ISSN 2616-5880 Vol. 6, Issue 1: 29-35, DOI: 10.25236/AJMC.2025.060103

Effect of trace rare earth Er on the properties of Sn-0.3Ag-0.7Cu-0.05Mn lead-free solder material

Yongfa Zheng[a], Qiming Zhu*, Jian Li[b]

School of Materials and Environment, Guangxi Minzhu University, Nanning, Guangxi, China
[a] 1634546707@qq.com, [b] 429057827@qq.com
**Corresponding author: aiyong2000@163.com*

Abstract: *The effect of adding trace rare earth Er on the properties of Sn-0.3Ag-0.7Cu-0.05Mn lead-free solder material is investigated. The experimental results show that the addition of Er elements can improve the Vickers hardness of lead-free Sn-0.3Ag-0.7Cu-0.05Mn solder. The wettability of lead-free Sn-0.3Ag-0.7Cu-0.05Mn-xEr solder exhibits an initial increase followed by a decrease with increasing Er content. Microscopic analysis of the solder's structure reveals that when the Er content is 0.1wt.%, the β-Sn matrix becomes significantly refined, and intermetallic compound (IMC) grain size is minimized and uniformly dispersed in the matrix, playing a role in grain refinement. However, when the Er content exceeds 0.1wt.%, the IMC grain size increases, and the presence of brittle large-sized IMCs adversely affects the reliability of the solder joints. The addition of rare earth Er noticeably suppresses the growth of the interface IMC layer. Furthermore, when the Er content at 0.1 wt.%, the surface smoothness of the solder joint interface reaches its optimal state, with virtually no observable Kirkendall voids.*

Keywords: *Sn-0.3Ag-0.7Cu-0.05Mn; Er; Microstructure of lead-free solder metal; wettability*

1. Introduction

Owing to the hazards posed by lead to both human health and the environment, numerous countries have enacted legislation to ban or restrict the use of Sn-Pb solder materials. Consequently, the research and application of lead-free solders in encapsulation technology are receiving increasing attention [1－4]. The researchers have been hoping to find a unique solder material that can replace Sn-Pb solder material [5]. The Sn-Ag-Cu solder alloy is regarded as the optimal choice for replacing traditional Sn-Pb brazing materials. This is attributed to its superior joint properties, appropriate melting point, excellent creep resistance, and high reliability [6].

The Sn-Ag-Cu (SAC) solder system includes both high-silver and low-silver variants. Compared to low-silver SAC solder, high-silver SAC exhibits superior wetting performance but incurs higher costs due to the elevated silver content. Additionally, during the solidification process, variations in the degree of supercooling can lead to the formation of coarse Ag_3Sn strips, which may further coarsen during subsequent service, potentially degrading the mechanical properties of the solder material. In contrast, low-silver solder materials reduce costs and rarely form large Ag_3Sn particles, leading to higher impact resistance. Consequently, developing new low-silver lead-free solders has become a trend. However, lower silver content also results in higher melting points, reduced thermal fatigue and wettability, lower shear and tensile strength compared to high-silver solders, and decreased reliability.

In response to the challenges associated with low-silver lead-free solders, researchers both domestically and internationally have commonly adopted the approach of single-element additions to enhance the performance of low-silver Sn-Ag-Cu (SAC) lead-free solder materials. Lu et al. [7] investigated the effects of rare earth element Er on the microstructure and performance of Sn-3.0Ag-0.5Cu lead-free solder alloy. They found that Er has minimal impact on the conductivity and corrosion resistance of the alloy but can lower the melting temperature zone while improving wettability. Additionally, with the addition of Er, the alloy's microstructure transitions from dendritic crystals to equiaxed crystals. Pan [8] investigated the effects of Mn on the interfacial reactions and mechanical properties of Sn-0.3Ag-0.7Cu lead-free solder. The study found that doping with trace amounts of Mn can thin the intermetallic compound (IMC) layer at the solder joint interface, inhibiting the growth of Cu_6Sn_5 and Cu_3Sn phases. Additionally, Mn doping increases the ultimate tensile strength and shear strength of the solder. In this work, we aim to enhance the overall strength of Sn-0.3Ag-0.7Cu lead-free

ISSN 2616-5880 Vol. 6, Issue 1: 29-35, DOI: 10.25236/AJMC.2025.060103

solder by incorporating the same Mn content while varying the amount of rare earth element Er. This work investigates its impact on the wettability of the solder material and conduct experimental observations and analyses of the microstructure and interfacial characteristics of the solder joints.

