J Mater Sci: Mater Electron (2015) 26:4021–4030
DOI 10.1007/s10854-015-2940-4

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High lead solder (over 85 %) solder in the electronics industry: RoHS exemptions and alternatives

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Received: 4 December 2014 / Accepted: 10 March 2015 / Published online: 20 March 2015
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Abstract The restriction of hazardous substances (RoHS) directive passed in 2006 prohibited the use of certain hazardous substances, including lead, in electrical and electronic equipment. However, high melting temperature type solders (i.e. lead-based alloys containing 85 % or more lead by weight) were exempted from the directive regardless of the application in which they were used. In 2011, a recast of the RoHS directive (RoHS2) was passed to set deadlines for eliminating exempt applications such as high lead (>85 % lead) alloys. These deadlines may only be extended through requests demonstrating that there are no acceptable alternatives. While there are no drop-in replacements for high lead solders, their use in a variety of applications has been eliminated and progress is being made on other application categories. As there is no proven reliable solution for some categories such as die attach and high temperature applications, it is likely that the European Union will extend the exempt for the use of high lead alloys but limit the scope of the exemption to those applications where no reliable alternative exists. Additionally, in light of the possible impending deadlines, there is an urgent need to conduct more studies to evaluate alternatives to high lead solder in different applications.

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1 Introduction

Prior to the restriction of hazardous substances (RoHS) directive, the European Union (EU) passed the waste electrical & electronic equipment (WEEE) directive in 2002 in response to the hazardous substances being dumped into landfills throughout Europe. The objective of the WEEE directive was to reuse, recycle, and recover electrical and electronic equipment waste to reduce the release of hazardous substances into the environment. Electrical and electronic equipment waste includes all components and subassemblies that are part of the product at the time the user discards it. The directive also required improving the environmental performance of all operators involved in the life cycle of electrical and electronic equipment, e.g., producers, distributors, and consumers, and in particular those operators directly involved in the treatment of WEEE.

The WEEE directive identified ten categories of electrical and electronic equipment including household appliances, IT and telecommunications equipment, lighting equipment, electrical and electronic tools (with the exception of large-scale stationary industrial tools), toys, leisure and sports equipment, medical devices (with the exception of all implanted and infected products), monitoring and control instruments, and automatic dispensers. The WEEE directive was applicable to all products falling into the ten categories placed in the market after August 13, 2005. Manufacturers were required to provide refurbishment, treatment, and reuse guidelines for each WEEE-compliant product. Additionally, WEEE required manufacturers to register their products and implement a plan to recycle in each EU country.

Realizing that controlling the waste stream alone would not solve the issues due to hazardous substances; efforts

were made to restrict hazardous substances at their origins [1]. As a result, the RoHS directive, adopted in February 2003 by the EU, restricted the use of certain hazardous substances in electrical and electronic equipment in EU member states and provided a mechanism for restricting additional substances in the future [2]. The RoHS directive (2002/95/EC) became effective on July 1, 2006. The RoHS directive prohibited the use of lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr^{+6}), polybrominated biphenyls (PBB), and polybrominated diphenyl ethers (PBDE) in electrical and electronic equipment. The RoHS directive was applicable to the ten categories of products listed in the WEEE directive and to electric light bulbs and luminaires in households. The maximum allowable level of each restricted substance found in a homogeneous material, according to the RoHS directive, is shown in Table 1. As per the RoHS directive, a homogeneous material is a material that cannot be mechanically disjointed into different materials. The term “homogenous” means that the material has uniform composition throughout; for instance, plastics, ceramics, glass, metals, alloys, and so on. The term “mechanically disjointed” means that the material can be separated by mechanical actions; for instance, unscrewing, cutting, crushing, grinding, and abrasive processes [3–5].

In order to add additional product categories for compliance with RoHS and to reduce the administrative overhead, the original RoHS directive was updated. The recast RoHS directive (2011/65/EU), also called RoHS 2, was published in the *Official Journal* on 1 July 2011 [6]. Updates to the original directive included setting compliance dates for two previously excluded product categories. Products under the medical devices category, must comply by July 2014, while products under the industrial control and monitoring instruments category must comply by July 2017. In a final step, unless explicitly excluded, the directive requires all other electronic equipment to compliance by July 2019. The electrical and electronic equipment explicitly excluded includes equipment used in military and space applications, large-scale stationary industrial tools, large-scale fixed installations, implantable medical devices, transportation applications (except for electrical two-wheel vehicles), non-road mobile machinery, photovoltaic panels designed for permanent use, and equipment designed solely for the purpose of research and development. [7].

