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Thermochemical processing with hydrogen of super-α_2 alloy

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Thermochemical processing (TCP) with hydrogen, including hydrogenation, intermediate heat treatment and dehydrogenation, of super-α_2, a type of Ti_3Al-based titanium aluminide alloy, was carried out in order to examine the microstructural variations in the alloy. It is shown that a number of microstructural changes, such as the amount, morphology and distribution of different phases in the alloy, can be brought about by TCP. Acicular or Widmanstatten α_2 was found to form in the retained B2 matrix under TCP with an intermediate heat treatment of furnace cooling from high temperature, instead of mainly equiaxed α_2 under the normal treatment. The precipitation in the microstructures for alloys undergoing TCP with the intermediate β-solution heat treatment followed by ageing while dehydrogenating was found to be more regular in morphology and homogeneous in distribution. Both the amount of primary α_2 and the size of the primary β grains in the microstructure could be controlled by suitable TCP. Some of the reasons leading to the microstructural variations caused by TCP are discussed.

1. Introduction

In recent years, considerable effort has been made to develop advanced titanium aluminide alloys based on Ti_3Al, due to their higher specific strength at elevated temperature and potential utilization as advanced aerospace materials to replace more conventional titanium alloys. However, low-temperature ductility in this type of alloy remains a major obstacle to their application, although large amounts of β-stabilizing elements, such as Nb, Mo and V, have been added to the alloys to give a considerable amount of deformable retained β phase in the microstructure. It has been shown by previous work that the microstructures of the Ti_3Al-based aluminide alloys can be varied by different heat treatments [1, 2], and that their mechanical properties are highly dependent on the microstructures of the alloys [3, 4], such as the amount of β or ordered β (B2), α_2 and O phases, as well as their morphologies and distributions. Therefore, improved mechanical properties of a Ti_3Al-based aluminide alloy may be obtained by modifying the microstructure of the alloy through suitable treatment.

Thermochemical processing (TCP) with hydrogen has been proved an effective method to modify the microstructure and enhance the properties of conventional titanium alloys [5], such as the well-known α + β alloy, Ti–6Al–4V [6–8]. It is known that hydrogen is a strong β-stabilizing element in titanium [9], and that it can easily be both charged into titanium alloys in large quantities and extracted out again by vacuum annealing at elevated temperature [5]. TCP with hydrogen of a titanium alloy is basically a series of processes including hydrogenation and intermediate heat treatment or hot-forming followed by dehydrogenation, either to modify the microstructure or enhance the hot-workability. The use of hydrogen as a temporary alloying element in the TCP of titanium alloys alters the α/β transformation behaviour and results in variations of the microstructures. The recent work of Chu and Thompson [10] showed that the microstructures of Ti–24Al–11Nb (at %), a type of Ti_3Al-based titanium aluminide alloy, had evidently been modified and also that the corresponding mechanical properties had been simultaneously improved. Thus it can be expected that TCP with hydrogen may be a prospective processing technique to improve the mechanical properties, especially the ductility, of Ti_3Al-based titanium aluminide alloys by microstructural modifications to improve the capacity for plastic deformation.

In the present investigation, TCP with hydrogen of super-α_2, another type of Ti_3Al-based titanium aluminide alloy, was carried out in order to examine the microstructural variations, such as the changes in amount, morphology and distribution of different phases in the alloy caused by the processing, to provide a preliminary basis for the optimization of this novel processing technique for the Ti_3Al-based titanium aluminide alloys.

2. Experimental procedure

The material used for this investigation had a nominal composition of Ti–25Al–10Nb–3V–1Mo (at %) and

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TABLE I Procedures for intermediate heat treatment and dehydrogenation

Designation	Heat treatment and dehydrogenation
FC	1100 °C/30 min/furnace cooling + 800 °C/120 min in vacuum
A18	1100 °C/30 min/air cooling + 800 °C/120 min in vacuum
A19	1100 °C/30 min/air cooling + 900 °C/60 min in vacuum
A28	1140 °C/30 min/air cooling + 800 °C/120 min in vacuum
A29	1140 °C/30 min/air cooling + 900 °C/60 min in vacuum

was received in the form of 10 mm diameter rolled bars. The bars were machined into specimens 9 mm in diameter and 40 mm in length and the surfaces were carefully cleaned. The specimens were then hydrogenated at 800 °C for 30 min in a pure gaseous hydrogen environment at pressures of 0.05 and 0.1 MPa, referred to in the text as 0.05 H and 0.1 H, respectively. For comparison, the unhydrogenated specimens, which underwent the same subsequent heat treatments as those for the hydrogenated specimens, are designated NH. The hydrogen content in the hydrogenated specimens could be estimated, from the relationship between hydrogen activity and hydrogen content at 800 °C for selected titanium alloys given by others [11], as approximately 8 at % for 0.05 H and 11 at % for 0.1 H. After hydrogenation, different intermediate heat treatments followed by dehydrogenation in a vacuum of 10^{-3} Pa were carried out for all the specimens, including both hydrogenated and unhydrogenated ones. The procedures for these intermediate heat treatments followed by dehydrogenation are given in Table I.

