | 98 |
| | 1200 | 2 | 0.21 | 4.0 | 33 |
| | | 4 | 0.24 | 7.6 | 101 |
| | | 8 | 0.41 | 1.8 | 113 |
| | | 17 | 0.46 | 1.0 | 98 |
| | 1300 | 2 | 0.33 | 1.4 | 52 |
| | | 4 | 0.36 | 2.7 | 126 |
| | | 8 | 1.10 | 0.22 | 290 |
| | | 17 | 1.20 | 0.64 | 1100 |


*Figure 1* Uncoated sapphire whiskers after 17 h at 1300° C.

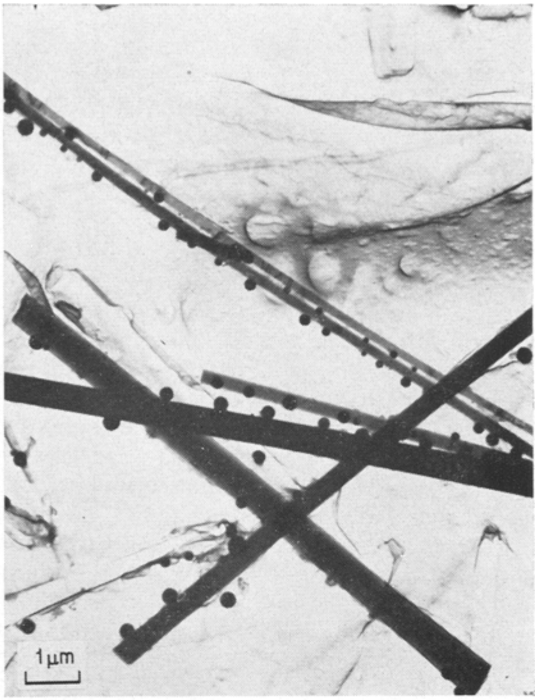



*Figure 3* Nickel particles and sapphire whiskers after 17 h at 1100° C.

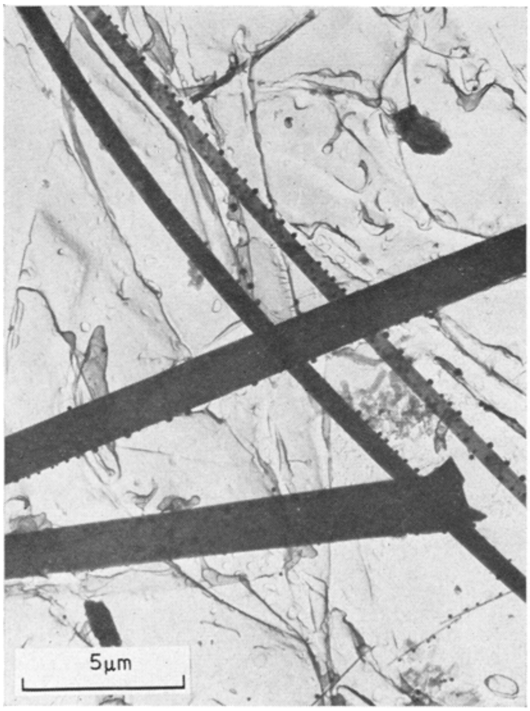



*Figure 2* Spheroidized nickel particles on sapphire whiskers after 2 h at 1100° C.

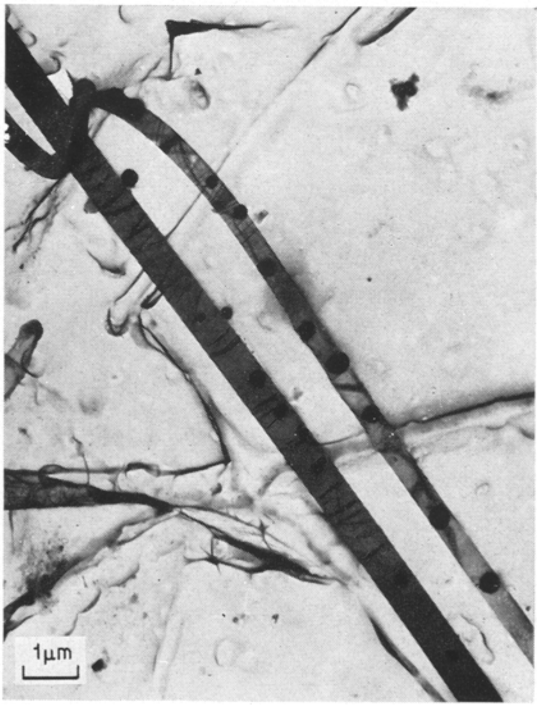



*Figure 4* Nickel particles and sapphire whiskers after 72 h at 1100° C.

