Effect of impurities (graphite) on the high-temperature creep properties of NiAl

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Previous high-temperature compression creep studies of NiAl have shown peculiar behaviour in the temperature range 700 to 900° C, which was perhaps due to precipitation of impurities in the matrix. To isolate the "impurity" effect, high-purity NiAl samples with 0.15 at% and 0.20 at% carbon (graphite) additions have been creep tested at four temperatures between 700 and 850° C. Addition of graphite has been shown to produce a significant reduction in the creep strength of the alloys. However, alloys with higher graphite concentrations have shown better creep resistance than those with lower graphite concentrations. Transmission electron microscopy indicates the presence of competing softening and hardening mechanisms in the alloys. Softening is due to the graphite particles acting as a dislocation source. Hardening results from a grain-boundary hardening mechanism due to the graphite particles segregating at grain boundaries and a dislocation−impurity (fine graphite) interaction, developing a Cottrell-like atmosphere.

1. Introduction

In recent years, the attention of researchers investigating the properties of intermetallic compounds has been drawn to their possible use in high temperature operations. Due to their excellent ordering and other thermodynamical properties, these alloys, which behave more like chemical compounds, exhibit mechanical properties superior to those of their parent metals. At higher temperatures this difference is much more significant.

The β-phase of stoichiometric NiAl, an intermetallic compound of nickel and aluminium, melts congruently at 1639° C. NiAl exhibits a long-range order which persists up to its melting temperature. The alloy has high hardness and shows good oxidation resistance, even at elevated temperatures. These properties of NiAl suggest the possibility that it has good creep resistance, particularly at high temperatures. With this possibility in mind, the mechanical properties of NiAl have been studied extensively [1−5], but the early expectations of outstanding creep behaviour have not been realized.

In the temperature range 700 to 900° C the compressive creep properties of polycrystalline NiAl were reported to be somewhat erratic [1]. Frequently, the steady-state creep rate at a particular temperature was found to be abnormally high when compared with data from specimens deformed at higher temperatures and of the same stress. This abnormal behaviour was attributed to the formation of unusual structures between 700 and 900° C resulting from the presence of impurities. Aluminium oxides and carbides were suspected to be the impurities responsible for the erratic behaviour. Subsequently Strutt *et al.* [2] put forward new experimental evidence to identify the impurity effects. They found that the creep activation energy in a decremental temperature compressive creep testing experiment was quite high. There was also the possible formation of impurity atom−vacancy complexes. Electron

microscopic studies of such specimens revealed precipitation of impurities on a fine scale. However, under these conditions, incremental temperature creep tests produced coarser precipitates and the creep activation energy was found to be equal to that for the diffusion of nickel in NiAl.

The above findings, which were reasonably supported by extensive metallography, indicated that there were some "impurities" always present in the alloy which were suspected to interact with the structure of NiAl, thereby controlling the high-temperature creep properties of the alloy. The most likely impurities were suspected to be Al_2O_3 and carbon.

The effect of Al_2O_3 additions on the structure of NiAl was studied by Tisone et al. [6] who found evidence of dislocation loop formation when aluminium oxide was added to pure NiAl. The effect of another probable impurity, carbon, has recently been studied [3] and some interesting abnormalities in the high-temperature creep behaviour of NiAl containing additions of 0.035 at%, 0.07 at%, 0.14 at% and 0.35 at% of graphite have been found. These alloys, both in the as-chill-cast condition and at temperatures above 750° C, showed softening characteristics at graphite concentrations up to 0.15 at% and then, at higher graphite levels, concentration hardening behaviour was observed. In the present investigation in order to identify further the effects of one of the suspected impurities, carbon, the high-temperature creep behaviour of NiAl with graphite additions has been studied, High-purity annealed NiAl samples containing graphite additions of nominally 0.00 at%, 0.15 at% and 0.20 at% have been creep tested in the temperature range 700 to 900° C under a compressive stress of 74.48 MPa. These load and temperature ranges have been selected in order to be consistent with other work [1, 3, 4]. The creep results show some peculiar behaviour in the relationship between creep rate and composition. An attempt has been made to explain this behaviour on the basis of transmission electron microscopic studies.

