International journal Of science, engineering, and information technology
Volume 04, Number 01, Desember 2019
Journal homepage: https://journal.trunojoyo.ac.id/ijseit

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

[a]Riswan Eko Wahyu Susanto, [b]Gita Novian Hermana

[a, b] The State Polytechnic of Malang PSDKU Kediri, Mayor Bismo Street No.27, Kediri City, Indonesia

A B S T R A C T

The Ni-Sn-W Alloy becomes an alternative as the Ni element could slow and block the forming of intermetalic. Beside, the existence of the W element could add the solder materials performance which is able to block the forming of intermetalic 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 Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4, solidus Sn (Sn), solidus Ni (Ni), NiW, Ni_4W, 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 (183ºC) 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. Nikel (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 intermetalic 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 attentionin recent years because it has high level of melting (3422ºC), 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 ºC 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 intermetalic substance. Besides, the existence of W element could add the ability of solder material and becomes additional barrier of intermetalic 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

* *Corresponding author*.
E-mail address: risone79@gmail.com

ISSN 2548-4214

Calculation of phase diagram (CALPHAD is one of the solutions for the lack of information about phase diagram for both systems, biner, or others systems above [8]. Computing method of CALPHAAD 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 temary Ni-Sn-W on different temperature.

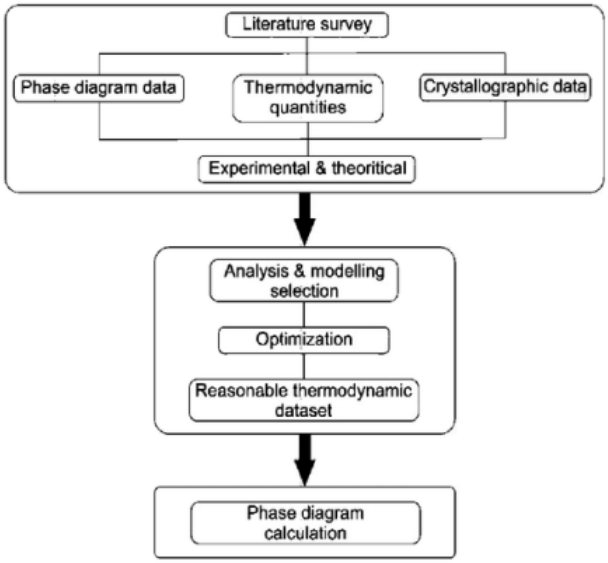

Figure 1. The flow chart of CALPHAD calculation method

2.1. Thermodyamic 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 ϕ and the reference of stable element (SER) from *i* if formulated below:

$$G_i^{0,\phi}(\mathrm{T}) = G_i^{\phi}(\mathrm{T}) - H_i^{SER} \quad (1)$$

Which

$G_i^{0,\phi}(T)$: Gibbs energy of pure element of Gibbs phase ϕ.

H_i^{SER} : enthalpy of element *I* on standard condition, P = 1 bar and T = 298.15 K.

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

$$G_i^{0,\phi}(T) = a + bT + cT\,lnT + \sum n\,dT^n \quad (2)$$

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

2.1.2. Sholidus 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.

$$G_m^{\phi}(T) = \sum_{i=1}^{n} x_i . G_i^{0,\phi} + RT \sum_{i=1}^{n} x_i . ln(x_i) + {}^{ex}G^{\phi} \quad (3)$$

$${}^{ex}G^{\phi} = \sum \sum x_i^{\phi} x_i^{\phi} L_{i,i}^{\phi}$$

which xi is a fraction mol from *i* element, R is the gas Constanta (8,3145 J/mol K), ${}^{ex}G^{\phi}$ is surplus Gibbs energy from a phase, and, $L_{i,j}^{\phi}$ is the interaction of *i* and *j* elements. Parameter interaction $L_{i,j}^{\phi}$ could be formulated by using the formula of Redlich-Klister:

$$L_{i,i}^{\phi} = \sum_k {}^{k}L_{i,i}^{\phi} (x_i^{\phi} - x_i^{\phi})^k \quad (4)$$

$$L_{i,i}^{k,\phi} = a^k + bT^k$$

The parameter interaction is also influenced by Alloy and temperature. .

2.1.3. Stoikiometry ubstance

The different Gibbs energy for pure element on the phase ϕ and the reference of stable element (SER) from *i* if formulated.

For the intermetalic, the energy Gibbs is formulated as follows:

$$G = \sum_{i=1}^{n} x_i G_i^{0,\phi} + G_f \quad (5)$$

Which Gf 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 750ºC 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 asc 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 750ºC 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 750ºC [5].

