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The stability of sapphire whiskers in nickel at elevated temperatures

Part 1 *General morphological and chemical stability*

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Composites of 1 to 20 vol % sapphire whiskers contained in a nickel matrix were produced by roll-bonding and by hot-pressing. The composites were examined using transmission electron microscopy, X-ray and electron diffraction, optical microscopy and mass spectrographic analysis. Composites were annealed in vacuum (1.3×10^{-3} N m^{-2}), in low-pressure air (13.3 N m^{-2}) and in dried hydrogen (101.3 N m^{-2}) in the temperature range 1100 to 1400° C for times up to 3800 h. Whiskers *in situ* and the whisker/matrix interface were observed by transmission electron microscopy; matrix dislocations were associated with whiskers and were stable after annealing at 1400° C. Whiskers extracted from annealed composites showed significant morphological changes. These were attributed to: (i) ovulation from the tips of whiskers by interfacial diffusion, (ii) waisting from surface undulations, (iii) Ostwald ripening and (iv) constant-volume shape changes.

1. Introduction

Considerable benefits to the power and efficiency of gas turbine engines would result from the use of turbine blades with improved strength and/or peak operating temperature. A nickel-based matrix unidirectionally reinforced with high strength fibres, such as sapphire whiskers, can in theory [1] develop creep-rupture properties well in excess of the minimum improvement sought [2] over existing materials. However, for the theoretical properties to be achieved and maintained during service the aspect ratio (length, l: diameter, d) of the reinforcement must remain in excess of a critical value (l_c/d). Physical processes that could lead to the degeneration of sapphire whiskers and a decrease in the aspect ratio include tip ovulation and waisting [3, 4], Ostwald ripening [5] and constant volume changes [6]. A decisive factor causing these changes is the difference in interfacial energy per unit volume between a whisker and an equiaxed particle of approximately the same diameter. Some approximate values for the interfacial energy of sapphire whiskers in nickel are derived in the present work.

Chemical processes which could decrease the aspect ratio of sapphire whiskers at elevated temperatures in nickel are spinel (nickel aluminate) formation, metastable phase formation, and reactions with impurities or intentional alloying additions in the nickel matrix.

Spinel formation has been observed [7] under oxidizing but not under reducing conditions. Formation of the spinel, $NiO.Al_2O_3$ in a nickel-alumina mixture requires the presence of oxygen. The main points of the phase equilibria of the nickel oxide-alumina system are as follows: (i) limited solid solution (less than 1 mol %) of $NiO.Al_2O_3$ into NiO at 1800° C, and reprecipitation during quenching to room temperature [8]; (ii) no solubility of NiO into the spinel at any temperature, and vanishingly small solubility of alumina into the spinel at temperatures below 1100° C. The spinel becomes non-stoichiometric at higher temperatures, containing 51 to 56 mol % alumina over the range 1100 to 1400° C [9]; (iii) limited solid solution of $NiO.Al_2O_3$ into alumina at 1400° C [10]; (iv) the liquidus curve shows a congruent melting maximum at the spinel composition and approximately 2020° C, with a minimum at about 1890° C and 8 mol % alumina, [11]; (v) a metastable phase, designated

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ϕ, of composition 11 Al_2O_3.NiO can be precipitated from non-stoichiometric spinel under certain conditions, e.g., by supersaturating the spinel with alumina at 1400°C or above, then annealing at a lower temperature, e.g., for 5 days at 1000°C, [9]. The phase decomposes at temperatures above 1200°C into spinel and α-alumina, and can no longer be regenerated by subsequent heating at 1000°C.

Some of the parameters governing the stability of ceramic whiskers in metal matrices have been shown [12] to be the solubility and diffusivity of the major components and any impurities in both phases, and the free energy of formation of potential reaction products. The data available on these parameters are especially incomplete for alumina. For example, only data on oxygen [13], aluminium [14] and iron [15] diffusion in alumina are known to the authors. The assumption that compatibility is assured so long as the ceramic reinforcement is chemically more stable than any known matrix compound has been demonstrated to be not always true [12]. A low solubility of a particular element in either of the two phases in the system may signify an early formation of a layer of the next phase out in the equilibrium diagram. An enhanced diffusivity of a particular species can also lead to instability [12], e.g., oxygen compared with aluminium in nickel [16].