2. Experimental procedure

Nickel and aluminium rods, both of 99.999% purity, and commercially-pure graphite were used in this investigation to prepare 50 at%–50 at% stoichiometric NiAl with graphite additions. The nickel was cleaned with 8 vol% nitric acid for 6 h and then rinsed with distilled water. The aluminium

was cleaned with an 8% sodium hydroxide solution and then washed with acetone. Nickel, aluminium and graphite were weighed in a fired alumina crucible to make a charge of approximately 80 g. It was observed that rubbing the graphite over the nickel and aluminium rods produced a better homogenity of graphite in NiAl. The melting was carried out in an induction furnace in a dry commercial argon atmosphere. After the charge was melted, the induction coil was run up and down the liquid metal level to achieve better homogenity in the melt. The furnace was then shut off and the melt was allowed to solidify. The average grain size was measured to be 0.45 mm.

From engineering considerations it has been suggested that for compressive creep testing the specimen length-to-radius ratio should be between 2 and 4. NiAl ingots were cut into small rods of dimensions approximately 3.1 mm × 3.1 mm × 6.2 mm using a high-speed diamond disc saw. The cut rods were annealed at 1300° C for 48 h in an argon atmosphere. The specimens were then mechanically polished and creep tested in a floor-type compression apparatus. The tests were carried out in an argon atmosphere. After each test the deformed specimens were quenched in order to retain the crept structure for further investigation, still with the load applied, by blowing air over the specimen enclosure tube. 100 and 1000 kV transmission electron microscopes were used for metallographic observations.

3. Results and discussion

Three NiAl alloys containing 0.00 at%, 0.15 at% and 0.20 at% graphite have been tested for compressive creep at four different temperatures 700, 750, 810 and 850° C. The tests were carried out at a constant compressive load of 74.5 MPa. The creep results are plotted as creep strain against time plots and are shown in Fig. 1. To check the reproducibility of the data of Fig. 1, one third of the creep tests were duplicated. The results from this second set of tests showed deviations from the first set of tests in the primary stage of creep deformation of between 5 and 10%; and the corresponding deviations for the secondary stage of creep (steady-state) deformation were less than 3%. In compressive creep tests the shifts observed in the primary stage are mostly due to variations in the initial settings of the compressive rams against the specimen surfaces. Due to experimental constraints, however, deformation rates
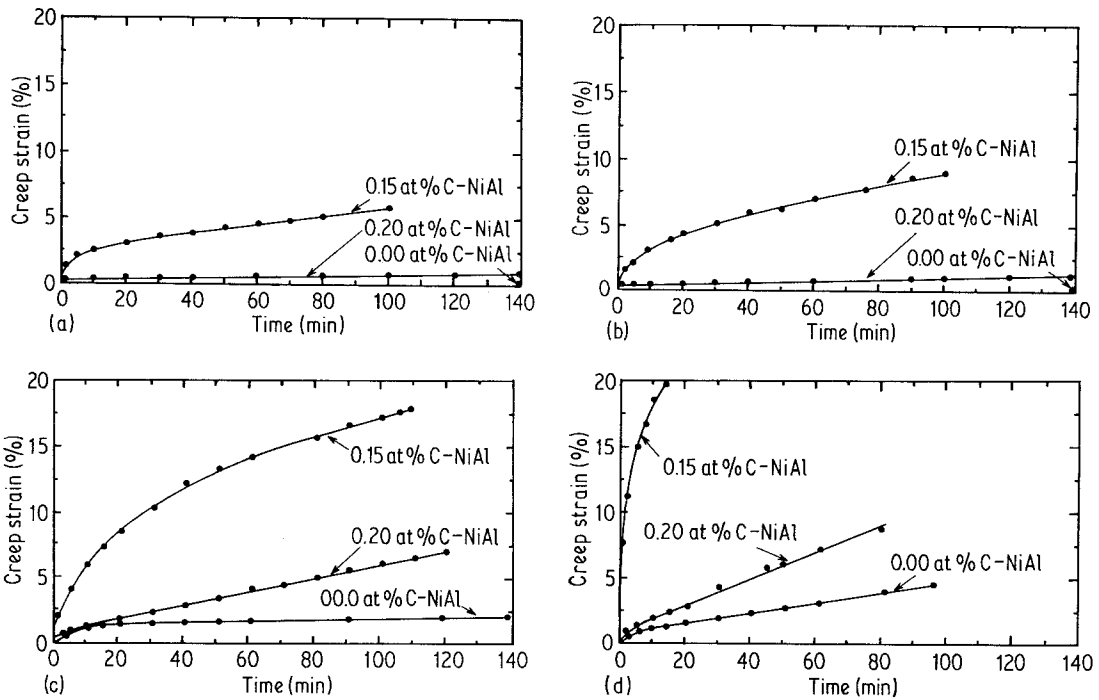
Figure 1 Creep strain against time behaviour at a compressive stress of 74.48 MPa of the three NiAl alloys at (a) 700° C (b) 750° C (c) 810° C and (d) 850° C. Note the extremely slow creep rates of the 0.00 at% C–NiAl alloy at 700° C and 750° C.
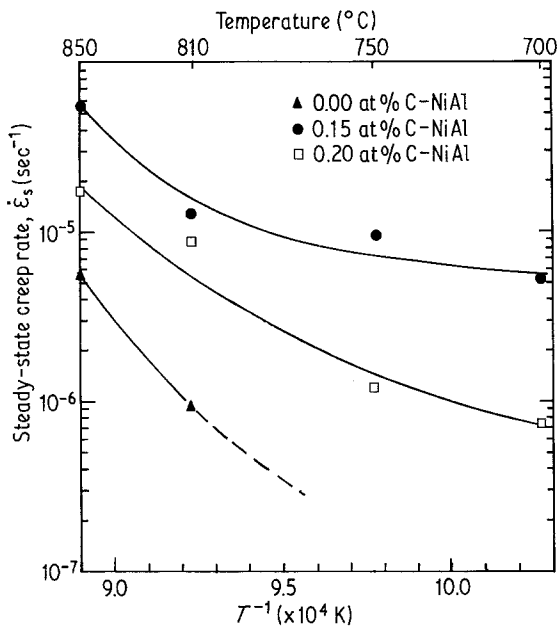

