

Influence of Thermal Aging on Microstructure and Property of Gold Alloy Joint Soldered by Sn-based Solder

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Abstract. As an undisputed material of choice to guarantee reliability in a broad range of high performance and safety-critical applications in the electrical contacts and connectors, AuAgCu alloy was soldered with Ag-plated Cu wire using Sn-based solder. To clarify the embrittlement and strength reduction of the gold soldered joint, the microstructure and its influence on the macro- and micro-mechanical properties of the soldered joint under various thermal aging conditions were studied. The result indicated that, taking the mechanical property consideration alone, Sn-based solder could be used to join AuAgCu alloy. Different from the embrittlement and strength reduction of the soldered joint of pure gold, although the brittle fracture features appeared in mechanical test of the soldered joints, the shear strength of soldered joint after thermal aging at 125 °C almost did not decrease in comparison with that before thermal aging. Nevertheless, too high temperature and long time still had bad influence on mechanical properties. Otherwise, thermal aging had a large effect on the IMCs layer, as aging temperature elevated and aging time increased, IMCs layer became thicker, more complex components and multiply-sublayers structure with different micro-hardness. The study provides a fundamental understanding for gold alloy soldering.

1 Introduction

Gold and its alloy have many unique advantages, such as high ductility, resistance to corrosion, oxidation and most other chemical reactions, and good conductivity of heat and electricity etc [1]. Its good conductivity and general resistance to oxidation and corrosion in other environments make it undisputed material of choice to guarantee reliability in a broad range of high-performance and safety-critical applications in corrosion resistant electrical connectors in all types of computerized devices, especially in electronic sliding contacts in highly humid or corrosive atmospheres, and in use for contacts with a very high failure cost (certain computers, communications equipment, spacecraft, and jet aircraft engines) [2, 3, 4]. Additions of silver and copper into gold will improve the electrical conductivity of pure gold based on maintaining its excellent chemical stability, enhance its hardness, strength and abrasive resistance, and decrease the temperature-resistance coefficient and thermoelectric potential to copper [5]. These versatility and unique properties make the AuAgCu alloy an indispensable and widespread industrial use in the electrical contacts and connectors, such as low resistance wire resistor, electronic brush, and electronic sliding ring etc [6, 7]. In most cases, gold and its alloy must be joined with other metal components,

Sn-based solder often provide the necessary electrical, mechanical, and thermal continuity [8].

A serious trouble emerges when Sn-based solder is used to join gold alloy that gold will rapidly dissolve into the molten Sn-based solder forming coarse, anisotropic, and brittle Au-Sn intermetallic compounds (IMCs) [9-18]. AuSn, AuSn₂ and AuSn₄ are the main IMCs between Au and Sn from Au-Sn binary phase diagram [19]. Both the brittle AuSn₄ phase and the weak interface between the Au-Sn IMCs and the solder matrix will lead to significant strength reduction and embrittlement of the gold soldered joint [20-26]. The thickness of Au layer, the soldering temperature and time, temperature and time of solid-state thermal cycling and aging have the important effect on the embrittlement [27-33]. As the aging temperature rises or the time increases, the dissolution rate of Au into Sn-based solder will increase largely. For a thin Au film, however, Au forms dispersed Au-Sn IMCs in the solder as a minor phase which does not cause embrittlement [34-37].

The extensive investigations have been mostly carried out on the solderability of Au and Au-Sn IMCs formation on gold-plated components [37-44]. But little information is available in the literature on the microstructure evolution and property of gold alloy soldered with Sn-based solder when gold alloy acts as a component with a certain thickness other than as the coating or layer on other metal components, especially

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for the effect of thermal cycling and temperature aging. Hence, with the increasing application of gold and its alloy in electrical contacts, more experimental evidence is required. The purpose of our present work is to clarify the microstructure evolution and its influence on mechanical property of AuAgCu alloy for Sn-based soldering under various thermal temperature and time by means of scanning electron microscope (SEM), mechanical tests, and micro-hardness tests. This study provides a fundamental understanding for the increasing applications of gold alloy.

