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Structural features of certain Ni-Al-Ta and Ni-Al-Hf alloys containing the γ'- and β-phases

A. BALDAN,* D. R. F. WEST
Department of Metallurgy and Materials Science, Imperial College, London SW7 2BX, UK

An investigation has been made of the structure of certain alloys of the Ni–Al–Ta and Ni–Al–Hf systems. The compositions chosen for investigation were: Ni–28.75 at % Al–2.5 at % Ta; Ni–26.75 at % Al–2.5 at % Ta; Ni–20.0 at % Al–7.5 at % Ta; Ni–20.0 at % Al–7.5 at % Hf; Ni–22.5 at % Al–5.0 at % Hf. The Ni–Al–Ta alloys consisted of $\gamma' + \beta$-phases (or β-phase transformed during rapid cooling to a martensitic product). Two types of morphology were observed in the transformed β-phase, one consisting of parallel sided plates and the other of acicular shaped plates; the plates contained fine twins on $\{1\,0\,1\}$ b c t planes. The as-cast Ni–Al–Nf alloys consisted of the γ'-phase, together with eutectic regions of β-phase and $(Ni, Al)_7Hf_2$; both lamellar and discontinuous eutectic morphologies were observed. Extensive solid solution of tantalum and hafnium in the γ'-phase occurred.

1. Introduction

In recent years attention has been given to the potential of the γ'-phase Ni_3Al, as a base for superalloy development and as a constituent of directionally solidified eutectic alloys. Various investigations of the mechanical properties of the γ'-phase have been reported (for example [1–4]); including work on ternary alloys, Ni–Al–X, where X includes refractory elements such as tantalum, hafnium and niobium. It was shown that considerable strengthening can be achieved by such alloy additions. However, the constitutional information published for these ternary systems (for example [5–7]) is insufficient for a detailed understanding of structure–property relationships.

The present investigation was concerned with certain alloys from the Ni–Al–Ta and Ni–Al–Hf systems; the compositions chosen corresponded to alloys which contained large volume fractions of the γ'-phase, together with another phase or phases. In particular, the work was aimed at investigating the influence of β-NiAl as a potential strengthening phase; the alloys studied from the Ni–Al–Ta system contained various proportions of aluminium and tantalum, giving β-phase contents of up to about 60 vol %. In the case of the Ni–Al–Hf system, the alloys consisted predominantly of the γ'-phase, together with relatively small volume fractions of the β-phase and of an intermetallic Ni–Hf compound.

The investigation explored microstructure, constitution and high temperature strength, and also the interrelationships of these features; three conditions of alloy treatment were studied, namely, alloys as-cast, homogenized and aged following homogenization.

2. Experimental procedure

The alloys, of composition as listed in Table I, were prepared as "ingots" of approximate weight 80 g by arc melting under an argon atmosphere; at least four "remelts" were made to achieve alloy homogeneity. The ingots were cast in a water-cooled rod-shaped hearth (of approximate dimensions 80 mm × 10 mm × 10 mm) and were allowed to cool completely before the furnace was opened to air. The weight variations during melting were small ($\lesssim \pm 1\%$) and the nominal compositions were taken as corresponding to the actual compositions.

For the homogenization and ageing treatments

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*Present address: Cukurova University, Adana, Turkey.

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TABLE I Alloy compositions and data for alloy phases

Alloy	Composition (at %)	Treatment	Constituents* (vol %)		Refractory element content† (at %)		Lattice parameters (Å)	
			γ'	β	γ'	β	γ'	β
1	Ni–28.75 Al–2.5 Ta	As-cast	42	58		1.0 Ta		
		Homogenized at 1260° C for 2 days	49	51	4.4 Ta	0.6 Ta	3.585	$a = 2.65$; $c = 3.245$; $c/a = 1.22$: b c t
		Homogenized and aged at 1000° C for 3 days	51	49	4.2 Ta	0.6 Ta	3.586	$a = 2.859$: b c c
2	Ni–26.75 Al–2.5 Ta	As-cast			3.2 Ta	1.1 Ta		
		Homogenized at 1260° C for 2 days	71	29	3.7 Ta	0.4 Ta	3.587	$a = 2.68$; $c = 3.25$; $c/a = 1.21$: b c t
		Homogenized and aged at 1000° C for 3 days	75	25	5.2 Ta	0.6 Ta	3.592	$a = 852$: b c c
3	Ni–20.0 Al–7.5 Ta	As-cast	80	20	8.4 Ta		3.612	$a = 2.880$: b c c
		Homogenized at 1260° C for 2 days	80	20	8.3 Ta		3.611	$a = 2.869$: b c c
		Homogenized and aged at 1000° C for 3 days	80	20	7.0 Ta		3.605	$a = 2.861$: b c c
4	Ni–20.0 Al–7.5 Hf	As-cast	76		6.7 Hf		3.625	
5	Ni–22.5 Al–5.0 Hf	As-cast	92		3.0 Hf			
		Homogenized at 990° C for 4 days	96		4.6 Hf		3.615	

*Estimated accuracy typically about ± 2%. Note: in the Ni–Al–Ta alloys aged at 1000° C where γ'-phase precipitation occurred within the β-phase areas it has been point counted as β-phase; thus, the data for the aged state overestimates the percentage of β-phase present (see Fig. 6).

