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Electron microprobe investigation of lower melting regions in the as-cast structure of DS200 + Hf single crystal

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The elemental characteristics of incipient melting (or lower melting) regions in as-cast DS200 + Hf single crystal were investigated in detail. In addition to the Ni_5Hf phase, the Ni_7Hf_2-type compound was observed to exist in the incipient melting regions. Ni_7Hf_2 and Ni_5Hf showed considerable solubilities for chromium, cobalt and aluminium. Chromium and cobalt replace nickel in the Ni_7Hf_2 phase. A large variability of composition was observed in the incipient melting regions. For example, nickel and hafnium contents varied between 27.35 and 59.94 wt% and 14.47 and 54.87 wt%, respectively.

1. Introduction

Although the addition of 1.5 to 2.0 wt % Hf to directionally solidified superalloys can increase the transverse mechanical properties of alloys at intermediate temperatures [1], it is known that hafnium lowers the incipient melting temperature to below the solid solution treatment of ($\gamma + \gamma'$) eutectic and made full dissolution difficult [2]. The incipient melting region, which contains the Ni_5Hf intermetallic compound, has the lowest melting point in the hafnium-bearing alloys. It was considered [3] that the melting of the Ni_5Hf phase may be one of the main factors affecting incipient melting. Ni_5Hf occurs generally in nickel-base superalloys containing more than 0.4 wt % Hf. It was pointed out [4] that the Ni_5Hf was responsible for hot tearing along the grain boundaries during directional solidification.

Because the incipient melting region mainly consists of elemental nickel and hafnium it was decided to consider the Ni–Hf phase diagram briefly. Nash and West [5] constructed a composite Ni–Hf phase diagram, the data of which were taken from different sources. This phase diagram shows that in the Ni–Hf system the following intermetallic compounds occur: Ni_5Hf, Ni_7Hf_2, Ni_3Hf, $Ni_{21}Hf_8$, Ni_7Hf_3, $Ni_{10}Hf_7$, $Ni_{11}Hf_9$, NiHf and $NiHf_2$. The Ni–Hf phase diagram suggests that the intermetallic compounds formed exist as stoichiometric compounds. Ni_5Hf forms according to the following peritectic reaction [6]

$$\text{L (liquid)} + Ni_7Hf_2 \rightarrow Ni_5Hf \text{ at } 1240^\circ\text{C} \quad (1)$$

The Ni_7Hf_2 compound occurs congruently at 1477° C.

Although it has very important implications for the mechanical properties of the alloys, incipient melting has not been properly investigated in terms of the segregations of the elements in this microconstituent. Therefore, the aim of this study was to investigate the elemental characteristics of incipient melting regions.

2. Experimental procedure

For this study DS200 + Hf single-crystal alloy was chosen in the as-cast state. The chemical composition of this alloy is given in Table I. This alloy was supplied as a single-crystal rod grown at the rate of $4\,\text{mm min}^{-1}$ 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 the ZAF correction computer programme. Sections, perpendicular to the solidification axis, were taken from the top, middle and bottom of the rod. Specimens from these sections were used for electron microprobe investigation. X-ray maps of the major elements, including nickel, cobalt, chromium, aluminium, titanium, tungsten, niobium and hafnium were also obtained.

3. Results and discussion

Investigation of incipient melting regions in DS200 + Hf alloy has shown the following type of morphologies. (i) A cellular form or small particles in the interdendritic region (Figs 1a and 2a). (ii) Columnar- or branch-like particles in the interdendritic region (Fig. 1b). (iii) Grain-boundary-type morphology (Figs 1c and d).

As can be seen in Figs 1 and 2, the incipient melting regions always occur in the vicinity of the rosette-type ($\gamma + \gamma'$) eutectic pools. There are also carbide particles which are connected to or very close to the incipient melting regions. These types of carbide were quantitative analysed as the (Hf,Nb)C- and ~HfC-type carbides [7]. Usually, in these carbides very high hafnium contents were observed, up to 78 wt % [7]. Fig. 2a shows an incipient melting region with the carbide particles connected to it. As can be seen in Figs 2b to e the incipient melting region is enriched in nickel, hafnium and chromium and depleted in titanium. The carbide particles labelled A and B in

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TABLE I The chemical 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

Fig. 2a are enriched in hafnium and titanium, and depleted in chromium and nickel.

