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Effects of Annealing Temperature and Ag_3Sn Intermetallic Compound Particles on the Electrical Resistivity of Sn/Ag Eutectic Material

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Abstract

This work aims to study a new lead-free solder alloy as a substitute for lead-tin alloys in order to solve the problem of protecting human health. The effect of thermal aging on the electrical resistivity of a eutectic Sn-3.5wt%Ag lead-free solder alloy has been investigated. The samples have been aged at the temperature range of 100°C - 160°C. During aging, the precipitation behavior has been followed by the electrical resistivity measurements. The resistivity change of Sn-3.5wt%Ag eutectic alloy rises to a maximum value and then decreases to a constant value at each aging temperature. The maximum value increases as aging temperature increased. The little reduction in resistivity after the maximum value is due to the coalescence and growth of precipitates and then decreasing in the scattering effect to the electrons. Microstructural characterizations using scanning electron microscope (SEM) were conducted to follow in detail the precipitation behavior. The SEM results cleared that the precipitation process increases with increasing thermal aging time and the coarsening of fine precipitates occurs in the samples aged at a long time.

Keywords; Electrical resistivity; thermal aging; scattering centers; conduction electrons; precipitation process

Introduction

In the electronic devices, the solders serve as electrical interconnections. In order to the solder does not affect the functionality of the electronic circuits, the variations of the electrical resistivity during thermal work should be determined. Sn-Pb soldering for metal interconnections has a long history, dating back 2000 years. These materials are the dominant solders used widely in manufacture because of their unique combination of material properties, such as easy handling, low melting temperatures, good workability, ductility and excellent wetting on Cu substrate and its alloys. It is well known that conventional Pb- containing solders are harmful to both people’s health and environment, so the exploration of lead-free solders as substitute of lead-tin alloys is paid more attention [13].

The lead-free solders used in electronic industry need to meet a series of standards: good wettability, low melting point, low cost, adequate strength and good electrical/thermal conductivity. At present, a number of investigations have been carried out on such promising lead-free solder alloys as Sn-Ag, Sn-Cu, Sn-Zn, Sn-Bi and Sn-In. Among these alloys, Sn-Ag solder alloys have been considered strong candidates to replace the Sn-Pb solder alloys because of two main reasons: (i) their properties are reasonably compatible with those of the Sn-Pb solder alloys (ii) they have better mechanical properties (ductility, creep resistance and thermal resistance) than the Sn-Pb solder alloys in addition to their low cost. The eutectic composition for the Sn-Ag binary system occurs at Sn-3.5Ag and the eutectic temperature is 221°C. By comparison with Pb-Sn alloys, the Sn-3.5wt%Ag alloy has limited solid solubility of Ag in Sn, making it more resistant to coarsening. As a result, Sn-3.5wt%Ag forms more stable and uniform microstructure [6]. The microstructure of the eutectic Sn-3.5wt%Ag consists of β-Sn matrix phase and Ag_3Sn intermetallic compound (IMC). The Ag_3Sn IMCs dispersed in the β-Sn phase make the Sn-Ag alloys have better mechanical properties by a dispersion-strengthening effect [7].

It has been known that the electrical resistivity of alloys increases linearly with the amount of elements in solid solution. Only a part of the elements is usually found in solution and the rest is found in precipitates. During aging, some of an alloying element precipitates from the supersaturated solution into precipitates since the degree of precipitation depends on aging temperature and aging time [9].

The reaction of precipitation is initiated by cooling or quenching the alloys from a temperature at which a single-phase solid solution to a temperature where the phase is supersaturated. Slow cooling and low temperature annealing tend to promote precipitation while rapid cooling tends to suppress precipitation [2].

The electrical resistivity measurement is used to investigate the decomposition and the nucleation of the precipitates that occur in the solid solution state. It has been reported that the formation of fine precipitates causes an increase in the electrical resistivity while large precipitates cause a decrease in the electrical resistivity. Depending on the testing variables such as aging temperature and aging time, redissolving or coarsening of the precipitates may be occurred. The annealing process is an important processing variable that significantly affects the microstructure and therefore determines its conductivity behavior [2, 1].

