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Effect of Magnesium Addition on Microstructure and Mechanical Properties of Lead-Free Zinc-Silver Solder Alloys

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Abstract

Replacing the lead (Pb)-containing solders with the Pb-free solders in electronic products has been a global trend due to environmental and human health concerns for Pb toxicity. Many kinds of Pb free solder alloys have been proposed to date. Zinc (Zn) based Pb-free solder can be a promising alternative of Sn-Pb solder because of its competitive price and mechanical properties. In this research, Zn based solder alloys were developed by addition of silver (Ag) and magnesium (Mg) through conventional casting method. The changes in tensile strength, microhardness microstructure associated with the addition of relatively high melting point noble metal namely Ag were investigated in this work. Furthermore, the effects Mg addition on these mechanical properties and microstructure of the promising candidate Zn-Ag based alloys were extensively reported. Chemical composition of the alloys was confirmed by XRF analysis. A significant change in microstructure, microhardness and strength were found with the change of Ag content. A more interesting point is that the addition of Mg with Zn-Ag alloy increases the microhardness and strength to a large extent as well as ternary eutectic phases in the microstructures.

***Keywords:** High temperature solder; Pb-free solder; Zn-based solder; Mechanical properties; Microhardness*

Introduction

In the electronic industry, high temperature lead containing solder alloys provide conductive path required to achieve connection from one circuit element to another also provide mechanical and thermal connections between the components. In recent years, environmental regulations worldwide have targeted the elimination of Pb usage in electronic assemblies, due to the inherent toxicity of Pb. This has made the search for suitable “Pb-free” solders.

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For high-temperature solder, typical properties requirements are melting temperature in the range of 260°C to 400°C, good thermal conductivity, small volume expansion at reflow treatment that does not break a package, sufficient workability to be thin wires or sheets, good mechanical properties, especially fatigue resistance etc. [1,2]. In addition, the melting range between solidus and liquidus temperature should be narrow for good solder alloys. A few candidate alloys have been proposed as alternative solders to high temperature high lead solders. However, none of them can fulfill all the requirements to replace the current high lead solders. Zn-based solders have a lot of prospects due to its competitive price and mechanical properties [3-9]. The Zn-Al alloys are considered as ultrahigh temperature solders, for which the solidus temperature should be higher than 643 K, and the liquidus temperature should be less than 673 K [10]. Zn-Sn and Zn-Al alloys are more ductile compared to others as there found no intermetallic compounds in these alloys, have proper melting range, and good thermal/electrical conductivities [11]. However, Zn based die attach/solder is difficult to handle practically due to its highly active characteristics.

New Zn based alloys are still under development. It is scientifically meaningful and industrially urgent to carry research on the mechanical and metallurgical analysis of Zn based die attach/solder system to give solutions to the lead-free reliability problems. Research on Ag added Zn based solders are very scarce. Ag is one of the non-toxic elements having antibacterial properties which lead to the removal of toxicity of Pb on the environment. The present attempt has therefore been taken to investigate the effect of addition of Ag on the physical, thermal, and mechanical properties of Zn-based solder alloy. Also, Small amount of Mg has been added to investigate the effects on the properties of Zn-Ag binary alloy.

Experimental Procedure

The lead-free solder alloys were developed from commercially available pure Zn and Ag. Alloys that were used for the respective study were divided into six Zn based alloys. Primarily three binary alloys of different Ag compositions, i.e., 1.0 mass %, 2.0 mass %, and 5.0 mass % were prepared by conventional casting method. From the binary phase diagram of Zn-Ag alloys it is found that Zn forms a eutectic composition with 5 mass % Ag. This composition was prepared to see what major change occurs at this eutectic point compared to hypereutectic composition. After that three ternary alloys were prepared by adding different Mg compositions, i.e., 1.5 mass %, 2.0 mass %, and 2.5 mass % into Zn-2% Ag alloy. At first Zn was placed in to a graphite crucible and melted in a gas fired pit furnace. Then required amount of preheated Ag and Mg were mixed slowly in to the molten Zn by manual stirring at about 640°C. Finally, the alloy was homogenized for few minutes at a temperature of 550°C before pouring.

