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Compatibility limits in sapphire whisker-nickel composites

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The effects of anneals at 1200 to 1300° C on the compatibility of sapphire whiskers coated with nickel, with the coatings ranging from 20 to 320 nm in thickness, have been investigated.

It was found that at 1200° C, all the coatings, which were initially continuous, spheroidized to form a series of adherent particles. The particles coarsened with continued time at temperature, but the whiskers remained coherent. In contrast, at 1300° C, most of the whiskers degraded after anneals > 2 h, an event which was preceded by a transition in the wetting characteristics of the particles and hole formation in some whiskers. The whisker breakdown was correlated with the diffusion of iron impurity into the nickel particles.

1. Introduction

In a previous investigation [1], it was demonstrated that, provided the impurity concentration is maintained at a low level, individual sapphire whiskers are compatible with a 50 nm thick nickel coating at temperatures up to 1200° C. At higher temperatures ($\geqslant$ 1300° C) a reaction occurs between sapphire and nickel, which leads ultimately to whisker degradation. The significance of these events is in suggesting a possible fabrication procedure for a sapphire whisker-nickel matrix composite; i.e. utilizing a controlled exposure at 1300° C to form a chemical bond, followed by operation at a temperature (< 1200° C) at which the reaction does not proceed. Clearly such a method demands a precise knowledge of the reaction kinetics and one attendant difficulty is the interpretation of the data for the 50 nm thick nickel coating in terms of the greater "coating" thickness in an actual composite. Consequently a study has been made of the compatibility of individual purified sapphire whiskers with evaporated nickel coatings of various thicknesses (from 20 to 320 nm). The structural changes produced by anneals at 1200 and 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 series of nickel coatings (20, 80, 160 and 320 nm) by evaporation in a vacuum chamber. Samples of the nickel coated whiskers were annealed at 1200 and 1300° C for 2 to 17 h, in high purity argon, and were then prepared for electron microscope and microprobe examination using the "replication-transmission" technique described previously [3].

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

Element (%)	CTH	TFI
Si	0.15	0.07
Ca	0.01	0.02
Fe	0.35	0.07
Mg	0.06	0.04

3. Results

3.1. Anneals at 1200° C

On both TFI and CTH whiskers, all the nickel coatings investigated (20, 80, 160 and 320 nm) broke up after anneals at 1200° C to form a series of spheroidal particles. As shown in the example in Fig. 1, most of the particles adhered

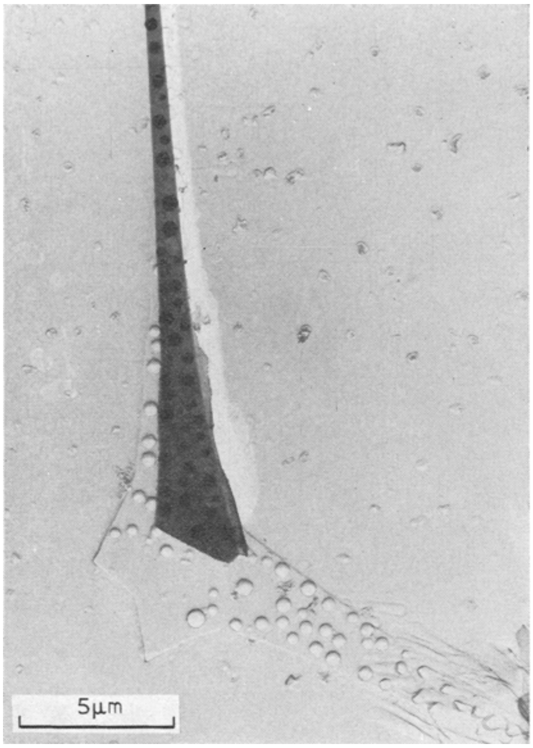


Figure 1 Nickel particles on a TFI whisker after 2 h at 1200° C (initial coating 80 nm).

to the whisker and were not detached by the replication procedure. In general, for any given initial coating thickness, the particles increased in diameter (and decreased in number) with time at temperature. Alternatively, at any given time, the particle size increased as the initial coating thickness was increased. These results are summarized in Table II.

The larger particles tended to develop facets and a greater area of contact, as shown in Fig. 2. However, there was no evidence for nickel wetting the whisker surface, as the angle of contact was consistently $> 90°$.

