JOURNAL OF MATERIALS SCIENCE 25 (1990) 4054–4059

Microsegregation of cast DS200 + Hf single crystal

A. BALDAN
Division of Materials Science and Technology, CSIR, P. O. Box 395, Pretoria 0001, Republic of South Africa

Data from electron microprobe have been used to investigate the segregation characteristics of DS200 + Hf single-crystal superalloy. Dendritic and $(\gamma + \gamma')$ eutectic reaction segregations have been investigated in detail. The results showed that segregations of aluminium, titanium, niobium, hafnium and nickel elements increased from dendritic structure towards the interdendritic and eutectic regions, whereas cobalt, tungsten and chromium showed the reverse segregation characteristics.

1. Introduction

Cast nickel-base superalloys, which are used for the production of turbine blades, typically consist of approximately 60 vol % γ' phase coherently precipitated in an fcc matrix, together with the $(\gamma + \gamma')$ eutectic structure and carbide phases. Because the as-cast structure of DS200 + Hf alloy cannot be solution treated completely because of the incipient melting problem, the properties of this alloy are governed by the as-cast microstructure which, in turn, depends upon the casting parameters, such as solidification rate and thermal gradient. The microsegregation behaviour of the elements of an as-cast alloy has a great effect on properties such as toughness, creep strength, corrosion resistance, as well as determining suitable heat treatment for the alloy. The aim of this study was to investigate the microsegregation characteristics of primary and secondary arm dendrites, interdendritic and eutectic regions in the as-cast condition of DS200 + Hf single crystal.

2. Experimental procedure

To study the degree of segregation in this alloy, a single-crystal rod was sectioned into three parts, top, middle and bottom, which are perpendicular to the solidification direction. The microsegregation of the top section of the rod was studied in the present work; the other sections will also be investigated in the future.

The bulk composition of DS200 + Hf alloy is given in Table I. This alloy was supplied as a single-crystal rod grown at the rate of 4 mm min^{-1} along the $\langle 0\,0\,1 \rangle$ direction.

Electron microprobe analysis was carried out on polished and unetched specimens at 20 kV using a Jeol 733 instrument. Computer correction procedures were performed using a ZAF correction computer program. The concentrations of the major elements including aluminium, cobalt, chromium, nickel, niobium, titanium, tungsten and hafnium within the dendrites, and the interdendritic and eutectic regions were determined on sections cut normal to the solidification direction and therefore to the columnar structure. This ensured that the complete range of compositions was exposed.

3. Results

Examination of the as-cast DS200 + Hf single crystal reveals a prominent dendritic solidification pattern containing various classes of carbides and incipient melting regions (Figs 1 and 2). The results of an investigation on carbides and incipient melting regions are also reported and will be published elsewhere. Fig. 2 shows the typical dendritic structure of the alloy, with a schematic illustration of it. An important aspect of a dendritic structure is the occurrence of microsegregation between the dendrites. Therefore, in order to control the properties of cast alloys, it is necessary to understand the mechanism and characterization of microsegregation.

As illustrated in Fig. 2b, the compositional variations along the lines A–B and C–D were measured in the dendrite, and the results are given in Figs 3 and 4, respectively. As Fig. 3 indicates, there are periodic changes of elements along the primary dendrite arm; this can clearly be seen for hafnium, chromium, niobium and nickel, in particular. These periodic changes in concentration show the differences between the γ matrix and γ'-precipitates. The differences in concentration within primary and secondary arms of dendrites are illustrated in Fig. 4. This figure clearly indicates that the niobium, titanium and chromium contents have segregated to the secondary arm whereas tungsten has segregated to the primary arm. In other words, elemental niobium, titanium and chromium have segregated to the remaining liquid as the solid–liquid interface grows during the solidification process, and the primary dendrite arm becomes deficient in these elements. It is also evident in Fig. 4, that niobium and tungsten are the most heterogeneously distributed within the primary and secondary dendrite arms. The distribution of elements within the eutectic and

0022–2461/90 $03.00 + .12

TABLE I The bulk composition (wt %) of DS200 + Hf alloy

Alloy	Cr	Co	Al	Ti	W	Nb	C	B	Zr	Hf	Ni
DS200 + Hf	9.0	10.0	5.0	2.0	12.0	1.0	0.11	0.015	< 0.05	1.75	Balance

dendritic regions is illustrated in Fig. 5. It is important to mention that the eutectic composition in this figure represents the composition of the remaining liquid at the end of the ($\gamma + \gamma'$) eutectic solidification. As is evident in Fig. 5, elemental nickel, aluminium and hafnium have segregated to the eutectic region, whereas elemental cobalt, chromium and tungsten have segregated to the dendritic region, which indicates that the remaining liquid was enriched in nickel, aluminium and hafnium during eutectic solidification.