†Estimated accuracy ± 1% Ta (relative) for alloys 1–3 and ± 0.2% Hf (absolute) for alloys 4 and 5.

the specimens were sealed in silica capsules under 1/3 atmosphere of argon; on completion of the heat treatment the capsules were quenched in water, being broken on contact with the water to ensure a rapid quench. The homogenization treatment used for the Ni–Al–Ta alloys consisted of heating to a temperature of 1260 ± ~ 5° C for 2 days. In the light of data on eutectic reactions, in the Ni–Al–Hf system [7], a treatment of 4 days at a temperature of 990° C was chosen for alloys 4 and 5. Specimens of the Ni–Al–Ta alloys were also subjected to an ageing treatment of 3 days (alloys 1 and 2) or 4 days (alloy 3) at 1000° C followed by water-quenching.

Specimens for examination by light microscopy were etched with alcoholic ferric chloride. A point-counting technique was used for determining the proportions of the phases. Three millimetre diameter discs were spark-machined from slices of the ingots of thickness about 0.4 mm. These discs were ground to about 70 μm thickness, and then ion-beam thinned for transmission electron microscopical examination. X-ray examination of specimens was carried out by diffractometry from a flat specimen surface using CuKα radiation. Some electron microprobe analysis was carried out on the β- and γ'-phases.

3. Results and discussion

3.1. Ni–Al–Ta alloys

The Ni–Al–Ta alloys consisted of γ'- and β-phases or body-centred tetragonal martensite β-phase [8] (see Table I). There was extensive solubility of tantalum in the γ'-phase (approximately 8 at %) in contrast to the small solubility in the β-phase ($\lesssim$ 1 at %). The γ'-phase lattice parameters were in reasonable agreement with previous work [9] and were greater than those for binary Ni_3Al [10] as a result of the greater atomic size of tantalum, compared with that of aluminium.

The homogenization temperature of 1260° C was in the $\beta + \gamma'$ region [11]. On quenching, the β-phase transformed martensitically in alloys 1 and 2, while it was retained in alloy 3. Light microscopical examination showed that the martensite formed with a plate-like (banded) morphology, the plates having straight and parallel sides. For example, Figs. 1a and b show this type of struc-

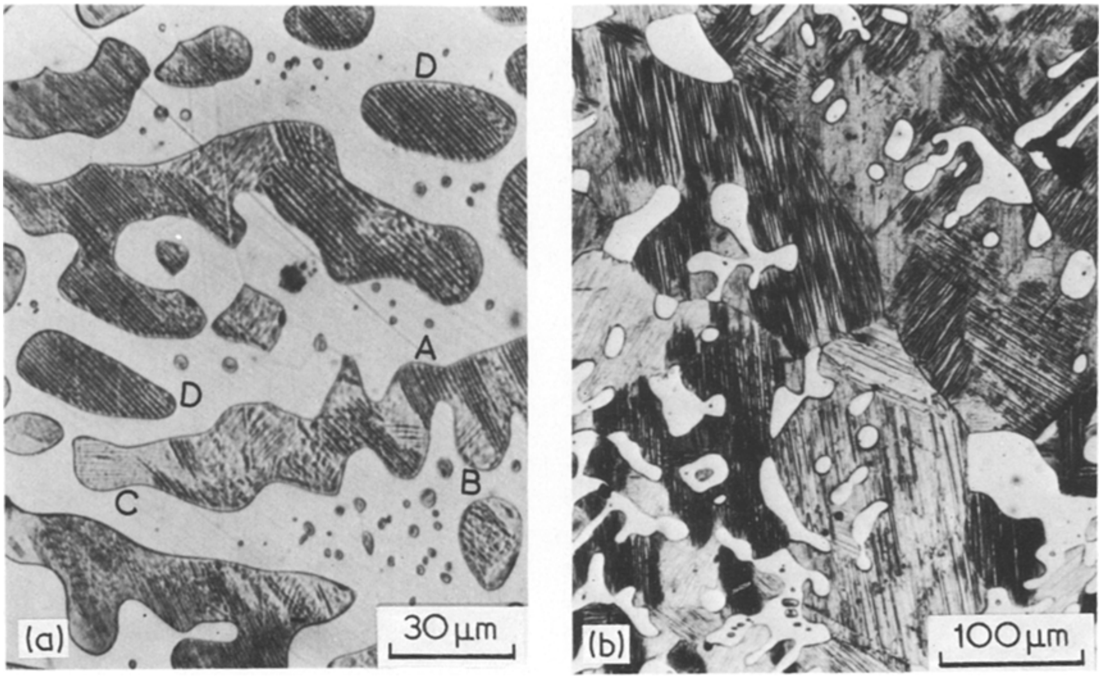


Figure 1 Alloy 1: Ni–28.75 at % Al–2.5 at % Ta. (a) Homogenized at 1260° C for 48 hours and water quenched. Banded β-martensite structure showing straight, parallel-sided plate morphology; some regions contain three differently orientated sets of plates, e.g. at A, B, and C, while other (smaller) regions contain only one set of plates e.g. at D. (b) Homogenized at 1350° C for 5 hours and water quenched. Shows a larger proportion of β-martensite structure.

