

# Periodicity of Interaction Coefficients of Al and Si in Molten Fe-Based Alloys Arranged with Periodical Table and Phase Diagrams

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**Abstract:** Periodicity of the interaction coefficients of Al and Si;  $\epsilon_{Al}^j$  and  $\epsilon_{Si}^j$  in molten iron was analyzed to try generalization of the interaction coefficients. The coefficients of both Al and Si, which are important for deoxidation of molten steels, arranged with periodic table show periodicity with each Period from 2 to 5. Referring to the phase diagrams of Al-j systems, the melting point of the first compound from the Al-j liquid solution was focused on. It was found that the interaction coefficients increased with increasing the melting point of the compounds. The empirical correlations were found as  $\epsilon_{Al}^j = 0.019 \cdot T_M (\text{compound}) - 19.48$  (Al-system) and  $\epsilon_{Si}^j = 0.053 \cdot T_M (\text{compound}) - 74.35$  (Si-system)  $T_M$  is the melting point of the compound. The periodicity was more improved by applying the above equations than the first plots.

**Keywords:** Interaction Coefficient, Al, Si, Periodic Table, Periodicity

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## 1. Introduction

In the last two decades, a number of interaction coefficients  $e_i^j$  have been measured by various researchers. Those include minor elements of Si, Al, Mg, Ca and Ti to particularly respond the control of non-metallic inclusions. A committee in Japan published a book [1] allowing researchers to apply relevant equilibrium constants as well as the interaction coefficients depending on what reaction each researcher works on.

Much attention has been paid to the coefficients in terms of the effect of Ti on Si in molten iron owing to the importance of behavior of Ti in molten iron [1-6] that occasionally leads to problems in practice such as nozzle clogging attributed to the formation of TiN or Ti oxide inclusions [7]. The coefficients were on discussion due to the significant scattering to determine what values are closest to the truth. Some researchers have made great efforts to clarify the value [1-6]. A research group has paid attention to the periodicity of the coefficient of the effect of Ti on Si and N to verify the value obtained by the group [5]. The work shows that the significance of the coefficient is not as much.

Most recently, a special issue of "Thermodynamics of

Deoxidizing Elements, Transition Metals and Tramp Elements in Steel" [8] was published to clarify the relevant interaction coefficients. The author demonstrated the periodicity of the coefficients of the effects of j elements on Al and Si arranged with periodical table in the issue [9] indicating that periodicities have been confirmed studying the previous articles [10-12]. The periodicity of the effect of j elements on C in the molten iron is most well-known for the metallurgists in charge of blast furnaces and converters. In the paper [10], the periodicity was comprehensively described referring to thermochemical values of excess free energy. This challenge to discover a rule tells us that generalization of the coefficients has been being tried until recent days.

In the research field of solid solution (partially liquid) of alloys, H; heats of solution for binary alloys were empirically deduced by the summation of the electron densities of the free atoms situated at the lattice positions at  $T=0$  (K) [13]. H is well-known as the excess free energy expressed by activity coefficient and the solute content. As recognized, activity coefficient is the summation of the

products of the relevant interaction coefficients and the solute contents. This concept appears quite alike the previous work [10-12] because the electron densities of the free atoms situated at the lattice positions obey the periodical table. A model of Lennard-Jones type interatomic potential to estimate the interaction parameters was applied for the vacancy properties in ordered  $\text{Ni}_3\text{Al}$  alloys by cluster variation method [14]. The model suggests the calculation of the affinity of two atoms.

On the basis of the above investigations, a trial followed by the previous studies [5, 9] has been carried out to clarify the periodicity of the interaction coefficients in the molten iron using the accumulated data [1, 5, 8, 15, 16]. This study aims at finding some regulations of the coefficients referring to the periodical table and thereafter focusing on the phase diagrams of the  $i$ - $j$  systems. The goal is to estimate the unknown coefficients but are necessary to describe some reactions. Sometimes, experimentations themselves are difficult, dangerous or costly particularly for the combinations of active elements. The coefficients of  $j$  elements on Al and Si are studied because the values corresponding these elements are quite inevitably used to calculate the oxygen content in equilibrium after the treatment of deoxidation of the steels. Thereafter, physical significance is discussed on an estimation basis.

