

Enthalpy of Formation of B2-Fe_{1-x}Al_x and B2-(Ni,Fe)_{1-x}Al_x

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The enthalpy of formation of the ordered B2 phases in the Fe-Al and Fe-Ni-Al systems was measured with very good accuracy using a special, laboratory-built differential-solution calorimeter. The measurements were performed at 1073 K as a function of composition, with an accuracy of about 1 pct. The enthalpy of formation of B2-FeAl is most negative for the composition Fe_{0.50}Al_{0.50} (-36.29 kJ/mol). Compounds with Al contents less than about 40 at. pct show a deviation from the linear dependence of the enthalpy of formation with composition which prevails for Al contents larger than 40 at. pct. Upon replacing Fe by Ni while maintaining a constant Al content, the enthalpy of formation of B2-(Fe,Ni)Al compounds becomes more negative. With decreasing Al content and for a constant Fe/Ni ratio, the enthalpy of formation of the ternary phase becomes less negative.

I. INTRODUCTION

SOME intermetallic compounds with a CsCl structure (B2 type) are stable over a relatively wide range of compositions at normal temperatures and pressures, *e.g.*, CoAl, NiAl, FeAl, CoGa, NiGa, and PdAl (*e.g.*, Reference 1). A wide range of homogeneity for ordered compounds always entails the existence of constitutional defects (in addition to defects that are due to thermal disorder), since the surplus of one or the other component has to be balanced in order to maintain the overall ordered structure (*i.e.*, to preserve the number of sites on all sublattices).

The defect equilibrium as function of composition and temperature at constant pressure may be described by statistical thermodynamic models (*e.g.*, References 1 through 3). The validity of a model for a particular phase can be tested by comparing measured and calculated data for the Gibbs free energies of formation as a function of composition. Then, the experimental values for the Gibbs free energy of formation have to be known with sufficient accuracy.

Calorimetric measurements of the enthalpy of formation of several B2 compounds (*e.g.*, refer to Reference 4 for B2-NiAl and to Reference 5 for B2-CoAl) were conducted in the past. It was shown^[3,4,5] that applying a Wagner-Schottky or Bragg-Williams approach for the description of the interaction between pairs of species in the compounds (atoms/atoms and atoms/defects), the enthalpy of formation, the Gibbs free energy as well as the defect structure of these compounds, can be described very well (refer, in particular, to Reference 3).

To our knowledge, the enthalpy of formation as a function of composition of the B2-phase Fe_{1-x}Al_x has not been measured over a distinct composition range with, for the modeling, necessary accuracy. The present study is devoted to such experiments, to enable a subsequent model description.

To this end, a special, laboratory-built differential calorimeter was used, which allows heat-of-dissolution measurements to be made with high accuracy.

Recently, enthalpy-of-formation values were reported for the ternary B2-phase (Ni,Co)_{1-x}Al_x.^[6] It was shown^[3] that, with some modifications of the binary model used to describe the data of the binary phases B2-Ni_{1-x}Al_x and B2-Co_{1-x}Al_x, it is possible to provide a satisfactory model description for the thermodynamic properties and the defect structure of the ternary phase as well. Against this background and in addition to the enthalpy-of-formation measurements of the binary B2 compound Fe_{1-x}Al_x, in this work, measurements of the enthalpy of formation of the ternary B2-phase (Fe,Ni)_{1-x}Al_x were performed too.

