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Developing phase diagrams for nano binary system by MATLAB

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1-Introduction

In the recent years, the use of nanomaterials has been significantly developed, including various industries such as electronics, catalysis, ceramics, magnetic data storage and etc. Nano materials obtain several properties such as high surface area which strongly influences energy states of the constituents leading to higher mechanical strength, lower melting point and different equilibrium phase diagram.

Many studies have been conducted in order to investigate the effect of particle size on the melting point of nanoparticles and their equilibrium phase diagram. Mirjalili and et al. provided a model for predicting the melting point of nanoparticles based on the average coordination number, which demonstrated that the melting temperature was proportional to the mean atomic coordination number. This number in nanoparticles is lower than the bulk material, so the melting temperature of nanoparticles decreases with decreasing particle radius. Lee and et al. examined the effect of particle size on the melting temperature of Ag-Pb alloy. The results of their studies showed that the melting temperature of the particles is linearly related to the particle diameter.

This paper proposes an innovative algorithm for drawing nanoscale phase diagrams in regular and irregular systems by using MATLAB software which affords to draw phase diagrams in bulk and nano state with acceptable accuracy in the shortest possible time.

2- Experimental

In this study, in order to simplify the calculations, the Gibbs free energy equations of all phases were first calculated with two variables of temperature and atomic percentage. Actually, at a certain temperature, the free energy of each phase was calculated according to the partial percentages of constituents. In considered temperatures, the Gibbs free energy diagrams of each phase at all atomic percentages were compared with each other and the phase with the lowest energy was stored in a matrix (Table 1 and Figure 1). This process was repeated for all temperatures.

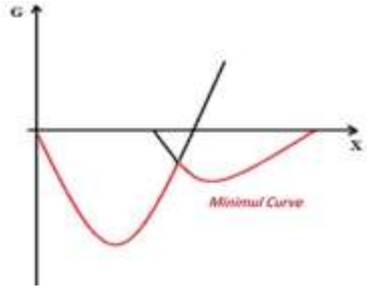

Figure 1- Finding the minimum free energy curves at a given temperature in all atomic percentages

Table 1- Finding the minimum free energy matrix at a given temperature in all atomic percentages

	X_s	X_s+X_{step}	…	X_f
G_1	$G_1(X_s)$	$G_1(X_s+X_{step})$	…	$G_1(X_f)$
⋮	⋮	⋮	…	⋮
G_{nL}	G_{nL}	$G_{nL}(X_s+X_{step})$	…	$G_{nL}(X_f)$
G_{nL+1}	G_{nL+1}	$G_{nL+1}(X_s+X_{step})$	…	$G_{nL+1}(X_f)$
⋮	⋮	⋮	…	⋮
G_{nL+nS}	G_{nL+nS}	$G_{nL+nS}(X_s+X_{step})$	…	$G_{nL+nS}(X_f)$
G_{min}	G_{min}	$G_{min}\ (X_s+X_{step})$	…	$G_{min}\ (X_{f..})$

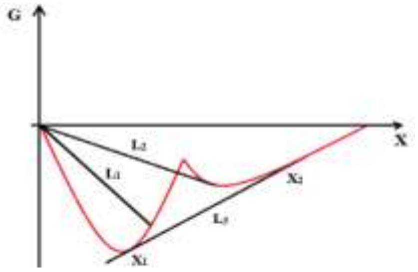

Figure 2- Calculating the connected lines at a given temperature and comparing them with the minimum free energy curve. It is clear that only the L3 line is below the minimum curve at all X-axis intervals, so X1 and X2 points were saved in the final matrix.

Finally, tangent lines of two points were drawn on minimal curve. For this purpose, each point from the curve was connected by the line to all subsequent points on the curve. Then, each line drawn was compared with the minimal curve for all longitudinal axis values (atomic percentage). The tangent line must be completely lower than the values of minimal curve at all atomic percentage (Figure 2). Consequently, the points of the minimal curve which were connected by the tangent line were collected in a final matrix. In the last step, the phase diagram was obtained by drawing the final matrix.

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3- Results and Discussion

There are several models to calculate the melting point and phase diagram of the nano systems. According to Haiming model, the melting enthalpy H_m and melting temperature T_m are proportional to the bond energy and have been deduced to have the same size-dependences as the cohesive energy, namely.

$$\frac{T_m(D)}{T_m(\infty)} \approx \frac{H_m(D)}{H_m(\infty)} \approx \left[1-\frac{1}{12D/D_0-1}\right] exp\left[\frac{-2S}{3R}\frac{1}{12D/D_0-1}\right] \quad (1)$$

$$\frac{\Omega(x,D)}{\Omega(\infty)} = \left[1-\frac{1}{12D/D_0-1}\right] exp\left[\frac{-2S}{3R}\frac{1}{12D/D_0(x)-1}\right] \quad (2)$$

Where $\Omega_{(x, D)}$ is atomic interaction energy. S= $H_{b(\infty)}/T_{b(\infty)}$ is the bulk solid-vapor transition entropy of crystals with $H_{b\ (\infty)}$ and $T_{b\ (\infty)}$ which are the bulk enthalpy of vaporization and boiling temperature, respectively.

