JMEPEG (2012) 21:629–637
DOI: 10.1007/s11665-012-0125-3

©ASM International
1059-9495/$19.00

Current Problems and Possible Solutions in High-Temperature Lead-Free Soldering

Ales Kroupa, Dag Andersson, Nick Hoo, Jeremy Pearce, Andrew Watson, Alan Dinsdale, and Stuart Mucklejohn

(Submitted October 23, 2011; in revised form December 10, 2011)

The substitution of lead in the electronics industry is one of the key issues in the current drive towards ecological manufacturing. Legislation has already banned the use of lead in solders for mainstream applications ($T_M \approx 220$ °C), but the use of lead in the solders for high-temperature applications (>85% lead, $T_M \approx 250$-350 °C) is still exempt in RoHS2. The search for proper substitutes has been ongoing among solder manufacturers only for a decade without finding a viable low cost alternative and is the subject of intensive research. This article tries to map the current situation in the field of high-temperature lead-free soldering, presenting a short review of current legislation, requirements for substitute alloys, and finally it describes some existing solutions both in the field of promising new materials and new technologies. Currently, there is no drop-in replacement for lead-containing solders and therefore both the new materials and the new technologies may be viable solutions for production of reliable lead-free joints for high-temperature applications.

Keywords lead-free soldering, materials for high-temperature LF solders, new technologies for HT lead-free soldering

1. Introduction

Public awareness of environmental issues including the use and disposal of potentially toxic materials has never been greater, with lead being the subject of particular scrutiny. Lead-containing materials are among the most important posing a great threat to human life and the environment. The main reason is the danger of lead accumulation in the human body; it leads to disorders of the nervous and reproductive systems, delays in neurological and physical development, it causes cognitive and behavioral changes and reduces the production of hemoglobin resulting in anemia and hypertension. Currently, lead poisoning is assumed to have occurred if the level of lead in the blood exceeds 500 µg/mL, but recent studies have found that a level of lead below the official threshold could be hazardous to a child's neurological and physical development (Ref 1).

This article is an invited submission to JMEP selected from presentations at the Symposia "Wetting, soldering and brazing" and "Diffusion bonding and characterization" belonging to the Topic "Joining" at the European Congress and Exhibition on Advanced Materials and Processes (EUROMAT 2011), held September 12-15, 2011, in Montpellier, France, and has been expanded from the original presentation.

Ales Kroupa, Institute of Physics of Materials, AS CR, Zizkova 22, 61662 Brno, Czech Republic; **Dag Andersson**, Swerea IVF, Mölndal, Sweden; **Nick Hoo** and **Jeremy Pearce**, ITRI Ltd., Curo Park, St. Albans, UK; **Andrew Watson**, SPEME, University of Leeds, Leeds, UK; **Alan Dinsdale**, National Physical Laboratory, Teddington, UK; and **Stuart Mucklejohn**, Ceravision Limited, The Mansion, Bletchley Park MK3 6EB, UK. Contact e-mail: kroupa@ipm.cz.

In industry, there has been increasing pressure to eliminate lead-containing materials, which has had significant support of the legislative process throughout the EU. Despite the fact that the electronic industry is not the largest user of lead and lead-containing chemicals (the electronics industry is only the 6th largest consumer of lead but 80% of its consumption is in solders), electronic products and processes were (and still are) significant sources of lead contamination, through the both occupational exposure and waste disposal of electronic assemblies, causing, e.g., the contamination of underground water sources. In addition, there is the possibility of lead containing effluents entering sewage disposal systems. Although there seems to be no generally accepted description of the actual mechanisms by which lead from disposed electronic products enters the ground water stream and from there the animal or the human food chain, it is generally agreed that the effect occurs. Apparently it is connected with the action of water containing oxygen, carbon dioxide, and possibly chloride on the lead-containing solder materials.

Recent EU legislation DIRECTIVE 2002/95/EC, Restriction of the use of certain Hazardous Substances (RoHS) in electrical and electronic equipment (EEE), and the recast version (RoHS 2, DIRECTIVE 2011/65/EU) restricted the use of lead-containing solders in many industries from July 1, 2006. A related directive (DIRECTIVE 2002/96/EC, Waste EEE, WEEE) was launched to promote the collection and recycling of electronic equipment and the work with an update to this directive is ongoing, Despite the fact that the materials for high-temperature soldering are among materials currently not affected by this deadline, the pressure to remove hazardous substances continues and spreads to other, currently exempt fields. Likewise, market pressures due to economies of scale are already having an impact on industries currently exempt by the dwindling availability of lead-containing high-temperature solders (for use in the temperature intervals between 250 and 350 °C), thereby causing another source of pressure for switching to lead-free materials.

2. EU Legislation

As mentioned in a previous part, two EU directives, RoHS Directive 2002/95/EC (Restriction of Hazardous Substances in EEE) and the recast version RoHS 2 2011/65/EU that has to be implemented in national law by January 2, 2013 and WEEE Directive 2002/96/EC (Waste Electrical & Electronic Equipment) are currently defining the use and availability (RoHS) and collecting and recycling (WEEE) of lead-containing solders. There is also another legislation [REACH Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals), EC/1907/2006] which regulates the use and exploitation of chemicals in industry in general.

2.1 RoHS Directive

The RoHS Directive of 2002 has recently been recast as Directive 2011/65/EU of the European Parliament and published in the Official Journal of the European Union on 01 July 2011. This Directive entered into force on July 22, 2011. Member states are required to comply with the recast Directive by January 02, 2013.

The main objective of the RoHS Directive is to contribute to the protection of human health and the environmentally sound recovery and disposal of waste EEE. The top priority in the legislation is given to prevention in waste. Prevention is defined as measures that reduce the content of harmful substances in materials and products. Restrictions on the use of certain substances in materials and products must take into account technical and economic feasibility, including the impact on small and medium enterprises (SMEs).

The decision on exemptions and on the duration of possible exemptions should take into account the availability of substitutes and the socioeconomic impact of substitution. Life-cycle thinking on the overall impact of exemptions should apply, where relevant. Substitution of the hazardous substances in EEE should also be carried out in such a way as to be compatible with the health and safety of users of EEE.

Exemptions from the restriction for certain specific materials or components are limited in their scope and duration. Once it becomes possible to substitute substances that have been subject to exemptions, and following a detailed review, a gradual phase out of the substances in EEE is then usually implemented.