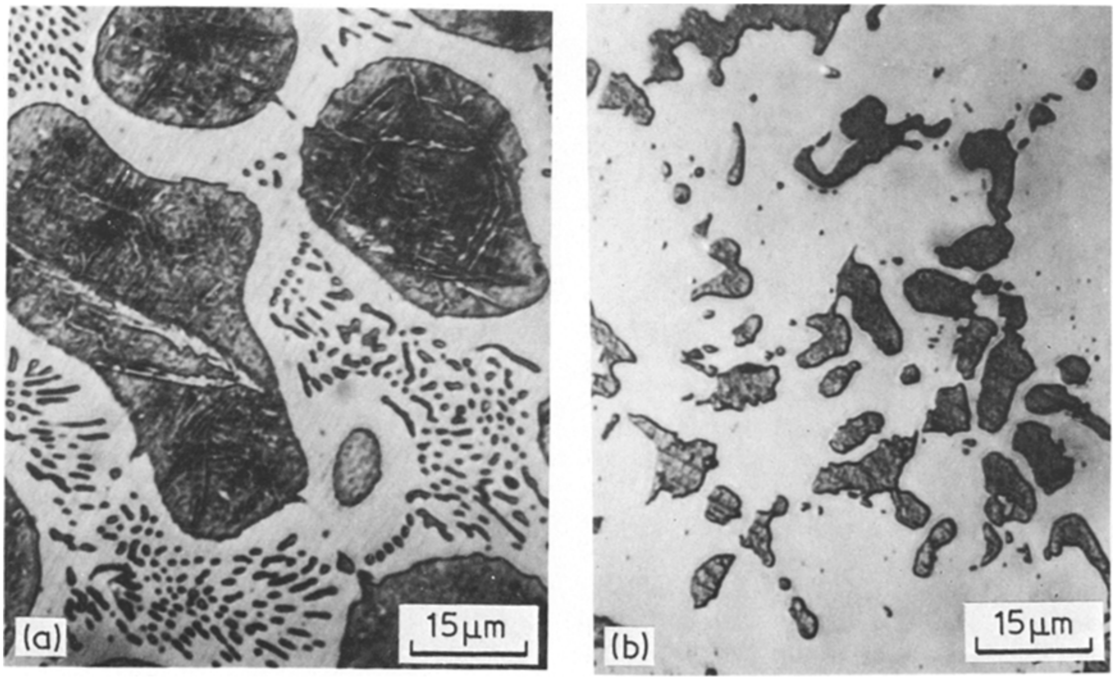


Figure 2 (a) Alloy 1: Ni–28.75 at % Al–2.5 at % Ta; as-cast. Primary β-phase regions (martensitic) plus eutectic regions (β + γ'-phases). (b) Alloy 3: Ni–20.0 at % Al–7.5 at % Ta; as-cast. γ' + β-phases.

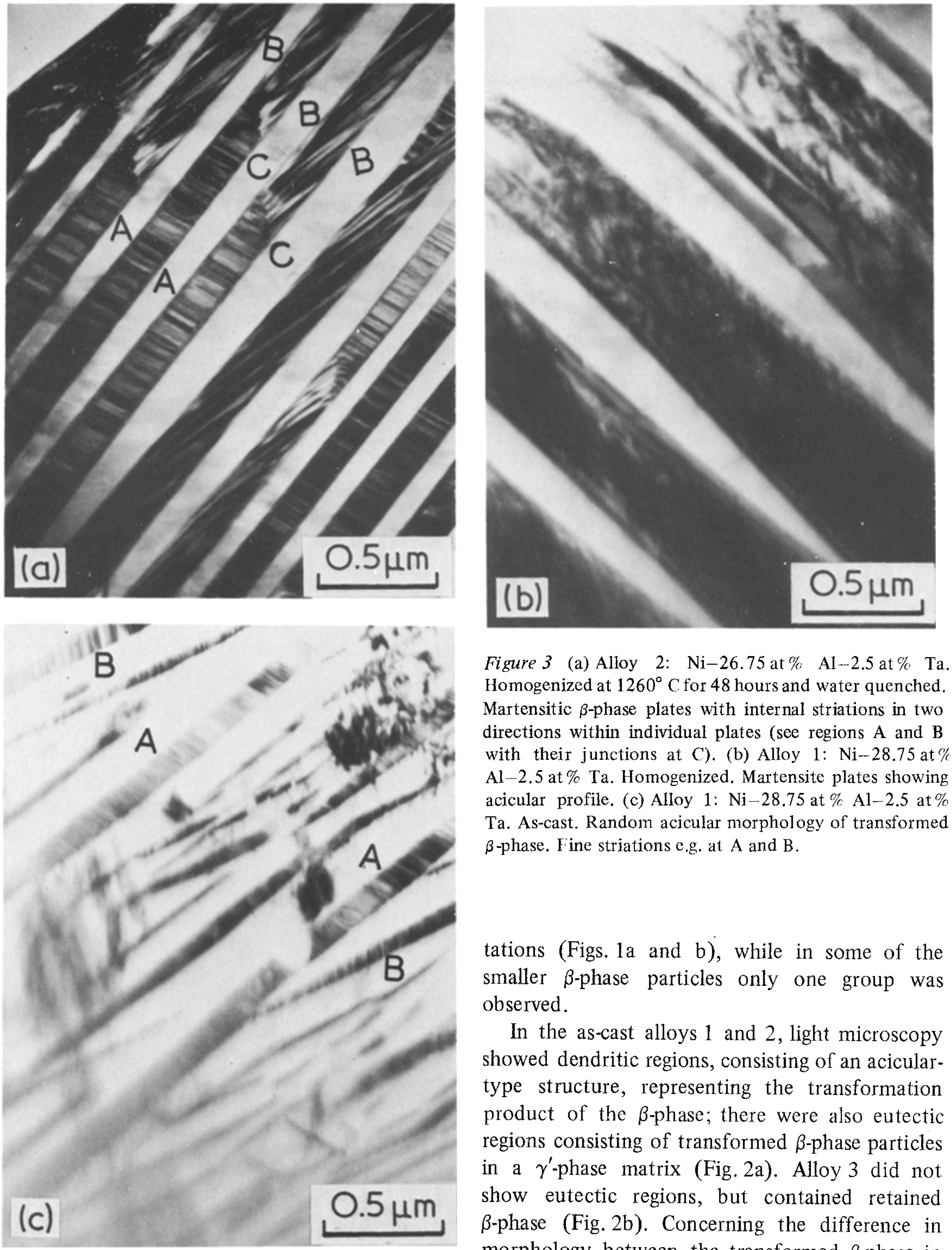
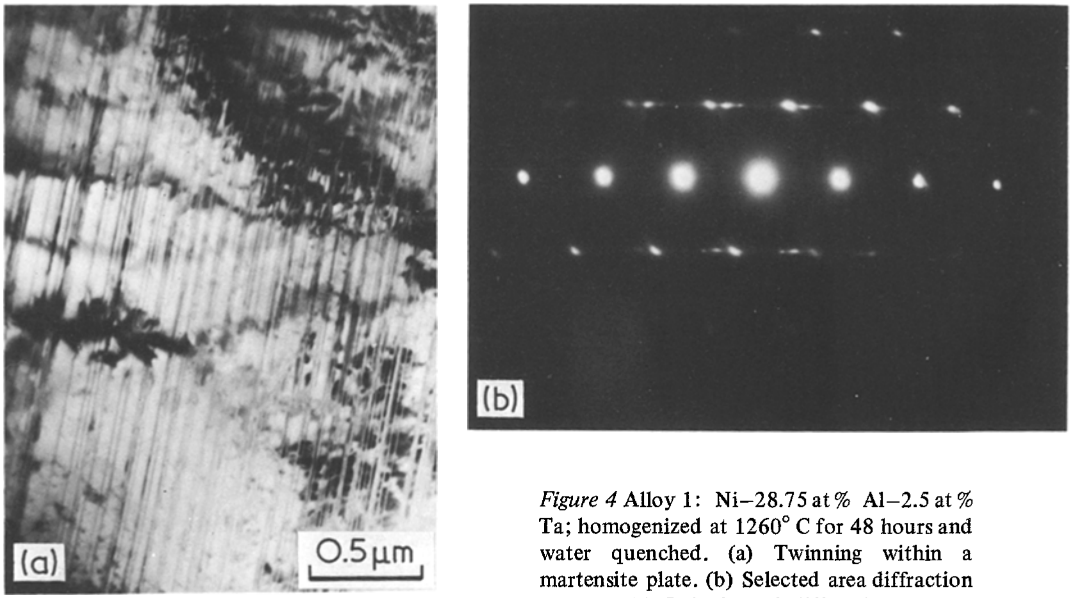


