Heats of Formation and Heat Capacities in the System Iron-Nickel-Chromium

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The heats of formation from the component metals of 47 alloys in the system iron-nickel-chromium have been measured at about 1300° C. using an adiabatic high-temperature calorimeter. The present results together with the previously published heats of formation in the binary systems have been used to interpolate the isoenthalpy contours in the ternary system. A maximum heat absorption of 2200 cal. per gram-atom was found at a composition of about 10 atomic % Fe, 60 atomic % Cr, and 30 atomic % Ni. The true heat capacities of a nickel-chromium alloy with 35 atomic % Cr and of the component metals have also been measured between 850° and 1220° C. The deviation from Neumann-Kopp's rule is positive, of the order of ΔCp = 0.7–0.4 cal. per °C. gram-atom. The heat of the order-disorder transformation of an alloy, $FeNi_3$, was $\geq$ 667 cal. per gram-atom.

THIS LABORATORY has started an investigation of the thermodynamic properties of the system iron-nickel-chromium. So far, the determination of the integral heats of formation at about 1300° C. has been completed. Some heat capacities in the binary systems have also been measured, and vapor pressure and e.m.f. measurements have begun. However, since a complete study of the free energies in the ternary system will require considerable time, it is believed to be desirable to put the experimental results so far obtained on record.

The heats of formation of the binary alloys have previously been determined in this laboratory by Dench (*2*), who devised the adiabatic calorimeter which has been used in the present investigation.

EXPERIMENTAL

The high-temperature calorimeter has been described in detail by Dench (*2*). A specimen made of compacted metal powders may be held under adiabatic conditions at elevated temperature, and measured quantities of energy may be supplied to the specimen via an internal heater.

Since the publication of the first paper (*2*), the control system of the calorimeter has been modified by the addition of an automatic controller to replace the hand-operated furnace control resistances. The purpose of the controller is to maintain adiabatic conditions during the heating of the specimen through the reaction range (ca. 40 minutes) and also during the period of time when the reaction is going to completion at high temperature. The controller is operated from the differential thermocouples, two forms of control being applied. One controls the mean power dissipated in the furnace winding; the other superimposes small increases or decreases of power on this mean level during a given small time interval and thus has the effect of adding to or subtracting from the system small pulses of energy while maintaining the mean power at an approximately constant level. A fuller description of this semi-automatic controller has been given by Dench (*1*).

Electrolytic chromium flake was ball-milled for 8 hours and then sieved, the fraction between 300- and 400-mesh being used. Carbonyl iron powder was reduced with dried high-purity hydrogen at 400° C. for 45 minutes. The partly sintered powder was ground and sieved, the fraction less than 400-mesh being used. Carbonyl nickel powder was prepared in the same way as the iron but received hydrogen treatment for 30 minutes at 450° C. Vacuum fusion analyses for oxygen and nitrogen made at this stage gave the following results: iron, 0.07% O_2 and 0.02% N_2; nickel, 0.04% O_2 and 0.007% N_2; chromium, 0.45% O_2 and 0.015% N_2.

The compacted mixture of the metal powders was enclosed in a double-walled capsule made from 0.05-mm. tantalum sheet. At certain compositions, where the tantalum tended to alloy with the compact, the inner wall was made from 0.05-mm. tungsten sheet.

In each case, a specimen prepared as indicated above was initially heated in the calorimeter to about 400° C. using the outer furnace only. The specimen was then brought to the starting temperature of 503.5° C. using the internal heater and automatic control. This is approximately the highest temperature to which the specimen may be heated without the reaction proceeding at an appreciable rate. The specimen was held in equilibrium at this temperature for about 10 minutes and was then heated through the reaction range to 1291.7° C. by means of the internal heater, adiabatic conditions being maintained by means of the automatic controller. At 1291.7° C. the internal heater was switched off and the heat input recorded. Adiabatic conditions were maintained until it was evident that the reaction had gone to completion. This took up to one hour and was indicated by the attainment of either a constant temperature in the specimen or of a small constant rate of change of temperature owing to small errors in the differential thermocouple system.

The change in heat content of the pure component metals, the capsule, and the calorimeter was measured over the same range of temperatures in separate experiments. Their mean heat capacities in the range 1274° to 1310° C. were also measured. The heat of formation was obtained by subtracting the total change in heat content from the energy put into the specimen by the internal heater during the reaction.

A binary nickel-chromium alloy (35 atomic % Cr) was selected on which heat capacities were measured in the range 850° to 1250° C. in 100° intervals. Heat capacities were also measured in the same temperature range on a composite specimen made up of two cylinders of pure nickel and two cyclinders of chromium, the metals being in the same atomic proportion as in the alloy. The use of the calorimeter for *Cp* measurements has been described by Dench and Kubaschewski (*3*) who investigated pure iron.

