THE MELTING TEMPERATURE FOR BINARY ALLOYS AB AT VARIOUS PRESSURES

Pham Dinh Tam

Military Technical Academy

Abstract. *The equations for melting temperature of the metals and binary alloys AB in the f.c.c and b.c.c structures are obtained by the moment method. The values of the melting temperature obtained by solving these equations are in good agreement with experimental data.*

I. INTRODUCTION

There are various methods of investigation of the fusion for crystal such as Lindemann method, Simon equation [1] , pseudo - potential method [2,3] . These methods help to successfully investigate the fusion of some simple metals. The development of the equation for melting temperature of the metals and binary alloys having the same lattice structures at various pressures is a task which has been paid attention to but has not been satisfactorily resolved. The recent use of the limiting condition of absolute stability for the crystalline state, and the moment method has given the equation for melting temperature of the metals and binary alloys AB with a very small concentration of atoms B at pressure p = 0 and the equation for the melting temperature of the metals at various pressures. The numerical results are very well agreed with the experiment[4] .

In difference to the above authors, in this work, by using the Lindemann assumption [1] and the results obtained from the moment method of the works [5, 6, 7] , we have developed the equations for melting temperature of the metals and alloys AB with f.c.c and b.c.c structures at various pressures. The calculation results are in good agreement with the experimental data.

II. THE EQUATIONS FOR MELTING TEMPERATURE OF THE METALS AND BINARY ALLOYS AB.

Using the Lindemann assumption [1] , the equation for melting temperature of the metals and binary alloys AB is given in the form:

$$\frac{\langle u^2 (T_m, P)\rangle}{a^2 (T_m, P)} = const, \tag{1}$$

where $\langle u^2\rangle$ - the mean square displacement of atoms in the lattice vibration; a - The lattice spacings; T_m - The melting temperature for crystal at pressure p.

For to the binary alloys in the f.c.c and b.c.c structures, the $\langle u^2 \rangle$ is given in the form [5]

$$\langle u^2 \rangle = \sum_{\alpha\beta} \nu_\beta P_\alpha^\beta \langle (u_\alpha^\beta)^2 \rangle, \tag{2}$$

where ν_β - the concentration of the lattice point of type β ($\beta = a, b$); P_α^β - the probability of atoms α ($\alpha = A, B$) located in the lattice point β; $\langle (u_\alpha^\beta)^2 \rangle$ - the mean square displacement of atoms in the lattice vibration of the effective system ($\alpha\beta$) .

Similar to [6] , we have

$$\langle (u_\alpha^\beta)^2 \rangle \simeq \frac{\theta}{k_\alpha^\beta} + \frac{\gamma_\alpha^\beta \theta^2}{\left(k_\alpha^\beta\right)^3}. \tag{3}$$

Substituting $k_\alpha^\beta, \gamma_\alpha^\beta$ defined in [5] into (3) , we obtain

$$\langle (u_\alpha^\beta)^2 \rangle \simeq \frac{\theta}{k_\alpha} + \frac{\theta^2 \gamma_\alpha}{k_\alpha^3} - \frac{\theta n_1 P_{\alpha\alpha'}}{4c_\alpha} \left[\left(\frac{1}{k_\alpha^2} + \frac{3\theta\gamma_\alpha}{k_\alpha^4} \right) \Delta\varphi^{(2)}(a) - \right.$$

$$\left. - \frac{\theta}{k_\alpha^2} \left(\frac{\Delta\varphi^{(4)}(a)}{6} + \Delta\varphi_{xy}^{(4)}(a) \right) \right]. \tag{4}$$

Put (4) into (2) and take into accout the condition of probalities P_α^β [5] , we obtain the following result

$$\langle u^2 \rangle = c_A \langle u_A^2 \rangle + c_B \langle u_B^2 \rangle -$$

$$- \frac{\theta n_1 P_{AB}}{4} \left\{ \left[\frac{1}{k_A^2} - \frac{1}{k_B^2} + 3\theta \left(\frac{\gamma_A}{k_A^4} - \frac{\gamma_B}{k_B^4} \right) \right] \times \right.$$

$$\left. \times \Delta\varphi^{(2)}(a) - \theta \left(\frac{1}{k_A^2} - \frac{1}{k_B^2} \right) \left(\frac{\Delta\varphi^{(4)}(a)}{6} + \Delta\varphi_{xy}^{(4)}(a) \right) \right\}, \tag{5}$$

where $\langle u_\alpha^2 \rangle$ - the mean square displacement of atoms in the metals α ($\alpha = A, B$)

$$\langle u_\alpha^2 \rangle \simeq \frac{\theta}{k_\alpha} + \frac{\gamma_\alpha \theta^2}{k_\alpha^3}. \tag{6}$$