The restricted substances are referred to in Article 4(1) of 2011/65/EU. Currently, the limits are 0.1% for lead, mercury, hexavalent chromium, and polybrominated diphenyl ethers (PBDE). Stricter limits of 0.01% are imposed on Cd and polybrominated biphenyls (PBB). The limits are defined as the maximum concentration values in weight percent tolerated in homogeneous materials. Examples of the exemption are shown in the Table 1. Out of 34 currently valid exemptions, only those related to lead-free soldering are shown in the table. The exemptions 7(a,b) currently govern the use of lead-containing solders for high-temperature application.

2.2 The REACH Regulation

The aim of the REACH Regulation is to improve the protection of human health and the environment through the better and the earlier identification of the intrinsic properties of chemical substances. At the same time, innovative capability and competitiveness of the EU chemicals industry should be enhanced. The basic principle of this directive can be described as "No data, no market." No product will be allowed to enter the market without a clear and detailed description of contained substances and the registration of the information in a central database run by the European Chemicals Agency (ECHA) in Helsinki.

The REACH Directive gives greater responsibility to industry to manage the risks from chemicals and to provide safety information on the substances. Manufacturers and importers are required to gather information on the properties

Table 1 The exemptions in the RoHS Directive 2011/65/EU related to the use of lead in solders

Exemption no.	Description of the exemption	Other comments
7(a)	Lead in high melting temperature type solders (i.e., lead-based alloys containing 85 wt.% or more lead)	
7(b)	Lead in solders for servers, storage and storage array systems, network infrastructure equipment for switching, signalling, transmission, and network management for telecommunications	
14	Lead in solders consisting of more than two elements for the connection between the pins and the package of microprocessors with a lead content of more than 80 wt.% and less than 85 wt.%	Expired on January 1, 2011 and after that date may be used in spare parts for EEE placed on the market before January 1, 2011
15	Lead in solders to complete a viable electrical connection between semiconductor die and carrier within integrated circuit flip chip packages	
24	Lead in solders for the soldering to machined through hole discoidal and planar array ceramic multilayer capacitors	
27	Lead alloys as solder for transducers used in high-powered (designated to operate for several hours at acoustic power levels of 125 dB SPL and above) loudspeakers	Expired on September 24, 2010
31	Lead in soldering materials in mercury-free flat fluorescent lamps (which, e.g., are used for liquid crystal displays, design, or industrial lighting)	
33	Lead in solders for the soldering of thin copper wires of 100 μm diameter and less in power transformers	

of their chemical substances, which will allow their safe handling and discharging.

2.3 The WEEE Directive

The aims and objectives of the WEEE Directive are closely related to those of the RoHS Directive. The WEEE Directive sets out a framework for the collection, recycling, and safe disposal of EEE thereby limiting the amount of toxic waste that is put into landfill. Producers of EEE are responsible for financing the disposal of their products at end-of-life and hence are legally responsible for compliance with national WEEE legislation. Most producers meet their obligations by joining a WEEE producer compliance scheme (currently the unification of local legislation in progress). A proposed update to the WEEE directive suggests that higher amounts should be collected and that collection goals should be related to sales volumes.

3. State of the Art in the Field of Lead-Free Soldering

A considerable amount of research has already been conducted on the formulation of new lead-free soldering materials, not only in Europe but also in USA and Japan. A number of promising materials, e.g., SnAgCu- or Sn-Zn-based alloys reviewed recently by Zhang et al. (Ref 2), have been developed to replace the (near-)eutectic Sn-Pb solders for mainstream applications (with the melting temperatures approximately 220 °C), but there is still no single "drop-in" alternative. Nevertheless, according to the industrial internal market research, 65% of the global market has now converted to lead-free soldering.

However, research was seriously lacking until recently into replacements for high-temperature, high-lead containing alloys, where the lead levels can be above 85 wt.%, and this is reflected in the fact that these materials are, at present, exempt from the valid RoHS legislation. Some of the problems associated with replacement of these alloys have been discussed in recent papers by both Japanese and American authors (Ref 3-6). Lately, a major research programme addressing the issue of high-temperature lead-free soldering has been initiated in Japan.

The main applications for high-temperature ($T_M > 250$ °C) solders within the electronics industry are for the advanced packaging technologies, e.g., die-attach and Ball Grid Array (BGA) solder spheres, chip-scale package (CSP), and multichip module (MCM). The die-attach material should withstand normal working temperatures, thermal loading during soldering and also be sufficiently thermally conducting to transfer heat away from the device. High-lead alloys in die-attach applications are also used in power circuits where very high levels of conductivity are required. These are normally found in automotive under bonnet applications owing to the high current and low voltage produced by car batteries and the high temperatures occurring within the engine bay.

In the case of MCM technology, the so-called step soldering approach is employed. This method is used to solder various levels of the package with different solders of different melting points. One of the solders currently used in this technology is the Pb95-Sn5 alloy with a melting temperature between 308 and 312 °C. New lead-free high-temperature solders should replace the current alloys for a broad range of melting temperatures, and therefore, a good understanding of the melting behavior is paramount. The upper limit of the process temperatures in the MCM technology is around 350 °C, which is defined by the polymer materials used in the substrate. The subsequent process temperatures are defined by the melting point of previously used solders.

A soldered assembly may also be subject to large mechanical or long-term fatigue stresses. Solder interconnects should also not corrode in the presence of high humidity at elevated temperatures. They must also be resistant to air pollutants, such as NO_2 and H_2S. It is also clear that the reliability of solder joints is related to the wettability of the substrate by the molten solder and to the morphological evolution inside interconnects during fabrication and service. In addition, the ongoing miniaturization in the electronics industry poses serious questions concerning reliability, since a clear size effect has been demonstrated for solder joints; with a decrease in the size of the solder gap, the joints become considerably more brittle and this effect is exacerbated with high Sn solders typical in lead-free applications. Traditional barrier metals used in Si device manufacture are also proving unsuitable for use in high technology, unpackaged, miniaturized devices, such as flip chip technology. In these instances, the use of solders with a high Sn content in combination with multilayered metallizations (e.g., Ag, Ti, W, Cu, Ni, V) results in complex interactions during soldering and operational life, leading to galvanic corrosion and destruction of the chip-side interconnections, resulting in a barrier to miniaturization for some devices (Ref 7). In addition, the influence of reaction products at the solder/substrate interface on the mechanical behavior of the joints becomes more significant. Last, but not least, the problem of material cost plays an important role in the selection of the solder.

