

Enthalpy and Heat Capacity from 0° to 900° C of Three Nickel-Chromium-Iron Alloys of Different Carbon Contents

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The enthalpy relative to 0° C of three alloys was measured at nine temperatures from 100° to 900° C by a precise "drop" method. The alloys contained approximately 76 percent of nickel, 15 percent of chromium, and 8 percent of iron, with carbon contents of 0.02, 0.07, and 0.11 percent, respectively. The results are almost independent of the several variations in prior heat treatment investigated, and the heat-capacity-temperature curves of the three alloys are almost coincident, but there is a marked shift in each curve within the interval 500° to 600° C.

1. Introduction

The National Advisory Committee for Aeronautics has had underway a program of acquiring basic physical data important in the aerodynamic heating of the construction materials used in supersonic airplanes and guided missiles. As a part of the program, the Committee sponsored at the National Bureau of Standards measurements of the thermal conductivity, thermal expansion, total thermal emissivity, and heat capacity of nickel-chromium-iron alloys commercially produced as Inconel.

The investigation of these properties covered Inconel specimens whose carbon contents spanned more than the range normally encountered. The measurements of heat capacity are reported in this paper. The results of the measurements of heat capacity, thermal conductivity, thermal expansion, mechanical properties, electrical resistance, and emissivity of these Inconel alloys are summarized elsewhere [2].¹

2. Alloys Investigated

The heat capacity was derived from enthalpy measurements on specimens that had been cut from hot-rolled, unannealed rods of ½-in. diameter furnished by the International Nickel Company, who

supplied the chemical analyses of the three alloys given in table 1.² Before measurement of their enthalpy, the samples were subjected to the various annealing treatments specified in footnotes to the tables of enthalpy data (tables 3 to 5, section 4), and the average values of hardness found after annealing [2] are given in the last two columns of table 1. The enthalpy data of table 6 are preliminary values determined in an attempt to ascertain whether certain variations in prior annealing treatment affected the enthalpy appreciably. Although the hardness values were determined on various Rockwell superficial hardness scales, these results have been converted to approximate values on the Vickers scale, which also are given to afford ready comparison.

3. Calorimetric Method

The apparatus and method used in measuring the enthalpy were described in detail in a recent paper [3]. Briefly, the sample in a helium-filled container of the alloy 80 Ni-20 Cr was held inside a silver-core furnace in an atmosphere of helium until, as determined by preliminary "relaxation-time" tests [4], the sample had time to reach the furnace temperature within 0.01 deg C. The sample and container were

² Although these alloys were not reanalyzed at the Bureau to confirm these compositions, there are reasons for believing that in the temperature range investigated their enthalpies are insensitive to errors in composition. The heat capacities per unit mass of the three principal elements (nickel, chromium, and iron) are approximately the same, and there are no transitions in their ternary phase diagram near the compositions of the present alloys [1].

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Chemical compositions of the alloys

Sample number	Chemical composition (weight %)									Hardness	
	C	Ni	Cr	Fe	Mn	Si	Cu	S	Total	Rockwell, 15-T scale	Approximate equivalent value, Vickers scale
1-----	0.02	75.99	14.42	8.87	0.28	0.17	0.22	0.007	99.98	78	97
2-----	.07	76.45	14.96	7.89	.26	.19	.15	.007	99.98	80	106
3-----	.11	75.64	15.32	8.17	.33	.21	.19	.007	99.98	83	123

then dropped into a precision Bunsen ice calorimeter, the heat they delivered in cooling to 0° C being determined by the mass of mercury entering the calorimeter because of the reduction in volume caused by the melting of ice. Similar measurements were made on the empty container to account accurately for (a) the part of the heat due to the container when a sample was present, and (b) the heat lost elsewhere than to the calorimeter during the drop. The net heat contributed by the sample itself equals its difference in enthalpy between the furnace temperature and 0° C.

