Solubility of Titanium and Carbon in Molten Fe–Ti Alloys Saturated with Carbon

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Synopsis
The solubilities of titanium and carbon in Fe–C sat–Ti alloys were determined at temperatures from 1300°C to 1500°C. Some of the already reported values of titanium solubility were determined by measuring the acid-soluble titanium dissolved in rapidly cooled samples which inevitably contain the particles of titanium carbide sedimented during cooling. The sedimentation of titanium carbide results in the difficulty in determining the accurate solubility of titanium. In order to solve this difficulty, methods were newly devised to measure the total titanium content in rapidly cooled samples.

The results obtained are as follows:
(1) The solubility of titanium at temperatures from 1300°C to 1500°C was expressed as,
\[ \log [\%Ti] = (-6760/T) + 3.906 \]

(2) By the use of the carbon solubility in iron with different concentrations of titanium, the temperature dependence of the interaction coefficient, \( e_{Ti} \), at temperatures from 1350°C to 1500°C was determined as,
\[ e_{Ti} = (-221/T) - 0.072 \]

(3) The change of standard Gibbs free energy for the reaction, \( Ti + C_{sat} = TiC_2(s) \), was obtained as \( AG^0 = -30500 - 13.3T \) (cal/mol).

II. Experimental Method for Determining Titanium Solubility

1. Experimental Apparatus and Procedure
Figure 1 shows the sketch of the experimental arrangement. Seven small graphite crucibles, which contained 28 g of Fe–C alloy, were placed in a large graphite crucible which was set in the constant-temperature hot zone of a porcelainous tube. The inner diameters of the small crucibles and the large crucible were 13 mm and 65 mm, respectively. After the heating to the experimental temperature, a TiC-tablet (10 mm × 5 mm H) of the weight of 1.5 g was placed on the surface of molten Fe–C alloy in each of the small crucibles. Before this step, TiC-tablets were preheated just above the large crucible. The reaction system was held at the settled temperature for 13 to 21 days in order to be in the equilibrium. During this period each of the small crucibles was taken out for analysis.

The atmosphere of the reaction system was controlled by flowing argon of high purity (>99.999 vol%) at a rate of 20 l/min through the bottom of the porcelainous tube and also at a rate of 0.5 l/min into the large graphite crucible through a graphite tube inserted from the top of the apparatus.

The experimental temperature was regulated by a controller connected to a Pt-6Rh/Pt-30Rh thermocouple positioned in a mullite sheath touching the outside of the constant-temperature hot zone of the porce-
The temperature in the reaction zone inside the large graphite crucible was accurately monitored by another thermocouple introduced through the top of the apparatus, and the fluctuation of the temperature was within ±0.2°C at each temperature. The measurement of the temperature distribution in the small graphite crucible revealed that the temperature at the top of the crucible was higher than that at the bottom by 2°C. The experimental temperatures were 1304°C, 1348°C, 1391°C, 1450°C and 1501°C.

The experimental method described above is referred to as "the diffusion method" because the reaction velocity is determined by the diffusion of titanium in iron.

2. Microscopy of Cooled Samples and Sample Preparation for Chemical Analysis

The cooled metal samples in the small graphite crucibles were cut into two pieces in the way shown in Photo. 1. The polished sections of the pieces were examined under a microscope. As shown in Photo. 2, the boundary between the TiC-tablet and the metal bulk was clearly recognized, although pores in the TiC-tablet were filled with metal because of the high wettability of TiC with molten iron. No small TiC particles which possibly separated from the TiC-tablet were observed in the metal bulk.

On the other hand, TiC particles which sedimented from iron melt during cooling or during being held at the experimental temperature were observed in such parts as the center and the middle of the metal phase, and also at the metal-crucible boundary. These three parts were schematically shown in Fig. 2.

In the center and middle of the metal phase two types of TiC particles are identified (Photo. 3). One type of the particles is of 3 to 10μ which contacts closely with graphite sedimented during cooling, and the other is of 1 to 3μ which is observed independently rather in the middle of the metal phase. If these particles in the central and middle parts sedimented during the period when the metal samples were held at the experimental temperatures, these would become a source of error in determining the solubility of titanium. However, the following characteristics observed in each sample indicate that the particles sedimented during cooling:

(1) In the parts where there were graphite particles, TiC particles sedimented in close contact with them (Photo. 3(a)). Usually, the crystal starts its growth at a solid as a kernel. This suggests that during cooling the growth of TiC crystal easily starts at the graphite crystal sedimented in advance of the TiC crystal growth.

