"BUTTERFLY" PRECIPITATES IN δ-$TiN_{0.53}$ → δ'-$TiN_{0.53}$ ORDERING TRANSFORMATION①

Du Jun*#, Yang Gaiying*#, Portier R#, Shi Likai*
* *General Research Institute for Non-Ferrous Metals, Beijing 100088*
# *Ecole Nationale Superieure de Chimie de Paris, 75231 Paris, France*

ABSTRACT The morphology of the hyperstoichiometric δ'-$TiN_{0.53}$ long-range ordered precipitates during δ-$TiN_{0.53}$ → δ' $TiN_{0.53}$ ordering transformation was investigated by transmission electron microscopy. It was found for the first time that the δ'-$TiN_{0.53}$ ordered precipitates present a "butterfly" microstructure, which is greatly similar to that found in some martensite transformations, but quite different from the general lamellar microstructures observed in stoichiometric δ'-$TiN_{0.5}$ and in many other cubic→tetragonal phase transformations. In general, δ'-$TiN_{0.53}$ precipitates consist of three "butterfly" branches whose geometrical symmetry axes are intersected one another at a common point, these "butterflies" are all formed by the three equivalent orientation domains of the δ'-$TiN_{0.53}$ and their growth directions are parallel to ⟨111⟩ directions of the d-$TiN_{0.53}$ matrix.

Key words "butterfly" precipitates δ'-$TiN_{0.53}$ ordering transformation

1 INTRODUCTION

Titanium nitride is a high melting point compound with high resistance to wear and to corrosion, good thermodynamic and chemical stabilities, thus making it a widely used coating material in cutting tools and an ideal passive diffusion barrier material in microelectronic device applications[1, 2]. The disordered δ-TiNx phase of *fcc* structure exhibits a large nonstoichiometry with x varying from 0.38 to 1.10[3]. When isothermally annealed below 800℃, the δ-TiN_x phase of a composition in the vicinity of stoichiometry ($x = 0.50$) will undergo an ordering transformation: δ-TiN_x → δ'-TiN_x. The ordered δ'-TiN_x phase presents a tetragonal structure with space group $I4_1/amd$[4]. It is important to note that a common feature of many such cubic→tetragonal phase transformations is that there always exist three equivalent orientations for the new tetragonal phase, that is, with tetragonal distortions (i.e., c axis) along [100], [010] and [001] directions of the parent cubic phase[5]. This typical orientation relationship is responsible for the three equivalent orientation domains of the δ'-TiN_x phase during δ-TiN_x→ δ' TiN_x ordering transformation. In previous work[6] it has been shown that the δ'-TiN_x phase usually exhibits a lamellar microstructure formed by combination of any two of its three orientation domains, which is consistent with many other cubic→tetragonal phase transformations.

In this paper, we report for the first time a new "butterfly" morphology of δ'-TiN_x precipitates with a hyperstoichiometric composition ($x = 0.53$). In the general case, this kind of "butterfly" precipitation has only been observed in a few martensite transformations, e.g. in Fe-Ni-C and Fe-Ni-Cr-C systems[7, 8].

2 EXPERIMENTAL

Based on Joule effects, the δ'-TiN_x parent phase ($x = 0.53$) was obtained by direct nitridation of titanium plates with a purity higher than 99.99% in high vacuum (10^{-5} Pa) and at high temperature (1 440 ± 10℃), followed by high

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temperature homogenization annealing at 1370 ± 10 ℃ for 500 h. The δ-$TiN_{0.53}$ → δ'-$TiN_{0.53}$ disorder → order phase transformation was realized under the following vacuum annealing conditions: 10^{-5} Pa, 750 ℃ and 11 h. TEM observations were carried out using JEOL-2000FX electron microscope with an accelerating voltage of 200 kV.

3 RESULTS AND DISCUSSION

Table 1 shows the orientation relationships of the three crystallographically equivalent orientation domains of δ'-$TiN_{0.53}$ in relation to the parent phase δ-$TiN_{0.53}$, this is for the purpose of easily analyzing and understanding the growth features of the new δ'-$TiN_{0.53}$ phase from δ-$TiN_{0.53}$ matrix.

