



Article

# Round-Robin Measurement of Surface Tension for Liquid Titanium by Electromagnetic Levitation (EML) and Electrostatic Levitation (ESL)

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Abstract: To accurately measure the surface tension of liquid titanium free of contamination from chemical reaction with the supporting materials and dissolution of atmospheric oxygen, the measurement was performed by using electromagnetic levitation (EML) and electrostatic levitation (ESL) in consideration of the influence of oxygen partial pressure of the measurement atmosphere,  $P_{O_2}$ . When liquid titanium was maintained at 2000 K under Ar–He gas with  $P_{
m O_2}$  of 10 Pa flowing at 2 L·min $^{-1}$ using EML, the surface tension decreased with time due to the dissolution of atmospheric oxygen into the sample. When the  $P_{O_2}$  of the gas was decreased to  $10^{-2}$  Pa, the oxygen content and the surface tension were confirmed to not vary, even after 120 min. Even though  $P_{O_2}$  further decreased to  $10^{-11}$  Pa under Ar–He–H $_2$  gas, the surface tension slightly increased with time due to gas phase equilibrium between  $H_2$  and  $H_2O$  that allowed for a continuous dissolution of atmospheric oxygen into the liquid titanium. The surface tension of liquid titanium measured by ESL, which prevents contamination of the sample from supporting materials and the high  $10^{-5}$  Pa vacuum inhibits the dissolution of oxygen, showed almost the same value as that measured under Ar-He gas at PO, of  $10^{-2}$  Pa by EML. From the measurement results of EML and ESL, the surface tension of the 99.98 mass % pure liquid titanium, free from any contaminations from chemical reactions, with the supporting material and dissolved oxygen was expressed as  $\sigma_{99.98\%} = 1613 - 0.2049(T - 1941) (10^{-3} \text{ N·m}^{-1}).$ 

**Keywords:** surface tension; liquid titanium; oxygen dissolution; oxygen partial pressure; round-robin measurement; electromagnetic levitation; electrostatic levitation



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#### 1. Introduction

To improve and optimize various high-value-added high temperature melt processes, such as the reliable welding and precise casting of aerospace parts, numerical simulation is playing an increasingly important role. Thus, accurate data of the surface tension and its temperature dependence for the surface tension of liquid metals and alloys are indispensable when considering the effects of a free surface shape of a melt and the heat/mass transportation through Marangoni convection. However, the reported data of surface tension for liquid titanium show a large-scale scattering [1–16].

One possible reason for the scatter in the literature data is that the influence of the partial oxygen pressure of the atmospheric gas,  $P_{\rm O_2}$ , on the surface tension has not been sufficiently considered in many studies. The adsorption of atmospheric oxygen often lowers the surface tension of metallic melts [17–23]. Moreover, the oxygen content in liquid titanium may increase with time due to the dissolution from the atmosphere until

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saturation during surface tension measurements since oxygen solubility in titanium is significantly high. Although Brillo et al. [2] reported on the influence of oxygen content on the surface tension of liquid titanium using electromagnetic levitation (EML), their measurement results showed a large scatter beyond their suggested influence of oxygen, even when the oxygen content in the sample was almost the same, indicating that some inherent error may have been affecting their measurement.

Another possibility is the difficulty in suppressing the contamination of the sample from the supporting materials at high temperature when the measurement is carried out using a container method. The surface tension of liquid metals is usually affected by trace impurities.

In the present study, the surface tension of liquid titanium was measured with the oscillating droplet method using the electromagnetic levitation (EML) technique [21–26]. The EML technique enables us to measure the surface tension of liquid metals over a wide temperature range, including undercooling conditions. This is attributed to the sample not being in contact with the container, which is chemically reactive with the sample at high temperatures and plays a role in the nucleation site below the melting point. An extension of the temperature range of the measurement would result in a reduction in the uncertainty of the measurement for the temperature coefficient. Furthermore, the  $P_{O_2}$ of the measurement atmosphere can be controlled in the EML technique. Although the electrostatic levitation (ESL) technique can also realize a container-free condition, it is very difficult to control the  $P_{O_2}$  due to a discharge from electrodes when an ambient gas is introduced. One purpose of this study was to accurately measure the surface tension of liquid titanium under contamination-free conditions, even at a very high temperature, while considering the influence of dissolved atmospheric oxygen in the sample. After the influence of  $P_{O_2}$  on the surface tension had been confirmed, a round-robin measurement was carried out using the electrostatic levitation (ESL) technique [27–29] to confirm the validity of the measurement results using EML.