Chemical analysis of the as-cast alloys was done by XRF (SHIMADZU XRF-1800). Cubic samples of 10 mm × 10 mm × 10 mm were prepared for microstructural analysis. The as-cast alloys were fine polished on a polishing wheel where γ-alumina powder was used as polishing medium. Non-ferrous metallographic fine polishing standard technique was carried out with 0.5 µm γ-Al_2O_3 particles in order to obtain the microstructure. Ethanol-5% HCl solution was used as etching reagent. Each specimen was observed under optical microscope both in un-etched and etched conditions. The samples were observed using field emission scanning electron microscope (FESEM: JEOL JSM 7600F). Backscattered electrons were used to see microstructures and EDS (Energy Dispersive X-ray Spectroscopy) analysis.

The polished samples were placed in the Hardness tester machine to make the indentations for Vickers Hardness test (FV-800, FUTURE-TECH, Japan). Ten kg load was applied to the sample for 10 seconds at room temperature. The solder ingots were then mechanically machined into tensile specimens with a gauge length marked 25.00 mm for each sample as per sub-standard size of the ASTM E8/E8M-11 and the width and thickness of the samples were 6.00 mm and 5.00 mm respectively. Tensile tests were carried out with a universal testing machine (Instron 3369 Universal Testing Machine) at a strain rate of 3.00 mm/min at 25°C to obtain data on the stress-strain curves containing information of elongation at fracture and UTS. The fracture surfaces were observed under SEM to see fracture behavior.

The electrical conductivity of each alloy was measured in %IACS (International Annealed Copper Standard) by using conductivity meter for non-ferrous alloys (TECHNOFOUR CONDUCTIVITY METER TYPE 979). From %IACS data the resistivity and conductivity can be determined using the rules: Resistivity=172.41/%IACS and conductivity=1/Resistivity, respectively. For the test, each sample was polished and cleaned. The conductivity meter was calibrated with standard data. At least six data were taken for each alloy at different spots on the surface.

Results and Discussion

XRF analysis

The main chemical compositions of alloys were confirmed by XRF analysis. The measured compositions are given in TABLE 1.

TABLE 1. **XRF Analysis**

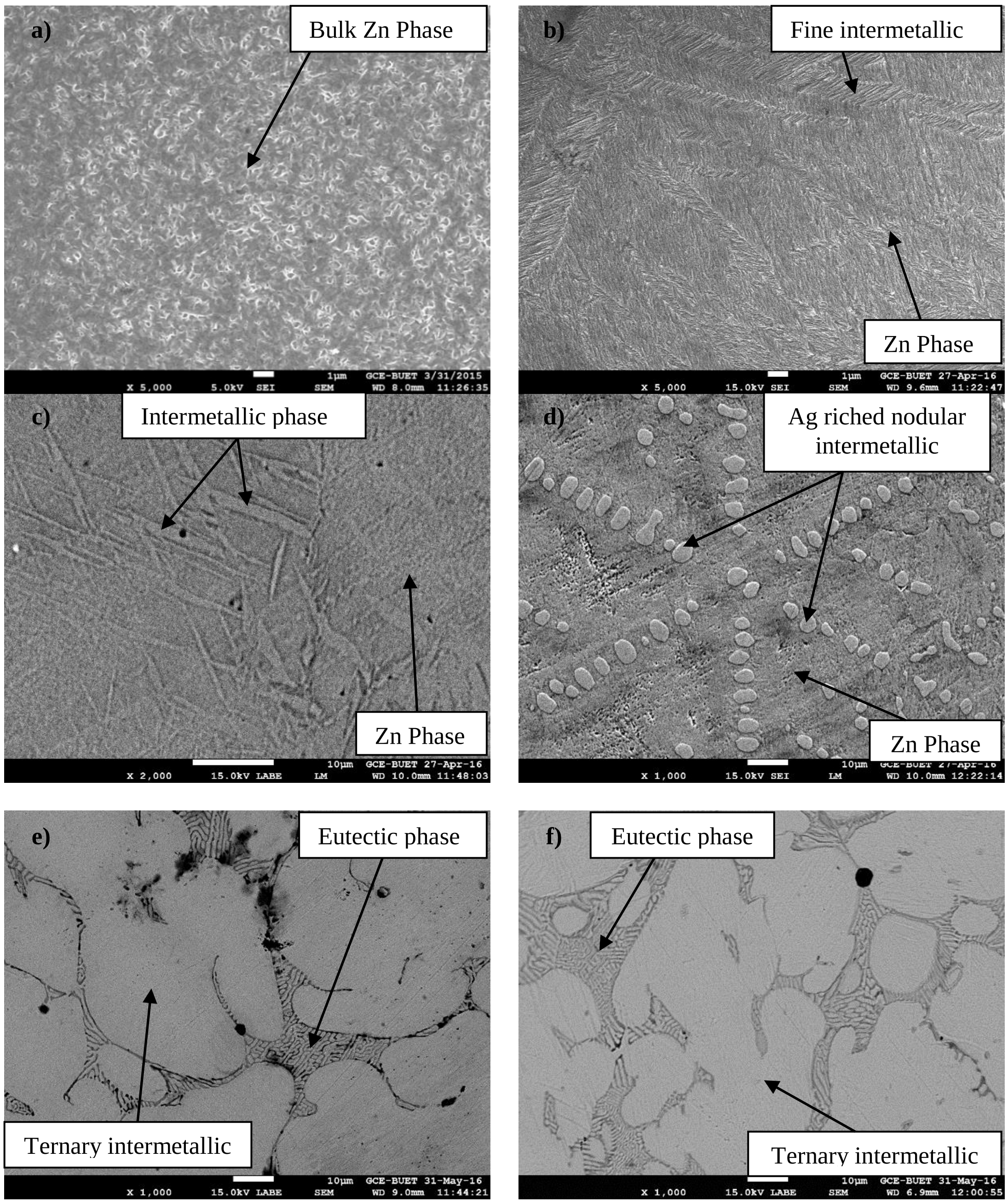
Sample	Zn (wt%)	Ag (wt%)	Mg (wt%)	Si (wt%)	Fe (wt%)	Al (wt%)
Commercially Pure Zn	99.02	-	-	0.75	0.12	0.11
Commercially Pure Ag	-	99.76	-	0.12	0.03	0.08
Commercially Pure Mg	-	-	99.78	0.13	-	0.08
Zn-1Ag	97.53	0.99	-	1.30	0.08	0.10
Zn-2Ag	96.12	2.18	-	1.56	0.07	0.06
Zn-5Ag	93.42	5.67	-	0.71	0.04	0.15
Zn-2Ag-1.5Mg	95.19	2.24	1.48	0.88	0.06	0.14
Zn-2Ag-2Mg	95.07	2.28	1.99	0.43	0.04	0.17
Zn-2Ag-2.5Mg	94.48	2.43	2.33	0.57	0.06	0.12