Figure 2 Inverse temperature (1/T) dependence of the steady-state creep strain rate at an applied compressive stress of 74.48 MPa. The creep rates of the 0.00 at% C–NiAl alloy at 700 and 750° C were below the detection limit (6×10^{-7} sec^{-1}) of the experiment.

lower than 6×10^{-7} sec^{-1} and higher than 1×10^{-3} sec^{-1} could not accurately be recorded. This is the reason for not detecting any significant strain of the alloy containing no addition (0.00 at%) for the tests at 700 and 750° C, since under these conditions the creep rates were observed to be very low.

At temperatures above half the absolute melting-point temperature, $T > 0.5\,T_{\mathrm{m}}$, diffusional processes are the dominant rate controlling processes in high-temperature creep and the activation energy for creep in this temperature range is often found to be independent of temperature. In Fig. 2 the logarithm of the steady-state creep rate of various NiAl alloys has been plotted against T^{-1}. These curves may be compared with an Arhenius-type high-temperature creep rate behaviour of the form:

$$\dot{\epsilon}_{\mathrm{s}} \propto \sigma^n \exp \frac{-Q_c}{RT}, \qquad (1)$$

where $\dot{\epsilon}_{\mathrm{s}}$ is the steady-state creep rate, σ is the applied stress, n is a constant, Q_{c} is the apparent activation energy for steady-state creep, R is the gas constant and T is the absolute temperature.
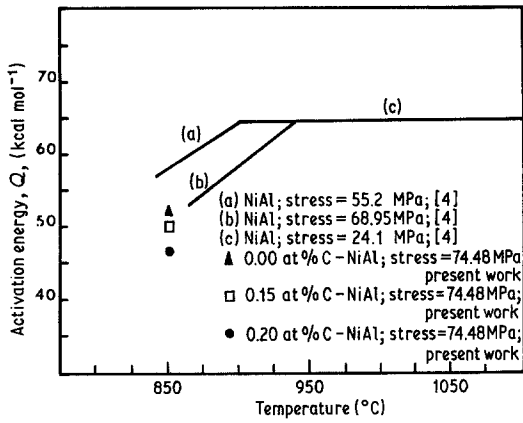
Figure 3 Temperature dependence of creep activation energy. Activation energies found during the present work have been calculated over the temperature range 840 to 850° C, see Fig. 2.

