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No Hope for Ceramic Whiskers or Fibres as Reinforcement of Metal Matrices at High Temperature

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A study has been made of the incorporation of aligned alumina whiskers (from both USA and French commercial sources) and aligned alumina fibres (0.01 in. diameter) into nickel and the resultant tensile properties at 20 and 1100°C studied. Conditions have been established which preclude significant whisker/fibre break-up, densify the matrix and promote chemical bonding between the whisker/fibre and the matrix. The factors which influence these aspects are described, viz. impurities on the whisker surface, classification of the whiskers, deposition of nickel on aligned whiskers or fibres from pure nickel carbonyl, hot-pressing conditions to promote bonding and effect densification.

High strengthening efficiency (up to 75%) can be ascribed to the use of whiskers or fibres in tests at 20°C but at high temperatures (1100°C) this efficiency is poor, 10% or less. This poor efficiency is ascribed to the rupture of the chemical bond between whisker or fibre and matrix during the first reheat after composite manufacture. Strong chemical bonding is vital for a successful composite since in any practical ceramic whisker/fibre-metal matrix composite the inherent disparity in thermal expansion coefficients acts to disrupt the chemical bond. Moreover, even if the chemical bond was sufficiently strong not to rupture as a result of the thermal expansion disparity, the implication of increased chemical affinity to produce the strong bond would lead to complete erosion of a whisker in times of about 100 h. Even in the case of fibres with a large diameter (0.010 in.) there is sufficient degradation of mechanical properties although without apparent loss of the cylindrical form to markedly reduce composite properties.

Apart from any economic consideration, therefore, it is concluded on technical grounds that the reinforcement of metals by ceramic whiskers or fibres for high temperature (>700°C) use is impossible.

1. Introduction

The availability of high strength ceramic whiskers (albeit at a price ~ £6000 per lb) and the proven concept [1] of composite strengthening has, for some little time, presented the metallurgist with the challenge of incorporating such whiskers into refractory and oxidation resistant alloys to improve strengthening and rigidity over what can be gained by either dispersion or precipitation strengthening.

The turbine of the aero-engine was an obvious choice for initial study. Nickel-chromium alloys, with their inherent oxidation resistance had been fully developed using conventional metallurgical methods and the higher strength alloys, based on niobium and molybdenum were, and still are, unsatisfactory because of the failure to develop reliable oxidation protection coatings.

Simple theory predicts that incorporation of 25 vol% of alumina whiskers in a nickel-chromium matrix would result in mechanical properties comparable with those achieved in the high strength niobium and molybdenum alloys. Accordingly, work was initiated at AWRE in 1966 and later in 1967 supported by Mintech to investigate the strengthening of a whisker/metal matrix system at high temperature (1100°C) conditions.

The choice of matrix and whisker species was for various reasons limited to nickel and alumina.

Nickel was chosen as matrix because of the high inherent oxidation resistance obtained by alloying with 20 wt% chromium and it was judged that initially work should be restricted to the major component of the intended binary (Ni/Cr) system. Alumina whiskers proved to be the only available strengthening material. Of the stable oxides available, viz. CaO, MgO, Al_2O_3, ThO_2, BeO, the first two are cubic and deformable, the last two are toxic and unavailable.

The general approach made was to establish as satisfactory each stage in the manufacture of the composite before making a tensile evaluation. Accordingly the following aspects have been studied.

(i) whisker strength,
(ii) chemical bonding of alumina to nickel which is vital if the interface between the whisker and matrix (with differing thermal expansion coefficients) is to remain an integral part of the composite during thermal cycling,
(iii) provision of nickel matrix by powder metallurgy,
(iv) provision of nickel matrix by chemical decomposition of a gas phase,
(v) evaluation of the product.

The first three aspects have already been published [2-7]. This work showed the strength and chemical bonding to be satisfactory but the incorporation of nickel as powder resulted in unacceptable break-up of whiskers. This latter observation lead to the study of the final two aspects which are the subject of the present paper and the unfavourable conclusion that whiskers in metals will not provide a satisfactory composite for high temperature service use. In short, the disparity in thermal coefficient of expansion between whisker and matrix disrupts any chemical bond so far produced between the whisker and matrix during heating to the service temperature. Even if this was not so, it is considered that the necessity to promote chemical interaction in the system $Ni\text{-}Al_2O_3$ is inconsistent with ensuing chemical stability at 1100°C which is vital if the whiskers are not to be consumed in an oxidising environment at 1100°C.

Use of thicker reinforcements would minimise the effect of any surface dissolution of the reinforcement. Accordingly, the use of thick (0.010 in. diameter) alumina single crystal fibres as reinforcement for a nickel matrix has been studied.

This work has involved a hot pressing study to consolidate nickel/alumina composites in which the form of the nickel matrix was varied between being plated directly onto the fibres from carbonyl vapour and as powder. The resulting composites have been mechanically tested at 20 and 1100°C together with measurement of fibre break-up as a function of the matrix form. Results of this investigation have indicated that the use of such composites for high temperature materials is extremely doubtful due to a disruption of the fibre/matrix bond as a consequence of thermal cycling (one and a half cycles) and also as a result of degradation of fibre strength when the interfacial reaction is increased to enhance bonding.

2. Preparation of Composites

2.1. Materials

2.1.1. *Whiskers and fibres of α-alumina*

Whiskers used in the investigations have been obtained from two sources:

(*a*) Thermokinetic Fibres (TKF). These whiskers were in the form of sapphire wool mats containing whiskers with a diameter of 1 to 3 μm and an aspect ratio (length/diameter) of 500 to 5000:1.

(*b*) Compagnie Francaise Thompson Houston-Hotchkiss Brandt (FTH). These whiskers were generally of a larger diameter (up to 10 μm) and with a smaller aspect ratio than TKF whiskers.

The strength characteristics of these two types of whisker are similar; room temperature strength varies in the range 10^5 to 10^6 psi (0.7 to 7 GNm^{-2}) depending on cross-sectional size of the crystal and the strength at 1100°C is in the range 2.5 to 2.8×10^5 psi (1.75 to 1.96 GNm^{-2}).

Table I compares the impurity elements in the two types of whisker. The high silicon content associated with FTH whiskers is concentrated in a globular phase which occurs on the surface of these whiskers as a result of the growth process. The phase is thought to be a complicated silicate (microhardness of DPN 1113) containing $\sim$ 35% silicon, 53% oxygen and 12% aluminium and can be removed by treatment in a 10% HF-10% H_2SO_4 solution at 140° C for times as low as 15 min. This etching treatment does not reduce the 20°C strength of the whisker itself.

The alumina single crystal fibres, 0.010 in. diameter, were obtained from Tyco Inc. These fibres are prepared by a drawing process from the melt, and results in fibres with the $\langle 0001 \rangle$ direction parallel to the fibre axis. A number of surface and volume imperfections have been noted which can be interpreted as arising from the method of preparation. These imperfections are (i) surface striations due to unevenness in the drawing speed, (ii) random areas of surface imperfection caused possibly by entrapped gases and (iii) inclined stringers of bubbles (~ 1 μm diameter) inclined at 30° to the growth direction. These bubbles may arise as a result of a rotation during the drawing process giving rise to a spiral of bubbles or may be due to the formation of gas bubbles on certain preferential crystallographic planes. The tensile strength at 20°C varies between 2.14 to 4.22 × 10^5 psi (1.5 to 3.0 GNm^{-2}) with an average strength over ten determinations of 3.16 × 10^5 psi (2.2 GNm^{-2}). At 1100°C, the strength is less variable and shows a value of 10^5 psi (0.7 GNm^{-2}). A study of the fracture surface of such crystals reveals possible initiation of fracture at bubble defects. Fig. 1 shows the almost explosive fracture behaviour at the site of one of these bubbles. The fibres are extremely pure; table II shows the level of impurities in the fibres.

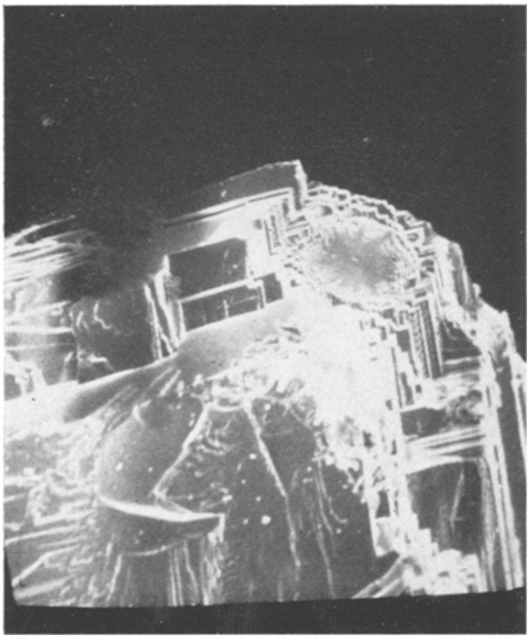

Figure 1 Fracture at a bubble defect in Tyco alumina fibre (× 650).

