HIGH TECHNOLOGY LETTERS | Vol. 24 No. 1 | Mar. 2018 | pp. 113 ~ 116

doi:10.3772/j.issn.1006-6748.2018.01.014

Hillock Sn whiskers growth behaviors in Sn0.3Ag0.7Cu/Cu solder joints during corrosion①

Zhang Liang (张 亮)②* **, Liu Zhiquan**, Sun Lei*, Yang Fan*, Zhong Sujuan***
(*School of Mechanical & Electrical Engineering, Jiangsu Normal University, Xuzhou 221116, P. R. China)
(**Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, P. R. China)
(***State Key Laboratory of Advanced Brazing Filler Metals & Technology,
Zhengzhou Research Institute of Mechanical Engineering, Zhengzhou 450001, P. R. China)

Abstract

Hillock Sn whiskers in Sn0.3Ag0.7Cu solder are investigated in 20 seconds in corrosive climate (95% methanol and 5% nitric acid), and the growth mechanism of hillock Sn whiskers is studied. The results indicate that hillock Sn whiskers are formed near the interface of Sn0.3Ag0.7Cu/Cu solder joints, and small corrosion pits provide conceive sites for Sn whiskers. Moreover, compressive stress induced by IMC reaction and oxidation for the whisker growth may be suggested as the driving force.

Key words: Sn whisker, solder joints, corrosion pits, conceive sites

0 Introduction

In the past, Sn-base solders containing Pb were widely used in chip attachment and surface-mount processes in electronic packaging industry. Owing to the increasing environmental and health concerns of toxicity of lead, the use of Pb was required to be removed from manufacturing consumer electronic products in 2006 by international legislation (EU RoHS), which has led to an extensive R&D study of lead-free solder materials[1,2]. Among series of lead-free alloys, SnAgCu near eutectic solders were proposed as the most promising alternatives for traditional SnPb solders[3,4] due to their good material performance. Therefore, SnAgCu solders are extensively used as the interconnection materials in BGA, CSP, CCGA, etc.

In recent years, in order to reduce the cost of SnAgCu solders, low-Ag SnAgCu solders have been studied by lots of researchers. It has been found that the low-Ag SnAgCu solders, such as the Sn0.3Ag0.7Cu and Sn1.0Ag0.5Cu, exhibit both higher bulk compliance and higher plastic energy dissipation than Sn4.0Ag or Sn3.0Ag0.5Cu[5]. Liu[6] reported that Fe_2O_3 nanoparticles added could remarkably improve the wettability of Sn1.0Ag0.7Cu solder alloys and inhibit the formation and the growth of the interfacial IMCs between the nano-composite solders and Cu substrate. Wu[7] found that with the addition of TiO_2 nanoparticles, the thickness of intermetallic compound layer could be reduced obviously at Sn0.3Ag0.7Cu/Cu interface. EI-Daly[8] demonstrated that 2.0wt.% Zn into Sn1.0Ag0.3Cu soldering resulted in an excessive tensile strength and low ductility, 3.0wt.% Zn exhibited both the highest strength and large ductility. The addition of Ti, In, Sb, Zn, Al, Fe, and Co to low-Ag-content SAC solder has the potential to improve the thermal-cycling reliability of joints without sacrificing the drop-impact performance[9].

In this study, the hillock Sn whisker in Sn0.3Ag0.7Cu solder is investigated with 20 seconds corrosion, the reaction mechanism of hillock Sn whisker is studied, which can provide a reference for the research of low-Ag lead-free solders.

1 Experiment

Sn0.3Ag0.7Cu alloys are prepared from pure Sn, Sn-Cu alloy and Sn-Ag alloy. Raw materials for SnAgCu solders are melted in a ceramic crucible, and melted at 550 ± 1℃ for 40 min. And mechanical stirring is needed to homogenize the solder alloy. In order to protect the solder for oxidation during melting, KCl + LiCl (1.3:1) are used over the surface of liquid

