

# Surface Tension and its Temperature Coefficient of Liquid Sn-X (X=Ag, Cu) Alloys

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The surface tension of liquid Sn-X (X=Ag, Cu) alloys was measured by the constrained drop method in the temperatures between 700 and 1500 K across whole composition range. Surface tension of the alloys increased with the content of Ag and Cu, and the temperature coefficient of the surface tension ( $d\sigma/dT$ ) had both positive and negative values. Experimental results were compared with the calculated results based on Butler's model. The calculated results reasonably accorded with the measurements. The effect of thermo-physical parameters on the surface tension and the temperature coefficient were examined using the model. It was found that the temperature coefficient increases as the difference in the surface tension of component metals or the excess free energy increases in the high composition range of the component metal having higher surface tension, because of the surface enhancement of the other component metal.

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**Keywords:** metal, surface tension, temperature coefficient, liquid tin-silver alloys, liquid tin-copper alloys, large drop method

## 1. Introduction

Due to the difficulties in direct investigation on the surface concentration of liquid metals, it is usually estimated by calculations with available information such as the temperature and concentration dependences on surface tension. Butler's model can be applied in the calculations.<sup>1)</sup> Butler considered that the condition of equilibrium between the surface and the bulk is expressed by eq. (1).

$$\sigma = \frac{\mu_1^s - \mu_1^b}{A_1} = \frac{\mu_2^s - \mu_2^b}{A_2} = \dots = \frac{\mu_n^s - \mu_n^b}{A_n} \quad (1)$$

where  $\sigma$ ,  $A_i$ ,  $\mu_i^s$  and  $\mu_i^b$  denote the surface tension of the liquid alloy, the molar surface area of pure liquid  $i$ , the chemical potential of component  $i$  in the surface, and that in the bulk, respectively. Many researchers including the authors have shown that the surface tension of liquid alloys can be predicted by Butler's model using thermodynamic database within experimental errors.<sup>2-12)</sup> Using Butler's model, the temperature coefficient of surface tension ( $d\sigma/dT$ ) for liquid alloys can also be obtained by calculating the surface tension with changing temperature at a fixed composition. Generally, the temperature coefficients of liquid metals and alloys are negative.<sup>13)</sup> However, it is reported that positive temperature coefficients can be observed for liquid alloys having very positive excess free energies.<sup>14)</sup> For liquid alloys having negative excess free energies, it has not been clarified whether the temperature coefficient can have a positive value. For example, Moser *et al.*<sup>12)</sup> obtained negative temperature coefficients for liquid Sn-Ag in their experiments, while positive temperature coefficients for some alloys in their calculations. In order to explain the discrepancy between them, the reason causing the positive temperature coefficients in thermodynamic calculations should be verified with experiments of high accuracy.

In the present work, the surface tension of liquid Sn-Ag and Sn-Cu alloys was evaluated across the whole composi-

tion range with varying temperature widely by both experiments and thermodynamic calculations. Recently, the authors showed that more reliable surface tension values could be obtained by the constrained drop method.<sup>15-17)</sup> (For example, the surface tension of liquid Au showed very small relative errors from the mean value less than  $\pm 0.5\%$ .<sup>17)</sup>) In the present work, the constrained drop method was applied to measure the surface tension. The apparatus and experimental techniques have been described in Ref. 16. The experimental measurements were compared with the calculation results. In addition, to clarify the major factors determining the temperature coefficient, thermodynamic calculations for more general cases has been conducted.

## 2. Experimental Results

### 2.1 Surface tension of pure liquid Ag, Cu and Sn

In the calculation of surface tension of liquid alloys, the accurate surface tension of the component pure liquid metals is indispensable. Therefore, in the present work, the surface tension of liquid Ag, Cu and Sn (component metals in the Sn-Ag, Sn-Cu alloys) was measured. In Fig. 1, the surface tension of liquid Ag in 10% $H_2$ -Ar gas atmosphere is shown with the temperature between 1269 and 1474 K. (Every experiment in this article was performed in 10% $H_2$ -Ar gas atmosphere to prevent oxygen contaminations.) As the temperature increases, the surface tension of liquid Ag decreases, yielding a negative temperature coefficient. The surface tension of liquid Ag, then, could be expressed as eq. (2).

$$\sigma_{Ag}/\text{mNm}^{-1} = 1207 - 0.228 \times T \quad (2)$$

The deviation of measurements from eq. (2) is less than  $\pm 0.9\%$ . In Fig. 1, reported measurements are also drawn for comparison.<sup>16,18-30)</sup> Keene<sup>30)</sup> asserted in his review that the surface tension of liquid metal measured using the sessile drop method could be lowly estimated due to the contamination from the substrates (mainly oxides), and the surface tension measured by the levitation method usually showed