## 2. Results and Discussion

### 2.1. Arrangement with Periodical Table

#### 2.1.1. Case of $i=\text{Al}$

Figure 1 shows the coefficients of  $\epsilon_{\text{Al}}^j$  arranged by the

atomic number, where the values of  $e_i^j$  have been converted by the following well-known equation [1]:

$$\epsilon_i^j = 230 \frac{M_j}{M_{\text{Fe}}} e_i^j + \left(1 - \frac{M_j}{M_{\text{Fe}}}\right) \quad (1)$$

where  $M$  is atomic weight of the  $j$  element.

One can understand focusing on the periods 2 and 3 that C and Si take the peak values lighter than which the coefficients are smaller and heavier than which those smaller as well. As understood, period 4 behave the tendency same as the 2 and 3 except at  $j=\text{Co}$  plotted above the curve. Period 5 does not have the values corresponding to the lighter side elements; however, the heavier side shows the similar slope to the period 4. It is noted that the value of  $j=\text{Mo}$  is taken by the estimated one in the previous study [9]. Period 6 has merely a value of  $j=\text{Pb}$  indicating that the tendency is unknown. Summarizing the plots one can evidently understand that Periods 2, 3 and 4 obey a regulation except at  $j=\text{Co}$  that the values of  $j=\text{C}$ , Si and Ti take the peaks with smooth curves.

Taking the measured values into consideration, the coefficients of  $j=\text{Mo}$  [17] and Sn [18] are apart from the curves. This result might tell us that the regulation has to be accounted for with the background of physics.

Due to the characteristics of Eq. (1), the lighter the  $j$  elements are the more significant the coefficients are as far as engineers prefer to mass% as the unit of the solute contents. Figure 2 shows the case with  $j=\text{Cr}$ , Mo and W assuming that the reported coefficient of  $\epsilon_{\text{Al}}^{\text{Cr}}=2.12$  obeys the regulation stated above. The following equation is available:

$$\epsilon_{\text{Al}}^{\text{Mo}} = \epsilon_{\text{Al}}^{\text{W}} = 2.12 \quad (2)$$

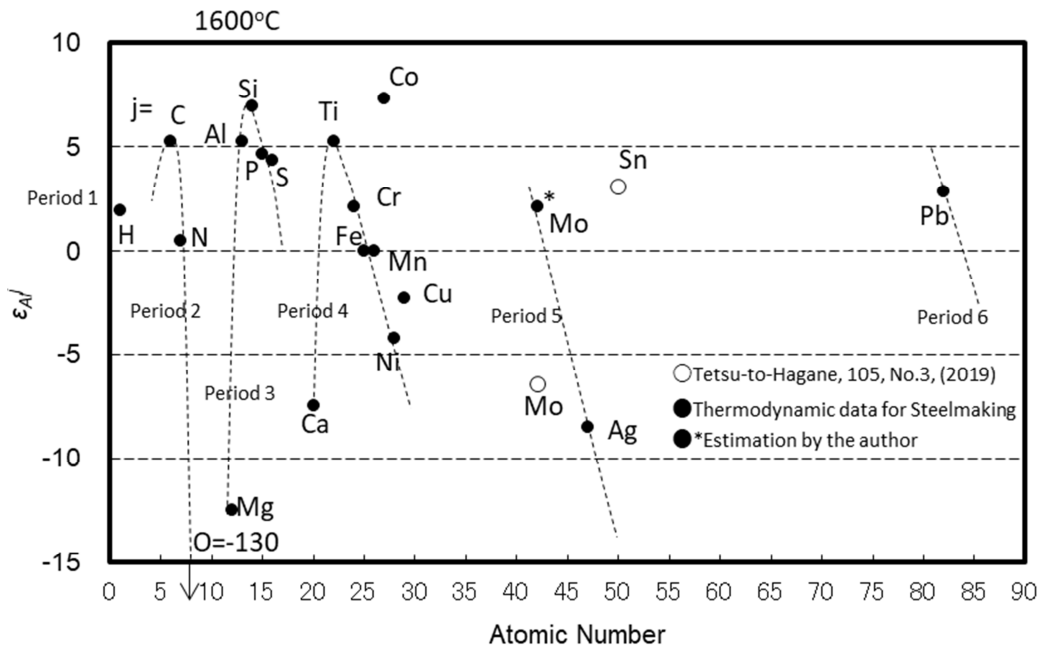


Figure 1. Interaction parameters of effects of  $j$ -elements on Al arranged with atomic number.