El-Daly et al. [1] measured the electrical resistivity of Pb-65.5Sn-3.4Zn eutectic and Pb-65.0Sn-1.0Zn ternary alloys at various aging temperatures for various aging times. They found that the Pb-Sn-Zn ternary alloys show reduction in the electrical resistivity compared with the Pb-Sn binary eutectic composition. This is a result of the nature of the internal stresses induced by the Zn particles and the multiplicity of types of inter-phase boundary that causing enhancement in the driving force for the coarsening process.

The eutectic solder alloy Sn-9Zn has been studied by Kamal et al [5]. They found that the additions of the elements Bi, Cu and In to the eutectic alloy improve its properties. The results showed that the composition Sn-9Zn-1Bi-2Cu-2In has a lower melting point, a lower resistivity and a higher value of Young's modulus compared with the eutectic binary alloy.

Yassin [12] investigated the effect of annealing temperature on the electrical resistivity of Sn-12Sb solder alloy. He found that the volume fraction of SnSb IMCs reduces during annealing. This is attributed to the dispersion of SnSb IMCs in Sn-matrix. The fine particles of SnSb-phase were treated as isolated scattering centres for conduction electrons and accordingly, the scattering of conduction electrons increases with the increasing of the tiny SnSb-phase.

Although there have been some investigations on the relationship between the thermal aging and mechanical properties in Sn-Ag solder alloys, research on the effect of thermal aging on the electrical resistivity with microstructural variations is still limited. The effects of aging temperature and aging time on the microstructural precipitation and electrical resistivity of Sn-3.5wt%Ag eutectic lead-free solder alloy is still absent. The purpose of this research is to characterize the effects of isothermal aging and aging time on the electrical resistivity of Sn-3.5wt%Ag eutectic solder alloy through experimental measurements of resistivity with various aging temperature and various aging time.

Experimental procedure

96.5wt%Sn-3.5wt%Ag lead-free eutectic composition was prepared from pure (99.99%) Sn and Ag. These two elements have been melted in furnace at 250°C. The ingot rod has been rolled to wire samples of diameter 0.8 mm and length of 100 mm. Different materials may be found as impurity atoms in solid solution in the Sn matrix. As the impurity content is less than 0.01%, these impurities have a negligible effect on the results in comparison with that of Ag content. The samples were homogenized at 150°C for 6 hours in furnace with temperature-controlled ±1K and were rapidly quenched in water at 0.0°C to obtain specimens of different preliminary microstructures. The samples were mounted in the furnace between two rods of copper of 10 mm in diameter and 30 mm in length. DC electric current of 50 mA has been used for all measurements. The temperature was monitored by steel temperature sensor mounted close to the middle of the specimens. The samples were aged at aging temperatures ranging from 100 to 160°C. At each temperature, the sample was aged at different time ranging from 1 to 60 min. The electrical resistivity ρ (t) at aging temperature was calculated for each aging time (t). In all measurements, the specimens were mounted within a few seconds and immediately measured beginning from room temperature (27°C).

In order to explain the effects of isothermal aging on the electrical resistivity, scanning electron microscope (SEM) has been conducted to investigate the microstructure of specimens after quenching and after aging.

Results and Discussion

The electrical resistivity measurements have been widely used as a characterization method of the decomposition states of precipitation in structure [2, 8]. The change in electrical resistivity is direct proportional to the number of scattering centers that has formed during aging. According to the Sn-Ag phase diagram, the Ag element added into Sn is easy to combine with Sn and form a stable Ag_3Sn intermetallic compound (IMC) phase. The electrical resistivity strongly depends on the degree and size of precipitation and increases with increasing IMC precipitates in the structure [4].

