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Relative strength of phase stabilizers in titanium alloys

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Titanium alloys exhibit three distinct crystal structures: α, β, and ω. For various applications alloying elements can be used to stabilize the desired phase. Extensive data exist to determine the thermodynamic equilibrium phase, typically phase coexistence. However, the normal state of commercial alloys is a quenched solid solution. While alloy designers have well-established rules of thumb, rigorous theory for nonequilibrium single-phase crystal stability is less well established. We develop a theory to predict which phase a particular alloy will adopt, as a function of minor element concentration. We use two different methods based on density functional theory with pseudopotentials and plane waves, with either explicit atoms or the virtual crystal approximation (VCA). The former is highly reliable, while the latter makes a number of drastic assumptions that typically lead to poor results. Surprisingly, the agreement between the methods is good, showing that the approximations in the VCA are not important in determining the phase stability and elastic properties. This allows us to generalize, showing that the single-phase stability can be related linearly to the number of d electrons, independent of the actual alloying elements or details of their atomistic-level arrangement. This leads to a quantitative measure of β stabilization for each alloying transition metal.

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I. INTRODUCTION

Titanium alloys are important for many applications, especially in the aerospace industry, where low density, high strength, and corrosion resistance are paramount. Most commercial alloys contain secondary alloying elements such as V, Cr, Mo, Fe, Nb, Zr, La, Sn, or Al.

After some years of controversy, it is now generally accepted that at zero temperature the ω phase of Ti has the lowest free energy.[1,2] At finite temperature, vibrations and entropy play an important role. Under ambient conditions the α (hcp) phase becomes stable, and at high temperatures (above 1150 K) the β phase (bcc) is stabilized by a combination of electronic and phonon entropy. This complicated behavior is possible because the free energy of all three phases is very similar. Relatively small amounts of alloying elements alter these free energies, and can have a significant effect on the transformation temperature, perhaps eliminating it altogether.[3–5] There are also significant alloying effects on high-pressure structures.[6] The most common additives in Ti alloys are Al, which stabilizes α, and V and Cr, which favor β. Additives also play additional roles in machinability, corrosion, and hardening; however the unanticipated side effects on phase stability can be problematic: For example, La was expected to improve machinability by lowering melting points of β alloys, but in fact forms brittle LaSn precipitates which actually hinder machining.[7]

Density functional theory (DFT) calculations provide a reliable technique for calculating the Gibbs free energy, which determines the stability of crystal phases at ambient pressure. This is normally done by separately evaluating two contributions: H_0, the electronic ground-state enthalpy, and F_{vib}, a phonon contribution involving zero point energy, vibrational energy, and entropy.

A general rule appears to be that sp elements are α stabilizers while transition metals, even Zn and Cd which adopt the hcp structure, are β stabilizers. However, the strength of the stabilization effect is unquantified. Here we apply DFT to show that the effects of alloying with different elements may be treated quantitatively as a function of d-band filling only. This provides a modern confirmation and specific application of ideas that date back to Hume-Rothery.[8–12]

II. COMPUTATIONAL METHOD

The calculations are performed using CASTEP,[13] a plane-wave code with ultrasoft pseudopotentials[14] that we have thoroughly tested.[15] The generalized gradient approximation of Perdew and Wang with the Perdew-Burke-Ernzerhof parametrization[16] is used for the exchange-correlation energy. For chromium, scandium, titanium, and vanadium, we treat the semicore $3s$ and $3p$ states as valence states, in addition to the usual $3d$ and $4s$ states. Supercell sizes of up to 24 atoms are used to get impurity levels down to 4 at. %. A plane-wave cutoff of 500 eV is used to ensure energy convergence. The k-point mesh density used for each configuration is 0.05/Å. For supercells containing more than one impurity atom, a number of different chemical decorations were tried, using the special quasirandom structure (SQS) approach.[17] These lead to representative error bars in Fig. 1 and multiple points in Fig. 2. The small scatter of these points shows that local ordering typically contributes only a few meV per atom, although we note in passing that the local ordering does have a significant effect on the lattice parameter.