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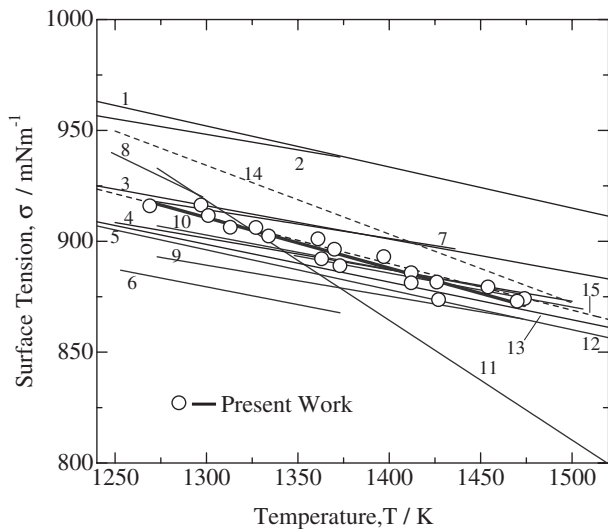


Fig. 1 Surface tension of pure liquid Ag as a function of temperature in 10% $H_2$ -Ar atmosphere. (1. Kasama *et al.*,<sup>18</sup>) 2. Rhee,<sup>19</sup>) 3. Brunet *et al.*,<sup>20</sup>) 4. Bernard *et al.*,<sup>21</sup>) 5. Nogi *et al.*,<sup>22</sup>) 6. Sangiorgi *et al.*,<sup>23</sup>) 7. Krause *et al.*,<sup>24</sup>) 8. Kingery *et al.*,<sup>25</sup>) 9. Metzger,<sup>26</sup>) 10. Lauer mann *et al.*,<sup>27</sup>) 11. Libmann,<sup>28</sup>) 12. Egry *et al.*,<sup>29</sup>) 13. Lee *et al.*,<sup>16</sup>) 14. Keene (suggested),<sup>30</sup>) 15. Keene (mean of the reported)<sup>30</sup>).

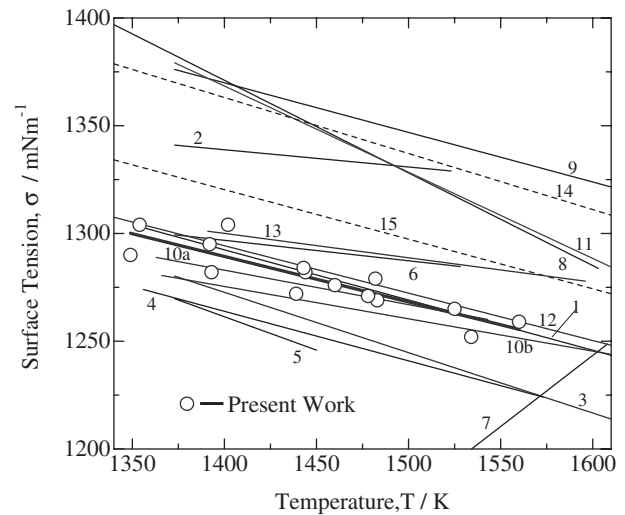


Fig. 2 Surface tension of pure liquid Cu as a function of temperature in 10% $H_2$ -Ar atmosphere. (1. Kasama *et al.*,<sup>18</sup>) 2. Lauer mann *et al.*,<sup>27</sup>) 3. Gans *et al.*,<sup>31</sup>) 4. Pawlek *et al.*,<sup>32</sup>) 5. Allen,<sup>33</sup>) 6. Metzger,<sup>26</sup>) 7. Krause *et al.*,<sup>24</sup>) 8. Soda *et al.*,<sup>34</sup>) 9. Keene *et al.*,<sup>35</sup>) 10. Lang *et al.*,<sup>36</sup>) 11. Kawai *et al.*,<sup>37</sup>) 12. Egry *et al.*,<sup>29</sup>) 13. Lee *et al.*,<sup>16</sup>) 14. Keene (suggested),<sup>30</sup>) 15. Keene (mean of the reported)<sup>30</sup>).

higher surface tension values than that by the sessile drop method because the sample in the levitation method might not be contaminated from the substrate. However, Egry *et al.*<sup>29</sup>) showed that the surface tension of liquid metal droplets measured by the levitation method had been highly estimated due to the electromagnetic pressure on the liquid metal. The apparent surface tension of liquid Ag at the melting temperature was about  $1060 \pm 40$  mN/m without considering the effect of the magnetic pressure, whereas that corrected with the effect of the magnetic pressure was  $910 \pm 20$  mN/m. The agreement between the present measurements and those by Egry *et al.* is acceptable. The scatter in the measurements of the present work ( $\pm 0.9\%$ ) is smaller than that by Egry *et al.* (about  $\pm 2\%$ ). On the contrary, the suggested mean values by Keene<sup>30</sup>) (broken line in Fig. 1) were probably highly evaluated, because they contained uncorrected levitation data.

