metals

Article

Measurement of Interfacial Tension between Liquid Pb and a Molten LiCl-NaCl-KCl Mixture via a Floating Drop Method

Masashi Nakamoto [1,*], Toshihiro Tanaka [2] and Takaiku Yamamoto [2]

[1] Low Temperature Center, Osaka University, 2-1 Yamadaoka, Suita 565-0871, Osaka, Japan
[2] Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita 565-0871, Osaka, Japan; tanaka@mat.eng.osaka-u.ac.jp (T.T.); tyamamoto@icems.kyoto-u.ac.jp (T.Y.)
* Correspondence: nakamoto@mat.eng.osaka-u.ac.jp; Tel.: +81-6-6879-7985

Abstract: The floating drop method has the potential for high-accuracy measurement of liquid–liquid interfacial tension. It was applied here to measure the interfacial tension between liquid Pb and a molten mixture of 8.9% LiCl, 50% NaCl, and KCl (mass%). The heavier Pb droplet floated on the lighter molten salt and enabled the acquisition of data at 673 K, 723 K, and 773 K under vacuum. The results agreed with previous reports. The temperature (*T*) dependence of the interfacial tension *s* was given by *s* = 459–1.27 *T* mN/m.

Keywords: interfacial tension; measurement; liquid Pb; molten salt; floating drop method

check for updates

Citation: Nakamoto, M.; Tanaka, T.; Yamamoto, T. Measurement of Interfacial Tension between Liquid Pb and a Molten LiCl-NaCl-KCl Mixture via a Floating Drop Method. *Metals* **2022**, *12*, 1198. https://doi.org/10.3390/met12071198

Academic Editor: Gunter Gerbeth

Received: 27 May 2022
Accepted: 12 July 2022
Published: 14 July 2022

1. Introduction

Many issues regarding liquid–liquid interfacial phenomena are encountered in a wide variety of industrial processes. Thus, interfacial tension is a critically important physical property, and numerous investigations have been reported for liquid–liquid systems [1–3]. Recently, the authors [4–6] proposed the floating drop method for measuring liquid–liquid interfacial tension based on the submerged profile of a floating droplet on another liquid. Specifically, high-accuracy measurements were obtained at room temperature for canola oil and a 1% aqueous solution of detergent as a floating droplet and a solvent. A very small variation of the interfacial tension (0.6~1 mN/m) was measured [4]. In addition, the interfacial tension between rapeseed oil and an aqueous solution with a 0.2% polyoxyethylene alkyl-ether sulfuric-acid ester salt was measured to confirm the reliability of the interfacial tension result with Neumann's triangle [5]. The floating drop method was effective for measuring the liquid–liquid interfacial tension of a heavy liquid paraffin droplet floating on relatively lighter water [6].

A heavier droplet can float on a lighter solvent at high temperatures because of the balance between the densities of the two liquids and their interfacial properties. This could be a serious issue affecting various high-temperature material processes. For example, relatively high-density floating Fe droplets on lower-density molten slags were observed by Han and Holappa [7] and also by Taniguchi and Seethraman [8]. A heavier Cu droplet, or Cu matte, on a lighter molten slag was reported by Terashima et al. [9]. Utigard et al. [10] reported flotation characteristics of heavier liquid-metal droplets and lighter sodium flux systems. Here, we applied the floating drop method to the measurement of the interfacial tension between liquid Pb and a molten mixture of LiCl, NaCl, and KCl to verify the potential of the method for high-temperature systems. It was reported that a Pb droplet floated on molten salt in an LiCl-NaCl-KCl system [11]. In addition, the data on the interfacial tension between a liquid Pb and a molten salt in an LiCl-NaCl-KCl system are available [12]. Moreover, the molten salt in LiCl-NaCl-KCl shows relatively low melting temperatures, such as 673 and 773 K [13]. This realizes the observation by a normal optical system with LED light and camera through molten salt and borosilicate glass instead of specific apparatus with an X-ray beam. In addition to the measurement of interfacial tension, the floatability of a heavier Pb droplet on molten salt was examined based on a model that uses a balance of the droplet weight, buoyancy, and surface tension.

