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Analysis of Thermal Properties of Solder Material Sn-Bi-Al using Differential Scanning Calorimetry (DSC)

D. Tamara Dirasutisna[*,1,a], *B. Soegiono*[2,b], *B. Kurniawan*[2,c], *M. Yudi Masduki*[2,d]

[1]Departement of Mechanical Engineering, FTI, Universitas Trisakti, Indonesia.
[2]Departement of Materials Science, Faculty of Mathematic and Natural Science, University of Indonesia, Indonesia.
[*]*tamaradirasutisna@yahoo.com;* [a]*bambangsg@yahoo.com;* [b]*bkuru06@gmail.com;* [c]*myudims@yahoo.com*

Abstract – *The thermal properties on Sn-Bi-Al based solders has been studied using differential scanning calorimetry (DSC). Thermodynamics characteristics the materials on melting point, heat capacity, entropy, enthalpy and Gibbs free energy was obtained. The Sn-xBi melted at 600 ^oC in controlled atmospheric to avoid the oxidation. The results show the melting point of Sn-xBi was decreased while the composition of Bi increased. The heat capacity, entropy and enthalpy of Sn-xBi were also decreased while the composition of Bi increased. The lowest melting point of the Sn-52Bi was added by Al to form Sn-52Bi-xAl. The results show the melting point of Sn-52Bi-xAl were increased compared the Sn-52Bi. The melting point of Sn-52Bi-xAl slightly higher than Sn-30Bi and Sn-70Bi.*

Keywords: Sn-Bi; Melting Point, Heat Capacity, Entropy, Enthalpy, Gibbs Free Energy

1.0 INTRODUCTION

The Sn-37Pb based solder material was at eutectoid composition having the lowest melting point at 182.2 ^oC. The ideal melting point value for solder material in range 180 ^oC to 300 ^oC [1]. The Sn-37Pb alloy had a good wettability, high thermal conductivity and corrosion resistance. The disadvantage of Sn-37Pb, this material is toxicity that naturally from Pb element. Alternative for solder material without Pb has been developed such as Sn-Ag Sn-Pb,Sn-Cu,Sn-Bi,Sn-Al, Sn-Zn [2].

Some studies for solder material has been done on Sn-58Bi, Sn-Zn-Bi system, Sn-Ag-Cu system, eutectic Sn-3.5Bi alloy and eutectic Sn-0.7Cu alloy [3]. Solder material heat capacity influenced to their physic characteristic. There are two types thermal response in material during heated which are endothermic and exothermic [4]. Solder material should response endothermic during heated. This was intended to protect the electrical component from heat during joining process by solder material.

In this study, we presented on thermal analysis on Sn-Bi-Al solder material. The thermal properties all solder materials were done by differential scanning calorimetry technique.

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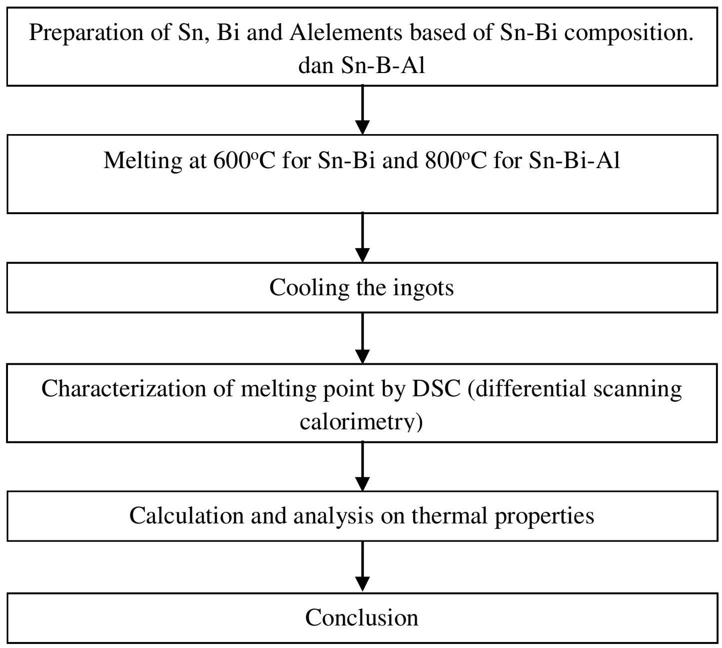
2.0 EXPERIMENTAL

Solder materials were prepared by melted the metal powder at 600 ^{o}C. The composition of Sn-xBi alloy is x=0, 10, 30, 52, 70 and the aluminum was added to the Sn-52Bi alloy with x=0.05, 0.11, 0.14, 0.19, 0.25. The compositions each of variation tabulated at Table 1.

