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Theoretical estimation of coefficient of thermal expansion for solder alloy

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Coefficient of thermal expansion (CTE) of solder alloy Sn-37%Pb was estimated by using cluster expansion method. Five phases with available experimental CTE in Sn-Pb system were employed to derive the correlation coefficient, q_i. Monte-Carlo simulation was carried out to obtain the correlation functions, ξ_i. With the derived q_i and ξ_i, CTE of Sn-37%Pb was calculated, which is in excellent agreement with experiment. This study may provide a simple approach for the CTE prediction of disordered structures.

1. Introduction

The estimation of coefficient of thermal expansion (hereafter, CTE or α) is important in the design of new materials [1]. For example, in designing the next generation lead-free solder alloy, a key requirement is that the CTE of new solder alloy should be compatible with that of the joint materials so that thermal stress will not be developed when the device experiences thermal cycling. Therefore, it is desirable to establish a general theoretical technique that can be used routinely for CTE prediction of different materials.

A major hurdle of developing a general approach for CTE calculation is how one should model the phonon contributions to the free energy. First principles molecular-dynamics as well as lattice dynamics methods have been attempted on CTE calculation for different systems [2–3]. However, the general applicability of these methods is rather limited due to either high computational cost or the theoretical invalidity below Debye temperature [4]. In addition, these methods were performed on relatively simple crystal structure, and none of them have been used for CTE calculation of disordered alloys (such as solder alloy).

The motivation of this paper is to explore the possibility of using cluster expansion theory [5–6] for CTE calculation of solder alloy. As an example, CTE of a widely used solder composition, Sn-37%Pb, will be examined with cluster expansion theory. The success of this exploration will enable us to extend the approach to predict CTE of designed new solder composition.

2. Theory of cluster expansion

Detailed explanation and application of cluster expansion theory could be found in many references [7–12]. Here, only a brief description will be given.

The basic idea of cluster expansion theory is that any quantity (for example CTE, α) which is related to atomic configuration, can be expanded as the sum of terms which involves the series of correlation functions:

$$\alpha(m) = \sum_i q_i \xi_i \quad (1)$$

where m is a phase in the system, for instance, Sn or Pb in Sn-Pb system. q_i is the coefficient term, and it is transferable from one phase to another when the system is fixed [13]. ξ_i is the correlation function [14] for i-cluster. For example, the entire lattice of Sn can be decomposed into various clusters: empty cluster ($i = 0$), point cluster ($i = 1$), pair cluster ($i = 2$), triangle cluster ($i = 3$), tetrahedron cluster ($i = 4$), etc.

To apply Equation 1 for CTE calculation, we employed Connolly and Williams scheme [12]. In Connolly and Williams's scheme, it was assumed that only the clusters consisting of entirely nearest neighbors are important. Therefore, the largest cluster we need to consider is the tetrahedron one, i.e. Equation 1 can be truncated at the fourth order:

$$\alpha(m) = q_0\xi_0 + q_1\xi_1 + q_2\xi_2 + q_3\xi_3 + q_4\xi_4 \quad (2)$$

If we know q_i and ξ_i, we can apply Equation 2 to calculate CTE of Sn-37%Pb. As has been mentioned before, q_i is transferable from phase to phase (i.e. q_i derived from one phase can be applied on another in the same system), hence, we can obtain it by employing five other phases with available CTE in Sn-Pb system. The five phases we used include Sn, Sn-30%Pb, Sn-50%Pb, Sn-80%Pb and Pb. Table I lists their experimental [15] CTEs. Once we obtained correlation functions for them, we can perform matrix inversion of

TABLE I Thermal expansion coefficients of five phases at room temperature [15]

%Pb	%Sn	CTE $\times 10^{-6}$ in K^{-1}
0	100	23.8
30	70	21.6
50	50	23.4
80	20	26.5
100	0	29.1