In addition to the generally spheroidal shape, some particles developed an elongated profile with the long axis perpendicular to the whisker axis (Fig. 3). These particles, in contrast to the spheroidal particles, frequently became detached during replication.

Two other effects noted exclusively on CTH whiskers were the formation of irregular particles (Fig. 4) and the occasional presence of possible reaction rings outlining the positions

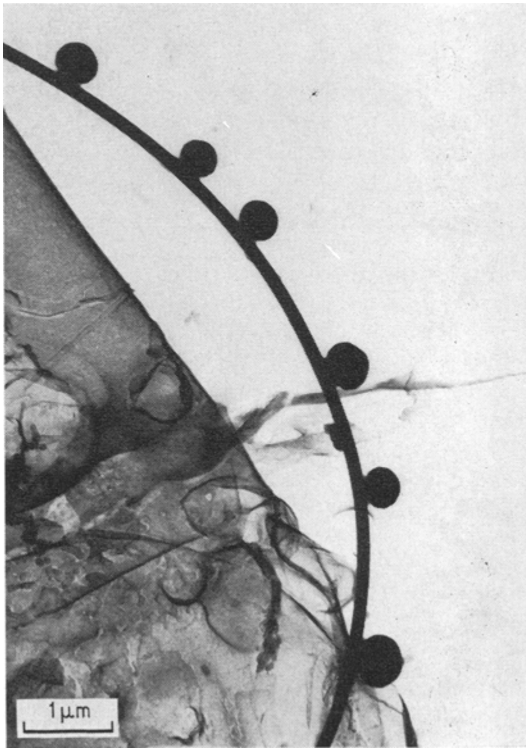


Figure 2 Faceted nickel particles on a TFI whisker after 4 h at 1200° C (initial coating 320 nm).

TABLE II The variation of average Ni particle diameter ($\bar{d}$) with time (t) at 1200°C

Whisker type	Original Ni coating thickness (d_0) (μm)	Average diameter ($\bar{d}$) (μm)			($\bar{d} - d_0$) (μm)		
		After 2 h	After 4 h	After 17 h	After 2 h	After 4 h	After 17 h
TFI	0.02	0.23	0.31	0.36	0.21	0.29	0.34
CTH	0.02	0.20	0.37	0.42	0.18	0.35	0.40
TFI	0.08	0.33	0.35	0.40	0.25	0.27	0.32
CTH	0.08	0.30	—	0.81	0.22	—	0.73
TFI	0.16	0.47	0.60	0.71	0.31	0.44	0.55
CTH	0.16	0.56	0.68	—	0.40	0.52	—
TFI	0.32	0.55	0.70	1.2	0.22	0.38	0.88
CTH	0.32	—	0.72	1.0	—	0.40	0.68

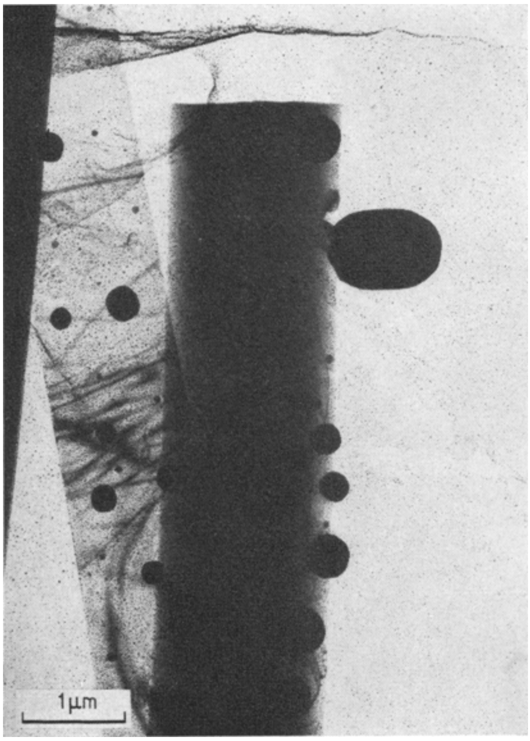


Figure 3 Elongated nickel particle on a CTH whisker after 17 h at 1200° C (initial coating 160 nm).

occupied on the whisker by detached particles (Fig. 5).

