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Calculation of the surface energy of hcp metals by using the modified embedded atom method

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Abstract

With MEAM, the surface energies of three kinds of representative surfaces, (h 0 l), (h h l) and (h k 0) belong to [0 1 0], [1 $\bar{1}$ 0] and [0 0 1] crystal band, respectively, have been calculated for 13 closed-packed hexagonal (hcp) metals Co, Dy, Er, Gd, Ho, Mg, Nd, Pr, Re, Sc, Tb, Tl and Zr. For all 13 hcp metals, the basal plane (0 0 1) has the minimum surface energy. So from surface energy minimization, the (0 0 1) texture should be favored in the hcp films, this is consistent with the experimental results. The fact that the short termination corresponds to much lower surface energy than long one implies the former is more stable for those surfaces having two possible terminations. Such as the prism plane (1 0 0), only the short termination was observed in experiment.

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Keywords: hcp metals; Surface energy; MEAM; Calculation

1. Introduction

A detailed knowledge of the structure and energy of surfaces is important for the understanding of many surface phenomena such as adsorption, oxidation, corrosion, catalysis, crystal growth, etc. [1–4]. Compared with the bulk materials, thin films have a relatively large surface and interface. The anisotropy of the surface and interface energy can supply an additional driving force for abnormal grain growth and texture formation or change in a thin polycrystalline film on a substrate. Lee suggested that the texture of vapor deposits changes from the orientation that places the lowest energy crystal facets parallel to the substrate under the condition of low atom or ion concentration adjacent to the deposit, to the orientation that places the higher energy crystal facets parallel to the substrate as the atom or ion concentration adjacent to the deposit increases [5,6]. It is necessary to know the surface energies of various surfaces.

In our previous papers, the surface energies for materials with face-centered cubic (fcc) [7], body-centered cubic (bcc) [8] and diamond cubic [9] structures have been calculated by using embedded atom method (EAM) developed by Daw and Baskes [10,11] and modified embedded atom method (MEAM) extended by Baskes [12–14] by including directional bonding. Besides fcc- and bcc-films, the third important structure of polycrystalline films is closed-packed hexagonal (hcp) structure. Although there are many experimental and theoretical studies of the surfaces of hcp metals [15–19], only the low-index crystal surfaces were considered. In previous papers [20,21], we have studied various surfaces of hcp metals from the strain energy point of view. In this paper, the surface energies of 35 surfaces for 13 hcp metals Co, Dy, Er, Gd, Ho, Mg, Nd, Pr, Re, Sc, Tb, Tl and Zr have been calculated by using the MEAM [22], and some properties of the surface structures for hcp metals have been also discussed.

2. Summary of MEAM

In the MEAM [12–14], the total energy E of a system of atoms is given by the expression

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right] \quad (1)$$

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where the embedding function $F_i(\bar{\rho}_i)$ represents the energy to embed an atom i into the background electron density $\bar{\rho}_i$ at site i, $\phi_{ij}(r_{ij})$ is a pair interaction between atoms i and j separated by a distance r_{ij}. The term in square brackets in Eq. (1) denotes the contribution to the total energy from the ith atom

$$E_i = F_i(\bar{\rho}_i) + \frac{1}{2}\sum_{j(\neq i)} \phi_{ij}(r_{ij}) \tag{2}$$

The following form of the embedding function is adopted [22]

$$F_i(\bar{\rho}_i) = AE_c\left(\frac{\bar{\rho}_i}{\rho_e}\right)\ln\left(\frac{\bar{\rho}_i}{\rho_e}\right) \tag{3}$$

where A is a parameter to be determined, E_c the cohesive energy, and ρ_e the background electron density for a reference structure in which the individual atoms are on their exact lattice points. Normally, the equilibrium crystal structure is taken as the reference structure. The background electron density $\bar{\rho}_i$ consists of a spherically symmetric partial electron density $\rho_i^{(0)}$ and the angular contributions $\rho_i^{(1)}$, $\rho_i^{(2)}$ and $\rho_i^{(3)}$. Each partial electron density is expressed as

$$\rho_i^{(0)} = \sum_{j(\neq i)} f^{(0)}(r_{ij}) \tag{4}$$

$$(\rho_i^{(1)})^2 = \sum_{\alpha}\sum_{j,k(\neq i)} f^{(1)}(r_{ij}) f^{(1)}(r_{ik}) \frac{r_{ij}^{\alpha} r_{ik}^{\alpha}}{r_{ij} r_{ik}} \tag{5}$$