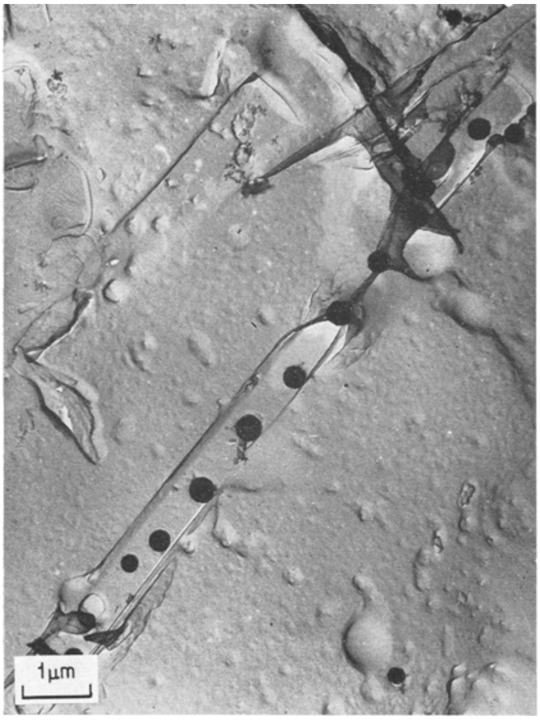



*Figure 5* Nickel particles detached by replication after 17 h at 1100° C.


*Figure 6* Nickel particles and sapphire whiskers after 2 h at 1200° C.

times up to 4 h and complete adhesion was established after ~3 h. However, after longer times the particles became considerably larger, as is shown by a comparison of Fig. 7 (1300° C/2 h) with Fig. 8 (1300° C/17 h). After 8 to 17 h the particles appeared adherent to the whisker surface as shown by the replica in Fig. 8, but there was also evidence, both for the initiation of whisker breakdown in the vicinity of the particles (Figs. 9 and 10), and for whisker debris (Figs. 11 and 12). The total volume of nickel measured on the remaining coherent whiskers, after anneals which gave whisker breakdown, increased to levels greatly in excess of that expected from the original coating alone (Table II). This effect appeared to occur after a shorter time and to be more extensive on the TFI whiskers than on the CTH whiskers.

## 4. Discussion

At the temperatures investigated in the interval 1100 to 1300° C the initially coherent nickel coating spheroidized to form a series of discrete nickel particles. With continued time at temperature there were changes in the total volume of nickel per unit area of surface and the size, number and shape of the particles. The implications of these changes are considered in turn.

### 4.1. Total volume of nickel per unit area of surface

The replication technique used in the preparation of the annealed whiskers for microscopic examination, provided an effective test of the interfacial adhesive bond of the nickel particles to the sapphire whisker. It was observed that the proportion of detached particles decreased progressively with continued time at 1100 to 1300° C. The extent of adhesion was also assessed by relating the total volume of nickel per unit area at any given time to the original volume per unit area. These combined approaches indicated that times of ~72, 4 and 3 h were required at 1100, 1200 and 1300° C, respectively for 100% adhesion of the nickel particles to the sapphire whisker. Substituting in the rate equation:

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

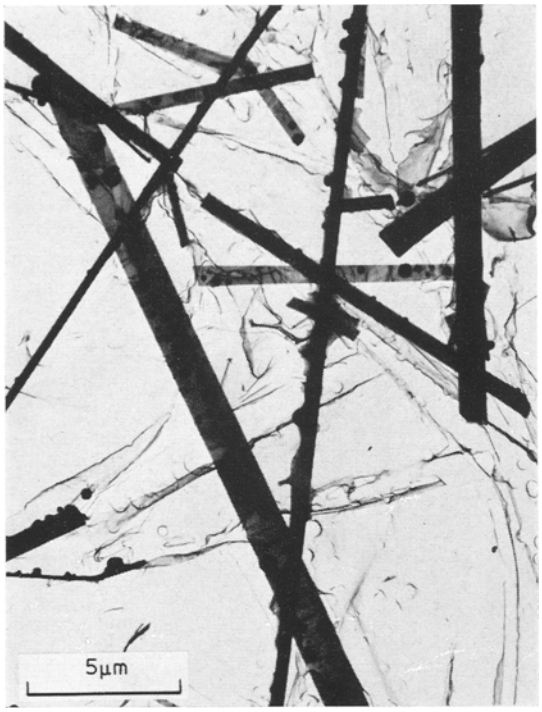



*Figure 7* Nickel particles and sapphire whiskers after 2 h at 1300° C.

