Prediction of Density of Carbon Steels

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The change in the density of carbon steel with phase at a temperature range from 1 000 to 1 973 K has been studied by a sessile drop profile method. Measurement of the density by a sessile drop profile method has to be carried out under heating conditions to avoid the influence of both undercooling and the shrinkage within the sample during solidification. The density of carbon steel was dependent on the phase but not carbon, silicon, manganese, phosphorus and sulfur contents.

The density in L, δ and γ single phase regions, (L+ δ), (L+ γ), (δ + γ) two phases regions and (L+ δ + γ) three phase region could be predicted using the experimental results for Fe–C binary steel and steel contained alloying elements.

These estimated values are in good agreement with experimental results.

KEY WORDS: density; carbon steel; phase; transformation; sessile drop.

1. Introduction

Density is an important factor to decide continuously cast conditions for improving the quality of products, and is indispensable for simulation of heat conduction, solidification, elastic-plastic deformation and fluid flow in many processes. Therefore, many researchers^{1–14)} have studied density at high temperature range.

Solidification modes of carbon steel are very complicated and are changed by carbon content according to the equilibrium phase diagram. The primary phase during solidification is either δ phase or γ phase, and then solidification is completed either as a single phase or as two phases where δ/γ transformation occurs during solidification. Furthermore, the phase after solidification may become two phases through δ/γ transformation. Though the density of carbon steel seems to vary with phase during solidification as well as the Fe–Cr–Ni ternary alloys,¹⁵⁾ the relationship between density and phase for carbon steels was unclear in previous studies.

To study the relationship in the present paper, the density of Fe based alloys, that change with both carbon and alloying elements, were measured by a sessile drop profile method, and the phases of sample changes with concentration of both carbon and alloying elements were predicted by equilibrium thermodynamic calculation.¹⁶⁾ From these results, the relationship between density and phase has been made clear, and the validity of the rule of additivity¹⁷⁾ as a first approximation to estimate the density of (δ + γ) coexisting phase region is discussed.

2. Experimental Procedures

2.1. Composition of the Samples

The chemical compositions of the Fe–C binary steel

samples and Fe based samples accompanied with alloying elements are listed in **Tables 1** and **2**, respectively. In order to investigate the influence of phase on density, the carbon contents of the samples were varied, and silicon, manganese, phosphorous and sulfur were added to Fe–C alloy samples. The steel ingots were produced using electrolytic iron and alloying elements in a vacuum furnace, and then were hot forged at a temperature of 1 473 K. The samples were machined to the given size and shape from round bars of 2.5×10^{-2} m.

2.2. Experimental Apparatus

The density of carbon steel was measured by a sessile drop profile method.^{7,13–15)} **Figure 1** shows a schematic diagram of the experimental apparatus. A sample 6×10^{-3} m in diameter and 6×10^{-3} m in height was set on a plate made

Table 1. Chemical composition of the Fe–C binary samples (mass%).

Sample	C	Fe
FE00	0.005	bal.
FE04	0.039	bal.
FE08	0.079	bal.
FE10	0.097	bal.
FE14	0.14	bal.
FE16	0.16	bal.
FE18	0.18	bal.
FE28	0.28	bal.
FE56	0.56	bal.

Table 2. Chemical composition of the steel samples with alloying elements (mass%).

Sample	C	Si	Mn	P	S
ULC	0.005	0.01	0.12	0.014	0.0028
LC	0.04	0.04	0.19	0.026	0.006
MC1	0.11	0.10	0.48	0.020	0.008
MC2	0.14	0.16	0.54	0.016	0.003
HC	0.55	0.15	0.91	0.021	0.001

Fig. 1. Schematic diagram of the experimental apparatus for measurement of density.

of magnesia in a vacuum vessel. The atmosphere in the vacuum vessel was replaced by argon gas after evacuation with a rotary pump. The argon gas was purified through a dehydrating cartridge-type device connected to a deoxidizing cartridge-type device. The heating and cooling rate of the sample changed with temperature, and the rate was $0.21 \text{ K} \cdot \text{s}^{-1}$ for the temperature range from room temperature to 1400 and $0.083 \text{ K} \cdot \text{s}^{-1}$ for the range from 1400 to 1973 K. Measurements were carried out after 120 s holding at a given temperature. The temperature of the sample was controlled by the output voltage of a B-type (Pt–Rh) thermocouple that was held at $2 \times 10^{-3} \text{ m}$ above the sample. The B-type thermocouple is accurate at a high temperature range up to 1973 K, but accuracy is lower below 773 K. Accordingly, the density was measured in the temperature range from 1000 to 1973 K in this experiment.