II. EXPERIMENTAL

A. Calorimeter

An isoperibolic heat-flow differential-solution calorimeter has been employed for the measurements of the enthalpy of solution reported in the present study. The apparatus has been described in detail elsewhere;^[4,6] therefore, here only a short description will be given. The calorimeter is made up of four compartments which are arranged in a large cylindrical nickel block. Each calorimeter compartment contains an alumina crucible with liquid Al as the metallic solvent (mass of Al on the order of 20 to 30 g). The four samples (mass of about 0.5 g) are mounted on small alumina stirrers above the four baths. Between each two of the compartments, a differential thermopile (Reference 4) is located, which measures the temperature difference between the two adjacent calorimeters. This is why each temperature effect as a function of time, which is induced when a stirrer is moved down into the liquid Al and the sample dissolves in the Al solvent, is recorded by two adjacent thermopiles. During one measurement run, four samples are dissolved consecutively and eight temperature-time areas are recorded. These areas are "translated" into amounts of energy, on the basis of a calibration for each calorimeter compartment performed by electrical resistance heating. The arithmetic mean of the two measurements for each heat effect in each calorimeter compartment provides the experimental result presented here.

For the accuracy of the measurement, the constancy of the

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Table I. Heat Effect of Dissolution of Solid Fe in Liquid Al and the Corresponding Enthalpy of Solution, at 1073 K

Solvent n_{Al} (Mol)	Sample n_{Fe} (Mol)	Fe Content of Bath x_{Fe}	Heat Effect $\Delta h_{L,Fe}$ (kJ)	Enthalpy of Solution $\Delta H_{L,Fe}$ (kJ/mol)	
1.06684	0.00683	0.0064	-0.7615	-111.5	$\Delta H_{L,Fe}^0 = -112.6 \pm 1.3$
0.99965	0.00672	0.0067	-0.7504	-111.7	
0.99626	0.00734	0.0073	-0.8440	-115.0	
0.98892	0.00711	0.0071	-0.8129	-114.3	
1.05918	0.00424	0.0040	-0.4713	-111.2	
1.05911	0.00451	0.0042	-0.5032	-111.7	
1.05804	0.00398	0.0038	-0.4510	-113.3	
1.05150	0.00870	0.0082	-0.9775	-112.3	

calorimeter block temperature is most important. To ensure this temperature stability, the apparatus is equipped with an elaborate heating and temperature control system. It is designed with six individual units which allow the regulation of the constant temperature of the calorimeter block.

The measurements reported in this study are performed under dynamic vacuum conditions ($<10^{-2}$ Pa) at a constant temperature of 1073 K. The stability of the block temperature for the time of the experiments was found to be better than $\pm 10^{-3}$ K/day, yielding a resolution of the heat effects (enthalpy of solution) on the order of 1 J and a very good accuracy of the measurements, on the order of 1 pct for the enthalpy of formation. The reproducibility of the results (Section III) of individual measurements is excellent.

B. Sample Preparation

Iron (99.98 wt pct), aluminium (99.999 wt pct), and nickel (99.98 wt pct) were used for the preparation of the samples (alloys and pure iron) and the solvent (Al). The intermetallic compounds (each sample weighing about 20 to 25 g) were prepared by melting the constituents under an argon atmosphere in an induction furnace and casting into copper molds. The alloys thus prepared were sealed in silica glass tubes under a protective atmosphere ($5 \cdot 10^4$ Pa argon) and annealed for 10 days at 1323 K. To avoid contamination with Si from the tubes during annealing, alumina underlays were used. A spark-erosion device was used to cut the alloys into cylindrical discs (diameter of 6 to 7 mm and thickness of 1.5 to 2 mm) and to provide them with a hole for the ceramic stirrer. The disc surfaces were ground and cleaned with acetone. The homogeneity of the samples was verified metallographically and by X-ray diffraction analysis. The compositions of the compounds were checked by chemical analysis of a randomly selected specimen of each alloy prepared.

III. RESULTS AND DISCUSSION

In the following text, the enthalpy of formation of solid B2 (Fe,Ni)_{1-x}Al_x phase is defined such that solid B2 (Fe,Ni)_{1-x}Al_x is formed from solid Fe, solid Ni, and liquid Al.