① Supported by the National Natural Science Foundation of China (No. 51475220), the State Foundation of Laboratory of Advanced Brazing Filler Metals & Technology (Zhengzhou Research Institute of Mechanical Engineering) (No. SKLABFMT-2015-03) and High Level Talent Plan of Jiangsu Normal University (No. YQ2015002).
② To whom correspondence should be addressed. E-mail: zhangliang@jsnu.edu.cn
Received on Jan 4, 2017

solder. Then the molten alloys are chilled and cast ingots in a mold and solidified by nominally air-cooling. At last for stabilizing the microstructure of the solder alloys, all solder specimens are heated and treated at 125℃ for an hour. SnAgCu solder is put on the surface of Cu substrate, and interconnection between Cu and solder is carried out by reflow soldering with peak temperature 245℃ (Fig. 1). SnAgCu samples are mechanically polished with 1μm diamond paste for microstructural observation. The etching solution contains 95% methanol and 5% nitric acid, the samples in corrosion climate are 20 seconds. The microstructures of these solders are examined by scanning electron microscopy (SEM) with a voltage of 20 KeV.

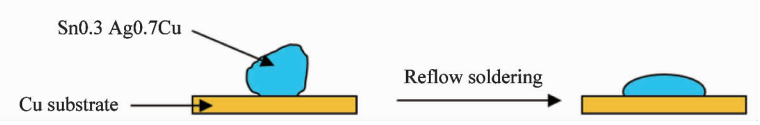

Fig. 1 Schematic illustration of Sn0.3Ag0.7Cu solder joint

2 Results and discussion

Fig. 2 shows the surface morphologies of Sn0.3Ag0.7Cu/Cu solder joints after corrosive climate. The corrosion pits can be observed well with the SEM figures, and the hillock Sn whiskers are developed mainly in the corrosion pits, the length of the whiskers may be as long as 6μm. Moreover, some hillock Sn whiskers are formed near the interface of Sn0.3Ag0.7Cu/Cu solder joints. Due to the small period for corrosion, no long whisker can be observed in the samples. Horváth, et al[10,11] reported the tin whisker grew from micro-alloyed SnAgCu solders in corrosive climate. The larger the copper content is in an alloy, the more stress will develop in the layer due to the larger expansion of the corrosion product within the alloy. Jiang[12], et al. reported that the whisker growth on tin finishes produced by three different plating baths (sulfate-based, alkaline stannate-based and stannous chloride-based) was observed by both optical and scanning electronic microscopy. With the corrosion climate, the corrosion pits can play an important role on improving the whisker growth.