Another model is offered by Tanaka. This model assumes regular solution to investigate the effect of particle size on the solid solution diagram as follows:

$$\Delta G^{Total.Liq} = \Delta G^{Bulk.Liq} + \Delta G^{Surface.Liq} \quad (3)$$

$$\Delta G^{Total.Liq} = \Delta G^{Bulk.Liq} + \Delta G^{Surface.Liq} \quad (4)$$

In the above relations, $\Delta G^{Bulk.Liq}$ and $\Delta G^{Bulk.Sol}$ are the Gibbs free energies of the liquid and solid bulk solutions. The effect of the surface on the overall Gibbs energy, $\Delta G^{Surface.Liq}$ and $\Delta G^{Surface.Sol}$ is also assumed to be as follows:

$$\Delta G^{Surface.Liq} = \frac{2\sigma^{Liq}V^{Liq}}{r} - \frac{2\left(X_A\sigma_A^{Sol}V_A^{Sol}+X_B\sigma_B^{Sol}V_B^{Sol}\right)}{r} \quad (5)$$

$$\Delta G^{Surface.Sol} = \frac{2\sigma^{Sol}V^{Sol}}{r} - \frac{2\left(X_A\sigma_A^{Sol}V_A^{Sol}+X_B\sigma_B^{Sol}V_B^{Sol}\right)}{r} \quad (6)$$

In these relations, r is the particle radius, σ^{Liq} and σ^{Sol} are the surface tension of liquid and solid alloys, V^{Liq} and V^{Sol} are the molar volumes of liquid and solid alloys. Also, σ_A^{Sol} and σ_B^{Sol} are the surface tension of pure solids A and B and V_A^{Sol}, and V_B^{Sol} are their molar volumes.

In this study, in order to simplify the relations, the following assumptions have been applied in the calculations:

1- The molar fraction of the alloying elements is the same at surface and bulk.
2- The temperature dependence of the molar volumes of liquid and solid has been neglected.
3- The liquid and solid surface tensile stresses are considered independent to the temperature and are equal to $\sigma_{X,m}^{L}$ and $1.25\sigma_{X,m}^{L}$, respectively.

With above assumptions, two models of Heming and Tanaka were applied to the Ag-Pb system, and the diagram of this system was plotted for nanoparticles with a diameter of 10 nm as well as for the bulk state (Figure 3).

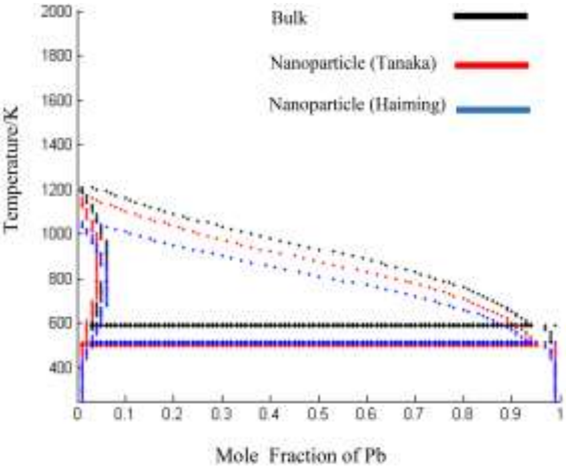

Figure 3- Ag-Pb phase diagram in bulk and nano system (10 nm for particle diameter) based on Haiming and Tanaka models

According to Figure 3, as the particle size decreases, the melting points decrease and the solidus and liquidus lines move downwards due to the effect of the surface factor. Furthermore, in nano scale, the 2-phase region became more limited and the solid solution regions expanded.

4- Conclusion

In this study, a program was developed by MATLAB which can be used for plotting phase diagrams in regular and irregular systems. The basis of the used algorithm was to find the minimum free energy at each temperature and composition. In the second step, the nanoparticles phase diagram for the Ag-Pb binary system was plotted according to the Haiming and Tanaka models. In addition, the results confirmed that the liquidus and solidus lines in the nano scale system move downwards and the 2-phase region becomes limited than that of the bulk system. Furthermore, reaching to nanoscales decreases the solid solubility limits.