Phase formed on the temperature of 750ºC are Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4, solidus Sn (Sn), solidus Ni (Ni), NiW_2, NiW, Ni_4W, solidus W (W), and solidus liquid (L). On the equilibrium phase, it could be concluded that Ni-Sn-W on the temperature of 750 ºC 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 750ºC [7]

All authors are required to complete the Procedia exclusive license transfer agreement before the article can be published, which they can do online. This transfer agreement enables Elsevier to protect the copyrighted material for the authors, but does not relinquish the authors' proprietary rights. The copyright transfer covers the exclusive rights to reproduce and distribute the article, including reprints, photographic reproductions, microfilm or any other reproductions of similar nature and translations. Authors are responsible for obtaining from the copyright holder, the permission to reproduce any figures for which copyright exists.

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.

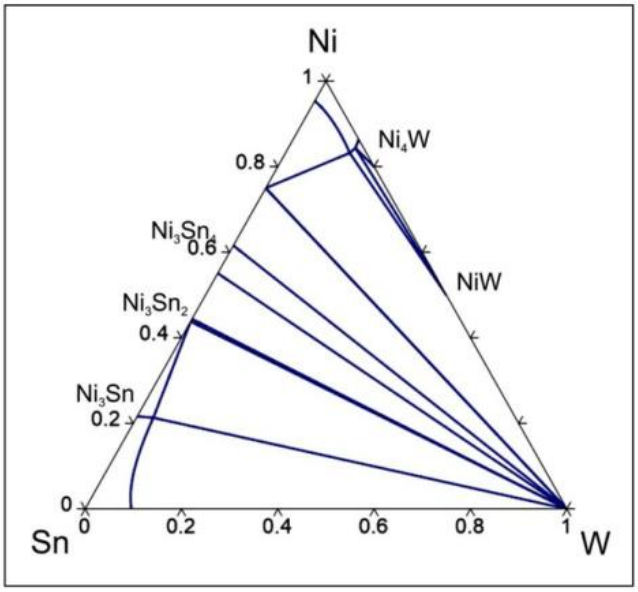

Figure 2. Equilibrium Phase Calculation on Ni-Sn-W on the temperature of 750ºC.

The picture 2 above shows the result of calculation of Equilibrium Phase from Ni-Sn-W on the temperature 750ºC and Table 1 shows the thermodinamic parameter. From the result is gained that Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4, solidus Sn (Sn), solidus Ni (Ni), NiW, Ni_4W, solidus W (W), and solidus liquid (L) as the result of research conducted by Hermana [5].. The previous calculation still needed data reparation and addition from the unpublished experiments.