Figure 3 (a) Alloy 2: Ni–26.75 at% Al–2.5 at% Ta. Homogenized at 1260° C for 48 hours and water quenched. Martensitic β-phase plates with internal striations in two directions within individual plates (see regions A and B with their junctions at C). (b) Alloy 1: Ni–28.75 at% Al–2.5 at% Ta. Homogenized. Martensite plates showing acicular profile. (c) Alloy 1: Ni–28.75 at% Al–2.5 at% Ta. As-cast. Random acicular morphology of transformed β-phase. Fine striations e.g. at A and B.

ture in alloy 1 after homogenizing at 1260° C and 1350° C, the latter treatment producing a larger proportion of β-phase and hence of martensite. Some of the transformed β-phase particles contained three groups of plates of different orientations (Figs. 1a and b), while in some of the smaller β-phase particles only one group was observed.

In the as-cast alloys 1 and 2, light microscopy showed dendritic regions, consisting of an acicular-type structure, representing the transformation product of the β-phase; there were also eutectic regions consisting of transformed β-phase particles in a γ'-phase matrix (Fig. 2a). Alloy 3 did not show eutectic regions, but contained retained β-phase (Fig. 2b). Concerning the difference in morphology between the transformed β-phase in the homogenized and as-cast material, the cooling rate from the β-phase range to room temperature in the as-cast alloys (i.e. in the arc-melting furnace) was less rapid than the water-quenching applied following homogenization; thus, a diffusional component in the β-phase transformation is to be



