The Density of Liquid Iron-Carbon Alloys

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The density of liquid Fe-C alloys at temperatures ranging from 1250 °C to 1550 °C was measured by the sessile drop profile method. An accurate method of digital image processing was developed to capture, enhance, and determine the coordinates of the X-ray shadow image of the droplet. Laplace's equation was then solved to obtain the volume and density of the droplet. The density of iron-carbon alloys was then determined as a function of carbon content (from 0 to 4 wt pct) and temperature (1250 °C to 1550 °C). A least-squares analysis of our data points gives an equation for the density of liquid iron-carbon alloys as a function of temperature T [K] and carbon content [pct C] [wt pct]:

$$\rho[\text{g/cm}^3] = (7.10 - 0.0732[\text{pct C}]) - (8.28 - 0.874[\text{pct C}]) \times 10^{-4}(T - 1823)$$

These results will give a value to within ±1.5 pct of the data of Lucas,[3] Widawski and Sauerwald,[2] and the present work.

I. INTRODUCTION

ACCURATE determination of densities in liquid iron-carbon alloys is essential to allow realistic calculations of gravitationally driven and interfacial phenomena; however, there is a large scatter in the reported density values of iron-carbon alloys at 1600 °C (Figure 1) which can lead to a significant error in any derived value. Thus, the densities of liquid iron-carbon alloys were redetermined using a sessile drop profile method to assess the reliability and accuracy of current literature values.

II. EXPERIMENTAL

An X-ray radiographic technique was used to image the droplet profile, and then the image was digitized by means of a sophisticated image analyzer developed by the authors.[7,8] The droplet volume was calculated from computer generated solutions of the Young-Laplace equation.

A. Experimental Method

Figure 2 shows a schematic for the experimental apparatus with the X-ray device. Details for the apparatus and procedure are described elsewhere.[7,8] The iron used in this study was 99.99 pct metallic purity iron (from Noah Technology, San Antonio, TX). Impurities in the iron are summarized in Table I. The Fe-C alloys were made of the iron metal and high-purity grade (99.95 pct) graphite powder (by Johnson Matthey, Ward Hill, MA). The mixture of iron and carbon was heated in the atmosphere-controlled induction furnace at around 1500 °C for 30 minutes and then quickly cooled by an ultrahigh-purity CO jet in the furnace. Each sample piece was prepared cutting 1 to 1.5 g from the mother alloy. The piece was polished with sandpaper, cleaned with acetone in an ultrasonic washer, and dried.

For each run, a sample crucible (McDanel 998 High-Purity Alumina, Conical, 22-mm top diameter × 33-mm height), which is also the pedestal material, was charged from the top of the furnace tube onto a shallow alumina crucible. An alumina powder layer is placed in the shallow crucible to prevent the sample crucible from cracking by thermal shock and to avoid contamination of the pedestal when the sample crucible breaks by accident. The atmosphere in the furnace was a reducing dehydrated gas mixture of ultrahigh-purity carbon monoxide (99.999 pct) and ultrahigh-purity argon (99.999 pct) (by Matheson Gas Products). The decrease in weight of sample during the experiment was found to be within 0.2 pct of the initial weight.

The experimental conditions are shown in Table II. Carbon content for each mother alloy was analyzed by a LECO* Carbon Analyzer. For each condition, at least

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*LECO is a trademark of LECO Corporation, St. Joseph, MI.

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four individual runs were accomplished. For each individual run, at least four X-ray pictures were taken every 20 minutes after confirming that the sample had melted. The equilibrium shape was quickly obtained after the sample melted. Each individual run was completed within 2 hours after melting. From each X-ray picture, two hard copies were processed independently through the image digitizing and analyzing process to ensure consistency.

