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DEVELOPMENT OF HIGH MELTING POINT, ENVIRONMENTALLY FRIENDLY SOLDERS, USING THE CALPHAD APPROACH

PROJEKTOWANIE WYSOKOTEMPERATUROWYCH, PRZYJAZNYCH DLA ŚRODOWISKA LUTÓW PRZY POMOCY METODY CALPHAD

An attempt has been made using the CALPHAD approach via Thermo-Calc to explore the various possible chemical compositions that adhere to the melting criterion i.e. 270-350°C, required to replace the traditionally used high lead content solders for first level packaging applications. Various ternary combinations were extrapolated iteratively from well assessed binary systems using the COST 531 (version 2) and SSOL2 thermodynamic databases. The ternary combinations that met the solidification requirement were optimized for a narrow solidification range. Taking advantage of the CALPHAD approach meaning that Scheil's equation could now be applied to multicomponent alloys in a more efficient way than the traditional; the optimized ternary compositions were subjected to non-equilibrium solidification simulations. Effort has also been made to predict the phase fractions during solidification of promising solder alloy candidates.

The ternary combinations that satisfied the primary solidification requirement were scrutinized taking into account the commercial interests i.e. availability, cost-effectiveness, recyclability and toxicity issues. Technical issues like manufacturability and surface tension have also been considered. Special focus has been given to toxicity related issues since the main ideology of looking for an alternative to high lead containing solders is not related to technical issues but due to environmental concerns.

Keywords: CALPHAD, COST 531 (solder database), SSOL2 (solution database)

Przy pomocy metody CALPHAD, używając pakietu ThermoCalc, dokonano próby wytypowania bezołowiowych stopów trójskładnikowych, o temperaturze topnienia 270-350°C, jako zamienników lutów wysokoołowiowych, stosowanych do wstępnego montażu układów elektronicznych. Rozpatrzono różne typy stopów z bazy danych COST 531, wersja 2, oraz bazy SSOL2 dobierając te o najmniejszej różnicy temperatur solidus-likwidus. Dla tak dobranych stopów wykonano następnie symulację krzepnięcia równowagowego i symulację z zastosowaniem modelu Scheila. Na podstawie otrzymanych ścieżek krzepnięcia próbowano przewidzieć skład fazowy stopów przy obydwu rodzajach krzepnięcia. Grupa wybranych stopów była dalej oceniana z punktu widzenia technicznego, ekonomicznego i ekologicznego ze szczególnym uwzględnieniem tego ostatniego.

1. Introduction

Solder is a critical material that physically holds electronic assemblies together while allowing the various components to expand and contract, to dissipate heat and to transmit electric signals. Increasing the lead content and reducing the tin content results in solders with substantially higher melting points. Common versions are Pb-10Sn/Pb-5Sn, having a melting range of 275°C to 302°C and 308°C to 312°C respectively. These alloys solder the terminations within electronic components. High melting point solders prevent the solder joint within the component from remelting when the component is subsequently soldered to the printed circuit board (PCB), a step that typically involves lower melting point solders. High lead containing solders in general have better fatigue performance, higher tensile strengths and slightly reduced wettability when compared to the lower melting point tin-lead compositions [1]. Reducing gas atmospheres, such as forming gas or pure hydrogen are effective fluxing agents at high soldering temperatures and often substitute for chemical fluxes that may char at high soldering temperatures. Despite of all the beneficial attributes and familiarity associated with these alloys, the presence of lead and its potential environmental impact when products are discarded to landfills has caused the industry to seek for lead free alternatives.

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The Latin word for lead, plumbum may have derived from the original Sankrit bahumala, meaning "very dirty" [2]. Throughout recorded history, lead has been known to be toxic. H.L. Needleman [3, 4] points out that evidence of lead toxicity existed in $2000_{B.C.}$ Having been phased out of western civilization's staples such as gasoline, paint and water distribution lines, the elimination of lead in electronic products is imminent. The toxic metal's last major refuge is automobile batteries which demand more than 70% of global assets but are largely recycled with notable fugitive emissions that contaminate the environment world wide [5]. Unlike automobile batteries; the use of recycled lead for electronics application can be severely limited since recycled lead displays higher α-particle emission than virgin lead. This can have detrimental effects on the performance of integrated circuits because α-particle emission leads to the occurrence of soft errors [6].

