JOURNAL OF MATERIALS SCIENCE 2 (1967) 365–370

The Growth of Single Crystals of the Intermediate Phases NiAl and Ni_3Al

B. R. MCDONNELL, R. T. PASCOE, G. F. HANCOCK, C. W. A. NEWEY
Department of Metallurgy, Imperial College, London, SW7, UK

Received 10 January 1967, and in revised form 2 May

Single crystals of stoichiometric NiAl, nickel-rich Ni_3Al, and aluminium-rich $Ni_3(Al, Ti)$ have been grown by a modified Bridgman technique; a strain-anneal method has also been used to produce small, single crystals of non-stoichiometric NiAl.

1. Introduction

The intermediate phases based on the stoichiometric compositions NiAl and Ni_3Al are currently the subject of considerable research, both in the field of high-temperature alloys and in fundamental studies of the properties of structures which exhibit long-range order and which exist over a range of composition. Detailed investigations of these materials require them in the form of high-purity single crystals.

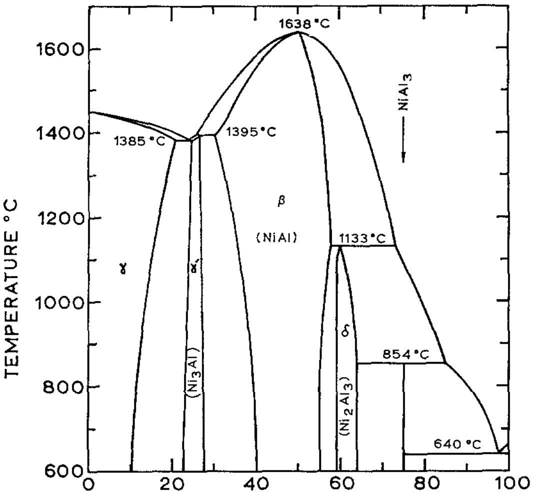

Figure 1 The Ni/Al phase diagram (after Hansen [1]).

The Ni/Al phase diagram, fig. 1, shows that the β phase, NiAl, exists over a wide range of composition, with a maximum melting point of 1638° C at the stoichiometric composition. The γ' phase, Ni_3Al, also exists over a range of composition, see fig. 2; compositions between 24.4 and 25.51 and between 25.51 and 26.25 at. % Al are produced via a eutectic reaction at 1385° C and a peritectic reaction at 1395° C respectively.

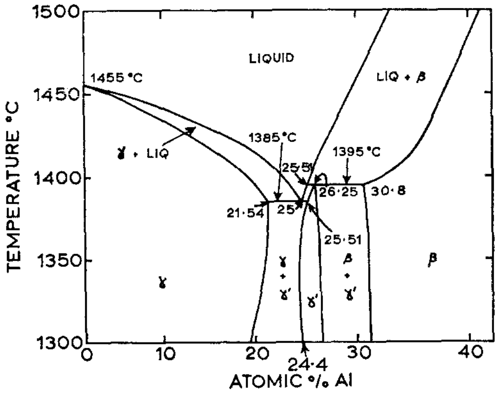

Figure 2 The nickel-rich region of the Ni/Al system (after Phillips [2]).

This paper describes a modified Bridgman technique which has been used to grow single crystals of stoichiometric NiAl and Al-rich Ni_3Al alloys from the melt, and a strain-anneal technique for the production of single crystals of non-stoichiometric NiAl.

2. The Production of Ni/Al Alloys

In the production of high-purity Ni/Al alloys of the required composition and volume, for use as starting material for the growth of single crystals from the melt, two serious difficulties were encountered: the strong affinity which aluminium has for oxygen and the violent exothermic reaction which occurs when nickel and aluminium are melted together. These problems were overcome by casting the alloy under a very pure argon atmosphere in a horizontal, water-cooled, copper boat using rf induction heating.

