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A THIRD LAW OF THERMODYNAMICS ANALYSIS OF THE ENTHALPY CHANGE OF THE ORDER–DISORDER TRANSFORMATION IN Ni_3Fe *

CHARLIE R. BROOKS and SUJIT DAS

Materials Science and Engineering Department, The University of Tennessee, Knoxville, TN 37996-2200 (U.S.A.)

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ABSTRACT

For the alloy Ni_3Fe, the heat capacity–temperature curves for the ordered and the disordered condition have been constructed from experimental data from 300 to 773 K (the experimental order–disorder transformation temperature), and from 0 to 300 K from heat capacity models and low temperature (1–4 K) experimental data. From the most reliable value of the enthalpy of the transformation at 773 K, the entropy of disordering is calculated to be 2.40 (± 0.8) J g-atom^{-1} K^{-1}. The value calculated from the heat capacity curves is 4.76 (± 0.18). This implies that the calculated heat capacity curve for the ordered state is too low, and thus there may be a low temperature (e.g. < 500 K) phase transition in the ordered structure.

INTRODUCTION

There has been a resurgence in interest in calculating the Ni–Fe phase diagram. This has involved the use of experimental thermodynamic data (e.g. heats of alloy formation, activities, etc.) and experimental phase boundaries. Generally, models are used to represent the dependence of the thermodynamic properties on chemical composition from which the phase boundaries are calculated. In some treatments specific parts of the experimentally determined phase diagram are taken as correct, and the models must meet these restrictions. Treatments are usually considered best if the models predict well the experimental phase diagram from the liquidus to the lower temperature limit of reliable experimental data (e.g. 500 K).

Such analyses are of interest because they contribute to an understanding of the thermodynamics of alloys, and in the specific case of Ni–Fe alloys, to the influence of magnetic effects on the thermodynamic behavior. Another

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* Dedicated to Professor E.F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

area where the calculation of the Fe–Ni phase diagram is of interest is in understanding the structures which have formed in Fe meteorites. These extraterrestrial bodies are basically Fe-rich Fe–Ni alloys (e.g. 10% Ni) which have cooled in the solid region extremely slowly (i.e. 1 K every 10^5 years). Practical equilibration experiments are limited to about 500 K, and thus the phase diagram used below about 500 K must be that calculated from the thermodynamic models. That structures not predicted by the thermodynamic calculations can form below this range is evidenced by the discovery in meteorites of intermetallic compounds which have never been made in the laboratory (e.g. Fe_3Ni [1] and NiFe [2–4]) or only under very specialized conditions (NiFe) [5,6].

The only intermetallic compound in the Ni–Fe system that exists at high temperatures is Ni_3Fe [7]. The alloy of the composition Ni_3Fe is configurationally long-range ordered (LRO) below 773 K, and magnetically ordered below 871 K [7]. In the calculations of the phase diagram, a thermodynamic quantity of interest is the heat of formation of this compound. This can be determined from experimental data of the free energy of formation of the disordered alloy, of the enthalpy change of the disorder-to-order transformation, and of the temperature dependence of the heat capacity of the alloy in both the LRO and the disordered condition.

The reliability of the experimental values of the enthalpy change of the transformation can be assessed by a third law of thermodynamics analysis. If heat capacity data are available from 0 to 773 K for the LRO and the disordered condition, the entropy change at 773 K can be calculated. This value should differ from that obtained by dividing the enthalpy change by 773 by the configurational entropy of ordering. It is the purpose of this paper to estimate the entropy of the transformation at 773 K, and make this comparison.

