

Article

Tin Whisker Growth Inhibition in RE-Doped Sn-Zn Soldered Joints

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Abstract: The tin whisker inhibition in RE-doped Sn-Zn soldered joints was investigated. The results indicated that after aging treatment at 150 °C, with the proper addition ratio of Ga and Nd, no obvious NdSn₃ phase nor tin whisker growth was observed in the soldered joints. By replacing the Sn-Nd phase with a Ga-Nd phase, the risk of tin whisker growth caused by the oxidation of RE-phase was significantly inhibited even in soldered joints with additional excessive contents of Nd. The IMC layer in soldered joints with optimal addition showed a relatively regular shape after aging treatment, making the soldered joint maintain preferable mechanical performance. The results would be available for guiding the study of tin whisker growth inhibition method.

Keywords: tin whisker inhibition; RE-doped; soldered joints; aging treatment

1. Introduction

With the increasing requirements of environmental protection in the electronics industry, Sn-Pb series solder were banned in electronic packaging products, therefore the development of lead-free solders has attracted special attention in the past years [1–3]. Among all the lead-free solders, Sn-Zn series solders have the advantage of relatively low melting temperature, higher mechanical properties, and a relatively low cost [4,5]. However, poor wettability limits the application of Sn-Zn solders in industry due to the easy oxidation of zinc [6]. In the previous research, a small addition of rare earth elements (RE) can evidently improve the wettability and mechanical properties of Sn-Zn solders [7], however, an excessive addition of RE would be harmful to the solder which may induce the tin whisker growth phenomenon.

Tin whiskers are 10–500 μm long pure tin crystal filaments which can cause short circuits in electronic devices. It is reported that the tin whisker growth phenomenon has caused great losses in satellites, missiles, radars, and other equipment during the past decades [8]. Although a tin whisker would bring immense risk of device failure, the uncertainty of whisker growth under various conditions brings great difficulties to the study. The compressive stress has been considered as the main reason which induced the tin whisker growth, nevertheless, the mechanism of tin whisker growth remains unclear. In consideration of the high tin content in lead-free solders, tin whisker growth in lead-free soldered joint should be paid sufficient attention.

Recent research has discovered that tin whiskers grow in solder with excessive addition of rare earth element, which provides a novel approach to explain the mechanism of whisker growth [9,10]. In this paper, the behavior and mechanism of tin whisker growth in Sn-Zn series soldered joints

bearing rare earth Nd were investigated. The results could provide a feasible method to inhibit tin whisker growth, and the method has been successfully tested over a long time aging treatment.

2. Experimental Procedure

All alloys were made from pure Sn (99.95 wt.%), pure Zn (99.95 wt.%), pure Ga (99.95 wt.%), and pure Nd (99.5 wt.%). Under vacuum atmosphere (10–3 torr), Sn-5Nd master alloy ingots were prepared by melting Sn and Nd at 90 °C for 15 min. Then the master alloy was added into the melted SnZn alloy which was held for about 5 min while mechanical stirring was performed every 1 min. The melting temperature was controlled below 400 °C. The melted solder was chilled to cast and cut into solder bars of 40 mm length. The compositions of alloys were analyzed by inductively coupled plasma emission spectrometer (ICP-AES).

The interfacial microstructure of soldered joints after aging treatment were observed by Su8010 field emission scanning electron microscope (FE-SEM, BSE mode, Hitachi Co., Ltd., Tykyo, Japan) equipped with energy dispersive X-ray spectroscopy (EDS). Phase composition analysis was determined through Rigaku ultima IV x-ray diffractometer (XRD) with following parameters: Cu-K α target, working voltage 40 kV, operating current 40 mA, scanning speed 5°/min, and scanning range 20° to 100°.

According to the Japan Industry Standard JIS Z 3198-2 test methods for lead-free solders—Part7: methods for shear strength of solder joints on chip components, the shear strength of soldered joints after aging treatment was tested with STR-1000 Micro-joint strength tester (Rhesca Co., Ltd., Tykyo, Japan).

