JOURNAL OF MATERIALS SCIENCE **39** (2004) 2529–2530

# Vacancy formation energy of small particles

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Vacancies play an important role in the kinetic and thermodynamic properties of materials. The formation energy of a vacancy is the key to understanding the processes occurring in materials during heat treatment and mechanical deformation. Vacancy formation energy can be measured by positron annihilation experiment [1, 2] or calculated by ab initio theory [3–5].

In recent decades, researchers have paid more attention to the special properties of small particles [6, 7]. When dealing with the properties of these particles, such as catalytical or diffusional, the vacancy formation energy is needed as an important parameter. It is difficult to determine the vacancy formation energy of small particles experimentally, and thus some researchers refer to theoretical predictions. Gladkikh and Kryshtal [8] have developed a semi empirical method to calculate the vacancy formation energy of a small particle. In this method, the input parameters are the variation of lattice parameter, the vacancy volume, and the oscillation entropy. All these parameters are the quantities of small particle, and errors in these parameters will lead to uncertainty in the final result. The present letter aims at developing a simpler and physical method to account for the size dependent vacancy formation energy of small particles.

In 1970s, Enderby and March [9] proposed a simple relationship between the vacancy formation energy and Debye temperature from their studies of the structure factor in the liquid metals. Meanwhile, Mclachlan and Jr. [10] have obtained a relationship between the cohesive energy and the Dyeby temperature when they discussed the phenomenon of melting. These two relationships were combined by Tiwari and Patil [11], which lead to a relation between the vacancy formation energy $E_{\mathrm{V}}$ and the cohesive energy $E_0$, i.e.,

$$E_{\mathrm{V}} = k \cdot \frac{m \cdot n}{Z} \cdot E_0 \tag{1}$$

where $K$ is a numerical constant, equal to $8.557 \times 10^{-2}$, $Z$ denotes the coordination number, both $m$ and $n$ are constants given by reference [12]. $K$, $m$, $n$ and $Z$ are all constants for a certain metal without structural variation. Equation 1 shows that the vacancy formation energy is linear to the cohesive energy, consequently, if the cohesive energy of small particles is obtained, Equation 1 can be used to calculate the vacancy formation energy of these particles. Therefore, the key to the problem is to get the formula for the cohesive energy of small particles.

Cohesive energy is an important parameter to estimate the metallic bond, which equals to the energy that can divide the metal into isolated atoms by destroying all metallic bond. However, similar to ionic bond, we can regard the metallic bond as the interaction between different atoms. For simplicity, the interactions between the nearest atoms are only considered in the following calculation. Taking the ideal simple cubic lattice for instance, there are 6 nearest atoms for each interior atom. The interior atoms are emphasized here to distinguish from the surface atoms. According to our assumption, a pair of nearest atoms forms a bond, so each atom in simple cubic lattice forms 6 bonds with its nearest neighbor atoms. However, each bond belongs to two atoms, so the effective number of bonds of an atom is just half of its coordination number. Then for simple cubic lattice, the effective number of bonds of an atom is 3. Of course, the total energy of 3 bonds equals to the cohesive energy if an interior atom. Then the cohesive energy of metal is the sum of all the bond energy of the metal system.

According the scheme discussed above, we can obtain the cohesive energy of metallic particles. Here we assume the particle is in an ideal cubic form, and composed of the same number of unit cells in three dimensions. If the size of the edge of the cubic particle denotes $D$, the volume and the surface of the particle are $D^3$and $6D^2$. For the structural change from simple cubic to body centered-cubic or face centered cubic with little change of particle volume, so it is acceptable to ignore the structure difference of different crystal lattice. Here, we assume all the crystal lattices are in simple cubic structure. Then the total number of the atoms ($n$) of the cubic metallic particle is $D^3/d^3$, here $d$ denotes the size of an atom, in other words, when we change the volume of an atom into an cubic form, $d$ is the size of edge. Furthermore, the number of its surface atoms ($N$) is $6 \cdot D^2/d^2$. Then the number of the interior atoms is $D^3/d^3 - 6 \cdot D^2/d^2$. We denote the number of bonds of an interior atom as $\alpha$ and the number of the bonds of a surface atom as $\frac{1}{2} \cdot \alpha$, because half of the total bonds of the surface atom are dangling bonds. The cohesive energy of the particle ($E_{\mathrm{p}}$) can be written as

