

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% H_2 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 (TiO_x), on which MnS and TiN is precipitated to be used as a nucleation site of the $\gamma \rightarrow \alpha$ phase transformation inside the grain.¹⁾ 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 steel solidification front.^{2–4)} 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.⁶⁾ 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)⁷⁾ 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 by compensating for the oxygen contamination effect ($\sigma_{Fe} = \sigma_{Fe-O} + 7\,490 \cdot [at\%O]^9$) 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% H_2 atmosphere at 1 823 K. In the experiments, we applied the constrained drop method, recently developed by the authors.^{7,10)} This method considerably decreases the experimental scatter. For example, the experimental scatter of pure liquid iron has been reduced to $\pm 2.4\%$ 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 $\pm 6.8\%$.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 ($T_{\text{Max.}}=1973\text{ K}$) with a high-resolution CCD camera (1636×1236 pixels) as shown in Fig. 1. A He–Ne laser rays ($\lambda=632.8\text{ nm}$) 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 $\pm 1\text{ K}$. 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 Ti_2O_3 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% H_2 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 the liquid metal was calculated with a computer program. 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

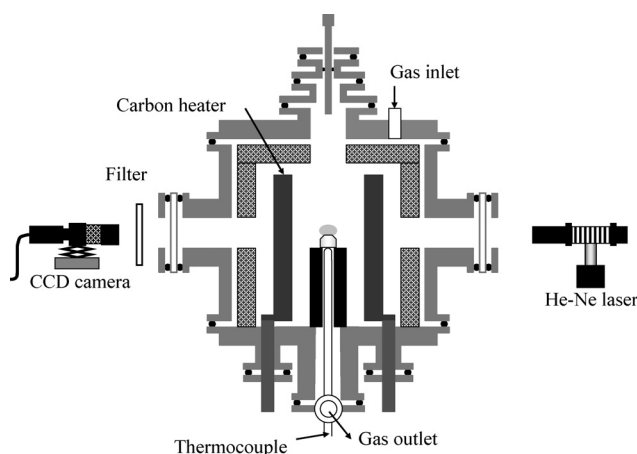


Fig. 1. Schematic diagram of the experimental apparatus.

Table 1. Chemical composition of the samples.

alloys	Chemical composition / mass%							
	C	Si	Mn	P	S	Ti	O*	N
No.1	0.0017	0.007	<0.002	<0.002	<0.0003	0.22	0.0092	0.0013
No.2	0.0021	0.007	<0.002	<0.002	<0.0003	0.33	0.0078	0.0014
No.3	0.0021	0.007	<0.002	<0.002	<0.0003	0.46	0.0084	0.0013
No.4	0.0034	0.008	<0.002	<0.002	<0.0003	0.91	0.0082	0.0012
No.5	0.0019	0.006	<0.002	<0.002	<0.0003	1.80	0.0100	0.0017

*total oxygen

Table 2. Oxygen content in the samples after experiments.

	Oxygen content / mass ppm				
	No.1	No.2	No.3	No.4	No.5
Total O (Meas.)	12	12	8	24	18
Soluble O (Cal.)	7	7	8	15	106*

* It is considered that the soluble oxygen content was highly evaluated due to uncertainty of thermodynamic data such as interaction parameters.

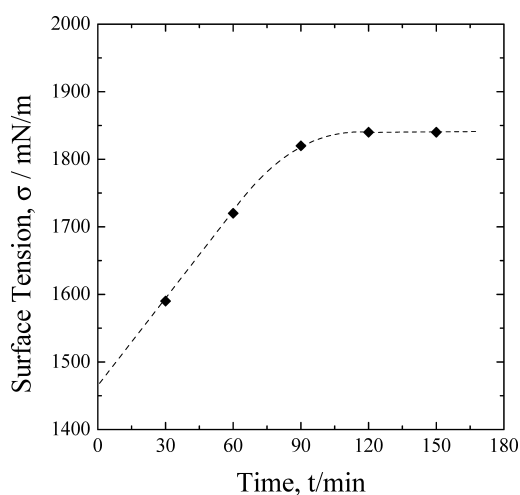


Fig. 2. Variation of the surface tension of liquid Fe–0.46 mass%Ti alloy with increasing time.

