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Electronic Origins of Anomalous Twin Boundary Energies in Hexagonal Close Packed Transition Metals

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Density-functional-theory calculations of twin-boundary (TB) energies in hexagonal close packed metals reveal anomalously low values for elemental Tc and Re, which can be lowered further by alloying with solutes that reduce the electron per atom ratio. The anomalous behavior is linked to atomic geometries in the interface similar to those observed in bulk tetrahedrally close packed phases. The results establish a link between TB energetics and the theory of bulk structural stability in transition metals that may prove useful in controlling mechanical behavior in alloy design.

Twinning is a common deformation mechanism in materials where the number of active dislocation slip systems is limited [1–5]. In such materials, understanding of the mechanisms underlying twin boundary (TB) formation can thus be essential for optimizing mechanical properties [6–9]. Theories of the crystallography of twinning and its relation to bulk deformation are well developed, and the mechanisms of twin nucleation and growth have been investigated in many technologically important systems [2]. However, the degree to which deformation twinning can be significantly influenced through variations in composition for materials design has been investigated in only a limited number of systems (e.g. [10–13]).

In this Letter we report results of a study of the properties of commonly observed deformation twins in hexagonal close packed (HCP)-structured transition metals, a class of materials that finds use in diverse applications including aerospace alloys, cladding for nuclear fuel, and magnetic recording. Through the use of density-functional-theory (DFT) calculations, we demonstrate anomalously low TB energies (γ_t) for the group VII transition metals, Re and Tc. This finding correlates with the unique mechanical properties of HCP-structured Re, which displays pronounced deformation twinning [14–17], and a unique combination of high temperature strength and low-temperature ductility [18] that have made it of interest for structural applications in extreme environments [18, 19]. To investigate the electronic origins of this anomalous twinning behavior, we introduce a new method for computing the composition dependence of γ_t in alloys. Results derived with this approach demon-

strate that TB energies in Re can be decreased even further through alloying with elements that lower the average number of d electrons per atom relative to pure Re. These predictions are consistent with experimental characterization studies undertaken in this work, demonstrating pronounced differences in deformation microstructures in Re versus Re-10 at. % W alloys. The anomalous TB energetics in the group VII metals are correlated with the presence of structural units near the TB plane that are similar to the Frank-Kasper polyhedra characterizing the tetrahedrally-close-packed (TCP) transition-metal intermetallic compounds that are stable near half d -band filling [20–24]. Through an analysis of the electronic structure, a link between the theory of bulk structural stability and TB energies is established, which may be useful in controlling the energetics underlying twin formation in the design of transition metal alloys with targeted mechanical properties.

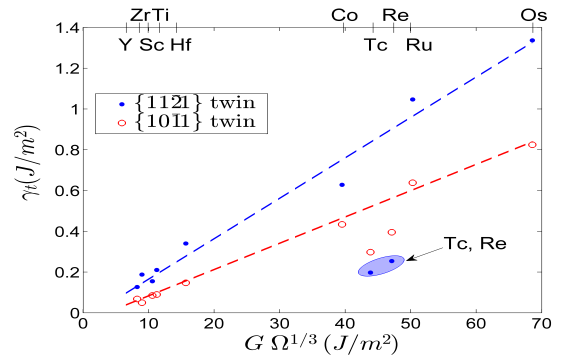


Figure 1: Calculated $\{10\bar{1}1\}$ and $\{11\bar{2}1\}$ twin boundary energies versus calculated values of the $G\Omega^{1/3}$, where G and Ω are shear modulus and atomic volume, respectively. Dashed lines are least-squares fits excluding the data for Re and Tc.