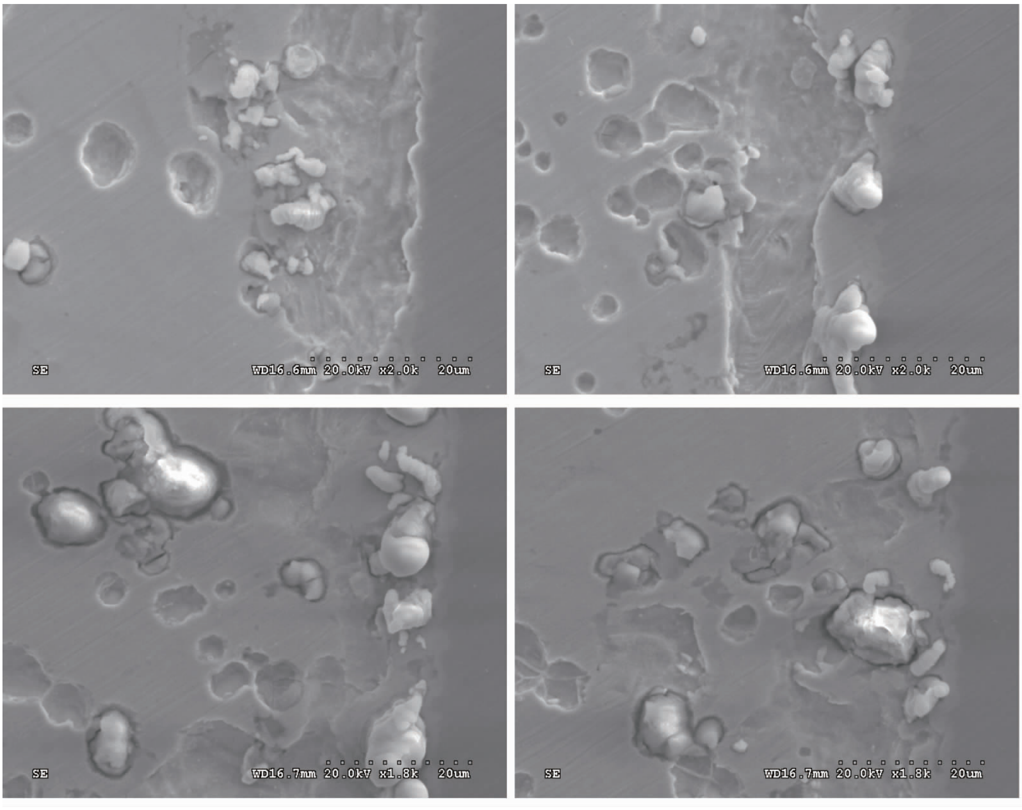

Fig. 2 Hillock Sn whiskers in SnAgCu/Cu solder joints

In order to further analyze the growth of Sn whisker, the whiskers near the interface of solder joints are magnified as shown in Fig. 3 and Fig. 4. At the initial stage, the reflow soldering of Sn0.3Ag0.7Cu solder on Cu substrate is completely stress-free. After soldering, chemical force can be induced during corrosion. Tu[13,14] found that the origin of the chemical force was induced by the reaction between Sn and Cu to form Cu_6Sn_5 intermetallic compound with room temperature, and the chemical reaction provided a sustained driving force for spontaneous growth of whiskers as long as the reaction kept going with unreacted Sn and Cu, which represents that the reaction of Cu and Sn can provide the stress of whisker growth. In addition, Hua[15] suggested that possible mechanism causing this growth was that product volume of metal interreaction or oxidization in solder alloy expanded to induce compression stress, during the release of stress, Sn was extruded out. Therefore, the interface reaction and volume variation during corrosion could provide the driving force: compressive stress. During corrosion, the part of Sn matrix could be etched away, so small corrosion pits could be formed likely among the Sn grains, which could be the weak point for the squeezing of Sn whiskers.