The Ni_3Fe alloy can be obtained at 300 K in the equilibrium LRO condition by very slow cooling from above 773 K, or by annealing at a temperature just below 773 K. Also, at 300 K the alloy can be obtained in the non-equilibrium, disordered condition by rapid cooling (e.g. water quenching) from above 773 K [8]. Thus at 300 K the alloy can be obtained in either the LRO or the disordered condition. This has allowed measurement of the heat capacity from 1.4 to 4.4 K for both conditions [8]. Further, the kinetics of ordering from the disordered condition are sufficiently slow that the heat capacity of the disordered alloy has been measured from 300 to 773 K by a rapid pulse method [9]. Thus there are accurate heat capacity data for the LRO and for the disordered condition at very low temperatures, and from 300 K to the transformation temperature, 773 K. However, there are no data for either condition from 4.4 to 300 K. In this paper, we present an estimate of C_p from 0 to 300 K for the LRO and the disordered condition. These results are combined with the experimental C_p data for both conditions from 300 to 773 K to calculate the entropy change of the disorder-to-order transformation. This is then compared with the value obtained from the experimental enthalpy change at 773 K.

C_p FOR THE LRO AND THE DISORDERED CONDITION

300–773 K

The data of Kollie [10] were used for the heat capacity from 300 to 773 K. A pulse calorimeter technique was used by which the heat capacity is measured using a thin wire as it is heated directly by passage of electric current [9]. The error in C_p by this method is about $\pm 0.5\%$ in the temperature range 300–800 K [10,11]. The heating rates were sufficiently rapid (of the order of 50 K s^{-1}) that the disordered condition, obtained by prior rapid cooling from above 773 K, was retained to 773 K. For the LRO ordered condition, prior to measurement the specimen was annealed below 770 K for 63 days, which developed a LRO parameter of 0.96 [10].

The measurements began at about 400 K. To obtain a value of C_p at 300 K for both conditions, the data values every 10 K from about 500 to 400 K were plotted, then extrapolated linearly to 300 K. The value at 300 K so obtained and the experimental data to 773 K were fitted to a polynomial (Table 1) and the resulting C_p curves are shown in Fig. 1. From these equations the entropy change from 300 to 773 K for each condition was calculated (Table 2).

0–300 K

In this temperature range, the only C_p data for both conditions are those of Kollie et al. [12] from 1.4 to 4.4 K. For the LRO condition, measurements were made only for a LRO parameter of ~1.0 *.

TABLE 1

The polynomials used to represent the heat capacity from 300 to 773 K of Ni_3Fe in the LRO and in the disordered condition

LRO condition	Disordered condition
$C_p = 17.3169 + 0.03720\ T - 5.112\times10^{-5}\ T^2 + 3.739\times10^{-8}\ T^3$	$C_p = 17.3358 + 0.03742\ T - 4.503\times10^{-5}\ T^2 + 3.329\times10^{-8}\ T^3$ C_p in J g-atom^{-1} K^{-1} T in K

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* Kollie et al. [12] give a value of the LRO parameter of 0.69. However, it is clear from other work [13] that it is close to unity. It appears that the reported value is a misprint.

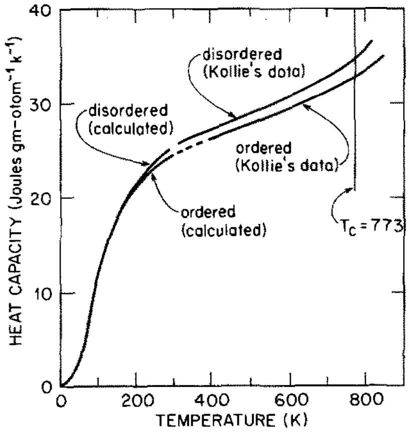

Fig. 1. The heat capacity of Ni_3Fe in the LRO and in the disordered condition from 0 to 773 K.

From the C_p data they obtained the low temperature heat capacity coefficient γ and the Debye temperature θ_D, which we have used to estimate the contribution to the heat capacity at constant volume from the excitation of electrons and lattice vibrations.
Thus

$$C_v = \gamma T + C_v^D \tag{1}$$

where C_v^D is given by the Debye integral using a single Debye temperature θ_D. However, to obtain C_p a dilation correction must be applied [14]. Unfortunately, there are no data of isothermal compressibility and thermal expansion which allow this calculation, so we have used the Nernst–Lindemann approximation [15]. Thus we have

$$C_p = \gamma T + C_v^D + AC_p^2 T \tag{2}$$

where A is the Nernst–Lindemann constant. For the LRO and the disordered condition, we obtained a value of A by using the value of C_p at 300 K and the values of γ and θ_D in Table 3. The equation above, with the appropriate parameters, was used to calculate C_p values at approximately