2 Experimental Procedures

The parent metals used were a gold alloy with a composition of 60Au-34Ag-6Cu (wt %) and silver plated copper wire. The gold alloy sheets with 1 mm in thickness, 20 mm in length, 5 mm in width and the copper wire with 20 mm in length and 1 mm in diameter were prepared for soldering. The lap length was 1.5 mm. The commercial eutectic SnPb solder (Sn 63 wt% and Pb 37 wt%) was used to join two parent metals in conjunction with the flux of ZnCl₂+NH₃Cl solution. The solder was placed on the gold surface, heated up to 230 °C until it was melted completely. The copper wire was inserted into the molten solder. Then they were cooled down to the room temperature. The Au/Sn-based solder/Cu soldered joint was produced. Thermal aging test, microstructure observation and mechanical test will be conducted for all the soldered joints.

Thermal aging of the soldered joints were performed at 125 °C, 150 °C, and 175 °C for 4, 10, 30, 60 and 90 days. The mechanical property of the soldered joints were evaluated by shear testing at room temperature using a tensile testing machine (Instron) with a machine displacement rate of 0.5 mm/min. The average shear strength of five joints was used to contrast the mechanical properties under different aging conditions. Micro-hardness was tested using a Vickers micro-hardness tester (Mitutoyo HM-113) with 0.246 N indentation force, and 10 s holding time. The microstructure of soldered joint was observed using a scanning electron microscope (SEM). The Hitachi S-530 SEM coupled with an energy dispersive X-ray spectroscopy (EDS) was used to determine the chemical composition of compound phases and the thickness of IMCs layer presented in the soldered joint. EDS analysis and mapping were performed with an acceleration voltage of 20 kV.

3 Results and Discussion

3.1 Microstructure and the thickness of IMCs layer

The rapid dissolution of Au into the molten Sn-based solder will induce a large amount of Au-Sn IMCs formation along the interface between Sn-based solder and gold alloy [9-18]. Meanwhile, Au will continue to dissolve into solid state Sn-based soldered zone forming

the new Au-Sn IMCs during thermal aging [27-33]. Figure 1 gives the microstructures of the soldered interface close to AuAgCu alloy after soldering and different aging conditions.