In Fig. 2, the surface tension of liquid Cu is shown with temperature in the range of 1349~1560 K and expressed as a function of temperature by eq. (3).

$$\sigma_{Cu}/mNm^{-1} = 1585 - 0.21 \times T \quad (3)$$

The deviation of measurements from eq. (3) is less than  $\pm 1.0\%$ . The accordance in the surface tension between the present work, our previous work and that by Egry *et al.*<sup>29</sup>) is acceptable. The deviation in the present work markedly reduced compared to our previous results ( $\pm 2.0\%$ ). Hence, the surface tension and the temperature coefficient obtained in the present work are considered more reliable. The temperature coefficient is very close to the value ( $-0.22$ ) obtained by Egry *et al.*<sup>29</sup>)

Figure 3 shows the surface tension of liquid Sn with temperature. The temperature range of the experiments is 510~1334 K. From a linear regression of the measurements, the surface tension of liquid Sn is given by eq. (4).

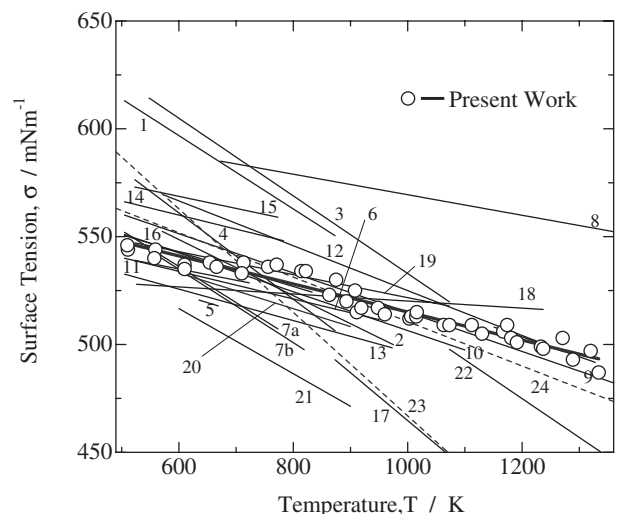


Fig. 3 Surface tension of pure liquid Sn as a function of temperature in 10% $H_2$ -Ar atmosphere. (1. Goumiri *et al.*,<sup>38</sup>) 2. Yatsenko,<sup>39</sup>) 3. Pelzel,<sup>40</sup>) 4. Matsuyama,<sup>41</sup>) 5. Hogness,<sup>42</sup>) 6. Lang,<sup>43</sup>) 7. Lang *et al.*,<sup>36</sup>) 8. Kawaii *et al.*,<sup>37</sup>) 9. Kasama *et al.*,<sup>18</sup>) 10. Nogi *et al.*,<sup>22</sup>) 11. Ofitserov *et al.*,<sup>44</sup>) 12. Naidich *et al.*,<sup>45</sup>) 13. Abdel-Aziz *et al.*,<sup>46</sup>) 14. Melford *et al.*,<sup>47</sup>) 15. Mukai,<sup>48</sup>) 16. White,<sup>49</sup>) 17. Adachi,<sup>50</sup>) 18. Bircumshaw,<sup>51</sup>) 19. Bircumshaw,<sup>52</sup>) 20. Moser *et al.*,<sup>12</sup>) 21. Yuan *et al.*,<sup>53</sup>) 22. Kaufman *et al.*,<sup>54</sup>) 23. Keene (suggested),<sup>30</sup>) 24. Keene (mean of the reported)<sup>30</sup>).

$$\sigma_{Sn}/mNm^{-1} = 580 - 0.065 \times T \quad (4)$$

The deviation of measurements from eq. (2) is less than  $\pm 0.9\%$ . In the surface tension measurements of liquid Sn, oxygen contamination from atmosphere can be a problem, because  $SnO_2$  is readily created even in the low oxygen partial pressure atmosphere (e.g.  $p_{O_2} = 4.19 \times 10^{-9}$  Pa at 1253 K<sup>55</sup>). Recently, Yuan *et al.*<sup>53</sup>) reported that the surface tension of liquid Sn had a non-linear relationship with the temperature when oxygen adsorption occurs on the surface of

liquid Sn. The present results shows a linear relationship in the wide temperature range, so that we may conclude that the present measurements were conducted in the atmosphere of very lower oxygen partial pressures, having not affected the surface tension values, viz,  $p_{O_2} \leq 4 \times 10^{-9}$  Pa.

