Surface Tension of Liquid Fe–Ti Alloys at 1 823 K

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Surface tension of liquid Fe–Ti alloys has been determined by using the constrained drop method at 1 823 K in Ar–10%H2 gas atmosphere. It was found that the surface tension of liquid Fe–Ti alloy decreases slightly with increasing titanium content. In addition, the surface tension of Fe–Ti alloy was also obtained by a theoretical calculation. It was found that the experimental results became slightly lower than the calculated results with increasing titanium content. This paper also discusses the possible reasons for the slight decrease in the surface tension with increasing the titanium content.

KEY WORDS: surface tension; liquid Fe–Ti alloys; constrained drop method.

1. Introduction

Titanium is added into steel to increase toughness of the heat affected zone of a thick steel plate. Titanium forms titanium oxide (TiOx), on which MnS and TiN is precipitated to be used as a nucleation site of the γ→α phase transformation inside the grain. This titanium is generally added during refining process of molten steel. Surface tension of liquid iron containing titanium and its interfacial tension to titanium oxide are very important thermo-physical properties to the understanding of the nucleation and the growth of titanium oxide inclusions as well as the behavior of gas bubbles or titanium oxide inclusions in front of an advancing solidification front. Basically, the estimation of the interfacial tension requires the knowledge of the accurate surface tension of liquid steel and solid oxide as well as the contact angle between them according to Young’s equation. Therefore, the surface tension data of liquid Fe–Ti alloys are very essential to develop titanium added steels.

Despite the importance of the surface tension of liquid Fe–Ti alloy, only few investigations have been performed due to the difficulties of experiments such as reactions with atmosphere or substrates. Smirnov5) firstly investigated the surface tension of liquid iron containing 0–2.12 mass% Ti and found that the surface tension slightly increased with increasing titanium content. Kishimoto et al.6) found that the surface tension of liquid Fe–Ti alloys decreases with increasing titanium content in the concentration region of 0–2.70 mass% Ti. They suggested that hydrogen used in their experiments might adsorb on the surface site of titanium, because titanium naturally has a lower electro-negativity to form a hydrogenic compound easily, whereas not on the surface site of iron having a higher electro-negativity. Therefore, it was anticipated the adsorbed hydrogen atom decreased the surface tension by about 400 mN/m at most.

In two sets of the previous experiments, however, the surface tension value for pure liquid iron was lowly estimated than the more reliable recent data (1 842(±44) mN/m at 1 823 K). It is considered that the samples used in the experiments might have been contaminated by surface-active impurities such as oxygen and sulfur, which may considerably lower the surface tension of liquid iron-based alloys. Recently, Yokoyama et al.8) examined the surface tension of liquid iron alloys containing 0–0.5 mass% Ti and found that the surface tension decreased when titanium content was lower than 0.1 mass%, but it slightly increased for the higher concentration region. They considered that the surface tension was decreased due to oxygen contamination as well as hydrogen adsorption. They examined the surface tension in argon atmosphere, and concluded that oxygen contamination is inevitable in their experiments. It is very remarkable that the re-estimated surface tension of liquid iron with compensating for the oxygen contamination effect (σFe–O = σFe–O + 7 490 · [at%O]9)) became 1 852 mN/m, almost the same value as the measurements for pure iron by Lee et al.7) Applying the same rule to liquid Fe–Ti alloy, the surface tension was re-estimated to be 1 674 and 1 705 mN/m for the alloys containing 0.15 and 0.5 mass% Ti, respectively. These values are much lower than that of pure iron, which reason has not been clarified properly. Accordingly, it is considered that the surface tension of liquid Fe–Ti alloys has not been properly estimated by experiments.

In the present work, the surface tension of liquid Fe–Ti alloys has been determined in the concentration region of 0.22–1.80 mass% Ti in Ar–10%H2 atmosphere at 1 823 K. In the experiments, we applied the constrained drop method, recently developed by the authors. This method considerably decreases the experimental scatter. For example, the experimental scatter of pure liquid iron has been reduced to ±2.4% by employing the constrained drop
method.7) Typical sessile drop method with the same experimental apparatus for pure liquid iron yields experimental scatter as large as ±6.8%.7) In addition, in the present work the surface tension of Fe–Ti alloy was also obtained by a theoretical calculation, and compared with the experimental results in order to discuss possible reasons of changes in the surface tension with increasing the titanium content.