The volume of the sample was calculated by a method of image sectioning of the sample profile assuming that the shape of the sample was symmetrical. Thus, from knowledge of the weight of the sample, the density of the sample could be easily calculated. Both the shape and the size of the sample were analyzed by using a computer from a two-dimensional shadow image photographed by a CCD camera. The shadow image of the sample was made using flash facing the CCD camera. Both the shape and the size of the sample at a given temperature were measured from four directions by rotating the sample slowly at an interval of 0.25π radian in the horizontal plane. The average value of the volumes of the sample taken from the four directions was regarded as the volume of the sample, and the density was calculated. In order to increase the accuracy of measurement for both the shape and size of the sample, the CCD camera was connected to a telescopic lens and a magnified image was displayed on the screen of a computer. The resolution of this measurement system was $3.0 \times 10^{-5} \text{ m}$ and the measuring error was within 1.5%.

From the results of observation of solidification microstructure for a Fe–Cr–Ni sample in the previous study,¹⁵⁾ it was found that an undercooling occurred and a cavity

formed during solidification. Therefore, in this experiment the density of the sample was measured under heating conditions to avoid these influences which will cause errors in measurement.

3. Results

3.1. Phase Transformation of Fe–C Binary Steel

Figures 2(a)–2(i) show the relationship between the L, δ or γ phase fraction and temperature given by the equilibrium thermodynamic calculation. The relationship between phase and temperature of Fe–C binary steel was also predicted by that calculation.

Figure 2(a) shows the relationship between mass fraction of phase and temperature for sample FE00. The primary phase of this sample during solidification was the δ phase and the δ/γ transformation was completed immediately at solidus temperature, and then the γ single phase was formed. When the temperature decreased, the α phase was precipitated in the γ phase and the structure became the α single phase.

Figures 2(b) and 2(c) show the change of phase fraction with temperature for samples FE04 and FE08, respectively. The primary phase of these samples during solidification was the δ phase and the phase just after solidification remained a single δ phase. The γ phase was precipitated after complete solidification and a $(\delta + \gamma)$ coexisting phase region was formed. The γ phase fraction increased with decreasing temperature, and the δ phase fraction became zero. The behavior of δ phase fraction was opposite to that of γ phase. After precipitation of the α phase, the γ phase fraction decreased and the α phase fraction increased.

Figures 2(d) and 2(e) show the relationship between phase fraction and temperature for samples FE10 and FE14, respectively. Mass fractions of phase in these samples changed with temperature. Though the primary phase of these samples during solidification was the δ phase, the same as sample FE00–FE08, the single δ phase was not formed after solidification. After the δ/γ phase transformation started, the γ phase fraction increased with decreasing temperature. On the other hand, the δ phase fraction decreased with decreasing temperature.

The change in phase of sample FE16 with temperature is shown in Fig. 2(f). The primary phase of this sample was the δ phase and the fraction of δ phase increased before the γ phase precipitation, and fraction of the δ phase showed the maximum value which was smaller than unity. δ/γ phase transformation was completed during solidification and the γ single phase formed at solidus temperature. When the temperature decreased, the γ/α transformation started and the fraction of γ phase decreased.

Figures 2(g) and 2(h) show the relationship between phase of sample FE18 and FE28 and temperature, respectively. The primary phase of these samples was the δ phase, and the fraction of δ phase showed the maximum value during solidification which was as large as lower carbon concentration. After the γ phase precipitating, the $(L + \gamma)$ phase structure formed and the structure became the γ single phase at solidus temperature. The γ/α transformation started at low temperature in this experiment.

Figure 2(i) shows the relationship between phase and

Fig. 3. Change in density with temperature for Fe-C binary samples. Closed circles represent the experimental results on heating condition and solid line represents the calculated result.
(a) Sample FE00, (b) FE04, (c) FE08, (d) FE10, (e) FE14, (f) FE16, (g) FE18, (h) FE28 and (i) FE56.

