Microstructure and elevated-temperature shear strength of Zn–4Al–3Mg–xSn high-temperature lead-free solders

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ABSTRACT

The microstructure and shear strength of the high-temperature Zn–4Al–3Mg, Zn–4Al–3Mg–7Sn, and Zn–4Al–3Mg–13Sn solder alloys were investigated in the temperature range of 25–200 °C. The results revealed that the shear yield stress (SYS) and ultimate shear strength (USS) of all three alloys decrease with increasing test temperature. The ternary base alloy showed higher strength levels up to 145 °C above which all alloys behave similarly. The superiority of the ternary alloy is ascribed to the higher volume fraction of the fine α–γ eutectic and eutectoid structures and the hard MgZn2 particles. Introduction of Sn into the base alloy, however, resulted in substantial decrease in the strength, due to the presence of the soft Sn that reduces the volume fraction of the eutectic structure and the hard second phase particles. Despite the weakening effects of Sn, the strength of quaternary alloys is still higher than those of the Zn–Sn and Pb–Sn high-temperature solders.

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1. Introduction

Tin-based lead-free solder alloys are considered as suitable substitutes for the toxic tin–lead solders, which have long been used for the joining of electronic devices as well as mechanical components. These tin-based solders are principally considered for intermediate-temperature applications, due to their relatively low melting range [1]. There are, however, some severe thermal environments, in which solders are supposed to withstand higher temperatures and thus new materials with higher melting points are required. For such conditions, various lead-free solders such as Au–Sn, Bi–Ag, Zn–Sn, and Zn–Al based alloys have been proposed to replace the commonly used Pb–Sn alloys containing 85–97 wt.% Pb. The application of Au–Sn and Bi–Ag solders is restricted due to their high cost. On the other hand, the zinc-base Zn–Sn and Zn–Cu–Al alloys have shown strength [2,3] and creep resistances [4,5] which are remarkably higher than those of the conventional Pb–55Sn solder.

Due to the high service temperatures, the high-temperature solder materials should possess reasonable strength that can be attained at elevated temperatures. The ultra-high temperature Zn–Al alloys with relatively high liquidus temperatures of less than 400 °C and solidus temperatures of higher than 370 °C are considered as suitable candidates for the high temperature applications. This family of materials, however, suffers from a relatively low creep resistance at even moderately elevated temperatures [6]. It has been suggested that the addition of different alloying elements to the binary Zn–Al alloy system can modify both soldering and mechanical properties. Addition of Cu enhances hardness and tensile strength [7,8], while Mg and Sn are mainly added for lowering the melting temperature of the base alloy [9]. The detrimental effects of Sn additions on the tensile strength and ductility of Mg–4Al–3Mg solder alloy has been documented. It has been reported that although Sn significantly weakens the alloy, the strength of Zn–4Al–3Mg–6.8Sn alloy at 200 °C is still comparable to that of the Pb–55Sn solder alloy [10].

The strength of the high-temperature lead-free solders are mostly investigated by the conventional tensile test [8,10–12] and in some cases by the shear testing of the joints made on different substrates [13]. Recently, however, the high-temperature shear strength of the bulk Zn–Sn [2] and Zn–Cu–Al [3], and Sn–Sb–Ag [14] solders has been studied by the localized shear punch testing (SPT) technique. There are many reports in the literature indicating that the SPT is an efficient method being capable of producing strength data which are well correlated with those found by the conventional tensile tests [15,16]. This method can be particularly advantageous when the material is available only as small test pieces or there are difficulties with the machining of samples made of very soft materials such as solder alloys. The evaluation of high-temperature strength of the Zn–Al–Mg alloy and its variants by SPT has not been reported before and thus will be attempted in this study.
2. Experimental procedures

2.1. Materials and processing

This investigation involved three alloys with the nominal chemical compositions of Zn–4Al–3Mg–xSn (x = 0, 7, and 13 wt%). They were prepared from high-purity (99.97%) zinc, tin, and Zn–20Al and Zn–40Mg master alloys, melted in a graphite crucible at 580 °C in an electrical furnace under inert argon atmosphere. Alloys were remelted twice at 480 °C, held at this temperature for 30 min, and then stirred mechanically for 2 min using a stainless steel rod to provide a homogeneous composition. The molten material was then poured into a 16-mm-diameter steel die. The cast bars were cut into 4- and 1-mm thick slices using an electro-discharge wire-cutting machine. The thicker slices were used for microstructural analysis and hardness measurement, and the thinner ones were used for the assessment of shear strength. The specimens were polished with 0.3-mm diamond paste, followed by polishing on an abrasive-free microcloth. Etching was implemented using 20 g CrO₃, 1.5 g Na₂SO₄, and 100 mL H₂O at room temperature. Microstructural examination was carried out for the phase and composition analysis using optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2.2. Mechanical property measurements