2. Experimental

2.1. Apparatus and Materials

In the present work, the surface tension was measured by using a graphite-heating-element furnace (T_max = 1 973 K) with a high-resolution CCD camera (1 636×1 236 pixels) as shown in Fig. 1. A He–Ne laser rays (λ=632.8 nm) was used to capture a much clearer image profile of the liquid metal drop. The temperature was measured with a Pt–30%Rh/Pt–6%Rh thermocouple set under the crucible. The temperature was controlled manually within ±1 K. The samples used in the present study were prepared in a cold crucible furnace. Applying this technique, majority of inclusions can be removed from the samples, because large-scale inclusions are gathered on the bottom side of the samples. The chemical composition of each sample is shown in Table 1. Total oxygen content before experiments was about 80–100 mass ppm, but after experiments it reduced to about 8–24 mass ppm. (Table 2) If the samples are in a state of equilibrium with Ti2O3 inclusions before experiments, most of oxygen in the samples might exist as oxide inclusions, because the equilibrium soluble oxygen content is less than 20 mass ppm in most cases. We will discuss this problem later. During experiments, oxygen partial pressure of the sample was controlled by the equilibrium between hydrogen and trace moisture in gas atmosphere, so that it is believed that oxygen as a state of oxide was removed by the reaction with hydrogen gas. In addition, since sulfur content was less than 3 mass ppm, it is considered that the surface tension values obtained in the present work have not been lowered by the contamination of surface-active element sulfur. After experiments, it was confirmed that the change in the composition of titanium was negligible.

2.2. Procedure

The sample metal was prepared as cylindrical pieces of 8 mm in diameter, and used after removing surface contaminants with a grit paper and washed in acetone using an ultrasonic cleaner. After the sample was placed in a specially designed alumina crucible7) at the center of the furnace, the reaction furnace was sealed and evacuated, and then a purified Ar–10%H2 gas mixture was introduced for 12 h. Then, the furnace was heated to the experimental temperature in 2–2.5 h. After the sample melted, the surface tension measurements started. The shape of a sample was investigated with a high-resolution CCD camera. Then, the surface tension of liquid Fe–Ti alloy gradually increased with time. In Fig. 2, a typical example of the surface tension change for the Fe–0.46 mass% Ti alloy is shown as a function of time. With increasing time, the surface tension gradually increases and reaches an equilibrium value. The higher the concentration of titanium, the longer the time to reach the equilibrium value. As can be found in the following section, it may be related to the stronger affinity of oxygen to titanium rather than iron. The whole image processing sequences and experimental details are reported in our previous contribution.7)
3. Results and Discussion

The surface tension of liquid Fe–Ti alloys in the concentration region of 0.22–1.80 mass% Ti was measured at 1823 K, and all measurements were plotted in Fig. 3. It is noteworthy that the surface tension slightly decreases with increasing the titanium concentration. In addition, the present results show higher values than the reported ones.5,6,8) As addressed before, it is considered that the samples used in the previous experiments might have been contaminated by surface-active impurities such as oxygen and sulfur.

Theoretically, the surface tension of liquid Fe–Ti alloys can be calculated by applying Butler’s model with available thermodynamic and thermo-physical data.11) Butler’s model is expressed by Eq. (1) for the Fe–Ti binary alloys.