At present there are Pb-free solders which can replace eutectic SnPb, but there is none to replace high Pb containing solders used for first level packaging applications. One well known binary alloy which could be considered for this application is Au-20Sn (weight-percent) with a eutectic point of 280°C, yet this eutectic alloy is known to have poor reflow properties because it does not readily react with Cu or Ni. The Sn in the alloy tends to stay with Au because it is eutectic consisting of two Au-Sn compounds. In order to react with Cu or Ni, the Sn atoms must dissociate themselves from the Au atoms so that the driving force is reduced. Thus only ternary alloys could possibly provide an amicable solution [7].

Experimental determination of a ternary system is extremely time consuming. If thermodynamic descriptions of all the constituent binary systems are available, it is possible to estimate a phase diagram of a higher component system from the extrapolation of the binary systems. The quality of the extrapolation to a ternary system from the descriptions of the three binary systems depends not only on the accuracy of the calculation of each binary system but also on the magnitude of possible ternary interactions and the occurrence of ternary intermetallic compounds. The probable magnitude of these ternary interactions can be estimated from the properties of the binary systems. In most cases the excess Gibbs free energies of the solution phases in the binary systems relevant to solder alloys are relatively small in magnitude, indicating that their ternary interactions are less significant [8, 9].

2. Methods

Using Thermo-Calc version R, various ternary combinations were extrapolated iteratively from all the well assessed binary systems in the COST 531 version 2.0 [10] and SSOL2 [11] thermodynamic databases to determine the ones that adhere to the melting criterion i.e. 270-350°C. Ternary combinations which could probably meet the solidification requirement but are not well assessed have not been considered. The extrapolations have been carried out without taking into account the possibility of formation of any ternary phases. The ones that met the equilibrium solidification requirement were further optimized for technically preferred narrow solidification ranges.

The optimized ternary combinations were scrutinized taking into account the commercial and technical interests like availability, commercial cost, wetting and toxicity. Primary focus has been given to toxicity related issues since the main ideology of looking for an alternative to high lead content solder is not related to technical issues but due to environmental concerns. The promising ternary combinations that are deemed to be non-toxic were further subjected to non-equilibrium simulations as one of the main strengths of CALPHAD is that Scheil's equation could now be applied for muticomponent systems in a more efficient way than the traditional Scheil's approach. Microsegregation during solidification of potential environmentally friendly solders has been predicted by studying the composition profiles of each phase under both equilibrium and non-equilibrium conditions during solidification. The elements were classified as segregated during non-equilibrium solidification simulations if their compositions in the solidified material were greater than the one predicted by equilibrium solidification.

3. Results and discussion

3.1. Solidus/Liquidus

The ternary combinations that met the primary solidification requirement are listed in table 1. The results show that the promising solder alternatives could be either Au based or Sn based ones. There are many Au based ternary systems (Table 1) that could be considered for this application since Au undergoes a eutectic reaction with Sn, Sb, Ge and Si. The ternary combinations Au-32Sn-0.01Ag, Au-0.31Sn-0.01Cu, and Au-0.30Sn-0.01Zn have a very narrow solidification range as they are close to the eutectic Au-Sn composition but the content of Ag, Cu and Zn could be increased to a maximum of Au-0.35Sn-0.03Ag, Au-0.33Sn-0.04Cu and Au-0.30Sn-0.09Zn and still meet the solidification criterion for this application but with a broader solidification range. The Bi based system cannot be considered for this application due to its poor thermal and electrical properties which are critical for solder applications.

