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Why Twins Do Not Grow at the Speed of Sound All the Time

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Deformation twinning occurs in various materials including metals, intermetallics, ceramics, superconductors, and even geological systems. The rate of twin growth depends on the material system, but there are no crystallographic models to understand the mechanisms of slow twin growth. The physics of twin growth is presented for bcc-Ti alloys where it is shown that octahedral interstitial sites are not conserved at the twin-matrix interface where oxygen resides. The predicted activation energy for twin growth correlated well with experimental values for the diffusion of oxygen. These models will have a broad application in understanding the twinning process and designing advanced materials.

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Twinning is a deformation process in crystalline materials where the lattice of the twin becomes the mirror image of that of the untwinned matrix across the twin-matrix interface. This process is known to occur in various materials including metals [1–3], ceramics [4], intermetallics [5], nanocrystalline materials [6], superconductors [7,8], and geological systems [9,10]. The actual rate of twin growth depends on the material system. For instance, it is noted that in minerals, the twin walls may be pinned at impurities in the lattice [10]. Twin growth may occur on a geological time scale owing to a low thermal energy for diffusion as compared to the energy for depinning. Moreover, sapphire doped with Ti^{4+} ions on the order of 0.1 wt. % shows slower twin growth than undoped sapphire, as the dopant may contribute to the formation of stacking faults which impede twin propagation [4]. In metals, however, the twin-growth rate is expected to be much higher, namely, the speed of sound (340 m/s) [2]. It has long been understood how twins can grow at the speed of sound, but recently it was observed [11,12] that twin growth in hexagonal close-packed, hcp (α) titanium, and bcc (β) titanium alloys can occur at rates on the order of 1 nm/s, which is many orders of magnitude smaller than the speed of sound. It is not clear why twins in metals can grow very slowly, and to date there are no crystallographic models available to explain this phenomenon. In this investigation we have presented models for slow growth of twins using a body-centered cubic β-titanium alloy as the model system. This model is expected to help explain the twinning phenomenon in crystalline materials in general and metals in particular.

While the slow growth of twins was observed in bcc and hcp titanium alloys, we selected a bcc alloy as the model system because experimental values are available for the activation energy of the twin-growth process and for the diffusion of oxygen in the material. Consider a bcc crystal structure, the projection of which onto the **(1$\bar{1}$0)** plane is shown in Fig. 1(a). Figure 1(b) shows the twinning shear on the **(112)** plane in the **[11$\bar{1}$]** direction. Normally, once the shearing in this twinning process in the crystalline metal starts, the twin can grow at the speed of sound. Therefore, it is normally difficult to record the sequential process of twin growth, and some aspects of the twin-growth process are not well understood. As shown in Fig. 1(a), if one considers only lattice sites corresponding to the substitutional atoms, shown as open circles, the twinning proceeds as shown in Fig. 1(b) where all lattice sites are translated to

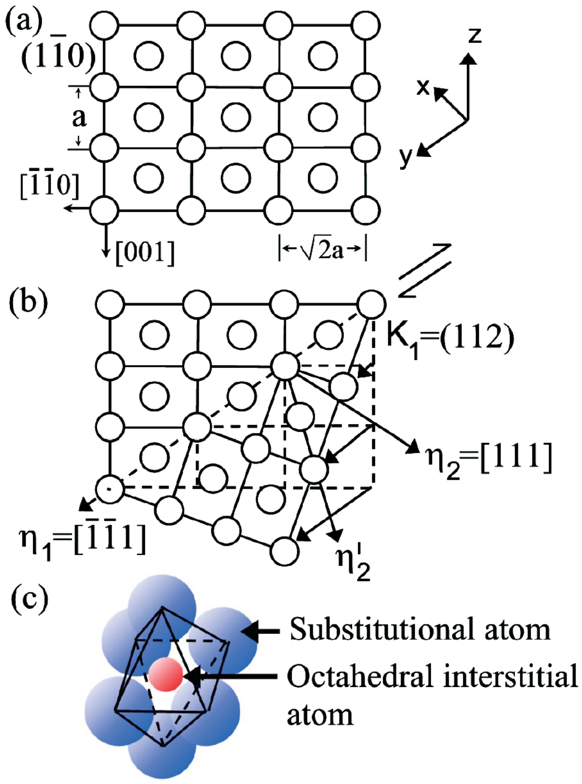

FIG. 1 (color). (a) Projection of bcc substitutional atoms onto (1$\bar{1}$0) plane. (b) [$\bar{1}$ $\bar{1}$ 1] twinning shear of **(112)** planes results in mirror reflection across twin boundary. (c) Interstitial atom located at an octahedral site.

