A Study of Brittle to Ductile Fracture Transition Temperatures in Bulk Pb-Free Solders

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Abstract

The fracture toughness of bulk Sn, Sn-Cu, Sn-Ag and Sn-Ag-Cu lead-free solders was measured as function of the temperature by means of a pendulum impact test (Charpy test). A ductile to brittle fracture transition was found for them, i.e. a sharp change in their fracture toughness, compared to no transition for the eutectic Sn-Pb. The transition temperature of high purity Sn, Sn-0.5%Cu and Sn-0.5%Cu(Ni) alloys is around -125°C. The Ag-containing solders show a transition at higher temperatures: in the range of –78° to–45°C. The highest transition temperature of –45°C was measured for Sn-5%Ag, which is ductile only above –30°C. The increase of the Ag content shifts the transformation temperature towards higher values, which can probably be related to the higher volume fraction of $SnAg_3$ particles in the solder volume. These result are believed to be very important for the selection of the best lead-free solder composition.

Key words: Lead-free solders, brittle to ductile transition temperature, Impact (Charpy) test.

Introduction

By July 2006 the use of lead in electronics in Europe will be forbidden and lead-free solders should replace the Sn-Pb solder, commonly used in microelectronics for more than 50 years. Many Sn-based solders are under intensive study in the last years, such as Sn-Ag, Sn-Cu, Sn-Ag-Cu etc., but the work is far from finished in particular concerning their reliability. Since the "soft" Pb is taken out of the solder, the Pb-free solders deform less easy and the level of locally accumulated stresses grows, which increases also the probability of crack nucleation. This influences significantly the major failure mode of solder joints, namely the solder fatigue. It is well known that some metals loose their ductility at low temperature and show a brittle fracture mode. Therefore, the ductile-to-brittle transition temperature is an important parameter. To our knowledge, the only existing data for Pb-free alloys, see Meyer [1], shows a transition temperature of -25°C for Sn-5%Ag, compared to no transition for Sn-93.5%Pb-1.5Ag. This fact is rather disappointing, because many standard thermal cycling tests start from a temperature as low as –40 or even -60°C, which will affect the failure mode. Moreover this temperature is also in the range of some applications, as aerospace for instance. The purpose of this paper is to study the brittle to ductile fracture transition temperature for several bulk Pb-free solders.

Experimental

A pendulum impact test, well known as "Charpy test", was performed in order to determine the amount of energy dissipated during fracture, which is a measure for the fracture toughness of the material, as function of the temperature. The experimental set-up is shown in Figure 1.

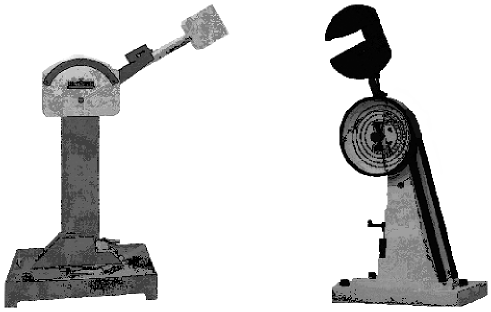


Figure 1: Experimental set-up for the pendulum impact (Charpy) test.