3.2. Anneals at 1300° C

Anneals at 1300°C produced some whisker fragmentation and degradation of nickel-coated TFI and CTH whiskers, for all the conditions investigated, as demonstrated in Fig. 6. The number of completely degraded whiskers increased with time at temperature and with an increase in the initial nickel coating thickness. Estimates of the percentage of whiskers degraded were $< 50\%$ for the 2 h (all coatings) anneals, $> 50\%$ for the 4 h (all coatings) and 17 h (20 and 80 nm coatings) anneals and $\sim 95\%$ for the 17 h (160 and 320 nm coatings) anneals. Accompanying this disintegration on both types of whisker was a change in the wetting characteristics from a non-wetting (contact angle $> 90°$) to a wetting (contact angle $< 90°$) situation, as illustrated in Figs. 7 and 8. It should be noted that all the non-wetting particles observed after 1300°C anneals were adherent to the whiskers. During the transition in wetting characteristics, some examples of an interfacial structure between the particles and whisker were noted (Fig. 9).

On both TFI and CTH whiskers surface pits adjacent to some particles were formed. In addition, for the 160 and 320 nm coatings on CTH whiskers complete holes were noted after anneals at > 2 h, which were either associated with a particle (Fig. 10) or reflected the outline of a particle (Fig. 11).

3.3. Microprobe analysis after 1200 and 1300° C anneals

It was established that electron beam microprobe analysis was effective as a means of monitoring the presence of Ni (in the coating or particle) or Al (in the whisker) for the size range investigated. However, calibration experiments on non-heat-treated specimens with continuous nickel coatings, revealed that the ratio of the Ni to Al signal peaks was sensitively dependent on the thickness of the nickel layer (Table III). Consequently an interpretation of the Ni/Al ratio, to assess any changes in the particle composition with time at temperature, was in general complicated by the corresponding changes in the particle diameter. An exception to this was provided when the particles were observed in

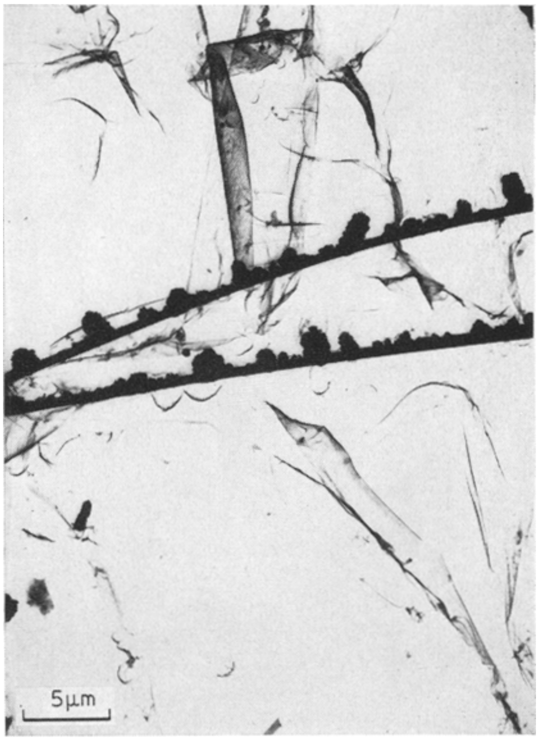


Figure 4 Irregular nickel particles on CTH whiskers after 17 h at 1200° C (initial coating 80 nm).