The apparatus, see fig. 3, was basically the "silver boat" equipment obtained from Stanelco Industrial Services Ltd* (early versions of this equipment were described by Sterling and Warren [3]) used in conjunction with a 25 kW rf generator. The closed system containing the boat and charge was traversed manually through the rf coil. The original, multitube, silver boat was replaced by a more simple boat, see fig. 3, which was constructed from a single copper tube. High-purity argon was produced by passing argon of commercial purity through P_2O_5 to remove water, and over titanium and chromium chips at 1000° C to remove oxygen and nitrogen respectively. Gaseous contamination of the closed system was reduced as much as possible by evacuating to a pressure of 10^{-5} torr prior to melting the main charge of 99.99 wt % Al and 99.999 wt % Ni. The first ingot of a series was often contaminated by the small traces of oxygen remaining in the system and was discarded. The alloy was produced and consolidated by moving the boat and accessories through the coil; careful manipulation of the boat was required to produce an ingot of satisfactory shape and homogeneity. The eddy currents induced in the melt only provided good mixing in the top half of the ingot, and homogeneity was improved by turning the ingot over and remelting.

Sterling and Warren [3] attempted to produce single crystals from the melt using the horizontal boat method, but were unsuccessful.

3. Growth of Single Crystals from the Melt

3.1. NiAl (β Phase)

The Ni/Al phase diagram, fig. 1, indicates that stoichiometric and near-stoichiometric NiAl alloys have a congruent melting point; consequently, single crystals of these compositions can be produced from the melt more readily than other compositions of the phase. In the present work, this has been achieved using the Bridgman technique; although, hitherto, this technique has not been used successfully for the growth of crystals with melting points above 1500° C because of the problems associated with container materials. The alternative methods of growing crystals from the melt, the floating-zone and Czochralski techniques, were considered to be impracticable because of the considerable technical problems involved.

The apparatus developed in the present work, fig. 4, was similar to that described by Hall [5] for the growth of iron-alloy single crystals, but, to withstand operating temperatures of 1700° C and to minimise the loss of aluminium at these temperatures, it differed in several important features.

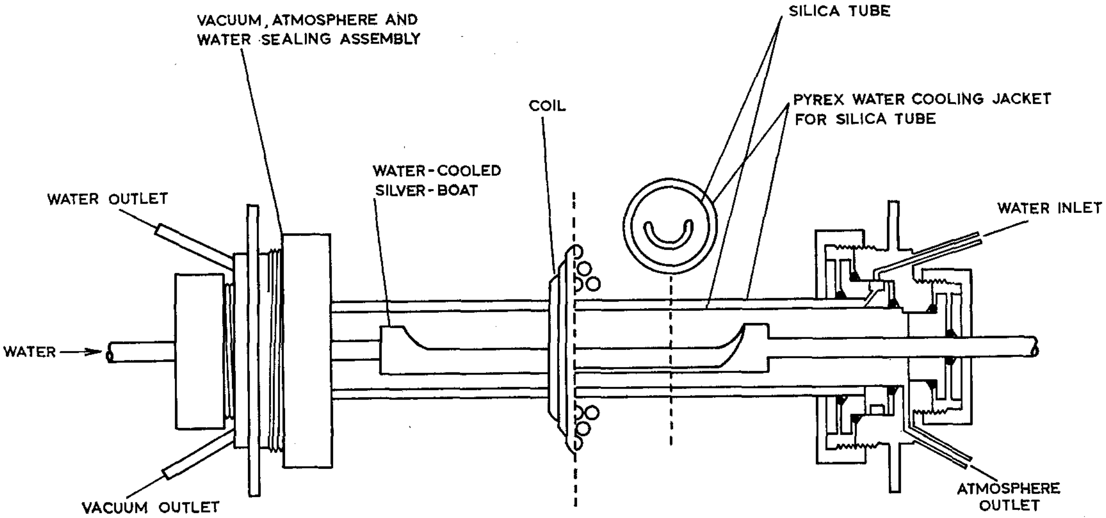

Figure 3 Schematic diagram of the horizontal casting apparatus.

