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Investigation on properties of Sn–8Zn–3Bi lead-free solder by Nd addition

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ABSTRACT

In this paper, effects of a rare earth element (neodymium) on the properties of the Sn–8Zn–3Bi alloys were investigated. Spreading test and wetting balance method were used to display the wettability of the Sn–8Zn–3Bi–*x*Nd alloys. Results showed that addition of Nd improved the wettability of the Sn–8Zn–3Bi alloys in air condition. Maximum bubble pressure measurement was employed to evaluate surface tension of the solder melts. It was found that the surface tension of the solder melts at the temperature between 200 °C and 240 °C decreased with the Nd addition, which was considered as one of the reasons for the improvement of wettability. Another cause of the improved wettability would be the decrease of oxidation at the solder melts surface. Thermo-gravimetric analysis (TGA) was used to demonstrate the effect of Nd addition on the oxidation resistance of the solder melts, and Auger Electron Spectra (AES) analysis was applied to investigate the oxidation process. The results indicate that formed Nd_2O_3 at the surface of the solders delayed oxygen atoms diffusing into the solders. Moreover, the ultimate tensile strength (UTS) of the solder increased to 97 MPa with addition of 0.1 wt% Nd, and the elongation of the alloy approached 30%.

1. Introduction

Due to environmental and health concerns, a variety of new lead-free solders have been developed to eliminate the usage of Sn–Pb solders in electronic industry in recent years [1,2]. Sn–Zn-based alloys are considered to be very promising candidates for their substantially same melting points as Sn–Pb solder, excellent mechanical properties and low cost [3–5]. Sn–8Zn–3Bi alloy is the typical one with acceptable comprehensive properties and has already been used in commercial products. But wettability and oxidation resistance of the alloy used in air condition are not satisfactory enough for its extensive use [6,7]. Two factors have been considered responsible for the unsatisfactory wettability of the Sn–Zn solders. The first one is that the surface tension of the alloys is excessively high. Although Bi additive can decrease the surface tension, the alloys with a small amount Bi (≤3 wt%) hardly obtain the same surface tension with the Sn–Pb solders. Otherwise, massive ZnO formed at the surface of the solders usually prevents the solder melts from spreading out or wetting on substrate surface [8–10]. The main objective of this work is to demonstrate the effect of the fourth additive Nd on the surface tension and the oxidation resistance of Sn–8Zn–3Bi solders, and to find out the way to improve the wettability of the solders. Additive Bi into Sn–Zn alloys leads to loss of the ductility, but the elongation of the alloys is desired to improve with the addition of Nd.

2. Experimental procedures

The amount of alloying elements is very little, especially for the rare earth element Nd. In order to reduce the burning loss, two steps were taken to melt the alloys. Firstly, Sn–5Nd master alloy ingots were prepared by melting Sn and Nd in N_2 atmosphere at 720 °C for 20 min. Composition analysis was carried out by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Secondly, the master alloy, Zn and Bi were added into the molten Sn. To obtain the homogenous alloys, the mixture was stirred continuously. The melting temperature was controlled below 450 °C. To reduce burning loss, the whole melting process was as short as possible. The designed chemical compositions of the alloys studied in this paper are given in Table 1.

Spreading test was conducted in air at 240 °C, and complied with GB11364-89. Wetting balance tests were performed with SAT-5100 of Rhesca Co. As shown in Fig. 1, the piece was suspended from a sensitive balance. It was immersed at a predetermined speed before the end of it reached a controlled depth into the solder melt at a specific temperature. The resultant vertical force of buoyancy and wetting force of the Cu piece could be detected by a transducer and recorded. Wettability was determined by the examination of the vertical forces as a function of time. In the present experiments, the Cu piece was immersed at a speed of 20 mm s^{-1}, before the immersion depth reached to 2 mm. After keeping it for 5 s, the Cu piece was taken out. A middle active rosin flux (RMA) was used in the wetting balance experiments.