In the expressions (5) and (6) , the parameters $k_\alpha, \gamma_\alpha, \Delta\varphi^{(2)}(a), \Delta\varphi^{(4)}(a), \Delta\varphi_{xy}^{(4)}$ (are defined by the interaction potential between atoms in metals. In the approximate limit of the two first and second coordination spheres, we have found the following expressions

* *For the f.c.c lattice:*

$$k_\alpha = 2\varphi_\alpha^{(2)}(a) + \frac{4}{a}\varphi_\alpha^{(1)}(a) + 2\varphi_\alpha^{(2)}(a_2) + \frac{1}{a_2}\varphi_\alpha^{(1)}(a_2), \tag{7a}$$

$$\gamma_\alpha = \frac{2}{3}\varphi_\alpha^{(4)}(a) + \frac{1}{a}\varphi_\alpha^{(3)}(a) + \frac{4}{a^2}\varphi_\alpha^{(2)}(a) - \frac{4}{a^3}\varphi_\alpha^{(1)}(a) +$$

$$+\frac{2}{3}\varphi_\alpha^{(4)}(a_2)+\frac{2}{a_2}\varphi_\alpha^{(3)}(a_2)-\frac{7}{2a_2^2}\varphi_\alpha^{(2)}(a_2)-\frac{7}{2a_2^3}\varphi_\alpha^{(1)}(a_2), \tag{7b}$$

$$\Delta\varphi^{(2)}(a)=\frac{1}{3}\left[\varphi_B^{(2)}(a)-\varphi_A^{(2)}(a)\right]+\frac{2}{3a}\left[\varphi_B^{(1)}(a)-\varphi_A^{(1)}(a)\right], \tag{7c}$$

$$\Delta\varphi^{(4)}(a)=\frac{1}{6}\left[\varphi_B^{(4)}(a)-\varphi_A^{(4)}(a)\right]+\frac{1}{a}\left[\varphi_B^{(3)}(a)-\varphi_A^{(3)}(a)\right]-$$

$$-\frac{1}{2a^2}\left[\varphi_B^{(2)}(a)-\varphi_A^{(2)}(a)\right]+\frac{1}{2a^3}\left[\varphi_B^{(1)}(a)-\varphi_A^{(1)}(a)\right], \tag{7d}$$

$$\Delta\varphi_{xy}^{(4)}(a)=\frac{1}{12}\left[\varphi_B^{(4)}(a)-\varphi_A^{(4)}(a)\right]+\frac{3}{4a^2}\left[\varphi_B^{(2)}(a)-\varphi_A^{(2)}(a)\right]-$$

$$-\frac{3}{4a^2}\left[\varphi_B^{(1)}(a)-\varphi_A^{(1)}(a)\right]. \tag{7e}$$

**For the b.c.c lattice:*

$$k_\alpha=\frac{4}{3}\varphi_\alpha^{(2)}(a)+\frac{8}{3a}\varphi_\alpha^{(1)}(a)+\varphi_\alpha^{(2)}(a_2)+\frac{2}{a_2}\varphi_\alpha^{(1)}(a_2), \tag{8a}$$

$$\gamma_\alpha=\frac{14}{27}\varphi_\alpha^{(4)}(a)+\frac{2}{9a}\varphi_\alpha^{(3)}(a)+\frac{8}{9a^2}\varphi_\alpha^{(2)}(a)-\frac{8}{9a^3}\varphi_\alpha^{(1)}(a)+$$

$$+\frac{1}{6}\varphi_\alpha^{(4)}(a_2)+\frac{2}{a_2}\varphi_\alpha^{(3)}(a_2)-\frac{2}{a_2^2}\varphi_\alpha^{(2)}(a_2)+\frac{2}{a_2^3}\varphi_\alpha^{(1)}(a_2), \tag{8b}$$

$$\Delta\varphi^{(2)}(a)=\frac{1}{3}\left[\varphi_B^{(2)}(a)-\varphi_A^{(2)}(a)\right]+\frac{2}{3a}\left[\varphi_B^{(1)}(a)-\varphi_A^{(1)}(a)\right], \tag{8c}$$

$$\Delta\varphi^{(4)}(a)=\frac{1}{9}\left[\varphi_B^{(4)}(a)-\varphi_A^{(4)}(a)\right]+\frac{4}{3a}\left[\varphi_B^{(3)}(a)-\varphi_A^{(3)}(a)\right]-$$

$$-\frac{4}{3a^2}\left[\varphi_B^{(2)}(a)-\varphi_A^{(2)}(a)\right]+\frac{4}{3a^3}\left[\varphi_B^{(1)}(a)-\varphi_A^{(1)}(a)\right], \tag{8d}$$

$$\Delta\varphi_{xy}^{(4)}(a)=\frac{1}{9}\left[\varphi_B^{(4)}(a)-\varphi_A^{(4)}(a)\right]+\frac{2}{3a^2}\left[\varphi_B^{(2)}(a)-\varphi_A^{(2)}(a)\right]-$$

$$-\frac{2}{3a^3}\left[\varphi_B^{(1)}(a)-\varphi_A^{(1)}(a)\right]. \tag{8e}$$

In the expressions (7a ÷ e) and (8a ÷e) , φ_α - the interaction potential between two atoms in metal α ($\alpha = A, B$); upper indexs of potential φ - order of derivative; a, a_2 - radii of the two first and second coordination spheres, they have been defined in [7] .

