Size-Dependent Formation Enthalpy of Nanocompounds

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Size-Dependent Formation Enthalpy of Nanocompounds

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A quantitative thermodynamic model for the size-dependent formation enthalpy of nanocompounds is proposed. The model reveals that the thermal stability of nanocompounds decreases because of the size dependence of formation enthalpy when the size of these nanostructures decreases. This stability loss is related to some general phenomena such as interface alloying of immiscible systems and phase segregation of miscible systems with reducing system sizes. The predictions from the model are in agreement with the results from density function theory calculation for MgH_2, the experimental measurement of SnTe nanoparticles, and quantum chemistry consideration.

1. Introduction

As the sizes of crystals and devices decrease, the properties of materials become different from those of the corresponding bulks. For example, the thermal stability of nanomaterials decreases compared with that of the bulk ones,[1−10] which affects directly the application of nanoscale devices. It has been shown that both melting enthalpy and cohesive energy of nanocrystals are size-dependent.[5−10] For nanocompounds, one may naturally ask whether formation enthalpy is also size-dependent. Here, the formation enthalpy is the enthalpy change associated with the formation of a compound from its constituent substances or elements. The answer to this question could be very significant in determining phase diagram of nanoscale multi-element systems and in understanding physical and chemical properties of nanocompounds and multilayers, which are of great interest not only in fundamental research but also in technology application. For example, the formation enthalpy and interface energy of Cu/Ta binary system play a key role in ultralarge scale integration circuit. It is well-known that the formation enthalpy of bulk Cu/Ta system is positive and large, therefore, their interface is stable and safe for the circuit. The stability of the interface actually depends on the ratio of the formation enthalpy to interface energy of the system. When the ratio is smaller than 1, with reducing scale of the nanodevices, despite positive formation enthalpy, the alloys can be formed because of the instability of the larger interface energy,[11] that is, Cu or Ta atoms can diffuse badly through the interface, which will lead to the failure of the circuit.

In this paper, on the basis of the size dependence of latent heat of melting-phase transition, a quantitative thermodynamic model for the size dependence of formation heat of nanocompounds is proposed. The size-dependent formation enthalpies predicted from our model are compared with those from density function calculation for nanoscale MgH_2, the experimental

measurement of SnTe nanoparticles, and quantum chemistry consideration, and good agreements are found.

2. Model

In recent years, a physical model for the size-dependent melting enthalpy $H_m(D)$ function has been established. The model's predictions are consistent with the experimental results of nanocrystals.[7−8] $H_m(D)$ decreases with reducing crystals' size D and the decrease rate depends on such parameters as bulk melting entropy S_{mb} and the critical size D_{cm}.[7,8] The $H_m(D)$ function as a general function for the size dependence of the phase transition heat is also suitable for other transitions.[9,12] For example, it is applicable for the determination of size-dependent cohesive energy $E_c(D)$ function if the corresponding transition entropy S_{cb} for the solid−vapor transition is used to substitute S_{mb} and the critical size D_{cc} for the corresponding transition is employed instead of D_{cm}.[9]

For nanocompounds of two different elements, the formation enthalpy should also be size-dependent. Similarly to the size-dependent melting enthalpy[7,8] and cohesive energy,[9] with the formalism of a product of the exponential function and the linear one of D, the size-dependent formation enthalpy $H_f(D)$ function of nanocompounds can be written as

$$\frac{H_f(D)}{H_{fb}} = \exp\left(-\frac{2S_{fb}}{3R}\frac{1}{D/D_{cf}-1}\right)\left(1-\frac{1}{D/D_{cf}-1}\right) \quad (1)$$

where D denotes the diameter of compound nanocrystals or the thickness of alloy layers for binary metallic films, H_{fb} is the bulk formation enthalpy, S_{fb} is the bulk entropy corresponding to the formation of compounds and is expressed as

