AN ANALYTICAL ELECTRON MICROSCOPY STUDY
OF THE RECENTLY REPORTED "Ti$_2$Al PHASE" IN γ-TiAl ALLOYS

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Introduction

In a recent series of papers, Loiseau and coworkers (1-3) reported that a low volume fraction of Ti$_2$Al precipitates can be produced in TiAl alloys for compositions in the range 50-56Al (all compositions in at.pct unless otherwise stated). The structure of these precipitates was identified as being hexagonal with lattice parameters a ≈ 0.30 nm and c ≈ 1.40 nm, which are related to those for the hexagonal α-Ti phase as follows: a ≈ a$_{α-Ti}$, c ≈ 3c$_{α-Ti}$. This is not the first time a Ti$_2$Al phase has been proposed in the literature. For example, Ence and Margolin (4) reported a Ti$_2$Al phase to be stable between 25 and 40Al, though the lattice parameters proposed were much different than the above, i.e. a = 0.5775 nm, c = 0.4638 nm. However, this latter identification failed to be substantiated in subsequent investigations (5,6) of the binary Ti-Al system. In fact, in these latter studies the phase Ti$_2$Al was not present in any alloy containing up to 57Al which includes the composition range recently studied by Loiseau, et al. (1-3). In view of the lack of agreement between the previous studies (5,6) and those of the recent past (1-3), it is necessary to review closely the analysis used in the identification of the phase Ti$_2$Al (1-3). When this is done, three disturbing aspects emerge. Firstly, it is somewhat surprising that only a small volume fraction of Ti$_2$Al phase was observed, even after extended annealing treatments. Secondly, the phase was present only in alloys with very large Al contents (i.e. > 50%) and never in the presence of the Ti$_3$Al (α$_2$) phase; this indeed is surprising in view of the expected stoichiometry of the Ti$_2$Al compound which involves 33% Al. Finally, the composition of the reported Ti$_2$Al phase was based on high resolution images rather than a more direct technique such as energy dispersive x-ray spectroscopy (EDXS). The present study was initiated because of both these disturbing features and also the potential alloy development possibilities which would be obvious were the stable Ti$_2$Al phase field to exist in actuality. The effort has concentrated on the identification and characterization of this so-called Ti$_2$Al phase using a variety of analytical electron microscopy (AEM) techniques: EDXS, convergent beam electron diffraction (CBED), and electron energy loss spectroscopy (EELS).

Experimental Procedure

Binary Ti-Al alloys containing 33, 45 and 52Al were prepared by non-consumable electrode arc melting in a purified (pumped, purged, and Ti gettered) partial pressure of Ar gas, using vacuum melt consolidated EL-60 grade Ti sponge (99.95 wt. percent pure) and 99.999 percent pure Al as the starting materials. Homogeneity was insured by melting each button five times, with the buttons inverted between melts. After electropolishing, the alloys were loosely wrapped in Ta foil and sealed inside previously evacuated (to a vacuum of ~2x10^{-4}Pa) fused silica tubes, containing a partial atmosphere of the exchange gas. Subsequently, the 33, 45, and 52Al ingots were given equilibration heat treatments of 1100°C (14 days), 1000°C (11 days) and 1000°C (11 days), respectively, and subsequently ice-water quenched. The interstitial contents of the homogenized alloy buttons were determined by chemical analyses from which it was found that the dilute alloy (33 Al) contained 1170 ppm (by wt.) oxygen and 2080 ppm (by wt.) nitrogen whereas the more concentrated alloys (45 and 52 Al) contained 120 ppm oxygen and 40 ppm nitrogen. The high interstitial contents in the former alloy have been attributed to a leak in the encapsulation tube during the heat treatment. Thin slices of these ingots were cut with a slow speed diamond saw and thin foils suitable for analytical transmission electron microscopy (AEM) were jet polished in a solution of (by volume) 60% methanol, 35% butanol and

6% perchloric acid (70% concentrated) at a temperature of approximately -50°C. Analysis was performed in transmission electron microscopes operating at nominal accelerating voltages of either 120 or 300 kV.