Put (5) into (1) we obtain the equation for melting temperature in the binary alloys AB

$$c_A\langle u_A^2\rangle+c_B\langle u_B^2\rangle-$$

$$-\frac{\theta n_1 P_{AB}}{4}\left\{\left[\frac{1}{k_A^2}-\frac{1}{k_B^2}+3\theta\left(\frac{\gamma_A}{k_A^4}-\frac{\gamma_B}{k_B^4}\right)\right]\Delta\varphi^{(2)}(a)-\right.$$

$$\left.-\theta\left(\frac{1}{k_A^2}-\frac{1}{k_B^2}\right)\left(\frac{\Delta\varphi^{(4)}(a)}{6}+\Delta\varphi_{xy}^{(4)}(a)\right)\right\}=a^2.const. \tag{9}$$

In the equation (9) , const. is determined by the experimental data for the melting temperature of the alloys at pressure p = 0 (or at pressure p≠ 0) . Thus, if the potential energy $\varphi_\alpha(\alpha = A, B)$ is known, from (9) we can determine the melting temperature for binary alloys AB at various pressure. Put (6) into (1) we obtain the equation for melting temperature in the metals

$$\frac{\theta}{k_\alpha} + \frac{\gamma_\alpha \theta^2}{k_\alpha^3} = a_\alpha^2 .const, \tag{10}$$

where k_α, γ_α are determined by expressions (7a) , (7b) (for the f.c.c lattice) or (8a) , (8b)(for the b.c.c lattice); a_α - the lattice spacings of metal α, they are determined in [6] ; const is determined by the experimental data for the melting temperature of the metal α at pressure p = 0.

III. THE NUMERICAL CALCULATION AND DISCUSSION.

For numerical calculation we choose the interaction potential between two atoms in metal in the form of the Lennard - Jones potential [8] :

$$\varphi(r) = \frac{D}{n-m}\left[m\left(\frac{r_0}{r}\right)^n - n\left(\frac{r_0}{r}\right)^m\right], \tag{11}$$

where D, r_0 are determined by experiment and n, m are determined by experience (Table 1) ; r - radius of the coordination sphere, defined in [7] .

Metals	Al	Ag	Cu	Ni	Pd	Pt
D/k (K)	2995,6	3658,9	4125,7	4782,0	5478,1	7039,3
r_0 (Å)	2,8541	2,8760	2,5487	2,4780	2,7432	2,7689
n	12,5	9,5	9,0	8,5	9,5	10,5
m	4,5	5,5	5,5	5,5	5,5	5,5

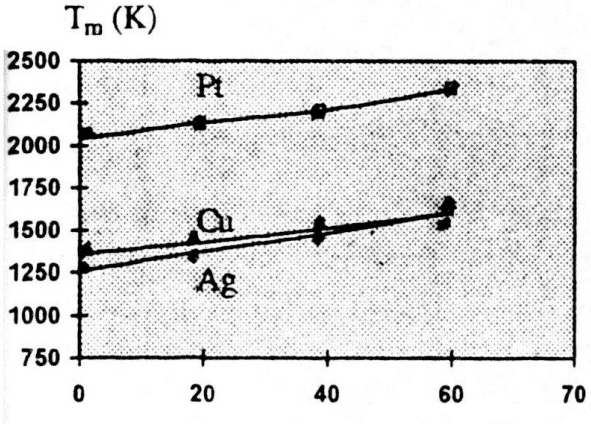
Table 1. The value of parameters D, r_0, n and m of the metals

Metals	P(Kbar) const		0	10	20	30	40	50	60	$\frac{dTm}{dp}\left(\frac{K}{kbar}\right)$
Al	75.10^{-4}	Cal	935	933	1048	1100	-	-	-	6.0
		Exp	933	933	1053	1110	-	-	-	6.5
Cu	69.10^{-4}	Cal	1355	-	1430	-	1510	1580	1600	4.0
		Exp	1357	-	1430	-	1510	1580	1600	4.0
Ag	73.10^{-4}	Cal	1255	-	1373	-	1480	1590	1610	5.5
		Exp	1234	-	1373	-	1472	1588	-	6.0
Pt	46.10^{-4}	Cal	2040	-	2136	-	2210	2290	-	4.0
		Exp	2043	-	2136	-	2210	2303	-	4.2

Table 2. The calculation (Cal) and experimental (Exp) [9] values of the melting temperature of the metals.