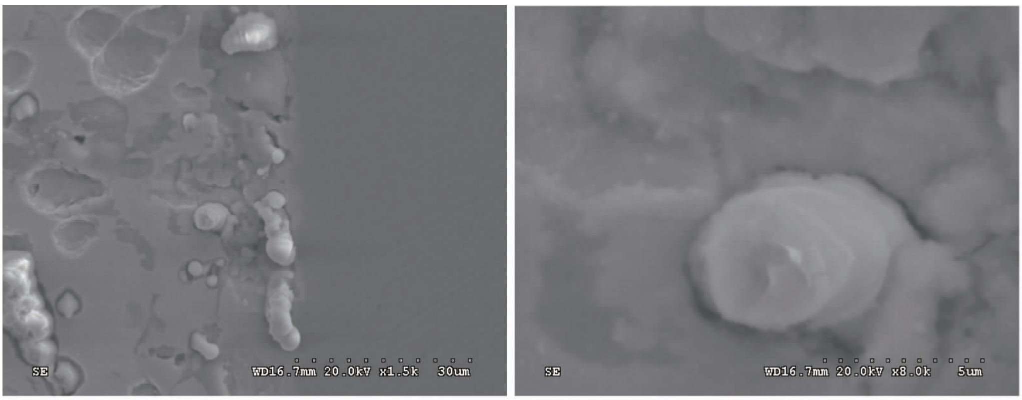

Fig. 3 Hillock Sn whiskers in SnAgCu/Cu solder joints

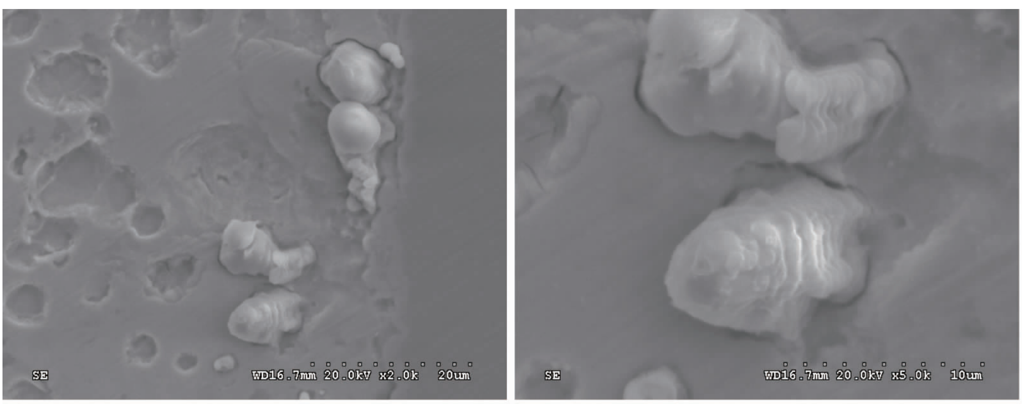

Fig. 4 Hillock Sn whiskers in SnAgCu/Cu solder joints

In order to illustrate the formation of Sn whisker, the formation mechanism of Sn whiskers is shown in Fig. 5. During reflow soldering, Cu atoms from Cu substrate can diffuse into solder to react with Sn to form Cu_6Sn_5 intermetallic compound. Moreover, after the soldering, the IMC layer will grow significantly (Fig. 5(a)), the volume expansion of IMC will develop, the compressive stress for the whisker growth may be formed. When these samples are corroded, tin will be transformed to SnOx, the compressive stress can be generated. With a period of corrosion, some corrosion pits may occur on the surface of solder joints (Fig. 5(b)), meanwhile, with the formation of corrosion pits, part compressive stress induced from the corrosion will be decreased, some small corrosion pits in the boundaries of Sn grains will be the conceive site of hillock whisker (Fig. 5(c)). So some hillock Sn whiskers can be observed in the Sn matrix near the interface of solder joints. Ma[16] suggested that crack among the Sn grains with the maximum divergence in orientation, the growth of Sn whiskers was promoted at this site due to the compressive stress originating from the bottom of the crack.

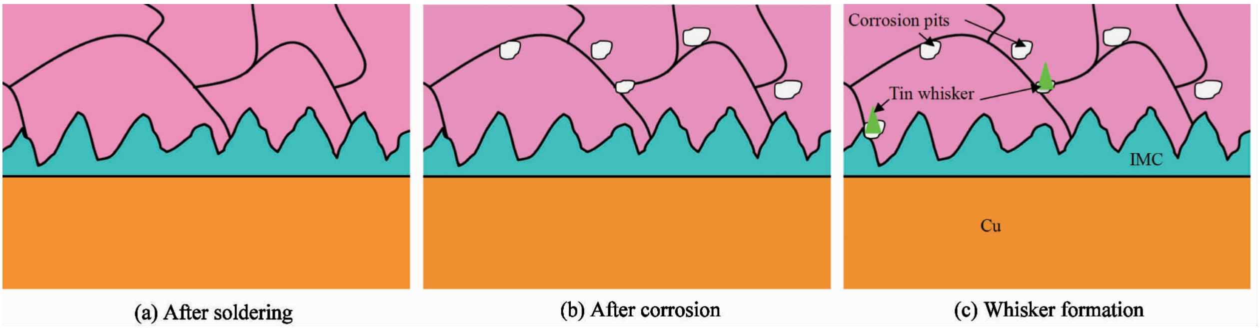

Fig. 5 Schematic illustration of Sn whiskers formation

3 Conclusions

Sn0.3Ag0.7Cu solders are put on Cu substrate to form low-silver solder joints with reflow soldering, and the hillock Sn whisker is observed after 20 seconds in corrosive climate (95% methanol and 5% nitric acid). The results indicate that hillock Sn whiskers are formed near the interface of Sn0.3Ag0.7Cu/Cu solder joints, and small corrosion pits provide the conceive site for Sn whiskers. Moreover compressive stress induced by IMC reaction and oxidation for the whisker growth may be suggested as the driving force.