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In Fig. 1, results of DFT calculations of γ_t are plot-

ted for two commonly observed twins in HCP transition metals, which we will refer to by the twinning plane: $\{11\bar{2}1\}$ and $\{10\bar{1}1\}$. The calculations have been performed within the framework of the local density approximation to DFT [25, 26], using the Vienna ab-initio simulation package [27–29], as described in the Supplemental Material [ref]. The γ_t results in Fig. 1 are plotted as a function $G\Omega^{1/3}$, where G is the Voigt-Reuss-Hill averaged isotropic shear modulus [30]) and Ω is the atomic volume. With the notable exception of the group VII metals (Tc and Re), the results in Fig. 1 show (i) an overall trend towards increasing values of γ_t with the magnitude of $G\Omega^{1/3}$, and (ii) lower energetics for $\{10\bar{1}1\}$ relative to $\{11\bar{2}1\}$ TBs. The first observation is consistent with similar correlations reported previously for grain and twin boundaries in metals [31, 32], and is found to hold for TBs in other HCP metals based on the calculated values given in the Supplemental Material [ref.].

The results in Fig. 1 for the group VII elements Tc and Re stand out in two ways. First, the magnitudes of γ_t are lower than expected based on the dashed trend lines fit to all the other transition metals. This is particularly true for the $\{11\bar{2}1\}$ TB, for which γ_t for Tc and Re is more than a factor of five lower than that for Ru or Os, the neighboring elements in the periodic table. Second, Tc and Re are the only elements in the transition-metal series for which the $\{11\bar{2}1\}$ TB has a lower calculated energy than the $\{10\bar{1}1\}$ TB. Interestingly, the second of these two results is qualitatively consistent with experimental observations in deformed Re samples, which show a predominance of $\{11\bar{2}1\}$ twins [14, 15, 17]. An example is given in Fig. 2, which shows electron back scattered diffraction images for Re and Re-10 at. % W alloys deformed in compression at room temperature to strains of 6.8 % and 7.8 %, respectively. A detailed investigation of the dominant twin type was undertaken for these deformed polycrystalline samples, as described in the Supplemental Material [ref.]. Out of 1,040 twins investigated in pure Re all but 5 were found to be $\{11\bar{2}1\}$ type (the other five were of $\{10\bar{1}2\}$ type), and similarly 68 twins were analyzed in the Re-10 at. % W sample, all of which were of $\{11\bar{2}1\}$ type.

To further investigate the anomalous twinning behavior in the group VII transition metals, we focus on Re and examine the effect on γ_t resulting from alloying with neighboring elements in the periodic table. For this purpose we have developed a methodology for computing the energies of planar defects in substitutional alloys based on the special quasirandom structure (SQS) formalism. In the SQS approach a structure with a number of atoms small enough to be considered in DFT calculations is constructed with an atomic configuration for which the correlation functions for the near-neighbor shells mimics as closely as possible those for a random substitutional alloy [33–35]. In the present generalization of the approach we generate SQS which, in addition, give correlation func-

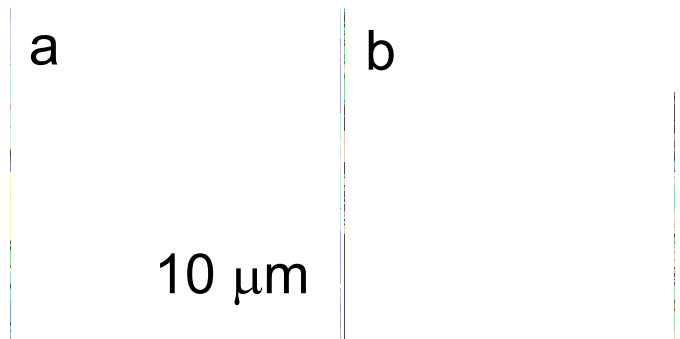


Figure 2: Electron back-scattered diffraction scans of a) pure Re deformed 6.8 % and b) a Re-10 at. % W alloy deformed 7.8 %. The colors represent crystallographic orientation as described by the legend top right. Black areas represent regions that were unable to be indexed due to surface pitting.

tions close to random values within the *local* vicinity of a plane where cleavage or shearing/shuffling operations are imposed to create a surface or TB, respectively. The accuracy of the scheme developed in this work has been assessed for model alloys described by classical potential models, as described in the Supplemental Material [ref.].