\[
\sigma = \sigma_{Fe} + \frac{RT}{A_{Fe}} \ln \left( \frac{1 - N_{c}^{s}}{1 - N_{c}^{b}} \right) + \frac{1}{A_{Fe}} \left( \bar{G}^{Ex,s}_{Fe} (T, N_{c}^{s}) - \bar{G}^{Ex,b}_{Fe} (T, N_{c}^{b}) \right)
\]

\[
= \sigma_{Ti} + \frac{RT}{A_{Ti}} \ln \left( \frac{N_{c}^{s}}{N_{c}^{b}} \right) + \frac{1}{A_{Ti}} \left( \bar{G}^{Ex,s}_{Ti} (T, N_{c}^{s}) - \bar{G}^{Ex,b}_{Ti} (T, N_{c}^{b}) \right) \quad \text{(1)}
\]

where \( R \) is universal gas constant; \( T \) is temperature; \( N_{c}^{s} \) is the mole fraction of \( i \) in the surface; \( N_{c}^{b} \) is the mole fraction of \( i \) in the bulk; \( G^{Ex,s}_{i} (T, N_{c}^{s}) \) is the partial excess free energy of \( i \) in the surface as a function of \( T \) and \( N_{c}^{s} \); \( G^{Ex,b}_{i} (T, N_{c}^{b}) \) is the partial excess free energy of \( i \) in the bulk as a function of \( T \) and \( N_{c}^{b} \); \( A_{c} \) is the molar surface area of component \( i \) (\( A_{c} = 1.091 \times (6.02 \times 10^{23})^{1/3}, V_{r}^{23} \), where \( V_{r} \) is the molar volume of the element \( i \). The constant 1.091 is introduced on the hypotheses of the close-packed configuration in a monolayer.12) The partial excess free energy in the surface is obtained using Eq. (2) assuming that the partial excess Gibbs energy in the bulk and the surface have the same concentration dependence.

\[
\bar{G}^{Ex,s}_{i} (T, N_{c}^{s}) = \bar{G}^{Ex,b}_{i} (T, N_{c}^{b}) \quad \text{(2)}
\]

The constant \( \beta \) (0.83) is the value of pure metals determined from the bonding energy difference between the surface and the bulk, which is generally applied to alloys.14) Solving Eq. (1) by instituting the thermo-physical data and the excess free energy of liquid Fe–Ti alloys listed in Table 3, the surface tension is calculated as a function of the bulk concentration at 1823 K.

The calculated surface tensions (solid line) are plotted in Fig. 4 together with the experimental results. There are slight differences between the calculations and the measurements, and this difference increases with increasing the titanium concentration (67 mN/m at most). In order to make the measurements and the calculation results accord with

| Table 3. Thermodynamic and thermo-physical data for calculation. |
|---|---|---|
| Data | ref | at \( T = 1823 \text{ K} \) |
| \( \sigma_{Fe} (\text{mN/m}^{-1}) = 2110 - 0.1437T \text{(K)} \) | 7) | 1849 (mN/m\(^{-1}\)) |
| \( \sigma_{Ni} (\text{mN/m}^{-1}) = 1860 - 0.1567T \text{(K)} \) | 15) | 1576 (mN/m\(^{-1}\)) |
| \( V_{c}^{Fe} \left( \text{m}^{3}\text{mol}^{-1} \right) = 7.94 \times 10^{-2} + 0.13 \times (T - 1811) \) | 16) | 7.95 \times 10^{-2} (m\(^{3}\)mol\(^{-1}\)) |
| \( V_{c}^{Ni} \left( \text{m}^{3}\text{mol}^{-1} \right) = 11.6 \times 10^{-2} + 0.56 \times 10^{-2} \times (T - 1914) \) | 16) | 1.15 \times 10^{-2} (m\(^{3}\)mol\(^{-1}\)) |
| \( G^{Ex,s}_{Fe} \left( \text{kJmol}^{-1} \right) = X_{c}^{Fe} X_{f}^{Fe} [(-6.7589 + 9.8093T) - 4731] \) | 17) | -54438X_{c}^{Fe} X_{f}^{Fe} (kJmol\(^{-1}\)) |

Fig. 3. Surface tension of liquid Fe–Ti alloys at 1823 K.

Fig. 4. The calculated results of the surface tension and the surface concentration of Fe–Ti alloys.
each other, the surface tension of liquid Ti should be
836 mN/m at 1823 K, which is about half of the reported
value in the state of under-cooling.\(^\text{13}\) Thus, it is considered
that the experimental results in the present work has been
lowly estimated due to some reasons.