## 2.2 Surface tension of liquid Sn-Ag and Sn-Cu alloys

The surface tension of liquid Sn-Ag alloys with concentrations of 10, 30, 50, 70 and 90 at% Ag was measured in the temperatures between 700 and 1500 K, and all measurements were plotted in Fig. 4. Experimental data for each composition were estimated with a linear regression method (solid lines in the figure), and listed in Table 1. It is noteworthy that the temperature coefficient for liquid Sn-50 and 70 at% Ag alloys have positive values:  $+0.012$  and  $+0.044$  mNm $^{-1}$ K $^{-1}$  respectively. It can be speculated that the positive temperature coefficients were not the result of the oxygen contamination, because we confirmed negative temperature coefficients for pure liquid metals (Ag and Sn). In Fig. 5, the surface tension of liquid Sn-Cu alloys with concentrations of 10, 30, 50, 70 and 90 at% Cu is shown. Positive temperature coefficients are also found for liquid Sn-50 and 70 at% Cu alloys. (See Table 1) We will discuss on this problem later.

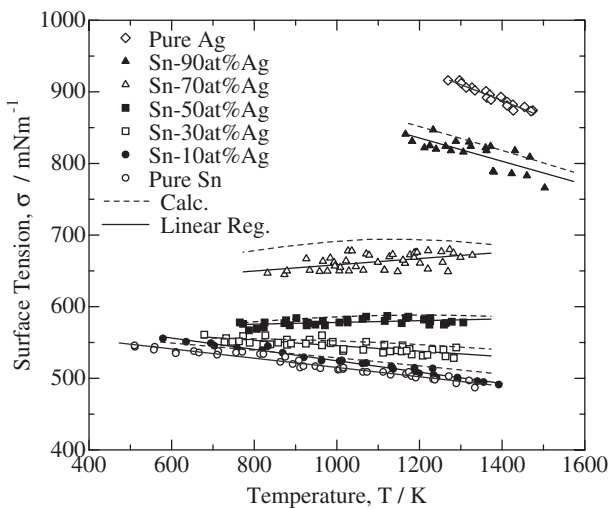


Fig. 4 Temperature dependence of the surface tension of liquid Sn-Ag alloys.

Table 1 The surface tension for liquid Sn-X (X=Ag,Cu) alloys as a function of temperature.

at% X	$\sigma = \sigma_{T=0K} - (d\sigma/dT)T$ (mN/m)	
	Sn-Ag	Sn-Cu
0	580 - 0.065T	
10	604 - 0.079T	590 - 0.068T
30	584 - 0.038T	566 - 0.032T
50	566 + 0.012T	555 + 0.014T
70	615 + 0.044T	595 + 0.060T
90	1031 - 0.163T	1076 - 0.064T
100	1207 - 0.228T	1585 - 0.211T

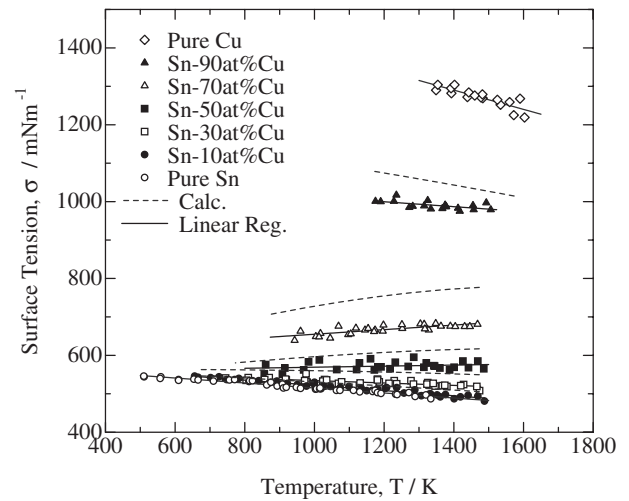


Fig. 5 Temperature dependence of the surface tension of liquid Sn-Cu alloys.

## 3. Thermodynamic Calculations

Butler's model was applied to estimate the thermodynamic quantities of the surface such as surface tension, surface concentration and relationships between them. Butler's model is expressed by eq. (5) for Sn-based binary alloys.

$$\begin{aligned} \sigma &= \sigma_{Sn} + \frac{RT}{A_{Sn}} \ln \left( \frac{1 - N_i^s}{1 - N_i^b} \right) \\ &+ \frac{1}{A_{Sn}} (\bar{G}_{Sn}^{Ex,s}(T, N_i^s) - \bar{G}_{Sn}^{Ex,b}(T, N_i^b)) \\ &= \sigma_i + \frac{RT}{A_i} \ln \left( \frac{N_i^s}{N_i^b} \right) \\ &+ \frac{1}{A_i} (\bar{G}_i^{Ex,s}(T, N_i^s) - \bar{G}_i^{Ex,b}(T, N_i^b)) \end{aligned} \quad (5)$$

where  $R$  is universal gas constant;  $T$ , is temperature;  $N_i^s$  is the mole fraction of  $i$  in the surface ( $N_{Sn}^s = 1 - N_i^s$ );  $N_i^b$  is the mole fraction of  $i$  in the bulk ( $N_{Sn}^b = 1 - N_i^b$ );  $\bar{G}_i^{Ex,s}(T, N_i^s)$  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  $N_i^b$ . The molar surface area of component  $i$  can be obtained by eq. (6).<sup>2,3)</sup>

$$A_i = 1.091 \cdot (6.02 \cdot 10^{23})^{1/3} \cdot V_i^{2/3} \quad (6)$$

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. The partial excess free energy in the surface is obtained using eq. (7) assuming that the partial excess Gibbs energy in the bulk and the surface have the same concentration dependence.

