Nanometric phase diagram of Bi-Sn system in the solid state

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The purpose of this research is to create a model of the nanometric, binary eutectic system Bi-Sn studied experimentally by Jesser and Schamp[*] at room temperature. The nano particles in system separate into two phases as a function of composition (Fig 1.) In the two phase region of the nanometric phase diagram of Bi-Sn, increased solubility in the two solid phases is observed relative to the bulk (Fig 2.).

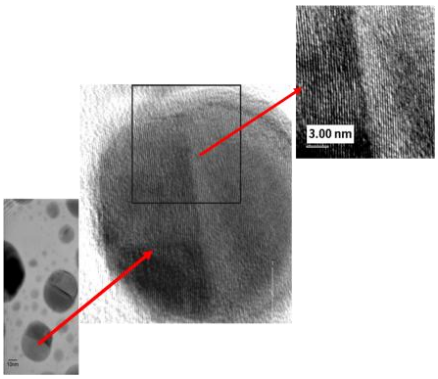


Fig 1:Experimental observation of the Bi-Sn system in TEM[*] showing a planar interface between two phases.

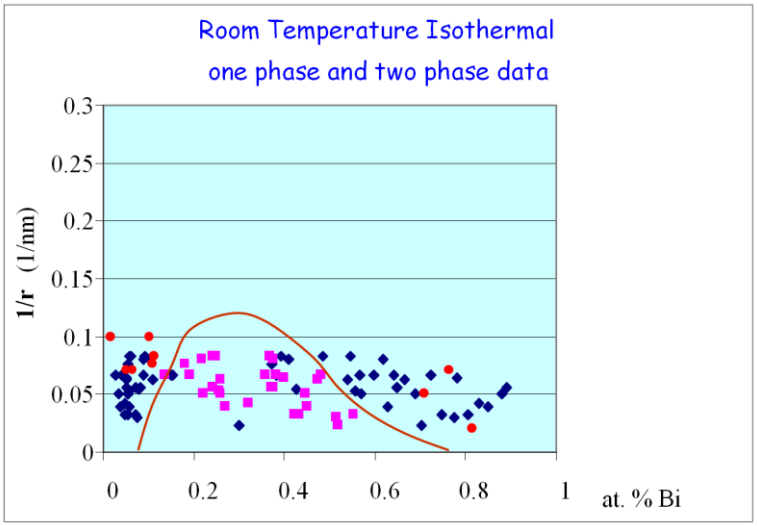
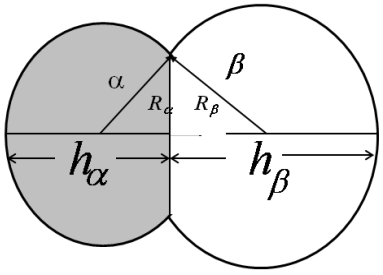


Fig 2: Isothermal cross section of the experimental phase diagram of Bi-Sn at room temperature in the size-composition phase space. Red points represent single phase particles. Pink points represent two-phase particles at their average composition. Blue points represent the compositions of the two-phases at equilibrium.



The geometric model that we used to describe the two phase nano-particles is displayed -

We formulated a semi empirical Gibbs free energy function for the two-phase nano-system relative to the single phase homogeneous solution nanoparticle within the regular solution approximation.

$$\Delta G = n^{\beta}\left[x_{Sn}G_{Sn}^{0,\beta} + RT\left[x_{Sn}\ln x_{Sn} + x_{Bi}\ln x_{Bi}\right] + x_{Bi}x_{Sn}\left(L_0^{\beta} + L_1^{\beta}\left(x_{Sn} - x_{Bi}\right)\right)\right] +$$

$$n^{\alpha}\left[x_{Bi}G_{Bi}^{0,\alpha} + RT\left[x_{Sn}\ln x_{Sn} + x_{Bi}\ln x_{Bi}\right] + x_{Bi}x_{Sn}\left(L_0^{\alpha} + L_1^{\alpha}\left(x_{Sn} - x_{Bi}\right)\right)\right]$$

$$+\sigma^{\alpha}A^{\alpha} + \sigma^{\beta}A^{\beta} - G^{ref}$$

The parameters a_i and L_i are the surface energy series coefficients and the interaction parameters of the regular solution respectively.

$$\sigma^{\alpha} = \sigma_{Sn}^{0} + a_1^{\alpha}\left(x^n - 1\right) + a_2^{\alpha}\left(x^m - 1\right)$$

$$\sigma^{\beta} = \sigma_{Bi}^{0} + a_1^{\beta}x^k + a_2^{\beta}x^l$$

To fit the experimental results (the solubility in the two solid phases), we found that it was necessary to require that the surface energies of both phases decrease strongly with additional solute, deviating considerably from any reasonable interpolation of the bulk values. In addition it was necessary to modify the interaction parameters obtained in the CALPHAD database, so that when we consider the surface effect on the free energy we obtain the required mutual solubility while retaining the bulk properties.