### 2. Experimental Procedure

## 2.1. Electromagnetic Levitation (EML)

Two titanium samples with the different mass purities of 99.98% (99.95 at. %) and 99.5% (98.1 at. %) were used. Tables 1 and 2 show the nominal compositions of the samples. A rectangular sample with a mass of 410–680 mg cut from an ingot was chemically cleaned in a fluonitric acid solution using an ultrasonic cleaning machine and then placed on a quartz holder. The sample was electromagnetically levitated and then inductively melted under a mixture of high-purity Ar, He, and  $O_2$  gases with  $P_{O_2}$  of  $10^{-2}$  and 10 Pa flowing at 2 L·min<sup>-1</sup>. For comparison, the sample was also melted under Ar–He–10 vol. %  $H_2$ mixed gas, which has often been used to lower the  $P_{O_2}$  in many studies of the surface tension measurement of metallic melts. The nominal partial pressure of  $H_2O(g)$  in the Ar–He–10 vol. % H<sub>2</sub> gas was about  $2.7 \times 10^{-1}$  Pa. The  $P_{O_2}$  of the inlet gas was measured using a zirconia-type oxygen sensor operated at 1008 K, which was calibrated using the oxidation and reduction reactions of metals such as nickel and iron [30]. Semiconductor laser heating was superimposed on the levitated droplet sample sufficiently above its melting temperature. The temperature of the levitated droplet was controlled by varying the output power of the laser, and the partial pressure of argon and helium gases. A monochromatic pyrometer was used to measure the temperature of the levitated droplet.

**Table 1.** Nominal composition of titanium sample with mass purity of 99.98% (mass ppm).

Al	С	Ca	Cr	Cu	Fe	K	Mg	Mn
0.69	<10	<1	0.39	0.4	0.35	< 0.01	< 0.01	0.1
N	Ni	O	S	Si	Th	U	V	Zn
<10	0.54	110	<10	1.4	< 0.0001	< 0.0001	0.03	< 0.05

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<b>Table 2.</b> Nominal co	mposition of titanium s	sample with mass	purity of 99.	.5% (mass ppm).

С	Fe	Н	N	О
800	2000	150	300	1800

After the indicated temperature and  $P_{\rm O_2}$  values had become constant, the oscillation behavior of the droplet was observed from above using a high-speed video (HSV) camera (500 FPS for 16 s). The frequencies of the surface oscillations of  $m=0,\pm 1$ , and  $\pm 2$  for the l=2 mode and those of the center of gravity (oscillations of the m=0 and  $\pm 1$  for the l=1 mode) were analyzed from time-sequenced data of the HSV images using fast Fourier transformation (FFT) and the maximum entropy method (MEM). The influence of the apparent droplet rotations, induced from the phase differences between m=+1 and m=-1, and m=+2 and m=-2 was considered, as well as that of a real rotation in the analysis [22–26]. The surface tension of liquid titanium was calculated from these frequencies using the following Rayleigh equation [31], calibrated with the Cummings and Blackburn equation [32].

$$\sigma = \frac{3}{8}\pi M \left[ \frac{1}{5} \sum_{m=-2}^{2} f_{2,m}^{2} - f_{t}^{2} \left\{ 1.905 + 1.200 \times \left( \frac{g}{8\pi^{2} f_{t}^{2}} \sqrt[3]{\frac{3M}{4\pi\rho}} \right)^{2} \right\} \right]$$
 (1)

where  $\sigma$  is the surface tension, M is the sample mass,  $f_{2,m}$  is the frequency of surface oscillation for the l=2 mode,  $f_t$  is the frequency of motion of the center of gravity of the droplet, g is the gravitational acceleration, and  $\rho$  is the density of liquid titanium.  $\rho$  was determined from the following equation, measured by ESL [33].

$$\rho = 4193 - 0.23762(T - 1941) \left( \text{kg·m}^{-3} \right), \tag{2}$$

where T is the temperature. The details of our EML facility and measurement method can be found elsewhere [21–26].

