Energy consideration for variant selection in precipitation on dislocations

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Abstract

Preferential precipitation on dislocations has been discussed by considering interaction energy between transformation strains to change the crystal structure and stress fields around dislocations. For quantitative calculation, precipitation of the hcp α phase from the bcc β matrix in a Ti alloy is analyzed. A previous experiment shows that a certain variant of precipitates among crystallographically equivalent ones was formed preferentially on a given dislocation. The present analysis is successful in explaining such variant selection. Comparison with other studies has revealed that the stress always plays an important role in the early stage of phase transformation to change the crystal structure. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Upon precipitation of a second phase from a solid matrix crystal, dislocations frequently act as preferential nucleation sites [1–3]. The precipitates so formed on a given dislocation often belong to one or a few particular variants among many crystallographically equivalent ones [4]. Such heterogeneous nucleation associated with the variant selection is sometimes considered detrimental to microstructure refinement since the eventual growth and coalescence of the precipitates may result in the formation of large domains with the same orientation.

It is well known that internal and external stresses promote the formation of preferential variants of precipitates [5–7] and martensites [8–11]. It is, therefore, reasonable to consider that stress fields around a dislocation also play an essential role on the variant selection of precipitates. Although some previous studies have discussed this possibility [2–4], it appears that no quantitative analysis has yet been performed so far. The present research is aimed to quantitatively evaluate the role of the stress fields around a dislocation on the preferential formation of specific precipitate variants. As a tool for the analysis, the same idea of interaction energy that has been applied successfully to discuss the external stress effects [5–11] will be adopted by considering the interaction between transformation strains upon precipitation and stress fields around dislocations.

2. Analysis

2.1. Transformation matrix

As an example of the quantitative analysis, let us use the results of an experimental study by Furuhara et al. [4]. They have examined the precipitation of the hcp α-phase in a β-phase matrix of a titanium alloy and observed the strong variant selection of precipitates formed on dislocations. The Burgers orientation relationship described as

\[(1\overline{1}0)_{\beta} / (0001)_{\alpha}, \quad [111]_{\beta} / [1\overline{2}0]_{\alpha}\]  

has been observed between the α precipitates and the β matrix. Fig. 1 shows the atomic arrangements of the two phases. By adopting the apparent lattice correspondence between the grey rectangles in Fig. 1, i.e.

\([1\overline{1}0]_{\beta} \Leftrightarrow [001]_{\alpha}, \quad [001]_{\beta} \Leftrightarrow [\overline{1}2\overline{1}0]_{\alpha}, \quad [1\overline{1}0]_{\beta} \Leftrightarrow [10\overline{1}0]_{\alpha}\]  

together with the lattice constants of the two phases (\(a_\beta = 0.3232\) nm, \(a_\alpha = 0.2956\) nm and \(c_\alpha = 0.4693\) nm [4]), the lattice deformation matrix \(A\) to change the \(\beta\) lattice into the \(\alpha\) lattice can be written as

\[
A = \begin{pmatrix}
1.1202 & 0 & 0 \\
0 & 0.9146 & 0 \\
0 & 0 & 1.0267
\end{pmatrix}.
\]  

(2)

Here, the \(x_\beta^0 - x_\alpha^0 - x_\alpha^0\) coordinates shown in Fig. 1 were used to express Eq. (2). In the actual bcc → hcp transformation, in addition to the homogeneous deformation \(A\),
atomic shuffling by shear on every other (0001)α planes is necessary. However, since this shuffling does not change the overall shape and size of the two crystals, Eq. (2) does represent the actual lattice deformation matrix.

In addition to A, rigid-body rotation R by 5.26° is necessary to realize the Burgers orientation relationship shown in Eq. (1) and Fig. 2:

$$R = \begin{pmatrix} \cos 5.26° & -\sin 5.26° & 0 \\ \sin 5.26° & \cos 5.26° & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$  

Therefore, the total transformation matrix D to induce the β → α change in the crystal structure becomes

$$D = RA = \begin{pmatrix} 1.1155 & -0.0839 & 0 \\ 0.1028 & 0.9107 & 0 \\ 0 & 0 & 1.0267 \end{pmatrix}.$$  

Of course, Eq. (4) expresses the transformation matrix of a specific Burgers variant. As pointed out by Furuhara et al. [4] and as listed in Table 1, there are 12 Burgers variants, V1–V12, that can be discriminated by transmission electron microscopic (TEM) observation. With these notations, we find that the transformation matrix of Eq. (4) belongs to that of the V4 variant.