Firstly, we may consider the changes of oxygen affinity
to the surface of molten Fe–Ti alloys by increasing titanium
concentration as a reason. Recently, Lee \textit{et al.}\(^\text{18}\) found that
the oxygen adsorption on liquid Fe–Cr alloys remarkably
increased with increasing chromium content at constant
oxygen partial pressure. They considered that alloying ele-
ments (in this case, chromium) having stronger affinity to
oxygen than iron increased the oxygen adsorption.
Similarly, it is likely that titanium of liquid Fe–Ti alloy rein-
forced the adsorption of oxygen on the surface. Chemically,
the oxygen adsorbed on the metal surface can be equilibra-
ted with the soluble oxygen in the bulk metal. The soluble
oxygen content is calculated by using the standard Gibbs
energy change of the dissolution of titanium and oxygen in
liquid iron.\(^\text{19,20}\)

\[
\text{Ti}_2\text{O}_3 (s) = 2\text{Ti} + 3\text{O} \quad \cdots \cdots \cdots \cdots (1)
\]

\[
\Delta G^\circ = 403000 \text{ [J]} \quad \text{(at 1823 K)} \quad \cdots \cdots \cdots \cdots (2)
\]

\[
\log K_e = 2 \log [\%\text{Ti}] + 2 \log f_{\text{Ti}} + 3 \log [\%\text{O}] + 3 \log f_o - \log a_{\text{IO}_2} \quad \cdots \cdots \cdots \cdots (3)
\]

\[
\log f_{\text{Ti}} = e_{\text{Ti}}^{(\circ)}[\%\text{Ti}] + e_{\text{Ti}}^{(\circ)}[\%\text{O}] \quad \cdots \cdots \cdots \cdots (4)
\]

\[
\log f_o = e_o^{(\circ)}[\%\text{Ti}] + e_o^{(\circ)}[\%\text{O}] \quad \cdots \cdots \cdots \cdots (5)
\]

where \(e_{\text{Ti}}^{(\circ)}, e_o^{(\circ)}\) and \(e_o^{(\circ)}\) are 0.043, \(-3.49\), \(-1.15\) and
\(-0.20\), respectively.\(^\text{14}\) The calculated soluble oxygen con-
tent in most samples (except the sample containing
1.8 mass\% Ti) is as low as 7–15 mass ppm, which is very
lower level than those before experiments, but closer to
those after experiments. (Table 2) During experiments, a
strong reducing atmosphere was maintained by flowing Ar–
H\(_2\) gas. Accordingly, the following reaction mechanism can
be considered: 1) initially at the surface soluble oxygen is
removed by the reaction with hydrogen gas, 2) a concentra-
tion gradient of oxygen in the sample or surface layer oc-
curs and, Marangoni flow by local difference in surface ten-
sion might cause a mass transportation of oxygen from bulk
to surface, and 3) successive dissolution of the titanium
oxide (Ti\(_2\)O\(_3\)) in bulk is followed. In such a case, however,
oxygen on the surface can have the same as or lower chemi-
ical potential than that of the oxygen in the bulk. Assuming
that the oxygen contamination is the major reason for the
lower surface tension in measurements, it is considered to
be related to the strong affinity of titanium to oxygen. Thus,
desorption of oxygen can be the rate-determining step.
However, it is impossible to evaluate quantitatively the ef-
fect of oxygen on the surface tension of Fe–Ti alloys at the
moment.