(2) The sedimented TiC particles in the central and middle parts were observed not only in the sample of the final stage of the heat but also in the sample of the initial stage.* Figure 4 shows that in the initial stage of the heat the melts were not in equilibrium with TiC placed on the top of the melts. The sedi-

* The meanings of the terms, initial and final, are explained in Fig. 4.
The sedimentation of TiC crystal from molten iron, which is not in equilibrium with TiC, can not occur under the small fluctuation, within ±0.2°C, of the experimental temperature. (3) The number of the sedimented particles were more at the higher experimental temperatures than at the lower temperature. The number of particles depends on the experimental temperature. For samples held at higher temperatures it takes more time to cool down. The longer the cooling time, the more the number of sedimented particles is.

(4) As shown in Fig. 3, the line analysis, by an electron microprobe, of the metal phase closely near the TiC particles which sedimented in contact with graphite particles revealed that in the region between 8 and 32 μ from the TiC-metal boundary the concentration of titanium was lower than that in the region more than 32 μ away from the boundary. The high titanium concentration in the region up to 8 μ from the boundary is attributed to the presence of a part of the TiC crystal just beneath the very thin metal layer through which X-ray penetrates.

The above described phenomenon was also observed in the metal phase near the smaller TiC particles not in contact with graphite particles. On the basis of the above mentioned facts, the titanium of the TiC particles in the central and middle is regarded as the solute in the molten iron held at the experimental temperature.

Besides the small particles described above, as shown in Photo. 4, the sedimentation of large TiC and graphite grains were observed at the boundary between the metal phase and the wall of the graphite crucible. At the experimental temperature of 1304 °C, the size of the TiC grains was 50 to 60 μ which were ten times larger than the TiC particles observed in the central and middle parts of the metal bulk. Those grains were identified in the samples in the final stage of the heats, however no such grains in the initial stage. While in the final stage the molten iron was in the state of equilibrium with TiC placed on the top of the melt, in the initial stages not. This indicates that, if the metal once gets into the state of equilibrium with TiC, the sedimentation and growth of TiC crystals on the wall of graphite crucible occur...
by a small fluctuation of the experimental temperature. The size of the TiC grains became larger at lower experimental temperatures: 5 to 15 µ at 1 450°C and 1 501°C, 10 to 30 µ at 1 348°C, and 50 to 60 µ at 1 304°C. This is consistent with the general observation concerning the effect of temperature on the crystal size. At any rate, the size of the TiC grains on the wall of the graphite crucible was invariably larger than that of the particles observed in the central and middle parts of the metal bulk. When molten metal in a crucible is cooled down, the peripheral part of the metal solidifies faster than the central and middle parts. So the TiC grains with larger size indicate that these grew during the period when the metal samples were held at the experimental temperatures, and not during cooling. In consequence, the TiC grains on the crucible wall should be eliminated so as not to be a source of error in determining the titanium solubility.

On the basis of the results of the microscopic examination, the samples for chemical analysis were prepared in the following way; the upper half, including the TiC tablet, of the solidified metal (cf., Photo. 1) was first eliminated by cutting horizontally at the level of 5 mm under the TiC tablet-metal boundary, then the peripheral part was cut off by a thickness of about 1.5 mm, and the rest was crushed into powder with the size of under 150 µ.

3. Experimental Result

The experimental result is shown in Fig. 4 as the relationship between the titanium content in iron saturated with carbon and the holding time of the reaction system at the experimental temperatures: 1 304°C, 1 348°C, 1 391°C, 1 450°C and 1 501°C. The content of titanium in the iron was determined by atomic absorption spectrometry.

III. Experimental Method for Determining Carbon Solubility in Iron with Different Concentrations of Titanium

1. Experimental Apparatus and Procedure

The experimental apparatus is schematically shown in Fig. 5. 1.2 kg of Fe–C alloy in a graphite crucible with the inner diameter of 70 mm was heated up to experimental temperature in a porcelainous tube in an atmosphere of argon of high purity. Then a small amount of TiC was put on the surface of molten iron which was followed by stirring for 5 to 10 days until the TiC completely dissolved. The adding amount of the TiC was so adjusted as the concentration of titanium in iron to be 58 to 84% of the solubility. The control of the atmosphere and temperature of the reaction system was the same as in the case of the experiment for the determination of titanium solubility.

