Enthalpies of Formation of $L1_2$ Intermetallics Derived from Heats of Reordering

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(Received 25 November 1996)

A new method is proposed for estimating the enthalpies of formation of $L1_2$ (fcc-ordered) intermetallics from the heat release measured during ordering of their disordered polymorphs. The method is applied to Cu₃Au, Ni₃Al, and Ni₃Si. The resulting estimates of enthalpies of formation are close to values obtained by high temperature dissolution calorimetry. They also appear to be more precise than estimates based on Miedema's correlations provided that care is taken to account properly for the magnetic and lattice stability contributions to the formation enthalpies in the ordered and disordered states. [S0031-9007(97)03482-0]

The stability of various phases depends on their thermodynamic potentials such as the Gibbs free energy G which depends on concentration and external variables such as temperature. At constant pressure, the molar free energy of a chemically ordered or disordered alloy structure is determined by the enthalpy $\Delta H_{\text{formation}}$ and the entropy $\Delta S_{\text{formation}}$ change that accompanies its formation from the pure constituents. While the formation entropy $\Delta S_{\text{formation}}$ can often be approximated by the well-known configurational entropy associated with the combinatorics of arranging atoms on the lattice sites of the chosen structure with a given state of chemical order [1], smaller contributions such as the vibrational entropy and the magnetic entropy also depend on the state of chemical order. For example, it has been found [2] that for Ni₃Al, the vibrational entropy difference between the disordered-fcc and ordered-fcc ($L1_2$) states is of the order of a third of the configurational entropy.

In the present work, we are concerned with the determination of the enthalpy of formation $\Delta H_{\text{formation}}$ of ordered intermetallics, which is difficult to obtain and is usually measured by high temperature dissolution calorimetry. However, for most intermetallics such data are not available. In the absence of such data, a quick estimate of $\Delta H_{\text{formation}}$ can be obtained using the correlations of Miedema [3]. We will show that for certain ordered intermetallics, $\Delta H_{\text{formation}}$ can be estimated with good accuracy, from the easily measurable enthalpy difference $\Delta H_{\text{ordering}}$ between the disordered and ordered states.

The thermodynamic modeling of ordered intermetallic phases is usually performed using a sublattice model and has a long history [4,5]. It has been more recently described by the calorimetry and phase diagrams (CALPHAD) method [6,7]. For a binary ordered alloy of the type $(A_{y'}B_{1-y'})p(A_{y''}B_{1-y''})q$ with the first sublattice preferentially occupied by A atoms and the second preferentially occupied by B atoms, the enthalpy per mole of the phase is usually written as

$$H_m - H_{\text{ref}} + H_{\text{ex}},$$

where the first term refers to the enthalpy of formation of the stoichiometric (perfectly ordered) state. For site fractions y'_A and y''_A of A atoms and y'_B and y''_B of B atoms on the two sublattices,

$$H_{\text{ref}} = y'_A y''_A {}^{\circ}H_{ApAq} + y'_A y''_B {}^{\circ}H_{ApBq} + y'_B y''_A {}^{\circ}H_{BpAq} + y'_B y''_B {}^{\circ}H_{BpBq}, \qquad (1)$$

where ${}^{\circ}H_{ApAq}$ and ${}^{\circ}H_{BpBq}$ represent the enthalpies of the constituent elements A and B in the same crystal structure and ${}^{\circ}H_{ApBq}$ and ${}^{\circ}H_{BpAq}$ the enthalpies of the stoichiometric compounds A_pB_q and B_pA_q, and we assumed that $y'_A + y'_B = y''_A + y''_B = 1$ (no vacancies). The second term, H_{ex}, expresses enthalpy changes due to deviations from stoichiometry and is written as

$$H_{\text{ex}} = y'_A y'_B [y''_A L_{A,B:A} + y''_B L_{A,B:B}]$$
$$+ y''_A y''_B [y'_A L_{A:A,B} + y'_B L_{B:A,B}]$$
$$+ y'_A y'_B y''_A y''_B L_{A,B:A,B}, \qquad (2)$$

where $L_{i,j:i}$ and $L_{i:i,j}$ are interaction parameters between atoms on a sublattice for a given site-occupancy of the

other. However, in fully ordered stoichiometric compositions with no antisite defects (A and B atoms on their respective sublattices only), $y'_A = y''_B = 1$ and $y'_B = y''_A = 0$, and so is H_{ex} of Eq. (2), as expected. Furthermore, H_{ref} becomes just the enthalpy of formation $°H_{ApBq}$ of the stoichiometric compound,

$$H_{ref} = °H_{ApBq}, \qquad (3)$$

which is usually measured by dissolution calorimetry.