Fig. 1 shows the electron micrographs of δ'-$TiN_{0.53}$ ordered precipitates in δ-$TiN_{0.53}$ matrix. The incident electron beam was parallel to the $[12\bar{2}]_M$ direction of the parent *fcc* phase (Here M is referred to *fcc* coordinate system of the parent phase). Fig. 1(a) is a bright field image; Fig. 1(b) and 1(c) are two dark field images obtained by using superlattice reflections $101\ p1$ and $01\bar{1}\ p2$ belonging to $p1$ and $p2$ orientation domains, respectively. As indicated by the circles shown in Fig. 1(a), the precipitates, beginning from one point, are extended in forms of "butterfly" along some special crystallographic directions. It can be seen by inspection of the orientation relationships between the three orientation domains ($p1$, $p2$, $p3$) and the δ-$TiN_{0.53}$ matrix (Table 1) that the superlattice reflections owing to $p1$, $p2$ and $p3$ can never appear simultaneously in the same diffraction pattern[6]. However, $p3$ orientation domains could be easily confirmed by comparison of the bright and dark field images for this particular crystal orientation in Fig. 1. From the above micrographs, the following general facts can be extracted:

(1) δ'-$TiN_{0.53}$ precipitates almost always consist of three "butterfly" branches whose geometric symmetry axes are intersected one another and that their growth directions are just along

Table 1 Orientation relationships between δ-$TiN_{0.53}$ and δ'-$TiN_{0.53}$

$p1$	$p2$	$p3$
$[100]_{\delta}//[100]_{\delta'}$	$[100]_{\delta}//[010]_{\delta'}$	$[100]_{\delta}//[001]_{\delta'}$
$[010]_{\delta}//[010]_{\delta'}$	$[010]_{\delta}//[001]_{\delta'}$	$[010]_{\delta}//[100]_{\delta'}$
$[001]_{\delta}//[001]_{\delta'}$	$[001]_{\delta}//[100]_{\delta'}$	$[001]_{\delta}//[010]_{\delta'}$

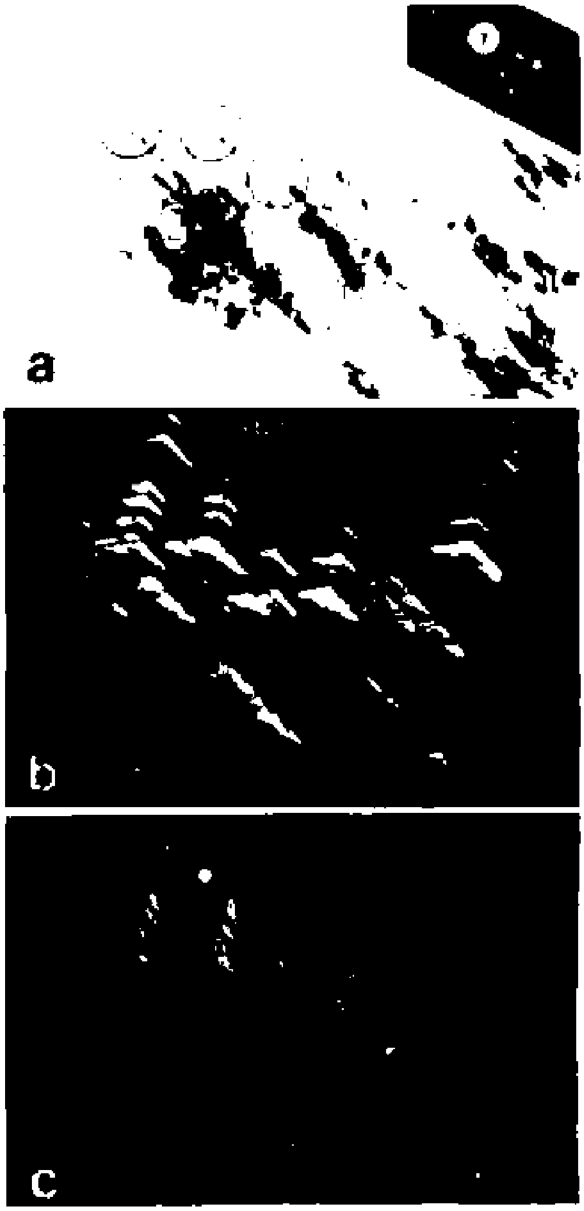

Fig. 1 Projected "butterfly" morphology of δ'-$TiN_{0.53}$ precipitates along $[12\bar{2}]_M$ direction

(a)—Bright field image, (b) and (c) Dark field images taken respectively with $g1 = 101\ p1$ and $g2 = 011\ p2$ superlattice reflections their symmetry axes.