A nickel matrix is used in the present investigation for ease of preparation and fabrication and in order to study the feasibility of reinforcement. The requirement for an oxidation resistant matrix coupled with the necessity for minimizing spinel formation means that composites for gas turbine blades will probably have an alloyed nickel-chromium matrix.

2. Experimental

The techniques and some results of thin foil electron microscopy on composites containing 1, 2, 5, 15 and 20 vol % of sapphire whiskers are given in [3]. Specimens in the form of sandwiches were prepared by settling and by roll sandwiching and composites were prepared by hot-pressing, as described previously [3].

A comparison sample was pressed at room temperature at 260 MN m^{-2} from 5 vol % sapphire whiskers dispersed and mixed with type 255 nickel powder. On removal from the 12.7 × 38.1 mm double-acting die set it was decarburized and reduced in wet hydrogen at 664°C for 14 h followed by 18 h sintering at 1000°C in dried hydrogen. The density of the specimen was then 86% of theoretical and was possibly further slightly increased during its final treatment of 33% reduction by cold-rolling.

For the majority of the stability determinations, samples were held in a high alumina fireclay combustion boat and separated by aluminous porcelain thermocouple insulators. To minimize the evaporation of the nickel matrix from the specimens, the combustion boat containing up to five samples was inserted into a nickel tube of 21.2 mm bore and 127 mm length. The whole assembly was put into a recrystallized alumina sheath and evacuated to 0.7 mN m^{-2} during heat-treatments. A number of specimens were annealed at 1400°C under higher pressures (*ca.* 1.3 N m^{-2}) for studies of spinel formation. For those stability tests at 1100°C lasting over 100 h, samples were sealed into evacuated silica capsules after an outgassing period of 2 to 4 h at up to 800°C and 13 mN m^{-2}. These samples were separated from the silica walls of the capsules by aluminous porcelain thermocouple insulators. Despite the precautions taken, five out of six samples annealed in this way suffered various degrees of oxidation.

The whisker/metal interface was examined by thin foil electron microscopy using methods already outlined [3]. The extraction of the whiskers from the composites for X-ray powder diffraction, mass spectrographic analysis and electron microexamination have also been described previously [3].

3. Results and discussion

3.1. Observations of whisker-matrix interfaces

Bonfield and Markham have carried out transmission electron microexamination of silicon nitride [17] and alumina [18] whiskers annealed after coating with a surface film of nickel. They found that annealing above 800°C caused the nickel coating to break up into a series of spheroidal particles.

Transmission electron microexamination of thin composite foils of sapphire whiskers in nickel revealed that in all cases electrothinning had exposed parts of whiskers so that they emerged from the surface of the foils, e.g., Fig. 1. Because of this and the excessively thin (< 0.2 μm) foils required in order to transmit 100 kV electrons, the dislocation structures observed near the whiskers may well have been altered from the original state prior to thinning. Never-

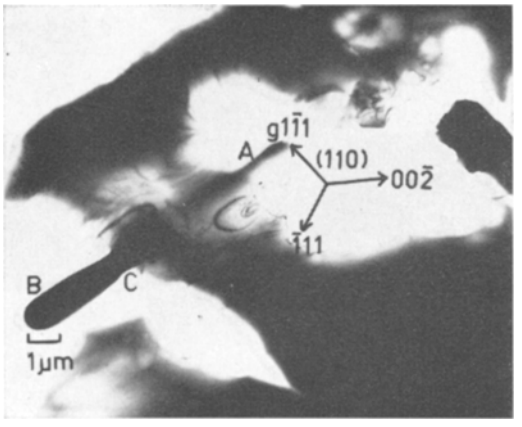

Figure 1 A whisker projecting into a perforation of a 1 vol % composite annealed for 500 h at 1200°C.

theless, the observations have demonstrated the feasibility of transmission electron microscopy of composites and three possible improvements in techniques are suggested below.