Research roadmap:



Sn-Bi-Al was done by mixed the element of Sn, Bi and Al. The elements were melted at 600 ^{o}C for Sn-Bi and at 800 ^{o}C for Sn-Bi-Al. The melting process was done in open air and added an oxidation inhibitor. The Sn-Bi material was done in five compositions, Sn-0Bi, Sn-10Bi, Sn-30Bi, Sn-52Bi dan Sn-70Bi.

The best composition of Sn-Bi added the element Al to form new material (Sn-yBi)-xAl. Calculation of alloy density was used pure the Sn and Bi element as standard in this research. The Sn-Bi and Sn-Bi-Al ingots showed in Fig. 1.

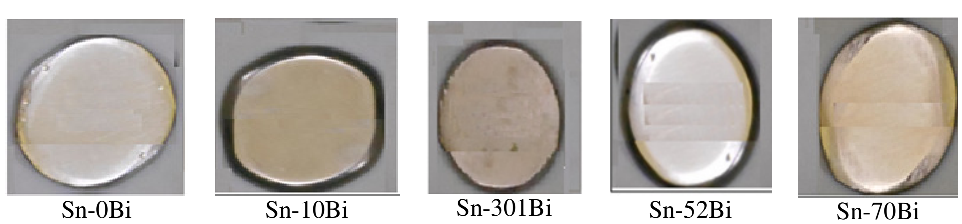


Figure 1: Ingots of Sn-Bi and Sn-Bi-Al

These materials were analyzed by different scanning calorimetry (DSC) at range 30 ^{o}C to 450 ^{o}C with heating rate at 10 ^{o}C/min. The acquired heat flow data was used to calculate the heat capacity, determined the melting point. Others thermal parameters such as enthalpy, entropy and Gibbs free energy were also derived for Sn-Bi-Al systems. Measurement heat capacity by

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DSC data was done with procedures three measurements of blank-blank crucible, blank-standard crucible and blank-sample crucible. In this measurement Zn standard was used.

Table 1: Sample variation compositions of Sn-Bi-Al solder material.

Sample	Composition (g)		
	Sn	**Bi**	**Al**
Sn-0Bi	20.06	0	-
Sn-10Bi	17.94	2.1	-
Sn-30Bi	14.07	6.01	-
Sn-52Bi	9.6	10.42	-
Sn-52Bi-0.05Al	3.6999	4.0082	0.0010
Sn-52Bi-0.11Al	3.6955	4.0035	0.0023
Sn-52Bi-0.14Al	3.6926	4.0003	0.0030
Sn-52Bi-0.19Al	3.6882	3.9955	0.0040
Sn-52Bi-0.25Al	3.6855	3.9926	0.0051
Sn-70Bi	6.04	14.08	-

Calculation of heat capacity was done by Eq. 1

$$C_p = (m_0/m)C_0\left(\frac{(S_3 - s_1)}{S_2 - S_1}\right) [5] \quad (1)$$

m_o = standard mass (mg)
m = sample mass (mg)
C_0 = heat capacity of standard (J/mg.K)
Zn standard use $C_0 = 114.8 + 0.0128x10^5 T + 35.4T^{-2}$ [5]
S_1 = heat flow measurement of blank-blank crucible (mW)
S_2= heat flow measurement of blank-standard crucible (mW)
S_3= heat flow measurement of blank-sample crucible (mW)

Result from Eq. 1 tabulated in Appendix 1. The heat capacity under constant pressure, entropy and its free energy Gibbs can be calculated. The calculation was done by polynomial regression (Appendix 2) then the heat capacity value at 20^0C, 25^0C, 142.28^0C, and 190.12^0C can be determined.

Entropy calculated by equation

$$S = Cp\ln\left(\frac{T}{273}\right) \quad (2)$$

Enthalpy (H) calculated by equation

$$H = (Cp + nR)T - 273(Cp + nR) \quad (3)$$

Gibbs free energy calculated by equation:

$$G = (Cp + nR)T - CpT\ln\left(\frac{T}{273}\right) - 273(Cp + nR) \quad (4)$$

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with $R = 8.3143 \dfrac{Joule}{molK}$ [4]

n is the composition of elements in mol that tabulated in Table 2.