$$\bar{G}_i^{Ex,s}(T, N_i^s) = \beta \cdot \bar{G}_i^{Ex,b}(T, N_i^s) \quad (7)$$

The constant  $\beta$  ( $= 0.83$ ) is used the value of pure metals determined from the bonding energy difference between the surface and the bulk.<sup>3,4)</sup> Solving eq. (5) by instituting the thermo-physical data and the excess free energy of liquid Sn-X (X=Ag, Cu) alloys listed in Table 2, we can calculate the surface tension and the surface concentration as a function of the bulk concentration and the temperature. In Fig. 6, the

Table 2 Thermo-physical data and partial excess Gibbs energies for the calculation of the surface tension of Sn-X (X=Ag, Cu) alloys.

$V_i/\text{m}^3\text{mol}^{-1}$	$V_{\text{Sn}} = 17.0 \cdot 10^{-6}\{1 + 0.87 \cdot 10^{-4}(T - 504.99)\}^{13}$ $V_{\text{Ag}} = 11.6 \cdot 10^{-6}\{1 + 0.98 \cdot 10^{-4}(T - 1233.65)\}^{13}$ $V_{\text{Cu}} = 7.94 \cdot 10^{-6}\{1 + 1.0 \cdot 10^{-4}(T - 1356.15)\}^{13}$
$G^{\text{Ex}}/\text{Jmol}^{-1}$	$N_{\text{Ag}}N_{\text{Sn}}\{(-4902.5 - 4.30532T) + (-16474 + 3.12507T)(N_{\text{Ag}} - N_{\text{Sn}}) + (-7298.6)(N_{\text{Ag}} - N_{\text{Sn}})^2\}^{59}$ $N_{\text{Ag}}N_{\text{Sn}}\{(-8124 - 6.553T) + (-23970 + 7.037T)(N_{\text{Cu}} - N_{\text{Sn}}) + (-25124 + 13.566T)(N_{\text{Cu}} - N_{\text{Sn}})^2 + (-10213 + 10.042T)(N_{\text{Cu}} - N_{\text{Sn}})^3\}^{61}$

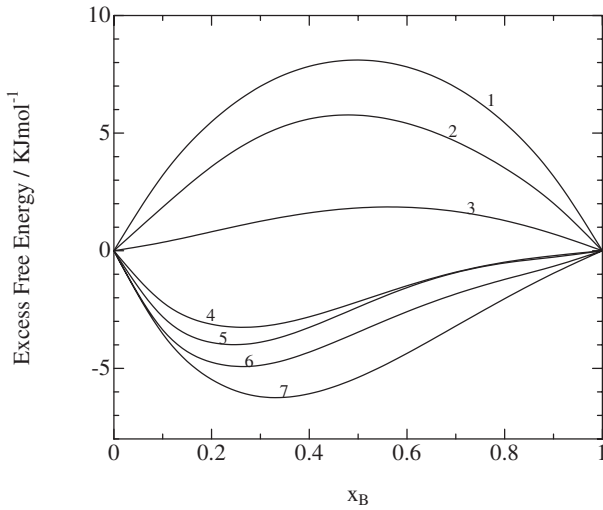


Fig. 6 Excess free energy of liquid A-B binary alloys. (1. Cu-Fe (Servant *et al.*<sup>56</sup>), 2. Pb-Cu (Wang *et al.*<sup>57</sup>), 3. Pb-Ag (Lee *et al.*<sup>58</sup>), 4. Sn-Ag (Kattner *et al.*<sup>59</sup>), 5. In-Cu (Liu *et al.*<sup>60</sup>), 6. Sn-Cu (Miettinen<sup>61</sup>), 7. In-Ag (Moser *et al.*<sup>62</sup>)).

Gibbs excess free energies of various binary alloys are given.<sup>56-62</sup> It is found that liquid Sn-Ag and Sn-Cu have negative values.

The calculated surface tensions are also plotted in Figs. 4 and 5 with broken lines. There is slight difference between the calculations and the measurements, but the agreement between them is acceptable. Nevertheless, it is noteworthy that the positive temperature dependence is also reproduced in the calculations for liquid Sn-50 and 70 at% Ag alloys and liquid Sn-50 and 70 at% Cu alloys.