Formation of clusters, phonons, and structure imperfections cause an initial increase in resistivity. This is attributed to the increasing number of scattering centers of electrons by these factors as is shown in the Pb-Sn eutectic solder alloy [1, 4]. In order to follow the various precipitation processes during aging, the samples were aged at temperatures of 100, 120, 140, and 160°C and the change of resistivity has been calculated at different aging times. Figure1 Shows the variations of electrical resistivity change [$\Delta\rho/\rho_0 = (\rho_t - \rho_0)/\rho_0$] with time for Sn-3.5wt%Ag eutectic alloy, where ρ_0 is the resistivity immediately after quenching and ρt is the resistivity at aging time(t). This Figure shows that the resistivity change rises with a decreasing rate to a maximum value (dependent on aging temperature) and then decreases to a steady state value. This behavior occurs at each aging temperature. The peak value increases as the aging temperature increases and the increasing in resistivity with temperature can be observed at each aging time. The peak values may be due to the lack of coarse particles clusters in the eutectic structure which allows more fine precipitation. From curves shown in Fig. 1 it can be seen that the peak value reaches in an earlier time as the aging temperature is raised. This behavior may be attributed to the enhancement of formation of precipitates by increasing aging temperature. As the aging time increases there is a little reduction in resistivity after the peak value and is attributed to the coalescence of Ag_3Sn precipitates and growth of their size which leads to the decreasing scattering effect. In the SnAg2.5 solder alloys, Ruo-Wei Yang ey al demonstrated that the large particles of Ag_3Sn intermetallic compounds have been observed after 10 min [13]. All these observations indicate that the number and size of precipitated particles are principally controlled by the aging temperature.

In order to determine the relationship between resistivity change and aging temperature, the resistivity change as a function of temperature has been plotted at different aging times, as shown in Figure 2. As the temperature increased, the effect of the quantized elastic waves (phonons) increases and the number of imperfections increases and therefore lead to increase number of scattering centres and resistivity as shown in Figure 2.

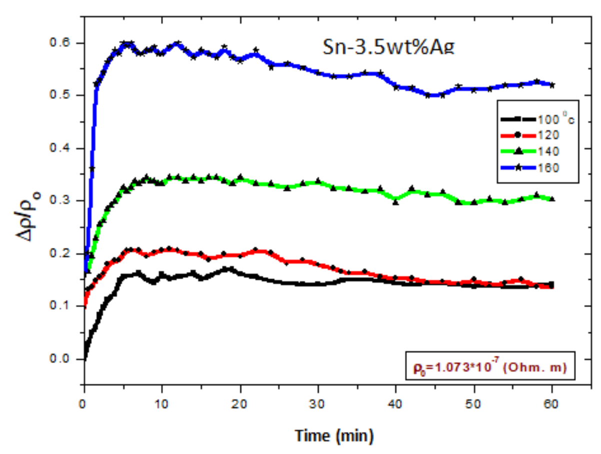

Figure 1: Aging time dependent of the resistivity change at different aging temperature.

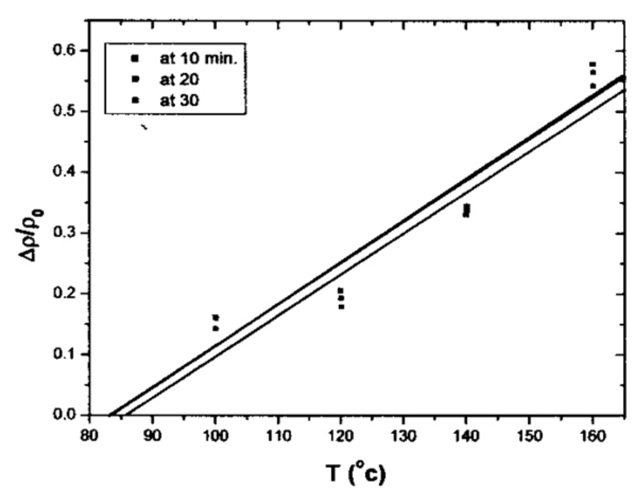

Figure 2: Aging temperature dependent of the resistivity change at different aging time.

