Empirical Relation of Melting Temperatures of CsCl-Type Intermetallic Compounds to Their Cohesive Energies

Chonghe Li and Ping Wu*

Institute of High Performance Computing of Singapore, 1 Science Park Road, 01-01 The Capricorn, Singapore 117528

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An empirical linear relationship between melting temperatures and cohesive energies, which was first derived on the basis of the universal binding energy theory and the Debye model, is reexamined by using 78 pure element solids. The results show that, although a general trend is observed, many elements deviated far from this regularity. However, it is further found that this empirical relationship works very well for element solids that have a common crystal structure (e.g., bcc). Similar behaviors are observed among intermetallic compounds of the same structure. For CsCl-type intermetallic compounds the obtained linear relationship is $T_m = 0.030\Delta E/k_B$, which may be applied to predict the melting point of unknown alloys.

1. Introduction

Despite abundant experimental and theoretical information,[1−7] prediction of melting temperatures of intermetallics on the basis of atomic parameters of constituent elements is a very challenging problem, although some successes are reported in the literature. By analyzing melting point data of nearly 500 AB-type intermetallic compounds, Chelikowsk and Anderson[4] reported that Vegard's Law of melting points works quite well for transition−transition binary alloys, but only moderately well for compounds involving simple metals. For RT_2-type and RT_2X_2-type compounds, the dependence of melting point on crytallographic properties was studied,[6] and it was found that the melting point is inversely proportional to the cubic root of molar volume for these compounds. In China a correlation/data-mining technology[3,8−10] has been proposed to study the melting of binary alloys, using atomic properties of constituent elements or their combinations as the inputs of artificial neural networks. Some regularities of melting temperature were obtained by this method for compounds with specific crystal structures (i.e., CsCl-type compound, $AuCu_3$-type compound, and Laves phases).

The melting temperature sometimes can be taken as a measure for the coefficient of thermal expansion[11] and elastic property[12] in the design of advanced materials. Therefore, it is considered as a critical index[13,14] to assess alloys in search for advanced materials such as high-temperature structural parts in aircraft and space industries. The study of the melting behavior of intermetallic compounds has attracted significant interests. Prediction methods that can quickly screen multicomponent systems to estimate the melting temperature of unknown compounds are necessary for new materials design.

Intermetallic compounds with CsCl structure form one of the largest groups of compounds. Alloys that possess this kind of ordered structure include AlNi, AlCo, AlFe, AlRu, NiTi, FeTi, CoTi, FeCo, and CuZn, which have versatile applications as functional or structural materials.[15−17] It is practical to study the regularities of melting of these compounds.

In this paper, the scaling relation (of melting temperatures of pure metals to their cohesive energies) deduced from the universal binding theory of solids[18] is further studied, especially on its reliability for pure metals of the same crystal structure (i.e., bcc structure).

* Corresponding author. E-mail: wuping@ihpc.nus.edu.sg.

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Melting temperatures and formation enthalpies of CsCl-type binary intermetallic compounds are collected and used to verify this empirical linear relationship. And finally an empirical model is built up, which can quickly estimate or predict the melting temperature of multicomponent intermetallic compounds with CsCl crystal structure.

2. Relation of Melting Points of Pure Metals to Their Cohesive Energies

In the 1980s, Rose, Smith, and Ferrante[19−21] proposed a universal model about the equation of state of solids, which is also called the universal binding energy theory. It has shown that the total internal energy of solids as a function of volume per atom exhibits a universal scaling feature, and can be written as eq 1

$$E(r_{ws}) = \Delta E\ E^*[(r_{ws} - r_{wse})/l] \quad (1)$$

where $E(r_{ws})$ is the total energy as a function of the Wigner Seitz radii r_{ws}, ΔE is the cohesive energy at the equilibrium lattice constant, and r_{wse} is the Wigner Seitz radii at equilibrium. $E^*[(r_{ws} - r_{wse})/l]$ is an approximately universal function which describes the shape of the binding energy curve. The variable l is a scaling length which describes the curvature of the above-mentioned function near the minimum; it can be related to the equilibrium value of the isothermal bulk modulus, B, as

$$l = (\Delta E/12\pi r_{wse}B)^{1/2} \quad (2)$$

According to the Debye model at high temperature,[22] and assuming that the Debye temperature for metals can be accurately computed by the supposition that the longitudinal speed of sound is given by $(B/\rho)^{1/2}$, then the root-mean-square of vibration of each atom about its lattice site is

$$\langle \boldsymbol{u}^2 \rangle^{1/2} = (0.827 k_B T/r_{wse}B)^{1/2} \quad (3)$$

where ρ is mass density of the solid and T is temperature.