TABLE 1

Equilibrium ternary combinations optimized for a narrow solidification range

S.No	Ternary Compositions (mole-fraction)	Solidus T (°C)	Liquidus T (°C)	Range (°C)
1.	Sn-0.25Au-0.20Sb	282.83	305.18	22.35
2.	Sn-0.36Au-0.08Zn	302.95	327.69	24.74
3.	Sn-0.33Au-0.02Ge	314.29	343.43	29.14
4.	Sn-0.30Au-0.08Ag	300.50	334.03	33.53
5.	Sn-0.29Au-0.08Cu	291.75	330.94	39.19
6.	Au-0.18Ge-0.10In	338.69	339.03	0.34
7.	Au-0.16Sb-0.22In	285.83	287.05	1.22
8.	Au-0.30Sn-0.24In	280.54	289.14	8.6
9.	Au-0.30Sn-0.01Zn	274.96	284.11	9.15
10.	Au-0.31Sn-0.01Cu	279.15	291.44	12.29
11.	Au-0.35Sn-0.21Sb	312.43	329.23	16.80
12.	Au-0.26Ge-0.02Bi	331.50	351.42	19.92
13.	Au-0.26Sb-0.20Bi	292.44	313.59	21.15
14.	Au-0.13Sn-0.10Si	312.23	333.67	21.44
15.	Au-0.32Sn-0.01Ag	280.86	307.08	26.22
16.	Au-0.15Ge-0.12Sn	285.58	314.16	28.76
17.	Au-0.24Ge-0.05Sb	285.40	347.88	62.48
18.	Bi-0.16Sb-0.04In	269.11	335.84	66.73

3.2. Scrutinization based on commercial interests

It is very essential to take into account some of the commercial interests like availability, comercial cost, toxicity and recyclability issues, during the design of replacement solders for first level packaging applications.

3.2.1. Availability

One of the global concerns is, will the chosen replacement be available in sufficient quantity to supply the needs globally? Thus, it is essential for developing a replacement solder that does not have a scarce major constituent. The availability of elements being considered for this application till the end of 2007 [12] is listed in Table 2.

TABLE 2

Metal reserves (31December 2007)

Elements	Reserve (thousand metric tons)
Tin	17100
Antimony	6400
Copper	1430
Zinc	1150
Bismuth	1000
Silver	840
Gold	132
Indium	27

3.2.2. Commercial cost

The microelectronics industry is extremely cost conscious. The history of the industry has been to continuously produce higher performance at lower costs. The cost of the product is the resultant of the cumulative cost of the components, hence the cost of Pb-free solder alloys can impact the cost of the finished product. Cost competitiveness in the electronics industry is maintained by reducing the cost of individual components to a minimum, in order to maximise the overall cost reduction. The commercial cost of the elements being considered for this application is listed in table 3 [13-15].

TABLE 3

Cost of metals per kg[a]

Metals	Cost (28 March 2008) (US$/Kg)
Gold	29910
Indium	925
Silver	575
Bismuth	33
Tin	20.595
Copper	8.535
Antimony	7.71
Zinc	2.325

[a] Metal cost only, does not include fabrication costs, margins, etc.

3.2.3. Environmental issues

The extent to which Pb-free solders themselves are 'environmentally friendly' is also relevant. There are two basic requirements here i.e., toxicity and recyclability. While a solder might be Pb-free, it might contain other toxic metallic elements violating the whole motivation behind the drive for Pb-free solders development. Of particular importance here are the acceptable concentrations in ground water and potable water, and the leachability of solder alloys. Recent research indicates that according to California's hazardous waste classification criteria, most electronic products might still be considered hazardous even if all electronic product manufacturers replace lead-tin solders by solders with high content of copper, nickel, antimony and zinc and abide according to European RoHS mandate [16-18].

The metals being considered for first level packaging applications are ranked in descending toxicity in table 4 based on EPA (Environmental Protective Agency- US) [19] which takes into account leaching by ground water and OSHA (Occupational Safety and Health Administration) [20] which deals with occupational exposure, inhalation and other exposure in the work place. Thus the sole objective of developing not only lead free but also environmentally friendly high melting point solders could be accomplished only by Au based or Sn based solder alloys.