---

*Address: Boreham Wood, Herts, UK.

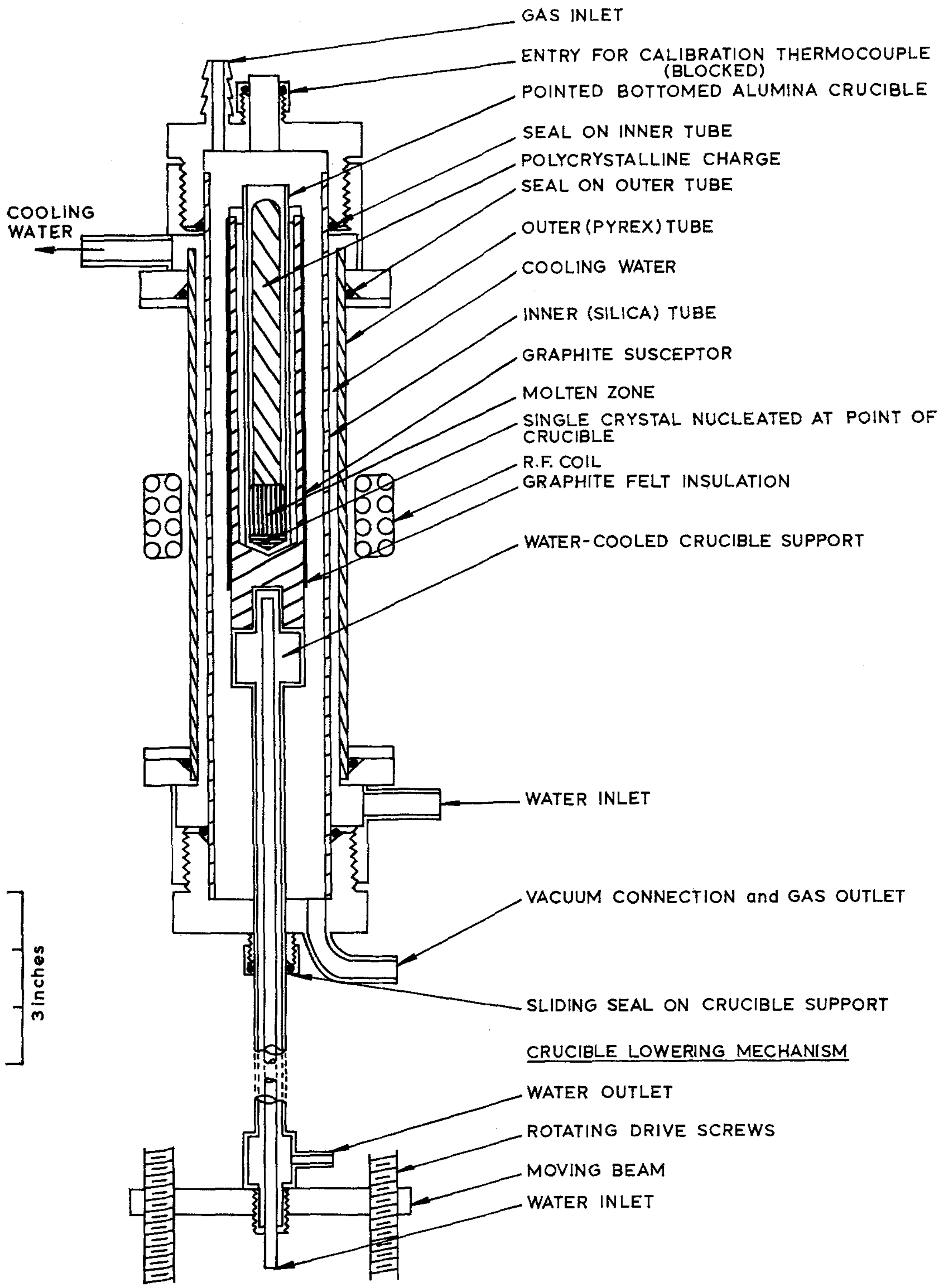

Figure 4 Schematic diagram of modified Bridgman apparatus (1 in. = 2.5 cm).