Results and Discussion

Typical micrographs from the Ti-33Al and Ti-45Al alloys are shown in Fig. 1(a) and (b), respectively. In the former alloy the microstructure consists only of α_2 (Ti₃Al) while both α_2 and γ (TiAl) are present in the Ti-45Al sample. These results are consistent with the phase diagrams proposed in previous studies (5,6) and with the experimental observations of Loiseau et al. (1-3). However, micrographs from the Ti-52Al alloy (e.g. Fig. 2(a)) indicated that, even though the matrix phase is γ, there is indeed a small volume fraction of a second phase which appeared similar to the "Ti₂Al" phase reported in the previous references (1-3).

(a)   (b)
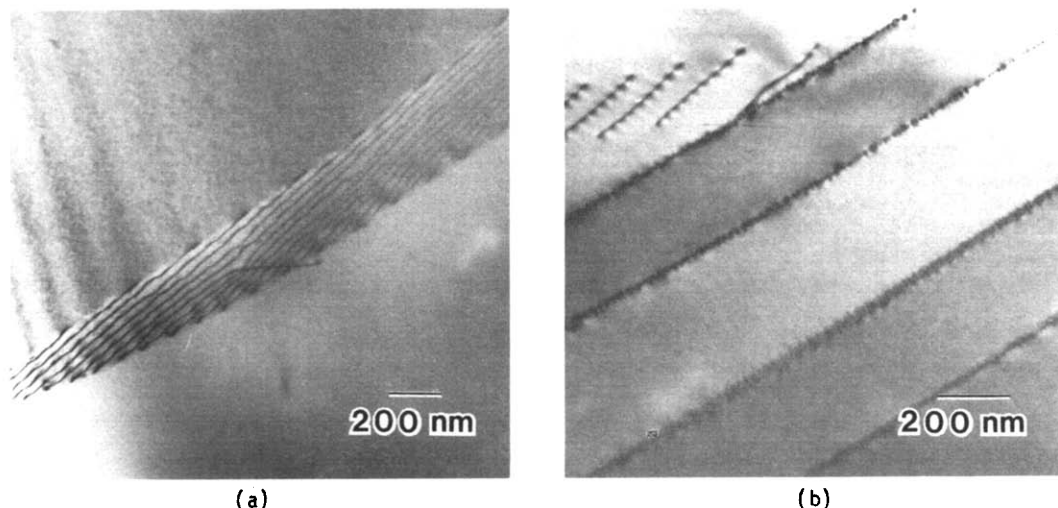
Fig. 1   Transmission electron micrographs showing typical areas of the two most dilute alloys;
        a) Ti-33Al; b) Ti-45Al.

In order to establish that the second phase detected in the Ti-52Al alloy is identical to that reported to be Ti₂Al in Refs. 1-3, conventional and analytical electron microscopy (CTEM and AEM) have been utilized. Firstly, a bright field image (Fig. 2(a)) indicates that the shape of the phase of interest at the orientation chosen is lenticular with a substantial aspect ratio, in agreement with Fig. 9 in Ref. 1. Secondly, from selected area diffraction patterns (SADPs) obtained from the second phase particle (Fig. 2(b,c)), it may be deduced that this phase is hexagonal (a ≈ 0.304 nm and c ≈ 1.389 nm) with an orientation relationship given by $(0001)_{ppt}$ ∥ $(111)_{TiAl}$ and $[11\overline{2}0]_{ppt}$ ∥ $[1\overline{1}0]_{TiAl}$: again, consistent with that proposed by the previous authors (1-3). Thirdly, an analysis of the particles using EDXS reveals the presence of only Ti and Al with an approximate Ti to Al composition ratio of 2:1, consistent with the composition of Ti₂Al. Thus, it can be concluded that the second phase of interest in the present work appears to be identical to that identified as being Ti₂Al in the previous studies (1-3).