In addition to extending the number of products that must comply with the material restrictions, the directive provided deadlines for all exempted applications. Exempt application which were previously include in the original RoHS directive define when restricted materials may be used, In addition to setting deadlines, a process for extending or revoking exemptions was also provided. For all product categories that were subject to the original RoHS directive, the deadline for expiration of exempt applications was set for 5 years (2017). Under Annex III of the RoHS2 directive, application exemptions were provided for lead in high melting temperature type included:

- Exemption 7: “(a) Lead in high melting temperature type solders” (i.e. lead-based alloys containing 85 % by weight or more lead), Exemption 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 % and less than 85 % by weight”.
- Exemption 15: “Lead in solders to complete a viable electrical connection between semiconductor die and carrier within integrated circuit flip chip packages”.

Current uses of high temperature solders exempted under 7(a) include soldered electrical connections, soldered thermal interfaces to semiconductor devices and internal solder joints of passive modules [8]. Though originally exemption 7(a) was supposed to include allowance for flip chip interconnections, it was determined that 7(a) was insufficient. Exemption 15 was therefore introduced in the RoHS recast to represent all alloy constructions of flip chip interconnections at that time [9].

While transportation applications are exempt from RoHS, automobiles fall under the purview of the European Union’s end of life vehicle (ELV) directive. The ELV directive, adopted 2000, aimed to make vehicle dismantling and recycling more environmentally friendly; to set clear quantified targets for reuse, recycling and recovery of

Table 1 Maximum allowable concentration values of restricted substances in RoHS-compliant products [2]

Restricted substance	Maximum concentration value in a homogeneous material	
	% by weight	ppm
Lead (Pb)	0.1	1000
Mercury (Hg)	0.1	1000
Cadmium (Cd)	0.01	100
Hexavalent chromium (Cr^{+6})	0.1	1000
Polybrominated biphenyl (PBB)	0.1	1000
Polybrominated diphenyl ether (PBDE)	0.1	1000

vehicles and their components; and to push producers to manufacture new vehicles with a view to their recyclability. This directive also called for the reduction and elimination of hazardous substances in automobiles. In particular, with the exception of explicit exemptions, it prohibited the use of lead, mercury, cadmium, and hexavalent chromium. At the time of its initial implementation, exemptions were provided for lead in solder for electronic circuit boards and other applications. This directive has been annexed periodically since adoption. In 2011, it's the ELV directive set the exemption for using lead in solder to attach electrical and electronic components to electronic circuit boards and lead in finishes on terminations of components to expire on 1 January 2016. The exemption for lead in high melting temperature solders (i.e. lead-based alloys containing 85 % by weight or more lead) is under review in 2014 [10].

Since the high lead exemption in RoHS will expire for a large portion of the industry in 2017 unless a technical reason for extending it is provided, the electronics industry needs to find alternative or provide justification for maintaining the exemption. The objective of this paper is to examine the currently available alternative solders and technologies for high lead solders if the RoHS exemption 7(a) were to expire. The background on why high lead (>85 %) solders became a popular choice for high reliability and high power/performance applications is discussed in Sect. 2.1. The reasons for the exemption of high lead solders in RoHS directives are provided in Sect. 2.2. The alternatives to high lead solders and their advantages are discussed in Sect. 3. The limitations associated with the existing alternatives are discussed in Sect. 4. In Sect. 5, a summary of what we can expect in the next RoHS revision is provided, along with the viewpoints of certain leading manufacturers in the electronics industry.

2 High lead (>85 %) solder

High melting temperature type solders (i.e. lead-based alloys containing 85 % by weight or more lead) are typically used in the die attach process, step soldering (attaching heat sinks and lead pins), direct chip attachment, internal connections of passive devices, and flip chip assembly, as well as some circuit boards for automotive, space, oil and gas, and avionics applications. These high melting temperature solders have stringent requirements, including corrosion resistance, high ductility, high thermal shock reliability, high thermo-mechanical fatigue resistance, small volume expansion during reflow, and sufficient workability to be thin wires or sheets, among others [11, 12].