The droplet and the crucible were carefully examined after the experiment. Keene[9] noted that measurements in the Fe-C system should be treated with caution as metal/substrate reactions occur which can lead to changes in the melt composition. For example, Nizhenko and Floka[10] observed that an Fe-C melt of eutectic composition, when held on an alumina support for 10 minutes at 1600 °C, acquired an alumina content of 0.14 wt pct, which rose to 0.33 wt pct after 4 hours. Bubbles were observed at the interface between the melt and the alumina. Kozakevich and Urbain[11] also observed reaction between high carbon alloys and alumina at 1550 °C and suggested that bubbles of CO were formed. These experiments were carried out in a carbon monoxide atmosphere rather than argon, and the crucible surface in our experiment was completely clean without any

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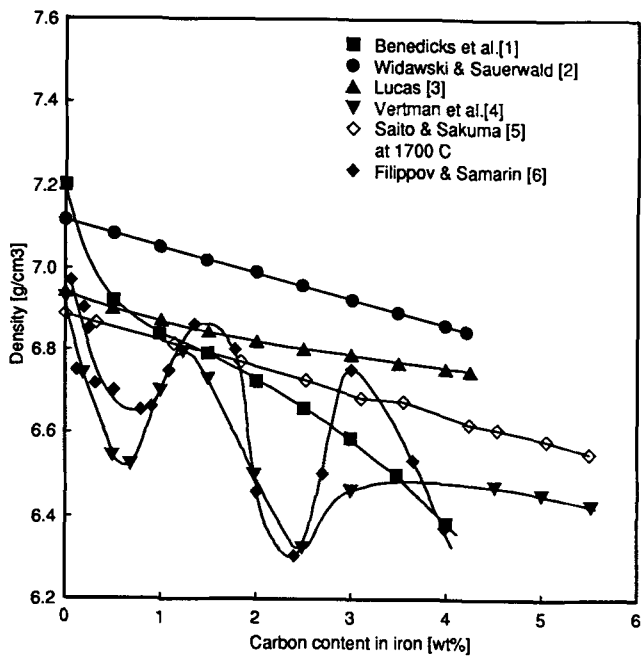Manuscript submitted March 19, 1992.

Fig. 1—Density of Fe-C alloys at 1600 °C.

Table I. Impurity Data for High-Purity Iron Used in the Experiment (Unit: Ppm)

Si	Mn	Cu	O	H	N	P	S
5	27	16	14	2	26	11	6

Table II. Experimental Conditions and Results

	Temperature (°C)	Carbon Content (Wt Pct)	Density (g/cm^3)
1	1550	0.00	7.124
2	1550	1.91	6.926
3	1450	1.91	6.982
4	1550	3.91	6.837
5	1450	3.91	6.893
6	1350	3.91	6.925
7	1250	3.91	7.005

discoloration or contamination. No trace of interaction between the alumina crucible and iron droplet or of bubble formation was observed during these experiments.

B. Calculation Method

The shape of a sessile drop or pendant drop can be calculated, and assuming that the droplet is symmetrical, its volume can also be calculated. Thus, from a knowledge of the droplet's weight, the density of the metal can be easily calculated.

A solution to the Young-Laplace equation for sessile droplets was first developed in 1883 by Bashforth and Adams,[12] who derived the theoretical form of a sessile or hanging drop and calculated tables of droplet contours. Based on these tables, a number of previous workers have used a simplified method to calculate droplet properties in which only the horizontal diameter of the drop and the distance from the equator of the drop to its
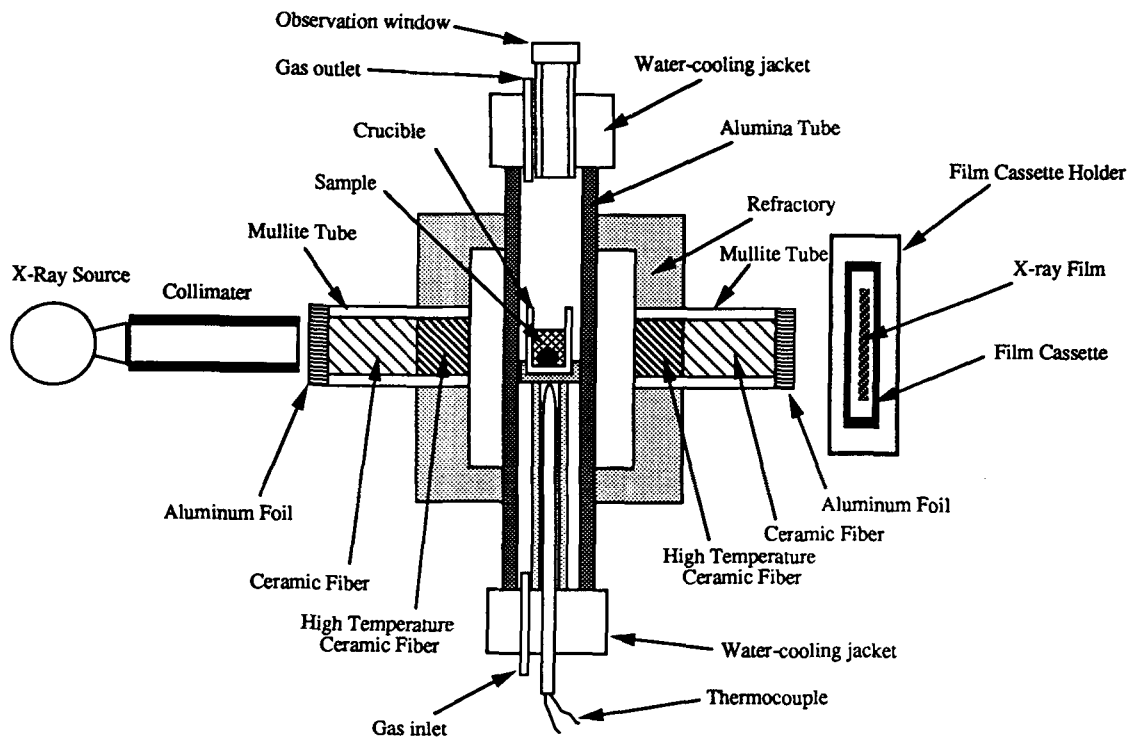