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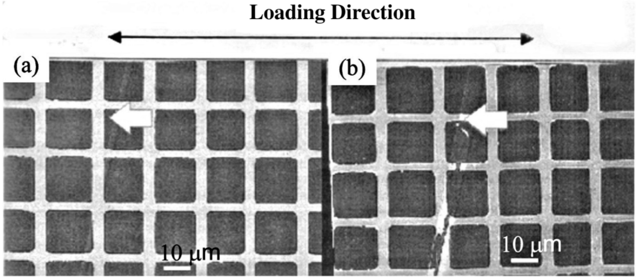

FIG. 2. (a),(b) Creep (time-dependent deformation) specimen, β Ti-14.8 wt. % V. Arrows indicate location and growth of twins between (a) and (b) in a time of 1.62 h. Creep tests conducted at 298 K at a stress level of 95% YS. Horizontal and vertical gold grid lines were put on the specimen as a reference to indicate extent of deformation [11].

the correct twinned position or conserved. However, in the crystal, there are gaps or interstices throughout the lattice. An interstice at the center of an octahedron bound by the substitutional atoms is shown in Fig. 1(c). All these interstitial sites are present in the bcc lattice. Thus, the question arises whether these interstitial sites are conserved when the twinning process occurs, particularly at the twin-matrix interface. Such a consideration is essential because oxygen, or other interstitials, reside in octahedral interstitial sites in the bcc lattice [13]. Indeed, Magee *et al.* [14] have described the effect of a **(112)** twinning shear on the octahedral interstitial sites in a bcc lattice when describing deformation twinning in cubic martensites. The slow growth of twins mentioned before was observed when titanium alloys were subjected to creep, or time-dependent plastic deformation, at a constant stress of 95% yield stress (YS). The models presented in this Letter are for the twins shown in Figs. 2(a) and 2(b) [11] where the crystal structure is bcc and the twins are of the type **{332}**⟨**113**⟩, as identified by transmission electron microscopy.

The **{332}**⟨**113**⟩ twinning in β-titanium alloys has been attributed to shear mechanisms [15] and alternatively to dislocation mechanisms [16], but these analyses have not considered what happens to the interstitial sites near the twin-matrix interface. The shear mechanism considers atomic positions in terms of their untwinned matrix position and their final twin position. Figures 3 and 4 illustrate the growth of a twin that involves shears and shuffles and are based on the scheme first proposed by Crocker [15], with the inclusion of octahedral interstitial sites. Figure 3(a) shows the untwinned bcc crystal structure including octahedral sites projected onto the **(1$\bar{1}$0)** plane. The **[113]** shear direction is also indicated. The displacement of the lattice as a result of the twinning shear is such that a mirror angle is created between the twin and the untwinned matrix. Figure 3(b) shows the projection of the final twinned structure, the mechanism of which is described below.

The details of the twin-matrix interface corresponding to the first three **(332)** planes of substitutional atoms to the right of the twin-matrix interface of Fig. 3 are shown in Fig. 4. Figure 4 shows that after shear of the untwinned lattice seen in Fig. 4(a) in the **[113]** direction, only half of the substitutional atoms, those in the plane of the projection, are sheared to the correct twin position. An additional displacement known as a shuffle is required to move the substitutional atoms above and below the plane of projection to the final twin position and is illustrated in Fig. 4(c). It should be noted that shuffles alternate in opposite directions, **[113]** or $[\bar{1}\,\bar{1}\,\bar{3}]$, such that mass balance is maintained [17]. The shuffle, however, reorients the substitutional atoms at the twin-matrix interface such that the octahedron in which the interstitial atom could sit is eliminated. Such an interstitial site is indicated by a green triangle in Fig. 4(c). If an oxygen atom occupies such a site, it must diffuse to another interstitial site in either the twin or the untwinned matrix. For each **(332)** plane of substitutional