Uncertainty for the measurement was evaluated on the basis of the ISO Guide to the Expression of Uncertainty in Measurement (GUM) [34]. The oxygen content of the sample after the surface tension measurement was analyzed using an inert-gas fusion oxygen analyzer.

### 2.2. Electrostatic Levitation (ESL)

A cubic sample with side lengths of about 1.7 mm (about 22 mg) was placed between a pair of disk electrodes in a vacuum chamber. The chamber was evacuated to the order of  $10^{-5}$  Pa using a turbomolecular pump backed up by a scroll pump. The sample was electrostatically levitated by applying a high voltage between the electrodes. The levitated sample was melted and then heated by irradiation with  $100 \text{ W CO}_2$  lasers from three directions to minimize the horizontal movement of the levitated sample and to enhance temperature homogeneity [28,29]. The sample temperature was measured using a monochromatic pyrometer. The rotation of levitated droplet was controlled by a rotating magnetic field from four coils beneath the bottom electrode or by appropriately aligning the  $CO_2$  laser beams. The surface tension measurement system used in ESL is described in [35]. The surface oscillations of m=0 for the l=2 mode was induced in the levitated droplet by superimposing a small sinusoidal electric field on the levitation field.

The oscillation behavior of the droplet was monitored from the horizontal direction by an oscillation detection system composed of a power meter with a vertical slit. A collimated laser beam projects a shadow of the levitated sample onto the power meter, and the fluctuation of the vertical diameter of the molten sample was measured using the sampling frequency of 4096 Hz. The measured signal was analyzed through a fast Fourier transformation to obtain the frequency of the m = 0 oscillation for the l = 2 mode.

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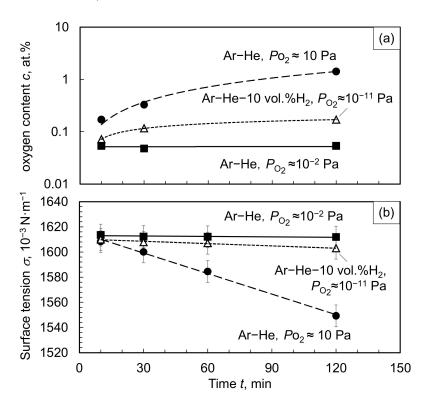
The surface tension of liquid titanium was calculated from the frequency of m = 0 oscillation using the following Rayleigh equation [31,36], modified for nonuniform surface charge distribution [27,37].

$$\sigma = \frac{r_0^3 \rho}{8} \left\{ (2\pi f_{2c})^2 - \frac{Q^2}{8\pi^2 r_0^6 \rho \epsilon_0} \right\} (1 - F), \tag{3}$$

where  $r_0$  is the radius of spherical droplet,  $f_{2c}$  is the frequency of surface oscillation of the m = 0 for the l = 2 mode, Q is the sample charge, and  $\varepsilon_0$  is the permittivity under vacuum.

### 3. Results

Figure 1 shows the time dependence of oxygen content in 99.98 mass % pure liquid titanium and the corresponding surface tension when it was maintained at 2000 K under flowing Ar–He–O<sub>2</sub> gas and Ar–He–10 vol. % H<sub>2</sub> gas using EML. The largest value of uncertainty in each measurement plot of the surface tension was  $\pm 9.6 \times 10^{-3}~\rm N\cdot m^{-1}$  for a selected coverage factor of  $k_{\rm p}=2$  corresponding to a 95.45% confidence interval. The corresponding uncertainty budget is shown in Table 3. When the liquid titanium was maintained under a flowing mixture of Ar–He–O<sub>2</sub> gas at  $P_{\rm O_2}$  of ~10 Pa (•) by EML, the oxygen content in the sample increases with time, resulting in a decrease in surface tension. This confirms that oxygen dissolves into the liquid titanium from the Ar–He gas at  $P_{\rm O_2}$  of ~10 Pa during heating the sample. When the  $P_{\rm O_2}$  of the Ar–He gas decreases to ~10<sup>-2</sup> P (■), no detectable variations in the oxygen content and the surface tension of liquid titanium are confirmed, even after 120 min.



