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Effect of Vacancy on Elastic Deformation of Metallic Materials

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Based on the theory of material thermodynamic surface tension, a research has been conducted on the relationship between vacancy formation energy and elastic deformation parameter of metal materials-Young modulus so as to establish an internal correlation mechanism between microscopic vacancy defect and macroscopic mechanical properties. According to the research results, vacancy formation energy and Young modulus are the external reflection of the binding energy with a regular linear relationship between them, and the proportionality coefficient ranges from 0.005 to 0.008. The mechanism provides a reference for the mutual prediction of macroscopic mechanical properties and microscopic vacancy defect in metallic materials.

1. Introduction

Vacancy is one of the most common microscopic defects in materials. The researches have shown that vacancy concentration and distribution have a great effect on the macroscopic physical and chemical properties of materials (Jordan and Deevi, 2013), such as hardness, melting point (Wang, 1959), boiling point, conductivity and Young modulus (Wan et al., 2009). And the energy required for forming a vacancy can be characterized by vacancy formation energy (Tiwari and Patil, 1975). Thus, it is of great value to carry out an in-depth discussion of the internal mechanism of vacancy formation energy and macroscopic physical properties for preparation and processing of materials.

At present, researches on vacancy formation energy are mainly on two levels: experimental research and simulation fitting. At the experimental research level, Qi et al., estimated vacancy formation energy of 51 kinds of common metals; Zhao et al., used diffraction matrix method to measure the vacancy of point defect; Guedes et al., (2011) measured the vacancy formation energies of BN and BxCyNz and analyzed the formation kinetics of vacancy. Cai et al., (2013) calculated the vacancy formation energy of He and the (001) plane iron atoms. These results are quite decentralized and do not infer from the perspective of metal bond energy from a deep level. At the simulation fitting level, Zhu et al., (1998) used Density Functional Theory to fit the vacancy formation energy; Zhang et al., (2008) synthesized the Tiwari and patil models and introduced the shape factor, correcting the formation energy of vacancies in different shapes; Hu et al., (1999) introduced energy influence factor based on the Brooks model and simulated the vacancy formation energy of different lattices. In fact, the above simulation models are relatively complex with too many semi-quantitative factors. Besides, the part of the simulation superposition process does not truly reflect the overall performance. To more concisely and accurately characterize the essence of the vacancy formation energy, an internal correlation mechanism between microscopic vacancy defect and macroscopic mechanical parameter has been established. Based on the theory of material thermodynamic surface tension, this paper conducts a study on between the vacancy formation energy and elastic deformation parameter of metal materials—Young modulus, which provides some references for the mutual prediction of macroscopic mechanical properties and microscopic vacancy defect in metallic materials.

2. Model

At equilibrium, the forces of atoms come from different directions and can be cancelled out to a certain extent. Suppose that an atom is extracted from the perfect lattice, the extraction process needs to overcome the mutual attraction between the atoms and to break the metal bonds of the atom and the surrounding atoms

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(usually, the formed vacancy is a sphere). According to the material thermodynamic surface tension theory, the relationship between the vacancy formation energy and surface tension can be expressed as (Yu et al., 2014):

$$E_f = \sigma \cdot 4\pi R_0^{\ 2} \tag{1}$$

Where, E_f is the energy required to form a spherical vacancy with unit of *J/mol*; R_0 is the radius of the sphere with unit of *m*. At the same time, the increase of macroscopic surface energy can also be used to express the size of the vacancy formation energy

$$E_f = W_{surface} = -2A \bullet \sigma \tag{2}$$

Where, A is the increase of the superficial area caused by the formation of vacancy with unit of m^2. At the same time, in the process of the formation of vacancy, the radius R before the formation of vacancy is greater than the radius R_1 after the formation of vacancy due to the contraction of the bond energy. According to the law of conservation of mass, the following can be obtained:

$$\frac{4}{3}\pi R_1^{\ 3} \cdot \rho_1 = \frac{4}{3}\pi R^3 \cdot \rho \tag{3}$$

$$R_1 = R\left(\frac{\rho}{\rho_1}\right)^{\frac{1}{3}} \tag{4}$$

Where, ρ is the mean density after the formation of vacancy, and ρ_0 is the mean density before the formation of vacancy. Therefore, the increase of the superficial area is expressed as:

$$A = 4\pi R_1^{\ 2} = 4\pi R^2\left(\frac{\rho}{\rho_1}\right)^{\frac{2}{3}} \tag{5}$$

