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Some Electron Microscope Observations of Alumina Whisker/Nickel Composites

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Alumina whiskers separated from Thermokinetic Fibres sapphire wool mat type 1A have been incorporated into nickel by roll-bonding and by hot-pressing. The roll-bonded composites containing up to 5 vol % whiskers were successfully electrothinned to allow transmission electron microscope examination of alumina whiskers contained in the nickel matrix. In the hot-pressed composites which contained 20 vol % whiskers, examination of the whiskers was only possible after extraction from the composite. The roll-bonding process resulted in whisker break-up but the whisker segments retained their monocrystalline form. The whiskers in these composites also retained extensive dislocation tangles in the adjacent nickel matrix after annealing at temperatures up to 1400° C.

The whiskers extracted from the as-hot-pressed composites had a monocrystalline form and gave no indication of spheroidisation. In hot-pressed samples annealed at 1400° C for up to 100 h the whiskers exhibited evidence of spheroidisation. In some instances the whiskers developed strong crystallographic morphologies with faces parallel to the $<11\bar{2}0>$ directions of the approximated close-packed hexagonal lattice of α-alumina.

1. Introduction

The calculated creep rupture properties of nickel alloys reinforced with dispersed alumina whiskers are encouraging [1] and make these composites potential successors to the present precipitation-hardened Ni/Cr/Co alloys. However, future use of such composites requires that successful fabrication and long-term high-temperature stability are achieved. The critical transfer length l_c for the reinforcement of nickel by alumina whiskers can be estimated from existing theories [2] and typical values are as follows: 20° C 90 μm; 1100° C, 100 μm; and 1200° C, 170 μm. Fabrication techniques must allow amongst other factors the introduction of whiskers of length greater than l_c and also generate a strong whisker-matrix bond. In service at elevated temperatures the strength of the whisker and whisker-matrix bond must be retained together with a whisker length greater than l_c if the desired strength levels of the composite are to be achieved.

The observations presented in this paper describe results concerned with the integrity of alumina whiskers in nickel. Electron microscope techniques have been used to study alumina whisker/nickel composites containing varying volume fractions of whiskers and of composites fabricated in different ways and subsequently heat-treated.

2. Experimental

2.1. Preparation of Whisker Composites

Thin sheets of nickel containing dispersed alumina whiskers were prepared by three methods: settling and roll-bonding; (see section 2.1.1) roll-sandwiching (see section 2.1.2); and hot-pressing (see section 2.1.3).

The materials used were High Purity Material nickel* sheet, sapphire wool mat type 1A†, and a nickel-alumina composite tape made at AWRE, Aldermaston. This composite tape is made by a slurry extrusion technique similar to that of Raynes [3] in which the alumina whiskers are

*International Nickel Limited, D & R Laboratory, Birmingham, UK.
†Thermokinetic Fibres Inc, Nutley, NJ, USA.

suspended in a nickel powder-ammonium alginate slurry sol and aligned in the extrusion direction. Subsequent gelling, drying and heat-treatment in hydrogen at 1100° C results in a composite tape, 25 mm wide and 0.05 mm thick, which is approximately 75% porous. This process can be used to introduce up to 20 vol % of alumina whiskers into the nickel tape.