2. Experimental materials and methods

The experimental Sn-0.3Ag-0.7Cu-0.05Mn-*x*Er (x = 0, 0.05, 0.1, 0.25, 0.5 wt.%) solder alloys were prepared using 99.9% pure Sn, Ag, Cu, Mn, and Er. The raw materials were weighed and placed in a WK-II type non-self-consuming vacuum arc furnace. The furnace was evacuated to a pressure of 5×10^{-1} Pa, followed by three argon gas washes. Under argon protection, the specimens were repeatedly melted three times to ensure uniformity. After melting, the samples were naturally cooled to obtain Sn-0.3Ag-0.7Cu-0.05Mn-xEr solder alloys with varying Er content.

The wettability performance test was conducted according to the national standard GB/T 11364-2008 "Solder Material Wettability Test Method." Specimens of purple copper sheets (20 mm × 20 mm × 1 mm) were prepared by polishing their surfaces with 800# sandpaper and cleaning them ultrasonically to remove surface contaminants. After drying, a flux paste was applied to the center of each specimen, and a solder ball weighing (0.2 ± 0.01) g was placed on it. The specimens were then heated in a vacuum tube furnace at 300°C for 2 minutes, followed by air cooling. Photographs were taken, and the spreading area was calculated using AUTOCAD. The experimental results represent the average of three trials.

To measure the wetting angle, wire cutting was used to section the solder joints centrally, ensuring accurate measurement of the wetting angle. Due to potential electrochemical corrosion, wire cutting may introduce pores at the interface. The samples were then mounted and polished using an XQ-1 metallographic specimen setting machine. The wetting angle was measured using a SOPTOP IE500M metallographic microscope, which observed the angle formed between the cross-section of the solder joint and the copper sheet. The microstructure of the solder was examined using the same microscope, while the thickness of the reaction layer and phase composition analysis were performed using a scanning electron microscope (SEM) and energy-dispersive spectrometer (EDS).

Mechanical property test specimens were prepared from the remaining melted samples. The samples were mounted and polished, and Vickers hardness tests were conducted using an HV-55PA digital microhardness tester. Hardness measurements were taken at six random points on the sample surface, with each measurement performed under a test force of 0.098 N and a holding time of 15 seconds. The experimental results represent the average of the six measurements.

3. Results and analysis

3.1 Microstructure analysis

The microstructure of the Sn-0.3Ag-0.7Cu-0.05Mn-*x*Er (x = 0~0.50) solder alloy is shown in Fig. 1. The alloy consists of a grey fibrous phase and a light white matrix phase. Specifically, the grey phase represents a reticulated eutectic structure, while the light white matrix phase is rich in Sn with a massive distribution. Intermetallic compounds (IMCs) are dispersed within the matrix as strips and particles. The addition of Er gradually refines the β-Sn primary phase, increases the formation of eutectic phases, and reduces the size of IMC particles. The morphology of the primary crystalline phase significantly influences the fluidity of the alloy. Finer grains result in a smoother solidification interface, lower flow resistance, and improved fluidity [9]. As shown in Fig. 1c, the microstructure is most refined and uniform when the Er content is 0.1 wt.%, and it gradually coarsens as the Er content increases. The addition of an appropriate amount of Er achieves grain refinement primarily because Sn and Er have a strong mutual attraction, leading to Er enrichment at phase interfaces or grain boundaries, which inhibits the growth of primary crystals and eutectic structures [7].

