β Phase Precipitation and α/β Interface Phase in Commercially Pure Titanium

By A. Lasalmonie* and S. Naka*

Iron rich β precipitates were observed in single crystals of unalloyed T40 titanium. It is inferred that the solubility of Iron in α is smaller than 600 ppm. An *fcc* phase, with parameters $a=0.432$ nm and $c=0.467$ nm was identified at the α - β interfaces; it was identical to the interface phase reported in several α - β alloys. We show that, in T40, this phase is, most likely, a titanium hydride due to the preparation of the thin foils.

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I. Introduction

For a long time the maximum value of the solubility of Fe in titanium was thought to be around 2000 ppm at 873 K (600°C)⁽¹⁾⁽²⁾ (873 K is the eutectoid temperature between Ti and TiFe). It was recently shown that the maximum solubility occurred at 1063 K (790°C) and was 660 ppm⁽³⁾.

In a commercially pure titanium such as T40, where the amount of Fe can be as high as 2500 ppm, a precipitation of metastable β or of TiFe may be expected.

The work reported here on T40 titanium provides direct evidence of β precipitation; we shall also discuss the nature of the *fcc* layer observed at the β - α interfaces. This phase which has been reported in a number of α or α - β alloys^{(4)~(7)} was never observed previously in unalloyed titanium.

II. Experimental

The T40 titanium provided by Ugines has the following composition: Ti-800 ppm Fe-1500 ppm oxygen.

The specimens were cut from rods which had been used to grow single crystals by a float zone electron beam method.

The heat treatment of the samples can be roughly described as a rapid cooling from the melting point to 1073 K (rate ≈ 1 K/s) followed by a slower cooling at 0.2 K/s

The foils for electron microscopy were prepared by conventional electropolishing techniques.

III. Results

1. β phase precipitation

The optical micrograph of Photo. 1 was taken in a single α grain; etching reveals the subgrain boundaries and long plate-shaped precipitates which lie often along subgrain boundaries.

The volume fraction of these precipitates is in the range 0.1 % to 0.3 %.

Photo. 1 Optical micrograph showing subgrain boundaries and long precipitates.

* ONERA-Châtillon 92320-France.

An analysis in the electron microprobe gave an amount of iron of 18% in the precipitates. From these results we can calculate the amount of Fe in the α phase: it is between 200 ppm and 600 ppm, which is coherent with the work of Matyka *et al.*⁽³⁾

Electron diffraction patterns proved that the precipitates were the metastable iron rich β phase in the Burgers orientation. ω precipitates were present in all the β particles as shown on the dark field image of Photo. 2.

2. The crystallography of the interfacial phase

In freshly prepared foils, an interfacial layer was observed at the β - α boundaries. By analogy with papers of Chenu *et al.*⁽⁶⁾⁽⁷⁾ we shall call it L phase. An example is given on Photo. 3(a): the β precipitate has the shape of a T-square with faces A parallel to $(0001)\alpha$ and faces B parallel to $(10\bar{1}0)\alpha$. Along the interface the L layer has a thickness varying from 50 nm to 80 nm.

The diffraction pattern of the area is given on Photo. 3(b). The spots from the $(1\bar{2}10)\alpha$ zone and $(1\bar{1}1)\beta$ zone are nearly superposed.

All the extra spots originate from the interfacial layer, which is nearly *fcc* with parameter $a=0.467$ nm. The complete indexation is shown on Fig. 1. Three families of the L phase are found:

Photo. 2 Dark field image of ω in a β precipitate.

Photo. 3(a) β precipitate with $(0001)\alpha$ and $(10\bar{1}0)\alpha$ interfaces.
(b) Diffraction pattern: $(1\bar{2}10)\alpha$ zone/ $(1\bar{1}1)\beta$ zone.

Fig. 1 Indexation of the diffraction pattern.

Family 1 such that: $\left. \begin{array}{l} (0001)\alpha // (110)\beta // (111)_L \\ \langle 1\bar{2}10 \rangle_\alpha // \langle 1\bar{1}1 \rangle_\beta // \langle 1\bar{1}0 \rangle_L \end{array} \right\}$
I

Family 2 is a twin of 1 as respect to (111), it gives rise to the same orientation relationship.

Family 3 such that: $\left. \begin{array}{l} (0001)\alpha // (110)\beta // (001)_L \\ \langle 1\bar{2}10 \rangle_\alpha // \langle 1\bar{1}1 \rangle_\beta // \langle 1\bar{1}0 \rangle_L \end{array} \right\}$
II

Actually, the splitting of the (220) spots of family 3 and the spreading of the (111)_L spots around their ideal positions are better explained by a face-centered tetragonal structure with $c/a=1.08$. The parameters of L are then $a=0.432$ nm, $c=0.467$ nm.

Dark field images (Photo. 4(a)(b)) show that families 1 and 2 precipitate on interface A (parallel to $(0001)\alpha$) where the interface layer is finely twinned; Family 3 has only a few twins due to the tetragonality of L, and precipitates on interface B (parallel to $(10\bar{1}0)\alpha$) (Photo. 4(c)).

These observations evince a close correlation between the type of orientation relationship and the plane of interface.