Maximum bubble pressure measurement was employed to evaluate surface tension of the solder melts. Fig. 2 shows the process of forming a bubble. At the end of the tubule, curvature radius (r) of the bubble decreased firstly with the increasing of pressure difference (ΔP) between inside and outside of the bubble. After r reached the radius of the tubule (R), r increased with the volume increasing of the bubble, and ΔP decreased. So the following relation could be proposed by Laplace formula ($\Delta P_{max} = 2\sigma/R$), where σ was the surface tension of the melt. If the end of the tubule was just immerged in the melting solder, ΔP could be displayed by the pressure gauge. σ could be expressed by the equation $\sigma = R\Delta P_{max}/2$.

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Table 1
The designed chemical compositions of alloys (wt%).

Alloy no.	Zn	Bi	Nd	Sn
1	8	3	–	Bal.
2	8	3	0.05	Bal.
3	8	3	0.10	Bal.
4	8	3	0.15	Bal.

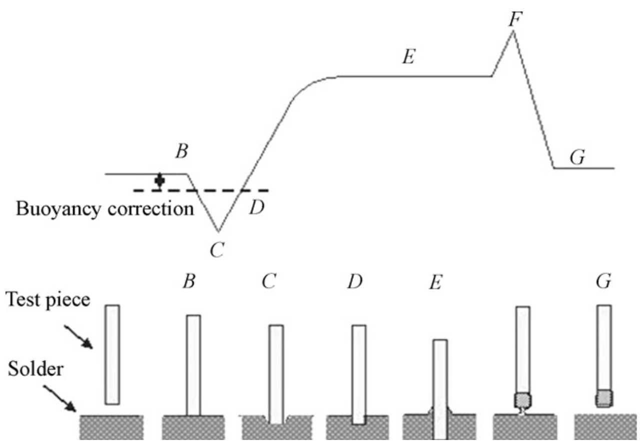

Fig. 1. A schematic diagram of wetting balance measurement.

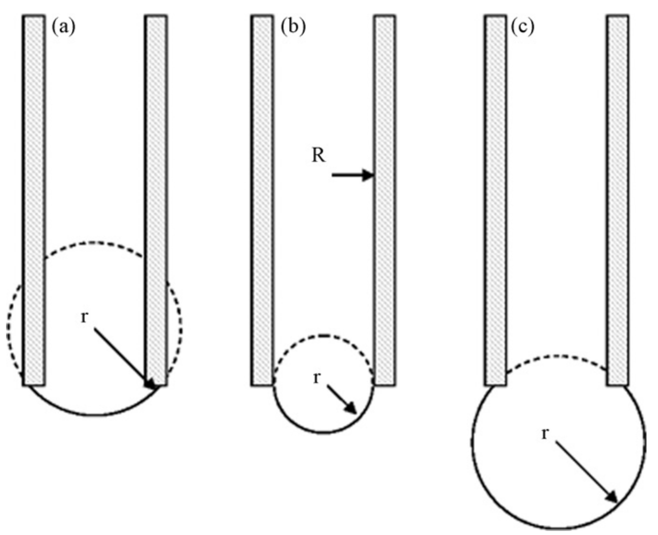

Fig. 2. A schematic diagram of a bubble in forming.

The oxidation behavior was examined by a thermo-gravimetric analyzer (TGA) in a TA DMTA-Q600 for 10 mg powder samples. Heating was carried out at rate of 5 °C/min from 170 °C to 240 °C in air, then insulation for 10 min. The oxides formed at surface of the solder alloys were determined with Auger Electron Spectra (with AES-350 of ANELVA Co.). During depth profile analysis of AES, Ar^+ ion beam with 3.0 keV energy was used to sputter the sample surface. The Ar^+ ion beam was incident at an angle of 30° with respect to the sample surface. The beam of Ar^+ ions was focused to a 1 mm × 1 mm area and the sputtering rate was about 5 nm/min.

The tensile specimen is shown in Fig. 3, and the tensile tests were carried out at room temperature with a strain rate of 10^{-5} s^{-1}.