According to the standard of the Department of Defense of the USA [11], the samples were placed in an oven maintained at a constant temperature to perform the high temperature storage test. The aging temperature was 150 °C and storage time set as 720 h, 1200 h, 3000 h, and 6000 h for different samples.

3. Results and Discussion

In the previous research of solders doped with rare earth, the excess of rare earth addition would cause the formation of mass RE-phase. Therefore, the oxidation of these RE-phase was considered as the main reason which induced the tin whisker growth in the solder matrix [12–14]. However, there are various situations of tin whisker growth in soldered joints as shown in Figure 1. It can be concluded that the tin whisker sprouted out from RE-phase near the interface layer in Figure 1a was similar to the whisker growth in the solder matrix, moreover, Figure 1b,c demonstrated the whisker growth without the participation of RE-phase in Nd-doped soldered joint. The EDS results in Figure 1d,e have shown that the compositions of the microstructure near the tin whisker root were Cu-Zn-Sn intermetallic compounds (IMC), which indicated that the tin whisker directly sprouted out from the twisted interfacial intermetallic compound layer.

The tin whisker growth near the interface of soldered joint is greatly affected by the formation and conversion of interfacial IMC layer [15]. The diffusion between atoms caused stress to accumulate during the aging process while the stress further accelerated the diffusion reaction. Moreover, the volume change caused by the growth of IMC layer was blocked by the solder matrix, which also caused stress to accumulate in the corresponding grain boundaries. When the stress reached a certain level, voids, and fractures appear in the IMC layer which aggravate the stress concentration and finally induced tin whisker growth. Considering about the reliability of the soldered joint, besides the formation of RE-phase which may induce the tin whisker growth in RE-doped soldered joints, the growth of IMC layer should also be well controlled.

The compositions of IMC layer in Sn-Zn series soldered joint could be determined as Cu₅Zn₈ after soldering [16]. The thickness of IMC layer increased with aging time, however, an IMC layer which was too thick would deteriorate the mechanical properties of the soldered joint since the IMC is hard and brittle [17]. It was reported that Sn-Zn series solder possess favourable mechanical properties compared with Cu₆Sn₅/Cu₃Sn IMC layer in Sn-Ag-Cu and Sn-Cu series solder [18].