The ongoing research in the field of high-temperature lead-free solders indicates that it is necessary to abandon traditional Sn-based soldering technology that corresponds closely to that used with eutectic Pb-Sn solders but for a lower melting range. Attempts to adjust the melting temperature of Sn-based solders by the use of appropriate alloying elements have not yet been successful, as possible additives tend to lower the melting temperature. Therefore, attention has turned towards different base elements and at the present time several combinations are under consideration. Hypo-eutectic Bi-Ag alloys, among the most promising under investigation, are very good from the point of view of the liquidus temperature and exhibit mechanical properties close to those of the Pb-based solders, and are affordable. Other interesting materials are Zn-Al eutectic systems alloyed with Mg, Ge, Ga, Sn or Bi, Sb-Sn, and Au-Sn-Sb systems. Some materials are already in use—e.g., Au-Sn-based solders, but replacements are being sought since these alloys are quite expensive and therefore these materials are used only in niche markets, in equipment, where the cost is not one of the key issues.

Mechanical and other properties of joints involving high-temperature solders also need to be understood. In fact, little work has been done for any lead-free solder joints. It is important to characterize the associated diffusion processes in ternary and in particular in quaternary alloy solder joints and their subsequent effect on the long-term mechanical properties of the joint. The formation and growth of intermetallic phases during solder joint reflow and service has been addressed

extensively in the literature, although almost exclusively for the Cu-Sn-X alloy systems. Studies on the effect of intermetallic compound growth on the joint strength of the resulting solder have been focused primarily on lead-free solder alloy systems for mainstream applications. These studies have demonstrated that, owing to their brittle nature and lattice mismatch with the copper substrate, an increased intermetallic thickness weakens the solder joint, especially when subjected to thermal or mechanical fatigue. The research work that does exist has often treated the kinetics of alloy formation, evolution, and corrosion (Ref 8-13) separately and also independently from their corresponding effect on the mechanical and thermophysical properties of the joint (Ref 14-16). Only recently have studies dealing with properties of potential materials for high-temperature lead-free soldering appeared (Ref 17-21).

As a result of increasing computing power, great attention is also paid to the theoretical modelling of processes in complex multi component systems, e.g., the description of their thermodynamic and thermophysical properties and responses on mechanical loading. These methods are currently being applied to both the model systems, and to real materials and joint/interfaces, saving the time and cost incurred for complex experimental studies (Ref 22-25).

4. Search for Solutions

The requirements that are associated with the expected transfer from lead-containing to lead-free materials for high-temperature applications have been summarized by Chidambaram et al. (Ref 23) and are shown in Table 2.

As the ideal solution for industry would involve as few changes as possible, especially from the point of view of the complexity of materials, changes in technologies, etc., the search for substitution has been limited by other less explicit requirements by the manufacturers, than those shown in Table 2. Therefore, the development of lead-free solutions is split into two categories—the development of new materials and the development of new technologies.

New materials should have as few component elements as possible and not in extremely low amounts (microalloying). The materials should be as simple as possible (3, max. 4 elements) and there should be reasonable tolerance with respect to composition.

New technologies should use existing equipment if possible, and avoid higher complexity of the processes. Otherwise the new approach will be hindered by increased costs associated with changing the production lines.

Currently, there is no single drop-in replacement material suitable for applications and no promising universal candidate. There exist, however, high cost solder materials for special niche markets—space industry, power semiconductor devices, etc. (Ref 26-28). New technologies that go beyond traditional soldering can be more promising for the future—Transient Liquid Phase Bonding (TLB), nanotechnologies, adhesives, etc. (see section 4.2)

Recent achievements in the search for alternatives for lead-containing solders can be illustrated by the current situation in new patent applications (Fig. 1, 2).

The results shown in both Fig. 1 and 2 indicate a relatively low number of patent applications in the years 2005-2009, with a significant majority of them associated with new technologies rather than with new materials. Most of the patents were submitted by Japan-based companies, reflecting the significant attention and financial support given to this topic by Japanese manufacturers.

4.1 Possible New Materials for High-Temperature Lead-Free Soldering

A review of the literature reveals a number of subjects that are the focus of study, both with respect to new materials and new technologies. The properties of Zn-based alloys have been the subject of a number of studies (e.g., Zn-*x*Sn and Zn-Al-Cu) (Ref 19, 20, 29-32), and much attention has been given to Bi-based alloys; e.g., Bi-*x*Ag-0.4Ni-0.2Cu-0.1Ge (x = 2, 5, 8, 11, 14) (in wt.%) (Ref 33), Bi-Ag solders doped by Ce (Ref 34), Bi-5 wt.% Sb-(0.5-5.0) wt.% Cu (Ref 35), and Bi-(0-11) wt% Ag (Ref 36). The other systems studied are Au-based alloys (Au-Sn-X, Au-Ge-X). Here, the main problem is the cost of such materials, but good properties make them suitable for special applications (e.g., space research) (Ref 25-27, 37-41).

Two reviews of new materials and technologies for lead-free soldering have been published recently by Suganuma et al. (Ref 42) and Takaku et al. (Ref 28). Suganuma et al. (Ref 42) suggested several candidates for high-temperature soldering applications; nevertheless none of them fulfil all requirements. Three candidate alloys were considered to cover most of the requirements for high-temperature applications, and again Zn-Sn-X, Au-Sn-X, and Bi-based alloys were highlighted.

An overview of materials was published by Takaku et al. (Ref 28). Based on their own results and a survey of the literature, they proposed several candidate alloys covering most of the high-temperature applications. Their study is an excellent example of the application of *Calphad*-type thermodynamic modelling for the development of new materials. This approach exploits the significant progress achieved in the development of software packages allowing the modelling of phase diagrams and thermodynamic properties of multicomponent systems (Ref 43-46).

