The structure of consolidated rapidly solidified powders of Ni₃Al

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Rapidly solidified powders of stoichiometric Ni_3Al and Ni_3Al containing boron and titanium have each been consolidated by two distinct routes, namely hot extrusion or hot compaction. The resulting microstructures have been examined by optical microscopy, scanning electron microscopy and transmission electron microscopy. The consolidated material did not retain the non-equilibrium structure of the rapidly solidified powders. The addition of titanium and boron produced material with a larger final grain size, a decreased incidence of twinning and, in the extruded material, led to cracking. Although all processing was performed in inert atmospheres, oxides were present in all consolidated products.

1. Introduction

Aluminide intermetallics are strong, microstructurally stable and oxidation-resistant at elevated temperatures, thus they are potentially useful in advanced energy-conversion systems. However, whilst they show ductility as single crystals in polycrystalline form, they are generally brittle under ambient conditions. For this reason they are not utilized as engineering materials. A way to improve the ductility of polycrystalline aluminides may be to produce grain sizes smaller than that at which the brittle-to-ductile transition occurs [1, 2]. One route to fine-grained Ni_3Al is through deformation and subsequent recrystallization of single crystals [3]. The route described here is through the consolidation of powders produced by rapid solidification. This technique has the advantage that not only may small grain sizes be achieved but microsegregation is minimized in the powders, no macrosegregation occurs in the powder compact (often a problem in producing stoichiometric Ni_3Al) and the solid solubility of alloying elements may be increased [4]. A possible disadvantage is that surface contamination of the powder could lead to undesirable properties [5].

Two alloys were prepared from rapidly solidified and consolidated powders, one of stoichiometric Ni_3Al and one of Ni_3Al containing boron and titanium in an approximate 2 : 1 ratio. The latter was prepared with previous research in mind; namely, titanium diboride precipitates stabilize boundaries in DO_3-structured Fe_3Al prepared by hot extrusion of rapidly solidified powders [6]. Boron (up to 0.5 at %) has also been shown to increase the room-temperature tensile ductility of nickel-rich Ni_3Al polycrystals from $\sim 0\%$ to over 50% [7, 8].

In previous papers [9–11] the microstructure of the rapidly-solidified powders was shown to consist of aluminium-enriched martensitic dendrites (and interdendritic lamellae in the stoichiometric Ni_3Al powder)

in an $L1_2(Ni_3Al)$ matrix. This paper presents some observations of the structure of the consolidated powders. The room-temperature mechanical properties of the consolidated powders have been presented elsewhere [12].

2. Experimental procedure

Ingots of Ni_3Al containing 24.4 at % Al, 2.8 at % B, 1.5 at % Ti and of stoichiometric Ni_3Al were prepared by United Technologies, East Hartford, Connecticut. The principal impurities (> 0.01 at %), as measured in the consolidated powders, are indicated in Table I.

The ingots were remelted and solidified into powders at Pratt & Whitney Aircraft, Government Products Division, West Palm Beach, Florida, using the P & W Rapid Solidification Rate (RSR) process [13–15]. This process utilizes rotary/centrifugal atomization in which molten droplets of various sizes are convectively cooled by high-velocity helium. Quench rates, which vary with droplet size (typically 10 to 80 μm), are greater than $10^5 \, K \, sec^{-1}$ [14]. Particles larger than 175 μm were separated by screening and discarded. The remainder was stored under a protective nitrogen atmosphere. Consolidation occurred by two distinct routes:

1. Extrusions to rods of (further) size-separated powders were performed (see Table II for conditions)

TABLE I Impurity levels (> 0.01 at %) in the consolidated powders

Impurity	Impurity level (at %) in compound	
	Ni_3Al	Ni_3Al (B, Ti)
Fe	0.05	0.05
Cr	0.05	0.02
Si	0.05	0.09
H	0.02	0.02
C	0.04	0.02
O	0.04	0.02

TABLE II Extrusion data for Ni_3Al and Ni_3Al (B, Ti) rod

Alloy	Particle size (μm)	Extrusion temperature (K)	Area reduction ratio	Extrusion constant, K (MPa)*	Grain size (μm)	Hardness (Rockwell A)
Ni_3Al (coarse)	100 to 175	1503	30:1	392	11	60 ± 2
Ni_3Al (fine)	< 100	1533	25:1	407	15	60 ± 2
Ni_3Al (B, Ti) (coarse)	100 to 175	1533	25:1	357	23	75 ± 2
Ni_3Al (B, Ti) (fine)	< 100	1533	25:1	360	23	75 ± 2

