Computational Materials Science 92 (2014) 166–171

Contents lists available at ScienceDirect

Computational Materials Science

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

Scaling behavior of the surface energy in face-centered cubic metals

Minho Jo [a], Y.W. Choi [a], Y.M. Koo [a,b], S.K. Kwon [a,*]

[a] Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
[b] Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

ARTICLE INFO

Article history:
Received 3 February 2014
Received in revised form 17 May 2014
Accepted 20 May 2014

Keywords:
Surface energy scaling
Universal binding energy curve
Molecular dynamics simulation

ABSTRACT

The binding energy of metals shows a universal feature which can be described by an equation of state. We explore the scaling behavior of the surface energy in face-centered cubic metals and propose the concept of equivalent structures. The surface energies were calculated on various orientations using the modified embedded-atom method. A strong linear correlation was observed between the surface energies of different metals. Based on the results, we established a scaled surface energy-to-element relationship. This scalability suggests an efficient scheme to estimate the orientation dependency of the surface energy by two characteristic parameters.

1. Introduction

The surface energy, defined by the excess energy of surface atoms compared to bulk, is a fundamental physical quantity to understand surface-related phenomena in materials science. For examples, surface morphology, surface reconstruction, and the shape of nano-sized particles have been described in terms of the surface energy [1–7]. Nonetheless, experimental determination of the surface energy is still difficult and inaccurate. The surface energy in experiments is usually derived by extrapolating the surface tension of liquid phase to low temperature, which involves unavoidable errors [8]. Meanwhile, extensive theoretical studies have been performed on the surface energy of various metals by using *ab initio* method [9–14] and semi-empirical method [15,16]. Although the surface energy of low indexed surfaces can be obtained with accuracy, determination of the surface energy of high indexed surfaces is time-consuming with *ab initio method* and semi-empirical values are suspicious in reliability. Therefore, in order to identify the orientation dependency of the surface energy, it is essential to understand a general behavior of the surface energy.

It is well known that the binding energy of metals exhibits a universal behavior regardless of the crystalline structure [17–19]. In other words, the binding energy curves of different metals can be merged into a single curve through a scaling with the ground state quantities: cohesive energy, equilibrium lattice constant, and bulk modulus. Considering that the surface energy of metals can be roughly estimated by counting the number of broken bonds of the nearest-neighbor [20,21], one may imagine a possibility of an element-independent description of the surface energy, similarly to the binding energy.

In this work, we examine the scalability of the surface energy in face-centered cubic (fcc) metals. Surface energies of various orientations were obtained by using the modified embedded-atom method (MEAM) [22,23]. We show a linear relationship among the surface energies of different metals. Based on the result, the variation of the surface energy on orientation is successfully scaled to a single energy curve. We discuss the scalability and the binding energy in a general view of the structure–element–energy correlation.

2. Computational method

We employed the second nearest-neighbor MEAM potential for eight fcc metals to obtain the total energy by molecular dynamics method: Al, Ni, Cu, Pd, Ag, Pt, Au, and Pb [23]. The universality of the binding energy of the fcc metals was checked with the total energy calculation by changing the lattice constant. Surfaces were modeled by the double-sided slab geometry using the bulk equilibrium lattice parameter. For each metal, we considered 16 (12) different surface orientations normal to the $[1\bar{1}0]$($[100]$) direction as listed in Table 1. The slab thickness was taken to be more than 20 atomic layers depending on the surface orientation, which guarantees that the surface energy in the calculations was converged within the numerical error of less than 0.01 eV/surface atom. The surface energies of both unrelaxed and relaxed structures were considered to inspect how the atomic relaxation modifies the structure–energy correlation.

---

* Corresponding author. Tel.: +82 54 2799024.
E-mail address: sekk@postech.ac.kr (S.K. Kwon).

http://dx.doi.org/10.1016/j.commatsci.2014.05.042
0927-0256/

Table 1
The surface orientations and angles for calculation. The angles are measured relative to the (1 1 0) and (0 0 1) surface orientation.