Fig. 2. Change in fraction of phase with temperature for Fe-C binary samples.
(a) sample FE00, (b) FE04, (c) FE08, (d) FE10, (e) FE14, (f) FE16, (g) FE18, (h) FE28 and (i) FE56.

temperature of sample FE56. Primarily the γ phase solidified during the solidification sequence which differed from other samples and the δ phase did not exist. The γ single phase formed at solidus temperature and the γ phase remained before the γ/α transformation began.

3.2. Density of Fe–C Binary Steel

Figures 3(a)–3(i) show the change of density with temperature measured under heating conditions. The relationship between phase and temperature is also shown in Figs. 3(a)–3(i).

The density of sample FE00 plotted against temperature is shown in Fig. 3(a). Under heating conditions, the density decreased with increasing temperature. The difference of density between liquidus and solidus temperature was large. In the liquid phase region, the density decreased with increasing temperature. There was an irregular change in the density at the δ/γ transformation temperature.

Figures 3(b) and 3(c) show the relationship between density of samples FE04 and FE08 and temperature, respectively. The density decreased with increasing temperature and the change of density in the solidification temperature range was large. The difference of density between liquidus and solidus temperature was almost the same as that of sample FE00.

Figures 3(d) and 3(e) show the change of density of sample FE10 and FE14 with temperature, respectively. In the liquid phase region, the density decreased with increasing temperature. The difference in density between liquidus and solidus temperature was large and the density in the $(\delta+\gamma)$ phase region increased with decreasing temperature. The density of γ phase changed linearly with temperature the same as the other samples.

Figure 3(f) shows the relationship between density of sample FE16 and temperature. The primary phase of this sample was the δ phase, and then a single γ phase was formed just below the solidus temperature. The density of sample FE16 decreased with increasing temperature and the density between liquidus and solidus temperature changed a lot.

Figures 3(g) and 3(h) show the density of sample FE18 and FE28 varying with temperature, respectively. The primary phase of this sample was the δ phase and the γ phase was precipitated, and the γ single phase was formed below the solidus temperature. The density of these samples decreased with increasing temperature and the change of density between liquidus and solidus temperature was large.

Figure 3(i) shows the relationship between density of sample FE56 and temperature. The primary phase was the γ phase and the δ/γ transformation during solidification did not exist unlike in the other samples. The density of sample FE56 decreased with increasing temperature and the difference of density between liquidus and solidus temperature was large. In the liquid phase, the density decreased with increasing temperature. In the γ phase, the density increased linearly with decreasing temperature.

From the results shown in Fig. 3, the density of Fe–C binary steel seemed to be governed either by the L, δ or γ phase fraction and not to be determined simply by the carbon content.

4. Discussion

4.1. Phase Dependence of Density of Fe–C Binary Steel

In order to investigate the dependence of density upon the L, δ or γ phase, the density was arranged by the temperature difference on the basis of the start temperature of phase transformation as shown in Fig. 4.

Figure 4(a) shows the change of density in the liquid phase region for samples FE00 to FE56 and previous results for stainless steel samples¹⁵⁾ and carbon steel samples^{1,2,13)} with temperature difference. The temperature difference was defined on the basis of liquidus temperature. The density for all the samples decreased with increasing temperature difference from the liquidus temperature. When the temperature difference was the same, the density of all the samples had almost the same value.

In many previous studies on Fe–C binary alloy, the dependency of the density upon carbon content at constant temperature in the liquid phase region was investigated. As the liquidus temperature varied with carbon content, superheat above the liquidus temperature was different for each carbon content under the constant temperature conditions in the liquid phase region. Therefore, it would seem to be hard to investigate the dependence of density upon carbon content under constant temperature conditions.

The dependence of density upon the temperature difference on the basis of the liquidus temperature was summa-

Fig. 4. Relationship between density and temperature difference. (a) Liquid phase, (b) δ phase and (c) γ phase.

rized by Jimbo *et al.*¹¹⁾ The regression line based on the present experimental results shown here, was within the range of previous results. For the δ and γ single phase, density was thought to be arranged by temperature difference because density depended on temperature the same as liquid phase.

