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Mechanism of Reaction Between Nd and Ga in Sn-Zn-0.5Ga-*x*Nd Solder

PENG XUE,[1] SONG-BAI XUE,[1,4] YI-FU SHEN,[1] FEI LONG,[2] and HONG ZHU[3]

1.—College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China. 2.—School of Material Science & Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China. 3.—The 14th Research Institute, China Electronics Technology Group Corporation, Nanjing 210013, China. 4.—e-mail: xuesb@nuaa.edu.cn

The mechanism of reaction between Nd and Ga in Sn-Zn-0.5Ga-*x*Nd solder was investigated in order to enhance the reliability of soldered joints. It was found that, after aging treatment at ambient temperature and 125°C for over 3000 h, no Sn whisker growth was observed in Sn-9Zn-0.5Ga-0.08Nd soldered joints. X-ray diffraction (XRD) analysis and thermodynamic calculations indicated that Ga reacted with Nd instead of Sn-Nd intermetallic compound (IMC), eliminating Sn whisker growth. Shear force testing was carried out, and the results indicated that Sn-9Zn-0.5Ga-0.08Nd solder still had excellent mechanical properties after aging treatment. This new discovery can provide a novel approach to develop high-reliability solder without risk of Sn whiskers.

Key words: Sn whisker, Nd, Ga, Sn-Zn-Ga-Nd solder

INTRODUCTION

It is well known that adding rare-earth elements (RE) to lead-free solder is the most useful way to improve the properties of lead-free solders.[1–6] In recent years, many reports have certified that, with moderate addition of RE such as Ce, Pr, and Nd, the wettability and mechanical properties of lead-free solders can be evidently improved.[7–10] However, when the RE addition exceeds a certain value, spontaneous growth of Sn whiskers in lead-free solder appears unavoidable. It has been proved that Sn whiskers are responsible for great losses in satellites, missiles, radars, and other equipment, so addition of rare-earth elements should be strictly controlled.[11–13]

The mechanisms of whisker growth are still unclear. Previous research has shown that the inevitable oxidation of Sn-RE phases would cause high stress accumulation, which would serve as the driving force to induce whisker growth.[14,15] Moreover, it has already been proved that Ga can improve the oxidation resistance and reduce the surface tension of Sn-Zn-based lead-free solders.[16] Based on previous results, we tried to further improve the reliability of solder and seek an alternative route to develop Sn-whisker-free solder by studying the inhibiting effect of Nd and Ga on Sn whisker growth in Sn-9Zn lead-free solder. It was found that, after aging treatment at ambient temperature and 125°C, no Sn whisker growth was observed in Sn-9Zn-0.5Ga-0.08Nd. This new discovery can provide a novel approach to develop Sn-whisker-free solder.

EXPERIMENTAL PROCEDURES

Experimental alloys were made from pure Sn (99.95 wt.%), pure Zn (99.95 wt.%), pure Ga (99.99 wt.%), and pure Nd (99.5 wt.%). Under vacuum atmosphere (10^{-3} torr), a Sn-5Nd master alloy ingot was prepared by melting Sn and Nd at 900°C for about 15 min. Then, the master alloy and pure Ga were added into melted Sn-9Zn alloy and the molten alloy was held for about 5 min while mechanical agitation was performed every 1 min. The melting temperature was controlled below

