The Calculation of Ni-Sn-W Alloy Phase Diagram Using CALPHAD Method As New Soldering Material

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ABSTRACT

The Ni-Sn-W Alloy becomes an alternative as the Ni element could slow and block the forming of intermetallic. Since, the existence of the W element could add the solder materials performance which is able to block the forming of intermetallic substance. Calculation of phase diagram (CALPHAD) is able to become a solution for the limited information about phase diagram whether two system (biner) or others systems above. Computing method of CALPHAD used the factual approach and assumed that it is the characteristic of thermodynamic. From the calculation, the result gained are NiSn, NiSn2, NiSn3, solidus Sn (Sn), solidus Ni (Ni), NiW, NiW, solidus W (W), and solidus liquid (L).

Keywords: Ni-Sn-W, Calphad, Phase Equilibria

Article History
Received 01 September 19 Received in revised form 11 September 19 Accepted 02 October 19

1. Introduction

The selection of substance materials Alloy is an important part in understanding the development of materials especially as the alternative materials and the material substitution for existing material. It needs much experiment and time to understand and determine one material Alloy.

The Sn-Pb Alloy has a unique attraction especially in electronic. The melting temperature is relatively low in the area of eutectic (183°C) makes the Sn-Pb becomes irreplaceable materials. However, European Union Waste Electrical and Electronic Equipment Directive (WEEE) dan Restriction of Hazardous Substances Directive (RoHS) has banned the use of timbale on electronic device because it contained toxic which endangers the environment on June 2006 [1-2].

Sn is a main substance of the free timbale solder due to the electroplated Sn layer on substart is able to raise the wettability between subtract and solder. Nickel (Ni) is considered as the barrier because it has low reactivity. It makes the materials Sn/Ni often used as diffusion barrier materials on the connection of Under Bump Metallization (UBM) and Ball Grid Away (BGA0 during the process of soldering. The interfacial between melted solder materials and subtract happen and produces intermetallic substance (IMC) on the interface. IMC is formed during the process of soldering which give transformation phase effect. The development of IMC and its characteristic will influence the reliability of solder connectivity [3].

The existence of Ni will reduce the development of IMC because the Ni layer is diffused right before the interfacial process with the solder. To reduce the development of IMC between Ni and solder materials, minor materials like P, B, Co, Mo or W needed to add into the Sn-Ni alloy [4].

Tungsten (W) attracted attention in recent years because it has high level of melting (3422°C), good heat stabilization, and low diffusion coefficient to Ni [5]. Adding the W will make the Alloy more stable in high temperature. The W has high potential to combine with Ni and the Ni-W alloy is used as diffusion barrier materials.

To understand the interfacial reaction, phase diagram is the only tool to use. So far, there is only one information about the equilibrium phase from the Ni-Sn-W alloy component on 750 °C known. The lack of information about the equilibrium phase on the component of the Ni-Sn-W alloy becomes obstacle to understand the interfacial reaction exists. To handle that, thermodynamic approach using CALPHAD is a solution to predict equilibrium phase to some temperature

The Ni-Sn-W alloy is an alternative due to the Ni element in it which cloud slow and block the forming of intermetallic substance. Besides, the existence of W element could add the ability of solder material and becomes additional barrier of intermetallic substance.

To determine alloy of each element and to understand the phase formed during the heating process due to soldering process, the understanding of phase diagram is important. The limited information and the lack of research on phase on the Ni-Sn-W alloy especially and the other three systems in general become obstacle of the development of materials

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ISSN 2548-4214
Calculation of phase diagram (CALPHAD) is one of the solutions for the lack of information about phase diagram for both systems, binary or others systems above [8]. Computing method of CALPHAD uses factual methods and seen as a phase diagram of thermodynamic. For short, calculate the phase diagram with thermodynamic to all phase in a system is possible.

2. Methodology

The phase flow chart calculation using CALPHAD shown on the picture1. The first step for producing the thermodynamic calculation is by finding the phase diagram data like solidus and liquidus temperature, enthalpy, hot capacity, and crystallographic from each solid phase. Energy Gibbs model for every phase according to the different crystal structure. Data from the experiment needed for gaining the data of the optimal thermodynamic. The data gained is used to calculate the phase diagram from the ternary Ni-Sn-W on different temperature.