3. Results and discussion

3.1. Wetting behaviors

The addition of Nd has improved the wettability of Sn–8Zn–3Bi solders on Cu substrate. As shown in Fig. 4, the spreading area

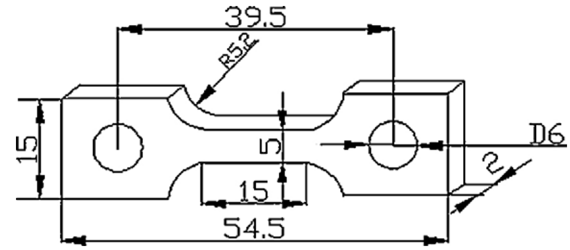

Fig. 3. Schematic illusion of tensile test for specimens.

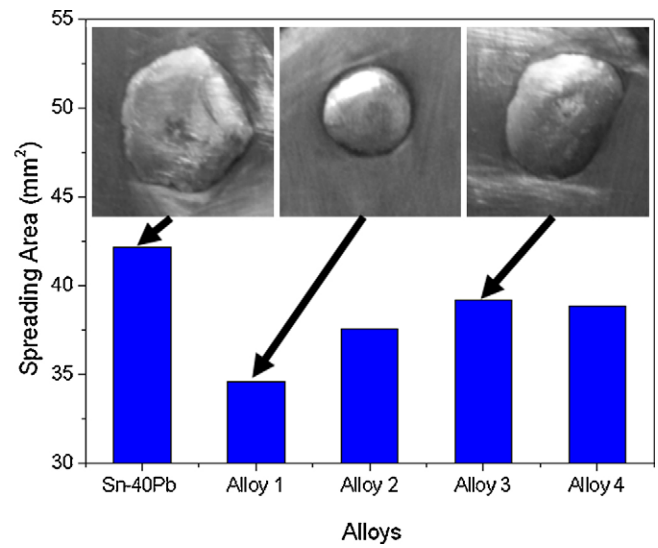

Fig. 4. The spreading area as a function of Nd concentration.

Table 2
Spreading areas of solder alloys (mm^2).

	Alloy no.				Sn–40Pb
	1	2	3	4	
Spreading area	34.6	37.6	39.6	38.9	42.2

increases with Bi concentration from 0.05 wt% to 0.10 wt%. By doping 0.10 wt% Nd into the alloy, the solder obtains the maximum spreading area (39.6 mm^2). The results of spreading test are given in Table 2. It is close to the spreading ability of the Sn–40Pb solder

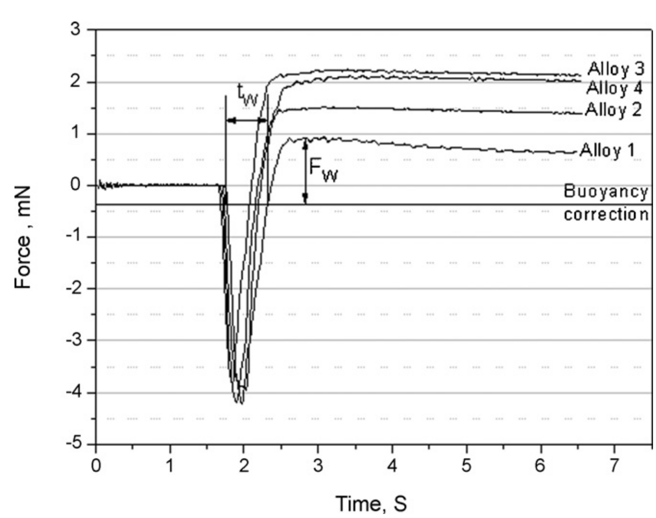

Fig. 5. The wetting balance curves of Sn–8Zn–3Bi–(0–0.15)Nd.