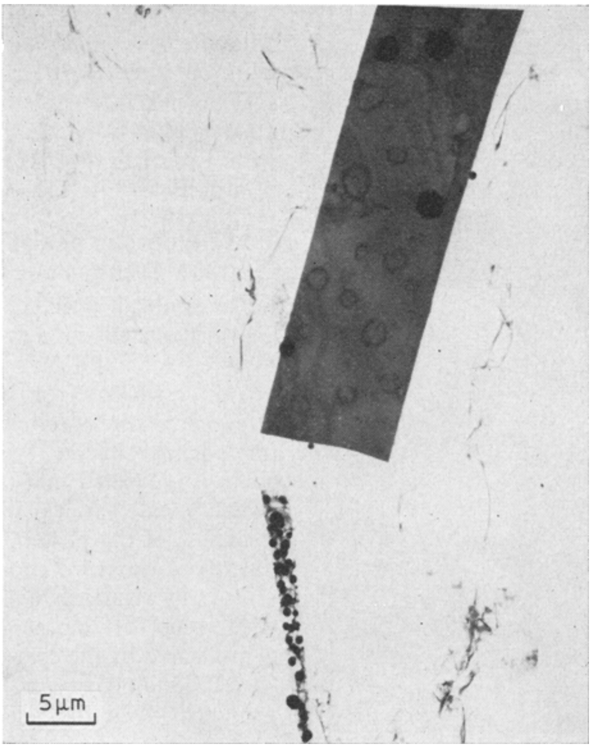


Figure 5 Possible "reaction rings" on CTH whiskers after 4 h at 1200° C (initial coating 320 nm).

TABLE III Effect of coating thickness on the Ni/Al signal ratio

Coating thickness (nm)	Ni/Al signal ratio
20	0.24
80	0.62
160	1.12
320	2.35

profile on the "side" of the whisker (e.g. Fig. 2). In this case for particles of diameter $\geqslant 0.5$ μm, the particle size is sufficient to preclude an aluminium signal due to secondary electrons scattered from the adjacent sapphire substrate. Consequently, any diffusion of aluminium into the nickel particle could be assessed. In fact, using this technique, it was not possible to detect the presence of aluminium in the nickel particles for any of the experimental conditions investigated. Similar experiments were performed for the major impurity elements (Si and Fe) present in the sapphire whiskers. No diffusion of Si into

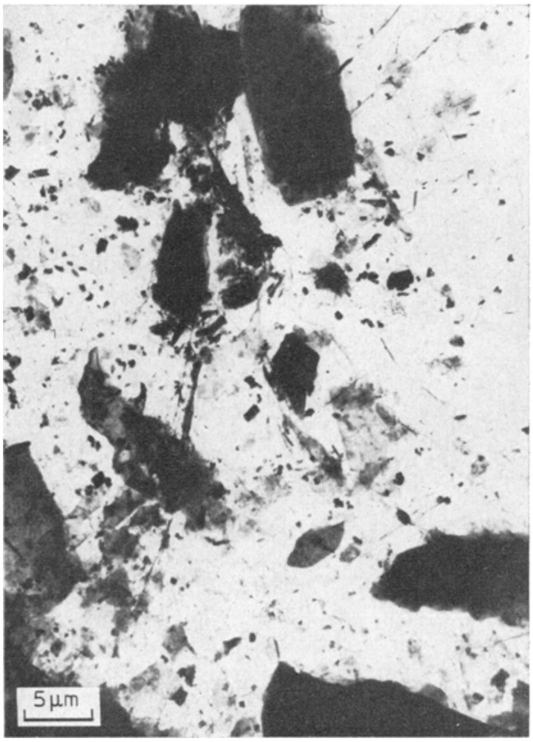


Figure 6 Fragmented and degraded TFI whiskers after 17 h at 1300° C (initial coating 20 nm).

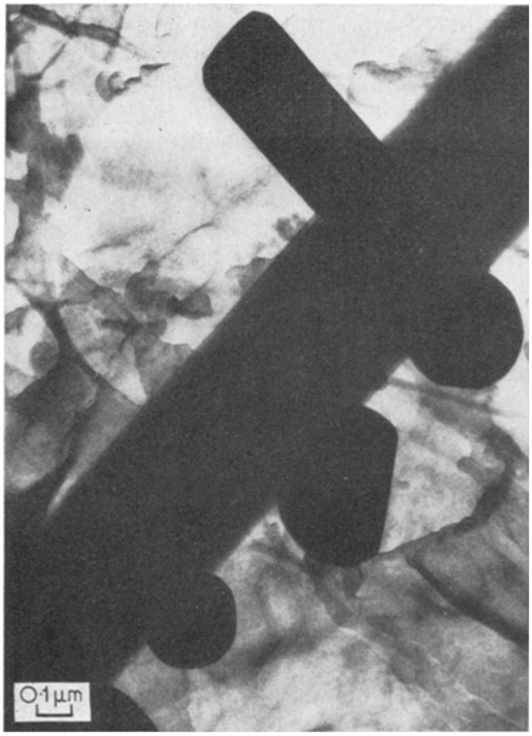


Figure 7 Non-wetting particles on a TFI whisker after 2 h at 1300° C (initial coating 80 nm).

the particles was detected. However, it was established that, first, iron diffused into the nickel particles (Fig. 12) and second, that the concentration increased with time (Table IV). For any given time, the concentration of iron in the particles on the CTH whiskers was always greater than that in the particles on the TFI whiskers (Table IV).

