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Enthalpy and Specific Heat of Nine Corrosion-Resistant Alloys at High Temperatures [1]

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Specific heats from 0 to 900 °C that are believed to be accurate in general to within ±0.3 percent are reported for two alloys: 90 Ni–10 Cr and stainless steel, type 316. These values were calculated from enthalpies measured with a drop method and a precision Bunsen ice calorimeter. For reference and comparison, high temperature specific heats of seven other base-metal alloys, determined similarly at the Bureau and previously published, also are tabulated. These seven alloys are 80 Ni–20 Cr, 76 Ni–15Cr–9 Fe (three slightly different samples), stainless steel, types 347 and 446, and Monel (67% Ni, 30% Cu).

1. Introduction

Certain base-metal alloys which are relatively resistant to corrosion find practical applications at elevated temperatures, where a knowledge of their specific heats and other physical properties is often needed. For many of these, specific heats only at or near room temperature have been reported. During the past few years the specific heats of nine such alloys have been measured accurately (from 0 to 900 °C in all but one case) at the National Bureau of Standards. The values for seven of these alloys and complete details have been published previously [1, 2] [2], but for ready reference and comparison are tabulated here alongside the newly reported values for the other two alloys. Several of these alloys are so similar in chemical composition that the comparison of their specific heats may afford some assistance when it is desirable to estimate values for analogous compositions. It should be pointed out, however, that the specific heats of many alloys depend appreciably on their previous histories, and in many cases small changes in composition introduce into the specific-heat—temperature curve large anomalies attributable to the appearance of phase changes.

2. Alloys Recently Measured

Enthalpy measurements were made on three samples (A, B, C) of the alloy 90 Ni–10 Cr (commercially designated as Chromel P) and on one sample of stainless steel type 316 (Am. Iron & Steel Inst. designation). Table 1 gives the compositions of these alloys as determined by their analyses at the Bureau,[3] and also affords a comparison with the ranges of composition associated with the nominal designations "Ch P" [3] and "SS 316" [4]. No attempt was made to correct the measured enthalpies to the basis of a different composition.

The enthalpy measurements on 90 Ni–10 Cr were made on rolled strips. As indicated in section 4, a few of these measurements were on specimens that had been previously annealed by heating to approximately 1,100 °C for about 5 minutes [5].

[1] The measurements on 90 Ni-10 Cr were supported by the Diamond Ordnance Fuze Laboratory, Department of the Army, Washington, D.C. Those on stainless steel type 316 were supported by the Wright Air Development Center, Department of the Air Force, Wright-Patterson Air Force Base, Ohio.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The samples of 90 Ni-10 Cr were analyzed by chemical methods. The analysis of the stainless steel type 316 was determined spectrochemically, and is to be considered approximate only, since suitable spectrochemical standard samples were not available. However, the enthalpy and specific heat of the latter alloy are insensitive to errors in composition, since the heat capacities per unit mass of the three principal elements (iron, chromium, and nickel) are approximately the same.

TABLE 1. *Chemical compositions of the alloys thermally measured and of the corresponding nominal alloys*

Alloy designation	Sample	Chemical composition (weight percent)											
		Ni	Cr	Fe	Si	Zr	Co	Cu	Mn	Nb	Mo	C	Total
Ch P	Measured (A)	89.1	9.6	0.63	0.42	0.12	0.08	0.01	0.01	------	------	------	100.0
	----do----(B)	89.3	9.3	.34	.44	.11	.03	.01	.02	0.26	------	------	99.8
	----do----(C)	89.4	9.3	.35	.46	.11	.03	.01	.02	.26	------	------	99.9
	Nominal	90	10	------	------	------	------	------	------	------	------	------	100
SS 316	Measured	12.6	17.0	([a])	.4	([a])	([a])	([a])	1.4	([a])	2.0	([a])	------
	Nominal	10–14	16–18	------	[b] 1.0	------	------	------	[b] 2.0	------	2–3	[b] 1.0	------

[a] Not determined.
[b] Maximum.