Quantitative analysis of the incipient melting regions was performed, and the results are given in Tables II and III. These tables indicate the large variability of the major elements including nickel, hafnium, chromium, cobalt, aluminium and niobium. The variability limits of the elements observed are as follows: Ni, 27.35 to 47.28 wt %; Hf, 18.54 to 54.87 wt %; Cr, 1.58 to 10.61 wt %; Co, 3.93 to 10.32 wt %. The variability of the composition in the incipient melting regions has led us to construct curves as a function of

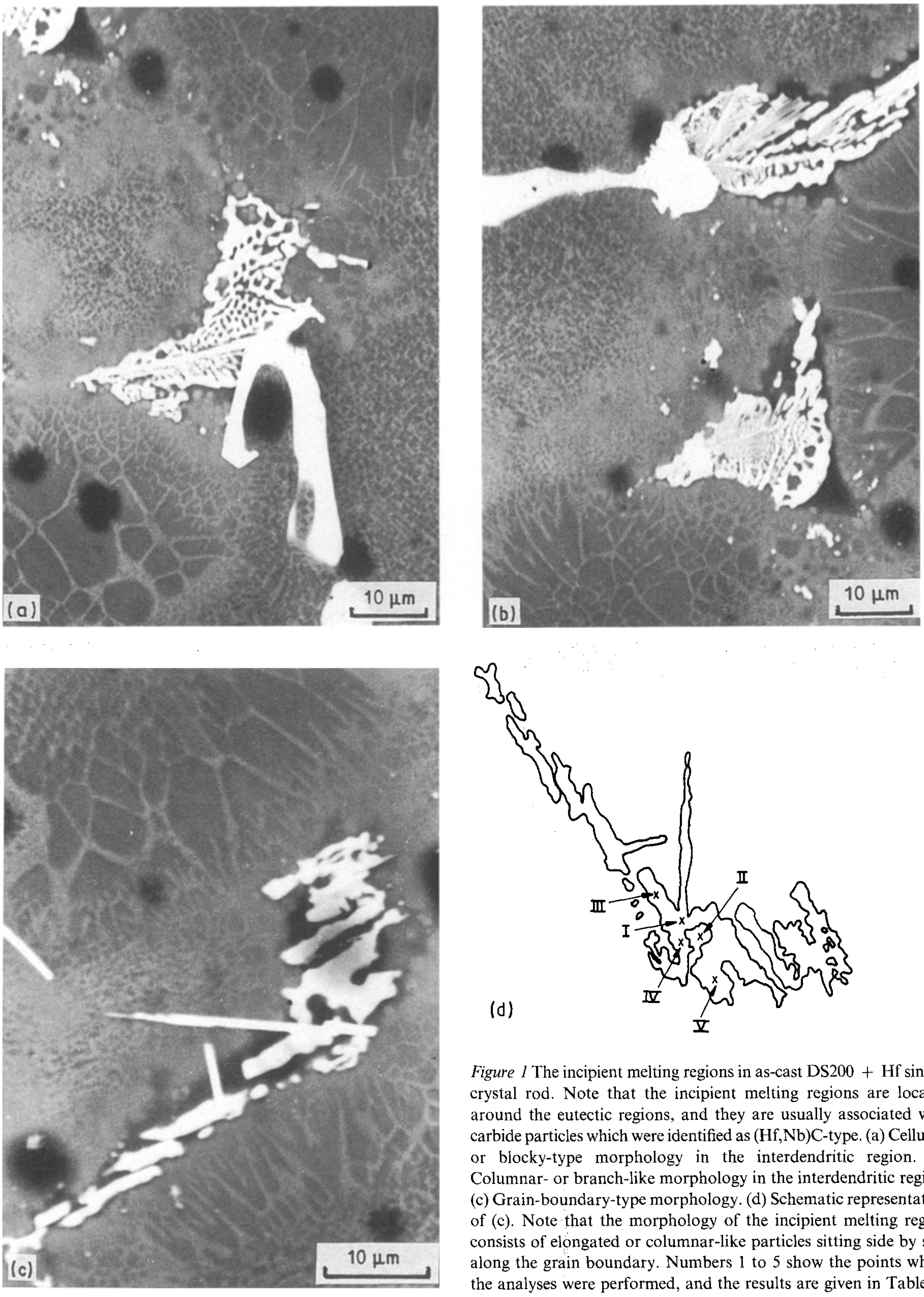


Figure 1 The incipient melting regions in as-cast DS200 + Hf single-crystal rod. Note that the incipient melting regions are located around the eutectic regions, and they are usually associated with carbide particles which were identified as (Hf,Nb)C-type. (a) Cellular- or blocky-type morphology in the interdendritic region. (b) Columnar- or branch-like morphology in the interdendritic region. (c) Grain-boundary-type morphology. (d) Schematic representation of (c). Note that the morphology of the incipient melting region consists of elongated or columnar-like particles sitting side by side along the grain boundary. Numbers 1 to 5 show the points where the analyses were performed, and the results are given in Table II.

