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Homogenization of single crystal superalloys

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ABSTRACT

The homogenization of nickel-base superalloys is best carried out at a temperature within the γ phase field, provided that the alloy does not undergo incipient melting before the γ′ solvus is reached. The temperature range between the γ′ solvus and the solidus of the inhomogeneous alloy is called the heat-treatment window. This work is an investigation of the factors determining the heat-treatment window, as a function of alloy composition for a range of single crystal superalloys. The homogenization behaviour is followed using various microanalysis techniques.

It is found that the heat-treatment window variations can be qualitatively understood in terms of the effect of Ti on the solidus temperature of superalloys and in terms of its ability to increase the amount of γ/γ′ eutectic obtained in as-cast single crystal superalloys. Some clear trends in the segregation behaviour of various alloying elements are also established and discussed.

INTRODUCTION

The creep properties of investment-cast superalloy turbine blades can be improved by reducing the amount of transverse grain boundary area per unit volume, to form a directionally solidified structure of coarse columnar grains oriented along the maximum stress axis (VerSnyder and Guard (1960)). Like conventional turbine blades, which consist of equiaxed grains, directionally solidified blades cannot easily be homogenised after casting. Homogenization can only be achieved within a reasonable time if the alloy is heat-treated at a temperature within the single phase γ region when all the alloying elements are taken into solution. Equiaxed and columnar structured alloys both contain grain boundary strengthening elements, such as Zr and Hf, which significantly lower the alloy solidus causing incipient melting to occur before all the γ′ precipitates have entered the γ solid solution, thus making it impossible to fully homogenize such alloys.

Single crystal turbine blades have no high angle grain boundaries and, therefore, the alloys used in their manufacture do not need nor do they contain grain boundary strengthening additions. It is, therefore, possible to fully homogenize these alloys in the single phase region, resulting in a more uniform microstructure with mechanical properties far superior to those of the conventional materials (VerSnyder and Shank (1970)). Homogenization is carried out in the temperature range between the solidus of the segregated alloy and the solvus of the γ′ precipitate; this region is termed the heat-treatment window. The present work is a microanalysis based study of the homogenization of several cast single crystal Ni-base superalloys in which the Ti concentration was systematically varied. The work is part of a programme on the influence of Ti on the defect energies and creep properties of single crystal superalloys.

DETERMINATION OF THE HEAT-TREATMENT WINDOW

The alloy compositions are given in Table 1; they contain between 1.8 and 2.7 at. pct. Ti. The alloys were prepared in the form of cast-single crystal rods. Under the influence of the very high temperature gradient constitutional supercooling occurs and solidification progresses dendritically with the γ′ forming elements generally being partitioned to the liquid phase. The enriched inter-dendritic liquid ultimately solidifies by eutectic decomposition to a coarse γ/γ′ mixture shown in fig. 4. The overall microstructure (fig. 3) consists of a fine dispersion of γ′ particles (∿ 0.6 vol. frac.) within the large γ dendrites with the coarse γ/γ′ eutectic visible in the inter-dendritic spaces. Due to severe coring, the γ′ morphology at the centre of the dendrites (fig. 1a) is considerably different from that at the edge (fig. 1b). Some very fine dendritic Ta-rich MC carbides were also

TABLE 1 Bulk compositions of the alloys studied (at. pct.)

Element	A	B	C	D	E	F	G
	Alloy						
Ni	67.7	68.2	67.8	68.2	68.3	68.1	68.9
Al	11.8	11.4	12.0	11.9	11.8	11.8	11.9
Ti	2.7	2.5	2.4	2.2	2.1	2.1	1.8
Cr	9.3	9.4	9.3	9.3	9.4	9.4	9.3
Co	4.8	4.8	4.8	4.7	4.8	4.8	4.8
Ta	0.9	0.9	0.9	0.9	0.9	0.9	0.9
W	2.8	2.8	2.8	2.8	2.8	2.8	2.8

TABLE 2 Averaged EDS/STEM analyses (at. pct.) for γ and γ' after homogenization for 32 hours at 1300°C

Element	γ	γ'
Ni	63.0 ± 1.7	67.8 ± 0.5
Al	9.7 ± 1.7	18.6 ± 1.5
Ti	1.7 ± 0.6	3.9 ± 0.2
Cr	17.1 ± 2.3	3.9 ± 0.2
Co	6.3 ± 0.6	3.1 ± 0.3
Ta	-	1.2 ± 0.2
W	2.3 ± 0.6	1.4 ± 0.1

observed. These precipitate ahead of the main alloy solidification front and are unchanged by subsequent heat-treatment.

