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Environment-dependent phase equilibria in a small volume system in the case of decomposition of Bi-Sb solid solution

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Abstract

Regarding phase transitions in systems of a very small volume it is necessary to take some considerable dissimilarities into account. They are due to the contribution of the all interphase boundary's surface free energy in the system's full energy, that grows as the system's size decreases. In this study, external environment influence on the phase equlibria in nanoparticles with core-shell configuration where one of the phases doesn't touch the system's external boundary, of binary stratifying solid solution with upper critical solution temperature (UCST) was investigated using the methods of equilibrium chemical thermodynamics. That configuration has two thermodynamically stable states, which differ in mutual position of co-existing phases. In macro-systems, where the contribution of the surface energy is negligible, the energies of both states are equal. In nano-systems the state, whose surface energy is higher, becomes metastable. Each state corresponds to its own phase diagram, which is different from the phase diagram of a macro-system. External environment was modeled by the value of surface free energy on the system's external boundary. It is shown, that a change of the external environment leads to a change of equilibrium composition of all co-existing phases and the UCST. The UCST can both increase and decrease, depending on what solid solution is in the shell-position. Nanosystem's phase diagram depends on its external environment, what is of interest for many nanotechnology application fields.

References

[1] L.H. Liang, D. Liu, Q. Jiang. Size-dependent continuous binary solution phase diagram. *Nanotechnology*. **2003**. Vol.14. No.4. P.438-442.
[2] T. Tanaka, S. Hara. Thermodynamic evaluation of binary phase diagrams of small particle systems *Zeitschrift fuer Met*. **2001**. Vol.92. No.11. P.467-472.
[3] V.B. Fedoseev, E.N. Fedoseeva. Size effects during phase transformations in stratifying systems. *Russian Journal of Physical Chemistry*. **2014**. No.3. Vol.88. P.436-441. (russian)
[4] V.B. Fedoseev, A.V. Shishulun, E.K. Titaeva, E.N. Fedoseeva. On the possibility of the formation of a NaCl-KCl solid-solution crystal from an aqueous solution at room temperature in small-volume systems. *Physics of the Solid State*. **2016**. No.10. Vol.58. P.2020-2025. (russian)
[5] J. Park, J. Lee. Phase diagram reassessment of Ag-Au system including size effect. *CALPHAD*. **2008**. Vol.32. No.1. P.135-141.
[6] D. Hourlier, P. Perrot. Au-Si and Au-Ge phase diagrams for nanosystems. *Material Science Forum*. **2010**. Vol.653. P.77-85.
[7] T. Ivas, A.N. Grundy, E. Povoden-Karadeniz, L.J. Gauckler. Phase diagram of CeO_2-CoO for nano-sized powders. *CALPHAD*. **2012**. No.36. P.57-64.
[8] B. Straumal, B. Baretzky, A. Mazilkin, S. Protasova, A. Myatiev, P. Straumal. Increase of Mn solubility with decreasing grain size in ZnO. *Journal of the European Ceramic Society*. **2009**. Vol.10. No.29. P.1963-1970.

[9] V.B. Fedoseev, A.A. Potapov, A.V. Shishulin, E.N. Fedoseeva. Size and shape effect on the phase transitions in a small system with fractal interphase boundaries. *Euras. Phys. Tech. J*. **2017**. Vol.1 (27). No.14. P.18-24.
[10] M. Ghasemi, Z. Zanolli, M. Stankovski, J. Johansson. Size- and shape-dependent phase diagram of In-Sb nano-alloys. *Nanoscale*.**2015**. Vol.7. P.17387-17396.
[11] G. Guisbiers, S. Khanal, F. Ruis-Zepeda, J. Roque de la Puente, M.J. Yakamán. Cu-Ni nano-alloy: mixed, *core-shell* or *janus* nano-particle. *Nanoscale*. **2014**. Vol.24.No.6.
[12] M.A. Bykov, G.F. Voronin, N.M. Mukhamedzhanova. Direct and inverse problems of chemical thermodynamics. *Novosibirsk: Nauka.* **1987**. P.30-33.
[13] Yu.K. Tovbin. Lower size boundary for the applicability of thermodynamics. *Russian Journal of Physical Chemistry*. **2012**. No.9. Vol.86. P.1356-1369.
[14] F. Aqra, A. Ayyad. Surface free energy of alkali and transition metal nanoparticles. *Applied Surface Science*. **2014**. Vol.314. P.308-313.
[15] W. Tyson, W. Miller. Surface free energies of solid metals. Estimation from liquid surface tension measurements. *Surf. sci.* **1977**. Vol.62. No.267.
[16] A.P. Babichev, N.A. Babushkina, A.M. Bratkovsky et al. Physical quantities. *A Reference Guide*. **1991**. *Moscow: Energoatomizdat.* 1232 p. (russian)
[17] V.B. Fedoseev. Splitting of the phase diagram of a stratified solid solution in micro- and nanosized systems. *Physics of the Solid State*. **2015**. No.3. Vol.57. P.599-604. (russian)
[18] B. Bouillot, T. Spyriouni, S. Teychené, B. Biscans. Solubility of pharmaceuticals: A comparison between SciPharma, a PC-SAFT-based approach, and NRTL-SAC. *The European Physical Journal, Special Topics*. **2017.** Vol.226. No.5. P.913-929.
[19] V.M. Kiselev, O.A. Golovanova, V.B. Fedoseev, M.A. Polyntseva. Study of calcium phosphates crystallization process using the method of fractal analysis. *Butlerov Communications.* **2017**. Vol.49. No.3. P.36-43. ROI: jbc-02/17-49-3-36.
[20] A.A. Kimyashov, A.V. Syromolotov. The isothermal section of diagram lgP_{O2}-composition-temperature of the system Fe–Si–O at the temperature 1373 K. *Butlerov Communications.* **2017**. Vol.50. No.6. P.132-136. ROI: jbc-02/17-50-6-132.