Specimens for microstructural examination after TCP, as well as for comparative treatments, were prepared as longitudinal sections by standard metallographic procedures and etched with Kroll's reagent. All the microstructural observations were carried out in a Hitachi S-530 scanning electron microscope (SEM). The X-ray energy-dispersive spectrometer on a Philips 501 SEM was also used to identify the phases in some typical microstructures.

3. Results and discussion

From Table I it can be seen that TCP with hydrogen of super-α_2 alloy in this investigation has been concentrated on two aspects. One was to apply a complete intermediate heat treatment to the alloy between hydrogenation and dehydrogenation, in order to study the influence of hydrogen on the microstructure during continuous cooling at a slow rate from the α_2–β transus temperature. The other was concentrated on studying microstructural variations of the alloy during ageing while dehydrogenating (ageing in vacuum), after it had been β-solution treated. Since the α_2–β transus temperature for the super-α_2 alloy has been reported to be in the range of 1065–1093 °C [12], higher temperatures (1100 and 1140 °C) were chosen for the β-solution treatment temperature and a single β-phase microstructure at these temperatures was expected. Representative SEM micrographs showing the microstructural variations of super-α_2 alloy subjected to TCP, compared with the normal treatment (unhydrogenated), are shown in Figs 1 to 6.

The different phases expected in the microstructures of Ti_3Al-based super-α_2 alloys have been documented in recent years. It has been shown [2, 4, 13, 14] that the b.c.c. β phase, or B2 (an ordered β phase that forms below a certain transformation temperature), may decompose to several different phases, including secondary α_2 (ordered h.c.p.), O phase with an ordered orthorhombic structure, or ω phase (h.c.p.), either on continuous cooling from the β region or during high-temperature ageing following a β-solution treatment. Since hydrogen is a strong β-stabilizing element in titanium alloys, both the addition of hydrogen and the following release of it should have a strong influence, thermodynamically or dynamically, on both the stability of β (or B2) and the decomposition of β (or B2) to α_2 or O phases during heat treatment. Consequently, the microstructures of super-α_2 alloys subjected to TCP with hydrogen should vary in comparison with those undergoing normal treatment.

It is shown in Fig. 1a that the microstructure of a specimen heat-treated at 1100 °C for 30 min followed by furnace cooling (FC) exhibits a homogeneous distribution of mainly equiaxed α_2 (dark blocky area) within a retained B2 matrix (light area). Some evidence of dark-etching acicular α_2 phase is also observable within the lighter B2 matrix regions. However, in the specimens hydrogenated and followed by the same FC heat treatment, different microstructures were obtained. Acicular or Widmanstatten precipitation of α_2 is more apparent in the B2 matrix along with a smaller amount of undissolved primary α_2 for the specimen hydrogenated at lower pressure (Fig. 1b). A microstructure of Widmanstatten α_2 plates separated by retained B2 phases within moderately sized colonies, with little evidence of primary α_2 and a much larger size of primary β grains, is obtained at higher hydrogen pressure (Fig. 1c and d). It can be seen from Fig. 1d that smaller precipitates also exist within the retained B2 matrix for the specimen hydrogenated at higher pressure (0.1 H). These precipitates are most probably the decomposition products of the subsequent dehydrogenation, for the hydrogen-stabilized retained B2 phase should gradually lose its stability and begin to decompose also during the dehydrogenation treatment.

Generally, the concentration of Nb, a β-stabilizing element in titanium alloys, should be different in the separate phases in the microstructure of Ti_3Al–Nb titanium aluminide alloys [4]. It should be relatively higher in the retained B2 matrix and lower in the Ti_3Al-based α_2 phases (both primary and secondary) than the average in the alloy, and be at an intermediate level in the Ti_2AlNb-based O phases. This can provide a simple method to identify the different phases in the microstructure. Table II lists the relative Nb content of the different phases (identified accord-