4. Discussion

At 1200° C all the nickel coating investigated (20 to 320 nm) spheroidized on both CTH and TFI sapphire whiskers to form a series of discrete nickel particles, the average diameter ($\bar{d}$) of which increased with time (t) at temperature. At any given time the particle diameter increased with an increase in the initial coating thickness. However, if the initial coating thickness is considered

TABLE IV Variation of Fe/Ni signal ratio at 1300° C

Type of whisker	Time at 1300° C (h)	Fe/Ni signal ratio
CTH (320 nm coating)	2	0.14
CTH (320 nm coating)	17	0.28 to 0.37
TFI (320 nm coating)	17	0.10

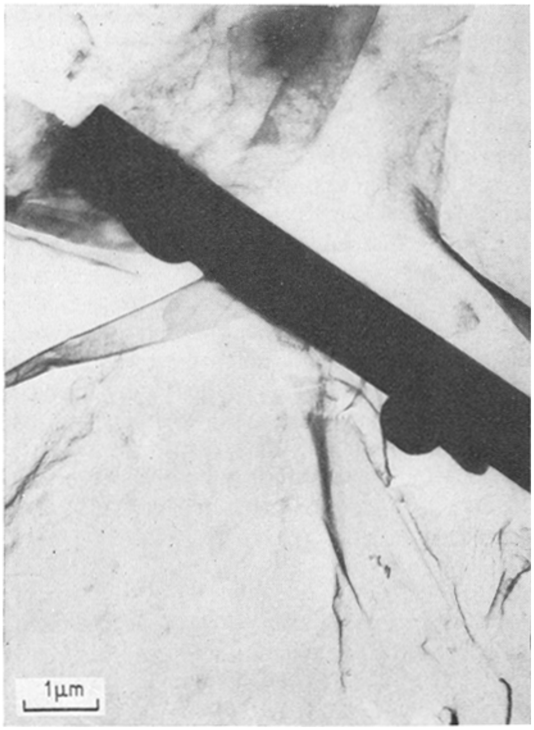


Figure 8 A non-wetting and wetting particle on a TFI whisker after 17 h at 1300° C (initial coating 320 nm).

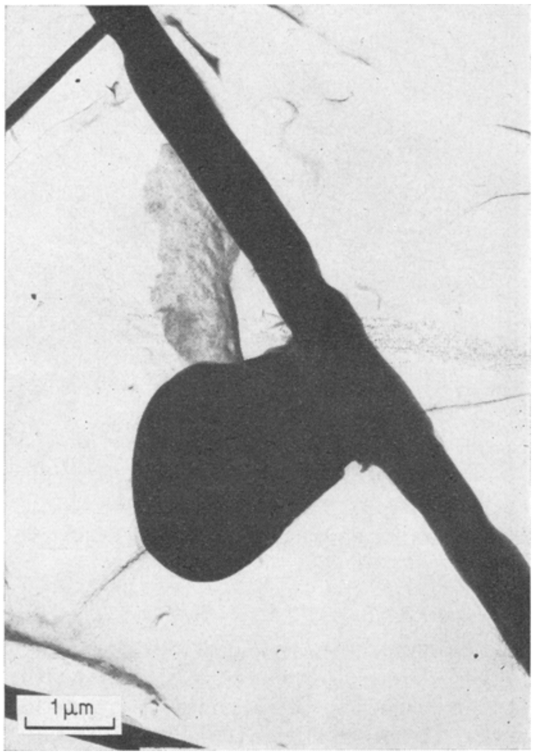


Figure 9 A possible interfacial structure formed on a TFI whisker after 17 h at 1300° C (initial coating 160 nm).

