CALCULATION OF MELTING TEMPERATURE APPLIED TO FCC ALLOYS

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Abstract: A method for calculation of melting temperature and application to fcc alloys have been developed based on the vibrational or Lindemann theory. Analytical expressions for the effective force constant, mean square displacement and Lindemann melting temperature have been derived. This temperature depends on the mass proportion of alloy components. The *eutectic* point has been determined. Numerical calculations have been carried out for the fcc binary alloy CuAg, and the results are found to be in good agreement with experiment.

1. Introduction

The melting of materials, especially of alloys, is studied widly by theory and by experiment [1-10]. The vibrational theory has been succesfully applied by Lindemann and others [1-5] according to which an alloy is melted when the atomic mean square displacement reaches an critical value at a melting temperature, i., e., the Lindemann temperature. The melting is also studied recently experimentally by the X-ray absorption fine structure (XAFS) [7] for crystals.

The purpose of this work is to develop a vibrational theory for the melting of binary alloys. Our development is the derivation of analytical expressions for the effective force constant, mean square displacement (MSD) and Lindemann melting temperature. The derived theory is focus especially to *eutectic* alloys, which are the binary alloys having the phase diagram with two melting curves, the point connecting this two curves is called *eutectic point* corresponding to the alloy-ratio at which the alloy has the lowest phase trasition temperature. Numerical calculations have been carried out for the fcc binary alloy CuAg showing the *mean melting curve*, i., e., the dependence of melting temperature on the mass-ratio of *eutectic* alloy CuAg, and the existence of a ratio corresponding to the minimum melting temperature. The calculated ratio and *eutectic* temperature of CuAg are found to be in good agreement with experiment [3, 10].

2. Theory

We deal with the alloy lattice including two metals having face centered cubic structure (fcc).

If each of fcc lattice shell has on average s atoms of type 1 and 4-s atoms of type 2, we have the mean net displacement :

$$\mathbf{U}_n = \frac{1}{8}\sum_q \left\{ [s\mathbf{u}_{1q} + (4-s)\mathbf{u}_{2q}]e^{iqR_n} + \left[s\dot{\mathbf{u}}_{1q} + (4-s)\dot{\mathbf{u}}_{2q}\right]e^{-iqR_n}\right\} \quad (1)$$

We calculate the MSD or Debye-Waller factor (DWF) [8, 11]

$$W = \frac{1}{2}\sum_q \left|K\ \overline{u_q}\right|^2,\quad \overline{u_q} = \frac{s u_{1q} + (4-s)u_{2q}}{4}. \tag{2}$$

We have the lattice energy

$$E = \sum_q \overline{\varepsilon_q} = \sum_{k,q} NM_k \left|\dot{u}_{kq}\right|^2 = N.s.M_1\omega_q{}^2\left|u_{1q}\right|^2 + N(4-s)M_2\omega_q{}^2\left|u_{2q}\right|^2, \tag{3}$$

where, M_1, M_2 are the masses of atoms of types 1 and 2, respectively.
We have the mean energy of fcc lattice shell

$$\overline{\varepsilon_q} = N.\omega_q^2\left|u_{1q}\right|^2\left[s.M_1 + (4-s)\frac{M_1^2}{M_2}\right];\qquad \overline{\varepsilon_q} = 4\left(\overline{n_q} + \frac{1}{2}\right)\hbar\omega_q\ . \tag{4}$$

Hence

$$\left|u_{1q}\right|^2 = 4\frac{\left(\overline{n_q} + \frac{1}{2}\right)\hbar}{N.M_1\omega_q\left[s + (4-s)\frac{M_1}{M_2}\right]} \tag{5}$$

We have the expressions for 1 and all 3 polarizations, respectively

$$\left|Ku_q\right|_1^2 = \tfrac{1}{3}K^2\left|u_q\right|^2;\quad \left|Ku_q\right|_3^2 = K^2\left|u_q\right|^2 = 3\frac{1}{48}K^2\left[s + \frac{M_1}{M_2}(4-s)\right]^2\left|u_{1q}\right|^2. \tag{6}$$

Hence, the Debye-Waller factor is given by

$$W = \frac{1}{32}K^2[s + (4-s)m]\frac{\hbar}{M_1}\hbar\int_0^{\omega_D} 4\left\{\frac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1} + \frac{1}{2}\right\}\frac{3\omega^3}{\omega_D^3\hbar\omega}d\omega,\qquad m = \frac{M_1}{M_2}. \tag{7}$$

Since we consider the melting, so it is sufficient to take the hight temperature quantity

$$W = \frac{3}{8}\frac{[M_2 s + (4-s)M_1]\hbar^2 TK^2}{M_1M_2k_B\theta_D^2} \tag{8}$$

From(2) and (6) we obtain

$$\sum_q \left|u_{1q}\right|^2 = \frac{96}{K^2[s + (4-s)m]^2}W \tag{9}$$

Comparing the following expressions for the lattice energy

$$E = \sum_{k,n} M_k\left|\dot{U}_{kn}\right|^2 = \sum_{k,n}\sum_q M_k\left|\dot{U}_{knq}\right|^2 = \sum_{k,n}\sum_q M_k\omega_q^2\left|U_{knq}\right|^2;\quad E = \sum_{k,q} NM_k\omega_q^2\left|U_{kq}\right|^2 \tag{10}$$

we obtain

$$\sum_{k,n} M_k\left|U_{kn}\right|^2 = \sum_{k,q} NM_k\left|U_{kq}\right|^2. \tag{11}$$