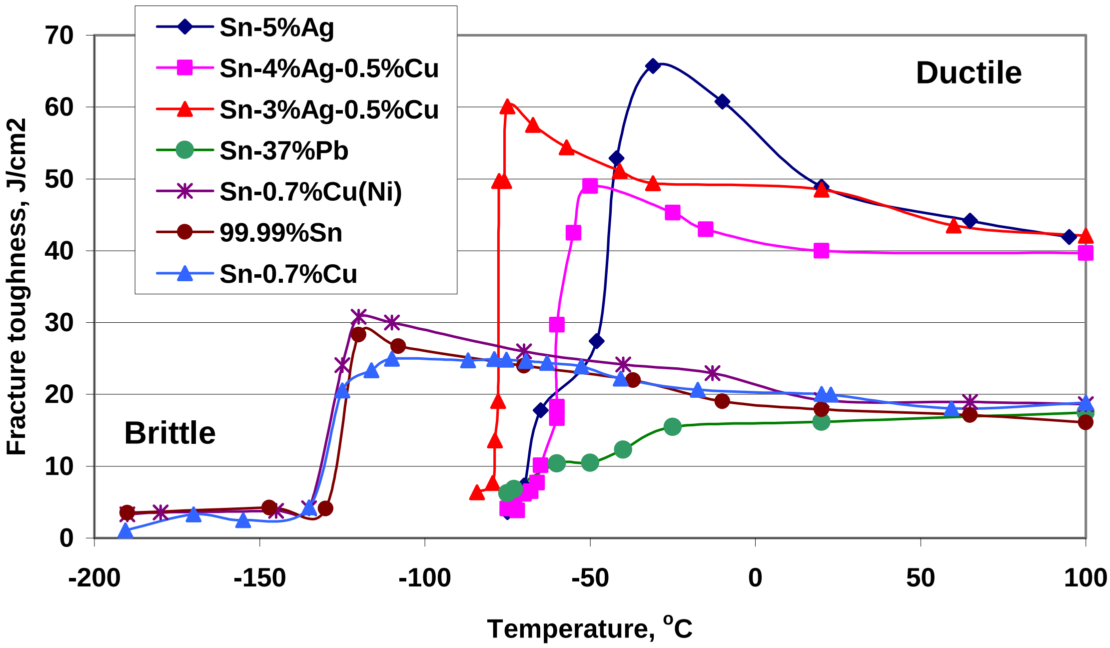


Figure 2: Fracture toughness of the studied solders as function of the test temperature.

Bulk samples of 7 alloys were tested, as follows:

- 99.99wt.%Sn
- Sn-0.7wt.%Cu,
- Sn-0.7wt.%Cu (0.1wt.%Ni)
- Sn-3wt%Ag-0.5wt%Cu,
- Sn-4wt%Ag-0.5wt%Cu
- Sn-5wt%Ag
- Sn-37wt.%Pb, as a reference.

The tests were performed according to ASTM E23 standard with V-notch samples of size 10x10x55mm. For some alloys a sample size of 5x5x55mm was used due to the limited material available. The hammer energy was 50J and the impact velocity was 3.8 m/s. A hammer of energy 358J was used for several measurements when the absorb energy was higher than 50J. The results are normalized by surface of the sample cross-section. The temperature of the sample was varied in the range: -195°C to 100°C, by means of an off-line heating/cooling system. The heating was performed in hot water and the cooling in dry ice (powder CO_2) or liquid ethanol cooled with liquid N_2. Following the ASTM E23 standard, the sample was tempered 10 minutes at the required temperature and then transferred to the machine and tested in less than 10 seconds.

Results

The results, given in Figure 2, show that the Pb-free solders change their fracture mode from brittle to ductile. For all of them the fracture toughness increased with the decrease of the temperature, reaching its maximum just before the transition temperature. The fracture toughness is a combination of strength and ductility. The elastic properties (E-modulus and yield strength) of Pb-free solders are increasing significantly with the temperature decrease, without significant change in ductility [2], which causes increase in fracture toughness as well. At the transition temperature, a drastic change of the fracture toughness happens. The change in the absorbed energy is about one order of magnitude, which is a clear indication for a change in the failure mode from ductile to brittle. The transition temperature, the “safe” application interval and the type of transition are summarized in Table I. A gradual loss of ductility at low temperatures was noticed for Sn-Pb solder, but no sharp transition was found. On the contrary, sharp transitions were noticed for the Pb-free solders. The transition temperatures are relatively low. All studied solders are ductile above -30°C, which is sufficient for most applications. The analyzed Pb-free solders can be divided in 2 groups: with a low transition temperature and a higher one. The first group consist of 99.99%Sn, Sn-0.7wt%Cu and Sn-0.7wt%Cu(Ni) solder with a transition temperature of about -130°C and a “safe” range above -120°C. This is probably related to the intrinsic properties of pure Sn and a small amount of Cu or Cu(Ni) do not cause significant change. On the contrary, the increase of the Ag content clearly shifts the transition temperature towards higher values in the range of –78° to –45°C. The highest transition temperature of –45°C was measured for Sn-5wt.%Ag, which corresponds rather well to the already published data [1].