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⁾

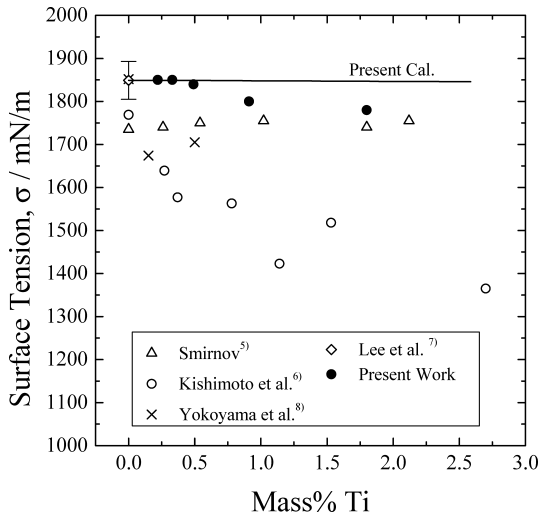


Fig. 3. Surface tension of liquid Fe-Ti alloys at 1823 K.

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.

$$\begin{aligned} \sigma &= \sigma_{Fe} + \frac{RT}{A_{Fe}} \ln \left(\frac{1 - N_{Ti}^s}{1 - N_{Ti}^b} \right) \\ &+ \frac{1}{A_{Fe}} (\bar{G}_{Fe}^{Ex,s}(T, N_{Ti}^s) - \bar{G}_{Fe}^{Ex,b}(T, N_{Ti}^b)) \\ &= \sigma_{Ti} + \frac{RT}{A_{Ti}} \ln \left(\frac{N_{Ti}^s}{N_{Ti}^b} \right) \\ &+ \frac{1}{A_{Ti}} (\bar{G}_{Ti}^{Ex,s}(T, N_{Ti}^s) - \bar{G}_{Ti}^{Ex,b}(T, N_{Ti}^b)) \dots\dots\dots(1) \end{aligned}$$

where R is universal gas constant; T , is temperature; N_i^s is the mole fraction of i in the surface; N_i^b is the mole fraction of i in the bulk; $\bar{G}_i^{Ex,s}(T, N_i^s)$ is the partial excess free energy of i in the surface as a function of T and N_i^s ; $\bar{G}_i^{Ex,b}(T, N_i^b)$ is the partial excess free energy of i in the bulk as a function of T and N_i^b . A_i is the molar surface area of component i ($A_i = 1.091 \cdot (6.02 \cdot 10^{23})^{1/3} \cdot V_i^{2/3}$, where V_i 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.

Table 3. Thermodynamic and thermo-physical data for calculation.

Data	ref	at T=1823K
$\sigma_{Fe}(mNm^{-1}) = 2110 - 0.1437(T)$	7)	1849 (mNm^{-1})
$\sigma_{Ti}(mNm^{-1}) = 1860 - 0.1567(T)$	15)	1576 (mNm^{-1})
$V_{Fe}(m^3mol^{-1}) = 7.94 \times 10^{-6} \times [1 + 1.3 \times 10^{-4} \times (T - 1811)]$	16)	$7.95 \times 10^{-6}(m^3mol^{-1})$
$V_{Ti}(m^3mol^{-1}) = 11.6 \times 10^{-6} \times [1 + 0.56 \times 10^{-4} \times (T - 1914)]$	16)	$1.15 \times 10^{-5}(m^3mol^{-1})$
$G_{Fe,Ti}^{Ex}(Jmol^{-1}) = X_{Fe}X_{Ti}\{-67589 + 9.809 \times T\} - 4731$	17)	$-54438X_{Fe}X_{Ti}(Jmol^{-1})$

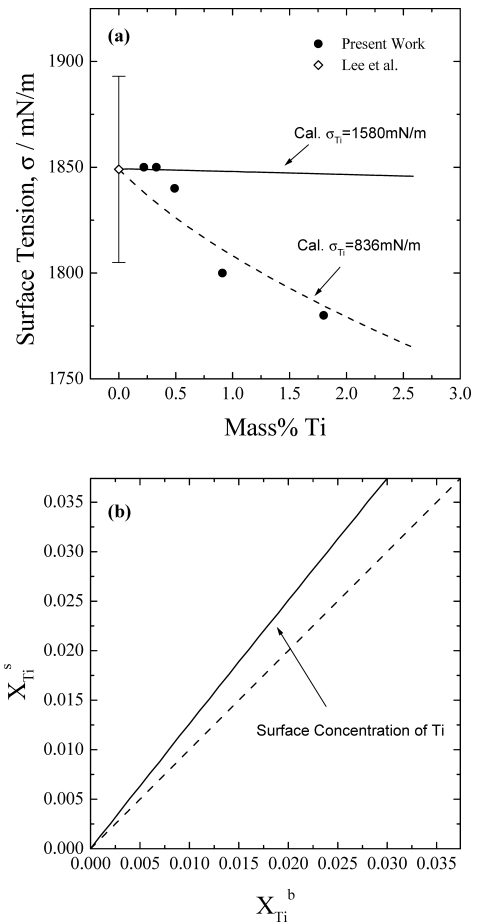


Fig. 4. The calculated results of the surface tension and the surface concentration of Fe-Ti alloys.

