Surface energy and its anisotropy of hexagonal close-packed metals

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ABSTRACT

The surface energy and its anisotropy of 13 hexagonal close-packed (HCP) metals have been investigated via a broken-bond based geometric model. The model can assess arbitrary orientations which are difficult to construct in atomistic simulations. Using only three material dependent parameters, our results are in good agreement with the majority of reported experimental values. An exception occurs in the cases of divalent sp metals, namely Mg, Zn and Cd, for which the calculated values are lower by a factor of 2. For all 13 metals, the stereographic projections of surface energy demonstrate strong six-fold symmetries with a global minimum on (0001) pole, whereas the actual projection patterns are unique for every element. The overall anisotropy is found to be 15% to 21%. The equilibrium crystal shape of HCP metals is found to be a truncated hexagonal bi-prism, with the (0001) facets always shown, but the bi-prismatic facets vary from one metal to another. The detailed anisotropy of surface energy is found to be largely determined by an anharmonicity factor η. The results of metals possessing comparatively low η, namely Be, Sc, Ti, Y, Zr and Hf, are in better agreement with experimental findings. We believe the surface energy anisotropy of these elements is more representative for HCP metals.

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1. Introduction

Surface energy is one of the most important fundamental quantities in the context of surface science. It has a significant impact on the structure and properties of a material [1–3], and controls how it reacts to its surroundings [4,5]. In contrast to its counterpart of non-crystalline phases, the surface energy of crystalline substances exhibits orientation-dependent behaviour [6,7], which is originated from the long-range structural order. The surface energy anisotropy of a crystalline substance is dependent on its lattice structure as well as the physical and chemical environments under which the surface is presented. As such, an improved understanding of the surface energy and its anisotropy helps with the manipulation of not only surface properties such as its energy absorption and catalytic capacity, but also bulk properties including toughness and fatigue resistance.

Direct measurement of the surface energy remains challenging. By far the best experimental approach relies on analysis of carefully equilibrated crystallites [8–10]. Such process is reliable for some materials but not the others, and has low reproducibility. Alternatively, a large part of modern understanding on the topic of surface energy is obtained via computational methods, such as density-function theories (DFT), embedded-atom methods (EAM) and other semi-empirical approaches [11–24]. Substantial computational resource is required to calculate the full anisotropy of surface energy for atomically complex surfaces.

Being regarded as brittle materials thus overlooked in the past, hexagonal close-packed (HCP) metals attract a recent resurgence of interests, owing to some of the unique properties they possess. Nonetheless, compare to cubic metals, the knowledge regarding HCP metals in the context of surface energy, particularly its anisotropy, is somewhat limited. Following our recent work on face-centred cubic (FCC) metals [25], an improved Mackenzie's broken-bond model has been developed for HCP metals. Combining with the Rose–Vinet universal potential, the new model is used to study the absolute unrelaxed surface energy and its orientation-dependence of 13 HCP metals. Only three input parameters, namely the lattice constant, the bulk modulus and the cohesive energy, are employed in the model. The method allows construction of three-dimensional γ-plots which lead to some new interesting understandings of the subject. The naturally favoured facets of HCP metals are revisited base on these findings.

The remainder of this paper is organized as follows. Section 2 introduces the theoretical parts of our model. Results and discussions are presented in Section 3. Section 4 concludes our work.

2. Theory

According to Herring [26], the excessive energy of surface with orientation $\hat{\mathbf{n}}$ can be expressed as

$$\Gamma(\hat{\mathbf{n}}) = \frac{1}{2}\sum f_{\mathbf{b}}(\mathbf{b})\phi_{\mathbf{b}} \tag{1}$$

where $\phi_{\mathbf{b}}$ denotes the energetic contribution from a two-body type interaction between atoms linked by vector $\mathbf{b}$, and $f_{\mathbf{b}}$ is the amount of