1. The incorporation of the thinnest whiskers, selected by a classification method, into composites should result in more areas suitable for examination after thinning.
2. The use of an ion beam for thinning should eliminate excessive localized attack on the matrix at the edges of exposed whiskers.
3. Because of the need to view through comparatively thick composite foils, this type of investigation is an obvious task for the million volt electron microscope. The samples most suitable for thin foil electron microscopy proved to be the 1 vol % hot-pressed composites.

In foils annealed for 500 h at 1200°C, the structures shown in Figs. 1 and 2a to c were observed. In Fig. 1 the whisker AB is seen to be at least partly contained in the nickel matrix and "waisting" of the whisker is evident at C.

Fig. 2a to c all shows one area of foil at different angles of tilt. It was previously observed [3] that dislocations were associated with sapphire whiskers in settled and in roll-sandwiched composites. In Fig. 2a dislocations in the nickel matrix can be seen to be closely associated with whiskers in hot-pressed composites. These dislocations near the whisker have may persisted from the deformation during hot-pressing or they may result from differential thermal contraction on cooling after annealing. In Figs. 2a to c one side of the whisker appears to be fully embedded in the matrix. From Fig. 2b measurement of the

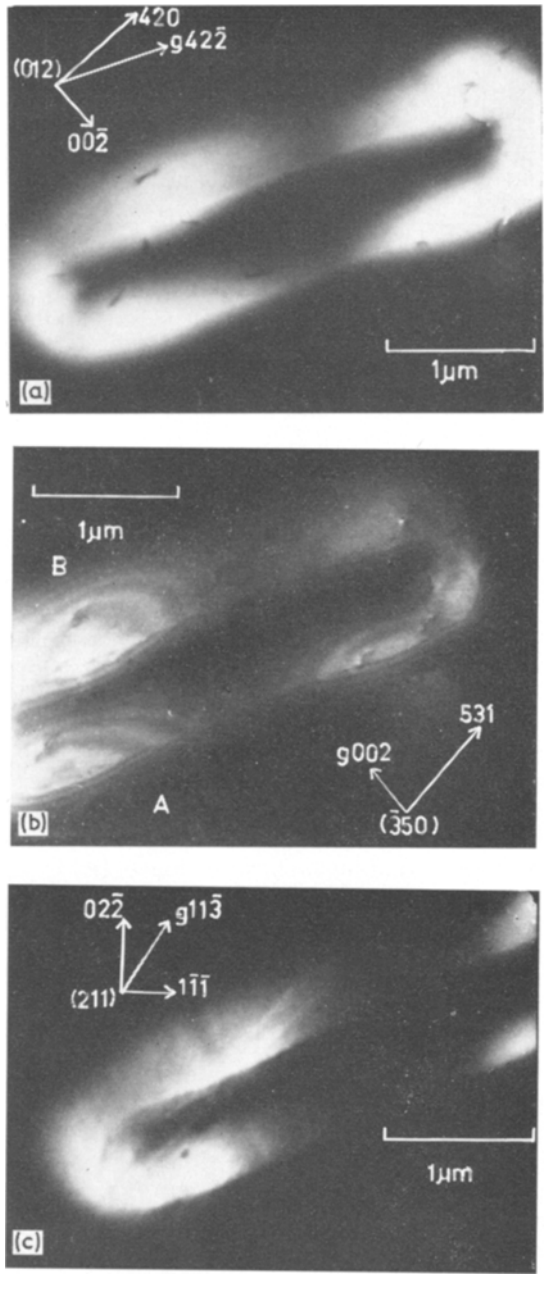

Figure 2 (a) (b) and (c). An area of a 1 vol % composite viewed at different angles of tilt and showing the structure in the region of the whisker/matrix interface.

bright fringe spacings allows the construction of a contour section through AB, Fig. 3. Each bright fringe spacing corresponds to the 28 nm extinction distance for the operating (002) reflection. Fig. 3 shows that these fringes are consistent with one side of the whisker being