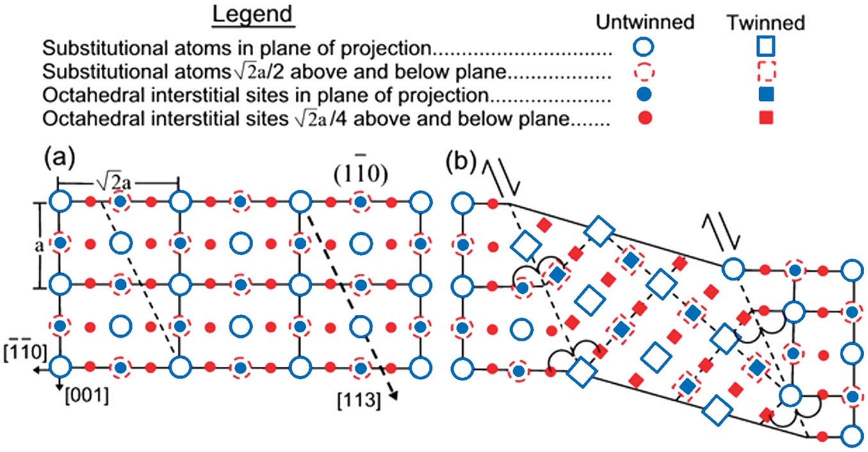

FIG. 3 (color). Projection of bcc substitutional and octahedral interstitial atoms onto **(1$\bar{1}$0)** plane. (a) Untwinned structure showing direction of **[113]** twinning shear, and (b) Final twinned structure showing mirror symmetry across twin-matrix interface.

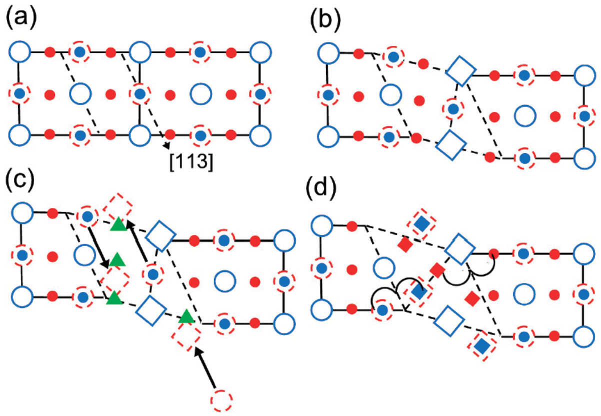

FIG. 4 (color). Details of the twinning mechanism for the first three **(332)** planes from Fig. 3 showing elimination of octahedral sites indicated by green triangles. (a) Projection of untwinned bcc crystal structure onto $(\mathbf{1\bar{1}0})$ plane with direction of [**113**] twinning shear indicated; (b) twinning shear moves only in-plane substitutional atoms to correct twin position; (c) shuffles to create mirror symmetry across interface; (d) final twinned structure.

atoms that move to the twin position along the **[113]** shear direction, one **(332)** plane of octahedral interstitial sites is eliminated at the twin-matrix interface. After the shuffle of the substitutional atoms to the final twin positions, the octahedral sites will be reformed in new locations. The final twinned structure, including reformed octahedral sites is shown in Fig. 4(d). It should be noted that, while Fig. 4 illustrates the shear and shuffle of the first three **(332)** planes of substitutional atoms simultaneously, in reality the twin growth will occur one **(332)** plane at a time and one **(332)** plane of octahedral sites will be reformed before the next is eliminated.

The large shears and shuffles, particularly in a direction opposite that of the twinning shear, required of the shear twinning mechanism first described by Crocker call into question whether such a mechanism is energetically favorable. Therefore, Litvinov and Rusakov [17] propose two dislocation mechanisms of twinning, which are not illustrated, as an alternative to account for the twinning transformation. One of the dislocation mechanisms involves twin growth via the gliding of $\frac{5a}{22}[\bar{1}\,\bar{1}\,3]$ twinning dislocations in a stack of **(332)** planes. In this case, the final twin-matrix interface is similar to that shown in Fig. 4(d). An alternative twinning dislocation mechanism proposed by Litvinov and Rusakov [17] involves the gliding of $\frac{a}{22}[11\bar{3}]$ partial dislocations. The movement associated with these dislocations is similar to that of the $\frac{5a}{22}[\bar{1}\,\bar{1}\,3]$ dislocation but is smaller in magnitude and of opposite direction on the same **(332)** planes. This dislocation mechanism, however, requires the subsequent shuffling of the substitutional atoms by $\pm\frac{a}{22}[332]$ in order to move the atoms to their correct twin positions. Even in this case, the twin-matrix interface is similar to that shown in Fig. 4(d). The net result is no matter which mechanism is operating the octahedral sites near the twin-matrix interface are not conserved. If interstitial atoms such as oxygen are present in these sites, the oxygen has to move out before twinning can proceed, resulting in the slow growth of twins.