For the accurate determination of carbon solubility, the sedimentation of graphite in the metal phase during sampling was prevented by applying rapid suction of molten iron through a silica tube from the metal pool in the graphite crucible in the way shown in Fig. 6. Before the rapid suction, the tube nose, holding 30 to 50 g of molten sample, was held for an instant just above the surface of the metal pool. By means of this method, the shape of the solid sample sucked into the silica tube was tubelike instead of being rodlike, and the tubelike shape made it possible for the sucked samples to be rapidly cooled. The thickness of the tubelike metal was about 0.5 mm.

2. Microscopy of Cooled Samples and Sample Preparation for Chemical Analysis

Microscopy of the solid samples revealed that there was much less sedimented graphite in the tubelike samples than that usually expected in rodlike samples, and also there was no trace of undissolved TiC particles. After the microscopy, the thin oxide layer on the outer surface of the tubelike samples was polished off. Then the polished samples were crushed into particles with the size of 0.5 to 1 mm for the analysis of carbon, and also with the size of under 150 µ for the analysis of titanium. The carbon con-
tent was determined by conductometric titration, and the titanium by atomic absorption spectrometry.

3. Experimental Result

Figure 7 and Table 1 show the carbon solubility in iron with different concentrations of titanium at the experimental temperatures of 1350°, 1400°, 1450°, and 1500°C. Each point plotted in the figure is the arithmetical average of the values obtained by 5 to 10 times repeated analysis of the same sample. The standard deviation of the values was about 0.028%, and this was much smaller than the value, 0.1%.

Table 1. Carbon solubility in molten Fe-C sat-Ti alloys.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>[Ti]sat (%)</th>
<th>[C]sat (%)</th>
<th>[Ti] sat (%)</th>
<th>[C]sat (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350</td>
<td>0.00</td>
<td>4.80</td>
<td>0.00</td>
<td>4.90</td>
</tr>
<tr>
<td>1400</td>
<td>0.00</td>
<td>4.82</td>
<td>0.00</td>
<td>4.93</td>
</tr>
<tr>
<td>1450</td>
<td>0.18</td>
<td>4.85</td>
<td>0.18</td>
<td>4.93</td>
</tr>
<tr>
<td>1500</td>
<td>0.36</td>
<td>4.88</td>
<td>0.36</td>
<td>4.91</td>
</tr>
</tbody>
</table>

The carbon solubility in Fe-C system, obtained in the present work, was in good agreement with the already reported values. For the sake of reference, Fig. 7 includes the values at 1550° and 1680°C after Neumann and Schenck.

IV. Discussion

1. The Solubility of Titanium in Fe-C sat-Ti System

In the present experimental method ("the diffusion method"), as shown in Fig. 4, the concentration of titanium in iron saturated with carbon attained to a limiting value after a reaction time of 7 or 8 days. After this limiting value was observed, the reaction system was regarded as to be in the equilibrium. This was confirmed as follows. Figure 8 shows the distribution of titanium along the axial direction of the cooled samples. The concentration in the figure is expressed as the counts of the characteristic X-ray per second. There was no concentration gradient in the samples which were held at 1348° and 1450°C.
for more than 10 days. This uniformity in the concentration indicates that the reaction system was in the equilibrium.

The solubility of titanium was determined in terms of the arithmetic mean of the values plotted around the horizontally straight part, which shows the limiting value, of the curve drawn in Fig. 4: 0.46% (1304°C), 0.66% (1348°C), 0.82% (1391°C), 1.09% (1450°C) and 1.43% (1501°C). On the basis of these values, the temperature dependence of the solubility is represented as Eq. (1).

$$\log [\% Ti] = \frac{-6760}{T} + 3.965 \quad (1)$$

In Fig. 9 the values are plotted with those already reported. The values of the present work are higher compared with others. In order to verify the reliability of the present values, another experimental method was devised as follows. The method was based on the elimination of excess titanium dissolved in iron by sedimenting as TiC which floats on the surface of molten iron because of its smaller specific gravity, and this method is hereinafter referred to as “the excess TiC flotation method” in contrast with “the diffusion method” described in the foregoing section. Figure 10 shows the experimental procedure. The experimental result is shown in Fig. 11 in which the data obtained by “the diffusion method” is reproduced for comparison. The concentration of titanium decreased with time, approaching to a limiting value which is in close agreement with the value obtained by “the diffusion method”. The close agreement between the two values obtained by both “the diffusion method” and “the excess TiC flotation method” indicates the reliability of the solubility determined by the present work.