**Figure 1.** Time dependence of (a) oxygen content and (b) surface tension of liquid titanium maintained at 2000 K under different oxygen partial pressure,  $P_{O_2}$ , of Ar–He and Ar–He–10 vol. % H<sub>2</sub> gases using EML.

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Table 3. Uncertainty budget of surface tension measurements of liquid titanium by EML when the
calculation result of uncertainty for the measurement plot showed the largest value.

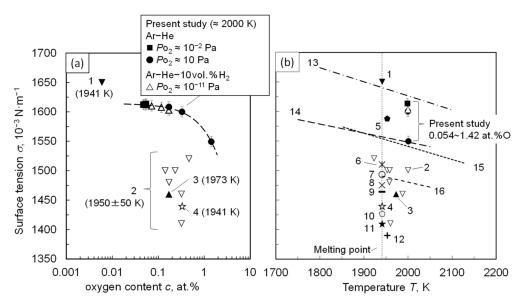
Source of Uncertainty	Value $\pm$	Divisor	Standard Uncertainty, u(i)	Sensitivity Coefficient, c(i)	Uncertainty Contribution, $u_s(\mathbf{i})$	
Density, ρ [33]	62.36 kg⋅m <sup>-3</sup>	2	31.18 kg⋅m <sup>-3</sup>	$-6.423 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-2}$	$-2.003 \times 10^{-4} \ \text{N} \cdot \text{m}^{-1}$	
Sample mass, M	$7.277 \times 10^{-7} \text{ kg}$	1	$7.277 \times 10^{-7} \text{ Kg}$	$3976  \mathrm{s}^{-2}$	$2.893 \times 10^{-3} \ \text{N} \cdot \text{m}^{-1}$	
Translation frequency of	· ·		· ·			
m = -1 for the $l = 1$ mode,	$6.104 \times 10^{-2}  \mathrm{s}^{-1}$	$\sqrt{3}$	$3.524 \times 10^{-2}  \mathrm{s}^{-1}$	$1.618 \times 10^{-3} \text{ kg} \cdot \text{s}^{-1}$	$5.702 \times 10^{-5} \text{ N} \cdot \text{m}^{-1}$	
$f_{1,-1}$ Translation frequency of						
m = 0 for the $l = 1$ mode,	$6.104 \times 10^{-2} \text{ s}^{-1}$	$\sqrt{3}$	$3.524 \times 10^{-2} \mathrm{\ s}^{-1}$	$2.325 \times 10^{-3} \text{ kg} \cdot \text{s}^{-1}$	$8.193 \times 10^{-5} \text{ N} \cdot \text{m}^{-1}$	
$f_{1,0}$ Translation frequency of	0.101 × 10 3	VS	0.021 × 10 5	2.020 × 10 - Rg 5	0.135 × 10 14 III	
m = +1 for the $l = 1$ mode,	$6.104 \times 10^{-2}  \mathrm{s}^{-1}$	$\sqrt{3}$	$3.524 \times 10^{-2} \ \mathrm{s}^{-1}$	$1.823 \times 10^{-3} \text{ kg} \cdot \text{s}^{-1}$	$6.425 \times 10^{-5} \ \mathrm{N \cdot m^{-1}}$	
$f_{1,+1}$ Surface oscillation frequency of m = 0 for the $l = 2$ mode, $f_{2,0}$	$6.104 \times 10^{-2}  \mathrm{s}^{-1}$	$\sqrt{3}$	$3.524 \times 10^{-2} \mathrm{s}^{-1}$	$9.349 \times 10^{-3} \text{ kg} \cdot \text{s}^{-1}$	$3.294 \times 10^{-4} \text{ N} \cdot \text{m}^{-1}$	
Surface oscillation frequency of $m = \pm 1$ for the $l = 2$ mode, $f_{2,\pm 1}$	$6.104 \times 10^{-2}  \mathrm{s}^{-1}$	$\sqrt{3}$	$3.524 \times 10^{-2} \mathrm{s}^{-1}$	$2.228 \times 10^{-2} \mathrm{kg \cdot s^{-1}}$	$7.852 \times 10^{-4} \text{ N} \cdot \text{m}^{-1}$	
Surface oscillation frequency of $m = \pm 2$ for the $l = 2$ mode, $f_{2,\pm 2}$	$6.104 \times 10^{-2}  \mathrm{s}^{-1}$	$\sqrt{3}$	$3.524 \times 10^{-2} \text{ s}^{-1}$	$2.531 \times 10^{-3} \text{ kg} \cdot \text{s}^{-1}$	$8.918 \times 10^{-4} \text{ N} \cdot \text{m}^{-1}$	
Repeatability of surface tension measurement, $\sigma_{\text{rep}}$	$\begin{array}{c} 3.618 \times 10^{-3} \\ N \cdot m^{-1} \end{array}$	1	$3.618 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$	1	$3.618 \times 10^{-3} \; N{\cdot}m^{-1}$	
Combined uncertainty, $u_c(\sigma)$ : $4.800 \times 10^{-3}  \mathrm{N \cdot m^{-1}}$						
Expanded uncertainty, $U: 9.600 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ (coverage factor $k_p = 2$ is selected)						