Fig. 2—A schematic diagram of the experimental apparatus with X-ray devices.

apex are measured in order to determine the droplet profile. This method suffers from difficulties in locating the equator accurately and is subjective due to difficulties in manual determination of the droplet circumference.

To avoid the errors which are caused by the above subjectivity and simplification, several workers[13,14,15] have developed a curve-fitting method, which can be used to generate solutions to the nonlinear differential equation which describes the theoretical curve and to adjust the parameters of the equation to provide the best fit to the experimental measurements. The advantages of this method are that measurements at a larger number of points along the drop contour are used to determine the value of the surface or interfacial tension and the value derived is less subjective as the errors involved in manual contour determination are minimized.

In the actual computer program, an objective function which expresses the error between the physically observed and a theoretical Laplacian curve is constructed. This objective function is minimized numerically using the method of incremental loading in conjunction with the Newton-Raphson method. A very useful explanation for this calculation scheme has been given by Roetenberg et al.[15]

C. Data Acquisition

The actual droplet size is 6 to 8 mm in equator diameter and 4 to 6 mm in height. Hard copies of the magnified image (times 20 to 25) are directly taken from the X-ray negative pictures using a Canon microfilm copier.

In recent years, a number of workers have developed techniques of digital image processing in order to measure the surface tension of organic materials using a pendant droplet technique at room temperature.[16,17] Due to the benefits of automated digital image processing, a similar type of system was developed to process the sessile drop X-ray pictures which were obtained under steelmaking temperatures and conditions.

In order to develop a quick image capturing system, the authors purchased a QuickCapture board from Data Translation, Inc. (Marlboro, MA), which enables a MACINTOSH* II to capture images from a TV camera

*MACINTOSH is a trademark of Apple Computers, Inc., Cupertino, CA.

or VCR in real time. The authors also acquired the image processing software *Image* from the National Institute of Health.

To digitize the shadow image, it is convenient to make a binary image (*i.e.*, where the X-ray shadow image is completely black and the surroundings are white). The computer can then recognize the circumference of the shadow image and automatically digitize the image by means of an image recognition program. The authors then developed a program which allowed the binary image to be recognized and the circumference of the image to be traced. The merit of this program is that image recognition and digitizing can be automatically accomplished using a MACINTOSH. Figure 3 shows a schematic of the process flow.