## 4. Discussion

### 4.1 Temperature coefficient

The theoretical temperature coefficient of the surface tension for a pure liquid metal ( $d\sigma/dT$ ) is given by eq. (8).<sup>13</sup>

$$\frac{d\sigma}{dT} = \frac{\sigma}{T_C - T} \left( \frac{2(T_C - T)}{3\rho} \frac{d\rho}{dT} - 1 \right) \quad (8)$$

where  $T_C$  and  $\rho$  are the critical temperature and the density of the liquid metal. Since  $d\rho/dT$  of pure liquid metals is negative, the temperature coefficient ( $d\sigma/dT$ ) for the pure liquid metals should have a negative value. On the other hand, positive temperature coefficients can be observed in liquid alloys. The positive temperature coefficient has been reported especially with the system having very positive excess free energies. (Fig. 6) Joud *et al.*<sup>14</sup> observed positive

temperature coefficients for liquid Ag-Pb alloys (4.78, 12.08, 29.10 and 53.22% Pb) having positive excess free energies. Keene *et al.*<sup>63</sup> investigated positive temperature coefficients for Fe-based alloy systems containing surface active elements such as sulfur and oxygen, yielding very positive excess free energies.<sup>5,7</sup> For liquid alloys having a negative excess free energy, however, it has not been clarified whether the positive temperature coefficient be found. Moser *et al.*<sup>12</sup> observed negative temperature coefficients for liquid Sn-Ag alloys, but they pointed out that the predicted values by thermodynamic calculations showed positive temperature coefficients in the concentration range of 30 ~ 60 at% Sn at the lower. In the present work, some liquid Sn-Ag and Sn-Cu alloys having negative excess free energies showed positive temperature coefficients both in the measurements and the calculations. In order to clarify the effect of the thermo-physical parameters on the temperature coefficient, we testified simplified imaginary systems in the next section.

### 4.2 Effect of thermo-physical parameters on the temperature coefficient

Considering an imaginary A-B binary regular solution system, we calculate the surface tension using Butler's model. The melting temperature ( $T_m$ ) and the surface tension at  $T_m$  of pure liquid A and B are taken as 1000, 500 K and 1000, 500  $\text{mNm}^{-1}$ , respectively. In addition, the temperature coefficient and the molar volume of pure liquid metals were assumed as  $-0.1 \text{ mNm}^{-1}\text{K}^{-1}$  and  $10^{-5} \text{ m}^3\text{mol}^{-1}$ , respectively. Parameters used in this calculation are summarized in Table 3.

Firstly, the effect of the interaction parameter ( $\Omega = +10, 0, -10 \text{ kJmol}^{-1}$ ) was examined with fixing other variables. (In the regular solution system, the excess free energy is given by  $\Omega N_A N_B$ .) The calculation was conducted across the whole composition range, but we explain with the results of two representative compositions ( $N_B^b = 0.3$  and  $0.7$ ) for better understanding. If we solve the eq. (5) at a fixed bulk composition with changing the temperature, the surface tension is obtained as a function of temperature. Differentiating it with respect to the temperature, we can obtain the temperature coefficient. In Fig. 7, variations of the calculated temperature coefficient are shown. It is noteworthy that the temperature coefficient of the A-rich alloy ( $N_B^b = 0.3$ ) has very positive values at low temperatures and it markedly decreases with temperature to negative values, while that of the B-rich alloy ( $N_B^b = 0.7$ ) has negative values and moderately decreases with temperature. In Fig. 8, corresponding surface concentrations are plotted. The A-rich alloy ( $N_B^b = 0.3$ ) shows considerable changes in the surface

Table 3 Parameters used in the calculation of the surface tension of A-B alloys.

	Melting temp., $T_m/K$	Surface tension at $T_m$ , $\sigma/mNm^{-1}$	Molar volume, $V_i/m^3mol^{-1}$	Interaction parameter $\Omega/kJmol^{-1}$
A	1000	1000	$10^{-5}$	-10, 0, +10
B	500	300, 500, 800	$10^{-5}$	

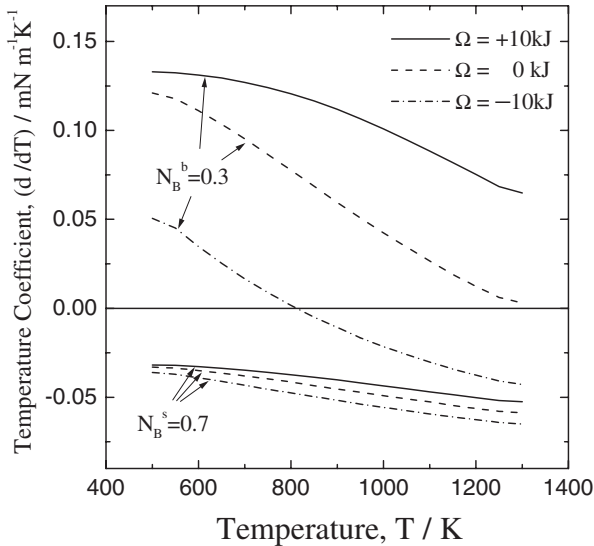


Fig. 7 Calculated results of the temperature coefficient with systematic change of  $\Omega$  on the basis of the regular solution model for liquid A-B alloys when  $N_B^b = 0.3$  and  $0.7$ .