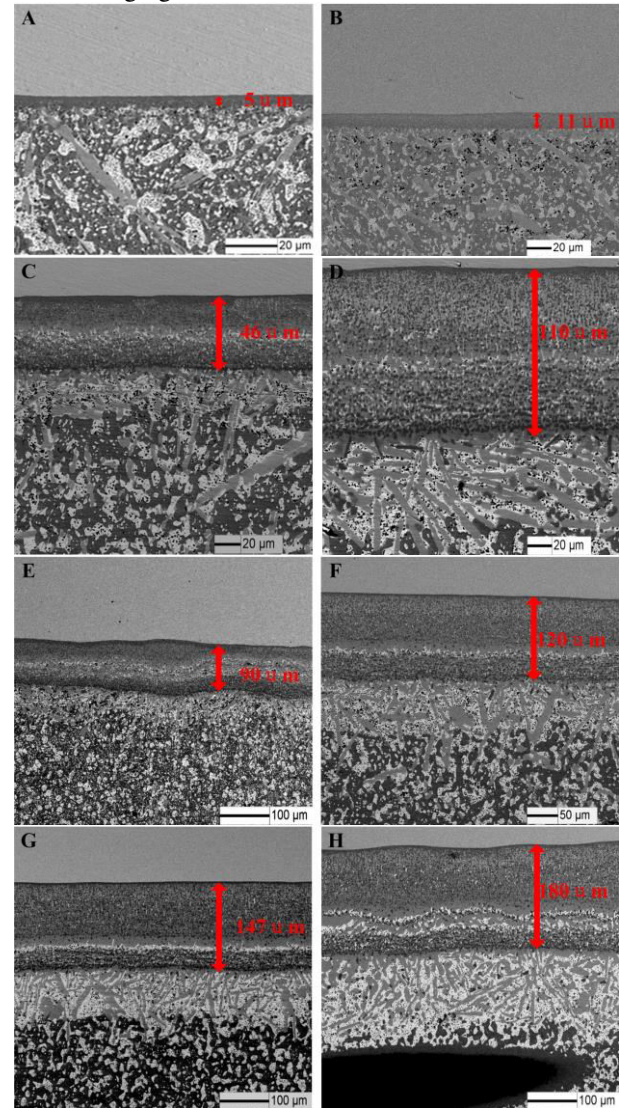


Fig. 1. The microstructures of the soldered interface close to AuAgCu alloy after soldering and different aging conditions. A) after soldering; B) after 4 days at 125 °C; C) after 4 days at 150 °C; D) after 4 days at 175 °C; E) after 10 days at 150 °C; F) after 30 days at 150 °C; G) after 60 days at 150 °C; H) after 90 days at 150 °C

It is found from Figure 1A that the obvious IMCs layer formed at the interface close to AuAgCu alloy, and some long columnar Au-Sn IMCs also appeared in the Sn-based solder zone close to the IMCs layer boundary. After solid state thermal aging, the IMCs layer became thicker, and the columnar Au-Sn IMCs in the soldered zone also became more. As aging temperature elevated and aging time increased, IMCs layer divided into the different compound layer, indicating different composition IMCs layer formed.

To clarify the effect of aging parameters on the IMCs, the relationship between the thickness of IMCs and aging parameters is illustrated as Figure 2. Figure 2a

shows the thickness of IMCs layer varying with aging temperature, and Figure 2b shows the thickness of IMCs layer varying with aging time. It is found that whatever the aging time is, the thickness of IMCs layer is almost linear with the increasing range of aging temperature from 125 °C to 175 °C.

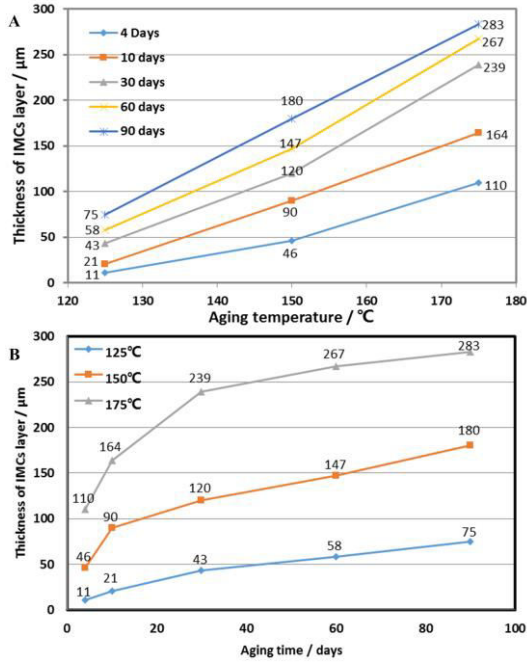


Fig. 2. The relationship between the thickness of IMCs layer and aging parameters. A) The thickness of IMCs layer varying with aging temperatures under different aging time; B) The thickness of IMCs layer varying with aging time under different aging temperatures

However, the relationship of thickness of IMCs layer with aging time is slightly different. Under the aging temperature of 125 °C, the thickness of IMCs layer is almost linear with the increasing of aging time. But under the aging temperature of 150 °C and 175 °C, as the aging time increases from 4 days to 30 days, the thickness of IMCs layer increases quickly, and from 30 days to 90 days, the thickness increasing rate becomes slower.

3.2 Chemical composition and Micro-hardness of IMCs layer

It was found from microstructure observation that IMCs layer was not a certain compound, but a mixture of some IMCs. And as the thermal aging temperature elevated and aging time increased, not only IMCs layer became thicker, but also different IMCs combinations formed. Another obvious result could be obtained, so the chemical composition of the IMCs was analyzed by SEM coupled with EDS technology.