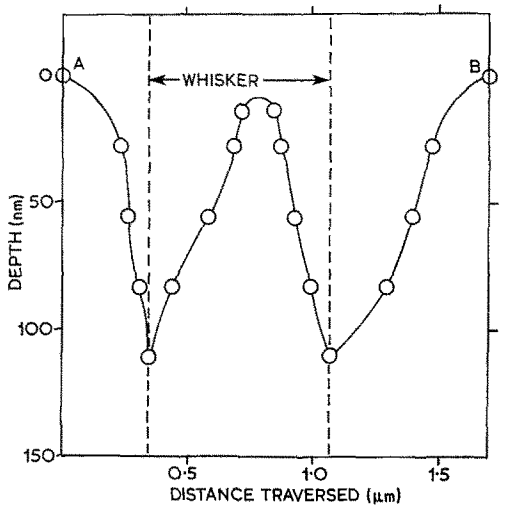

Figure 3 A thickness contour section for the line AB across the matrix and whisker shown in Fig. 2b.

exposed at the surface of the foil. Since the whisker itself can be assumed to be under multiple beam conditions the curve within the area of the whisker in Fig. 3 denotes the thickness of nickel, rather than the position of the surface of the whisker. Whilst the contrast effects in Fig. 2b could be interpreted as resulting from lattice strains, they could equally well be due to thickness variations as shown in Fig. 3. In Fig. 2c the cause of the lines of light contrast running diagonally across the whisker and matrix is not known.

3.2. Bicrystals and measurements of interfacial energy

Many whiskers presented a segmented appearance (Fig. 4) due to the presence of transverse grain boundaries associated with surface grooves. Electron diffraction patterns from either side of the boundary demonstrate a difference in orientation. These bicrystals were observed in both the extracted whiskers (Fig. 4) and in whiskers partly contained in a thinned composite foil (Fig. 5). The latter observation (Fig. 5) demonstrates that similar structures present among extracted whiskers (Fig. 4) are not artifacts resulting from the method of extraction and mounting. The bicrystals were observed in hot-pressed composites and in annealed hot-pressed composites but not in the as-grown whiskers nor in the AWRE tape. The following observations support the conclusion that bicrystal whiskers are a reality: (i) the extent of the necking at the

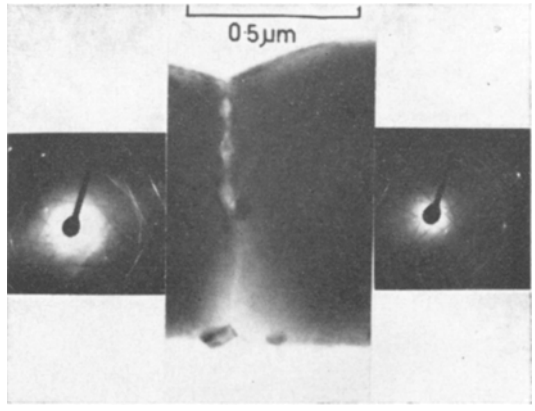

Figure 4 A bicrystal extracted from an as-hot-pressed 20 vol % composite.

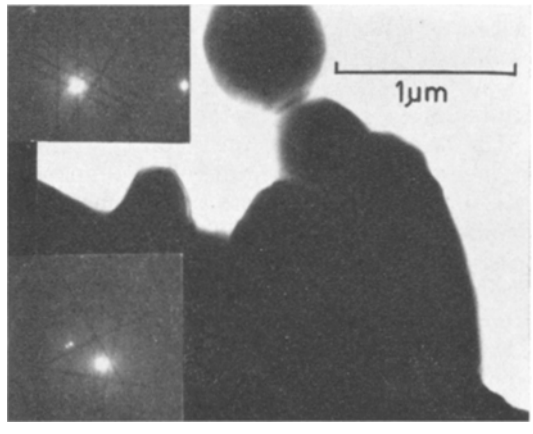

Figure 5 A bicrystal projecting from the edge of a foil of a 1 vol % composite annealed 100 h at 1400° C.

boundary increased with the annealing temperature and time of anneal; (ii) tilting about the length axis of the bicrystals showed that they were not artifacts resulting from superimposed whiskers; (iii) break-up of the carbon film supporting the extracted whiskers by increasing the electron beam intensity failed to separate the component crystals.