To ensure a constant alloy feed, the ingot produced in the horizontal boat was ground to fit easily into a tapered, alumina crucible with a pointed bottom. The charge was heated by rf currents induced in a nuclear-purity graphite susceptor in the form of a tube around the crucible; a small gap between the susceptor and crucible minimised reduction of the alumina by the graphite. The crucible and susceptor were contained in a gas-tight, water-cooled jacket consisting of concentric silica (inner) and Pyrex tubes. Crystal growth was achieved by lowering the crucible and assembly, at the required temperature, through the rf coil by means of a mechanical drive. The crystal was grown in an argon atmosphere of commercial-purity argon; no attempt was made to purify the argon in this case, since carbon is a very efficient oxygen-getter at the operating temperatures used (about 1700° C). The apparatus was degassed by evacuating to a pressure of 10^{-4} torr at dull-red heat prior to carrying out the growth procedure.

During the initial experiments with this apparatus, the radiation from the susceptor was sufficient to cause devitrification and collapse of the silica tube. This problem was overcome by the incorporation of a radiation shield of graphite felt (Le Carbone (GB) Ltd,* Grade RVG200). This shield, sewn as a sleeve around the susceptor using graphite thread, proved to be extremely efficient and reduced considerably the power required to maintain the molten zone at 1700° C.

A control thermocouple was not used because its presence in the crucible would have interfered with the feeding of material into the molten zone. Instead, the power supplied by the rf generator was calibrated against temperatures achieved in blank experiments under growth conditions, and the operating temperature during crystal growth was then controlled by the power supplied. The temperature was found to be constant to within 20° C in successive calibrations at 1700° C.

The most satisfactory conditions for producing NiAl single crystals were a growth rate of 0.2 mm/min using an rf coil which heated a small zone of the susceptor about 2.5 cm wide; this size of zone prevented excessive volatilisation of aluminium from the melt and chemical attack of the crucible by the melt. Single crystals, 6 cm in length and 1 cm in diameter, have been grown; they did not adhere to the crucible and their surfaces were quite clean and oxide-free. The growth faces of these crystals were close to $\{100\}$ and $\{110\}$ – the most closely packed planes in the NiAl crystal structure.

3.2. Ni_3Al (γ' Phase)

According to the phase diagram, when alloys of composition between 24.4 and 25.0 at. % Al are cooled from the melt, primary γ dendrites separate out. At the eutectic temperature, the remaining liquid freezes as a two-phase mixture of $\gamma + \gamma'$. The final, single-phase, γ' structure is achieved by a solid-state transformation involving the precipitation of γ' in the primary γ dendrites and transformation of the eutectic to massive γ'.

Kear and Copley [6], using a 22.5 at. % Al alloy, have shown that, if growth is promoted from one end of a molten ingot by gradient cooling, the final cast structure is such that the primary γ dendrites are continuous throughout the crystal in the growth direction; consequently, on annealing, transformation of the residual γ should result in a homogeneous single crystal of γ'.

Provided the phase diagram is correct, in detail it should also be possible to grow single crystals of 25.51 at. % Al from the melt, since, at this unique composition, solidification occurs through the reactions liquid $\rightarrow \gamma' +$ liquid $\rightarrow \gamma'$ without the formation of any intermediate β. It may also be possible to grow crystals of compositions in the range 25.51 to 26.25 at. % Al, provided that a single nucleus of the β phase can be produced on cooling through the $\beta +$ liquid field, and that the nucleation and growth of γ' from this nucleus can be suitably controlled on cooling through the peritectic temperature. A considerable experimental difficulty for these compositions is the prevention of large amounts of segregation during growth from the melt. Thornton [7] has recently described a technique for producing single crystals of ζ Cu/Ge and ζ Ag/Sn, both of which are the products of a peritectic reaction. His technique involves a three-stage melting procedure which is difficult to apply to materials with melting points greater than about 1100° C.