TABLE II The differences in composition between the various parts of an incipient melting region (Fig. 1d) in the as-cast structure of DS200 + Hf single crystal

Element	Composition (wt %)				
	1	2	3	4	5
Al	0.33	2.15	0.76	2.33	0.55
Co	3.93	10.32	6.19	7.66	6.08
Cr	1.58	10.61	2.36	6.99	2.08
Ni	27.35	47.12	47.23	43.58	47.28
Nb	5.06	2.30	2.67	3.72	2.36
Ti	1.57	1.24	0.70	1.34	0.81
W	1.68	4.48	1.31	4.88	1.34
Hf	54.87	18.54	36.99	27.29	38.54

TABLE III Analysis of an incipient melting region at different positions (Fig. 4)

Element	Composition (wt %)			
	1	2	3	4
Al	5.07	1.66	1.67	1.76
Co	7.76	8.32	9.20	7.47
Cr	4.20	7.14	7.89	12.56
Ni	59.94	47.67	49.49	42.40
Nb	1.49	1.43	1.32	1.37
Ti	2.38	0.66	0.73	0.85
W	2.63	3.27	3.96	6.57
Hf	14.48	28.32	24.09	22.37

nickel and hafnium contents, respectively, in order to determine the relationships (if any) between the element contents in the incipient melting regions. Fig. 3 shows these curves. Increasing the nickel content up to about 54 to 57 at % Ni increases cobalt, chromium and aluminium contents, and on the other hand, decreases the hafnium content (Fig. 3a). Above the 54 to 57 at % Ni content, the behaviour of these elements reverses. However, tungsten, niobium and titanium contents do not vary significantly as the nickel content increases (Fig. 3a). In Fig. 3b, on the other hand, chromium and cobalt contents decrease as the hafnium content increases up to about 17.5 at % Hf. However, above about 17.5 at % Hf the contents of all the elements do not show any significant change while the hafnium content increases. Tables II and III give the results of the analyses performed from the different positions of the two incipient melting regions in Figs 1d and 4. These tables indicate the variability of the elements from one position to another within an incipient melting region. As stated in Section 1, assuming that the compounds in incipient melting regions occur as stoichiometric phases, as in the binary Ni–Hf system, only position 2 in Fig. 1d represents the Ni_5Hf-type compound. Positions 3, 4 and 5 are close to the Ni_7–HF_2-type compound. The composition of position 1 is somewhere between Ni_7Hf_2- and Ni_7Hf_3-type compounds. No such compounds exists in the Ni–Hf system. When considering the result in Table II for Fig. 4, the analyses indicate that 2, 3 and 4 represent the Ni_5Hf_2-type phase, whereas the composition of analysis point 1 is close to the Ni_7Hf_2-type compound. Examination of cellular- or columnar-type structures (Figs 1 and 2) suggests that more than one phase could exist in the incipient melting regions.

There is a close crystallographic relationship between Ni_5Hf and Ni_7Hf_2 [8], and Ni_7Hf_2 could be formed from Ni_5Hf by deletion of alternate nickel layers and several atomic displacements. This might give low interfacial energies which may be the reason