TABLE I Chemical analyses of the impurity elements in α-Al_2O_3 whiskers.

Impurity element	TKF	FTH
Si	0.290%	6.0%
Na	0.013%	0.550%
K	0.002%	1.100%
Ca	0.007%	0.005%
Mg	0.028%	0.025%
Cl	0.120%	0.070%

TABLE II Generalised table of impurities in Tyco fibre.

Impurity element	(ppm) Impurity level
Fe	50-100
Si	100
Cu	50-100
Mn	5
Mo	5
Na	<500
Be	ND <10
Mg	20-50
Cr	<5
Ni	<20
V	<5
Pb	50
Ca	50
Ti	10-20

2.1.2. Nickel matrix

In the course of this work, the nickel matrix was supplied from two sources (i) by the decomposition of nickel carbonyl (on to both whiskers and fibres) and (ii) from nickel powder (fibres alone).

In the case of nickel carbonyl, $Ni(CO)_4$*, the fibres and whiskers were heated to 170°C in the presence of carbonyl vapour. At this temperature, the carbonyl vapour decomposes into nickel and carbon monoxide in the vicinity of the whiskers or fibres producing an even coating of nickel around each whisker or fibre. Bonding of nickel, deposited in this way onto α-Al_2O_3 single crystal plaques under a temperature and pressure of 1100°C and 1 tsi (15.4 MNm^{-2}) respectively gives rise to an interfacial shear strength at the nickel/alumina interface of ~ 7 × 10^3 psi (50 MNm^{-2}) [6]. From this value of interfacial shear strength, then, according to the criterion that the critical aspect ratio of the fibre is $\sigma_f/2\tau$ (where σ_f is the fibre strength and τ is the interfacial shear strength), the critical aspect ratio necessary for efficient strengthening at room temperature is 70 (for whiskers) and 30 (for fibres). Efficient strengthening at room temperature should therefore be easily attainable. Further, assuming

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* Supplied by International Nickel Co Ltd.

that at 1100° C the effective interfacial whisker or fibre/matrix bond is the shear strength of nickel at this temperature [~ 1.85 × 10^3 psi (12.95 MNm^{-2})], then the critical aspect ratios necessary for efficient strengthening are 75 (for whiskers) and 25 (for fibres); full strengthening efficiencies of both whiskers and fibres at 1100°C should therefore be possible.

2.2. The Whisker Classification

The size distribution of whiskers in an as-grown mat can vary considerably. In view of the arguments set out in section 2.1.2 above, it is essential that the whiskers used in a nickel matrix composite for projected use over the range 20 to 1100°C be of a minimum aspect ratio of 75. A simple method of classifying the whiskers into fractions containing similar whisker sizes (as defined by their length) has been devised. This method, based on the development at ERDE, Waltham Abbey, involves passing a mixture of whiskers in water through a series of meshes of decreasing mesh size. Whiskers of a differing size fraction separate out on the meshes. Typical results are shown in table III. In the preparation of composites, the first four classified fractions were used in the case of TKF whiskers and the first two in the case of FTH.

2.3. Whisker Alignment

To obtain the full strengthening efficiency from whiskers arranged in a metal matrix, the whiskers need to be aligned in the direction of maximum stress. Alignment also allows a much increased packing efficiency to be realised. Calow and Wakelin [8] have shown how whisker alignment can be produced by extruding a plasticised mixture of the whiskers plus the matrix powder through a thin slit, gelling the plasticiser and drawing off a continuous strip of material. Using this method, aligned whisker tape can also be made exclusive of any metal powder, there being sufficient misorientation of the whiskers to cross link the bulk which is aligned and so ensure a handleable tape after firing. This method of producing aligned whisker paper was used in this investigation.

2.4. Composite Manufacture

2.4.1. *From the carbonyl technique (whiskers and fibres)*

The decomposition of nickel carbonyl referred to earlier affords a method of plating directly onto both aligned Al_2O_3 whisker tapes and individual Al_2O_3 fibres. In the case of whiskers, whisker paper 2 in. wide and 0.001 in. thick can be plated with a very even distribution of nickel (1 to 5μm thick) (fig. 2) and, in the case of alumina fibres an intermittent plating process allows much thicker coatings to be produced (0.010 in. thick); this process results in very even coatings with the "ring" structure shown in fig. 3 resulting from the intermittent plating.

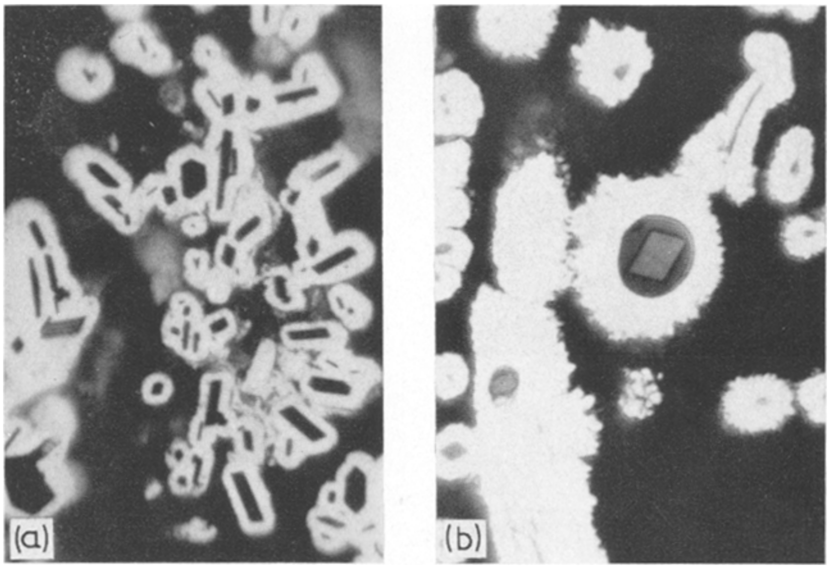


Figure 2 Nickel plated whiskers by nickel carbonyl decomposition. (b) shows the silicon rich impurity phase around the whisker ((a) × 800, (b) × 1100).

TABLE III Classification of whiskers.

Sieve size, μm	Average l/d range		% by weight	
	TKF	FTH	TKF	FTH
500	> 350	> 100	16.8	34.8
150	> 180	> 50	45.0	35.9
75	> 120	> 36	16.8	13.0
53	> 75	> 23	5.1	6.5
26	> 30	> 10	4.3	2.2
Fines	< 30	< 10	12.0	7.6

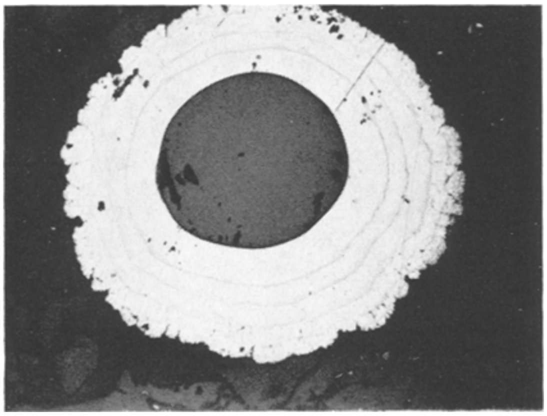


Figure 3 Nickel plated Tyco fibre by nickel carbonyl decomposition. The ring structure of the deposit results from intermittent plating (× 100).

Densification of these plated materials containing 0.10 to 0.20 volume fraction of the fibrous phase was carried out in two stages. The as-plated whiskers or fibres were given a vacuum heat-treatment at 1100° C for up to 22 h duration to remove carbon monoxide from the structure of the deposit. The entrainment of this gas arises during decomposition of nickel carbonyl and if not removed from the system impairs the bond between nickel and alumina by reducing the small amount of nickel oxide in the nickel which is necessary to react with alumina to form the bond producing spinel ($NiAl_2O_4$). Hot-pressing follows the heat-treatment step; this is carried out at 1100 to 1300° C under pressures of 0.5×10^3 to 6.0×10^3 psi (3.5 to 42.0 MNm^{-2}) for $\frac{1}{4}$ to 3 h in vacuum (3×10^{-3}mm Hg) to produce composites $3 \times 0.5 \times 0.1$ in. in size.