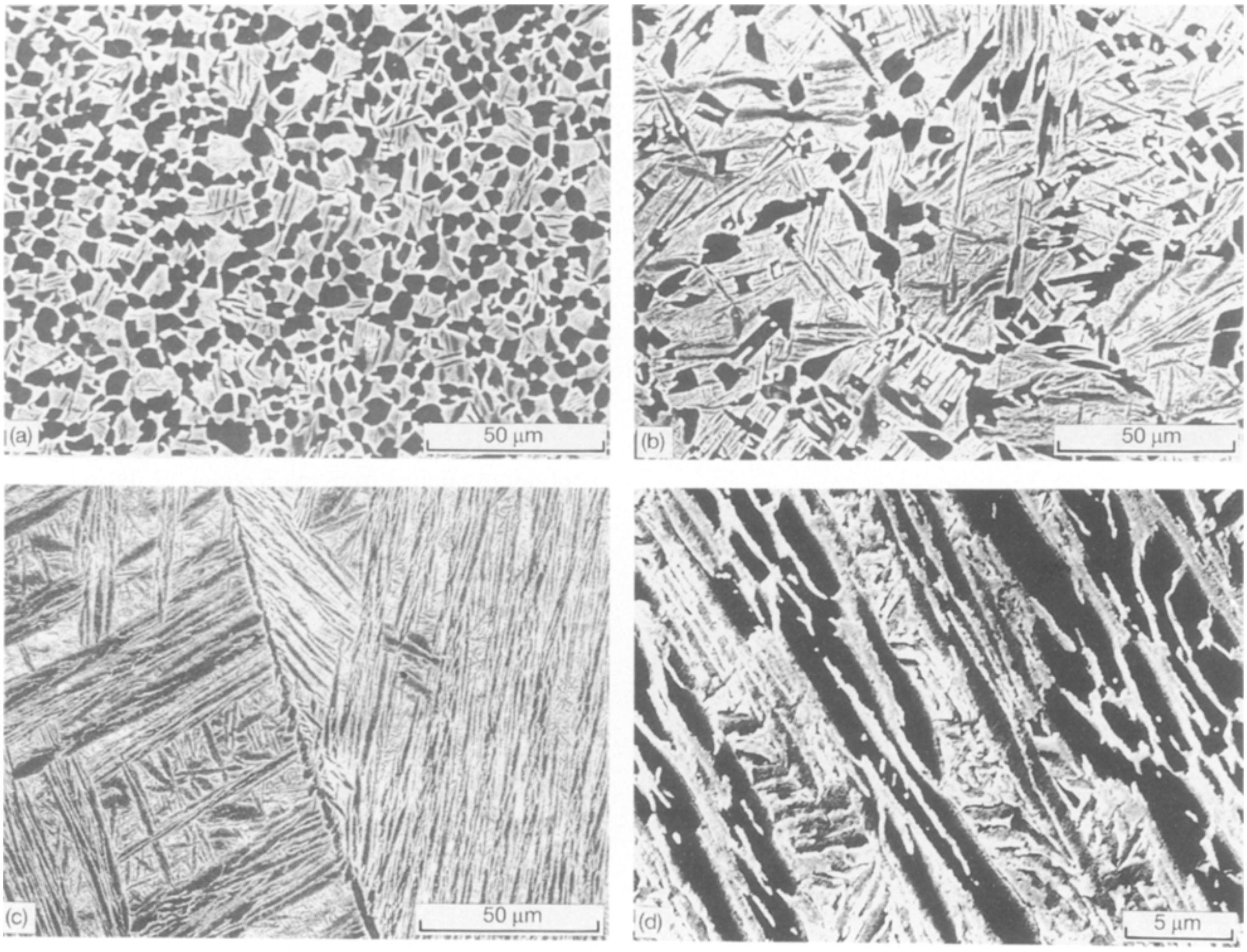

Figure 1 Microstructural variations caused by TCP with furnace cooling: (a) NH; (b) 0.05 H; (c, d) 0.1 H.

TABLE II Identification of different phases in the microstructures

Treatment and characterization		Relative Nb content over average	Phase
FC(NH)	Dark blocky area	0.658	α_2
	Light matrix	1.285	B2
FC(0.1 H)	Dark thin area	0.611	α_2
	Decomposition products in light matrix	0.958	O or α_2 + O
A29(NH)	Dark blocky area	0.728	Primary α_2
	Grain-boundary phase	0.927	α_2 + O
	Dark precipitates	1.053	α_2 + O
	Light area	1.218	B2
A29(0.1 H)	Dark precipitates	0.890	α_2 + O
	Light area	1.013	B2

ingly) in the microstructures using the X-ray energy-dispersive spectrometer on the SEM. The same counting time was used and the data were obtained as a relative atomic ratio of Nb content to the average content that can be easily used for comparison. From the relative Nb contents shown in Table II it can be confirmed that the decomposition products during dehydrogenation should be either O phase with an ordered orthorhombic structure (and intermediate level of Nb), or a mixture of secondary α_2 and O phase, which is consistent with the time–temperature–transformation (TTT) curve for the super-α_2 alloy aged at the same temperature, 800 °C, given by Peters and Bassi [2].