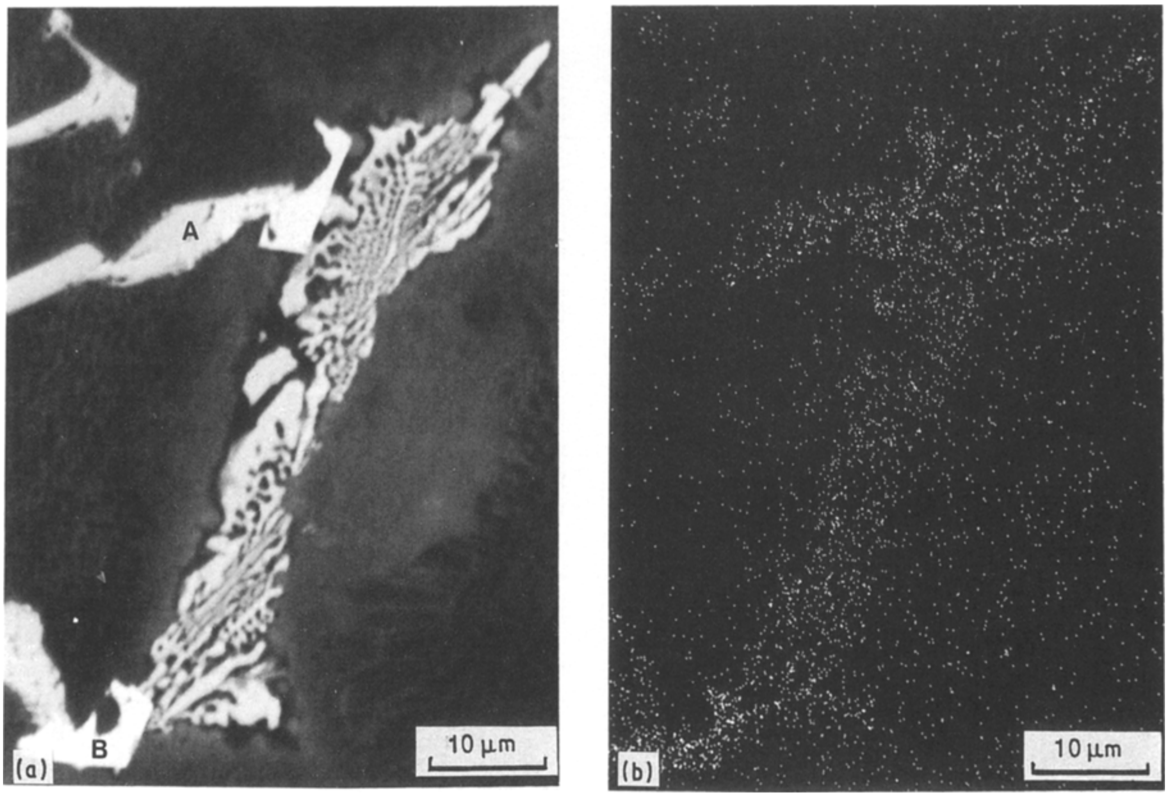


Figure 2 An incipient melting region in the DS200 + Hf alloy. (a) Cellular- and columnar-like morphology. A and B are carbide particles connected to the incipient melting region: (b) hafnium, (c) nickel, (d) titanium, (e) chromium.

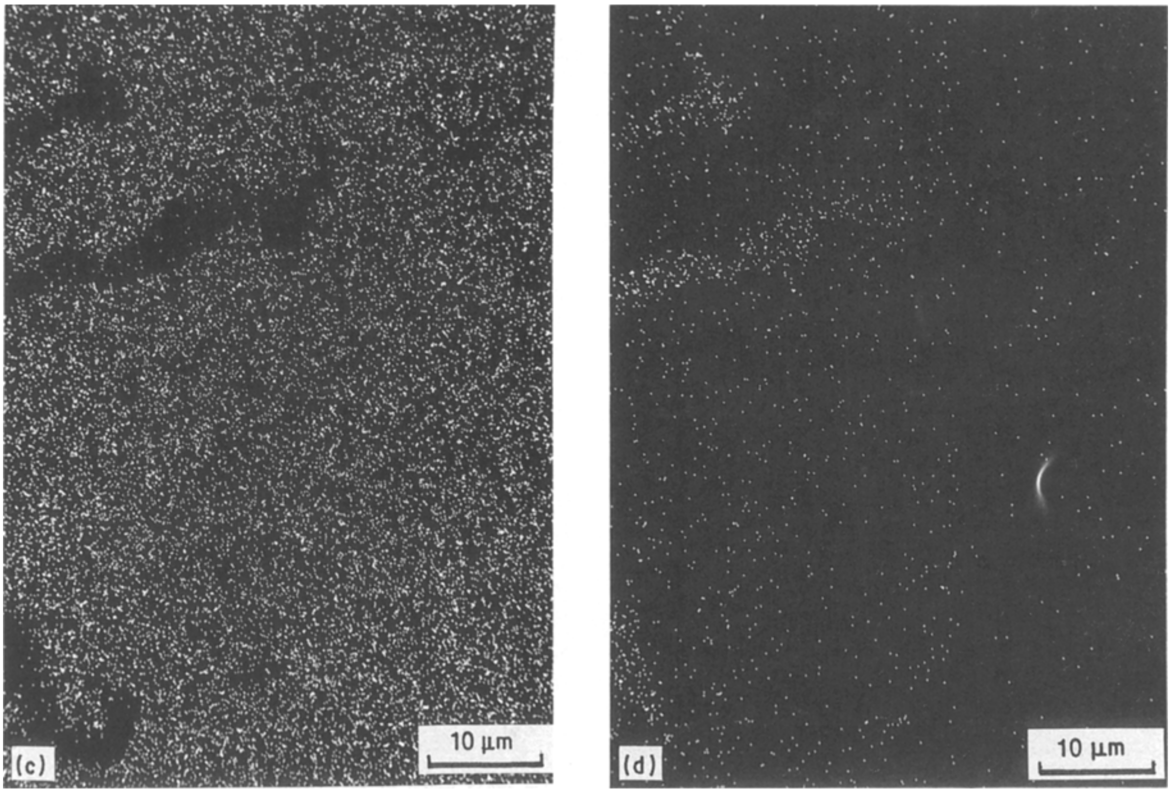


Figure 2 Continued.

why the microstructure of the incipient melting regions is fine. Returning to Fig. 3a, this figure clearly indicates that below about 54 to 57 at % Ni the Ni_5Hf-type phase occurs. Therefore, as Fig. 3a shows the behaviour of elemental hafnium, cobalt, chromium and aluminium is reversed in the Ni_7Hf_2 and Ni_5Hf phase regions. Further, Fig. 3a also indicates that in Ni_7Hf_2, nickel is replaced by elemental cobalt and chromium. The substitution of cobalt and chromium by nickel is in agreement with previous observations [5, 9].