2.1 Thermal and mechanical properties of high lead (>85 %) solders

Tin and lead have melting points of 232 and 323 °C, respectively, with their alloys having lower melting temperatures with a minimum melting point of 183 °C (eutectic tin–lead solder). As the lead content increases, the liquidus points of the Sn–Pb solder alloys also increase. The increase in the liquidus point of high lead content Sn–Pb solder alloys is one of the primary reasons for its continued use in high temperature electronic applications.

The melting temperatures of high lead solders are typically greater than 250 °C. The melting temperatures of typical high lead solders are provided in Table 2. The high melting temperature of high lead solders made them an ideal interconnect candidate in high power applications. Additionally, the high melting temperatures enabled these solders to withstand secondary reflows of lower melting temperature solders.

High lead solders are considered soft alloys due to their low modulus. This enables the alloy to maintain a reliable joint structure by relaxation of thermal stresses. The coefficient of thermal expansion (CTE), modulus, and 0.2 % yield strength of typical high lead solders are provided in Table 3.

High lead solders have a well-established knowledge base of the physical metallurgy, mechanical properties, flux chemistries, manufacturing processes, and reliability of leaded solders. High lead content solders have been shown to have stable microstructures that do not change at temperatures up to 176 °C (see Fig. 1).

2.2 Why was high lead (>85 %) solder exempted from RoHS legislation?

When RoHS was implemented in 2006, no suitable alternatives existed that matched the reliability and performance of high lead solders for a variety of applications previously mentioned. As a result, the use of lead in high melting temperature type solders (containing >85 % lead)

Table 2 Melting temperatures of typical high lead (>85 %) solders

Solder composition	Melting temperature (°C)
Pb85/Sn15	183–288
Pn88/Sn10/Ag2	268–290
Pb89.5/Sn10.5	275–302
Pn90/Sn5/Ag5	292
Pb92.5/Sn5/Ag2.5	287–296
Pb95/Sn5	308–312
Pb95.5/Sn2/Ag2.5	299–304

Table 3 Mechanical properties of typical high lead (>85 %) solders

Solder composition	CTE (ppm/°C)	Modulus (GPa)	0.2 % Yield strength (MPa)
Pb85/Sn15	27.2	–	–
Pn88/Sn10/Ag2	29	–	15.5
Pb90/Sn10	29	19.0	13.9
Pn90/Sn5/Ag5	27	–	–
Pb92.5/Sn5/Ag2.5	25	13.8	–
Pb95/Sn5	28.4	–	13.3
Pb95.5/Sn2/Ag2.5	299–304	–	–

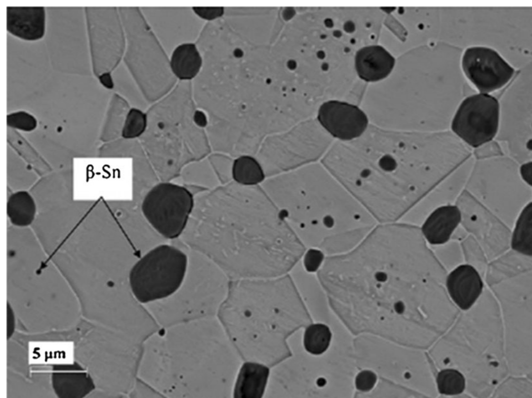

Fig. 1 Microstructure of Pb–10Sn solder in the as-cast state [13]

were exempted in RoHS. The properties that enabled high lead solders to perform well under high reliability and high power/performance applications were high melting temperatures, thermal fatigue resistance, electromigration resistance, resistance to the formation of intermetallic compounds (IMCs), and known long-term reliability (see Fig. 2). Thermal fatigue resistance of chip-to-substrate interconnects is important due to the difference in the CTE between the silicon chip and the substrate. Due to the CTE mismatch, temperature fluctuations can impose cyclic strain on the interconnects; resulting in crack initiation and propagation. The complete loss or partial loss of a solder interconnect can produce device failure. With their long history of use, the thermal cycling reliability of high lead (>85 %) tin–lead solders has been established in a wide range of applications. At the time of implementation of the original RoHS directive in 2006, tin–silver–copper (SAC), tin–copper (SnCu), and tin–silver (Sn–Ag) solders were considered as potential alternatives to high lead solders by the RoHS committee. In 2006, there was not enough field data on the long-term reliability of these lead-free solders. Additionally, several manufacturers had reported failure of SAC bumps in very short duration during accelerated testing conditions, forcing them to continue using high lead tin–lead solder for high reliability applications [4, 9]. The use of gold bumps was also limited due to the unknown long-term reliability and high cost.