From XRF analysis it was found that some loss of Mg wt% in alloy compositions. It might be due to its high reactivity. A significant amount of silicon is present which may be obtained from alloying elements and during casting as impurities. Most of the samples show the gain of Ag compared to the amount added. It may be due to localized segregation and sampling position from a large ingot.

Microstructures

The microstructures of different Zn-xAg and Zn-2Ag-xMg alloys of FESEM are as shown in FIG. 1. FIG. 1(a) shows the microstructure of commercially pure zinc in as cast condition. A significant amount of intermetallic is formed with the addition of small amount of Ag i. e, (Zn-1Ag, Zn-2Ag) as shown in FIG. 1(b) and FIG. 1(c). This needle like intermetallic phase increases its amount and size with the increase of Ag content. A sharp change in structure is observed at peritectic composition (Zn-5Ag) shown in FIG.1(d). Silver riched phase of round shaped regular pattern was found which contains almost 24 per cent Ag as per EDS result.

When Mg is added in Zn-2Ag alloys a clear and fine alternate layer of eutectic phase is found around the Zn riched white phase grains as shown in FIG.1(e), FIG. 1(f) and FIG. 1(g). The eutectic phase is mainly Zn-Mg riched and almost all Mg is present in this eutectic region. The white large grains contain only Zn-Ag with a very minor amount of Mg.



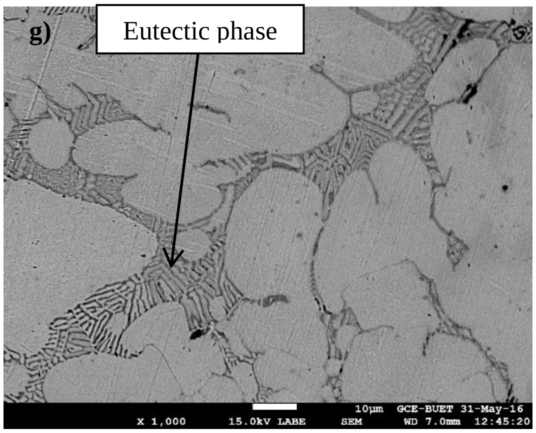


FIG.1. **SEM images of a) Pure Zn, b) Zn-1Ag, c) Zn-2Ag, d) Zn-5Ag, e) Zn-2Ag-1.5Mg, f) Zn-2Ag-2.0Mg and g) Zn-2Ag-2.5Mg.**

Pure Zn showed moreover homogenous grains. Most of the phases in Zn-Ag alloys are homogeneously distributed. The needle like phases for Zn-2Ag composition is replaced by large grains with eutectic phases due to the addition of Mg. With the increase of Mg in Zn-2Ag alloy, no major change in microstructure is found rather than the increase of small amount of eutectic phase.