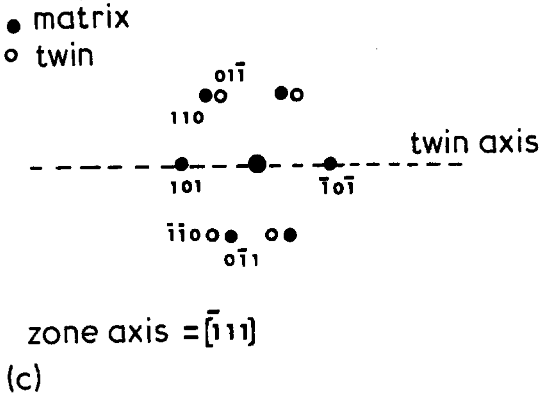


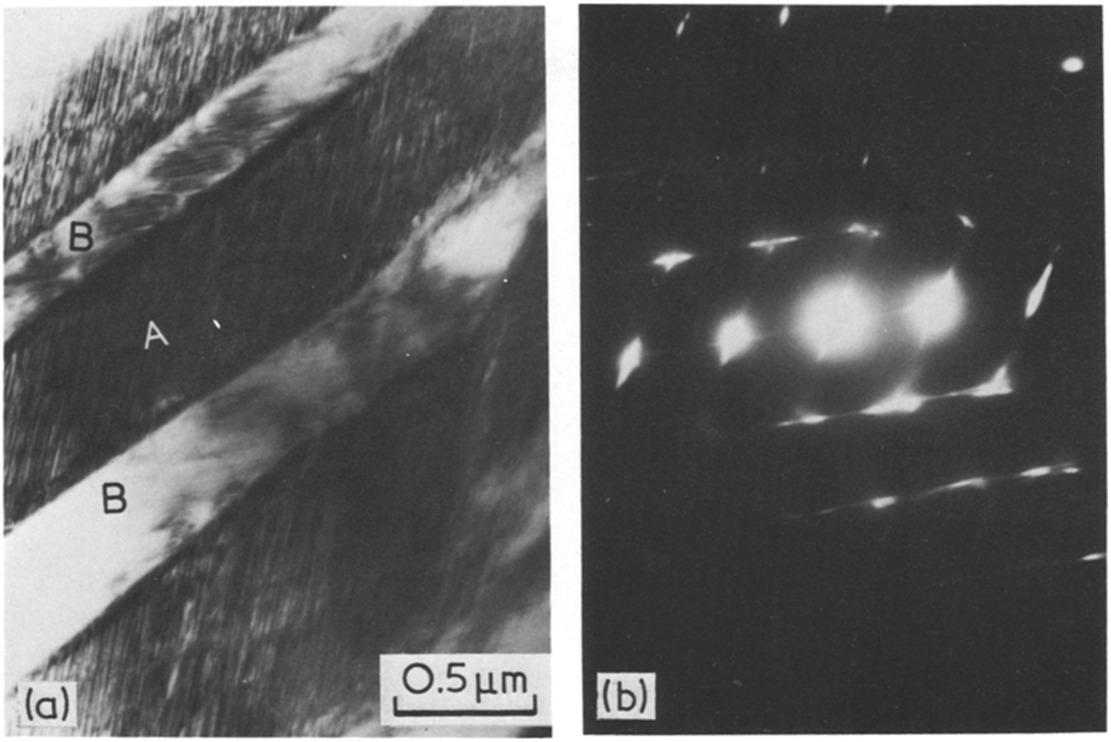
Figure 4 Alloy 1: Ni–28.75 at% Al–2.5 at% Ta; homogenized at 1260° C for 48 hours and water quenched. (a) Twinning within a martensite plate. (b) Selected area diffraction pattern. (c) Indexing of diffraction pattern shown in Fig. 4b.

expected. A further feature, found in alloy 1, but not in alloy 2, was a higher nickel content (as determined by electron microprobe analysis) in the as-cast β-phase combined with an associated higher micro-hardness value in comparison with the homogenized β-phase. This higher nickel content could result from a departure from equilibrium during solidification and the resultant higher martensite "start" temperature, M_s [12] could influence the nature of the β-phase transformation.

The present work has not involved a comprehensive study of the changes in crystal structure and microstructure associated with martensite formation. However, transmission electron microscopical examinations were made of alloy 1 in the as-cast and homogenized conditions and of alloy 2 in the homogenized condition and it is of interest to note certain features in the context of previous work involving electron microscopy and X-ray diffraction [13–19].

From previous work, it appears that the structural changes are complex and are not yet completely understood. The martensite has been found to be body-centred tetragonal in structure [8] but, in addition, a body-centred orthorhombic form has been found [8]. Martensite plates have been found to be internally twinned on {1 0 1} bct planes [8]. Various streaking effects have been observed in diffraction (for example [8, 17–19]) which can originate from the fine twins. Also, streaking along the ⟨1 1 0⟩ direction in the β-phase has been attributed to the presence of fine planar precipitates on {1 1 0} matrix planes, involving rapid decomposition of the β-phase during quenching by the formation of Ni_3Al clusters [8]. The occurrence of pre-martensitic lattice instability has also been proposed [17] associated with anomalous structural features such as diffraction streaking, and a "mottled" structure observed in transmission electron microscopy.

In the present work, the martensite morphology, as observed by electron microscopy, generally consisted of parallel, straight-sided plates forming a "banded" structure with fine internal striations (see Fig. 3a); examples were seen of plates tapering to an acicular profile (Fig. 3b) and areas showing a more random arrangement of plates were also seen in the as-cast condition of alloy 1 (Fig. 3c). Fine internal striations observed within martensite



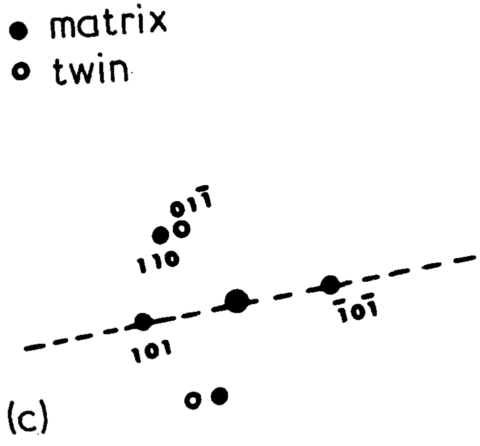


Figure 5 Alloy 1: Ni–28.75 at % Al–2.5 at % Ta; homogenized at 1260° C for 48 hours and water quenched. Martensitic β-phase plates showing internal faulting on two variants of the $\{1\,0\,1\}$-planes in adjoining plates. (a) Bright field electron micrograph. (b and c) Selected area diffraction pattern from plates A and B in Fig. 5a. Zone axis $\simeq$ $[\bar{1}\,1\,1]$ martensite.