In soldered zone of AuAgCu joint as shown in Figure 1A, the upper zone was the microstructure of AuAgCu alloy, its chemical composition was that 61.88Au-32.47Ag-5.65Cu (wt%) and 44.62Au-42.76Ag-12.62Cu (at%). The middle zone was the IMCs layer with the thickness of 5µm, its chemical composition was that

15.05Au-15.2Ag-1.09Cu-67.89Sn-0.77Pb (at%), it should be the mixture phase of AuSn₄ and Ag₃Sn. The bottom zone was the Sn-based solder zone, some long columnar Au-Sn IMCs appeared in this zone. The chemical composition of the Au-Sn IMCs was that 18.90Au-78.89Sn-2.21Pb (at%), indicating that it was AuSn₄ IMCs. And the gray-white microstructure was Pb-rich phase for its chemical composition of 6.07Sn-93.93Pb (at%), the gray-black microstructure was Sn-rich phase for its chemical compositions of 94.87Sn-5.13Pb (at%).

After thermal aging, because of Au diffusion into solid state SnPb solder zone, the IMCs layer became thicker, and the obvious change happened in the chemical compositions of IMCs layer. EDS results of the IMCs layer in Fig.1B indicated that chemical compositions of the upper part of IMCs layer should be AuSn₂+Ag₃Sn+(AuCu)Sn₂, and the chemical compositions of the bottom part was AuSn₄+Ag₃Sn. The IMCs layer shown in Figure 1C could be segmented into four sublayers with different chemical compositions, the upper sublayer close to the interface of AuAgCu alloy, the second sublayer, the middle sublayer, and the bottom sublayer close to Sn-based solder zone. The EDS analysis indicated that the compound mixture of the upper sublayer close to the interface of AuAgCu was AuSn₂+(AuCu)Sn₂+Ag₃Sn, the second sublayer was Ag₃Sn+AuSn₄+AuSn₂, the middle sublayer was AuSn₄+Ag₃Sn, and the bottom sublayer was AuSn₄+Ag₃Sn+AuSn₂. The similar cases happened in Figure 1D~Figure 1H.

Figure 3 shows the microstructure of the soldered joint of AuAgCu alloy at aging temperature of 175 °C for 60 days. Table 1 gives the chemical compositions of different phases in the soldered joint. It was found that the microstructure of the soldered joint could be segmented into several parts as follows:

- 1) (AuCu)Sn₂+AuSn₂+Ag₃Sn was close to AuAgCu interface;
- 2) The second sublayer was Ag₃Sn+AuSn₄+AuSn₂, maybe little Cu₆Sn₅ also existed in IMCs;
- 3) The middle sublayer was AuSn₄+Ag₃Sn;
- 4) The bottom sublayer was AuSn₄+Ag₃Sn+AuSn₂;
- 5) The Sn-based solder zone consisted of a lot of long columnar AuSn₄ compounds and Pb-rich phase, little Sn-rich phase;
- 6) Cu₆Sn₅ compound appeared in the interface close to silver plated copper wire.

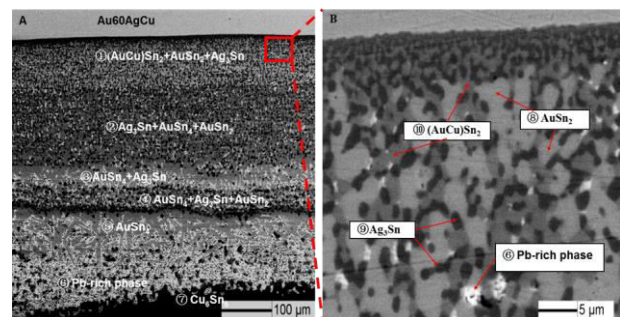


Fig. 3. The microstructure of the soldered joint of AuAgCu alloy at aging temperature of 175 °C for 60 days.