2. Determination of Interfacial Tension

In the floating drop method, the interfacial tension between two liquids was measured based on the submerged profile of a floating droplet on another liquid [4–6]. Figure 1 shows the cross-sectional profile of an axisymmetric floating droplet L_1 on a liquid L_2. The profile of the droplet is theoretically expressed by:

$$\frac{dx}{d\phi} = R \cdot \cos\,\phi \tag{1}$$

$$\frac{dz}{d\phi} = -R \cdot \sin\,\phi \tag{2}$$

$$R = \frac{1}{\left\{ -\frac{\Delta\rho g}{\sigma_{L_1/L_2}}(h - z) + \frac{2}{b} - \frac{\sin\,\phi}{x} \right\}} \tag{3}$$

$$\Delta\rho = \rho_{L_1} - \rho_{L_2} \tag{4}$$

where x and z are coordinate axes; R is the curvature radius normal to the surface at a selected point on the curve of the sectional plan of the droplet, as shown in Figure 1; ϕ is the angle between the normal line passing through the coordinates (x,z) in the profile of the droplet and the central axis; g is gravitational acceleration; h is the height of the droplet; b is the radius of the curvature at the vertex of the droplet; σ_{L_1/L_2} is the interfacial tension between droplet L_1 and liquid L_2; $\Delta\rho$ is the density difference; and ρ_{L_1} and ρ_{L_2} are the densities of droplet L_1 and liquid L_2, respectively. The liquid-liquid interfacial tension, σ_{L_1/L_2}, was obtained by determining the optimal σ_{L_1/L_2}, h, and b that fit the calculated droplet profile to that obtained experimentally, with known $\Delta\rho$.

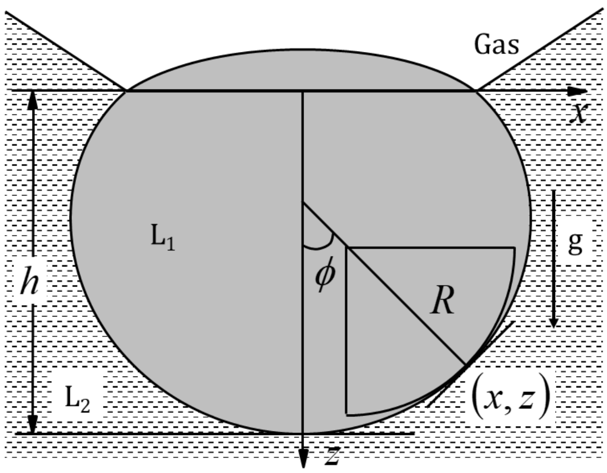

Figure 1. Coordinate system for a floating droplet L_1 on a liquid L_2. (Figure modified from [6]).

3. Experiment

Pb (>99.999% purity) was used as a droplet. LiCl, NaCl, and KCl powders were used for molten 8.9% LiCl, 50% NaCl, and KCl (mass%). The experimental setup (see Figure 2) consisted of an image-capturing system and a horizontal furnace with a $MoSi_2$ heating element. The image-capturing system used light-emitting diodes (LEDs) on one side that illuminated the submerged droplet and a charge-coupled device (CCD) camera (Sony Corp., Tokyo, Japan) fitted with an optical-zoom lens on the other side. An alumina tube was covered with stainless foil to protect it from the molten salt vapor. Approximately 1.8 g of the LiCl, NaCl, and KCl mixed powder filled a borosilicate glass cell (10 mm × 10 mm × 50 mm). A Pb sample was placed on the mixed powder. Its weight varied over approximately 0.015–0.1 g to investigate the effect of droplet size on its floatability on the molten salt. The mass of the Pb sample was measured before the start of experiment. The inside of the tube was evacuated to approximately 0.6 Pa. The system was heated to 673 K to melt the materials, and the temperature was held for 30 min.