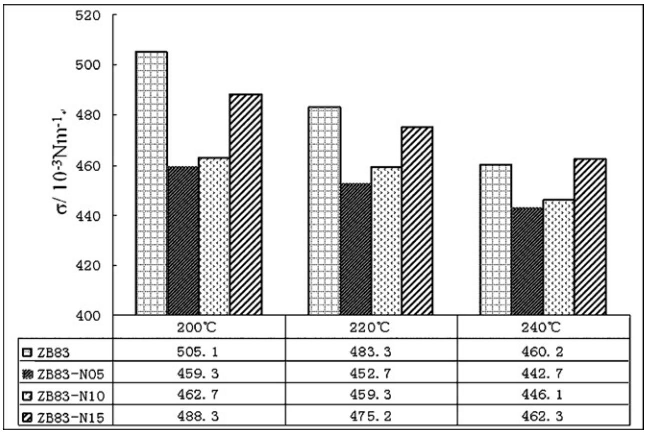

Fig. 6. The surface tension of Sn–8Zn–3Bi–*x*Nd melts as a function of temperature.

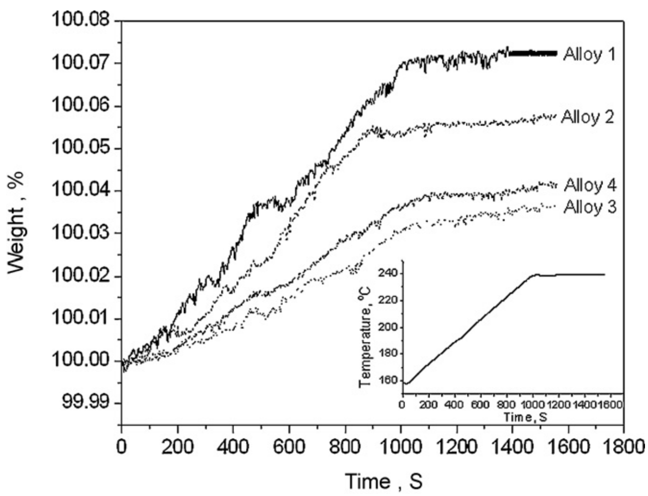

Fig. 7. TGA curves for Sn–Zn–Bi–*x*Nd solders showing formation of oxide at surface (heating the solders from 160 °C to 240 °C, then holding the solders at 240 °C for 600 s).

(42.2 mm^2). When the concentration of Nd reaches 0.15 wt%, the effect of Nd on spreading area is detrimental.

The contact angle θ between solder and Cu substrate is the parameter representing the wettability. When θ decreases, the solder must spread out with the increasing of the spread area. Therefore, the increased spreading area of the solder indicates the decrease of contact angle. Wetting force (F_W) is a common parameter to evaluate wetting behavior of solders on substrates. Because of $F_W = L\sigma_{lg}\cos\theta$ (where L is the perimeter of Cu piece and σ_{lg} is the surface tension of solder), the decrease of θ causes the increase of F_W [11,12]. Therefore, the increase of spread area conforms to the increase of F_W. Fig. 5 shows the wetting balance curves of the Sn–8Zn–3Bi–*x*Nd solder melts on Cu substrate. It was obvious that the wetting force of the solders increased with minute amount of Nd added into the base alloy. The results both in the spreading test and in the wetting balance test can demonstrate that additive of Nd has improved the wettability of the Sn–8Zn–3Bi solders. The optimal additive of Nd was 0.10 wt%. The wetting force decreased when Nd content reached 0.15 wt%. Moreover, the additive of Nd shortened the wetting time of the solder melts on Cu substrate, as shown in Fig. 5.

Table 3
Tensile properties of solder alloys.

	Alloy no.			
	1	2	3	4
UTS (MPa)	93.3	96.4	97.8	85
Elongation (%)	15.7	16.8	29.4	30.0