Using the expressions

$$\left|U_{1n}\right|^2 = \left(\frac{M_2}{M_1}\right)^2\left|U_{2n}\right|^2;\quad \left|u_{2q}\right|^2 = \left(\frac{M_1}{M_2}\right)^2\left|u_{1q}\right|^2 \tag{12}$$

we obtain :

$$\frac{1}{N}\sum_n\left|U_{2n}\right|^2 = m^2\sum_q\left|u_{1q}\right|^2 \tag{13}$$

Hence, the mean value of vibrational squared amplitude is resulted as

$$\frac{1}{N}\sum_n\left|U_{2n}\right|^2 = \frac{36m^2\hbar^2T}{M_1[s + (4-s)m]k_B\theta_D^2}. \tag{14}$$

The lattice will be melted when this value reach a crictical value $x_m^2 r_s^2$, where r_s is the radius of Wigner-Seitz lattice shell. From this we determined the Lindemann's melting temperature T_m

$$T_m = \frac{[sM_2 + (4-s)M_1]}{36m}\chi \; ; \; \chi = \frac{x_m^2 k_B \theta_D^2 r_s^2}{\hbar^2}, \quad x_m^2 = \frac{1}{Nr_s^2}\sum_n |U_{2n}|^2 . \tag{15}$$

We use (15) to calculate the melting temperature of CuAg alloy at *eutectic* mass proportion 71,9% Ag. Defining t as the percent mass ratio of Ag in alloy, the average number of Ag atoms appeared in each alloy lattice shell is given by

$$s = \frac{4.t}{m(1-t)+t} \; ; \quad m = \frac{M_{Ag}}{M_{Cu}} . \tag{16}$$

To consider the dependence of χ and m on atomic mass proportion of alloy, we take average

$$m = \frac{-[t-(1-t)(M_{Ag}/M_{Cu})] + \sqrt{\Delta}}{2(1-t)}, \quad \Delta = [t-(1-t)(M_{Ag}/M_{Cu})]^2 + 4t(1-t)(M_{Cu}/M_{Ag}). \tag{17}$$

The parameter χ after taking average is given by

$$\chi = \frac{[s\chi_{Ag}^{1/2} + (4-s)\chi_{Cu}^{1/2}]^2}{16}. \tag{18}$$

Using (15), (17) and (18), we perform the investigation of the dependence of alloy melting temperature on its mass proportion (see the figure).

3. Numerical calculation and discussions

Now we apply the expressions derived in the above section to numerical calculation. The results are compared to experiment [3, 10]. Using the atom mass of Cu and Ag we obtain t = 0.719 , s = 2.4. The caculated result of the melting temperature of CuAg alloy at *eutectic mass proportion* 71.9% Ag is 1064.2 K. It agrees with the experimental result (1053 K) with an accuracy of 3.85%.

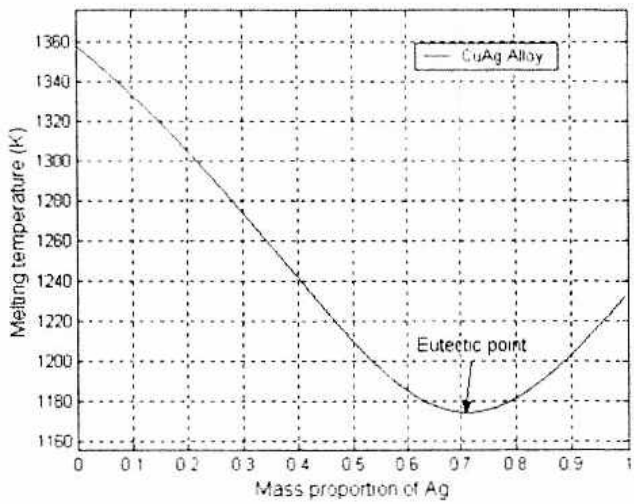

Fig.1. Mean melting curve for the dependence of melting temperature on the atom mass proportion of binary alloy CuAg and the *eutectic point.*

The dependence of the melting temperature on the mass proportion of the component element Cu and Ag in the binary alloy Ag is calculated and the result is illustrated in Figure 1. This curve has a minimum at the mass proportion 71.2%Ag corresponding to the melting temperature 1170K and the experimental information from the phase diagram of CuAg alloy gives us the *eutectic* point with mass proportion 71.9%Ag and minimum liquid phase transition temperature 1053 K, respectively. Based on the comparison, we have concluded that, mass proportion of Ag the alloy ratio corresponding to the minimum melting point of this theoretical curve is the *eutectic ratio*. (the relative difference between experiment and theory with respect to this ratio only is 0.97%).

The above theoretical curve above is compatibly the *mean melting curve* for a binary alloy. However, the existence of a minimum point of this curve is intimately connected with the *eutectic* alloy of CuAg experimental diagram. Therefore, to somewhat, we can provide an explaination of the existence of a special point with minimum liquid phase transition temperature (*eutectic point*) in the diagram of CuAg alloy.

1. Conclusions

Based on the Lindemann's theory we developed further the vibrational theory. Our development is the derivation of analytical expressions for the melting temperature depending on the atomic mass proportion of a binary alloy, i. e., *the mean melting curve*, and a method for determination of the *eutectic point*.

The calculated *mean melting curve* and the *eutectic point* for the binary alloy CuAg are found to be in a reseanable agreement with experiment. This curve provides the information on the dependence of alloy's melting characteristic on its mass proportion. The *mean melting curve* has pointed out an ratio of Cu-Ag alloy having the lowest melting point, this atomic mass ratio nearly coincide with the *eutectic ratio* in the experimental diagram of this alloy.

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