2.1.1. Setting and Roll Bonding

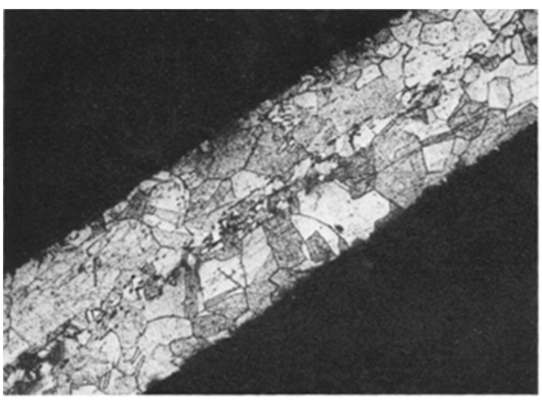
The Thermokinetic sapphire wool mat was dispersed in ethylene glycol using a kitchen mixer and the suspension sieved through 52 and 500 BSI standard mesh sieves. The 500 mesh fraction was discarded and the remaining 52-500 mesh whiskers dispersed in a small volume of ethylene glycol and poured on to 0.25 mm thick nickel sheet contained in a Petri dish. The whiskers were allowed to settle on the nickel sheet and the remaining liquid removed by evaporation. In some instances this process led to the local agglomeration of whiskers on the nickel sheet. A further 0.25 mm sheet of nickel was clamped on top of the "whiskered" surfaces and the composite heat-treated in purified hydrogen at 1000° C for 24 to 60 h. Cold-rolling to 90% total reduction in thickness with intermediate anneals at 1400° C completed the bonding of the nickel sheet and the composite. Optical microexamination of these composites revealed a low density of whiskers, in the centre of the sandwich in association with small recrystallised grains.

2.1.2. Roll-Sandwiching

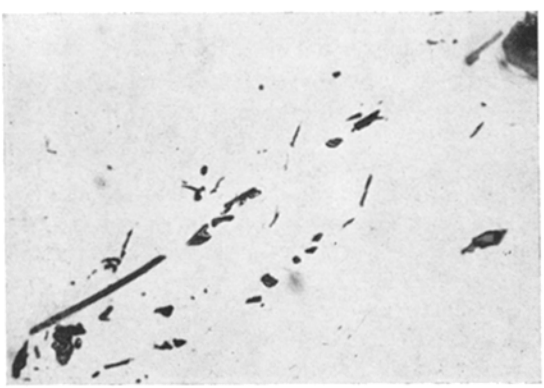
In this approach, the AWRE tape containing 5 vol % alumina whiskers was bonded between two sheets of nickel. To prepare these composites it was necessary to achieve complete densification and also to obtain material in sheet form which would produce electron microscope specimens by electrothinning. Previous work [4] on roll-densification of porous sintered nickel/alumina composites had shown that a minimum of 60 to 80% reduction in thickness was necessary before the composites approached their full theoretical density. These conditions were satisfied by spot-welding the 0.05 mm thick tape between 0.25 mm thick nickel surface layers and cold-rolling to 0.05 to 0.10 mm thick, with intermediate anneals at 1000° C in a vacuum of better than 10^{-5} torr. Metallographic observations revealed that this treatment resulted in a good bond between the tape and nickel sheets.

2.1.3. Hot-Pressing

Composites were obtained from AWRE, tape (5 vol % whiskers) sandwiched between surface layers of nickel by hot-pressing for 1 h at 1100° C under a pressure of 1 tsi (1.0 tsi = 1.0 ton/in.^{2} = 157 kg/cm^2) in a vacuum of approximately 10^{-3} torr. These composites had the structures shown in figs. 1a and 1b, the matrix grain-size being much finer in the central layer containing the whiskers. This finer grain-size may be a consequence of the particle-size (5 μm) of the initial nickel powder, used to produce the AWRE tape. It may on the other hand be due to the restriction of grain-growth by the presence of the whiskers. A number of composites made from 20 vol % alumina whisker tape by hot-pressing without the surface nickel sheets were supplied by AWRE.



(a)



(b)

Figure 1 Cross sections of a hot-pressed sandwich with 0.05 mm nickel surface layers and AWRE 5 vol. % alumina whisker-tape core layer. (a) × 160, etched; (b) × 800.

2.2. Preparation of Thin Foils for Transmission Electron Microscopy

The composites made by settling and roll bonding and by roll-sandwiching had uniform thicknesses of 0.05 to 0.10 mm. These materials yielded suitable thin foils by electropolishing, using the window method, with a solution containing 12.5% sulphuric acid, 55.5% phosphoric acid and 32% water by volume, maintained at a temperature of 70°C.