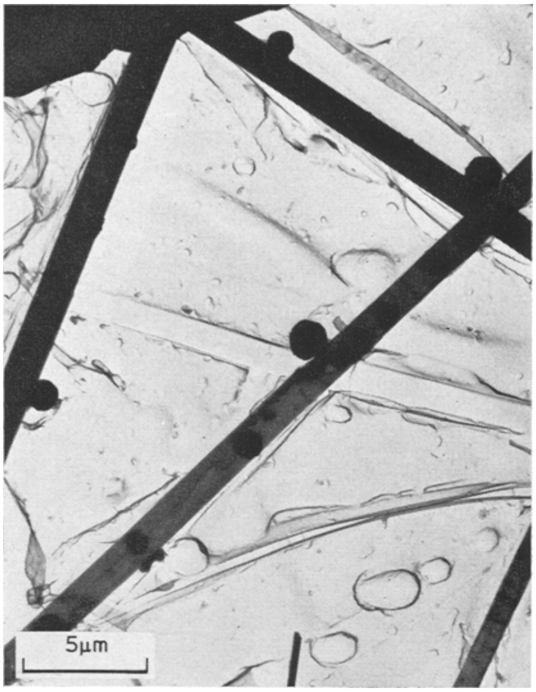



*Figure 9* Whisker pitting on TFI sapphire whiskers after 17 h at 1300° C.

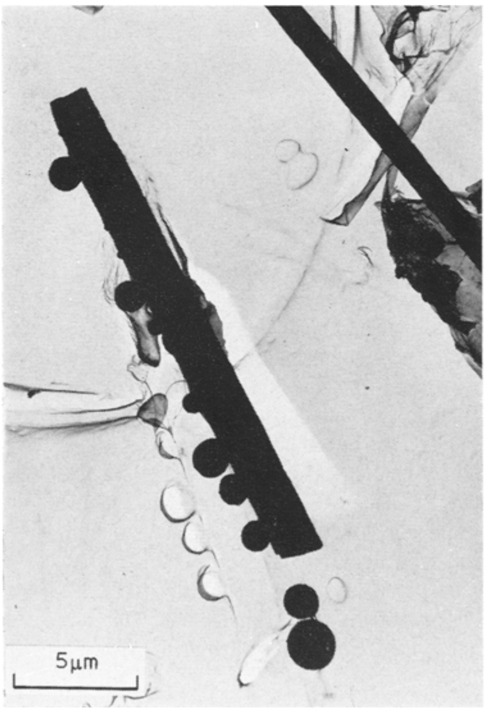



*Figure 8* Nickel particles and sapphire whiskers after 17 h at 1300° C.