The coefficients of  $\epsilon_{\text{Al}}^j$  ( $j=\text{Cr}$ , Mo, W) are becoming smaller with atomic number due to the use of mass% as the unit of

weight apparently implying that the significance of the coefficients is less with the heavier solutes.

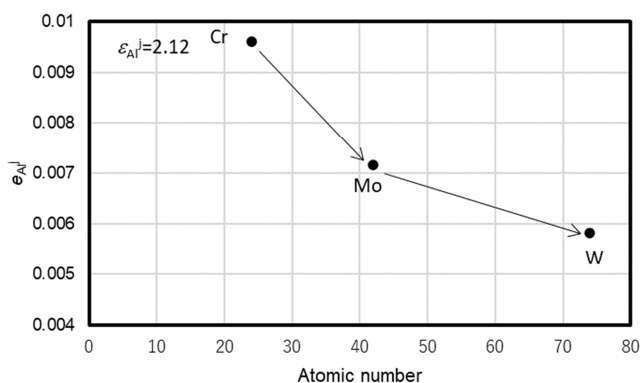


Figure 2. Interaction coefficients of  $e_{Al}^j$  taking  $j$  as Cr, Mo and W.

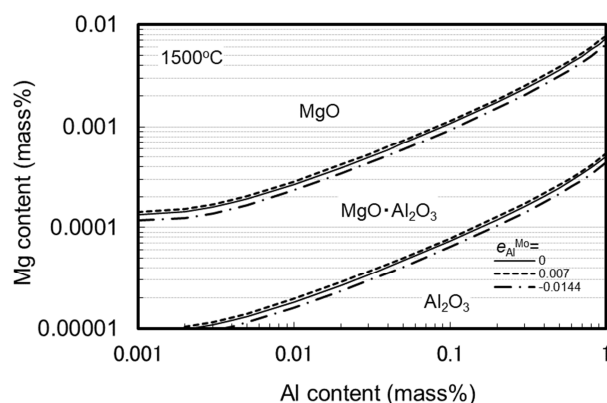


Figure 3. Oxide stability diagram of MgO, MgO·Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in molten Fe-23.5mass%Cr-22mass%Ni-6.2mass%Mo alloy.

An oxide stability diagram relevant to MgO, MgO·Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in the molten Fe - 23.5mass%Cr - 22mass%Ni - 6.2mass%Mo alloy was calculated originally ignoring the interaction coefficient of  $e_{Al}^{Mg}$  as zero [19]. The diagram has been recalculated applying the interaction coefficients of the

previously estimated [9] and measured [17]. Figure 3 shows the comparison of the applications of the three cases with which it is evidently understood that the coefficients are not very significant. This is because the lines are very close to each other supporting the tendency shown in Figure 2.

It is noted that the relationship between  $\epsilon_{Al}^j$  and  $e_{Al}^j$  has to be careful of the plus and minus in values. The positive value of  $\epsilon_{Al}^j$  usually gives positive value of  $e_{Al}^j$ ; however, some exceptions exist. For example, when  $j=N$ ,  $\epsilon_{Al}^j=0.25$  while  $e_{Al}^j=-0.004$ . Hence, it is occasionally risky to judge that when  $e_i^j$  is negative, the affinity between  $i$  and  $j$  is intimate. The conversion to  $\epsilon_i^j$  is necessary to discuss the affinity between  $i$  and  $j$  elements.

### 2.1.2. Case of $i=Si$

Figure 4 shows the interaction coefficients of  $\epsilon_{Si}^j$  in molten iron arranged by atomic number applying the same manner as in the previous section. In the case of  $j=Ti$  wide scattering is obvious [1, 2, 6, 21]. The corresponding reason has not been clarified yet. Once, taking Y axis up to 60, Figure 5 can be obtained in which the tendency similar to the case of  $i=Al$  is obvious as is seen in Figure 1. Periods 2 and 3 suggest the peaks with  $j=C$  and  $Si$  while Period 4 indicates somewhat scattering. Focusing on Period 4, the coefficients of  $j=Ti$  are higher than the others and the value of  $j=Fe$  is principally zero implying that the coefficients of  $j=Cr$ ,  $Mn$  and  $Ni$  seem to be with experimental error. Therewith the author has drawn the curved line the same as the case of  $i=Al$  shown in Figure 1. Period 5 has the value with  $j=Mo$  obtained by Taguchi et al. [22] while no data were found as for Period 6. Therefore, it is concluded here that Periods 2 and 3 show the same tendency as is in the case of  $i=Al$  while Period 4 somehow scatters to some extent, however, the values of  $j=Ti$  shows higher than the others.