plates corresponded to twinning on $\{1\,0\,1\}$ bct planes, (for example in Figs. 3a, 4 and 5). Fig. 3a shows striations in two directions within individual plates: the diffraction data suggest that two variants of the $\{1\,0\,1\}$ bct faulting systems exist within one martensite plate, but it is possible that the effect may result from impingement of plates during growth. In Fig. 5 selected area diffraction patterns from martensite plates A and B, respectively, show streaks along the $(0\,1\,1)$ and $(1\,0\,1)$ plane normals, respectively. These streaks are perpendicular to the striations in the respective plates, and it appears that these adjoining plates are internally faulted on two variants of the $\{1\,0\,1\}$-type plane. A diffraction pattern from plates A and B (Fig. 5) is consistent with twinning, which could indicate a twin relationship between the plates, as well as internal twinning.

Considering precipitation effects, ageing of alloys 1 and 2 at a temperature of 1000° C for 3 days produced γ'-phase precipitation (see Fig. 6); the β-phase did not undergo the martensite transformation after its composition had been changed by this ageing treatment, that is, depletion of the nickel content lowered the M_s below room temperature [20, 21]. A very fine "tweed-like" structure was observed in the retained β-phase in alloy 1 after ageing (Fig. 7); diffraction streaking suggests the presence of fine precipitates on $\{1\,1\,0\}$-planes, consistent with previous work [8, 16, 22].

3.2. Ni–Al–Hf alloys

The γ'-phase was the main phase present in alloys 4 and 5 (see Table I and Fig. 8). Hafnium showed

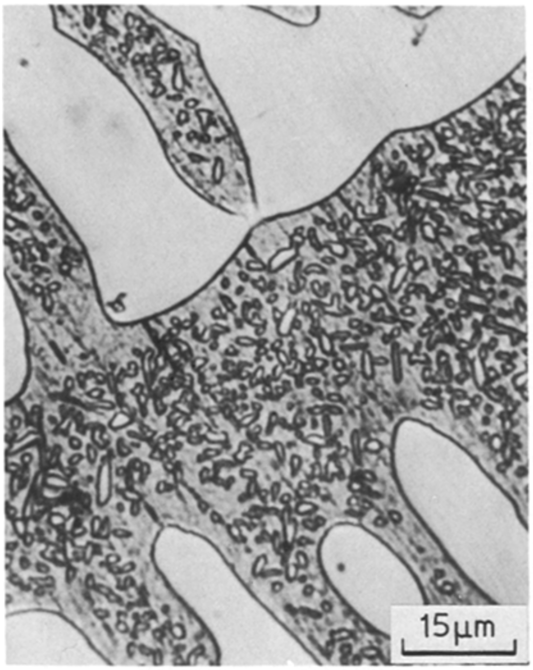


Figure 6 Alloy 1: Ni–28.75 at % Al–2.5 at % Ta; homogenized at 1260° C and then aged at 1000° C for 3 days and water quenched. γ'-phase precipitation within β-phase areas.

Figure 7 Alloy 1: Ni–28.75 at % Al–2.5 at % Ta; homogenized at 1260° C and then aged at 1000° C for 3 days and water quenched. "Tweed" sub-structure in β-phase.

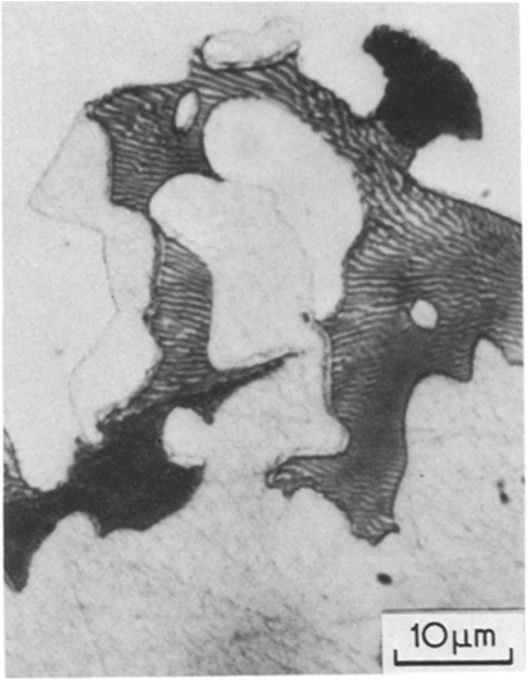


Figure 8 Alloy 4: Ni–20.0 at % Al–7.5 at % Hf; as-cast. Primary γ'-phase + eutectic of β + $(Ni, Al)_7Hf_2$.

an extensive solubility in the γ'-phase [23] and the lattice expansion was greater than that produced by tantalum in accordance with atomic size considerations. The β-phase was present as a constitute of eutectic regions (Figs. 8 and 9); the individual eutectic particles were too small for electron microprobe analysis but, as discussed below, the other eutectic constituent has been identified as an intermetallic compound. Both "lamellar" and "discontinuous" eutectic morphologies were observed (Fig. 9). Homogenization of alloy 5 for 4 days at a temperature of 990° C removed the eutectic regions.