This figure provides direct information of the precipitation process. It can be seen that the lowest temperature for initiating precipitation process occurs at the same temperature, 85°C. This means that the mechanism of the precipitate reaction remain the same at any aging time. In order to determine the average energy required to formation precipitates, the activation energy was calculated from the slope of the linear relation between $Ln(\Delta\rho/\rho_o)$ and (1000/T) K^{-1} [12] for different ageing times, as shown in Figure 3. The calculated values of the activation energies ranged from 0.34eV to 0.37eV.

The scattering of conduction electrons takes place in metallic alloys due to: (1) quantized elastic waves (phonons) (2) lattice imperfections (3) impurity atoms and (4) precipitates (phase's precipitates).

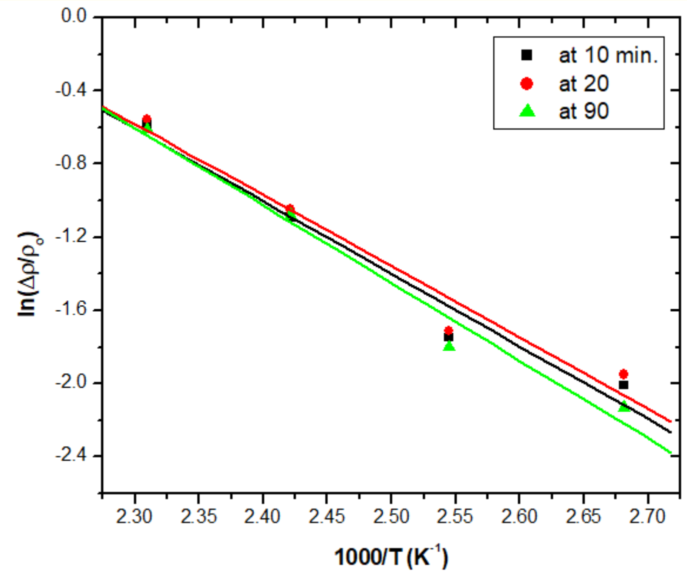

Figure 3: Variation of ln $(\Delta\rho/\rho_o)$ and $(1000/T)K^{-1}$ at different aging time.

The total electrical resistivity in the alloys can be represented according to the Matthiessen's rule by the following formula [9, 3].

$$\rho = \rho_m + \rho_p \qquad (1)$$

Where, ρ_m: contribution from the matrix phase and ρ_p: contribution from the precipitates. The precipitation process may be due to the combined effects of the matrix Sn and the Sn-Ag intermetallic phases. Moreover, number of vacancies may be nucleate because of the quenching process. These vacancies are stabilized by silver atoms [3]. Because the diffusion rate of silver atoms increases with temperature, the number of these stabilized vacancies increases and act as scattering centers for the conduction electrons.

In the region of low ageing time, the formation of Ag_3Sn fine precipitates occurs during aging and the number of these precipitates increases with aging time. This behavior has been observed in the work of Taillard et al [10]. The precipitation of NiAl IMCs has been occurred during isothermal aging for aging times less than 1.0 min. and the mean precipitate size increases proportionally to the aging time. The effect of phonons, resulting due to thermal vibration, increases as aging temperature increased. The examined alloy may contain lattice imperfections that cause irregularities in the electrostatic fields within alloy. These irregularities act as scattering centres and reduce the mobility and the mean free path of conduction electrons [4]. All these factors increase resistivity in the equation (1) and resistivity change observed in Figure1. However, these effects will be having fewer contributions to the scattering centers, as the aging time increased as is observed in the work of El-Daly et al [1]. As the aging time increased, the contribution of the second term of the equation (1) will be decreases due to the coalescence of precipitated particles. The coalescence of particles increases and grow with increasing ageing time as is shown in Figure 4 which is in agreement with works of Yassin [12] and Xiao et al [11]. This explains the little reduction in resistivity observed (Figure1) at long ageing time.