The application of the *Calphad* method for the development of new materials has been demonstrated elsewhere (Ref 47-50),

Table 2 The requirements for the substitution materials in high-temperature lead-free soldering (from Chidambaram et al. (Ref 23))

Manufacturing	Reliability and performance
Solidus/liquidus (250-350 °C)	Good thermal and electrical conductivity
Wetting (low surface tension, high wetting force, low wetting time)	Less variation in co-efficient of thermal expansion
Cost-effective	Good shear and tensile strength
Availability and manufacturability	Fatigue and creep resistance
Environmental friendly and recyclability	Oxidation and corrosion resistance
Miniaturization (low natural radius of curvature, easily electroplatable)	IMC formation (wetting reaction and solid state aging)

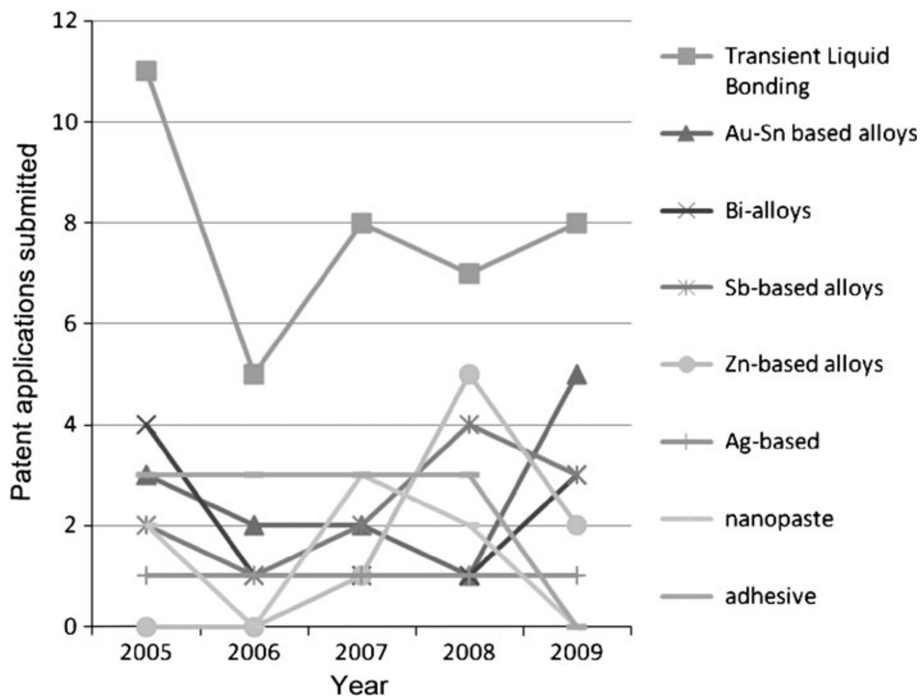

Fig. 1 The distribution of patent applications submitted in the years 2005-2009 by material or technology

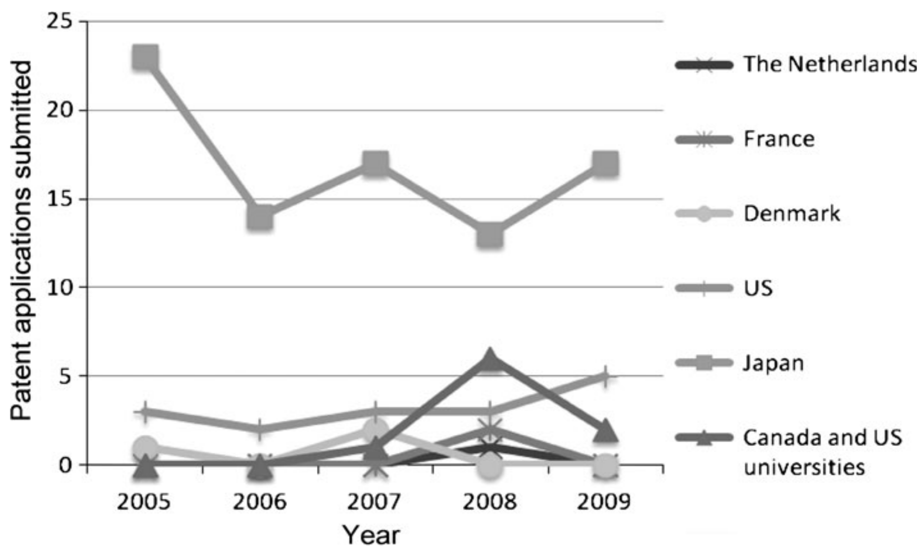

Fig. 2 The distribution of patent applications submitted in the years 2005-2009 by country of origin

and it is itself not the topic of this review. Nevertheless, the existence of a self-consistent thermodynamic database is crucial for such an approach and therefore great attention has been paid recently to the development of thermodynamic databases. Currently, two databases (SOLDERS, Ref 51 and ADAMIS, Ref 52) for the modelling of materials suitable for lead-free soldering are available and their development is still in progress.

Takaku et al. (Ref 28) used the ADAMIS database (Ref 52) to develop alloy compositions before testing the materials to verify the assumptions used in their design. The first group of alloys they proposed is a Bi-based composite solder. Here, they exploited the existence of a metastable liquid miscibility gap in Bi-Cu binary system which becomes stable on the addition of Al. Also Mn is added to the proposed alloy to promote the precipitation of suitable particles. The resulting structure after solidification consists of a Bi matrix reinforced by fine Cu-Al-Mn particles. These particles allow for relaxation of thermal stresses and inhibition of crack growth in the solder.

The second proposed alloy is a Zn-Al-based solder with the addition of Cu. This alloy system contains two invariant reactions (monotectoid at approximately 285 °C and eutectic at approximately 380 °C) and can withstand the thermal stresses and temperature hysteresis between −40 and 250 °C, necessary for the packaging of power semiconductor devices.

Following a survey of the literature, the authors also mentioned Zn-Sn alloys as possible lead-free soldering materials.

These alloys have quite a wide solid/liquid region (solidus temperature at 199 °C, liquidus temperature at approximately 360 °C) and it is therefore important to avoid liquid formation at reflow temperatures at around 250 °C during the soldering process. Also, there is a danger of oxidation on the surface from ambient gas.

Another example of the application of *Calphad*-type theoretical modelling for the development of new materials was described by Ref 25, 37-41, where phase diagram modelling was used for the development of candidate alloys using the SOLDERS database (Ref 51). Two main candidate systems were considered in these studies. The first is a ternary system Au-Sn-X (X = Ag, Cu), where compositions close to the binary eutectic Au-Sn composition (Ref 40, 41) were exploited. Thermodynamic calculations were used to predict the alloying conditions necessary to suppress the precipitation of the brittle Au_5Sn phase while simultaneously not significantly increasing the melting temperature. Thermodynamic calculations were also used for the design of the low Au, Sn-rich solder composition Sn-28Au-8Ag (at.%). The same approach was used for the study of the second candidate system, Au-Ge-X (X = In, Sb, Sn). Some examples of predicted compositions are shown in Table 3 (Ref 23).