In fact relationship I, where the close-packed planes of the three phases remain parallel is readily understood:

The transition from α Ti to an *fcc* structure

can be realized by introducing stacking faults in the $(0001)\alpha$ planes (from α Ti is thus built an *fcc* structure with parameter $a=a_\alpha\sqrt{2}=0.417$ nm; the *fcc* to β transformation is then given by the Bain transition.

This relationship I provides a bad fit of the lattices at the interfaces: in the case of interface A (parallel to $(0001)\alpha$) for instance, the $(112)\beta$ planes going normal to the interface are parallel to the $(10\bar{1}0)\alpha$ planes, which have very different spacings (Fig. 1) and no planes of L are parallel to them.

This gives rise to large strains in the interfacial layer and explains the fine twinning of the L layer along A (Photo. 4(a)(b)).

On the contrary, relationship II may allow a better fit in the case of a $(10\bar{1}0)\alpha$ interface since the three sets of planes $(0002)\alpha$, $(002)_L$ and $(110)\beta$ normal to the interface have almost the same spacing.

The interfacial phase described above has the same morphology, crystallography and orientation relationship with α and β as that described in other alloys such as TA6V⁽⁵⁾ or Ti 685⁽⁶⁾⁽⁷⁾.

In the case of alloy 685 a tetragonal distortion with $c/a>1$ of the *fcc* layer was also reported⁽⁶⁾. In all these alloys the interfacial layer was assumed to be an intermediate phase, probably enriched in β stabilizing elements. The following experiments show that it is not the case in T40.

3. The nature of the interfacial phase

In T40, the interfacial layer is, most likely, an artifact due to electropolishing: when the thin foils were heated in the electron microscope, the interfacial layer disappeared rapidly at a temperature as low as 323 K (50°C); the precipitate of Photo. 3 is shown on Photo. 5(a) after heating 300 s (5 min) at 373 K (100°C), the associated diffraction pattern evince the disappearance of L (Photo. 5(b)). The L phase did not reappear on cooling. We also noticed that no L phase could be found in thin foils kept several months at room temperature. In our case we think that the interfacial layer is a titanium hydride. TiH_2 has indeed a fluorite *fcc* structure with $a=0.445$ nm, which may transform to *fcc* at low temperature⁽⁸⁾

Photo. 4 Dark field images of the interface layer.
(a) Family 1, (b) Family 2, (c) Family 3

Photo. 5(a) Same precipitate as on Fig. 3 after 300s (5 min) at 373K (100°C).
(b) Associated diffraction pattern (compare to Photo. 3(b)).

or when the hydrogen concentration decreases⁽⁹⁾.

The puzzling fact is that titanium hydride has $c/a < 1$ whereas we found $c/a > 1$; the observed phase could be a metastable hydride TiH similar to the metastable hydride ZrH ($c/a = 1.08$) which has been observed in zir-

conium instead of the normal ZrH_2 ⁽¹⁰⁾⁽¹¹⁾.

In other specimens of T40 we could obtain platelets of hydride inside the α grains by changing the electropolishing conditions; these platelets had the same *fcc* structure as L with $c/a \approx 1.08$.

The possibility of a hydrogen stabilized in-

terface phase had been proposed previously by Hall *et al.*⁽¹²⁾; in our case, the low temperature at which L vanishes shows that it is not formed in the bulk specimen but, most likely, during the polishing, due to a concentration of hydrogen at the β - α interface.

Although it is identical in structure and morphology, this does not mean that the interfacial phase described in the other alloys is also a hydride; previous works in TA6V⁽⁴⁾ and Ti 685⁽¹³⁾ showed, indeed, that the L layer did not vanish during heating up to high temperatures. Our observations emphasize, however, the care, which must be taken in the study of this interfacial phase in Ti alloys; it might be suitable to avoid any electropolishing artefact to prepare some foils by an ion-thinning technique.

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REFERENCES

- (1) D. H. Polonis and J. G. Parr: Trans AIME, 200, (1954), 1148.
- (2) L. P. Luznikov, W. M. Novikova and A. P. Mareev: Metalloved i Term, Obrabotka Metal, 2 (1963), 13.
- (3) J. Matyka, F. Faudot and J. Bigot: Scripta Met., 13 (1979), 645.
- (4) C. G. Rhodes and J. C. Williams: Met. Trans A, 6A (1975), 1670.
- (5) C. G. Rhodes and N. E. Paton: Met. Trans A, 10A, (1979), 209.
- (6) F. Chenu, C. Servant, T. Manoubi and P. Lacombe: C. R. Ac. Sc. Paris t. 288, Serie C, p. 521.
- (7) F. Chenu, C. Servant and P. Lacombe: Scripta Met., 13 (1979), 951.
- (8) J. P. Blackledge and C. G. Libowitz: *In Metal Hydrides*, Ed. by W. Mueller. Academic Press (1968), p. 336.
- (9) V. V. Sofina, Z. M. Azarkh and N. N. Orlova: Kristallografiya, 3(5) (1958), 539.
- (10) S. S. Sidhu, Le Roy Heaton, F. P. Campos and D. D. Zaubers: Advances in Chem. Series, Am. Chem. Soc., No. 39 (1963).
- (11) J. S. Bradbrook, G. W. Lorimer and N. Ridley: J. Nucl. Mat., 42 (1972), 172.
- (12) J. W. Hall and C. Hammond: Metal. Science, No. 7 (1978), 339.
- (13) C. Servant: unpublished results.