Figure 4(b) shows the relationship between density and temperature difference in the δ phase region. The results for samples FE00, FE04, FE08 and previous results for stainless steel samples¹⁵⁾ and carbon steel samples^{1,2,13)} which were primarily in the δ phase before solidification and in the single δ phase after solidification, were summarized. In either case, the density increased with increasing temperature difference. When the temperature difference was the same, the density of all samples had almost the same value.

In the γ phase region, the relationship between density and temperature difference is shown in Fig. 4(c). Samples FE16, FE18, FE28, FE56 and previous results for stainless steel samples¹⁵⁾ and carbon steel samples¹⁾ which were the single γ phase after solidification. The density was given by the temperature difference the same as in the case of the liquid phase and the δ phase, and the density increased with increasing temperature difference. There was no influence from carbon content under these conditions.

It was found that the density of Fe-C binary steel was dependent on the phase, for example the L, δ and γ phase under these experimental conditions and the density in the L, δ or γ phase region was given by the temperature difference in all three cases. The regression lines shown in Fig. 4(a)–4(c) are given by the following equations, respectively:

$$\rho_L = -7.50 \times 10^{-4} \Delta T_L + 7.02 \quad \text{.....(1)}$$

$$\rho_\delta = 3.07 \times 10^{-4} \Delta T_\delta + 7.27 \quad \text{.....(2)}$$

$$\rho_\gamma = 4.80 \times 10^{-4} \Delta T_\gamma + 7.41 \quad \text{.....(3)}$$

4.2. Prediction of Density of Fe-C Binary Steel during and after Solidification

The density of single L, δ and single γ phase can be expressed in terms of the temperature difference as shown in Fig. 4. On the other hand, if the temperature difference on the basis of the equilibrium thermodynamic calculation is known, the density of L, δ or γ phase can be predicted. Besides either the δ single phase or the γ single phase, ($\delta + \gamma$), (L + δ), (L + γ) phase and (L + $\delta + \gamma$) phase was present during solidification of carbon steel. Therefore, in order to estimate the density of carbon steel, it seems to be necessary to know the density of both binary and ternary phases.

In the present study, the density of both binary and ternary phases that were composed of L, δ and γ phase was estimated using the rule of additivity as a first approximation. By comparing estimated values with measured values, the validity of the estimation method was investigated.

The density in the ($\delta + \gamma$) phase region is represented by the rule of additivity as follows:

$$\rho_{(\delta+\gamma)} = \rho_\delta \cdot f_\delta + \rho_\gamma \cdot f_\gamma \quad \text{.....(4)}$$

ρ_δ and ρ_γ were calculated from Eqs. (2) and (3), respectively, and f_δ and f_γ were used by the relation shown in Fig.

2.

The density in the (L + δ) phase region was given using the difference of density between liquidus and solidus temperatures, and the mass fraction of δ phase:

$$\rho_{(L+\delta)} = \rho_L^0 + \Delta \rho_{L/\delta} \cdot f_\delta \quad \text{.....(5)}$$

The densities in the (L + γ) phase region and (L + $\delta + \gamma$) phase region were given by:

$$\rho_{(L+\gamma)} = \rho_L^0 + \Delta \rho_{L/\gamma} \cdot f_\gamma \quad \text{.....(6)}$$

$$\rho_{(L+\delta+\gamma)} = \rho_L^0 + \Delta \rho_{L/\delta} \cdot f_\delta + \Delta \rho_{L/\gamma} \cdot f_\gamma \quad \text{.....(7)}$$

Predicted values of density are represented by solid lines in Figs. 3(a)–3(i) and were compared with measured values.

Figure 3(a) shows the relationship between the predicted value of density and the temperature of sample FE00. The estimated values of L, δ and γ phase were in good agreement with the measured values and varied linearly with temperature in either phase.

The estimated density of samples FE04 and FE08 change with temperature as shown in Figs. 3(b) and 3(c), respectively. The mass fraction of phase changed with temperature as shown in Figs. 2(b) and 2(c). The estimated density varied with both temperature and phases fraction, and was in good agreement with the measured values.

Figures 3(d) and 3(e) show the change of estimated density of samples FE10 and FE14 with temperature, respectively. The solidification sequence of samples FE10 and FE14 were different from those of samples FE04 and FE08 and the δ single phase was not formed and the phase became the ($\delta + \gamma$) phase at the solidus temperature. The estimated values of density agreed with the measured values.