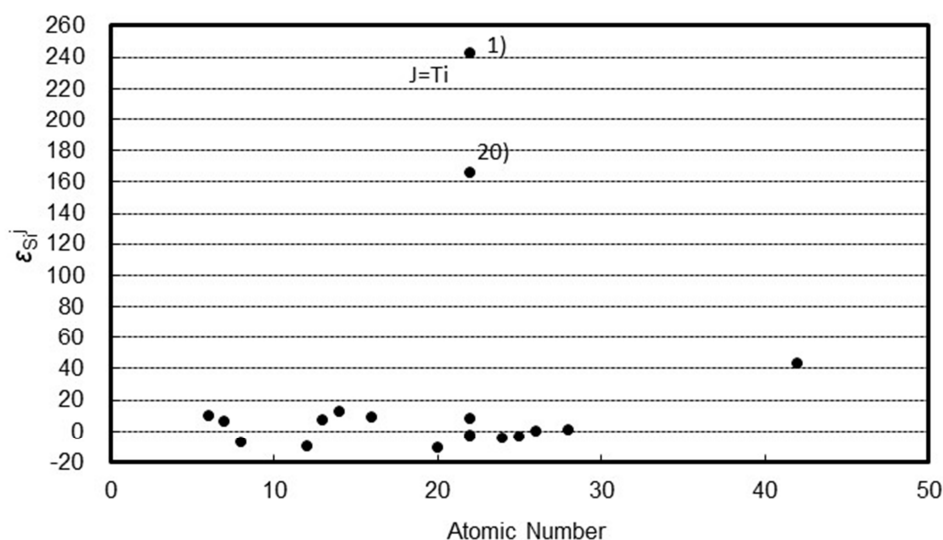


Figure 4. Interaction coefficients of  $\epsilon_{Si}^j$  in molten iron arranged by atomic number.

## 2.2. Relation to Phase Diagrams

Learning the empirical relation and bonding energy [13, 14],

phase diagrams [23] are focused on because they are created with a lot of thermochemical information. Figure 6 shows the typical diagrams of Al- $j$  systems with  $j=Ti$ ,  $S$  and  $Mn$ . The

author accounts for the nearest Al·j compounds referring to the Al sides with another assumption that the compounds have significance with the first ones from the homogeneous Al-j system liquid solutions and the compounds should have non-stoichiometric regions that are solid solutions. Unless compounds were found, the j end was selected instead of the compound.

Figures 7 (a) and (b) show the results of the interaction coefficients plotted against the melting points as for Al and Si, respectively. As understood, in both cases, the coefficients increase with increasing the melting points of the compounds which obey the above rule. One can see that the lowest values

begin with Mg and Ca and then transition metal elements including Fe, Cr, Mn and Ni. At the higher positions, S, Si and Ti stay and at the highest position Mo is plotted. Taking the least squares, the following relations are empirically obtained:

$$\varepsilon_{Al}^j = 0.019 \cdot T_M (\text{compound}) - 19.48 \quad (\text{Al-system}) \quad (3)$$

$$\varepsilon_{Si}^j = 0.053 \cdot T_M (\text{compound}) - 74.35 \quad (\text{Si-system}) \quad (4)$$

where  $T_M$  is the melting temperature ( $^{\circ}\text{C}$ ) of the compound under the above assumption.