Table II shows the average concentrations of elements in the primary and secondary arm dendrites, eutectic and interdendritic regions, as well as the segregation ratios. The segregation ratio is defined as the ratio of the solid composition to the remaining liquid composition. The segregation ratio is of importance in the study of the segregation of solute elements during liquid–solid transformation. Although the equilibrium segregation ratio is generally assumed to be constant in the binary systems, in the case of multicomponent systems, such as in the present alloy, it may vary because of solute interactions in the liquid. The data in Table II were used to construct Fig. 6. This figure indicates more clearly the segregation characteristics of the elements in the microconstituents. Note that each composition value was taken as the average value of five microprobe analyses.

4. Discussion

It is evident in Figs 4 to 6 that the γ- and γ'-forming elements show the reverse segregation characteristics. Namely, the segregations of elemental aluminium, titanium, niobium, hafnium (which are the γ'-forming elements) and nickel increase from the dendritic structure towards the interdendritic and eutectic regions, whereas the γ-forming elements, cobalt, tungsten and chromium, show the reverse segregation behaviour. The maximum and minimum segregations occur in the primary dendrite and eutectic region. The segregation ratios, $K(C_i/C_e)$ and $K(C_p/C_e)$, of chromium, tungsten and cobalt solutes are greater than 1, which indicates that these elements are depleted in the eutectic region and enriched in the primary and interdendritic regions. The segregation ratio $K(C_p/C_e)$ of hafnium is

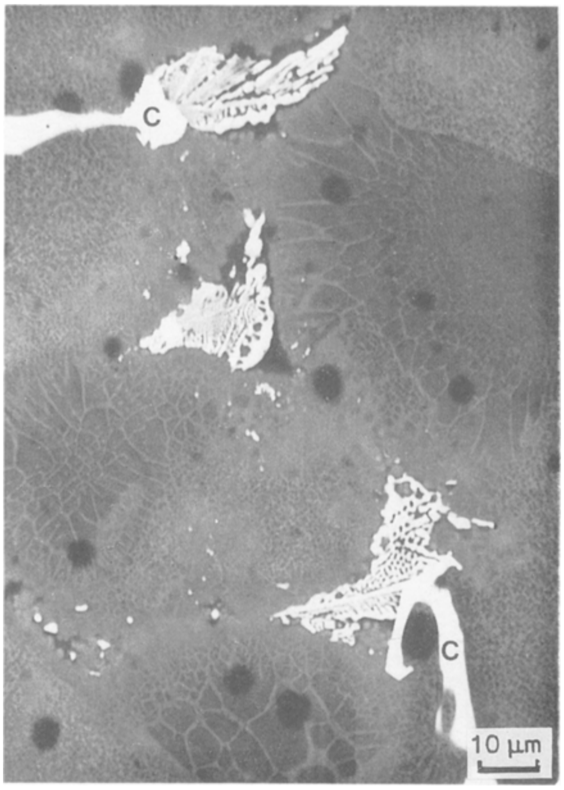

Figure 1 The rosette-type ($\gamma + \gamma'$) eutectic pools, incipient melting region, carbide particle (C), and cuboidal-like γ' morphology in the interdendritic regions.