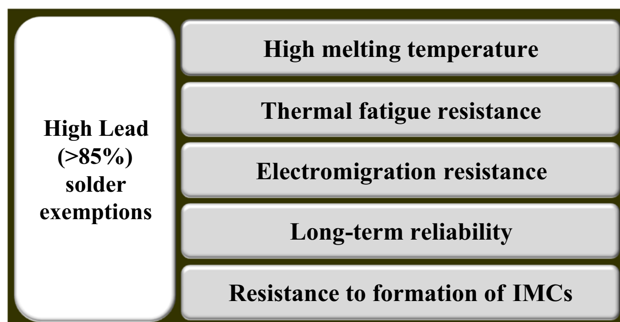

Fig. 2 Properties of high lead (>85 %) solder that favored its exemption from RoHS directives

Since the current-carrying capability is approximately a function of melting point for many solders, the high melting points of high lead (>85 %) solders correlate to the ability to carry the high electrical currents required for high power/performance applications. A primary failure mechanism for current-carrying solder joints is electromigration. Electromigration is the transport of electrons through the conductor, causing atoms to move between the thin conducting traces on the silicon chips and the solder bumps. The high lead tin–lead solder has been primarily used in high power/performance applications due to its having better electromigration resistance than other solders. At the time of the implementation of the RoHS directive in 2006, research on electromigration in lead-free solders showed contradictory results, often showing lead-free solders to be inferior to high-lead solders [9].

Additionally, high-lead tin–lead solder does not contain IMCs, thereby forming a ductile interconnection. The alternatives considered at the time of RoHS implementation (in 2006) readily form IMCs, thereby resulting in a less reliable interconnections. For instance, in flip chips, the small size of solder bumps results in the IMCs occupying a significant volume of the solder bump. Due to the brittle nature of IMCs, cracking can occur at the solder bumps under the application of a high strain load, resulting in unreliable interconnects [9].

3 High temperature lead-free alternatives

Considerable research has been ongoing in order to find replacements for the high lead content solders in high temperature applications. The promising replacements include lead-free solder alloys, conductive adhesives, and sinter technology. In this section, we discuss the currently available replacements for high lead content solder in high temperature electronic applications.

3.1 Solder alloys

Properties that need to be considered for alternative solders broadly cover the manufacturing process and reliability. Some of the factors in the manufacturing processes include melting temperature, repeatability, wettability, and surface compatibility. With regard to reliability, voiding, intermetallics, compliance, and thermal fatigue resistance should be taken into account. Table 4 presents some properties of select solders for high temperature applications.

3.1.1 Gold-based solder alloys

Gold-based solders materials have been widely accepted for use in high temperature electronics. Gold-based solders are often referred to as "hard" solders as a result of their higher melting temperatures, as compared to the "soft" solders such as SnPb. The reliability of soft solders, such as SnPb, however, is often restricted by thermal fatigue and creep rupture. The hard solder overcomes these disadvantages by remaining in the elastic deformation condition after bonding [14].

Among gold-based solders, the Au–Sn-based solders are the most widely used for high temperature electronic applications, including microwave devices, laser diodes, RF power amplifiers, and flip-chip bonding applications [15–17]. Au–Sn solders also offer many other advantages when making solder joints, such as the ability to solder without using flux, the formation of a hermetic seal, good mechanical and electrical properties, and low intermetallic growth rates when used over Ni, Pd, or Pt. However, Au–Sn is very stiff and transfers most of the thermo-mechanical stress to the die, making it viable only for small die applications. This solder in its pure state is limited to use at $T < 280$ °C [18]. However, if the eutectic mixture is exposed to gold in its pure form at a temperature at which the eutectic is in the liquid state but the pure element is in its solid state, then the liquid eutectic will dissolve some of the solid element, creating an off-eutectic combination with a higher melting point (solidus) than the eutectic mixture. This permits a joining material to be created with a high melting point for high temperature stability at a much lower processing temperature.