Even when the  $P_{\rm O_2}$  is further decreased to ~ $10^{-11}$  Pa through a gas phase equilibrium between H<sub>2</sub> and H<sub>2</sub>O under Ar–He–10 vol. % H<sub>2</sub> gas ( $\triangle$ ), the oxygen content in liquid titanium slightly increases with time, and the corresponding surface tension decreases.

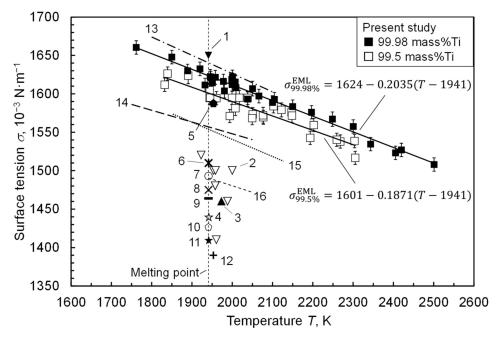
Figure 2 shows the surface tension of liquid titanium measured at about 2000 K as a function of oxygen content in the sample (Figure 2a) corresponding to the results of Figure 1, and its comparison with a scatter of the literature data (Figure 2b) [1–16]. Figure 2a confirms that the surface tension of liquid titanium continuously decreases with increasing oxygen content regardless of measurement atmosphere. The surface tension of liquid titanium measured in this study is higher than the data reported by Zhu [3], Flint [4], and Brillo et al. [5], even for similar oxygen content in the sample. The variation in the surface tension of liquid titanium with different oxygen contents measured in this study is so small that it would not be the main reason for the large scatter in the literature data, as shown in Figure 2b.

Figure 3 exhibits the temperature dependence of the surface tension of liquid titanium with the purity of 99.98 and 99.5 mass % measured under the flowing mixture of Ar–He gas at  $P_{\rm O_2}$  of  $10^{-2}$  Pa to eliminate the influence of the variation in oxygen content in the sample on surface tension during the measurement. The surface tension of liquid titanium is measured free from any contamination, chemical reaction with the supporting material, and dissolved atmospheric oxygen, over a wide temperature range from about 1700 to 2500 K including undercooling conditions. The surface tension of the 99.98 mass % purity liquid titanium ( $\blacksquare$ ) decreases linearly with elevating temperature, which agrees comparatively well with the data reported by Zhou et al. [13] using ESL.

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**Figure 2.** Surface tension of liquid titanium measured by EML at about 2000 K with respect to the oxygen content (**a**) and its comparison with a scatter of literature data (**b**) [1–16].



**Figure 3.** Temperature dependence of surface tension of liquid titanium with purity of (■) 99.98 mass % and (□) 99.5 mass % measured at  $P_{O_2}$  of  $10^{-2}$  Pa under Ar–He gas.