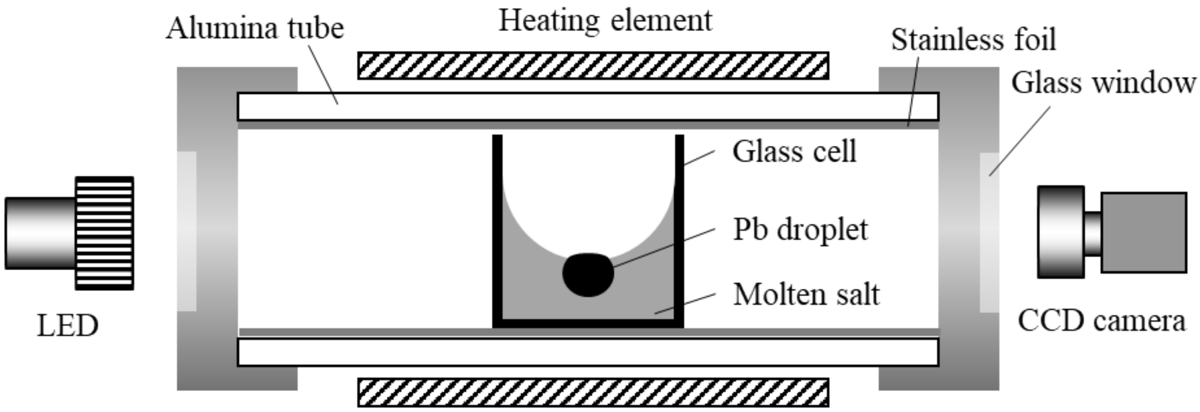

Figure 2. Schematic of the experimental arrangement for measuring the interfacial tension between liquid Pb and molten salt.

During the holding time, many gas bubbles were generated in the molten salt, as shown in Figure 3a. These bubbles are generated from the gas elements dissolved in the molten salt mixture when the inside of the apparatus is vacuumed. The Pb droplet was lifted by a large gas bubble formed on the droplet, which moved it to the liquid level of the molten salt (Figure 3b). The generation of bubbles was stopped after 30 min. Next, the submerged digital image profile of the Pb droplet was captured through the molten salt and the borosilicate glass cell at 0 min, 10 min, and 20 min. The image capturing was conducted similarly at 723 K and 773 K after heating and a 30-min holding time. The interfacial tension between the two liquids was obtained by comparing the experimental droplet profile with the theoretical droplet profile computed using the Laplace equation. The software package developed by Krylov et al. [14] was used to determine the interfacial tension. The density difference, D*r*, between the Pb droplet and the molten salt was calculated based on the previously reported temperature dependence of the liquid Pb density [15], given by 10.67–13.2 $\times$ 10^{-4} (T–600.5) (g/cm^3). The density of the molten salt was calculated from those of pure-liquid LiCl, NaCl, and KCl given in Table 1 [16], via the additive property of the molar volume.

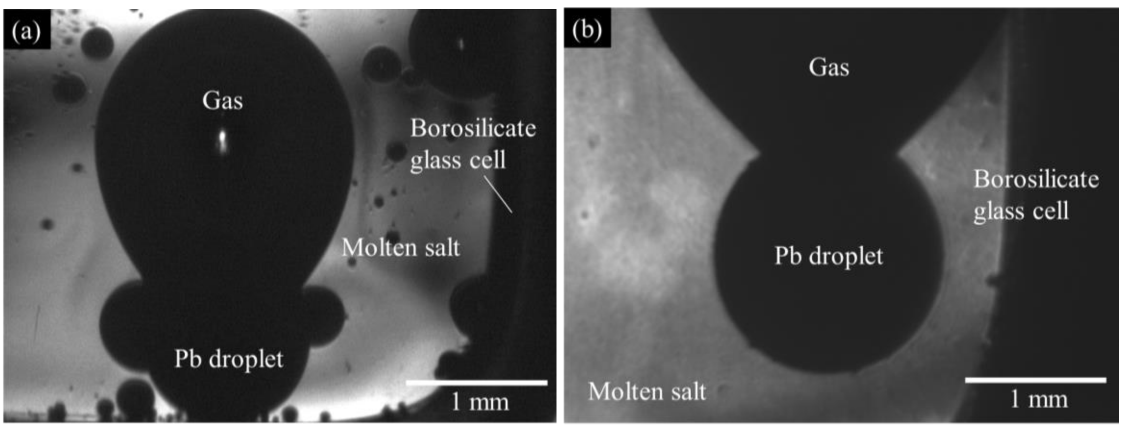

Figure 3. Example images of (**a**) gas generation, and (**b**) flotation of a Pb droplet on molten salt under vacuum.