Hardness

It was observed that with increasing Ag content in Zn-Ag alloys the hardness was increased. The addition of Ag and thus the increased amount of intermetallic phase could be the possible reason for this increase in hardness. For the addition of Mg in Zn-2Ag alloy the hardness value was increased to a great extent compared to Zn-2Ag even Zn-5Ag. This increment of hardness continues further with the increase of Mg addition. The hardness values of the Zn-xAg and Zn-2Ag-xMg alloys are shown in bar chart in FIG. 2.

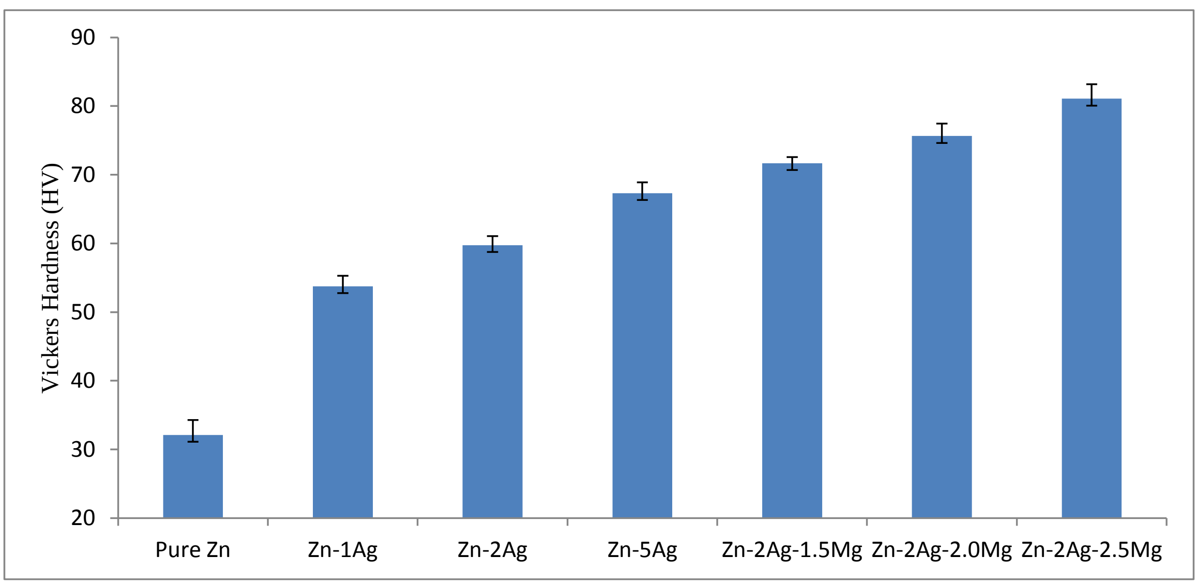


FIG. 2. **Change of Hardness in Zn-xAg and Zn-2Ag-xMg alloys.**

Tensile test

The effect of increasing Mg content of Zn based solder on tensile properties is given in TABLE 2. It shows that increasing Ag content increases both Ultimate Tensile Strength (UTS) and elongation. It does not seem to be normal as increase in UTS leads to the decrease in elongation.

TABLE 2. **Variation of tensile properties of the developed alloys.**

Sample	Average UTS (MPa)	Average %Elongation (G.L. 25 mm)
Zn-1Ag	61.08 ± 2.80	2.41 ± 0.88
Zn-2Ag	77.82 ± 9.38	4.00 ± 0.59
Zn-5Ag	103.87 ± 9.50	3.67 ± 0.68
Zn-2Ag-1.5Mg	117.32 ± 6.14	2.25 ± 0.35
Zn-2Ag-2.0 Mg	124.09 ± 9.53	2.18 ± 0.42
Zn-2Ag-2.5Mg	146.73 ± 15.56	2.18 ± 0.50

Mg addition plays a significant role for the increase in UTS and also the percentage of elongation gets lowered. It may be due to the addition brittle Mg which helps to form large brittle intermetallic phase. The range of UTS for a particular alloy was somewhat scattered. This may be occurred due to casting defects, internal fracture in the tensile sample or misalignment of the sample during loading.