2.2. Slip plane and dislocation geometry

Furuhara et al. [4] have reported that aging after a small amount of plastic deformation of a solution-treated β-titanium alloy causes the α phase precipitation on dislocations. The plastic deformation of the β matrix occurs by slip on (112)_β along [111]_β with \( b = (a_0/2)[111]_β \) the Burgers vector of the primary dislocations. Fig. 3 schematically shows the geometry of edge and screw dislocations on the (112)_β slip plane. In this figure, the atomic arrangement and orientation of the (110)_β and (0001)_a planes are also shown for the V4 variant. The reason why this V4 variant was chosen in Figs. 2 and 3 is that this is the variant that was found to be preferentially formed on primary dislocations [4].

2.3. Calculation of interaction energy

Now that the transformation matrix to change the crystal structure and dislocation geometry were identified, we are ready to calculate the interaction energy between the transformation strains and stress fields around a dislocation. For example, by expressing the \((i, j)\) components of \( D \) in Eq. (4) as \( D_{ij} \), the symmetric transformation strain tensors \( \varepsilon^T_{ij} \)

| Variant notation | Parallel planes | Parallel directions |
|------------------|----------------|--------------------|
| V1               | (110)_β/(0001)_α | [111]_β/[1120]_α |
| V2               | (110)_β/(0001)_α | [111]_β/[1120]_α |
| V3               | (110)_β/(0001)_α | [111]_β/[1120]_α |
| V4               | (110)_β/(0001)_α | [111]_β/[1120]_α |
| V5               | (011)_β/(0001)_α | [111]_β/[1120]_α |
| V6               | (011)_β/(0001)_α | [111]_β/[1120]_α |
| V7               | (011)_β/(0001)_α | [111]_β/[1120]_α |
| V8               | (011)_β/(0001)_α | [111]_β/[1120]_α |
| V9               | (101)_β/(0001)_α | [111]_β/[1120]_α |
| V10              | (101)_β/(0001)_α | [111]_β/[1120]_α |
| V11              | (101)_β/(0001)_α | [111]_β/[1120]_α |
| V12              | (101)_β/(0001)_α | [111]_β/[1120]_α |
can be obtained as [12]

$$\varepsilon_{ij}^T = \frac{D_{ij} + D_{ji}}{2} - \delta_{ij},$$

(5)

where $\delta_{ij}$ is the Kronecker delta.

For the stress fields $\sigma_{ij}$ around straight screw and edge dislocations, we will adopt the well-known elasticity solutions in an infinite isotropic medium [13]. It is more convenient to express the transformation strains $\varepsilon_{ij}^T$ on new $x_1 - x_2 - x_3$ coordinates fixed to a dislocation such that the dislocation line lies on the new $x_3$ axis. This can be done by a simple coordinate conversion of tensors. For example, from Eqs. (4) and (5) together with the conversion of coordinates, the transformation strains $\varepsilon_{ij}^T$ expressed on the new $x_1//[1\bar{1}1]_B - x_2//[\bar{1}12]_B - x_3//[1\bar{1}0]_B$ coordinates of the edge dislocation in Fig. 3 become

$$\varepsilon_{ij}^T = \begin{pmatrix} 0.0561 & -0.0934 & 0 \\ -0.0934 & -0.0299 & 0 \\ 0 & 0 & 0.0267 \end{pmatrix}.$$  

(6)

The interaction energy $E_{int}$ per unit volume between the transformation strains and the stress fields $\sigma_{ij}$ can now be calculated as [14]

$$E_{int} = -\sigma_{ij} \varepsilon_{ij}^T.$$  

(7)

Here, the usual summation convention over repeated indices was adopted. Negative and positive values of $E_{int}$ indicate that the stress $\sigma_{ij}$ assists and prohibits the transformation, respectively. Therefore, the stress effect in assisting the transformation becomes the largest when $E_{int}$ is the smallest, i.e., negative with the largest absolute value $|E_{int}|$.

For numerical calculation of Eq. (7), the stress fields at a distance $r$ from the dislocation center were considered, as shown in Fig. 4, by varying the angle $\theta$ from the $x_1$ axis. The values of the interaction energy $E_{int}$ were then calculated as a function of $\theta$. Fig. 5 shows, as an example, the calculated $\theta$-dependence of the interaction energy $E_{int}$ between the stress fields of a straight edge dislocation and the transformation strains of the V4 variant (Eq. (6)). The interaction energy was made dimensionless by multiplying $2\pi r/\mu b$ by $E_{int}$, where $\mu$ is the shear modulus and $b$ is the magnitude of the Burgers vector.

As can be seen in Fig. 5, the stress assists the transformation of the V4 variant most significantly at a point $\theta = \theta_{in} = 192.2^\circ$ with the minimum interaction energy of $(2\pi r/\mu b)E_{int} = -0.2998$. The same calculations were conducted for all the 12 variants in Table 1 and for both straight edge and screw dislocations.