Alloys	C_B	P(Kbar) Const	0	10	20	30	40	50	60	$\frac{dTm}{dp}\left(\frac{K}{kbar}\right)$
CuNI	30	84.1^{-4}	1513	1555	1595	1635	1675	1715	1750	4.0
NiCu	55	87.1^{-4}	1563	1605	1645	1685	1725	1765	1800	4.0
AuPt	30	58.1^{-4}	1723	1765	1815	1865	1910	1960	2010	5.0
PdCu	40	91.1^{-4}	1498	1545	1595	1640	1685	1730	1780	5.0
PdAg	40	81.1^{-4}	1663	1720	1770	1825	1875	1930	1985	5.5

Table 3. The melting temperature of the alloys at various pressures



'ig 1. *The melting temperature of metal at various pressures. (the dots correspond experimental values [9])*

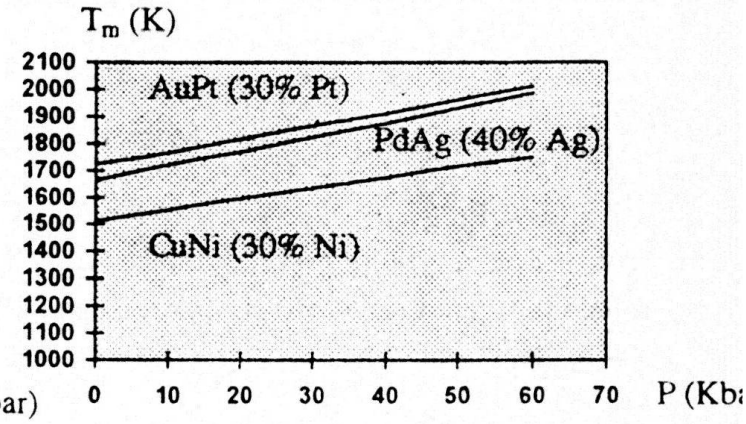


Fig 2. *The melting temperature for alloys at various pressures*

The values of the melting temperature for metals Al, Cu, Ag, Pt and for alloys CuNi, NiCu, AuPt, PdCu, PdAg are given in Tables 2, 3 and are shown in the Figs. 1,2.

Based on the numerical tables and the graphs obtained, we have the following comments

- The results of calculation of the melting temperature of metals by the moment method are well agreed with the experimental data (the difference is below 0,1%).

-The obtained fusion curve of metals and alloys has a form close to a straight line with an inclination of definite value for each metal and alloys. This result is also well agreed with the experimental data [9] .

Accordingly, the equations (9) and (10) allow to determine the melting temperature of the binary alloys and metals with f.c.c and b.c.c structures at various pressures.

REFERENCES

[1] V. E. Panhin. IU. IA. Hon. *Theory of Phase in Alloys* Novosibir Nauka, 1984 (In Russian).

[2] R. Jones. *Phys. Rev.* **(A8)**(1973) p.3215.

[3] D. Stroud, N.W. Ashcroft. *Phys. Rev.* **(B2)**(1972) p.371.

[4] Vu Van Hung, Nguyen Tang and Pham Dinh Tam. *Proc.* 2^{nd} *(IWOMS' 95)* Hanoi Oct. 1995 p.396.

[5] Nguyen Tang, Pham Dinh Tam and Vu Van Hung. *Comm. in Phys.* **3**(1997) p.47
[6] Nguyen Tang, Vu Van Hung. *Phys. Stat. Sol* (b). **149**(1988) p.611.
[7] Pham Dinh Tam. *Com. in Phys.* **2**(1998) p.78.
[8] M.N. Mogomedov. *J. Phys. Khimi.* **61**(1987)p.1003.
[9] E. IU. Tonkov. *Phase Transition of Compounds under High Pressure* M. 1968.

TẠP CHÍ KHOA HỌC ĐHQGHN, KHTN, t.XV, n^{0}2 - 1999

NHIỆT ĐỘ NÓNG CHẢY CỦA HỢP KIM THAY THẾ AB Ở ÁP SUẤT KHÁC NHA

Phạm Đình Tám

Khoa Lý Hóa - Kỹ thuật Học viện KTQS

Sử dụng giả thiết của Lindemann và mô hình hệ hiệu dụng của hợp kim đưa r trong các công trình trước, chúng tôi thu được các phương trình mới xác định nhiệt đ nóng chảy của kim loại và hợp kim thay thế AB cấu trúc LPDT và LPKT ở áp suất khá nhau. Kết quả tính số từ các phương trình thu được phù hợp tốt với các số liệu thự nghiệm