*K is the extrusion constant in the expression $p = K\ln A$ where p is the extrusion pressure and A is the extrusion ratio.

after canning powders (again, under a protective atmosphere) in pre-evacuated containers of 304 stainless steel (62 mm internal diameter, 5 mm wall thickness). The coarse powder (100 to 175 μm) of stoichiometric Ni_3Al was annealed for one hour at 1503 K prior to extrusion. All other powders were annealed for one hour at 1503 K and 30 min at 1533 K prior to extrusion.

2. Vacuum hot-compaction for 2 h at 1393 K at a pressure of 210 MPa was used to produce a disc of 50 mm diameter and 6 mm thickness from the screened powders (< 175 μm). After compaction the disc was slowly cooled (over 19 h) to room temperature.

The consolidated powders were thinned for examination in the TEM using an electrochemical technique [16], and mounted and polished in the standard manner before etching in Marble's Reagent for optical microscopy and scanning electron metallography.

3. Results and discussion
3.1. Hot extrusion
Fig. 1 shows the microstructure typical of the extruded rods. In both alloys the grains are equiaxed, indicative of a fully recrystallized product. The grains within the rod which was formed from the coarse stoichiometric Ni_3Al powder are smaller (11 μm) than those within the rod formed from the fine powder (15 μm). The grain size in the Ni_3Al (B, Ti) rods is 23 μm and is independent of the original powder size.

The grain-size difference between the two stoichiometric rods is not because the original powders differed in size, but because the coarse powder was extruded at a lower temperature and/or because this powder was given a slightly larger reduction during extrusion. The larger reduction would imply a larger stored energy and a larger number of recrystallization nuclei. The lower temperature would mean that less grain growth could occur immediately following recrystallization.

The similar grain sizes of the Ni_3Al (B, Ti) rods, formed from powders of different sizes (Table II), is in keeping with the view that the original powder size has little effect on the grain size of the extruded product.

Curiously, the grain size within the rod containing boron and titanium is greater than in the other, suggesting that grain growth following recrystallization is more rapid in the quaternary alloy. That faster grain growth is indeed the case in the quaternary alloy has been noted explicitly in experiments [17, 18] in which specimens of both alloys were annealed in flowing argon and metallographically examined. The reason for the more rapid grain growth in the quaternary

alloy is not clear. Possibly, the addition of titanium serves to "clean up" the grain boundaries by acting, for instance, as an oxygen getter. Or, perhaps, the boron by increasing the grain boundary dislocation motion [19] also makes grain-boundary migration easier. Alternatively, the boron may form a low melting-point alloy at the grain boundary which is near its melting point during extrusion.

The extruded quaternary alloy differed in three other respects. Firstly, although both alloys exhibited large hardness values (both also exhibited large extrusion constants, see Table II), the quaternary alloy has a higher hardness than the binary alloy ($R_a = 60 \pm 2$) despite the larger grains, implying that boron or titanium (or both) impart significant solution strengthening. Secondly, the stoichiometric Ni_3Al contained numerous twins whereas the Ni_3Al (B, Ti) contained fewer twins. This observation is reminiscent of an earlier one [20] where titanium was noted to reduce the incidence of twinning in Ni_3Al. It implies that titanium and/or boron raises the stacking-fault energy of Ni_3Al. Finally, the quaternary alloy was heavily flawed after extrusion. Numerous cracks and voids were present at grain boundaries (Fig. 2a). Examination of the interior of the larger cracks revealed a nodular structure (Fig. 2b). These nodules are smaller (of the order of 3 to 8 μm) than the original powder particles suggesting localized melting, presumably of an Ni_3Al–B eutectic analogous to the low melting-point eutectic in Ni–B [21]. Such voids and cracking have also recently been noted in Ni_3Al rods containing boron alone when extruded at 1522 K [22].
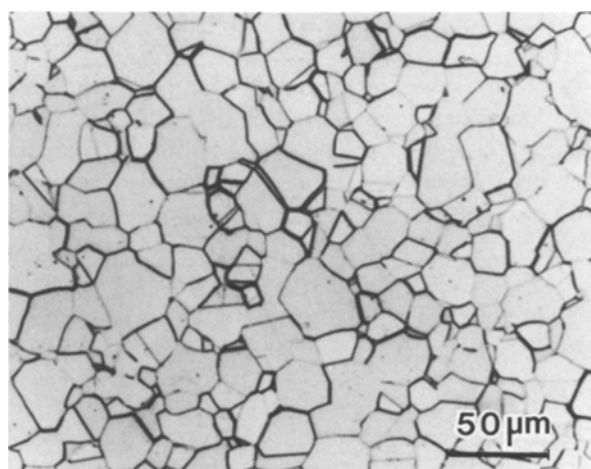
Occasionally, an area containing what appeared to