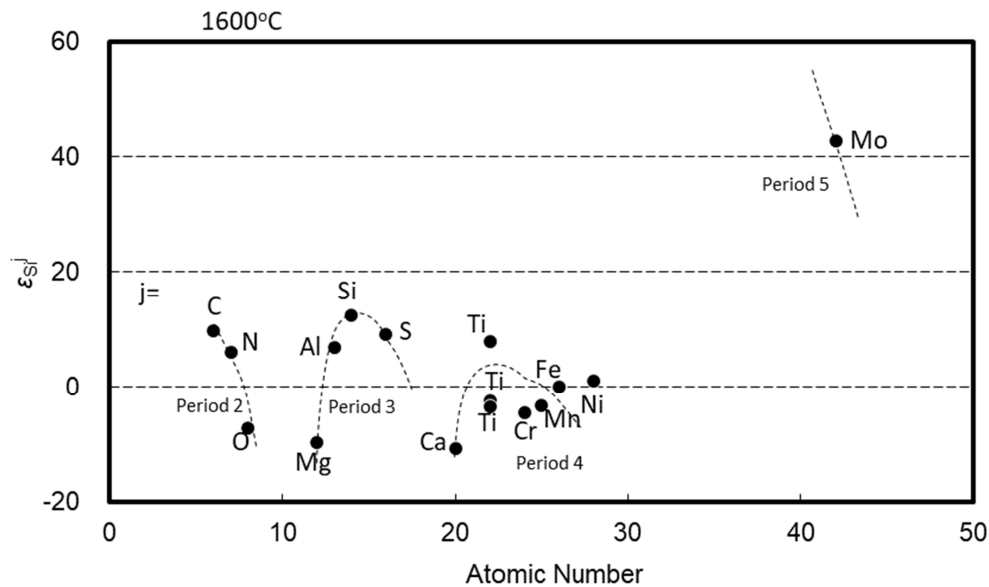


Figure 5. Interaction coefficients of  $\varepsilon_{Si}^j$  arranged with atomic number taking Y axis up to 60.