Suggestions for the mode of formation of bicrystal whiskers must be only speculative. The pressure of 15 MN m^{-2} applied during hot-pressing could, at regions of constraint such as positions of whisker overlap, exceed the resolved creep yield stress for slip on a suitably aligned slip system. However, it is difficult to see how deformation followed by recrystallization could then form only bicrystals and no polycrysals. The

bicrystal boundaries could also be either low-angle tilt boundaries caused by vacancy diffusion, or twin boundaries; the electron diffraction patterns are too complex to allow discrimination.

Measurements of the dihedral angle at the intersection of the grain boundary with the whisker surface permit an estimate to be made of the interface surface energy between the bicrystal and its environment. It was assumed that the grooves were formed as a consequence of surface tension effects and not by thermal etching. It was also assumed that the rate of cooling from the annealing temperature was rapid enough to retain the original high temperature morphology. The surface forces acting are shown in Fig. 6a. θ^1 and θ_2 were measured and the grain-boundary surface energy γ_{gb} is taken as 440 mN m^{-1} [19] at 1850°C and subsequently corrected for temperature using $d\gamma_{gb}/dT = -0.1$ mN m^{-1} [20]. The forces resolved along the bicrystal boundary give the relationship (Fig. 6b)

$$\gamma_{gb} = \gamma_i \cos \theta_1 + \gamma_i \cos \theta_2$$

from which γ_i, the surface energy which is assumed to have the same value in each component crystal, can be calculated. Results for a number of bicrystals are shown in Table I. In Fig. 4 there is an impurity particle associated with the bicrystal boundary/matrix intersection. The surface energy near the impurity particle was found to be 420 to 487 mN m^{-1} compared with 817 mN m^{-1} at the opposite boundary/matrix interface. Alumina/nickel and alumina/gas surface energies have been reported as 1860 to 2500 mN m^{-1} [21-23] and 485 to 515 mN m^{-1} [19] respectively over the temperature range 1100 to 1400°C. The values of γ_i in Table I are much nearer to the alumina/gas than the alumina/nickel surface energies. It seems unlikely, however, that all the whiskers had a gaseous environment due to localized porosity or lack of bonding to the nickel matrix. On the other hand, the possibility of a lowering of the nickel/alumina surface energy by impurities at the interface would appear to be supported by the observation presented in Fig. 4 and the results in Section 3.5 which show that impurities can be introduced during the preparation of composites.

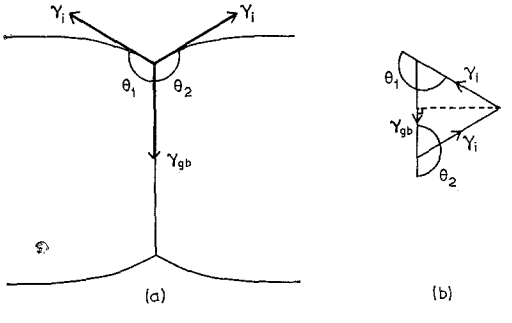

Figure 6 The surface forces acting at the bicrystal boundary/whisker surface intersection.

3.3. Spheroidization of whiskers

Examples of waisting and of rounding of the ends of whiskers annealed in a nickel matrix were presented in a previous publication [3]. In the present work both end-rounding and waisting were observed occasionally after hot-pressing for 1 h at 1100°C under a pressure of 15 MN m^{-2}. Quantitative determinations of the extent of spheroidization following anneals for various times within the temperature range 1100 to 1400°C are presented in Part 2 of the present publication. "Drumsticks" (Fig. 7) were also observed but unlike those reported by Barber [24] the globules were not composed of metallic aluminium. The partially spheroidized ends of the drumstick consist of α-alumina, the orientation of which is different from the remainder of the whisker (Fig. 7). Also unlike Barber's drumsticks only one of the present examples possessed an end globule of greater diameter than that of the parent whisker, this example was observed in a sample annealed for 500 h at 1200°C.