2.4.2. *From nickel powder technique (fibres)*

As an alternative to the route described above (section 2.4.1), two other routes were used in the case of alumina fibres, viz.:

(*a*) Al_2O_3 fibres/type A nickel powder.

(*b*) Al_2O_3 plated with nickel ex-carbonyl/type A nickel powder.

Fully dense composites were prepared by the hot pressing route referred to in section 2.4.1.

3. Evaluation of Composites

3.1. Nickel/Alumina Whisker Composites

3.1.1. *Metallography*

A comparison of the microstructures of composites prepared by the carbonyl method using FTH and TKF whiskers is shown in fig. 4. In the composite based on FTH whiskers a second phase can be clearly seen at the whisker/matrix interface completely surrounding the regular geometrical whisker shapes. The second phase is preferentially etched away by Carapellas reagent leaving voids around the whiskers; this can however be avoided using cathodic etching techniques. Microprobe analysis of the second phase material together with the analysis of the whisker itself are shown in table IV. Microhardness measurements gave values of 1300 DPN for the second phase and it is concluded, because of the hardness and compositional similarities, that the origin of the second phase in FTH composites is the globular phase appearing on the as-grown whisker surface. The irregular shape of this phase after pressing suggests that it has a low softening/melting point (< 1300° C).

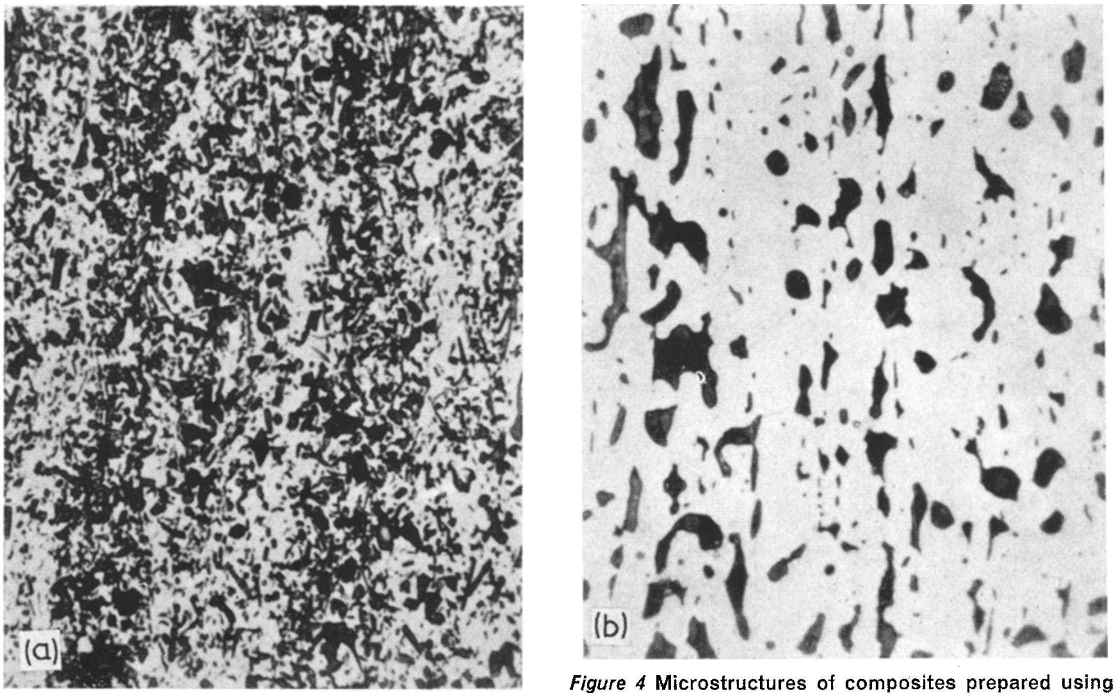
TABLE IV Analysis of the impurity phase in composites of $NiAl_2O_3$ (FTH) whiskers.

Element	Whisker (wt %)	Second Phase (wt %)
Al	53.0	15.5
Si	0.05	31.0
Ti	ND	0.9
Ni	0.6	0.7
K	ND	0.5
Ca	ND	0.6
O	46.4	50.6
Mg	ND	0.2
Cl	ND	ND
Na	ND	ND

3.1.2. *Tensile strength at 20 and 1100° C*

Table V indicates the UTS of composites prepared from Al_2O_3 whiskers by the previously described nickel plating/hot pressing route. The results show that:

(i) only in specimens in which the initial outgassing treatment (to remove carbon monoxide) was increased to 22 h at 1175°C does a degree



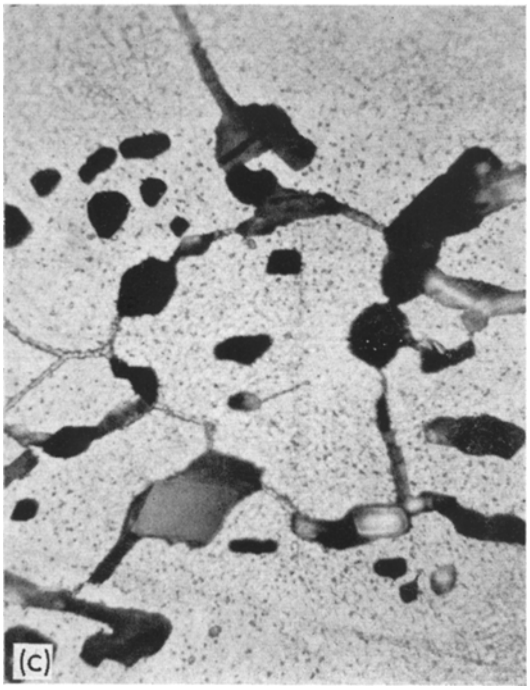


Figure 4 Microstructures of composites prepared using the carbonyl route. (a) and (b) show the cross section for TKF and FTH composites (× 410) respectively and (c) shows the impurity phase surrounding whiskers in FTH composites (× 1100).

of strengthening occur in a room temperature test,
(ii) assuming the maximum strength of α-Al_2O_3 whiskers is 0.45 × 10^6 psi (3.15 GNm^{-2}) (σ_f max), the UTS for carbonyl nickel is 0.45 × 10^5 psi (0.31 GNm^{-2}) and the yield point is 0.35 × 10^5 psi (0.25 GNm^{-2}), then the whisker strengthening efficiency of the best composite is 20 to 40% at 20° C depending on whether the comparison is made with the UTS or yield point of the matrix. Further, it is likely that in an actual composite the average strength of the whisker bundle is less than the one assumed (increasing efficiency by × 1.5) and that perfect alignment is not attained (increasing efficiency by × 1.2); an efficiency at 20° C of 75% is therefore not unreasonable,
(iii) etching of FTH whiskers to remove the surface silicon-rich impurity phase causes a loss in strengthening efficiency (i.e. composite strength is reduced from 51.7 × 10^3 psi (364 MNm^{-2}) to 43.2 × 10^3 psi (302.4 MNm^{-2})). Removal of the surface impurity by etching does not affect whisker strength;
(iv) extremely low strengthening efficiencies (~ 10%) are generated in tests carried out at 1100° C in argon (compare specimens 7, 8, 9). This efficiency falls to 5.70% in the case of FTH whiskers after removal of the surface impurity. Since analysis showed that the majority of whiskers had aspect ratios > 75 (this is con-

TABLE V Mechanical properties of $NiAl_2O_3$ composites.