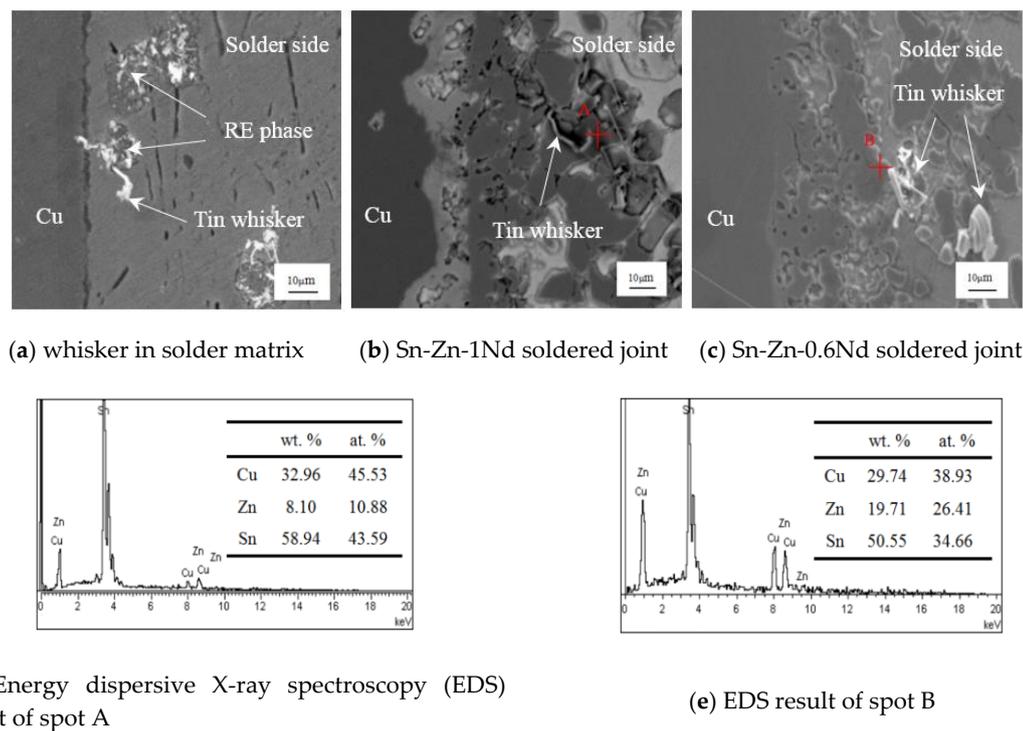


Figure 1. Various types of tin whisker growth in soldered joints.

Figure 2 showed the morphology of IMC layer in Sn-Zn-Ga-Nd solder at different aging time, the results indicated that in Figure 2a,b the thickness of IMC layer increased with aging time, while in Figure 2c,d the compositions of the IMC layer transformed into a mixture of Cu-Sn-Zn compounds. Meanwhile, the morphology of IMC layer was greatly affected by the discrepant atom distribution and diffusion rate. At the early aging process, the diffusion between Zn and Cu atoms is the leading factor of diffusion reaction, thus the thickness of Cu_5Zn_8 layer is increased with aging time. After an extended period, Kirkendall voids appear in the Cu_5Zn_8 layer as a result of the consumption of Zn atoms. Moreover, the leading factor of diffusion reaction change to the diffusion between Cu and Sn atoms owing to the depletion of Zn atoms near the interface, thus the IMC layer transform into Cu-Sn-Zn compounds as Figure 2e shows. Besides, the IMC layer in Sn-9Zn-0.5Ga-1Nd soldered joint couldn't be maintained uniformly and showed a stratification pattern. From the EDS results in the IMC layer as shown in Figure 2f, it can be inferred that the compositions of the IMC layer was approximate $\text{Cu}_5\text{Zn}_8/\text{Cu}_6\text{Sn}_5$ near the solder side, while the compositions of the IMC layer was approximate $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ near the Cu substrate side.

In addition, there were cracks of Cu_5Zn_8 IMC found near the solder side during the aging process as shown in Figure 3a. The formation of these cracks in solder matrix were caused by the discrepant distribution between Cu and Zn atoms. However, after 6000 h aging, the IMC layer in the Sn-Zn-1Nd soldered joint presented a collapsed and separating structure, while massive Cu_5Zn_8 IMC pieces could be found in the solder matrix as shown in Figure 3b. According to the theory of diffusion in solid [19,20], the formation of this periodic layer is related to the stresses induced by the different growth rate of diffusion couples in the interface layer. When the elastic deformation of the slow-growing diffusion couple reaches its limit value, it will be split up through the diffusion direction which cause the disintegration of the IMC layer. On the basis of the heterogeneous distribution of atoms near the interface, the diffusion couples in the IMC layer of Sn-Zn-Nd soldered joint could be mainly Cu_5Zn_8 and Cu_6Sn_5 during the aging process. With the consumption of Zn atoms, the growth rate of Cu_6Sn_5 is gradually greater than that of Cu_5Zn_8 , which means the slow-growing Cu_5Zn_8 diffusion couple would be split and even shattered from the IMC layer under the effect of diffusion stress during aging.