Table 2: Composition

Table 2.a: Sn-Bi composition		Table 2.b: Sn-Bi-Al composition	
%Wt.Bi	n mol	%Wt.Al	n mol
0	0.169	0.05	0.02174
10	0.1569	0.11	0.02172
30	0.1377	0.14	0.02170
52	0.1209	0.19	0.02168
70	0.1106	0.25	0.02166

3.0 RESULTS AND DISCUSSION

3.1 Sn-xBi systems

The melting point was determined from the heat flow. The melting point value is tabulated in Table 3.

Table 3: Melting point value of The Sn-xBi systems.

Sample	Melting point	
	^{o}C	K
Sn-0Bi	235.1	508.1
Sn-10Bi	220.39	493.39
Sn-30Bi	143.43	416.43
Sn-52Bi	142.28	415.28
	190.12	463.12
Sn-70Bi	143.74	416.74

The melting point value of Sn-52Bi at 142.28 ^{o}C as eutectic point and at 190.12 ^{o}C as eutectoid point. The melting point value measured on Sn-0Bi (pure Sn) has a good agreement to the theoretical value at 231.93 ^{o}C [6] with deviation at 1.34%. The lowest melting point value was at the Sn-52Bi. The Sn-52Bi heat capacity value was determined and tabulated in Table 4 at various temperature and compared to the Sn-37Pb.

Table 4: Heat capacity value of the Sn-52Bi compared to the Sn-37Pb.

Sn-52Bi						*Sn-37Pb*
t	**T**	a	b	c	*Cp*	*Cp*
C	K	J/mol.K	J/mol.K^2	(J/ mol)*K	*J/* mol.*K*	*J/* mol.*K*
20	293	7.060328	-0.01261	-36958.9	*2.93518*	32.58
25	298	7.060328	-0.01261	-36958.9	*2.88646*	32.83
142.5	415.5	7.060328	-0.01261	-36958.9	*1.60947*	38.71
190.12	463.12	7.060328	-0.01261	-36958.9	*1.04822*	41.10

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3.2 Sn-52Bi-xAl Systems

The melting point was determined from the heat flow data. The melting point value is tabulated in Table 5.

Table 5: Melting point value of The Sn-52Bi-xAl systems.

Sample	Melting point	
	°C	K
Sn-52Bi-0.05Al	144.38	417.38
Sn-52Bi-0.11Al	143.44	416.44
Sn-52Bi-0.14Al	145.05	418.05
Sn-52Bi-0.19Al	144.54	417.54
Sn-52Bi-0.25Al	144.6	417.6

Table 6: Heat capacity value of the Sn-52Bi-xAl systems.

Sample	*Cp*(J/mol.K)			
	20 °C	25 °C	142.28 °C	190.12 °C
Sn-52Bi-0.05Al	0.01512	0.064031	0.514163	0.488027
Sn-52Bi-0.11Al	-0.16344	0.004095	1.531795	1.432226
Sn-52Bi-0.14Al	1.094962	1.480245	4.724485	4.304881
Sn-52Bi-0.19Al	-0.25271	-0.07668	1.553836	1.467188
Sn-52Bi-0.25Al	-0.32254	-0.12317	1.706237	1.595852

Table 7: Entropy value of the Sn-52Bi-xAl systems.

Sample	*S* (J/mol.K)			
	(S1) 20 °C	(S2) 25 °C	(S3) 142.28 °C	(S4) 190.12 °C
Sn-52Bi-0.05Al	158.946	158.107	138.437	130.413
Sn-52Bi-0.11Al	368.786	365.626	291.508	261.274
Sn-52Bi-0.14Al	1225.03	1212.31	913.885	792.153
Sn-52Bi-0.19Al	359.028	356.222	290.409	263.563
Sn-52Bi-0.25Al	392.838	-389.31	306.549	272.789

Table 8: Entropy difference of the Sn-52Bi-xAl systems

Sample	*ΔS* (J/mol.K)		
	S2-S1	S3-S1	S4-S1
Sn-52Bi-0.05Al	-0.0102	-0.2001	-0.0657
Sn-52Bi-0.11Al	-0.0117	-0.2303	-0.0757
Sn-52Bi-0.14Al	-0.0027	-0.053	-0.0174
Sn-52Bi-0.19Al	-0.0093	-0.1826	-0.06
Sn-52Bi-0.25Al	-0.0136	-0.2677	-0.0879

Table 8 showed increased in temperature caused the heat value decreased. Decreasing in heat value, showed the heat that generated by the solder material wouldn't damage the component to be joined, as the ΔS value is less than 0. In this case the occurred process was reversible.

