Estimation of liquidus temperature of Sn-based alloys and its application to the design of Pb-free solder

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An interesting relation between the melting temperature and the alloy composition was discovered in Sn-based alloys through the evaluation of a series of experimental data on the liquidus temperatures (LTs) for 134 types of multi-component Sn alloys. In these Sn alloys, the degree of liquidus temperature drop with alloying was not affected by the kind of individual elements but by their total atomic fraction alone. The compositional dependence on the LT could be expressed by the equation, $LT(K) = 499.79 - 1.799X$, where X was the total mole percentage of alloying elements. It was demonstrated that the use of this equation would make it possible to develop Pb-free solder alloys more efficiently.

1. Introduction

Sn–Pb alloys are used currently as a solder in electrical and electronic industries. In recent years, however, it has been claimed that there is a possibility of polluting the environment with toxic Pb contained in the solder. Much attention has been paid to the development of Pb-free solder alloys in various countries [1–7].

For the development of new solder alloys, it is required first that the designed alloy has similar physical, chemical, and mechanical properties to those of the conventional Sn–Pb solder alloy. Among the properties, the melting temperature is one of the most important factors in the design of new Pb-free solder alloys from the viewpoint of soldering operation and heat damage to the electronic devices during the operation. It can be said that determining the alloy composition with optimum melting temperature is the first step in the alloy design, and this process requires a great deal of time. For this purpose, thermodynamic calculations have been employed and some phase diagrams of multi-component Sn alloys have been determined [8–11]. However, such an approach is limited only to those alloy systems in which the thermodynamic parameters are well established.

In this study, an experiment has been conducted in order to obtain the extensive data set concerning the effect of alloying elements on the melting temperature of Sn alloys. From the analysis of a series of experimental data, an interesting and simple rule was found for the melting temperature of Sn alloys.

2. Experimental procedures

Sn-based alloys containing Ag, Zn, In, Bi, Cu, and Ga were melted in a graphite crucible at 573 K in air. The total number of experimental alloys was 134. The compositional range of them is shown in Table I. The weight of each alloy was about 1 kg. The purities of the respective raw materials used for making these alloys were higher than 99.9%. The liquidus temperatures (LTs) of these alloys were measured from the cooling curves using a thermocouple. The thermocouple was calibrated carefully by measuring the melting temperatures of Sn,

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TABLE I Compositional range of multi-component Sn-based alloys prepared in this experiment

Alloying element	Compositional range (wt %)	Total number of alloys
Ag	0–3.5	
Zn	0–8.8	
In	0–25.0	
Bi	0–25.0	134
Cu	0–1.0	
Ga	0–2.0	
Sn	balance	

Pb, and Bi and the eutectic temperature of a Sn–Pb alloy. The average cooling rate was $0.025\,\mathrm{K\,s^{-1}}$

3. Results

The measured LTs of Sn alloys are plotted in Fig. 1 against the total amount of alloying elements in each alloy. Surprisingly, there was a good correlation between them. The LTs of Sn alloys decreased linearly with increasing total mole fraction of the alloying elements. As shown in this figure, a straight line was drawn by the least squares method, and it was expressed as,

$$\mathrm{LT(K)} = 499.79 - 1.799X$$

where LT is the liquidus temperature of the alloy and X is the total amount of alloying elements in mol %. The correlation coefficient, R, was as high as 0.981, according to the regression analysis. This experimental result apparently indicates that the liquidus temperature drop in Sn alloys does not depend on the individual alloying elements, but on the sum of mole percentages of alloying elements.

4. Discussion

4.1. Eutectic temperature and composition of Sn binary alloys

There have been no reports showing such a simple relation between the LTs and the alloy compositions

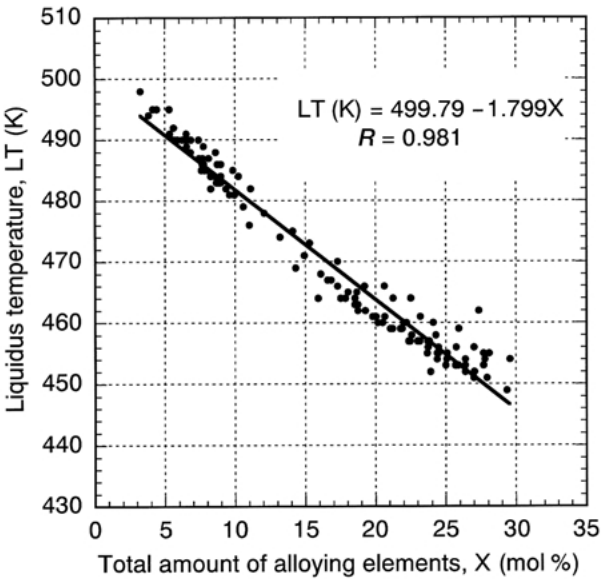

Figure 1 Relation between the LTs and total amount of alloying elements in the 134 types of Sn-based multi-component alloys.

shown in Fig. 1. This result seems to have significant meanings both theoretically and practically. The existence of such a relation in Sn alloys was further examined using fundamental information obtained from a series of Sn binary equilibrium phase diagrams [12].