The furnace temperature, which was held constant to ± 0.01 deg C during a heat measurement, was measured up to 600° C by a platinum thermometer and above 600° C by a platinum-platinum-10-percent rhodium thermocouple. Both measuring instruments, initially annealed and calibrated at the Bureau in terms of the International Temperature Scale of 1948, were recalibrated during the course of the present investigation; the thermometer had remained unchanged, and the temperature indications of the thermocouple had not changed by more than 0.1 deg C. The conversion factor of the ice calorimeter, 270.48 ± 0.03 abs j/g of mercury, had been determined earlier in hundreds of electrical calibrations of the calorimeter [3]. Minor corrections were made for the very small, unavoidable variations in temperature and masses of container materials entering the calorimeter.

The major material constituting the sample container, the alloy 80 Ni-20 Cr, has been shown to exhibit an anomaly in heat capacity [5] similar in magnitude and temperature range to those of the alloys of the present investigation. However, this effect always canceled completely in subtracting the empty-container heat to obtain that of the alloy sample, for the empty-container heat values were determined on the same container and at the same temperatures as those used for the alloy samples.

4. Enthalpy Data

The principal series of individual heat measurements are recorded in table 2 for the empty container and in tables 3, 4, and 5 for the three alloys, which are numbered as in table 1. All individual-run values in each of tables 3, 4, and 5 are given in chronological order, and all intervening periods of time when the samples were in the furnace but no heat measurements were being made also are recorded. (In table 2 the values for any one furnace temperature are listed chronologically, but the temperatures themselves are not.) Each value in the fourth column of tables 3, 4, and 5 was obtained by subtracting from the corresponding value in the third column the mean heat for the empty container at that furnace temperature (from table 2) and then dividing by the sample mass.

Although enthalpy values at some temperature between 500° and 600° C were also desired, no significance is to be attached to the particular choice of 557.5° C.

An investigation was made of the effect of different prior heat treatments on the relative enthalpy of alloy 2. Measurements on three specimens of this alloy that had had different treatments are recorded in table 6, in chronological order for each specimen. A sequence of several measurements at each of the successive temperatures 600°, 900°, and 600° C was adopted, and the pertinent values from table 4 are included for comparison ("specimen C"). The mean empty-container value of enthalpy (table 2) was used at each temperature.

TABLE 2. Enthalpy measurements—empty container

Furnace temperature, <i>t</i>	Measured heat		Furnace temperature, <i>t</i>	Measured heat	
	Individual run	Mean		Individual run	Mean
° C	<i>abs j</i>	<i>abs j</i>	° C	<i>abs j</i>	<i>abs j</i>
100.00	{ 510.2 509.5 }	509.8	500.00	{ 2,790.8 2,791.1 2,790.7 }	2,790.9
200.00	{ 1,050.2 1,049.9 1,049.6 }	1,049.9	557.50	{ 3,146.5 3,146.2 }	3,146.3
300.00	{ 1,611.8 1,614.9 1,612.1 }	1,612.9	600.00	{ 3,410.6 3,412.6 }	3,411.6
400.00	{ 2,192.1 2,196.2 2,197.6 2,193.7 2,200.2 2,192.1 }	2,195.3	700.0	{ 4,083.7 4,078.8 4,076.7 }	4,079.7
			800.0	{ 4,764.0 4,765.6 }	4,764.8
			900.0	{ 5,460.0 5,464.4 }	5,462.2

TABLE 3. Enthalpy measurements—alloy 1 (0.02% carbon)^a
(Sample mass=19.8559 g)