$$S_{fb} = -R(x_A \ln x_A + x_B \ln x_B) \quad (2)$$

at 0 K, where x is the atomic percentage of the components with the subscripts A and B corresponding to two components, respectively. It means that only configurational entropy contributes at 0 K and eq 2 is the same as the expression of ideal mixing entropy. When the temperature $T > 0$ K, S_{fb} is larger
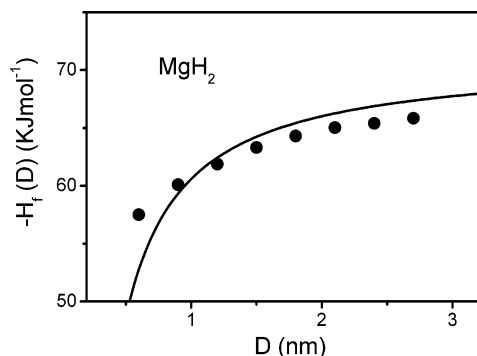
Figure 1. The size-dependent formation enthalpy $H_f(D)$ function of MgH$_2$. The solid line is the prediction of eq 1 and the symbols are the DFT calculation results at 0 K.[13] In eq 1, $H_{fb} = -71.1$ K J mol^{-1},[13] $h_{Mg-H} = 0.195$ nm,[14] $D_{cf} = h_{Mg-H}/2 = 0.0975$ nm, and $S_{fb} = 5.292$ J mol^{-1} K^{-1} in terms of eq 2 with $x_{Mg} = 1/3$ and $x_H = 2/3$.
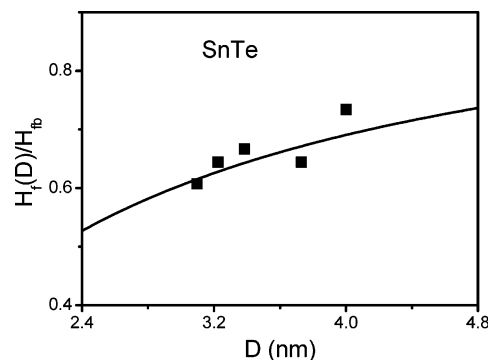

Figure 2. The size-dependent formation enthalpy $H_f(D)/H_{fb}$ function of SnTe nanoparticles. The solid line is the prediction of eq 1, $D_{cf} = (h_{Sn} + h_{Te})/4 = 0.1936$ nm with $h_{Se} = 0.3724$ nm and $h_{Te} = 0.4018$ nm,[15] $S_{fb} = -R(x_{Sn} \ln x_{Sn} + x_{Te} \ln x_{Te}) + [S_{cb}(Sn) + S_{cb}(Te)]/2 = 78$ J mol^{-1} K^{-1} with $x_{Sn} = x_{Te} = 1/2$ and $S_{cb} = H_{cb}/T_{cb}$, $H_{cb} = 295.80$ K J mol^{-1}, $T_{cb} = 2876$ K for Sn and $H_{cb} = 52.55$ K J mol^{-1}, $T_{cb} = 1261$ K for Te.[16] The symbols are experimental results from ref 17. The diameter of particles $D = 2^{1/3}h_a/(N^{-1/3})$ with the average atomic diameter $h_a = (h_{Sn} + h_{Te})/2 = 0.3871$ nm and the atomic numbers of the particles N, $H_{fb} = -0.64$ eV.[17]

usually because of the contribution of thermal entropy and also cannot be calculated simply by H_{fb} at T since the formation reaction of compounds is more complex than the simplex phase transition. D_{cf} in eq 1 is the critical diameter or thickness of compound particles or alloy layers.

Considering that a single atom or molecule cannot be identified whether it is in a single state or a compound state, when D is the size of only one atom, $H_f(D) = 0$. At the same time, according to eq 1, when $D = 2D_{cf}$, $H_f(D) = 0$, therefore, $2D_{cf}$ corresponds to the size of one atomic diameter h or the average bond length of compounds. Thus, the critical diameter or thickness D_{cf} is defined as a half of the bond length h_{A-B} between two element atoms of compound crystals, $D_{cf} = (h_A + h_B)/4$ for binary thin films. Another limit is $H_f(D) = H_{fb}$ when D increases up to the bulk size. From the point of view of the bulk approach, eq 1 satisfies the two limits. The formation enthalpy can be positive or negative, and the size effect of its absolute value is discussed here.

3. Results and Discussions

Equation 1 shows that the absolute value of the formation enthalpy decreases as the diameter of nanocompounds or the thickness of alloy layers decreases. The latest study has shown that the formation enthalpy (negative) of nanoscale MgH$_2$ increases as the size decreases.[13] Figure 1 shows the comparison between the prediction of eq 1 and the calculation results of MgH$_2$ by density function theory (DFT) method.[13] Clearly, it can be seen that they are in agreement with each other except for that in the minimum size (smaller than 1 nm). When the size of nanocompounds decreases to about 1 nm, these compounds may be some clusters whose structure and energy state are different from that of the corresponding crystals, the quantum or discrete size effect may be dominant, and the present model is not suitable for that case.

