Atomic-Scale Investigation of New Phase Transformation Process in TiO$_2$ Nanofibers

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1. The characterization results

Fig. S1 The detailed TEM analysis on the mixed-phase Ti$_3$O$_5$/TiO$_2$(B) nanofiber viewing along [110]$^{TB}$. (a) the HRTEM image; (b) the corresponding FFT image; (c) the intensity profile image; (d) the index of the two sets of diffraction patterns of Ti$_3$O$_5$ and TiO$_2$(B); (e) the stereographic projection image to prove the COR of [110]$^{TB}$/[034]$^T_3$; (f) the schematic interface between the two phases under this COR by using the Ti-O octahedron.
As it is known that the color Ti$_3$O$_5$ is black, the grey powder at 550 °C indicates that the existing of Ti$_3$O$_5$ phase. When the temperature is up to 700 °C, the color is back to the original white, proving that the anatase phase has been formed at this stage.

2. Invariant Line (IL) Model Explanation

In present study, the IL model was applied to study the phase transition from TiO$_2$ (B) to Ti$_3$O$_5$. According to the model, a habit plane must contain an edge dislocation with a Burgers vector $b$ for diffusional phase transformation. The virtual unit vector $P_1 = b / |b|$ is invariant in both length and direction during deformation. The vector $P_1$ is equivalent to but not the same as the invariant line in real space. $Q_1$ is invariant normal perpendicular to the Burgers vector $b$ (an edge dislocation in the habit plane). $P_1$ and $Q_1$ determine a one-step rotation matrix $R(u/\theta)(R$ is the rotation matrix, $u$ the unit rotation axis and $\theta$ the rotation angle). The rotation angle and the axis of a rotation matrix can be resolved by Euler’s equation dealing with rigid-body rotation:

$$
\frac{(P_2 - P_1) \times (Q_2 - Q_1)}{(P_2 + P_1) \cdot (Q_2 - Q_1)} = u \left( \tan \frac{\theta}{2} \right)
$$

(1)

Here, $Q_2$ is a deformation of vector $Q_1$ and $B$ is the generalized Bain strain. The vectors $P_2$, $Q_1$ and $Q_2$ are given by
\[
\begin{align*}
\begin{bmatrix}
P_2 & = B \cdot b / |B \cdot b| \\
\mathcal{Q}_1 & = [hkl] \\
\mathcal{Q}_2 & = \mathcal{Q}_1 \cdot B^{-1}
\end{bmatrix}
\end{align*}
\tag{2}
\]

And
\[
\begin{align*}
\begin{bmatrix}
P_1 \cdot \mathcal{Q}_1 &= 0 \\
|P_1| &= |P_2| \\
|\mathcal{Q}_1| &= |\mathcal{Q}_2|
\end{bmatrix}
\end{align*}
\tag{3}
\]

A one-stop rotation operation \( R(u/\theta) \) can be directly determined geometrically by using Euler’s equation (1). Thus, having found the total strain \( A (A = RB) \), the eigenvalues, eigenvectors (including invariant line) and eigenplanes (including habit planes) can be found by linear algebra. The orientation relationship between the matrix and the new phase can be directly deduced by considering the rotation matrix \( R(u/\theta) \) starting from the Bain strain lattice correspondence. Following this approach, it is very simple to define an OR.

### 2. The Detailed Calculation

The main strain matrix chosen in present calculation is:

\[
B = \begin{pmatrix}
\eta_1 & 0 & 0 \\
0 & \eta_2 & 0 \\
0 & 0 & \eta_3
\end{pmatrix} = \begin{pmatrix}
[001]_{TB} & |001|_{TB} & 0 & 0 \\
[106]_{TB} & |106|_{TB} & 0 & 0 \\
[100]_{TB} & |100|_{TB} & 0 & 0 \\
[010]_{TB} & |010|_{TB} & 0 & 0
\end{pmatrix} = \begin{pmatrix}
0.8108 & 0 & 0.7535 & 0 \\
0 & 0.8108 & 0 & 1.4042
\end{pmatrix}
\]

Based on the observed TEM result, the first axis \( \eta_1 \) was chosen as \([001]_{TB}/[100]_{TB}\). Similarly, the \([110]_{TB}/[010]_{TB}\) was donated as the second axis \( \eta_2 \). The third axis \( \eta_3 \) was obtained through searching the vector which is perpendicular with \( \eta_1 \) and \( \eta_2 \) in the stereographic projection 2.0 software. The obtained Bain strain lattice correspondence can be seen in Fig. S1.
Fig. S3 The Bain strain lattice correspondence for the phase transition from TiO\textsubscript{2} (B) to Ti\textsubscript{3}O\textsubscript{5}.

As the [100\textsubscript{TB}] parallels to one of Bain strain lattice correspondence \(\eta_1\), the IL model consequently was simplified to be two-dimensional case. Clearly, the rotation axis was [100\textsubscript{TB}].

As the total strain matrix for variant 1 can be written as:

\[
A = RB = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \theta & -\sin \theta \\
0 & \sin \theta & \cos \theta
\end{pmatrix}
\begin{pmatrix}
\eta_1 & 0 & 0 \\
0 & \eta_2 & 0 \\
0 & 0 & \eta_3
\end{pmatrix}
\]

(4)

We let \((A-I)X=0\), then we can obtain:

\[
|A-I| = \begin{vmatrix}
1 & 0 & 0 \\
0 & \cos \theta & -\sin \theta \\
0 & \sin \theta & \cos \theta
\end{vmatrix}
\begin{vmatrix}
\eta_1 & 0 & 0 \\
0 & \eta_2 & 0 \\
0 & 0 & \eta_3
\end{vmatrix} - \begin{vmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{vmatrix} = (\eta_1 -1)[1 + \eta_2 \eta_3 - (\eta_2 + \eta_3) \cos \theta] = 0
\]

(5)

Therefore, the rotation angle \(\theta\) can also be obtained as:

\[
\cos \theta = \frac{1 + \eta_2 \eta_3}{\eta_2 + \eta_3}
\]

(6)

In order to calculate the eigenvalue \(\lambda_i\) of the lattice deformation matrix, we let \(|A-\lambda I|=0\), then:
\[ |A - \lambda I| = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{vmatrix} \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} - \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & \lambda \end{pmatrix} \]

\[ = (\lambda - 1)(\lambda - \eta_2 \eta_3)(\eta_1 - \lambda) = 0 \]

Therefore, the three eigenvalues are determined to be \( \lambda_1 = 1, \lambda_2 = \eta_2 \eta_3, \lambda_3 = \eta_1. \)

Obviously, one of the eigenvalues always equals to 1. Hence, eigenvectors \( V_i \) of the matrix \( A \) can be calculated by letting \( AX = \lambda X \), then:

\[
(A - \lambda I)X = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} - \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & \lambda \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} (\eta_1 - \lambda)X \\ (\eta_2 \cos \theta - \lambda)Y - (\eta_3 \sin \theta)Z \\ (\eta_3 \sin \theta)Y + (\eta_3 \cos \theta - \lambda)Z \end{pmatrix} = 0
\]

After putting the eigenvalues and rotation angles \( \theta \) into Equation (8), we can obtain:

when \( \lambda_1 = 1 \), the eigenvector can be obtained to \( V = [0, 3, 2] \). This is the growth direction mentioned in paper. The eigenplane determined by the eigenvector can be calculated to be \( F = (100) \), and it is the habit plane in the phase transition.

Reference