The obvious differences in the microstructures shown in Fig. 1 can be explained by the fact that the addition of hydrogen to the super-α_2 alloy can effectively lower the α_2–β transus temperature [15] and thus affect the α_2–β transformation behaviour, owing to the β-stabilizing influence of hydrogen. Because of this effect of hydrogen, a homogeneous β-phase microstructure or one containing little primary α_2 would be achieved in the hydrogenated specimens with a consequent increase in the β grain size as observed. It appears that some undissolved primary α_2 remains in the microstructures, despite the fact that the 1100 °C solution treatment temperature chosen is above the reported α_2–β transus temperature for super-α_2 alloy [12]. At 1100 °C there was little or no undissolved α_2 left, depending on hydrogen pressure, in the hydrogenated microstructure, which clearly indicates that the α_2–β transus temperature has been lowered significantly by the addition of hydrogen. Correspondingly, the primary β grain size for the specimens hydrogenated at lower pressure (0.05 H) had reached about 0.4 mm and for those hydrogenated at higher pressure (0.1 H) had reached about 1.0 mm. The grain size of the unhydrogenated specimen was of the order of 20 μm.

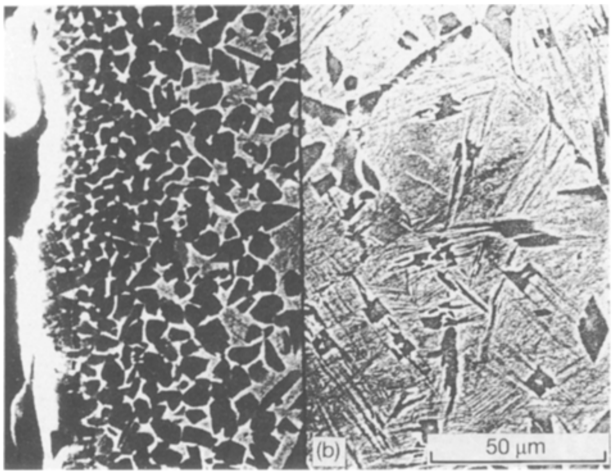

Figure 2 Microstructure close to the edge of the specimen treated by TCP with 0.1 H (FC): (a) at the edge, (b) near the edge.

The microstructure close to the edge of a specimen that was subjected to TCP with the 0.1 H(FC) treatment is shown in Fig. 2 and is different from that shown in Fig. 1c and d, these being more typical of the microstructure throughout the bulk of the specimen. At the edge of the specimen very fine equiaxed α_2 phase was found, which became coarser away from the edge (Fig. 2a). Eventually, acicular α_2 appeared (Fig. 2b) and the microstructure became similar to Fig. 1b. This happened in a range of 0.5 to 1 mm from the edge. This difference in microstructure within one specimen is considered to be due to the effect of a variation in hydrogen concentration along the radial direction of the specimen, i.e. hydrogen loss occurred near the surface during the intermediate heat treatment, although the total hydrogen content in the specimen might not be much affected.

The effects of TCP for the intermediate β-solution heat treatments of 1100 and 1140 °C, followed by ageing while dehydrogenating at high temperatures, on the final microstructures of the super-α_2 alloy are compared with the more customary heat treatment routes in Figs 3 to 6. Again, it can be seen that for the