3. Results

3.1. Interaction with an edge dislocation

Using the stress fields around a straight edge dislocation, the minimum interaction energy value $E_{int}^{\text{min}}$ was calculated for each of the 12 Burgers variants. Table 2 shows the results together with the position $\theta_{in}$ at which the minimum interaction energy is realized. The Poisson ratio was taken to be 0.3 for this calculation.

We find in Table 2 that the V4 variant has the smallest $E_{int}^{\text{min}}$ with the largest absolute value among all the 12 Burgers variants. Aside from V3, the absolute values of all the other variants are much smaller than that of V4. This indicates that the formation of the V4 variant is most strongly aided by the stress field around the edge dislocation.

![Fig. 3. The (\{1\bar{1}2\}_B[1\bar{1}1]_B) slip system and orientation of primary edge and screw dislocations. The $\alpha$ crystal shown satisfies the specific Burgers relationship in Fig. 2.](image-url)

![Fig. 4. Coordinates fixed to a dislocation. A straight dislocation line is on the $x_3$ axis. The stress fields around the dislocation were chosen at various points $(r, \theta)$ on the circle of radius $r$.](image-url)

![Fig. 5. Interaction between the stress fields around a straight edge dislocation and the transformation strains of the V4 variant. Dimensionless interaction energy was plotted as a function of $\theta$ in Fig. 4. The Poisson ratio $\nu = 0.3$.](image-url)
Table 2
Minimum interaction energy $E_{\text{int}}^m$ and the position $\theta_m$ around a straight edge dislocation at which the minimum interaction energy is realized for 12 Burgers variants. Poisson ratio: 0.3

| Variant notation | $(2\pi r/\mu b)E_{\text{int}}^m$ | $\theta_m/\text{deg}$ |
|------------------|---------------------------------|---------------------|
| V1               | $-0.1651$                       | 188.4               |
| V2               | $-0.1651$                       | 188.4               |
| V3               | $-0.2991$                       | 188.0               |
| V4               | $-0.2998$                       | 192.2               |
| V5               | $-0.0976$                       | 18.9                |
| V6               | $-0.1114$                       | 14.3                |
| V7               | $-0.1555$                       | 349.1               |
| V8               | $-0.1638$                       | 343.5               |
| V9               | $-0.1114$                       | 14.3                |
| V10              | $-0.0976$                       | 18.9                |
| V11              | $-0.1555$                       | 349.1               |
| V12              | $-0.1638$                       | 343.5               |

with a close next candidate of the V3 variant. As mentioned previously, this is in complete agreement with the experimental observation of the variant selection [4].

The transformation strain components of the V4 variant are shown in Eq. (6) and their directions are schematically drawn in Fig. 6. Similarly, directions of the stress components around the edge dislocations are drawn in Fig. 7 together with the angle $\theta_m = 192.2^\circ$ for the V4 variant in Table 2. It can be seen that the directions of the stress components at $\theta_m = 192.2^\circ$ (Fig. 7) and the transformation strain components (Fig. 6) much exactly at $\theta_m = 192.2^\circ$. This is the easy way to understand the physical reason why the V4 variant has the minimum interaction energy at $\theta_m = 192.2^\circ$.

3.2. 3.2. Interaction with screw and mixed dislocation

Table 3 shows the calculated results for a straight screw dislocation. In this case, because of the crystallographic equivalence, some variants have the same $E_{\text{int}}^m$ values. We note, however, that the absolute values for variants V3, V4, V7 and V8 are nearly twice as large as those of other eight variants. Therefore, the above four variants can be expected to be formed more preferentially. As a result, the V4 variant selection is again consistent with the calculation even when the stress effect of a pure screw dislocation is considered, although the superiority of V4 over V3, V7 and V8 cannot be pointed out.

In reality, however, pure screw dislocations can hardly exist and many dislocations must be of a mixed character. Around a mixed dislocation, superimposed stress fields of edge and screw dislocations develops. Therefore, from the calculated results in Tables 2 and 3, the V4 variant selection on a general mixed dislocation is remains very plausible.