It is evident from Fig. 2 that the slope (Q_c) of the log $\dot{e}_s$ against T^{-1} curve is not constant but is increasing with increasing temperature. In "pure" NiAl the high-temperature creep behaviour has been found to follow Equation 1 only at temperatures above 1000° C (i.e. $T > 0.67\,T_m$). However, below 1000° C the activation energy for creep has been found to decrease with temperature and is dependent on the stress [4]. This is shown in Fig. 3. Although this is not an accurate method,
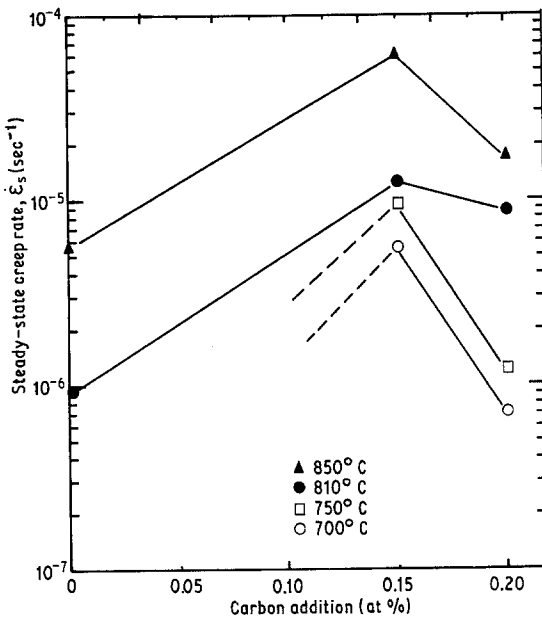

Figure 4 Effect of carbon (graphite) concentration on the steady-state creep strain rate at an applied compressive stress of 74.48 MPa. Creep rates of 0.00 at% C–NiAl alloy at 700 and 750° C were below the detection limit (6 × 10^{-7} sec^{-1}) of the experiment.

TABLE I Grain size and lattice parameters of NiAl–C alloys

Alloy	Grain size (mm)	Lattice parameter (nm)
NiAl + 0.00 at% graphite	0.45	0.28815
NiAl + 0.15 at% graphite	0.40	0.28820
NiAl + 0.20 at% graphite	0.40	0.28815

the "activation energy" values, as determined by the slope of the curves of Fig. 2 around 850° C, have been plotted in Fig. 3 with other [4] data and seem to be, to within a reasonable accuracy, to agree with the results of the earlier study of "pure" NiAl. However, because the test temperature (850° C) is much lower than the high-temperature regime of NiAl alloy, i.e. approximately 1000° C, and because of the error associated with the measurement of the activation energy from the slope of Fig. 2, the activation energy values of NiAl–C alloys can be taken to be, at best, tentative. With this consideration, the temperature dependency of creep rate of NiAl–C alloys seems to be consistent with that of NiAl.

Fig. 4 shows the effect of carbon addition on the creep properties of NiAl. This behaviour seems to be somewhat "abnormal". (Chill-cast NiAl–C alloys also showed similar properties above 750° C [3].) The addition of carbon to stoichiometric NiAl, in general, is found to decrease the compressive creep strength of the alloy. As shown in Fig. 4, this softening behaviour is not a direct function of carbon concentration. The steady-state creep rates of alloys with 0.15 at% and 0.20 at% carbon additions, at any of the test temperatures, are higher than those of the "pure" NiAl. However, the low carbon alloy (i.e.
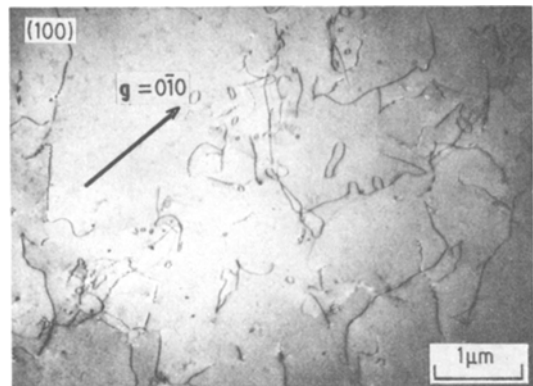