TABLE 2

Calculated entropy change from 0 to 773 K of Ni_3Fe in the LRO and in the disordered condition

LRO condition	Disordered condition
$S^{773} - S^{\circ} = S^{773} - S^{300} + (S^{300} - S^{\circ})$	$S^{773} - S^{\circ} = 27.511 + 26.236$
$= 26.435 + 24.912$	$= 53.747$
$= 51.347$	ΔS in J g-atom^{-1} K^{-1}

TABLE 3

Parameters used to calculate the heat capacity from 0 to 300 K of Ni_3Fe in the LRO and in the disordered condition

Parameter	Ordered	Disordered
Debye temperature (K)	400 (±8)	431 (±5)
γ (Joules g-atom^{-1} K^{-2})	3.301×10^{-3} (±0.010)	4.178×10^{-3} (±0.009)
A (g-atom J^{-1})	7.837×10^{-6}	8.8873×10^{-6}

every 2 K. The values so obtained were then fitted to polynomials for ease of integrating to obtain the entropy change from 0 to 300 K for each condition (Table 2). The C_p curves based on these polynomials are shown in Fig. 1.

ENTROPY OF DISORDER-TO-ORDER TRANSFORMATION AT 773 K

The values of the entropy change from 0 to 773 K (Table 2) were subtracted to obtain an entropy change Δs^{O-D} of the disorder-to-order transformation at 773 K of 2.40 J g-atom^{-1} K^{-1}. This value is dependent upon the values of the parameters used in eqn. (2). Note that the uncertainity in the Debye temperatures is about ± 5 K (Table 3). If the Debye temperatures are taken to be 10 K different than the values in Table 3, with $\theta_D^O = 420$ and $\theta_D^D = 450$, then the entropy change is about 3.2 J g-atom^{-1} K^{-1}. If the extremes of the uncertainity in the γ values in Table 3 are used to calculate Δs^{O-D} (with the same θ_D values as in the table), a value of about 2.44 is obtained, a small change. It thus appears that the calculated entropy change of 2.40 has an uncertainty of about ± 0.8.

Values of the enthalpy change upon disordering are tabulated in Table 4. The differences reflect experimental errors and probably differences in the degree of LRO obtained prior to the measurements. We take the value of Kollie [10] to be the best. From this, the entropy change is 4.76 J g-atom^{-1} K^{-1} (±0.18).

TABLE 4

Experimental values of the enthalpy change (J g-atom^{-1}) of the disorder-to-order transformation at 773 K for Ni_3Fe

Reference	Value
Kaya (1938) [16]	3034
Leech and Sykes (1939) [17]	3350
Iida (1952) [18]	3716
Kollie (1969) [10]	3680 (±140)

DISCUSSION

The entropy change at 773 K of 4.76, based on the reliable enthalpy change at this temperature, is much higher than the value of 2.40 calculated from the heat capacity curves. This implies that the heat capacity curve of the disordered state is too high, or that of the ordered state is too low, or both. Below 773 K both alloys are magnetically ordered, so that this effect cannot account for the discrepancy. Also, it appears unlikely that the heat capacity curve for the disordered condition is in error enough to account for the difference. The most likely explanation is that there is a phase transformation between 0 and 773 K in the ordered structure. This would manifest itself in a discontinuity in the heat capacity, associated with an enthalpy of transformation, or a maximum in the heat capacity curve, depending on the type of transformation, as the ordered structure changed to another type of ordered structure. (It would also alter the low temperature data (e.g. 1–4 K) and affect the θ_D and γ values.) This would give a higher entropy than that calculated. In the higher temperature range (e.g. above 500 K), such a change would probably occur rapidly enough to be observed or at least to affect physical properties and hence hint at such a possibility; there do not appear to be reports of such an effect at high temperature. Thus it is most likely that the change occurs below 500 K, where the rate of transformation is too low for it to have been observed.

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