All the enthalpy measurements on stainless steel type 316 were made on the sample (sawed from a large ingot) in the condition in which it was received, without further heat or mechanical treatment. The thermal history of the sample is unknown, but supposedly it had been annealed by heating in a salt bath and quenching, which is the standard procedure for austenitic stainless steels [4].

3. Calorimetric Procedure

The apparatus and method used in measuring the enthalpy were described in detail in a recent paper [6]. 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, the sample had time to reach the furnace temperature within 0.01 deg C. The sample and container were 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 outside the calorimeter during the drop.

The furnace temperature, which was held constant to ±0.01 deg C during a heat measurement, was measured up to 600 °C by a strain-free platinum resistance thermometer and above 600 °C by a platinum—platinum-10-percent rhodium thermocouple. Both instruments were actually read up to 600 °C in order to be able to detect any unusual departure of either from its calibration. The thermocouple had been calibrated on the International Temperature Scale of 1948. The calibration factor of the ice calorimeter was taken to be 64.646 defined thermochemical calories [4] per gram of mercury, which is based on hundreds of electrical determinations made earlier at the Bureau [6].

4. Enthalpy and Specific Heat of 90 Ni-10 Cr

The mean observed values of enthalpy relative to 0 °C are shown for the four samples in columns 2 to 5 of table 2. For each case where more than one run was made on the sample at a given furnace temperature, the standard deviation of the mean is stated as a tolerance, and takes into account not only the precision of the runs with sample but also that of the runs on the empty container at the same temperature. (No runs were actually made on the empty container at 350 and 650 °C, but the enthalpy values used at these temperatures were obtained from smooth deviation plots of the runs at the other temperatures.) The few values in columns 3 to 5, which were run to compare several similar samples, differ by 0.15 percent or less from the values in column 2 (amounts within the accuracy of the measurements), and will not be further considered.

The values in table 2, column 2, show smoothly varying differences up to and including 600 °C, but in comparison an anomalous rate of increase with temperature between 600 and 700 °C. Three empirical equations were derived to fit the enthalpy in the respective temperature ranges 0 to 600°, 600 to 700°, and 700 to 900 °C, and their deviations from the mean observed values are given in the last column of table 2. The coefficients of the enthalpy equation for 0 to 600 °C were derived by the method of least squares; those for the equation from 700 to

[4] The "defined" thermochemical calorie (=4.1840 absolute joules) is the unit of heat used throughout this paper.

TABLE 2. *Relative enthalpy of 90 Ni-10 Cr*

Furnace tempera-ture t	Mean observed enthalpy, $H_t - H_{0\,°C}$ [a]				Mean observed (col 2) minus smoothed enthalpy
	Sample A unannealed	Sample A annealed	Sample B unannealed	Sample C annealed	
°C	cal g⁻¹	cal g⁻¹	cal g⁻¹	cal g⁻¹	cal g⁻¹
100. 00	10. 75±0. 005	-----------	-----------	-----------	0. 00
200. 00	22. 08±0. 020	-----------	-----------	-----------	−. 01
300. 00	33. 91±0. 010	-----------	-----------	-----------	−. 01
350. 00	40. 01±0. 005	-----------	-----------	-----------	+. 01
400. 00	46. 20±0. 025	-----------	-----------	-----------	+. 01
500. 00	58. 87±0. 005	58. 87±0. 005	58. 82±0. 015	58. 90±0. 065	. 00
600. 00	71. 93±0. 010	-----------	-----------	-----------	−. 01
650. 0	78. 78±0. 030 [b]	-----------	-----------	-----------	−. 03
700. 0	85. 81±0. 020 [b,c]	85. 86 [d]	85. 68±0. 045	85. 75 [d]	. 00
800. 0	99. 84±0. 025	-----------	-----------	-----------	. 00
900. 0	114. 28±0. 010	-----------	-----------	-----------	. 00

[a] Each value represents the mean of two runs on the sample except where otherwise indicated.
[b] The mean of three runs on the sample at this temperature.
[c] A fourth run on the sample, discarded because of very inferior precision, is not included in the tabulated mean or its stated tolerance.
[d] Only one run was made on the sample at this temperature.