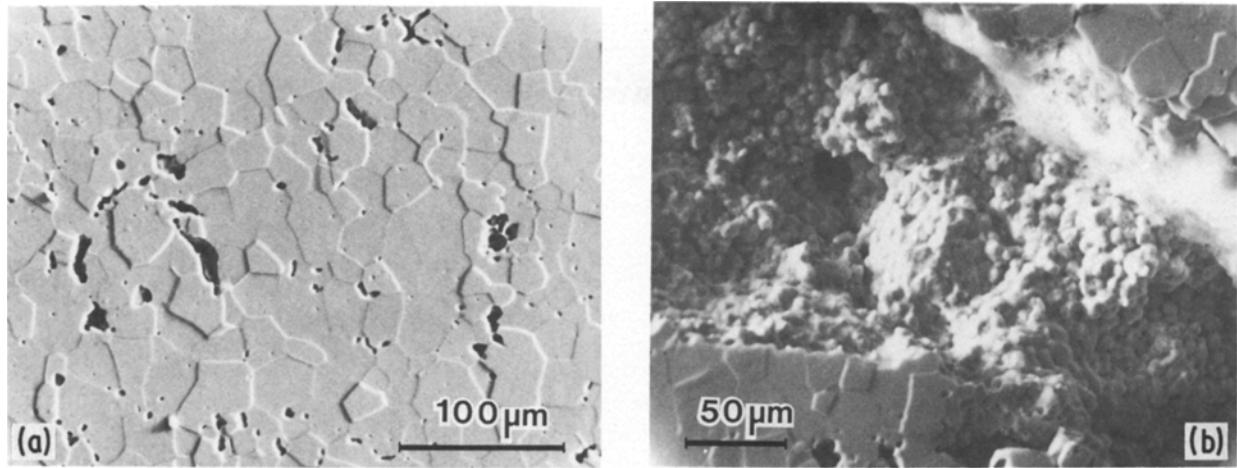Figure 1 Optical micrograph of structure of extruded rod of stoichiometric Ni_3Al.

Figure 2 Scanning electron micrograph of transverse section showing (a) cracks and voids in extruded Ni_3Al (B, Ti) powder, (b) interior of a crack. The nodules in (b) are smaller than the mean powder size (23.5 μm), suggesting they are not unconsolidated powder.

be very fine grains was observed (Fig. 3). These were rare, and only two or three such regions were present in each cross-section of the extruded stoichiometric Ni_3Al rod. An X-ray spectroscopic (EDS) analysis was performed on one of these regions and on the nearby matrix. The results shown in Fig. 4 indicate that this region contained various contaminants. Erosion of the nozzle through which the molten metal passes at high speed is a problem in rapid solidification rigs, and could be the source of the cobalt and silicon here. The result also suggests that the contaminants retard recrystallization and/or grain growth in Ni_3Al.

Transmission electron metallographical examination revealed no additional differences between the two alloys: both were essentially dislocation-free and, when examined using superlattice reflections revealed no antiphase boundaries. Both alloys contained particles which, although rare, could be large, $\sim 2\,\mu$m, (Fig. 5). No diffraction information could be obtained from these particles and they showed no changes in diffraction contrast during tilting, suggesting that they were not crystalline.