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

Phase	Model	Parameter	Ref
Liquid	(Ni,Sn,W)	${}^0L^{liquid}_{Ni,Sn}$ = -105002.87+197.8089 T-21.6959 T Ln(T)	[6]
		${}^1L^{liquid}_{Ni,Sn}$ = -28342.17+52.5528 T-7.56094 T Ln(T)	[6]
		${}^2L^{liquid}_{Ni,Sn}$ = 5582.31	[6]
		${}^0L^{liquid}_{Ni,W}$ =16290-10.25 T	[7]
		${}^1L^{liquid}_{Ni,W}$ = -22450	[7]
FCC	(Ni,Sn,W) : (Va)	${}^0L^{fcc}_{Ni,Sn:Va}$ = -69460.28+77.6267 T-8.89084 T Ln(T)	[6]
		${}^1L^{fcc}_{Ni,Sn:Va}$ = -8295.19	[6]
		${}^0T^{fcc}_{Ni,Sn:Va}$ = -6000	[6]
		${}^1T^{fcc}_{Ni,Sn:Va}$ = 3000	[6]
		${}^0L^{fcc}_{Ni,W:Va}$ = 2556+11.6 T	[7]
BCC	(Ni,W):(Va)	${}^1L^{fcc}_{Ni,W:Va}$ = -52900	[7]
		${}^0L^{bcc}_{Ni,W:Va}$ = 82000	[7]
Ni_3Sn_HT	$(Ni,Sn)_{0.25}$:(Ni,Sn)$_{0.25}$:$(Ni)_{0.5}$	${}^0G^{Ni_3Sn\_HT}_{Ni:Ni:Ni}$ = ${}^0G^{fcc}_{Ni}$	[6]
		${}^0G^{Ni_3Sn\_HT}_{Sn:Ni:Ni}$ = 13557.12-2.4434	[6]
		${}^0G^{Ni_3Sn\_HT}_{Ni:Sn:Ni}$ = -21744.79+1.7049	[6]
		${}^0G^{Ni_3Sn\_HT}_{Sn:Sn:Ni}$ = 24069.79+12.1937	[6]
		${}^0L^{Ni_3Sn\_HT}_{Ni,Sn:Ni}$ = -16726.09	[6]
		${}^0L^{Ni_3Sn\_HT}_{Ni,Sn:Ni}$ = 6635.72	[6]
Ni_3Sn_2 _HT	$(Ni)_{0.33}$:(Ni,Sn)$_{0.33}$:$(Sn)_{0.33}$	${}^0G^{Ni_3Sn_2\_HT}_{Ni:Ni:Sn}$= -22448.65+0.2828	[6]
		${}^0G^{Ni_3Sn_2\_HT}_{Ni:Ni:Sn}$= -4935.38+7.5571	[6]
		${}^0G^{Ni_3Sn_2\_HT}_{Ni:Sn:Sn}$ = -78783.2	[6]
Ni_3Sn_4	$(Ni)_{0.25}$:(Ni,Sn)$_{0.25}$:$(Sn)_{0.5}$	${}^0G^{Ni_3Sn_4}_{Sn:Ni:Sn:Ni}$ = -26138.15+4.912 T+0.5	[6]
		${}^0G^{Ni_3Sn_4}_{Ni:Ni:Sn:Sn}$ = 7613.24+8.749	[6]
		${}^0G^{Ni_3Sn_4}_{Ni:Sn:Sn:Sn}$ = -50828.16	[6]
Ni_4W	$(Ni)_4$: (W)	${}^0G^{Ni_4W}_{Ni:Ni:Ni:W}$ = -12862-4.747 T+4${}^0G^{fcc}_{Ni}$+${}^0G^{bcc}_{W}$	[7]
NiW	(Ni): (W)	${}^0G^{NiW}_{Ni:W}$= -8885.91+3 T+${}^0G^{fcc}_{Ni}$+${}^0G^{bcc}_{W}$	[7]
NiW_2	(Ni): $(W)_2$	${}^0G^{NiW_2}_{Ni:W}$ = -8888.282+3T+${}^0G^{fcc}_{Ni}$+ 2${}^0G^{bcc}_{W}$	[7]

4. Conclusion

The phase of equilibrium calculation on Ni-Sn-W has done successfully. The phase form on the temperature of 750 ºC are phase of Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4, solidus Sn (Sn), solidus Ni (Ni), NiW, Ni_4W, 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.

REFERENCES

[1] WEEE EU-Directive 2002/96/EC, Official Journal of the European Union L37 **(2003)** 24. Doi: 10.1109/ECODIM. 2003.1322630
[2] RoHs EU-Directive 2002/95/EC, Official Journal of the European Union L37 **(2003),** pp. 19 Doi:10.1109/ECODIM.2003.1322630.

[3] Y. Liu, A. Hu, T. Luo, andM. Li, “Interfacial reaction of Sn–2.0 Ag–2.5 Zn solder on Cu and Ni–W substrates”, Journal of Materials Science: Materials in Electronics, 24(3),**(2013)**, pp. 1037-1044.

[4] A. S. M. A. Haseeb, S. Chew, M. R. Johan, “Interfacial reactions between Sn-3.5 Ag solder and Ni–W alloy films”, Journal of Materials Science: Materials in Electronics, 22(9), **(2011)**, pp. 1372-1377.

[5] G. N. Hermana, Y. W. Chang, P. Y. Chen, C. W. Chiu, and Y. W. Yen, “Phase equilibria of the Sn-Ni-W ternary system at 750 ºC”, IEEE, **(2016)**,pp. 201-204.

[6] H.S.Liu, J.Wang, Z.P.Jin,”Thermodynamic optimization of the Ni-Sn binary system”, CALPHAD, 28 **(2004)**, pp. 363-370.

[7] Popovič, J., P. Brož, and J. Buršík, "Microstructure and phase equilibria in the Ni–Al–W system" Intermetallics 16.7 **(2008)**: 884-888.

[8] B. Fabrichnaya, and Olga, “Thermodynamic Data, Models, and Phase Diagrams in Multicomponent Oxide Systems : an Assessment for Materials and Planetary Scientists Based on Calorimetric”, Volumetric and Phase Equilibrium Data, Springer Berlin Heidelberg, Berlin, **(2004)**.

[9] A. T. Dinsdale, “SGTE Data for Pure Elements”Calphad, 15(4),**(1991)**, pp. 317-425.