The preparation of thin foils from the hot-pressed sandwiches presents a number of problems. The maximum starting thickness for successful electrothinning in these composites is ~ 0.20 mm. On the other hand the minimum specimen thickness which can be successfully hot-pressed between alumina platens and subsequently detached from the platens without extensive deformation is ~ 0.45 mm [5]. Attempts to reduce thickness prior to electrothinning by mechanical polishing and spark-machining tended to introduce deformation into the specimens, and chemical polishing resulted in extensive pitting.

3. Results

3.1. Structure of Alumina Whiskers before Incorporation into Nickel

Thermokinetic Fibres sapphire wool mat type 1A was dispersed in a solution of ethylene glycol and water and the whiskers allowed to settle on to microscope grids. After drying, a carbon film was deposited on the whiskers to prevent electrostatic charging and movement in the microscope. All the whiskers exhibited single-crystal diffraction patterns. The ends of the whiskers exhibited either a growth tip (fig. 2), or facets characteristic of a surface formed by cleavage fracture (fig. 3).

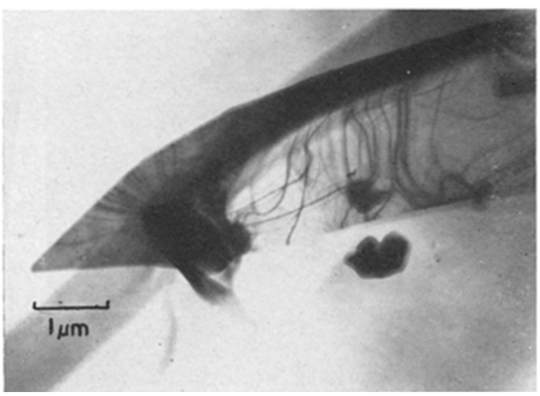


Figure 2 A growth tip in an alumina whisker as separated from the as-grown wool mat.

3.2. Settled and Roll-Bonded Composites

Fig. 4 is an example of the structure observed in the cold-rolled composite. Whiskers were only observable at the edges of the foils and detailed examination was not possible due to thickness fringes and the presence of intense dislocation tangles. The selected-area diffraction pattern (inset fig. 4) shows strong reflections from the nickel in a (2 1 1) orientation and the faint spots are attributed to the whisker.

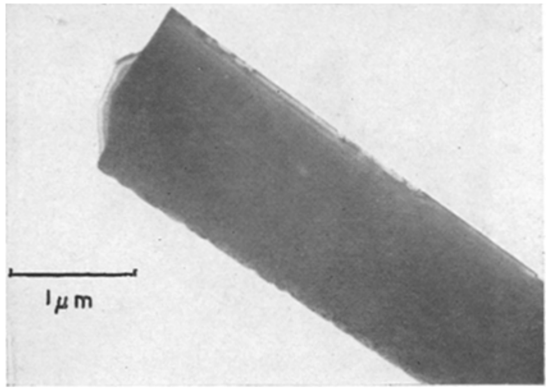


Figure 3 A fracture face in an alumina whisker as separated from the as-grown wool mat.

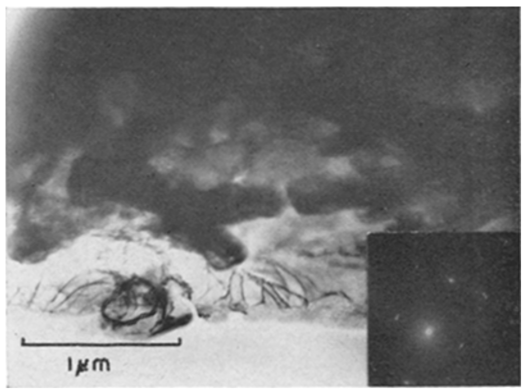


Figure 4 Alumina whiskers in a settled and roll-bonded sandwich, as cold-rolled. Inset: selected area diffraction on a whisker plus the matrix.