Finally, the heat of transformation of an iron-nickel alloy of composition $FeNi_3$, which forms an ordered structure below 500° C., was determined in the calorimeter. Specimens containing 25.0 atomic % Fe were alloyed at 1000° C. for several hours and then annealed (as indicated in Table III) to form a superlattice. The order-disorder transformation occurred over the range 540° to 580° C. At this temperature the sheathed thermocouple normally used did not give an accurate measurement of the temperature of the specimen and so a thermocouple making direct contact with the specimen was used, being tied to it with tantalum wire.

The specimens were heated through three successive temperature intervals, arranged so that the transformation occurred in the middle interval. The other intervals acted as a check that the transformation did in fact occur completely in the middle interval. The calorimeter was then cooled down and the specimen reheated through the same three intervals, the difference in the input energy required giving the heat of transformation.

RESULTS AND DISCUSSION

The measured integral heats of formation of the ternary alloys from the component metals are recorded in Table I. Recent results on some binary iron-nickel alloys are included. The accuracy of such measurements with the present calorimeter has been discussed by Dench (*2*). The maximum error in the individual heats of alloying may be taken to be ±150 cal. per gram-atom. This includes both chemical and physical errors.

The bulk of the results on the binary alloys in the systems iron-nickel, nickel-chromium, and chromium-iron may be taken from Dench's paper. The heats of formation of iron-nickel alloys obtained by Steiner and Krisement (*9*), who applied liquid-tin solution calorimetry at 800° C., agree reasonably well with those of Dench and should also be taken into account. All this information has been used to construct smoothed isoenthalpy contours at 500 cal. per gram-atom intervals, shown in Figure 1, obtained by graphical interpolation of the tabulated results.

Figure 1 shows that the isoenthalpy curves show a relatively simple pattern. The maximum heat effect seems to occur in the ternary range, at a composition of about 60 atomic % Cr and 30 atomic % Ni, where 2200 calories are absorbed in the formation of 1 gram-atom of alloy. Discussion of the significance of the enthalpy changes would require a more intimate knowledge of the equilibrium diagram, which can be worked out only when a complete set of free energy data is also available.

Table I. Integral Heats of Formation from the Component Metals of Ternary Iron-Nickel-Chromium Alloys at 1292° C., and Binary Iron-Nickel Alloys at 1050° C.

Atomic Per Cent			ΔH_f, Cal./ G.-Atom	Atomic Per Cent			ΔH_f, Cal./ G.-Atom
Cr	Fe	Ni		Cr	Fe	Ni	
0	25	75	−1060	30	30	40	+450
0	25	75	−1045	30	30	40	+410
0	90	10	−195	30	40	30	+770
0	90	10	−290	30	40	30	+970
0	90	10	−140	30	50	20	+860
10	10	80	−650	30	60	10	+860
10	20	70	−490	40	10	50	+850
10	30	60	−740	40	20	40	+950
10	40	50	−510	40	30	30	+1340
10	50	40	−450	40	40	20	+1700
10	60	30	−80	40	50	10	+1610
10	65	25	−170	50	10	40	+1440
10	70	20	−130	50	20	30	+1650
10	80	10	+250	50	30	20	+1810
20	10	70	−270	50	40	10	+1680
20	20	60	−80	60	10	30	+2270
20	30	50	−310	60	20	20	+1850
20	40	40	−30	60	30	10	+1620
20	40	40	−120	60	30	10	+1300
20	50	30	+100	65	10	25	+1940
20	60	20	+550	70	10	20	+1800
20	70	10	+810	70	20	10	+1610
30	10	60	+340	80	10	10	+1730
30	20	50	+360				

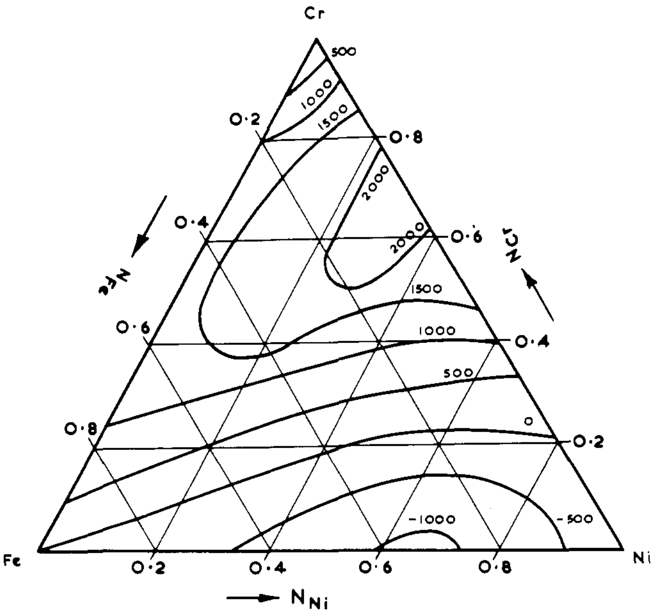

Figure 1. Isoenthalpy contours (in calories per gram-atom) in the system iron-nickel-chromium for the range of temperature covered by the experimental work

Table II records the measured, true, heat capacities of a chromium-nickel alloy with 35.0 atomic % Cr as well as those for the pure metals, the values for which agree reasonably well with the ones calculated additively from the heat capacities of chromium and nickel selected by Hultgren *et al.* (*5*). The values of $\Delta Cp = Cp$ (alloy) − Cp (metals) show that there is a substantial deviation from Neumann-Kopp's rule indicating that the heat of formation of Ni-Cr solid solutions depends on temperature. The original experimental data are indicated in Figure 2.