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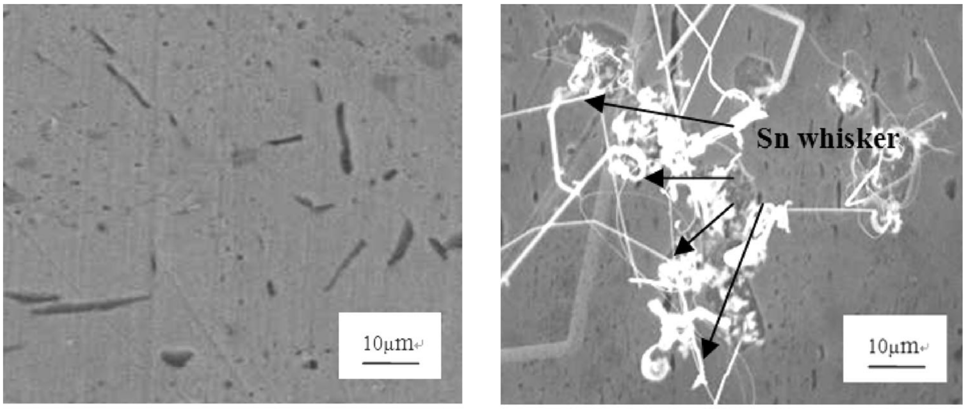
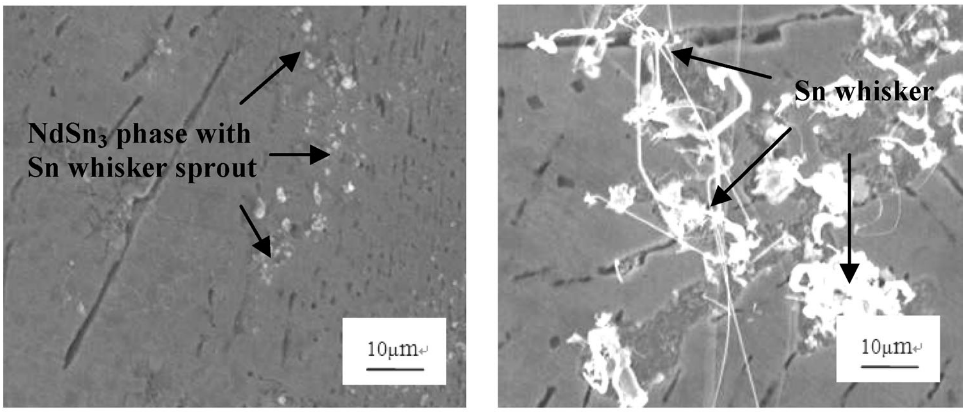


(a) Sn-9Zn-1Nd after 60h at room temperature

(b) Sn-9Zn-1Nd after 720h at room temperature



(c) Sn-9Zn-1Nd after 60h at 125℃

(d) Sn-9Zn-1Nd after 720h at 125℃

Fig. 1. Microstructures of Sn-9Zn-1Nd after aging treatment for (a) 60 h and (b) 720 h at room temperature, and (c) 60 h and (d) 720 h at 125°C.

400°C, and the melted solder was chilled to cast and cut into solder bars of about 40 mm length. The compositions of the alloys were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

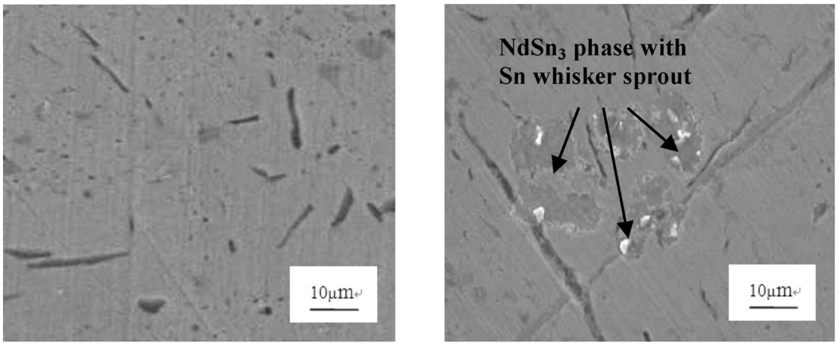
According to US standard MIL-STD-883[17] (Test method military standard for microelectronics[S] Columbus: AMSC N/A, 1990), the samples were placed in an oven maintained at a constant temperature to perform the high-temperature storage (HTS) test. The aging temperature was ambient or 125°C, and the storage (aging) time was 120 h, 1080 h or 3000 h. Before the aging treatment, the samples were prepared by polishing with 0.3-μm Al_2O_3 powder and etched with 4% HNO_3 alcohol solution. Microstructures were observed by scanning electron microscopy (SEM), chemical compositions were determined by energy-dispersive x-ray (EDX) analysis, and phase composition was detected by XRD after aging treatment.

The shear force of the soldered joints was tested at room temperature using an STR-1000 joint strength tester (Rhesca Co., Ltd., Japan) according to Japanese industry standard JIS Z 3198-6:2003.[18] The shear speed was set as 2 mm/min.