The cold-rolled material was vacuum-annealed at 800° C for 1 h. Fig. 5 shows an alumina whisker partially contained in the nickel matrix and the whisker (A on the micrograph) is associated with matrix dislocation tangles. The inset

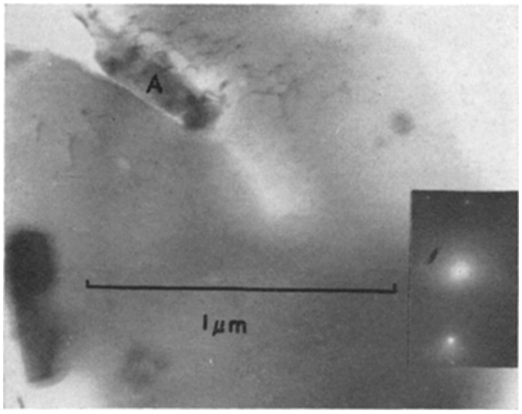
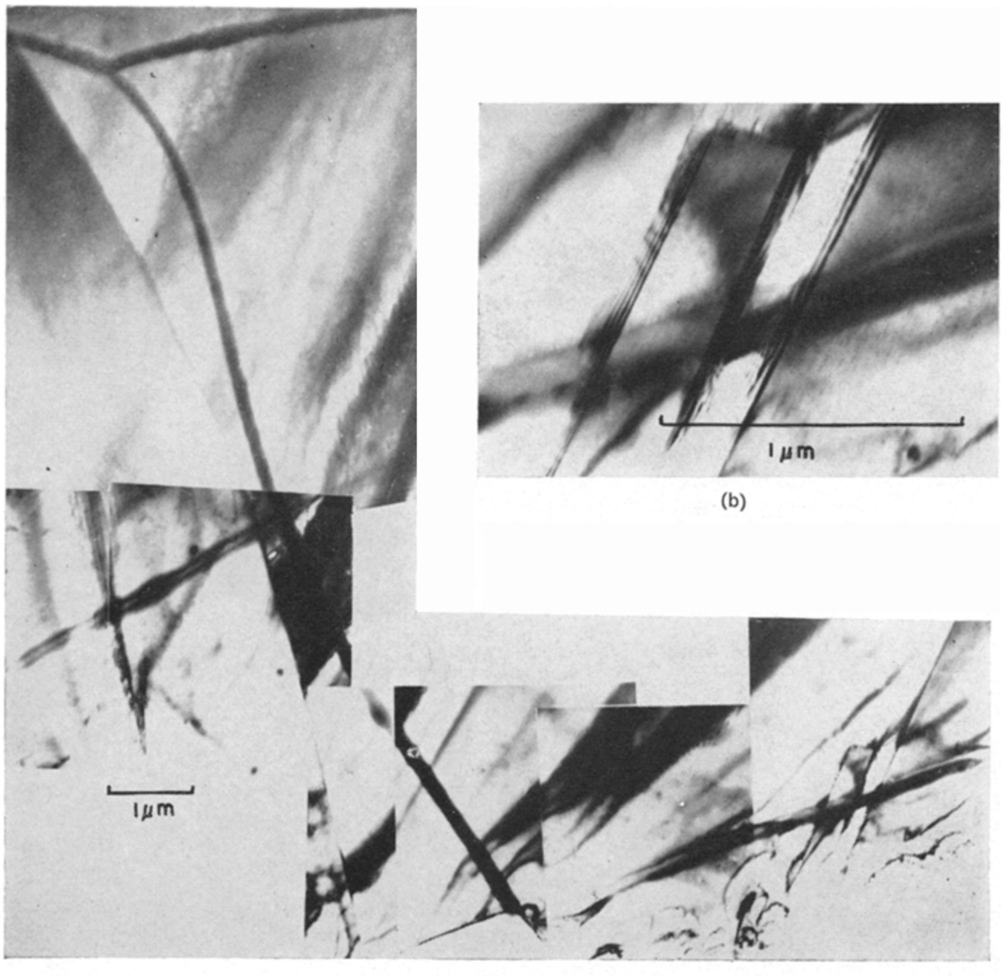


Figure 5 Alumina whiskers in a settled and roll-bonded sandwich after vacuum-annealing for 1 h at 800° C. Inset: selected-area diffraction from the whisker and matrix on the right.