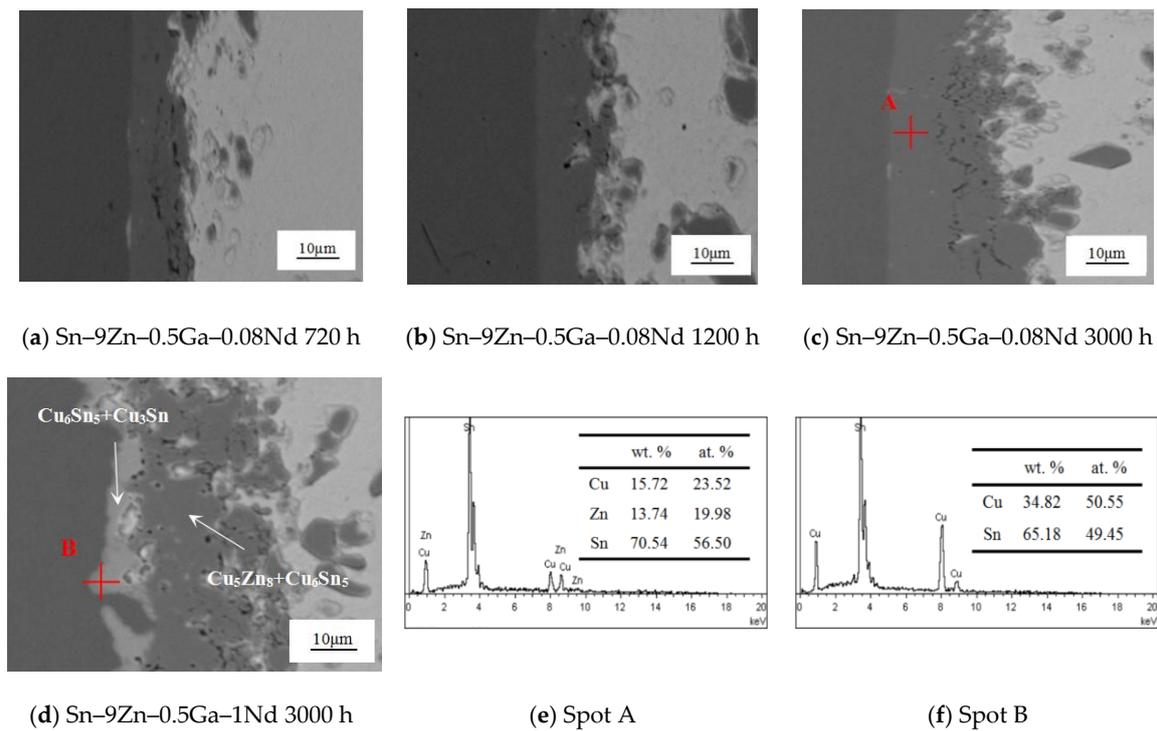


Figure 2. Morphology of intermetallic compounds (IMC) layer at different aging time.

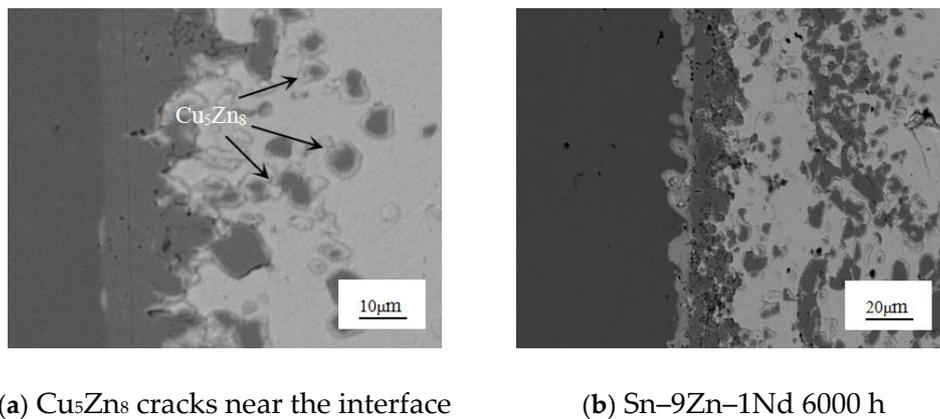


Figure 3. Results of stress release induced by diffusion.

It is worthwhile that there was no tin whisker growth or Sn-Nd phase found near the interface of Sn-Zn-Ga-Nd soldered joints, while the IMC layer maintained relatively regular shape and the amount of voids and cracks in IMC layer were decreased after long time aging treatment. Our early research indicated that no obvious tin whisker growth observed in Sn-Zn-0.5Ga-0.08Nd and Sn-Zn-0.5Ga-1Nd solder matrix after aging treatment [21]. The element Ga was proved to inhibit the growth of tin whisker in solder matrix by replacing the transformation of Sn-Nd phase to Ga-Nd phase. To further research the inhibition effect of Ga, the microstructure observation of soldered joints with additional excessive contents of Nd after long time aging treatment were performed to validate the research results.