(2) For this particular crystal orientation, the trace sections of the "butterflies" determined from the micrographs, are parallel to $[223]_M$ $[1\bar{3}2]_M$ and $[\bar{4}1\bar{1}]_M$ directions of the δ- $TiN_{0.53}$ matrix. Their angles are respectively: 112° for $[223]_M$ and $[2\bar{3}\bar{2}]_M$, 124° for $[223]_M$ and $[\bar{4}1\bar{1}]_M$, 124° for $[2\bar{3}\bar{2}]_M$ and $[\bar{4}1\bar{1}]_M$.

(3) Meanwhile, each "butterfly" is always formed by the three equivalent orientation domains of δ' -$TiN_{0.53}$ in forms of lamellae. In fact, $p1$ and $p2$ types of domains appear in pair along $[\bar{4}1\bar{1}]_M$ direction with a habit plane of $(011)_M$, $p2$ and $p3$ along $[223]_M$ with a habit plane of $(1\bar{1}0)_M$ and $p1$ and $p3$ along $[2\bar{3}\bar{2}]_M$ with a habit plane of $(101)_M$. Exactly such a lamellar structure is really coherent with that found in stoichiometric δ'- $TiN_{0.5}$ phase[6].

(4) Finally, the width of the "butterfly" decreases away from the intersected point along the growing direction. This implies that, at the first stage, δ'- $TiN_{0.53}$ phase is precipitated firstly at the intersected points as marked by circles in Fig. 1(a), and then the precipitates continue growing along the special directions mentioned above, by way of combining any two of the three orientation domains.

The following paragraph deals with the elucidation of the growth directions of δ'- $TiN_{0.53}$ "butterflies" with the help of stereographic projection. Fig. 2 is the $[12\bar{2}]_M$ stereographic projection showing the habit planes, trace directions of the "butterflies" and projected directions of $\langle 111\rangle_M$. It was noted that $[8, 7, 11]_M$ and $[8, \bar{11}, \bar{7}]_M$, the projected directions of $[111]_M$ and $[1\bar{1}\bar{1}]_M$ are located at the large circle as well as $[223]_M$, $[2\bar{3}\bar{2}]_m$ and $[\bar{4}1\bar{1}]_M$ directions, and that the angles betwen $[8, 7, 11]_M$ and $[223]_M$ and between $[8, \bar{11}, 1]_M$ and $[2\bar{3}\bar{2}]_M$ are quite small($<2.7°$). This may suggest that, considering the measurement accuracy on micrographs, the growing directions of δ' -$TiN_{0.53}$" butterflies" be along the $\langle 111\rangle_M$ directions of the parent phase.

For further confirmation of the above results , many TEM observations and analyses have

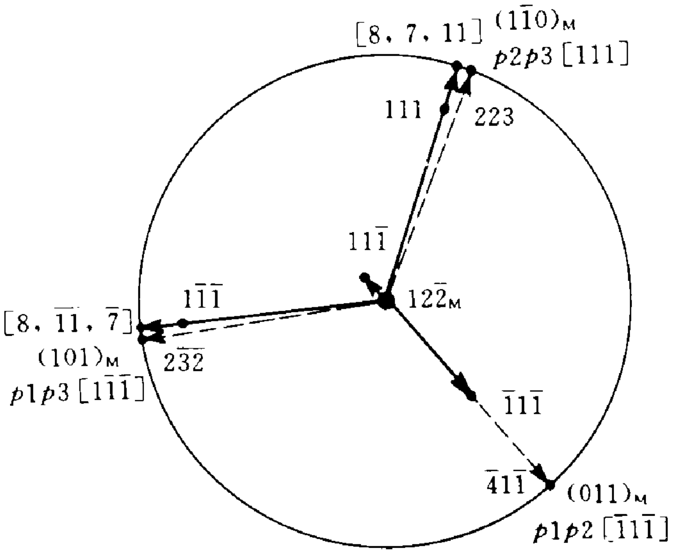

Fig.2 $[12\bar{2}]_M$ **stereographic projection**

been carried out, all showing the same. Here, we take an example as given in Fig. 3, in which the micrographs were taken with the incident electron beam parallel to $[11\bar{2}]_M$ direction of the δ- $TiN_{0.53}$ matrix. Fig. 3(a) is a bright field image; Fig. 3(b) is a dark field image realized using 011 $p1$ superlattice reflection (diffraction pattern was embedded in Fig. 3(b) only with the superlattice reflections owing to $p1$ orientation domains excited in this crystal orientation). Fig. 3(b) also indicates the three projected directions of the "butterflies": $[111]_M$, $[\bar{3}1\bar{1}]_M$ and $[1\bar{3}1]_M$. Fig. 4 shows the combination relationship of the three orientation domains of δ' – $TiN_{0.53}$ and their habit planes.