Hultgren and Land (*4*)measured heat contents of nickel-chromium alloys with 2 to 11 atomic % Cr between 400° and 1500° K. by means of a diphenyl ether calorimeter. At the higher temperatures, they generally also found positive deviations from Neumann-Kopp's rule. Though smaller than the deviations for the 35% alloy, they increase with chromium content and are thus consistent with the present findings.

Taylor and Hinton (*10*) studied the atomic heat of an alloy, "$CrNi_3$," and found some evidence of superlattice formation in that the *Cp vs. T* curve showed the typical λ shape with the maximum at 814° K. At higher temperatures, ΔCp again assumes positive values.

Table II. True Heat Capacities of a Ni-Cr Alloy with 35 Atomic % Cr and the Corresponding Composite of Chromium and Nickel

Temp., ° C.	Alloy, *Cp*, Cal./ ° C., G.-Atom	0.35 Cr + 0.65 Ni *Cp*, Cal./ ° C., G.-Atom	ΔCp, Cal./ ° C., G.-Atom
900	8.79	8.10	0.69
950	8.91	8.23	0.68
1000	8.97	8.36	0.62
1050	9.05	8.48	0.57
1100	9.14	8.61	0.53
1150	9.19	8.74	0.46
1200	9.28	8.87	0.42

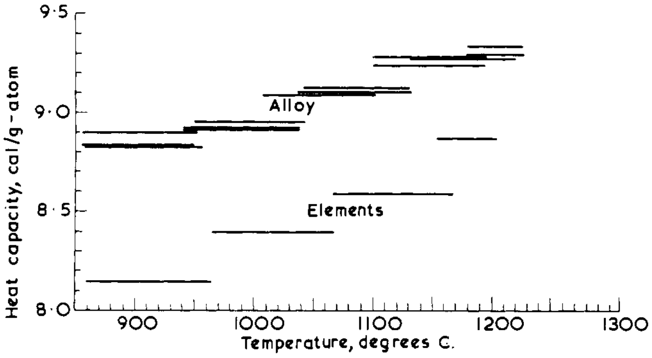

Figure 2. Mean heat capacity vs. temperature for a 35 atomic % Cr-Ni alloy and for a composite specimen containing the same mass of chromium and nickel unalloyed

Table III. Experimental Conditions and Heats of the Order-Disorder Transformation of $FeNi_3$

Specimen	Pretreatment: Annealing Temp., ° C. and Time, Hr.	*Cp* Measmt. Temperatures, ° C.	L_t, Cal./ G.-Atom
1	490°, 935 & 455°, 720	443-608	647
2	435°, 270 & 400°, 550	503-569	357
3	490°, 22 & 490° to 350° 550	506-603	596
4	490°, 1030 & 490° to 350°, 550	503-584	667

The annealing conditions, the temperature ranges of measurement, and the heats of the order-disorder transformation derived therefrom for an iron-nickel alloy containing 75.0 atomic % Ni are given in Table III. The degree of ordering achieved by the present pretreatment is difficult to ascertain because, for most x-ray wavelengths, the atomic scattering factors of iron and nickel are similar—that is, the superlattice lines are very weak. One is therefore inclined to choose the highest value, L_t = 667 cal. per gram-atom, as likely to be nearest the true value for the heat of transformation. The value is in excellent agreement with Iida (*6*), who determined the heat of disordering of an alloy with 74 atomic % Ni, 25 atomic % Fe, and 1 atomic % Mn at 490° C. and found L_t = 650 cal. per gram-atom.

At about 600° C., $FeNi_3$ undergoes a magnetic transformation, and measurements of *Cp* that extended much beyond this temperature consequently produced higher heats of transformation—i.e., those of the order-disorder transformation plus the magnetic energy. Leech and Sykes (*8*) heated an alloy with 74.3 atomic % Ni from 270° to 620° C. and found a heat effect of 825 cal. per gram-atom corresponding to the λ anomaly. The peak occurred at 544° C. Kaya and Nakayama (*7*) found a somewhat higher heat of transition—namely, 1000—at 75 atomic % Ni. In both cases, the temperature range in which the magnetic transformation occurs was entered, so that some magnetic energy was contained in the calorific value.

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