Noticeable by its absence in the extruded alloy is the two-phase structure observed in the rapidly solidified powders [9–11], implying that the thermomechanical
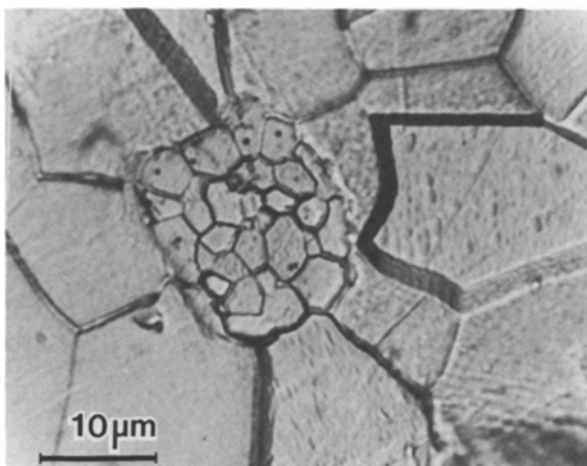
processing (extrusion) is sufficient to homogenize the alloys. In fact, a one-hour anneal of the original powders at 1073 K is sufficient to cause most particles ($> 80\%$) to develop a grain structure [9], implying that (because the powders were annealed for at least one hour at 1503 K) the powders had probably fully transformed to the $L1_2$ structure prior to extrusion.

A separate stoichiometric rod was extruded from powder once at 1473 K (6:1 area reduction), again at 1373 K (6:1 area reduction) and again at 1023 K (4.5:1 area reduction); the rod was sheathed in stainless steel. Each extrusion produced a recrystallized product of low dislocation density. The doubly and triply extruded products had grain sizes of 10 and 2.6 μm, respectively.

3.2. Hot compaction

Hot compaction at 1393 K of rapidly solidified powders produced a heavily twinned, recrystallized grain structure of 85 μm grain size for Ni_3Al and a less twinned 99 μm grain size for Ni_3Al (B, Ti). Again the titanium and boron additions led to faster grain growth and a decreased incidence of twinning. The long, slow cool after compaction (over 19 h) allowed considerable grain growth after recrystallization and is the reason for the much larger grain size in the compacted product compared with the extruded rod.

This time voids were not present in the quaternary alloy, possibly because the hot-compaction temperature was too low to cause localized melting.

Prominent features of the compacted powders were necklace-like strings of particles. The diameter of the necklaces suggests that they correspond to the former powders' surfaces (Fig. 6). Particles outlining prior powder surfaces have also been observed in iron-based superalloys produced by powder metallurgy [23–25]. In those alloys, however, the particles were (assumed to be) carbides.

The particles found here, 50 to 100 nm in diameter, were also observed in the TEM. Often they appeared in lines and occasionally in rings (Fig. 7). Since these particles are present in both compacted alloys their formation did not depend on the boron and titanium additions.

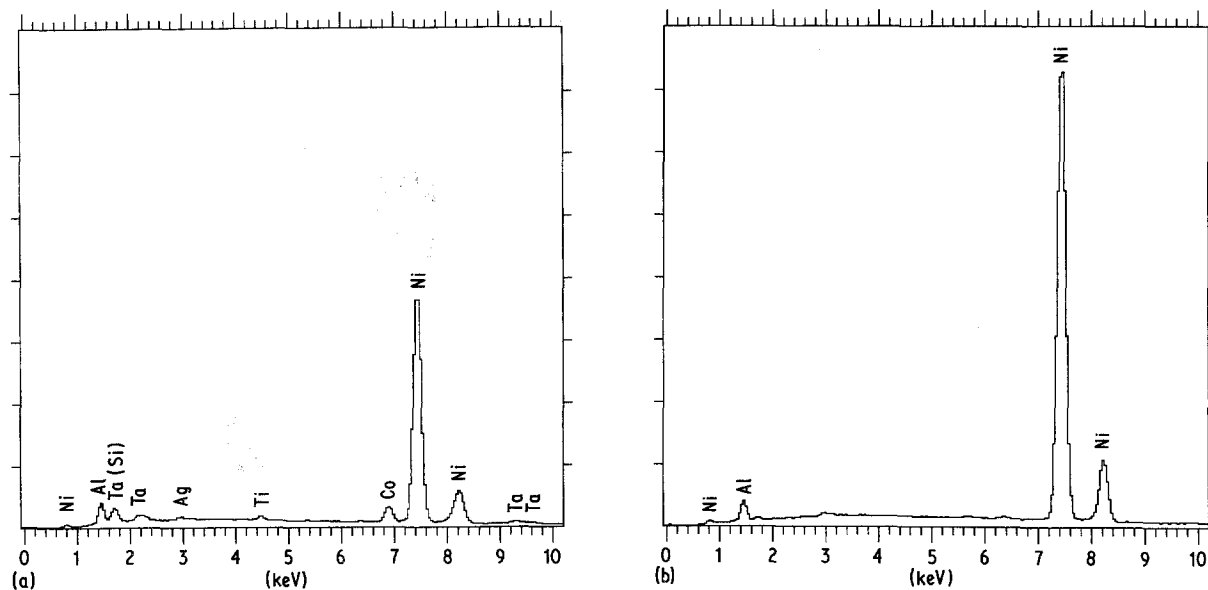*Figure 3* Optical micrograph of fine-grained area in extruded Ni_3Al rod.