ISSN 2616-5880 Vol. 6, Issue 1: 29-35, DOI: 10.25236/AJMC.2025.060103

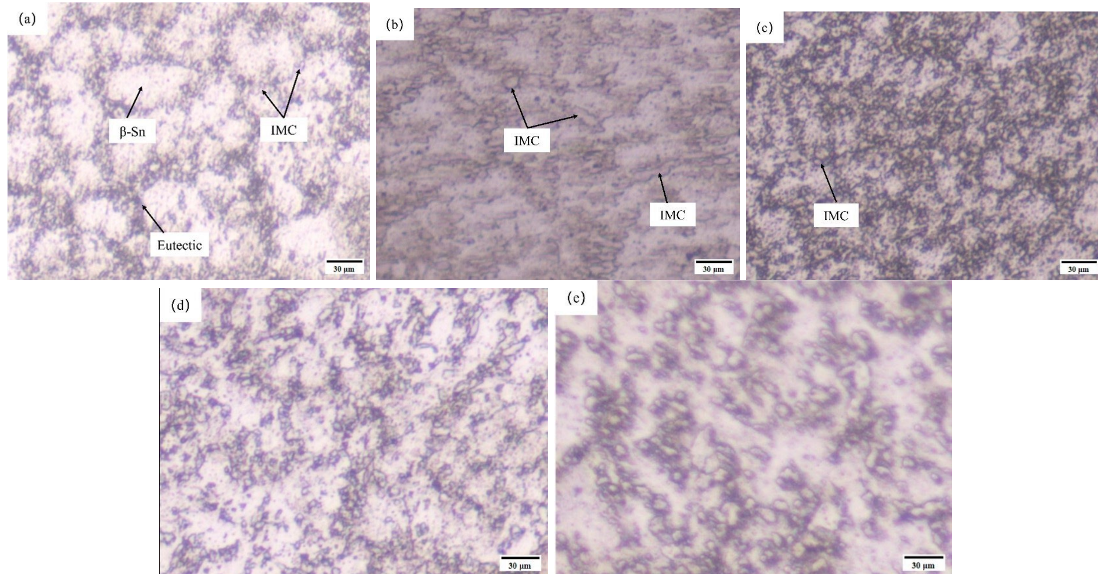

Fig. 1. Microstructures of Sn-0.3Ag-0.7Cu-0.05Mn-xEr solders: (a) x=0(OM); (b) x=0.05(OM); (c) x=0.10(OM); (d) x=0.25(OM); (e) x=0.50(OM).

3.2 Hardness

The hardness curve of the Sn-0.3Ag-0.7Cu-0.05Mn-*x*Er solder alloy is shown in Fig. 2. The Fig. 2 illustrates that the hardness initially increases and then decreases with the addition of Er, remaining higher than that of Sn-0.3Ag-0.7Cu-0.05Mn solder throughout. The maximum hardness is achieved when the Er content is 0.05 wt.%. The variation in hardness is closely related to the degree of microstructure refinement, phase solid solubility, and the formation of intermetallic compounds (IMCs). As shown in Fig. 1, the microstructure of Sn-0.3Ag-0.7Cu-0.05Mn solder with 0.05 wt.% Er is the most refined. According to the fine grain strengthening mechanism, this refinement increases the number of grain boundaries. Under applied stress, dislocations tend to aggregate at these boundaries, impeding their movement and thereby increasing the hardness of the solder [10].