diffraction pattern obtained from an area containing the whisker at A gave *d* spacings which were in reasonable agreement with those for α-alumina. Figs. 6a and 6b show whiskers associated with the nickel matrix after an anneal at 1400° C for 1 h. From the appearance of the extinction fringes of the twin boundaries the whisker is lying on the surface of the foil, possibly in a shallow valley. The foil thickness near the twin-whisker intersection can be estimated since the orientation of the matrix is within 5° of (1 1 0); the thickness (approximately 400 Å) implies that the whisker (diameter 1000 Å) is protruding from the surface of the matrix. It should also be noted that the dislocation tangles associated with the whiskers in fig. 5 are not present in fig. 6.



(a)

Figure 6 (a) A branched alumina whisker 21 μm long in a settled and roll-bonded sandwich annealed for 1 h at 1400° C. (b) Enlarged view of the area at the right of fig. 6a.

3.3. Roll-Sandwiched Composites

After a 30 h vacuum anneal at 800° C of the roll-bonded AWRE tape composite, short segments of whiskers with rounded ends were observed in the thinned foils (fig. 7). After annealing the composite for 30 min at 1400° C the structures presented in fig.8a and 8b were observed. These results show the presence of a series of similarly aligned whiskers. There are intense dislocation tangles associated with the whiskers in the adjoining matrix (point A in fig. 8b). There is also some fragmentation of the whiskers (fig. 8b) which could have occurred during the production of the composite.

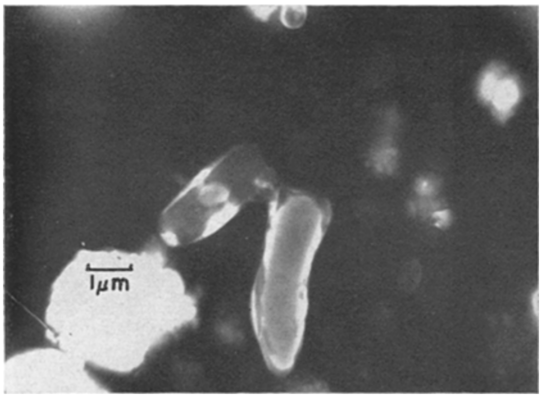


Figure 7 Alumina whiskers in roll-sandwiched AWRE 5 vol % tape after vacuum-annealing for 30 h at 800° C.