Whisker type	Etched to remove silicon phase	Heat treatment prior to hot-pressing	Hot-pressing condition			Density (g cc^{-1})	Whisker volume fraction	Ultimate tensile strength (psi × 10^3)			Efficiency
			T°C	Pressure psi	t h			At RT (20°C)	At 20°C after heat treatment	At 1100°C	
1. FTH	No	2 h at 1100°C in vacuum	1100	2240	2		~0.20	28 [196 MNm^{-2}]			
2. FTH	No	,,	1300	700	$\frac{1}{2}$	7.04	>0.20	36 [252 MNm^{-2}]			
3. TKF	No	,,	1300	1120	$\frac{1}{2}$	7.70	0.24	40-43.7 [280-306 MNm^{-2}]			
4. FTH	No	,,	1300	1120	3	7.93	0.13	27.30 [189-210 MNm^{-2}]			
5. FTH	No	22 h at 1175°C in vacuum	1175	2750	$\frac{1}{4}$	7.96	0.12	51.3-52.03 [359-364 MNm^{-2}]			
6. TKF	No	,,	1175	2750	$\frac{1}{4}$	7.90	0.15	51.0-53.0 [357-371 MNm^{-2}]			
7. TKF	No	,,	1175	2750	$\frac{1}{4}$		0.20			6.90 [48 MNm^{-2}]	
8. FTH	No	,,	1175	2750	$\frac{1}{4}$	8.02	0.20			6.62 [46 MNm^{-2}]	
9. FTH	Yes	,,	1175	2750	$\frac{1}{4}$	7.87	0.21			5.40 [38 MNm^{-2}]	
10. FTH	Yes	,,	1175	2750	$\frac{1}{4}$	7.87	0.21	43.2 [302 MNm^{-2}]	47.2 [330 MNm^{-2}]		
11. TKF	No	,,	1175	2750	$\frac{1}{4}$	7.98	0.13		52.6-53.3 [368-373 MNm^{-2}]		
12. Carbonyl nickel		,,	1175	2750	$\frac{1}{4}$		0.0	45.00 [315 MNm^{-2}]		3.70 [26 MNm^{-2}]	

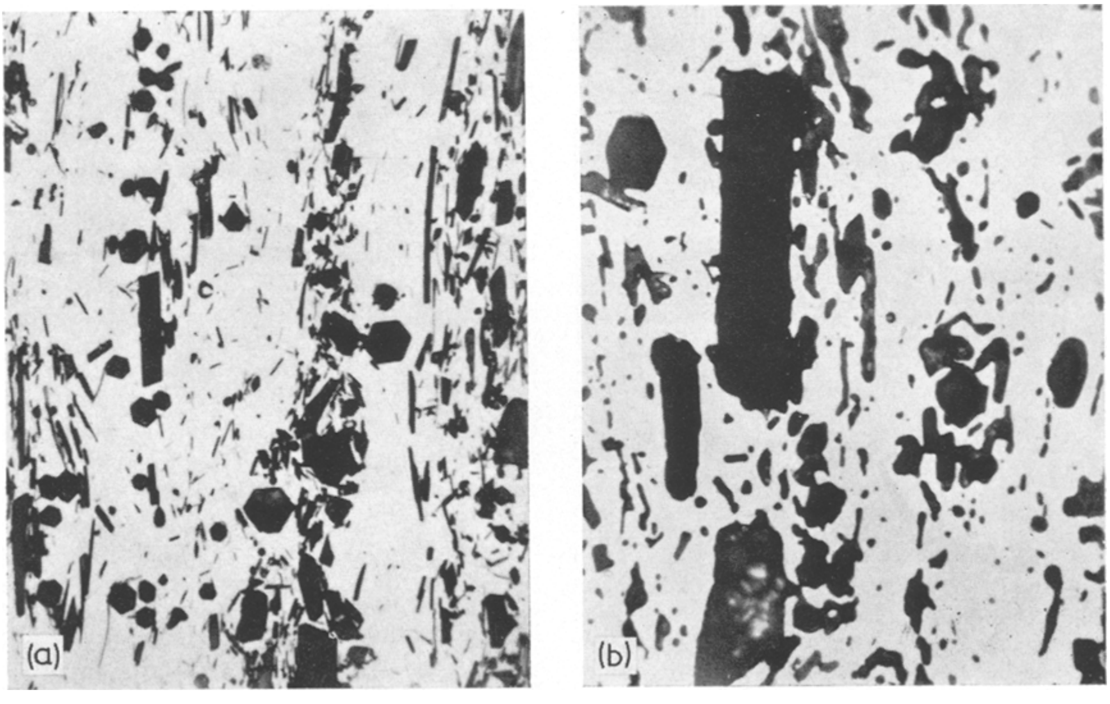


Figure 5 The effect of heat treatment on composites prepared from acid cleaned FTH whiskers (a) before the treatment and (b) after 300 h at 1100°C (× 400).

sidered essential for full utilisation of whisker strength at 1100°C), then this lack of strengthening is considered as being due to a very poor interfacial bond strength,

(v) after heat treatments of 1100°C for 300 h, room temperature tensile testing revealed that little degradation in mechanical properties had occurred (specimens 10 and 11). Metallography, however, revealed several important affects of the heat-treatment. In etched whisker composites (FTH), the well-defined whisker shapes become extremely uneven and a second phase (probably

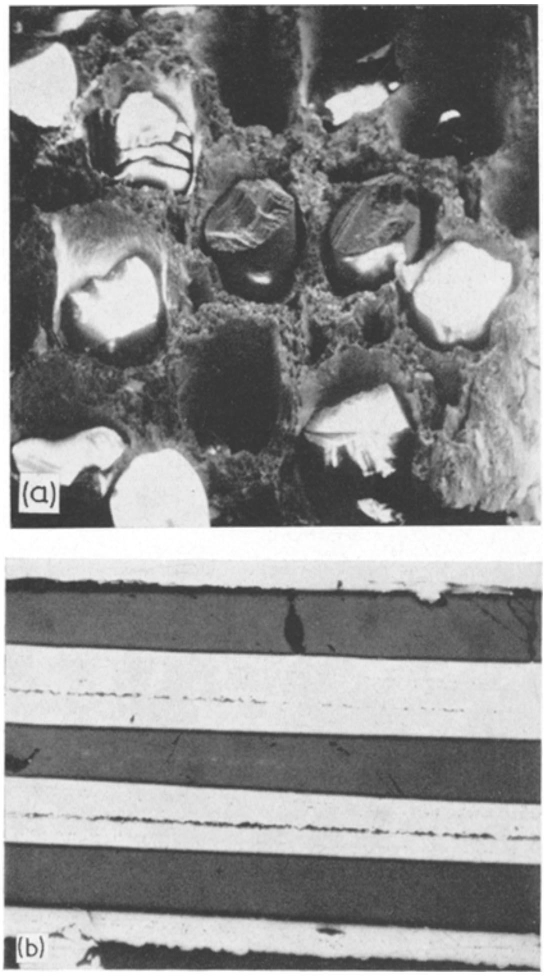


Figure 6 Lack of matrix densification in nickel/alumina fibre composites. (a) appearance of the fracture surface showing porosity in the matrix between fibres (× 67) and (b) continuous porosity in between fibres (× 40).

$NiAl_2O_4$) surrounds the whiskers (fig. 5). In contrast, unetched whiskers (with the silicon impurity phase) were not grossly attacked although some surface serration and transverse cracking were observed. With TKF composites, this treatment caused complete dissolution of the finest whiskers and considerable rounding and loss of geometrical form of the coarser fractions.

3.2. Nickel/Alumina Fibre Composites

Preliminary work has indicated that the usual pressing procedure used in the nickel/alumina whisker system (1175° C, under 3000 psi (21 MNm^{-2}) for 15 min) was insufficient to cause full densification in the nickel/alumina fibre system (fig. 6). Further pressing treatments on small specimens 1 × 0.15 × 0.10 in. using increased temperatures (up to 1300° C) and pressures (up to 6000 psi (42 MNm^{-2})) were carried out and a future consolidation procedure defined; this was defined as a pressure of 4.5×10^3 psi (31.5 MNm^{-2}) and a temperature of 1200 to 1250° C. Such a treatment produced a fully dense composite (8.16 $g.cc^{-1}$) with a strength in three point bending of 104×10^3 psi (728 MNm^{-2}) (fig. 7).

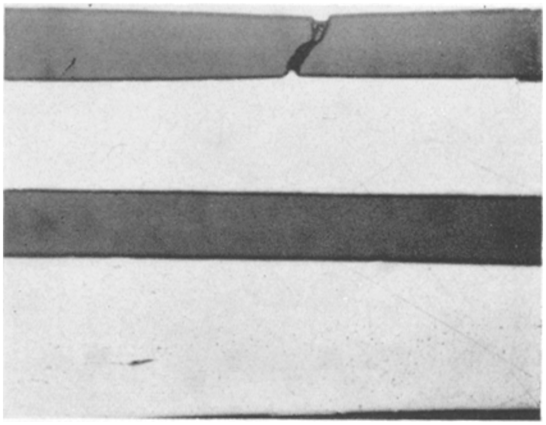


Figure 7 Densified matrix in nickel/alumina fibre composite (× 40).

Pressing at higher temperatures (300° C) resulted in the formation of $NiAl_2O_4$ and low composite strength (80×10^3 psi (560 MNm^{-2})) on bending.