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Table 9: Enthalpy value of the Sn-52Bi-xAl systems.

Sample	*H* (J/mol)			
	(H1) 20 °C	(H2) 25 °C	(H3) 142.28 °C	(H4) 190.12 °C
Sn-52Bi-0.05Al	520.6325	519.1148	483.5144	468.9925
Sn-52Bi-0.11Al	429.13	427.09	379.1524	359.5997
Sn-52Bi-0.14Al	401.0817	401.9801	423.0547	431.6513
Sn-52Bi-0.19Al	422.253	420.7234	384.844	370.2084
Sn-52Bi-0.25Al	478.9895	476.0404	406.8659	378.6488

Table 10: Enthalpy difference of the Sn-52Bi-xAl systems

Sample	*ΔH* (J/mol.K)		
	H2-H1	H3-H1	H4-H1
Sn-52Bi-0.05Al	-1.5178	35.6004	14.5218
Sn-52Bi-0.11Al	-2.0436	47.9335	19.5527
Sn-52Bi-0.14Al	0.8985	21.0745	8.5966
Sn-52Bi-0.19Al	-1.5296	35.8793	14.6356
Sn-52Bi-0.25Al	-2.9491	69.1744	28.2171

Table 10 showed the thermal process occurred at the Sn-52Bi-0.05Al, Sn-52Bi-0.11Al, Sn-52Bi-0.19 Al and Sn-52Bi-0.11Al was exothermic and the other samples were the endothermic occurs.

Table 11: Gibbs free energy value of the Sn-52Bi-xAl systems.

Sample	*G* (J/mol)			
	(G1) 20 °C	(G2) 25 °C	(G3) 142.28 °C	(G4) 190.12 °C
Sn-52Bi-0.05Al	16.26	6.2813	-134.4234	-147.7224
Sn-52Bi-0.11Al	-3246.06	-4987.92	-26501	-26149.79
Sn-52Bi-0.14Al	2386.18	6491.16	80154.8	99529.38
Sn-52Bi-0.19Al	87113.86	89627.05	169769.69	212460.07
Sn-52Bi-0.25Al	38.6569	26.329	-133.547	-137.7624

Table 12: Gibbs free energy difference of the Sn-52Bi-xAl systems.

Sample	*ΔG* (J/mol.K)		
	G2-G1	G3-G1	G4-G1
Sn-52Bi-0.05Al	-9.98	-140.70	-13.30
Sn-52Bi-0.11Al	-1741.86	21513.08	351.21
Sn-52Bi-0.14Al	4104.99	73663.64	19374.57
Sn-52Bi-0.19Al	2513.19	80142.63	42690.39
Sn-52Bi-0.25Al	-12.33	-159.88	-4.22

The Gibbs free energy show does a reaction could occur spontaneously or needed an external energy. Table 12 showed the Sn-52Bi-0.05Al, Sn-52Bi-0.11Al and Sn-52Bi-0.25Al had the Gibbs free energy difference less than 0. The Gibbs free energy difference of the Sn-52Bi-0.14Al and Sn 52Bi-0.19Al showed the alloy occurs energy conversion along the process and the others alloy remain unchanged.

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4.0 SUMMARY

The melting point value of Sn-xBi were decrease with increased of Bi. The Sn-52Bi was the ideal composition having the lowest melting point at 142.28 ^{o}C. This alloy was formed at two point, the melting point at eutectic at 142.28 ^{o}C and the point at eutectoid at 190.12 ^{o}C. The melting point of Sn-52Bi-xAl increased with increased of Al. The Sn-xBi showed endotherm process during heated that good agreement to requirement of solder material compare to the Sn-37Pb with its exothermic process. Adding an Al in Sn-52Bi was increased their melting point.