Au–Ge is another promising alternative for high-temperature soldering, since it does not have any intermetallic phases. The melting temperature of the Au–Ge (28 at.% Ge) eutectic composition is 360 °C, which is relatively high. The addition of small amounts of In, Sb, or Sn to the Au–Ge eutectic, however, decreases the melting point of this alloy. Apart from lowering melting temperatures, the addition of Sb to the AuGe eutectic has also been shown to improve its ductility, transforming it from a "hard" to a "soft" solder alloy (see Fig. 3) [19].

Other alloys of gold that have been developed for die attach applications include Au–Si and Au–In alloys. Chin et al. [20] reported successful GaAs device bonding using AuIn alloys at low temperatures of 200 °C with subsequent use up to 450 °C. Au–Si systems have also been studied for use with SiC mono-crystal surfaces at high temperatures of 1500 °C [21]. The addition of Si to Au increased the interaction of the alloy with the SiC surface by reducing the interfacial tension and contact angle.

3.1.2 Zinc-based alloys

Zinc (Zn) based alloy systems used as high temperature die attach materials have gained popularity due to their low cost. The high price of Au has forced the development of cheaper and more abundantly available material (such as zinc) that would be conducive for a mass manufacturing scenario. Zinc has a melting temperature of 419.5 °C. By alloying zinc with such materials as aluminum and tin, the melting temperature of zinc can be lowered to a suitable range of 300–400 °C. The Zn–Sn alloy has a simple binary eutectic phase diagram without any IMC in the whole

Table 4 Major properties of select high temperature solders

Solder composition	Melting temperature (°C)	CTE (ppm/°C)	Modulus (GPa)
Au80/Sn20	280	16	59.0
Au88/Ge12	356	13	72.7
Au97/Si3	363	12	83.0
Bi89/Ag11/Ge0.05	262–360	–	37.2
Ag80/In20	695		
Zn–(4–6)Al(–Ga, Ge, Mg, Cu)	~380	–	–
Zn–(10 ~ 30)Sn	360	30	–

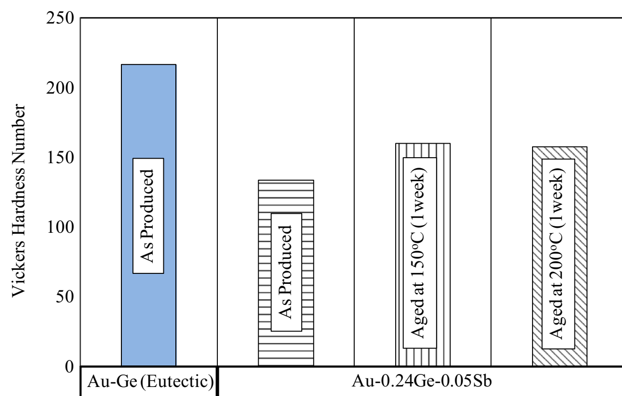

Fig. 3 Microhardness values using 100 g load illustrating the softness induced by micro-alloying Sb to the Au–Ge eutectic [19]

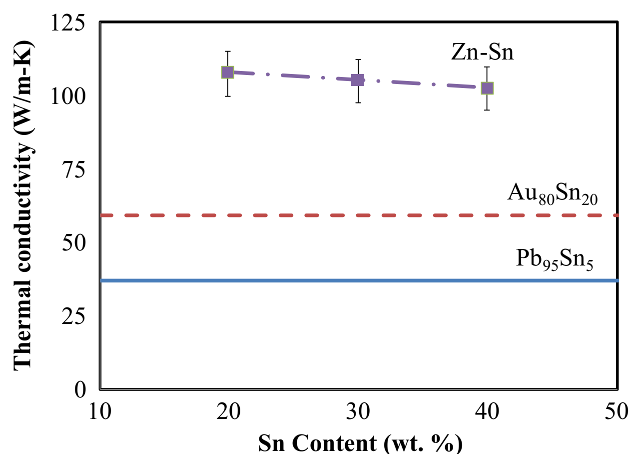

Fig. 4 Thermal conductivity of Zn–Sn alloys as a function of tin content [22]

range of composition and is believed to be one of the best choices.

The absence of IMCs in the Zn–Sn alloy system results in the Zn–Sn solder alloys being extremely ductile. The thermal conductivity of Zn–Sn alloys has also been shown to be higher than that of some of the more traditionally used Au–Sn and Pb–Sn solder systems, as shown in Fig. 4.