From the thermal effects of dissolution at infinite dilution, the enthalpies of formation of the solid B2 compounds (ΔH_{B2}) at the temperature of the bath ($T = 1073$ K) were calculated using the following equation, utilizing Hess' law of constant heat summation (*i.e.*, the enthalpy is a state variable):

Table II. Partial Enthalpy of Mixing at Infinite Dilution for Liquid Fe in Liquid Al (Error Limits as Given by the Corresponding Authors)

$\Delta \bar{H}_{Fe}$ (kJ/mol)	Measurement Temperature (K)	Reference
-128.5	971	8
-114.7 \pm 1.2	994	9
-123.4 ($x_{Fe} = 0.0082$)	1023	10
-124.7 \pm 1.3	1073	this work
-106.7 \pm 1.8	1073	11
-110.8 \pm 3	1212	12
-95.2	1873	13

$$\Delta H_{B2} = x_{Fe}\Delta H_{L,Fe}^0 + x_{Ni}\Delta H_{L,Ni}^0 - \Delta H_{L,B2}^0 \quad [1]$$

where $\Delta H_{L,i}^0$ ($i = Fe, Ni,$ and B2) denotes the enthalpy of the solution at infinite dissolution of the pure solid elements Fe and Ni and of the solid B2 compound, respectively. The molar fractions of Fe and Ni are given by x_{Fe} and x_{Ni} , respectively. An "infinitely large" reservoir of liquid aluminium is used in the present study as the solvent. At infinite dilution, the enthalpies of solution of Fe and Ni, separately, are equal to the enthalpy of solution both Fe and Ni simultaneously, and this leads to Eq. [1].

A. Enthalpy of Solution of Solid Fe in Liquid Al and Partial Enthalpy of Mixing Liquid Fe in Liquid Al

The measured heat effect and the enthalpy of solution of pure solid Fe in liquid Al have been given in Table I. Each heat-effect value ($\Delta h_{L,Fe}$) given in the table represents the mean value of two measured heat effects (Section II-A). A dependence on the amount of the dissolved Fe was not observed, so $\Delta H_{L,Fe}^0$ is obtained as the arithmetic mean of the results of all experiments (Table I). Note that this statement is valid for the relatively narrow compositional range considered.

The partial enthalpy of mixing at infinite dilution for liquid iron in liquid aluminium ($\Delta \bar{H}_{Fe}$) is given by

$$\Delta \bar{H}_{Fe} = \Delta H_{L,Fe}^0 - \Delta H_{Fe}^m \quad [2]$$

For the enthalpy of melting of Fe extrapolated to the measurement temperature (ΔH_{Fe}^m), a value of 12.08 kJ/mol^[7] was used. The result obtained in this study for the partial enthalpy of mixing at infinite dilution is compared with literature data in Table II. It follows that the present result is in good agreement with the value reported in Reference 10 for about

Table III. Heat Effect of Dissolution of Solid B2-Fe_{1-x}Al_x Compounds in Liquid Al and the Enthalpy of Formation of Solid B2-Fe_{1-x}Al_x at 1073 K, as Calculated by Applying Equation [1] (The Error Ranges Indicated Represent the Standard Deviation of the Measurements)