From the analyses performed on the incipient melting regions, the Ni_5Hf- and Ni_7Hf_2-type compounds are found to have the following stoichiometric formulae in the DS200 + Hf alloy

$$[Ni_{(0.65-0.75)}, Co_{0.13}, Cr_{(0.12-0.22)}, Nb_{0.02}]_5$$

$$[Hf_{(0.45-0.62)}, Al_{(0.26-0.45)}, Ti_{(0.06-0.11)}, W_{(0.07-0.15)}],$$

$$[Ni_{(0.57-0.89)}, Co_{0.11}, Cr_{(0.04-0.11)}]_7$$

$$[Hf_{(0.23-0.79)}, Ti_{(0.04-0.14)}, Al_{(0.05-0.55)}, Nb_{(0.05-0.11)}, W_{(0.03-0.07)}]_2$$

The existence of the Ni_7Hf_2 compound in nickel-base superalloys has also been observed previously [9–11]. As mentioned in Section 1, Ni_7Hf_2 forms congruently at 1477° C. Therefore, the Ni_7Hf_2 intermetallic compound in DS200 + Hf alloy is assumed to form when the liquid is enriched in hafnium upon solidification. The fact that the majority of the observations are of the Ni_7Hf_2-type compound rather than the Ni_5Hf phase suggests that the Ni_7Hf_2 phase consumes much of the hafnium enriched in the liquid, because this phase forms earlier than Ni_5Hf compound (see Reaction 1). In the present results, the Ni_7Hf_2 phase exhibits a large solubility for cobalt, chromium and aluminium. The maximum solubilities observed for these elements are ~8 at % for Co, ~10 at % for Cr and ~12 at % for Al. However, the solubilities of titanium, niobium and tungsten in the Ni_7Hf_2 phase are low. In nickel-rich Ni–Al–Hf systems the Ni_7Hf_2 phase shows a similar solubility for aluminium (~14 at %) at 1200° C [5], which suggests that the solvus boundary for aluminium in DS2000 + Hf alloy is similar to those in the Ni–Al–Hf system, and that there is no considerable diffusion during the solid state

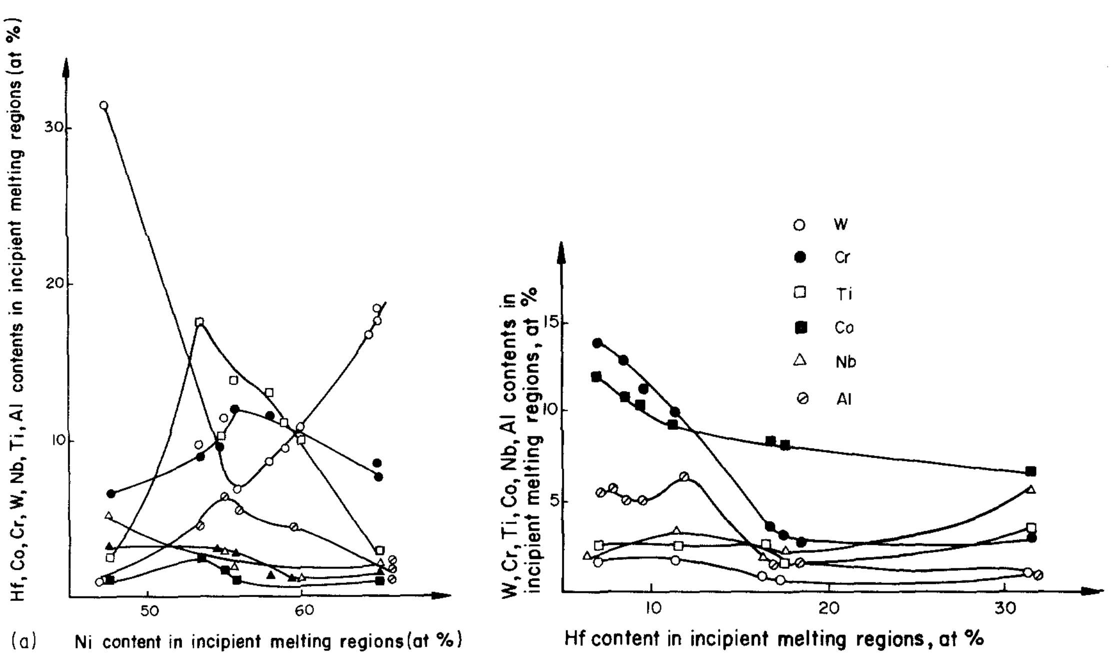


Figure 3 Variation of elements in the incipient melting regions, as a function of (a) nickel content, (b) hafnium content. (○) hafnium, (●) cobalt, (□) chromium, (■) tungsten, (△) niobium, (▲) titanium, (⊘) aluminium.

cooling. In the Ni–Cr–Hf system, on the other hand, the maximum solubility of chromium in Ni_7–HF_2 was observed [12] to be 8.3 at % at 1200° C, which is also similar to those in the DS200 + Hf alloy (~ 10 at %). These and the present results for aluminium and chromium suggest that there are no considerable chemical interactions between aluminium, chromium and the rest of the solutes upon solidification. In different as-cast nickel-base superalloys containing different hafnium concentrations (from 0.05 to 0.35 at %), the Ni_7Hf_2-type compound was observed [11], which contained high contents of hafnium (28 at %) and titanium (~ 11 at %), whereas in the present case the solubilities of hafnium and titanium observed were 17 and 3 at %, respectively. Considerable solubilities of chromium (maximum 14 at %), cobalt (maximum 12 at %) and aluminium (maximum ~ 6 at %) were also observed in the Ni_5Hf compound. However, the solubilities of tungsten, titanium and niobium were not appreciable ($\leqslant$ 2.5 at %).