The incipient melting point of each alloy was determined by heating 15 mm x 10 mm diameter single crystal cylinders to temperatures between 1280-1340°C, at 10°C intervals for one hour periods, followed by rapid air cooling to ambient temperature. Incipient melting locally alters the microstructure and was detected on polished and electrolytically etched samples using optical and scanning electron microscopy. The temperature at which the coarse γ/γ' eutectic entered solution was similarly determined; we note that these are the standard methods used to determine heat-treatment windows for commercial alloys. The results are presented in Fig. 2 which shows that the incipient melting point decreases rapidly with increasing Ti content; the eutectic solvus rises relatively slowly with increasing Ti, and the overall effect is to narrow the heat-treatment window with increasing Ti.

The effect of increasing Ti is to increase the volume fraction of liquid which decomposes to the γ-γ' eutectic; higher Ti levels thus lead to a higher volume fraction of the eutectic mixture (2% in alloy A and 0.3% in alloy G). This means that for a given homogenization temperature, high Ti alloys will require longer times for the dissolution of the eutectic, when the homogenization temperature is close to the eutectic solvus. Because the heat-treatment window establishment procedures involve a constant 1 hr period, high Ti alloys are expected to show an apparent increase in the γ/γ' solvus temperature.

In the absence of detailed phase diagram data, the effect of Ti on the incipient melting point cannot be properly discussed, but we note that the observed effect is consistent with the influence of Ti (at levels less than about 15 at. pct.) on the solidus temperature of Ni-Ti-Al alloys (Nash et al. (1983)).

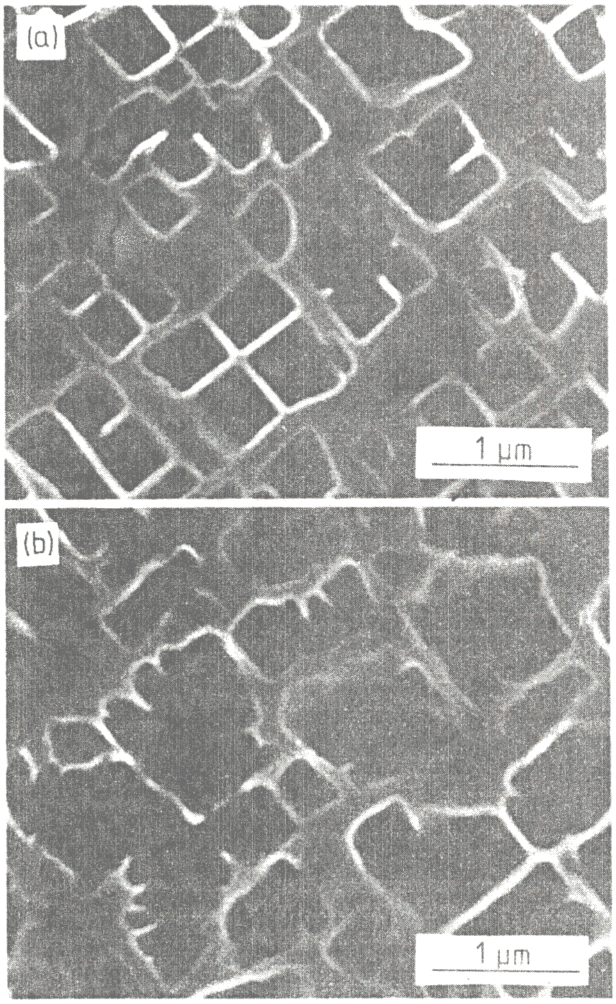


Fig. 1 Scanning electron micrographs showing the as-cast γ´ morphology at (a) the centre and (b) the edge of the dendrite arms.

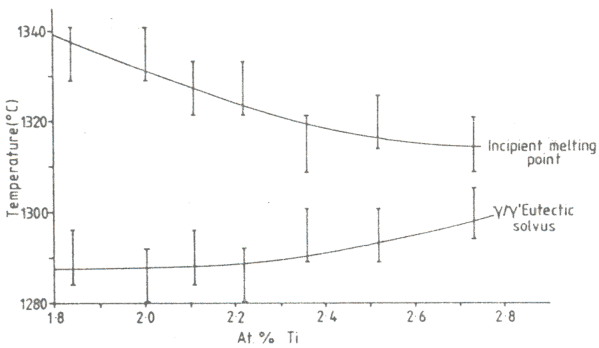


Fig. 2 Temperature dependence of the γ/γ´ eutectic solvus and the incipient melting point on the bulk alloy composition.

