Construction of Unbalanced Cluster Binding Energy Theory Model

Shuai Zhang¹, Lei Chen², Wanli Zhu³, Ruixin An⁴

¹College of Materials Science and Engineering, Jilin Jian Zhu University, Changchun 130118, China
²College of municipal and environmental engineering, Jilin Jian Zhu University, Changchun 130118, China
³School of Geomatics and Prospecting Engineering, Jilin Jian Zhu University, Changchun 130118, China
⁴School of Transportation Science and Engineering, Jilin Jian Zhu University, Changchun 130118, China

Abstract

This paper builds three models about the surface volume ratio \( \delta \), the bonds ratio \( Ba / Bt \) and the binding energy \( Ec (N) \) of the Wulff construction with the total number of atoms, \( N \), in the system as a variable. The results from model prediction are consistent with those from the appropriate cluster experiment and the computer simulation. In allusion to the uncertainty of the structure of atomic clusters, the geometry and energy model of Wulff construction is used to approximately describe the energy and morphology of clusters.

Keywords: The Surface Volume Ratio \( \delta \), The Bonds Ratio, Construction of Unbalanced Cluster.

1. INTRODUCTION

It is well-known that the Wulff construction (available by taking the minimum surface energy per unit volume) is a standard method to get an equilibrium structure of bulk crystals. Although the atomic cluster differs from the Wulff construction, it has the lowest system surface energy just as crystals have. At this point, the cluster morphology and energy may be similar to Wulff construction (Zhu et al., 2011; Li et al., 2009; Li et al., 2013; Jiang et al., 2000).

2. MODEL

In view of the closed-packed arrangement of atomic clusters, a Wulff sphere construction of face-centered cubic crystal is referenced in this paper. The Wulff sphere is available by symmetrically shearing the six vertices of the octahedron, thereby (100) faces of six squares and (111) faces of eight hexagons are formed on surface. The Wulff sphere is just a chamfered octahedron TO structure. As shown in Fig. 1, for the (111) faces, there are three edges common to the (100) faces of the squares, on each of which the number of atoms is supposed to be \( n_{squ} \). The number of atoms on the other three edges is supposed to be \( n_{hex} \). As the number of bonds depends on the dimension and structure of the system simultaneously, in this paper, the geometric characteristics of the Wulff sphere construction are described with bonds ratio \( Ba / Bt \) as the variable, then,

\[ \delta = N_s/N \]  

Where \( N_s \) represents the number of atoms on the surface of the system. For the Wulff sphere construction, the surface atoms cover the atom \( N_{(111)} \) on the (111) faces, the atom \( N_{(100)} \) on the (100) faces, the atom \( N_e \) on the edge and the atom \( N_v \) on the vertex. According to the Wulff sphere geometrical characteristics given in Fig. 1, \( N_{(111)} \), \( N_{(100)} \), \( N_e \) and \( N_v \) are expressed as follows:

\[ N_{(111)} = 4(n_{squ}+n_{hex})(n_{squ}+n_{hex}+9)+2n_{squ}n_{hex}+14 \]  

\[ N_{(100)} = 6(n_{squ}+2)^2 \]  

\[ N_e = 12(2n_{squ}+n_{hex}+6) \]  

And \( N_v = 24 \)

48
Figure 1. A sketch of a general TO structure with eight hexagonal (111) and six square (100) facets at surfaces

(Gu et al., 2001; Coyle et al., 2001)

By adding the above formulae, the number of atoms on the surface of the system can be available, namely: \( N_s = N_{111} + N_{100} + N_e + N_v \). Besides, as a function of \( n_{squ} \) and \( n_{hex} \), the total number of atoms in the system, \( N \), is determined by the following formula:

\[
N = \left\{2[2(n_{squ} - 1) + n_{hex}]^3 + 2(n_{squ} - 1) + n_{hex}\right\}/3 - 2(n_{squ} - 1)^3 - 3(n_{squ} - 1)^2 - (n_{squ} - 1) \tag{5}
\]

By defining the ligancy of the surface atoms in different positions and combining the number of corresponding surface atoms, the average ligancy \( Z_s \) of the surface atoms can be available,

\[
Z_s = (Z_{111}N_{111} + Z_{100}N_{100} + Z_eN_e + Z_vN_v)/N_s \tag{6}
\]