RESULTS AND DISCUSSION

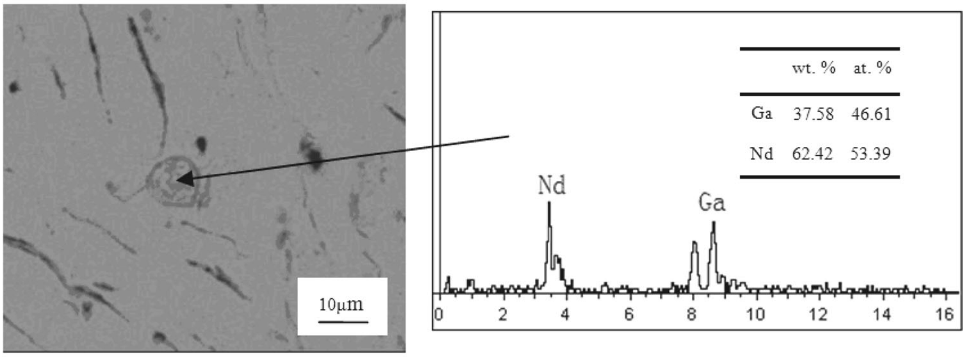
Sn whiskers have been proved to be responsible for billions of dollars of losses in satellites, missiles, radars, and other equipment,[11–13] so research on the mechanisms of Sn whisker initiation and growth is a hot issue. Based on the results of adding different amounts of Nd/Ga to Sn-9Zn solder and after aging treatment for 3000 h at ambient temperature and 125°C, we obtained several new findings from experimental results compared with previous research.

It has been proved that, with excess addition of Nd, $NdSn_3$ phase appears at the solder interface.[19] Figure 1 shows the microstructures of Sn-9Zn-1Nd after aging treatment at ambient temperature and 125°C. It can be observed that Sn whiskers grew continuously with aging time in Sn-9Zn-1Nd. Moreover, massive $NdSn_3$ phase was also observed plus Sn whiskers around the rare-earth phase. The lengths of the longest whiskers could be



(a) Sn-9Zn-0.5Ga-1Nd at at room temperature after 120h

(b) Sn-9Zn-0.5Ga-1Nd at room temperature after 1080h



(c) Sn-9Zn-0.5Ga-1Nd at at room temperature after 3000h

Fig. 2. Microstructures of Sn-9Zn-0.5Ga-1Nd after aging treatment at room temperature for (a) 120 h, (b) 1080 h, and (c) 3000 h.

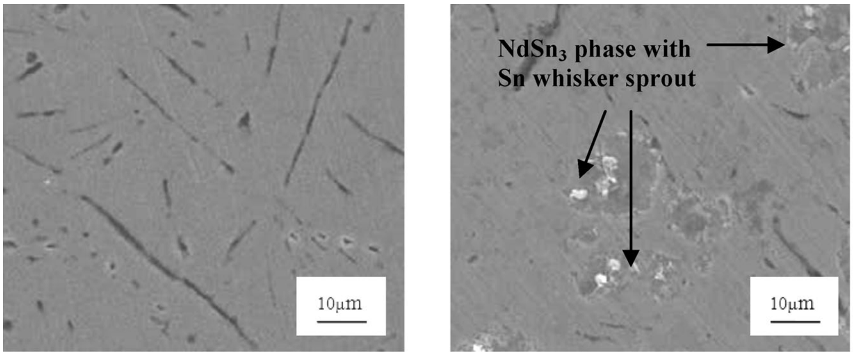
approximately 60 mm. These lengths were longer than 50 mm, which has been chosen as the maximum whisker length at device end-of-life.[20]

Figure 2 shows the microstructure of Sn-9Zn-0.5Ga-1Nd after aging treatment at ambient temperature. Compared with Fig. 1, we can see that fewer Sn whiskers sprouted from $NdSn_3$ in Sn-9Zn-0.5Ga-1Nd until the time was extended to 1080 h and 3000 h, and the amounts of $NdSn_3$ phase decreased significantly. Moreover, Ga-Nd intermetallic compound could be observed under 1000× magnification. Figure 3 shows the microstructures of Sn-9Zn-0.5Ga-1Nd after aging treatment at 125°C. Fewer Sn whiskers can be observed in Sn-9Zn-0.5Ga-1Nd until the aging time was extended to 1080 h and 3000 h, similar to the situation at ambient temperature. As a result, Sn whisker growth was observed in all solders with excessive addition (1 wt.%) of Nd after long-time aging. With addition of 0.5 wt.% Ga, growth of Sn whiskers was retarded.