2. The Estimation of the Interaction Coefficient, $\psi_{i}$, in Fe-Csat-Ti System

According to the values plotted in Fig. 7, the solubility of carbon increases linearly with increasing the concentration of titanium. On the basis of the slopes, calculated by the method of least squares, of the straight lines in the figure, the solubility of carbon in Fe-Csat-Ti alloy is represented as follows:

- 4.18+0.17 [\%Ti] for 1350°C
- 4.90+0.186 [\%Ti] for 1400°C
- 5.03+0.181 [\%Ti] for 1450°C
- 5.15+0.171 [\%Ti] for 1500°C

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**Fig. 8.** Variation of titanium concentration in Fe-Csat-Ti alloys with distance from the boundary of metal-TiC tablet, examined by an electron microprobe.

**Fig. 9.** Comparison of the experimental values of titanium solubility in Fe-Csat-Ti alloys at different temperatures.

**Fig. 10.** Procedure for measuring titanium solubility in a molten Fe-Csat-Ti alloy by “the excess TiC flotation method”.

**Fig. 11.** Comparison of the solubility of titanium in a molten Fe-Csat-Ti alloy between “the excess TiC flotation method” and “the diffusion method”.
With these results, the interaction coefficient, \( \varepsilon_T^{\text{th}} \), was estimated by the use of the following four equations:\(^{10} \)

\[
-(\partial \ln N_i/\partial N_{Ti}) = aT_i^0 \\
\varepsilon_T^{\text{th}} = aT_i^0(1+\varepsilon_T^{\text{w}}N_iC) \\
\varepsilon_T^{\text{th}} = 0.00434 \left[N_{Fe}^0 + N_{Fe}^C \frac{M_C}{M_{Fe}^0} \right] \left(\varepsilon_T^{\text{w}} - 1\right) \frac{M_{Fe}^0}{M_{Ti}^0} + 0.00434 \left[1 - \frac{M_{Fe}^C}{M_{Ti}^C}\right] + 1 \\
\varepsilon_T^{\text{w}} = \frac{-0.00434 \left[1 - \frac{M_{Fe}^C}{M_{Ti}^C}\right]}{M_{C}^0 \left(1 - \frac{C}{C} \right)} \\
\varepsilon_T^{\text{th}} = \frac{-0.00434 \left[1 - \frac{M_{Fe}^C}{M_{Ti}^C}\right]}{M_{C}^0 \left(1 - \frac{C}{C} \right)} \\
\varepsilon_T^{\text{w}} = \frac{-0.00434 \left[1 - \frac{M_{Fe}^C}{M_{Ti}^C}\right]}{M_{C}^0 \left(1 - \frac{C}{C} \right)}
\]

where, \( N_i \): mole fraction
\( M_i \): atomic weight
\( C_i \): the weight percent of carbon
\( \varepsilon_T^{\text{w}} \): interaction coefficient on the mole fraction basis
\( \varepsilon_T^{\text{th}} \): interaction coefficient on the weight percent basis.

The value of \( \varepsilon_T^{\text{th}} \) was calculated by Eq. (6).

\[
\ln \tau_i = \ln \tau_i^C (or \ ln \tau_i^C) + \varepsilon_T^{\text{w}} N_i C_i \ (or \ \varepsilon_T^{\text{th}} N_i C_i) \\
\ln \tau_i = \ln \tau_i^C (or \ ln \tau_i^C) + \varepsilon_T^{\text{w}} N_i C_i \ (or \ \varepsilon_T^{\text{th}} N_i C_i)
\]

where, \( \tau_i \): the activity coefficient of carbon
\( \tau_i^C \): the activity coefficient of carbon at infinite dilution
\( \tau_i^C \): the activity coefficient of carbon at austenite saturation
\( \Delta N_i \): the difference of the mole fraction of carbon between arbitrary concentration and infinite dilution or austenite saturation.

Rist and Chipman\(^7 \) and Schenck et al.\(^8 \) found that approximately linear relationship between the logarithm of the activity coefficient of carbon and the mole fraction of carbon holds for the liquid phase in the temperature range up to 1760°C. In the present work, the value of \( \varepsilon_T^{\text{th}} \) was calculated as 10.0 by assuming the linear relationship.\(^9 \) The value of \( \varepsilon_T^{\text{th}} \) was calculated as 0.13 in terms of the conversion formula\(^{10} \) which relates \( \varepsilon_T^{\text{th}} \) with \( \varepsilon_T^{\text{w}} \).