Where, \( Z_{111} \), \( Z_{100} \), \( Z_e \) and \( Z_v \) are the ligancies of the atoms on the (111) faces, on the (100) faces and at the vertices, then \( Z_{111} = 9 \), \( Z_{100} = 8 \), \( Z_e = 7 \) and \( Z_v = 6 \). For face-centered cubic crystals, the ligancy of atoms in the bulk is 12, i.e. \( Z_b = 12 \). Therefore, the number of corresponding bonds in \( B_s = \lceil(N, Z_s + (N - N_s)Z_b)/2 \right\rangle \) and \( B_t = NZ_b/2 \), that is:

\[
\frac{B_s}{B_t} = \frac{NZs}{NZ_b} \tag{7}
\]

It is difficult to determine arithmetic values \( \delta \) and \( B_s/B_t \) for the Wulff sphere construction of different substances since there are two variables contained in the above formula, \( n_{squ} \) and \( n_{hex} \). The two variables are therefore incorporated into one to simplify the calculation process, which can be achieved by considering the Wulff sphere construction formation conditions. For any Wulff sphere construction, the following conditions must be met:

\[
\frac{\gamma_{100}}{\gamma_{111}} = \frac{D_{100}}{D_{111}} \tag{8}
\]

Where \( \gamma_{100} \) and \( \gamma_{111} \) are the surface energies of (100) faces and (111) faces, respectively. \( D \) is the distance from the face to the center of the chamfered octahedron. It follows that the Wulff sphere construction depends on the substance itself, and its geometrical characteristics depend on the ratio \( \gamma_{100}/\gamma_{111} \). In the formula (8), \( D_{100}/D_{111} \) can be expressed as: \( D_{100}/D_{111} = d_{100}/d_{111} \) and \( d_{100} \) and \( d_{111} \) are the interlayer spacings of the (100) faces and the (111) faces, respectively. For face-centered cubic crystal, \( d_{100}/d_{111} = \sqrt{3}/2 \). \( \xi_{100} \) and \( \xi_{111} \) are the number of layers of (100) faces and (111) faces at the intervals of 2\( D_{100} \) and 2\( D_{111} \), respectively. For a typical TO structure consisting of a hexagonal and a square facets, there is a relationship: \( \xi_{100} = \frac{2n_{squ} + 2n_{hex} - 4}{2n_{squ} + 2n_{hex} - 3} \)

According to the formula (8), this formula can be re-expressed as:

\[
\frac{2\gamma_{100}}{\sqrt{3} \gamma_{111}} = \frac{2n_{squ} + 2n_{hex} - 4}{2n_{squ} + n_{hex} - 3} \tag{9}
\]
The relationship between \(n_{\text{hex}}\) and \(n_{\text{squ}}\) can be determined from the formula (9) and based on the ratio \(\gamma_{(100)}/\gamma_{(111)}\) for different substances. As shown in the Table 1, there are ratios of \(\gamma_{(100)}/\gamma_{(111)}\) of the known face-centered cubic crystals. \(\gamma_{(100)}\) is generally greater than \(\gamma_{(111)}\) since the (100) face has more missing bonds, such that \(\gamma_{(100)}/\gamma_{(111)}>1\).

**Table 1** The values of \(\gamma_{(100)}\) and \(\gamma_{(111)}\) and the corresponding ratios \(\gamma_{(100)}/\gamma_{(111)}\) for FCC metallic elements. The presented \(\gamma_{(100)}/\gamma_{(111)}\) values respectively for R-TO and OH structures are determined according to Wulff theorem (Eq. (8)) for comparison.