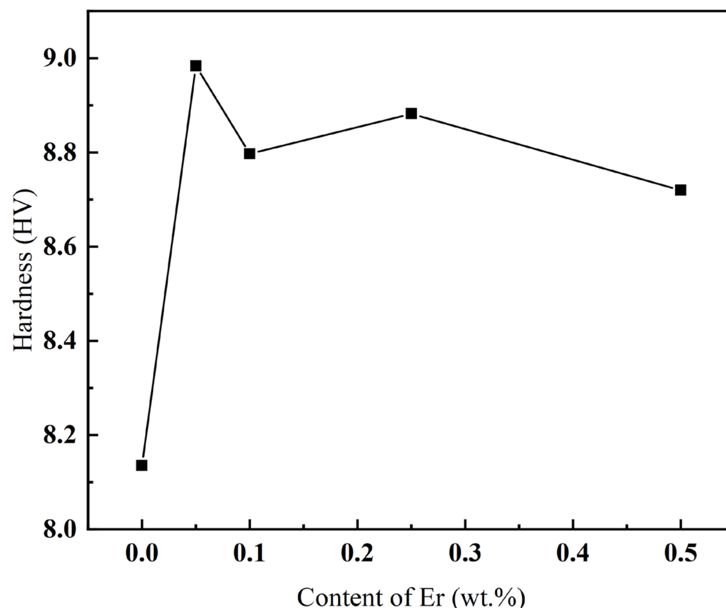

Fig. 2. The hardness of Sn-0.3Ag-0.7Cu-0.05Mn-xEr (x=0,0.05,0.1,0.25,0.5 wt. %) composite solders.

3.3 Wetting properties

For solder alloys, wettability is a critical factor that directly determines the solderability of the process. The ability of the solder to wet the substrate effectively is essential for forming reliable welded

ISSN 2616-5880 Vol. 6, Issue 1: 29-35, DOI: 10.25236/AJMC.2025.060103

joints. Factors influencing wettability include intrinsic factors such as the composition of the solder and base material, surface roughness, and degree of oxidation, as well as environmental factors like temperature and the presence of fluxes or surface-active substances. Various methods are used to measure and evaluate the wetting performance of solder alloys, including assessing the spreading area, wetting angle, spreading rate, wetting time, and wetting force. In this study, the spreading area and wetting angle of the Sn-0.3Ag-0.7Cu-0.05Mn-*x*Er composite solder on Cu substrates were measured and calculated. The effect of adding Er elements on the wetting performance of the solder alloy was then compared and analyzed.

The spreading area of the Sn-0.3Ag-0.7Cu-0.05Mn-*x*Er solder alloy is shown in Fig. 3. As the Er content increases, the spreading area also increases. This phenomenon may be attributed to the high melting point of Er compared to other elements. When a small amount of Er is added to the SAC0307 matrix, the Er particles do not fully melt but instead infiltrate the matrix, forming a microscopic framework structure within the solder joints. This framework creates capillary action within the solder matrix, promoting the diffusion of molten solder and enhancing wettability [11]. When the Er content reaches 0.1 wt.%, the spreading area achieves its maximum value of 56.0398 mm^2 . However, as the Er content continues to increase beyond this point, the spreading area gradually decreases. This decrease can be attributed to the rising viscosity of the solder fluid and the tendency of excess tiny particles to agglomerate, which produces a pinning effect on the grain boundaries of the molten solder material, hindering its flow and thus reducing the spreading area.

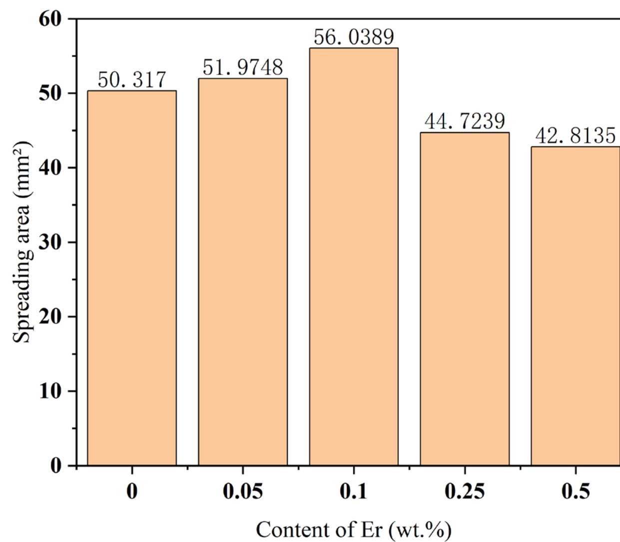

Fig. 3. Spreading area of Sn-0.3Ag-0.7Cu-0.05Mn-xEr solder alloy.