Figure 2 illustrates the model's prediction and the experimental results for the size-dependent formation enthalpy of SnTe nanoparticles.[17] In the experiment, SnTe nanoparticles were obtained by the vapor deposition method, and the condensation of the molecules is similar to the inverse process of sublimation.[17,18] To compare with the experimental measurement, S_{fb} in eq 1 is assumed to be equal to a sum of the configurational entropy determined by eq 2 and the average value of S_{cb} of two components as a first-order approximation, $S_{cb} = H_{cb}/T_{cb}$, with vaporization enthalpy H_{cb} and boiling point T_{cb}.[9]

The size effect of the formation enthalpy can also be corroborated by the interface or surface alloying[11,20-21] and by the formation of nanosized compounds of immiscible binary

systems.[19,22-23] For immiscible binary systems in the bulks, the formation enthalpy is positive and larger than the interface energy of the systems, the interface between two elements is stable, and thus the formation of compounds or interface alloying is impossible. However, for the same systems at the nanoscale, such as Cu/Ta, Fe/Cu, and Au/Ni systems, and so forth, the interface alloying or nanosized compounds have been observed experimentally,[11,19-20,22-23] and this plausible contradiction can be explained by our model. When the formation enthalpy reduces to be smaller than the interface energy of the systems because of the size effects, the nanocompounds can be obtained and the interface alloying can occur at certain size range or layer thickness. This interpretation consummates the previous interface energy analysis.[21] For immiscible systems, the positive formation enthalpy decreases with reducing size, implying an increase of the miscible capability, which constitutes an important guideline to powder metallurgy field and electronic industry.

On the other hand, for two miscible elements, the negative formation enthalpy increases with decreasing size as demonstrated by Figures 1 and 2. The result reflects a decrease of the miscible capability of miscible systems at nanoscale. Another evidence is the experiment on nanostructured Ni/Co thin films, which did not form the alloy as expected from their bulk phase diagram,[24] and this miscibility decline is directly related to general surface phase segregation phenomena in miscible systems.

The one describes that the original immiscible state in the bulks loses its stability and tends to be miscible, and the other shows that the stable miscible state in the bulks becomes unstable and phase segregation reinforces with reducing size. Both of them are from the stable state in the bulks to the metastable state in the nanostructures because of the higher energy and activity of the nanostructures. The mechanism behind this effect may be related with the complementary changes of electronegativity and electron density differences between two elements with reducing size.

Considering the approximation of $\exp(-x) \approx 1 - x$ for small x, eq 1 can be simplified as $H_f(D)/H_{fb} \approx 1 - 2S_{fb}D_{cf}/(3RD)$ when D is large. This result is in accordance with the general quantum chemistry consideration that the size-dependent change of thermodynamic quantities is roughly proportional to $1/D$[25] and with the classical thermodynamic droplet model: the slope

of $H_f(D)$ changing with $N^{-1/3}$ in our model is about 1.85 eV, which is 1.62 eV in the droplet model.[17] Moreover, the atomic interaction energy between two elements related to the mixing enthalpy is also the function of $1/D$.[26] This correspondence implies that the decrease of the thermodynamic quantities is essentially induced by the increase of the surface/volume ratio and by the lower coordinate number of surface atoms[10] related to the higher surface energy of nanomaterials. As the size of the nanostructures decreases further to smaller than $5-10$ nm, the size effect of the thermodynamic quantities is stronger than the above simplified linear form, because the energetic state of interior atoms of the nanostructures in small size is also higher than that of the corresponding bulk crystals.

Moreover, eq 1 shows that the size dependence of the enthalpy decreases as the parameters S_{fb} and D_{cf} decrease. For the positive formation enthalpy of three components, the decrease of the enthalpy compared to the bulk is stronger than that of two components, since $S_{fb} = 9.134$ J mol^{-1} K^{-1} for three components with $x = \frac{1}{3}$ is larger than 5.763 J mol^{-1} K^{-1} for two components with $x = \frac{1}{2}$ in terms of eq 2, considering the same x of every component at 0 K, and D_{cf} of three components is also larger. This may explain to some extent why the amorphous alloys with three components are easier to form than those with two components.