Another possible reason is the adsorption of hydrogen on
the surface as suggested by Kishimoto \textit{et al.}\(^\text{6}\) In the present
work, we investigated the change in surface tension of Fe–
0.91 mass\% Ti alloys during reduction by switching the at-
mosphere Ar–H\(_2\) → Ar → Ar–H\(_2\). In Fig. 5, the surface ten-
sion change of the liquid Fe–Ti alloy due to the change in
atmosphere is shown. It is found that when the gas atmos-
phere was switched from argon gas (open circles) to
Ar–H\(_2\) gas mixture (solid circles), surface tension suddenly
decreased by 50 mN/m. Initially, the surface tension in-
creased with time, because the oxygen was removed by hy-
drogen. When the gas atmosphere was shifted into argon
gas, oxygen cannot be removed further more and the sur-
face tension maintains almost a constant value, whereas by
re-introducing Ar–H\(_2\) gas mixture the surface tension sud-
denly decreased. After about 70 min, surface tension starts
to re-increase because hydrogen reduces the oxygen in the
surface again, and finally it reaches to the value shown in
Fig. 3. In pure argon gas atmosphere, it was impossible to
investigate the surface tension values as high as those in
Ar–H\(_2\) gas mixture as reported by Yokoyama \textit{et al.}\(^\text{8}\)
Probably, it is related to residual oxygen in the introducing
argon gas. From the Butler’s model, it is found that without
oxygen or hydrogen the surface concentration of titanium
is almost the same as that of the bulk. (Fig. 4(b)) Con-
sequently, it can be anticipated that the hydrogen adsorbs
on the titanium site of the surface, and the hydrogen adsorp-
tion increases with increasing the concentration of titanium,
qualitatively. On the other hand, in the presence of oxygen,
once oxygen previously occupies the surface sites, the
chance for hydrogen to adsorb on the metal surface will de-
crease, because oxygen would occupy both titanium and
iron sites (or preferentially on the titanium sites). Then, the
adsorption of hydrogen along with oxygen would show
smaller effect on the surface tension decrease than that
without oxygen, \textit{i.e.}, the surface tension at the point (b)
in Fig. 5 would have stronger effect by hydrogen than the
point (a) in Fig. 5. Namely, surface tension of Fe–
0.91 mass\% Ti in a hypothetical condition of pure hydrogen
atmosphere without oxygen may be decreased by more than
50 mN/m compared with the calculated values without oxy-
gen and hydrogen. As found in Fig. 4, the difference in sur-
face tension between the measurement and calculation for

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Variation of the surface tension of liquid Fe–0.91 mass\% Ti alloy with increasing time. During experi-
ments, gas atmosphere was switched into Ar for 2 h. In
the atmosphere of Ar gas (open circles), the surface ten-
sion maintains almost a constant value. Once the gas at-
mosphere returns to Ar–10\%H\(_2\), the surface tension sud-
denly decreases by about 50 mN/m.}
\label{fig:fig5}
\end{figure}
the sample of the Fe–1.8mass%Ti alloys is 67 mN/m. Based upon this, it seems that the hydrogen adsorption decreases the surface tension values with increasing the concentration of titanium in Ar–H₂ atmosphere. In addition, it should be noted that even if hydrogen adsorption decreased the surface tension of liquid Fe–Ti alloys, the decrease in surface tension would not be so considerable as suggested by Kishimoto et al. (400 mN/m). It is considered that the reported values were lowly estimated due to both oxygen and hydrogen adsorption.

At the moment, however, it is very difficult to say which element dominantly affects the surface tension decrease in the present measurements (even though it is believed that the effect of hydrogen adsorption on the surface tension decrease is much stronger than oxygen in the present experimental condition), because the adsorption mechanism of hydrogen adsorption without oxygen was not investigated directly. In order to clarify the mechanism of the competitive adsorption of oxygen and hydrogen, additional experimental data and an acceptable adsorption model are anticipated. Nevertheless, in the present work, the surface tension of liquid Fe–Ti was determined by the constrained drop method more precisely, and it was confirmed that the surface tension of liquid Fe–Ti alloys shows much smaller dependence on the titanium content than the reported ones.

4. Conclusions

In the present study, the surface tension of liquid Fe–Ti alloys has been determined by using the constrained drop method at 1 823 K in an atmosphere of Ar–10%H₂ gas mixture. It was found that the surface tension of liquid Fe–Ti alloy slightly decreases with increasing titanium content. It is considered that the slight decrease in surface tension values with increasing the titanium content in the present study is due to the adsorption of oxygen and/or hydrogen on the surface at the titanium sites. However, even if hydrogen or oxygen adsorption decreases the surface tension of liquid Fe–Ti alloys, the decrease in surface tension would not be so considerable as suggested by previous researchers.

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