Figure 4 showed the interface morphology of Sn-Zn-0.5Ga-2Nd soldered joints. According to the previous research on RE-doped solders, 1 wt.% amount of RE means excessive addition and will deteriorate the properties of solders. Comparing with Sn-Zn-0.5Ga-1Nd, Sn-Nd phase was observed in Sn-Zn-0.5Ga-2Nd soldered joints after aging at 15 °C for 120 h, while no obvious tin whisker growth was found near the interface after aging for 720 h. This result indicated that 0.5 wt.% of Ga couldn't react with all 2 wt.% of Nd, thus the rest of Nd reacted with Sn and formed Sn-Nd phase. Due to the

amount and size of Sn-Nd phase were fewer and smaller, the driving force caused by the oxidization of Sn-Nd phase which may induce tin whisker growth was insufficient. In addition, influenced by the variation of concentration gradient near the interface, the Sn-Nd phase may diffusely distributed in the solder matrix during the aging process, therefore no obvious whisker growth appeared in the interface of Sn-Zn-0.5Ga-2Nd soldered joints.

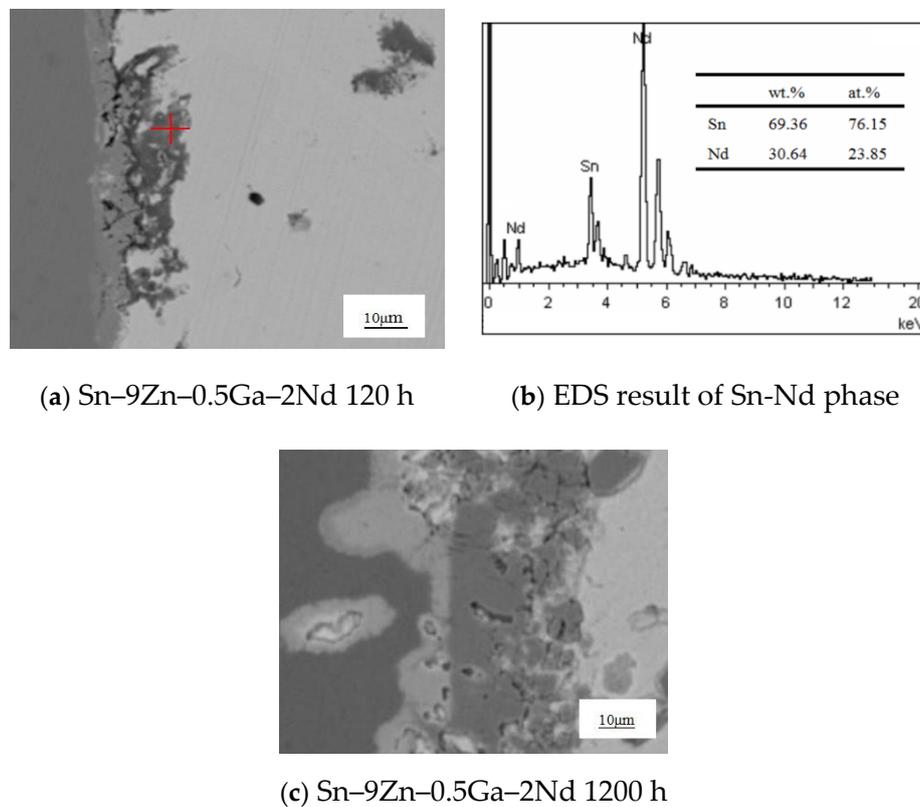


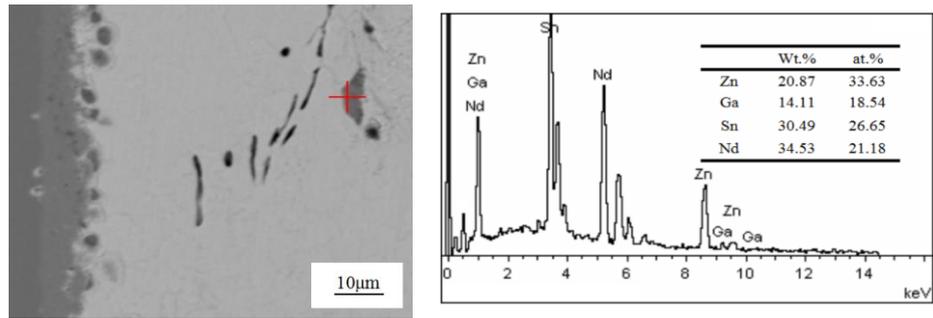
Figure 4. Interface morphology of soldered joints with additional excess content of Nd.

Figure 5 showed the interface morphology of Sn-Zn-1Ga-2Nd soldered joints. After adjusting the addition ratio of Ga and Nd to 1:2, no Sn-Nd phase observed near the interface of soldered joints. Instead, there's a small amount of Sn-Zn-Ga-Nd phase found in the side of solder matrix as shown in Figure 5b. The atom ratio of Sn and Nd is nearly 1:1 which is far from 1:3 in NdSn_3 phase, while the atom ratio of Ga and Nd is nearly 1:1. According to the previous research, it can be assumed that the 1 wt.% addition of Ga replaced the 2 wt.% addition of Nd which reacted with Sn in soldered joints, thus no Sn-Nd phase and tin whisker observed after aging treatment. Meanwhile, due to the excessive addition of Ga and Nd, the thickness of IMC layer Sn-Zn-1Ga-2Nd soldered joints after aging treatment was obviously larger than that in soldered joint with the optimal addition.