![Figure 1. The flow chart of CALPHAD calculation method](image)

2.1. Thermodynamic model

On the model of thermodynamic, a selection of phase from each must be selected. Each phase is needed for different model of thermodynamic

2.1.1. Unary phase

The different Gibbs energy for pure element on the phase \( \Phi \) and the reference of stable element (SER) from \( i \) if formulated below:

\[
G^{\Phi, i}(T) = G^{i}(T) - H^{SER}_i
\]  

Which

- \( G^{\Phi, i}(T) \): Gibbs energy of pure element of Gibbs phase \( \Phi \).
- \( H^{SER}_i \): enthalpy of element \( i \) on standard condition, \( P = 1 \) bar and \( T = 298.15 \) K.

The above similarity (1) above is formulated as follows;

\[
G^{\Phi, i}(T) = a + bT + cT \ln T + \sum n \alpha^n
\]

which the parameter score \( a, b, c, \ldots \) taken from SGTE (Scientific Group Thermodata Europe) [9].

2.1.2. Solidus phase

The solidus phase consists of liquid phase, FCC, HCP, dan BCC modeled by single-lattice random solution. This model is the function of temperature and Alloy.

\[
G^S(T) = \sum_{i=1}^{N} x_i G^{i}(T) + R \sum_{i=1}^{N} x_i \ln(x_i) + \sum_{i=1}^{N} x_i \sum_{j=1}^{N} x_j \xi_{ij}
\]

which \( x_i \) is a fraction mol from \( i \) element, \( R \) is the gas Constanta (8.3145 J/mol K), \( \xi_{ij}^S \) is surplus Gibbs energy from a phase, and, \( L_{x_i}^S \) is the interaction of \( i \) and \( j \) elements. Parameter interaction could be formulated by using the formula of Redlich-Klister:

\[
L_{x_i}^S = \sum_{k=1}^{N} L_{x_i}^k = \sum_{k=1}^{N} \xi_{ik}^S (x_i^k - x_j^k)^k
\]

\[
L_{x_i}^S = \sum_{k=1}^{N} L_{x_i}^k = a^k + b^k
\]

The parameter interaction is also influenced by Alloy and temperature.

2.1.3. Stoikiometry substance

The different Gibbs energy for pure element on the phase \( \Phi \) and the reference of stable element (SER) from \( i \) if formulated. For the intermetallic, the energy Gibbs is formulated as follows:

\[
G = \sum_{i=1}^{N} x_i G^{i} + G_j
\]

Which \( G_j \) is Gibbs energy for the form of Stoikiometri Substance.

3. Result and Discussion

The result of experiment on phase equilibria system the Ni-Sn-W alloy on the temperature 750°C was introduced for the first in 2016. The method used on that research was arc melting. The number is 21 metals alloy with Ni – Sn – W alloy. The different alloy were applied by using arc melting up to 6 times melting sintering. Each metal alloy is put into glass cube and vacuumed to avoid the contamination on the sintering process. Then each metal Alloy heated into 750°C for 720 hours. Beside, each sample is quenched with water. The quenched metal then analyzed.
using Scanning Electron Microscopy (SEM) with energy dispersive spectroscopy (EDS), and x-ray diffraction analysis (XRD) temperature for the next identified phase formed on temperature of 750°C [5].

Phase formed on the temperature of 750°C are Ni₃Sn, Ni₄Sn₁₂, Ni₅Snₓ, solidus Sn (Sn), solidus Ni (Ni), NiW₂, NiW, Ni,W, solidus W (W), and solidus liquid (L). On the equilibrium phase, it could be concluded that Ni-Sn-W on the temperature of 750 °C has 9 single phases, 13 double phases, and 7 three areas. Meanwhile, ternary was not found IMC on system of Ni-Sn-W on the temperature of 750°C [7].

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The phase diagram calculation of ternary Ni-Sn-W using CALPHAD method referenced on the result of experiment existed. For the Biner phase Ni-Sn using thermodynamic from Liu [6] and Popovic for Ni-W [7]. For W-Sn phase was not calculated and assumed as perfect solidus.

![Figure 2. Equilibrium Phase Calculation on Ni-Sn-W on the temperature of 750°C.](image)

The picture 2 above shows the result of calculation of Equilibrium Phase from Ni-Sn-W on the temperature 750°C and Table 1 shows the thermodynamic parameter. From the result is gained that Ni-Sn, Ni₄Sn₁₂, solidus Sn (Sn), solidus Ni (Ni), NiW₂, NiW, Ni,W, solidus W (W), and solidus liquid (L) as the result of research conducted by Hermena [5]. The previous calculation still needed data reparation and addition from the unpublished experiments.