The error involved in all the steps of experimental procedures and the digitizing process lies within 1.8 pct of
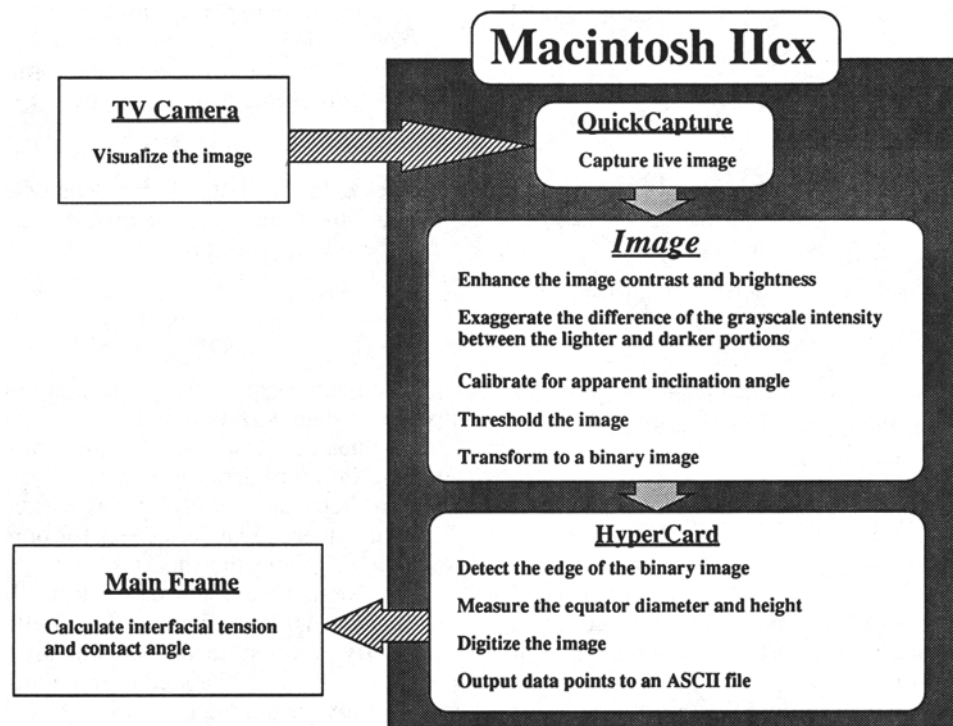

Fig. 3—A schematic diagram of the process flow for the image capture. (HYPERCARD is a trademark of Apple Computers, Inc., Cupertino, CA.)

Table III. Density of Liquid Iron at 1550 °C [g/cm³]

| References	Density	Measurement Method
Present work	7.124	sessile drop
Lucas[18]	7.02	maximum bubble pressure
Koeniger and Nagel[19]	7.16	Archimedean
Kirshenbaum and Cahill[20]	7.00	Archimedean
Frohberg and Weber[21]	7.06	maximum bubble pressure
Vertman et al.[22]	7.02	sessile drop
Dragomir et al.[23]	7.00	maximum bubble pressure
Dzhemilev et al.[24]	7.13	sessile drop
Saito et al.[25]	7.03	maximum bubble pressure
Maekawa and Suzuki[26]	6.98	maximum bubble pressure
Morita et al.[27]	7.13	Archimedean
Adachi et al.[28]	6.95	levitation
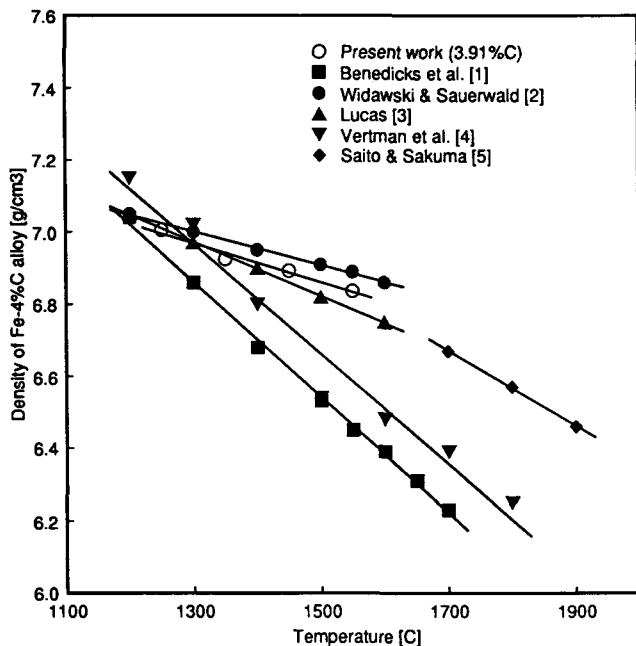
Fig. 4—Density of Fe-4 pct C alloys as a function of temperature.

the absolute value of the measured density, though the error which occurs in the digitizing process itself is less than 0.17 pct.