In the present work, Ni_3Al (22.8 at. % Al) and a number of Ni_3 (Al, Ti) single crystals were grown using the modified Bridgman apparatus, but employing a higher growth rate (0.5 mm/min) than for the growth of NiAl crystals. The starting material was supplied by

---

*Address: Portslade, Sussex, UK.

International Nickel Ltd* in ingot form and this was machined to a loose fit in the pointed-bottomed crucible.

The composition of the binary alloy is similar to that of the nickel-rich crystals produced by Kear [6]. According to fig. 2, the composition of this alloy and also that of the crystals grown by Kear is in the $\gamma' + \gamma$ phase field. After a homogenisation anneal at 1200° C for 48 h, optical microscopy showed the apparent presence of small traces of γ at the original dendrite boundaries. However, electron-probe micro-analysis was unable to detect any change in nickel or aluminium composition on traversing these boundaries.

Table I lists the compositions of the $Ni_3(Al, Ti)$ crystals which were grown. Since titanium atoms are substituted for aluminium atoms on the Ni_3Al crystal lattice, alloys 1 and 2 can be regarded as aluminium-rich; the presence of a small amount of titanium is not expected to have a significant effect on the phase diagram and so these alloys should solidify by a peritectic reaction. Chemical analysis indicated that, after homogenisation at 1300° C for 48 h, there was no significant segregation (0.2% along a 7 cm length of crystal).

TABLE I

Alloy No.	Aluminium (at. %)	Titanium (at. %)
1	22.05	4.3
2	21.34	4.94
3	20.52	4.4

Alloy 3 is essentially stoichiometric and again no significant segregation was observed.

The above results are to be contrasted with those for the binary alloys, where no success was achieved with the growth of crystals having compositions lying between stoichiometric and the aluminium-rich limit of the phase field.

All crystals produced had growth axes close to <211>, in contrast to the work of Kear and Copley [6] where growth axes close to <100> were invariably found.

4. The Strain-Anneal Technique

Since in the NiAl phase field, fig. 1, the liquidus and solidus diverge rapidly with departure from stoichiometry, particularly on the aluminium-rich side, it was felt that a solid-state method would provide the best means of growing single crystals of non-stoichiometric NiAl. The strain-anneal technique [4], which is based on the controlled recrystallisation and grain growth of a work-hardened polycrystalline sample of the required composition, was chosen. In its conventional form, this method consists of introducing a previously determined, "critical", tensile strain into a fine-grained, strain-free specimen; the specimen is then annealed at successively higher temperatures in a stepwise fashion or by passing it through a steep temperature gradient.

Hot-extruded NiAl with a grain size of 50 μm, supplied by International Nickel Ltd, was cut into specimens of typical dimensions 15 × 2.5 × 2.5 mm using a diamond-impregnated slitting wheel.

The brittle nature of NiAl in tension, at temperatures below which appreciable recovery occurs, prevented the use of a tensile pre-strain, and so the specimens were pre-strained in compression using apparatus which is described elsewhere [8]. The deformed specimens were then annealed in batches by placing them in a closed-end, alumina tube, over which was passed a temperature-gradient furnace. The furnace, which had a gradient of 150° C/cm at an operating temperature of 1500° C, was traversed at 0.5 cm/h. The specimens were annealed in a stream of argon which was purified by the process described earlier.

A critical strain value that leads to the growth of a single crystal was not found; this was probably a consequence of the slight inhomogeneities of deformation produced during the pre-straining of the long, narrow specimens. It was found, however, that specimens with large grains were often obtained after strains of greater than 0.5% and that many of the grains were sufficiently large for useful single crystals to be isolated, see fig. 5.