The result of the estimation of \( \varepsilon_T^{\text{th}} \) is shown in Fig. 12: -0.205 (1350°C), -0.209 (1400°C), -0.200 (1450°C) and -0.195 (1500°C). The temperature dependence of the interaction coefficient is represented as follows in terms of the method of least squares:

\[
\varepsilon_T^{\text{th}} = (-221/T) - 0.072 \\
\varepsilon_T^{\text{th}} = (-221/T) - 0.072
\]

Schenck and Steinmetz reported\(^{10} \) the value of the interaction coefficient as -0.229 at temperatures of 1580°C to 1680°C. On the basis of their experimental data\(^3 \) on the carbon solubility (cf. Fig. 7), the interaction coefficient was recalculated as -0.188 by applying the thermodynamic data used and also obtained in the present work. The recalculated value is in good agreement with the value estimated by Eq. (7) (cf. Fig. 12).


For the formation reaction of TiC out of the melt of Fe-Csat-Ti:

\[
Ti + C_{sat} = TiC (s) \\
\]

the standard Gibbs free energy change is written as follows:

\[
\Delta G^o = A + B \cdot T = -RT \cdot \ln K \\
K = a_{TiC}(a_{C2} \cdot a_i) = a_{TiC}(f_{Ti}([%Ti] \cdot a_i) \\

\]

where, \( T \): absolute temperature
\( K \): equilibrium constant
\( a_i \): the activity of species \( i \)
\( f_{Ti} \): the weight percent activity coefficient of Ti.

As the activities of TiC and carbon are allowed to be fixed as unity, the following equation is derived by the rearrangement of Eqs. (9) and (10).

\[
\log [%Ti] + \log f_{Ti} = (\Delta G^o/2.3R T) = (A/2.3RT) + (B/2.3R) \]

where,

\[
\log f_{Ti} = \varepsilon_T^{\text{th}} [\%Ti] + \varepsilon_T^{\text{w}} [\%C]
\]

The enthalpy change, \( \Delta H^o (A) \), is obtained as the slope of the linear relation between the reciprocal of absolute temperature and the left-hand-side terms of Eq. (11) as shown in Fig. 13. The value was -3.05 × 10^4 cal in which the contribution of the temperature dependence of \( \varepsilon_T^{\text{th}} \) was not taken into account, and the value of \( \varepsilon_T^{\text{th}} \) was fixed as 0.042.\(^{11} \) The values of \( \varepsilon_T^{\text{th}} \), \( [%Ti] \) and \( [%C] \) were those obtained in the present work. After the estimation of the enthalpy change, the entropy change, \( \Delta S^o (B) \), was calculated as 13.3 by the use of Eq. (11).

In consequence, the standard Gibbs free energy change for the reaction (8) is expressed as,

\[
\Delta G^o = -30500 + 13.3T \ (\text{cal/mol}) \]

For comparison, the standard Gibbs free energy changes for the reaction (8), calculated by combining the standard Gibbs free energy changes for the reactions (13) and (14), are summarized in Table 2. The value by the present work is approximately the average of those by other researchers.
The standard Gibbs free energy changes for the reaction (14), except for that reported by Chipman, were calculated by the use of the activity coefficients of Ti at infinite dilution, assuming the melt is a regular solution.

V. Summary

(1) The solubility of titanium in Fe-Csat-Ti system was determined in argon atmosphere: 0.46% (1304°C), 0.66% (1348°C), 0.82% (1391°C), 1.09% (1450°C) and 1.43% (1501°C). The temperature dependence of the solubility was expressed as:

\[ \log[\%Ti] = (-6760/T) + 3.965 \]

(2) The solubility of carbon in Fe-Csat-Ti system with different contents of titanium in argon atmosphere was determined as functions of titanium concentration: 4.81% + 0.178[\%Ti] for 1350°C, 4.90% + 0.186[\%Ti] for 1400°C, 5.03% + 0.181[\%Ti] for 1450°C and 5.15% + 0.171[\%Ti] for 1500°C.

(3) On the basis of the relationship between carbon solubility and titanium concentration in Fe-Csat-Ti alloys, the interaction coefficient, \( e_{Ti} \), was estimated as the following: -0.205(1350°C), -0.209(1400°C), -0.200(1450°C) and -0.195(1500°C). The temperature dependence of the coefficient was represented as:

\[ e_{Ti} = (-221/T) - 0.072 \]

(4) The standard Gibbs free energy change for

\[ Ti(s) + C(s) = TiC(s), \quad \Delta G^\circ = -44400 + 3.41T^{1.6} \]  
\[ Ti(s) = Ti \]  \[ TiC(s) \]

was calculated, on the basis of the thermodynamic data obtained by the present work, as the following:

\[ \Delta G^\circ = -30500 + 13.3T \text{ (cal/mol)} \]

REFERENCES