Composition	Solvent <i>n</i> _{Al} (Mol)	Sample <i>n</i> _{B2} (Mol)	Heat Effect $\Delta h_{L,B2}$ (kJ)	Enthalpy of Formation ΔH_{B2} (kJ/mol)	
Fe _{0.70} Al _{0.30}	1.02548	0.01512	-0.7831	-27.05	-27.15 ± 0.21
	1.02660	0.01287	-0.6599	-27.57	
	1.02248	0.01158	-0.5994	-27.04	
	1.02344	0.01327	-0.6866	-27.06	
	0.72390	0.01426	-0.7386	-27.01	
Fe _{0.675} Al _{0.325}	0.73321	0.01021	-0.4990	-27.15	-27.23 ± 0.08
	0.72668	0.01024	-0.5000	-27.18	
	0.72078	0.01023	-0.4981	-27.30	
	0.70314	0.01015	-0.4943	-27.30	
Fe _{0.65} Al _{0.35}	0.73275	0.01457	-0.6619	-27.75	-27.83 ± 0.29
	0.74408	0.01494	-0.6827	-27.48	
	0.73275	0.01514	-0.6815	-28.17	
	0.72747	0.01485	-0.6717	-27.95	
Fe _{0.6375} Al _{0.3625}	0.73291	0.01015	-0.4367	-28.75	-28.35 ± 0.29
	0.74128	0.01022	-0.4484	-27.92	
	0.73291	0.01025	-0.4450	-28.35	
	0.74128	0.01024	-0.4442	-28.39	
Fe _{0.63125} Al _{0.36875}	0.64504	0.00531	-0.2271	-28.30	-28.61 ± 0.33
	0.67953	0.00508	-0.2154	-28.68	
	0.61190	0.00520	-0.2186	-29.06	
	0.64504	0.00518	-0.2210	-28.44	
Fe _{0.625} Al _{0.375}	1.07694	0.01007	-0.3911	-31.65	-31.19 ± 0.32
	1.05869	0.01004	-0.3955	-30.99	
	1.07694	0.01005	-0.3926	-31.30	
	0.84425	0.01005	-0.3977	-30.82	
Fe _{0.6125} Al _{0.3875}	0.70676	0.00917	-0.3516	-30.63	-30.53 ± 0.33
	0.74246	0.00914	-0.3459	-31.14	
	0.70671	0.00906	-0.3500	-30.34	
	0.74246	0.00919	-0.3553	-30.31	
	0.74128	0.00918	-0.3556	-30.25	
Fe _{0.60625} Al _{0.39375}	0.64403	0.00501	-0.1910	-30.12	-30.52 ± 0.36
	0.64900	0.00502	-0.1905	-30.32	
	0.70503	0.00499	-0.1873	-30.73	
	0.64874	0.00499	-0.1862	-30.91	
	1.02277	0.01464	-0.5375	-30.73	
Fe _{0.60} Al _{0.40}	1.02465	0.01459	-0.5375	-30.73	-30.81 ± 0.11
	1.02519	0.01408	-0.5153	-30.97	
	1.01698	0.01113	-0.4090	-30.81	
	0.98874	0.00997	-0.3130	-33.35	
	0.72302	0.00990	-0.3114	-33.30	
Fe _{0.575} Al _{0.425}	0.74418	0.00991	-0.3144	-33.02	-33.12 ± 0.22
	0.74418	0.00988	-0.3155	-32.80	
	0.70676	0.00888	-0.2482	-33.98	
	0.74246	0.00824	-0.2326	-33.70	
Fe _{0.55} Al _{0.45}	0.73291	0.00881	-0.2404	-34.63	-34.10 ± 0.39
	0.70676	0.00837	-0.2331	-34.08	
	0.84425	0.00999	-0.2353	-35.57	
	0.98874	0.00989	-0.2308	-35.77	
Fe _{0.525} Al _{0.475}	0.75578	0.00994	-0.2304	-35.94	-35.72 ± 0.15
	0.74117	0.01001	-0.2356	-35.58	
	0.82358	0.01378	-0.2783	-36.11	
	0.84980	0.01435	-0.2967	-35.74	
Fe _{0.50} Al _{0.50}	0.71805	0.01251	-0.2484	-36.44	-36.29 ± 0.32
	0.74408	0.01424	-0.2807	-36.59	
	0.74117	0.01003	-0.1980	-36.56	

the same temperature. The values reported in Reference 11 for Fe, Ni, and Co are systematically less negative than the ones obtained in this study for Fe and in the earlier study^[6] for Ni and Co. The data given in Table II show that with

increasing temperature, the partial enthalpy of mixing at infinite dilution becomes less negative.

