Surface Science 624 (2014) 103–111

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Influences of the third and fourth nearest neighbouring interactions on the surface anisotropy of face-centred-cubic metals

Yongkun Luo, Rongshan Qin *

Department of Materials, Imperial College London, SW7 2AZ London, United Kingdom

ARTICLE INFO

Article history:
Received 7 October 2013
Accepted 6 February 2014
Available online 15 February 2014

Keywords:
Surface energy
Surface anisotropy
Surface structure
Equilibrium crystal shape

ABSTRACT

The structure and the anisotropic properties of the surfaces of face-centred-cubic (FCC) metals have been studied using the broken-bond model while considering the third and fourth nearest neighbouring (3rd and 4th NN) interactions. The pair potential expressions are obtained using the Rose–Vinet universal potential equation. The model is suitable for calculation of the property of a surface with arbitrary crystallographic orientations and can provide absolute unrelaxed surface energy values using three input parameters, namely the lattice constant, bulk modulus and cohesive energy. These parameters are available for the majority of FCC metals. The numerical results for 7 FCC metals have been obtained and compared with these obtained from ab initio calculations and experimental measurements. Good agreement is observed between the two. Taking into account up to the 4th NN interactions, the overall surface energy anisotropy for FCC metals was found to be between 12% to 16%, and the ratio between the surface energies at (100) and (111) planes was found to be 1.05. These values are less than those reported by conventional calculations but more similar to experimental measurements. It is found that the strength of 3rd and 4th NN interactions differs from one element to another, the Ni and Cu interactions being the most significant while the Au, Pt and Pb interactions are the least significant. This suggests that the polar diagrams of the surface energy of Ni and Cu are different from those of Au, Pt and Pb by showing cusps of the unconventional {110} and high-index {210}, {311} and possibly {135} poles. This provides explanations to the recent experimental observations of the {110}, {210}, {311} and {135} facets in equilibrated Ni and Cu crystallines.

1. Introduction

The interaction between the surface of a crystal and its surroundings is orientation-dependent. Examples include the enhanced catalytic capability of some high-index facets of a Pt nanocrystal [1–4], the texture evolution of abnormal grains on metallic thin films [5,6] and the anisotropic growth of corrosion pits in engineering alloys [7]. All of these phenomena are attributed to the orientation-dependent surface energy, which appears to be the nature of crystalline materials that possess structures of long-range order. The study of surface energy anisotropy is of fundamental importance in the understanding of the behaviours of engineering metals.

In order to form a complete analysis of surface anisotropy and completely grasp its nature, its value at all possible crystallographic orientations must be known. However, there is no sophisticated experimental method that can guarantee the creation of a surface of desired orientation. The closest experimental feat achievable is usually an equilibrated crystal containing facets of a few specific orientations. Most of the orientations are rarely seen in experiments. In addition, the surface energy is a thermodynamic term that varies with temperature, pressure and also extremely sensitive to the atmosphere [8–13]. Direct measurements of surface energy anisotropy are unlikely to be achieved. Computational methods, e.g. the embedded-atom models (EAM) [14–16], have shown considerable success. Nonetheless, these methods calculate one particular surface orientation at a time and have only proposed information on a few low-index facets.

In this study, a broken-bond model which considers up to the fourth nearest neighbouring (4th NN) interactions has been implemented to study the structure and properties of FCC metal surfaces. The Rose–Vinet universal potential equation has been implemented within the model, which is able to provide the absolute unrelaxed surface energy of FCC metals at all crystallographic orientations. It relies on only three input parameters, namely the lattice constant a, the bulk modulus B and the cohesive energy E_c. The numerical results for 7 FCC metals at 0 K zero and pressure show good agreement with experimental findings and ab initio calculations. By considering the 3rd and 4th NN interactions, the overall anisotropy for FCC metals is found to be roughly 12% to 16% and the ratio between the surface energy at (100) and (111) is obtained as 1.05. The values are smaller than conventional findings but in better agreement with recent experimental measurements. We also discover that, contrary to popular belief, the {110}, {210}, {311} and {135} facets

* Corresponding author.
E-mail addresses: yongkun.luo08@imperial.ac.uk (Y. Luo), r.qin@imperial.ac.uk (R. Qin).

http://dx.doi.org/10.1016/j.susc.2014.02.010
0039-6028/

are actually favoured for FCC metals. This explains the existence of these facets in recent studies on equilibrated Ni and Cu crystallites.