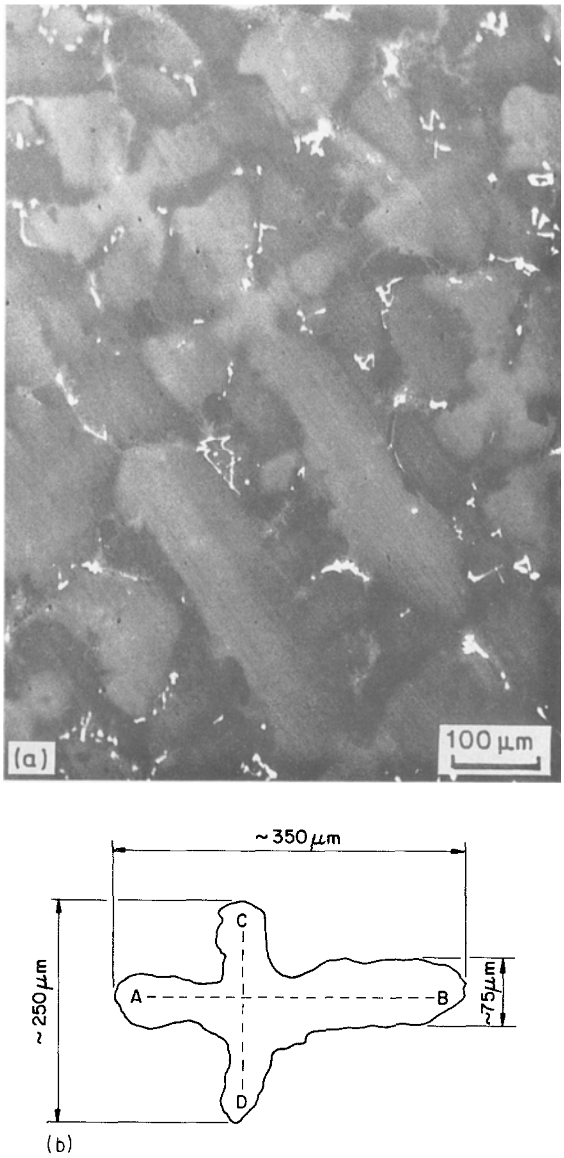

Figure 2 Dendritic structure of the alloy. (a) General view. (b) Schematic representation of a dendrite. Note that for the construction of the curves in Figs 3 and 4 the analyses were performed along the lines A–B and C–D, respectively.

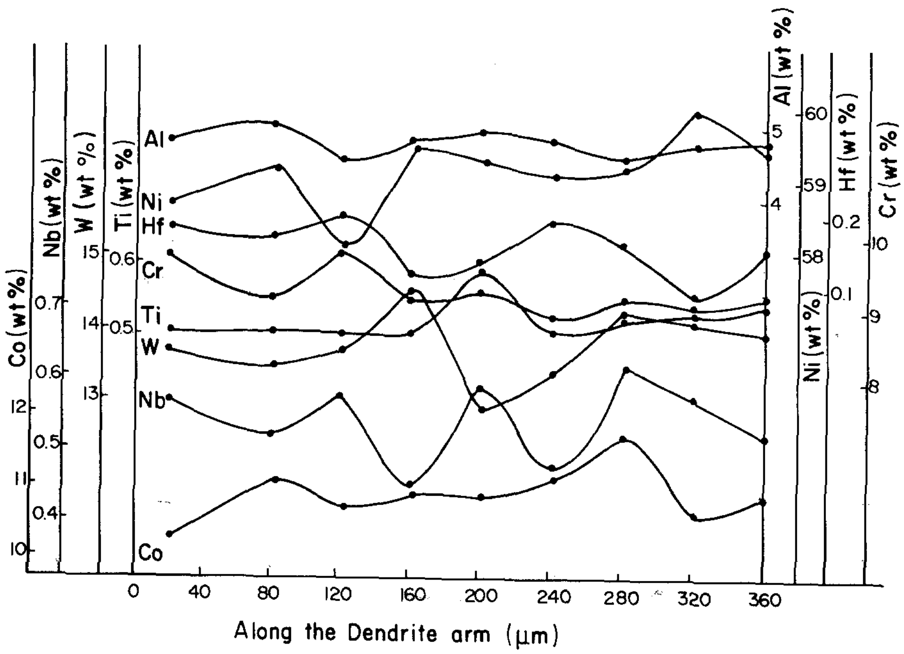

Figure 3 Distribution of the elements along the primary dendrite arm, as indicated along A–B in Fig. 2b.