Figure 4 EDS output for (a) fine-grained area in Fig. 3 and (b) nearby matrix.

As in the extruded rods, the particles are dark and do not change contrast during tilting. Again, diffraction information could not be obtained from them, even using a stationary 10 nm diameter probe in a scanning transmission electron microscope (STEM). Microanalyses of particles in the stoichiometric Ni_3Al using a Philips FEG EM400T STEM only detected nickel and aluminium in the same ratio as in the Ni_3Al matrix. In the Ni_3Al (B, Ti) some particles appeared aluminium-enriched (compared to the matrix compositions), presumably because the Ni_3Al (B, Ti) is itself aluminium-rich (particularly so if the titanium substitutes for aluminium only). There was no evidence of any TiB_2 precipitation. The particles' spatial distribution and measured composition suggest that they are oxides formed by surface contamination; oxygen is not, of course, detectable using a standard EDS system. The particles in the extruded alloys are presumably also oxides, the larger particle size being due to greater coarsening at the higher temperature of the extrusion.* Mixed oxides of nickel and aluminium have been found in dilute Ni–Al alloys which have been internally oxidized [27].

An interesting feature of the particles observed here is that they do not appear to be associated with grain boundaries, suggesting that the particles offer little impediment to grain growth.

The hot-compacted alloys showed features in common with the extruded alloy, namely the lack of a multiphase structure and no antiphase boundaries. In the compacted alloys some dislocations were found, often as networks or low-angle boundaries. Strangely, the latter were not always associated with the particles in this material (Fig. 8).

4. Summary

Examination of both extruded and hot-compacted alloys of stoichiometric Ni_3Al and of Ni_3Al (B, Ti) established the following points:
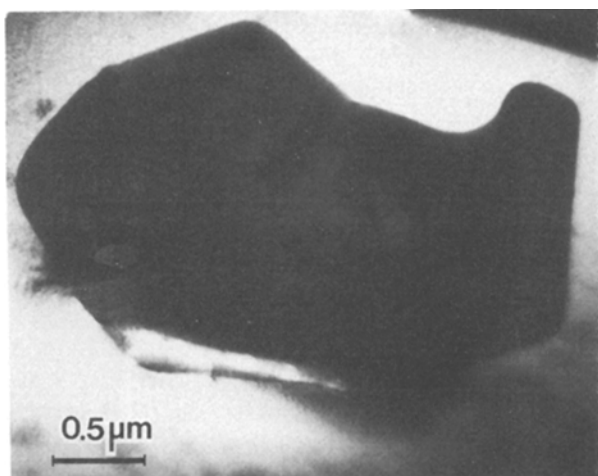

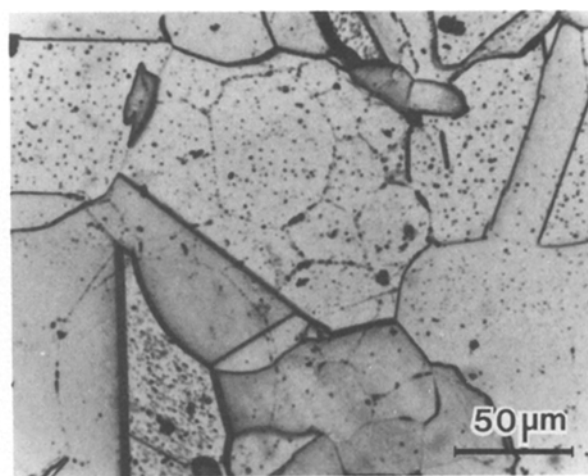Figure 5 TEM micrograph showing a large particle in extruded stoichiometric Ni_3Al rod.