Table 1. Temperature (K) dependence of the density and surface tension for pure LiCl, NaCl, and KCl [16].

Substance	Density (g/cm^3)	Surface Tension (mN/m)
LiCl	1.8842–4.3280 × $10^{-4}T$	187.6507–0.0617810T
NaCl	2.1390–5.444 × $10^{-4}T$	187.0–0.068T
KCl	2.1359–5.831 × $10^{-4}T$	176.8–0.075T

4. Results and Discussion

Figure 4 shows a 0.0236-g Pb droplet floating on molten LiCl-NaCl-KCl at 723 K. The contour of the droplet below the surface of the molten salt was clearly observed. Although the liquid level (i.e., the surface of the molten salt) dropped toward the droplet, the droplet did not sink, but instead floated on the molten salt. The relationship between the weight of the droplet and its floatability on the molten salt is shown in Figure 5. Pb droplets with weights less than approximately 0.032 g floated on the molten salt, whereas no droplets with weights greater than 0.04 g floated under these experimental conditions.

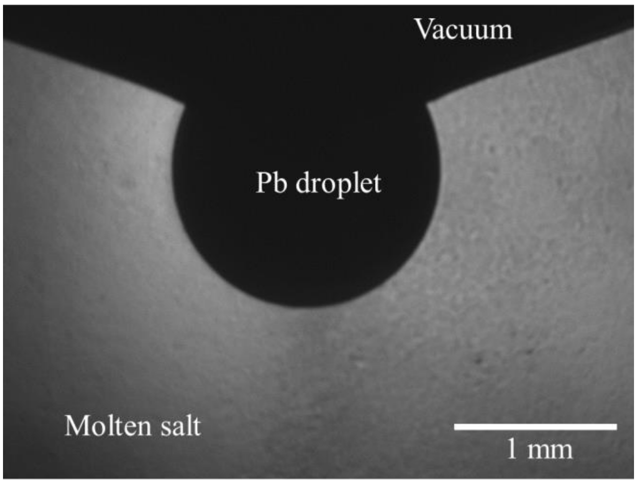

Figure 4. Submerged part of a floating Pb droplet on a molten LiCl-NaCl-KCl mixture at 723 K.

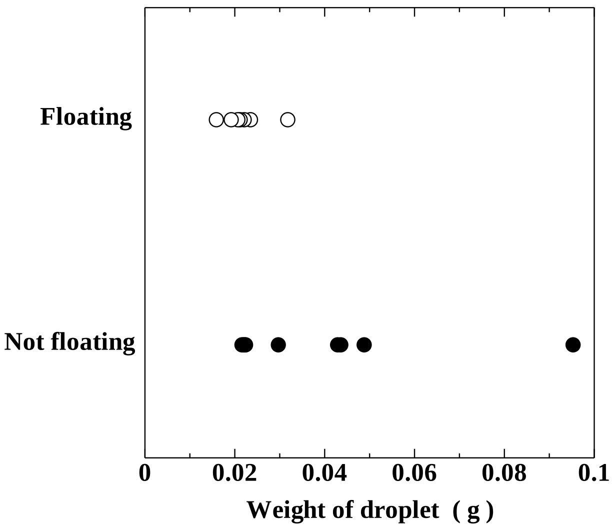

Figure 5. Effect of Pb droplet weight on its floatability on molten salt.