In the top panel of Fig. 3 we plot the variation of the DFT-calculated $\{11\bar{2}1\}$ γ_t for $\text{Re}_{0.912}\text{X}_{0.098}$ alloys, as a function of the solute species X . In the middle panel we also plot, for comparison, calculated basal-plane ($\{0001\}$) surface energies (γ_s) for the same alloys. The lower panel plots the value of an intrinsic ductility parameter $D = \gamma_s/\gamma_t$, which has been proposed for HCP metals where cleavage occurs on the basal plane, and where deformation twinning is the primary mechanism for plasticity under tensile loading parallel to the c axis [3, 4]. It can be seen that γ_t calculated for $\{11\bar{2}1\}$ TBs display a pronounced dependence on solute species: alloying with elements to the left (right) of Re is seen to give rise to a significant decrease (increase) in γ_t . Calculated γ_t values decrease by approximately 50 % when Re is alloyed with 9.8 at. % W or Ta, and increases by approximately the same magnitude with a comparable amount of alloying with Os or Ir. The $\{10\bar{1}1\}$ TB energy on the other hand (see Supplemental Fig. S4) shows an order of magnitude smaller variation for the same compositions. Similarly, the surface energy is seen to show relatively small variations with solute addition, and, as a consequence, alloying with elements to the left (right) is predicted to lead to a sharp increase (decrease) in the intrinsic ductility parameter D .

The computational prediction that alloying with W leads to a pronounced decrease in γ_t for the $\{11\bar{2}1\}$ TB is supported by a comparison of the deformation microstructures for Re and Re-10 at.% W alloys shown in Fig. 2. Specifically, the spacing (λ) between TBs in the twin variants for the Re-W alloy is considerably smaller than for pure Re. Generally, it is expected that a de-

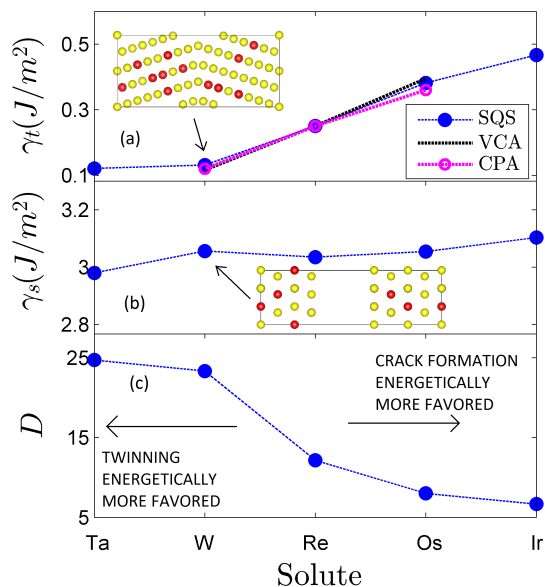


Figure 3: For Re-9.8 at. % X alloys, variations as a function of solute X, for (a) the $\{11\bar{2}1\}$ TB energy as calculated from SQS, VCA and KKR-CPA, (b) $\{0001\}$ surface energy calculated from SQS and (c) a ductility parameter, $D = \gamma_s/\gamma_t$.

crease in γ_t leads to a decreased value of λ [36] when all other conditions are roughly equal. This was verified by measuring twin thickness in approximately 50 grains from each material. Twins in the deformed Re and alloys samples were found to have an average thickness of 720 nm and 440 nm, respectively.