$$(\rho_i^{(2)})^2 = \sum_{\alpha,\beta}\sum_{j,k(\neq i)} f^{(2)}(r_{ij}) f^{(2)}(r_{ik}) \frac{r_{ij}^{\alpha} r_{ij}^{\beta} r_{ik}^{\alpha} r_{ik}^{\beta}}{(r_{ij} r_{ik})^2} - \frac{1}{3}\sum_{j,k(\neq i)} f^{(2)}(r_{ij}) f^{(2)}(r_{ik}) \tag{6}$$

$$(\rho_i^{(3)})^2 = \sum_{\alpha,\beta,\gamma}\sum_{j,k(\neq i)} f^{(3)}(r_{ij}) f^{(3)}(r_{ik}) \frac{r_{ij}^{\alpha} r_{ij}^{\beta} r_{ij}^{\gamma} r_{ik}^{\alpha} r_{ik}^{\beta} r_{ik}^{\gamma}}{(r_{ij} r_{ik})^3} \tag{7}$$

where $f^{(h)}(r)$ (h = 0–3) are radial functions, the subscripts j and k indicate neighboring atoms to the atom i in question, and the α, β and γ summations are over the three coordinate directions. Combining the partial electron densities to give the total background electron density

$$\bar{\rho}_i = \rho_i^{(0)} \exp\left(\frac{1}{2}\sum_{h=1}^{3} t^{(h)}\left(\frac{\rho_i^{(h)}}{\rho_i^{(0)}}\right)^2\right) \tag{8}$$

where $t^{(h)}$ (h = 1–3) are parameters to be determined. The radial functions that represent the decrease in the contribution with increasing distance are given by

$$f^{(h)}(r) = \exp\left[-\beta^{(h)}\left(\frac{r}{r_e} - 1\right)\right] \tag{9}$$

where $\beta^{(h)}$ (h = 0–3) are parameters to be determined and r_e is the equilibrium nearest-neighbor distance.

In the reference structure for an atom of type i, Eq. (2) has the following form

$$E_i^u(r) = F_i(\bar{\rho}_i^0(r)) + \frac{Z_i}{2}\phi_{ii}(r) \tag{10}$$

where r is the nearest-neighbor distance, $\bar{\rho}_i^0(r)$ the background electron density and Z_i the number of the nearest-neighbor atoms in the reference structure.

The energy per atom in the reference structure is generally presented by a universal energy function [23]

$$E^u(r) = -E_c\left[1 + \alpha\left(\frac{r}{r_e} - 1\right)\right]\exp\left[-\alpha\left(\frac{r}{r_e} - 1\right)\right] \tag{11}$$

with

$$\alpha = \sqrt{\frac{9B\Omega}{E_c}} \tag{12}$$

here B and Ω are bulk modulus and equilibrium atomic volume, respectively.By combining Eqs. (10) and (11), the form of $\phi_{ii}(r)$ can be obtained as

$$\phi_{ii}(r) = \frac{2}{Z_i}\left\{-E_c\left[1 + \alpha\left(\frac{r}{r_e} - 1\right)\right] \times \exp\left[-\alpha\left(\frac{r}{r_e} - 1\right)\right] - F_i(\bar{\rho}_i^0(r))\right\} \tag{13}$$

3. Surface structure of the hcp metals

Fig. 1 shows a crystal cell of the hcp lattice. Three axes (a_1, a_2, c) or four axes (a_1, a_2, a_3, c) are used to denote the indices of the crystal planes and directions usually. The former is adopted in this paper for simplicity. Three kinds of representative surfaces, (h 0 l), (h h l) and (h k 0) belong to [0 1 0], [1 $\bar{1}$ 0] and [0 0 1] crystal bands, respectively, were studied.

Different from cubic lattice, the hcp lattice has some specific structural properties. For example, the (1 0 0) surface, as illustrated in Fig. 2 (view along the c axis), has two possible

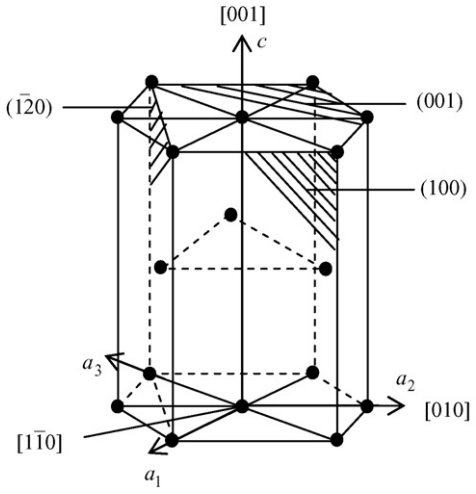

Fig. 1. Crystal cell of the closed-packed hexagonal lattice.