The generation of vacancy makes a new interface appear inside the material, which increases the superficial area and decreases the binding energy (Yu et al., 2014). According to the law of conservation of energy, the decreased binding energy will be translated into the material's internal energy and lattice distortion energy. In this process, the material's internal energy is far greater than the lattice distortion energy. Thus, assuming that the binding energy can be completely translated into internal energy, then we can obtain:

$$\triangle U = \triangle W_{sur\ face} \tag{6}$$

In the process of stretching of the material, the elastic deformation of the material overcomes the maximum of the binding energy of the material. According to the interaction curve of atoms, the σ-ε curve of the material in the elastic deformation phase can be expressed by a sine function as

$$\sigma = \sigma_{\max} \sin(\frac{2\pi x}{T}) \tag{7}$$

Therefore, the increase of internal energy caused by broken bond of a single atom can be expressed as

$$U = \int_0^{\frac{T}{2}} \mathrm{a}_0^2 \sigma_{\max} \sin(\frac{2\pi x}{T}) dx = \frac{T}{\pi}\sigma_{\max}\mathrm{a}_0^2 \tag{8}$$

Where, σ_{max} is the stress value of the rock bottom of the interaction curve of atoms, x is elongation of stretching of curve of the material in the elastic deformation phase can be expressed by a sine function as, T is the period of the sine curve. Thus, the increase of internal energy can also be expressed by the specific surface energy γ of curve of the material in the elastic deformation phase can be expressed by a sine function as

$$U = \frac{T}{\pi}\sigma_{\max} a_0^2 = 2a_0^2 \cdot \gamma \tag{9}$$

By simplifying, it is

$$\sigma_{\max} = \frac{2\pi\gamma}{T} \tag{10}$$

Elastic deformation parameter of metal materials—Young modulus is the specific value of stress and strain in the axis, characterizing the tensile strength of the material. In the process of elastic deformation of the material, the greater the Young modulus is, the better the tensile strength of the material is. The formula is expressed as

$$E = \sigma \frac{L}{\triangle L} = \frac{\sigma}{\triangle L} \cdot L \tag{11}$$

Where, σ is stretching stress; *L* is the original length of the material with unit of *m*; $\triangle L$ is tensile elongation of the material. When the formula (7) and the formula (11) are differential simultaneous, namely $\triangle x$ is $\triangle L$, then

$$\frac{E}{L} = \sigma_{\max} \frac{2\pi}{T} \cos(\frac{2\pi x}{T}) \tag{12}$$

$\cos(\frac{2\pi x}{T}) \propto 1$, so, formula (11) can be simplified as

$$\sigma_{\max} = \frac{ET}{2\pi L} \tag{13}$$

When the formula (10) and the formula (13) are simultaneous, the specific surface energy of the material is

$$\gamma = \frac{ET^2}{4\pi^2 L} \tag{14}$$

In the process of breaking of a single atom, the period of the binding energy sine function is approximately equal to the atomic bond length, namely, T≈L (Yu et al., 2014), then

$$\gamma = \frac{Ea}{4\pi^2} \tag{15}$$

Substitute formula (15) into formula (9), the change in internal energy caused by breaking of a single atom can be expressed as

$$U = 2a_0^2 \cdot \gamma = 2a_0^2 \frac{Ea_0}{4\pi^2} = \frac{Ea_0^3}{2\pi^2} \tag{16}$$

When the formula (2) and the formula (16) are simultaneous, we can obtain

$$\frac{Ea_0^3}{2\pi^2} = 2A \cdot \sigma \rightarrow \sigma = \frac{Ea_0^3}{4A \cdot \pi^2} \tag{17}$$

Substitute formula (17) into formula (1), then

$$E_f = \frac{Ea_0^3}{4A \cdot \pi^2} \cdot 4\pi R_1^2 = a_0^3 \cdot \frac{E}{4\pi^2} \cdot \left(\frac{\rho}{\rho_1}\right)^{\frac{2}{3}} \tag{18}$$

It can be seen from formula (18) that the vacancy formation energy of the material has a linear relationship with the Young modulus of the material. The larger the Young modulus is, the greater the vacancy formation energy of the material is.

