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Improvement of mechanical properties of Sn−58Bi alloy with multi-walled carbon nanotubes

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Abstract: Carbon nanotubes (CNTs) reinforced Sn−58Bi composites were successfully fabricated through ball-milling method and low temperature melting process. The influence of multi-walled carbon nanotubes (MWCNTs) on the mechanical strength and ductility of Sn−58Bi lead-free alloy was studied. The mechanical test results show that the bending strength of Sn−58Bi−0.03CNTs (mass fraction, %) composite is increased by 10.5% than that of the Sn−58Bi alloy, which can be attributed to the reduction of Sn-rich segregation and the grain refinement. The toughness of Sn−58Bi−0.03CNTs composite is increased by 48.9% than that of the matrix materials. It is indicated that the influence of CNTs on the strength of Sn−58Bi−*x*CNTs composite is insignificant. In addition, the fracture mechanism of CNTs reinforced Sn−Bi composite was analyzed. The corresponding fracture surface comparison between the Sn−58Bi−0.03CNTs composite and the monolithic Sn−58Bi alloy was made to identify the influence of CNTs on the fracture behavior and the reinforcing effect of CNTs.

Key words: carbon nanotubes; metal-matrix composites; mechanical properties; fracture mechanism

1 Introduction

For the past few years, the investigation of the carbon nanotubes (CNTs) functionalized Sn−Ag−Cu composite showed that the CNTs which distributed around the Ag_3Sn compounds can improve the mechanical properties of the composite, such as micro hardness and tensile strength [1−3]. Carbon nanotubes functionalized 63Sn−37Pb solder was synthesized by powder metallurgy methods. Mechanical properties of the composites showed that the ultimate tensile strength is increased by 30% with the 0.3% (mass fraction) addition of CNTs [4].

Sn−58Bi alloy is considered as an alternative substitute for Sn−Pb solders and an ideal step solder for applications with Sn−Cu−Ag candidate solders, because of its low melting temperature (139 °C), excellent flowability and good oxidation resistance [5−11]. Therefore, it is suitable for use in microelectronic packaging industry. Moreover, it has been found that the thermal shock resistance, creep resistance and tensile strength of the Sn−58Bi solder are higher than that of the eutectic Sn−Pb solder [11]. However, the elongation of Sn−58Bi alloy is lower than that of Sn−Ag−Cu and Sn−Pb alloys. Thus, it is urgent to discover how to improve its ductility. Several reports have indicated that addition of small amounts of elements, such as Ag, Cu and rare earth elements, is an effective way to refine the microstructure and improve the properties [5, 6, 11]. However, the influence of CNTs on the mechanical properties and the micro-fracture mechanisms of Sn−58Bi alloy has not been discussed. Thus, in the present work, CNTs were attempted to incorporate into

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Sn−58Bi alloy to fabricate Sn−58Bi−CNTs composite. The effects of CNTs on the mechanical properties, including tensile test properties and bending test properties were investigated. The strengthen mechanism of CNTs and its influence on the micro-fracture mechanism of the composite were also discussed.

2 Experimental

Commercial gas-atomized Sn−58Bi alloy powder with the diameter ranging from 25−75 μm was used as the metal matrix material. The average diameter and the length of the multi-walled CNTs (CNano Co. Ltd.) were 11 nm and 10 nm, respectively. Various systems of Sn−58Bi powder with 0, 0.03%, 0.06%, 0.1% CNTs (mass fraction) were pre-weighted and then mechanically mixed by ball milling method in an argon atmosphere, then Sn−58Bi−*x*CNTs composites were obtained after heating at 180 °C for 60 s under the cover of molten organic salt.

The three-point bending tests, applying on rectangular bend specimens of 16 mm×4.5 mm×0.6 mm, were conducted on an electron-mechanical universal material testing machine (Instron 1186), which was produced by Instron Limited. The bending rate was 2 mm/min.

For tensile tests, the composite alloys were cut into pieces with the dog-bone shape using electrical discharge wire-cutting process. A dog-bone tensile specimen is shown in Fig. 1. The ambient temperature tensile tests were conducted on electron-mechanical universal material testing machine (Instron 1186) with a tensile rate of 1 mm/min. The microstructure characterization was carried out on the fracture surface of the tested Sn−58Bi−CNT composite with field emission scanning electron microscope (QUANTA 200F, FEI). The average value of the tensile strengths and the elongations were determined from three tests of tensile samples that were achieved under the same condition.