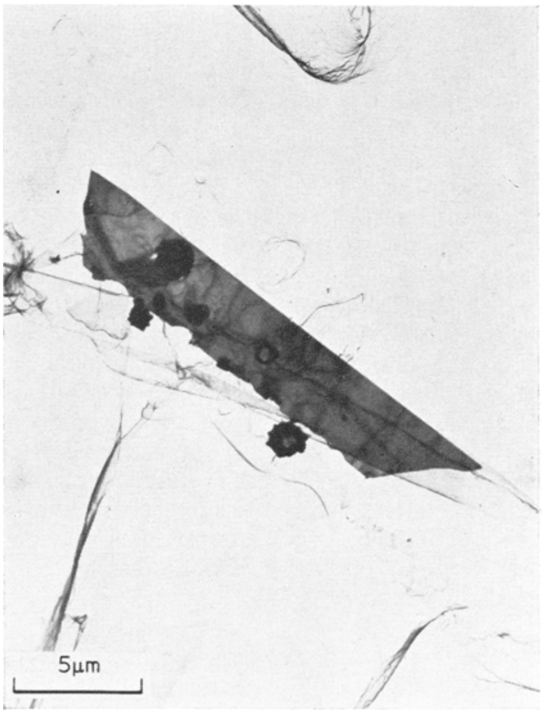
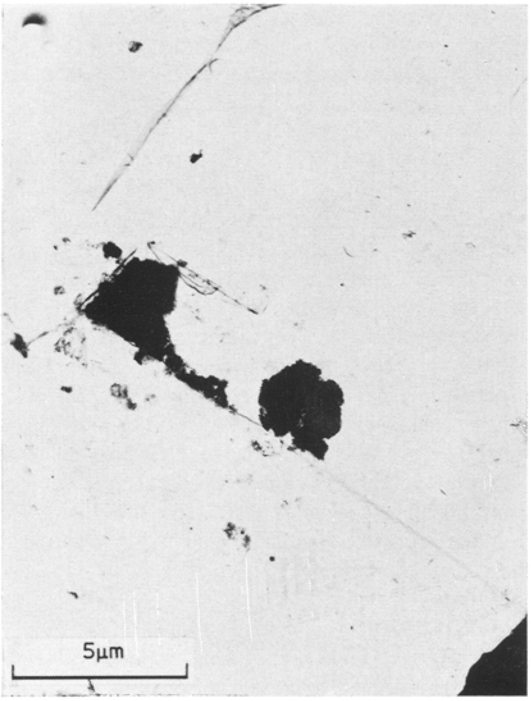
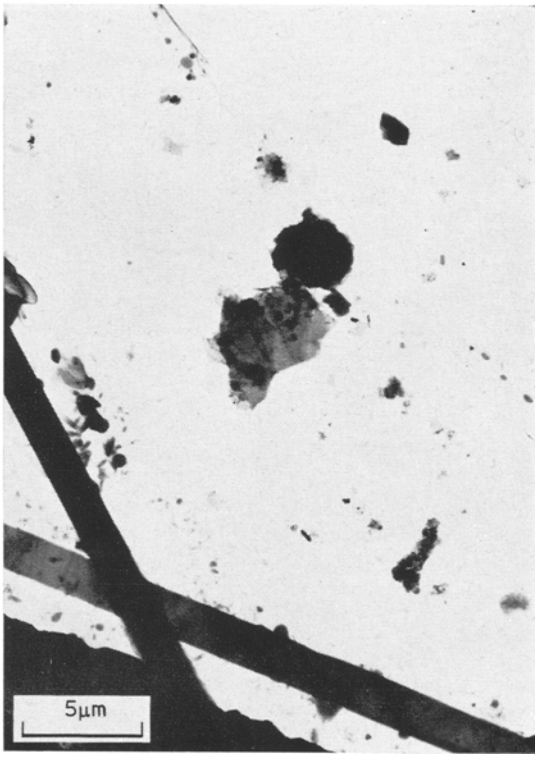



*Figure 10* Nickel sapphire reaction on CTH sapphire whiskers after 8 h at 1300° C.




*Figures 11 and 12* Whisker debris after 17 h at 1300°C.

in which $t$ represents time, $K$ a pre-exponential constant, $R$ the gas constant and $T$ absolute temperature, an approximate activation energy ($Q$) for adhesion of 70 kcal/mol is obtained. This value may be compared with activation energies of 74 and 110 kcal/mol derived for the diffusion of nickel into silicon nitride whiskers [3] and carbon fibres [4], respectively, under similar experimental conditions.

When 100% adhesion of the nickel particles is achieved, it would be expected that continued annealing would not significantly alter the total volume of nickel per unit area of surface. Within experimental scatter, this appears to be the situation at 1200°C (Table II). However, at 1300°C, the total volume of nickel per unit area after 17 h had increased to 5 to 10 times the level expected on the basis of the original coating thickness. An explanation for this effect from the microscopic evidence of whisker pitting and debris, could be that some of the whiskers had disintegrated due to a sapphire-nickel reaction and hence created an additional source of "nickel" for the remaining coherent whiskers, although further experiments are required to establish the nature of the reaction product.