To gain further insight into the nature of the reported Ti₂Al phase, a more complete structure determination (i.e. point and space groups) has been performed using CBED (7,8). Various zone axes have been examined and the convergent beam patterns (CBPs) used for the point group analysis are shown in Fig. 3. From the [0001] CBP shown in Fig. 3(a,b), it can be seen that the projection diffraction (Fig. 3(a)) and whole pattern symmetries (Fig. 3(b)) are both 6mm. Using Table 2 in Buxton et al. (7), it can be deduced that the diffraction group for this zone axis is either 6mm or 6mml$_R$. Similarly, for the [11$\overline{2}$0] CBP (Fig. 3(c)) the whole pattern symmetry is 2mm; the reflections in the zero order Laue layer are spaced extremely closely, such that it is not possible to obtain a useful pattern from which to determine the projection diffraction symmetry. However, for a whole pattern symmetry of 2mm,
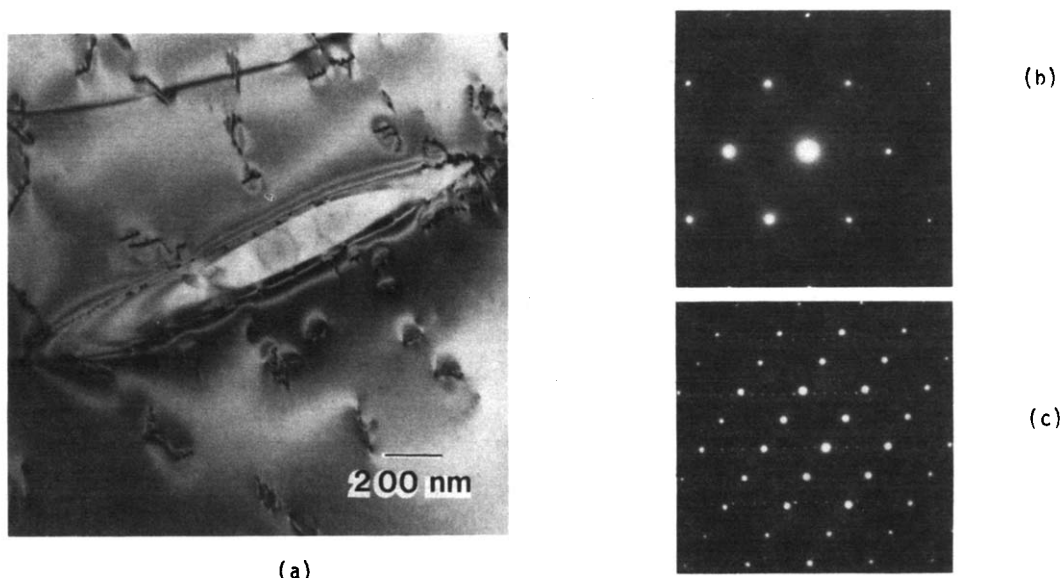
Fig. 2 a) Transmission electron micrograph of a second phase particle found in the alloy Ti-52Al; b) SAD pattern obtained from the second phase shown in (a), with the electron beam parallel to [0001] in the particle (see text); (c) SAD pattern obtained from the particle and matrix (γ-TiAl), with the electron beam parallel to [1$\bar{1}$0]$_γ$, and [11$\bar{2}$0] particle.

the corresponding diffraction group is either 2mm or 2mm1$_R$ (again obtained by referring to Table 2, reference (7)). A combination of the symmetry information from these two zone axes and utilization of Table 3 in Buxton, et al. may be used to show that the only consistent point group for this phase is 6/mmm (Table 2, reference (7)).

