



Cohesion and coordination effects on transition metal surface energies



Judit Ruvireta, Lorena Vega, Francesc Viñes*

Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1, 08028 Barcelona, Spain

ARTICLE INFO

Keywords:

Surface energy
Transition metals
Broken-bond model
Stefan equation
Surface tension
Wulff construction

ABSTRACT

Here we explore the accuracy of Stefan equation and broken-bond model semiempirical approaches to obtain surface energies on transition metals. Cohesive factors are accounted for either *via* the vaporization enthalpies, as proposed in Stefan equation, or *via* cohesive energies, as employed in the broken-bond model. Coordination effects are considered including the saturation degree, as suggested in Stefan equation, employing Coordination Numbers (CN), or as the ratio of broken bonds, according to the bond-cutting model, considering as well the square root dependency of the bond strength on CN. Further, generalized coordination numbers CN are contemplated as well, exploring a total number of 12 semiempirical formulations on the three most densely packed surfaces of 3d, 4d, and 5d Transition Metals (TMs) displaying face-centered cubic (fcc), body-centered cubic (bcc), or hexagonal close-packed (hcp) crystallographic structures. Estimates are compared to available experimental surface energies obtained extrapolated to zero temperature. Results reveal that Stefan formula cohesive and coordination dependencies are only qualitative suited, but unadvised for quantitative discussion, as surface energies are highly overestimated, favoring in addition the stability of under-coordinated surfaces. Broken-bond cohesion and coordination dependencies are a suited basis for quantitative comparison, where square-root dependencies on CN to account for bond weakening are sensibly worse. An analysis using Wulff shaped averaged surface energies suggests the employment of broken-bond model using CN to gain surface energies for TMs, likely applicable to other metals.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Surfaces are the main defect on an otherwise infinite material. In fact crystalline materials periodically repeat their bulk structure along the three-dimensional space up to the surface terminations. Material nanoparticles, micrograins, up to macroscopic single crystals expose certain preferential surface endings, which in turn outline the particle shape. Infinite plane endings exist within a crystal, yet groups of them are equivalent due to the materials bulk intrinsic crystal group symmetry. The natural observed trend is that materials expose those terminations or surfaces families that are more stable, typically being the most close-packed ones. The rationalization is simple; those terminations where surface atoms are more saturated lack less bonds, and so, the fewer bonds are missed, the more stable the surface is.

The stability of a given surface termination is quantified by the so-called surface energy, γ , also known as surface tension, given per exposed surface area—typically in J m^{-2} or N m^{-1} units. Ideally, when a bulk is truncated into two surface endings, the cleavage energy equals to both surface energies added up. Surface energies include immediate post-cleavage effects such as surface relaxation or atomic reconstruc-

tions. These processes are considered secondary though, and the materials bulk cohesive strength is actually normally regarded as the main property sizing the surface energy. Again the concept is straightforward; the stronger the bonds in the material are, the most costly to create a surface is, and, therefore, the higher the surface energy.

The surface energy is the main energetic descriptor of a crystal termination, and many physicochemical surface properties hang upon it. For instance, Wulff construction procedure is used as a top-down approach to ascertain the crystal equilibrium shape from independent surface energies [1]. The moiety shape can affect the overall electronic structure of material nanoparticles, and even alter their magnetic solution [2,3]. Furthermore, the presence of certain surface terminations can induce particular moiety aggregations, such as metal nanowires from isolated nanoparticles [4]. The different surface terminations differ in their electronic structures, and so surface properties depend on them, e.g. the work function, of vital importance in processes where electrons are ejected from the material, like in electrochemical processes, or surface science techniques like the X-ray photoemission spectroscopy and scanning tunneling microscopy.

On top of that one has to regard that surfaces are the main region where materials interact with media, and so, of pivotal importance in

* Corresponding author.

E-mail address: francesc.vines@ub.edu (F. Viñes).

cutting-edge surface-driven processes where nowadays research focus onto, e.g. chemical resolution of enantiomers [5], CO₂/CH₄ gas separation [6], patterning of two-dimensional organic frameworks [7], electron/hole separation in photocatalysis [8], and heterogeneous catalysis [9], to cite a few examples of technological relevance. Moreover, a given structural shape in turn expresses other lower dimensionality defects such as edges and corners, which may also feature, due to their lower atomic coordination, a markedly different chemical activity [10–12]. Shape, size, and surface tension are determining factors of transition metal nanoparticles reactivity [13–15], where surface energies have been claimed as a main indicator of the overall metal surface activity [16], and because of this posed as a descriptor of its catalytic activity [17]. As it happens, other coordination [18] and electronic [19] descriptors are intimately linked to a particular surface termination.

The experimental measurement of a solid metal surface energy is challenging: On the one hand it is important to measure a system without impurities, which otherwise could substantially affect the determined γ . On the other hand, the employed techniques typically require having the metal (nearly) molten. Different procedures can be employed, such as sessile and pendent drops, drop weight, capillary rise, and maximum bubble or drop pressures, for whose detailed description we refer to the literature [20]. In all cases, the γ drops with the temperature, but only ranging 0.1–0.4 mN m⁻¹ K⁻¹, this is, the effect of the temperature only becomes significant at very large temperatures above 1000 K [21]. In any case, from the linear dependence of γ with respect to the temperature T one can gain extrapolated surface energy values at 0 K, with multiple acquired values over the last decades, ensuring finite values with an overall associated error of $\pm 2\%$ [21].