3.2.1. *Tensile testing of composites with a matrix of carbonyl plated nickel*

Using the defined manufacturing parameters (1220° C, 4.5×10^3 psi (31.5 MNm^{-2}) for 15 min), a 20 vol % composite was manufactured from 0.010 in. diameter Al_2O_3 fibres plated to 0.022 in. diameter with carbonyl nickel. In these full size composites (3 × 0.5 × 0.1 in.), densification was still a problem at this fibre loading resulting in low composite tensile strengths of ~ 26.0×10^3 psi (182 MNm^{-2}). However, when the nickel plating thickness was increased to produce coated fibres with overall diameters of 0.026 to 0.030 in. (volume fractions of 0.15 to 0.11), hot-pressing produced fully dense composites with a strength of 41.0×10^3 psi (287 MNm^{-2}) (< 40 % strengthening efficiency), a lack of fibre/matrix interaction (average strength of fibres removed from composite was 2.14×10^5 psi (1.54 GNm^{-2})) and lack of fibre break-up (fig. 8). The lack of strengthening

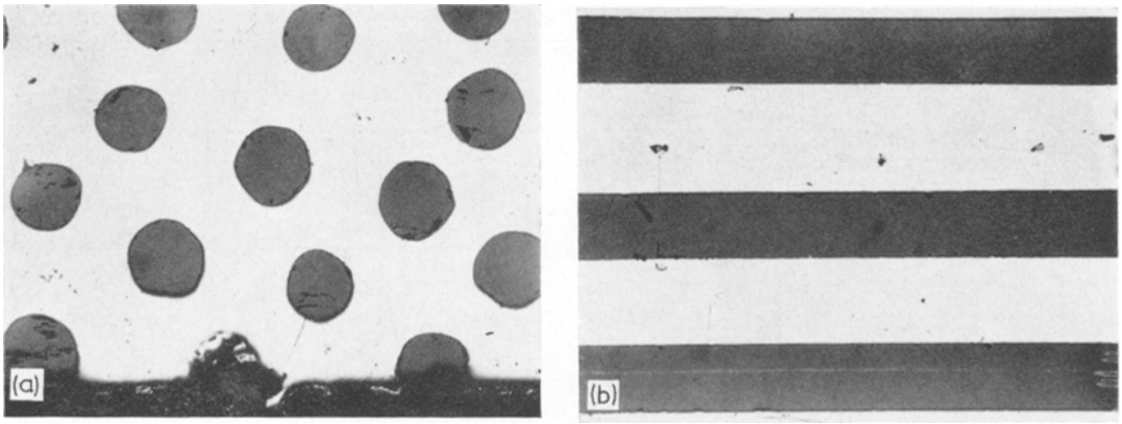


Figure 8 Fully densified composite prepared with fibres coated to a final thickness of 0.028 to 0.030 in. (× 40).

efficiency (compared with whisker strengthening) is due possibly to the increased difficulty in producing fully dense composites in the case of Al_2O_3 fibre reinforcement. The effect of fibre gripping by differential expansion would be reduced on cooling if porosity existed in the matrix giving rise to the lower strengthening efficiency.

3.2.2. *Tensile testing of composites with a matrix from nickel powder*

Specimens have been prepared by hot pressing uncoated alumina fibres with nickel (A type) powder to a nominal 0.20 fibre volume fraction. The hot pressing was carried out at 1200 ± 20°C under 3×10^3 psi (21 MNm^{-2}) for $\frac{1}{2}$ h in a vacuum of $5 \mu m$. These specimens showed a UTS of 50.7×10^3 psi (354.9 MNm^{-2}) (30% strengthening efficiency) and an extension on a 0.25 in. gauge length of 30%. Fig. 9 shows micrographs of this material showing (i) the high densification of the specimens, (ii) lack of gross chemical matrix/fibre interaction; (iii) lack of fibre pull-out and (iv) the gross fibre break-up.

3.2.3. *Tensile testing of composites with a matrix from nickel plating (ex-carbonyl)/ powder combination*

A series of tests have been carried out to vary the matrix constitution between one comprised totally of nickel powder and one comprised totally of nickel ex-carbonyl plating in an attempt to combine the best of both techniques, i.e. strengthening of the former case and the lack of fibre break-up of the latter condition. The volume fraction of all the specimens was 0.20 and the pressing procedure of 1200°C under 3000 psi for $\frac{1}{2}$ h common to all the composites. Table VI shows the matrix constitution and the resulting composite UTS. Fig. 10 shows a plot of these results together with the conditions when the matrix constitution

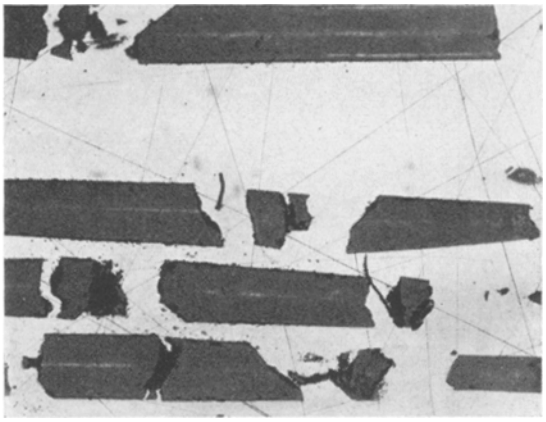


Figure 9 Fibre break up occurring in composites prepared from a mixture of unplated fibres and nickel matrix (× 40).

$$\frac{\text{wt. of nickel as powder}}{\text{Total wt. of nickel}} \text{ or } \left(\frac{P}{T}\right)$$

is 0 (all carbonyl nickel) and 1 (all powder). A strength improvement in excess of the original all carbonyl nickel condition does not occur until the P/T ratio is > 0.50 and a maximum in the strength curve arises at a P/T ratio of 0.995. A composite, however, prepared under identical conditions to the $P/T = 0.995$ composite and tested at 1100°C showed a poor UTS (4.7×10^3 psi (33 MNm^{-2})) corresponding to a strengthening efficiency of $< 5\%$.

All the specimens referred to above showed a

TABLE VI Composite properties as a result of matrix constitution changes.

Matrix constitution $\dfrac{\text{Wt. of nickel as powder}}{\text{Total wt. of nickel}}\left(\dfrac{P}{T}\right)$	Testing temp. °C	Density g. cc^{-1}	UTS psi [MNm^{-2}]	Strengthening efficiency %
0.975	20	7.48	53.5×10^3 [374]	31.4
0.865	20	7.60	47.8×10^3 [335]	24.0
0.450	20	7.55	40.0×10^3 [280]	13.3
0.995	1100	—	4.7×10^3 [33]	5

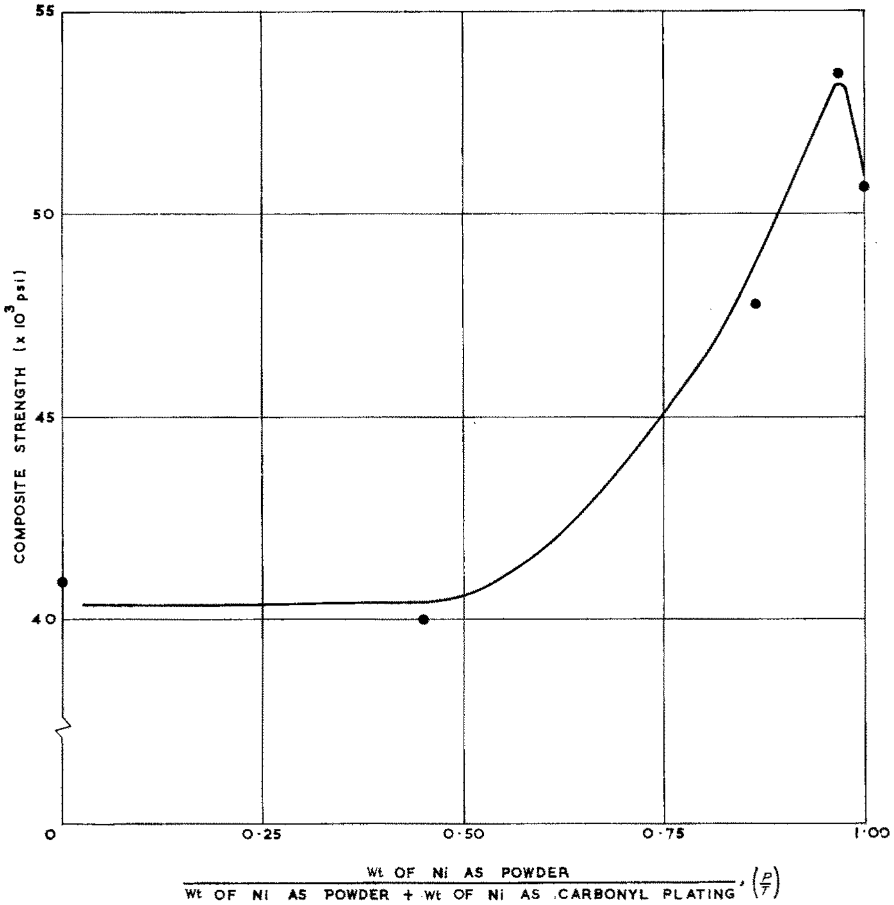


Figure 10 Composite strength as a function of matrix constitution.

