

On the size dependence of the vacancy formation energy

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The possibilities for estimating the vacancy formation energy in small particles are considered. The values obtained for vacancy formation energy for a number of metals agree with the literature ones. We also find the size dependence of the formation energy of both volume and surface vacancies. These dependencies are obtained from experimental data on the melting temperature and lattice parameter decreasing in small metal particles.

Рассматриваются возможности для оценки энергии образования вакансий в малых частицах. Вычисленные значения согласуются с имеющимися литературными данными. На основании экспериментальных данных по понижению температуры плавления и уменьшению параметра решетки в малых частицах получена размерная зависимость энергии образования объемных и поверхностных вакансий соответственно.

1. Introduction

The crucial role of defects, specifically, of vacancies, in determining the physico-chemical properties of crystalline solid bodies is well known. It becomes vital when dealing with small particles due to their enormous activity (catalytical, diffusional etc). For the first time the conclusion on the increase of the vacancy concentration in small particles was made in paper [1] resulting from the analysis of experimental data on the melting temperature lowering with the particle size decreasing. Later an attempt was made to investigate the size dependence of the vacancy formation energy in quasi-chemical approximation, taking into account the role of the surface and the ejecting Laplace pressure [2]. It was found that for fcc metals with $V_v \sim 0.5\Omega$ (V_v is the single vacancy volume and Ω is the atomic volume) the concentration of vacancies actually does not depend on particle size. Recently the concept of Laplace pressure has failed

to describe the properties of small-size particles [3], thus stimulating further development of the concept of size dependence of the vacancy concentration in small particles. Fundamentally it can be reduced to the determination of the size dependence of the vacancy formation energy.

2. Estimating vacancy formation energy

Let us use the fact of proportionality between the vacancy formation energy and the melting temperature T_s [4-6],

$$E_v = \gamma T_s, \quad (1)$$

where γ is a constant depending on the structure type. As the particle of radius r has lower melting temperature T_r than the bulk samples, then the passage from bulk samples to small particles the decrease in melting temperature $\Delta T = T_r - T_s$ corresponds to the decrease of the vacancy formation energy

Table. Comparison of calculated values of the vacancy formation energy E_v with the available ones [8].

Element	E_v, eV [8]	E_v, eV , cacluated on (5)	λ , kJ/mol [27]	σ_l , erg/cm ² [27]	$\frac{d\sigma}{dT}$ [27]	σ_s , erg/cm ² [9]	δ , % [27]	T, °C
Ag	0.92	0.71	11.3	903	0.16	1140	3.8	750
Au	1.08	0.8	12.37	1140	0.52	1450	5.1	970
Al	0.77 [26]	0.68	10.47	866 [9]	0.15 [9]	1140	6.5	180
Cu	1.11 [26]	0.7	13.02	1350	0.24	1720	4.2	1006
Pt	1.58	1.16	19.7	1800	0.17	2340	6.6 [29]	1310
In	0.53	0.5	3.27	585 [9]	0.1 [9]	633	2.0	142
β -Sn	0.52	0.4	7.08	544	0.07	673	2.3	215
Pb	0.49	0.35	4.98	468	0.13	560	3.5	309
Fe	-	1.01	13.8	1872	0.49	2320	3.5	1410
Bi	-	0.41	11.0	378	0.07	521	-3.35	239

$$\Delta E_v = \gamma \Delta T. \quad (2)$$

Also it is well known, that with the decrease of the size of a small spherical particle, the evaporation energy decreases, because the particle before evaporation still has the surface energy $4\pi r^2 \sigma$. It was Frenkel [6] who had shown that processes of vacancy evaporation and formation were similar to each other and therefore the formation energy of vacancies should have the order of the evaporation energy of vacancies. Consequently, for a particle of radius r the formation energy is decreased by the quantity

$$\Delta E_v = \frac{3\sigma_s \Omega}{r} \quad (3)$$

According to the triple point model [7], the lowering of the melting point of free particles on decreasing their size is given by the expression

$$\frac{T_s - T_r}{T_s} = \left(\frac{3}{\lambda \rho} \frac{\sigma_s - \sigma_l(1 + \delta/3)}{r} \right), \quad (4)$$

So, from the equality of ΔE_v values determined from expressions (2) and (3) together with (4) one can obtain the expression for the vacancy formation energy in the bulk

$$E_v = \frac{\lambda \rho \Omega}{1 - \sigma_l(1 + \delta/3)/\sigma_s}. \quad (5)$$