$$\varepsilon_{Al}^{Ti} = 5.27$$

$$\varepsilon_{Al}^S = 4.39$$

$$\varepsilon_{Al}^{Mn} = 0.02$$

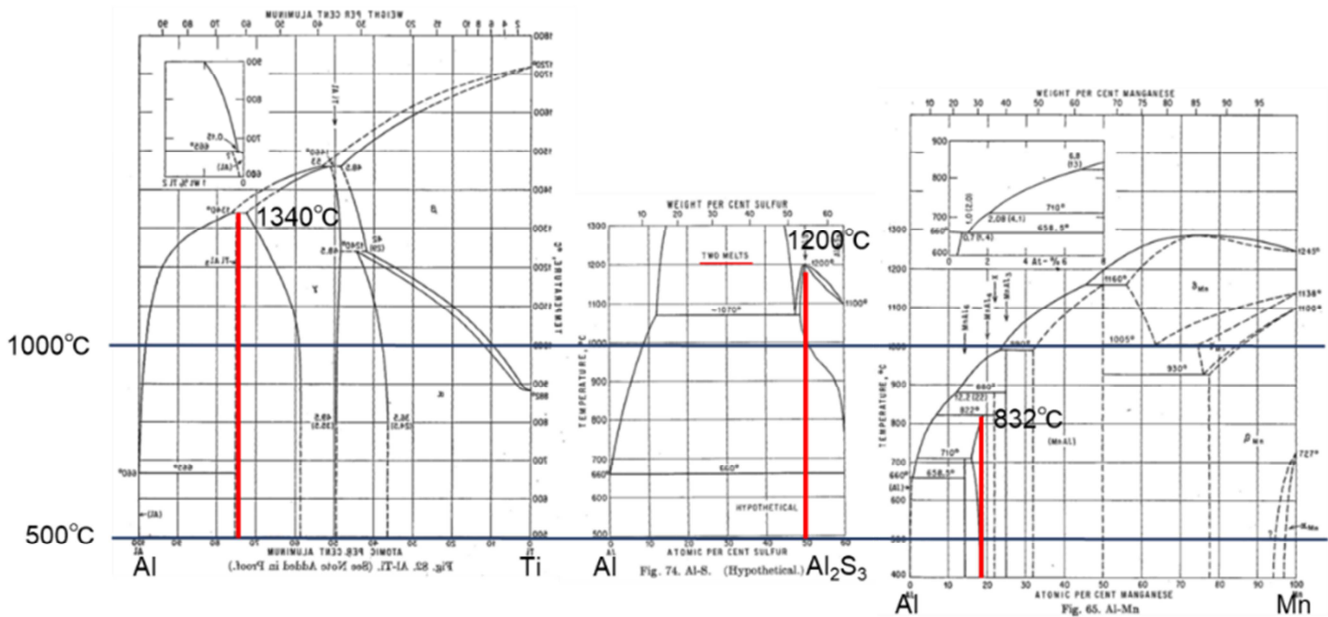
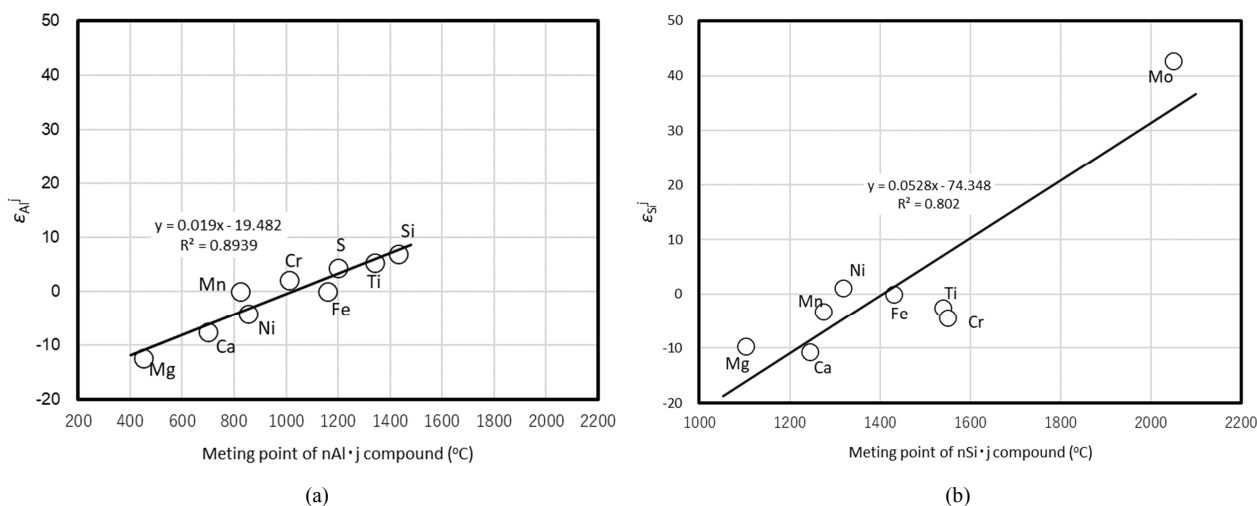
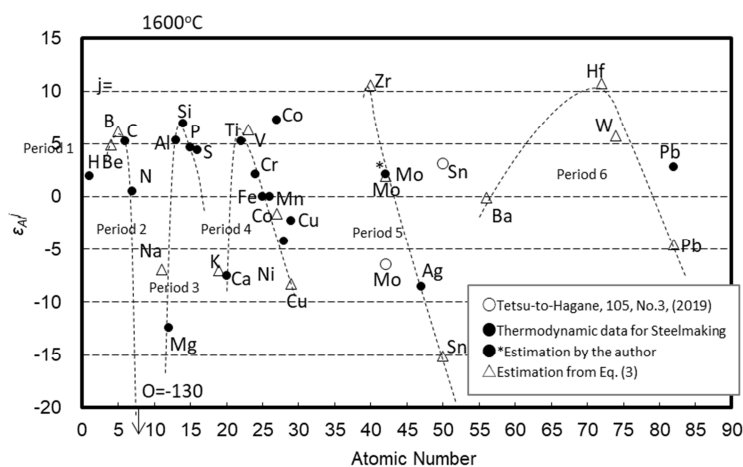


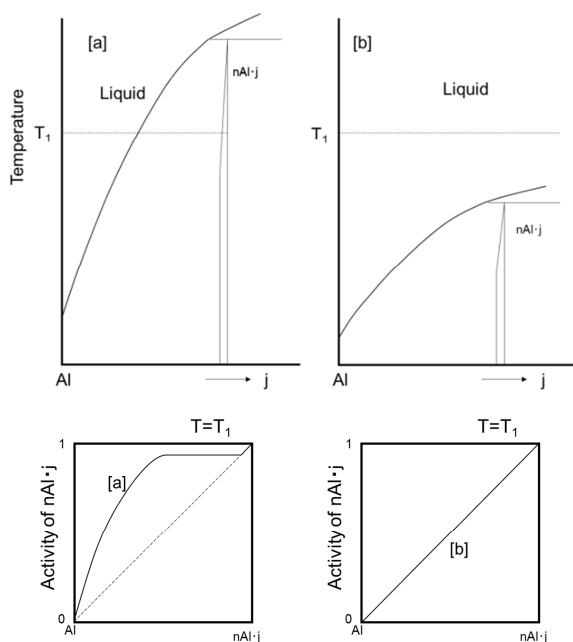
Figure 6. Phase diagrams of Al-Ti, Al-S and Al-Mn systems adjusting temperature with interaction coefficients.