In what follows we will show that in the particular case of stoichiometric binary phases in which all the nearest neighbors of one of the two sublattices (say the q sublattice) are on the other sublattice, the enthalpy of formation of the intermetallic phase $°H_{ApBq}$ can be obtained from the "enthalpy of ordering" of its disordered state. This procedure, which to our knowledge has not been previously used, is of practical importance because it allows ordering enthalpies to be obtained easily from differential scanning calorimetric analysis instead of more difficult methods such as dissolution calorimetry. Furthermore, the method allows the determination of the enthalpies of formation of permanently ordered intermetallics such as Ni$_3$Al from the reordering enthalpies of their metastable disordered polymorphs obtained by simple methods such as ball milling.

Consider a phase A_pB_q, of the type Cu$_3$Au-$L1_2$ (ordered fcc) structure in which the B atoms occupy the sublattice of the cube-edge atoms (y'') of the fcc unit cell and the A atoms are on the sublattice of cube-face sites (y'). In this structure, which can be referred to as A_pB_q with $q = \frac{1}{4}$ and $p = \frac{3}{4}$, the B atoms of the y'' sites have all their $Z = 12$ nearest neighbors (nn) on the p sublattice corresponding to the absence of any BB nearest neighbors (nn) while atoms on the y' sites have only $\beta Z = (q/p)Z = 4$ on the q sublattice (AB nn) and $(1 - \beta)Z = 8$ on their own p sublattice (AA nn). If we approximate the enthalpy of such a structure in terms of

the contributions to the internal energy, of the various nearest-neighbor pairs E_{AA}, E_{AB}, and E_{BB} (and neglecting next nn effects), the enthalpy per mole (N_A atoms) takes the form:

$$\begin{aligned} H(\text{intermetallic}) &\equiv n_{AA}E_{AA} + n_{AB}E_{AB} + n_{BB}E_{BB} \\ &= N_AZ[0.5p(1 - q/p)E_{AA} + qE_{AB}] \\ &= (\tfrac{1}{2})N_AZ[(p - q)E_{AA} + 2qE_{AB}], \quad (4) \end{aligned}$$

where the factor $(\frac{1}{2})$ serves to avoid counting the A atoms on p sites twice. In order to get the enthalpy of formation $\Delta H_{formation}$, we must subtract the enthalpies of the pure constituents $pH_A + qH_B$ in the same crystal structure:

$$pH_A + qH_B \equiv (\tfrac{1}{2})N_AZ[pE_{AA} + qE_{BB}] \qquad (5)$$

and

$$\begin{aligned} \Delta H_{formation}(A_pB_q) &= (\tfrac{1}{2})N_AZ[(p - q)E_{AA} + 2qE_{AB}] \\ &\quad - (pH_A + qH_B) \\ &= N_AZq[E_{AB} - (\tfrac{1}{2})(E_{AA} + E_{BB})]. \end{aligned}$$
$$(6)$$

Consider now the enthalpy $H(\text{solid-sol.})$ of a disordered solid-solution of composition identical to that of the intermetallic A_pB_q. In this case the two sublattices disappear as the site occupancy will be random for both A and B atoms. Assuming a similar nn approximation for estimating the enthalpy with AA, BB, and AB bond energies the same as in the ordered state, bond counting as in Eq. (4) yields

$$H(\text{solid-sol.}) = (\tfrac{1}{2})N_AZ[p^2E_{AA} + 2qpE_{AB} + q^2E_{BB}]$$
$$(7)$$

and the formation enthalpy $\Delta H_{formation}(\text{solid-sol.})$ is obtained after deduction of the pure constituent enthalpies of Eq. (5):

$$\begin{aligned} \Delta H_{formation}(\text{solid-sol.}) &= (\tfrac{1}{2})N_AZ\{[p^2E_{AA} + 2qpE_{AB} + q^2E_{BB}] - [pE_{AA} + qE_{BB}]\} \\ &= N_AZqp[E_{AB} - (\tfrac{1}{2})(E_{AA} + E_{BB})], \qquad (8) \end{aligned}$$

which is commonly known as the regular solution expression and where we have used $p + q = 1$. The ordering enthalpy is then given by

$$\Delta H_{ordering}(\text{solid-sol.}) = \Delta H_{formation}(A_pB_q) - \Delta H_{formation}(\text{solid-sol.}) = N_AZq^2[E_{AB} - (\tfrac{1}{2})(E_{AA} + E_{BB})]. \qquad (9)$$