Elastic modulus calculations were carried out using finite stresses, with the internal positions allowed to rerelax. Changes in energies and analytic stresses then give two semi-independent (and consistent) measures of bulk and shear moduli. We found that the bulk modulus is insensitive to either local order or composition, but the shear moduli, particularly in β alloys, vary greatly between compositions.

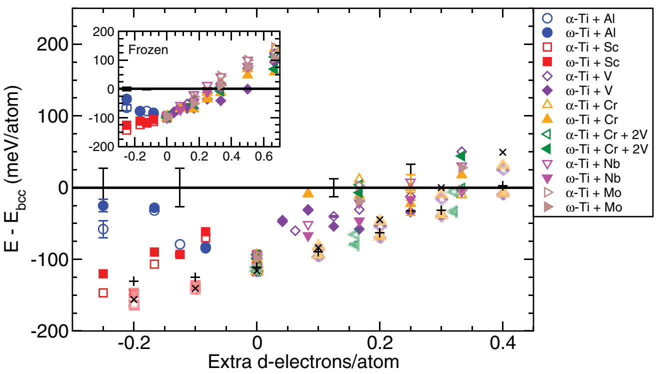

FIG. 1. (Color online) Phase stability of Ti-based alloys against number of valence electrons, calculated with the supercell method (dark symbols) and with VCA (light symbols). Open symbols denote the hcp phase and filled symbols denote the ω phase. Bcc is the reference. Alloying elements are coded on a color scale, with blue circles, Al; red squares, Sc; violet diamonds, V; orange up triangles, Cr; green left triangles, Cr + 2V; magenta down triangles, Nb; brown right triangles, Mo. Pluses are charged hcp and crosses are charged ω.

III. RESULTS AND DISCUSSION

The relative stability of Ti-X (X = Al, Cr, Mo, Nb, Sc, V) alloys for a range of concentrations is shown in Fig. 1. The inset shows results when the atoms are constrained to their crystal lattice sites, while the main figure allows all atoms to be relaxed within the broken symmetry due to the added impurities. In cases where the bcc structure is not mechanically stable, this full relaxation gives an unrepresentatively low energy for bcc, leading to the large apparent scatter on the left-hand part of the graph. The results show that the stabilization effect is insensitive to the short-range atomistic order in the cell, and ternary data show that the stabilizing effect is additive. Adding Sc, an α stabilizer,[18,19] counters the effects of V and Cr in exact proportion to its effect in reducing the number of valence electrons. By contrast the nontransition metal Al, although correctly found to be an α stabilizer, does not follow the linear relation. This observation leads us to propose that the effect of Sc, Nb, V, Cr, and Mo comes from the same mechanism, the filling of the d band. Furhermore, these results agree well with previous theoretical results on low-modulus Ti alloys[20–22] and with recent experimental results.[23]