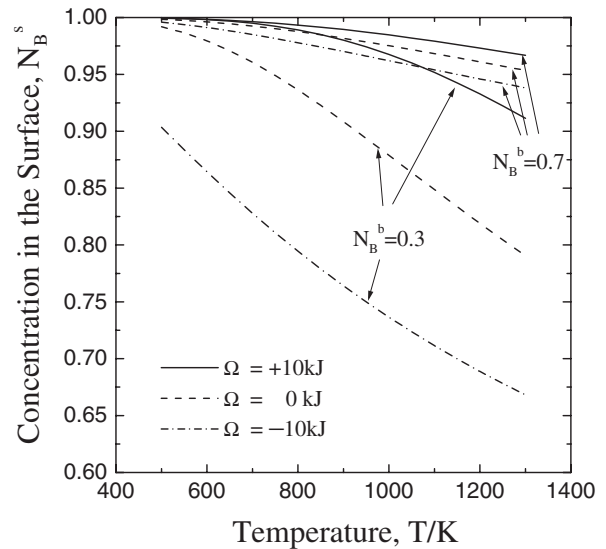


Fig. 8 Calculated results of the surface concentration with systematic change of  $\Omega$  on the basis of the regular solution model for liquid A-B alloys when  $N_B^b = 0.3$  and  $0.7$ .

concentration with temperature, while the B-rich alloy ( $N_B^b = 0.7$ ) decreases a little. Hence, it is believed that the dramatic change of the temperature coefficient is due to the remarkable change in the surface concentration. From Fig. 7, we can determine the maximum temperature to have a positive temperature coefficient. Applying the maximum temperature to Fig. 8, we can get the surface and bulk concentrations yielding the positive temperature coefficient. It is found that the temperature coefficient is positive when  $N_B^s/N_B^b > 2.67$  regardless the excess free energy. Thus, the enhanced level of B in the surface is considered as the main reason to cause the positive temperature coefficient. In addition, it is considered that the excess free energy contributes to the increase in the surface enhancement.

It is found that the temperature coefficient increases as increasing the excess free energy from Fig. 7. Nevertheless, it is still interesting that the temperature coefficient shows positive values even for the system having a negative excess free energy ( $\Omega = -10 \text{ kJmol}^{-1}$ ) in the low temperature region. Simulations for the system were conducted by changing the surface tension of pure B. In Figs. 9 and 10, the calculated temperature coefficient and surface concentration with varying the surface tension of pure B are shown, respectively. ( $\sigma_B$  (at  $T_m$ ) = 800, 500, 300) The simulation was conducted in the condition as follows:  $N_B^b = 0.3$  and  $0.7$ ,  $\Omega = -10 \text{ kJmol}^{-1}$ . It is considerable that the temperature coefficient of the A-rich alloy ( $N_B^b = 0.3$ ) becomes more positive as the difference of the surface tensions between pure A and B increases. It is considerable that the positive

temperature coefficient is found at the same criteria as in the calculation of the effect of interaction parameters; viz,  $N_B^s/N_B^b > 2.67$ .

In order to clarify the effect of the bulk composition, the simulations have been conducted with different compositions. In Fig. 11, the relationship between the bulk and the surface concentration to have the zero temperature coefficients is shown. Regardless the excess free energy and the surface tension differences, the zero temperature coefficient is only described as a function of the concentration ratio between the bulk and the surface. Since we assumed that the temperature coefficient and the molar volume of pure liquid metals are constants in the present calculations, the Gibbs adsorption equation is valid.

$$d\sigma = -\frac{S^s}{A}dT - \sum \Gamma_i d\mu_i = -\frac{S^s}{A}dT - \frac{dG^{s,\text{Mix}}}{A} \quad (9)$$

where  $\Gamma_i$  and  $G^{s,\text{Mix}}$  are the adsorption of  $i$  and the Gibbs free energy of mixing in the surface. From eq. (9), we obtain

$$\frac{d\sigma}{dT} = -\frac{S^s}{A} - \frac{dG^{s,\text{Mix}}}{AdT} \quad (10)$$

The first and second terms on the right side denote the surface entropy ( $S^s$ ) and the ordering effect by the surface enhancement in unit area. Therefore, when the temperature coefficient is zero, the surface entropy is equal to the surface mixing entropy. For a regular solution, the surface mixing entropy will not depend on the interaction parameter and the surface tension difference between component metals. On the