The present article is organised as follows. Section 2 provides details for the theoretical aspects of the model and introduces the role of the Rose–Vinet universal potential equation. Section 3 reviews the conventional broken-bond model by Mackenzie et al. [17] and explains the method to investigate the breaking of NN interactions on surface. Section 4 presents the numerical results, including both the absolute surface energy and the polar-diagram of surface energy (γ-plot), together with comparison and discussion with both experimental and other theoretical works. Finally Section 5 summarises the work.

2. Theory

In this paper we only consider mono-atomic metals. A simple interpretation of surface energy is the amount of energy required to break all the chemical bonds during the creation of a pair of new surfaces. In this sense, the specific surface energy for a surface with outward normal $\hat{\mathbf{n}}$, $\Gamma(\hat{\mathbf{n}})$, could be expressed simply as half of the summation of binding energy 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 bond strength or pair-wise interaction energy between two atoms linked by vector $\mathbf{b}$, and $f_{\mathbf{b}}$ is the amount of $\mathbf{b}$ type interactions destroyed for the creation of a pair of such surface. Eq. (1) is straightforward for covalently bonded crystals. In the case of metallic materials, on the other hand, the atomic potential energies could not be fully divided into two-body bondings, thus the term $\phi_{\mathbf{b}}$ is not clearly defined. As suggested by Baskes, EAM type N-body potential yields the following expression for surface energy [18]:

$$E^f_{(x)} = \sum \frac{E_c\frac{Z_i - Z_d}{Z_i} + F_i\frac{\overline{\rho}_i^{\,x}}{Z_i} - \frac{Z_d}{Z_i}\cdot F_i\frac{\overline{\rho}_i^{\,0}}{Z_i}}{A_{(x)}} \tag{2}$$

where E_c is the cohesive energy of reference lattice; $\overline{\rho}_i^{\,x}$ and $\overline{\rho}_i^{\,0}$ refer to the background electron density of surface sites and bulk (reference) site respectively; Z_d and Z_i denote the coordination number of the surface site and bulk site atoms respectively; $A_{(x)}$ represents the area per atom near surface; and finally F_i, the embedding function, generally takes the following form [18,19]:

$$F(\overline{\rho}) = \alpha_i E_c \overline{\rho}\ln\overline{\rho} \tag{3}$$

where α_i is an adjustable parameter. We make a coarse assumption that $\frac{\overline{\rho}_i^{\,x}}{\overline{\rho}_i^{\,0}} \propto \frac{Z_d}{Z_i}$ for unrelaxed mono-atomic lattice with fixed structure. Combining the above assumption with Eqs. (2) and (3) gives:

$$E^f_{(x)} = \sum \frac{E_c\frac{Z_i - Z_d}{Z_i} + \alpha_i E_c \overline{\rho}_i^{\,0}\frac{Z_d}{Z_i^2}\ln\left(\frac{Z_d}{Z_i}\right)}{A_{(x)}}. \tag{4}$$

Note that the second part of Eq. (4) scales with $1/{Z_i}^2$. This means that the impact of this N-body part is reduced if many coordination shells are exploited in pair-potential expansion. Such finding is in agreement with the work by Vitos et al. [20], who proposed that neglected N-body terms can be partly "renormalized" into the so called "effective pair interactions" when many coordination shells are used. A similar concept of "effective pair potential" is also mentioned by Da silva et al. [21]. Da silva and co-authors performed ab initio calculation on the surface energy of 15 different Cu facets and found an "almost perfect" linear relationship between the surface energy and the number of broken NN bonds. Such linear scaling of surface energy as a function of the number of broken NN interactions is also confirmed in ab initio studies on pure Pb [22] and Ni [23] surfaces.