Useful single crystals were grown in a range of compositions containing excess nickel and these have been used in studies of slip systems. No satisfactory, aluminium-rich, single crystals have yet been grown, although considerable grain growth has been observed. The growth of aluminium-rich crystals is complicated by their vacancy defect structure, which renders these alloys completely brittle at room temperature, even in compression. Specimens of these compositions must, therefore, be strained at an elevated temperature; 650° C was found to be

---

*Address: Wiggin Street, Birmingham 16, UK

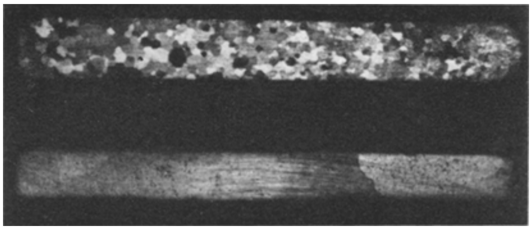

Figure 5 Effects of the strain-anneal treatment on grain size; each specimen has been given the same annealing treatment (heated to 1500° C in a travelling gradient). Top – specimen undeformed before annealing. Bottom – specimen given 1% plastic strain in compression before annealing.

the most effective, because the initial rate of work-hardening is greatest at this temperature, and a high rate of work-hardening aids a uniform distribution of strain. The specimens were rapidly cooled to room temperature immediately after deformation at 650° C, to prevent recovery

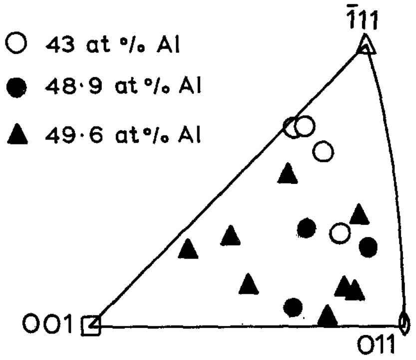

Figure 6 Orientations of the compression axes of polycrystals related to the resultant single crystals grown by the strain-anneal technique.

reducing the stored energy introduced by the deformation.

Crystalline perfection, indicated by the sharpness of X-ray reflections, was higher for crystals grown by the solid-state method than for those grown from the melt. This difference could be removed by annealing the melt-grown crystals at 1500° C in an argon atmosphere for about 12 h. There was no obvious relationship in the strain-anneal specimens between the orientations of the crystals produced and their original compression axes, see fig. 6; crystals with orientations covering a wide area of the unit stereographic triangle were produced.

Acknowledgements

The authors would like to thank Professor J. G. Ball for the provision of research facilities at Imperial College, and the Science Research Council for a Grant for Special Research, and the Ministry of Aviation for support.

The provision of materials by International Nickel Ltd (Ni_3Al, high-purity Ni, and extruded NiAl), British Aluminium Research Laboratories (high-purity Al), and Dr D. A. Young of Imperial College (graphite rod and felt) are also gratefully acknowledged.

References

1. M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill, 1958), p. 118.
2. H. W. L. PHILLIPS, Annotated Equilibrium Diagram No. 18, Institute of Metals (1958).
3. H. F. STERLING and R. W. WARREN, *Metallurgia* **67** (1963) No. 404.
4. "Art and Science of Growing Crystals", edited by J. J. Gilman (Wiley, 1963), p. 415.
5. R. C. HALL, *Trans. Met. Soc. AIME* **209** (1957) 1267.
6. B. KEAR and S. COPLEY, Pratt & Witney Aircraft Report No. 66-026 (September 1966).
7. P. H. THORNTON, *Trans. Met. Soc. AIME* **236** (1966) 592.
8. R. T. PASCOE, K. C. RADFORD, R. D. RAWLINGS, and C. W. A. NEWEY, *J. Sci. Instr.* **44** (1967) 366.