TABLE 4

Toxicity Metrics

Metals	EPA (US) drinking water standard (mg/L)	OSHA PEL (mg/m3)
Lead	0.015	0.05
Silver	0.05	0.01
Antimony	0.006	0.5
Indium	none	0.1
Bismuth	0.05	none
Copper	1	0.1
Zinc	5	15
Tin	none	2
Gold	none	none

The alloys used must also be recoverable and recyclable, without significant increase in cost. At the present time, many recycling points are available for tin-lead alloys. By using gold, the initial costs would be higher but there would be potentially a value to the recycled product and no disposal costs associated with the solders resulting in lower lifetime costs for the product [21]. In addition, the issue of refining costs becomes important when considering initial material selection. For example, refining of gold recovered from electronic waste scrap is easier. It has been reported that 47% of the total consumption of gold was recycled in 2007 [12].

3.3. Scrutinization based on technical issues

3.3.1. Manufacturability

The substitute for lead-free solders would also have to be produced in all forms used by the electronics industry. Lead-free solder wire for repair and rework, lead-free powder for solder paste and lead free solder bar for wave soldering. Among all the metals being considered for this application a high bismuth content followed by antimony in the alloy would make drawing into wire very difficult due to the brittleness of the alloy [22].

3.3.2. Surface tension

The wetting behaviour of a molten solder is an important property which partially depends on the surface tension and viscosity of the liquid phase. Low surface tension generally ensures good wetting. The surface tension measured experimentally by Somol et al [23] for Pb-5Sn (weight-percent) and Pb-10% in protective Ar-H_2 atmosphere are 465 and 470 (mN/m) respectively. Surface tension measured experimentally for pure tin by Lee et al. at [23] at 50°C above the liquidus temperature was 540 mN/m in Ar-H_2 atmosphere. Under similar experimental conditions, the surface tension measured for gold by Krause et al. was 1090 mN/m [23].

3.4. Non-Equilibrium Solidification

The Scheil's equation is applicable only to dendritic solidification and even not to one where the solidification is mainly dendritic in nature but contains some final eutectic product. Furthermore it cannot be used to predict the formation of intermetallic compounds during solidification since the partition coefficient is assumed to be constant. However, the partition co-efficient is dependent on both temperature and/or composition and this is not taken into account in traditional Scheil's equation.

Using a CALPHAD route, all of the above obstacles can be overcome. The process that physically occurs during solidification can be envisaged. Any appearances of secondary phases can be easily taken into account in this approach with the assumption that no back diffusion is involved. Therefore all transformations can be handled including the final eutectic solidification. This approach is based on a series of isothermal steps but as the temperature step size becomes small it provides results which are almost completely equivalent to those which would be obtained from the continuous cooling [24].

The equilibrium calculations predicted that only Au and Sn based systems provide promising results that adhere to the melting criterion of high melting point lead free solders used for first level packaging applications. Taking into account the commercial cost and surface tension, initial focus has been given to Sn based solders compared to Au based ones. The promising Sn based ternary combinations listed in table 1 were subjected to non-equilibrium solidification simulations and are listed in table 5.

TABLE 5

Non-equilibrium solidfication simulations of Sn based systems

Ternary Compositions (mole-fraction)	Solidus (°C)	Liquidus (°C)
Sn-0.25Au-0.20Sb	273	290
Sn-0.33Au-0.02Ge	216	334
Sn-0.30Au-0.08Ag	122	335
Sn-0.29Au-0.08Cu	305	332
Sn-0.36Au-0.08Zn	156	328

Sn based combinations adhering to the solidification criterion generally undergoes a peritectic reaction. Equilibrium calculations are less valid for peritectic reactions and it is evident from table 5. Both Sn-Au-Cu and Sn-Au-Sb ternary combinations gave positive results. These combinations were optimized by non equilibrium solidification simulations. The Sn-Au-Cu system was optimized with an objective of reducing the solidification range and still meet the solidification criterion. The Sn-Au-Sb system was optimized with an objective of reducing the Sb content in the ternary system and still adhere to the solidification criterion since Sb is considered to be toxic The results are shown in Fig. 1 and Fig. 2 respectively.