Figure 3(f) shows the relationship between phase and temperature for sample FE16. The primary phase was the δ phase, and the γ phase precipitated and the δ/γ transformation was completed at the solidus temperature. The estimated density was good agreement with the measured values.

The estimated density of samples FE18 and FE28 change with temperature as shown in Figs. 3(g) and 3(h), respectively. The primary phase was the δ phase, and the γ phase precipitated and the δ/γ transformation completed during solidification. The estimated values of density in the L, δ and γ phase regions agreed with the measured values.

Figure 3(i) shows the change of estimated value of sample FE56 with temperature. The primary phase was the γ phase and the γ single phase was formed just after solidification unlike the other samples. The estimated value was in good agreement with the measured value.

From these results shown in Fig. 3, it seemed possible to estimate the density for a combination of L, δ and γ phases on the basis of the rule of additivity.

4.3. Change in Density during Solidification

The change in density is thought to depend on the phase transformation during solidification because the density changes according to the L, δ and γ phase. Therefore, it is necessary to clarify the change of density with δ/γ transformation during solidification in the continuously cast steel products.

Figure 5 shows the relationship between fraction of solid and carbon concentration at both the start and finish of δ/γ

Fig. 5. Relationship between fraction of solid and carbon concentration for δ/γ transformation of Fe-C binary samples.

Fig. 6. Change in (a) fraction of phase at solidus temperature and (b) difference of density between liquidus and solidus temperature with carbon concentration for Fe-C binary samples.

transformation for Fe-C binary steels. The fraction of solid at both the start and finish of δ/γ transformation decreased with increasing carbon concentration and the range of δ/γ transformation changed with carbon concentration. The lower the carbon concentration became, the higher the fraction of solid when δ/γ transformation began and finished in the range of carbon concentration from 0.09 to 0.53 mass%.

In previous studies, the difference of density has been measured between liquidus and solidus temperature. Both liquidus and solidus temperature varied with carbon contents and the difference of temperature between liquidus and solidus also varied with carbon. Therefore, the difference of density has been arranged by the difference of temperature between liquidus and solidus.

It is thought that the difference of density between liquidus and solidus is decided by the ratio of δ to γ phase at solidus temperature because the density depends on the phase state.

Figure 6 shows the change of mass fraction of phase and difference of density with carbon concentration.

Figure 6(a) shows the relationship between mass fraction of phase at solidus temperature and carbon concentration. The fraction of both δ and γ phase at solidus temperature

was changed with carbon concentration. The δ single phase was formed when carbon concentration was lower than 0.09 mass%, the $(\delta+\gamma)$ phase was formed the range from 0.09 to 0.18 mass% and the γ single phase was formed when carbon concentration was higher than 0.18 mass%.

Figure 6(b) shows the change in the difference in density between liquidus and solidus temperature with carbon concentration. The difference in density was defined as the difference either between L and δ phase, L and $(\delta+\gamma)$ phase or L and γ phase. The phase formed at solidus temperature is represented as δ , $(\delta+\gamma)$ and γ phase in this figure. The difference in density in both the δ phase and the γ phase was constantly independent of carbon concentration, because the density at both liquidus and solidus temperature was determined by the phase as shown in Fig. 6(a). The difference in density in the $(\delta+\gamma)$ phase region at fraction of solid 1.0 was given as follows:

$$\Delta\rho = \Delta\rho_{L/\delta} \cdot \Delta f_{\delta} + \Delta\rho_{L/\gamma} \cdot \Delta f_{\gamma} \dots\dots\dots(8)$$

The difference in density in the $(\delta+\gamma)$ phase region varied with carbon concentration because the fraction of the δ to the γ phase depended on carbon concentration. The difference in density in the $(\delta+\gamma)$ phase region at the solidus temperature was larger than in the δ phase region and lower than in the γ phase region.

Though the solidification shrinkage, that is, the change of density accompanied with δ/γ transformation during solidification has been thought to be one of causes for the longitudinal surface crack in continuously cast steel slabs, there were a few study which investigate the relationship between density and phase during solidification in detail. Therefore, the change of density accompanied with δ/γ transformation during solidification is investigated based on the experiment results, and these results are shown in Fig. 7.