In this situation, as shown in Figure 6, the weight of the floating Pb droplet, F_W, was balanced by its buoyancy, F_B, and the surface tension of the molten salt, F_S [9–11,17]. The following equation was derived based on this balance, as reported by Terashima et al. [9] and Ooi et al. [17]:

$$\frac{4}{3}\pi {r_D}^3 \cdot \rho_{Pb} \cdot g = \frac{4}{3}\pi {r_D}^3 \cdot \rho_{ms} \cdot g + 2\pi(0.87 r_D) \cdot \sigma_{ms} \cdot \sin\ \theta \ \cdots \quad (5)$$

where r_D is the radius of the Pb droplet, ρ_{ms} is the density of the molten salt, σ_{ms} is the surface tension of the molten salt, and θ is the angle of the molten salt surface from the horizontal. For simplicity, it was assumed here that the floating Pb droplet was spherical and that the volume used for the buoyancy calculations was same as that of the droplet weight, i.e., spherical. The chord length at the three-phase contact line was 0.87 times that of $2r_D$, which was obtained from the image in Figure 4. Based on Equation (5), r_D can be expressed by:

$$r_D = \sqrt{\frac{2.61\sigma_{ms} \cdot \sin\ \theta}{2(\rho_{Pb} - \rho_{ms}) \cdot g}} \ \cdots \quad (6)$$

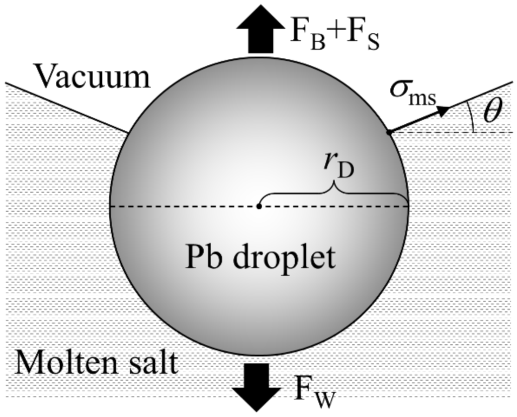

Figure 6. Model of Pb droplet floating on molten salt based on the balance among the droplet weight F_W, the buoyancy F_B, and the surface tension of molten salt F_S.

The surface tension, σ_{ms}, of molten salt in a ternary system was calculated from a model previously developed by the authors [18–20]. The surface tensions of pure LiCl, NaCl, and KCl [16] and the ionic radii for Li^+, Na^+, K^+, and Cl^- [21] in Table 2 were used for the calculation. These are the ionic radii for their configuration in a solid crystalline state at a given coordination, which may lead to the unexpected calculation results. However, the calculated surface tension with the ionic radii in Table 2 in molten binary LiCl-NaCl, LiCl-KCl, and NaCl-KCl systems, which consists of the components in the present work, provides reasonable predictions [18]. Therefore, we used the ionic radii for solids in this work.

Table 2. Ionic radii of cations and chlorine ions (Å) [21].

Li^+	0.68
Na^+	0.97
K^+	1.33
Cl^-	1.81

The molar volumes of pure LiCl, NaCl, and KCl were calculated from the densities [16] in Table 1. The angle θ was approximately 30°, and ρ_{Pb} and ρ_{ms} were the same as those in the interfacial tension measurement. The calculated weights of the floating Pb droplets at 673 K, 723 K, and 773 K were 0.044 g, 0.043 g, and 0.041 g, respectively. As shown in Figure 5, droplets with larger weights than the estimated ones did not float, and the weights that did float were smaller than the estimated ones. The floatability of the Pb droplet was roughly evaluated based on the simple model by considering the balance of droplet weight, buoyancy, and surface tension. However, some of the droplets did not float even when their weights were smaller than the estimated weights. This was attributed to experimental deviations from ideal conditions, such as fluctuations and convection due to the generation of bubbles. Although these fluctuations and convection affected the flowability of the Pb droplet, they did not affect the measurement of interfacial tension because the bubble generation finished before the measurement, as noted above.