Conductivity

The obtained result of electrical conductivity in terms of %IACS of Zn-xAg and Zn-2Ag-Xmg is graphically represented in FIG. 3. The conductivity was found to be decreased in increasing alloying element of Ag. Zn-2Ag-1.5Mg gives a %IACS value close to Zn-2Ag but somewhat smaller which get decreased further with increasing Mg content.

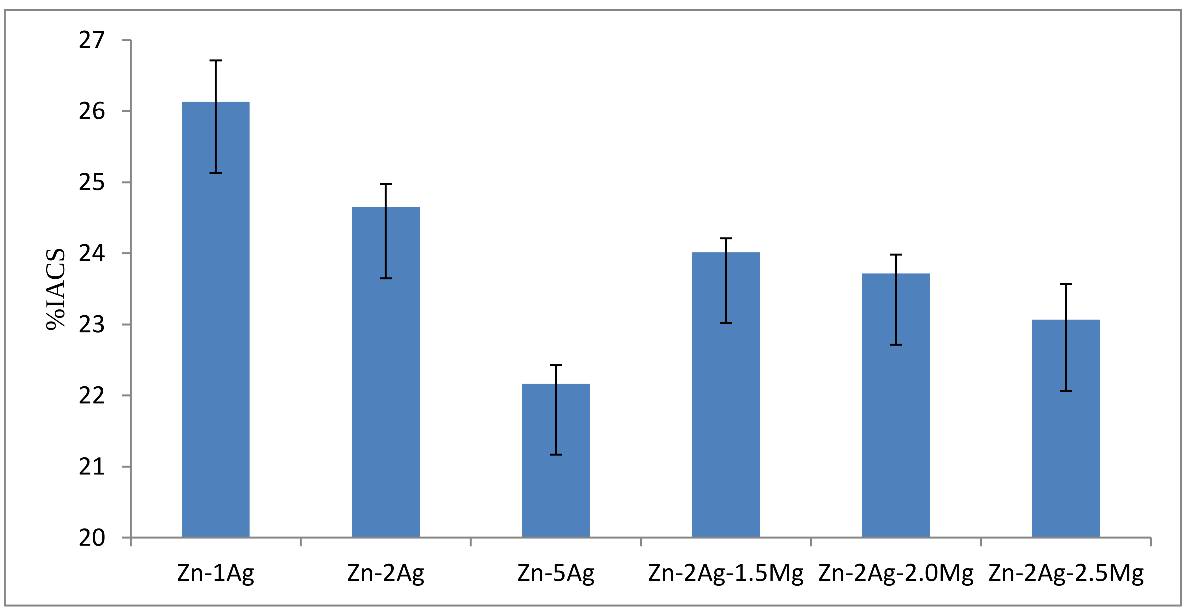


FIG. 3. **Effects of alloying elements on electrical conductivity of the alloys in terms of %IASC.**

In general, pure metal is a very good conductor of electricity which falls with increasing the amount of impurities. In case of copper, it is found that some specially formed copper shows conductivity of around 103% IACS, which is more than the standard copper. This occurs due to the enhanced purity of copper by sophisticated techniques. For the same reason, in this study the conductivity of developed alloys follows the basic theory.

Conclusion

High-temperature solders are widely used in various types of applications. Since each application has its own specific requirement, a single high-temperature solder cannot cover all the applications. Zn-xAg, Zn-xAg-yMg can be some promising candidates. Zn-xAg interconnect material was developed and effect on Ag content on the mechanical and thermal properties of prepared alloys has been investigated. It has been found that the addition of Ag had a major effect on microstructure as well as properties. The microstructure of solder alloys dramatically changed due to addition of Mg in Zn-Ag binary alloy. With the increase in Mg content increases the volume fraction of eutectic phase. The hardness of alloys increased with the formation of hard intermetallic. Moreover, UTS value increased and ductility decreases due to same reason. Most of the alloys show a regular trend in the change of microstructure, mechanical properties, homogeneity etc. the main drawbacks for developing Zn-Ag alloys may be the high cost of Silver, high brittleness with lower conductivity.

From the DTA curves, the solidus temperature and liquidus temperature of the Zn-xMg alloys were obtained, from which solidification range was found. Increasing Mg content decreased solidification range. In TMA analysis, it was revealed that with increasing Mg content in Zn-xMg alloys, CTE value decrease. Presence of eutectic and intermetallic phases is the main reason for lower CTE. Therefore, it can be concluded that Zn-xMg alloys have the potential thermal and mechanical properties for high temperature solder.

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