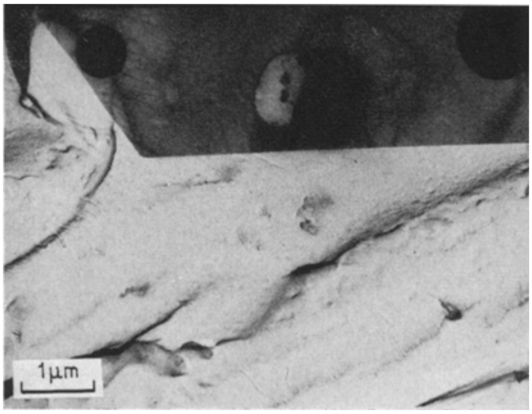


Figure 10 A hole in a CTH whisker, associated with a particle, after 4 h at 1300° C (initial coating 320 nm).

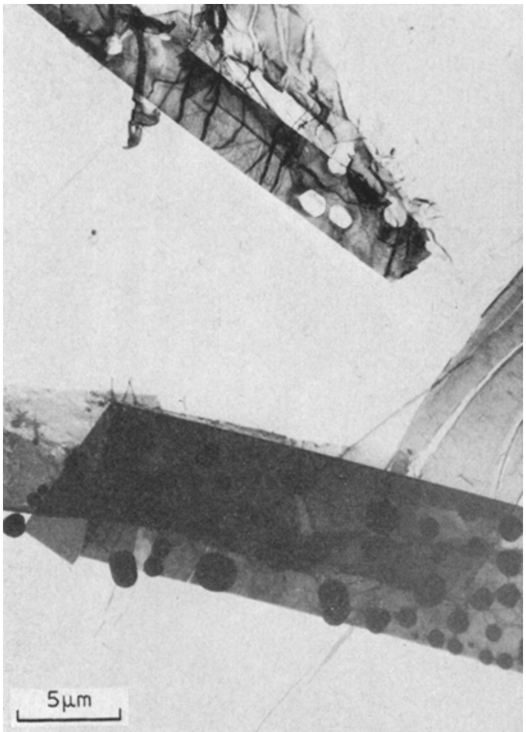


Figure 11 Holes in a CTH whisker compared with nickel particles on an adjacent whisker after 2 h at 1300° C (initial coating 320 nm).

as the initial diameter (d_0), it can be seen from Fig. 13 that a plot of ($\bar{d} - d_0$) versus t gives a similar result for all the initial coating thicknesses. Hence, it is concluded that the rate of particle coarsening is independent of the initial coating thickness. It also appears from Fig. 13 that the slope (m) is in reasonable agreement with the value $m = 0.33$ predicted for particle coarsening by a volume diffusion mechanism [4].

It is significant to note that all the various sized particles adhered to the whiskers, as the largest diameter ($\sim$ 1.2 μm) observed is comparable to the inter-whisker spacing in a composite. This result demonstrates that the adhesion between particle and whisker, even for the large particles, is sufficiently strong to withstand the interfacial stress generated by the differential contraction of nickel and sapphire on cooling from 1200° C to room temperature. Such evidence appears contrary to the recent suggestion [5] that there is an absence of "mechanical" bonding between sapphire whiskers and nickel at temperatures $> 700°$ C.

It appears that adhesion is developed in two stages. The continuous film spheroidizes to form discrete particles, which suggests that initially there is no adhesion between the coating and whisker, whereas subsequently the particles adhere firmly to the surface. As evidence for iron diffusion was obtained by electron microprobe analysis of the particles, such a transition could be attributed to the time required for the diffusion of iron from the sapphire whisker into the nickel. It appears that adhesion develops initially at the periphery of the particle, in a similar manner to that observed for metal sessile drops on sapphire plaques [6]. This effect probably accounts for the tendency of some particles to elongate perpendicularly to the whisker axis.