900 °C were obtained by direct substitution of the experimental points. The equation for 600 to 700 °C was then derived by requiring continuity of enthalpy and specific heat at 600 and 700 °C with the equations representing the other two temperature regions. The enthalpy and corresponding specific-heat equations (in terms of calories per gram and at t °C) are:

0 to *600 °C:*

$$H_t - H_{0\,°C} = 0.11680t + 1.652\,(10^{-5})t^2 - 8.11\,\log_{10}[(t+273.15)/273.15] \quad (1)$$

$$C_p = 0.11680 + 3.304\,(10^{-5})t - 3.52/(t+273.15) \quad (2)$$

600° to *700 °C:*

$$H_t - H_{0\,°C} = 182.977 - 0.74319t + 1.3310\,(10^{-3})t^2 - 6.680\,(10^{-7})t^3 \quad (3)$$

$$C_p = -0.74319 + 2.6620\,(10^{-3})t - 2.0040\,(10^{-6})t^2 \quad (4)$$

700 to *900 °C:*

$$H_t - H_{0\,°C} = -0.92 + 0.10955t + 2.050\,(10^{-5})t^2 \quad (5)$$

$$C_p = 0.10955 + 4.100\,(10^{-5})t. \quad (6)$$

The specific heats represented by eqs (2), (4), and (6) are shown by the solid curve in figure 1, and the "observed" points were computed from successive differences in table 2, column 2, with application of corrections for curvature derived from eqs (2) and (4). Though it is obvious that there is a local maximum between 600 and 750 °C, the enthalpy was measured at too few temperatures to define accurately the course of the specific-heat curve in this temperature region; the particular curve formulated is, however, consistent with all the enthalpy data obtained. The Curie temperature of this alloy lies below the range of measurement [8]. However, similar "anomalous" increases in heat capacity in the temperature range 500 to 800° C have been observed in many nickel-rich alloys containing chromium [1,2,7]. The effect is paralleled by irregularities in other physical properties of the same alloys, and has been attributed by some authors to the disordering of a lattice of short-range order in the neighborhood of the composition Ni_3Cr [8].

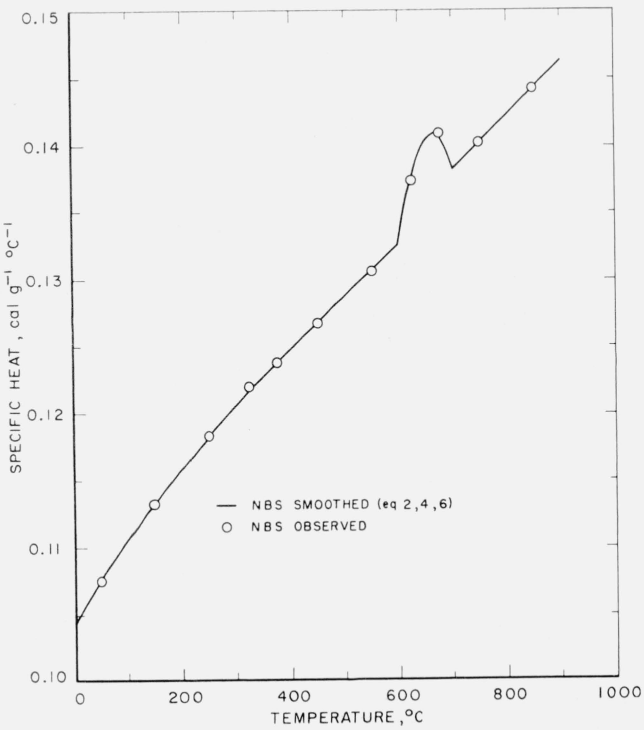

FIGURE 1. *Specific heat of 90Ni-10Cr.*

The precision of the enthalpy measurements on 90 Ni-10 Cr and their deviations from the empirical equations used to represent them are indicated in table 2. Considering also the known sources of possible systematic and instrumental errors, the authors believe that eq (2) represents the true specific heat between 100 and 600 °C within ±0.3 percent. Between 600 and 700 °C the uncertainty is much greater, for the reasons indicated above. Above 700 °C the uncertainty should be comparable to that below 600 °C.