Figure 4 shows the microstructures of Sn-9Zn-0.5Ga-0.08Nd after aging treatment at ambient temperature and 125°C. From Fig. 4, we can see that, for optimal addition of Ga and Nd, no Sn whisker growth was observed even when the aging time was extended to 3000 h in Sn-9Zn-0.5Ga-0.08Nd. However, comparing Fig. 1 with Fig. 2, one can see that, when adding 0.5 wt.% Ga to Sn-9Zn-1Nd, the $NdSn_3$ phase almost disappeared while Ga-Nd intermetallic compound appeared, causing a decrease of Sn whisker growth.

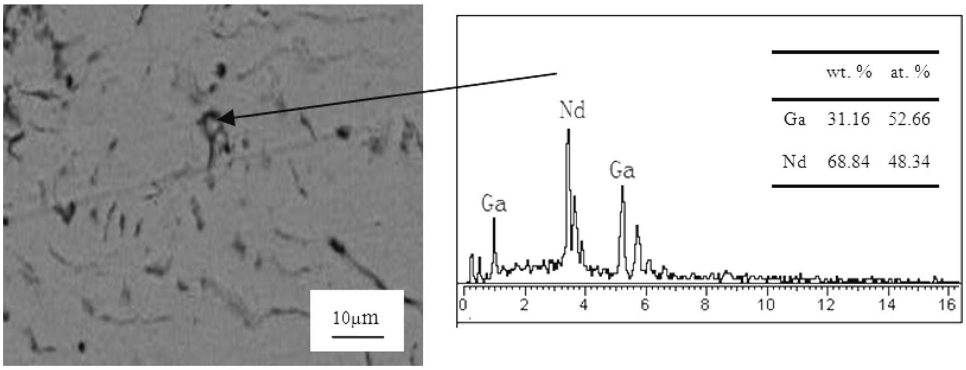
As a surface-active substance, Ga can improve the oxidation resistance and reduce the surface tension of Sn-Zn-based lead-free solder.[16] It has been reported that Ga is highly enriched on the surface of Sn-Pb solders and the degree of Ga enrichment can rapidly reach 34,000-fold for a nominal additive amount.[21] In the present work, we found that Ga-Nd IMC formed instead of $NdSn_3$, because the relative concentration of Ga was higher than that of Sn on the surface of the Sn-9Zn-0.5Ga-1Nd solder.

According to the Ga–Nd phase diagram, the Ga-Nd IMC may be GaNd, $GaNd_3$, Ga_3Nd_5, Ga_2Nd or Ga_5Nd.[22] Figure 5 shows the XRD result for Sn-9Zn-0.5Ga-0.08Nd after aging treatment for 3000 h, from which it can be observed that Ga-Nd IMC did indeed form and replaced the Sn-Nd IMC. Figure 6 shows the EDX result of Ga-Nd IMC in Sn-9Zn-0.5Ga-0.08Nd. The results shown in Figs. 2c, 3c, and 4a–d confirm that, after adding Ga and with Nd addition decreased from 1 wt.% to 0.08 wt.%, the $NdSn_3$ phase was completely replaced by the Ga-Nd IMC, as can be verified from the free energy of formation (ΔG°) data.



(a) Sn–9Zn–0.5Ga–1Nd at 125℃ after 120h

(b) Sn–9Zn–0.5Ga–1Nd at 125℃ after 1080h



	wt. %	at. %
Ga	31.16	52.66
Nd	68.84	48.34

(c) Sn–9Zn–0.5Ga–1Nd at 125℃ after 3000h

Fig. 3. Microstructures of Sn-9Zn-0.5Ga-1Nd after aging treatment at 125°C for (a) 120 h, (b) 1080 h, and (c) 3000 h.

Table I presents free energy data for $NdSn_3$, GaNd, and $GaNd_3$. According to physical chemistry, the more negative the free energy of formation,[23] the more stable a compound is considered to be.