Kim et al. conducted a study on the interfacial reaction of Zn–Sn alloys (with varying load percentages of tin) on A1N ceramic substrates for high temperature use. Their studies also concluded that Zn–Sn alloys exhibited good die shear strengths, excellent electrical properties, and oxidation resistance in high-temperature, high-humidity conditions [22–24]. Studies have also been conducted to examine the high temperature shear strengths of the Zn–Sn solders with varying Sn percentages [25]. In addition to the Zn–Sn solder system, Zn–Al-based solder alloys doped with varying percentages of magnesium (Mg) and gallium (Ga), as well as Zn–In-based systems, have also been studied in the literature as high temperature solder replacements [26–28].

3.1.3 Bismuth-based alloys

Another solution for high temperature electronics are Bismuth-based alloy systems, with Bi–Ag being the most popular choice. The Bi–Ag system has a eutectic melting point of 262 °C, corresponding to 2.6 wt% Ag. However, to overcome its brittleness, increasing the percentage of the Ag content in the eutectic Bi–Ag system has also been suggested in the literature. With an increase in the percentage of the Ag content in the Bi–Ag system, an improvement in tensile strength and elongation properties have been reported in the literature [29]. Alloying Bi with Sn has been reported to improve the wetting properties of the solder alloy [12, 30]. Microalloying Bi–Ag systems with rare earth elements have also been suggested to improve the wettability of Bi–Ag solder alloys [30]. The addition of copper to Bi has been reported to improve the embrittlement of copper substrate caused by grain boundary erosion [12]. Other Bi-based alloy systems include $Bi_{88.95}Ag_{11}Ge_{0.05}$ [31], Bi–Cu–X alloy system, where X represented antimony (Sb), tin (Sn), or zinc (Zn) [32]; and Bi doped with CuAlMn particles [33].

3.1.4 Silver-based alloys

Due to the high costs associated with gold, alloys based on silver provide a viable solution for high temperature applications. Silver has the best electrical conductivity and the second best thermal conductivity. It also demonstrates high temperature stability and has good mechanical properties. Chuang and Lee adopted an $Ag_{80}In_{20}$ alloy in a two-step fluxless bonding process at relatively low processing temperatures (206 °C) to form nearly void-free and uniformly thick joints between a die and substrate [34]. The melting point of these joints increased to between 765 and 780 °C when annealed for 26 h at 145 °C.

3.2 Conductive adhesives

Conductive adhesives have been used for die attach applications due to low processing temperature, low cost, and simple processing procedures [35]. These conductive adhesives typically consist of a polymer binder that provides the mechanical adhesion and conductive fillers that offer electrical and thermal conduction. The adhesives typically consist of a large percentage of metal fillers (approximately 80 %) that are used to improve the thermal and electrical characteristics of these adhesives. Usually, these fillers are Ag flakes and/or particles, as Ag has high thermal and electrical conductivity.

Table 5 Major properties of select high temperature conductive adhesives

Conductive adhesive	Degradation temperature (°C)	CTE (ppm/°C)	Modulus (GPa)
QMI 3555R[a]	~400	16	11.5
FO-3, FO-13[b]	450	25	
P1011[b]	389	32/225	
P1011S[b]	379	28/57	
E2001-6[b]	425	50/106	
E3001-6[b]	425	50/106	
H20E-175[b]	450	20/88	
H20E-PFC[b]	407	48/106	

[a] Adhesives made by Loctite

[b] Adhesives made by Epoxy Technologies

One of the major advantages of conductive adhesives is that these adhesives can be used on a wide range of surfaces, including ceramics, glass, and other non-solderable surfaces. The lower material moduli of the conductive adhesives, coupled with their relatively low curing temperatures, also allow for lower stress concentrations in the die [11, 36]. Table 5 presents some properties of commercially available conductive adhesives for high temperature applications.

3.3 Sintering

Sintering is a heating process that causes particles to bond together, resulting in significant strengthening and improved thermal, electrical, and mechanical properties. Sintering enables the formation of bonds at temperatures below the melting temperature of the interconnecting materials. Since the sintered materials usually have a denser microstructure than the original powder, they have significantly improved thermal, electrical, and mechanical properties. No phase transition occurs during the sintering process, as the bonding is achieved only by solid-state diffusion. Figure 5 provides a schematic of the sintering process.