3.4. Sapphire whiskers annealed in the absence of nickel

A sample of as-received whiskers was annealed for 100 h at 1400°C under a vacuum of 1.3 mN m^{-2}. The perforations in the whisker shown in Fig. 8 are similar to the thermal etch pits reported by Barber [24]. Bonfield and Markham [25] have also reported the formation of pits in annealed whiskers and attributed this to regions of high internal stress.

The whiskers showed no evidence of spheroid-

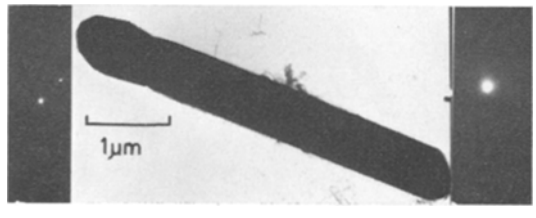

Figure 7 Spheroidization at the tip of a whisker extracted from a 20 vol % composite annealed for 500 h at 1200°C.

TABLE I Surface energy resolved along whisker edges as determined from bicrystal dihedral angles

Annealing time (hours/temperature, °C)	Estimated γ_{gb}(mN m^{-1})	Resolved γ_i(mN m^{-1})	No of determinations
As hot-pressed	515	550 ± 80	8
	515	512 ± 4	2
	515	817 420	2
100/1100	515	503 ± 53	8
	515	878 ± 125	6
100/1200	505	416 ± 91	12*
	505	408 ± 63	6
500/1200	505	419 ± 24	16
	505	434 ± 72	2
115/1400	485	533 ± 60	4†
100/1400	485	771 ± 18	2

*Tricrystal.
†Side growth.

ization as a result of the annealing treatment. The ends of the whiskers remained sharp and were consistent with either growth tips or fracture faces produced during preparation from the original whisker wool. Their aspect ratios were similar to the as-separated whiskers prior to the annealing treatment. No bicrystals were observed in the annealed sample and the X-ray diffraction patterns were unchanged by the annealing except for the introduction of an unidentified d-spacing at ~ 4.16Å.

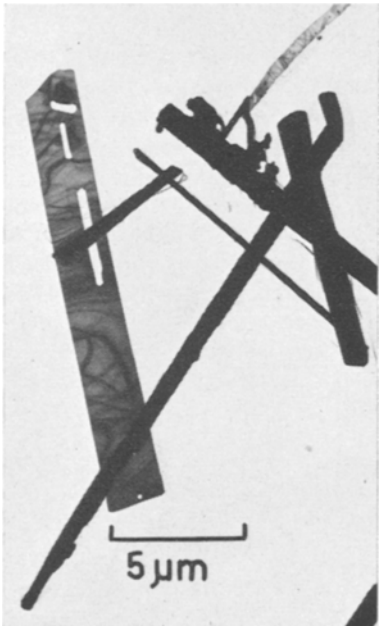

Figure 8 Thermal etch pits in whiskers annealed in the absence of nickel for 100 h at 1400° C under a vacuum of 1.3 mN m^{-2}.

3.5. Chemical reactions

The results of chemical activity between the whiskers and the nickel matrix were investigated using transmission electron microscopy, X-ray diffraction and mass spectrographic analysis.

The following observations were made on whiskers partially contained in foils of as hot-pressed samples. Figs. 9 and 10 show surface irregularities and whisker attack, the dislocation density evident in Fig. 9 is unusually high compared with as-grown whiskers. Also observed were "whiskers" having a polycrystalline or polyphase appearance with a ring diffraction pattern corresponding to nickel aluminate (Fig. 11) superimposed on strong reflections from single crystal α-alumina.