The values for the enthalpy of solution of solid Ni in liquid Al (used in this work; *cf.*, Eq. [1]) and for the partial

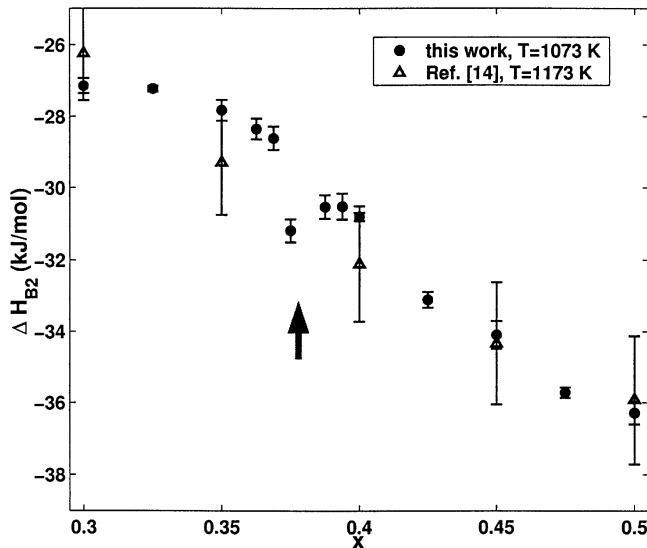


Fig. 1—Enthalpy of formation of solid B2-Fe_{1-x}Al_x compounds as a function of the atomic fraction of Al, x : ● represents results of the present study ($T = 1073$ K), error bars as determined in this work (refer to text); and △ represents data reported in Ref. 14 ($T = 1173$ K), error bars estimated to be 5 pct.

enthalpy of mixing liquid Ni in liquid Al have been reported in Reference 6.

B. Enthalpy of formation of B2-Fe_{1-x}Al_x

The heat effects measured and the corresponding calculated enthalpy-of-formation values for the solid binary B2 compounds Fe_{1-x}Al_x (Eq. [1], with $x_{Ni} \equiv 0$) have been summarized in Table III. Each indicated heat effect ($\Delta h_{L,B2}$) is the mean of two measured heat effects (Section II-A). The last value in each row of Table III is the arithmetic mean obtained from the experiments. The results obtained for the enthalpy of formation are shown in Figure 1 as a function of the atomic fraction of Al in B2-Fe_{1-x}Al_x. For comparison, the data reported in Reference 14, which were obtained from the measured temperature and composition dependencies of the thermodynamic activity, have been included in the figure as well. The data obtained in the present study (marked by a bullet in Figure 1) are the data with the smallest error margin. The data in Figure 1 derived from activity measurements^[14] are in good agreement with the present data, but are afflicted with relatively large errors of about 5 pct. (Note that the enthalpy-of-formation data do not depend strongly on temperature.)

The enthalpy of formation of the stoichiometric composition Fe_{0.50}Al_{0.50} is found to be the most negative one for the composition range investigated (Figure 1). The number of data points (*i.e.*, the number of alloys of different compositions) and the accuracy were much larger in this study than in the previous one. This may be the reason that interesting features are exhibited by the present data, which were not noted earlier (refer to Reference 14). In general, the enthalpy of formation becomes less negative with decreasing Al content. Additionally, the present results show a discontinuity at about 38 at. pct Al (refer to the arrow in Figure 1): the enthalpy curve for compounds with Al contents lower than