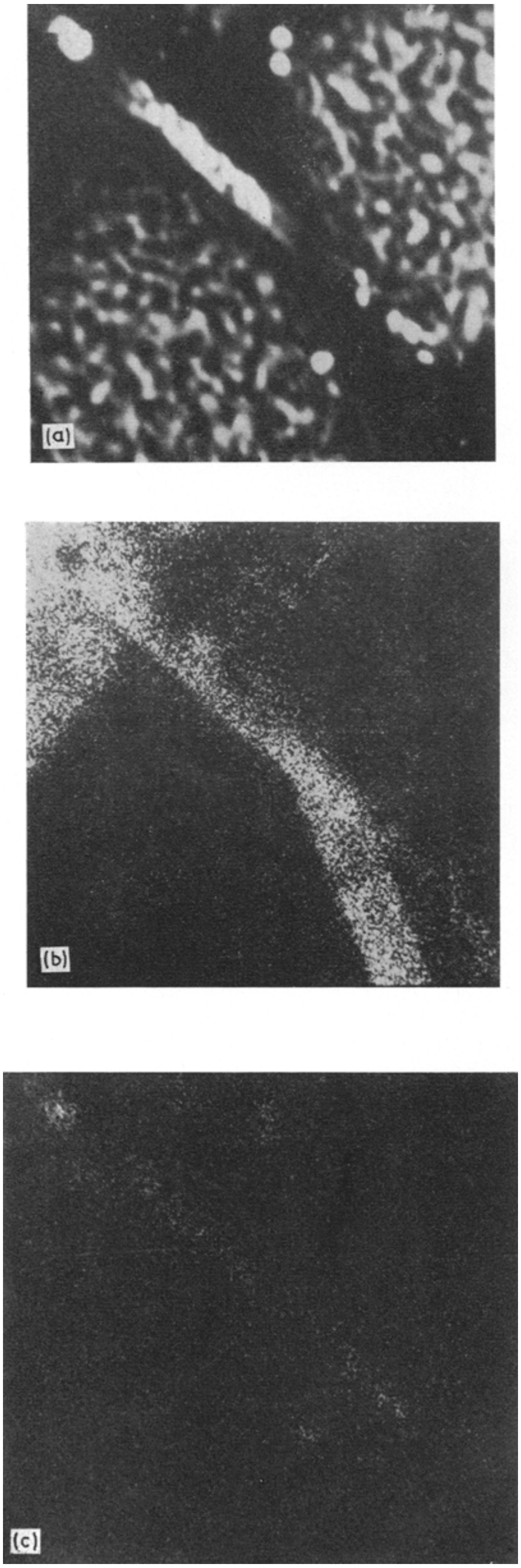
At 1300° C the results divided into two groups, namely, first, for 2 h anneals most of the whiskers remained coherent, and second, for > 2 h anneals, most of the whiskers were degraded. After the longer anneals at 1300° C, it was noted that some particles wetted the whiskers and that some pits and hole were created. These effects can be additive as the formation of a reaction ring or pits at the periphery of the particles promotes wetting of the whiskers by a modification of the equilibrium of the interfacial tensions [6]. Before reaction, the interfacial tensions (Fig. 14) are given by:

$$\gamma_A = \gamma_B \cos\theta + \gamma_C \,. \qquad (1)$$

However, after reaction γ_C is deflected downwards by some angle α, so that

$$\gamma_A > \gamma_B \cos\theta + \gamma_C \cos\alpha \,. \qquad (2)$$

Hence, the drop will spread outwards until equilibrium is restored, with the situation