Using Eqs. (6) and (10), the intermetallic's enthalpy of formation can be simply written as

$$\Delta H_{formation}(A_pB_q) = \Delta H_{ordering}/q, \qquad (10)$$

thus allowing its derivation from the measurement of the ordering enthalpy. It must be emphasized that the simple form of relation (10) is not only due to the assumption of pair-wise interactions and equality of "bond energies" E_{AA}, E_{BB}, and E_{AB} in the ordered and disordered structures, but also due to the absence of B-B nearest neighbors in the stoichiometric compound. (We will see later that if A, B, and A_pB_q do not all have

the same fundamental crystal structure or are magnetic, additional terms must be considered).

As a first example of application of Eq. (10), we consider the Cu$_3$Au-$L1_2$ structure. This intermetallic has been extensively studied because it is fairly simple (the constituent elements and the intermetallic are all fcc) and undergoes an order $\to$ disorder transformation near 500 K, and is thus available both in the intermetallic and the solid-solution (disordered) states corresponding to Eqs. (6) and (8).

In the case of isostructural Ni$_3$Al, the intermetallic decomposes by a peritectic reaction from its ordered state

and the disordered state of Eq. (8) can be obtained only by nonequilibrium processing (such as ball milling [8,9], vapor deposition [10], and to some degree by rapid-solidification [11]). In this case a magnetic contribution to the formation enthalpy must be included (because the Ni constituent is ferromagnetic while the intermetallic and its disordered state are paramagnetic down to 60 K or below, depending on purity)

$$\Delta H_{\mathrm{mag}} = H_{\mathrm{mag}}(\mathrm{alloy}) - (pH_{\mathrm{mag}}^{A} + qH_{\mathrm{mag}}^{B}) \qquad (11)$$

The magnetic enthalpy change upon alloying, ΔH_{mag}, is calculated using experimentally measured magnetic moments B_0^i (in μ_B Bohr magnetons per atom) and Curie temperatures T_c^i of each phase following a method proposed by Hillert and Inden [12,13] which fits well the data for pure elements or alloys with a single magnetic component following the simple dilution law:

$$H_{\mathrm{mag}}^{i}(T) = RT \ln(B_0^i + 1) h(T/T_c^i) \qquad (12)$$

and

$$h(T/T_c^i) = \{(-0.564/P)(T/T_c^i) + 0.954(1/P - 1)$$
$$\times [(T/T_c^i)^3/2 + (T/T_c^i)^9/15$$
$$+ (T/T_c^i)^{15}/40]\}/D,$$

where B_0^i and T_c^i are, respectively, the magnetization (in μ_B per atom) and the Curie temperature of phase i, R is the gas constant, $P = 0.28$ and $D = 2.34$ for fcc lattices. H_{mag} is negligible for $T/T_c > 1$.

As another example, we consider the $L1_2$ state of the intermetallic Ni$_3$Si which also can be disordered by heavy deformation (milling) as reported by Shou and Bakker [14]. While for Cu$_3$Au and Ni$_3$Al, all the constituent elements have fcc structures, as in the case of Ni$_3$Si, Si goes from the diamond cubic structure to fcc upon alloying. Usually when elements A with crystal structure α and B with crystal structure β mix to form an alloy with crystal lattice γ at a given temperature, the enthalpy of formation of the alloy includes a contribution given by

$$\Delta H^{\mathrm{LS}} = pH_{A(\gamma-\alpha)}^{\mathrm{LS}} + qH_{B(\gamma-\beta)}^{\mathrm{LS}}, \qquad (13)$$

where $H_{A(\gamma-\alpha)}^{\mathrm{LS}}$ and $H_{B(\gamma-\beta)}^{\mathrm{LS}}$ are the so-called lattice stability terms associated with enthalpy differences between the intermetallic lattice γ and the equilibrium room-temperature lattices α and β of the pure elements. They are experimentally available or calculated with good precision and are given in internationally compiled data bases such as