When the purity of the titanium sample is degraded from 99.98 to 99.5 mass % ( $\square$ ), the surface tension decreases by less than a few percentage points, which is smaller than the scatter in the literature of the surface tension of liquid titanium [1–16]. The oxygen content in the titanium sample with the purity of 99.5 mass % is a relatively large amount of 1800 mass ppm. The decrease in the surface tension of the sample corresponds well with the relationship between the surface tension and oxygen content shown in Figure 2a. It is reasonable that the decrease in the surface tension of liquid titanium with the purity of 99.5% is mainly due to the increase in oxygen content. Although the titanium sample with purity of 99.5% contains comparatively large amounts of iron and carbon, the influence of these elements on the surface tension of liquid titanium would be small.

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#### 4. Discussion

4.1. Influence of Atmospheric Gas Species on the Surface Tension of Liquid Titanium

When the  $P_{\rm O_2}$  of the atmospheric Ar–He gas flowing at 2 L·min<sup>-1</sup> was decreased from 10 to  $10^{-2}$  Pa, no detectable time dependence of the oxygen content and surface tension of liquid titanium was observed. Oxygen content in the liquid titanium slightly increased, and the corresponding surface tension decreased with time under the flowing Ar–He–10 vol.% H<sub>2</sub> gas, even though the  $P_{\rm O_2}$  of the gas was further decreased to ~ $10^{-11}$  Pa. This seemingly contradictory relationship among  $P_{\rm O_2}$ , oxygen content in liquid titanium, and surface tension can be explained by considering the difference of the rate-determining step in the dissolution of oxygen under Ar–He gas and Ar–He–10 vol. % H<sub>2</sub> gases. From the following standard Gibbs energy for the dissolution of oxygen gas into liquid titanium,  $\Delta G^{\circ}$ , reported by Belyanchikov [38], it was calculated that oxygen content in the original sample at about 0.03 at. % (0.01 mass %) is much smaller than the equilibrium value with oxygen partial pressure of  $P_{\rm O_2} \approx 10^{-11}$  Pa in the atmospheric Ar–He–10 vol. % H<sub>2</sub> gas.

$$\frac{1}{2}O_2(g) \ensuremath{\ensuremath{\rightleftarrows}} \underline{O} \ (\text{mass \% in liquid titanium}) \tag{4}$$

$$\Delta G^{\circ} = -494,500 + 95.54T \left( \text{J·mol}^{-1} \right)$$
 (5)

The saturated oxygen content in liquid titanium maintained at 2000 K under Ar–He–10 vol. %  $\rm H_2$  gas with  $\rm P_{O_2}$  of  $\rm 10^{-11}$  Pa was calculated to about 3 at. %. Therefore, oxygen dissolves into liquid titanium from the atmospheric gas. Even if the dissolution of atmospheric oxygen into liquid titanium would decrease  $\rm P_{O_2}$  locally and momentarily in the vicinity of the liquid surface, the variation in  $\rm P_{O_2}$  can be immediately buffered by gas phase equilibrium between  $\rm H_2$  and  $\rm H_2O$  since the partial pressure of these gases are much high than that of  $\rm P_{O_2}$ . In this case, atmospheric oxygen can continue to dissolve into the liquid titanium until it reaches saturation. Thus, oxygen content in liquid titanium maintained under Ar–He–10 vol. %  $\rm H_2$  gas can gradually increase, albeit slowly, even at very low  $\rm P_{O_2}$  at  $\rm 10^{-11}$  Pa, resulting in a decrease in surface tension.

On the other hand, no buffer effect for the variation of  $P_{\rm O_2}$  can be expected under the Ar–He gas used in this study because it contains trace amounts of  $H_2(g)$ . In this case, the flow rate of the gas can be the rate-determining step in dissolution of atmospheric oxygen into liquid titanium. Namely, the flow rate of the Ar–He gas at  $2 \text{ L·min}^{-1}$  is so slow that the oxygen content in liquid titanium could not be increased to detectable levels through dissolution from the atmosphere, even when the liquid titanium is maintained at a comparatively high  $P_{\rm O_2}$  of  $10^{-2}$  Pa for a long period of 120 min.