much less than 1, indicating that the hafnium content in the eutectic is much more than that in the primary dendrite. The segregation ratios, $K(C_p/C_e)$ of titanium, niobium, aluminium and nickel are less than 1, which indicates that these elements are segregated to the eutectic region. The enrichment of titanium, aluminium, hafnium and nickel and the depletion of tungsten and chromium in the eutectic region are in agreement with the previous observations in the dendritically solidified MAR-M200 [1–3] and the plane-front solidified MAR-M200 + Hf [4] alloys. However, in the case of chromium, in contrary to the present result, Sellamuthu and Giamei [4] observed that chromium was enriched in the eutectic region. In addition to the quantitative results given in Figs 5 and 6, and in Table II, Fig. 7 also clearly indicates that the rosette-type $(\gamma + \gamma')$ eutectic region is depleted in chromium. This figure also shows that the blocky-type γ' phase (white areas) is depleted in chromium and the γ matrix is enriched in chromium in the eutectic region.

In order to predict the solute interactions during the solidification of DS200 + Hf alloy, Table III was prepared. Data in this table were taken from the binary phase diagrams given by Hansen [5]. This table gives the segregation ratios of elemental aluminium, titanium, chromium, tungsten and niobium in the nickel-rich binary alloys at eutectic temperatures. Segregation ratios of aluminium vary from almost 1 to 0.82, which indicates that the segregation characteristic of aluminium changes during the course of solidification in DS200 + Hf alloy. In binary Ni–Al alloys, the segregation ratio is approximately 0.84, which is close to the segregation ratio $K(C_i/C_e)$. The segregation ratio of aluminium was almost the same [4] in the Ni–Al alloys and in MAR-M200, indicating that the interaction of aluminium with chromium, tungsten and titanium is not significant. However, the segregation ratio of aluminium in the MAR-M200 + Hf was different to that in the MAR-M200, which was attributed to the strong Al–Hf chemical interaction effect [4].

Table II indicates that the negligible partitioning of titanium occurs at the beginning of solidification,

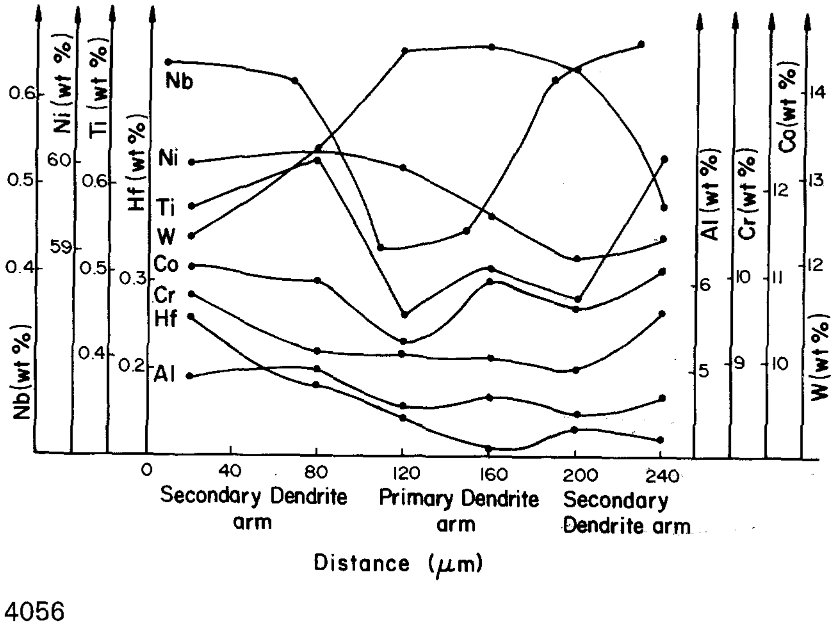

Figure 4 Distribution of the elements across the dendrite (primary and secondary dendrite arms), as shown along C–D in Fig. 2b.