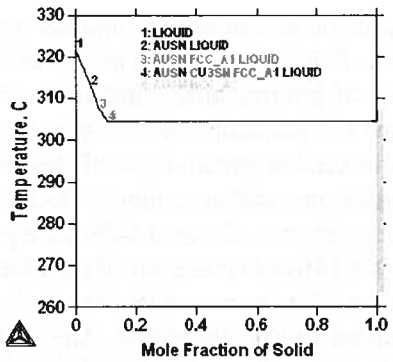

Fig. 1. Non-equilibrium solidification simulation of Sn-0.29Au-0.06Cu (mole-fraction)

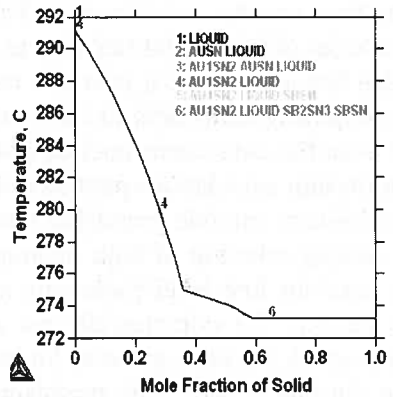

Fig. 2. Non-equilibrium solidification simulation of Sn-0.25Au-0.11Sb (mole-fraction)

Non-equilibrium solidification simulations predict that only two Sn based ternary compositions (among the elements being considered for this application) would satisfy the solidification criterion. Sn-0.29Au-0.06Cu has an edge over Sn-0.25 Au-0.11Sb since the latter includes a sizable proportion of antimony. Even though Sb is consider ed to be quite toxic but definitely not as toxic as lead.

3.5. Microsegregation

The composition profiles of each phase were studied under both equilibrium and non-equilibrium conditions during solidification of Sn-0.29Au-0.06Cu and Sn-0.25Au-0.11Sb. For equilibrium solidification there is no solute segregation and the composition of the solidified material is uniform. The elements were classified as segregated during non-equilibrium solidification simulations if their composition in the solidified material were greater than the one predicted by equilibrium solidification.

Microsegregation of Cu in FCC_A1 phase was observed during non-equilibrium solidification simulation of Sn-0.29Au-0.06Cu. Fig. 3 illustrates the deviation of Cu composition profile in FCC_A1 phase from the equilibrium one. Similarly microsegregation of Sb in SbSn phase was observed during non-equilibrium solidification simulation of Sn-0.25Au-0.11Sb. Fig. 4 illustrates the deviation of Sb composition profile in SbSn phase from the equilibrium one.

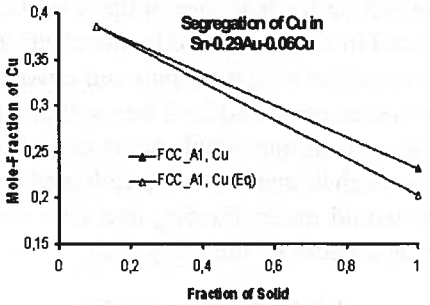

Fig. 3. CMicrosegregation of Cu predicted in FCC_A1 phase during non-equilibrium solidification of Sn-0.29Au-0.06Cu

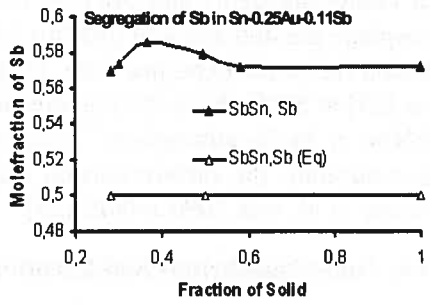

Fig. 4. Microsegregation of Sb predicted in SbSn phase du- ring non-equilibrium solidification of Sn-0.25Au-0.11Sb

The influence of segregation of elements during solidification on the thermo-mechanical properties probably depends on whether the segregated phase appears in the microstructure of the solidified material as a dispersed phase or as a matrix phase. It could have a small influence on the thermo-mechanical properties if the segregated phase appears as a dispersed phase while have a high influence on the thermo-mechanical properties if the segregated phase appears as a matrix phase in the final microstructure of the solidified material. The Thermo-Calc software version R is not capable of predicting the resulting microstucture for non-equilibrium solidification simulation. Thus, the final microstructures for the two promising solder alloys were predicted for optimized compositions that were determined by equilibrium calculations i.e., Sn-0.29Au-0.08Cu and Sn-0.25Au-0.20Sb. The results are depicted in Fig. 5 and Fig. 6 respectively.