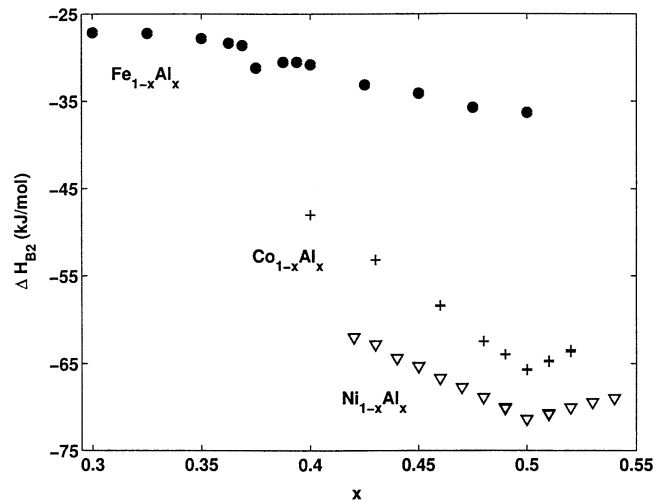


Fig. 2—Enthalpy of formation of binary aluminides, for the particular homogeneity range of the indicated B2 phases, as function of the atomic fraction of Al: ● represents results of the present study for B2-Fe_{1-x}Al_x ($T = 1073$ K), + represents data from Ref. 5 for B2-Co_{1-x}Al_x ($T = 1100$ K), and ▽ represents data from Ref. 4 for B2-Ni_{1-x}Al_x ($T = 1100$ K).

about 38 at. pct Al cannot simply be conceived as a continuation of the enthalpy curve for Al contents between about 38 and 50 at. pct.

As compared to B2-Ni_{1-x}Al_x and B2-Co_{1-x}Al_x, the enthalpy-of-formation values obtained for B2-Fe_{1-x}Al_x are the least negative ones (Figure 2). In contrast with (the present results for) B2-Fe_{1-x}Al_x, B2-Ni_{1-x}Al_x and B2-Co_{1-x}Al_x show linear dependencies for the enthalpy of formation on composition for $x < 0.5$ (and $x > 0.5$).

The unusual shape of the enthalpy vs composition curve for B2-Fe_{1-x}Al_x seems to bear a relationship to the phase diagram of the Fe-Al system, as reported in Reference 15. According to Reference 15, the composition range of the B2 phase is subdivided into three parts: the $\alpha_2(h)$ phase, the $\alpha_2(l)$ phase, and the α' phase. Following in this phase diagram, the isothermal line of 1073 K from the stoichiometric composition (50 at. pct Al) to lower Al contents, at about 38 at. pct Al, the boundary between the $\alpha_2(h)$ phase and the α' phase is crossed, which parallels the occurrence of the discussed discontinuity in the enthalpy of formation vs composition curve (Figure 1). The transformation of $\alpha_2(h)$ into α' was suggested by thermal analysis and dilatometry, but X-ray diffraction did not provide evidence.^[16] However, the subdivision of the B2-phase region of the Fe-Al system is controversial (refer also, *e.g.*, to the phase diagram given in Reference 17). To arrive at a better understanding of this phenomenon, systematic measurements of the heat capacity (c_p) in the questioned composition and temperature range are being carried out currently by our group.

C. Enthalpy of Formation of B2-(Fe,Ni)_{1-x}Al_x

The heat effects measured and the corresponding calculated (using Eq. [1]) enthalpy of formation for the solid ternary B2 compounds (Fe,Ni)_{1-x}Al_x have been given in Table IV. The indicated heat effects, again, are the mean of two recorded values. The results obtained for the enthalpy of formation are shown as a function of nickel content (relative to the sum of the iron and nickel contents) for various aluminium contents in Figure 3.

Table IV. Heat Effect of Dissolution of Solid B2-(Fe,Ni)_{1-x}Al_x Compounds in Liquid Al and the Enthalpy of Formation of Solid B2-(Fe,Ni)_{1-x}Al_x at 1073 K, as Calculated Applying Equation [1] (The Error Ranges Indicated Represent the Standard Deviation of the Measurements)