According to the Gibbs free energy equation at constant temperature,

$$\Delta G = \Delta G^\circ + RT\ln J \qquad (1)$$

$$\Delta G = \Delta G^\circ + RT\ln J = -RT\ln J^\circ + RT\ln J. \qquad (2)$$

when the concentrations of Ga and Nd are 0.5 wt.% and 0.08 wt.%, respectively, J can be expressed as

$$J^0 = C^0(GaNd_3)/\left(C^0(Ga) \times C^0(3Nd)\right). \qquad (3)$$

$$\begin{aligned} J &= C(GaNd_3)/(C(Ga) \times C(3Nd)) \\ &= 0.0267/(34,000 \times 0.5 \times 3 \times 0.0267) = 1/51,000. \end{aligned} \qquad (4)$$

$$\begin{aligned} \Delta G^\circ\#_{(GaNd_3)} &= \Delta G^\circ_{(GaNd_3)} + RT\ln J \\ &= -RT\ln J^0 + RT\ln J. \end{aligned} \qquad (5)$$

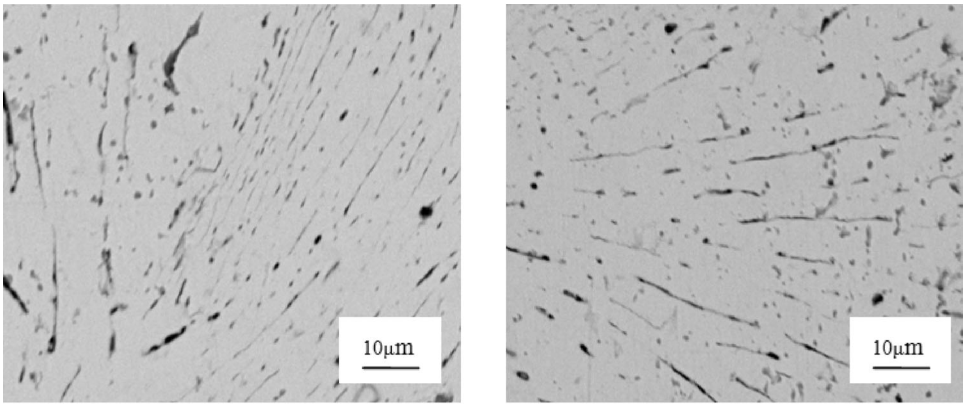
So, we can calculate the $\Delta G^\circ\#$ value of $GaNd_3$ as

$$\begin{aligned} \Delta G^\circ\# &= \Delta G^\circ + RT\ln J = -260.95 + 8.314 \\ &\quad \times (273 + 240) \times \ln(1/51,000) \\ &= -307.18\,\text{kJ/mol}. \end{aligned} \qquad (6)$$

The $\Delta G^\circ\#$ value of GaNd is

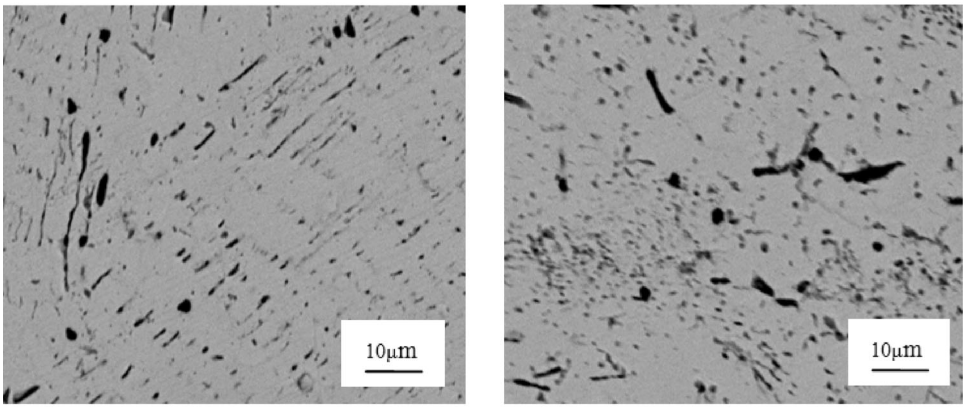
$$\begin{aligned} \Delta G^\circ\# &= \Delta G^\circ + RT\ln J = -178.14 + 8.314 \\ &\quad \times (273 + 240) \times \ln(1/17,000) \\ &= -224.370\,\text{kJ/mol}. \end{aligned} \qquad (7)$$

As shown in Table I, the negative ΔG° value of $GaNd_3$ (in the normal concentration state) approaches the ΔG° value of $NdSn_3$, while the $\Delta G^\circ\#$ value of $GaNd_3$ (in the enriched concentration state) is much larger than the ΔG° value of $NdSn_3$, meaning that $GaNd_3$ rather than $NdSn_3$ formation is favored during the soldering process. Due to the Ga enrichment effect, the negative $\Delta G^\circ\#$ value of GaNd (in the enriched concentration state) is greatly increased and approaches the ΔG° value of $NdSn_3$, promoting GaNd formation. From the XRD results shown in Fig. 5, one can see that GaNd and $GaNd_3$ IMCs formed instead of $NdSn_3$ IMC.