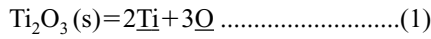
$$\bar{G}_i^{Ex,s}(T, N_i^s) = \beta \cdot \bar{G}_i^{Ex,b}(T, N_i^b) \dots\dots\dots(2)^{13}$$

The constant β ($=0.83$) 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

each other, the surface tension of liquid Ti should be 836 mN/m at 1 823 K, which is about half of the reported value in the state of under-cooling.¹⁵⁾ 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 *et al.*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 elements (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 reinforced the adsorption of oxygen on the surface. Chemically, the oxygen adsorbed on the metal surface can be equilibrated 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.^{19,20)}



$$\Delta G_1^\circ = 403\,000 \text{ [J]} \quad (\text{at } 1\,823 \text{ K}) \dots\dots\dots(2)$$

$$\log K_1 = 2 \log [\% \text{Ti}] + 2 \log f_{\text{Ti}} + 3 \log [\% \text{O}] + 3 \log f_{\text{O}} - \log a_{\text{Ti}_2\text{O}_3} \dots\dots\dots(3)$$

$$\log f_{\text{Ti}} = e_{\text{Ti}}^{\text{Ti}} [\% \text{Ti}] + e_{\text{Ti}}^{\text{O}} [\% \text{O}] \dots\dots\dots(4)$$

$$\log f_{\text{O}} = e_{\text{O}}^{\text{Ti}} [\% \text{Ti}] + e_{\text{O}}^{\text{O}} [\% \text{O}] \dots\dots\dots(5)$$

where $e_{\text{Ti}}^{\text{Ti}}$, e_{Ti}^{O} , e_{O}^{Ti} and e_{O}^{O} are 0.043, -3.49 , -1.15 and -0.20 , respectively.¹⁴⁾ The calculated soluble oxygen content 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–H₂ 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 concentration gradient of oxygen in the sample or surface layer occurs and, Marangoni flow by local difference in surface tension might cause a mass transportation of oxygen from bulk to surface, and 3) successive dissolution of the titanium oxide (Ti₂O₃) in bulk is followed. In such a case, however, oxygen on the surface can have the same as or lower chemical 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 effect 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 *et al.*⁶⁾ In the present work, we investigated the change in surface tension of Fe–0.91 mass% Ti alloys during reduction by switching the atmosphere Ar–H₂ → Ar → Ar–H₂. In Fig. 5, the surface ten-

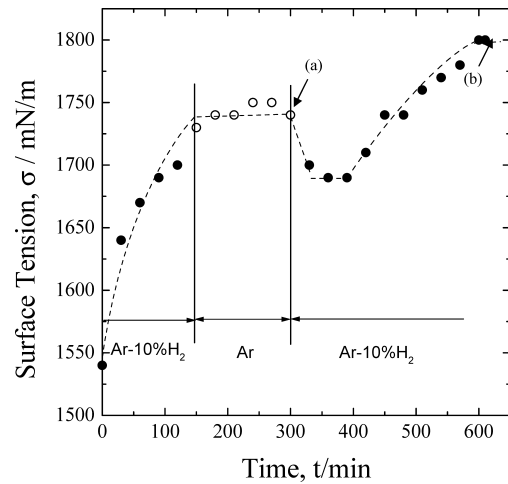


Fig. 5. Variation of the surface tension of liquid Fe–0.91 mass% Ti alloy with increasing time. During experiments, gas atmosphere was switched into Ar for 2 h. In the atmosphere of Ar gas (open circles), the surface tension maintains almost a constant value. Once the gas atmosphere returns to Ar–10% H₂, the surface tension suddenly decreases by about 50 mN/m.

sion change of the liquid Fe–Ti alloy due to the change in atmosphere is shown. It is found that when the gas atmosphere was switched from argon gas (open circles) to Ar–H₂ gas mixture (solid circles), surface tension suddenly decreased by 50 mN/m. Initially, the surface tension increased with time, because the oxygen was removed by hydrogen. When the gas atmosphere was shifted into argon gas, oxygen cannot be removed further more and the surface tension maintains almost a constant value, whereas by re-introducing Ar–H₂ gas mixture the surface tension suddenly 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–H₂ gas mixture as reported by Yokoyama *et al.*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)) Consequently, it can be anticipated that the hydrogen adsorbs on the titanium site of the surface, and the hydrogen adsorption 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 decrease, 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, *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 oxygen and hydrogen. As found in Fig. 4, the difference in surface tension between the measurement and calculation for

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).⁴⁾ 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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