5. Enthalpy and Specific Heat of Stainless Steel Type 316

The mean observed values of enthalpy relative to 0 °C are given in the second column of table 3. Each stated tolerance represents the standard deviation of the mean, and reflects the contribution from the lack of perfect agreement for both the empty container and the container with sample. The "smoothed" enthalpy referred to in the last column of the table is that given by an empirical equation whose coefficients were derived from the values in the second column by the method of least squares.

TABLE 3. *Relative enthalpy of stainless steel type 316*

Furnace temperature t	Mean observed enthalpy, $H_t - H_{0°C}$ [a]	Mean observed minus smoothed enthalpy
°C	*cal g^{-1}*	*cal g^{-1}*
100. 00	11. 43±0. 015	+0. 03
200. 00	23. 46±0. 010	−. 01
300. 00	36. 10±0. 020	+. 04
400. 00	49. 07±0. 015	−. 03
500. 00	62. 51±0. 010	−. 03
600. 00	76. 32±0. 015	−. 06
700. 0	90. 62±0. 020	+. 05
800. 0	105. 21±0. 045	+. 08
900. 0	119. 96±0. 025	−. 06

[a] Each value represents the mean of two runs.

This equation and the corresponding specific-heat equation (in terms of calories per gram and at t °C), applicable over the whole range 0 to 900 °C, are:

$$H_t - H_{0\,^\circ\mathrm{C}} = 0.12754t + 1.512\ (10^{-5})t^2 - 11.08\ \log_{10}\left[(t+273.15)/273.15\right] \qquad (7)$$

$$C_p = 0.12754 + 3.024\ (10^{-5})t - 4.81/(t+273.15). \qquad (8)$$

Considering both random errors and known sources of possible systematic errors, the authors believe that eq (8) represents the true specific heat between 100 and 800 °C within ±0.3 percent.

The three curves of figure 2 represent the smoothed values of the specific heat of stainless steel type 316

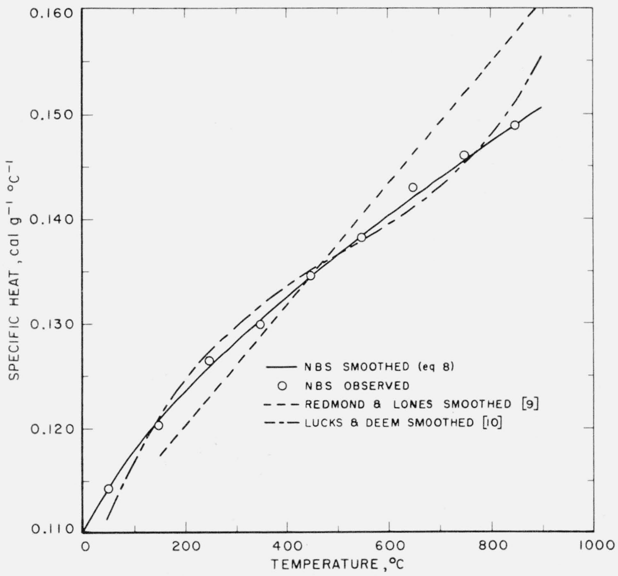

FIGURE 2. *Specific heat of stainless steel type 316.*

as given by the present work, by Redmond and Lones [9], and by Lucks and Deem [10]. Compared with the authors' curve (labeled "NBS"), that of Redmond and Lones agrees within their stated uncertainty of ±5 percent, and that of Lucks and Deem agrees in general to better than ±1 percent.

Because Lucks and Deem gave no unsmoothed values, estimates of accuracy, or sample analyses, there is no sound basis for making a truly objective comparison with the NBS curve. However, it seems likely that a major cause of the small differences may be their use of a positive-power series (of the form $C_p = A + Bt + Ct^2 + Dt^3$) to represent their smoothed values. As a general rule, if this form of equation does not indicate, in the temperature range of measurement, a radical change of slope for which there is no experimental evidence, it very often does so when extrapolated to higher temperatures. Knowing that extrapolation of empirical equations is widely indulged in by their users, and not without some practical justification, the present authors prefer forms of equation (such as eqs (6) and (8)) which give extrapolated curves similar in shape to the majority of known cases.