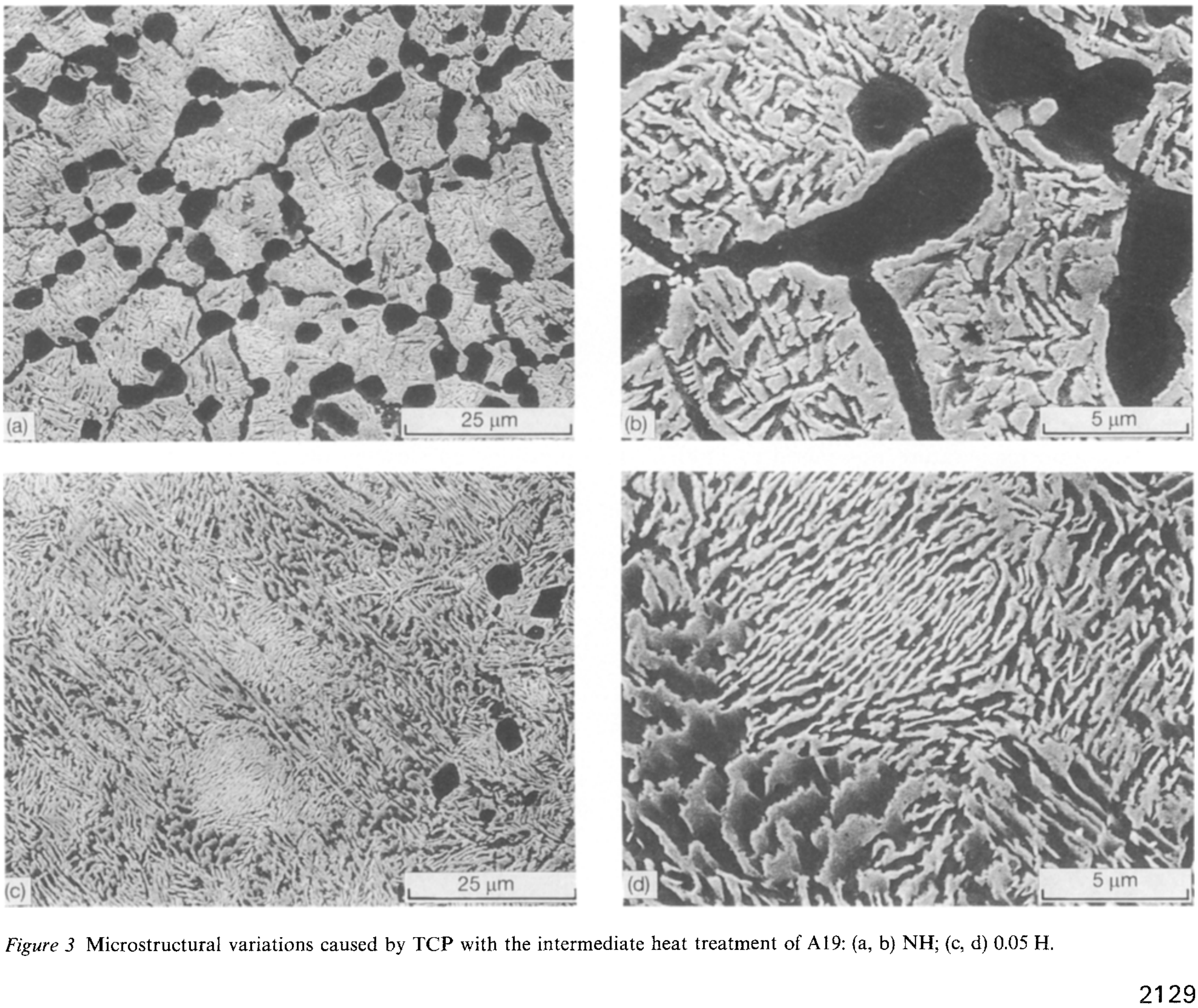

Figure 3 Microstructural variations caused by TCP with the intermediate heat treatment of A19: (a, b) NH; (c, d) 0.05 H.