To probe the origin of the effect of alloying on γ_t for the $\{11\bar{2}1\}$ TB in Re, additional DFT calculations were performed based on the virtual crystal (VCA) and coherent potential (CPA) approximations, as described in the Supplemental Material [ref]. In these calculations the individual Re and solute atoms are replaced by single effective atoms with a concentration-weighted number of valence electrons or scattering properties, but without accounting for displacement effects associated with atomic size mismatch. The calculations thus allow investigation of the relative importance of electronic versus size effects underlying the concentration dependence of γ_t . In Fig. 3 (a) the slope of the $\{11\bar{2}1\}$ TB energy is well reproduced (to within approximately 5 %) by both VCA and KKR-CPA calculations, suggesting a direct link with the band energy. This finding is consistent with a comparison of the calculated electronic density of states (DOS) for bulk HCP Re, and supercells of Re containing $\{11\bar{2}1\}$ and $\{10\bar{1}1\}$ twins. As detailed in the Supplemental Material [ref.], the calculated DOS show that within a rigid-band model a reduction in band filling leads to (i) a lowering of the band energy contribution to γ_t for the $\{11\bar{2}1\}$ twin, and (ii) a lowering of the band energy for this twin relative to that for $\{10\bar{1}1\}$; both findings are qualitatively consistent with the results for alloying effects on γ_t in Re

presented above, and in the Supplemental Material [ref.].

Additional insights into the origin of the effect of band filling on γ_t for the $\{11\bar{2}1\}$ twin can be obtained by examining the local atomic structure in the TB plane. As indicated in Fig. 4 the nearest-neighbor coordination polyhedron for atoms in the $\{11\bar{2}1\}$ TB plane takes the shape of a distorted icosahedron (pentagonal bipyramidal prism). This polyhedron increases the number of triangular faces by 2 and reduces the number of square faces by one as compared to the anti-cubooctahedron polyhedron characteristic of the bulk HCP structure. In contrast, atoms in the $\{10\bar{1}1\}$ TB plane have two distinctly coordinated sites: a 13 coordinated site with 2 additional triangular faces, and an 11 coordinated site with 2 less triangular faces than the anti-cubooctahedron shell of HCP. Therefore, for the $\{10\bar{1}1\}$ TB the total number of triangular and square faces averaged over the coordination polyhedra of the two interface sites are the same as in bulk HCP. An increase in the fraction triangular faces in the coordination polyhedra of the $\{11\bar{2}1\}$ TB makes the interface atomic structure similar to tetrahedrally close packed (TCP) structures, such as the well-known σ , χ and A15 Frank-Kasper structures, where coordination polyhedra have exclusively triangular faces. The TCP phases occur in transition metals and their alloys at characteristic valence electron/atom (e/a) ratios intermediate between Re and W [20].

A connection between these geometrical considerations, and the effects of band filling on γ_t for $\{11\bar{2}1\}$ twins in Re can be made through consideration of a moments analysis of the DOS [37, 38]. Previous work has demonstrated that for transition metals near half d -band filling, the relative stability of structures with similar second moments (i.e., with similar bond lengths and coordination numbers) can be understood based on the fourth moment of the DOS. It has been shown that near half d -band fillings, the nearest neighbor square clusters found in the HCP structure are penalized energetically relative to tetrahedral configurations (as found in TCP phases, and reflected by triangular faces on the coordination polyhedron), due to their contribution to the fourth moment [39–41]. This is consistent with our finding that the $\{11\bar{2}1\}$ twin shows an anomalous energetic stabilization with band fillings near to and slightly lower than Re: the atoms on and near the twin plane exhibit environments built from tetrahedra and distorted squares, instead of the planar nearest-neighbor square clusters found in the bulk HCP structure.