### 4.2. Particle size

At 1100, 1200 and 1300°C the nickel particles increased in diameter ($d$) with time ($t$) at temperature. It is useful to examine the variation of $\bar{d}$ with $t$ at the various temperatures, although the experimental scatter precludes an accurate evaluation. A plot of log $\bar{d}$ versus log $t$ at 1200°C (Fig. 13), for the times from 4 to 17 h when all the particles adhered to the whiskers, gave an average slope (by the least squares method) $m \sim 0.34$, which is in reasonable agreement with the $(\bar{d})^3 \propto t$ relationship predicted for particle coarsening by a volume diffusion mechanism [5].

At 1100°C a smaller slope, $m \sim 0.26$, which does not agree with the $(\bar{d})^3 \propto t$ relationship, was obtained, but these results were complicated by the variable number of particles detached at each time investigated. As it appeared that the size of the detached particles was generally smaller than that of the adherent particles

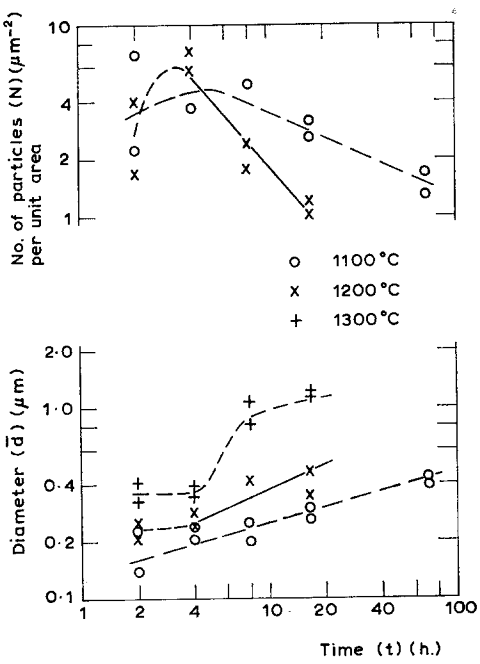



*Figure 13* Variation of nickel particle size and number on sapphire whiskers with time.

(Figs. 2 and 3), the measured diameter is probably not representative of that of all the particles. If the detached particles could be included in the results, their effect would be greatest at the shorter times (see Table II) and the net effect would be to increase the value of $m$.

At 1300° C there was no systematic variation between log $\bar{d}$ and log $t$ (Fig. 13) which is consistent with the observed onset of a nickel-sapphire reaction.

### 4.3. Particle number

It was shown in the previous section that at 1100° C, the average diameter of the adherent particles was probably not representative of that of all the particles (i.e. adherent and detached particles). Clearly, in addition, the number of adherent particles per unit area ($N$) measured at any given time prior to complete adhesion cannot be related to that at any other time due to the variation in the total volume of nickel. This is demonstrated by a plot of log $N$ versus log $t$ (Fig. 13), the slope of which does not correspond to the $N \propto t^{-1}$ relationship predicted by the volume diffusion particle coarsening model [5]. The only results which can be used to test this relationship are those measured at 1200° C for times >4 h, when the particles were adherent, and no reaction had occurred. These values give an approximate slope of $-1$ when plotted as log $N$ versus log $t$ (Fig. 13) and provide additional evidence for a volume diffusion process of particle coarsening at this temperature.

### 4.4. Particle shape

The times required for faceting of the nickel particles were considerably longer than those measured at the same temperature for nickel faceting on silicon nitride whiskers [4] (e.g. 8 h at 1100° C cf. 10 min at 1100° C). However, the present results were obtained on particles (and whiskers) 5 to 10 times larger in diameter and substitution in the rate equation (Equation 1) suggests an approximately similar activation energy for the initiation of faceting to that measured on silicon nitride (26 kcal/mol). Hence this finding is consistent with the conclusion [4] that faceting is a result of self diffusion within the nickel particles.

## 5. Conclusions

(1) A 500 Å thick nickel coating on CTH and TFI sapphire whiskers spheroidizes during anneals at 1100 to 1300° C in high purity argon.
(2) Complete adhesion between the nickel particles and the sapphire whiskers is developed after 72, 4 and 3 h at 1100, 1200 and 1300° C, respectively, which gives an activation energy of ~70 kcal/mol.
(3) Particle coarsening is noted at 1100, 1200 and 1300° C and can be related to a volume diffusion mechanism at 1200° C.
(4) Whisker breakdown occurs after 8 to 17 h at 1300° C and is attributable to a nickel-sapphire reaction.

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