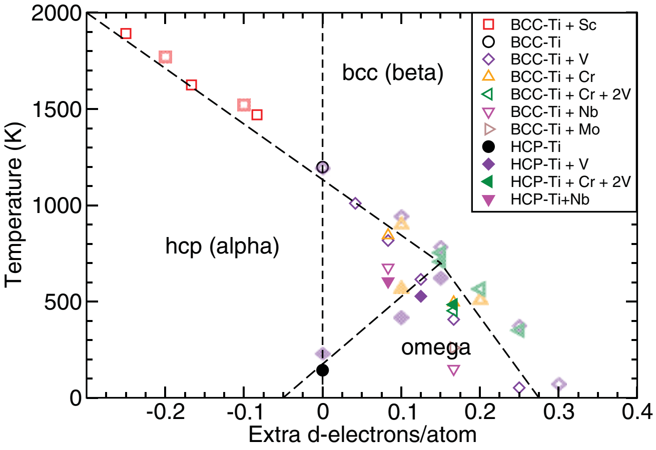

FIG. 2. (Color online) Phase diagram showing temperature against composition plotted as the number of valence electrons. Points show transition temperatures calculated with the supercell method (dark symbols) and with VCA (light symbols). Alloying elements are coded on a color scale as in Fig. 1. Approximate phase boundary lines are guides for the eye. The vertical dashed line is pure Ti, the reference. Binary diagrams can be deduced from this figure by considering only the data concerning a single alloying element and rescaling the x axis according to its valence.

To test this hypothesis, we repeat the calculations using the virtual crystal approximation (VCA)[24] as implemented in CASTEP.[13] The disordered alloy is modeled as a unit cell composed of mixture atoms defined by a pseudopotential that is generated as the weighted average of those for each atomic species. The same exchange correlation functional and other settings as in the supercell calculations above were used. The energy and stress tolerance for the cell relaxation is set to 5×10^{-5} eV and 2×10^{-2} eV/Å, respectively. The VCA has long been discarded as a method for reliable alloy calculations due to the inadequacy of relying on an "effective atom." For a metal, VCA produces the correct number of electrons per atom, but also an "averaged" density of states, which introduces an error if the local density of states is very different on the two atom types. Our d-filling hypothesis requires that the density of states is similar on all atoms, just as the VCA presupposes. Thus, we regard the VCA calculations not as a reliable description of the material, but as a test of the d-band filling hypothesis. As can be seen in Fig. 1, despite the lack of atomic detail, the VCA tracks the changes in phase stability well.

The d-band hypothesis implies that the VCA will fail completely to describe the p-band additive Al. Sure enough, we find this to be the case relaxing to unphysical volumes even with the same $1s2s2p$ core: This may be understood as due to the p band being full for the hybrid pseudoion, while it should not be for the Al ions.

A still-poorer approximation is to ignore alloying elements altogether and simply add electrons with a compensating background of positive charge. We use identical parameters as in the VCA calculations to investigate such "charged Ti" systems. Once again, Fig. 1 shows that the d-electron density alone stabilizes the β phase, in a way exactly equivalent to that obtained with electrons associated with supercells and explicit atoms.

The notion that d-electron density is the crucial quantity is only reasonable if the electronic density of states (DOS) is roughly composition independent. DOS calculated with both VCA and supercell calculations are shown in Fig. 3. It can be seen that they are indeed very similar in shape; the main effect of alloying is to move the Fermi level within the band. By contrast, the shape of the DOS for the Al-doped alloys is completely changed, once again showing that it is the d electrons, not the ionic charge, which is critical. Thus, we have shown that the enthalpy differences between the phases varies in proportion to the d-electron concentration.

To make contact with real materials for quantitative comparison, it is necessary to calculate free energy. Zero-point and finite temperature contributions to the free energy (F_{vib}) can be obtained in several ways.[25,26] A full quasiharmonic phonon calculation fails for bcc-Ti, because this has imaginary phonon frequencies and is in any case computationally impractical for the large supercells used here. Although self-consistent