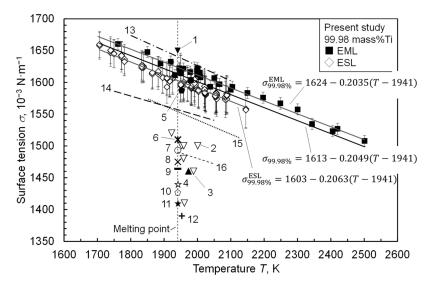
# 4.2. Round-Robin Measurement

The influences of the oxygen content and purity of the original sample on the surface tension of liquid titanium were so small that they would not be a reason for the large scatter in the literature data (cf. Figures 2 and 3). Some inherent error in measurement methods and/or contamination of the sample from the supporting materials may have affected the measurement results in some studies, including our measurement. In order to confirm the validity of the surface tension of liquid titanium measured by EML in this study, a round-robin measurement of surface tension for liquid titanium with a purity of 99.98 mass % was carried out using ESL. The ESL technique ensures a measurement free of sample contamination from the supporting materials, even at high temperature, as well as using EML. Since the experiment using EML clarified that the dissolution of oxygen in liquid titanium from the Ar–He gas flowing at  $2 \text{ L}\cdot\text{min}^{-1}$  was inhibited when the  $P_{O_2}$  of the gas was  $10^{-2}$  Pa, it is reasonable to suppose that the influence of the dissolution of oxygen can also be eliminated under the high-vacuum condition of  $10^{-5}$  Pa used in ESL. Figure 4 shows a comparison of the measurement results for the surface tension of liquid titanium with a purity of 99.98 mass % using ESL (♦) and EML (■). The largest uncertainty in each plot of the surface tension measured by ESL is  $\pm 28.03 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$  for a coverage factor Metals 2022, 12, 1129 8 of 11

of  $k_{\rm p}$  = 2. Table 4 shows the corresponding uncertainty budget. Although the measurement by ESL was carried out at temperatures lower than 2150 K to inhibit as much as possible the evaporation of high-temperature liquid titanium under a high-vacuum condition, the temperature range of the measurement is still relatively wide at over about 450 K, including undercooling conditions. The surface tension of liquid titanium measured by ESL agrees well with that by EML within a difference of less than 1.3%, implying the validity of our measurement results by EML and ESL. The temperature dependence of liquid titanium with a purity of 99.98 mass % free of any contamination,  $\sigma$ , can be expressed using a least-squares method from the measurement plots by EML and ESL as follows:

$$\sigma_{99.98\%} = 1613 - 0.2049(T - 1941) \left(10^{-3} \text{ N} \cdot \text{m}^{-1}\right),$$
 (6)

the intercept of which (1613  $\times$  10<sup>-3</sup> N·m<sup>-1</sup>) corresponds to the surface tension at the melting temperature of titanium (1941 K).



**Figure 4.** Comparison of the measurement results of the surface tension of liquid titanium with purity of 99.98 mass % by EML and ESL together with the literature data [1–16]. The averaged surface tension of liquid titanium from the measurement result by EML and ESL is expressed as  $\sigma_{99.98\%} = 1613 - 0.2049(T - 1941) (10^{-3} \text{ N·m}^{-1})$ .

**Table 4.** Uncertainty budget of surface tension measurements of liquid titanium by ESL when the calculation result of uncertainty for the measurement plot showed the largest value.