Base on the above consideration, we decide to neglect the N-body parts in Eq. (4), but instead consider further NN interactions to compensate such error. The main reason of such simplification is to avoid the usage of free parameter α, as the present model is intended to be kept readily assessable from minimal amount of experimental data. Qualitatively speaking, the above simplification overestimates the contribution of 1st NN interactions on surface energy, thus also overestimates the overall surface energy and anisotropy. The quantitative consequences of such simplification will be dependent on the actual N-body model employed. Based on the fact that the term $\frac{Z_d}{Z_i}$ typically ≥ 0.5 and our consideration includes 4th NN interactions, the multi-body term in Eq. (4) can be as large as 3% E_c depending on the choice of α. Therefore, it should be emphasised that the N-body term is still important and should be taken into account if reliable models are available.

Adopting above simplification, the expansion of the effective pair potentials based on Eq. (1) yields:

$$\Gamma(\hat{\mathbf{n}}) = \frac{1}{2}\left(f_{\mathbf{b}^1}\left(\mathbf{b}^1\right)\phi_{\mathbf{b}^1} + f_{\mathbf{b}^2}\left(\mathbf{b}^2\right)\phi_{\mathbf{b}^2} + f_{\mathbf{b}^3}\left(\mathbf{b}^3\right)\phi_{\mathbf{b}^3} + \ldots\right) \tag{5}$$

where $\mathbf{b}^{\mathbf{i}}$ represents a set of crystallographically equivalent vectors which belong to the ith NN interactions. Now we make an important assumption that all $\phi_{\mathbf{b}^{\mathbf{i}}}$ terms could be described using the same $\phi(r)$ potential function. It should be noted that this assumption is only true when all atoms share identical spherical atomic electron distributions, which turns out to be more realistic for pure metals. In covalent or ionic systems, where the atomic electron cloud is polarised, an atom's 1st NN and 2nd NN interactions cannot be described by a single potential function. Based on this assumption, by choosing a suitable potential function, the relative significances of the ith NN interactions could be determined from the difference in inter-atomic distance.

At this point we employ the Rose–Vinet universal interaction equation [24], which had been repeatedly treated as a fitting target for reference structures [19]. For a structure in thermal equilibrium the potential energy, E, of a lattice atom as a function of the inter-atomic distance, r, is expressed as

$$E(r) = -E_c\left(1 + a^* + 0.05{a^*}^3\right)e^{-a^*} \tag{6}$$

$$a^* = \eta\left(\frac{r}{r_e} - 1\right) \tag{7}$$

$$\eta = \sqrt{\frac{9\Omega B}{E_c}} \tag{8}$$

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 dimensionless anharmonicity term η controls the width of this potential well, which decreases as η increases. Adopting the Rose–Vinet potential function, the strength ratio between the ith NN and 1st NN interactions (the relative importance of ith NN as compared to 1st NN), $\frac{\phi_{\mathbf{b}^{\mathbf{i}}}}{\phi_{\mathbf{b}^1}}$, can be expressed as a function of interatomic distance ratio between the ith NN and 1st NN interactions, $\frac{|\mathbf{b}^{\mathbf{i}}|}{|\mathbf{b}^1|}$, and η, in the following form:

$$\frac{\phi_{\mathbf{b}^{\mathbf{i}}}}{\phi_{\mathbf{b}^1}} = \left(1 + \eta\left(\frac{|\mathbf{b}^{\mathbf{i}}|}{|\mathbf{b}^1|} - 1\right) + 0.05\eta^3\left(\frac{|\mathbf{b}^{\mathbf{i}}|}{|\mathbf{b}^1|} - 1\right)^3\right)e^{-\eta\left(\frac{|\mathbf{b}^{\mathbf{i}}|}{|\mathbf{b}^1|} - 1\right)}. \tag{9}$$

The next step is to determine a cut-off for the number of NN interactions beyond which $\frac{\phi_{\mathbf{b}^{\mathbf{i}}}}{\phi_{\mathbf{b}^1}}$ can be reasonably neglected. This depends on the value of $\frac{|\mathbf{b}^{\mathbf{i}}|}{|\mathbf{b}^1|}$ and η. The nature of the $\mathbf{b}^{\mathbf{i}}$ vectors, and their corresponding