These experimentally extrapolated γ values arise from (nearly) molten metal situations, with a highly dynamical admixing of particular surface endings, and because of that, difficult to assign to a particular crystallographic ending. This lack of atomistic knowledge on surface energies from the experimental point of view can be mended from the computational chemistry one, where Density Functional Theory (DFT) calculations on slab models are commonly used to mimic specific surface endings under study, and to obtain estimates of their surface energies. These estimates allow comparing the experimental surface energies with those obtained on slab models of most stable surfaces [22], as they are presumably those most exposed on a nanocrystallite according to Wulff construction [1,23], or even to a combination of surface endings of low Miller indices, profiting from a Wulff constructed shape [24].

Despite of the benefits on acquiring surface energy values from DFT calculations, some questions are to date under debate. Focusing only on transition metals as a large representative subset of metallic systems, one may wonder whether the employment of a given exchange-correlation (xc) functional may bias the surface energy estimates; in this regard, it seems clear that xc functionals within the generalized gradient approximation are best suited to describe metal bulks [22,25], although the question mark is still present when addressing metal surfaces. Furthermore, the modeling and optimization of surface slabs is computationally demanding, and thorough studies are limited nowadays to maximum miller indices of two [24], despite surfaces with higher Miller indices can be highly stable and so present in any system, or stabilized in case of their technological importance; see e.g. Cu(321) surface utilization in the catalysis of the water gas shift [26], or Cu(3117) chiral metal surfaces used for enantioselective chemical separation [27], to mention a couple of cases.

In that sense, the usage of semiempirical equations to estimate the surface energies of a particular surface ending becomes quite appealing, given their easiness and rapid utilization, more if, in addition, they are able to deliver surface energies with a high degree of accuracy. Historically, one has to remark the Stefan equation [28], in which the surface energy can be obtained as;

$$\gamma = \frac{\Delta H_{vap}^o \rho^{2/3} CN_s}{M^{2/3} N_A^{2/3} CN_b} \quad (1)$$

where ΔH_{vap}^o is the material vaporization at standard conditions of pressure and temperature —10⁵ Pa and 273.15 K—, ρ is the material density, M the molar mass, and N_A the Avogadro constant. Aside from these variables, the surface energy depends on the relation in between the Coordination Number (CN) of the surface (CN_s) with respect that of the material bulk (CN_b). The Stefan equation can be then decomposed into two clearly differentiated terms; the CN_s/CN_b, which quantifies the degree of saturation of surface atoms with respect bulk conditions, and the rest of the equation, which is a weighted value of ΔH_{vap}^o , accounting for the materials atomic cohesion. Hence, these terms account for the above-stated cohesion and coordination dependences, and stem from the experimental observation of dependence of γ with respect ΔH_{vap}^o [20], and CN_s/CN_b terms [29].

The other extendedly used empirical adjustment is that of the bond-broken model, also known as bond-cutting model [30]. There the surface energy γ is expressed as

$$\gamma = \frac{CN_b - CN_s}{CN_b} E_{coh} \quad (2)$$

where E_{coh} is the material cohesive energy, which naturally accounts for the material cohesion dependence. At variance with Stefan equation, the saturation proportionality term depends on CN_b-CN_s, this is, the number of broken bonds when creating the surface. Criticism arose on the broken-bond model in the sense that ignores the variation of bond strengths with respect CN [31], such as in the above commented surface relaxation processes, and lower dimensionality defects. Tight-binding theory showed a square root dependency on CN for covalent bonds [32], and so the broken-bond equation could be reformulated as

$$\gamma = \frac{\sqrt{CN_b} - \sqrt{CN_s}}{\sqrt{CN_b}} E_{coh} \quad (3)$$

where its usage on transition metals has been advised, claiming an agreement compared to *ab initio* estimates being improved by 20–50% [33–35], although the explicit agreement or improvement with respect experimental values was not addressed.

At this point, it is clear that many questions remain open when using these empirical equations: What cohesion term is better suited, standard vaporization enthalpies or cohesive energies? Moreover, is surface saturation better treated in terms of coordination, or as broken bonds? Would the above commented square root dependency apply when comparing to experimentally determined surface energies? On top of that, recently generalized coordination numbers (\overline{CN}) have been suggested and employed as better geometric descriptors of the transition metals surface activity compared to CN [36,37], allowing distinguishing different similarly packed surfaces, by considering the saturation of sub-surface and vicinal lower-dimension sites. In this sense, would \overline{CN} be a better coordination parameter to quantify the surface stability in terms of γ ? To solve these questions, we here present a profound analysis on the parameterization and dependences employed for the cohesion and coordination effects, by comparing surface energies obtained based on Stefan equation and broken-bond models, compared to precise values of surface energies considering 26 transition metals as a broad and representative study set.

2. Computational details

Different empirical equations have been tested, either based on Stefan equation employing standard vaporization energies as cohesion descriptor, or based on the broken-bond model, and, therefore utilizing cohesive energies for this purpose. The list of experimental standard vaporization energies, densities, and cohesive energies is found in the Supplementary Information. These cohesion terms are combined with the above stated

$$(1) \frac{CN_s}{CN_b}, (2) \frac{CN_b - CN_s}{CN_b}, \text{ or } (3) \frac{\sqrt{CN_b} - \sqrt{CN_s}}{\sqrt{CN_b}} \quad (4)$$

Download English Version:

<https://daneshyari.com/en/article/5421108>

Download Persian Version:

<https://daneshyari.com/article/5421108>

[Daneshyari.com](https://daneshyari.com)