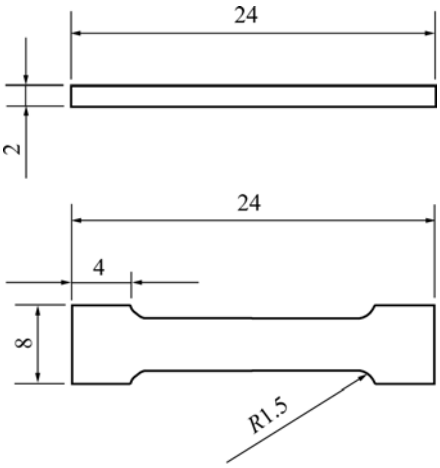

Fig. 1 Schematic diagram of tensile specimens (Unit: mm)

3 Results

3.1 Bending strength of Sn−58Bi−*x*CNTs composite

The bending strength of Sn−58Bi−*x*CNTs composite is given in Table 1. Compared with the Sn−58Bi alloy, the bending strength of Sn−58Bi−0.03%CNTs composite is increased by 10.5%. However, the bending strength of composites is decreased with the increase of CNTs contents.

Table 1 Bending strength of Sn−58Bi−*x*CNTs composite

Material	Bending strength/MPa
Sn−58Bi	167.68±2.8
Sn−58Bi−0.03CNTs	184.12±3.5
Sn−58Bi−0.06CNTs	170.76±3.2
Sn−58Bi−0.10CNTs	159.58±2.1

3.2 Tensile test results of Sn−58Bi−*x*CNTs composite

The tensile test results are given in Table 2. The results show that the influence of CNTs on the strength of Sn−58Bi−*x*CNT composite is insignificant. The elongation measurements reveal an increasing trend of the elongation with the increase of the CNTs content. Compared with Sn−58Bi alloy, the elongation of Sn−58Bi−0.03%CNTs composite is increased by 48.90%. However, when the addition of CNTs content exceeds 0.03%, the elongation of the composite samples decreases. A proper addition of CNTs will improve the elongation of the Sn−58Bi, which is inconsistent with the reported results in Refs. [1−4].

Table 2 Mechanical properties of monolithic and composite alloy

Material	Ultimate tensile strength/MPa	Elongation/%
Sn−58Bi	91.65±3.9	14.56±1.2
Sn−58Bi−0.03CNTs	94.24±3.0	21.68±0.9
Sn−58Bi−0.06CNTs	93.16±2.2	20.95±1.0
Sn−58Bi−0.10CNTs	93.00±2.1	18.39±0.8

4 Discussion

4.1 Influence of CNTs on bending property of Sn−58Bi−*x*CNTs composite

Figure 2 shows the microstructures of Sn−58Bi alloy and Sn−58Bi−0.03CNTs composite. It displays that Sn−58Bi alloy consists of the lamellar eutectic and Sn-rich dendrite phases. When the addition of CNTs content is 0.03%, the number of dendrites of composite decreases significantly. Furthermore, the microstructure of the composite becomes finer with the presence of CNTs which can hinder the growth of the grains. As a consequence, the bending strength increases because of the refinement of the Bi-rich phase. Moreover, since the eutectic lamellar space becomes smaller, the deformation of the composite becomes uniform. Finally, the thermal expansion coefficient mismatch of CNTs (-5.86×10^{-9}/K) and Sn−58Bi (1.5×10^{-6}/K) can bring dislocations which will punch at the interface [12,13]. The high dislocation density would also increase the bending strength of the composites.