TABLE II Concentrations of elements within the primary (C_p) and secondary (C_s) arm dendrites and the interdendritic (C_i) and eutectic (C_e) regions

Element	Concentration (wt %)				Segregation ratios			
	C_p	C_s	C_i	C_e	C_p/C_s	C_s/C_i	C_i/C_e	C_p/C_e
Al	4.70	4.74	5.27	6.43	0.99	0.90	0.82	0.73
Co	10.97	10.78	10.56	8.39	1.02	1.02	1.26	1.31
Cr	9.21	9.28	9.25	6.07	0.99	1.00	1.52	1.52
Ni	59.12	59.63	61.59	64.71	0.99	0.97	0.95	0.91
Ti	0.53	0.55	0.78	1.05	0.96	0.71	0.74	0.50
Nb	0.55	0.60	1.06	1.43	0.92	0.57	0.74	0.38
Hf	0.15	0.17	0.94	3.21	0.88	0.18	0.29	0.05
W	13.79	13.41	9.56	6.78	1.03	1.40	1.41	2.03

whereas at the end of solidification titanium preferentially partitions to the liquid to a greater extent as the segregation ratio varies between 0.96 and 0.74. However, in the binary alloy (Table III) the segregation ratio of titanium is approximately 0.92, indicating preferential partitioning of this element to the liquid. The increased partitioning tendency of titanium was attributed [4] to the strong chemical interaction of titanium with aluminium, chromium and tungsten in the liquid phase.

As the segregation ratio of chromium varies from almost unity at the beginning of solidification to 1.52 at the end of solidification, the tendency to segregate to the growing solid phase increases during the course of the liquid–solid transformation. In nickel-rich Ni–Cr alloys, the segregation ratio is approximately 0.92, indicating that the chromium preferentially segregates to the liquid in the binary system. At the beginning of solidification of DS200 + Hf, the segregation ratio is similar to that in the Ni–Cr alloys, which suggests that there is no strong interaction between chromium and the rest of the solutes in DS200 + Hf, whereas the segregation ratio is high at the end of solidification indicating a strong chemical interaction of chromium with the other solutes.

The segregation of tungsten to the growing solid increases from almost negligible partitioning to a much larger amount during the course of liquid–solid transformation as the segregation ratio varies from almost unity to 1.41 (Table II). In Ni–W alloys, the segregation ratio is approximately 0.97, which is similar to that in DS200 + Hf alloy. This suggests that there is no strong interaction between tungsten and the other solutes at the beginning of solidification. However, this chemical interaction should become strong towards the end of solidification as the segregation ratio increases.

The segregation ratio of niobium decreases from 0.92 to 0.74 during solidification, indicating increased preferential partitioning of niobium to the remaining liquid phase. In Ni–Nb alloys the segregation ratio is approximately 0.87 which indicates the preferential partitioning of niobium to the remaining liquid in the binary Ni–Nb alloys. The similarity of the segregation ratio of niobium in DS200 + Hf at the beginning of solidification with that in Ni–Nb alloys suggests that there is no strong interaction of niobium with the rest of the solutes in the liquid. However, this chemical interaction increases towards the end of solidification because the segregation ratio of niobium decreased to the value of 0.74.

The segregation ratio of hafnium varies from 0.88 to 0.29 during solidification, indicating increased preferential partitioning of hafnium to the remaining liquid phase. In Ni–Hf binary alloys, the segregation ratio is approximately 0.13 indicating preferential