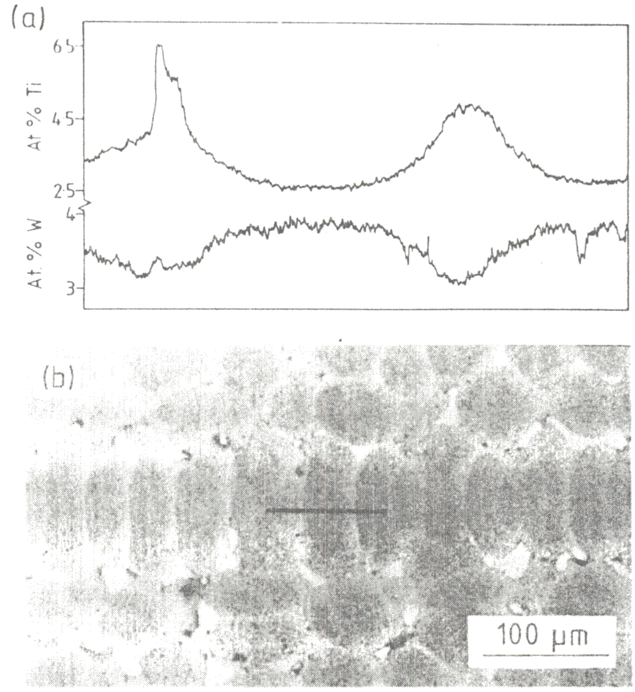


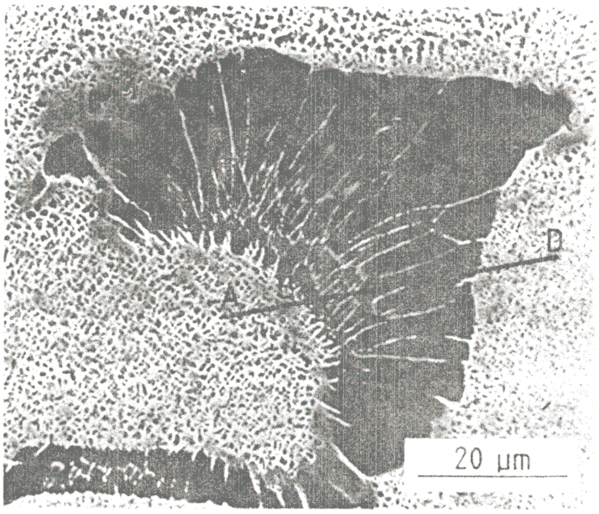
Fig. 3 (a) Election microprobe traces for Ti and W across two of the secondary dendrite arms illustrated in (b).

HOMOGENIZATION EXPERIMENTS

A homogenization temperature of 1300°C was chosen for these experiments, since this lies within the heat-treatment window of all the present alloys. Homogenization was carried out on samples of alloy A sealed in a silica tube, containing a partial pressure of pure Ar. The experiments were interrupted after 4, 8, 16, 32 and 64 hours at temperature, for metallographic and micro-analytical studies. Microanalysis was carried out on a microprobe and also on an energy dispersive sytem on an SEM. Thin foils prepared from the homogenised specimens were also examined for very fine scale compositional variations in a Philips 400T using a STEM probe and a Link 860 EDS unit. The experiments thus gave micro-analytical information on three scales, the diameter of the analysing spot being ∿ 2 µm for the microprobe, 1 µm for the SEM and 200 A° for the STEM probe (after allowing for beam broadening in the thin foil).

MICROANALYSIS OF THE AS-CAST STRUCTURE

Probe and EDS traces across dendrite arms show relatively high concentrations of Al and Ti (both strong γ´ forming elements) at the edges of dendrites, while W showed high concentrations in the central regions, see Fig. 3. Quantitative metallography on a Quantimet 720 image analysing computer showed that, consistent with the above microanalysis results, the γ´ volume fraction was larger at the edges than at the centres of dendrites. Alloy A contained 0.60 volume fraction of γ´ at the edges of dendrites, with 0.55 at the centres; the corresponding figures for the Ti



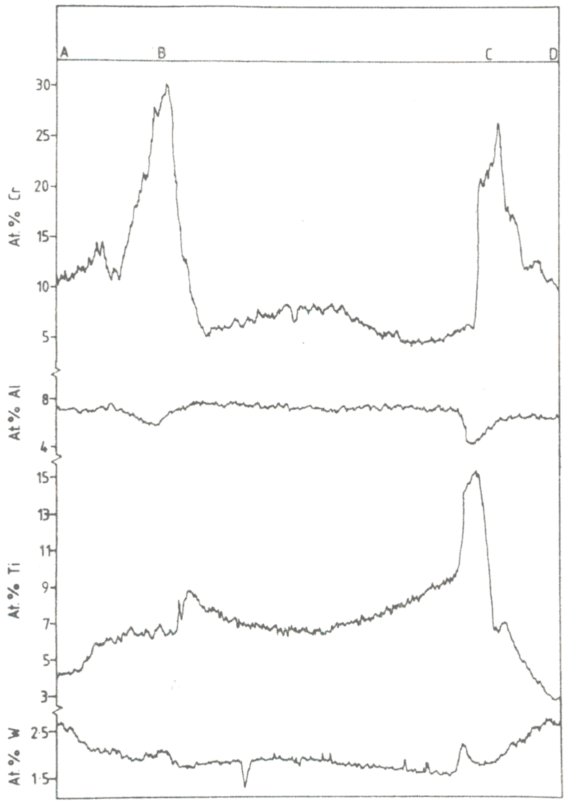


Fig. 4 Electron microprobe traces for Cr, Al, Ti and W across a typical γ/γ' eutectic colony.