Figure 5 Dislocation structure after 2% creep in a 0.00 at% C–NiAl alloy deformed at 810° C.
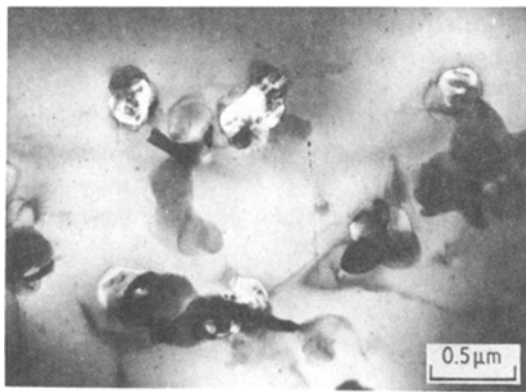
Figure 6 A 0.15 at% C–NiAl alloy, cast and annealed at 1300° C for 48 h. Apart from the fine precipitates, believed to be graphite, large particles of graphite (confirmed by electron diffraction analysis) can also be seen.

Figure 8 A source punching-out dislocation in a 0.15 at% C–NiAl alloy after 4% creep at 750° C.

with 0.15 at% carbon addition) has deformed more quickly than the high carbon alloy. The "pure" alloy and the alloy with addition of 0.20 at% carbon reached the steady-state creep stage after a relatively short primary creep stage while the alloy with addition of 0.15 at% carbon usually exhibited a much longer primary creep stage and reached steady-state creep only for specimens which were deformed below 750° C. The grain-size measurements made before and after each creep test did not show any evidence of recrystallization. Similarly the X-ray data did not show any appreciable change in lattice parameters due to carbon addition into NiAl. The respective values of grain size and lattice parameters are given in Table I. In view of these observations the creep behaviour of the alloy seems to be governed by a precipitate–matrix interaction mechanism.

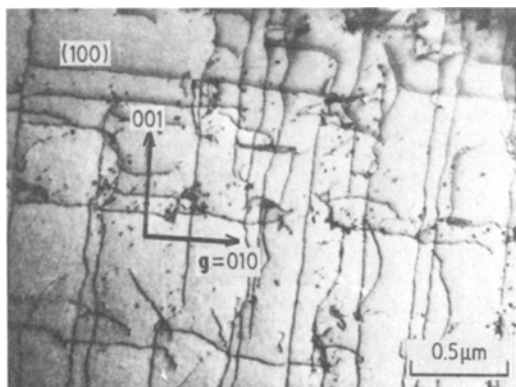Fig. 5 shows the structure of the "pure" NiAl

after 2% creep deformation, as observed by TEM. The presence of dislocation loops has been attributed to the presence of trace amounts of impurities in the pure NiAl in the earlier studies [1]. Adding trace amounts of aluminium oxide also produced dislocation loops in NiAl [6]. The structure of the alloys containing carbon are shown in Figs 6 to 10. It has been observed that the NiAl–C alloys have a higher dislocation density which consists of loops, jogs and series of punched-out dislocations. During the creep process, as a result of the different moduli of the matrix and the precipitate, the stress levels in these phases are different. To accomodate the deformation at the precipitate–matrix interface, dislocation loops are punched-out. This seems to be the reason for the higher dislocation densities observed in alloys with 0.15 at% and 0.20 at% carbon additions. The increase in dislocation density eventually decreases the creep strength of the

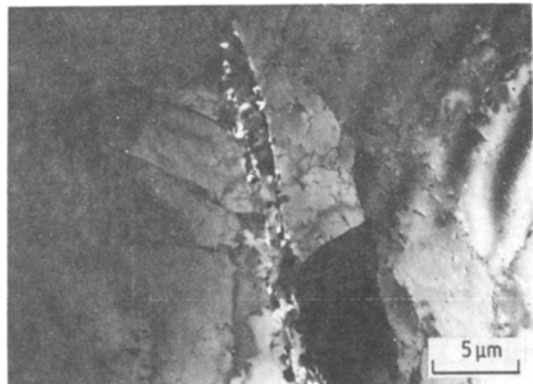*Figure 7* Dislocation and precipitate structure in a 0.15 at% C–NiAl alloy after 4% creep at 850° C.