Frequently, it is possible to determine the space group of an unknown phase by analyzing the dynamic absences which are formed in the CBP's (8-10). Such absences, indicating the presence of glide planes and/or two-fold screw axes, are observed in kinematically forbidden reflections where intensity has been generated by dynamical (double) diffraction (11). Cursory examination of the CBP's in Fig. 3 does not allow a clear determination of whether any such absences are present at these orientations. However, close examination of the first order Laue zone (FOLZ) in the [0001] CPB (Fig. 3a) indicates that absences may be present in the 33$\bar{6}$1 type reflections: however, there is some uncertainty in this conclusion due to the presence of other lines of deficient intensity which intersect in these reflections. Thus, in order to establish whether these are indeed dynamic absences, thereby indicating the presence of {10$\bar{1}$0} glide planes (11), the sample was tilted away from the [0001] zone axis about a 10$\bar{1}$0 systematic row to determine whether other CBP's might contain such absences. After tilting approximately 18° to the [1$\bar{2}$12] zone, the necessary CBP was obtained shown in Fig. 4a. The dynamic absence in the 1$\bar{2}$13 reflection is revealed more clearly as a black cross when the specimen is tilted to the Bragg condition (Fig. 4b), and this confirms the presence of the {10$\bar{1}$0} glide plane. It should be mentioned that the black cross in this reflection is also consistent with the presence of a [1$\bar{2}$13] two-fold screw axis, but that such a symmetry element is not allowed in any crystal structure (12). Upon inclusion of this symmetry information and use of the tables in Ref. 12, it was determined that the only consistent space group is hexagonal P6$_3$/mmc. Obviously, this determination does not preclude the Ti$_2$Al possibility proposed in the previous studies (1-3). Thus, further clarification was obtained by a more complete determination of the composition of this phase as described below.

As mentioned above, EDXS has been used to show that of the elements subject to detection using a conventional detector (i.e. with a Be window), only Ti and Al were detected, and that
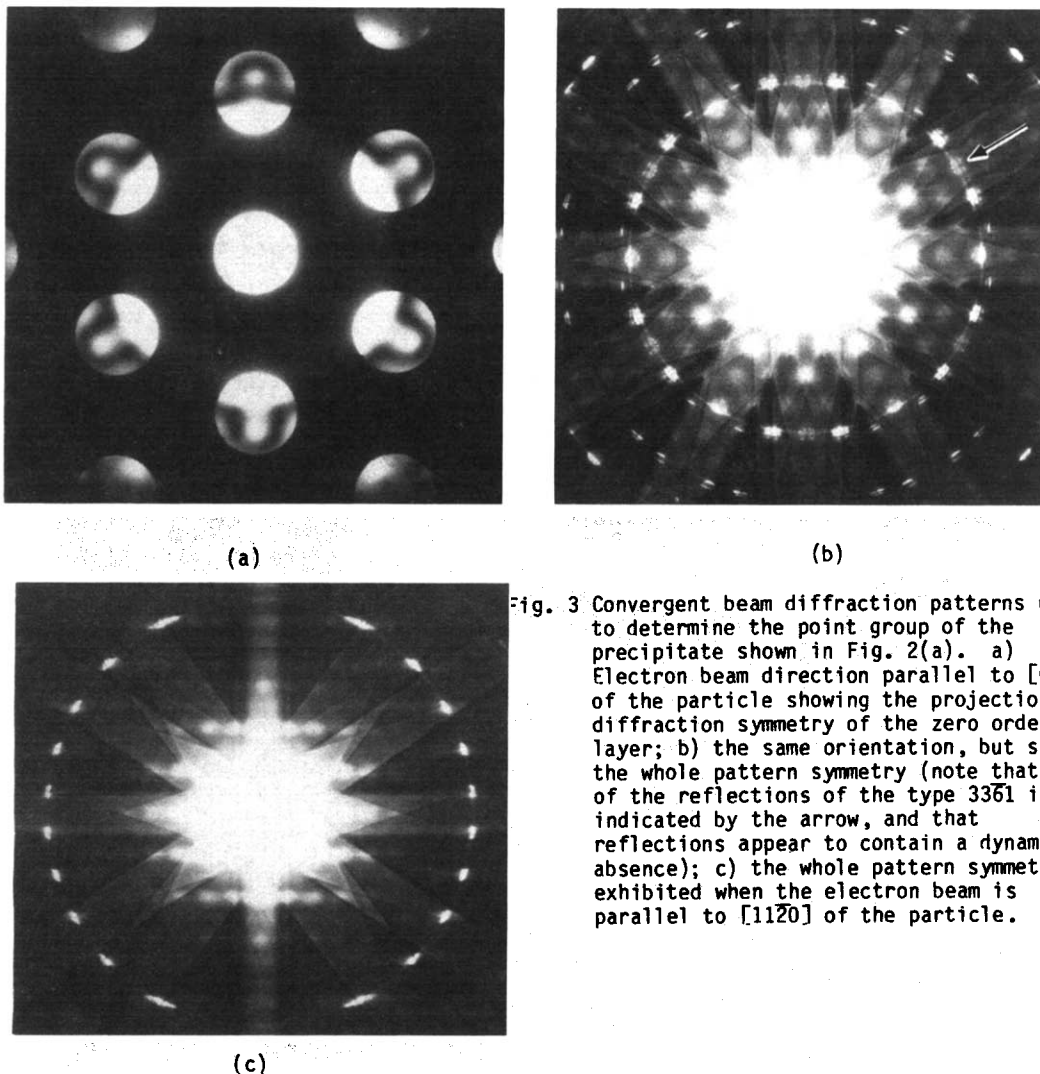
(a)