	Orientation	Angle (°)
Normal to $[1\bar{1}0]$	(1 1 0)	0.0
	(4 4 1)	10.0
	(3 3 1)	13.3
	(2 2 1)	19.5
	(3 3 2)	25.2
	(5 5 4)	29.5
	(1 1 1)	35.3
	(3 3 4)	43.3
	(2 2 3)	46.7
	(1 1 2)	54.7
	(2 2 5)	60.5
	(1 1 3)	64.8
	(1 1 4)	70.5
	(1 1 6)	76.7
	(1 1 8)	80.0
	(0 0 1)	90.0
Normal to [1 0 0]	(0 0 1)	0.0
	(0 1 8)	7.1
	(0 1 5)	11.3
	(0 1 4)	14.0
	(0 1 3)	18.4
	(0 2 5)	21.8
	(0 1 2)	26.6
	(0 3 5)	31.0
	(0 2 3)	33.7
	(0 3 4)	36.9
	(0 4 5)	38.7
	(0 1 1)	45.0

3. Results and discussion

It was shown by Rose et al. [17] that the binding energy of metals can be scaled into a single energy curve through three steps; (i) the total energy is divided by the cohesive energy, (ii) the lattice parameter is shifted and scaled with the equilibrium lattice constant, and (iii) the width of the total energy curve is adjusted with the bulk modulus. We followed an equivalent procedure as above except the last step. For a simplification, the width of the total energy curve was scaled by the difference of the lattice constant between at the equilibrium and half of the cohesive energy. We show the results of the fcc metals in Fig. 1(a). It is clear that all scaled binding energy curves are well fitted into a single curve throughout the interatomic distance. This indicates that the employed interatomic potentials provide reliable cohesive properties of considering materials.

The total energy of a crystalline material generally depends on two factors, lattice structure and constituent elements. It is an interesting question to what extend the two factors can be decomposed to be dealt with independently. When it is the case, the total energy can be described solely with the element-dependent factor after confining the structural factor. Definitely, even for a given structure the system energy relies on the composition of constituent elements and it is not an easy task to estimate the total energy. However, there are cases in which two system energies of different compositions or elements can be matched by a relationship in the structural parameter space and a universal class can be identified. In that circumstance, we define the pair of structures as an *equivalent structure*. In other words, all pair of equivalent structures between the structural group A and A' having a different composition α and β, respectively, will satisfy a relation $E_{\alpha,\,A} = f(E_{\beta,\,A'})$ where f is a correlation function. Note that the equivalent structures need not be the same structure.

The binding energy is an example of the equivalent structure. As demonstrated above, the binding energy behavior of metals is universal with the scaled interatomic distance. Although we figured out only several discrete points in Fig. 1(a), the curve is continuous and every point on it can be reached by all the elements. When such a scaled energy curve is available for a class of material systems, we will define the group of material structures which belongs to the same point of the scaled curve as an equivalent structure. Thus, there is an infinite number of equivalent structure sets in a scaled energy curve and the equilibrium structures of metals, as a trivial example, are equivalent to each other. Note that the structures in an equivalent structure set do not have the same lattice parameter and total energy; the equivalent structure imposes a capability to occupy the same point in the scaled energy curve for the structures of different materials.

The equivalent structure implies a very remarkable feature. In Fig. 1(b), we denoted eleven equivalent structures of seven fcc metals, which are matched with those of Al. Each of seven points located along the vertical axis are equivalent and able to be overlapped by the scaling of the cohesive energy. Reminding the prescribed scaling steps, it can be understood that the scaling step (ii) and (iii) identify the group elements of the equivalent structure and the step (i) equalize the energy values in the same equivalent structure. From the fact, we give an energy relationship

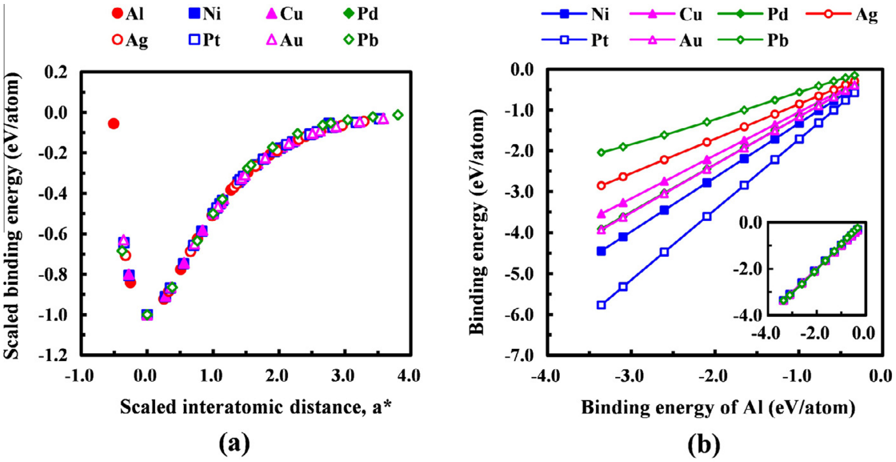

Fig. 1. (a) The scaled binding energy of fcc metals as a function of the scaled interatomic distance. (b) The energy–energy correlation of the binding energies with Al as a basis. Inset is the scaled binding energy between the equivalent structures. The equivalent structure is defined as a group of structures which occupies the same points in the scaled energy curve.