Table 1. Chemical compositions of different phases in the soldered joint (as shown in Figure 3) by EDS analysis.

Position	Chemical compositions (at%)					The possible compound phase
	Au	Ag	Cu	Sn	Pb	
①	21.25	19.61	10.18	48.96	—	(AuCu)Sn ₂ +AuSn ₂ +Ag ₃ Sn
②	16.47	20.08	3.41	59.04	—	Ag ₃ Sn+AuSn ₄ +AuSn ₂
③	17.20	13.64	—	65.73	3.43	AuSn ₄ +Ag ₃ Sn
④	14.53	24.02	—	60.36	1.09	AuSn ₄ +Ag ₃ Sn +AuSn ₂
⑤	20.59	—	—	79.41	—	AuSn ₄
⑥	0.88	—	—	4.89	94.23	Pb-rich phase
⑦	—	—	55.45	44.55	—	Cu ₆ Sn ₅
⑧	33.66	1.05	—	65.29	—	AuSn ₂
⑨	—	74.08	—	25.92	—	Ag ₃ Sn
⑩	25.30	—	25.04	49.66	—	(AuCu)Sn ₂

It was found from the above results and analysis that as aging temperature elevated and aging time increased, not only IMCs layer was thicker, but also the chemical compositions of IMCs changed, especially for the upper zone close to AuAgCu alloy interface. Because of the similar high atomic concentrations of Au and Ag in AuAgCu alloy compared with that of Cu, two IMCs of AuSn₄ and Ag₃Sn first formed between gold alloy and the molten Sn-based solder. After thermal aging, because Au and Ag atoms diffused into Sn-based solder, IMCs layer was thicker and segmented into several sublayers with different IMCs combinations. Ag₃Sn was the main component of all the IMCs layer. AuSn₄ in the IMCs layer was partly transformed into AuSn₂, AuSn₂ and AuSn₄ were the main components of the IMCs layer. In the zone closest to AuAgCu alloy, Au and Cu atoms of AuAgCu alloy reacted with Sn atom to form the ternary IMC of (AuCu)Sn₂.

Different IMCs components would produce different mechanical properties. The micro-hardness test was used to measure the properties of different IMCs. Figure 4 shows the micro-hardness measurement of four IMCs sublayer in the soldered joint at the aging temperature of 150 °C for different aging time.

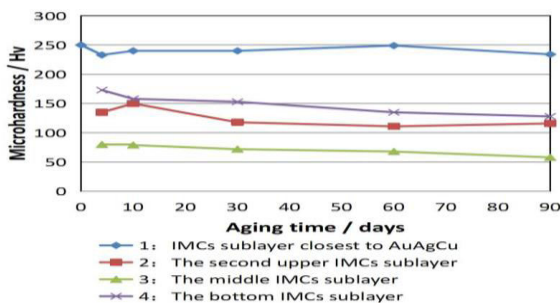


Fig. 4. The micro-hardness values of four IMCs sublayers in soldered joint at aging temperature of 150 °C for different aging time.

It is found from Figure 4 that the highest hardness value appeared in the upper sublayer closest to AuAgCu alloy with the combinations of

(AuCu)Sn₂+Ag₃Sn+AuSn₂ IMCs, and the lowest hardness value appeared in the middle sublayer of AuSn₄+Ag₃Sn IMCs. The hardness values of the second sublayer and the bottom sublayer were very close because of the similar chemical compositions of AuSn₂+AuSn₄+Ag₃Sn IMCs. And the hardness values of the same positions in IMCs layers of the soldered joints at 150 °C for different aging time had little difference.

3.3 Mechanical property analysis

Figure 5 shows the micro-fractography of the two soldered joints as soldering and after thermal aging, respectively. It was found that the obvious brittle fracture features appeared in the mechanical test of the soldered joints, whatever thermal aging test was done or not and there is no yield phenomenon happened. It is also clearly seen that the failure happened at the interfacial compound layer close to gold alloy. There were almost no any dimple and tear ridges on the micro-fractography of two joints.