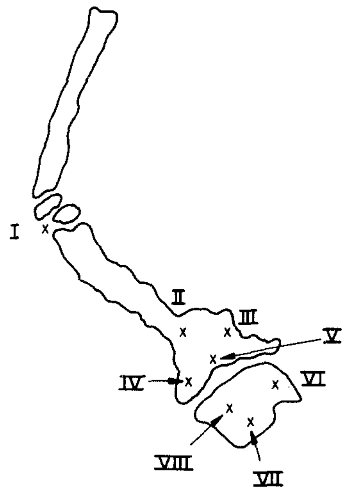
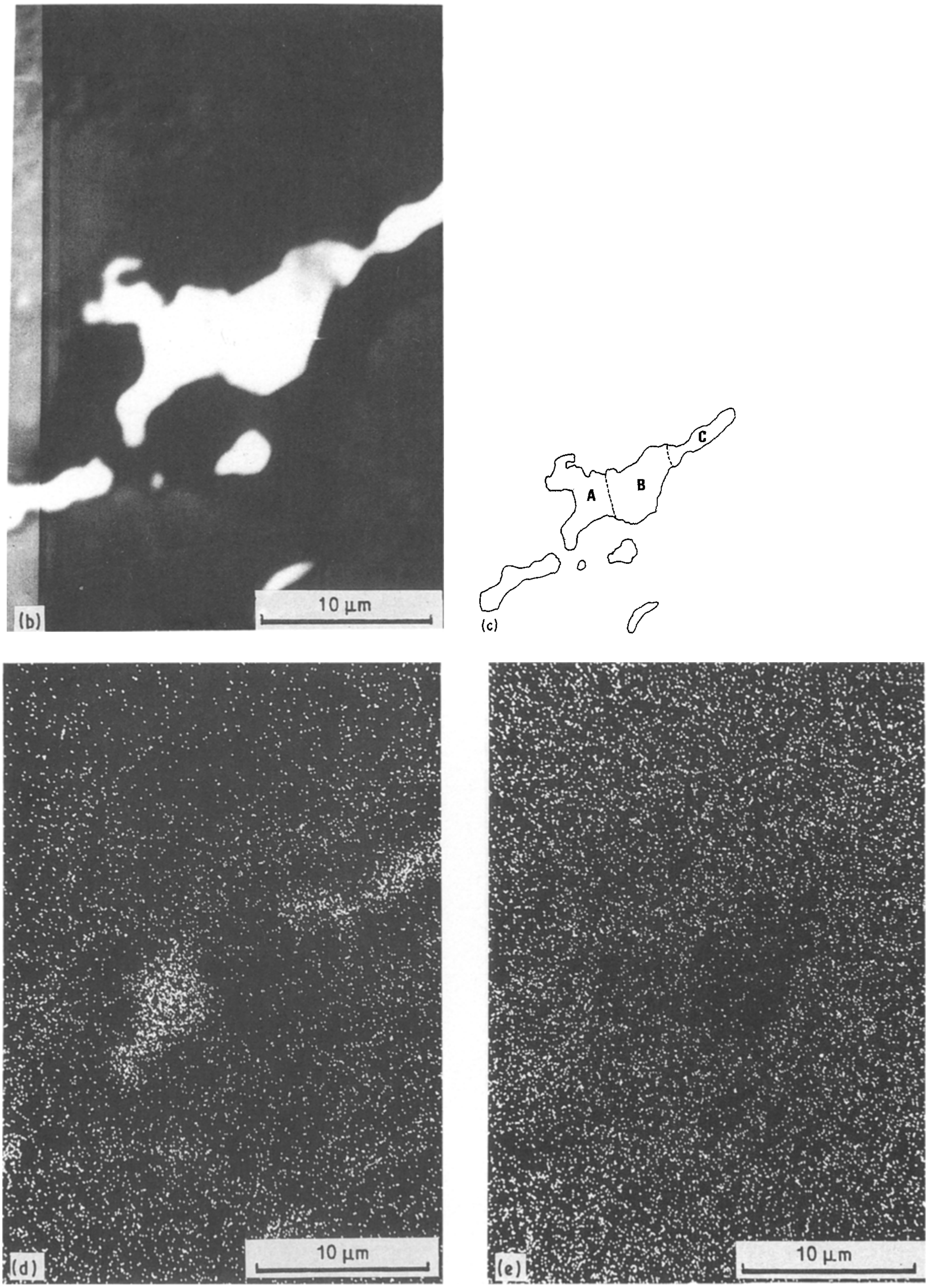


Figure 4 Schematic illustration of an incipient melting region. Numbers 1 to 4 represent the positions where the analyses were performed. (The results are given in Table III.)