The X-ray diffraction studies were carried out on whiskers extracted from composites. For comparative purposes as-received whiskers were annealed for 100 h at 1400° C under a vacuum of 1.3 mN m^{-2} in the absence of nickel and subsequently subjected to the acid leaching treatment used for the composites. Neither the annealed nor annealed and leached alumina whiskers exhibited significant differences in "d" spacings to those of the as-received alumina. Diffraction studies were carried out on cold-pressed and on settled samples, on hot-pressed samples and after annealing of all these samples in the temperature range 1100 to 1400° C. From

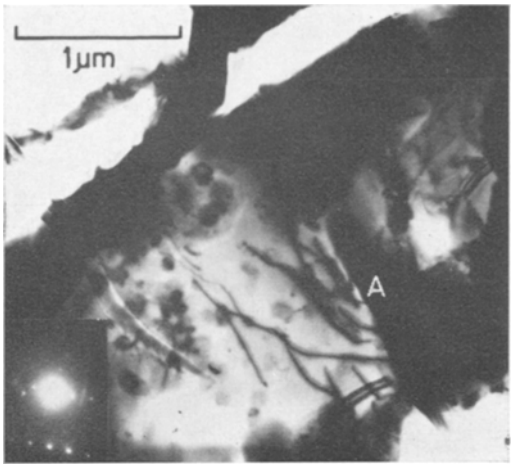

Figure 9 A whisker extracted from an as-hot-pressed sandwich and exhibiting a high dislocation density.

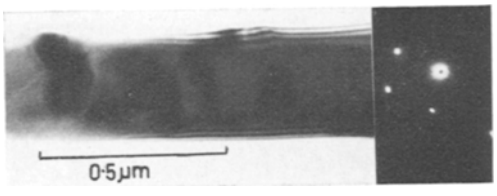

Figure 10 A whisker extracted from an as-hot-pressed sandwich and showing evidence of reaction with the matrix.

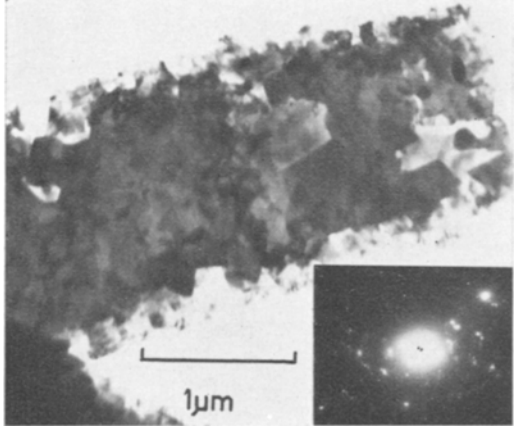

Figure 11 A whisker extracted from an as-hot-pressed composite. The diffraction pattern has a ring appearance superimposed on the strong reflections associated with the single crystal alumina (cf. Figs. 9 and 10). This suggests that only the surface layer is polycrystalline.

these specimens "*d*" spacings* consistent with the spinel compound $NiAl_2O_4$ were obtained. The occurrence and intensity of the lines increased with annealing temperature and time. A further strong factor was the vacuum maintained during the anneal; the higher the pressure the more intense the spinel lines.

The results from mass spectrographic analysis of samples before and after annealing are presented in Tables II and III respectively. The level of many elements varied considerably from one treatment to another but in many cases there is no systematic variation with time or temperature of heat treatment. The tables do show however, the presence in significant proportions of nickel following high temperature anneals under "poor" vacuum conditions. The sulphur and sodium levels can possibly be related to the use of teepol in the extraction of the whiskers. Calcium, magnesium and to some extent potassium show marked increases above their as-grown levels and these were possibly introduced through the use of ammonium alginate as a binder in the preparation of the AWRE tape.

Bonfield and Markham [25] have carried out an electron microscope examination of the thermal response from 800 to 1500°C of Thompson Houston (high silicon content) and Thermo kinetic whiskers (used in the present investigation). They found extensive second phase formation in the high silicon content whiskers but reduced activity in the Thermo kinetic whiskers with some impurities present and also some whisker disintegration. In the present work, there was little evidence of chemical activity from the X-ray diffraction and electron microscope studies of whiskers annealed at 1400°C. The present results are in accord with previously published observations [3] and indicate a rather lower level of chemical activity than that reported by Bonfield and Markham [25] and this may have arisen from slight differences in whisker samples and annealing procedures used in the two investigations. In both cases, thermal pitting was observed after annealing at 1400°C but appears to have been rather more intense in the case of the Bonfield and Markham [25] experiments.