Furnace temperature, <i>t</i>	Time in furnace	Measured heat (sample plus container)	Net enthalpy of sample, $H_t - H_{0^\circ\text{C}}$	
			Individual run	Mean
° C	<i>min</i>	<i>abs j</i>	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>
100.00	{ 32 34 54 }	{ 1,404.7 1,407.8 1,410.4 }	{ 45.07 45.23 45.36 }	45.22
200.00	{ 34 34 }	{ 2,896.9 2,895.8 }	{ 93.02 92.96 }	92.99
300.00	{ 49 44 50 }	{ 4,435.6 4,439.6 4,441.8 }	{ 142.16 142.36 142.47 }	142.33
400.00	{ 44 44 }	{ 6,032.7 6,035.5 }	{ 193.26 193.40 }	193.33
500.00	{ 49 44 }	{ 7,678.1 7,675.9 }	{ 246.14 246.02 }	246.08
600.00	{ 44 44 54 }	{ 9,396.7 9,406.9 9,406.2 }	{ 301.43 301.94 301.91 }	301.76
700.0	{ 44 44 }	{ 11,242.0 11,237.3 }	{ 360.71 360.47 }	360.59
800.0	{ 44 44 }	{ 13,116.1 13,117.0 }	{ 420.60 420.64 }	420.62
900.0	{ 79 44 }	{ 15,048.6 15,050.6 }	{ 482.80 482.90 }	482.85
557.50	{ 45 45 }	{ 8,657.8 8,657.1 }	{ 277.58 277.54 }	277.56

^a Prior treatment: Annealed at 1,010° C (1,850° F) and then quenched.

TABLE 4. Enthalpy measurements—alloy 2 (0.07% carbon)^a

(Sample mass=19.9070 g)

Furnace temperature, <i>t</i>	Time in furnace	Measured heat (sample plus container)	Net enthalpy of sample, $H_t - H_{0^\circ\text{C}}$	
			Individual run	Mean
$^\circ\text{C}$	<i>min</i>	<i>abs j</i>	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>
100.00	{ 45 45	{ 1,405.1 1,407.4	{ 44.97 45.09	{ 45.03
200.00	{ 45 45	{ 2,891.4 2,892.4	{ 92.50 92.55	{ 92.53
300.00	{ 45 45	{ 4,440.9 4,439.9	{ 142.06 142.01	{ 142.04
400.00	{ 45 45	{ 6,043.8 6,046.6	{ 193.32 193.46	{ 193.39
500.00	{ 45 45	{ 7,697.8 7,699.3	{ 246.50 246.57	{ 246.53
600.00	{ 45 45 45 45	{ 9,435.7 9,424.9 9,425.1 9,423.3	{ ^b (302.61) 302.07 302.08 301.99	{ 302.05
700.0	{ 45 45	{ 11,258.1 11,257.7	{ 360.60 360.57	{ 360.58
800.0	{ 45 45	{ 13,143.1 13,146.9	{ 420.87 421.06	{ 420.97
900.0	{ 45 45	{ 15,085.2 15,084.3	{ 483.40 483.35	{ 483.38
557.50	{ 45 45	{ 8,674.1 8,673.8	{ 277.68 277.67	{ 277.67
557.50	{ 170 183	{ 8,667.6 8,666.9	{ 277.36 277.32	{ 277.34
557.50	{ 45 50	{ 8,669.6 8,667.1	{ 277.45 277.33	{ 277.39
400.00	{ 45 50	{ 6,040.1 6,042.5	{ 193.14 193.26	{ 193.20
900.0	70	15,083.1	483.29	483.29
557.50	{ 45 50	{ 8,674.5 8,674.3	{ 277.70 277.69	{ 277.69

^a Prior treatment: Annealed by heating at 1,120° C (2,050° F) for 7½ min and cooling in air, and then by heating at 1,010° C (1,850° F) for 20 min. In the latter case the method of cooling is not known.

^b Omitted from the mean because of inferior precision.

TABLE 5. Enthalpy measurements—alloy 3 (0.11% carbon)^a

(Sample mass=19.8347 g)