From eqs 3 and 2, and supposing $\langle \boldsymbol{u}^2 \rangle^{1/2} = l$ when melting occurred at $T = T_m$, Guinea[18] deduced a long known empirical correlation between cohesive energies ΔE and melting points T_m for pure metals

$$T_m = 0.032\Delta E/k_B \quad (4)$$

Because the effect of crystal structure of solids was not included, the rule expressed by eq 4 works only moderately well for 78 pure solid elements as shown in Figure 1. For those elements with a complex structure, for example, C(diamond structure), Tm(complex hcp), Ga(orthorhombic), and Np(orthorhombic), there exist obvious deviations.

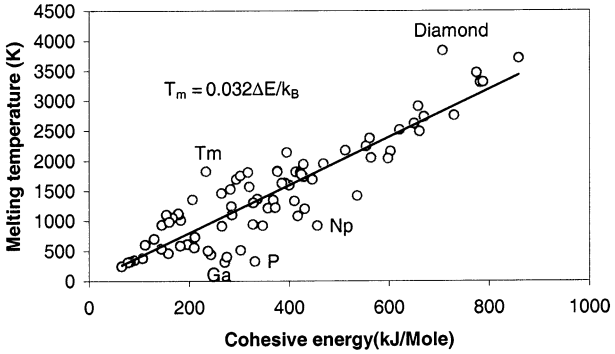

Figure 1. Melting temperature vs cohesive energy for pure elements (the solid line is the regression line).

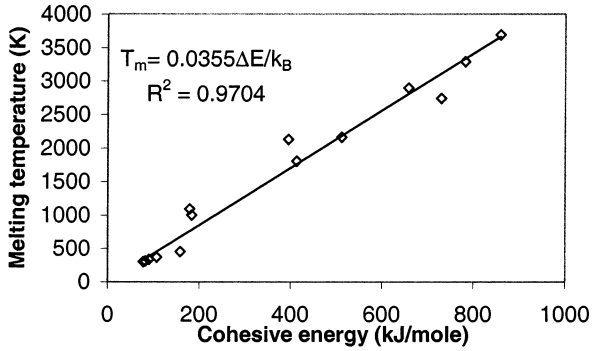

Figure 2. Melting temperature vs cohesive energy for bcc metals (the solid line is the regression line).

According to previous works[22,23] the crystal structure is not insignificant when studying melting of solids. Therefore, to show the effect of crystal structure, elements that have the same structure and do not undergo polymorphy reaction (i.e., Li, V, Cr, and etc., 14 bcc metals), are chosen to test the melting points versus cohesive energies relationship, as shown in Figure 2. A better linear correlation between melting temperatures and cohesive energies for these metals does exist, and the regression coefficient is $R^2 = 0.97$. For pure fcc metals a similar behavior is observed.

3. Relation of Melting Points of CsCl-Type Compounds to Their Cohesive Energies

Because empirical correlation of melting temperatures and their cohesive energies works well for pure metals of the same structure, it would be interesting to search for similar regularities of melting points for multicomponent intermetallic compounds. A big challenge in this research is to obtain reliable cohesive energy data of intermetallic compounds, which are either from experiment or from first principles calculations.

Although the interactions in solids are well understood, it is not an easy task to calculate cohesive energies of solids by first principles method. Chelikowsky once wrote a famous comment[24] "... the energy of an isolated heavy atom ... can be estimated to be on the order of $\sim 10^6$ eV/atom or more, but the cohesive energy ... only about 6 eV/atom. ... To obtain a reason-