3.4. Hot-Pressed Alumina Whiskers/Nickel Composite

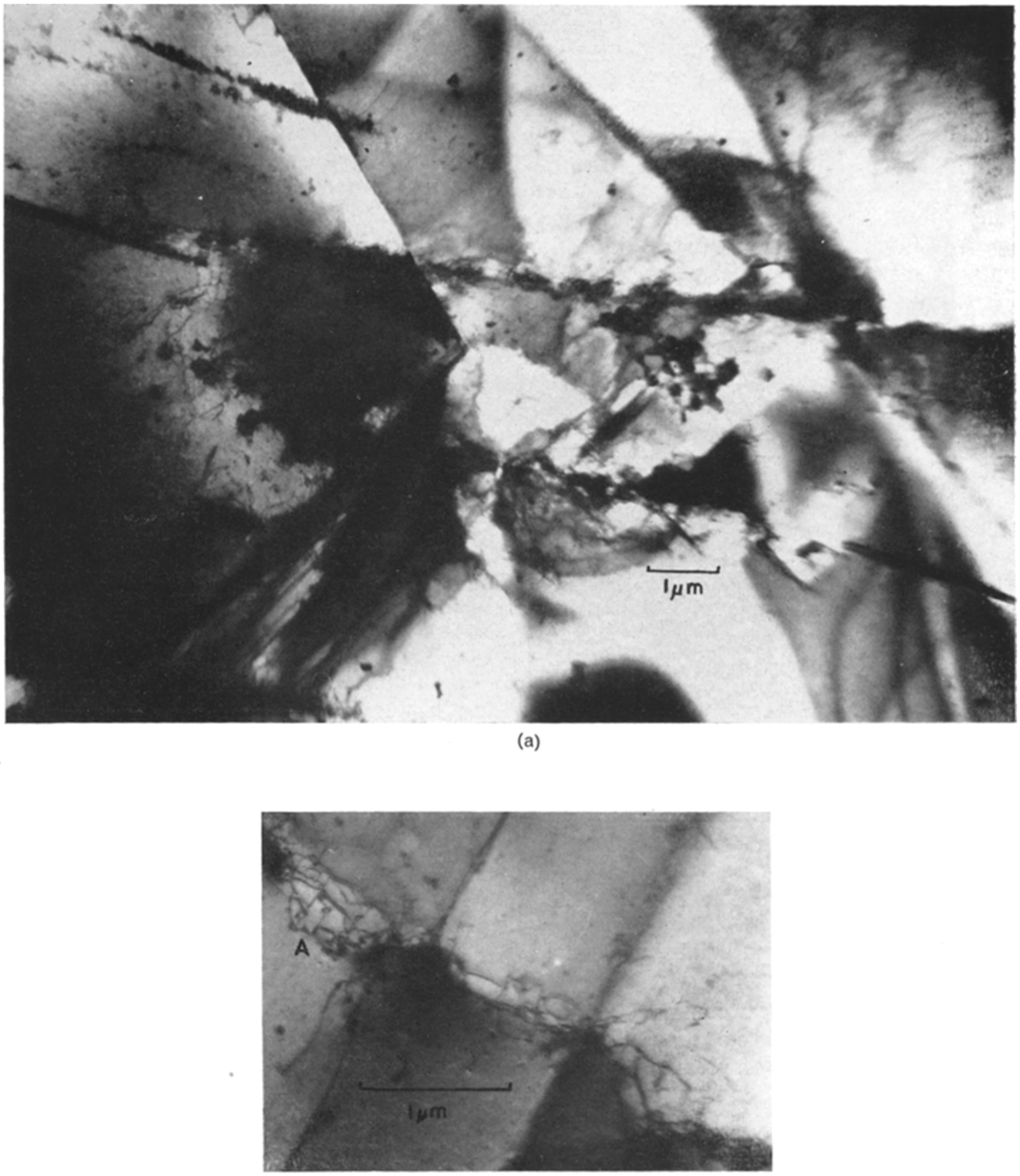
The hot-pressed composites contained a higher volume-fraction of whiskers than the other materials. As a consequence, premature thinning of the nickel matrix occurred between regions of overlapping whiskers (fig. 9) and only small regions of transparent matrix were obtained. In the hot-pressed composites containing 20 vol % whiskers a further problem, namely that of the formation of an obscuring felt of whiskers on the surface of the foils, made detailed examination of both the whisker and matrix very difficult. Whiskers were therefore separated from the matrix by dissolution of the nickel in a solution containing by volume 60% nitric acid, 10% sulphuric acid and 30% water. Whisker samples prepared by filtration and washing were subsequently settled on electron microscope grids together with an evaporated carbon film. In some instances a silver film was also evaporated on the whiskers to give a diffraction standard.

Whiskers extracted from composites as hot-pressed, containing 20 vol % whiskers are shown in fig. 10. The whiskers had a general angular form with sharp fracture faces and the diffraction patterns showed that the whiskers retained their monocrystalline form during the hot-pressing operation. After heat-treatment at 1400° C for 115 h in a vacuum of 10^{-5} torr, whiskers with rounded and hexagonal profiles were extracted (fig. 11) from a 20 vol % composite. In fig. 11 the hexagon edges of the whisker were parallel to the $<11\bar{2}0>$ directions in the approximated close-packed hexagonal lattice of α-alumina. A further feature of heat-treatment at 1400° C was the formation of necks or "waists" in the whiskers (fig. 12).