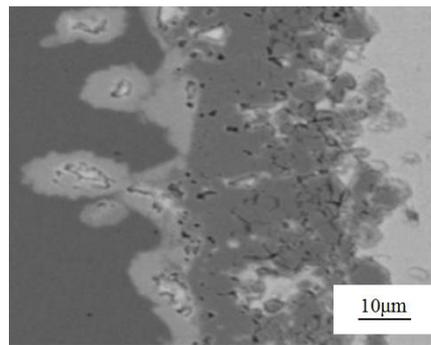
The XRD result of Sn-9Zn-1Ga-2Nd soldered joint, as Figure 6 illustrated, could further verify the result, by replacing Sn-Nd phase to Ga-Nd phase, no obviously Sn-Nd phase or tin whisker growth found near the interface of soldered joint doped with exceeding content of Nd. Considering about the existence of Sn-Zn-Ga-Nd phase, there could be probably little Sn-Nd phase disperse in the interfacial microstructure of soldered joints or the amount of these Sn-Nd phase are too low to be detected after long time aging treatment. Therefore, the risk of tin whisker growth could be significantly reduced with the combined effect of Ga and Nd.

The transformation in the interfacial microstructure would directly affect the mechanical property of soldered joint. Figure 7 showed the shear force of soldered joints after aging treatment, it can be seen that after eliminating the risk of tin whisker growth, the shear force of soldered joint doping excessive addition of Nd and Ga (Sn-Zn-1Ga-2Nd) is lower than Sn-Zn-0.06Nd soldered joint, while

soldered joint with optimal addition (Sn-Zn-0.5Ga-0.08Nd) could maintain preferable performance after long time aging treatment. Compared with SnAgCu and SnPb soldered joints in Table 1, the shear strength of SnZnGaNd soldered joints after long term aging treatment was significantly improved. This phenomenon can be explained as both Ga and Nd are surface activity elements, they can enhance the interface reaction during the soldering process, making the solder and Cu substrate well bonded. However, with excessive addition of Ga and Nd, the results of drastic interface action could cause the formation of a too thick IMC layer which will perform an adverse impact on the reliability of soldered joints.