4. Conclusion

In summary, on the basis of the size dependence of melting-phase transition heat of nanocrystals, we have proposed a thermodynamic model for size-dependent formation enthalpy of nanocompounds. The size effect results from the large surface/volume ratio of nanostructures and reflects the instability of nanostructures compared to the bulks. More importantly, the model reveals the mechanism behind some general phenomena such as interface alloying of immiscible systems and phase segregation of miscible systems with reducing size of the systems. The predictions from our model are consistent with those results from density function theory (Figure 1), the experiment (Figure 2), and other estimates.

References and Notes

(1) Takagi, M. *J. Phys. Soc. Jpn.* **1954**, *9*, 359.
(2) Goldstein, A. N.; Echer, C. M.; Alivisatos, A. P. *Science* **1992**, *256*, 1452.
(3) Kellermann, G.; Craievich, A. F. *Phys. Rev. B* **2002**, *65*, 134204.
(4) Kim, H. K.; Huh, S. H.; Park, J. W.; Jeong, J. W.; Lee, G. H. *Chem. Phys. Lett.* **2002**, *354*, 165.
(5) Jackson, C. L.; McKenna, G. B. *J. Chem. Phys.* **1990**, *93*, 9002.
(6) Lai, S. L.; Guo, J. Y.; Petrova, V.; Ramanath, G.; Allen, L. H. *Phys. Rev. Lett.* **1996**, *77*, 99.
(7) Jiang, Q.; Shi, H. X.; Zhao, M. *J. Chem. Phys.* **1999**, *111*, 2176.
(8) Zhang, Z.; Lü, X. X.; Jiang, Q. *Physica B* **1999**, *270*, 249.
(9) Jiang, Q.; Li, J. C.; Chi, B. Q. *Chem. Phys. Lett.* **2002**, *366*, 551.
(10) Sun, C. Q.; Wang, Y.; Tay, B. K.; Li, S.; Huang, H.; Zhang, Y. B. *J. Phys. Chem. B* **2002**, *106*, 10701.
(11) Kwon, K. W.; Lee, H. J.; Sinclair, R. *Appl. Phys. Lett.* **1999**, *75*, 935.
(12) Jiang, Q.; Cui, X. F.; Zhao, M. *Appl. Phys. A* **2004**, *78*, 703.
(13) Liang, J. J. *Appl. Phys. A* **2005**, *80*, 173.
(14) Wimmer, E. *Atomistic Approaches in Industrial Materials Engineering*; Physics Spring School in Toulouse: Toulouse, 2003; p 33.
(15) King, H. W. *Physical Metallurgy*; Cahn, R. W., Ed.; North-Holland Pub. Co.: Amsterdam, 1983; p 64.
(16) *Periodic Table of the Elements*; Sargent-Welch Scientific Company: Skokie, IL, 1980; p 1.
(17) Schäfer, R. *Z. Phys. Chem.* **2003**, *217*, 989.
(18) Bachels, T.; Tiefenbacher, F.; Schäfer R. *J. Chem. Phys.* **1999**, *110*, 10008.
(19) Yavary, A. R.; Desre, P. J.; Benameur, T. *Phys. Rev. Lett.* **1992**, *68*, 2235.
(20) Nielsen, L. P.; Bensenbacher, F.; Stensgaard, I.; Laegsgaard, E.; Engdahl, C.; Stoltze, P.; Jacobsen, K. W.; Norskov, J. K. *Phys. Rev. Lett.* **1993**, *71*, 754.
(21) Tersoff, J. *Phys. Rev. Lett.* **1995**, *74*, 434.
(22) Yang, G. W.; Lai, W. S.; Lin, C.; Liu, B. X. *Appl. Phys. Lett.* **1999**, *74*, 3305.
(23) Yin, L. W.; Li, M. S.; Liu, Y. X.; Sui, J. L.; Wang, J. M. *J. Phys.: Condens. Matter* **2003**, *15*, 309.
(24) Chow, G. M.; Goh, W. C.; Hwu, Y. K.; Cho, T. S.; Je, J. H.; Lee, H. H.; Kang, H. C.; Noh, D. Y.; Lin, C. K.; Chang, W. D. *Appl. Phys. Lett.* **1999**, *75*, 2503.
(25) Müller, H.; Opitz, Ch.; Strickert, K.; Skala, L. *Z. Phys. Chem. (Leipzig)* **1987**, *268*, 634.
(26) Liang, L. H.; Liu, D.; Jiang, Q. *Nanotechnology* **2003**, *14*, 438.