[15]. Such a contribution must be included for the Si constituent in the formation enthalpy Ni$_3$Si. Thus, globally, Eq. (10) becomes

$$\Delta H_{\mathrm{formation}}(A_p B_q) = \Delta H_{\mathrm{ordering}}/q + \Delta H_{\mathrm{mag}} + \Delta H^{\mathrm{LS}}. \qquad (14)$$

Ni$_3$Al and Ni$_3$Si were disordered by heavy deformation (ball milling). Disordering was followed by the gradual disappearance of superstructure Bragg peaks from the x-ray diffraction spectra and by low temperature susceptibility measurements. The heat release that accompanies reordering $\Delta H_{\mathrm{ordering}}$ was then measured by differential scanning calorimetry [14,16]. Many others also reported such experiments on Ni$_3$Al [8,9]. However, Ni$_3$Al is mechanically very hard and gets contaminated by fragments from the milling device. We therefore use the results of Zhou and Bakker [14] (as given in Table I) who disordered their intermetallics in a device made of tungsten-carbide, a material harder than Ni$_3$Al. Table I also gives the lattice stability, and magnetic contributions to the enthalpy of formation of the intermetallics. Since both the disordered and ordered states of Ni$_3$Al and Ni$_3$Si are paramagnetic at room temperature and above, they have equal magnetic enthalpy and there is no magnetic contribution to the enthalpy of ordering. However, ΔH_{mag} of the intermetallics as well as the lattice stability contributions must be included in their formation enthalpies as in Eq. (14). The lattice stability terms have been calculated using standard CALPHAD equations [15] at 500 K and the magnetic terms using Eqs. (11) and (12) with $T_c^{\mathrm{Ni}} = 633$ K and $B_0^{\mathrm{Ni}}(500 \mathrm{\ K}) \approx 0.4\mu_B$. $T = 500$ K was selected because the transformations back to the ordered state during annealing were found to occur near this temperature, depending on the composition and heating rate (the lattice stabilities are not strongly temperature sensitive). Using the values of Table I together with Eq. (14), we derive $\Delta H_{\mathrm{formation}}$ and compare it in Table II to estimations with the Miedema model and $\Delta H_{\mathrm{formation}}$ values obtained from other experimental results (high temperature dissolution calorimetry). It can be seen that agreement between enthalpies of formation derived from the heats of reordering measured by differential scanning calorimetry are in good agreement with independently obtained experimental data. Our new procedure seems to give somewhat better results than Miedema's semiempirical method.

TABLE I. Lattice stability, magnetic and experimental ordering enthalpies of $L1_2$-type Cu$_3$Au, Ni$_3$Al, and Ni$_3$Si (in kJ/mole of atoms).

Ordered fcc ($L1_2$) intermetallics (enthalpies in kJ/mole of atoms)	ΔH^{LS} Lattice stability	ΔH_{mag} (Compound)	ΔH_{mag} (Disordered)	$\Delta H_{\mathrm{ordering}}$ Experimental, DSC
Cu$_3$Au	0	0	0	-2 ± 0.1 [16]
Ni$_3$Al	0	1.4	1.4	-8.5 ± 0.5 [17]
Ni$_3$Si	1.3	1.4	1.4	-10 ± 0.2 [14]

TABLE II. Enthalpies of formation of $L1_2$-type Cu_3Au, Ni_3Al, and Ni_3Si derived from their heats of reordering using Eq. (14) as compared to values obtained by dissolution calorimetry and by Miedema's method (all in kJ/mole of atoms).

Ordered fcc ($L1_2$) intermetallics (enthalpies in kJ/mole of atoms)	$\Delta H_{formation}$ (intermetallic) (Dissolution calorimetry [3])	$\Delta H_{formation}$ (intermetallic) (Miedema [3])	$\Delta H_{formation}$ (intermetallic) from $\Delta H_{ordering}$ [Eq. (14)]
Cu_3Au	-7 ± 0.5	-10	-8 ± 0.4
Ni_3Al	-38 ± 3	-33	-33 ± 5
Ni_3Si	-36	-26	-37 ± 5