Table I: Transition temperatures of the studied solders.

Solder	Transition temperature, °C	Safe above, °C	Transition type
99%Sn	-125	-120	Sharp
Sn-0.7%Cu	-130	-120	Sharp
Sn-0.7%Cu(Ni)	-130	-120	Sharp
Sn-37%Pb	---	--	Gradual change
Sn-3%Ag-0.5%Cu	-78	-70	Sharp
Sn-4%Ag-0.5%Cu	-60	-45	Sharp
Sn-5%Ag	-45	-30	Sharp

The fracture surfaces of three representative samples are shown in Figures 3-5, namely of pure Sn, of Sn-5%Ag and Sn-37%Pb. The Figures 3-5, a. are corresponding to the ductile type of fracture (at high temperature) and the figures 3-5, b: to the brittle one (at low temperature). The two type of fracture surfaces of the Pb-free alloys are clearly different. The ones at high temperature are dull and fibery indicating ductile fracture after high plastic deformation. The ones at low temperature, which are shiny and crystalline indicate brittle fracture. On the other hand, the fracture surfaces of the Sn-Pb solder do not differ significantly; they both are dull. The fractography results correspond very well to the pendulum impact test measurements, showing a clear brittle- to- ductile transition for the Pb-free solders and no sharp transition in the case of the Sn-Pb solder.

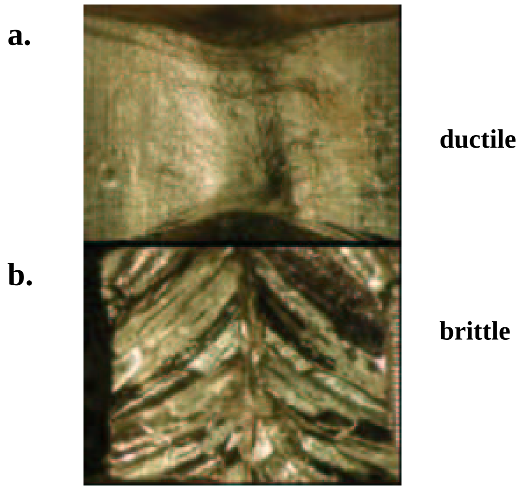


Figure 3: Fracture surface of 99.99%Sn at high (a) and low temperature (b).

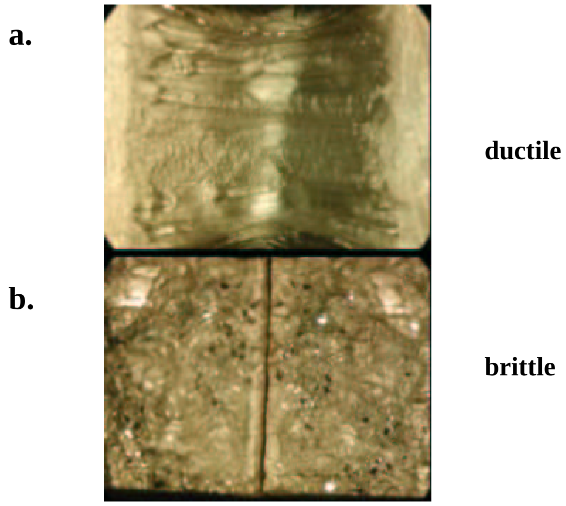


Figure 4: Fracture surface of Sn-5%Ag at high (a) and low temperature (b).

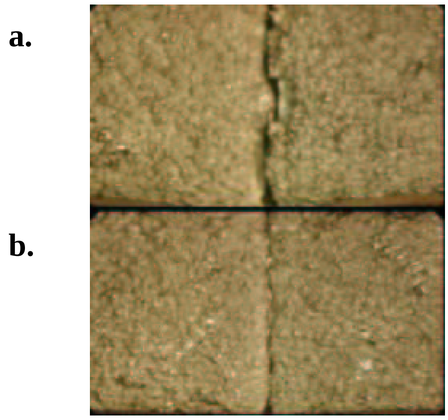


Figure 5: Fracture surface of Sn-Pb at 100°C (a) and at-75°C (b).