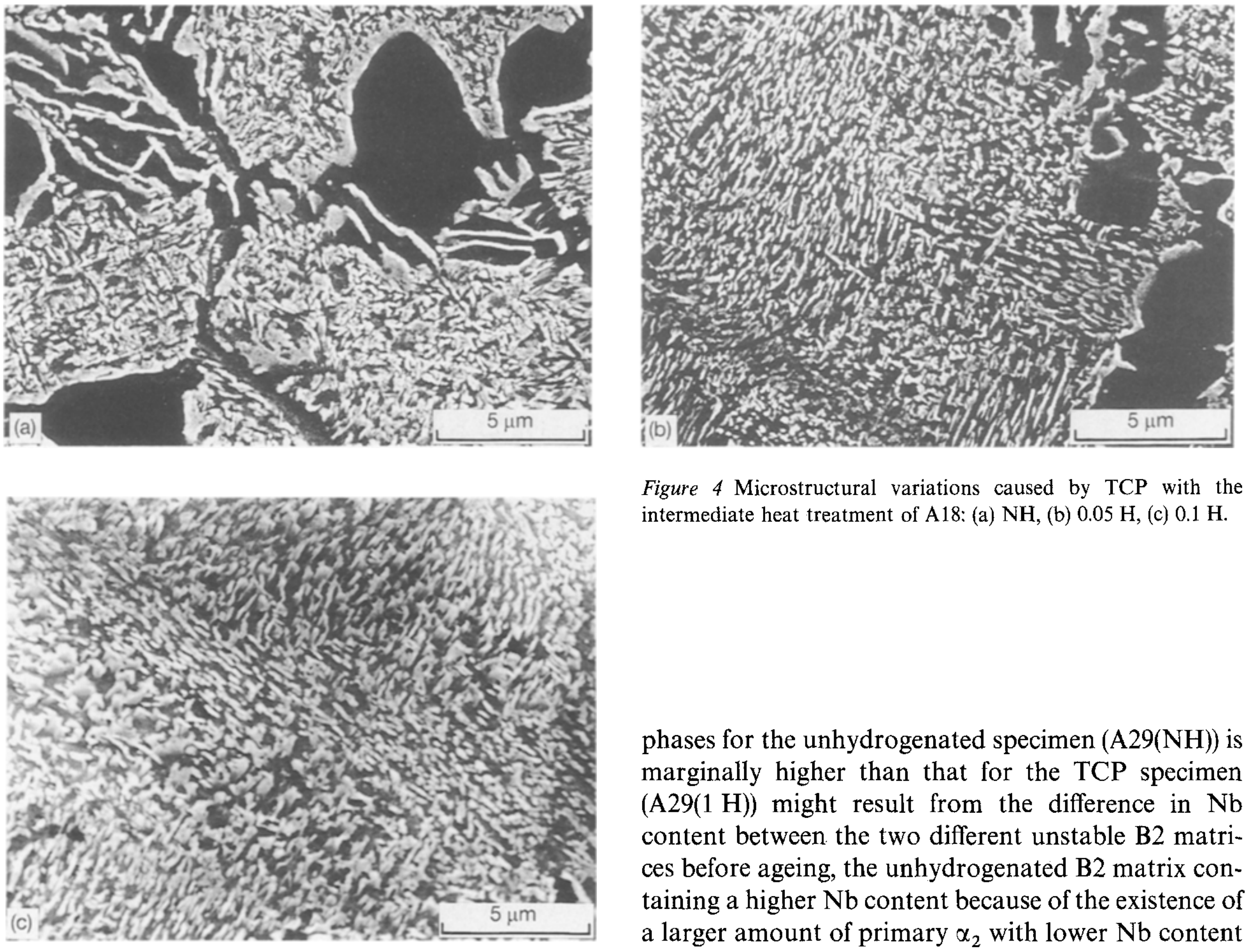

Figure 4 Microstructural variations caused by TCP with the intermediate heat treatment of A18: (a) NH, (b) 0.05 H, (c) 0.1 H.

specimens β-soloution treated at 1100 °C (Figs 3 and 4), a large amount of undissolved primary α_2 (dark blocky features) has been left in the microstructure of the unhydrogenated specimens (Figs 3a and 4a), although the solution temperature was higher than the reported α_2–β transus temperature for super-α_2 alloy [12]. Once again, however, less primary α_2 can be found in the microstructures of specimens treated to give a lower hydrogen content (0.05 H), as shown in Figs 3c and 4b, and no primary α_2 exists for those with the higher hydrogen content (0.1 H), which is once more consistent with lowering of the α_2–β transus temperature by the addition of hydrogen. Even after the β-solution temperature was raised to 1140 °C, a certain amount of undissolved primary α_2 persisted in the microstructure for the unhydrogenated specimens, accompanied by slight growth of the primary β grain size, as shown in Figs 5a, 5b and 6a, but this time no primary α_2 has been left in either of the hydrogenated specimens (Fig. 5c to f). Therefore, both the amount of primary α_2 and the size of the primary β grains in the microstructure of super-α_2 alloy can be expected to be controlled by suitable TCP with hydrogen.

From the measurement of relative Nb concentration of the phases in the microstructure given in Table II, the decomposition products of the unstable B2 matrix can be identified as mainly O phase, or a mixture of secondary α_2 and O phases, according to estimations from the TTT curves given previously [2]. The reason why the Nb content in both O and B2 phases for the unhydrogenated specimen (A29(NH)) is marginally higher than that for the TCP specimen (A29(1 H)) might result from the difference in Nb content between the two different unstable B2 matrices before ageing, the unhydrogenated B2 matrix containing a higher Nb content because of the existence of a larger amount of primary α_2 with lower Nb content in the microstructure.

Another significant difference between the microstructures under TCP and normal treatments, which can be seen from Figs 3 to 6, is in both the morphology and the distribution of the secondary precipitation (α_2 + O) after the ageing treatment. For specimens undergoing the normal ageing treatment, this precipitation (dark phases in white areas) is irregular in morphology and randomly distributed, and the higher the ageing temperature, the coarser the precipitates, as shown in Figs 3b, 4a, 5b and 6a. The existence of undissolved primary α_2 contributes to the inhomogeneity, as for example in the case of the cellular region around the primary α_2 shown in Fig. 4a and the regions denuded of α_2 around the primary α_2 shown in Figs 3b and 5b. There is not much difference in precipitation between the microstructures β-solution treated at 1100 and 1140 °C, except for the higher density of precipitation for the latter owing to the lower amount of primary α_2 in the microstructure. In comparison, precipitation in the microstructures for specimens under TCP appears more regular and homogeneous in both morphology and distribution. The precipitation and matrix are well mixed and it can be difficult from the micrographs to differentiate between the phases (e.g. Figs 3d, 4c, 6b and c). Several orientations of the precipitates are apparent, and in some areas similarly oriented precipitates are grouped to give the appearance of packets of acicular plates within the primary β grains (e.g. Figs 3c, 3d, 4b, 4c, 5c, 6b, and 6c). It has been previously reported that relatively small subgrains could be formed in the microstructure of super-α_2 alloy air-cooled from the β