The amount of density change in the $(\delta+\gamma)$ coexisting phase region during solidification is not determined with fraction of phase alone, because the density of δ and γ phase are different. The fraction of density change varied with ratio of δ/γ transformation during solidification. As shown in Fig. 5, the ratio of δ/γ transformation depended on the carbon concentration. By the way, it is thought that the solidification shrinkage, that is, density change will not influence the dynamic behavior of solidified shell until fraction of solid 0.8 the same as tensile strength and elongation¹⁸⁾ where dendrites form a network¹⁹⁾ during solidification. Therefore, the density change was investigated over fraction of solid 0.8.

Figure 7(a) shows the relationship between difference in density and carbon concentration of both δ and γ phase in the range of δ/γ transformation during solidification. The difference in density of δ phase in δ/γ transformation region was a value which multiplied $\Delta\rho_{L/\delta}$ by fraction of δ phase. Similarly, the value $\Delta\rho_{L/\gamma}$ was used for calculation difference in density of γ phase. For both δ and γ phase, the difference in density increased with increasing carbon concentration and showed a maximum value, then decreased. The difference in density of γ phase was larger than that of δ phase in each carbon concentration.

To relate the behavior of δ/γ transformation and the cooling conditions of continuously cast steel products, it is necessary to understand the difference in fraction of solid

Fig. 7. Change of (a) difference in density, (b) difference of fraction in solid during δ/γ transformation and (c) rate of density change with carbon concentration.

between start and end of δ/γ transformation. Figure 7(b) shows the change of difference in fraction of solid with carbon concentration during δ/γ transformation. The difference in fraction of solid depended on carbon concentration and increased with increasing carbon concentration and showed a maximum value, then decreased. It seems that the larger the difference in fraction of solid, the slower the δ/γ transformation rate under same cooling conditions because change of fraction of solid relates cooling rate.

The ratio of difference in density obtained in Fig. 7(a) to difference in fraction of solid obtained in Fig. 7(b) during δ/γ transformation is thought to show the rate of density change in the range of δ/γ transformation during solidification. As this rate is different in either δ and γ phase, it seems to be necessary to evaluate the rate in the region of δ/γ transformation by product of rate of δ and γ single phase.

Figure 7(c) shows the relationship between rate of density change during δ/γ transformation and carbon concentration. The rate of density change during δ/γ transformation was large in the range of carbon concentration 0.09–0.24 mass%. As the amount of solidification shrinkage is also different when the amount of density change in solidified shell is different, the thermal stress is thought to be generated in the shell of continuously cast steel products. The

higher the rate of density change during δ/γ transformation, the larger the difference in density and also the larger the thermal stress generated in solidified shell under same cooling conditions.

Moreover, the relationship between normalized index of longitudinal surface crack occurrence in continuously cast steel slabs and carbon concentration is also shown in Fig. 7(c). However, the range of carbon concentration in which frequency of longitudinal surface crack was high^{20,21)} did not corresponded to the range of carbon concentration in which rate of density change was high. Therefore, it is thought that longitudinal surface crack is not determined with solidification shrinkage alone, that is, change of density alone, and is influenced also by tensile strength and elongation during solidification.

4.4. Influence of Alloying Elements on Density

Though the change of density Fe–C binary steel has been examined, silicon, manganese, phosphorus and sulfur are contained in commercial steel as the main solute elements. Firstly, it is necessary to clarify the influence of alloying element on the solidification behavior to understand the density of commercial steel.

Figure 8 shows the relationship between mass fraction of phase for δ and γ , and fraction of solid for Fe–0.12mass%C steels which are contained with either silicon, manganese, phosphorus or sulfur.

Figure 8(a) shows the change of mass fraction of phase and fraction of solid for a Fe–0.12mass%C steel. The δ phase was formed as a primary phase during solidification. The fraction of δ phase increased with increasing fraction of solid and reached with the maximum value. At this time, the γ phase precipitated and δ/γ transformation began, and then the fraction of δ phase decreased with increasing the fraction of γ phase.

Even if alloying elements are added to a Fe–0.12mass%C steel, the solidification mode seems to be almost the same as a Fe–0.12mass%C binary steel. However, the fraction of solid which the γ phase precipitated and the fraction of both δ and γ phase at solidus temperature are thought to change with alloying elements.