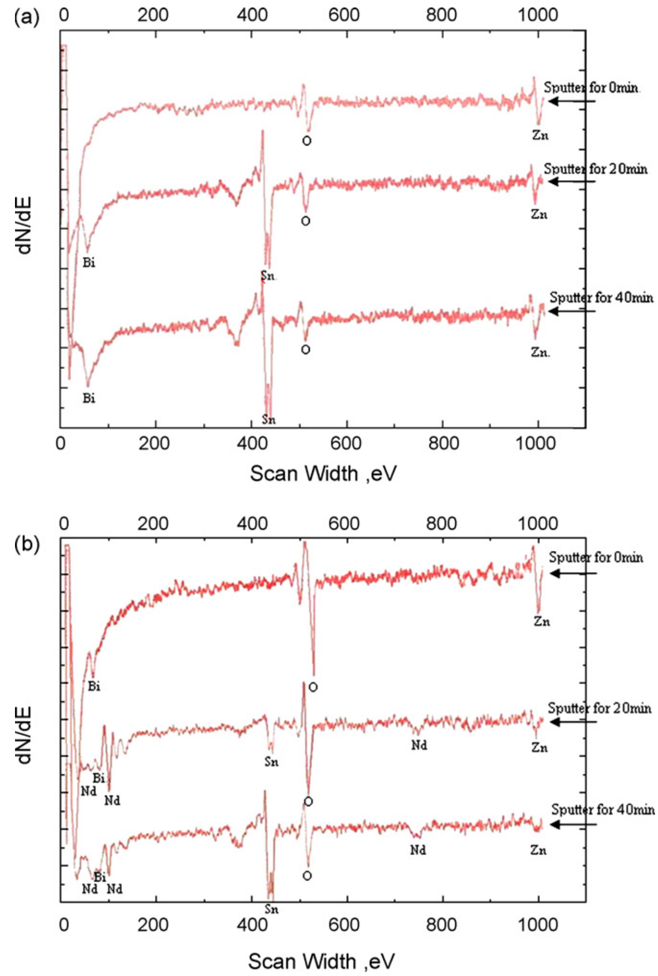

Fig. 8. AES catalogues for (a) Sn–8Zn–3Bi and (b) Sn–8Zn–3Bi–0.1Nd.

Fig. 6 shows the surface tensions of Sn–8Zn–3Bi–(0–0.15)Nd solder melts in air at 200 °C, and up to 240 °C. It was clear that the surface tension of the solders decreased with the increase of temperature. Adding minute amount of Nd into the base alloy caused decrease of the surface tension. With addition of 0.05 wt% Nd, the

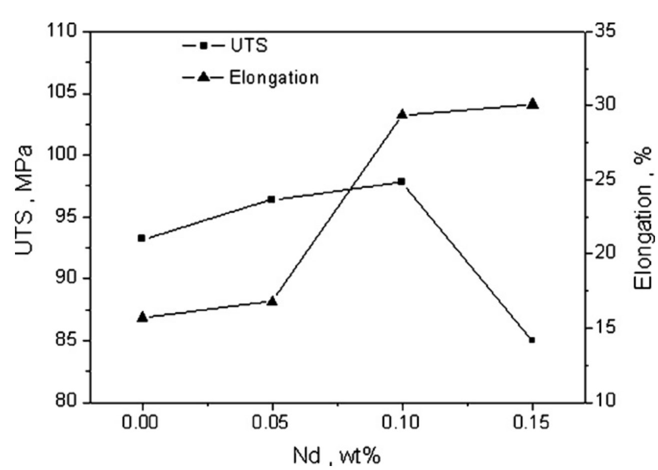

Fig. 9. UTS and elongation as a function of Nd concentration.

surface tension reached the minimum. When additive of Nd rised to 0.15 wt%, the surface tension at 240 °C increased above the base alloy, and the surface tensions at 200 °C and 220 °C were still lower than that of the base alloy.

According to Young–Dupre formula, there is $\theta = \cos^{-1} (\sigma_{gs} - \sigma_{ls})/\sigma_{lg}$ (where σ_{gs} is the surface tension of Cu and σ_{ls} is the interfacial tension between solder and Cu). It reveals that the contact angle θ degrades with the decrease of σ_{lg}, so the increased spreading area and the increased wetting force were usually caused by the decrease of the surface tension of the solders. Considering the results in maximum bubble pressure measurement, the decrease of surface tension is one of the reasons for the increased wettability of the Sn–8Zn–3Bi–*x*Nd solders, but is not the only one. Attention must be paid to that the minimum surface tension of Sn–8Zn–3Bi–0.05Nd alloy has not lead to the optimum wettability. The wettability of the solder should be affected by other factors such as oxidation.