Fig. 5a shows blocky-type small and large particles in a grain boundary. In terms of the elemental distribution (Figs 5d to k), the carbide particle in Fig. 5b was divided into three sections, labelled A, B and C. Sections A and C are enriched with nickel, hafnium,

Figure 5 Showing the blocky-type particles along the grain boundary (a) at low magnification, (b) at high magnification. (c) A schematic representation of (b). This particle was sectioned into three, A, B and C. Sections A and C are enriched with nickel, hafnium, cobalt and chromium and poor in niobium and tungsten, whereas section B is enriched with niobium and tungsten and poor in cobalt, chromium, aluminium and nickel. The distribution of these elements is: (d) hafnium, (e) titanium, (f) aluminium, (g) nickel, (h) tungsten, (i) cobalt, (j) chromium, (k) niobium.



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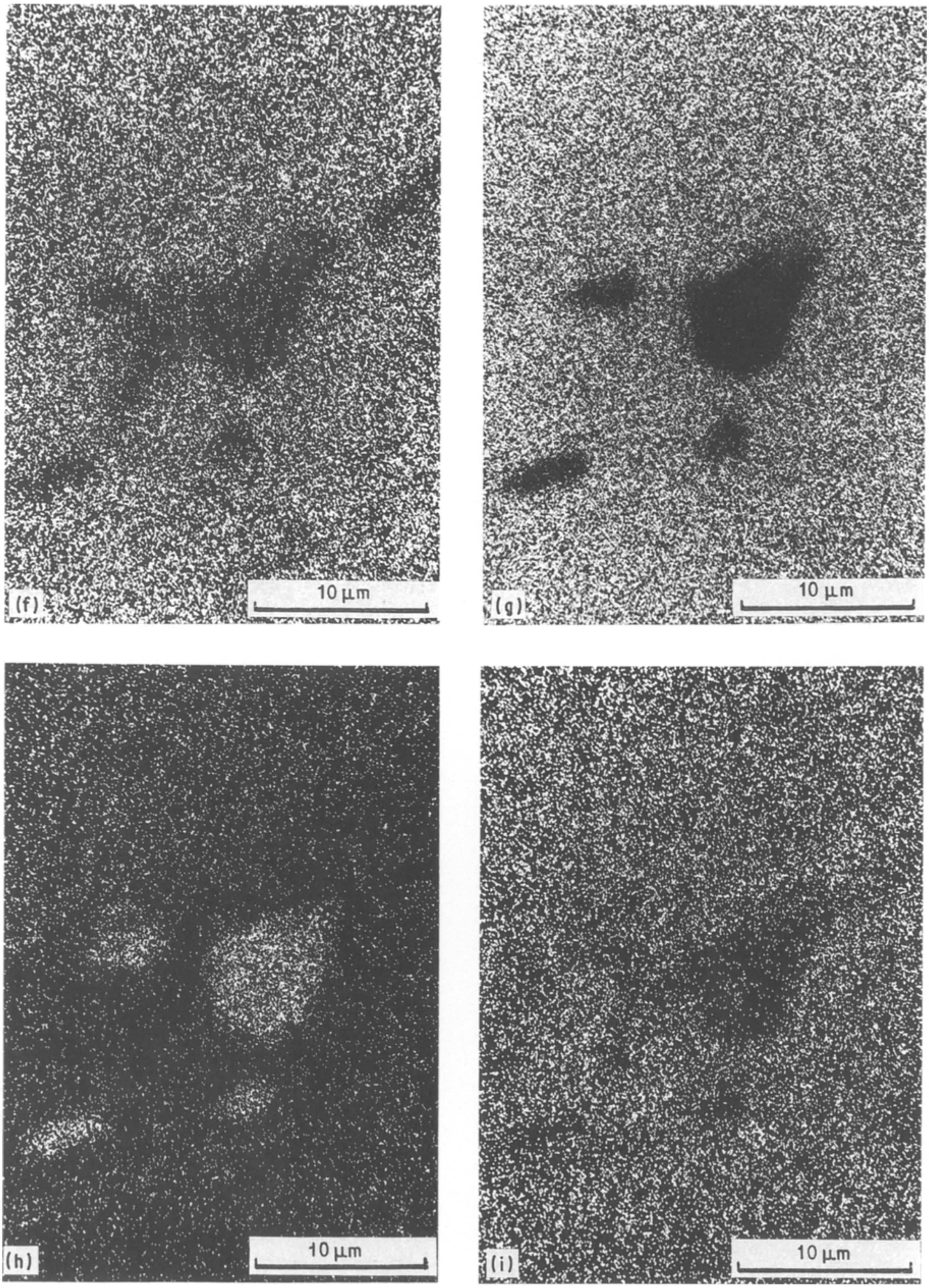
cobalt and chromium, and depleted in niobium and tungsten, whereas the section B is enriched with niobium and tungsten, and depleted in cobalt, chromium, aluminium and nickel. Unfortunately, quantitative analyses of these sections are not available. However, if the present results and the results for the carbides given previously [7] are taken into account, it is possible that sections A and C represent the incipient melting regions, and section B corresponds to (Nb,W,Ti)C carbide. From this observation it is tentatively proposed that there might be some kind of interaction (or reaction) between the phase (or phases) in the incipient melting region and the MC-type carbide.