The Au-Ge-X system was also studied intensively by Wang et al. and Leinenbach et al. (Ref 25, 37-39). They brought theoretical calculations to practical application, as the Au-Ge alloys developed on a theoretical basis were used for the Heated conversion surface assemblies for the ESA/JAXA Mission BepiColombo to Mercury (Launch 2014) (Ref 26, 27).

4.2 New Technologies for High-Temperature Soldering (Joining)

As the search for material substitution proved to be difficult and no easy solution is available, the development of new technologies is also underway and many new approaches are being investigated.

Suganuma et al. (Ref 42) discussed not only possible new and prospective materials in his article but also described several new approaches based on different technologies offering excellent stability and maintaining interconnection stability after reflow treatment. The conductive adhesive technologies, technologies based on nanoparticles with or without Ag particles (Ref 53-56), and epoxy adhesives filled with metallic solders (Ref 57) were indicated as the most promising. Despite their generally good properties, there are still problems to be solved, e.g., Suganuma et al. (Ref 57) studied the degradation mechanism of the interface between Ag epoxy conductive adhesives (CAs) and Sn plating under humid conditions. Two different types of oxide phases, SnO and SnO_2, were found to be formed at the interface and are the root cause of the interfacial degradation.

Other promising technologies included solutions based on Ag foils or sintering (Ref 58, 59). For example, Ag foil was chosen to bond silicon (Si) chips and copper (Cu) substrates by Dupont et al. (Ref 58). Prior to bonding, the Si chips were coated with thin Cr and Au layers. The Si chip, Ag foil, and Cu substrate were bonded together in one step at 250 °C under a reduced pressure of approximately 7 Pa (50 mtorr), Au/Ag and Ag/Cu bonds forming at the interfaces by short-range interdiffusion. The resulting joints exhibit nearly perfect quality. No voids are observed at the Si/Ag and Ag/Cu bonding interfaces.

Ceramic packaging was described by Liu et al. (Ref 60). High frequency localized induction heating technology was applied to packaging a ceramic crust. It took only about 5 s to complete the packaging process. The temperatures on the cover edges near the solder-loop and at the bottom of the ceramic package were about 320 and 100 °C, respectively. Results showed that owing to the solder reflow, a hermetic seal of the ceramic package was accomplished.

High-temperature lead-free solder joints can be also prepared by means of the high-energy droplet deposition technique. The theoretical background of this method, together with some application examples was described by Conway et al. (Ref 61).

Another promising approach is joining by means of intermetallics. These technologies included evaporating films on the interface (Ref 62, 63) or TLB technology (Ref 64, 65). The former approach consists of replacing a lead-based solder with an intermetallic compound (IMC) to join a Si chip with evaporated Ag, Cu, and Sn films onto a Ag-plated Cu substrate at 250 °C for 10 s. As a result, the evaporated films were completely transformed into intermetallic compounds (Ag_3Sn, or Cu_6Sn_5, $(Ag, Cu)_3Sn$, and Cu_3Sn layers depending on the complexity of films) which were formed under heat treatment at 300 °C for 30 s. The IMC joint showed sufficient strength at 270 °C.

The second approach is based on creating interlayers between joined interfaces, which are designed to form a thin or partial layer of a transient liquid phase, creating bonds through a brazing-like process, in which the liquid phase disappears isothermally. In contrast to conventional brazing, the liquid is substituted by an intermetallic phase with a higher melting point (Fig. 3). Various alloys can be used in this technology; any system, where the liquid phase disappears by means of diffusion or other processes is suitable for this approach. The Sn and Ag layers were used in Ref 64, 65 creating the layer Cu_6Sn_5 IMC, where Ag layer can prevent the

Table 3 The solidus and liquidus temperatures and the extent of mushy zone calculated using the *Calphad* approach (Ref 23)

Alloy no.	Alloy compositions (at.%)	Solidus, *T* (°C)	Liquidus, *T* (°C)	Temperature difference, *T* (°C)
1.	Sn-25Au-20Sb	273	290	17
2.	Sn-29Au-8Cu	305	322	17
3.	Au-18Ge-10In	338.7	340	1.3
4.	Au-16Sb-22In	285.7	288	2.3
5.	Au-30Sn-24In	280.5	290	9.5
6.	Au-31Sn-1Cu	278	292	14
7.	Au-26Ge-2Bi	332	352	20

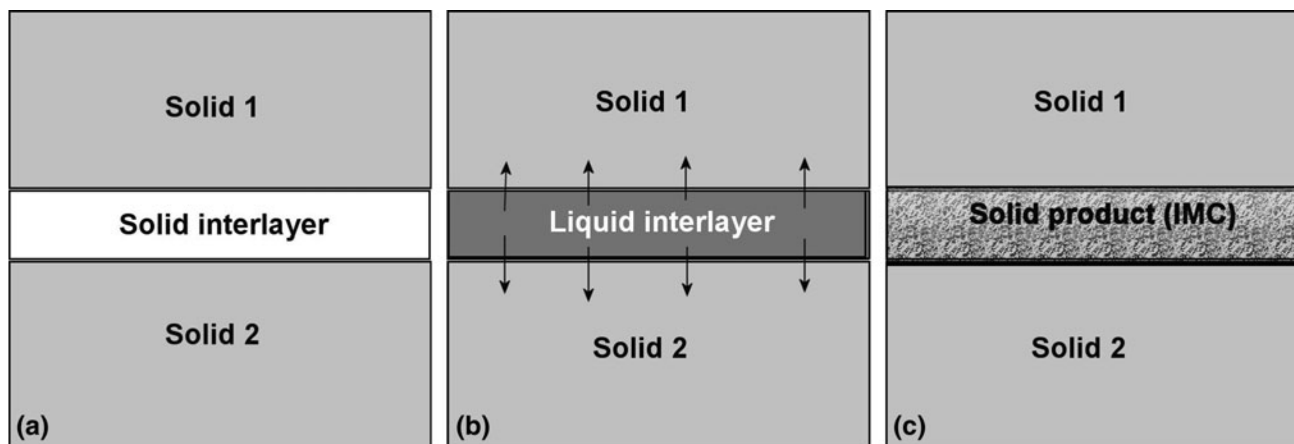

Fig. 3 The TLB approach. The initial state at the temperature lower than the melting point of the interlayer (a), the liquid interlayer phase transforms by isothermal process (b) into the intermetallic compound with a melting point higher than the working temperature (c) (Ref 65)

creation of voids caused by the Kirkendall effect. Kodentsov (Ref 65) also showed results of using the Bi layers on Ni substrate to create the $NiBi_3$ bonding layer. Currently, longer annealing times are still needed for the creation of the IMC layer, which hinder the practical application.