6. Compilation of the Specific Heats of Nine Alloys as Determined at the National Bureau of Standards

The purpose of this section is indicated in the introduction (section 1), where the original references to the seven alloys not discussed in this paper are cited. The chemical compositions as determined by chemical analysis are given in table 4, and the smoothed values of specific heat are given in table 5.

The authors thank several members of NBS who aided the present investigation: the samples of 90 Ni–10 Cr were chemically analyzed by R. K. Bell and E. E. Maczkowske, while the sample of stainless steel type 316 was furnished by L. L. Wyman and spectrochemically analyzed by R. E. Michaelis.

TABLE 4. *Chemical compositions of nine alloys (in % by weight)*

Element \ Alloy	Stainless steel			90Ni–10Cr	80 Ni–20 Cr	76Ni–15Cr–9Fe [b]			Monel
	316	347	446	Sample A		Sample 1	Sample 2	Sample 3	
	%	%	%	%	%	%	%	%	%
Fe	(a)	(a)	(a)	0.63	0.45	8.87	7.89	8.17	1.6
Ni	12.6	11.1	0.32	89.1	77.4	75.99	76.45	75.64	66.9
Cr	17.0	18.3	25.58	9.6	19.5	14.42	14.96	15.32	-----
Cu	-----	-----	-----	0.01	-----	0.22	0.15	0.19	29.8
Mn	1.4	1.30	0.42	.01	0.59	.28	.26	.33	1.0
Nb	-----	0.86	-----	-----	-----	-----	-----	-----	-----
Si	0.4	.52	.68	.42	1.4	.17	.19	.21	0.07
C	(a)	.08	.23	(a)	0.04	.02	.07	.11	.15
S	-----	-----	.016	-----	-----	.007	.007	.007	-----
P	-----	-----	.019	-----	-----	-----	-----	-----	-----
Zr	-----	-----	-----	.12	-----	-----	-----	-----	-----
Mo	2.0	-----	-----	-----	-----	-----	-----	-----	-----
Co	-----	-----	-----	.08	-----	-----	-----	-----	-----
Total accounted for, %	-----	-----	-----	100.0	99.4	99.98	99.98	99.98	99.5

[a] Not determined. [b] Alloys commercially produced as Inconel.

TABLE 5. *Specific heats of nine alloys (in cal g^{-1} deg C^{-1})*[a]

Temperature (°C) \ Alloy	Stainless steel 316	Stainless steel 347	Stainless steel 446	90Ni–10Cr Sample A	80Ni–20 Cr	76Ni–15Cr–9Fe[b] Sample 1	76Ni–15Cr–9Fe[b] Sample 2	76Ni–15Cr–9Fe[b] Sample 3	Monel
0	0.110	0.110	0.108	0.104	0.103	0.105	0.104	0.105	0.101
25	.1122	.112	.110	.1058	.105	.1068	.1061	.1066	.102
50	.1142	.114	.113	.1076	.107	.1084	.1077	.1082	.103
100	.1177	.118	.118	.1107	.111	.1112	.1108	.1111	.105
200	.1234	.123	.129	.1160	.117	.1160	.1160	.1162	.110
300	.1282	.128	.140	.1206	.122	.1202	.1207	.1208	.114
400	.1325	.133	.151	.1248	.126	.1240	.1249	.1251	----------
500	.1364	.137	.163	.1288	.131	.1276	.1290	.1292	----------
600	.1402	.141	.21	.1326	.14	.1379	.1377	.1396	----------
700	.1438	.145	.170	.138	.147	.1421	.1422	.1430	----------
800	.1472	.149	.163	.142	.152	.1462	.1467	.1465	----------
900	.151	.152	.162	.146	.156	.150	.151	.150	----------

[a] 1 cal=4.1840 abs joules. See table 4 for chemical compositions of the alloys.
[b] Alloys commercially produced as Inconel.

7. References

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