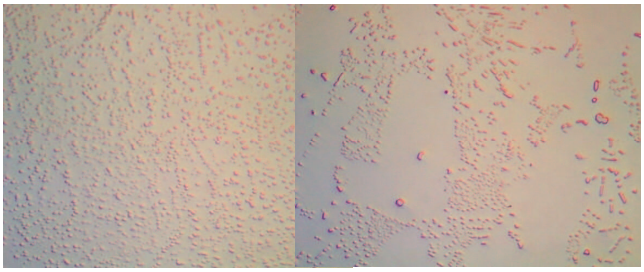
The microstructure of the studied alloys is shown in Figure 6. The comparison of Figures 6, a and b, shows no difference between the microstructures of the initial pure Sn samples and the one of the same alloy after a brittle fracture. The other samples show also the typical microstructure: Sn dendrites and eutectic areas, consisting of Sn_5Cu_6 and/or $SnAg_3$ particles, depending of the alloy composition, in Sn-matrix, see Figures 6,c-g. The typical eutectic α–β microstructure of the Sn-37%Pb is shown in Figure 6, h. No unexpected phases were found, as for instance the diamond cubic “gray tin”, which is responsible for the dangerous “tin pest” and which is able to change drastically the mechanical properties of the studied alloys.

Discussion

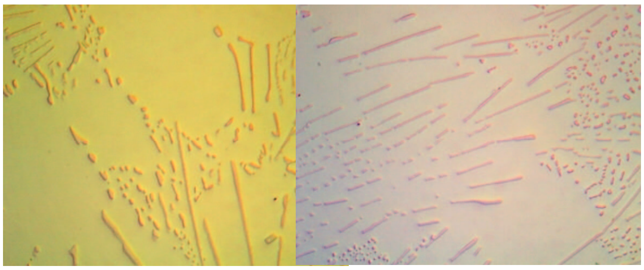
The present results clearly show that high purity Sn, Sn-0.5%Cu and Sn-0.5%Cu(Ni) alloys have a ductile to brittle transition temperature, around -125°C. Our results do not match very well to the graph presented in Metals Handbook, [2], where a transition is shown for Sn, but at a temperature of about -30°C. We have no clarification for this discrepancy.

While most of the commercially important metals do not show low temperature brittleness, some of the body-centered cubic metals do, the most important being the Fe in all its forms. It has to be noted that the structure of the white Sn, under study here, is also body centered, but tetragonal.

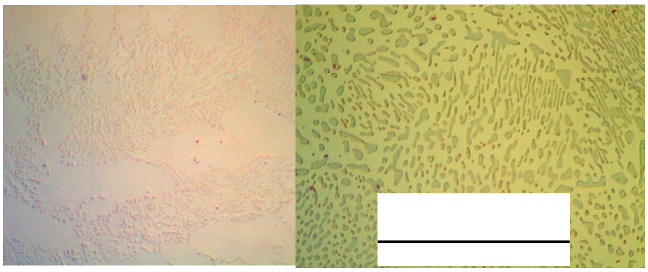
a. Sn **b. Sn, brittle fracture**



c. Sn-0.7%Cu **d. Sn-0.7%Cu(Ni)**



e. Sn-3%Ag-0.5%Cu **f. Sn-4%Ag-0.5%Cu**



g. Sn-5%Ag **h. Sn-37%Pb**

Figure 6: Microstructure of the studied solders.

Another issue of pure Sn is that it can transform from the normal body-centered tetragonal metal (bright tin) to a diamond cubic form (grey tin), which has very different properties. Since this allotropic transformation is accompanied by a change in density from 7.3 to 5.75 g/cm^3 the resulting expansion causes disintegration of the metal, well known as ‘tin pest” [2]. The equilibrium temperature of the transformation is 13°C, but its maximum velocity is at about -40°C. It is very difficult to initiate this transformation and even after initiation the rate is very small. It takes 1.5 years at -20°C in order to transform 40% of the surface of a Sn-0.5%Cu ingot into gray tin [3]. This transformation is significantly influenced by impurities; Bi and Sb suppress it successfully and Ge, Al, Mn, Mg, Co can accelerate it. Although the cooling of the samples during our test was comparatively short, about 10 minutes, we checked the microstructure of the pure Sn sample and compared it to the one, which showed a brittle fracture mode (at -195°C), see Figures 6,a and b. No difference was found on optical inspection level (with a resolution of several micrometers). Actually the 99.99%Sn shows very simple microstructure, because of the lack of second phase particles. Therefore we have no reason to suggest any link between the allotropic transformation and the ductile to brittle fracture transformation observed in this work.