The temperature dependence of the interfacial tension between the liquid Pb and the molten LiCl-NaCl-KCl system is plotted in Figure 7. The data points were averages of the three measurements acquired every 10 min, and the error bars reflected the largest values for each point as the upper limit and the smallest values as the lower limit. The scatter of the measured values was roughly within 5% at 673 K and 723 K, and 5–10% at 773 K. The larger scatter at 773 K could be attributed to devitrification of the borosilicate glass cell, which decreased the sharpness of the Pb droplet profile. The devitrification also prevented some measurements below 773 K, even though the Pb droplet floated on the molten salt. Therefore, the results obtained from two measurements are shown in the figure. The interfacial tension between the liquid Pb and the molten LiCl-NaCl-KCl system exhibited a negative temperature dependence, which was consistent with the sessile-drop method used by Ishii et al. [12]. In addition, our results were similar. The temperature dependence can be expressed as:

$$s = 459 - 1.27T \text{ mN/m} \tag{7}$$

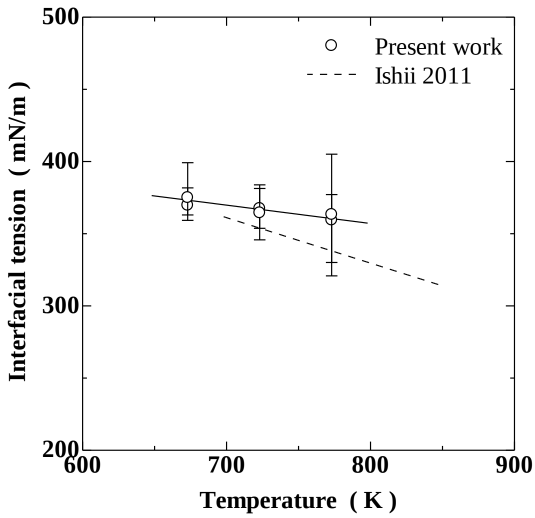

Figure 7. Temperature dependence of the interfacial tension between liquid Pb and molten salt [12].

In the sessile-drop method, the data on interfacial tension between liquid Pb and molten NaCl, which is similar to our system, show the error of about ±2~10%, and those between liquid Cu and molten NaCl show about ±15% [10]. Therefore, it is thought that the accuracy of the measurement for interfacial tension obtained by the floating drop method in the present work is comparable with that by the sessile drop method. However, because the measurement for only one system was conducted in the present work, we think it is necessary to apply the measurement to the other system more in the future in order to strictly discuss the accuracy of the measurement by the floating drop method.

Overall, we verified that the floating drop method can be used to measure interfacial tension between a liquid metal and a molten salt.

5. Conclusions

We measured the interfacial tension between liquid Pb and a molten mixture of LiCl, NaCl, and KCl via a floating drop method under vacuum. A heavy Pb droplet could float on the lighter salt mixture, and its floatability was roughly evaluated with a simple model that considered the balance of the droplet weight, buoyancy, and surface tension. The temperature dependence of the interfacial tension *s* was fit by *s* = 459–1.27*T* mN/m, which was in agreement with a previously reported value.