3. Results and Discussion

In order to verify the correctness of the theory, this paper uses data of Young modulus and vacancy formation energy of 16 kinds of common metals (Mei, 1991; Martienssen and Warlimont, 2005; Hu anf Qi, 1999). Based on the crystal structure of different kinds of metals, these metal materials are classified into face-centered cubic crystals, body-centered cubic crystals and close-packed hexagonal crystals. Through collation and analysis of data, the following results have been obtained:

Table 1: Young's modulus and vacancy formation energy

Lattice type	Element	Young's modulus/GPa	vacancy formation	Lattice type	Element	Young's modulus/GPa	vacancy formation
FCC	Co	204	1.75	BCC	Mo	330	3.20
FCC	Cu	128	1.11	BCC	K	1.28	0.39
FCC	Au	78	0.94	BCC	V	127	1.32
FCC	Ag	80	1.00	BCC	Li	4.24	0.46
FCC	Al	70.2	0.77	HCP	Ti	102	1.50
FCC	Fe	211	1.92	HCP	Mg	44.4	0.94
BCC	Cr	145	1.74	HCP	Be	286	2.37
BCC	W	407	3.60	HCP	Cd	62.3	1.23

Figure 1 shows the relationship between Young modulus and vacancy formation energy of six common face-centered cubic lattice materials. In the figure, the abscissa is Young Modulus E of different materials with unit of *GPA*; and the ordinate is the vacancy formation energy E_f of the corresponding element with unit of *eV*. It can be seen from the figure that the larger Young modulus is, the greater the vacancy formation energy is. Both are approximately linear relationship where the data is linearly fitted with the proportionality coefficient being 0.0072 and intercept being 0.3288.

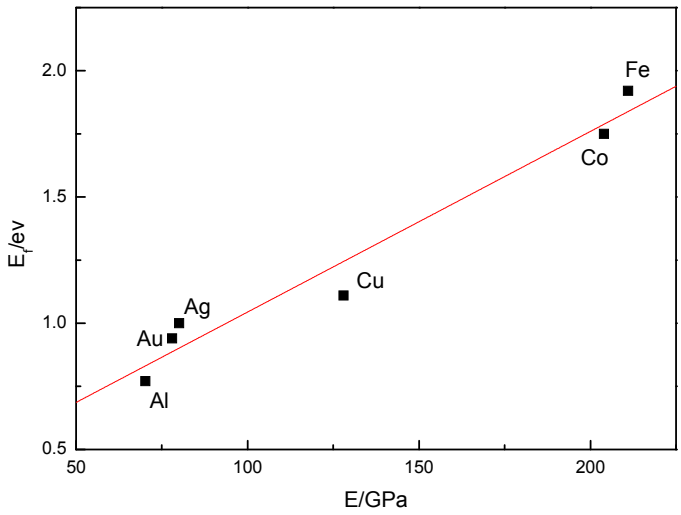

Figure 1: The correlation between FCC lattice metal Young's modulus and vacancy formation energy

Figure 2 and Figure 3 respectively show the relationship between Young modulus and vacancy formation energy of six common body-centered cubic lattices and four close-packed hexagonal lattices. It can be seen from the figures that the relationship between the two is still a linear relationship to a certain degree, in which the proportionality coefficient of the body-centered cubic is 0.0081 and the intercept is 0.4188; the proportionality coefficient of close-packed hexagonal cubic is 0.0055 and the intercept is 0.8318.