It is seen from $[11\bar{2}]_M$ stereographic projection (Fig. 4) that $[2\bar{4}1]_M$ and $[\bar{4}2\bar{1}]_M$ projections are parallel respectively to those of $[1\bar{1}\bar{1}]_M$ and $[\bar{1}1\bar{1}]_M$, and their angles with $[1\bar{3}1]_M$ and $[\bar{3}1\bar{1}]_M$ are all 9. 27°. The angle between $[11\bar{1}]_M$ and $[11\bar{2}]_M$ is 19.47°. Therefore, it can be concluded that δ'- $TiN_{0.53}$ phase grows along $\langle 111\rangle_M$ directions of the parent phase.

4 CONCLUSIONS

(1) In contrast to the lamellar precipitate morphology of stoichiometric δ'- $TiN_{0.5}$ and in many other cubic→tetragonal phase transformations, hyper-stoichiometric δ' -$TiN_{0.53}$ precipita-

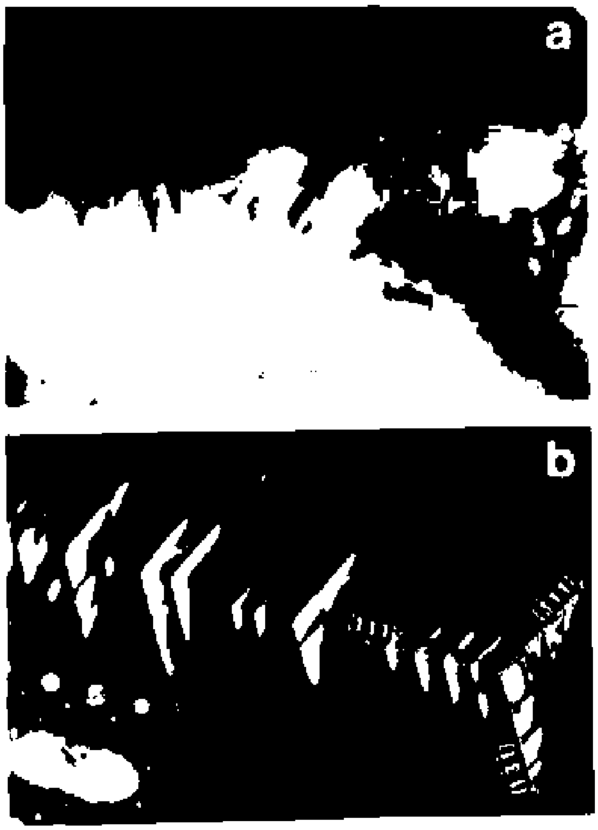

Fig.3 "Butterfly" morphology of δ'-$TiN_{0.53}$ precipitates projected along $[11\bar{2}]_M$ direction

(a)—Bright field image; (b)—Dark field image taken with $g1 = 011p1$ superlattice reflection

tes exhibit a new "butterfly" morphology.

(2) In general, the δ'-$TiN_{0.53}$ precipitates consist of three "butterfly" branches whose symmetry axes are intersected one another.

(3) These "butterflies" are all formed by the three equivalent orientation domains of δ'-$TiN_{0.53}$ and their growth directions are parallel to $\langle 111 \rangle_M$ directions of the δ-$TiN_{0.53}$ matrix.

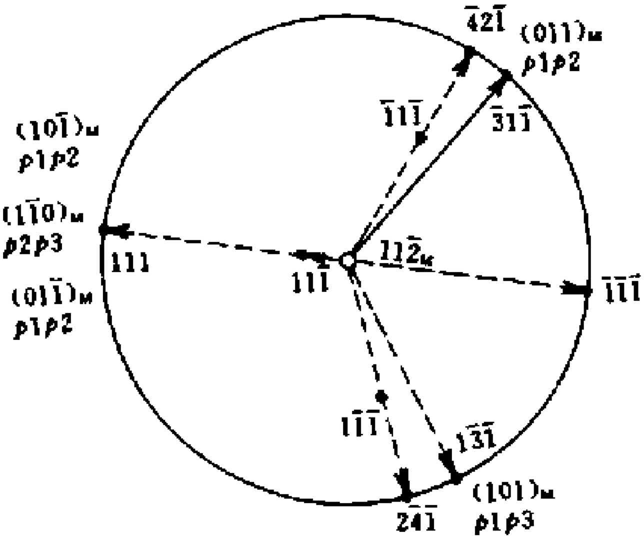

Fig.4 $[11\bar{2}]_M$ stereographic projection

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