high degree of ductility (viz. 30% on a ¼ in. gauge length.) This ductility is due to the increased fibre diameter (cf Al_2O_3 whiskers) as described by Kelly and Cooper [9]. These workers showed that in the fracture of a fibre reinforced composite, the matrix material deforms plastically either side of the fracture and the extent of this deformed zone is dependent on the diameter of the fibre by the equation

$$x = \left(\frac{1 - V_f}{V_f}\right)\frac{\sigma_M d}{4\tau}$$

where V_f is the fibre volume fraction, σ_M is the matrix strength, τ is the interface shear strength, d is the fibre diameter and x is the extent of extensive plastic flow of the matrix either side of the fracture. In the case of alumina fibres (0.010 in. diameter) when $V_f = 0.20$, $\sigma \sim 40 \times 10^3$ psi (280 MNm^{-2}), $\tau = 10^4$ psi (70 MNm^{-2}) then $x = 0.040$ in. (i.e. plastic flow occurs over a region $2x = 0.080$ in.) For tensile specimens with a 0.25 in. gauge length, deformation over 0.080 in. gives rise to measurable amounts of plastic deformation. For whiskers ($d = 0.0005$

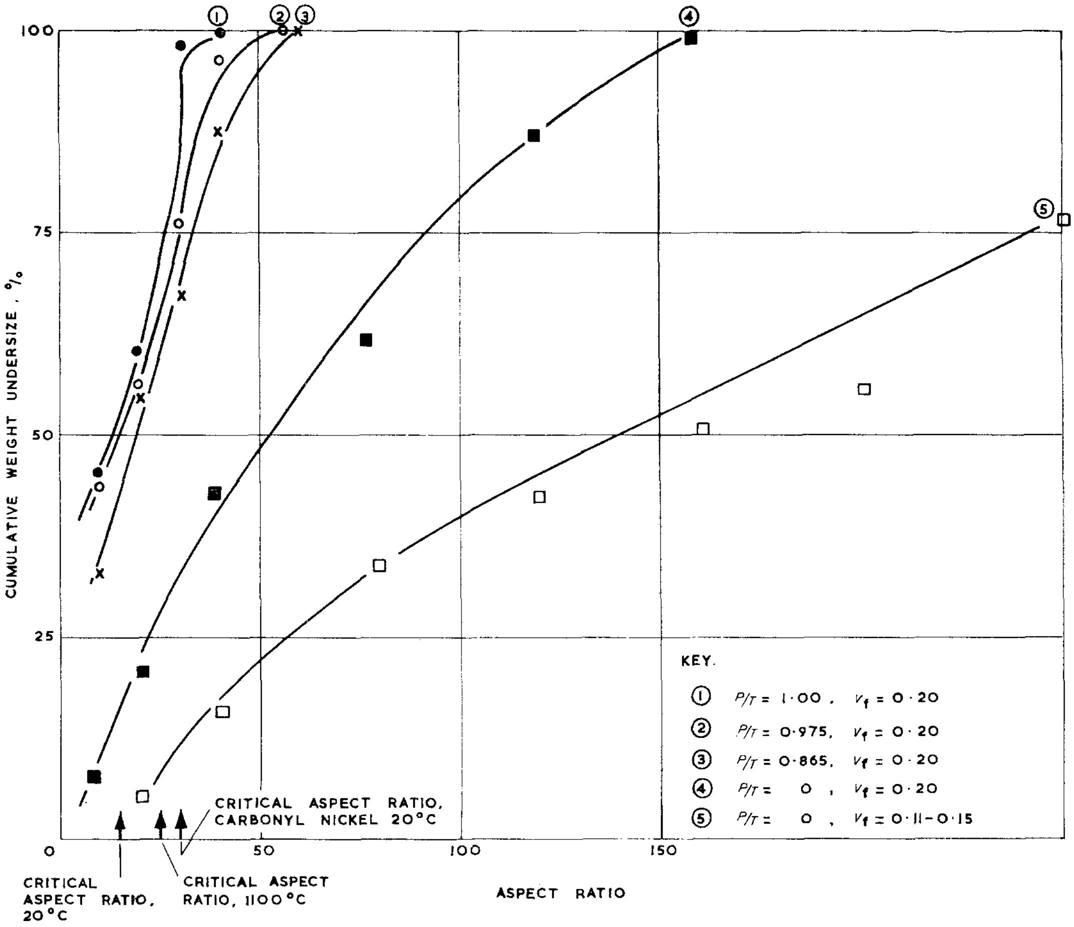


Figure 11 Fibre break-up as a function of matrix constitution.

in.), the deforming zone would be fifty times smaller than in the case of the fibres and would not be measurable in a usual tensile test.

3.3. Analysis of Fibre Break-up in Nickel/Alumina Fibre Composites

In all the specimens studied, fibre break-up occurs to some degree as a result of the hot compaction procedure. The critical aspect ratio of the fibres to allow full theoretical strengthening by the fibres in the composite has been discussed previously (section 2.1.2) and it was shown that at 20 and 1100°C the critical aspect ratios are 15 (or 30) and ≥ 25. Fig. 11 shows the results of an analysis of fibre size after composite preparation by different routes; the fibre fragments were removed from the composite by acid dissolution of the matrix. These results show:

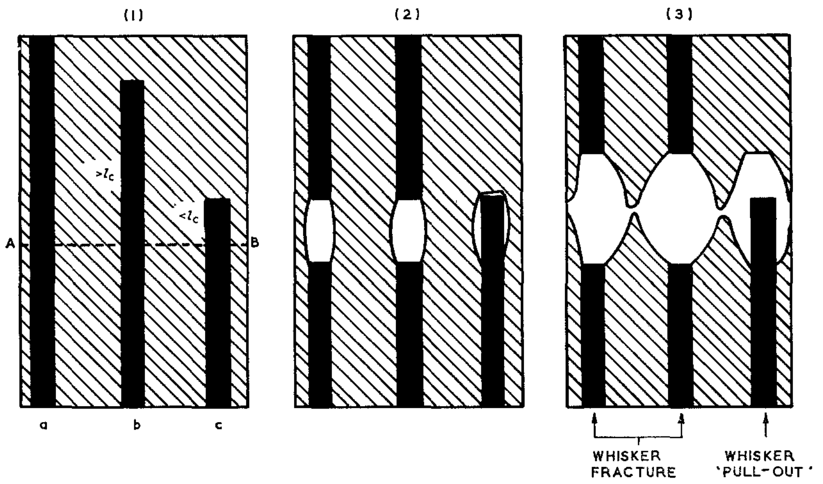
(1) That in any of the processes in which nickel powder was involved in the matrix constitution (curves 1 to 3) considerable fibre break-up occurred. By using nickel-coated fibres combined with powder (curve 2, 3), break-up is marginally improved.

(2) By increasing the thickness of the nickel carbonyl-plated layer (in the all plated carbonyl nickel matrix) from 0.006 to 0.010 in. (curve 4 and 5 respectively), the break-up is lessened.