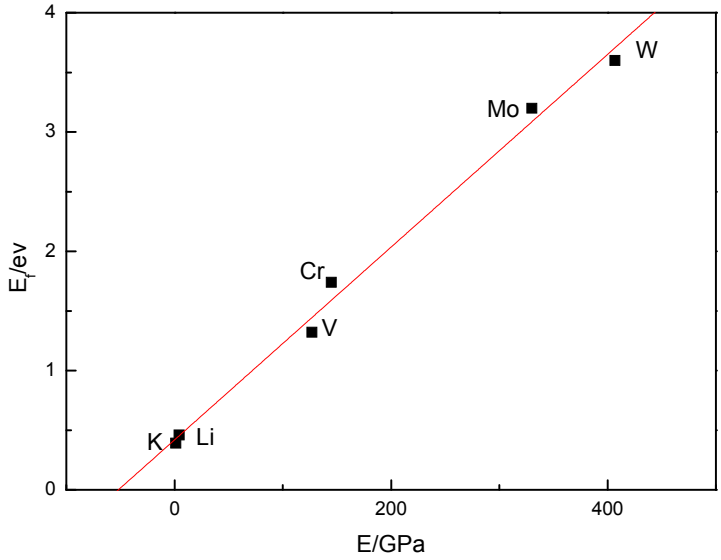

Figure 2: The correlation between BCC lattice metal Young's modulus and vacancy formation energy

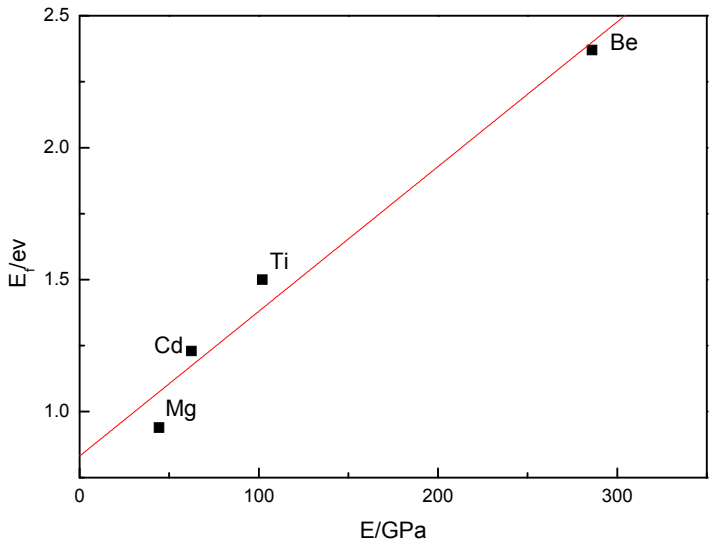

Figure 3: The correlation between HCP lattice metal Young's modulus and vacancy formation energy

From the relationship between Young modulus and vacancy formation energy in Figure1, Figure 2, and Figure 3, it can be concluded that in the FCC, BCC and HCP lattices, there is a linear relationship between Young modulus and vacancy formation energy. The proportionality coefficient is between 0.005 and 0.008. At the same time, there is a small amount of error between the actual value and the true value of vacancy formation energy of different elements for the effect of defects in the material and the lattice shrinkage in the process of vacancy formation energy of the material. It can be known from an in-depth inference; the material's bulk modulus and shear modulus are proportional to Young modulus. Therefore, the bulk modulus and shear modulus are also proportional to the vacancy formation energy of the material.

4. Conclusions

1. In fact, Young modulus of the material is related to the bond energy of the lattice, and vacancy formation energy of the material can also be characterized by the surface energy of the material. Therefore, there is a certain relationship between Young modulus and vacancy formation energy of the material.
2. Based on the formulas of Young modulus and vacancy formation energy, we can know that there is a linear relationship between the two, and the proportionality coefficient is between 0.005 and 0.008. The macroscopic mechanical properties of materials are effectively combined with microscopic vacancy defects.
3. According to the transformational relations of the three elastic modulus, the shear modulus, bulk modulus and Young modulus are proportional to each other, so it is deduced that there is a linear relationship among the shear modulus, bulk modulus and vacancy formation energy.

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