(a) Sn–9Zn–0.5Ga–0.08Nd at room temperature after 1080h

(b) Sn–9Zn–0.5Ga–0.08Nd at room temperature after 3000h



(c) Sn–9Zn–0.5Ga–0.08Nd at 125℃ after 1080h

(d) Sn–9Zn–0.5Ga–0.08Nd at 125℃ after 3000h

Fig. 4. Microstructures of Sn-9Zn-0.5Ga-0.08Nd after aging treatment for (a) 1080 h and (b) 3000 h at room temperature, and (c) 1080 h and (d) 3000 h at 125°C.

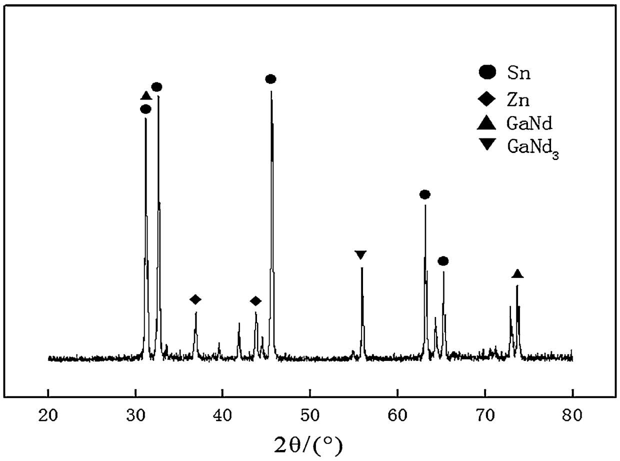


Fig. 5. XRD result of Sn-9Zn-0.5Ga-0.08Nd after aging treatment for 3000 h.

It has been reported that Sn-RE IMCs such as $NdSn_3$ easily induce Sn whisker growth.[14,15] However, unlike Sn-Nd IMC, Ga-Nd IMCs cannot feed Sn atoms to promote Sn whisker growth. In Sn-9Zn-0.5Ga-0.08Nd solder with optimal Nd addition, we believe that Ga reacted with all the content of Nd and totally eliminated the formation of $NdSn_3$, thus inhibiting Sn whisker growth. Meanwhile, in Sn-9Zn-0.5Ga-1Nd solder with excessive Nd addition, only part of the Nd reacted with Ga while the rest of the Nd formed $NdSn_3$, finally inducing Sn whisker growth.

Figure 7 shows the shear force of the Sn-Zn-0.5Ga-0.08Nd soldered joint after aging treatment. The shear force of the Sn-Zn-0.5Ga-0.08Nd soldered joint was further increased compared with Sn-Zn-0.06Nd, being remarkably higher than that of the original Sn-9Zn soldered joint. Moreover, the shear force of the Sn-Zn-0.5Ga-0.08Nd soldered joint decreased with aging time, although more slowly than for the Sn-Zn-0.06Nd and Sn-9Zn soldered joints. In particular, the shear force of the Sn-Zn-0.5Ga-0.08Nd soldered joint after aging treatment for 1080 h remained higher than that of the original as-soldered Sn-9Zn joint.