3.2. Oxidation resistance

Fig. 7 shows TGA curves of the four alloys heated in air. TGA analysis shows that the alloys undergo a slight progressive increment of weight during heating in air in the temperature range between 160 °C and 240 °C, after which the sample weight has kept stable. As can be seen from Fig. 7, minute amount of Nd addition decreases the weight of oxide formed at the surface of the solder, which shows the oxidation process is suppressed. Oxidation at the solder surface inhibits the molten solder from contacting with the solid substrate, which usually causes non-wetting behavior. Flux has been used to clean up the oxide formed at the surface on heating. But when the oxide is massive, or the oxide quickly generates, the flux cannot perfectly remove the oxides, and the wettability will degrade. According to the results of TGA, 0.1 wt% Nd addition has resulted in less quantity of oxidation, which could be considered as an important reason for the optimum wettability of the Sn–8Zn–3Bi–0.1Nd solder.

Auger Electron Spectra (AES) analysis was applied to determine the identity of the oxide formed in the Sn–Zn–Bi–Nd quaternary alloys. The AES catalogue was shown in Fig. 8. As can be seen from Fig. 8a, there was a lot of ZnO at the inner surface of Sn–8Zn–3Bi. As for the solder containing Nd, beside with ZnO, Nd_2O_3 existed at the surface of the Sn–8Zn–3Bi–0.1Nd solder, as can be seen from Fig. 8b. Comparing with Fig. 8a, Zn concentration of the inner surfaces of the Nd contained solder obviously decreased, which indicated enriched Nd at surface prevented Zn atom from forming ZnO.

3.3. Mechanical properties

Fig. 9 shows the results of tensile test for Sn–Zn–Bi–(0–0.15)Nd solder alloys as a function of Nd concentration. The results of the test for tensile properties of the alloys are given in Table 3. The ultimate tensile strength (UTS) of the solder increases to 97.8 MPa with the increasing of Nd content. However, it decreases to 85.0 MPa when the Nd addition increases to 0.15 wt%. As for the elongation, it does