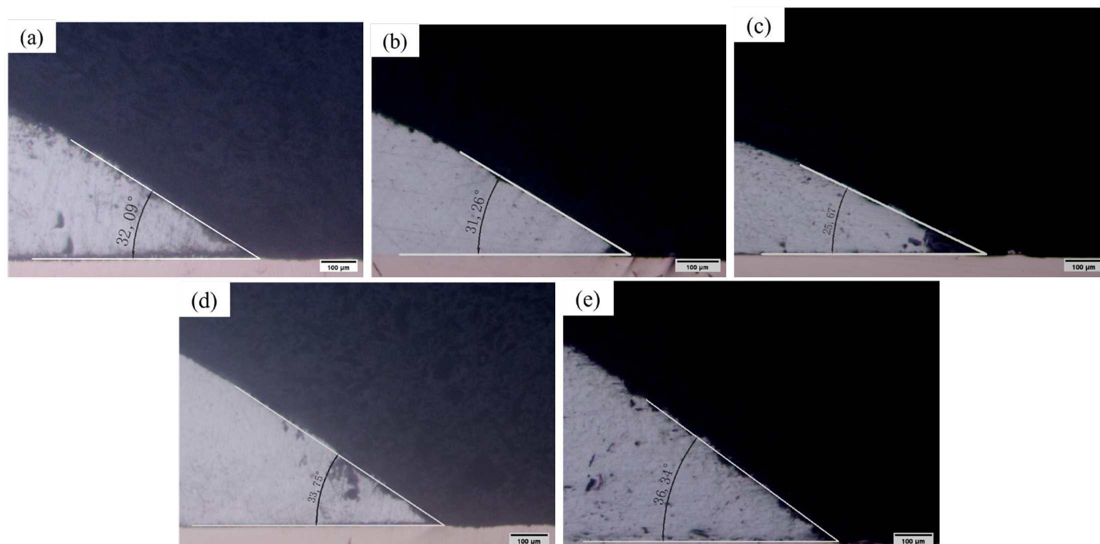

Fig. 4. OM image of wetting angle of Sn-0.3Ag-0.7Cu-0.05Mn-xEr solder alloy: (a) x=0; (b) x=0.05; (c) x=0.10; (d) x=0.25; (e) x=0.50.

ISSN 2616-5880 Vol. 6, Issue 1: 29-35, DOI: 10.25236/AJMC.2025.060103

Fig. 4 shows the optical microscopy (OM) images of the wetting angles for solder alloys with varying Er contents. As shown in Fig. 4, it can be observed that the wetting angle initially decreases and then increases with the addition of Er. The minimum wetting angle of 25.67° is achieved when the Er content is 0.1 wt.%. This behavior can be attributed to the surface-active nature of the rare earth element Er, which has a low surface tension. When Er is distributed on the surface of the liquid solder alloy, it reduces the surface tension, thereby decreasing the wetting angle. However, as the Er content increases, its chemical reactivity leads to the formation of rare earth compounds and oxides on the liquid solder alloy surface. This layer of film-like compounds hinders the spread of the liquid solder, resulting in an increase in the wetting angle.