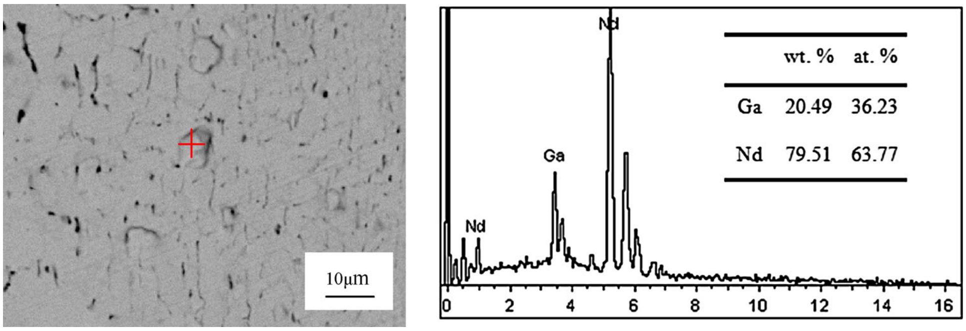


Fig. 6. EDX result of Ga-Nd IMC in Sn-9Zn-0.5Ga-0.08Nd.

Table I. Free energy data for RE compounds ($\Delta G°\#$ calculated supposing Ga concentration enrichment of 34,000-fold)

Compound	$\Delta G°$	Compound (Normal Concentration State)	$\Delta G°$	Compound (Enriched Concentration State)	$\Delta G°\#$
$NdSn_3$	−270.02	$GaNd_3$	−260.95	$GaNd_3$	−307.18
		GaNd	−178.14	GaNd	−224.37

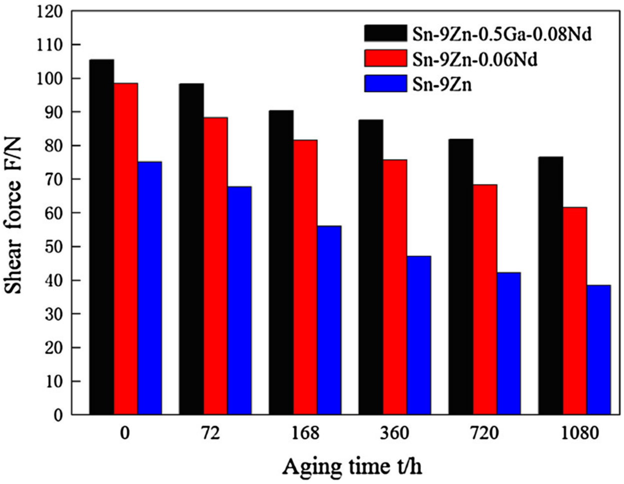


Fig. 7. Shear force of Sn-Zn-Ga-0.08Nd at different aging times.

In industrial production, increasing attention is being paid to optimal RE addition. In this case, Sn-9Zn-0.5Ga-0.08Nd solder was absolutely sufficient to meet the requirements of the electronics industry. In particular, our experimental results and theoretical analysis confirm that formation of GaNd and $GaNd_3$ IMCs to replace Sn-Nd IMC is the key factor inhibiting Sn whisker growth. This new discovery of Sn-9Zn-0.5Ga-0.08Nd solder provides a novel approach to develop Sn-whisker-free solder.

CONCLUSIONS

1. Ga can disperse Nd in Sn-9Zn-0.5Ga-*x*Nd solder to avoid $NdSn_3$ formation, thus reducing the risk of Sn whisker growth. Without feeding of Sn atoms, no obvious spontaneous Sn whisker growth was observed in Sn-9Zn-0.5Ga-*x*Nd after aging treatment.
2. Experimental results indicated that, in Sn-9Zn-0.5Ga-0.08Nd solder, GaNd and $GaNd_3$ IMCs formed and no Sn whisker growth was observed. The results of XRD and EDX analyses indicate that the key factor for Sn whisker growth inhibition in Sn-9Zn lead-free solder is the formation of GaNd and $GaNd_3$ IMCs to replace Sn-Nd IMC.
3. According to the theory of IMC free energy of formation, it was verified that, due to the Ga enrichment on the surface of the Sn-9Zn-0.5Ga-0.08Nd solder, the negative value of $\Delta G°\#$ of $GaNd_3$ is much larger than that of $NdSn_3$ while the $\Delta G°\#$ of GaNd is close to the $\Delta G°$ value of $NdSn_3$, so GaNd and $GaNd_3$ rather than $NdSn_3$ IMC formation is favored.
4. Shear force testing was carried out, and the results indicated that the Sn-9Zn-0.5Ga-0.08Nd soldered joint still had excellent mechanical properties after aging treatment. These results demonstrate a novel approach to develop high-reliability, Sn-9Zn-0.5Ga-0.08Nd solder without risk of Sn whisker formation.

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