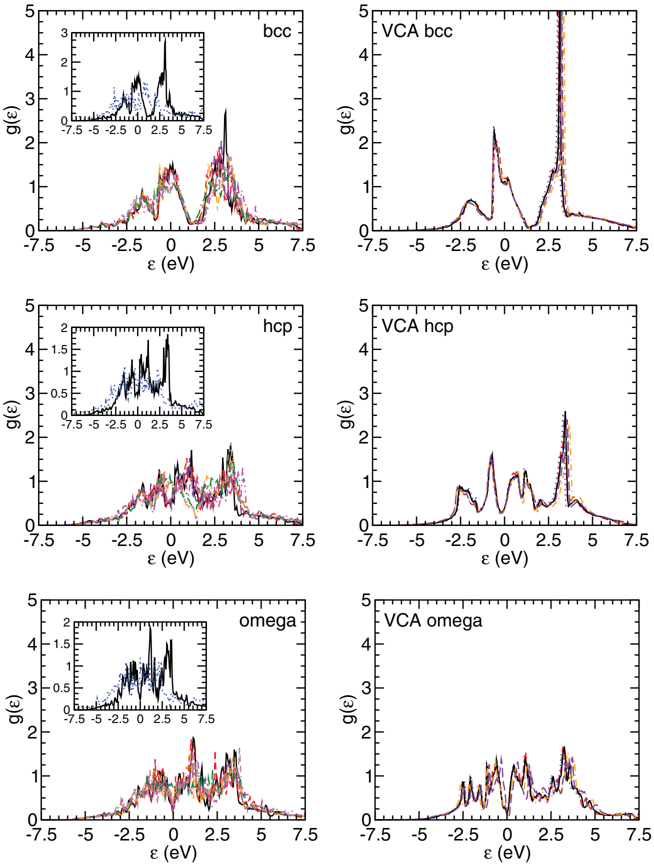

FIG. 3. (Color online) (Left) Density of electronic states for alloys in the different phases, calculated with pure Ti (solid black line), Ti + 25% Sc (dashed red line), Ti + 33% V (long-dashed violet line), Ti + 33% Nb (dot-dot-dashed magenta line), Ti + 16% Cr (dot-dashed orange line), Ti + 16% Mo (dash-dash-dotted brown line) and Ti + 8% Cr + 16% V (dot-long-dashed green line). The inset shows the DOS for Ti + 16% Al (dotted blue line), compared with pure Ti. (Right) The corresponding plots for VCA, calculated with $-0.2e$ charged Ti (dotted blue line), Ti + 20% Sc (dashed red line), pure Ti (solid black line), $+0.4e$ charged Ti (dot-dashed orange line), and Ti + 40% V, (long-dashed violet line).

phonon theory[27] has been shown to work for bcc-Ti, this is even more computationally demanding. A proven and practical method suitable for our purposes is to use the Debye approximation for the vibrational free energy.[28,29] The vibrational free energy per atom F_{vib} can then be expressed as

$$F_{\text{vib}}(\Theta_D,T) = \tfrac{9}{8}k_B\Theta_D - k_BT[D(\Theta_D/T) - 3\ln(1-\mathrm{e}^{-\Theta_D/T})], \qquad (1)$$

where $D(\Theta_D/T)$ is the Debye function.

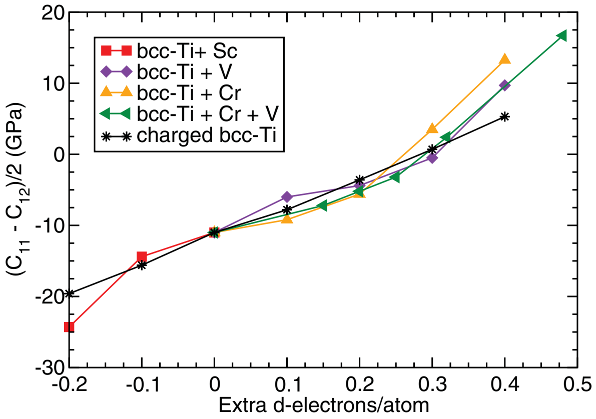

FIG. 4. (Color online) Elastic stability of bcc Ti-based alloys against number of valence electrons, calculated using VCA. The straight line, derived from simply adding electrons to a Ti supercell, gives $C' = -11.6 + 42\Delta n_d$.

We can determine the Debye temperature from

$$\Theta_D = \frac{\hbar}{k_B}[6\pi^2 v^{1/2}]^{1/3} v_D, \qquad (2)$$

where v is the volume per atom and v_D is the Debye sound speed, obtainable from the elastic constants, using the approach by Chen and Sundman.[30]

For pure Ti this gives $\Theta_D = 395$ K for the ω phase, $\Theta_D = 364$ K for the α phase,[29] and $\Theta_D = 276$ K for the β phase.[30] This is in good agreement with previous work and shows the correct ω-α-β sequence with increasing temperature.