Furnace temperature, <i>t</i>	Time in furnace	Measured heat (sample plus container)	Net enthalpy of sample, $H_t - H_{0^\circ\text{C}}$	
			Individual run	Mean
$^\circ\text{C}$	<i>min</i>	<i>abs j</i>	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>
100.00	{ 45 45	{ 1,406.1 1,406.0	{ 45.19 45.18	{ 45.18
200.00	{ 45 60 50	{ 2,890.8 2,892.3 2,890.6	{ 92.81 92.89 92.80	{ 92.83
300.00	{ 45 45	{ 4,437.7 4,436.7	{ 142.41 142.36	{ 142.39
400.00	{ 45 45	{ 6,039.7 6,037.1	{ 193.82 193.69	{ 193.75
500.00	{ 45 45 45	{ 7,690.9 7,688.5 7,691.9	{ 247.04 246.92 247.09	{ 247.02
557.50	{ 45 50 45	{ 8,676.0 8,669.5 8,669.8	{ 278.78 278.46 278.48	{ 278.57
600.00	{ 45 45	{ 9,412.9 9,410.4	{ 302.57 302.44	{ 302.50
700.0	{ 45 45 45 45	{ 11,256.2 11,251.5 11,257.3 11,250.4	{ 361.81 361.57 361.87 361.52	{ 361.70
800.0	{ 45 45	{ 13,139.1 13,137.8	{ 422.20 422.14	{ 422.17
900.0	{ 45 45 60 45	{ 15,070.6 15,064.8 15,063.1 15,069.2	{ 484.42 484.13 484.04 484.36	{ 484.24
200.00	{ 45 45	{ 2,892.1 2,890.6	{ 92.88 92.80	{ 92.84
500	180	(^b)	-----	-----
200.00	45	2,890.1	92.78	92.78

^a Prior treatment: Annealed by heating at 1,120° C (2,050° F) for 7½ min and cooling in air, and then by heating at 1,010° C (1,850° F) for 20 min. In the latter case the method of cooling is not known.

^b No runs.

TABLE 6. Variation of the relative enthalpy of alloy 2 with heat treatment and hardness

Specimen	Prior treatment	Resulting hardness		Mean relative enthalpy, $H_t - H_{0^\circ\text{C}}$ ^a	
		Rockwell scales	Vickers scale (approx.)	<i>t</i> =600° C	<i>t</i> =900° C
A	{ Hot-rolled, then machined to rod (diam, 0.5 in.).	31(Rc)	309	{ <i>abs j g⁻¹</i> 301.35 ±0.02(3) 301.07 ±0.00(2)	{ <i>abs j g⁻¹</i> 483.37 ±0.06(5)
B	{ Annealed at 1,000° C (1,830° F) for 1 hr and air-cooled. Then cold-rolled from 0.5- to 0.03-in. thickness in 3 steps, each followed by annealing at same temperature.				
C	{ Annealed at 1,120° C (2,050° F) for 7½ min, then at 1,010° C (1,850° F) for 20 min. Cooled in quiescent air.	80(15T)	106	302.05 ±0.02(3)	483.35 ±0.02(3)

^a The number of individual measurements is given in parentheses, and the stated tolerance is the probable error of the mean. The second value at 600° C for each of specimens A and B was determined after the measurements on the specimen at 900° C. The results for specimen C have been repeated from table 4 for comparison.

5. Smoothed Values of Enthalpy and Heat Capacity

The mean observed values of relative enthalpy in the last columns of tables 3, 4, and 5 were smoothed by fitting to them empirical functions of temperature whose coefficients were determined by the method of least squares. The temperature derivatives of such functions give reliable smooth values of the instantaneous heat capacity in those temperature regions where there is evidence that inadequately represented irregularities, such as those often caused by transitions, do not occur.

The relative enthalpies of the three alloys per unit mass are obviously so nearly the same at the same temperature that a single equation to represent all three would be of some practical value. The best quadratic function of temperature giving in absolute joules per gram the enthalpy at t° relative to 0° C was found to be

$$H_t - H_{0^\circ\text{C}} = 0.43954t + 1.0832(10^{-4})t^2. \quad (1)$$

The corresponding heat capacity is

$$C_p = 0.4395 + 2.166(10^{-4})t. \quad (2)$$

The average deviation between the mean observed enthalpy for the three alloys and that calculated from eq (1) (without regard to sign) is 0.2 percent, and the maximum deviation is 0.8 percent. By dividing the difference between the mean observed enthalpies at two adjacent temperatures by the temperature difference, an "observed" value of heat capacity at the mean temperature is obtained for each alloy. These observed values are compared with eq (2) in figure 1.³ The average deviation between mean and observed heat capacities is 0.75 percent, and the maximum deviation is 2 percent.