Measurements of the twin growth for the $\mathbf{\{332\}\langle 113\rangle}$ twin taken from Figs. 2(a) and 2(b) show a growth of approximately 3.45 μm in a time period of 1.62 h, indicating a twin-growth rate of approximately 0.590 nm/s. Thus, based on a bcc titanium lattice constant, a, of 0.339 nm, the twin advances by the distance a from the twin-matrix interface in 0.58 s. This corresponds to one **{332}** plane of substitutional atoms moving to the twin position and the corresponding elimination of one **{332}** plane of octahedral interstitial sites every 0.27 s. In this alloy, oxygen is the main interstitial element present and is present at a concentration of approximately 920 ppm. All the other interstitial elements such as nitrogen are at extremely small levels. Oxygen interstitials will diffuse from eliminated sites either in the direction of twin growth, or opposite, as interstitial sites in other directions are also eliminated. The nearest available octahedral interstitial site is a distance of approximately $\frac{a}{2}$, or 0.17 nm from the eliminated site [18]. If it is assumed that the movement of the twin-matrix interface is similar to a moving concentration front associated with concentration driven diffusion [2], then it holds that the effective diffusion distance, x_{eff}, can be related to the diffusion constant, D, and time, t, by Eq. (1) [18,19]:

$$x_{\mathrm{eff}} = \sqrt{Dt}. \tag{1}$$

It is realized the driving force, however, is not constant as the process is opposed by other growing twins and grain boundaries. As such, the twin-growth rate slows with time. Solving for D when $t = 0.27$ s and $x_{\mathrm{eff}} = 0.17$ nm as determined above gives a value for D of 1.07×10^{-15} cm^2/s. For the diffusion of oxygen in β-Ti, the diffusion constant at temperature, T, is related to the activation energy for diffusion, Q, by Eq. (2) as given by Claisse and Koenig [20]:

$$D = 0.083 \times \exp\left(\frac{-Q}{RT}\right). \tag{2}$$

Solving for Q when $D = 1.07 \times 10^{-15}$ cm^2/s and $T =$ 300 K gives an activation energy, Q, of 105 kJ/mol. This value is close to the experimental activation energy of 122 kJ/mol for the diffusion of oxygen in β-Ti determined by Claisse and Koenig [20]. The difference between the calculated value in this investigation and the value determined by Claisse and Koenig may be related to the various assumptions made in computing the Q values. Additional experimental support for the computed values comes from Hudson and Ankem [21]. They have measured the activation energy for the creep deformation of the β-Ti alloy seen in Figs. 2(a) and 2(b), and obtained a range of values from 39–112 kJ/mol. This range of values was attributed to different operating mechanisms of slip or twinning, depending on the creep strain. The value of 112 kJ/mol corresponds to the strain region where twinning is the predominant mechanism and twinning in turn is controlled by diffusion of oxygen as postulated above. Further indirect support to our model comes from the review of twinning in bcc alloys by Christian and Mahajan, which notes that the presence of interstitial oxygen, even at very low levels, hinders twin formation [22].

Slow growth of twins was also observed in a high-temperature superconductor, namely $YBa_2Cu_3O_{7-x}$ [7,8] with a perovskite-type crystal structure. Studies of the kinetics of twin growth in this material show that twinning dislocations glide in conjunction with oxygen jumping between lattice sites at the twin boundary, i.e., diffusion of oxygen. The activation energy for this twinning mechanism in $YBa_2Cu_3O_{7-x}$ was found to be close to that for oxygen diffusion in crystals with low oxygen content [7,8]. These studies are consistent with our twin models in metals which suggest that if oxygen is required to diffuse the activation energy for the twinning process is close to that of the activation energy for oxygen diffusion in the respective materials. However, the reason for the necessary diffusion of oxygen during the twinning process is different. In metals it is due to the elimination of octahedral sites, while in the superconductor the diffusion of oxygen is to maintain symmetry across the twin-matrix interface. Our model also has relevance to twin growth in geological systems, in that the slow growth of twins in geological materials has been attributed to the presence of impurities, and our model clearly explains how impurities that are present at the interstitial site can make the twinning process dependent on the diffusion of these interstitial impurity elements.

Given that the diffusion of oxygen, and hence the rate of twin growth in β titanium, depends on the number of interstitial sites occupied by oxygen, these results clearly suggest that a small variation in the amount of oxygen in the alloys can have a significant effect on the amount of ambient temperature creep deformation. Further, the twin-matrix boundary can act as a nucleation site for fatigue cracks, and the extent of creep deformation can have a direct effect on the structural integrity of components. The control of the amount of oxygen in the material, and hence the mechanical properties, can be optimized. In addition, this analysis can also be applied to the effect of other interstitials such as nitrogen. Our model can certainly explain why twins do not grow at the speed of sound all the time in metals. Further, our models can also help understand slow twin growth in various other crystalline materials including high-temperature superconductors as well as geological systems where slow twin growth was attributed to impurities in these materials.

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