Other technologies, which obviate the need for any specific materials to be used for joining, are also under development. For example, direct Cu bonding (Ref 66) is based on electroless copper deposition producing all-copper chip-to-substrate connections. The PCB process (Ref 67) is another alternative method for electronic assembly that completely bypasses the traditional high-temperature soldering process. The new process reverses the traditional approach to electronic assembly by placing components first and then making the electrical interconnections using traditional printed circuit board (PCB) manufacturing processes.

5. Conclusion

The search for a replacement for lead-containing solders for high temperatures has proved to be difficult. Current research focuses both on the development of new technologies suitable for the many different applications of the high-temperature soldering industry and the extensive search for new materials. No universal lead-free high-temperature solder material is or will be available in the near future and therefore attention has been directed to the selection of different alloys, technologies and processes which can be used in specialized fields in the electronic industry.

References

1. E.B. Smith, Health and Environmental Effects of Lead and Other Commonly Used Elements in Microelectronics, *Handbook of Lead-free solder technology for Microelectronic Assemblies*, K.J. Puttlitz and K.A. Salter, Eds., Marcel Dekker Inc., 2004, ISBN 0-203-02148-7, p 49–81
2. L. Zhang, S.-B. Xue, L.-L. Gao, Z. Sheng, H. Ye, Z.-X. Xiao, G. Zeng, Y. Chen, and S.-L. Yu, Development of Sn–Zn Lead-Free Solders Bearing Alloying Elements, *J. Mater. Sci. Mater. Electron.*, 2010, **21**, p 1–15. doi:10.1007/s10854-009-0014-1
3. F.W. Gayle, G. Becka, J. Badgett, G. Whitten, T.Y. Pan, A. Grusd, B. Bauer, R. Lathrop, J. Slattery, I. Anderson, J. Foley, A. Gickler, D. Napp, J. Mather, and C. Olson, High-Temperature Lead-Free Solders for Microelectronics, *J. Manag.*, 2001, **53**(6), p 17–21
4. T. Shimizu, H. Ishikawa, I. Ohnuma, and K. Ishida, Zn-Al-Mg-Ga Alloys as Pb-Free Solder for Die-Attaching Use, *J. Electron. Mater.*, 1999, **28**(11), p 1172–1175
5. M. Rettenmayr, P. Lambracht, B. Kempf, and C. Tschudin, Zn-Al Based Alloys as Pb-Free Solders for Die Attach, *J. Electron. Mater.*, 2002, **31**(4), p 278–285
6. J.H. Kim, S.W. Jeong, and H.M. Lee, Thermodynamics-Aided Alloy Design and Evaluation of Pb-free Solders for High-Temperature Applications, *Mater. Trans.*, 2002, **23**, p 1873–1878
7. Z.H. Huang, P.P. Conway, E. Jung, R.C. Thomson, C.Q. Liu, T. Loeher, and M. Minkus, A Reliability Issue for Pb-Free Solder Joint Miniaturisation, *J. Elec. Mater.*, 2006, **35**(9), p 1761–1772
8. N.S. Bosco and F.W. Zok, Strength of Joints Produced by Transient Liquid Phase Bonding in the Cu–Sn System, *Acta Metall.*, 2005, **53**, p 2019–2027
9. T.K. Lee, S. Zhang, C.C. Wong, A.C. Tan, and D. Hadikusuma, Interfacial Microstructures and Kinetics of Au/SnAgCu, *Thin Solid Films*, 2006, **504**(1–2), p 441–445
10. T.C. Chang, M.C. Wang, and M.H. Hon, Growth and Morphology of the Intermetallic Compounds Formed at the Sn-9Zn-2.5Ag/Cu Interface, *J. Alloys Compd.*, 2005, **402**(1–2), p 141–148
11. T.C. Chang, J.W. Wang, M.C. Wang, and M.-H. Hon, Solderability of Sn-9Zn-0.5Ag-1In Lead-Free Solder on Cu Substrate: Part 1. Thermal Properties, Microstructure, Corrosion and Oxidation Resistance, *J. Alloys Compd.*, 2006, **422**(1–2), p 239–243
12. K.-L. Lin and T.-P. Liu, The electrochemical Corrosion Behaviour of Pb-Free Al-Zn-Sn Solders in NaCl Solution, *Mater. Chem. Phys.*, 1998, **56**(2), p 171–176
13. F. Rosalbino, E. Angelini, G. Zanicchi, and R. Marazza, Corrosion Behaviour Assessment of Lead-Free Sn-Ag-M (M = In, Bi, Cu) Solder Alloys, *Mater. Chem. Phys.*, 2008, **109**, p 386–391
14. Z. Wang, I. Dutta, and B.S. Majumdar, Thermal Cycle Response of a Lead-Free Solder Reinforced with Adaptive Shape Memory Alloy, *Mater. Sci. Eng. A*, 2006, **421**, p 133–142
15. F. Gao and T. Takemoto, Mechanical Properties Evolution of Sn-3.5Ag Based Lead-Free Solders by Nanoindentation, *Mater. Lett.*, 2006, **60**(19), p 2315–2318
16. C. Andersson, Z. Lai, J. Liu, H. Jiang, and Y. Yu, Comparison of Isothermal Mechanical Fatigue Properties of Lead-Free Solder Joints and Bulk Solders, *Mater. Sci. Eng. A*, 2005, **394**(1–2), p 20–27
17. P. Zimprich, U. Saeed, B. Weiss, and H. Ipser, Constraining Effects of Lead-Free Solder Joints During Stress Relaxation, *J. Electron. Mater.*, 2009, **38**, p 392–399
18. Y. Plevachuk, W. Hoyer, I. Kaban, M. Köhler, and R. Novakovic, Experimental Study of Density, Surface Tension and Contact Angle of Sn–Sb Based Alloys for High Temperature Soldering, *J. Mater. Sci.*, 2010, **45**(8), p 2051–2056