(3) Even in the worst break-up condition (curve 1), 50% by weight of the fibres have aspect ratios greater than the critical value at 20°C and 30% at 1100°C. In the best condition (specimen 5), 90% of the fibre fragments are greater than the critical aspect ratio values at both 20 and 1100°C

3.4. Fractography of Composites

The features of the fracture region of composites prepared from both alumina fibres and alumina whiskers in nickel have been studied. The surface is generally comprised of a series of holes, matrix



(1) REPRESENTATION OF A COMPOSITE CONTAINING WHISKERS (abc) ABOUT TO FRACTURE ALONG AB WHEN a & b FRACTURE INTO TWO HALVES $>l_c$ & c PULLS OUT SINCE THE FRACTION OF WHISKER IN THE FRACTURE ZONE IS $<l_c$

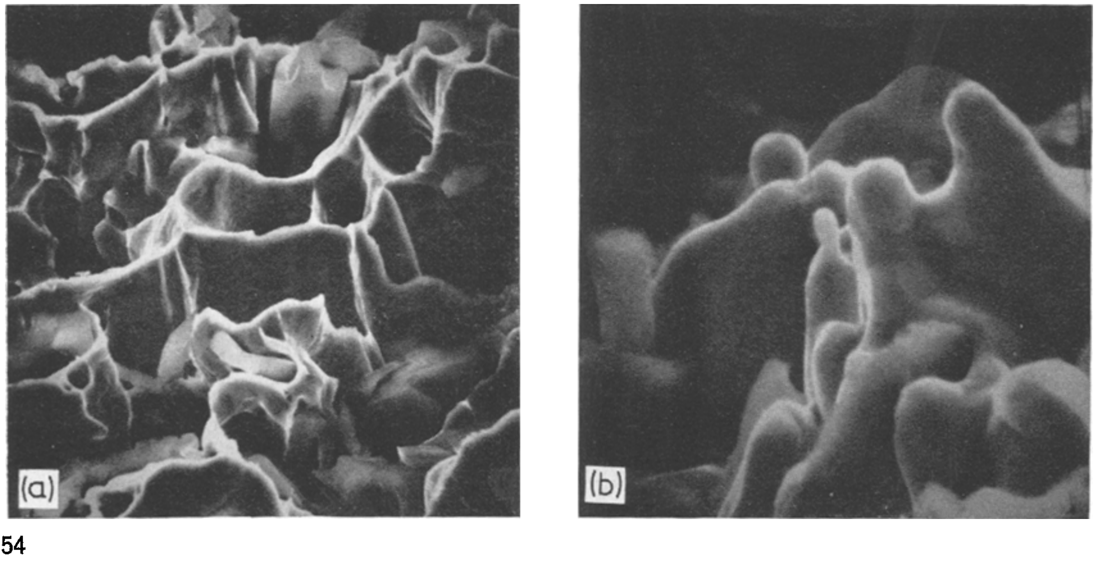
(2 & 3) AFTER WHISKER FRACTURE, THE MATRIX BETWEEN WHISKERS NECKS AND FINALLY FRACTURES, REVEALING A SERIES OF CRATERS WITHOUT WHISKERS SHOWING (WHEN WHISKER FRACTURE OCCURS) & WITH WHISKERS SHOWING (WHEN PULL OUT OCCURS)

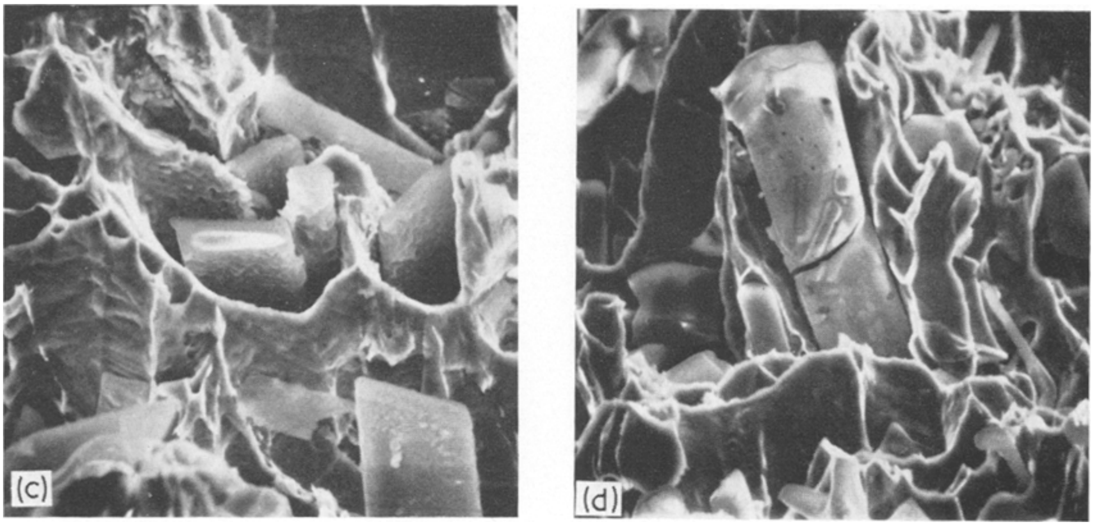
Figure 12 Model for fracture of composites.

ridges and pulled-out fragments of the whiskers or fibres.

A model system is proposed to clarify the general features of the composite fracture surface for a discontinuous fibre system. Alumina whisker composites clearly fall into this category and, it is argued, that in view of fibre break-up on pressing, then alumina fibre composites also comply.

Fig. 12 represents the stages of the deformation of a model which is comprised of three whiskers or fibres (a, b and c) in a ductile matrix and in which fracture occurs along AB. The two whiskers (or fibres) a and b fracture into two halves since the lengths either side of the fracture zone are greater than l_c, the critical length; however, c, instead of fracturing, will pull-out of the matrix since the fraction of whisker in the fracture zone is $\leq l_c$. After whisker fracture, the matrix between the whiskers deforms further and





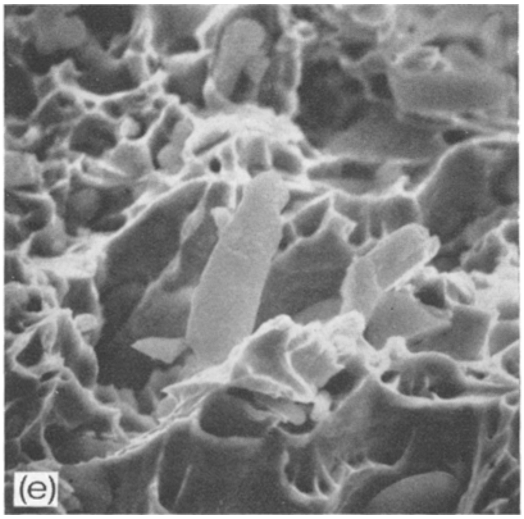


Figure 13 The appearance of the fracture surface of (a) composites prepared from uncleaned FTH whiskers, tested at 20° C; (b) as (a) tested at 1100° C; (c) composites prepared from acid cleaned FTH whiskers tested at 20° C; (d) as (c) tested at 1100° C; (e) as (c) tested at 20° C after a heat treatment at 1100° C for 300 h in argon (× 3000).

necks away from the whisker, finally fracturing. The structure produced, therefore, is comprised of a series of craters without whiskers showing above the general level of the ridge (if the whiskers have fractured) and with the whiskers showing above this level when pull-out occurs.

Fig. 13 indicates the major differences in the fracture region after testing composites of FTH whiskers (etched and unetched) in nickel at 20° C, 1100° C and after the heat-treatment. In the case of the elevated temperature test, the appearance of the pulled-out whisker fragments was dependent on whether or not etching of their surfaces was carried out. In the case of etched whiskers, the fragments are clean with no matrix material adhering whereas, for unetched whiskers the angular shape of the fragments is completely hidden by an adherent matrix phase. The matrix phase, too, shows structural differences after testing at 20°C and 1100°C. After a room temperature test, the matrix ridges are well defined whereas after a 1100°C test a more nodular structure occurs. Fig. 13e shows the fracture appearance after the 300 h heat-treatment. The serrated appearance of the chemically attacked whiskers is easily seen on the fragments of the pulled-out whiskers.

4. Discussion of Results

4.1. Metal/Whisker Composites

4.1.1. Differential thermal expansion effects

Table VII compares the thermal expansion coefficients for nickel and alumina at 100 and 1000°C. The difference in these properties suggests two effects may occur in a composite comprised of Al_2O_3 whiskers in a nickel matrix:

TABLE VII Comparison of coefficients of thermal expansion of Ni and Al_2O_3.