Figure 6 Optical micrograph of hot-compacted Ni_3Al powder. Necklaces of particles outlined prior powder surfaces.

*Similarly, extrusion to rod of FeAl powders at 1200 K led to strings of oxides outlining prior particle surfaces, whereas extrusion of FeAl at 1505 K produced larger ($\sim 1 \mu m$), more widely-spaced oxides [26].
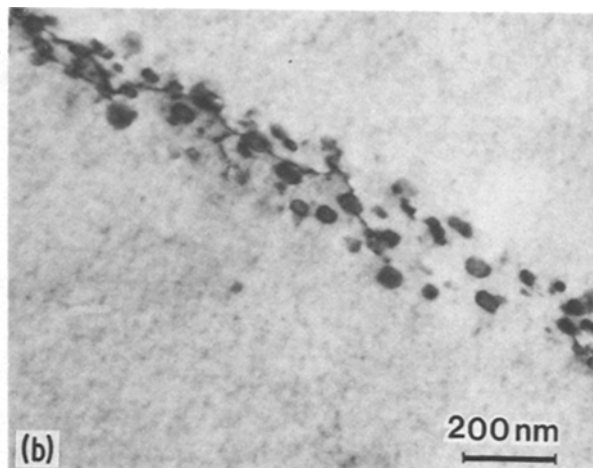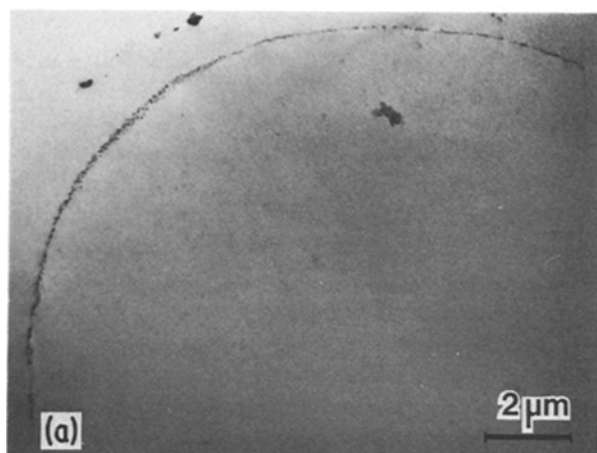
Figure 7 TEM micrograph of (a) a necklace of particles in Ni_3Al (B, Ti) and (b) higher magnification of (a).
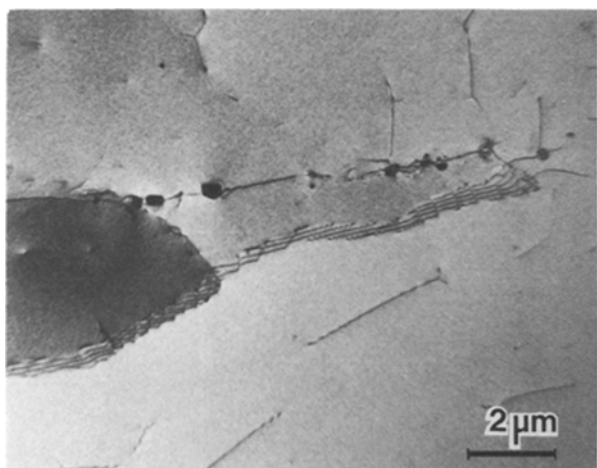

Figure 8 TEM micrograph of a dislocation network in hot-compacted Ni_3Al (B, Ti).

1. The two-phase structure of the rapidly solidified powders was removed by processing.

2. Addition of titanium and boron led to a larger final grain size (due to an increased grain growth rate), to a decrease in the incidence of twinning and to cracking in the extruded material.

3. Contamination was present in the form of possible ceramic debris (from the rapid solidification processing) and oxides (even though processing was performed under an inert atmosphere).

Acknowledgements

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