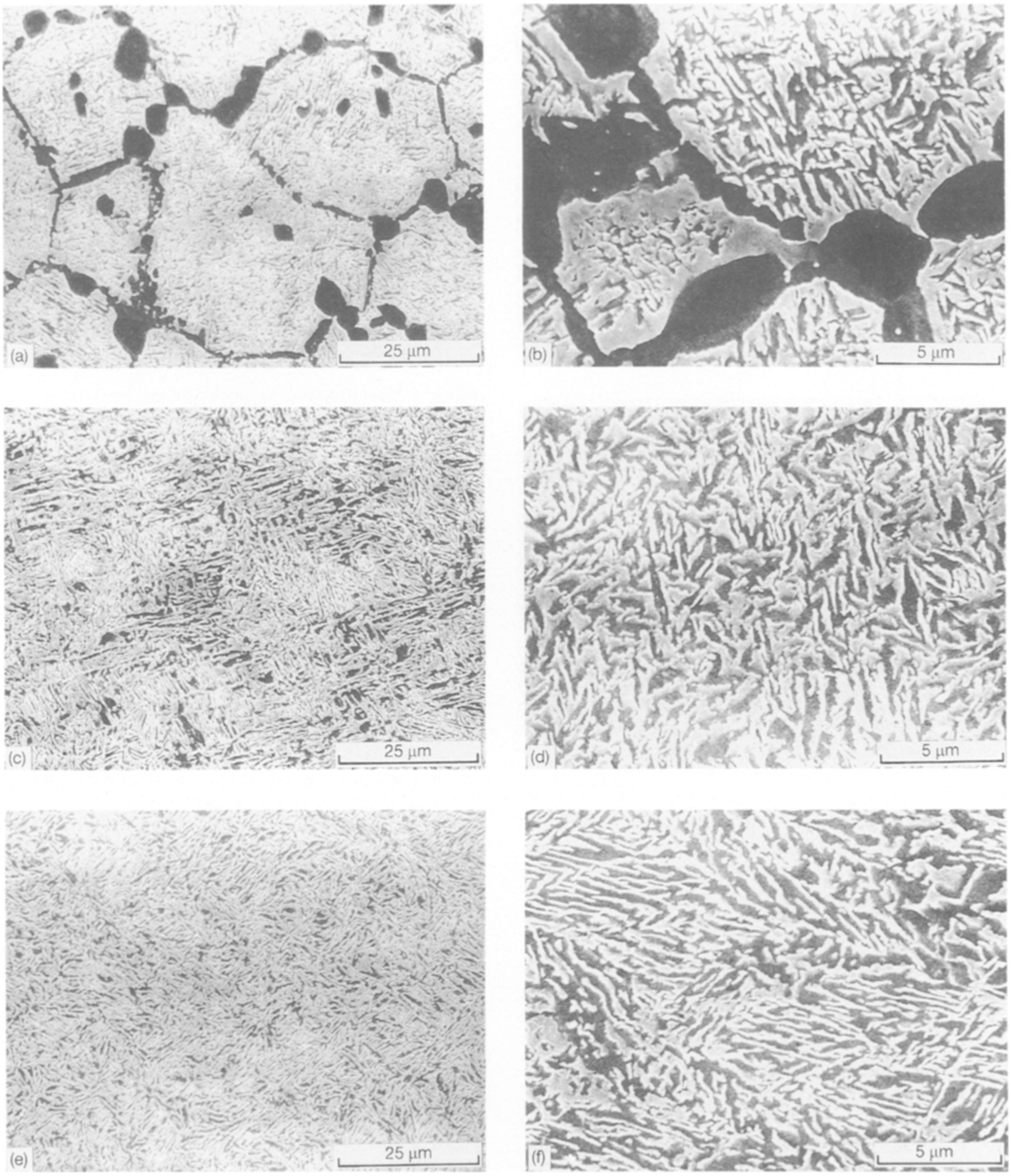

Figure 5 Microstructural variations caused by TCP with the intermediate heat treatment of A29; (a, b) NH; (c, d) 0.05 dH; (e, f) 0.1 H.

region [16], and this may be related to the formation of these small areas with similar orientations of precipitates observed in the present study.

