PHASE TRANSFORMATIONS IN A Ti-1.6 a/o N ALLOY

D. Sundararaman, V. Seetharaman and V. S. Raghunathan

Metallurgy Programme, Reactor Research Centre
Walpakkam-603102, India

Abstract

The martensitic transformation and the subsequent precipitation of Ti$_2$N were investigated in a Ti-1.6 a/o N alloy. On quenching, the alloy transforms completely to martensite consisting of several colonies of parallel crystals. While many of the adjacent martensite crystals were found to be twin related, some of them contained {1011}$\alpha$ type internal twins. On ageing, this martensite transforms to a mixture of $\alpha$ and Ti$_2$N. The orientation relationship between the $\alpha$ and the Ti$_2$N phases has been identified as

$$(10\overline{7}0)_\alpha \parallel (01\overline{1})\text{Ti}_2\text{N}$$

$$[12\overline{1}\overline{0}]_\alpha \parallel [01\overline{1}]\text{Ti}_2\text{N}$$

Introduction

It is very well documented that interstitial solutes like C, N and O exert profound influence on the mechanical properties and corrosion behaviour of titanium and zirconium base alloys. Among these, nitrogen is the most effective stabiliser of the $\alpha$ phase in titanium and also imparts maximum strength to the $\alpha$ phase at low temperatures. For example, addition of one atom percent of C, N or O leads to an increase in the tensile strength of titanium at room temperature by 64, 69 or 38 MPa respectively [1]. While several detailed investigations have been carried out on the phase transformations occurring in Ti-O and Ti-C systems, very few studies have been conducted on Ti-N alloys [2,3]. This paper reports some results obtained on the martensitic transformation and the subsequent precipitation reaction occurring in a Ti-1.6 a/o N alloy.

The phase diagram for the Ti-N system is shown in Fig. 1. The $\gamma$ phase corresponds to a composition Ti$_4$N and occurs over a very narrow range of compositions. It has a tetragonal (anti C4 type) structure with lattice parameters, $a=4.9414$ Å; $c=3.0375$ Å[4]. The $\delta$ phase corresponding to a TiN stoichiometry is a NaCl type compound with the lattice parameter, $a = 4.240$ Å.

Experimental Procedure

Iodide grade titanium foils of about 25 μm thickness were nitrided in an "ion-nitriding" apparatus described in detail elsewhere[5]. After evacuating the reaction chamber to a pressure of about 10$^{-6}$ torr, purified nitrogen gas was admitted
and the system pressure was maintained continuously in the range 1 to 5 torr. Pieces of titanium sponge maintained at 500°C were used as a getter to remove any trace of oxygen present in the nitrogen stream. Nitriding was carried out at 800°C and the temperature control of the sample was achieved by adjusting the ion current and the gas pressure. Typical values of the cathode voltage and the ion current used were 800V and 30mA respectively. The nitrogen concentration was estimated by the weight change technique.

Nitrided samples were homogenised at 1300°C in a vacuum better than 10^{-5} torr and then quenched. Subsequently some of the samples were aged at 200 and 400°C for different durations. Thin foils for electron microscopy were prepared by chemical polishing in a solution containing 33% HF, 50% HNO₃ and the rest water at 0°C. Since the total time required for polishing was less than five minutes, the hydrogen pick up as a result of polishing was expected to be very low. These foils were examined in a Philips EM400 transmission electron microscope at 120 KV.

Results

1. Quenched Microstructures

On quenching from the B phase the alloy transforms completely to the hcp \( \alpha \) phase by a martensitic mode. Fig.2 illustrates the typical acicular microstructure consisting of lenticular plates of martensite. No evidence for the occurrence of either retained B, the fcc martensite or the orthorhombic martensite was found in this work. Transmission electron microscopic examination showed that the martensite colonies, formed as a result of quenching, contained several plates stacked almost parallel to each other. Some of these were found to be internally twinned (Fig.3 (a) and (b)). Diffraction analysis showed that these twins were all strictly parallel to \( \{10T1\} \alpha \) planes. At the same time it was noticed that many of the adjacent martensite plates were also twin related; the twinning plane was identified as \( \{10T1\} \alpha \). The pair of bright and dark field micrographs shown in Fig.4(a) and (b) provides an example for this observation.