Using these results, we evaluate the phase transition temperatures for each composition. From this, we can construct phase diagrams for each binary and ternary system, and we find these to be in good agreement with experiment where available. However, to illustrate our central concept that structure depends on the *d* electrons, we plot a combined phase diagram with *d*-electron number involving all Cr (+2), V (+1), and Sc (−1) alloys (Fig. 2). Remarkably, the phase boundaries for the individual systems are coincident when scaled in this way, a data collapse that provides strong support for our theory.

Furthermore, we investigate the bcc-stabilizing behavior of the Cr ($\Delta n_d = +2$), V ($\Delta n_d = +1$), and Sc ($\Delta n_d = -1$) alloys by computing the zero temperature elastic constants C_{ij} and the shear constant $C' = (C_{11} - C_{12})/2$ versus number of *d* electrons, using VCA. C' is known to be negative for pure Ti, and tuned close to zero for Ti-based gum metal[31] reflecting the mechanical instability of the structure. The results are shown in Table I and Fig. 4, showing that the variation in C' is also accounted for by the number of *d* electrons alone. Once again, the even simpler charged Ti system is included for comparison,

TABLE I. Elastic constants (GPa) of bcc Ti-*X* alloys.

Extra *d* electrons	−0.2	−0.1	0	0.1		0.2			0.3		0.4	
X	Sc	Sc	Ti	V	Cr	V	Cr	V-Cr	V	Cr	V	Cr
C_{11}	60	79	90	107	101	119	115	117	132	137	154	159
C_{12}	109	108	112	119	120	127	126	128	133	130	134	132
C_{44}	46	45	41	41	33	48	39	45	51	46	51	50

and even this follows the same pattern. Although C' varies with temperature, this contribution is only weakly dependent on composition, so the near-linear relation should hold at all T.

Finally, we turn to the underlying cause of the unstable bcc structure. As can be seen in Fig. 3, the Fermi level in pure bcc-Ti is coincident with a peak in the DOS for Ti. This is an unstable situation, wherein a Peierls-type lattice distortion can split the peak and lower the enthalpy. As more electrons are added to the d band, through V and Cr alloying, the Fermi energy moves away from the peak. Although we are here only calculating properties of Ti alloys, this picture has much in common with that obtained for canonical d bands.[32] The unstable mode is the T1N phonon which, coupled with a lattice distortion, is the established pathway for the bcc-hcp transition.

We have shown the alloying effects to be additive in multicomponent homogeneous material systems; however, we recall that in many ternary and higher mixtures aging will cause phase separation with different compositions in the phases.

IV. CONCLUSIONS

In conclusion, we are considering alloys produced by quenching, and therefore unable to phase-separate to the thermodynamic equilibrium. We find that chromium and vanadium stabilize the β phase, while scandium destabilizes it. The strength of the effect is directly proportional to the additional d electrons present in the alloying element. The effect appears to be additive, and the positional effects of the impurities appear to be small.

In the case of aluminum, our calculations show that it stabilizes the α phase, but the simple d-electron sum rule does not apply to this sp element.

While the correct stabilization predictions of pseudopotential calculations are unsurprising, we have also tested our hypothesis using VCA and extra-electron calculations, which correctly capture the aspects of the physics we think are important. The accurate results obtained from these normally unreliable methods give strong support to the d-electron picture.

This puts the empirically known effects of α and β stabilization on a firm theoretical footing. It also enables alloy designers to anticipate the phase-stabilizing effects of additions which may be added for other purposes. Finally, it emphasizes the need for the d-electron concentration to be considered as a parameter in any multiscale modeling approach.

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