(b)

(c)

Fig. 3 Convergent beam diffraction patterns used to determine the point group of the precipitate shown in Fig. 2(a). a) Electron beam direction parallel to [0001] of the particle showing the projection diffraction symmetry of the zero order Laue layer; b) the same orientation, but showing the whole pattern symmetry (note that one of the reflections of the type 33$\bar{6}$1 is indicated by the arrow, and that reflections appear to contain a dynamic absence); c) the whole pattern symmetry exhibited when the electron beam is parallel to [11$\bar{2}$0] of the particle.

the atomic ratio of these elements was estimated to be ~ 2:1. To determine whether other elements with Z < 11 are also present in the phase of interest, EELS spectra have been recorded from the phase when situated near the edge of perforations in thin foils: spectra corresponding to the probe being placed on the matrix and precipitate are shown in Fig. 5. The spectrum from the matrix contains only the expected Ti L$_{2,3}$ absorption edge, whereas the precipitate spectrum exhibits an additional edge corresponding to that of N. It appears then that the phase of interest is a nitride. This is confirmed by noting that a nitride of composition described by Ti$_2$AlN, with the same space group as that, and essentially similar lattice parameter to those, determined in the present work, has been reported previously (13). In fact, Jeitschko, et al. (13) also characterized a carbide, Ti$_2$AlC, having the same structure and parameters as those deduced here, but since no significant carbon edge is observed in Fig. 5, the possibility that the phase of interest may also be a carbide is discounted. Consequently, it was concluded that the phase of interest in this and the previous studies was not a new binary phase having the Ti$_2$Al stoichiometry, but rather the nitride Ti$_2$AlN which forms presumably as a result of contamination of the alloy by N during preparation. Only a small concentration of N is required for the precipitation of this phase;
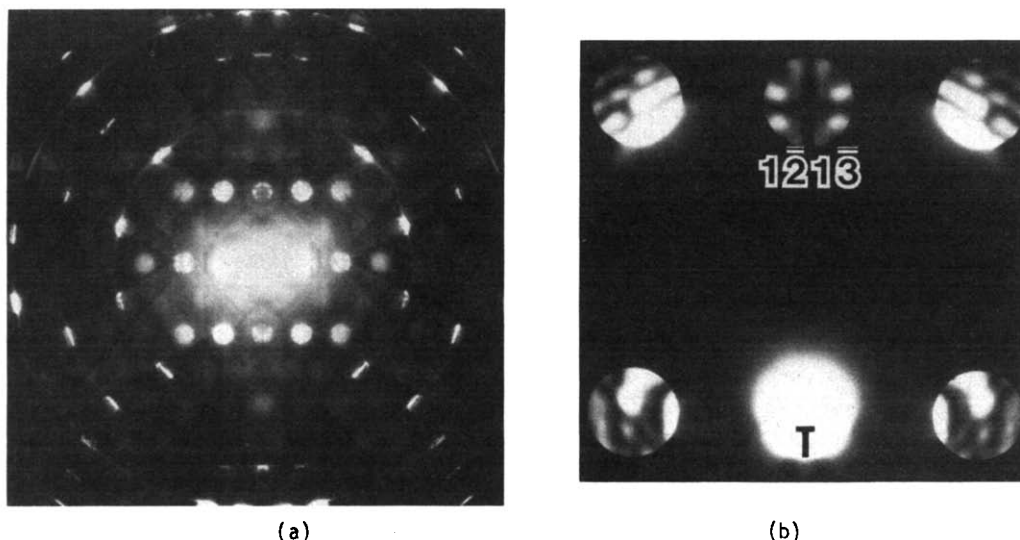
(a)   (b)