The scanning electron microscopy (SEM) of samples has been performed after aging for 60 minutes at 140°C and at an initial state (after quenching) as shown in Figures 4 and 5, respectively. The black areas represent β-phase (Sn) and the light areas represent eutectic phase of dispersed IMC within Sn-phase and a difference between two figures can be viewed. As in the work of Xiao et al [11], the distribution of Ag_3Sn precipitates is more dispersed in β-phase after aging than that after quenching. During low aging time the number of these dispersed particles increases and leads to the increase effect of scattering centers for conduction electrons [4].

El-Daly et al [1] and Xiao et al [11] found that coalescence of dispersed precipitates occurs in the grain and grain boundary of Sn as aging time increased. These precipitates coalescence and grow forming large precipitates [1, 12, 11] and then microstructure becomes less dense after aging than that directly after quenching as observed from Figures 4 and 5. Thus, formation of coarsening precipitates causes reduction in the effect of scattering centres as a result of the increase mean free path of conduction electrons.

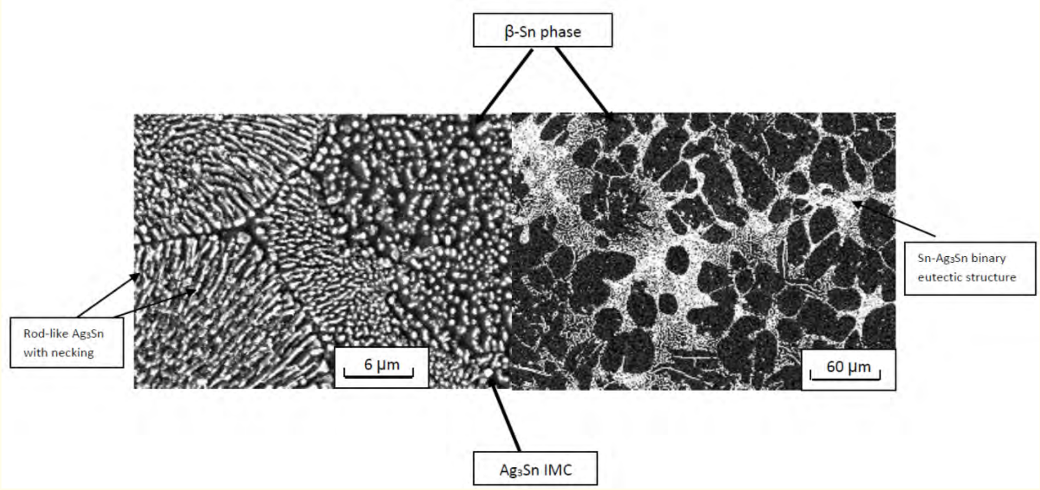

Figure 4: SEM structure of Sn-3.5wt%Ag alloy after ageing at 140°C for 60 min. (Dispersion of Ag_3Sn IMCs and β-phases in the eutectic can be viewed).