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Table 1. 27 CsCl-Type Compounds with Their Melting Point and Measured Cohesive Energy

no	compound	ΔH^f kJ/mol	ΔE kJ/mol	T_m K[b]	citation[a]	no	compound	ΔH^f kJ/mol	ΔE kJ/mol	T_m K[b]	citation
1	AuCd	19.4	259.4	629	(a)	15	ErPd	91.1	437.6	1540	(b)
2	AgCe	13.5	364	870	(b)	16	ScPd	89.3	465.3	1600	(b)
3	AgLa	16.9	374.4	880	(b)	17	AlNi	59.2	436.7	1638	(a)
4	AgPr	24.4	344.9	932	(b)	18	AlCo	55.3	430.8	1640	(a)
5	CuY	19.3	398.3	942	(b)	19	RhZr	75.9	654.4	1910	(b)
6	AgNd	19.8	325.8	952	(b)	20	RhTi	74.4	585.4	1940	(b)
7	CuSc	20.9	376.9	1125	(b)	21	IrZr	85.7	722.2	2050	(b)
8	AgY	26.8	379.8	1180	(b)	22	RuTi	77	636	2130	(b)
9	AgSc	26.2	356.2	1230	(b)	23	IrTi	84.3	653.3	2130	(b)
10	NiTi	33.1	481.1	1310	(b)	24	RuZr	68.7	695.2	2130	(b)
11	CoTi	41.3	487.3	1325	(b)	25	OsTi	68.5	696.5	2160	(b)
12	PdTi	51.6	473.6	1400	(b)	26	RhHf	95.8	683.3	2290	(b)
13	GdRh	72.4	549.4	1470	(b)	27	RuHf	91.8	727.3	2450	(b)
14	CoZr	35.8	549.3	1500	(b)						

[a] Formation enthalpy cited from (a) ref. 28, (b) ref. 25. [b] Melting temperatures of compounds cited from ref 5.

able estimate of the cohesive energy in this case, one must have a method that is accurate to one part in 10^6."

Another choice is to determine the enthalpies of formation of intermetallic compounds by experiment (i.e., precise calorimetry measurement), this is also a boring and time-consuming exercise. For example, it took about 20 years to measure only 273 data of formation energies of compounds of different structures.[25] Formation energy data of only 27 CsCl-type compounds are available in the literature, this is a large group of compounds with available data. So binary CsCl-type alloys are chosen as an example to verify this empirical rule.

The cohesive energy ΔE of compounds A_xB_{1-x} can be computed [4,26] using eq 5

$$\Delta E = xE^A + (1 - x)E^B + \Delta H^f \quad (5)$$

where E^A and E^B are the cohesive energy of element A and element B, whose values can be found in reference 27, and ΔH^f is the formation energy (enthalpy).

Table 1 lists 27 CsCl-type intermetallic compounds with their melting temperature, measured formation energy, and cohesive energy. All compounds in this table are congruent melting; the incongruent alloys are excluded because they do not completely melt and just decompose to a mixture of a liquid and a new solid compound at decomposing temperature.

A good linear relationship between melting temperatures of CsCl-type compounds and their measured cohesive energies is shown in Figure 3. This empirical correlation can be expressed as eq 6 with a regression coefficient $R^2 = 0.88$

$$T_m = 0.030\Delta E/k_B \quad (6)$$

This implies that the relationship between melting points and cohesive energies deduced by Guinea[18] for pure metals may be valid for intermetallic compounds under constraint of the same structure. And the melting temperature of unknown compounds with CsCl structure may be predicted or estimated by using this rule.

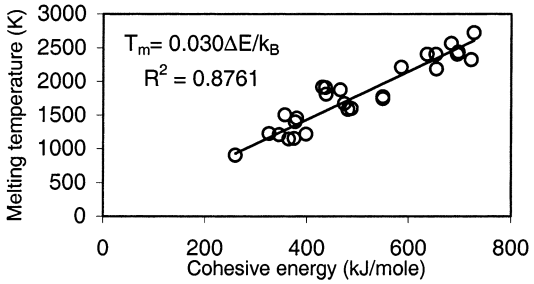

Figure 3. Melting temperature vs cohesive energy for compounds with CsCl structure (the solid line is the regression line).