3.4 Interface analysis of Sn-0.3Ag-0.7Cu-0.05Mn-xEr/Cu solder joints

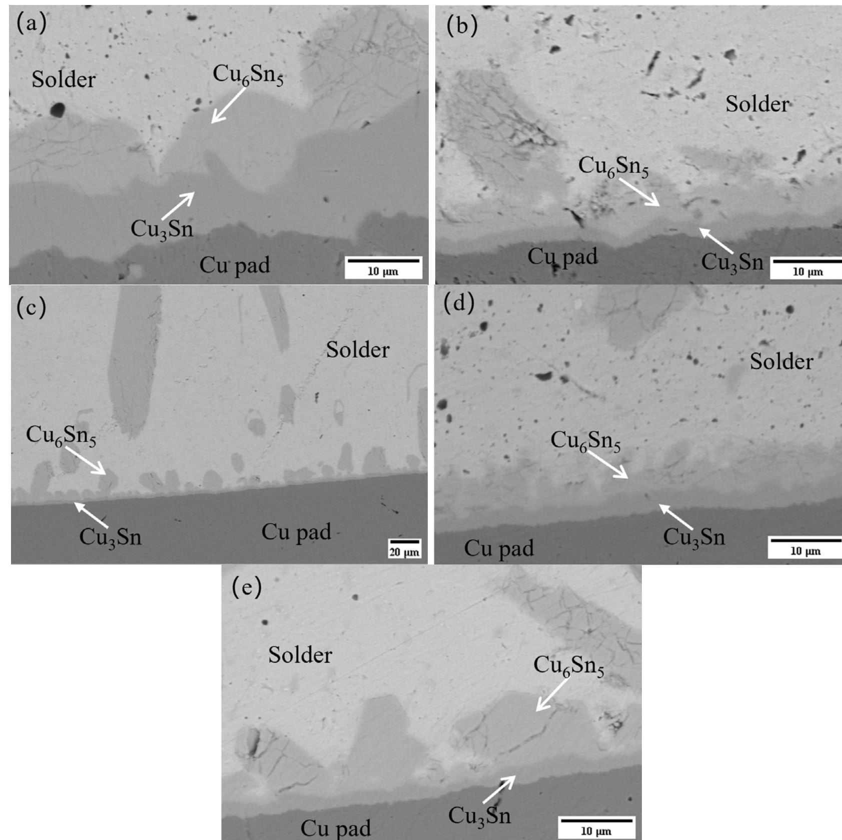

Fig. 5. Microstructure of Sn-0.3Ag-0.7Cu-0.05Mn-xEr/Cu solder joint interface: (a) x=0; (b) x=0.05; (c) x=0.10; (d) x=0.25; (e) x=0.50.

Fig. 5 presents the SEM image of the Sn-0.3Ag-0.7Cu-0.05Mn-*x*Er/Cu solder joint interface. As can be observed from the Fig. 5, a layer of IMCs is formed between Sn-0.3Ag-0.7Cu-0.05Mn-*x*Er and the Cu substrate, and the IMCs at the solder joint interface are of a double-layer structure. Fig. 6 displays the EDS spectra and elemental composition at points 1 and 2 of the Sn-0.3Ag-0.7Cu-0.05Mn-0.1Er/Cu interface in Fig. 5. It can be determined therefrom that the main components of the IMCs are Cu_3Sn and Cu_6Sn_5, with the Cu_3Sn layer adjacent to the Cu substrate and a Cu_6Sn_5 layer overlying it. During the melting process of the solder on the Cu substrate, the Sn atoms in the molten Sn-0.3Ag-0.7Cu-0.05Mn-xEr composite solder react with the Cu atoms on the substrate to generate a thick layer of IMCs, as shown in Reaction (1) [12];

$$6Cu + 5Sn \rightarrow Cu_6Sn_5 \quad (1)$$

Subsequently, the formation of Cu_3Sn mainly occurs in two manners: Firstly, the Sn atoms in the matrix diffuse to the Cu_6Sn_5/Cu_3Sn interface and react with the Cu atoms to form Cu_3Sn. Secondly, the Cu atoms on the substrate diffuse to the Cu_6Sn_5/Cu_3Sn interface and react with Cu_6Sn_5 to form Cu_3Sn, as depicted in Reactions (2) and (3) [13, 14].