It was found that the quenching rates achieved in this work were not sufficient to retain the \( \alpha \) phase completely in the supersaturated solid solution. Evidences for the very early stages of decomposition were seen within many martensite plates. Fig.5(a) represents a region which had presumably undergone a continuous transformation leading to the formation of a fine and highly coherent product microstructure. The striations were found to be parallel to \( (1121) \alpha \) and \( (1103) \alpha \). The selected area diffraction pattern taken from this region contained many additional spots which could be indexed as a slightly distorted (001) zone of \( Ti_3N \). The dark field micrograph shown in Fig.5(b) provides another example for the microstructure obtained after initial decomposition of the \( \alpha \) lattice. The diffraction pattern taken from this region (Fig.5(c) and (d)) reveals two
variants of the (011) reciprocal lattice sections of the Ti$_2$N phase superimposed on the matrix reflections. On analysis of such patterns the orientation relation between Ti$_2$N and the $\alpha$ matrix has been determined as follows:

\[(10\overline{1}0)_\alpha \parallel (011)_{\text{Ti}_2\text{N}}\]

\[[\overline{1}2\overline{1}0]_\alpha \parallel [011]_{\text{Ti}_2\text{N}}\]

Some of the twins in the martensite crystals were found to undergo a transformation: $\alpha \rightarrow \alpha + \text{Ti}_2\text{N}$ resulting in the formation of a large number of narrowly spaced parallel interfaces within them. Fig.6 (a) and (b) illustrate the microstructural features so obtained. It can be noticed that the $\alpha$ phase regions sandwiched between adjacent sheets of Ti$_2$N possess the same orientation as that of the matrix $\alpha$.

2. Aged Microstructures

On ageing at 200°C a large number of irregular shaped Ti$_2$N precipitates of 0.1 - 0.2 µm in length were found to form. Nucleation of such precipitates occurred preferentially on dislocations found within the martensite plates (Fig.7a). In addition to these, thin plate shaped precipitates of Ti$_2$N were also noticed in many regions of the foils. These plates were about 200 Å thick and about 0.4 µm long. The dark field micrographs shown in Fig.7(c) confirm that these plates are indeed Ti$_2$N. All these Ti$_2$N plates were found to be partitioned by a large number of closely spaced planar features (Fig.7(b)). Similar internal features have been observed in many precipitates and interpreted as strain relief twins [6] in systems such as Ta-O, Nb-O, Ni$_3$V, V-N etc. [7,8] and as internal faults in some other systems such as Nb-C, Hf-N etc. [9,10].

Ageing for one hour at 400°C resulted in the formation of large spherical precipitates of Ti$_2$N along the plate boundaries, besides a high density of fine Ti$_2$N precipitates formed within the plates (Fig.8). The adjacent martensite plates in this micrograph were found to be misoriented by a very small angle only. The pair of dark field micrographs shown in Fig.9(a) and (b) clearly reveal that the central plate of martensite is twin related to the adjacent plates. Since the $\alpha$ and Ti$_2$N reflections were so close that they could not be isolated, one set of Ti$_2$N and $\alpha$ reflections was enclosed by the objective aperture for obtaining each of these micrographs. Here again, the twin plane was identified as (1011)$_\alpha \parallel (210)$ Ti$_2$N. The stereographic projection shown in Fig.9(e) reveals that the angle between (0001)$_\alpha$ and (010)_{Ti$_2$N} is about 7°. It is seen that this finding is in reasonable agreement with the orientation relations mentioned earlier. When the duration of ageing was extended to three hours, it was noticed that the Ti$_2$N precipitates assumed a spherical or equiaxed morphology. This aspect is evidenced in the photograph shown in Fig.10.
Discussion

1. Morphology and substructure of the $\alpha$ phase

It is well known that addition of substitutional or interstitial solutes causes a change in the morphology and substructure of the titanium martensites. The exact concentrations at which such transitions occur would depend on the type of solute and its influence on the transformation temperatures as well as on the strength and the deformation mode of the parent and the product phases. For example, addition of 2.4 w/o Cr, or 6 w/o Cu or 20 w/o Zr to titanium brings about a change in morphology from the massive to the acicular type [11]. However, no such data are available for interstitial solutes in titanium. Though the scanning electron micrograph shown in Fig.2 suggests that the martensite obtained in the present alloy possesses an acicular morphology, it is clear from the transmission electron micrographs that martensite forms in this alloy both as plates and as laths. Thus it appears that the Ti - 1.6 w/o N alloy falls in the range of compositions over which a transition from lath to plate martensite takes place.

{1011} twins have been identified as the transformation twins in many titanium alloys [12]. However, in the present work only a limited number of the martensite crystals were found to contain such internal twins. Moreover, the spacing between these twins was found to be highly non-uniform. Therefore, it is proper to conclude that these twins could not have been caused by the transformation per se. Indeed it is likely that the post-transformation stresses generated within the martensite crystals could have led to the formation of such twins. In such a situation, the lattice invariant shear associated with the transformation must be accommodated by slip. Of course, the observed density of dislocations within the martensite crystals was quite low; this could be attributed to the fact that the $M_s$ temperature of this alloy was very high.