4. Discussion

It is impractical to estimate the melting temperature of intermetallic compounds using this empirical rule expressed as eq 6 because it may be more difficult to experimentally obtain their formation enthalpies than to measure their melting points. Fortunately, there exist some theories or models to predict or estimate formation enthalpy for different compounds.[29,30] For intermetallic compounds, Miedema's model is commonly accepted in the estimation of formation enthalpies.[30,31] With the estimated cohesive energies for unknown compounds, predictions of their melting temperatures by this empirical rule are possible. To predict the melting temperature of a new compound by eq 6, its formation energy is calculated by Miedema's model. Table 2 lists some CsCl-type intermetallic compounds with their formation enthalpies calculated by Miedema's model (ΔH^f), computed cohesive energy (ΔE), measured melting temperature (T_m), predicted melting temperatures (T_m^C) and prediction errors. It has shown that predicted melting points agree well with experiments. This implies that this rule can be applied to estimate the

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Table 2. Comparison Between Predicting Melting Temperatures of Some CsCl-Type Compounds and Their Measured Values

alloy	ΔE kJ/mol	ΔH^f kJ/mol	T_m K	T_m^C K	error %	alloy	ΔE kJ/mol	ΔH^f kJ/mol	T_m K	T_m^C K	error %
MgTl	168.5	5.0	631	604	−4.3	BaZn	172.4	15.9	613	618	0.8
PdSc	501.7	125.7	1873	1798	−4.0	ScNi	456.3	54.3	1573	1635	3.9
LaCd	332.8	61.3	1219	1192	−2.2	InLa	407.3	70.3	1398	1459	4.4
TiAu	487.9	69.9	1768	1748	−1.1	CeZn	324.8	51.3	1098	1164	6.0

melting point of unknown compounds together with Miedema's model.

Similarly, for ternary or multicomponent alloys, their formation enthalpy or cohesive energy can be estimated by Miedema's model,[26] and can be used to estimate their melting temperatures by this empirical rule. Therefore, it may provide a simple solution for materials scientists in the design of advanced materials, which are most likely to be multicomponent.

According to Sauthoff,[15] the melting temperature was roughly proportional to the formation enthalpy, not to the cohesive energy, for some AB-type compounds. This may be coincident. In his research, only four compounds were studied and three of them were aluminide (AlFe, AlNi, and AlCo). The term $(xE^A + (1- x)E^B)$ in eq 5 had almost the same value for these three aluminides, so he may be able to ignore this term and use only the formation enthalpy to express the trend of their cohesive energy. For general cases, melting temperatures of intermetallic compounds could be proportional to their cohesive energies.

It was reported[3,9] that the melting temperature of CsCl-type compounds can be predicted by a five-parameter modified cellular model of artificial neural networks. The five parameters are electronegativity difference, ΔX; valence electron density difference, $\Delta(Z/R^3)$,; electron−atom ratio, e/a; the average melting point, T_{avg}, and metallic radius ratio R_A/R_B of constituent elements. This concept is very similar to that of our current empirical model, because the parameters of ΔX and $\Delta(Z/R^3)$ in their model are the counterpart of $\Delta\varphi$ and $\Delta\eta_{ws}$ in Miedema's model, which can be used to calculate the formation enthalpy of compounds. The variables e/a and T_{avg} (which are considered as the cohesive-energy factor[32]) can be compared to the average cohesive energy of constituent elements $(xE^A + (1 - x)E^B)$ in our model; R_A/R_B is the measure of elastic energy for compounds with the same structure at some extent, and tthis term may be ignored because it is somehow insignificant.[33] In comparison to their model based on five-inputs artificial neural networks, the present study uses only one well-understood parameter.

5. Conclusion

An empirical relation of melting temperatures of metals to their cohesive energies, which was deduced on the basis of the universal bind energy theory as well as the Debye model,[18] was reexamined for pure elements and was tested using binary intermetallic compounds with CsCl structure, and the following conclusions can be obtained.

This empirical linear relationship between melting points and cohesive energies works only moderately well for all pure elements of different crystal structures, but quite accurately for pure metals of the same structure (i.e., bcc structure).

Melting temperatures of binary intermetallic compounds seem also proportional to their cohesive energies, for CsCl-type compounds this empirical correlation can be expressed by $T_m = 0.030\Delta E/k_B$, where ΔE is the cohesive energy in kJ/mol and k_B is Boltzman's constant.

Melting temperatures of CsCl-type alloys, including binary, ternary, or even multicomponent, may be estimated by combining this empirical rule and Miedema's model for rational materials design.

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