The identification by X-ray diffraction of the structure of the phase co-existing with the β-phase in the eutectic was hindered by the relatively small proportions present in the alloys and the proximity of some of the X-ray reflections to certain β-phase and γ'-phase reflections. However, selected area electron diffraction data using both as-cast and annealed samples were successfully indexed as a hexagonal cell; Fig. 10 shows two patterns from a range of zone axes studied. Transmission electron microscopy of alloy 5 annealed for 4 days at 990° C showed fine striations within the phase particles (Fig. 11); diffraction streaking effects

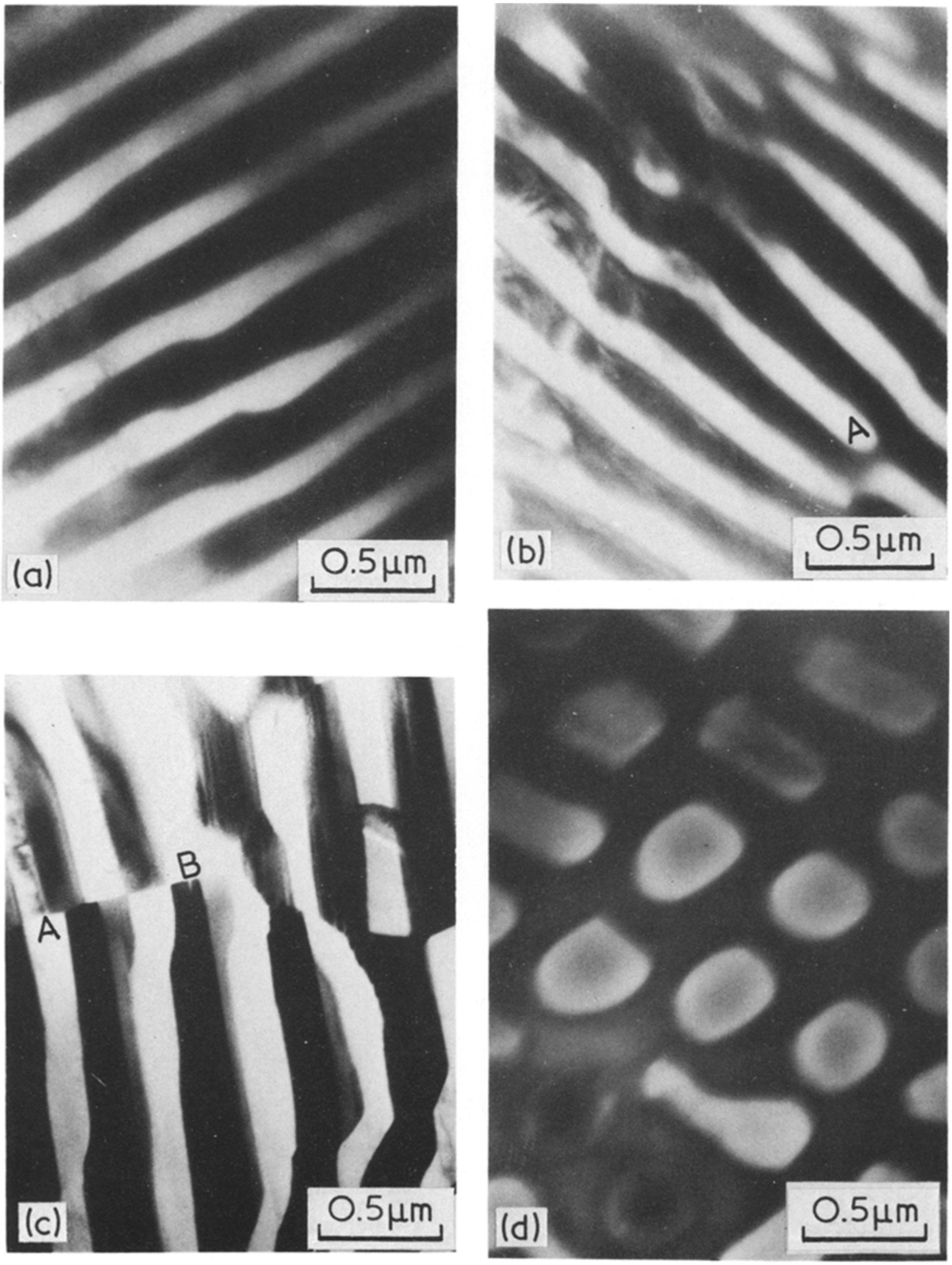


Figure 9 Alloy 4: Ni–20.0 at% Al–7.5 at% Hf; as-cast. Features of β + $(Ni, Al)_7Hf_2$ compound eutectic regions. (a) lamellar structure; (b and c) terminations of lamellae at A and B; (d) "discontinuous" eutectic.