$$3Cu + Sn \rightarrow Cu_3Sn \quad (2)$$

ISSN 2616-5880 Vol. 6, Issue 1: 29-35, DOI: 10.25236/AJMC.2025.060103

$$9Cu + Cu_6Sn_5 \rightarrow 5Cu_3Sn \quad (3)$$

With the formation of IMCs, Kirkendall voids emerge in the solder matrix structure. The analysis suggests that this might be attributed to the discrepant diffusion rates of Sn and Cu. When a substantial number of Sn atoms diffuse to the interface to react with the Cu atoms or Cu_6Sn_5, the vacancies left by the Sn atoms cannot be replenished promptly, thereby forming Kirkendall voids [15]. When 0.1 wt.% Er is added, the quantity of Kirkendall voids in the solder joint cross-section decreases. Due to Er is pinned in the Cu_6Sn_5 layer, suppressing the reaction between the Sn atoms and the Cu atoms, thereby decelerating the diffusion of the Sn atoms and reducing the formation of Kirkendall voids. The presence of Kirkendall voids will lead to stress concentration at the voids, exerting an influence on the reliability of the solder joint.

Fig. 6 illustrates the relationship between the average thickness of intermetallic compounds (IMCs) formed during the Sn-0.3Ag-0.7Cu-0.05Mn-xEr/Cu interfacial reaction and different Er additions. As shown in Fig. 6, it can be observed that the thickness of the IMC layer decreases significantly with the addition of 0.05 wt.% to 0.5 wt.% Er. Specifically, when 0.1 wt.% Er is added, the IMC layer thickness reaches its minimum value of 13.94 μm, compared to 18.97 μm without rare earth Er. Therefore, Er effectively inhibits the growth of the interfacial IMC layer.

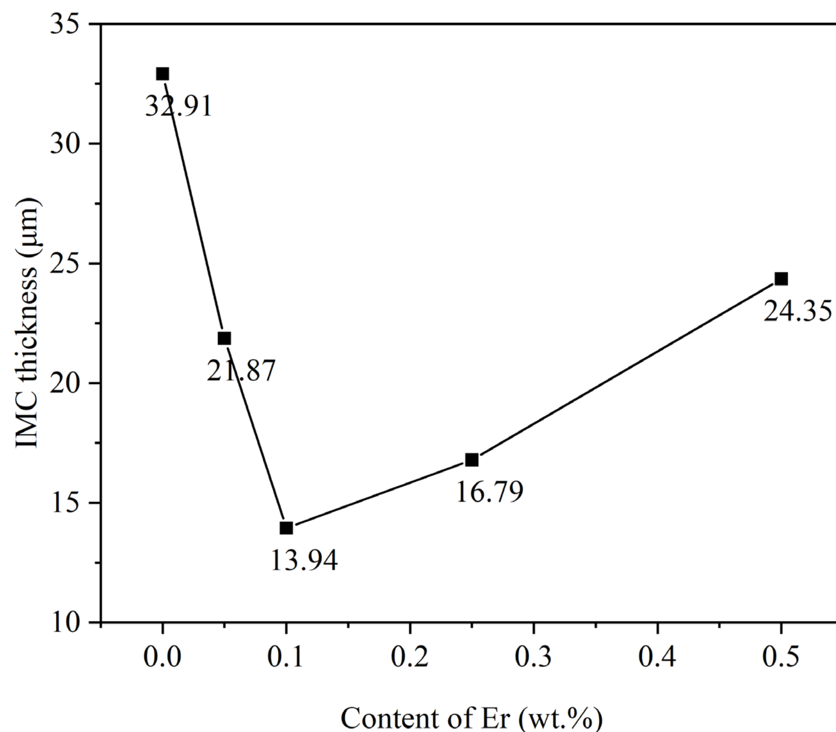

Fig. 6. IMC layer thickness at Sn-0.3Ag-0.7Cu-0.05Mn-xEr/Cu solder joint.

4. Conclusion

(1) Adding 0.1 wt.% Er to the Sn-0.3Ag-0.7Cu-0.05Mn solder alloy significantly refines the microstructure of the solder material, resulting in a marked reduction in the size of intermetallic compounds (IMCs).