4. Discussion

Alumina whiskers, prior to incorporation into the nickel by settling and roll-bonding, exhibited marked variations in length but in general these were greater than 100 μm. The observations in figs. 4 to 8 show that whiskers a few microns in length were present in composites after roll-bonding and in fig. 8 there is apparent disintegration of individual whiskers. Some whiskers appear to have survived the roll-bonding treatment as shown by the presence of a whisker 20 μm in length in fig. 6. The results in general however, do show that significant break-up of the whiskers must have occurred during roll-bonding. The occurrence of this mechanical damage was obviously predictable and the observations confirm that this form of fabrication would not generally be acceptable. The existence of short whisker lengths did show on the other hand that a sufficiently strong bond was developed in these composites for effective load transfer to occur between the alumina whiskers and the nickel matrix. Whilst the roll-bonding process resulted in whisker break-up, the whisker segments did retain their whisker form, that is they remained monocrystalline as evidenced by their diffraction patterns and also exhibited *d* spacings which were those for α-alumina (fig. 5).

Examination of roll-bonded composites containing both settled and tape whiskers revealed the presence of dislocation tangles at the whisker/nickel interface (fig. 5 and 8). These dislocation tangles survived annealing treatments at up to 1400° C and may be a consequence of the pinning or stabilisation of the cold-worked



(a)

(b)

Figure 8 (a) Alumina whiskers in roll-sandwiched AWRE 5 vol % tape after vacuum-annealing for 30 min at 800° C. (b) Another area in the foil of fig. 8a showing whisker fragments and associated matrix dislocations.

dislocation structure by the whiskers. A further factor, the differential thermal expansion of the alumina whiskers and the nickel, may have influenced the observations in figs. 5 and 8 and contributed towards the presence of the dislocations.

Examination of whiskers extracted from the composites as hot-pressed (fig. 10) revealed that their ends retained an angular form. The sharp ends of the whiskers were similar in nature to those of whiskers prior to incorporation into the nickel (fig. 3) and are presumed to be a result of

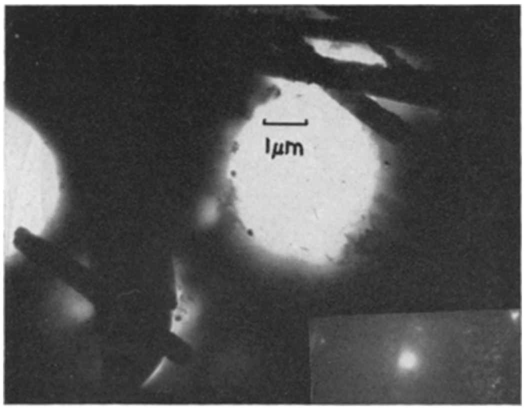


Figure 9 Overlapping whiskers and perforations in the nickel matrix in an AWRE 5 vol % tape sandwich as hot-pressed. Inset: selected-area diffraction from the small whisker and matrix at the lower left.

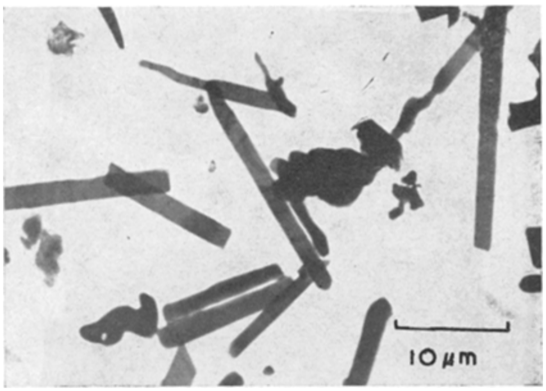


Figure 10 Alumina whiskers extracted from an AWRE 20 vol % tape composite as hot-pressed.

the fracture of the whiskers during the separation of the as-grown whisker wool. The whiskers also retained their monocrystalline form as shown in fig. 10. It would appear therefore, that as in roll-bonding, the hot pressing process did not result in any significant physical changes in the alumina whiskers. Annealing of the hot-pressed composites at 1400° C did result however, in marked changes in whisker morphology. By comparison with the whiskers in the as-hot-pressed condition (fig. 10) the whiskers following the annealing treatments exhibited rounded ends (fig. 11) and also "waisting" or local reductions in cross section (fig. 12). Similar observations of spheroidisation of alumina whiskers in nickel-rich matrices have also been reported by Walles [6], and Warnes and Cannell [7]. Morphological changes due to capillary-induced surface diffu-