IV. RESULT AND DISCUSSION

A. Result

The densities measured in this study are given in Table II. The measured density datum for liquid iron at 1550 °C by the authors is 7.124 [g/cm³]. Literature data are summarized and compared with the present work for pure liquid iron in Table III. As seen in the table, our result is very close to those from Dzhemilev et al.[24] and Morita et al.[27]
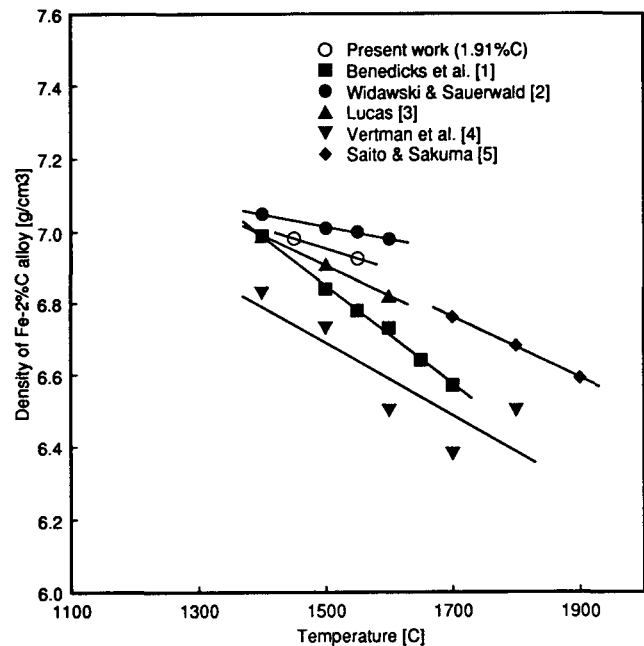

Fig. 5—Density of Fe-2 pct C alloys as a function of temperature.

The results of density determinations of liquid Fe-C alloys for 3.91 and 1.91 wt pct carbon are shown in Figures 4 and 5 as a function of temperature and in relation to previous data. In addition, the variation of density as a function of carbon content is given in Figure 6. The data of this study lie between the data from Widawski and Sauerwald[2] and of Lucas.[3]

B. Discussion

It is found experimentally that the temperature dependence of density for liquid metal and alloys is linear.[32,33] If we follow Steinberg's formula,[32] density data can be represented by the following equations:

$$\rho = \rho_m + \Lambda(T - T_m) \quad [1]$$

where ρ_m [g/cm³] stands for density at melting point T_m [K] and the temperature coefficient at constant pressure, Λ [g/cm³/K], is expressed as

$$\Lambda = \left(\frac{\partial \rho}{\partial T}\right)_p \quad [2]$$

The result of regression analysis by the authors on the previous data is shown in Table IV. As seen in the table, the values of $-\Lambda$ for pure liquid iron from most of the recent literature data lie between 8×10^{-4} and 1×10^{-3} [g/cm³/K]. Accordingly, it was reasonable that Steinberg gave the average value for $-\Lambda$ for pure Fe as 8.8×10^{-4} [g/cm³/K] from the literature data.[32]