The melting temperature of Sn, in most cases, decreases by the addition of the second elements, M, due to the occurrence of a eutectic reaction with M in it. Among the second elements, Sb is the only one exceptional element that increases the melting temperature of Sn by the onset of a peritectic reaction. The eutectic temperatures and compositions, which were well defined in binary phase diagrams, were selected and are listed in Table II. The eutectic temperatures are plotted in Fig. 2 against the eutectic compositions in mol %. As indicated by a straight line in the figure, a linear relationship can be seen clearly between the eutectic temperatures and the compositions. For comparison, a dotted line is also presented in the figure to show the relation between LTs and compositions obtained from Fig. 1. A straight line drawn from the compositional dependence of eutectic temperatures agreed well with the dotted line.

On the hypothesis that the liquidus line drawn by connecting the melting temperature of Sn, 505 K, with the eutectic point in the phase diagram is approximately linear, all the liquidus lines in the binary phase diagrams will be overlapped with each other and will fall on one straight line. As a result, the LT of the alloy has no alloying element dependence. The result shown in Fig. 1 can be understood by extending such an assumption to the liquidus surface of the multi-component Sn alloys. It is important to note here that such an explanation should

TABLE II Eutectic temperatures and compositions in Sn-binary phase diagrams

Alloy Sn–M	Eutectic temperature (K)	Eutectic composition, M (mol %)
Sn–Ag	494	3.8
Sn–Al	501	2.4
Sn–As	504.3	0.2
Sn–Au	490	6.3
Sn–Bi	412	43
Sn–Ca	503	~ 0.4
Sn–Cd	449*	33.45
Sn–Cu	500	1.3
Sn–Fe	504.96	0.001
Sn–Ga	293.5	91.6
Sn–Ge	504.1	0.26
Sn–In	393*	51.7
Sn–Li	495	5
Sn–Mg	476.5	9.6
Sn–Ni	504.15	0.3
Sn–Pb	456	26.1
Sn–Se	504	0.2
Sn–Sm	502	0.2
Sn–Sr	503	1
Sn–Te	504.5	0.01
Sn–Ti	504	~ 0.5
Sn–Tl	441	31
Sn–Y	502	1.6
Sn–Yb	503	1
Sn–Zn	471.5	14.9

*Eutectic reaction followed by peritectic reaction.

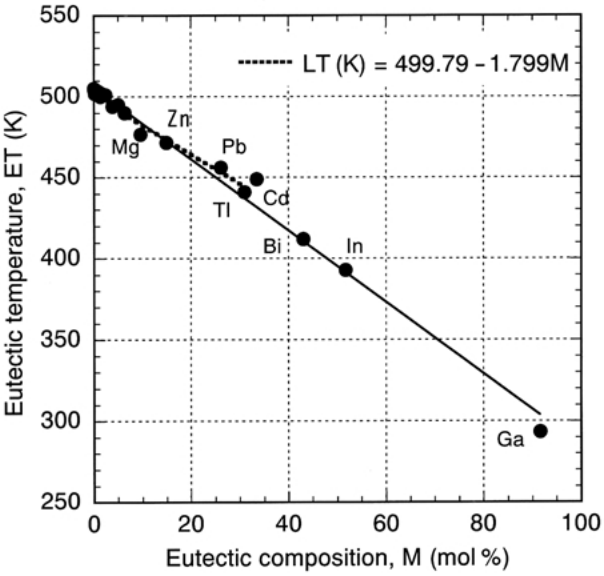

Figure 2 Relation between the eutectic temperatures and compositions in Sn-binary alloy phase diagrams.

be given only for the alloy with the hypoeutectic composition, i.e., where the alloy composition is less than the eutectic composition.

4.2. Compositional dependence of eutectic temperatures in simple- and transition-metal-based alloys

Sn belongs to a group of simple metals, and s- and p-electrons will mainly contribute to its physical and chemical properties. The same evaluation as done in Fig. 2 was carried out for other simple-metal-based alloys, such as Zn, Sb, and Bi binary alloys. The results are shown in Fig. 3 for Zn, Sb, and Bi. Such a strong correlation as observed in Sn alloys was not seen in these alloys. However, the eutectic temperature still tends to decrease with increasing amount of the second element at the eutectic point in these simple-metal-based alloys. The same attempt was also made for Ni-based binary alloys,