The strength of the materials was assessed by the shear punch testing. The 1-mm thick slices of the materials were ground to a thickness of about 0.7 mm, from which disks of 15 mm in diameter were punched for the SPT. A shear punch fixture with a 3.175 mm diameter flat cylindrical punch and 3.225 mm diameter receiving-hole was used for this experiment. Shear punch tests were performed in the temperature range of 25–200 °C using a screw driven SANTAM universal testing system equipped with a three-zone split furnace. After locating the specimen in the fixture, the assembly of the specimen and SPT fixture were accommodated by the split furnace. Then, the assembly was heated to the test temperature and held for 20 min to establish thermal equilibrium in the testing arrangement before the specimen was deformed by the punch. Tests were run with a load cell of 20 kN capacity and at a constant cross-head speed of 0.25 mm min⁻¹. After application of the load, the applied load P was measured automatically as a function of punch displacement; the data were acquired by a computer so as to...
to determine the shear stress of the tested materials using the relationship:

\[
\tau = \frac{P}{\pi dt}
\]

where \( P \) is the punch load, \( t \) is the specimen thickness, and \( d \) is the average of the punch and die diameters. Three different samples were tested for each condition and it was observed that the variation in the measured ultimate shear strength values was less than about 3%.

### 3. Results and discussion

To examine the shear deformation behavior of the materials tested by SPT, it was first necessary to calculate the shear stress-normalized displacement data. Although all SPT specimens had similar thicknesses in the range of 0.70–0.75 mm, the punch displacement was normalized to the specimen initial thickness in order to eliminate gage effects. Using Eq. (1), the punching load was converted to shear stress and plotted against the normalized displacement, as shown in Fig. 1a–c for all materials tested at different temperatures in the range of 25–200 °C. As can be seen, similar to tensile stress–strain curves, each of the individual curves exhibits a linear part, after which a deviation from linearity is observed. Further loading of the samples results in the load-instability, at which a maximum is observed in the stress-displacement curves. The deviation point is taken as the shear yield stress (SYS) and the stress corresponding to the maximum point is referred to as the ultimate shear strength (USS), as suggested for other solder alloys [2,14]. Regarding the reproducibility of the SPT data, at least three separate samples were tested and the obtained flow curves were very similar in such a way that the variations in SYS and USS values were less than 5%.

In all of the tested materials, increasing the test temperature from 25 °C to 200 °C results in a significant softening, as indicated by the lower levels of the SPT curves at higher temperatures (Fig. 1). To have an overall view on the softening behavior of the tested alloys, the SYS and USS data are plotted against test temperature in Fig. 2a and b, respectively. The results show that the highest SYS and USS at all test temperatures belong to the base Zn–4Al–3Mg alloy. Introduction of Sn into the base alloy causes a drastic drop in the strength, especially for the Mg–4Al–3Mg–13Sn alloy. Similar results have been reported for the tensile deformation of the same alloys tested in the temperature range 20–200 °C, where the base alloy exhibited superior strength and ductility with respect to the Sn-containing materials [10]. In the present work, the base alloy exhibited much higher strength up to 150 °C, after which it behaves very similar to the softer Sn-bearing alloys. This is in contrast to the tensile deformation results, in which the base alloy attains its higher strength even at 200 °C [10]. The observed difference can be attributed to the difference in the as-cast microstructure caused by various cooling rates imposed by the casting process.

It is worth comparing the strength of the present high-temperature solders with other solders designed for the same purpose. Unfortunately, the literature lacks any data for the shear strength of the bulk of high-Pb alloys to be compared with the shear strengths obtained for the Zn–4Al–3Mg–xSn solders in this work. However, the reported 14 MPa and 10 MPa tensile yield stresses of Pb–5Sn obtained respectively at 25 °C and 100 °C [17] are even much lower than the corresponding shear yield stresses of

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**Fig. 3.** SEM micrographs of: (a) Zn–4Al–3Mg, (b) Zn–4Al–3Mg–7Sn, and (c) Zn–4Al–3Mg–13Sn alloys.

**Fig. 4.** XRD patterns of the tested alloys.
Fig. 5. (a) SEM micrograph of the Zn–4Al–3Mg alloy showing dispersion of second phases in the Mg matrix, and the elemental maps of: (b) Zn, (c) Mg, and (d) Al.

Fig. 6. (a) SEM micrograph of the Zn–4Al–3Mg–7Sn alloy showing dispersion of second phases in the Mg matrix, and the elemental maps of: (b) Zn, (c) Mg, (d) Al, and (e) Sn.
100 MPa and 70 MPa, found for the weakest Zn–4Al–3Mg–13Sn alloy in the present work. The same is true for the reported 70 and 55 MPa shear strengths of the high-temperature lead-free Zn–20Sn obtained, respectively, at 25 and 100 °C [2]. These are considerably lower than the corresponding USS values of 200 and 130 MPa, found for Zn–4Al–3Mg, and 115 and 80 MPa for the Zn–4Al–3Mg–13Sn alloy in the present work. Nevertheless, our quoted shear strength values are lower than the corresponding USS values of about 215 and 175 MPa, found for the ultra-high-temperature Zn–3Cu–4Al alloy [3]. The observed strength inferiority becomes even more pronounced for the Sn-containing alloys, which provide shear strength levels of 115–130 and 80–100 MPa at the same test temperatures. Therefore, except for the Zn–Cu–Al alloys, it can be deduced that the present Zn–Al–Mg alloys possess comparable or even superior strength in comparison with the most of the other high-temperature solder materials.