Here σ_s and σ_l are specific surface energies in the solid and liquid phases, respective-

ly, at the particle melting temperature T_r , ρ is the density, λ is the melting heat, δ is the relative volume change under melting. Therefore, if the values of specific surface energies in the solid σ_s and liquid σ_l phases are known, one can estimate the value of the vacancy formation energy E_v . Note that expression (5) contains the surface energy of the liquid phase below the melting point of bulk samples. In this temperature region the energy is determined only for several easy-melting metals and only for small supercoolings. That is why in this work we extrapolate it below the melting temperature, as it was done in [7]. The results of estimations are presented in Table. One can see, that the values of the vacancy formation energy E_v , estimated according to expression (7), are in satisfactory agreement with the literature data. To our mind it is because experimental data, usually reported in the literature, correspond to temperatures close to the melting point. In this temperature region the temperature dependence of the specific surface energy in solid phase $\sigma_s(T)$ is already nonlinear and at the same time the accuracy of the values, estimated according to expression (7), is much lower. Basically, if one has the data on the temperature dependence of the quantity $\sigma_s(T)$ in the region where it is linear (e.g. far from the melting point) it will allow, probably, to estimate not only the value of the vacancy formation energy E_v but its temperature dependence too.

3. Size dependence of vacancy formation energy

For estimation of the size dependence of the vacancy formation energy it is sufficient to use expression (1). The particle of radius r has a lower melting temperature T_r than the bulk sample. Then neglecting the changes in structure type its vacancy formation energy E_r may be expressed as

$$E_r = E_v \frac{T_r}{T_s} \quad (6)$$

Figure 1 shows the dependence of the vacancy formation energy E_r as a function of the inverse radius of the particles. This dependence has been plotted using the experimental data on the melting temperature lowering for gold particles [10, 11] and associated naturally with the volume vacancies. Such dependence has the same shape for metals for which the measured data on the size dependence of the melting temperature are available in literature (Sn, Bi, Pb, In, Al).

Size dependence of the vacancy formation energy could also be estimated theoretically according to the molecular-kinetic considerations with usage of expression (3). This relationship has been plotted in Fig. 1 for gold particles with $\sigma=1500\text{erg/cm}^2$ and $\Omega=16.96 \cdot 10^{-24}\text{cm}^3$ (solid line). One can observe good agreement with the data calculated from the melting temperature lowering measured for small particles.

If we assume that the decrease of the lattice constant in small particles is due to the increased concentration of vacancies in them [13], then the experimental data on the decrease of this constant also allow us to estimate the size dependence of the vacancy formation energy. We have done this using the experimental data on the size dependence of the lattice parameter in Cu, Ag and Au island films [13]. The size dependence of E_r has been calculated from the following expression

$$E_r = kT \ln \left[\frac{1}{3} \frac{\Delta V_v}{\Omega} \frac{a_0}{\Delta a} e^{\frac{s}{k}} \right], \quad (7)$$

where $\Delta a/a_0$ is the relative decrease of the lattice parameter, $\Delta V_v = \Omega - V_v$, $e^{s/k}$ is the term related to the changes of the oscillation entropy under vacancy formation, k is Boltzmann's constant.

Figure 1 depicts the values of the vacancy formation energy calculated from the data on

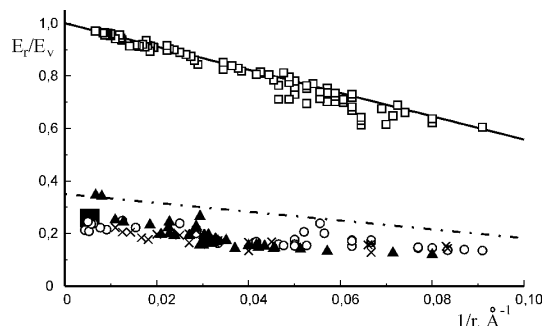


Fig.1. Size dependence of vacancy formation energy for small particles as a function of their inverse radius (\square denotes the data calculated from the melting temperature lowering for small gold particles [10, 11], solid line corresponds to expression (5), dash-dot line is for the estimates of surface vacancies formation energy [21,22], \circ , \blacktriangle , \times are the values, calculated from experimental data on the lattice parameter lowering for small Au, Ag and Cu particles, respectively [13-16, 23-25], \blacksquare is the measured value of the Ni surface vacancy formation energy [28].

the decrease of the lattice parameter for small Au, Ag and Cu particles [13-16, 23-25]. These values lie much lower than ones evaluated from the melting temperature lowering in small particles.

This difference seems to be natural and it is probably due to the following reasons. The population of surface and near-surface atoms in small particles with the size less than $100 \cdot \text{\AA}$ may attain the value of several tens percent. So it is the surface and near-surface vacancies that determine mainly the properties of such particles. This conclusion is supported by the following estimates.