The addition of Pb to Sn clearly changes the fracture behavior. The fracture toughness becomes smaller and it gradually decreases with decreasing the temperature. No clear transformation in the fracture mode was found in the studied Sn-37%Pb alloy.

The Sn-5%Ag and the Sn-Ag-Cu alloys show about two times larger fracture toughness than the pure Sn, which can be related to the second phase particles. They show a sharp ductile to brittle transition at higher temperature: in the range of –78° to–45°C. The highest transition temperature of –45°C was measured for Sn-5%Ag, which is ductile only above –30°C. This can decrease its possible range of applications, in particular the aerospace and automotive ones. It could be expected that this effect will be even higher if combined with vibrations as in the mentioned applications.

It seems also that the increase of the Ag content shifts the transformation temperature towards higher values. Ag is not a soluble element in Sn, it tends to precipitate as large and/or small $SnAg_3$ particles, see Figure 6, and their volume fraction increases with the increase of the Ag content. It is possible that just these particles, acting as obstacles for the dislocation motion serve as sources for cracks nucleation. It is generally agreed that such obstacles to slip must be very strong in order to stand the high stress at the head of the dislocation pile-up, but this was mainly related to grain boundaries and deformation twins [4].

Other factors that can influence the failure mechanism are the grain size and the stress state [4]. The influence of the grain size is a bit controversial. From one side the grain boundaries might serve as a crack nucleation site due to a dislocation pile-up, from another side they impede the motion of cracks, i.e. they can also block the brittle fracture mode. Existing stress state in the material is also important for the failure mode. Both brittle fracture crack nucleation and crack propagation are favored by high tensile stress and suppressed by shear stress [4].

If some of the Pb-free solders are used in its brittle fracture range, a significant change in the failure mode can be expected. Instead of the typical "solder fatigue" failure generated due to the thermal cycling, a catastrophic brittle fracture will be generated in the solder bulk. This failure mode will be significantly different than the brittle fracture at the interface due to cracking or delamination of intermetallic phases. This can happen at temperatures in the ductile zone close to the transition temperature, causing a mixed failure mode (for the solder only), which will be difficult to detect. Therefore, a "safe" for application temperature is considered at about 10°C away from the transformation temperature, as proposed in Table I.

The measured ductile to brittle fracture transition temperatures in bulk samples might differ from the one in real solder joints. This will be checked by means of a special "mini-Charpy test machine", which will be built for this purpose. It can be used also to study the failure mode in the transition temperature range, i.e. to observe the solder brittle fracture and the mixed failure mode.

Conclusions

A ductile to brittle fracture transition was found for bulk Sn, Sn-Cu, Sn-Ag and Sn-Ag-Cu lead-free solders, compared to no transition for the eutectic Sn-Pb. The transition temperature of Sn-0.5%Cu and Sn-0.5%Cu(Ni) alloys is around -125°C, which seems to be an inherited property from the high purity Sn. The Ag-containing solders show a transition at higher temperatures: in the range of –78° to–45°C. The increase of the Ag content shifts the transformation temperature towards higher values, which can probably be related to the higher volume fraction of $SnAg_3$ particles in the solder volume. They can serve as obstacles for the dislocation motion, causing dislocation pile-ups and crack nucleation. The highest transition temperature of –45°C was measured for Sn-5%Ag, which is ductile only above –30°C. This will influence considerably its range of applications. It is believed also that the failure mode in real solder joints can change considerably around and below the brittle fracture temperature, i.e. the ductile "solder fatigue" failure mode to change to a catastrophic brittle fracture into the solder.

Acknowledgements

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