The observed differences in the strength values and their variation with test temperature in the tested alloys are stemmed from their respective microstructures. According to the ternary Zn–Al–Mg phase diagram [18], the microstructure of the Zn–4Al–3Mg alloy should contain α-Al, Mg2Zn11, and η-Zn at room temperature. SEM micrograph of the Zn–4Al–3Mg base alloy, shown in Fig. 3a, consists of the bright primary η-Zn phase, lamellar α–η eutectic, the dark grey α–η eutectoid colonies, and some sparse dark Mg2Zn11 particles. It is evident that isolated patches of primary η-Zn are surrounded by the α–η eutectic structure. Similar results were reported in the Zn–Al–Mg–Ga [19], and Zn–Al–Mg alloys [20]. In the microstructure of the Sn-containing alloys depicted in Fig. 3b and c, however, the volume fraction of the eutectic structure decreases, where it appears as a continuous network in the grain boundary areas. It is further noted that in addition to the η-phase, eutectic, and eutectoid structures, some white Sn-rich particles are formed in the grain boundary areas. The volume fraction of this white phase increases with increasing the Sn content of the alloys.

The XRD patterns of the Sn-containing alloys together with that of the base alloy, exhibited in Fig. 4, indicate that in the base Zn–4Al–3Mg alloy, η-Zn, α-Al, MgZn2, and Mg2Zn11 are the present constituents. The same phases have been also identified in similar alloys reported in the literature [10]. It has been reported that MgZn2 is a metastable phase which acts as primary phase during the rapid solidification of the alloy. This phase will evolve into the Mg2Zn11 phase later through a peritectic reaction (MgZn2 + L → Mg2Zn11) [20]. With the addition of Sn, however, some new peaks corresponding to the pure Sn and Mg2Sn intermetallic compounds appear in the patterns. It can be inferred that as the Sn content increases, the intensity of the Sn peaks increases, but the
formation of the MgZn$_2$ and Mg$_5$Zn$_11$ seems to be suppressed. This can be attributed to the fact that Sn consumes the Mg content of the alloys, leaving less Mg for the formation of Mg–Zn compounds. As a different way of identifying constituent phases, it was decided to investigate the general distribution of Mg, Al, and Sn elements in the Zn matrix, by EDS mapping. From such maps illustrated in Fig. 5 the presence of $\eta$-Zn, $\alpha$-Al, and Mg–Zn particles is verified in the ternary base alloy. In the maps of the Sn-containing quaternary alloys shown in Figs. 6 and 7, the white phase corresponds to a Sn-rich phase. Although some weak peaks of Mg$_5$Sn were identified in the XRD patterns of these alloys, it is expected that these white areas are most probably pure Sn, which have been also detected by the stronger Sn peaks in the XRD patterns.

Concerning the microstructure-strength relationships, it is accepted that the overall deformation resistance of the material depends on the volume fractions and strength of the alloy constituents [21]. Microhardness testing is a useful technique to evaluate the mechanical properties of different phases of the microstructure. According to Li et al. [20], the microhardness values of the eutectoid structure, MgZn$_2$, and Mg$_5$Zn$_11$ are about 120, 200, and 250 Vickers, respectively. These are in sharp contrast to the very low hardness of Sn that has been reported to be only about 10 [2]. Therefore, the lower shear strength of the Sn-containing alloys with respect to the base alloy can be attributed to the lower volume fraction of the eutectic structure, lack of the hard MgZn$_2$ and Mg$_5$Zn$_11$ particles, and to the presence of the soft Sn that weakens the alloy, even at low temperatures. It is generally accepted that eutectics are often the hardest component in a phase diagram because of dispersion or phase-boundary strengthening [4]. However, the phase boundaries, which provide hardening at low temperatures, can also give rise to sliding at high temperatures, and cause softening. This can explain the strength drop of the base alloy at temperatures above 130 °C. The combination of these effects is believed to be the main reason for the inferior shear strength of the alloys containing Sn.

4. Conclusions

The high-temperature shear strength of Zn–4Al–3Mg and its variants containing 7 and 13 wt% Sn were tested by the shear punch testing method in the temperature range of 25–200 °C. The microstructure of the base alloy contained a high volume fraction of the fine $\alpha$–$\eta$ eutectic and eutectoid structures and the hard MgZn$_2$ and Mg$_5$Zn$_11$ intermetallic particles. According to the obtained shear strength data, introduction of Sn into the base alloy resulted in lower shear strengths at all test temperatures. This can be attributed to the dominant role of the soft Sn-rich particles that are formed in the grain boundary areas, decreasing the volume fraction of the eutectic structure and suppressing the formation of the hard MgZn$_2$ and Mg$_5$Zn$_11$ particles. The high shear strength of the present Zn–4Al–3Mg–xSn solders makes them suitable candidates to be used instead of high-Pb alloys in high temperature applications.

References