19. Y. Takaku, K. Makino, K. Watanabe, I. Ohnuma, R. Kainuma, Y. Yamada, Y. Yagi, I. Nakagawa, T. Atsumi, and K. Ishida, Interfacial Reaction Between Zn-Al-Based High Temperature Solders and Ni Substrate, *J. Electron. Mater.*, 2009, **38**(1), p 54–60
20. N. Kang, H.S. Na, S.J. Kim, and C.Y. Kang, Alloy Design of Zn-Al-Cu Solder for Ultra High Temperatures, *J. Alloys Compd.*, 2009, **467**(1–2), p 246–250
21. V. Sivasubramaniam, M. Galli, J. Cugnoni, J. Janczak-Rusch, and J. Botsis, A Study of the Shear Response of a Lead-Free Composite Solder by Experimental and Homogenization Techniques, *J. Electron. Mater.*, 2009, **38**(10), p 2122–2131
22. M. Maleki, J. Cugnoni, and J. Botsis, On the Mutual Effect of Viscoplasticity and Interfacial Damage Progression in Interfacial Fracture of Lead-Free Solder Joints, *Mater. Sci. Eng. A*, 2011, **40**(10), p 2081–2092
23. V. Chidambaram, J. Hald, and J. Hattel, Development of High Melting Point Environmentally Friendly Solders Using the CALPHAD Approach, *Arch. Metall. Mater.*, 2008, **53**(4), p 1111–1118
24. N. Moelans, A Quantitative and Thermodynamically Consistent Phase-Field Interpolation Function for Multi-Phase Systems, *Acta Mater.*, 2011, **59**, p 1077–1086
25. J. Wang, C. Leinenbach, and M. Roth, Thermodynamic Modeling of the Au-Ge-Sn Ternary System, *J. Alloys Compd.*, 2009, **481**, p 830–836
26. C. Leinenbach, N. Weyrich, H.R. Elsener, and G. Gamez, Soldering of Ti to Metallized Al_2O_3 Using Eutectic Au-Ge Filler Alloy—Influence of Ceramic Thermal Pre-Treatment on Joint Properties, *Int. J. Appl. Ceram. Technol.* (accepted)
27. H.R. Elsener, C. Leinenbach, J. Neuenschwander, P. Wurz, and D. Piazza, Fügen einer Beheizbaren Metall-Keramik-Struktur mit Eutektischem Au-Ge Lot, *Proceedings of 9th Proceedings of 9th International Conference on Brazing, High Temperature Brazing and Diffusion Bonding* 2010, Aachen, DVS-Berichte Band, Vol 263, p 93–97
28. Y. Takaku, I. Ohnuma, Y. Yamada, Y. Yagi, I. Nakagawa, T. Atsumi, M. Shirai, and K. Ishida, A Review of High temperature Solders for Power-Semiconductor Devices: Bi-Base Composite Solder and Zn-Al base Solder, *J. ASTM Int.*, 2011, **8**(1), JAI103042
29. K. Suganuma, K.-S. Kim, S.-S. Kim, D.-S. Kim, M. Kang, and S.-J. Kim, Joining Characteristics of Various High Temperature Lead-Free Interconnection Materials, *Proceedings of the Electronic Components and Technology Conference*, 2009, art. no. 5074255, p 1764–1768
30. S. Kim, K.-S. Kim, S.-S. Kim, K. Suganuma, and G. Izuta, Improving the Reliability of Si Die Attachment with Zn-Sn-Based High-Temperature Pb-Free Solder Using a TiN Diffusion Barrier, *J. Electron. Mater.*, 2009, **38**(12), p 2668–2675
31. S. Kim, K.-S. Kim, S.-S. Kim, and K. Suganuma, Interfacial Reaction and Die Attach Properties of Zn-Sn High-Temperature Solders, *J. Electron. Mater.*, 2009, **38**(2), p 266–272
32. G. Wnuk and M. Zielińska, Microstructural and Thermal Analysis of Cu-Ni-Sn-Zn Alloys by Means of SEM and DSC Techniques, *Arch. Mater. Sci. Eng.*, 2009, **40**(1), p 27–32
33. G. Meng and Z. Li, Shear Strength and Fracture Surface Analysis of BiAgNiCuGe/Cu Joint, *Trans. China Weld. Inst.*, 2009, **30**(10), p 45–48 (in Chinese)
34. Y. Shi, W. Fang, Z. Xia, Y. Lei, F. Guo, and X. Li, Investigation of Rare Earth-Doped BiAg High-Temperature Solders, *J. Mater. Sci. Mater. Electron.*, 2009, **21**(9), p 875–881
35. Y. Yan, L. Feng, X. Guo, K. Tang, and K. Song, Effect of the Content of Cu on Solderability and Mechanical Properties of Bi5Sb Solder Alloy, *Mater. Sci. Forum*, 2009, **610–613**, p 537–541
36. J.-M. Song and H.-Y. Chuang, Faceting Behavior of Primary Ag in Bi-Ag Alloys for High Temperature Soldering Applications, *Mater. Trans.*, 2009, **50**(7), p 1902–1904
37. C. Leinenbach, F. Valenza, D. Giuranno, H.R. Elsener, S. Jin, and R. Novakovic, Wetting and Soldering Behaviour of Eutectic Au-Ge Alloy on Cu and Ni Substrates, *J. Electron. Mater.*, 2011, **40**(7), p 1533–1541
38. J. Wang, S. Jin, C. Leinenbach, and A. Jacot, Thermodynamic Assessment of the Cu-Ge System, *J. Alloys Compd.*, 2010, **504**, p 159–165
39. J. Wang, C. Leinenbach, and M. Roth, Thermodynamic Assessment of the Au-Ge-Sb System, *J. Alloys Compd.*, 2009, **485**, p 577–582
40. V. Chidambaram, J. Hattel, and J. Hald, Design of Lead-Free Candidate Alloys for High-Temperature Soldering Based on Au-Sn Alloys, *Mater. Des.*, 2010, **31**, p 4638–4645
41. V. Chidambaram, J. Hald, and J. Hattel, Development of Au-Ge Based Candidate Alloys as an Alternative to High-Lead Content Solders, *J. Alloys Compd.*, 2010, **490**, p 170–179
42. K. Suganuma, S.-J. Kim, and K.-S. Kim, High Temperature Lead-Free Solders: Properties and Possibilities, *J. Manag.*, 2009, **61**(1), p 64–71
43. J.-O. Andersson, T. Helander, L. Höglund, P. Shi, and B. Sundman, Thermo-Calc & DICTRA, Computational Tools for Materials Science, *CALPHAD*, 2002, **26**, p 273–312