(a) Sn-9Zn-1Ga-2Nd 120 h (b) EDS result of Sn-Zn-Ga-Nd phase



(c) Sn-9Zn-1Ga-2Nd 1200 h

Figure 5. Interface morphology of soldered joints after composition adjustment.

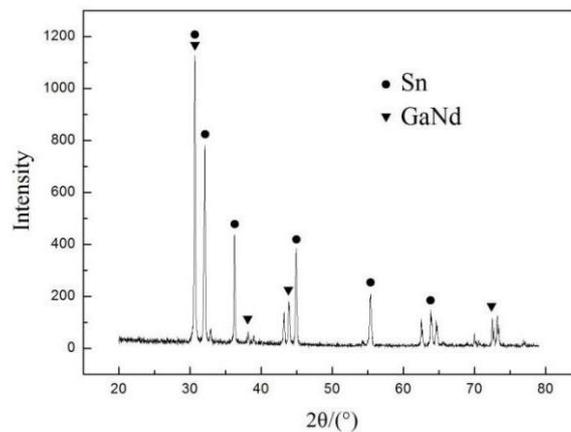


Figure 6. XRD result of Sn-9Zn-1Ga-2Nd soldered joint after 1200 h.

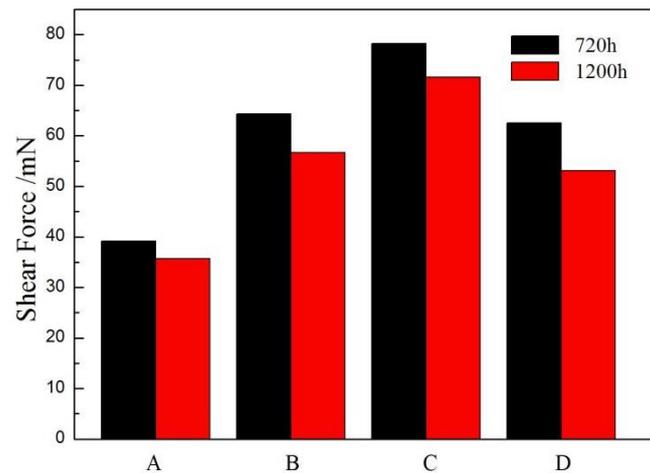


Figure 7. Shear force of soldered joints after aging treatment at 15 °C (A): Sn-9Zn, (B): Sn-9Zn-0.06Nd, (C): Sn-9Zn-0.5Ga-0.08Nd, (D): Sn-9Zn-1Ga-2Nd.

Table 1. Shear force of various soldered joints after aging treatment at 150 °C.

	Shear Strength (mN)					
	Sn9Zn	SnZn-0.06Nd	SnZnGa-0.08Nd	SnZn-1Ga-2Nd	Sn3.8AgCu	Sn63Pb37
720 h	39.13	64.32	78.27	62.55	37.65	27.93
1200	35.71	56.68	71.59	53.12	33.21	25.44

In summary, it can be determined that by controlling the total addition and appropriate ratio of Ga and Nd, Sn-Zn soldered joints with optimal properties and reliability could be obtained without the risk of tin whisker growth. The results would be available for guiding the study of tin whisker growth inhibition method.

4. Conclusions

The tin whisker inhibition in RE-doped Sn-Zn soldered joints was investigated. The morphology and mechanism of tin whisker growth in soldered joints are more complicated than whiskers in solder matrix. Based on the results, the following conclusions can be drawn:

The combined action of Nd and Ga could decrease the growth of the IMC layer in Sn-Zn soldered joints during aging process. The IMC layer maintained relatively regular shape after long time aging treatment and the amount of voids and cracks in IMC layer were decreased.

With the proper addition of Ga and Nd, no obvious NdSn_3 phase nor tin whisker growth observed in the soldered joints, therefore the risk of tin whisker growth caused by the oxidation of RE-phase was significantly inhibited even in soldered joints with additional excessive contents of Nd.

By controlling the total addition and appropriate ratio of Ga and Nd, soldered joints with optimal properties and reliability could be obtained without the risk of tin whisker growth.

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Conflicts of Interest: The authors declare no conflict of interest.

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