Composition	Solvent <i>n</i> _{Al} (Mol)	Sample <i>n</i> _{B2} (Mol)	Heat Effect $\Delta h_{L,B2}$ (kJ)	Enthalpy of Formation ΔH_{B2} (kJ/mol)	
Fe _{0.42} Ni _{0.08} Al _{0.50}	0.84506	0.01139	-0.1784	-42.58	-42.78 ± 0.28
	0.72112	0.01174	-0.1831	-42.64	
	1.08981	0.01350	-0.2043	-43.11	
Fe _{0.34} Ni _{0.16} Al _{0.50}	1.05933	0.00658	-0.0739	-48.95	-48.73 ± 0.22
	1.07099	0.00683	-0.0802	-48.44	
	1.06498	0.00671	-0.0764	-48.81	
	1.07926	0.00658	-0.0754	-48.73	
Fe _{0.25} Ni _{0.25} Al _{0.50}	1.06498	0.00641	-0.0519	-54.28	-54.42 ± 0.24
	1.05933	0.00650	-0.0495	-54.76	
	1.07114	0.00637	-0.0519	-54.23	
	1.02618	0.00813	-0.0648	-54.41	
Fe _{0.16} Ni _{0.34} Al _{0.50}	1.06933	0.00671	-0.0253	-60.78	-60.86 ± 0.23
	1.06990	0.00628	-0.0234	-60.84	
	1.07926	0.00629	-0.0212	-61.20	
	1.08423	0.00649	-0.0237	-60.91	
	1.07095	0.00618	-0.0246	-60.58	
	1.07562	0.00619	-0.0057	-65.58	
Fe _{0.08} Ni _{0.42} Al _{0.50}	1.02370	0.00702	-0.0070	-65.51	-65.74 ± 0.27
	1.02665	0.00702	-0.0028	-66.11	
	1.02549	0.00702	-0.0052	-65.77	
Fe _{0.46} Ni _{0.09} Al _{0.45}	1.07305	0.00905	-0.2170	-40.13	-39.87 ± 0.23
	1.06663	0.00898	-0.2203	-39.58	
	1.06030	0.00898	+0.2174	-39.90	
Fe _{0.37} Ni _{0.18} Al _{0.45}	1.06665	0.00857	-0.1767	-45.68	-45.74 ± 0.05
	1.06680	0.00863	-0.1779	-45.70	
	1.07006	0.00884	-0.1816	-45.76	
	1.07177	0.00893	-0.1830	-45.81	
Fe _{0.275} Ni _{0.275} Al _{0.45}	1.07248	0.00887	-0.1482	-51.91	-51.92 ± 0.14
	1.06237	0.00872	-0.1448	-52.00	
	1.05004	0.00859	-0.1452	-51.70	
	1.05789	0.00863	-0.1427	-52.08	
Fe _{0.18} Ni _{0.37} Al _{0.45}	1.06618	0.00891	-0.1138	-58.16	-58.07 ± 0.11
	1.06922	0.00944	-0.1216	-58.04	
	1.06818	0.00914	-0.1191	-57.90	
	1.06225	0.00867	-0.1105	-58.18	
Fe _{0.09} Ni _{0.46} Al _{0.45}	1.06793	0.00916	-0.0910	-63.16	-63.11 ± 0.06
	1.06732	0.00869	-0.0876	-63.03	
	1.06849	0.00925	-0.0929	-63.07	
	1.06762	0.00905	-0.0899	-63.17	
Ni _{0.55} Al _{0.45}	1.05526	0.00893	-0.0873	-65.51	-65.38 ± 0.10
	1.07083	0.00897	-0.0898	-65.28	
	1.05733	0.00901	-0.0889	-65.43	
	1.06487	0.00910	-0.0910	-65.30	
Fe _{0.59} Ni _{0.06} Al _{0.35}	0.64504	0.00961	-0.4228	-30.67	-30.92 ± 0.24
	0.64290	0.00949	-0.4129	-31.14	
	0.68224	0.00941	-0.4114	-30.94	
Fe _{0.53} Ni _{0.12} Al _{0.35}	0.72283	0.00962	-0.3953	-35.03	-35.46 ± 0.31
	0.67912	0.00963	-0.3928	-35.34	
	0.68224	0.00963	-0.3897	-35.62	
	0.72283	0.00958	-0.3857	-35.86	
Fe _{0.145} Ni _{0.505} Al _{0.35}	0.67953	0.01000	-0.3384	-51.62	-51.52 ± 0.29
	0.61190	0.01006	-0.3425	-51.40	
	0.64874	0.01008	-0.3375	-51.97	
	0.61190	0.01045	-0.3479	-52.16	