Equations (1) and (2) do not represent the data within their precision. In fact, it is evident from figure 1 that there are small but definite trends with temperature. A more refined representation of the

enthalpy of each alloy was obtained by dividing the whole temperature range investigated into three contiguous intervals and then fitting the mean observed values in each interval to an empirical equation of suitable form. In the case of each alloy the two equations for each pair of adjacent temperature intervals were required to give the same value of enthalpy at the temperature common to the two intervals.⁴

The resulting equations, which give the enthalpy of the alloy relative to 0° C in absolute joules per gram at t° C, are as follows:

Alloy 1 (0.02% carbon)—

$$H_t - H_{0^\circ\text{C}} = 0.49022t + 6.145(10^{-5})t^2 - 31.92 \log_{10} [(t+273.16)/273.16], \quad (3)$$

$$H_t - H_{0^\circ\text{C}} = -27.64 + 0.54737t, \quad (4)$$

$$H_t - H_{0^\circ\text{C}} = -12.65 + 0.47160t + 8.768(10^{-5})t^2. \quad (5)$$

Alloy 2 (0.07% carbon)—

$$H_t - H_{0^\circ\text{C}} = 0.48367t + 7.279(10^{-5})t^2 - 29.89 \log_{10} [(t+273.16)/273.16], \quad (6)$$

$$H_t - H_{0^\circ\text{C}} = -24.63 + 0.54231t, \quad (7)$$

$$H_t - H_{0^\circ\text{C}} = -9.55 + 0.46256t + 9.455(10^{-5})t^2. \quad (8)$$

Alloy 3 (0.11% carbon)—

$$H_t - H_{0^\circ\text{C}} = 0.47887t + 7.584(10^{-5})t^2 - 25.21 \log_{10} [(t+273.16)/273.16], \quad (9)$$

$$H_t - H_{0^\circ\text{C}} = 10.76 + 0.40369t + 1.3759(10^{-4})t^2, \quad (10)$$

$$H_t - H_{0^\circ\text{C}} = -22.06 + 0.49782t + 7.190(10^{-5})t^2. \quad (11)$$

The differences between the values of relative enthalpy given by the preceding equations and the corresponding mean observed values on which the equations are based are listed in table 7. No comparison is included based on eq (4), (7), and (10), as the agreement is automatically perfect in these short intermediate ranges of temperature because of the lack of data at additional temperatures in these ranges. Only the nonparenthesized entries in the table are significant with regard to the actually observed behavior of the alloys, as the parenthesized differences in a given column are based on extrapolated values of enthalpy calculated from the equation outside its temperature range of applicability.

Differentiation of eq (3) to (11) with respect to temperature gives the corresponding equations for instantaneous heat capacity, C_p . In the temperature ranges of their applicability the resulting equations provide the smoothed values of heat capacity given for round temperatures in table 9. A comparison between these equations and the corresponding mean "observed" heat capacities of the three alloys is afforded by figures 2, 3, and 4. It will be noted that these graphs do not include curves corresponding to eq (4), (7), and (10). These three equations give the best smoothed representation of the heat capaci-

³ Two sets of the points in figure 1 have been displaced by small amounts in a direction parallel to the graph line to avoid confusion from overlapping.

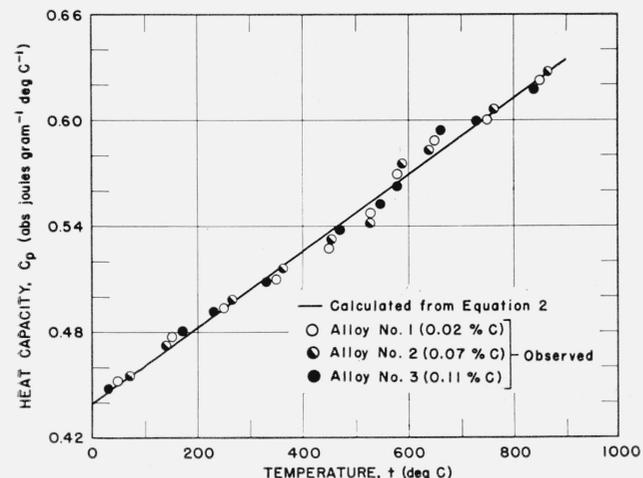


FIGURE 1. Heat capacity of the three alloys as represented by a single equation.