Equation 2 to derive q_i. The matrix inversion form of Equation 2 can be written as:

$$\begin{bmatrix} q_0 \\ q_1 \\ q_2 \\ q_3 \\ q_4 \end{bmatrix} = \begin{bmatrix} \xi_0^{\mathrm{Sn}} & \xi_1^{\mathrm{Sn}} & \xi_2^{\mathrm{Sn}} & \xi_3^{\mathrm{Sn}} & \xi_4^{\mathrm{Sn}} \\ \xi_0^{\mathrm{Sn-30\%Pb}} & \xi_1^{\mathrm{Sn-30\%Pb}} & \xi_2^{\mathrm{Sn-30\%Pb}} & \xi_3^{\mathrm{Sn-30\%Pb}} & \xi_4^{\mathrm{Sn-30\%Pb}} \\ \xi_0^{\mathrm{Sn-50\%Pb}} & \xi_1^{\mathrm{Sn-50\%Pb}} & \xi_2^{\mathrm{Sn-50\%Pb}} & \xi_3^{\mathrm{Sn-50\%Pb}} & \xi_4^{\mathrm{Sn-50\%Pb}} \\ \xi_0^{\mathrm{Sn-80\%Pb}} & \xi_1^{\mathrm{Sn-80\%Pb}} & \xi_2^{\mathrm{Sn-80\%Pb}} & \xi_3^{\mathrm{Sn-80\%Pb}} & \xi_4^{\mathrm{Sn-80\%Pb}} \\ \xi_0^{\mathrm{Pb}} & \xi_1^{\mathrm{Pb}} & \xi_2^{\mathrm{Pb}} & \xi_3^{\mathrm{Pb}} & \xi_4^{\mathrm{Pb}} \end{bmatrix}^{-1} \begin{bmatrix} \alpha(\mathrm{Sn}) \\ \alpha(\mathrm{Sn-30\%Pb}) \\ \alpha(\mathrm{Sn-50\%Pb}) \\ \alpha(\mathrm{Sn-80\%Pb}) \\ \alpha(\mathrm{Pb}) \end{bmatrix} \quad (3)$$

In the following section, we will present how to calculate ξ_i and q_i.

3. CTE calculation for Sn-37%Pb

3.1. Monte-Carlo simulation [16] of correlation functions ξ_i

3.1.1. Definition of correlation functions

The correlation function is defined as

$$\xi_i = \frac{1}{N_i} \sum_{p_i} \sigma_{p1}\sigma_{p2}\ldots\sigma_{pi} \quad (4)$$

where σ_{pi} is a spin-like operator that takes the value of $+1$ or -1, depending on whether the lattice point p is occupied by an A or B atom. N_i is the total number of lattice subset like point, pairs, triangles, tetrahedrons in a crystal, in which i equals to 1, 2, 3, 4, respectively (when $i = 0$, it is correspondent to an empty cluster, and ξ_0 is defined as 1 for all phases). To calculate $\xi_{i(i=1,4)}$ of Equation 4, the atomic configurations of five phases should be known and they were obtained through Monte-Carlo simulations.

3.1.2. Monte-Carlo simulation of the correlation functions

To simulate the equilibrium configuration of atoms for the five phases, a face centered cubic (FCC) lattice with cell dimension of $200 * 200 * 200$ was employed. Two types of atoms were labelled as A and B. Sites that occupied by A atom were assigned the number 1 while sites occupied by B atoms were identified by the number -1. The ratio of A and B atoms determined their relative concentration in each phase.

To perform Monte-Carlo simulation, the atomic interaction energy should be known. We derive the interaction energy through the following equation:

$$\begin{aligned} E^{\mathrm{total}} &= N_{aa}E_{aa} + N_{bb}E_{bb} + N_{ab}E_{ab} + N_{aaa}E_{aaa} \\ &\quad + N_{bbb}E_{bbb} + N_{abb}E_{abb} + N_{aab}E_{aab} + \cdots \end{aligned} \quad (5)$$