Figure 8(b) shows the relationship between mass fraction of phase and fraction of solid for a Fe–0.12mass%C–0.2mass%Si ternary steel. The fraction of solid at which δ/γ transformation started was almost the same as a Fe–0.12mass%C binary steel shown in Fig. 8(a) and the phase was the $(\delta+\gamma)$ phase at fraction of solid 1.0.

Figure 8(c) shows the change of mass fraction of phase with fraction of solid for a Fe–0.12mass%C–0.5mass%Mn ternary steel. The δ/γ transformation started earlier and the fraction of δ phase at fraction of solid 1.0 was smaller than that of a Fe–0.12mass%C binary steel.

Figure 8(d) shows the relationship between mass fraction of phase and fraction of solid for a Fe–0.12mass%C–0.03mass%P ternary steel. The phase was the $(\delta+\gamma)$ phase at fraction of solid 1.0 and the fraction of δ phase was larger than that of γ phase as shown in Figs. 8(a)–8(c).

Figure 8(e) shows the relationship between mass fraction of phase and fraction of solid for a Fe–0.12mass%C–0.01mass%S ternary steel. The fraction of solid at which δ/γ transformation started was higher comparing with the

Fig. 8. Change in fraction of phase with fraction of solid.
(a) Sample Fe-0.12mass%C, (b) Fe-0.12mass%C-0.2mass%Si, (c) Fe-0.12mass%C-0.5mass%Mn, (d) Fe-0.12mass%C-0.03mass%P and (e) Fe-0.12mass%C-0.01mass%S.

Fig. 9. Change in density difference between liquidus and solidus temperature with alloy concentration for Fe-0.12mass%C contained various elements.

other samples and the (L + δ + γ) phase was formed just before solidification. At a fraction of solid 1.0, the δ phase disappeared and the γ phase became the single phase.

As shown in Fig. 8, the behavior of fraction of both δ and γ phase was changed with alloying elements.

Figure 9 shows the relationship between difference of density between liquidus and solidus temperature and concentration of alloying elements. The difference in density changed with both kinds and the concentration of alloying elements. The effect of sulfur on the difference in density was largest because the fraction of γ phase which was formed at solidus temperature was largest as shown in Fig. 7.

Figures 10(a)–10(e) show the relationship between the L, δ or γ phase fraction and temperature given by the calculation for samples listed in Table 2. The relationship between phase and temperature was predicted by the equilibrium thermodynamic calculation the same as Fig. 2.

Figure 10(a) shows the relationship between mass fraction of phase and temperature for a sample ULC. The solidification behavior was the same as a sample FE00 shown in Fig. 2(a).

Figure 10(b) shows the change of phase with temperature for a sample LC. The phase change of this sample was the same as a sample FE04 and FE08 and a δ single phase was formed after solidification.

Figures 10(c) and 10(d) show the relationship between

mass fraction of phase and temperature for samples MC1 and MC2, respectively. The primary phase of this sample was the δ phase and the fraction of δ phase increased before the γ phase precipitation. The δ phase showed the maximum value which was smaller than unity and the (L + δ + γ) phase was formed during solidification. The (δ + γ) phase was formed at solidus temperature, and the structure became the γ single phase after completing the δ/γ transformation.

Figure 10(e) shows the relationship between mass fraction of phase and temperature for sample HC. The behavior of phase change of this sample was the same as the sample FE56 shown in Fig. 2(i), and the primary phase was the γ phase and the γ phase formed after solidification.

Figures 11(a)–11(e) show the change of density with temperature for samples listed in Table 2. The relationship between phase and temperature, and the predicted results of density are also shown in Figs. 11(a)–11(e).

Figure 11(a) shows measured and predicted density for sample ULC. The density decreased with increasing temperature and the change of density depended on phase state. The predicted values were in agreement with the measured values.

Figure 11(b) shows the relationship between measured and predicted density and temperature for sample LC. As predicted values almost corresponded to measured values, the density could be estimated by this method.

Fig. 10. Change in fraction of phase with temperature for steel samples.
(a) Sample ULC, (b) LC, (c) MC1, (d) MC2 and (e) HC.

Fig. 11. Change in density with temperature for steel samples. Closed circles represent the experimental results on heating condition and solid line represents the calculated result.
(a) Sample ULC, (b) LC, (c) MC1, (d) MC2 and (e) HC.