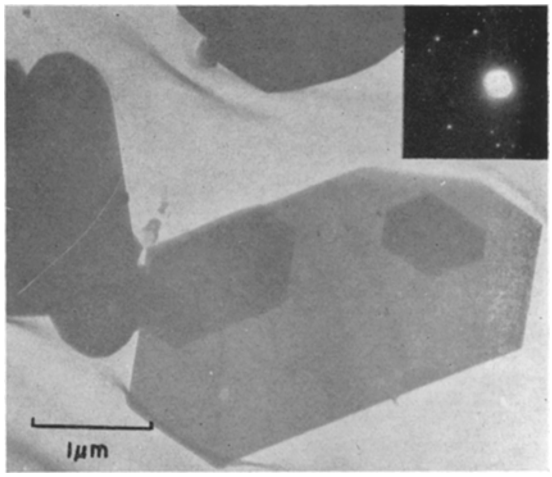


Figure 11 The hexagonal and rounded profiles of whiskers extracted from a hot-pressed AWRE 20 vol % tape composite after a vacuum anneal lasting 115 h at 1400° C. Inset: (0001) diffraction pattern from the hexagonal whisker.

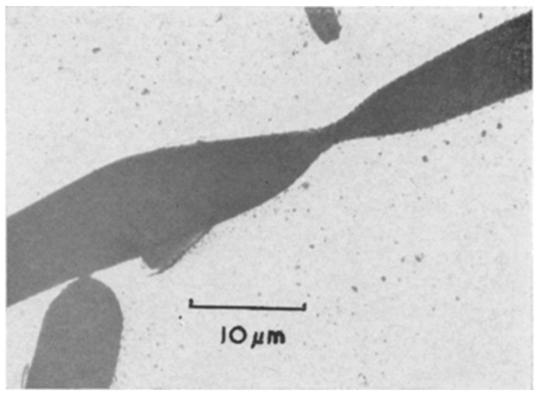


Figure 12 Waist formation in a whisker extracted from a hot-pressed AWRE 20 vol % tape composite after vacuum-annealing for 67 h at 1400° C. (Silver-shadowed extract replica.)

sion have been considered by Nichols and Mullins [8]. They concluded that a long cylindrical rod of initially uniform cross-section will become unstable and form a series of egg-shaped particles of equal size and shape, the ratio of the maximum radius to the initial rod radius at the time of "ovulation" being 1.65. It is of interest to note that the ratio of the major to minor axes of the alumina whisker fragments in figs. 11 and 12 is approximately 3. In some instances the whiskers exhibited a distinct crystallographic morphology (fig. 11) with the faces of the whiskers parallel to $\langle 11\bar{2}0 \rangle$

directions. This may represent a further stage in the diffusion-controlled shape change of the whiskers to attain a minimum surface energy condition. It would appear therefore that there is the possibility of diffusion-controlled instability when nickel-alumina composites are subjected to thermal exposure at 1400° C for periods of 100 h. Whether the same possibility exists for prolonged exposures at 1100 and 1200° C for these composites has still to be evaluated.

5. Conclusions

1. Electron microscope techniques can be used to examine alumina whisker-nickel composites if the volume-fraction of the whiskers does not exceed 2 to 5%.
2. The fabrication of alumina whisker/nickel composites by roll-bonding results in the break-up of whiskers but the whiskers retain their monocrystalline form.
3. Alumina whiskers introduced into nickel by hot-pressing at 1100° C retain their monocrystalline form and do not exhibit spheroidisation.
4. Alumina whiskers in nickel subjected to thermal exposure at 1400° C for 100 h undergo a diffusion-controlled shape change which could lead to whisker instability.

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