4. Conclusions

Variations in the microstructure of super-α_2, a type of Ti_3Al-based titanium aluminide alloy, have been found after subjecting the alloy to thermochemical processing with hydrogen, including hydrogenation, intermediate heat treatment and dehydrogenation. These variations include the amount, morphology and distribution of different phases in the microstructure. In the microstructure resulting from an intermediate heat treatment of slower furnace-cooling from a β-solution treatment temperature of 1100 °C, the α_2 in the B2 matrix can vary from mainly equiaxed under normal treatment to acicular or Widmanstatten under TCP. The amount of undissolved primary α_2, the morphology and distribution of the secondary precipitates, and the size of the primary β grains can also be varied according to the conditions of TCP. These changes can be related to the effect of hydrogen on the α_2–β transus temperature and corresponding transformation behaviour. Finally, it should be pointed out that this investigation addressed only a limited range

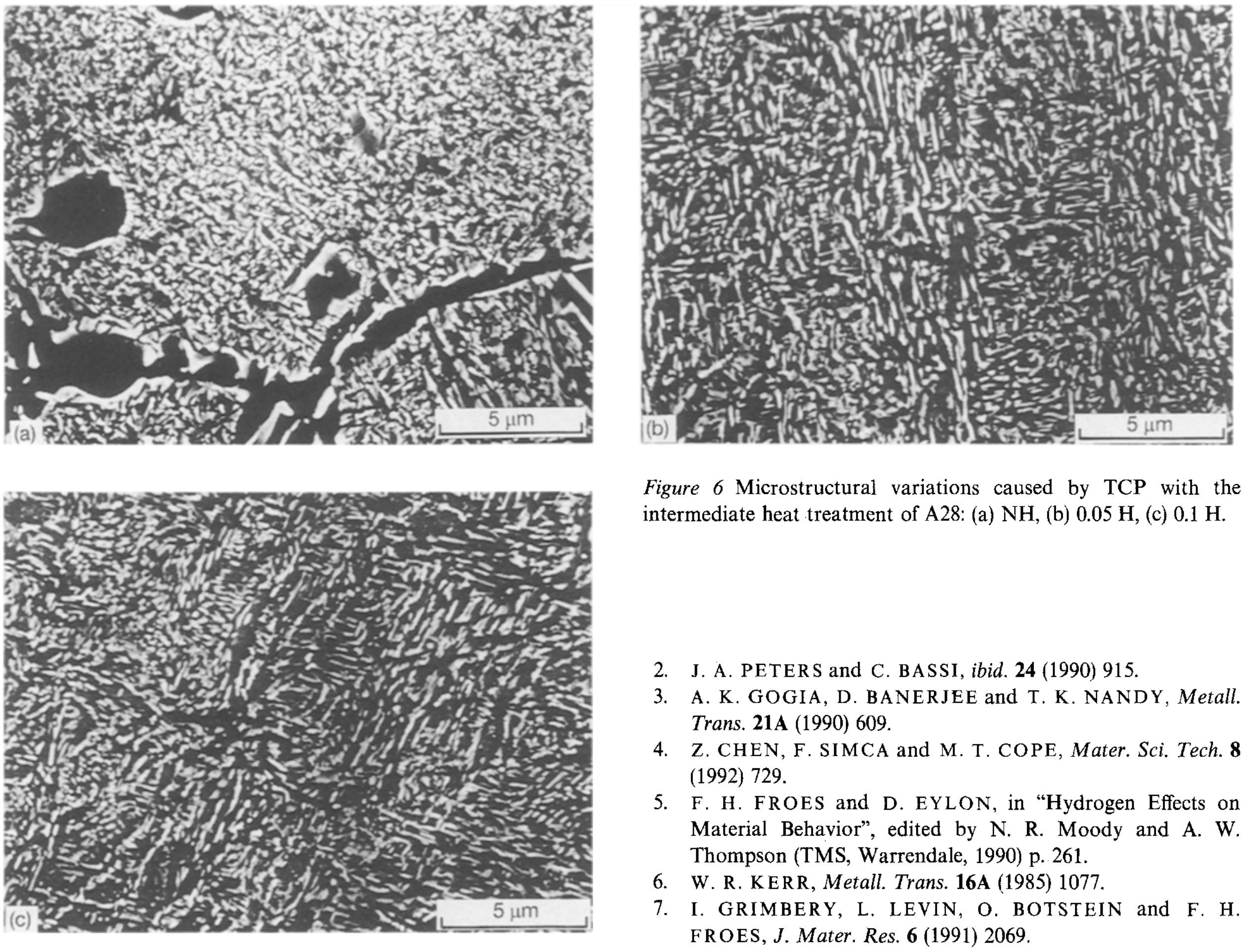

Figure 6 Microstructural variations caused by TCP with the intermediate heat treatment of A28: (a) NH, (b) 0.05 H, (c) 0.1 H.

of TCP conditions and more dramatic or different microstructural variations might be expected if a wider range of heat-treatment schedules and hydrogen pressures was employed.

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