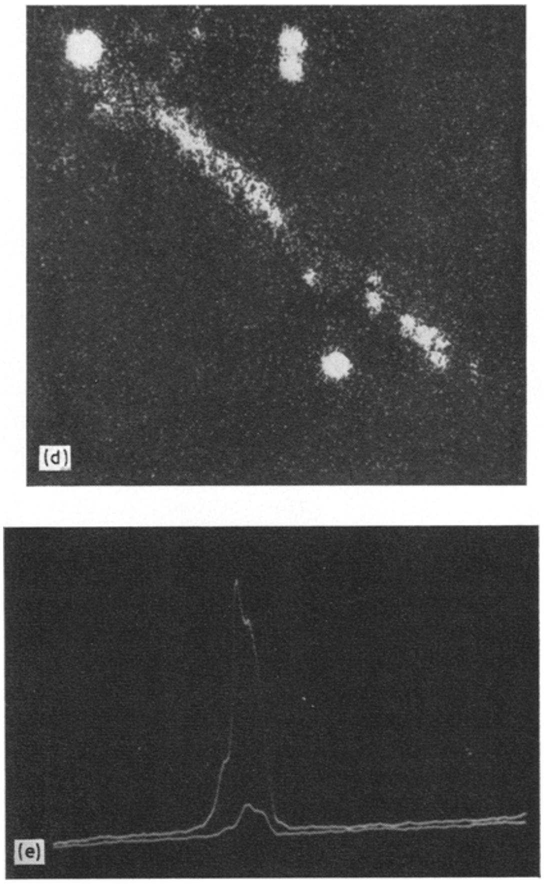


Figure 12 Electron microprobe analysis of nickel particles on CTH whiskers (initial coating 320 nm) after 2 h at 1300° C. (a) Optical, (b) Al signal, (c) Fe signal, (d) Ni signal, (e) Ni/Fe ratio.

recurring as the reaction proceeds.

Although the absence of detailed thermodynamic data precludes a quantitative description of the process responsible for whisker degradation at 1300° C, the present results allow an evaluation of the possible mechanism. Clearly, the melting of pure nickel particles (melting point 1453° C) is not responsible for this process. Equally, the presence of iron in the particles in concentrations up to 25%, which only depresses the melting point of nickel by ~ 20° C, does not produce particle melting at 1300° C. It has been suggested previously [7] that a spinel $NiAl_2O_4$ is formed at temperatures above 1100° C. Such a reaction requires initially the oxidation of Ni to NiO, but the oxygen partial pressure in the argon atmosphere is sufficient for this purpose. However, the alumina spinel reaction has been shown

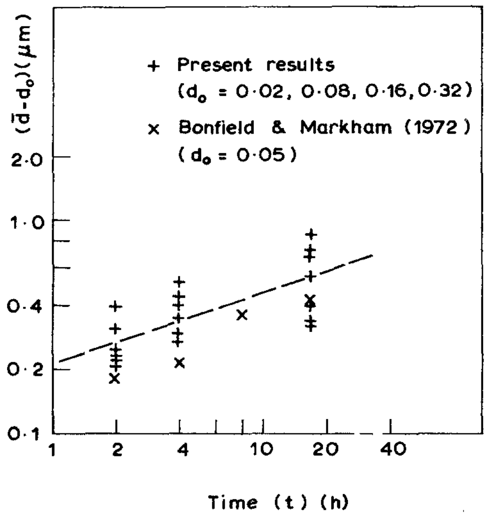


Figure 13 The variation of $(\bar{d} - d_0)$ with time, compared with previous measurements and a slope of $m = 0.33$ (dotted line).

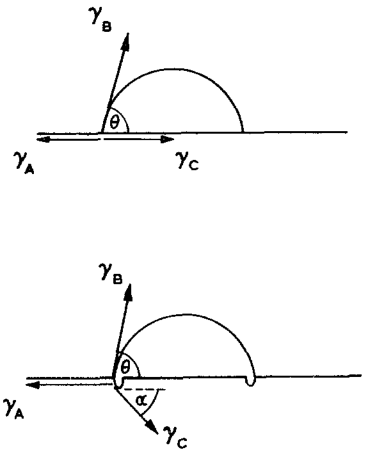


Figure 14 Schematic diagram of interfacial tensions before and after reaction.

[8] to proceed at a negligible rate at 1200°C (with no measurable spinel formation after 400h). In addition this reaction alone cannot account for the present results in which, first, aluminium was not detected in the nickel particles and, second, there was a difference in the rate of breakdown between the CTH and TFI whiskers. Therefore, it is suggested the diffusion of iron into the nickel particle is responsible for these additional effects. Although the formation of $FeAl_2O_4$ is possible, the most likely reaction product is $NiFe_2O_4$ which has been shown [9] to form rapidly on FeNi alloys above 600°C. Further work is required to establish the details of the degradation reaction products, but clearly iron impurity in the whiskers contributes significantly to the compatibility limit.

5. Conclusions

1. 20 to 320 nm nickel coatings on CTH and TFI sapphire spheroidize during anneals at 1200°C, but the whiskers remain coherent. The particles formed adhere to the whiskers and increase in size with time at temperature, with the rate of coarsening similar to that predicted by a volume diffusion mechanism.
2. Anneals at 1300°C for times > 2 h degrade most of the sapphire whiskers. The degradation is associated with the diffusion of iron impurity into the nickel particles.

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