Recent results on nickel alloy/alumina composites formed by liquid metal infiltration techniques have shown that the depth of interaction between the nickel and alumina was restricted to 6 μm, a small fraction of the diameter (0.25 mm) of the alumina reinforcement even after anneal-

*Details of all the X-ray diffraction studies are available [6].

TABLE II Results of mass spectrographic analysis before annealing

Element	Impurity concentration (atomic parts per million)				
	Sapphire whiskers		5 vol% h.p. sandwich	Whisker extracts from h.p. composites	
	As-grown	Comparison extracted		1 vol% h.p.	20 vol% h.p.
Zr	—	—	0.3	—	—
Zn	7	—	9	432*	1
Cu	<3	7.2	64	—	3
Ni	15	735	(matrix)	900	15
Fe	300	2725	300	440*	110
Mn	5	50	60	200	5
Cr	10	60	22	144	6
Ti	<18	162	8.2	—	<5
Ca	300	80	60	610	100
K	300	17000	—	4000	100
Cl	40	6650	1.8*	2430	26
S	48	300	120	2880	480
Si	1980	5350	60	42800	3300
Al	—	—	~3000	—	—
Mg	886	250	600	1200	1800
Na	3000	1700	10	4000	600
B	2.4	—	—	72000	12

Notes
h.p., as hot-pressed.
*Inhomogeneous distribution.

TABLE III Results of mass spectrographic analysis after annealing

	Extracts from hot-pressed composites					C.P.S. extract
Annealing time (h)	3800	67	100	100	940	100
Temperature (°C)	1100	1400	1400	1400	1400	1400
Pressure (mN m^{-2})	1.3	130	1.3	1.3	1.3	5980
Element	Impurity concentration (atomic parts per million)					
Zr	1200	—	—	—	—	—
Zn	72	54	18*	1440*	36	144
Cu	90	15	65*	3600*	100	<50
Ni	matrix	450000	4500	900	1500	160000
Fe	33000	3300	11000	660	2200	13200
Mn	40	150	20	20	1000	12000
Cr	24	180	120*	72	1200	4800
Ti	182*	90	18	108	3600	216
Ca	1000	600	10000	20600	2000	2060
K	1000	1000	20000	2000	2000	6000
Cl	242	400	1330	812	800	2430
S	1440	24000	48000	28800	48000	48000
Si	6480	10000	100000	8560	66000	128400
Al	200000	—	—	—	—	—
Mg	400	1800	2700	2000	8860	12000
Na	6000	10000	30000	120000	100000	120000
B	7	36	1200	480	360	720

Notes
C.P.S., cold-pressed and sintered composite.
*Inhomogeneous distribution.

ing for 300 h at 1100°C [26]. Under these conditions whiskers like the present ones, of 1 to 3 μm diameter would presumably have suffered marked attack.

Reaction between nickel and alumina can lead to the formation of nickel aluminate, $NiAl_2O_4$, if the annealing treatment is carried out in an oxidizing atmosphere [7]. In the present work the formation of the spinel $NiAl_2O_4$ was detected by X-ray diffraction. Its formation occurred more readily in samples with the higher partial pressure of oxygen In only two cases did extensive spinel formation occur and this was reflected in the nickel content of the extracted whiskers. In both samples the annealing treatment was carried out in a "poor" vacuum. These results are consistent with the observation that the formation of the spinel depends upon the availability of oxygen to the nickel/alumina system.

The results in Tables II and III show that many impurities were associated with the extracted whiskers. The extent of their reactions with alumina, or nickel however is not known as positive identification of compound formation was restricted to the spinel $NiAl_2O_4$.

4. Conclusions

1. Alumina whiskers contained in a nickel matrix can exhibit tip-ovulation and waisting as a consequence of annealing in the temperature range 1100 to 1400°C.
2. Mass spectrographic analyses, X-ray diffraction and electron microscope observations have shown that alumina whiskers react with the nickel matrix following anneals at 1100 to 1400°C for periods of 100 to 1000 h. One of the products of this reaction is nickel aluminate ($NiAl_2O_4$) and the extent of its formation increases with the partial pressure of oxygen.

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