Impurities Block the α to ω Martensitic Transformation in Titanium

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Impurities control phase stability and phase transformations in nature. Experiments and empirical databases are still central to tuning the impurity effects, since a broad theoretical underpinning is missing. Consider, for example, the titanium martensitic transformations, diffusionless structural transformations proceeding near the speed of sound. Pure Ti transforms from ductile α to brittle ω at 9 GPa creating serious technological problems for β-stabilized Ti alloys. Impurities in the Ti alloys A-70 and Ti-6Al-4V (wt. %) suppress the transformation up to at least 35 GPa enhancing their technological utility as lightweight materials. These and other empirical breakthroughs in technological materials call for broad theoretical understanding. Impurities pose two theoretical challenges: the effect on the relative phase stability and the energy barrier of the transformation. *Ab initio* methods calculate both changes due to impurities. In general, these effects are central to understanding structural phase transformations.

We have determined the energy and location of impurities in α and ω Ti and shown how they suppress the martensitic α → ω transformation (the phase diagram is shown in Fig. 1). Our approach exploits the basic observation that for any martensitic transformation the impurities are trapped in their local environment. We study a range of impurities, including those in the commercial Ti alloys A-70 and Ti-6Al-4V: interstitial O, N, C and substitutional Al and V. The interstitial impurities occupy the octahedral site in α and transform into the octahedral and hexahedral sites in ω. (See Fig. 2.)The impurities affect the transformation by shifting the relative stability of and energy barrier between the α and ω phases. Interstitial impurity effects are governed primarily by their size; they retard the transformation by increasing the energy barrier and shifting the relative stability. Substitutional impurities affect the transformation by changing the d-electron concentration; Al retards and V assists the transformation. (See Fig. 3.) The most important impurities, O in A-70 Ti and Al in Ti-6Al-4V, more than double the transition barrier and decrease the stability of ω, explaining the observed suppression of the transformation. The effect of impurities on relative energies and energy barriers is central to understanding structural phase transformations.

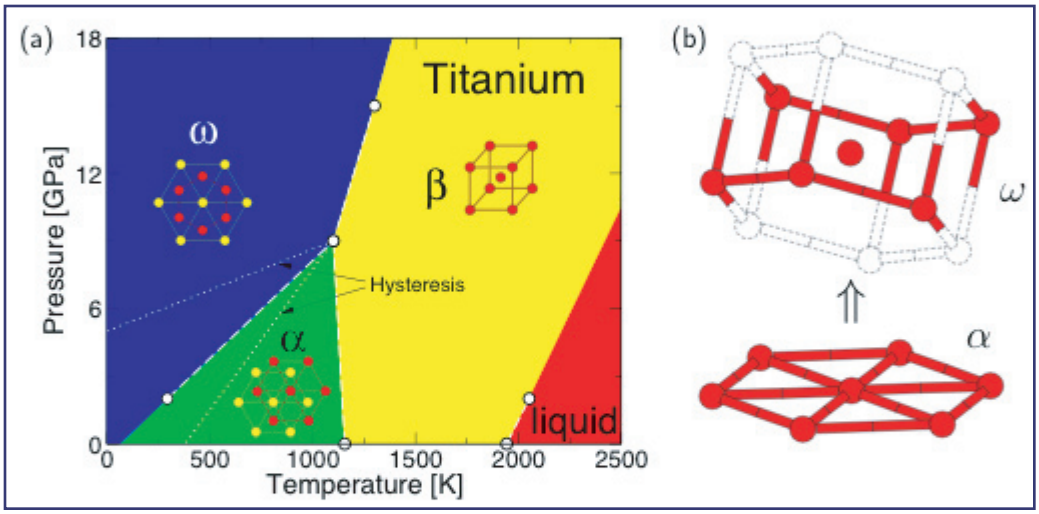

Figure 1—
Structural phase transitions in Ti. (a) The phase diagram of Ti as a function of temperature and pressure shows martensitic transformations between the α, β, and ω phases. (b) The transformation from α to ω proceeds via the TAO-1 mechanism [1]; shown is the transformation of one hexagonal basal plane of α to make the honeycomb and hexagonal planes in ω.

[1] D.R. Trinkle, R.G. Hennig, S.G. Srinivasan, D.M. Hatch, M.D. Jones, H.T. Stokes, R.C. Albers, and J.W. Wilkins, "A New Mechanism for the Alpha to Omega Martensitic Transformation in Pure Titanium," *Phys. Rev. Lett.* **91**, 025701 (2003).