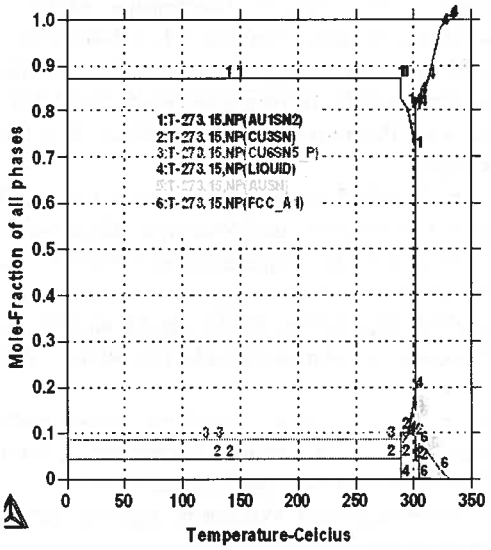

Fig. 5. Microstructure prediction by equilibrium calculation of Sn-0.29Au-0.08Cu solder alloy

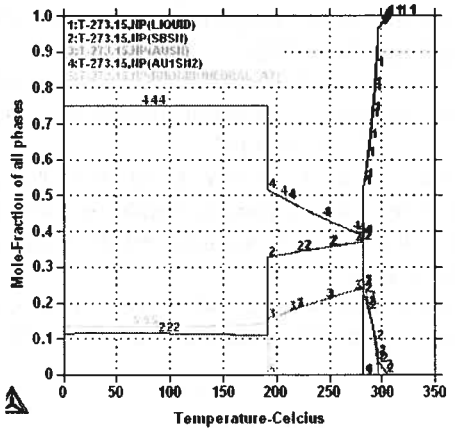

Fig. 6. Microstructure prediction by equilibrium calculation of Sn-0.25Au-0.20Sb solder alloy

The equilibrium calculation has predicted that in the final microstructure of Sn-0.29Au-0.08Cu, Cu6Sn5_P and Cu3Sn phases would be dispersed in the Au1Sn2 matrix phase. Similarly the equilibrium calculation has predicted that in the final microstructure of Sn-0.25Au-0.20Sb, Rhombohedral_A7 and SbSn phases are dispersed in the Au1Sn2 matrix phase. Segregation of Cu in FCC_A1 phase during solidification will have no influence on the thermo-mechanical properties since the FCC_A1 phase is not predicted in the final microstructure of the solidified material. Segregation of Sb in SbSn phase during non-equilibrium solidification may have a small influence on the thermo-mechanical properties as SbSn phase is predicted to occur only as a dispersed phase and not as a matrix phase in the final solidified material. However, the Thermo-Calc software version R is not capable of predicting the final microstructure for non-equilibrium solidification simulation. Thus, in order to confirm the predicttions of the final microstructure, it is necessary to perform the microstructure evaluation for the proposed solder candidates for the first level packaging applications i.e., Sn-0.29Au-0.06Cu and Sn-0.25Au-0.11Sb.

3.6. Sn-0.29Au-0.06Cu Vs Sn-0.25Au-0.11Sb

Sn-0.29Au-0.06Cu has relatively high solidus temperature. From a 'resistance to creep' perspective, it would be advantageous to use solder alloys with higher solidus temperature. Sn-0.29Au-0.06Cu is relatively more environmental friendly since the latter has a considerable proportion of Sb, even though Sb is considered to be quite toxic but definitely not as toxic as lead [18-20]. No segregation of alloying elements in the final solidified material of Sn-Au-Cu is predicted while a small segregation of Sb in SbSn phase is predicted in the final solidified material of Sn-Au-Sb. From the reliability point, one of the main advantages of using lead in the Pb-Sn alloy is that lead does not form any intermetallic compounds with Ni (solder wettable layer), commonly used in under bump metallization. This reliability issue could be satisfied only by Sn-Au-Cu since in addition to Sn, Sb also forms intermetallic compounds with Ni in the latter.