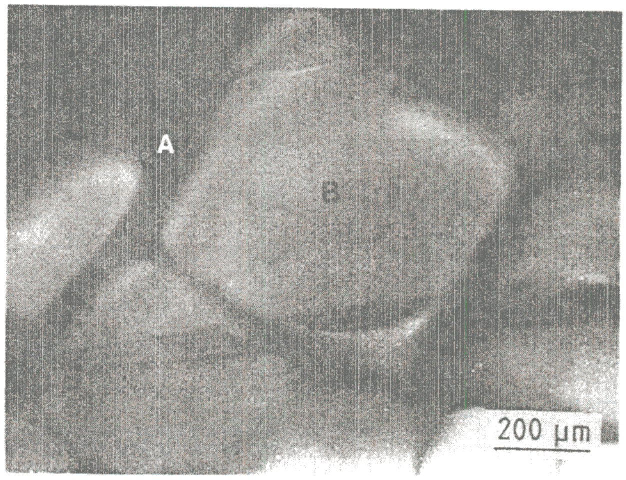


Fig. 5 Bright field transmission electron micrograph showing typical analysis points A and B used to obtain the γ and γ' compositions reported in Table 2.

poor alloy G show a greater difference, with 0.71 at the edge and 0.49 at the central regions (Fig. 1). Hence, the ragged morphology of the γ' particles at the edges of dendrites may arise through the onset of strong soft impingement effects.

The eutectic colonies themselves were found to be rich in Ti and Al and deficient in Cr and W, as shown in Fig. 4. The results generally indicate that the γ dendrites grow with the partitioning of γ' forming elements into the liquid phase.

HOMOGENIZATION

A fiducial line marked on the specimen was used to follow composition variations; after each heat-treatment, microprobe analyses were made on this line at 10 μm intervals, using a spot size of 1 μm. These experiments were only designed to show overall macroscopic composition variations. Heat-treatment for 8 hours at 1300°C made the microstructure appear uniform, without any eutectic colonies, but EDS analysis showed that the composition variations were still present. After 16 hours at 1300°C, the Ti, Ni, Al and Cr concentrations showed no significant variations while after 32 hours at 1300°C, none of the elements showed segregation beyond the range of experimental error.

Attempts were made to analyse the segregation profiles in terms of a relaxation time t, where $t = d^2/D$ (d = wavelength of composition wave, D is diffusivity of segregated element) but these were consistently found to overestimate the time necessary for homogenisation, presumably because of the serious lack of accounting for inter-element flux effects.

PARTITIONING OF ELEMENTS BETWEEN γ AND γ´

STEM microanalysis was conducted on the γ and γ´ phases present in thin foils from a homogenized (32 hours at 1300°C) specimen. At least ten separate areas were examined for each phase. Fig. 5 illustrates the typical areas analysed and the results are presented in Table 2. The results indicate that Al, Ti and Ta are strongly partitioned to the γ´ phase and that Cr, Co and W partition to the γ phase. Ta, when not bound up as an MC carbide, seems to virtually completely enter γ´ although Al and Ti are only partitioned in a 2:1 ratio. The results indicate the γ´ composition in the homogeneous alloy is close to $(Ni_{0.93}Co_{0.04}Cr_{0.03})_3(Al_{0.69}Ti_{0.14}Cr_{0.07}W_{0.05}Ta_{0.04})$ using the site occupancy data reported by Guard and Westbrook (1959) and Betteridge and Heslop (1974).

CONCLUSIONS

The results indicate that Ti decreases the width of the heat-treatment window for cast single-crystal superalloys due not only to the lowering of the solidus with increasing Ti content, but also because the volume fraction of γ/γ´ eutectic increases with overall Ti concentration. The effect could, however, be mitigated by means of longer heat-treatments, which would have the effect of reducing the apparent γ/γ´ eutectic solvus temperature. The alloys achieve adequate homogenization after annealing at 1300°C for 32 hours (within the heat-treatment window of all the alloys) and this homogeneity is both long range and on the level of individual γ´ particles.

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