**Figure 7.** Interaction coefficients of effects of  $j$  elements on Al (a) and Si (b) in relation with the compounds closest to the Al and Si sides from homogeneous liquid solutions which should have solid solutions, plotted against their melting points.



**Figure 8.** Coefficients assumed by Eq. (3).



**Figure 9.** Schematic illustration of phase diagrams along with supposed activity of  $nAl \cdot j$  at  $T=T_1$ .

According to the phase diagram of Al-Zr system [24], the compound under the assumption has the melting temperature of 1580°C. A value of 10.8 was obtained after inputting this temperature to Eq. (3). In addition, Al-Hf phase diagram [24] shows the melting point of the corresponding compound as 1590°C resulting in 10.7 as the coefficient. The other systems have been further calculated referring to the relevant phase diagrams [24]. Figure 8 shows the coefficient estimated as the above manner plotted as the open triangles. As clearly realized, the value of Zr is well consistent with the line extrapolated by the coefficients of  $j=Mo$  and Ag. The lighter side is unknown as for Period. However, the value of Hf shows the peak at Period 6 consistently with the calculated value of  $j=Pb$  with the slope consistent with Period 5 applying the estimated value of  $j=Pb$ . In addition, Period 4, the most important period due to a lot of alloying elements, shows the periodicity more evidently with  $J=Co$  and  $Cu$  adjusted by the calculated values. The coefficients of  $j=Na$  and  $K$  are close to  $j=Mg$  and  $Ca$ , respectively. The phase diagrams with Si- $j$  system were not found much. It is presumed that Al based alloys are widely applied for various use, whereas Si based alloys are not as much applied as the Al alloys.

The reason of this regulation has to be discussed from the viewpoints of thermochemical aspects. The author ponders that activity of  $n\text{Al} \cdot j$  at  $T=T_1$  should be considered to explain the affinity of Al with the  $j$  element. Figures 9 (a) and (b) show the schematic illustrations of the schematic phase diagrams along with the supposed activity of  $n\text{Al} \cdot j$  at  $T=T_1$ . The figures (a) and (b) show the illustrations in the cases of the higher and the lower melting points of the compounds, respectively. In (a), the system has the characteristics of repulsion due to the formation of  $n\text{Al} \cdot j$  at  $T=T_1$ . Therefore, the activity would take positive deviation in reference to Raoult's law. On the other hand, in (b), the activity would take almost ideal due to the homogeneous melt at  $T=T_1$ . Thus, the activity coefficient takes relatively high with the higher melting points leading to the higher coefficients of  $\varepsilon_{\text{Al}}^j$  consistently with Figure 7. It is desirable that software, today widely used, apply the equations of (3) and (4) to predict some unknown coefficients which would result in more accurate calculation than ignorance of the corresponding coefficients.

### 3. Conclusion

Analysis was conducted to try generalization of the interaction coefficients of Al and Si in Fe based alloys. The coefficients were arranged with periodic table and the phase diagrams. The following words summarize this study:

1. It was found that the coefficients of both Al and Si arranged with periodic table show periodicity with each Period from 2 to 5.
2. Referring to the phase diagrams of Al- $j$  system, the melting point of the first compound from the Al- $j$  liquid solution was focused on. It was found that the interaction coefficients increased with increasing the melting point of the compounds.
3. The empirical correlations were found as follows:
  - 1)  $\varepsilon_{\text{Al}}^j = 0.019 \cdot T_M (\text{compound}) - 19.48$  (Al-system)
  - 2)  $\varepsilon_{\text{Si}}^j = 0.053 \cdot T_M (\text{compound}) - 74.35$  (Si-system)

here,  $T_M$  is the melting point of the compound.

4. The periodicity was more improved by applying the above equations than the first plots.

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