The present data show that starting with binary B2-Fe_{1-x}Al_x and replacing Fe with Ni, while keeping the Al content at a constant value, the enthalpy of formation becomes more negative. Keeping the (Fe,Ni) content in (Fe,Ni)_{1-x}Al_x at a constant value, the enthalpy of formation becomes less negative with decreasing Al content. The

curves in Figure 3 represent mechanical mixing of the binary intermetallic phases at a constant Al content. It follows that the deviation from mechanical mixing for the enthalpy of formation is negative at the three Al contents investigated. This deviation increases distinctly with decreasing Al content. Note that for an Al content of 35 at. pct, the ternary

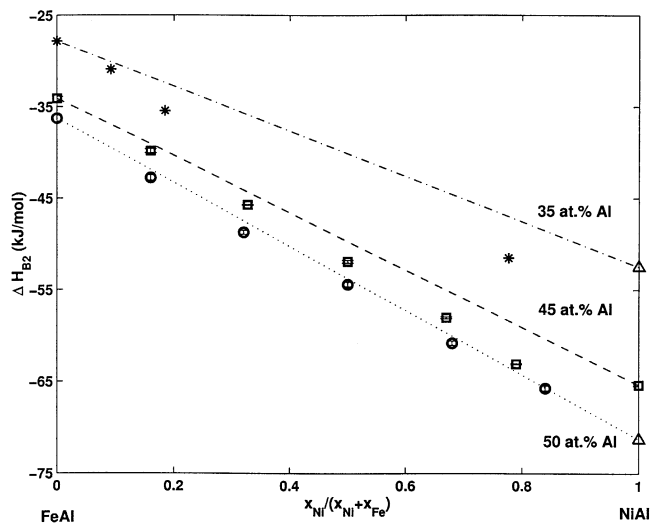


Fig. 3—Enthalpy of formation of solid B2-(Fe,Ni)_{1-x}Al_x compounds as a function of the relative amount of Ni (x_{Ni} and x_{Fe} denote the atomic fractions of Ni and Fe, respectively for various atomic fractions of Al. $x = 0.50$: ○, ...; $x = 0.45$: □, ---; $x = 0.35$: ★, -.-.; and △ represents data from Ref. 6 ($x = 0.50$) and data extrapolated from the data of Ref. 4 ($x = 0.35$). The error bars are of the size of the symbols. The curves represent the lines for the case of mechanical (ideal) mixing.

B2 phase is only stable at compositions near the binary phases B2-Fe_{1-x}Al_x and B2-Ni_{1-x}Al_x,^[18] and, therefore, the investigation of the enthalpy of the ternary B2 phase with this Al content could not be performed over the whole range of variable Ni/Fe atomic ratios.

IV. CONCLUSIONS

1. Application of special, laboratory-built isoperibolic heat-flow differential-solution calorimeter allowed determination of the enthalpy of formation of the B2 phases of the Fe-Al and Fe-Ni-Al systems with very good accuracy.
2. The enthalpy of formation of B2-Fe_{1-x}Al_x is most negative for the stoichiometric composition Fe_{0.50}Al_{0.50}. An

unusual discontinuity was found in the enthalpy of formation vs composition curve at about 38 at. pct Al. This result parallels the observation of a “phase transition” at this temperature and composition, as reported in the literature cited.

3. Upon replacing Fe by Ni atoms, while keeping the Al content constant, the enthalpy of formation of B2-(Fe,Ni)_{1-x}Al_x becomes increasingly more negative. Keeping the Ni/Fe atomic ratio constant, for decreasing Al contents (starting with 50 at. pct Al), the enthalpy of formation becomes less negative and shows an increasing deviation from the values predicted for the case of mechanical mixing of the two binary intermetallic phases B2-Fe_{1-x}Al_x and B2-Ni_{1-x}Al_x.

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