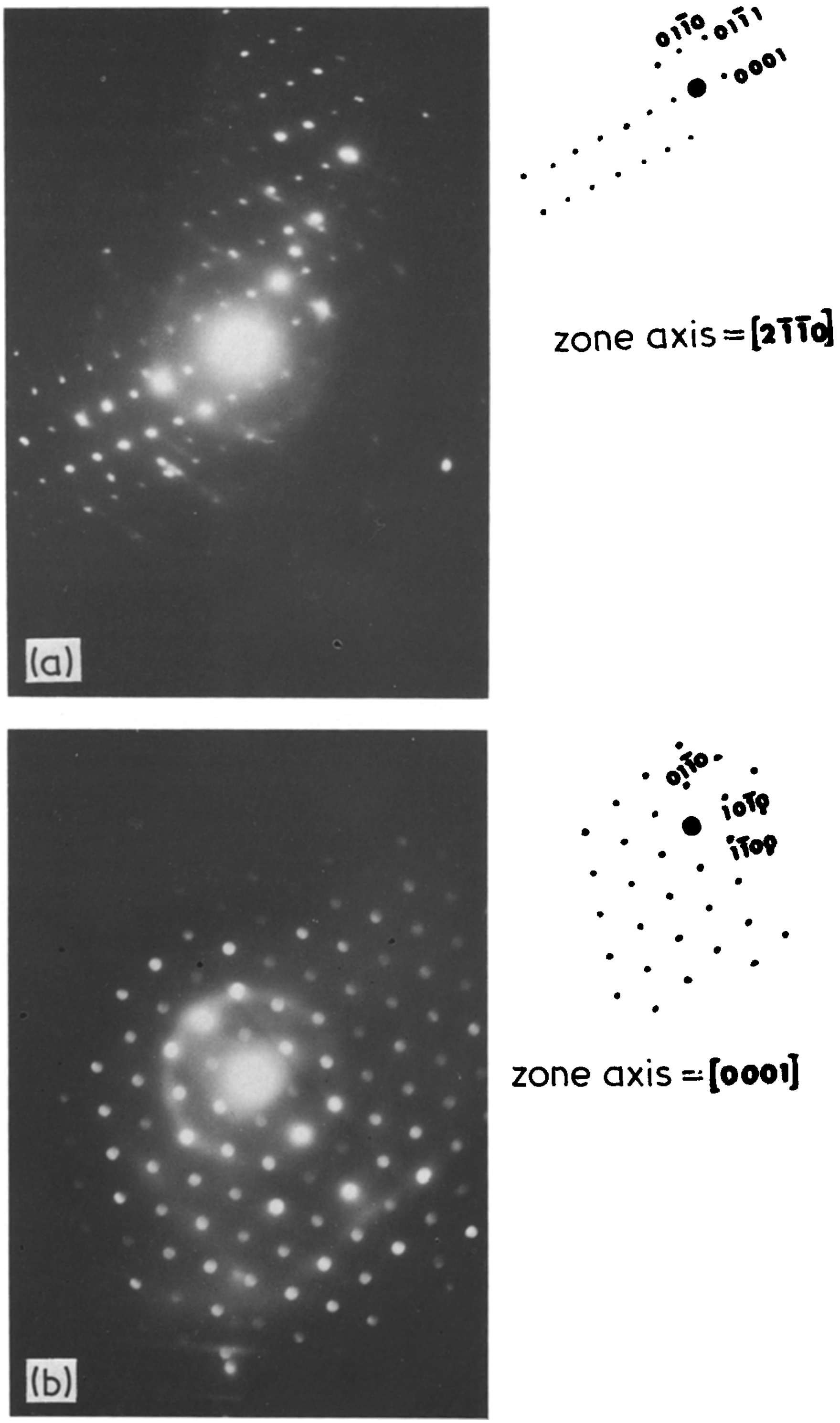


Figure 10 Ni–Al–Hf alloys. Selected area diffraction data from (Ni, Al)$_7$Hf$_2$ compound in eutectic regions. Indexed as a hexagonal structure (see Section 3.2); (0001) results from double diffraction.

Figure 11 Alloy 5: Ni–22.5 at % Al–5.0 at % Hf; annealed at 990° C for 4 days. Fine striations within a particle of (Ni, Al)$_7$Hf$_2$ representing faulting on the (0 0 0 1)-plane.

suggest that these features represent planar faults parallel to the basal plane.

Recent work by Nash [23] on the 1250° C isothermal section of the Ni–Al–Hf system has aided phase identification by means of electron microprobe and X-ray diffraction data for several alloys, including some with large proportions of the phase. The β-phase and γ'-phases were found to enter into equilibrium with a Ni–Hf intermetallic compound containing about 5 at % Al. Nash found that the X-ray data of the phase did not correspond to the structure of Ni$_3$Hf [24–26], but agreed well with the structure of Ni$_7$Hf$_2$: $a = 4.657$ Å; $b = 8.191$ Å; $c = 12.102$ Å; $\beta = 95.50°$ [27]. Ni$_7$Hf$_2$ is isotypic with Ni$_7$Zr$_2$ which has a pseudo-hexagonal atomic array [28], and a structure with a hexagonal translation group ($a \sim 4.6$ Å; $c \sim 5.9$ Å) has been reported in highly deformed Ni$_7$Zr$_2$ [27]. In the data obtained by Nash, the main diffraction lines of the monoclinic structure of the phase could also be indexed on the basis of a hexagonal cell ($a \sim 4.7$ Å; $c \sim 6.0$ Å) and these parameters agree well with the present diffraction data (Fig. 10). Thus, the evidence including electron microprobe data, indicates that the phase present, together with the β-phase, in the eutectic is (Ni, Al)$_7$Hf$_2$.

4. Summary and conclusions

(a) The structures of alloys containing Ni–28.75 at % Al–2.5 at % Ta; Ni–26.75 at % Al–2.5 at % Ta; Ni–20.0 at % Al–7.5 at % Ta consisted of $\gamma' + \beta$-phase (or marensitic β-phase). Martensite, formed by quenching β-phase from 1260° C, showed a "banded" morphology, whereas in the as-cast condition the transformed β-phase was acicular. The body-centred tetragonal martensite plates contained several types of fault including fine twins on {1 0 1} b c t.

(b) The as-cast structure of alloys containing Ni–20.0 at % Al–7.5 at % Hf and Ni–22.5 at % Al–5.0 at % Hf consisted of γ'-phase together with a eutectic of β-phase + (Ni, Al)$_7$Hf$_2$.

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