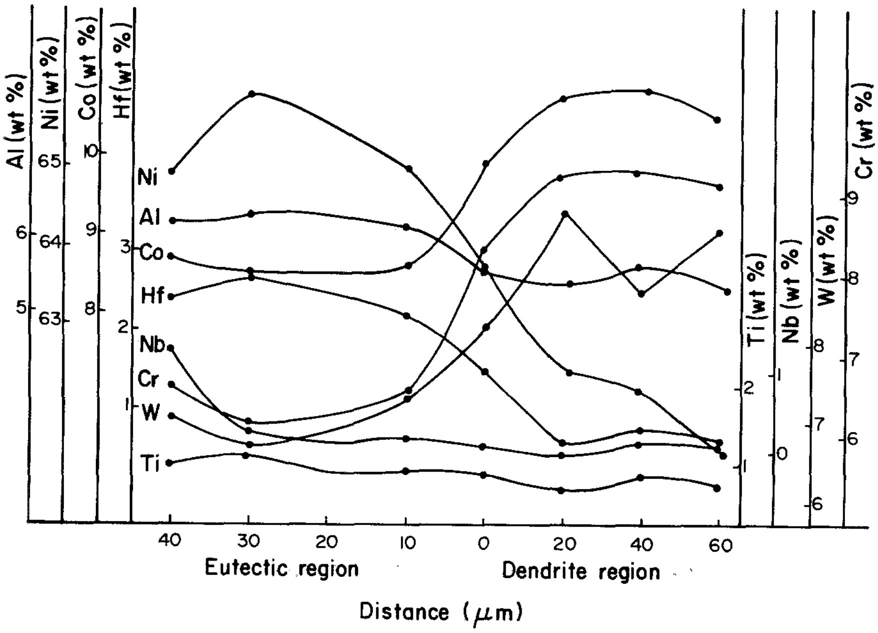

Figure 5 Distribution of elements within the eutectic and dendritic regions.

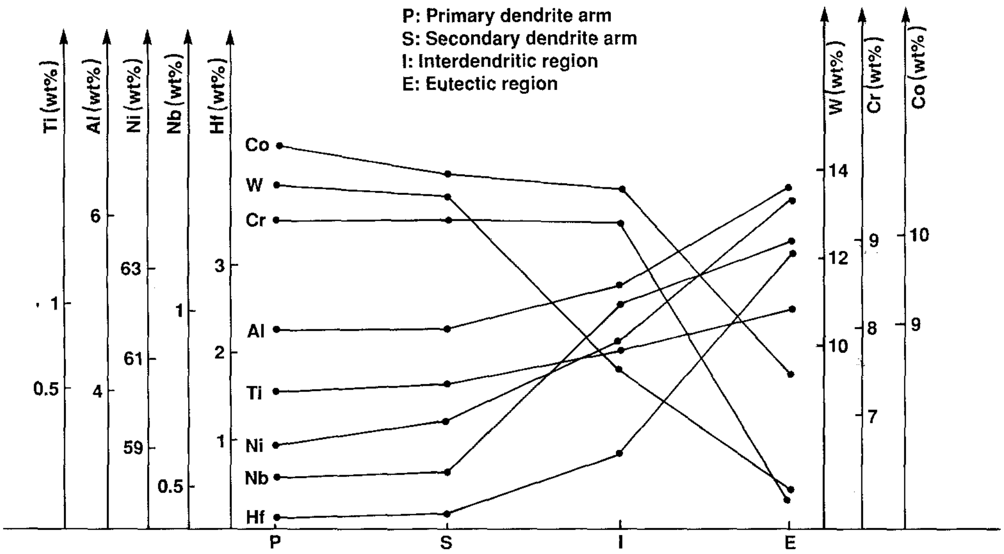

Figure 6 Segregation characteristics within primary and secondary dendrites, interdendritic and eutectic regions in the as-cast condition of DS200 + Hf single crystal.

segregation of hafnium to the liquid phase. From the segregation ratio of hafnium in DS200 + Hf and binary Ni–Hf alloys it can be concluded that there is a strong chemical interaction of hafnium with other solutes. The fact that the segregation ratio changes to a greater extent indicates that the degree of this interaction also changes.

The segregation ratio of nickel decreases from almost unity to 0.95 during solidification, indicating the increased tendency of nickel to segregate to the remaining liquid phase. This segregation may be related to the increased segregation tendency of tungsten, chromium and cobalt to the growing solid phase during solidification because the segregation ratios of tungsten, chromium and cobalt increase from almost unity at the beginning of solidification to much higher values at the end of solidification, whereas the segregation ratio of nickel shows the reverse behaviour.

5. Conclusions

The study of dendritic and eutectic structures in the as-cast state of DS200 + Hf single crystal has shown that the ($\gamma + \gamma'$) eutectic region was enriched in aluminium, titanium, hafnium, niobium and nickel, and depleted in tungsten, chromium and cobalt. The segregation characteristics and chemical interactions of these elements were discussed in detail.