An extensive amount of work has been carried out to determine Λ for liquid metals and alloys; however, it is currently impossible to theoretically predict these values.[34] If linearity between temperature and density for Fe-C alloys is assumed, $-\Lambda$ can be calculated (Tables V and VI for 4 and 2 pct carbon content, respectively), and regression analysis of the previous data indicates that the relationship between temperature and density obtained in
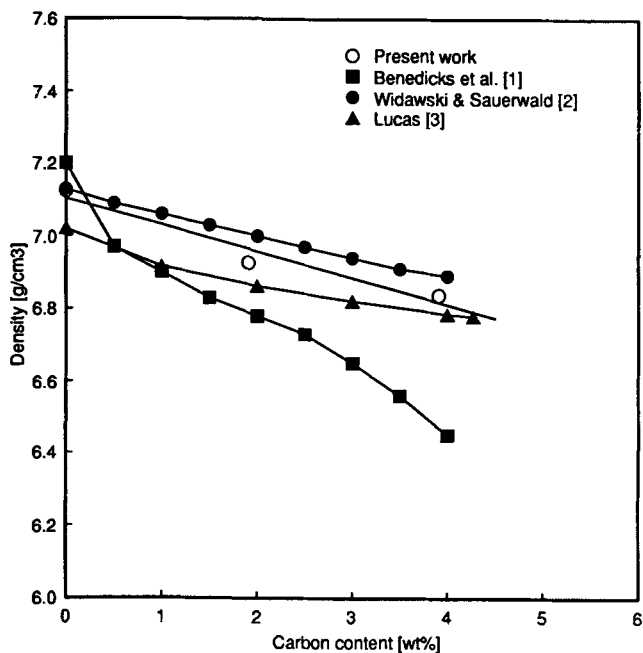
Fig. 6—Density of Fe-C alloys at 1550 °C as a function of carbon content.

Table IV. Relation between Temperature and Density of Liquid Fe
$$\rho \text{ [g/cm}^3] = \rho_m + \Lambda (T - T_m); \quad T_m = 1807 \text{ K}$$

References	ρ_m	$-\Lambda$
Benedicks et al.[1]	7.22	1.20×10^{-3}
Becker et al.[29]	7.13	1.05×10^{-3}
Kingery and Humenik[30]	7.28	1.60×10^{-3}
Lucas[8]	7.04	1.46×10^{-3}
Koeniger and Nagel[19]	7.19	1.60×10^{-3}
Kirschenbaum and Cahill[20]	7.01	8.35×10^{-4}
Froeberg and Weber[21]	7.08	1.23×10^{-3}
Vertman et al.[4]	7.04	8.00×10^{-4}
Saito and Sakuma[31]	7.03	8.50×10^{-4}
Saito et al.[25]	7.04	9.00×10^{-4}
Morita et al.[27]	7.15	9.32×10^{-4} *
Adachi et al.[28]	6.97	1.00×10^{-3}

*Below 1873 K.

Table V. Relation between Temperature and Density of Molten Fe-4 Pct C Alloy
$$\rho \text{ [g/cm}^3] = \rho_m + \Lambda (T - T_m); \quad T_m = 1458 \text{ K}$$

References	ρ_m	$-\Lambda$
Present work (3.91 pct C)	7.03	5.36×10^{-4}
Benedicks et al.[1]	7.05	1.60×10^{-3}
Widawski and Sauerwald[2]	7.05	4.63×10^{-4}
Lucas[3]	7.06	7.50×10^{-4}
Vertman et al.[4]	7.14	1.53×10^{-3}
Saito and Sakuma[5]	7.21	1.05×10^{-3}

Table VI. Relation between Temperature and Density of Molten Fe-2 Pct C Alloy
$$\rho \text{ [g/cm}^3] = \rho_m + \Lambda (T - T_m); \quad T_m = 1665 \text{ K}$$

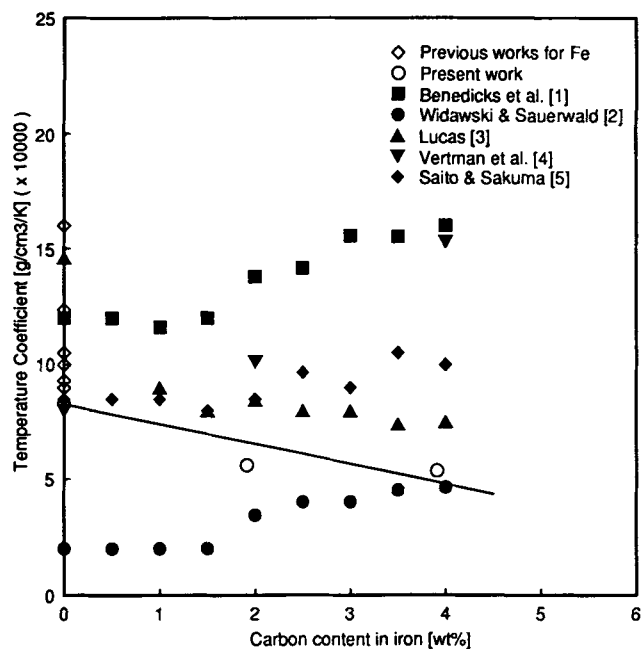| References	ρ_m	$-\Lambda$
Present work (1.91 pct C)	7.01	5.60×10^{-4}
Benedicks et al.[1]	7.00	1.38×10^{-3}
Widawski and Sauerwald[2]	7.05	3.43×10^{-4}
Lucas[3]	7.00	8.45×10^{-4}
Vertman et al.[4]	6.80	1.01×10^{-3}
Saito and Sakuma[5]	7.02	8.50×10^{-4}