2. Precipitation of Ti$_2$N

The experimental results obtained on the precipitation of Ti$_2$N from supersaturated $\alpha$ phase could be summarised as follows:

i) There exists a specific orientation relationship between the $\alpha$ phase and the Ti$_2$N phase.

\[ \begin{align*}
(\overline{1}0\overline{1}0)_{\alpha} & \parallel (011)_{\text{Ti}_2\text{N}} \\
[\overline{1}2\overline{1}0]_{\alpha} & \parallel [01\overline{1}]_{\text{Ti}_2\text{N}}
\end{align*} \]

The Ti$_2$N precipitates always form on definite habit planes.

ii) The transformation is very rapid - it initiates even during quenching.

iii) The volume change associated with the transformation $\alpha \rightarrow \text{Ti}_2\text{N}$ is very small ($\approx 5\%$).
iv) The Ti$_2$N plates contain many internal twin-like features.

The above mentioned observations suggest that this transformation could be described as 'bainitic' [13]. Similar results have been reported in Cu-Au, Ta-O, V-H etc. [13,14]. Flewitt et al [15] have succeeded in applying the phenomenological theories of martensitic transformation in order to predict the crystallographic features of the niobium hydride plates formed spontaneously in a Nb-Zr alloy.

The simplest lattice correspondence between $\alpha$ and Ti$_2$N is shown in Fig.11. The principal strains along the three mutually perpendicular directions are given below:

\[
\begin{align*}
\varepsilon_{[12\overline{1}0]} & = 4.88\% \\
\varepsilon_{[0001]} & = -5.52\% \\
\varepsilon_{[10\overline{1}0]} & = 1.28\%
\end{align*}
\]

The necessary and sufficient condition for a pair of planes to remain undistorted during a homogeneous deformation is that one of the principal strains be zero and the other two of opposite signs [16]. Since this condition is nearly satisfied for the present case, the amount of slip or twin which needs to be added to the pure lattice strain to produce an invariant plane strain is very small.

At temperatures below 200°C, it appears that the decomposition of $\alpha$ proceeds by a continuous transformation in the initial stages followed by the ordering of the solute rich phase. Fig.5 lends support to this 'spinodal ordering' mechanism. At temperatures above 200°C, the precipitation reaction occurs presumably by nucleation and growth processes. The observation of discrete and large precipitates along the lath boundaries (Fig.6) confirms this view.

Acknowledgements

The authors wish to thank Shri S. Vaidyanathan for his kind cooperation and assistance in carrying out the experiments. They are also grateful to Dr. P. Rodriguez, Senior Metallurgist for his keen interest and encouragement during the course of this investigation.

References

Fig. 1: Phase diagram for the Ti-N system.

Fig. 2: Scanning electron micrograph of the Ti-1.6 a/o N alloy quenched from the B phase. The micrograph reveals an acicular morphology characterised by a large number of parallel, lenticular plates of martensite.
Fig. 3: (a) Bright field and (b) dark field electron micrographs demonstrating the presence of narrow \( \{1011\} \) internal twins within martensite plates.

Fig. 4: Adjacent plates of martensite found to be mutually twin related, (a) Bright field and (b) dark field obtained using a twin reflection.
PHASE TRANSFORMATIONS IN Ti-N ALLOY 1529

Fig. 5: Evidences for the initial stages of decomposition of the α matrix found in the quenched sample. The diffraction pattern and the key shown in (c) and (d) respectively correspond to the micrograph shown in (b).

Fig. 6: Decomposition of the martensite within the internal twins resulting in a mixture of α and Ti₂N: (a) bright field (b) dark field. The α region within the transformed twins and the matrix have identical orientation.
Fig. 7: Microstructures observed on ageing at 200°C for one hour. Ti₂N plates containing 'strain relief twins' within them are visible. The dark field photograph shown in (c) confirms that these plates are indeed Ti₂N.

Fig. 8: Sample quenched and aged at 400°C for one hour. Besides fine and uniform precipitates formed within the martensite plates, large and discrete precipitates of Ti₂N are observed along the plate boundaries.
Fig. 9: (a) and (b) The dark field micrographs reveal precipitates of Ti$_2$N seen within the adjacent twin related martensite crystals. (c) Selected area diffraction pattern (d) key and (e) stereographic projection.
Fig. 10: Sample quenched and aged at 400°C for three hours. It is clear that the Ti$_2$N precipitates have grown and that their morphology has changed from ellipsoidal plates to more or less equiaxed crystals.

Fig. 11: Lattice correspondence between the α matrix and the Ti$_2$N precipitates.