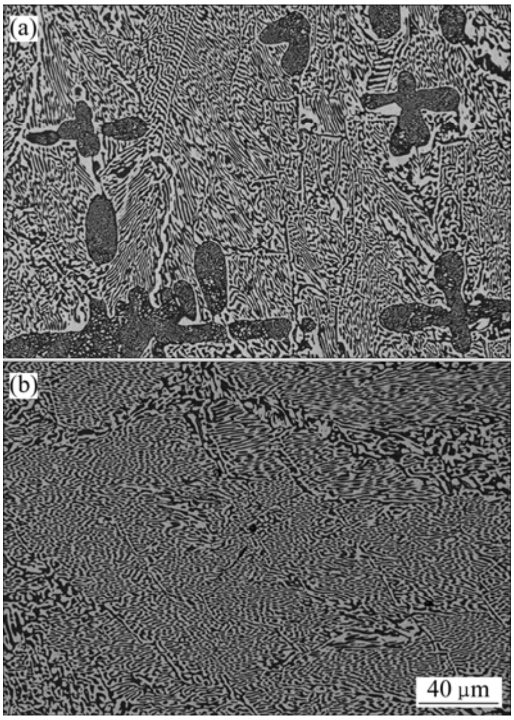

Fig. 2 Microstructure of composites: (a) Sn−58Bi; (b) Sn−58Bi−0.03CNTs composite

4.2 Influence of CNTs on tensile property of Sn−58Bi−*x*CNTs composite

The fracture surface of the Sn−58Bi−CNTs composite after tensile test has revealed the detailed fracture features. Due to the brittleness of the Bi-rich layer in Sn−58Bi alloy, there is no obvious plastic deformation behavior in the fracture surface, as shown in Fig. 3.

Figure 4 shows the high magnification images of the fracture surface of the Sn−58Bi−0.03CNTs composite sample. It indicates the presence of CNTs. Furthermore, the pseudo-dimples were observed in the fracture surface. CNTs are wrapped with the molten alloy and exist between the grain boundaries. The CNTs are at the edges of the pseudo-dimples. During the fracture process, CNTs were pulled out from the matrix alloy leading to the presence of pseudo-dimple which can elongate the micro-crack and increase the fracture area dramatically. Therefore, the toughness of the composite is improved. The existence of the pseudo-dimple indicates that the interface between the Sn−58Bi alloy and CNTs is strongly bonded.

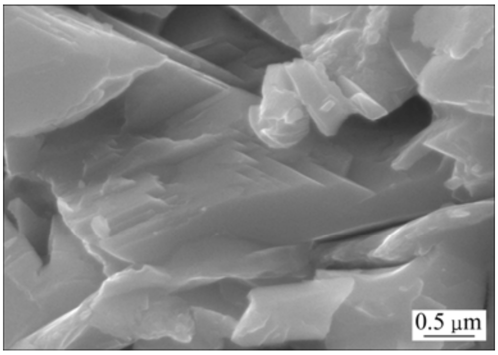

Fig. 3 Fracture surface of Sn−58Bi alloy

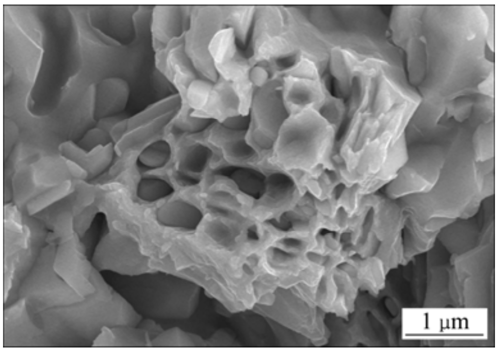

Fig. 4 Pseudo-dimple in Sn−58Bi−0.03%CNTs alloy

As shown in Fig. 5, it is indicated that the end of CNTs is pinned at the grain boundary. The “pinning effect” of CNTs would make a contribution to the fracture strength during fracture tests. The CNTs in the grain boundaries can inhibit the grain slipping during fracture test and improve the tensile strength. In addition, when the tensile stress is conducted on the composite, the CNTs, closing to the crack tip, are pulled out along the interfaces during fracture process. The pulling effect releases the stress at the crack tip and thereby hinders the crack growth.

The addition of CNTs introduces the bridging mechanism in the brittleness Bi-based solder matrix, as shown in Fig. 6. It would be beneficial for improving the interface bonding. Because of the high degree of orientation of carbon nanotubes, the interface dislocation was difficult to happen. The direction of crack propagation can only be the original direction. The CNTs closing to the crack tip would not break and thus erects as a bridge between the cracks. Therefore, the compressive stress at the crack surface will resist against the tensile stress, making the crack difficult to extend. As a result, the CNTs suffer significant stress by sharing a portion of the load and also make the matrix stronger by a bridging effect [14,15].