Figure 9 Graphite particles at grain boundaries and the formation of subgrain boundaries due to creep in a 0.20 at% C–NiAl alloy after 6% creep at 750° C.
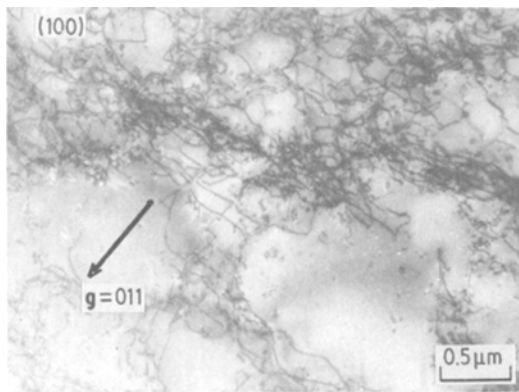
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Figure 10 Complex dislocation–precipitate network in a 0.20 at% C–NiAl alloy after 5% creep at 850° C (viewed at 1000 kV).

alloy, in a manner broadly explained by Taylor's relation:

$$\dot\epsilon \propto bv\rho \qquad (2)$$

where **b** is the burgers vector, **v** is the velocity and ρ is the density of the moving dislocations. The carbon particles also act as preferential sites for dislocation climb, hence increasing the softening mechanism by facilitating diffusive climb of the locked dislocations [7]. Thus the decrease in the creep strength of the alloys containing carbon is attributed to the carbon particles acting as (a) a dislocation source and (b) preferntial sites for dislocation climb.

The 0.20 at% C–NiAl alloy has shown a hardening behaviour superior to that of the 0.15 at% C–NiAl alloy. A TEM study of the 0.20 at% C–NiAl alloy, as shown in Fig. 9, shows segregation of graphite particles along the grain boundaries. This segregation would cause grain-boundary hardening and result in a reduction of the grain boundary contribution to the steady-state creep in the case of the 0.20 at% C–NiAl alloy. It is also suspected that, beyond a certain critical carbon concentration, the carbon atom–vacancy complexes and the high dislocation density would develop a Cottrell-like atmosphere, thus hindering the movement of the glide dislocations. The complex dislocation precipitate network was a common feature of the 0.20 at% C–NiAl alloy which could only be revealed in thicker specimens by using an electron microscope operating with a 1000 kV electron beam. This is shown in Fig. 10. The lowering in the creep rate of the 0.20 at% C–NiAl alloy is attributed to combination of the above two mechanisms, grain-boundary hardening and the formation of a Cottrell-like atmosphere.

4. Conclusion

Compressive creep tests have been carried out on three polycrystalline stoichiometric NiAl–C alloys containing 0.00, 0.15 and 0.20 atomic percentages of graphite and over a temperature range from 700° C to 850° C. The creep results show that at all the test temperatures the carbon-containing alloys exhibit a generally more marked softening than the pure NiAl alloy; however, the alloy with the higher carbon content (0.20 at%) has shown a sharper hardening with increase of creep rates at all test temperatures than the low carbon (0.15 at%) alloy. These observations indicate a typical coexistence of competing hardening and softening mechanisms.

The steady-state creep rates of the three alloys show an increase with increasing temperature which is consistent with earlier studies of NiAl. Transmission electron microscope studies of the deformed alloys have revealed that the carbon particles participate in punching-out of dislocations. As observed earlier, carbon particles may also act as preferential dislocation climb sites, thereby facilitating diffusive climb of the locked dislocations. The softening behaviour of the alloys containing carbon is attributed to the above mechanisms. However, further increase in carbon concentration seems to harden the grain boundaries and has been shown to act more as pinning points for moving dislocations. The lower steady-state creep rate of the 0.20 at% C–NiAl alloy compared with the lower carbon alloys may be attributed to the above two factors.

References

1. W. J. S. YANG, R. A. DODD and P. R. STRUTT, *Met. Trans.* 3 (1972) 2049.
2. P. R. STRUTT, R. S. POLVANI and B. H. KEAR, *Scripta Met.* 7 (1973) 949.
3. A. PRAKASH and R. A. DODD, Proceedings of the Second International Conference on the Mechanical Behaviour of Materials, Boston, August, 1976 (Federation of Materials Societies, ASM, Metals Park, Ohio, 1976) p. 370.
4. W. J. S. YANG and R. A. DODD, *Met. Sci. J.* 7 (1973) 41.
5. W. R. KANNE, Jr, P. R. STRUTT and R. A. DODD, *Trans. Met. Soc. AIME* 245 (1969) 1259.
6. T. C. TISONE, G. W. MARSHALL and J. O. BRITTAIN, *J. Appl. Phys.* 39 (1968) 3714.
7. G. W. MARSHALL and J. O. BRITTAIN, *Met. Trans. A.* 74 (1976) 1013.