44. R.H. Davies, A.T. Dinsdale, J.A. Gisby, J.A.J. Robinson, and S.M. Martin, MTDATA—Thermodynamics and Phase Equilibrium Software from the National Physical Laboratory, *CALPHAD*, 2002, **26**, p 229–271
45. S.-L. Chen, S. Daniel, F. Zhang, Y.A. Chang, X.-Y. Yan, F.-Y. Xie, R. Schmid-Fetzer, and W.A. Oates, The PANDAT Software Package and its Applications, *CALPHAD*, 2002, **26**, p 175–188
46. FactSage, CRCT—Centre de Recherche en Calcul Thermochimique/Centre for Research in Computational Thermochemistry and GTT-Technologies, http://www.factsage.com/
47. N. Saunders and A.P. Miodownik, *CALPHAD (A Comprehensive Guide)*, Pergamon Press, Oxford, 1998
48. H.L. Lukas, S.G. Fries, and B. Sundman, *Computational Thermodynamics—The Calphad Method*, Cambridge University Press, Cambridge, 2007
49. R. Schmid-Fetzer, D. Anderson, P.Y. Chevalier, L. Eleno, O. Fabrichnaya, U.R. Kattner, B. Sundman, C. Wang, A. Watson, L. Zabdyr, and M. Zinkewich, Assessment Techniques, Database Design and Software Facilities for Thermodynamics and Diffusion, *CALPHAD*, 2007, **31**, p 38–52
50. A. Dinsdale, A. Watson, A. Kroupa, J. Vrestal, A. Zemanova, and P. Broz, *Lead-free Solders: Materials Reliability for Electronics*, K.N. Subramanian, Ed., Wiley, 2012
51. A.T. Dinsdale, A. Watson, A. Kroupa, J. Vrestal, A. Zemanova, and J. Vizdal, Version 3.0 of the SOLDERS Database for Lead Free Solders, http://resource.npl.co.uk/mtdata/soldersdatabase.htm
52. ADAMIS, Alloy Database for Micro-Solders, http://www.materials-design.co.jp/adamis/adamisE.pdf
53. T.G. Lei, J.N. Calata, G.-Q. Lu, X. Chen, and S. Luo, Low-Temperature Sintering of Nanoscale Silver Paste for Attaching Large-Area (>100 mm^2) Chips, *IEEE Trans. Compon. Packag. Technol.*, 2010, **33**(1), p 98–104
54. A. Hirose, H. Tatsumi, N. Takeda, Y. Akada, T. Ogura, E. Ide, and T. Morita, A Novel Metal-to-Metal Bonding Process Through In-Situ Formation of Ag NANOPARTICLES USING Ag_2O Microparticles, *J. Phys. Conf. Ser.*, 2009, **165**, art. no. 012045
55. J. Janczak-Rusch, Research Approach Towards Knowledge Based Design of Lead Free Solder Joints, 3rd WUT-NIMS—Empa Workshop: New trends in Nanomaterials Design and Engineering, September 9–10, 2010, Dübendorf, Switzerland
56. J.N. Calata, T.G. Lei, and G.-Q. Lu, Sintered Nanosilver Paste for High-Temperature Power Semiconductor Device Attachment, *Int. J. Mater. Product Technol.*, 2009, **34**(1–2), p 95–110
57. K. Suganuma, K.S. Kim, S.S. Kim, D.S. Kim, M. Kang, and S.J. Kim, Joining Characteristics of Various High Temperature Lead-Free Interconnection Materials, *Proceedings of the Electronic Components and Technology Conference*, 2009, art. no. 5074255, p 1764–1768
58. L. Dupont, G. Coquery, K. Kriegel, and A. Melkonyan, Accelerated Active Ageing Test on SiC JFETs Power Module with Silver Joining Technology for High Temperature Application, *Microelectron. Reliab.*, 2009, **49**(9–11), p 1375–1380
59. P.J. Wang and C.C. Lee, Silver Joints Between Silicon Chips and Copper Substrates Made by Direct Bonding at Low-Temperature, *IEEE Trans. Compon. Packag. Technol.*, 2010, **33**(1), p 10–15
60. W.-M. Liu, M.-X. Chen, and S. Liu, Ceramic Packaging by Localized Induction Heating, *Nanotechnol. Precis. Eng.*, 2009, **7**(4), p 365–369 (in Chinese)
61. P.P. Conway, E.K.Y. Fu, and K. Willaims, Presicion Hightemperature Lead-Free Solders Interconnections by Means of High-Energy Droplet Deposition Technique, *CIRP Ann. Manuf. Technol.*, 2002, **51**(1), p 177–180
62. T. Takahashi, S. Komatsu, and T. Kono, Development of Ag_3Sn Intermetallic Compound Joint for Power Semiconductor Devices, *Electrochem. Solid-State Lett.*, 2009, **12**(7), p H263–H265
63. T. Takahashi, S. Komatsu, and T. Kono, Properties of Intermetallic Compound Joint Made from Evaporated Ag/Cu/Sn Films, *MRS Symposium Proceedings, Conference: Symposium V on Materials, Devices, and Characterization for Smart Systems held at the 2008 MRS Fall Meeting Location: Boston, MA*, 2008, Book Series: Materials

Research Society Symposium Proceedings, J. Su, L.P. Wang, Y. Furuya, et al. Eds., 2009, Vol 1129, p 335–340
64. K.K.Sosnowska, M. Pawelkiewicz, J. Janczak-Rusch, and R. Spolenak, Accelerating Transient Liquid Phase Bonding in Cu-Sn Interconnects, *Acta Mater.* (submitted)
65. A. Kodentsov, On the Merits of Transient Liquid Phase Bonding as a Substitute for Soldering with High-Pb Alloys, TMS 2010, Presented at 139th Annual Meeting, February, 14-18, Seattle, USA
66. T. Osborn, N. Galiba, and P.A. Kohl, Electroless Copper Deposition with PEG Suppression for All-Copper Flip-Chip Connections, *J. Electrochem. Soc.*, 2009, **156**(7), p D226–D230
67. J. Fjelstad; Solderless Assembly of Electronic Products—A More Reliable and more Cost Effective Approach to Electronics Manufacturing? *5th IEEE Vehicle Power and Propulsion Conference, VPPC '09*, 2009, art. no. 5289876, p 11–16