Metal-powder pastes, e.g., silver, silver–palladium, silver–indium, copper–tin, and nickel–tin pastes, are widely used in the fabrication of hybrid and co-fired microelectronic packages [37]. These metals have high tensile strength and high electrical and thermal conductivity, and they do not have the fatigue failure problem sometimes associated with solder. These metals also have high melting points that are much higher than any of the hard solders; thus, the sintered joint operates at a much lower homologous temperature, translating to low inelastic deformation or accumulation of damage during temperature or power cycling. Some properties of select sintering solutions are listed in Table 6.

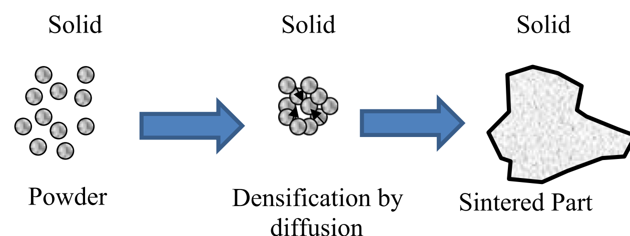

Fig. 5 Sintering process: atomic diffusion [35]

Transient liquid phase sintering (TLPS) combines the advantages of liquid phase joining with diffusion bonding. In this process, a low-melting-temperature constituent, A, melts, surrounds, and diffuses in a high-melting-temperature constituent, B. IMCs with high melting temperatures are formed by liquid–solid diffusion. IMCs of A and B form at the solid–liquid interface [37]. Their further growth is controlled by the solid state diffusion of A in B. A is consumed by IMC formation, and the concentration of B in the liquid phase increases until the concentration has reached the point where a phase transformation to a solid state occurs, leading to complete joint solidification. The process temperature (T_p) must exceed the melting temperature of A ($T_{m,A}$), but can be lower than the melting temperature of B ($T_{m,B}$). The final joint has the melting temperature of the IMCs (i.e. $T_{m,IMC} > T_{m,A}$). This enables the processing of joints at low temperature, and forms joints that can withstand high temperatures (>400 °C) (Fig. 6).

4 Limitations of lead-free alternatives for high-temperature applications

The electronics industry is still searching for a drop-in replacement for high-lead (>85 %) solders. The existing studies on alternatives to high-lead (>85 %) solders are scattered, and there is a lack comprehensive studies addressing the reliability of these lead-free alternatives under different environmental conditions. Combined with this, there is also very limited field data on the durability of these lead-free alternatives. Although there are many

Table 6 Major properties of select sintering solutions

Material	Operating temperature (°C)	Process temperature (°C)	CTE (ppm/°C)
Silver	961	250	19
Cu–Sn	>415	280	19
Sn–Ag	>600	250	
Sn–Ni	>400	300	14
Cu–In	>307	180	
Ag–In	>880	175	

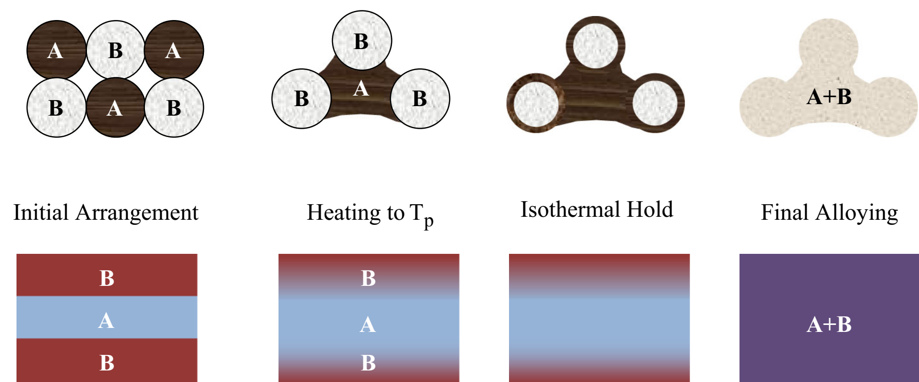

Fig. 6 Paste-based (*above*) and layer-based (*below*) TLPS approaches [37]

potential lead-free replacement alternatives, as has been discussed in Sect. 3, each alternative has some limitations prohibiting their universal acceptance. The following subsections discuss the potential drawbacks associated with the lead-free alternatives.