The number of broken bonds for atoms at face (111) of bulk fcc single crystals is equal to 3. Under formation of an adsorption atom, the atom leaves the surface where it has 9 nearest neighbours and arrives on the surface where it has 3 neighbours with simultaneous formation of a vacancy, the number of broken bonds being equal to 6. The value of the energy associated with this process is about 0.7eV whereas the energy value for the vacancy formation for volume vacancies is equal to 1eV. This value agrees with the measured data for face (111) of Cu single crystals [17,20]. One can estimate the formation energy of the surface vacancy as the difference between the energies the atom has "inside" the surface and at the fracture where the atom removed from

the surface should be placed in order to form a vacancy. As the atom at the fracture has 6 nearest neighbours, the number of broken bonds in the latter process is equal to 3 out of 9 available bonds and the formation energy of the surface vacancy has the value $\sim 0.33\text{eV}$.

As was established in paper [18], with the decrease of the crystal size the number of broken bonds for atoms at the surface of Wulf fcc polyhedron decreases and approaches 6. In this situation the formation energy of the surface vacancy also decreases to the value $\sim 0.3\text{eV}$ because for such small particles the formation of the surface vacancy leads to the number of broken bonds equalling 2-3 out of 6 available.

The estimates described above agree with the experimental results available in literature. For example, paper [28] obtained for the formation energy of surface vacancies the value 0.25eV studying the defects at nickel surface during ion bombardment. Moreover, the values of the vacancy formation and vacancy migration energies for intergrain boundaries decrease as compared with the volume ones, as follows from the results of experimental investigation of intergrain diffusion [21, 22]. These lowerings are such that the ratio of activation energies for diffusion at grain boundaries and in volume is equal to 0.35-0.55 for fcc metals. If we assume that the minimum value of the latter ratio holds for the ratio of formation energies of surface and volume vacancies, then the size dependence of the surface vacancy formation energy may be evaluated from the size dependence of the volume vacancy formation energy obtained from the data on the melting temperature lowering (dash-dot line in fig. 1). These values of the surface vacancy formation energy are slightly higher than the ones calculated from experimental data on the lattice parameter decreasing in small particles. This small difference is probably due not only to the changes in the atom coordination with the decrease of particle size described above. As was shown by a number of computer simulations [12], this difference is also caused by the decreasing of the absolute value of binding energy per atom with the decrease in particle size.

Let us extrapolate the experimental data on the decrease of the formation energy of both volume and surface vacancies up to the lowest sizes. It appears, that there is a critical size when one can't separate vacancies into vol-

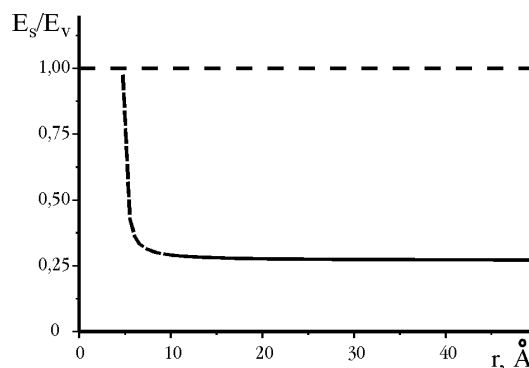


Fig.2. Size dependence of the ratio of formation energy of surface vacancies (obtained from the decrease of the lattice constant) to the volume vacancies (obtained from the melting temperature lowering)

ume and surface ones. The value of such size is about 5Å that agrees with the literature data and corresponds, probably, to the vacuum-particle transition layer. This fact is obvious from the curve in fig. 2 showing the ratio of the surface vacancy formation energy to the volume vacancy formation energy.

It is worth mentioning that the new size effect was established while studying small particles of ionic compounds of NaCl type. It was found that volume defects become surface ones with the crystal size decreasing [32]. This conclusion is also supported by the results of treating surface properties of closely packed clusters within the framework of different theoretical models [31] as well as by the results of molecular dynamic investigation of the melting process of clusters of atoms with binary interaction [12]. It was shown that at room temperature the vacancies mainly arise at the surface of a cluster and only then they pass to the outer vacant shell. This transfer disrupts the perfect cluster structure, existing at zero temperature when the next shell is filled after the preceding one. On increasing the temperature, the next shell begins to be filled before the preceding one is full, i.e., at room temperature the inner shells have vacancies.

Therefore the binding energy of the atom changes more smoothly with the increase of cluster size. As the vacancy formation energy in the inner shell exceeds the one at the surface shell substantially, this difference, according to the results of paper [31], is not so large. This fact is explained by interaction that converts vacancies in the outer shells to the inner

ones. All these facts point out that values of the vacancy formation energy obtained from the data on the decrease of the lattice parameter are associated with the surface vacancies. As the population of surface and near-surface atoms in small particles may attain the value of several tens percent, the decreasing of the lattice parameter in small particles is caused by the surface and near-surface vacancies.