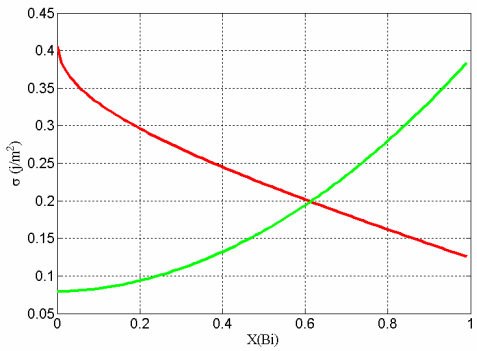


Fig 3: Surface energies of both phases in the system Bi-Sn showing the strong decrease in surface energy with increase of solute.

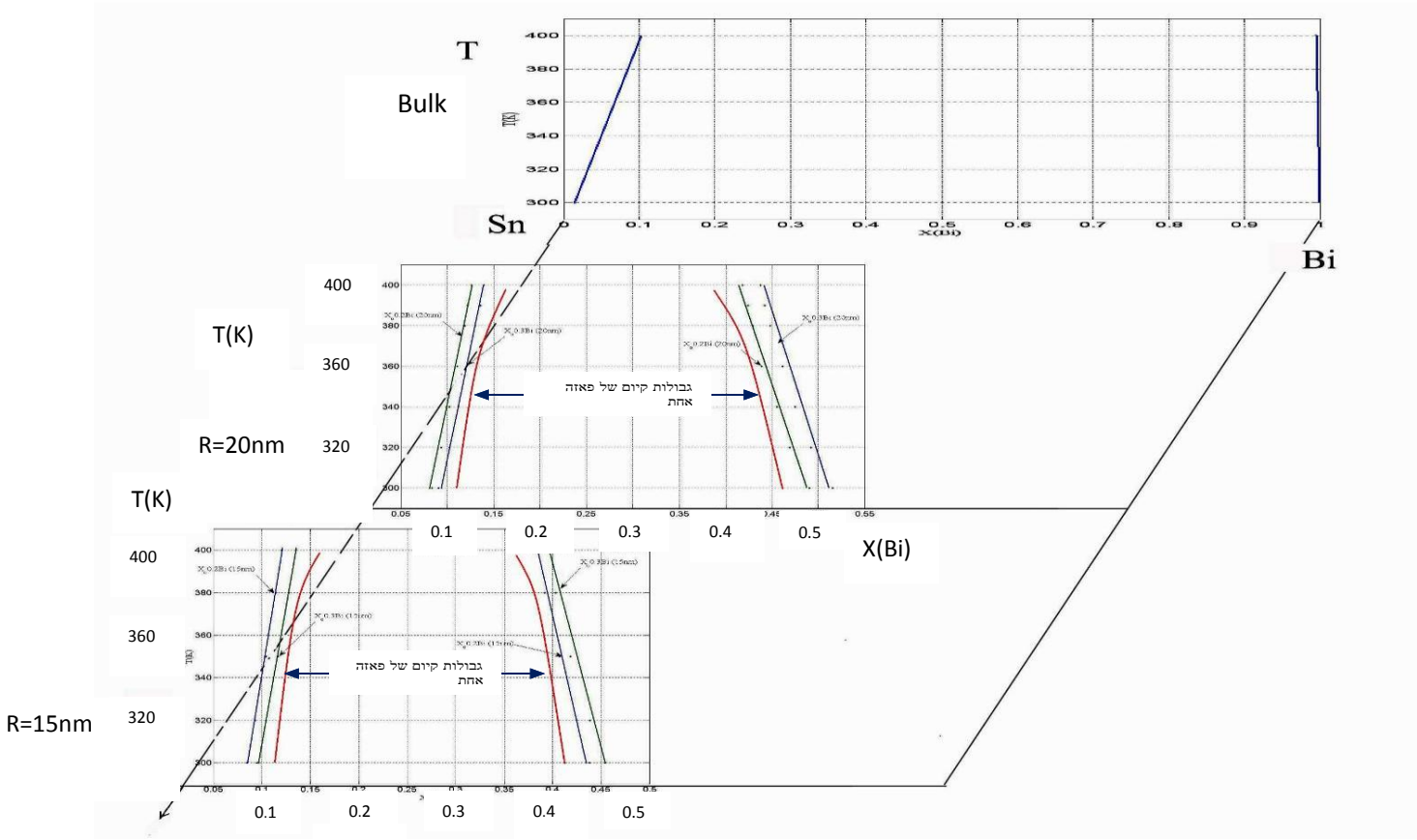


Fig 4: Three cross section of selected sizes of the three dimensional phase diagram, showing the separation of solubility lines and the increasing of solubility as the size

Summary

- In this research we constructed a 3D phase diagram of the nanometric Bi-Sn system as a function of composition, temperature and particle size.
- In Bi-Sn system it was observed[*] that with the decreasing size of the particle the solubility in both phases increases.
- To explain the increase of solubility in both phases we found it necessary to assume that the surface energy of both phases decreases strongly with the increase of the solute (Bi in Sn and Sn in Bi).

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[*] References: C.T. Schamp, MSc dissertation, *University of Virginia*.