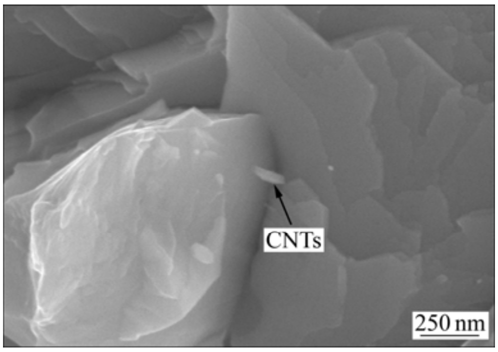

Fig. 5 CNTs inhibiting cracking of grain boundary of Sn−58Bi−0.03CNTs alloy

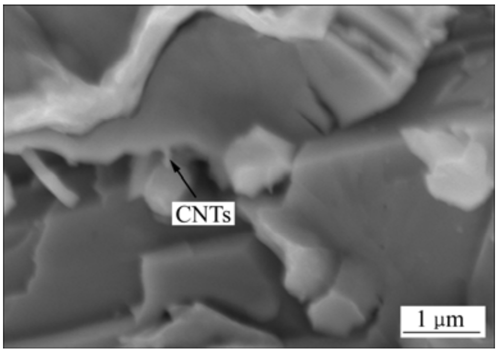

Fig. 6 Influence of CNTs on fracture mode of Bi rich phase in Sn−58Bi−0.03CNTs alloy

The presence of CNTs embedded in the matrix can produce a large number of cleavage steps, as shown in Fig. 7. The increase of disorder of the new generated cleavage stage can provide more fracture area and thus hinder the crack propagation. Consequently, the toughness of the composite can be improved.

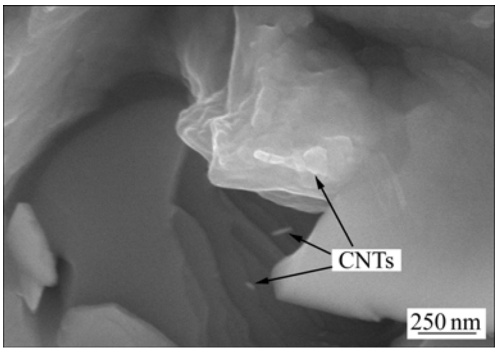

Fig. 7 Cleavage steps provided by CNTs in Sn−58Bi−0.03CNTs alloy

4.3 Effect of content of carbon nanotubes on properties of Sn−58Bi alloy

Based on the above results, with the increase of CNTs content from 0.03% to 0.06%, the strength and toughness of composites decrease. As shown in Fig. 8, compared to the microstructure of Sn−58Bi−0.03%CNTs composite, the grains of Sn−58Bi−0.06CNTs are much more coarse. In addition, degradation of the mechanical properties could be associated to the higher level of micro porosity observed at higher mass fraction of CNTs [1].

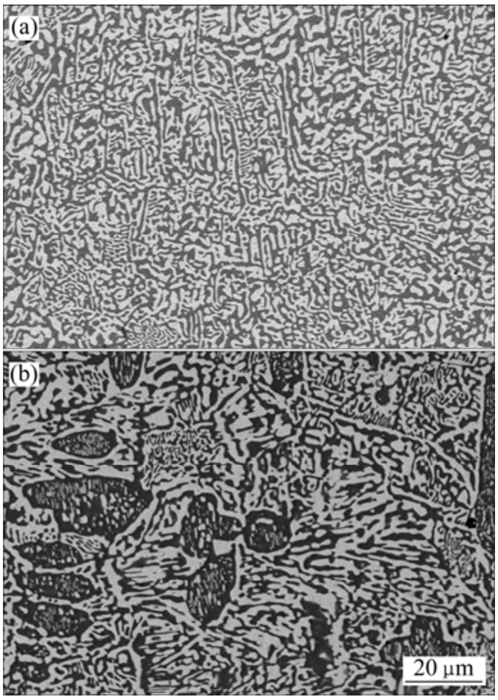

Fig. 8 Microstructuress of Sn−58Bi−0.03CNTs (a) and Sn−58Bi−0.06CNTs (b)

5 Conclusions

1) Both the bending strength and the elongation of Sn−58Bi alloy have been successfully enhanced by incorporation of Sn−58Bi alloy and CNTs with ball milling method and low temperature melting process. The mechanical strength and elongation of Sn−58Bi−0.03CNTs composite are higher than those of the composites with higher CNTs content, which is attributed to the reduction of Sn-rich segregation and the grain refinement.