Fig. 7—Comparison of temperature coefficient for densities of pure iron and Fe-2 pct C and Fe-4 pct C alloys.

the present work is very similar to that of Lucas[3] and Widawski and Sauerwald.[2] Assuming Steinberg's average value of $-\Lambda$ for pure Fe and incorporating the results of this study, the following regression equation describes $-\Lambda$:

$$-\Lambda \times 10^4 = 8.28 - 0.874 \text{ [pct C]} \qquad [3]$$

These results fall between those of Lucas and Widawski and Sauerwald (Figure 7).

The density of Fe-C alloys at 1550 °C also varies as a function of carbon content, and a linear regression gives the following equation (Figure 6) within the experimental error:

$$\rho = 7.10 - 0.0732 \text{ [pct C]} \qquad [4]$$

Therefore, if a linear relationship is assumed between density and temperature and between the density temperature coefficient and carbon content, a least-squares treatment of our data points gives the smoothed density equation for temperature T [K] and carbon content [pct C] [wt pct]:

$$\rho \text{ [g/cm}^3] = (7.10 - 0.0732[\text{pct C}])$$

$$- (8.28 - 0.874[\text{pct C}])$$
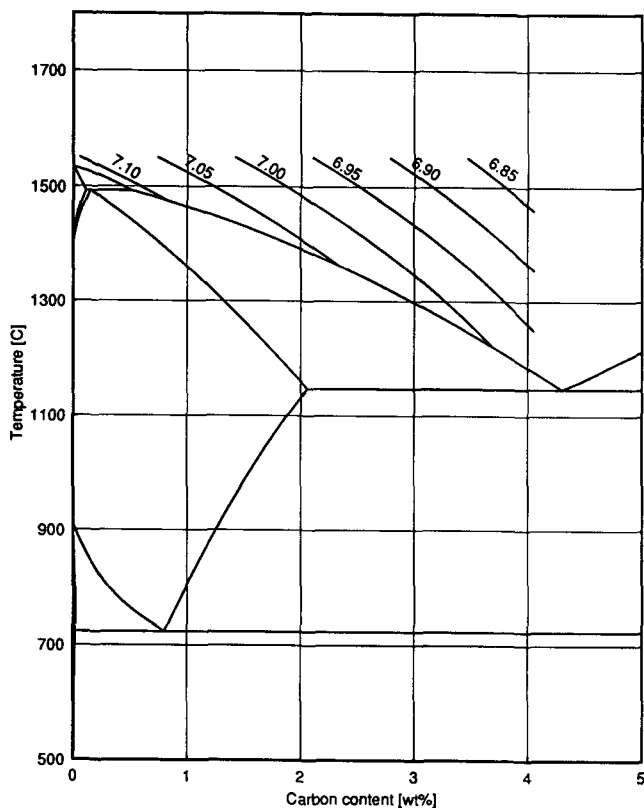
$$\times 10^{-4} (T - 1823) \qquad [5]$$

Fig. 8—Density diagram of Fe-C alloys for temperature and carbon content.

The curves derived by this equation can be shown on an Fe-C binary diagram (Figure 8). These results will give a value to within ±0.69 pct of present work and within ±1.5 pct of the data of Lucas[3] and Widawski and Sauerwald.[2]

V. CONCLUSION

The densities of liquid iron at 1550 °C and Fe-C alloys at temperatures ranging from 1250 °C to 1550 °C was measured. It was shown that the density values were quite similar to those of Lucas and of Widawski and Sauerwald. Based on these results, a density diagram and a regression equation for the calculation of the density of Fe-C alloys as a function of carbon content and temperature was developed.

ACKNOWLEDGMENTS

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