4. Summary

It was shown that the formation energy of both volume and surface vacancies decreases with the decrease in particle size. There is a critical size when all vacancies due to small size become the surface ones. These results allow one to explain from one viewpoint the various properties of small particles, for example, the enormous rate of sintering, catalytical activity, the «liquid-like» coalescence [19] discovered long ago etc.

Referencies

1. I.D.Morokhov, S. P.Chizhik et al, *Doklady akademii nauk SSSR*, **248**, 603 (1979).
2. I.D.Morokhov, V.I.Zubov et al, *Fiz. Tverd. Tela* **25**, 1, 312 (1983).
3. V.I.Gorchakov, E.L.Nagaev et al, *Fiz. Tverd. Tela* **30**, 4, 1068 (1988)
4. T.Gorecki, *High Temp. – High Press.* **11**, 83, (1979).
5. Ya.A.Kraftmakher, Works on Solid State Physics, Novosibirsk, Nauka, **1**, 30 (1967) [in Russian]
6. Ia I Frenkel, Kinetic Theory of Liquids, New York, Dover Publications, (1955)
7. N.T. Gladkikh, S.V. Dukarov, V.I. Larin, *Functional materials*, **1**, 50, (1994).
8. M.N.Magomedov, *Russian metallurgy*, **5**, 63 (1992)
9. V.I. Nizhenko, L.I. Floka, Surface Tension of liquid Metals and its Compounds, Moscow, Metallurgia (1981) [in Russian].
10. P.Buffat, J.P.Borel *Phys.Rev. A* **13**, 2287 (1976).
11. J.R.Sambles, *Proc. Roy. Soc. London* **A324**, 339 (1971).
12. B.M.Smirnov, *Soviet physics, Uspekhi*, **37**, 11 1079 (1994)
13. N.T.Gladkikh, O.P.Krystal, *VANT* 2(3) (1998).
14. M.Ya.Gamarnik, Yu.Yu.Sidorin, *Phys. Stat. Sol. B* **156**, k1 (1989).
15. Chr.Kuhrt, R.Anton, *Thin solid films* **198**, 301 (1991)..
16. N.T.Gladkikh, V.I.Larin et al, in: Proceedings of the conference “Structure and physical properties of thin films” Uzhgorod, Ukraine 35 (1977)
17. Yu.N.Devjatko, E.P.Gusev et al, in: Proceedings of the international conference “Interaction of ions with the surface” Zvenigorod, Russia, **1**, 114 (1997)
18. K. H.Behrndt, *Thin solid films* **7**, 415 (1971).
19. D.W.Pashley, *Advances in physics* **14**, 327 (1965).
- 20.H.M.Polatoglou, M.Methfessel, M.Scheffler, *Phys.Rev. B* **48**, 1877 (1993).
21. B S.Bokshtein et al, Thermodynamics and kinetics of grain boundaries in metals” Moscow, Metallurgija, (1986) [in Russian].
22. I.Kaur, W.Gust, Fundamentals of grain and interphase boundary diffusion, Ziegler Press, Stuttgart (1989).
23. A.G.Buntar’ et al, *Izv. Vuzov MV i SSO SSSR, Fisica VINITI 102-74 UDK 548.52.539.27* (1974)
24. A.G.Buntar’, A.M.Thorivskij et al, *Fiz. Met. i Metalov*, **37**, 4 790 (1974)
25. M.Ya, Gamarnik, Thesis of the doctor of science dissertation, Kharkov, Ukraine (1991).
26. M.W. Thompson, Defects and radiation damage in metals, Cambridge U.P., (1969)
27. Colin.I. Smithells, Metals reference book London, Butterworth and Co. Publishers, (1976)
28. M.A.Vasil’ev et al, Proceedings of the Eighth International Workshop on Ion Beam Surface Diagnostics Uzhgorod, Ukraine 144 (1998)
29. A.R.Ubbelohde, The molten state of the matter, John Wiley and Sons Ltd., (1978).
30. P.Varotsos, K.Eftaxias, V.Hadjicontis, *Phys. Rev. B* **38**, 4296 (1988)
31. B.M.Smirnov, *Soviet physics, Uspekhi*, **35**, 1 37 (1992)
- 32.V.M.Maevskii, N.N.Vitrikhovskii, E.R.Zusmanov, *Technical physics letters* **19**, 4 244 (1993)

Розмірна залежність енергії утворення вакансій

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Розглядаються можливості оцінки енергії утворення вакансій в малих частинках. Обчислені значення узгоджуються з наявними літературними даними. На підставі експериментальних даних по зменшенню температури плавлення та зменшенню параметра ґратки в малих частинках отримана розмірна залежність енергії утворення об’ємних та поверхневих вакансій відповідно.