The influence of aging time on mechanical properties of the soldered joints at different aging temperature is illustrated in Figure 6. It was found that aging time had the large effect on mechanical property of the soldered joint. At the aging temperature of 150 °C and 175 °C, as aging time increased from 4 days to 90 days, the mechanical properties of the soldered joints decreased obviously. But at the aging temperature of 125 °C, the mechanical property increased as the aging time increased from 4 days to 30 days, and then decreased from 30 days to 90 days. And for every aging temperature, the mechanical properties at short aging time (such as 4 days and 10 days) were all higher than that of the soldered joint without thermal aging, especially for the aging temperature of 125 °C, the shear strength of the soldered joint at the aging time of 30 days was also higher than that of the soldered joint without thermal aging. After 30 days, the mechanical properties were all lower than that of the soldered joints without thermal aging. The shear strength of the soldered joint at 125 °C for 90 days was almost 93.4% of that without thermal aging, indicating that thermal aging at 125 °C had little effect on mechanical property of soldered joint of AuAgCu alloy. However, the shear strength of the soldered joint at 175 °C for 90 days was only 60% of that without thermal aging.

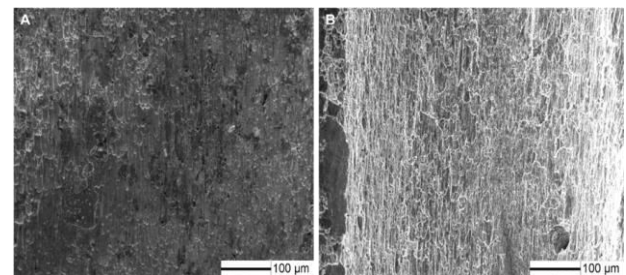


Fig. 5. The micro-fractography of the two soldered joints by SEM. A) The soldered joint as soldering; B) The soldered joint after thermal aging at 150 °C for 30 days.

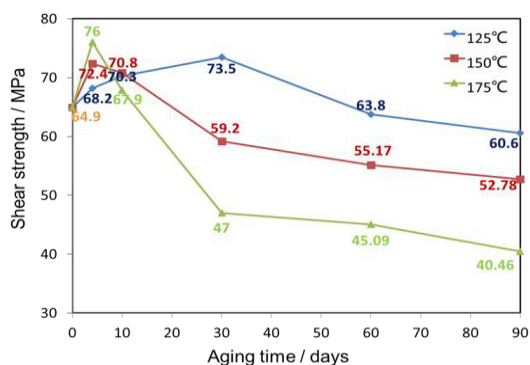


Fig. 6. The shear strength of the soldered joints at different thermal aging conditions.

4 Conclusion

In conclusion, aging temperature and time had large influence on the microstructure, thickness and phase compositions of IMCs layer, micro-hardness and mechanical property of the soldered joint of Au₆₀AgCu alloy and Ag-plated Cu wire. After soldering, the phase composition of IMCs layer in the soldered zone is mainly AuSn₄+Ag₃Sn mixed IMCs phase. Through thermal aging, IMCs layer became thicker, more complex compositions and multiply-sublayers structure. Ag₃Sn, AuSn₂ and AuSn₄ were the main components of the IMCs layer. (AuCu)Sn₂ ternary IMCs formed at the upper sublayer close to AuAgCu alloy.

Only considering the mechanical property, Sn-based solder could be used to join gold alloy. The reasons are that: 1) AuSn₄ was not the only IMCs at the interface close to gold alloy, any single IMCs was restricted by the mixture of various IMCs, and would not subsequently grow up to the coarse and brittle IMCs. 2) IMCs layer became a multiply-sublayers structure in which micro-hardness profile presented high-low alternating appearance after thermal aging, this would help to reduce the embrittlement of the joint. 3) The traditional aging temperature of 125 °C did not affect the mechanical property of the soldered joint. However, too high temperature for long time would obviously affect the mechanical property of soldered joint of AuAgCu alloy.

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