Author Contributions: Conceptualization, M.N. and T.T.; methodology, M.N.; validation, M.N., T.T. and T.Y.; formal analysis, M.N.; investigation, M.N.; resources, M.N.; data curation, M.N.; writing—original draft preparation, M.N.; writing—review and editing, M.N., T.T. and T.Y.; visualization, M.N.; supervision, T.T. and T.Y.; project administration, M.N.; funding acquisition, M.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by JSPS KAKENHI, grant number JP25820378.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author, M.N., upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bera, A.; Ojha, K.; Mandal, A.; Kumar, T. Interfacial tension and phase behavior of surfactant-brine–oil system. *Colloids Surf. A Physicochem. Eng. Asp.* **2011**, *383*, 114–119. [CrossRef]
2. Cong, Y.; Zhang, W.; Liu, C.; Huang, F. Composition and Oil-Water Interfacial Tension Studies in Different Vegetable Oils. *Food Biophys.* **2020**, *15*, 229–239. [CrossRef]
3. Ogino, K. *Chemistry of Interface at High Temperatures*; AGNE Gijutsu Center Inc.: Tokyo, Japan, 2008; Volume 1.
4. Nakamoto, M.; Tanaka, T.; Yamamoto, T. Measurement of Interfacial Tension Based on a Floating Droplet Profile on a Liquid. In Proceedings of the 6th International Symposium on Advanced Science Technology In Experiment Mechanics (ISEM 2011), Osaka, Japan, 5 November 2011.
5. Nakamoto, M.; Tanaka, T.; Yamamoto, T. Measurement of interfacial tension between oil and an aqueous solution via a floating drop method. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *529*, 985–989. [CrossRef]
6. Nakamoto, M.; Kasai, Y.; Tanaka, T.; Yamamoto, T. Measurement of liquid/liquid interfacial tension with water on liquid paraffin by the floating drop method. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *603*, 125250. [CrossRef]
7. Han, Z.; Holappa, L. Characteristics of Iron Entrainment into Slag Due to Rising Gas Bubbles. *ISIJ Int.* **2003**, *43*, 1698–1704. [CrossRef]
8. Taniguchi, Y.; Seethraman, S. Interfacial Phenomena among Liquid Iron-Carbon Alloy, Liquid Slag, and Solid CaO. *Metall. Trans. B* **2012**, *43*, 587–597. [CrossRef]
9. Terashima, H.; Nakamura, T.; Noguchi, F.; Ueda, Y. Floating Behavior of Molten Copper and Copper Matte Drops on Slag Surface—Study on interfacial phenomena in phase separation of copper smelting (3rd Report). *J. Min. Metall. Inst. Jpn.* **1990**, *106*, 881–885. [CrossRef]
10. Utigard, T.; Toguri, J.M.; Nakamura, T. Interfacial Tension and Flotation Characteristics of Liquid Metal-Sodium Flux Systems. *Metall. Trans. B* **1986**, *17*, 339–346. [CrossRef]
11. Poggi, D.; Minto, R.; Davenport, W.G. Mechanisms of Metal Entrapment in Slags. *J. Met.* **1969**, *21*, 40–45. [CrossRef]
12. Ishii, K.; Kitamura, S.; Shibata, H.; Maruoka, N.; Song, D.-Y. Measurement of interfacial tension between Pb/Al-Cu alloy and molten KCl-LiCl-NaCl salt. In Proceedings of the 32nd Japan Symposium on Thermophysical Properties, Yokohama, Japan, 21–23 November 2011.
13. Lin, P.-L.; Pelton, A.D.; Bale, C.W. Computation of Ternary Molten Salt Phase Diagrams. *J. Am. Ceram. Soc.* **1979**, *62*, 414–422. [CrossRef]
14. Krylov, A.S.; Vvedensky, A.V.; Katsnelson, A.M.; Tugovikov, A.E. Software package for determination of surface tension of liquid metals. *Non-Cryst. Solids* **1993**, *156–158*, 845–848. [CrossRef]
15. Iida, T.; Guthrie, R.I.L. *The Physical Properties of Liquid Metals*; Clarendon Press: Oxford, UK, 1993.
16. *NIST Molten Salt Database*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 1987.
17. Ooi, C.H.; Plackowski, C.; Nguyen, A.V.; Vadivelu, R.K.; St. John, J.A.; Dao, D.V.; Nguyen, N.-T. Floating mechanism of a small liquid marble. *Sci. Rep.* **2016**, *6*, 21777. [CrossRef] [PubMed]
18. Tanaka, T.; Kitamura, T.; Back, I.A. Evaluation of Surface Tension of Molten Ionic Mixtures. *ISIJ Int.* **2006**, *46*, 400–406. [CrossRef]
19. Nakamoto, M.; Kiyose, A.; Tanaka, T.; Holappa, L.; Hämäläinen, M. Evaluation of the Surface Tension of Ternary Silicate Melts Containing Al_2O_3, CaO, FeO, MgO or MnO. *ISIJ Int.* **2007**, *47*, 38–43. [CrossRef]

20. Nakamoto, M.; Tanaka, T.; Holappa, L.; Hämäläinen, M. Surface Tension Evaluation of Molten Silicates Containing Surface-active Components (B_2O_3, CaF_2 or Na_2O). *ISIJ Int.* **2007**, *47*, 211–216. [CrossRef]
21. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst. Sect. A* **1976**, *32*, 751–767. [CrossRef]