4.1 Solder alloys

Although Au-based systems have been proved to be a reliable alternative for high-temperature applications, the high cost of gold restricts the widespread use of gold-based, lead-free solders in the industry. Au-based systems are generally very stiff and transfer most of the thermo-mechanical stress to the die, making it viable only for small die applications.

Zinc-based solder alloys require complicated process control, as these solders must be processed significantly above their melting temperatures (20–50 °C above the melting temperature), as high processing temperatures are necessary for good joint quality. Elevated temperatures during processing can introduce high stresses on other package components, significantly reducing their remaining time to failure. The poor workability and poor stress relaxation of the Zn–Al solders under room temperature [27, 28] further limits their usage. Gallium inclusion in the Zn–Al system has been shown to create embrittlement failures [27, 28]. Severe zinc oxidation of Zn–In (indium loading of 30 % by weight) after 1000 h of testing at 85 °C and 85 % relative humidity has also been reported in literature [26].

The poor thermal and electrical conductivity possessed by Bi-rich phases hinders the development of Bi-based alloys for high-temperature soldering [19]. Bi–Ag alloys also exhibit poor wettability to metallizations used in electronic products, along with limited elongation capability, and are therefore susceptible to brittle fracture.

4.2 Conductive adhesives

The conductive adhesives provide low thermal and electrical conductivity compared to the solder alloys despite the addition of material fillers. The reduced conductivity values are due to the low contact area between the metal flakes within the adhesive [11, 36]. Furthermore, conductive adhesives also exhibit detrimental performance at elevated temperature and/or humidity, because polymers usually cannot be kept stable at these conditions. Since high electrical conductivity, high thermal conductivity, and high temperature stability are required for power semiconductor device attachment, conductive adhesives are not widely used in power device die attaches for industry practice.

4.3 Sintering

Silver sintering has considerable associated costs due to its complex processing with the synchronous application of pressure and temperature and silver as the joint materials. The porous structure of sintered silver joints also leads to significant steady state creep at elevated temperatures,

which might lead to reduced fatigue life under high thermo-mechanical loads. Also, although sintered joints can be formed at relatively low temperatures, once formed they cannot be reworked due to the high melting temperature of the sintered joint. Additionally, the application of sintered-Ag at the interconnect level is still in the nascent stage, and there is a need for additional investigations regarding the reliability and durability of these interconnects.

5 Summary

Although the RoHS legislation was adopted in 2006 to eliminate lead and other toxic materials from electronic assemblies, high-lead-content solders were exempt from the legislation. The high-lead-content-solder exemption appears to be offered primarily for die-attach applications and will be phased out in many products by 2017 unless renewal requests are submitted and accepted. Although efforts are being made to find suitable lead-free alternatives for high-temperature applications, at present there is no single drop-in replacement. This fact is evident from a joint study conducted by semiconductor suppliers to address Pb-free solder die attach technology development. The study claimed that "today's lead-free materials for semiconductor applications (die attach) are not ready to substitute high-lead solders in power applications" [38].

The choice of lead-free alternatives for high-temperature electronics continues to remain a challenge. Potential lead-free alternatives include solder alloys based on Au, Zn, Bi and Ag, conductive adhesives, and sintering (including TLPS). The applicability of these alternatives should be assessed case by case based on the application conditions and customer requirements. The key factors that influence the choice of high temperature attachment materials include the cost, the intended application, the characteristics of the intermetallics, the ease of manufacturing, and the field performance.

Although many of these alternatives have favorable characteristics with respect to their performance in soldering applications, further research is required to understand issues such as their long-term reliability as well as fatigue reliability. The fatigue reliability of alternatives needs to be assessed specific to the application conditions to which they will be subjected to. In addition to reliability data, there is insufficient knowledge on the reliability modeling of these lead-free alternatives. More research is needed in order to understand the physics of failure of these systems. It is likely that more than one technology will find its way into products.

While more research is needed, it is very likely that the general exemption provided in 7(a) and that exemption provided in the ELV directive will be modified to provide exemptions specific to applications where alternatives for high lead solder have not been proven reliable. Each manufacturer that is currently relying on these exemptions should be prepared to present the aspects of their unique requirements that make an exemption necessary.

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