<table>
<thead>
<tr>
<th>element</th>
<th>(\gamma_{(100)}) (J m(^{-2}))</th>
<th>(\gamma_{(111)}) (J m(^{-2}))</th>
<th>(\gamma_{(100)}/\gamma_{(111)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1.80</td>
<td>1.52</td>
<td>1.184</td>
</tr>
<tr>
<td>Ag</td>
<td>1.40</td>
<td>1.20</td>
<td>1.167</td>
</tr>
<tr>
<td>Ni</td>
<td>2.88</td>
<td>2.44</td>
<td>1.180</td>
</tr>
<tr>
<td>Pd</td>
<td>2.15</td>
<td>1.85</td>
<td>1.162</td>
</tr>
<tr>
<td>Ca</td>
<td>0.5</td>
<td>0.43</td>
<td>1.163</td>
</tr>
<tr>
<td>Sr</td>
<td>0.39</td>
<td>0.33</td>
<td>1.182</td>
</tr>
<tr>
<td>Cu</td>
<td>2.17</td>
<td>1.83</td>
<td>1.186</td>
</tr>
<tr>
<td>Pt</td>
<td>2.98</td>
<td>2.54</td>
<td>1.173</td>
</tr>
<tr>
<td>Rh</td>
<td>3.15</td>
<td>2.7</td>
<td>1.167</td>
</tr>
<tr>
<td>Ir</td>
<td>3.74</td>
<td>3.19</td>
<td>1.172</td>
</tr>
<tr>
<td>Pb</td>
<td>0.64</td>
<td>0.55</td>
<td>1.164</td>
</tr>
<tr>
<td>Al</td>
<td>1.68</td>
<td>1.45</td>
<td>1.159</td>
</tr>
<tr>
<td>Ac</td>
<td>1.14</td>
<td>1.03</td>
<td>1.107</td>
</tr>
<tr>
<td>Th</td>
<td>2.36</td>
<td>1.85</td>
<td>1.276</td>
</tr>
<tr>
<td>R-TO</td>
<td>2/(\sqrt{3}) = 1.155</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>(\sqrt{3}) = 1.732</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the formula (9), \(n_{\text{hex}}/n_{\text{squ}}\) is a monotone function of \(\gamma_{(100)}/\gamma_{(111)}\) and increases as the value of \(\gamma_{(100)}/\gamma_{(111)}\) goes up. It means that the substance with a higher value \(\gamma_{(100)}\) requires smaller (100) faces on its Wulff sphere construction surface. Note that, if \(n_{\text{hex}} = n_{\text{squ}}\), \(\gamma_{(100)}/\gamma_{(111)} = 2/\sqrt{3}\). This is a special Wulff sphere construction, also called as a regular chamfered octahedron (R-TO) whose surface is composed of regular hexagons and squares. It followed that, when \(\gamma_{(100)}/\gamma_{(111)}>2/\sqrt{3}\), \(n_{\text{hex}} > n_{\text{squ}}\) when \(\gamma_{(100)}/\gamma_{(111)}<2/\sqrt{3}\), \(n_{\text{hex}} < n_{\text{squ}}\). We note that there is a limit case, that is, for any value \(n_{\text{hex}}, n_{\text{squ}} = 1\). This means the complete octahedral structure (OH) without any chamfer. However, OH structures are generally unstable due to their high energy status.

In order to compare with the real cluster structure, the geometric parameters of IH and CO structures are imported:

\[
N_s = 10(v-1)^2 + 2 \quad \text{(IH, CO)}
\]

\[
N = \frac{10}{3} v^3 - 5v^2 + \frac{11}{3} v - 1 \quad \text{(IH, CO)}
\]

\[
\frac{B_s}{B_i} = \frac{20v^3 - 45v^2 + 37v - 12}{20v^3 - 30v^2 + 22v - 6} \quad \text{(IH)}
\]

\[
\frac{B_s}{B_i} = \frac{10v^3 - 24v^2 + 20v - 6}{10v^3 - 15v^2 + 11v - 3} \quad \text{(CO)}
\]

Where, since all the edges on the surfaces of the IH or CO structures are identical, \(v\) represents the number of atoms on each edge.

Due to the substitution of bonds which is directly correlated to the binding energy, based on the surface broken bond theory, the size-dependent binding energy function can be approximately expressed as follows:

\[
E_s(N/N) = \left| \frac{B_s}{B_i} \right|^{1/2} + \frac{B_s}{B_i}/2
\]
According to the formula (14), $E_a(N)$ is still in line with the broken bond theory, although the binding energy is proportional to $B_t$ or $\sqrt{B_a}$. Thus the formula (14) can also be used to describe the binding energy of any system.