2) The toughness of Sn−58Bi−0.03CNTs composite is increased by 48.9% than that of the matrix materials.

3) The presence of CNTs leads to the phenomenon of “pseudo-dimple”, “pinning effect” and “bridging effect”, which greatly influence the fracture behavior and thus improve the mechanical properties of Sn−58Bi−*x*CNTs composite.

References

[1] NAI S M L, WEI J, GUPTA M. Effect of carbon nanotubes on the shear strength and electrical resistivity of a lead-free solder [J]. Journal of Electronic Materials, 2008, 37(4): 515−522.

[2] NAI S M L, WEI J, GUPTA M. Lead-free solder reinforced with multi-walled crabon nanotubes [J]. Journal of Electronic Materials, 2006, 35(7): 1518−1522.

[3] KUMAR K M, KRIPESH V, TAY A A O. Single-wall carbon nanotube (SWCNT) functionalized Sn−Ag−Cu lead-free composite solders [J]. Journal of Alloys and Compounds, 2008, 450(1−2): 229−237.

[4] KUMAR K M, KRIPESH V, TAY A A O. Influence of single-wall carbon nanotube addition on the microstructural and tensile properties of Sn−Pb solder alloy [J]. Journal of Alloys and Compounds, 2008, 455(1−2): 148−158

[5] SU G K, SAKAI T, KIM K. Influence of Ag addition to Sn−Bi eutectic alloy on microstructure and on mechanical properties [J]. Journal of Japan Institute of Electronics Packaging, 2003, 6(5): 414−419.

[6] HISAAKI T, AKIRA Y, HIDEO H. Mechanical properties and solder joint relaibility of low-melting Sn−Bi−Cu lead free solder alloy [J]. R&D Review of Toyota CRDL, 2004, 39(2): 49−56.

[7] ZHANG Q K, ZOU H F, ZHANG Z F. Improving tensile and fatigue properties of Sn−58Bi/Cu solder joints through alloying substrate [J]. Materials Research Society, 2010, 25(2): 303−314.

[8] WANG J H, WEN L, ZHOU J W, CHUNG M. Mechanical properties and joint reliability improvement of Sn−Bi alloy [C]//Electronics Packaging Technology Conference. Singapore: IEEE, 2011, 13: 492−496.

[9] ZHAI Q J, GAO Y L, GUAN W B, XU K D. Role of size and cooling rate in quenched droplet of SnBi eutectic alloy [J]. Materials Science and Engineering A, 2006, 441: 278−281.

[10] LIANG Kun, TANG Xian-zhong, YU Li-jing, WANG Ni, HU Wen-cheng. Investigation of preparation and characteristics of Sn−Bi eutectic powders derived from a high shear mechanical approach [J]. Journal of Alloys and Compounds, 2011, 509(41): 9836−9841.

[11] DONG Wen-xing, SHI YAO-wu, XIA Zhi-dong, LEI Yong-ping, GUO Fu. Effects of trace amounts of rare earth additions on microstructure and properties of Sn−Bi-based solder alloy [J]. Journal of Electronic Materials, 2008, 37(7): 982−991.

[12] MANIWA Y, FUJIWARA R, KIRA H, TOU H, KATAURA H, SUZUKI S, ACHIBA Y, NISHIBORI E, TAKATA M, SAKATA M, FUJIWARA A, SUEMATSU H. Thermal expansion of single-walled carbon nanotube (SWNT) bundles: X-ray diffraction studies [J]. Physical Review B, 2001, 64(24): 1402−1404.

[13] XU Jun, HU Qiang, LIN Gang, ZHANG Fu-wen. Low temperature lead-free solder and its developing tendency [J]. Electronics Process Technology, 2009, 30(1): 1−4. (in Chinese)

[14] SHAO J C, XIAO B L, WANG Q Z, MA Z Y, YANG K. An enhanced FEM model for particle size dependent flow strengthening and interface damage in particle reinforced metal matrix composites [J]. Composites Science and Technology, 2011, 71: 39−45.

[15] GEORGE R, KASHYAP K T, RAHUL R, YAMDAGNI S. Strengthening in carbon nanotubes/aluminium (CNT/Al) composites [J]. Scripta Materialia, 2005, 53(10): 1159−1163.

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