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b type bonds broken upon the creation of a pair of such surface. It is generally questionable whether such two-body formalism is physically representative for metallic systems. However, in our latest work on FCC metals [25], we demonstrated how the many-body contribution in an EAM type potential can be renormalised into an expansion of pair-wise interactions by exploiting a large coordination shell. Following the same treatment, Eq. (1) can be rewritten as

$$\Gamma(\hat{\mathbf{n}}) = \frac{1}{2}\sum_i f_{\mathbf{b^i}}\left(\mathbf{b^i}\right)\phi_{\mathbf{b^i}} \tag{2}$$

where $\mathbf{b^i}$ represents a set of crystallographically equivalent vectors. The strength of $\phi_{\mathbf{b^i}}$ terms are estimated via the Rose–Vinet universal potential [27], which takes the following form

$$E(r) = -E_c\left(1 + a^* + 0.05a^{*3}\right)e^{-a^*} \tag{3}$$

$$a^* = \eta\left(\frac{r}{r_e} - 1\right) \tag{4}$$

$$\eta = \sqrt{\frac{9\Omega B}{E_c}} \tag{5}$$

where E_c is the atomic cohesive energy, Ω represents the atomic volume, B denotes the bulk modulus and r_e refers to the equilibrium nearest neighbour (1st NN) distance. The width of this potential well is inversely proportional to the dimensionless anharmonicity term η. The strength of $\phi_{\mathbf{b^i}}$ terms in Eq. (2) is related to the strength ratio between the ith NN and 1st NN interactions, $\frac{\phi_{\mathbf{b^i}}}{\phi_{\mathbf{b^1}}}$, which can be approximated given the interatomic distance ratio between the ith NN and 1st NN interactions, $\frac{|\mathbf{b^i}|}{|\mathbf{b^1}|}$, and η, as follows

$$\frac{\phi_{\mathbf{b^i}}}{\phi_{\mathbf{b^1}}} = \left(1 + \eta\left(\frac{|\mathbf{b^i}|}{|\mathbf{b^1}|} - 1\right) + 0.05\eta^3\left(\frac{|\mathbf{b^i}|}{|\mathbf{b^1}|} - 1\right)^3\right)e^{-\eta\left(\frac{|\mathbf{b^i}|}{|\mathbf{b^1}|} - 1\right)}. \tag{6}$$

For cubic structures, the neighbouring order of a particular set of $\mathbf{b^i}$ is indifferent from one crystal to another. For HCP structures, on the other hand, the ordering of neighbour is dependent on the actual c/a ratio which varies from one lattice to another, as the hexagonal metals are not exactly "close-packed". In addition, the symmetries presented in HCP lattice are more complicated as compared with cubic systems. In this paper, the 7 nearest $\mathbf{b^i}$ sets are considered in our calculation of surface energy regardless of their neighbouring order. The significant $\mathbf{b^i}$ sets are labelled alphabetically, rather than numerically as in our previous work. An example of each $\mathbf{b^i}$ set vector is given in Fig. 1. The co-ordination numbers and bond length (as a function of a and c) of the $\mathbf{b^i}$ vectors are listed in Table 1. The 0 K zero pressure value of the three input parameters, anharmonicity factor η, 1st NN bond strength $\phi_{\mathbf{b^1}}$ and the relative bond strengths (as compared to $\phi_{\mathbf{b^1}}$) of $\mathbf{b^i}$ vectors for 13 elemental HCP metals are given in Table 2.