Source of Uncertainty	Value $\pm$	Divisor	Standard Uncertainty, <i>u</i> (i)	Sensitivity Coefficient, c(i)	Uncertainty Contribution, $u_s(i)$	
Numerical fitting of droplet contour, <i>f</i>	0.6131 px	1	0.6131 px	$-5.717 \times 10^{-5}$ kg·s <sup>-2</sup> px <sup>-1</sup>	$-3.538 \times 10^{-5} \text{ N} \cdot \text{m}^{-1}$	
Diameter of droplet image, <i>r</i> <sub>img</sub>	0.5 px	$\sqrt{3}$	0.2887 px	$-5.717 \times 10^{-5}$ kg·s <sup>-2</sup> px <sup>-1</sup>	$-1.666 \times 10^{-5} \; N{\cdot}m^{-1}$	
Diameter of reference sphere $r_{ m ref}$	$5.0 \times 10^{-7} \text{ m}$	$\sqrt{3}$	$2.887 \times 10^{-7} \text{ m}$	-8.388 kg·m <sup>-1</sup> s <sup>-2</sup>	$-2.422 \times 10^{-6} \; N{\cdot}m^{-1}$	
Density, $\rho$ [33]	$65.46 \text{ kg} \cdot \text{m}^{-3}$	2	$29.33 \text{ kg} \cdot \text{m}^{-3}$	$-3.876 \times 10^{-4}$ m <sup>3</sup> ·s <sup>-2</sup>	$-1.269\times 10^{-2}\; N{\cdot}m^{-1}$	
Surface oscillation frequency $f_{2c}$	$0.5 \: { m s}^{-1}$	$\sqrt{3}$	$0.2887~{ m s}^{-1}$	$^{1.818 \times 10^{-2}}_{ ext{kg} \cdot  ext{s}^{-1}}$	$5.249 \times 10^{-3} \ N \cdot m^{-1}$	
Sample charge, Q	$1.359 \times 10^{-11} \text{ c}$	1	$1.359 \times 10^{-11} \text{ c}$	$-3.346 \times 10^{7}$ kg·s <sup>-2</sup> ·c <sup>-1</sup>	$-4.547 \times 10^{-4} \; N{\cdot}m^{-1}$	
Correction factor, F	$3.098 \times 10^{-10}$	1	$3.098 \times 10^{-10}$	$1.581 \ \mathrm{N \cdot m^{-1}}$	$4.898\times 10^{-10}\;N{\cdot}m^{-1}$	
Repeatability of surface tension measurement, $\sigma_{\rm rep}$	$2.781\times 10^{-3}\;N{\cdot}m^{-1}$	1	$2.781 \times 10^{-3}$ N·m <sup>-1</sup>	1	$2.781\times 10^{-3}\;N{\cdot}m^{-1}$	
Combined uncertainty, $u_c(\sigma)$ : $14.02 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ Expanded uncertainty, $U$ : $28.03 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ (coverage factor $k_p = 2$ is selected)						

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#### 5. Conclusions

The surface tension of liquid titanium was precisely measured free of any contamination from the supporting materials in consideration of the influence of oxygen partial pressure of measurement atmosphere,  $P_{\rm O_2}$ , with an oscillating droplet method using electromagnetic levitation (EML) and electrostatic levitation (ESL). When the measurement was carried out under Ar–He mixture gas showing  $P_{\rm O_2}$  of 10 Pa flowing at 2 L·min<sup>-1</sup> by using EML, the surface tension of liquid titanium decreased with time due to the dissolution of atmospheric oxygen into the sample. When the  $P_{\rm O_2}$  of the Ar–He gas was decreased to  $10^{-2}$  Pa, no detectable variations in the oxygen content and the surface tension of liquid titanium were confirmed even after 120 min. This was because the flow rate of the gas became the rate-determining step for oxygen dissolution in liquid titanium.

When the measurement was carried out under Ar–He–10 vol. %  $\rm H_2$  mixture gas flowing at 2 L·min<sup>-1</sup>, the surface tension of liquid titanium slightly decreased with time, even though the  $P_{\rm O_2}$  of the gas was further decreased to  $10^{-11}$  Pa since atmospheric oxygen slowly but continuously dissolved into the liquid titanium due to the gas phase equilibrium between  $\rm H_2$  and  $\rm H_2O$ .

The surface tension of liquid titanium decreased when the purity of the original sample was degraded from 99.98 to 99.5 mass %. However, the influence of the purity in the original sample on the surface tension was so small that it would not be a reason for the large scatter in the literature data.

As a round-robin test, the surface tension of liquid titanium was measured using ESL under a high-vacuum condition to suppress the contamination of the sample from the supporting materials and the dissolution of atmospheric oxygen as well as using EML. As a result, the surface tension for the liquid titanium measured by ESL showed almost the same value as that measured by EML with a difference of less than 1.3%. From the measurement results from EML and ESL, the temperature dependence of the surface tension of liquid titanium with a purity of 99.98% free from any contamination such as chemical reactions with the supporting materials and dissolution of atmospheric oxygen was expressed as  $\sigma_{99.98\%} = 1613 - 0.2049(T - 1941)$  ( $10^{-3}$  N·m<sup>-1</sup>).

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