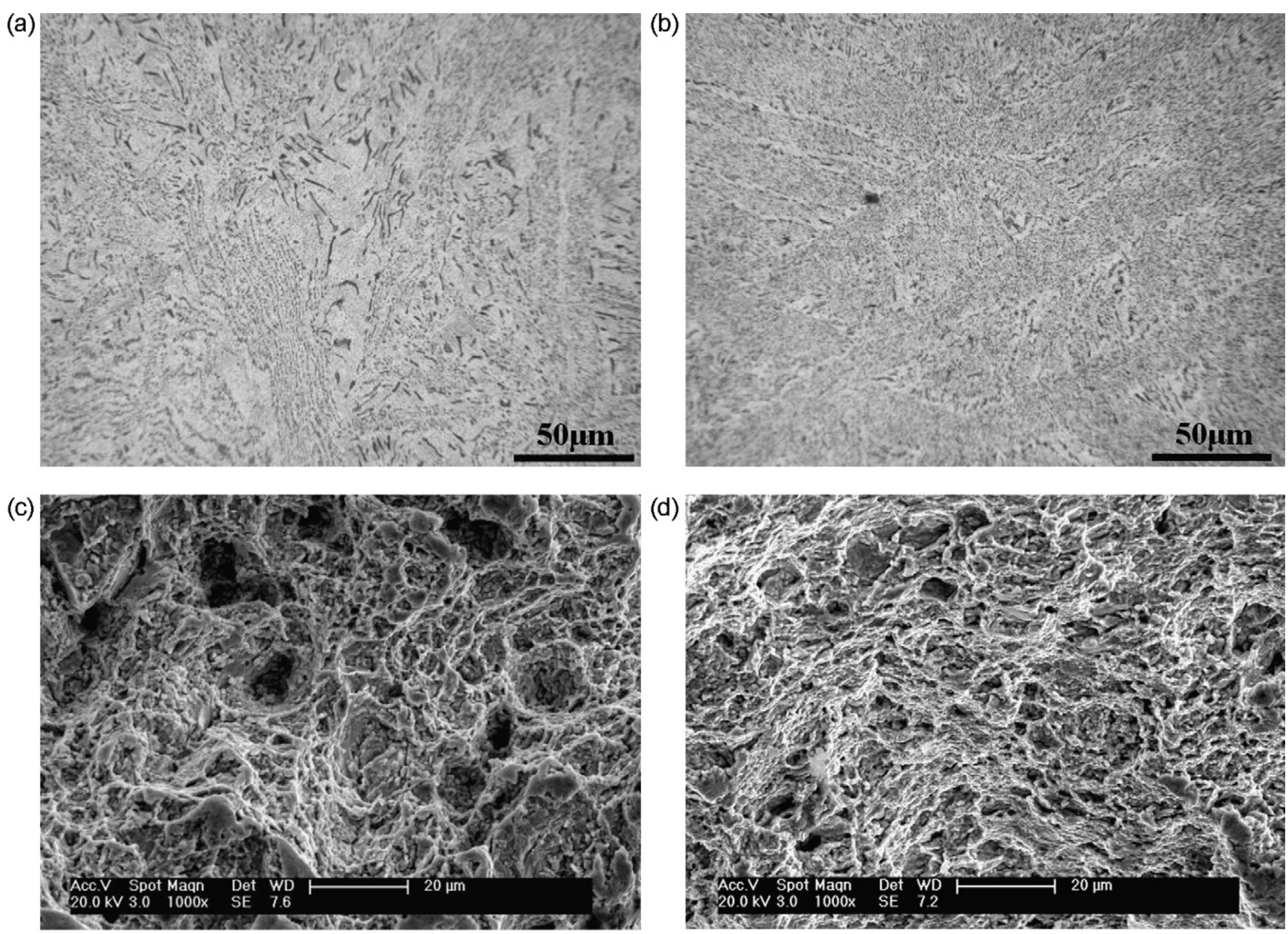

Fig. 10. Optical micrographs and SEM micrographs of fracture surface: (a) microstructure of Sn–8Zn–3Bi, (b) microstructure of Sn–8Zn–3Bi–0.1Nd, (c) fracture surface of Sn–8Zn–3Bi and (d) fracture surface of Sn–8Zn–3Bi–0.1Nd.

not obviously increase until Nd concentration reached 0.10 wt%. The elongation of the Sn–8Zn–3Bi–(0.10–0.15)Nd alloys is close to 30%, which leads to their better ductility.

Microstructure of the Sn–8Zn–3Bi in Fig. 10a shows dendritic segregation. Because the alloy has been cast into iron mould and frozen quickly, large Zn phase precipitates in the non-equilibrium microstructure. As can be seen from Fig. 10b, with addition of Nd, the microstructure of the alloy appears uniform (Zn + β) eutectic, and there is no large Zn phase. Fracture surfaces of the alloys have been checked and compared, as can be seen from Fig. 10c and d. The dimples in the fracture surface of the Sn–8Zn–3Bi–0.1Nd alloy is fine and uniform, but a small amount of large dimples appears at the fracture surface of the Sn–8Zn–3Bi alloy. It is indicated that all parts of the alloy doping with Nd can coordinately deform, which cause increase of the strength and increase of the elongation of the alloy.

4. Conclusions

(1) According to the present results, it is concluded that Nd addition could improve the properties of Sn–8Zn–3Bi base alloy. The wetting force of the solders increased, and the wetting time was shortened, indicating wettability of the solders improved.
(2) Adding trace amount Nd into the Sn–8Zn–3Bi alloy, the surface tension of the alloy is lower than that of the other alloys. It is one of the reasons for improved wettability.
(3) Zn atoms have been prevented from oxidation, which results from Zn concentration at the surface of solder melt has been reduced with addition of Nd. Nd atoms have been oxidated instead of Zn. But, the formation of Nd oxide is obviously slower than that of Zn oxide, which indicates that the diffusion of O atoms into the solder has been impeded.
(4) The elongation of the Sn–8Zn–3Bi–(0.10–0.15)Nd alloys is close to 30%, which leads to their better ductility.

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