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Appendix 1: Calculation data of Sn-52Bi Heat Capacity

t	T	S1	S2	S3	Co	Cp
C	K	mWatt	mWatt	mWatt	J/MK	J/M
32.95	305.95	-0.31	5.63	0.22	114.8004	6.014864
33.11	306.11	-0.31	5.74	0.21	114.8004	5.794078
33.27	306.27	-0.31	5.83	0.2	114.8004	5.599357
33.44	306.44	-0.31	5.92	0.19	114.8004	5.410263
33.6	306.6	-0.31	6	0.18	114.8004	5.234836
33.76	306.76	-0.31	6.07	0.17	114.8004	5.07174
33.92	306.92	-0.3	6.13	0.17	114.8004	0.738258
34.09	307.09	-0.3	6.19	0.16	114.8004	0.715871
34.25	307.25	-0.3	6.25	0.16	114.8004	0.709313
34.41	307.41	-0.3	6.3	0.16	114.8004	0.703939
34.58	307.58	-0.3	6.35	0.16	114.8004	0.698647
34.74	307.74	-0.3	6.39	0.18	114.8004	0.724664
34.9	307.9	-0.3	6.43	0.2	114.8004	0.750371
35.08	308.08	-0.29	6.47	0.22	114.8004	0.761982
35.23	308.23	-0.29	6.5	0.26	114.8004	0.818115
35.38	308.38	-0.29	6.53	0.3	114.8004	0.873754
35.56	308.56	-0.29	6.56	0.35	114.8004	0.94365
35.72	308.72	-0.29	6.59	0.4	114.8004	1.012936
35.88	308.88	-0.29	6.62	0.46	114.8004	1.096237
36.04	309.04	-0.29	6.65	0.53	114.8004	1.193372
36.21	309.21	-0.29	6.67	0.59	114.8004	1.277011
36.36	309.36	-0.28	6.7	0.66	114.8004	1.360172
36.53	309.53	-0.28	6.72	0.73	114.8004	1.457286
36.7	309.7	-0.28	6.74	0.8	114.8004	1.553846
36.85	309.85	-0.28	6.76	0.88	114.8004	1.664205
37.01	310.01	-0.28	6.78	0.95	114.8004	1.759632
37.19	310.19	-0.28	6.81	1.02	114.8004	1.851904
37.34	310.34	-0.27	6.82	1.09	114.8004	1.937377
37.5	310.5	-0.27	6.84	1.15	114.8004	2.017159
37.67	310.67	-0.27	6.86	1.22	114.8004	2.110659
37.83	310.83	-0.27	6.88	1.28	114.8004	2.18951
37.98	310.98	-0.27	6.9	1.34	114.8004	2.267922
38.16	311.16	-0.27	6.92	1.4	114.8004	2.345897
38.32	311.32	-0.27	6.94	1.46	114.8004	2.42344
38.47	311.47	-0.27	6.96	1.51	114.8004	2.486584
38.64	311.64	-0.26	6.98	1.56	114.8004	2.53895
38.8	311.8	-0.26	7	1.6	114.8004	2.587603
38.96	311.96	-0.26	7.02	1.65	114.8004	2.649863
39.12	312.12	-0.26	7.04	1.69	114.8004	2.697945
39.29	312.29	-0.26	7.06	1.73	114.8004	2.745765

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Appendix 2: Results calculation of Sn-52Bi heat capacity

Summary Output

Regression Statistics	
Multiple R	0.03139
R Square	0.000985
Adjusted R Square	0.000107
Standard Error	40.34747
Observations	2279

ANOVA

	df	SS	MS	F	Significance F
Regression	2	3654.49	1827.245	1.122443	0.3256638
Residual	2276	3705142	1627.918		
Total	2278	3708796			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	7.32873	19.05802	0.384548	0.700608	-30.04417	44.70163	-30.0442	44.70163
X Variable 1	-0.01302	0.026846	-0.48502	0.627708	-0.065666	0.039624	-0.06567	0.039624
X Variable 2	-52082.1	1254282	-0.04152	0.966882	-2511738	2407574	-2511738	2407574

T	T	a	B	c	Cp
C	K	J/MK	J/MK^2	(J/M)*K	J/MK
20	293	7.3287	-0.013	-52082.1	2.9069
142.5	415.5	9.7028	-0.0167	-185738	1.7047
190.12	463.12	9.7028	-0.0167	-185738	1.1213