⁴ None of the values of table 4 following the first two runs at 557.50° C was used in the derivation of the equations.

TABLE 7. Differences between mean observed and calculated relative enthalpy of the three alloys

Temperature, <i>t</i>	Mean observed minus calculated enthalpy $H_t - H_0^\circ \text{ C}$					
	Alloy 1 (0.02% C)		Alloy 2 (0.07% C)		Alloy 3 (0.11% C)	
	Eq (3)	Eq (5)	Eq (6)	Eq (8)	Eq (9)	Eq (11)
$^\circ \text{ C}$	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>	<i>abs j g⁻¹</i>
0	0.00	(+12.65)	0.00	(+9.55)	0.00	(+22.05)
100	-.09	(+9.83)	-.01	(+7.38)	-.04	(+16.74)
200	+.11	(+7.81)	+.01	(+5.79)	+.04	(+12.46)
300	+.01	(+5.61)	.00	(+4.31)	+.02	(+8.63)
400	-.08	(+3.31)	-.01	(+2.80)	-.05	(+5.18)
500	+.04	(+1.01)	+.01	(+1.17)	+.02	(+2.19)
557.5	(+.59)	+0.04	(-.14)	-0.02	(+.22)	(+0.76)
600	(+1.62)	-.12	(+.73)	+.03	(+.61)	-.02
700	(+4.95)	+.16	(+2.84)	+.02	(+3.24)	+.05
800	(+8.09)	-.13	(+5.21)	-.04	(+5.52)	-.05
900	(+12.09)	+.04	(+8.00)	+.02	(+7.79)	+.02

TABLE 8. Smoothed values of heat capacity of the three alloys

Temperature	Heat capacity (C_p) of alloy—		
	No. 1 (0.02% C)	No. 2 (0.07% C)	No. 3 (0.11% C)
$^\circ \text{ C}$	<i>abs j g⁻¹ deg C⁻¹</i>	<i>abs j g⁻¹ deg C⁻¹</i>	<i>abs j g⁻¹ deg C⁻¹</i>
0	0.4395	0.4362	0.4388
50	.4534	.4508	.4526
100	.4654	.4635	.4648
150	.4758	.4748	.4758
200	.4855	.4854	.4861
250	.4944	.4953	.4959
300	.5029	.5048	.5053
350	.5110	.5139	.5144
400	.5188	.5226	.5233
450	.5263	.5313	.5321
500	^a .5337	^b .5397	^c .5405
550	.547	.542	.555
600	.5768	.5761	^d .5841
650	.5856	.5855	.5913
700	.5944	.5950	.5985
750	.6032	.6044	.6056
800	.6119	.6139	.6128
850	.6207	.6233	.6200
900	.6295	.6328	.6272

^a Calculated from eq (3). ^b Calculated from eq (6).
^c Calculated from eq (9). ^d Calculated from eq (11).

ties afforded by the data in the short transition range 500° to 557.5° or 500° to 600° C. The heat capacities change rather rapidly with temperature in this region, and data were not obtained at a sufficient number of temperatures to establish the heat capacity in this temperature range with high accuracy. However, the temperature interval is small, so that the resulting percentage uncertainty in the enthalpy change of the alloy is small for a large temperature interval and is negligible when the interval includes the entire region of anomaly.

6. Discussion

The heat capacities of the simplest crystalline materials are usually found to have reproducible values that increase in a regular manner with temperature. The alloys of the present investigation depart from this uncomplicated type of behavior in two apparently distinct respects. In the first place, as the temperature increases and passes through the region between approximately 500° and 600° C, the heat capacity rapidly increases to a magnitude between 3 and 5 percent greater than that which would be

obtained by extrapolation from lower temperatures, and this change apparently takes place rapidly during either heating or cooling. Such an abnormally rapid rise of heat capacity with temperature was found to occur in the case of all three alloys investigated, the average temperature of rapid rise increasing slightly from alloy 1 to alloy 3. In the second place, much smaller and much slower changes in enthalpy (or mean heat capacity) appear to have occurred following changes in thermal history in the case of one of the alloys (No. 2).