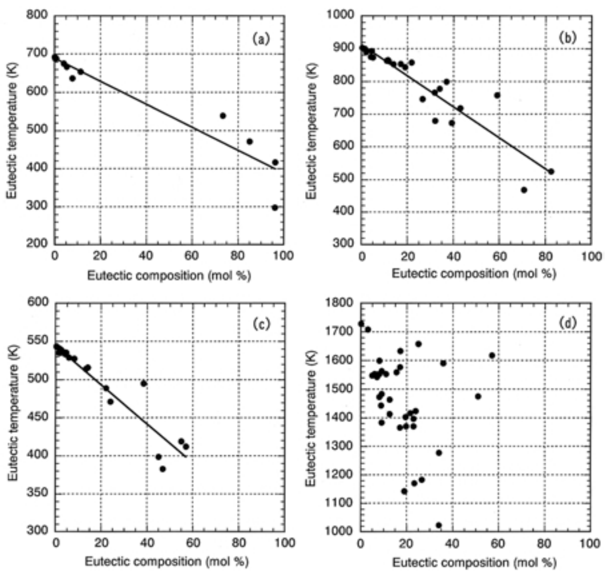

Figure 3 Relations between the eutectic temperatures and compositions in (a) Zn, (b) Sb, (c) Bi and (d) Ni binary-alloy phase diagrams.

one of the transition-metal-based alloys, and the result is shown in Fig. 3d. The data are scattered widely and any clear compositional dependence on eutectic temperatures is not found in the Ni binary alloys. These results indicate that the existence of a simple relation between eutectic temperatures and compositions is a peculiar feature of simple-metal-based alloys. As yet, a full explanation has not been given for why the LT drops irrespective of individual alloying element in the Sn-based alloys.

Here, it is simply noted that the melting temperatures of pure transition metals correlate well with the cohesive energy [13]. This is, however, not the case in the low melting temperature metals such as In, Sn, and Sb, in which the melting temperatures seem to correlate in some way with the Debye temperatures [13]. In other words, the contribution of thermal vibration energy to the free energy is probably significant near the melting temperature range of Sn. So, to account for the present result, it may be necessary to take such a vibrational term into consideration in a proper manner. Further study is now underway.

4.3. Application to the design of Pb-free solder alloy

A relation between the LT and the composition of Sn alloy will be useful for the design of Pb-free solder alloys. As described earlier, the melting temperature is one of the most important factors in the solder alloy. By utilizing Equation 1, the LT of the designed alloy can be estimated readily without doing any experiments. This will help us to save time and cost during the development of Pb-free solder alloys.

Actually, some Sn-based ternary and quaternary alloys listed in Table III were designed in order to confirm the validity of Equation 1 for the design of Sn-based Pb-free solder. All these alloys were designed to have a LT of 456 K, the same melting temperature as that of the current Sn–Pb eutectic solder. Here, the amounts of each alloying element were limited so as not to exceed the binary eutectic composition listed in Table II, except for Zn. The measured LTs of these alloys are shown in Fig. 4. It can be seen from this figure that the LTs of these designed alloys were well controled around 456 K. This result apparently supports the use of Equation 1 in the first-step of the design and it will lead to an efficient development of Sn-based Pb-free solder alloys.

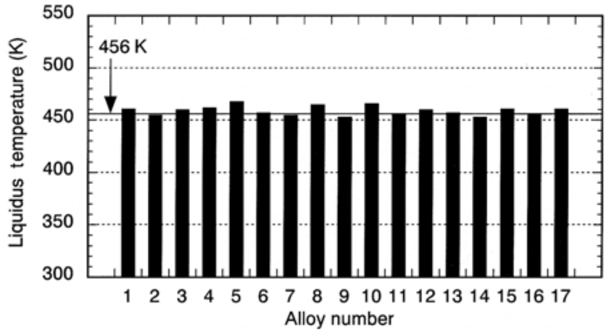

Figure 4 Measured LTs of designed alloys.

TABLE III Compositions of Sn-based alloys that were designed so as to have the LT of 456 K

Alloy no.	Alloying element (mol %)				
	Bi	Ag	Zn	In	Sn
1	8	—	—	16	
2	16	—	—	8	
3	12	—	—	12	
4	—	2	2	20	
5	—	2	20	2	
6	—	2	11	11	
7	18	1	5	—	
8	5	1	18	—	76
9	11.5	1	11.5	—	
10	5	1	—	18	
11	18	1	—	5	
12	11.5	1	—	11.5	
13	6	—	4	14	
14	14	—	4	6	
15	10	—	4	10	
16	6	—	14	4	
17	6	—	19	9	

5. Conclusions

The LTs were examined experimentally for the total of 134 types of Sn-based alloys. From the evaluation of the experimental data, a very simple relation was newly found between the LTs and alloy compositions. The LTs of Sn-based alloys decreased linearly with increasing total mole percentage of alloying elements. Such a relation was also found between the eutectic temperatures and compositions in Sn-binary phase diagrams. The LT of Sn-based alloys could be controled easily by using the relation obtained in this study.

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