This model is supported by calculations of the moments of the local DOS (LDOS) for atoms as a function of distance from the TB. The n -th moment of the LDOS (d_i) for atom i is defined as $\mu_i^{(n)} = \int_{-\infty}^{\infty} (E - \varepsilon_i)^n d_i(E) dE$, where ε_i is the center of gravity [42]. A “bimodality” parameter can be defined as $s = \{\mu^{(4)}\mu^{(2)} - (\mu^{(2)})^3 - (\mu^{(3)})^2\}/(\mu^{(2)})^3$ [42], such that a completely bimodal

LDOS corresponds to $s = 0$, while for $s < 1$ ($s > 1$) the LDOS is said to exhibit bimodal (unimodal) behavior. As shown in Fig. 4 (d), for the atoms near the $\{11\bar{2}1\}$ twin plane, $s < 1$ whereas far away from the twin $s > 1$. Hence, atoms on the twin plane exhibit a more bimodal LDOS that those in the HCP environment. Thus the low values of γ_t for the $\{11\bar{2}1\}$ TB can be understood by analogy with earlier work [23] showing that large stabilizing contributions to the atomic geometries of TCP structures, which are similar to those found in the twin plane, arise from hopping paths that produce a more bimodal DOS, with an associated enhanced energetic stabilization, near half d -band filling.

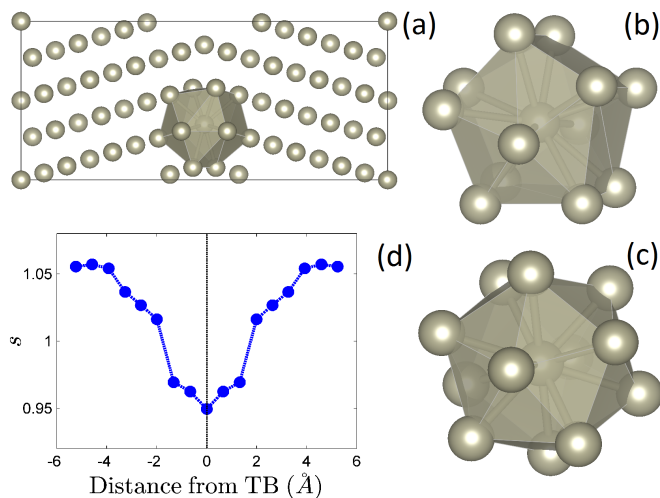


Figure 4: (a) The $\{11\bar{2}1\}$ TB, viewed in projection along an $[1\bar{1}00]$ direction, highlighting a distorted icosahedron on the TB plane, (b) detailed view of the distorted icosahedron as found in the $\{11\bar{2}1\}$ TB, (c) an undistorted Z12 icosahedron, and (d) the calculated bimodality parameter s as a function of distance relative to the TB plane.

In summary, we have undertaken DFT calculations demonstrating anomalously low energies for $\{11\bar{2}1\}$ TBs in the group VII transition metals. Additionally, we have shown for Re that the energy of this TB can be significantly lowered further by alloying with elements that decrease the filling of the d band relative to pure Re. The theoretical results are consistent with experimental observations of pronounced twinning in the deformation microstructures of Re and Re-W alloys, as γ_t is an important factor affecting twin nucleation (e.g. [43, 44]). Based on an analysis of the electronic and atomic structures of Re $\{11\bar{2}1\}$ and $\{10\bar{1}1\}$ TBs it is argued that the anomalously low energies of $\{11\bar{2}1\}$ twins originate from the presence of structural units at the interface which are stabilized for d band fillings intermediate between those characteristic of group VI and VII transition metals. The results thus suggest a strategy for the selection of alloying species that may be utilized to control twin activity in the design of transition metals with optimized mechani-

cal properties. In particular, the results suggest strategies for designing alloys that mimic the unique properties of Re by choosing combinations of alloying elements that lead to similar overall band fillings.

More generally, the results demonstrate a link between electronic structure and interfacial stability that may be effective in controlling interface-related properties of transition-metal alloys more generally. Specifically, the tuning of d band filling to stabilize specific atomic configurations may represent an effective strategy in stabilizing grain and twin boundaries that feature a high fraction of such structural units. Thus, classical theories of bulk phase stability in transition metals can provide guidelines for “interfacial engineering” of transition-metal alloys with properties controlled by their interfaces.

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