The first anomaly is shown in a simple way by the heat-capacity-temperature graphs of the three alloys in figures 2, 3, and 4. Each continuous curve represents a single empirical equation, but only the solid portion of the curve fits the observed data, the dashed portion constituting an extrapolation where the deviations are large. When each of the alloys passes through the temperature region of anomaly its heat capacity rather abruptly shifts onto the other curve, suggesting that in the process the alloy undergoes some type of transition accompanied by a change in its physical properties. Anomalies in the linear thermal expansion, the electrical resistivity, and the ultimate and yield strengths of the same alloys have been found to occur in approximately the same regions of temperature as the heat capacity [2, 6].

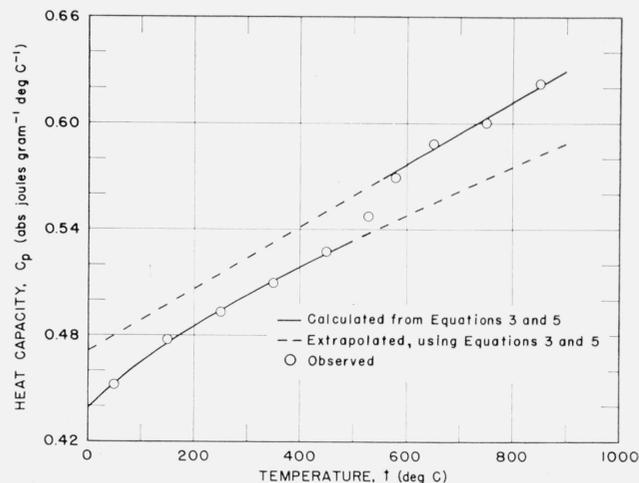


FIGURE 2. Heat capacity of alloy 1 (0.02% carbon).

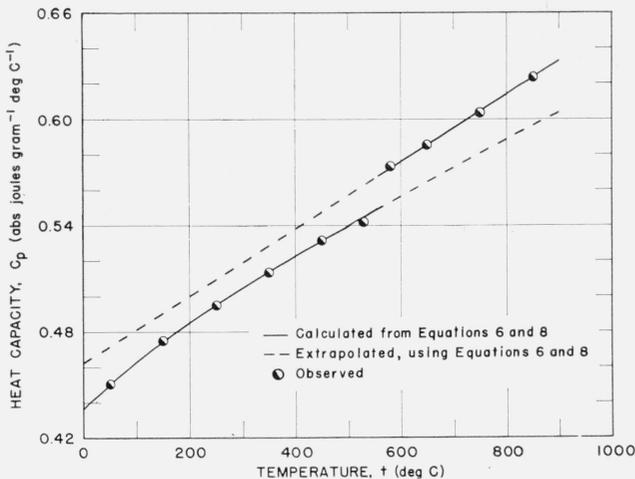


FIGURE 3. Heat capacity of alloy 2 (0.07% carbon).

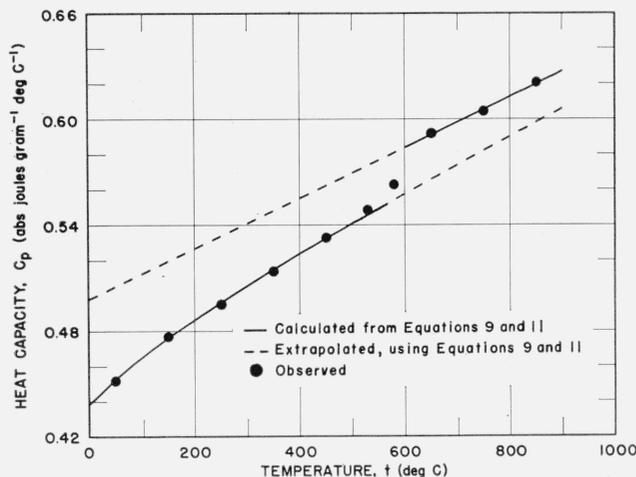


FIGURE 4. Heat capacity of alloy 3 (0.11% carbon).