As in the present case, Yunrong and Yulin [13] observed the Ni_5Hf phase near the $(\gamma + \gamma')$ eutectic pools in hafnium-bearing nickel-base alloys solidified with a dendritic structure. Sellamuthu and Giamei [14] have suggested that in addition to the usual $(\gamma + \gamma')$-type eutectic, another three-phase eutectic containing



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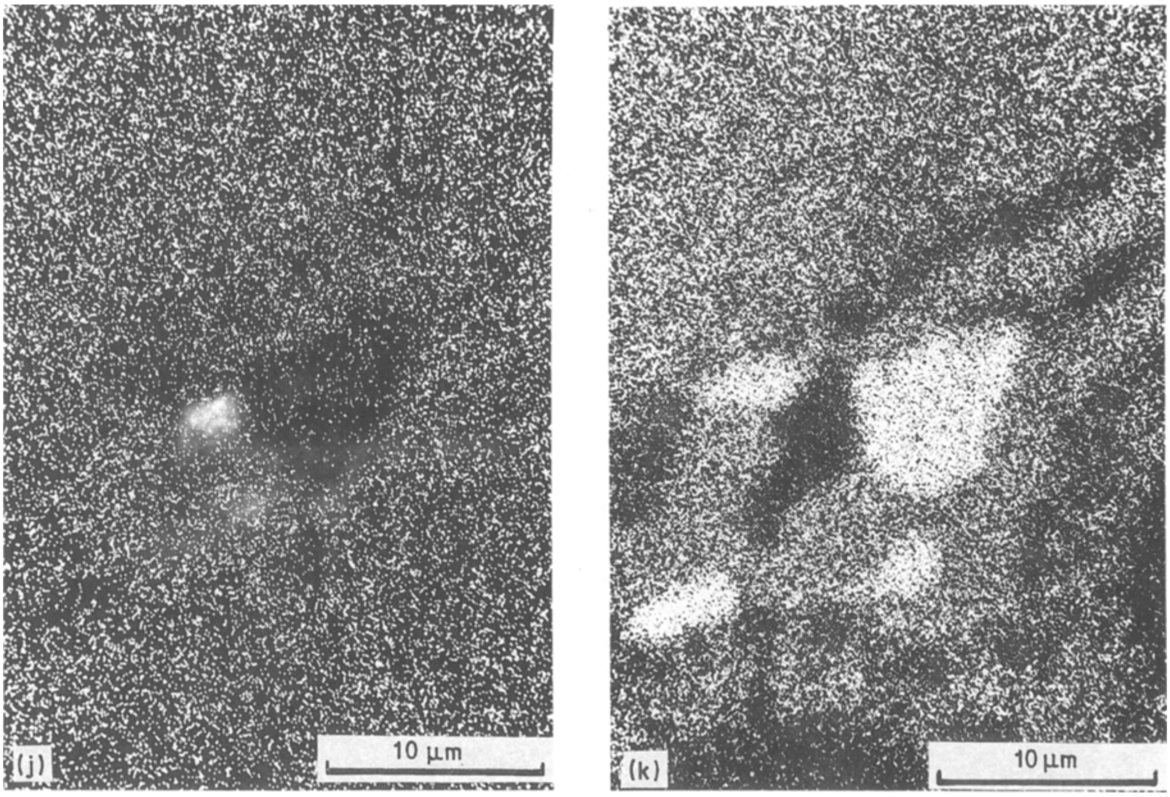
Ni_5Hf with a possibility of γ and carbide adjacent to it, existed in the dendritically solidified nickel-base alloys, a proposal with which the present observation agrees.

4. Conclusions

Electron microprobe data have been used to investigate the incipient melting (or lower melting) regions in as-cast DS200 + Hf single crystal. This investigation indicated that, in addition to the Ni_5Hf-type compound, the Ni_7Hf_2-type intermetallic phase exists in the incipient melting regions. Both Ni_5Hf and Ni_7Hf_2 show considerable solubilities for chromium, cobalt and aluminium. A large variability in composition was observed in the incipient melting regions. For example, nickel and hafnium contents vary between 27.35 and 59.94 wt % and 14.47 and 54.87 wt %, respectively. The incipient melting regions always



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occur in the vicinity of the rosette-type ($\gamma + \gamma'$) eutectic pools. Usually there are (Hf,Nb)C-type carbide particles which are connected to or very close to the incipient melting regions.

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