In a broken-bond method, the excessive energy of a surface with outward normal $\hat{\mathbf{n}}$ is calculated from the strength and number of destroyed bond vectors $\mathbf{b}$ upon the creation of the surface. For a specific $\mathbf{b}$ vector to be broken thus it contributes to the calculated surface energy, the following two conditions must be fulfilled: 1) the projection of $\mathbf{b}$ on $\hat{\mathbf{n}}$ must be in the same orientation as $\hat{\mathbf{n}}$, which gives $\hat{\mathbf{n}} \cdot \mathbf{b} > 0$; and 2) the parent atom of $\mathbf{b}$ vector must reside within the projection of the bond length on $\hat{\mathbf{n}}$ to be considered as a "surface atom". As such, if atomic
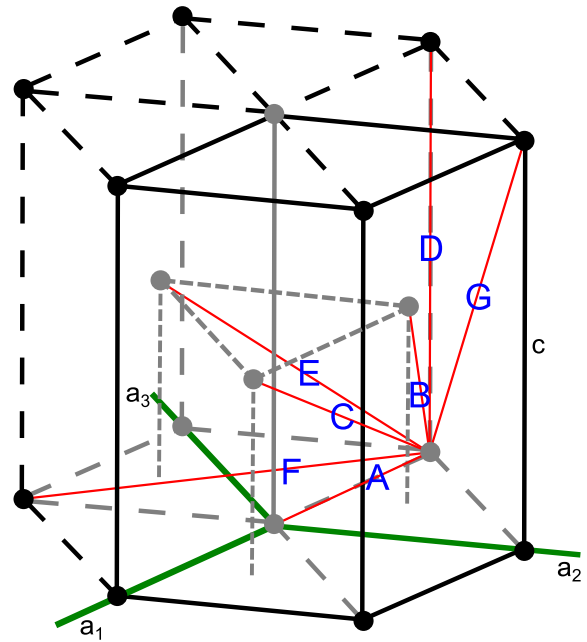

Fig. 1. A HCP cell showing the nature of $\mathbf{b^i}$ vectors. The vectors are labelled as referred to in Tables 1 and 2.

volume is denoted as Ω, the areal broken-bond density, $\overline{f}_{\mathbf{b}}$, can be expressed in the following piece-wise manner

$$\begin{aligned}\overline{f}_{\mathbf{b^i}} &= \frac{1}{\Omega}\sum_i \hat{\mathbf{n}} \cdot \mathbf{b^i} \quad \text{for} \quad \hat{\mathbf{n}} \cdot \mathbf{b} > 0 \\ &= 0 \quad\quad\quad\quad \text{for} \quad \hat{\mathbf{n}} \cdot \mathbf{b} \le 0\end{aligned} \tag{7}$$

Eq. (7) can be used for cubic systems without further modification. However, the concept of bonding geometry needs to be considered before applying Eq. (7) for hexagonal metals. Unlike the atoms in cubic crystals, which have a share of a fixed set of significant $\mathbf{b}$ vectors, the atoms in HCP crystals have two different sets of significant $\mathbf{b}$ vectors. In other words, an HCP atom has one of the two bonding ge-ometries associated with its lattice structure. An example on the $\mathbf{b^B}$ vectors is given in Fig. 2. It can be seen that the layer A atoms share a set of six $\mathbf{b^B}$ vectors coloured in blue, whereas all layer B atoms share the other set of six $\mathbf{b^B}$ vectors coloured in red. This discrepancy occurs when $\mathbf{b^B}$ vectors climb into alternative atomic layers, leading to two distinctive bonding geometries possessed by layer A atoms and layer B atoms respectively. This difference in bonding geometry affects the bond sets $\mathbf{b^B}$, $\mathbf{b^C}$ and $\mathbf{b^E}$. Consider the fact that layers type A and type B where each contains half of the total atoms in the lattice, the two bonding geometries will have equal chances to occur for a specific surface atom.

Table 1
The nature, the corresponding coordination number $Z_{\mathbf{b^i}}$ and the length of significant $\mathbf{b^i}$ vectors presented in HCP lattice.

	Nature of bond vector	Coordination number $Z_{\mathbf{b^i}}$	$|\mathbf{b^i}|$
$\mathbf{b^A}$	$\{11\overline{2}0\}$	6	a
$\mathbf{b^B}$	$\{2\overline{2}03\}$	6	$\sqrt{1/3a^2 + 1/4c^2}$
$\mathbf{b^C}$	$\{4\overline{4}03\}$	6	$\sqrt{4/3a^2 + 1/4c^2}$
$\mathbf{b^D}$	$\{0001\}$	2	c
$\mathbf{b^E}$	$\{12\overline{3}1\}$	12	$\sqrt{7/3a^2 + 1/4c^2}$
$\mathbf{b^F}$	$\{1\overline{1}00\}$	6	$\sqrt{3}a$
$\mathbf{b^G}$	$\{11\overline{2}1\}$	12	$\sqrt{a^2 + c^2}$