**Table 1. Ni-Sn-W Thermodynamic Parameter**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Model</th>
<th>Parameter</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>(Ni,Sn,W)</td>
<td>$\gamma_{\text{liquid}}$ = -105002.87+197.8089 T Ln(T)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Va)</td>
<td>$\gamma_{\text{liquid}}$ = 2,16959 T Ln(T)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Sn)</td>
<td>$\gamma_{\text{liquid}}$ = 7,56954 T Ln(T)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Ni,Sn)</td>
<td>$\gamma_{\text{liquid}}$ = 3,55823 T Ln(T)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Ni,Sn)</td>
<td>$\gamma_{\text{liquid}}$ = 16290-10.25 T</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>(Va)</td>
<td>$\gamma_{\text{liquid}}$ = -22450</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>(Sn)</td>
<td>$\gamma_{\text{liquid}}$ = -69460.28+77.6267 T</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Ni,Sn)</td>
<td>$\gamma_{\text{liquid}}$ = 8,89084 T Ln(T)</td>
<td>[6]</td>
</tr>
<tr>
<td>FCC</td>
<td>(Ni,Sn,W) : (Va)</td>
<td>$\gamma_{\text{liquid}}$ = -8295.19</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Va)</td>
<td>$\gamma_{\text{liquid}}$ = -6000</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Sn)</td>
<td>$\gamma_{\text{liquid}}$ = 2,556+11.6 T</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>(Ni,Sn,W)</td>
<td>$\gamma_{\text{liquid}}$ = -52900</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>(Va)</td>
<td>$\gamma_{\text{liquid}}$ = 7,82000</td>
<td>[7]</td>
</tr>
<tr>
<td>BCC</td>
<td>(Ni,W) / (Va)</td>
<td>$\gamma_{\text{liquid}}$ = 13587.12+2.4434</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni₃Sn₅</td>
<td>(Ni,Sn)₃/₂/₃(Ni)</td>
<td>$\gamma_{\text{liquid}}$ = -2,1744.79+1.7049</td>
<td>[6]</td>
</tr>
<tr>
<td>HT</td>
<td>,Sn₃/₂ (Ni)₃/₅</td>
<td>$\gamma_{\text{liquid}}$ = 2,4069.79+12.1937</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Ni,Sn)₇/₈</td>
<td>$\gamma_{\text{liquid}}$ = -16726.09</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>(Ni,Sn)</td>
<td>$\gamma_{\text{liquid}}$ = 6,635.72</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni₄Sn₂</td>
<td>(Ni)₃/₈ (Ni,Sn)</td>
<td>$\gamma_{\text{liquid}}$ = -2,2448.65+0.2828</td>
<td>[6]</td>
</tr>
<tr>
<td>HT</td>
<td>$\lambda_{\text{ht}}$(Sn₃)ₜ₀₈₀</td>
<td>$\gamma_{\text{liquid}}$ = -4935.38+7.5571</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni₅Sn₅</td>
<td>(Ni)₃/₅ (Sn₃)ₜ₀₈₀</td>
<td>$\gamma_{\text{liquid}}$ = -7,8783.2</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni₆Sn₄</td>
<td>(Ni)₁/₁₂ (Ni,Sn)</td>
<td>$\gamma_{\text{liquid}}$ = -2,6138.15+4.912 T+0.5</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{ht}}$(Sn₃)ₜ₀₈₀</td>
<td>$\gamma_{\text{liquid}}$ = 7,613.24+8.749</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni₄W</td>
<td>(Ni)₁/₁₀ (W)</td>
<td>$\gamma_{\text{liquid}}$ = -5,0828.16</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni₅W</td>
<td>(Ni)₁/₅ (W)</td>
<td>$\gamma_{\text{liquid}}$ = -7,888.28+3T</td>
<td>[7]</td>
</tr>
<tr>
<td>Ni₆W₂</td>
<td>(Ni)₁/₅ (W)₂</td>
<td>$\gamma_{\text{liquid}}$ = -8,888.28+2T</td>
<td>[7]</td>
</tr>
</tbody>
</table>

4. Conclusion

The phase of equilibrium calculation on Ni-Sn-W has done successfully. The phase form on the temperature of 750 °C are phase of Ni₃Sn, Ni₄Sn₁₂, solidus Sn (Sn), solidus Ni (Ni), NiW₂, solidus W (W), and solidus liquid (L) as the previous experiments, the result is categorized satisfied as the lack of experiments on Ni-Sn-W

**Acknowledgements**

The researcher would like to express the gratitude for the state polytechnic of Malang especially for financial support on this research.

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Doi:10.1109/ECDIM.2003.1322630.