where $N_{aa/bb/ab}$ and $N_{aaa/bbb/aab/abb}$ are the number of pairs and triangles in the system, and $E_{aa/bb/ab}$ and $\mathrm{E}_{aaa/bbb/aab/abb}$ are the pair and triangle interaction energies. A face centred cubic lattice (FCC) was employed to derive the interaction energies. For a binary system, there are a total number of 16 configurations when A or B atoms are inserted into the FCC lattice. Accordingly, 16 linear equations can be obtained based on Equation 5. The interaction energies were calculated by solving the 16 equations though singular value decomposition method. For each configuration, E^{total} was obtained by calculating the single point energy with density functional theory. In this paper, standard software CASTEP of MSI [17] was used to calculate the energy. The generalized gradient approximation of exchange-correlation function was employed. The basis set was chose to be FINE and the pseudopotentials used are in Kleinman-Bylander separable form. The summation over the Brillouin zone (BZ) is performed on a $6 \times 6 \times 6$ Monkhorst-Pack k-point mesh, which results in 18 k-points in the irreducible part of Brillouin zone.

For simulating the interdiffusion of atoms, the Kawasaki (spin exchange) dynamics was applied, that is the exchange of pairs of neighbouring Pb and Sn atoms in accordance with Metropolis *et al.* algorithm [18]. The goal of simulation was to produce a series of atomic configurations such that the probability of a configuration being generated is proportional to the probability of the configuration occurring in the statistical ensemble. The random number was generated by drand48 random number generator. In this study, each simulation runs up to 6×10^6 Monte-Carlo steps. At the equilibrium states, the total number of pairs, triangles and tetrahedrons were obtained. By using Equation 4, the correlation functions were calculated and listed in Table II.

3.2. Calculation of correlation coefficient term, q_i

By inserting the data of Tables I and II into Equation 3, the following correlation coefficients were

TABLE II Correlation functions for five phases at room temperature

Sn		Sn-30%Pb		Sn-50%Pb		Sn-80%Pb		Pb	
ξ_0	1	ξ_0	1	ξ_0	1	ξ_0	1	ξ_0	1
ξ_1	1	ξ_1	0.4	ξ_1	0	ξ_1	−0.6	ξ_1	−1
ξ_2	1	ξ_2	0.09311	ξ_2	−0.09073	ξ_2	0.32660	ξ_2	1
ξ_3	1	ξ_3	−0.03129	ξ_3	0.00059	ξ_3	−0.14402	ξ_3	−1
ξ_4	1	ξ_4	−0.05081	ξ_4	0.03517	ξ_4	0.03426	ξ_4	1

derived: $q_0 = 23.4974$, $q_1 = -4.5473$, $q_2 = 1.5859$, $q_3 = 1.8973$, $q_4 = 1.3668$. Although the coefficient terms were obtained from the five selected phases, according to cluster expansion theory, they can be applied to any other phase in Sn-Pb system.

3.3. CTE of Sn-37%Pb

With the coefficient terms for Sn-Pb system as well as the correlation functions for Sn-37%Pb ($\xi_0 = 1$, $\xi_1 = 0.26$, $\xi_2 = -0.0296405$, $\xi_3 = -0.0771827$, $\xi_4 = -0.022274$), the calculated CTE under room temperature is $22.1 \times 10^{-6}\ \mathrm{K}^{-1}$, which is in excellent agreement with experiment ($21.0 \times 10^{-6}\ \mathrm{K}^{-1}$ [1]).

4. Conclusion

This paper explored the possibility of applying cluster expansion theory on CTE calculation of disordered alloys. CTE of a typical solder alloys composition, Sn-37%Pb, was examined by using cluster expansion theory combined with Monte-Carlo simulations. Five phases were employed to derive the coefficient terms for Sn-Pb system. Correlation functions were calculated through Monte-Carlo simulations. Results showed that the theoretical CTE is in good agreement with experiment, indicating the feasibility of cluster expansion of CTE. Comparing to the existing CTE calculation approach, cluster expansion of CTE is simpler. It might be useful for the CTE estimate of both disordered and ordered alloys.

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