4. Concluding remarks

The preliminary assessment of various ternary combinations among the potential elements being considered for the first level packaging applications by the CALPHAD approach reveals that only Au based or Sn based systems could adhere to the primary solidification criterion for the first level packaging applications. The development of environmentally friendly solders could only be fulfilled by Au or Sn based systems. Taking into account the cost and surface tension issues, primary focus has to be given to Sn based solder alloys for this application if not the other alternative could be an Au based one. Among the proposed Sn based candidates, Sn-Au-Cu has an edge over Sn-Au-Sb.

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REFERENCES

[1] Y. Takaku, I. Ohnuma, R. Kainuma, Y. Yamada, Y. Yagi, Y. Nishibe, K. Ishida, Development of Bi-base high-temperature Pb-free solders with

second-phase dispersion: thermodynamic calculation microstructure and interfacial reaction, J.Electron.Jem. **35**, 1926-1932 (2006).

[2] P. Van der Krogt, Elementymology and Elements Multidict, http:// elements.Vanderkrogt.net/elem pb.html (accessed 04-02-07).

[3] H. L. Needleman, History of Lead Poisoning in the World, Lead Poisoning Prevention and Treatment: Implementing a National Program in Developing Countries, ed. A. M. George (Bangalore, India: The George Foundation), 1999.

[4] H. L. Needleman, Low Level Lead Exposure and Neuropsychological Performance, Lead versus Wealth, ed. M. Rutter and R. R. Jones (NewYork: John Wiley and Sons Ltd., 1983), 229-242.

[5] Blacksmith institute, The World's worst polluted places, www.blacksmithinstitute.org (accessed 04-02-07)

[6] J. F. Ziegler, G. R. Srinivasan, IBM J. Res. Dev.**40**, 1996.

[7] K. N. Tu, A. M Gusak, M. Li, Physics and materials ch- allenges for lead-free solders, J. App. Phy., 2003, 1335-1353.

[8] U. R. Kattner, C. A. Handwerker, Calcula-tion of Phase Equilibria in Candidate Solder Alloys, J.Z.Metallkd, July 2001.

[9] H. L. Lukas, S. G. Fries, B. Sundman, Computational Thermodynamics- The Calphad Method, Cambridge University press, 2007, 157-162.

[10] A. T. Dinsdale, A. Watson, A. Kroupa, A. Zemanova, J. Vrestal, J. Vizdal, COST 531 database V 2.0, Ja- nuary 2006.

[11] Scientific Group Thermo data Europe (SGTE), SSO- L-2 Solutions Database Version 2.1, 1999/ 2002/ 2003.

[12] United States Geological Survey, http:// minerals.usgs.gov/minerals/pubs/mcs/ (accessed 31-12-07).

[13] American Precious Metals Exchange, http://www. apmex.com/.

[14] London Metals Exchange, http://www.lme.co uk/.

[15] Indium Corporation, http://www.indium.com/.

[16] M. Warwick, Implementing Lead-free Soldering, SMTA, October 1999.

[17] Oladele A.Ogunseitan, Public Health and Environm- ental Benefits of Adapting Lead-Free Solders, JOM , July 2007, 12-17.

[18] J. D. Lincoln *et al.*, Leaching Assessments of Hazardous Materials in Cellular Telephones, J. Environ. Sci. and Technol., vol. 41, 2007, 2572-2578.

[19] U.S. Environmental Protective Agency (EPA), http:// www.epa.gov/.

[20] U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), http://www.osha. gov/.

[21] R. J. Holiday, Ch. W. Corti, Tren ds in the Use of Gold in Current Industrial Applications, World Gold Council, London, 2002.

[22] M. Abtew, G. Selvaduray, Lead -free Solders in Microelectronics, J. Material Science and Engineering, vol. 27, 2007, pp. 95-141.

[23] Z. Moser, W. Gasior, A. Dębski, J. Pstrus, Surface Tension and Density Databa- e, Institute of Metallurgy and Material Science, Polish Academy of Sciences, Krakow.

[24] N. Saunders, A. P. Miodownik, CALPHAD, Pergamon Materials Series **1**, 411-449 (1998).

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