Acknowledge

This study is funded by the Natural Science Foundation of China (51475220), the State Foundation of Laboratory of Advanced Brazing Filler Metals & Technology (Zhengzhou Research Institute of Mechanical Engineering) (SKLABFMT-2015-03), the Qing Lan Project, the China Postdoctoral Science Foundation Funded Project (2016M591464) and Six Talent Peaks Project in Jiangsu Province (XCL-022).

References

[1] Zhang L, Tu K N, Chen S W, et al. Development of lead-free solders in China during the past decade[J]. *Scientia Sinica Technologia*, 2016, 46(8):767-790
[2] Li C F, Liu Z Q, Shang P J, et al. In situ investigation on the oxidation behavior of a $RESn_3$ film by transamission electron microscopy[J]. *Scripta Materialia*, 2011, 65:1049-1052
[3] Zhang L, Han J G, Guo Y H, et al. Creep behavior of SnAgCu solders containing nano-Al particles[J]. *Journal of Materials Science: Materials in Electronics*, 2015, 26(6):3615-3620
[4] Sun L, Zhang L, Zhong S J, et al. Reliability study of industry Sn3.0Ag0.5Cu/Cu lead-free soldered joints in electronic packaging[J]. *Journal of Materials Science: Materials in Electronics*, 2015, 26(11):9164-9170
[5] Cheng F J, Gao F, Zhang J Y, et al. Tensile properties and wettability of SAC0307 and SAC105 low Ag lead-free solder alloys[J]. *Journal of Materials Science*, 2011, 46(10): 3424-3429
[6] Gu Y, Zhao X C, Li Y, et al. Effect of nano-Fe_2O_3 additions on wettability and interfacial intermetallic growth of low-Ag content Sn-Ag-Cu solders on Cu substrates[J]. *Journal of Alloys and Compounds*, 2015, 627:39-47
[7] Wu R W, Tsao L C, Chen R S. Effect of 0.5wt% nano-TiO_2 addition into low-Ag Sn0.3Ag0.7Cu solder on the intermetallic growth with Cu substrate during isothermal aging[J]. *Journal of Materials Science: Materials in Electronics*, 2015, 26(3):1858-1865
[8] EI-Daly A A, Hammad A E, AI-Ganainy G S, et al. Properties enhancement of low-content Sn-Ag-Cu lead-free solders containing small amount of Zn[J]. *Journal of Alloys and Compounds*, 2014, 614:20-28
[9] Shnawah D A, Said S B M, Sabri M F M, et al. High-reliability low-Ag-content Sn-Ag-Cu solder joints for electronics applications[J]. *Journal of Electronic Materials*, 2012, 41(9):2631-2658
[10] Horváth B, Shinohara T, Illés B. Corrosion properties of tin-copper alloy coatings in aspect of tin whisker growth [J]. *Journal of Alloys and Compounds*, 2013, 577:439-444
[11] Illés B, Horváth B. Tin whisker growth from micro-alloyed SAC solders in corrosive climate[J]. *Journal of Alloys and Compounds*, 2014, 616:116-121
[12] Jiang B, Xian A P. Whisker growth on tin finishes of different electrolytes[J]. *Microelectronics Reliability*, 2008, 48:105-110
[13] Tu K N, Li J C M. Spontaneous whisker growth on lead-free solder finishes[J]. *Materials Science and Engineering A*, 2005, 409:131-139
[14] Tu K N. Electronic Thin-Film Reliability. Cambridge: Cambridge University Press, 2010
[15] Hua L, Yang C. Corrosion behavior, whisker growth, and electrochemical migration of Sn-3.0Ag-0.5Cu solder doping with In and Zn in NaCl solution[J]. *Microelectronics Reliability*, 2011, 51:2274-2283
[16] Ma L M, Zou Y, Liu S, et al. Whisker growth behaviors in POSS-silanol modified Sn3.0Ag0.5Cu composite solders[J]. *Journal of Alloys and Compounds*, 2016, 657:400-407

Zhang Liang, born in 1984. He is Currently a professor in School of Mechatronic Engineering Jiangsu Normal University, China. He received his Ph. D degree from Nanjing University of Aeronautics and Astromautics, China in 2011. His interests include microelectronics welding, SMT, load-free solders etc. He has published over 100 papers.