(2) The IMC layer at the solder joint interface of the Sn-0.3Ag-0.7Cu-0.05Mn solder alloy with Er addition becomes thinner, and the thickness of the IMC layer at the interface is the thinnest at 13.94 μm when the Er addition is 0.1 wt.%. Kirkendall voids are almost not observed in the solder joint matrix.

(3) During the melting process, a certain amount of Er could promoting the diffusion of molten solder and enhancing wetting performance. When the Er content is 0.1 wt.%, the wetting area is maximized, the wetting angle is minimized, and the wetting performance is optimal. However, as the Er content continues to increase beyond this point, the wetting performance exhibits a decreasing trend.

ISSN 2616-5880 Vol. 6, Issue 1: 29-35, DOI: 10.25236/AJMC.2025.060103

References

[1] Wang M, Wang J, Ke W. Corrosion behavior of Sn-3.0Ag-0.5Cu lead-free solder joints[J]. Microelectronics Reliability, 2017, 73: 69-75.
[2] RanLi M I I, Salleh M A A M, Abdullah M M A B, et al. Formation and Growth of Intermetallic Compounds in Lead-Free Solder Joints: a Review[J]. Materials, 2022, 15(4): 1451.
[3] Wang X, Sun F, Han B, et al. Wetting characteristics of Sn-5Sb-CuNiAg lead-free solders on the copper substrate[J]. Soldering & Surface Mount Technology, 2021, 34(2): 96-102.
[4] Wang Q, Chen H, Wang F. Effect of Trace Zn Addition on Interfacial Evolution in Sn-10Bi/Cu Solder Joints during Aging Condition[J]. Materials, 2019, 12(24): 4240.
[5] Yang F, Zhang L, Liu Z Q, et al. Properties and Microstructures of Sn-Bi-X Lead-Free Solders[J]. Advances in Materials Science and Engineering, 2016.
[6] Shalaby R M, Kamal M, Ali E A M, et al. Design and Properties of New Lead-Free Solder Joints Using Sn-3.5Ag-Cu Solder[J]. Silicon, 2018, 10(5): 1861-1871.
[7] Lu B, Chestnut H, Wang Juanhui, et al. Effect of rare earth Er on the organization and properties of Sn-3.0Ag-0.5Cu lead-free solder alloy[J]. China Journal of Nonferrous Metals, 2007(4): 518-524.
[8] Pan Y C. Effect of manganese doping on interfacial reaction and mechanical properties of lead-free solder Sn-0.3Ag-0.7Cu[D]. South China University of Technology, 2014.
[9] Zhao L, Teng Y, Chen X, et al. Effect of Ce content on the properties of SnAg0.1Cu0.7 lead-free solder alloy[J]. Nonferrous Metal Engineering, 2020, 10(9): 25-29.
[10] Song, Shallow. Effect of Cr addition on the interfacial reaction and performance of Sn58Bi new lead-free solder joints [D]. Guangxi University, 2022.
[11] Guo F. Composite lead-free electronic solders[M]. Lead-Free Electronic Solders. Boston, MA: Springer US, 2007: 129-145.
[12] Li, Z L. Study on the effect of TiO_2 nanoparticle doping and solder joint size on the interfacial reaction of lead-free micro-solder joints [D]. South China University of Technology, 2016.
[13] QianQian S, WenChao Y, Yitai L, et al.Interfacial reaction and mechanical properties of Sn58Bi-XCr solder joints.pdf[J]. Vacuum, 2021, 194.
[14] Dele-Afolabi, Azmah Hanim M A, Ojo-Kupoluyi O J, et al. Impact of different isothermal aging conditions on the IMC layer growth and shear strength of MWCNT-reinforced Sne5Sb solder composites on Cu substrate [J]. Journal of Alloys and Compounds, Journal of Alloys and Compounds, 2019, 808.
[15] Tz-Cheng C, Kejun Z, Stierman R, et al. Effect of thermal aging on board level drop reliability for Pb-free BGA packages[J]. 2004,2:1256-1262.