Depending on the grain size, the measured heat release may include a contribution from grain growth occurring simultaneously with reordering where disordering has been accompanied by extreme grain refinement. This would lead to an overestimation of the formation enthalpy using Eq. (14). For example, in an intermetallic disordered by milling with nanocrystalline grain size, the grains were found to grow from a diameter of about 13 nm in the as-milled disordered state to 18 nm during ordering near 500 K (see [18]) corresponding to a grain-boundary specific surface reduction of 10^7 cm^2/mole of atoms with an expected heat release of less than 1 kJ/mole to be compared to the ordering enthalpies of ball-milled Ni_3Al and Ni_3Si in Table I. On the other hand, Okamoto *et al.,* using extended electron energy-loss fine-structure spectra (EXELFS), found that disordered Ni_3Al films developed some short-range chemical ordering below temperatures at which atoms can reorder back to the equilibrium $L1_2$ phase with long-range order (superstructure) [19]. They estimated that up to 20% of the ordering enthalpy could be released by short-range ordering. While such a contribution is usually convoluted with broad DSC (differential scanning calorimetry) exotherms measured for disordered Ni_3Al during reordering, in certain cases some short-range ordering may occur prior to calorimetric measurements, thus leading to an underestimation of the total ordering enthalpy and the calculated formation enthalpy. These considerations led us to the maximum error margins given with our values of $\Delta H_{formation}$ in Table II.

In conclusion, we have shown using a simple relation [Eq. (14)] based on nearest-neighbor pairwise interactions, that the heat of reordering of disordered stoichiometric $L1_2$ compounds can be used to estimate the enthalpies of formation with good precision. This simple relation between the enthalpies of formation and of reordering is obtained for the A_3B-type $L1_2$ structures because they do not contain any B-B nearest neighbors. In our development, all of the measured heat release during reordering has been attributed to changes in the number of A-A, A-B, and B-B nearest-neighbors pairs. While a fraction of the order of 10% or 20% of the binding energy may be expected to be due to next nearest-neighbor interactions and other contributions in a superlattice with long-range chemical order [20], the good agreement obtained using Eq. (14) is indicative of the dominant role of nearest-neighbor interactions in ordered fcc intermetallics. More generally, the approach is likely to be limited to cubic superstructures because the use of the assumption of equality of pairwise interaction energies in the disordered and ordered states requires little or no change in nn distances upon disordering. The method can be used with sputtered or ball-milled samples together with differential thermal analysis (DSC or DTA), thus avoiding high temperatures.

[1] D. de Fontaine, Solid State Phys. **34**, 73 (1979).
[2] B. Fultz, L. Anthony, L. J. Nagel, R. M. Nicklow, and S. Spooner, Phys. Rev. B **52**, 3315 (1995).
[3] F. R. de Boer, R. Boom, A. R. Miedema, and A. K. Niessen, *Cohesion in Transition Metal Alloys* (North-Holland, Amsterdam, 1989).
[4] M. Hillert and L. Steffanson, Acta Chem. Scand. **24**, 3118 (1970).
[5] C. Wagner, in *Thermodynamics of Alloys* (Addison Wesley, Cambridge, Massachusetts, 1952), pp. 54–58.
[6] B. Sundman and J. Agren, J. Phys. Chem. Solids **42**, 297 (1981).
[7] I. Ansara, B. Sundman, and P. Willemin, Acta Metall. Mater. **36**, 977 (1988).
[8] J. S. C. Jang and C. C. Koch, J. Mater. Res. **5**, 498 (1990).
[9] T. Benameur and A. R. Yavari, J. Mater. Res. **7**, 2971 (1992).
[10] J. S. West, J. T. Manos, and M. J. Aziz, Mater. Res. Soc. Symp. Proc. **213**, 859 (1990).
[11] A. R. Yavari and B. Bochu, Philos. Mag. A **59**, 697 (1989).
[12] M. Hillert and M. Jarl, CALPHAD **2**, 227 (1978).
[13] G. Inden, Physica (Amsterdam) **103B**, 82 (1981).
[14] G. Zhou and H. Bakker, Acta Metall. Mater. **42**, 3009 (1994).
[15] A. T. Dinsdale, CALPHAD **15**, 317 (1991).
[16] G. Zhou, Ph.D. thesis, Universiteit van Amsterdam, 1994.
[17] R. L. Orr, Acta Metall. **8**, 489 (1960).
[18] A. R. Yavari, Mater. Sci. Eng. (to be published).
[19] J. K. Okamoto, C. C. Ahn, and B. Fultz, J. Appl. Phys. **77**, 4380 (1995).
[20] P. Desre (private communication).