The present enthalpy measurements provide an upper limit to the time required for this transition to occur in these alloys. Some experimental estimates of cooling rates in the calorimeter indicate that when the samples had been initially brought to temperatures above the anomalous region, they cooled from 600° to 500° C in less than half a minute, a rate that is thus fairly rapid, but would in general be comparable to the rate of quenching only in the case of much more massive samples. The total heat thus evolved by the sample as it cooled to 0° C is given by eq (5), (8), or (11), which corresponds in part to the area under a combination of the low- and high-temperature *solid* curves of figure 2, 3, or 4, respectively.

In this process of cooling one of the alloys from a high temperature, the heat-capacity curve in the temperature region of anomaly which will complete the accounting for the total observed enthalpy change is not uniquely defined by the data but may be reasonably assumed to join smoothly the low- and high-temperature solid curves. The observed enthalpy changes prove that this short intermediate part of the curve possesses no hump except possibly a small one. In fact, it may be that no hump at

all exists, a situation approximating a zero heat of (first-order) transition. This situation is rather unusual, but has been reported in the cases of the similar alloy 80 Ni-20 Cr [5] and cobalt metal [7]. The sample of the former that was investigated had a composition analogous to that of the present alloys (77% Ni, 20% Cr, 0.4% Fe, 0.6% Mn, 1.4% Si, 0.04% C), and was found to have a very similar shift in its heat capacity-temperature curve.

Probably the most significant fact about the apparent *slow* changes of relative enthalpy observed with alloy No. 2 is their smallness. Strictly speaking, these small changes should be attributed not to the alloy specimen alone but to a combination of this alloy and the alloy 80 Ni-20 Cr constituting the container. All the heat measurements on the alloy specimen were carried out in this container, and the effect of prolonged times at elevated temperatures on the enthalpy of the empty container was not determined. For this reason there is no proof that the observed trends with time are not due, at least in part, to the container itself. However, as pointed out above, the chemical compositions of the two alloys involved are analogous. Hence if small changes were not actually exhibited by the alloy specimen, they must have been by a similar alloy.

The variation of the relative enthalpy of alloy 2 with hardness is shown in table 6. The first values at 600° C for the three specimens, determined immediately after the respective treatments indicated, show an increasing enthalpy with decreasing hardness, the total change of enthalpy amounting to 0.2 percent and lying well outside the limits of precision of the measurements. The subsequently determined enthalpies at 900° C show no systematic variation with hardness, but in the case of specimens A and B the enthalpy was then remeasured at 600° C and found somewhat lower than before. It will be noted from table 4 that holding specimen C for several hours at 557.5° C resulted in a decrease of relative enthalpy of 0.1 percent at this temperature, but that the original higher value (at 557.5° C) was restored after renewed exposure of the specimen to 900° C. The causes of these small systematic variations in enthalpy were not determined.

7. References

- [1] Metals Handbook, p. 1261, Am. Soc. Metals (Cleveland Ohio, 1948).
- [2] W. J. O'Sullivan, Jr., Some thermal and mechanical properties of Inconel to high temperatures for use in aerodynamic heating research, Am. Soc. Testing Materials, Proc., **55**, 757 (1955).
- [3] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Research NBS **57**, 67 (1956) RP2694.
- [4] D. C. Ginnings and R. J. Corruccini, J. Research NBS **38**, 593 (1947) RP1797.
- [5] T. B. Douglas and J. L. Dever, Enthalpy and specific heat of four corrosion-resistant alloys at high temperatures, J. Research NBS **54**, 15 (1955) RP2560.
- [6] P. Hidnert, Thermal expansion of some nickel alloys, J. Research NBS **58**, 89 (1957) RP2737.
- [7] K. K. Kelley, Contributions to the data on theoretical metallurgy. X. High-temperature heat-content, heat-capacity, and entropy data for inorganic compounds, U. S. Bureau of Mines Bull. **476**, 59 (1949).

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