Material	Coefficient of expansion in./in. °C × 10^{-6}	
	100°C	1000°C
Ni	13.25	16.50
Al_2O_3	6.00	8.20

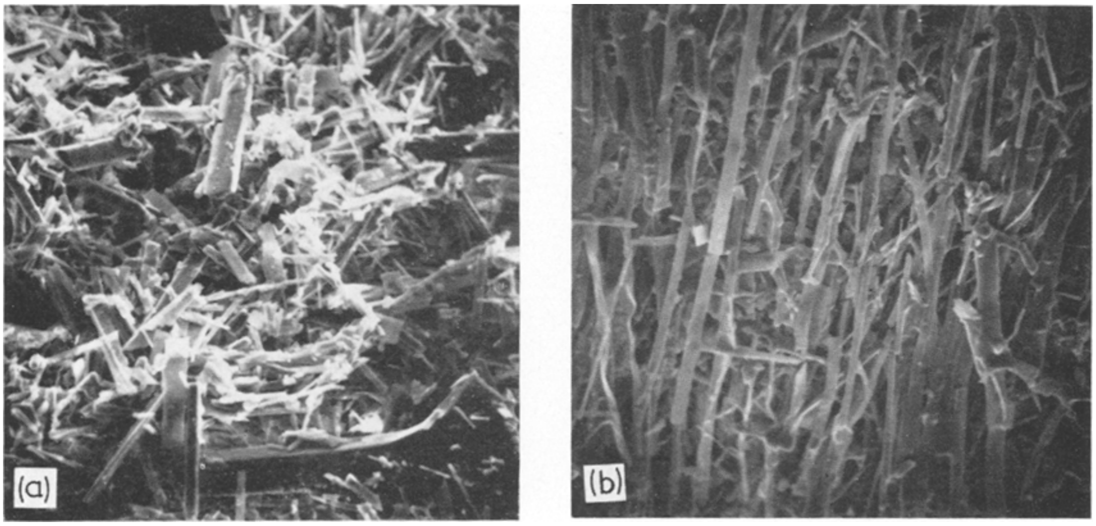


Figure 14 Whisker break-up in composites prepared from acid-cleaned whiskers (a) compared with whiskers from a composite prepared from as-received whiskers (b) (× 550).

(i) a lateral differential movement at the nickel/alumina interface on cooling, and

(ii) a circumferential gripping of the whisker by the matrix on cooling. Further, it is considered that (i) would disrupt any chemical bond produced at the interface on fabrication and (ii) would establish a mechanical bond. At room temperature, therefore, the mechanical bond allows the development of full theoretical strengthening in the composite; however, on reheating to some elevated temperature, the mechanical bond is relaxed due to differential expansion effects and a composite with poor strengthening efficiency is developed.

4.1.2. Role of the silicon rich impurity phase

The silicon rich impurity phase plays a minor part in determining the strength properties of the composite, the major role being played by the differential expansion effects. The three minor roles of this phase are:

(i) as a protection from chemical attack of the whisker by the matrix (see section 3.1.2)

(ii) as a promoter of bonding between the whisker and matrix giving rise to better strengthening efficiencies in the case of 20 and 1100° C tests.

(iii) as a soft phase at the compacting temperature which allows better densification and minimises whisker break-up during hot-pressing. Fig. 14 compares whisker debris taken from composites prepared from both as-received and etched whiskers.

4.2. Metal/Fibre Composites

Although a considerable degree of fibre break-up occurs during the course of composite manufacture, extensive fibre strengthening at both 20 and 1100° C would still be expected on theoretical grounds (even in the worst condition 50% of the fibres have aspect ratios greater than the critical value at 20° C assuming a bond of 6×10^3 psi (42 MNm^{-2}) and 25% at 1100° C). The conflict between theory and practice results from either a low bond strength (< the assumed values of 10×10^3 psi (70 MNm^{-2}) and 1.85×10^3 psi (MNm^{-2}) at 20 and 1100° C respectively) or from low fibre strength. Since the results cannot be accounted for in terms of fibre degradation (see section 3.2.1), it is therefore concluded that the overall lack of strength is due to a weak fibre/matrix bond. This major strength reducing effect is considered to be due again to the differential thermal expansion coefficients of the two components (as discussed above) which result in the extremely low fibre strengthening which occurs at both 20 and 1100° C in this system.

The development of the metal/alumina fibre system was based on the prognosis that the effect of chemical attack between matrix and fibre would not result in the rapid dissolution of the fibre into the matrix due to its size in contrast to the metal/alumina whisker system. Further, this also implies that the strength of the fibre/matrix interface can be improved by creating a stronger chemical bond (increased chemical reaction) at the interface without irrevocably damaging fibre properties. There is existing evidence, however, to show that this approach is not very promising; if the pressing temperature is increased to 1300° C (section 3.2) this caused sufficient reaction to occur to result in the appearance of the spinel $NiAl_2O_4$ and the resulting composite was weaker than the other conditions in which the presence of $NiAl_2O_4$ was not detected.

4.3. General

Our current observations on both strengthening at 20° C and the lack of strengthening at 1100° C have been adequately explained in terms of the disruption of the vital chemical interfacial bond between whisker and matrix during a single thermal cycle. The immediate conclusion that alumina whiskers are unsuitable for strengthening nickel is far more reaching. Wherever such a disparity in the coefficient of expansion exists there is risk of rupture of any similar interfacial bond. These conditions are likely to be met in every ceramic/metal situation and it follows therefore that reinforcement for high temperature service use of metals by ceramic whiskers is extremely unlikely. Moreover, should this conclusion be in error, and it be subsequently shown that a ceramic whisker bonded to a metal can be thermally cycled without rupture of the chemical interfacial bond, then the problem becomes that of ensuring compatibility between whisker and matrix. Even this alternative approach or possibility is fraught with difficulty.

Any metal matrix that has inherent oxidation resistance is likely to have a melting point in the range 1300 to 1650° C (chromium or nickel chromium alloys). If it is assumed that fabrication of the whisker composite is likely to be carried out in the solid state then the problem becomes that of promoting reaction between the components at $\sim$ 1300° C yet ensuring compatibility for long periods ($\sim$ 5000 h in the case of an aero-jet turbine) at temperatures only $\sim$100 to 200° C lower.

The alternative of considering liquid phase infiltration and consequential bond development at temperatures much higher than the service temperature of 1100° C is not a practical proposition. Whiskers would need to be aligned and preplaced and infiltrated at 2000° C under pressure, for suitable ceramics are not readily wetted by liquid metals. To promote wetting and so overcome this other difficulty may be proposed but any coating on the whisker must be chemically bonded to the whisker which recreates the initial problem.

Also from this work, no evidence has been collected to suggest that by using large diameter (0.010 in.), single crystal alumina fibres any benefit can be gained over the composite system involving fine, alumina whiskers (10 μm diameter). This system also suffers the disadvantage of differential thermal expansion effects which result in reduced interfacial bonds at room temperature (after one heating/cooling cycle) and almost zero bonding at elevated temperature (after a heating/coding/heating cycle) and further, the expected advantage of the thicker fibres being able to withstand higher degrees of fibre/matrix interaction is also doubtful. Initial results showed that by increasing the interfacial reaction, gross fibre degradation occurred after only moderate degrees of interaction.

Based on this work, it is concluded that the use of this system, both using Al_2O_3 whisker or fibres, as a high temperature composite is very doubtful.

5. Conclusions

(1) Both α-Al_2O_3 whiskers and fibres (0.01 in. diameter) have attractive high temperature mechanical properties, the tensile strengths at 1100° C being 2.5 to 2.8 10^5 psi (1.75 to 1.96 GNm^{-2}) and 10^5 psi (0.7 GNm^{-2}) respectively.

(2) The strengthening efficiency of such materials incorporated in a nickel matrix at 20° C is high (40 to 75 %) in consequence of a mechanical bond generated between whisker/fibre and matrix during cooling from the manufacturing temperature. The mechanical bond arises as a result of circumferential gripping of the whisker/fibre by the matrix due to the differential coefficient of expansions of the two components; such a differential also disrupts the elevated temperature chemical bond formed at the interface by relative longitudinal movement of the components. The lower 20° C strengthening efficiency in fibre composite is explained in terms of a reduced fibre gripping effect arising from possible matrix porosity.

(3) The strengthening efficiency of these composites at elevated temperature is very low ($<$ 10 %) since re-heating to conduct a high temperature test (1100° C) relaxes the 20° C mechanical bond and, in consequence, stresses are not shared by the whisker or fibre.

(4) To improve the strength of the interfacial chemical bond, the Al_2O_3 fibre (0.01 in.) composites have been subjected to increased manu-

facturing temperatures (1300° C). It was expected that these thicker fibres would be able to stand increased interfacial chemical reaction without suffering gross loss of form or mechanical properties in contrast to the thinner whiskers. Although no significant dissolution of the fibres occurred, nevertheless the increased chemical reaction resulted in poor composites.

(5) It is concluded, therefore, that mainly because of the inherent disparity of the coefficient of thermal expansion of metals and ceramics, the development of high temperature metal matrix composites is considered very unlikely.

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