Continuous Calorimetry in the Iron-Carbon System to 1900 K

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Calorimetric measurements were carried out in the iron-carbon system between 1900 and 900 K, from zero to 0.20 atom fraction carbon, using an improved version of Oelsen's continuous quantitative thermal analysis. Where equilibrium conditions are approached, they confirm recent thermodynamic data. The 95 pct confidence limits of the results are ±2.7 pct of the measured values.

A knowledge of the amount of heat that must be removed from molten iron-carbon alloys during freezing and cooling is important to metallurgists concerned with solidification of iron and steel. At the time this research was begun, information was available on the enthalpies of iron and graphite, and heat of formation data were available for cementite and austenite, but were not reliable for the liquid.\(^1\) It was, therefore, not possible to calculate the enthalpy-temperature relationships for any iron-carbon alloy into the liquid. More recently, the data have been revised\(^2\) and augmented. There has been no systematic calorimetric study of the system to compare with calculations made from the thermodynamic data compilations. The present work supplies the information to do this.

It was decided to use Oelsen's\(^3,\)\(^4,\)\(^5\) method of continuous quantitative thermal analysis, which permits a complete enthalpy-temperature diagram to be obtained from the results of a single experiment. His practice was used by Wittmoser\(^6\) and Genot\(^7\) to study foundry-type iron-carbon alloys containing the usual amounts of manganese and silicon. Their equipment was not suited to high-temperature work; Genot reported four successful runs out of sixteen trials. Several improvements were made to increase the reliability of the apparatus by using a novel heat sink\(^8\) to replace the water bath used by earlier investigators, and a hoist which permits the crucible-thermocouple assembly to be lowered in three to five seconds from the heating furnace into the calorimeter. These changes increased the frequency of successes to 50 pct.

APPARATUS

The major parts of the apparatus, which stands about three meters high, are shown in Fig. 1. It comprises a furnace for heating the sample; a heat sink for measuring the heat released by it, and a thermocouple to measure its temperature during this time; a mechanism for moving the sample and its thermocouple rapidly from furnace to heat sink; an adiabatic shield; and an enclosure surrounding these so that inert atmosphere or vacuum can be maintained.

The heat sink uses the principle described by Yamaguchi.\(^9,\)\(^8\) It is composed of three fixed coils and two movable ones wound from 1.63 mm diameter enamelled copper wire fixed in place by epoxy, and weighing a total of about 25 kilograms. The coils enclose a cavity 180 mm diam by 200 mm high. They are connected electrically in series and form one leg of a Wheatstone bridge circuit, whose unbalance is recorded by the Y-function of a high-speed X-Y recorder.

The coil assembly is surrounded by a heat barrier wound with 0.9 mm Chromel heating wire. Power input to this is controlled by a ten-junction array of differential thermocouples, with alternate junctions cemented to the heat barrier and to the outside of the coils.

A radiation shield, not shown in Fig. 1, hangs in the coil cavity, separating the crucible from the coil interior. It is constructed of thin copper foil mounted on an iron wire frame, and serves to slow down heat transfer from sample to coil.

The samples are contained in 50 ml recrystallized alumina crucibles. A crucible is suspended from the sliding steel tube shown at the top of Fig. 1, using a molybdenum wire harness. A thermocouple, made of 0.5 mm diam. Pt 6 Rh-Pt 30 Rh wires, with the junction protected by a short alumina tube, travels up or down with the crucible and sample.

When the crucible and charge are at their upper position, they are centered in a section of 52 mm OD alumina tube that is surrounded by a graphite susceptor induction furnace. In its lower position, it is centered within the radiation shield inside the copper coil assembly.

EXPERIMENTAL PROCEDURE

The samples are prepared from 25 mm diam Armco iron bar stock (principal impurity 0.08 pct oxygen) and nuclear grade graphite. Aluminum (0.12 pct by weight of the iron) is added to deoxidize the melts in order to prevent a carbon boil. This increases the enthalpy of the resultant Fe-Al-Al,O\(_3\) mixture by about 24 calories per gram-atom Fe, or 0.2 pct over the 900 to 1900 K temperature range. Graphite chips, along with the aluminum addition, are placed in the bottom of a 50 ml recrystallized alumina crucible. On top is placed a slug of Armco iron, drilled to receive a 3 mm OD recrystallized alumina thermocouple tube, which is cemented to an alumina disc lid. The charge weighs about 180 gm, while the crucible, thermocouple tube, and lid weigh 40 to 60 gm.

The crucible with its charge and thermocouple is...
A typical XY recorder trace is shown in Fig. 2. The X-axis shows thermocouple output, while the Y-axis gives the unbalance of the Wheatstone bridge circuit, indicating the increase in coil resistance as it warms up on receiving heat from the sample. The calorimeter coil is in parallel with a resistance box, whose resistance RB is changed as required during the run. A timer provides half-minute markings. From the start of the experiment to 3.7 min., the sample is liquid. Freezing through the austenite plus liquid range occurs from 3.7 to 6.1 min. This is followed by eutectic freezing from 6.1 to 0.5 min. The eutectoid reaction is noted at 22.2 to 24.5 min.

**EVALUATION OF DATA**

In addition to the information shown on Fig. 2, the data include a chart of radiation shield temperature. Data points are picked off the XY chart at suitable intervals on the temperature axis. For each point the temperature is obtained from the thermocouple calibration. The coil resistance is calculated from the bridge unbalance and the circuit constants, including the bridge voltage P-3 and the RB setting. The total heat absorbed by the coil during an interval is computed from the coil calibration, which must be corrected for the change in heat content of the radiation shield, calculated from its temperature change. This gives the heat that left the sample plus crucible assembly; the heat in the alumina and molybdenum is then deducted to obtain that lost by the alloy. This corrected heat is divided by the number of gram-atoms of alloy in the charge. Dividing it by the temperature difference gives the apparent specific heat in the interval and summing the heat increments over all the intervals yields the total heat. A computer is programmed to carry out all these calculations.

**CALIBRATIONS AND CORRECTIONS**

In the following sections, the ± items are 95 pct confidence intervals based on dispersion of the data and sample size, using Student's t-function at the 0.05 level.

The relation between heat absorbed by the coil and its resistance change was determined by electrical calibration,

\[ H_2 - H_1 = (R_2 - R_1)[42030 + 717.5(R_2 + R_1)] = 270 \text{ cal} \]

This relation was the same whether electrical energy was introduced uniformly in the entire coil, or only in the inner half of the winding, confirming that the calibration is independent of temperature distribution.

The thermocouple was calibrated in the apparatus, using gold and palladium fixed points.

The estimate of crucible temperature was arrived at as follows: two runs with Armco iron and one with nickel were made, and the heat content of alumina and so forth, were obtained by deducting the heat content of the metal, after Hultgren,\textsuperscript{10} from the total heat given off by the crucible assembly. Knowing the weights of alumina and of molybdenum wire, an equivalent weight of alumina, equal to grams Al\(_2\)O\(_3\) + 0.26 x grams Mo, was calculated. Kelley's\textsuperscript{11} enthalpy data was then used...