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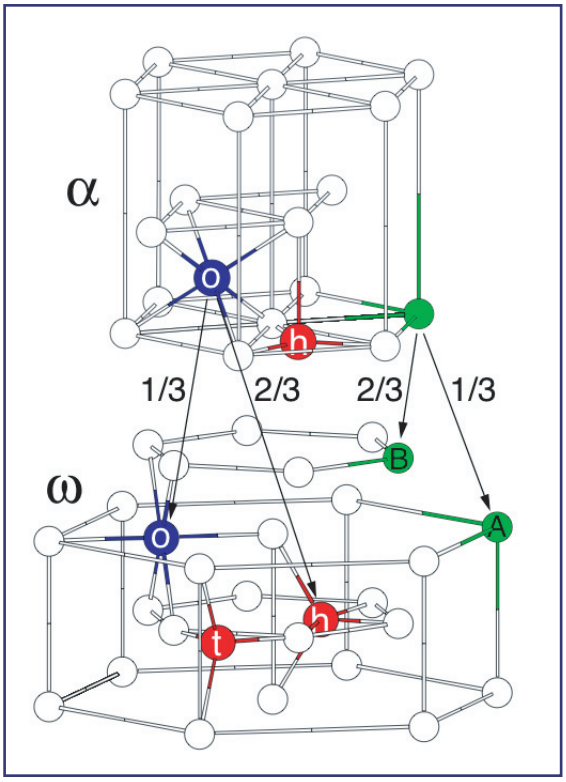

Figure 2—
Impurity sites in α and ω. Octahedral (o), tetrahedral (t), and hexahedral (h) sites for interstitial impurities as well as A and B sites for substitutional impurities in the α and ω phases. The α and ω phases each contain one unique o, t, and h site. The α_{tet} site relaxes to the nearby α_{hex} site for all three impurities (O, N, C). The hexahedral site is a distorted double-tetrahedral site with five neighbors. The arrows indicate the transformation of the impurity and lattice sites in the TAO-1 mechanism [1] and the relative ratios. For clarity, the relative orientation of α and ω in TAO-1 is not shown.

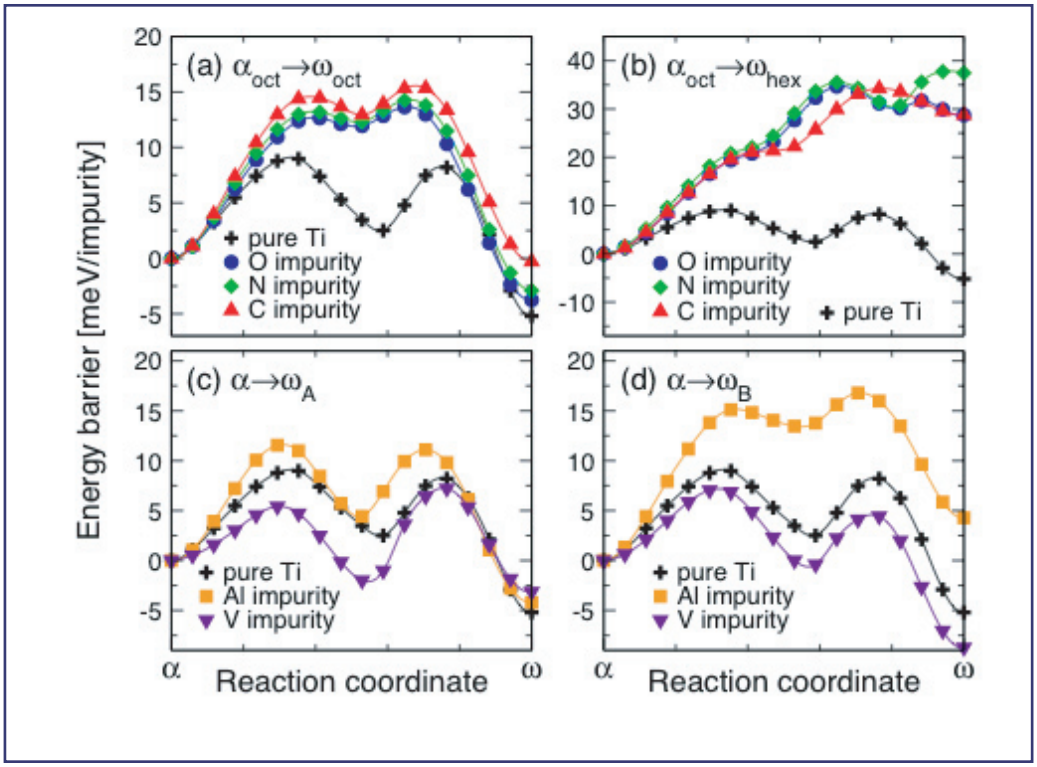

Figure 3—
Impurities change the energy barrier of the α→ω transformation. The energy barriers for the TAO-1 transformation [1] of interstitial and substitutional impurities in Ti are shown relative to the α phase in units of MeV per impurity atom. The defect concentration is 2 at. %. The endpoint energies match the formation energies for a defect concentration of 1 at. % within 1 meV/atom, providing an accuracy estimate for the barrier. The interstitial O, N, and C impurities occupy the α_{oct} and transform into either (a) ω_{oct} or (b) ω_{hex}, with a 1:2 ratio. The substitutional Al and V impurities transform in ω to either (c) the A site or (d) the B site, with a 1:2 ratio.