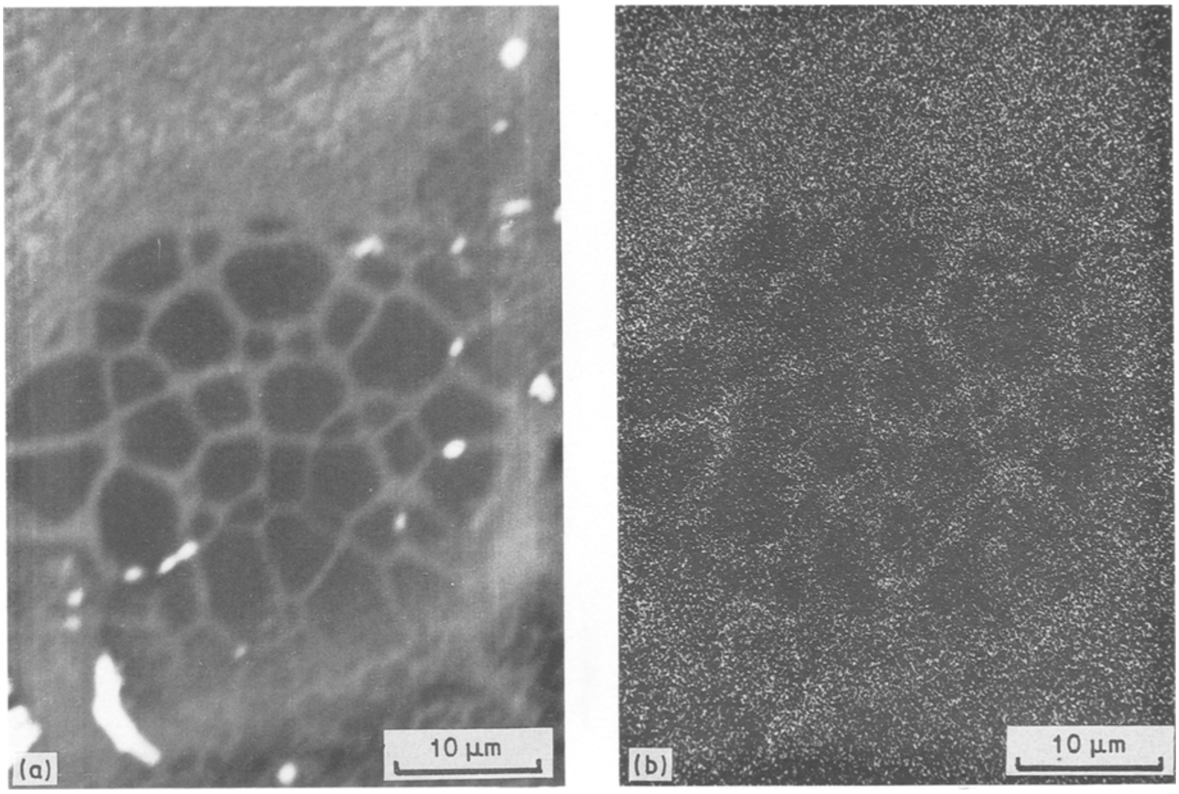

Figure 7 Distribution of chromium in the rosette-type eutectic region. (a) Morphology of the eutectic. (b) The eutectic region depleted in chromium.

TABLE III Segregation ratios of different elements in the binary nickel-rich Ni–X (X = Al, Ti, Cr, W, Nb and Hf) alloys at eutectic temperatures [5, 6]

Al	Ti	Cr	W	Nb	Nf
0.84	0.92	0.92	0.97	0.87	0.13

Acknowledgements

This work was supported by the Division of Materials Science and Technology, CSIR, South Africa. The author is grateful to Dr N. R. Comins for helpful discussion and comments on the manuscript.

References

1. B. J. PIEARCEY, B. H. KEAR and R. W. SMASHEY, *Trans. ASM* **60** (1967) 634.
2. R. A. GREGG and B. J. PIEARCEY, *Trans. AIME* **230** (1964) 599.
3. J. E. DOHERTY, B. H. KEAR and A. F. GIAMEI, *J. Metals*, November (1971) 59.
4. R. SELLAMUTHU and A. F. GIAMEI, *Met. Trans.* **17A** (1986) 419.
5. M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958).
6. P. NASH and D. R. F. WEST, *Metal Sci.* **15** (1981) 351.

Received 19 May
and accepted 23 October 1989