Figures 11(c) and 11(d) show the change of density with temperature for samples MC1 and MC2, respectively. The predicted values were in agreement with the measured values for both samples.

Figure 11(e) shows the change in density with temperature for sample HC. The change of density could be estimated because the predicted values were in agreement with the measured values.

From these results, it was found that the density of carbon steel contained with alloying elements could be estimated by this method.

5. Conclusions

The density of carbon steels were measured using a sessile drop profile method and the relationship between density and phase that was estimated by an equilibrium thermodynamic calculation was investigated. The density in the $(\delta+\gamma)$ coexisting phase region was estimated by the rule of additivity as a first approximation and the validity of this rule was investigated by comparing with the measured values.

(1) The density of carbon steel was determined by temperature and fractions of existing phases. Though the concentration of alloying elements besides carbon was the factor that determined fractions of phases, the influence of the alloying elements contained in the carbon steel on the density of each phase was small.

(2) The density in $(L+\delta)$, $(L+\gamma)$ and $(L+\delta+\gamma)$ phase regions of carbon steels were calculated by the following equations:

$$\rho_L = -7.50 \times 10^{-4} \Delta T_L + 7.02$$

$$\rho_\delta = 3.07 \times 10^{-4} \Delta T_\delta + 7.27$$

$$\rho_\gamma = 4.80 \times 10^{-4} \Delta T_\gamma + 7.41$$

(3) The density in L, δ and γ phase regions of carbon steels were calculated by the following equations:

$$\rho_{(L+\delta)} = \rho_L^0 + \Delta \rho_{L/\delta} \cdot f_\delta$$

$$\rho_{(L+\gamma)} = \rho_L^0 + \Delta \rho_{L/\gamma} \cdot f_\gamma$$

$$\rho_{(L+\delta+\gamma)} = \rho_L^0 + \Delta \rho_{L/\delta} \cdot f_\delta + \Delta \rho_{L/\gamma} \cdot f_\gamma$$

(4) The density of $(\delta+\gamma)$ phase was estimated by the rule of additivity as a first approximation.

$$\rho_{(\delta+\gamma)} = \rho_\delta \cdot f_\delta + \rho_\gamma \cdot f_\gamma$$

The estimated values were in good agreement with the measured values.

(5) The range of carbon concentration in which frequency of longitudinal surface crack of continuously cast steel slabs was high did not corresponded to the range of carbon concentration in which rate of density change was high.

(6) The behavior of the phase change in steel varied with the kind and the concentration of alloying elements. Even if the alloying elements were added to carbon steel, it was possible to predict the density using this method.

Nomenclature

ρ_L : the density in the liquid phase ($\times 10^3 \text{ kg} \cdot \text{m}^{-3}$)

ρ_δ : the density of the δ phase ($\times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 ρ_γ : the density of the γ phase ($\times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 $\rho_{(L+\delta)}$: the density of $(L+\delta)$ phase ($\times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 $\rho_{(L+\gamma)}$: the density of $(L+\gamma)$ phase ($\times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 $\rho_{(\delta+\gamma)}$: the density of $(\delta+\gamma)$ phase ($\times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 $\rho_{(L+\delta+\gamma)}$: the density of $(L+\delta+\gamma)$ phase ($\times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 ρ_L^0 : the density of the liquid phase at a temperature difference ΔT_L of 0 K ($7.02 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 $\Delta \rho$: the difference in density between liquidus and solidus temperature ($\times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 $\Delta \rho_{L/\delta}$: the difference in density between liquidus and solidus temperature of the δ phase ($0.25 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 $\Delta \rho_{L/\gamma}$: the difference in density between liquidus and solidus temperature of the γ phase ($0.39 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$)
 f_δ : the mass fraction of the δ phase
 f_γ : the mass fraction of the γ phase
 Δf_δ : the difference in mass fraction of the δ phase between liquidus and solidus temperature
 Δf_γ : the difference in mass fraction of the γ phase between liquidus and solidus temperature
 ΔT : the temperature difference between liquidus and solidus temperature (K)
 ΔT_L : the temperature difference on the basis of the liquidus temperature (K)
 ΔT_δ : the temperature difference on the basis of the solidus temperature of the δ phase (K)
 ΔT_γ : the temperature difference on the basis of the solidus temperature of the γ phase (K)

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