Fig. 4   Convergent beam diffraction patterns obtained with the electron beam parallel to
[1$\bar{2}$12] of the particle shown in Fig. 2(a); a) the pattern which results when the beam
is accurately parallel to [1$\bar{2}$12]; b) the pattern obtained when the particle is
oriented such that the reflection 1$\bar{2}$1$\bar{3}$ is at the Bragg condition. Note the presence
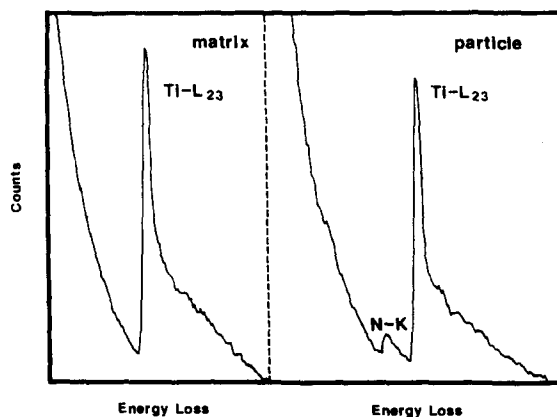of the black cross in the disk corresponding to this reflection.

Fig. 5   Electron energy loss spectra from areas such as that shown in Fig. 2(a) obtained when
the probe is focussed either on the matrix or the particle, as indicated.

the Ti-52Al alloy studied in the present investigation contained only 40 ppm (by wt.) N.
Thus, despite the various methods of preparation used in the previous studies (1-3), it is not
surprising that the Ti$_2$AlN phase was observed in all of their alloys.

Finally, it is useful to attempt to account for the fact that the Ti$_2$AlN phase was
observed only in alloys with Al concentrations greater than approximately 50% (i.e. in the
single phase γ-TiAl field on the binary diagram). Since a ternary Ti-Al-N phase diagram does
not exist (to our knowledge), it is only possible to speculate on the probable reason for this
result. Thus, it is noted that in our alloy Ti-33Al which contains a large amount of N (2080
ppm (by wt.)), the microstructure was found to consist of only single phase α$_2$. This
observation implies that essentially all the N is in solution, and so the solubility of N in

the α_2-Ti$_3$Al phase appears to be much greater than that in γ-TiAl. When the Al concentration is increased but still less than 50% such that at low temperatures the alloy exists in the two-phase α_2+γ phase field (on the binary Ti-Al phase diagram), presumably the N partitions to the α_2 phase and so remains in solution. This is consistent with the observation made on the Ti-45Al alloy in the present study. However, at greater Al contents where no α_2 is present, the TiAl phase quickly becomes supersaturated with respect to N and Ti$_2$AlN precipitates during heat treatments at elevated temperatures ($\sim$ 1000°C). Obviously, further work is required to substantiate these deductions as well as to study the possibility of using these precipitates in a beneficial fashion (as indicated in the creep study by Loiseau and Lasalmonie (3)).

Summary

A variety of experimental techniques has been utilized to establish that the phase reported previously to be a new stable Ti$_2$Al phase (1-3) is instead Ti$_2$AlN. The space group of Ti$_2$AlN has been determined to be P6$_3$/mmc with lattice parameters, a = 0.304 nm and c = 1.369 nm, in agreement with the results of Jeitschko, et al. (13). Also, since this phase is observed only in alloys which do not contain α_2-Ti$_3$Al, it was suggested that the solubility of N in α_2 must be rather large, while that in the γ(TiAl) phase is low. Finally, in light of the improved creep properties of γ alloys containing Ti$_2$AlN precipitates (3), it is suggested that an increase in the volume fraction of this phase, by increasing the N and/or C contents, in these alloys might be used to enhance the mechanical properties of this normally brittle compound.

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