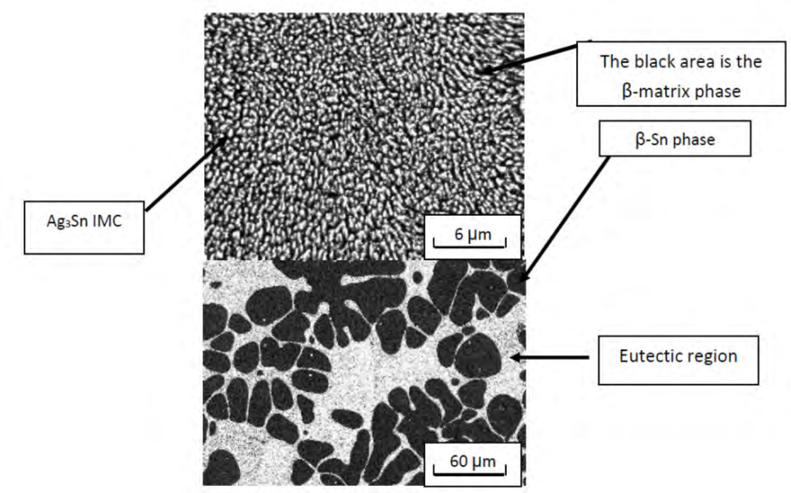

Figure 5: SEM structure of Sn-3.5wt%Ag alloy after quenching from 150°C.

Conclusions

1. During thermal aging up to about 0.4 of the melting point of the alloy, the electrical resistivity of Sn-3.5wt%Ag eutectic alloy varies with time in a characteristic manner summarized by:
    - Increasing at low time and
    - Steady-state following little reduction
2. The Sn-3.5wt%Ag eutectic alloy shows maximum and minimum values of resistivity and finally constant value during aging depending on the aging temperature. This behavior made this alloy to be useful in the future industry.

References

1. El-Daly AA, Abdel-Daiem AM and Yousf M. "Effect of Isothermal Ageing on the Electrical Resistivity and Microstructure of Pb-Sn-Zn Ternary Alloys". Mat. Chem. And Phys 9589 (2002): 1-8.
2. Gaber A, Afify N and Mostafa MS. "Investigation of the precipitation process in Al-Si alloys". J. Phys. D: Appl. Phys 23 (1990): 1119-1123.
3. Gaber A., et al. "Studies on Al-Mg solid solutions using electrical resistivity and microhardness measurements". Eur. Phys. J. AP 7 (1999): 103-109.
4. Kamal M and El-Blediwi Abu Bakr. "Structure, mechanical properties and electrical resistivity of rapidly solidified Pb-Sn-Cd and Pb-Bi-Sn-Cd alloys". Journal of Materials Science 9 (1998): 425-428.
5. Kamal M and Gouda ES. "Enhancement of solder properties of Sn-9Zn lead-free alloy". Cryst. Res. Technol 41.12 (2006): 1210-1213.
6. C. ML Wu., et al. "Properties of lead-free solder alloys with rare earth element additions". Mater. Sci. Eng., R 44. (2004): 1-44.
7. WR Osório., et al. "Mechanical properties of Sn-Ag lead-free solder alloys based on the dendritic array and Ag3Sn morphology". J. Alloys Compd 562.15 (2013): 194-204.
8. Naziri H and Pearce R. J. Inst. Met. 97 (1996): 326.
9. Ólafsson P and Sandstrom, R. "Calculations of electrical resistivity for Al-Cu and Al-Mg-Si alloys". Materials Science and Technology 17.6 (2001): 655-662.
10. Taillard R, Pineau A and Thomas BJ. "The precipitation of the intermetallic compound NiAl in Fe-19wt.%Cr alloys". Materials Science and Engineering 54 (1982): 209-219.
11. Xiao Q, Bailey HJ and Armstrong WD. "Aging Effects on Microstructure and Tensile Property of Sn3.9Ag0.6Cu Solder Alloy". Journal of Electronic Packaging Transactions of the ASME 126 (2004): 208-212.
12. Yassin AM. "Effect of Annealing Temperature on the Electrical Resistivity of Sn-12wt% Sb Lead Free Solder Alloy". Egypt. J. Solids 30.2 (2007).
13. Ruo-Wei Yang., et al. "Precipitation of large Ag3Sn intermetallic compounds in SnAg2.5 microbumps after multiple reflows in 3D-IC packaging". Materials Chemistry and Physics 134.1 (2012): 340-344.
14. ZHAO Xiao-yan., et al. "Effect of cerium on microstructure and mechanical properties of Sn-Ag-Cu system lead-free solder alloys". Transaction of Nonferrous Metals Society of China 17.4 (2007): 805-810.