$$E_{\mathrm{p}} = \frac{1}{2}\left[\frac{1}{2}\alpha \cdot 6 \cdot \frac{D^2}{d^2} + \alpha \cdot \left(\frac{D^3}{d^3} - 6 \cdot \frac{D^2}{d^2}\right)\right] \cdot E_{\mathrm{bond}} \tag{2}$$

where $E_{\mathrm{bond}}$ is bond energy. For simplicity, we can rewrite Equation 2 as

$$E_p = E_0 \cdot \left(1 - 3 \cdot \frac{d}{D}\right) \tag{3}$$

where

$$E_0 = \frac{1}{2}\alpha \cdot \frac{D^3}{d^3} \cdot E_{\mathrm{bond}}$$

$E_0$ is the cohesive energy of bulk metals. Equation 3 is the basic relation accounting for size dependence of the cohesive energy of metallic particles.

To account for the vacancy formation energy of small particles, it is necessary to replace $E_0$ in Equation 1 by $E_{\mathrm{p}}$, then we have

$$E_{\mathrm{VP}} = k \cdot \frac{m \cdot n}{Z} \cdot E_{\mathrm{P}} \tag{4}$$

where $E_{\mathrm{VP}}$ denotes the vacancy formation energy of small particles.

Inserting Equation 3 into Equation 4 and considering Equation 1, we have

$$E_{\mathrm{VP}} = E_{\mathrm{V}} \cdot \left(1 - 3 \cdot \frac{d}{D}\right) \tag{5}$$

Equation 5 is the basic relationship to calculate the size dependence of the vacancy formation energy of small particles.

To confirm our present method, we should compare our theoretical predictions with experimental values. However, we have not found any available experimental results on the vacancy formation energy of small particles. Here we compare our theoretical predictions with other theoretical results.

Fig. 1 shows our theoretical predictions for small gold particles by Equation 5. In order to compare our calculation results with that of literature, we chose the reciprocal of the half of the particle size $1/R(D = 2R)$ as variable. The diameter of gold atoms used here is 2.88 Angstrom [13]. It is reported that the vacancy formation energy of particle relates to its melting temperature [8]. The symbols in Fig. 1 denote the values of the vacancy formation energy of small gold particles, and which are calculated from their melting temperature [8]. Our theoretical results are consistent with the values given by the melting temperature variation. It is shown by the present results and the literature results that the vacancy formation energy of gold particles increases with increasing the particle size, and when the particle is large enough, their vacancy formation energy approaches to that of the corresponding bulk value.

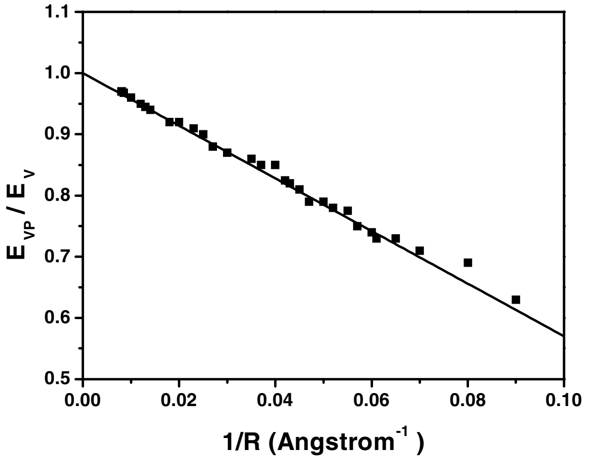

*Figure 1* Size dependence of the vacancy formation energy of small gold particles. Solid line is the calculation results given by Equation 5 ($D = 2R$), and symbols denote the values calculated from the melting temperature of small gold particles [8].

It is known that the melting temperature is a parameter to estimate the metallic bonds, and the melting temperatures of small particles decrease with decreasing the particle size, which means that metallic bonds of small particles are weaker than that of the corresponding bulk metals. Since the formation a vacancy requires the destruction of bonds between an atom and its surrounding atoms, therefore, the energy needed to form a vacancy in small particle, i.e., the vacancy formation energy, is lower than that of the corresponding bulk metal, which is consistent with our theoretical predictions.

In conclusion, a simple method accounting for the size dependent vacancy formation energy of small particles is developed in this letter. The theoretical predictions for the vacancy formation energy of small particles by present method are consistent with other calculation results. Furthermore, our method is better than others because there is only one input parameter (the atomic diameter) in the present one. Considering the importance of vacancy in affecting the properties of materials, the present method can be used widely in the research of the point defects in small particles.

## Acknowledgments

This work was supported by a grant from the National High Technology Research and Development Program of China (863 Program) (No. 2002AA302505).

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*Received 29 July*
*and accepted 29 October 2003*