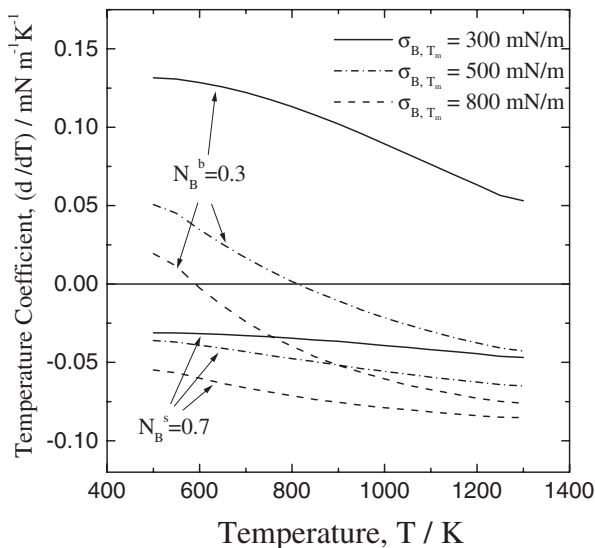


Fig. 9 Calculated results of the temperature coefficient with systematic change of  $\sigma_B$  when  $\Omega = -10$  kJ/mol.

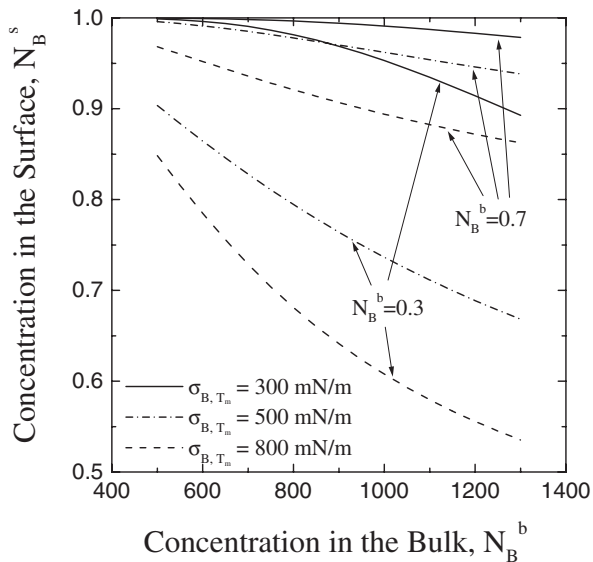


Fig. 10 Calculated results of the surface concentration with systematic change of  $\sigma_B$  when  $\Omega = -10$  kJ/mol.

other hand, the surface composition is closely related to the bulk composition. Therefore, the zero temperature coefficients are given as a function of the ratio between bulk and surface compositions, and the positive temperature coefficients are obtained for the surface enhancement.

Based on the results described above, it can be concluded that the temperature coefficient is determined by the surface enhancement, and it remarkably increase as the difference of the surface tensions and the excess free energy between the component metals increase. The simulation results are very helpful to understand the positive temperature coefficients in the Sn-Ag and Sn-Cu systems. Based on the present simulations, it is concluded that positive temperature coefficients in the Sn-Ag and Sn-Cu systems are mainly due to the enhanced level of Sn in the surface caused by the large difference in the surface tensions between the component

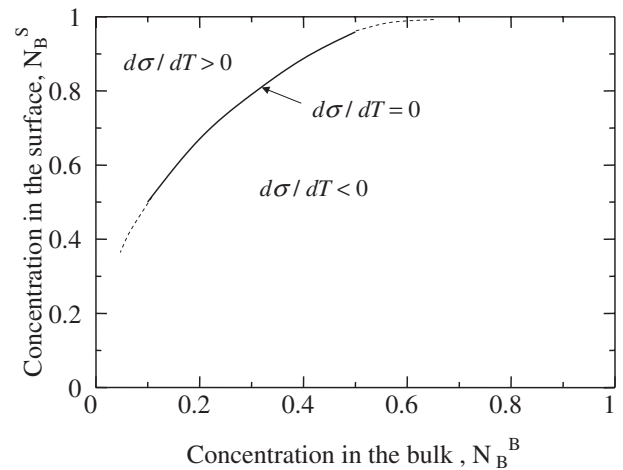


Fig. 11 Relationship of concentrations of B between the bulk and the surface when  $d\sigma/dT = 0$ .

metals, because the liquid alloys have very negative excess free energies.

## 5. Conclusions

In this paper, surface tension of liquid Sn-X (X=Ag, Cu) alloys was measured by the constrained drop method and compared with the calculated results by Butler's model using thermodynamic database. The temperature coefficients of the surface tension have both positive and negative values. From the simulation, the positive temperature coefficient was considered due to the large difference in the surface tensions between the component pure metals, yielding the enhanced level of Sn in the surface.

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