4. Discussion

4.1. Role of dislocations for the variant selection

We have found that the stress fields around a dislocation play an essential role in the variant selection. This means that the radius $r$ in Fig. 4 was tacitly assumed to be longer than the inner cut-off radius $r_0$ of the dislocation. On the
other hand, one may argue that not the stress fields obtained by elasticity but the atomic arrangement at the dislocation core plays an important role in assisting the formation of precipitate nuclei. Although it is true that continuum elasticity becomes invalid at the dislocation core, consistency should prevail between the outer stress fields and the inner atomic arrangement. In other words, if \( \sigma_{ij} \) as an elasticity solution has a positive value at a position \((r, \theta)\) with \(r > r_0\) in Fig. 4, the interatomic spacing along the \( x_1 \) direction at \((r, \theta)\) should be longer than the equilibrium spacing for both \(r > r_0\) and \(r < r_0\). Therefore, the elasticity solutions of the outer stress fields are still applicable to discuss relative distortions in atomic arrangement at the dislocation core. From this point of view, the present analysis is still valid even when the dislocation core structure is important. It should rather be understood that for a given dislocation, the outer stress fields are uniquely determined and, therefore, they become effective parameters to characterize both inside and outside of the dislocation core.

4.2. Comparison with other studies

The origin of the preferential precipitation at dislocations has been studied from different points of view. Cahn [1] thermodynamically discussed the activation barrier of nucleation and concluded that precipitation on dislocations became more important with increasing the Burgers vector and with increasing supersaturation. However, his analysis was limited to an incoherent precipitate lying along a dislocation and no discussion on the variant selection was made.

To explain experimental observations using the Al–Cu system, Thomas and Nutting [2] have proposed the idea that the preferentially formed variants are those that can efficiently relieve the strain fields around a dislocation. Although their idea is basically similar to ours, their analysis remains qualitative rather than quantitative.

More quantitative discussion has been developed by Kelly and Nicholson [3]. They have considered a coherent precipitate and defined a ‘misfit vector’ that is perpendicular to the atomic planes of largest misfit and with magnitude equal to the normal misfit strain. They concluded that the greatest strain energy reduction was realized if the misfit vector became parallel to the Burgers vector. Furuhara et al. [4] took along the same lines to explain their experimental results. Since only the direction of the largest normal misfit was taken into account, their analyses may be most useful for a precipitate with significantly unidirectional normal misfit strains, such as GP zones in Al–Cu [2,3]. However, they cannot be applied to coherent precipitates with rather isotropic misfit strains or to a semi-coherent precipitate with a shear-type misfit.

The present analysis, contrary to these previous ones, should be regarded as a general and quantitative one. This is because the energetic consideration naturally takes into account stress accommodation not only from the direction of the largest misfit but also from all other directions. Therefore, this analysis can be applied even to a coherent precipitate with nearly isotropic transformation strains. Furthermore, if only the transformation strains are identified, application to a semi-coherent precipitate is also possible, as done in the present study.

4.3. General stress effects on phase transformations

The necessary input parameters to conduct the present analysis were the crystal structures, lattice constants, lattice correspondence and the orientation relationship between the two phases. All of these parameters can be found easily and no information on the precipitate shape was needed. On the other hand, if the stresses are considered to assist the total shape change of the transformation product, its shape must be known, too. This is because not the transformation strains to change the crystal structure but the overall shape change strains must be used to calculate the interaction energy.

Whether the applied stress helps the change in the crystal structure or the change in the overall shape has been examined experimentally using single crystals. By applying two-step aging treatments with and without external stresses to Fe–N and Al–Cu single crystals, Mori and Horige [5], Eto et al. [6] and Tanaka et al. [7] have concluded that the stress plays a dominant role in the early stages of precipitation to change the crystal structure.

The fcc \(\rightarrow\) bcc stress-induced martensitic transformations in single crystals of various alloys have also been examined. Interestingly, the preferentially formed martensite variants have been found to belong to the identical Kurdjumov-Sachs variants regardless of the shape (lath [8], needle-like [9], spherical [10] or plate-like [11]) of the martensites. From these experimental results, Kato et al. have concluded that the stress effects, either on diffusion-controlled precipitation or on diffusionless martensitic transformation, always appear first and most significantly on the strains to change the crystal structure and, thereby, determine the preferentially formed variants [15]. The agreement with the experimental results in the present study leads us to conclude that the variant selection on a dislocation is also determined by the stress effect in assisting the change in the crystal structure.

5. Summary and conclusions

1. To find the origin of the variant selection of precipitation on dislocations, interaction energy between stress fields around dislocations and transformation strains has been calculated.
2. The \(\alpha\)-phase precipitates on edge and screw dislocations in the \(\beta\)-phase matrix of a Ti alloy have been considered for quantitative discussion. From the lattice correspondence and the orientation relationship between the \(\alpha\) and \(\beta\)
phases, transformation strains to change the crystal structure are identified and its interaction with stress fields around the dislocation is evaluated.

3. The analysis based on the interaction energy has been found successful in explaining the experimentally observed variant selection for precipitates on dislocations.

4. The present study as well as other studies on the stress effects on phase transformations show that stress plays an important role in the early stage of phase transformations to change the crystal structure.

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