3. RESULTS AND DISCUSSION

According to the formula (1), the surface volume ratios $\delta$ of IH, CO structures and Wulff sphere construction with different values of $\gamma_{100}/\gamma_{111}$ are subjected to change with the number of atoms $N$ in the system, as shown in Fig. 2. $\delta$ is the simplest function used to describe the geometrical characteristics of clusters, where values $\delta$ of the IH and CO structures are equal. It is obvious from Fig. 2 that the error between IH (or CO) and the Wulff sphere construction is lower and tends to zero as the value $N$ increases. The coincidence of function $\delta(N)$ of IH and Wulff sphere construction implies that the IH structure has a Wulff-like morphology. The relatively large $\delta$ error between IH and Wulff sphere construction suggests that even though the crystal structure takes the morphology of Wulff sphere, the number of atoms on its surface is still greater than the that on IH structure. Therefore, the morphology of clusters more tends to be spherical. On the other hand, when $N$ is a constant, the value $\delta$ of Wulff sphere construction depends on the ratio of $\gamma_{100}/\gamma_{111}$. As shown in Fig. 2, as the value of $\gamma_{100}/\gamma_{111}$ decreases, the $\delta$ value falls down accordingly, which means that a higher value $n_{sp}$ contributes to the formation of a spherical structure. This further explains that, compared with Wulff sphere construction,

![Figure 2. $\delta(N)$ functions for IH (and CO) and different Wulff constructions in terms of Eq. (3.1) (Biener et al., 2005; Volkert et al., 2006)](image)

CO structure has a lower value $\delta$. Therefore, the minimum and maximum of the Wulff sphere construction correspond to $\gamma_{100}/\gamma_{111} = 1$ and $\gamma_{100}/\gamma_{111} = \sqrt{3}$, respectively, where $\gamma_{100}/\gamma_{111} = \sqrt{3}$ means OH structure. It is worth noting that in Fig. 2, the errors of the values $\delta$ of different Wulff sphere constructions are extremely lower, that is to say, the geometric error of the Wulff caused by different ratios of $\gamma_{100}/\gamma_{111}$ are negligible. Therefore, the standard Wulff sphere construction - R-TO ($\gamma_{100}/\gamma_{111} = 2/\sqrt{3}$) can approximately describe the function $\delta(N)$ of any atomic cluster within the error range.

As shown in Fig. 3, the function values $B_s/B_t$ for different structures are compared. It is found that the $B_s/B_t$ is also correlated with structure and decreases as the number of atoms $N$ falls down. The $B_s/B_t$ of IH structure is greater than that of CO and Wulff in a full size range, which means that the total number of bonds in IH structure is highest. As shown in Fig. 3, it is also suggested that the $B_s/B_t$ in CO structure is lower than that in any Wulff sphere construction, although it is also face-centered cubic crystal with the lowest value $\delta$. Besides, a series of functions $B_s/B_t$ for Wulff sphere construction with $\gamma_{100}/\gamma_{111}$ between 1 and $\sqrt{3}$ are given in Fig. 3. It is found that the $B_s/B_t$ of OH structure is minimal, and the error in values $B_s/B_t$ between different Wulff sphere structures is also negligible. Values $B_s/B_t$ are correlated to the value $\delta$ on the one hand, or the surface morphology of the system and on the other hand have something to do with the binding energy $E_a(N)$. As a result, the Wulff sphere, the IH and the CO structures have similar values $B_s/B_t$. The Wulff construction can describe the characteristics of atomic clusters not only in morphology or structure, but also in binding energy.
Figure 3. The comparison the function values $B_a/B_t$ for different structures (Ouyang et al., 2006; Kofman et al., 1994; Jiang et al., 2001)

5. CONCLUSION

Based on the total number $N$ of atoms in the system, this paper gives three models for the surface volume ratio $\delta$, the bonds ratio $B_a/B_t$ and the binding energy $E_c(N)$ of the Wulff construction. The model prediction results are consistent with those of the corresponding atom cluster experiments and computer simulation. As a consequence, even if the atomic cluster structure is uncertain, the geometry and energy model of the Wulff construction can be used to approximately describe the energy and morphology of the cluster.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from Engineering Research Center of Geothermal Resources Development Technologies and Equipment, Ministry Education (Grant No. ERCGR201704).

REFERENCES